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Dynamical perspective of stability in glasses

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Jury:

Reviewer	Prof. Foivos Perakis
Reviewer	Prof. Marta Gonzalez Silveira
Examiner	Prof. Giancarlo Ruocco
Examiner	Prof. Roberto S. Brusa
Examiner	Prof. Noel Jakse
Supervisor	Prof. Giacomo Baldi
Supervisor	Prof. Jean-Louis Hazemann
Supervisor	Dott. Beatrice Ruta

PhD Candidate:

Irene Festi

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List of Abbreviations

AAT	Amorphous-Amorphous Transition
BP	Boson Peak
DAC	Diamond Anvil Cell
CRL	Compound Refractive Lens
DESY	Deutsches Elektronen-Synchrotron
DL	Debye Level
DOS	Density of States
DSC	Differential Scanning Calorimetry
DWP	Double-Well Potential
EH	Experimental Hutch
ESRF	European Synchrotron Radiation Facility
FSDP	First Sharp Diffraction Peak
FWHM	Full Width at Half Maximum
HDA	High-Density amorphous
HDL	High-Density Liquid
HET	Heterogeneous Elasticity Theory
HHLM	High-Heat-Load Monochromator
HP	High-Pressure
HRM	High-Resolution Monochromator
IF	Instrumental Function
ISF	Intermediate Scattering Function

KWW	Kohlrausch-Williams-Watts Function
LDA	Low-Density amorphous
LDL	Low-Density Liquid
LF	Low-Frequency
LLT	Liquid-Liquid Transition
MG	Metallic Glass
ML	MultiLayer mirror
MRO	Medium-Range Order
NRAIXS	Nuclear Resonant Inelastic X-ray Scattering
OG	Ordinary Glass
PCS	Photon Correlation Spectroscopy
PCM	Phase-Change Material
PEL	Potential Energy Landscape
PLD	Peierls-Like Distortion
PTM	Pressure-Transmitting Medium
PVD	Physical Vapor Deposition
QLM	Quasi-Localised Mode
SCBA	Self-Consistent Born Approximation
SCL	Supercooled liquid
SNR	Signal-to-Noise Ratio
SPM	Soft Potential Model
STM	Standard Tunnelling Model
SWP	Single-Well Potential
TTCF	Two-Time Correlation Function
TLS	Two-Level Systems
USG	Ultrastable Glass
XPCS	X-ray Photon Correlation Spectroscopy
XRD	X-ray Diffraction

Preface

Glasses have been essential materials since ancient times and today play a key role in the development of advanced technologies. Over the past century, the family of glasses has expanded to include organic, soft, chalcogenide, and metallic systems, each with distinct structural and functional properties. Glasses are inherently out-of-equilibrium materials, and this makes them prone to temporal evolution, which poses challenges for their use in high-performance and long-term applications. Understanding the concept of *glass stability*, and how it can be tuned, is therefore of both fundamental and practical importance.

Glasses are usually obtained by rapidly cooling a liquid, avoiding crystallisation. As the temperature decreases, particle motion becomes progressively slower until the viscosity rises so dramatically that the system falls out of thermodynamic equilibrium and becomes effectively frozen on experimental timescales. The system then enters the so-called glassy state, which retains the disordered, liquid-like structure. Glasses are characterised by the absence of long-range order, a feature that distinguishes them from crystalline solids [1].

Being out of equilibrium, glasses spontaneously evolve towards lower-energy, more stable configurations over time, a process known as *physical aging*. An important aspect of glass formation is that the stability of the final glassy state strongly depends on the cooling rate: the slower the cooling, the more stable the glass, as the particles have more time to arrange into lower-energy configurations [2].

However, achieving higher and higher stability is experimentally unfeasible due to the extremely slow cooling rates required. This challenge has driven the development of alternative approaches to produce highly stable glasses. A breakthrough in this direction is physical vapor deposition (PVD). In PVD, molecules are vaporised and deposited one by one onto a substrate, forming glasses of remarkably high stability. These *ultra-stable glasses* (USGs) exhibit thermodynamic and kinetic properties comparable to those of glasses aged for thousands of years or cooled at extremely low rates [2].

Macroscopic low-temperature studies have shown that PVD suppresses the so-called two-level systems (TLS), universal anomalies of glasses attributed to the quantum tunnelling of atoms or small groups of atoms between nearly degenerate configurations in a double-well potential. The suppression of TLS is associated with the enhanced stability of USG glasses compared to ordinary glasses [3].

Another approach to modify the glass stability is to apply external treatments to the final glass. Thermal annealing, mechanical deformation, or irradiation can either increase stability (aging) or induce the opposite effect, known as *rejuvenation*, leading to a higher-energy, less stable state. In particular, X-ray irradiation has been shown to trigger a yielding transition in certain oxide and chalcogenide glasses, resulting in rejuvenated states [4]. However, systematic studies across different glass families remain scarce. Unexpected behaviours have also been reported in metallic glasses (MGs) under high-pressure compression: not only can densification lead to rejuvenation, a counter-intuitive result, as denser states are usually associated with higher stability, but the pressure dependence of dynamics has been found to be non-monotonic [5, 6].

The primary goal of this Thesis is to explore how glass stability affects microscopic dynamics across the entire spectrum of timescales, from fast picosecond vibrations to slow structural relaxations on the order of hundreds of seconds. To address this, we combine different preparation methods and external treatments, focusing on three key routes: physical vapor deposition, X-ray irradiation, and high-pressure compression. The microscopic insight is obtained from the *intermediate scattering function* (ISF), $F(q, t)$, which quantifies the temporal evolution of density fluctuations [7]. Ultra-stable glasses prepared by PVD provide an ideal system to study how enhanced stability alters vibrational dynamics. As the ISF is extremely challenging to be directly accessed at picosecond timescales, we investigate it indirectly in the frequency domain through the vibrational density of states (DOS), $g(\nu)$. At much longer timescales, the influence of stability on structural relaxation is studied by applying X-ray irradiation and high-pressure compression to structural glasses. In this case, the ISF is directly probed.

In particular, to access the DOS of ultra-stable and ordinary glasses, we employ Nuclear Resonant Analysis to Inelastic X-ray Scattering (NRAIXS) [8], using a high-resolution spectrometer capable of measuring the DOS in absolute units down to frequencies of approximately 70 GHz. Complementary Raman spectroscopy provides a macroscopic perspective on vibrational anomalies. On the longer-timescale side, the ISF is directly measured using X-ray Photon Correlation Spectroscopy (XPCS) [9], which is applied to investigate relaxation dynamics under both X-ray irradiation and high-pressure

conditions. The high-pressure experiments are complemented by *ex-situ* fast nanocalorimetry, allowing us to directly correlate microscopic dynamics with macroscopic stability and to assess how densification tunes the glass stability.

Structure of this Thesis

This Thesis is organised as follows:

The **first Chapter** introduces the glassy state from a macroscopic perspective and then moves to a microscopic description, discussing the potential energy landscape framework and the role of density correlation functions such as the ISF. Relaxation processes in supercooled liquids and glasses are presented, followed by a discussion of *polyamorphism*, the coexistence of multiple amorphous forms sharing the same composition but differing in structure and thermodynamic properties. Finally, we review the anomalous low-temperature properties of glasses and the two main theoretical models proposed to explain them.

The **second Chapter** outlines the motivation of this work. Starting from the phenomenology of glass stability, we describe how it can be tuned either by employing different preparation methods, such as melt-quenching and physical vapor deposition, or by applying external treatments, like photo-irradiation and mechanical deformations. For each approach, we provide the state of the art and highlight the open questions that form the basis of this Thesis.

The **third Chapter** details the experimental methods used in this work. After a brief introduction to scattering processes, we describe in detail the NRAIXS technique for vibrational density of states measurements in ultra-stable and ordinary glasses, and XPCS for direct measurements of the intermediate scattering function under irradiation and high-pressure conditions. For both techniques, theoretical backgrounds, experimental setups, and data analysis procedures are presented. Complementary techniques, such as Raman spectroscopy and fast nanocalorimetry, are also discussed.

The **fourth Chapter** presents the results on the vibrational dynamics of ultra-stable and ordinary glasses. After describing the types of samples investigated, we report and extensively analyse the vibrational density of states measurements. A dedicated fitting procedure developed in this work allows a direct comparison with low-temperature specific heat data on equi-

valent samples. Raman measurements are then presented, and the results are discussed in light of the two main models of low-temperature glass anomalies.

The **fifth Chapter** focuses on the effect of photo-irradiation and high-pressure compression on structural relaxation dynamics. We first describe the investigated samples, and then present the results of X-ray irradiation, which induces a yielding transition whose effectiveness depends on the glass composition. We report the results obtained under high-pressure compression, revealing a polyamorphic transition and a non-monotonic pressure dependence of the dynamics. Fast-nanocalorimetry measurements show that densification leads to rejuvenation. For both case studies, the findings are interpreted and discussed in the context of existing literature.

The **sixth Chapter** summarises the main conclusions of this work and outlines future perspectives for further advancing the microscopic understanding of glass stability.

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Préface

Les verres sont des matériaux essentiels depuis l'Antiquité et jouent aujourd'hui un rôle clé dans le développement des technologies avancées. Au cours du siècle dernier, la famille des verres s'est élargie pour inclure des systèmes organiques, mous, chalcogénures et métalliques, chacun présentant des propriétés structurelles et fonctionnelles spécifiques. Les verres sont intrinsèquement des matériaux hors équilibre, ce qui les rend sujets à une évolution temporelle, posant ainsi des défis pour leur utilisation dans des applications de haute performance et de longue durée. Comprendre le concept de *stabilité du verre* et la manière dont elle peut être modulée est donc d'une importance à la fois fondamentale et pratique.

Les verres sont généralement obtenus par un refroidissement rapide d'un liquide, évitant ainsi la cristallisation. À mesure que la température diminue, le mouvement des particules ralentit progressivement jusqu'à ce que la viscosité augmente si fortement que le système sort de l'équilibre thermodynamique et devient effectivement figé sur les échelles de temps expérimentales. Le système entre alors dans l'état vitreux, qui conserve la structure désordonnée et semblable à celle du liquide. Les verres se caractérisent par l'absence d'ordre à longue portée, une caractéristique qui les distingue des solides cristallins [1].

Étant hors équilibre, les verres évoluent spontanément au cours du temps vers des configurations plus stables et à plus basse énergie, un processus connu sous le nom de *vieillessement physique*. Un aspect important de la formation vitreuse est que la stabilité de l'état vitreux final dépend fortement de la vitesse de refroidissement : plus le refroidissement est lent, plus le verre est stable, car les particules disposent de plus de temps pour s'organiser dans des configurations à plus basse énergie [2].

Cependant, atteindre des niveaux de stabilité de plus en plus élevés est expérimentalement irréalisable en raison des vitesses de refroidissement extrêmement lentes requises. Ce défi a conduit au développement d'approches alternatives pour produire des verres hautement stables. Une avancée majeure dans ce domaine est le dépôt physique en phase vapeur (*Physical Vapor Deposition*, PVD). Dans le PVD, les molécules sont vaporisées puis déposées une

à une sur un substrat, formant des verres d'une stabilité remarquable. Ces *verres ultra-stables* (USG) présentent des propriétés thermodynamiques et cinétiques comparables à celles de verres vieillis pendant des milliers d'années ou refroidis à des vitesses extrêmement faibles [2]. Des études macroscopiques à basse température ont montré que le PVD supprime les *systèmes à deux niveaux* (TLS), anomalies universelles des verres attribuées au tunnel quantique d'atomes ou de petits groupes d'atomes entre des configurations presque dégénérées dans un potentiel à double puits. Cette suppression des TLS est associée à la stabilité accrue des USG par rapport aux verres ordinaires [3].

Une autre approche pour modifier la stabilité d'un verre consiste à appliquer des traitements externes au verre final. Le recuit thermique, la déformation mécanique ou l'irradiation peuvent soit accroître la stabilité (vieillissement), soit induire l'effet opposé, connu sous le nom de *réjuvenation*, conduisant à un état de plus haute énergie et moins stable. En particulier, il a été démontré que l'irradiation X déclenche une transition de type *yielding* dans certains verres oxydes et chalcogénures, produisant des états rajeunis [4]. Cependant, les études systématiques sur différentes familles de verres restent rares. Des comportements inattendus ont également été observés dans les verres métalliques (MG) sous compression à haute pression : non seulement la densification peut entraîner une rejuvenation — un résultat contre-intuitif, car des états plus denses sont généralement associés à une plus grande stabilité — mais la dépendance en pression de la dynamique s'est révélée non monotone [5, 6].

L'objectif principal de cette Thèse est d'explorer comment la stabilité des verres affecte la dynamique microscopique sur l'ensemble des échelles de temps, des vibrations rapides de l'ordre de la picoseconde aux relaxations structurales lentes de l'ordre de centaines de secondes. Pour ce faire, nous combinons différentes méthodes de préparation et traitements externes, en nous concentrant sur trois voies principales : le dépôt physique en phase vapeur, l'irradiation X et la compression sous haute pression. L'information microscopique est obtenue à partir de la *fonction de corrélation intermédiaire* (ISF), $F(q, t)$, qui quantifie l'évolution temporelle des fluctuations de densité [7]. Les verres ultra-stables préparés par PVD constituent un système idéal pour étudier comment une stabilité accrue modifie la dynamique vibrationnelle. Comme l'accès direct à l'ISF aux échelles de temps picosecondes est extrêmement difficile, nous l'explorons indirectement dans le domaine fréquentiel à travers la densité d'états vibrationnelle (DOS), $g(\nu)$. À des échelles de temps beaucoup plus longues, l'influence de la stabilité sur la relaxation structurale est étudiée en appliquant l'irradiation X et la compression sous haute pression aux verres structurels. Dans ce cas, l'ISF est

mesurée directement.

En particulier, pour accéder à la DOS des verres ultra-stables et ordinaires, nous employons l'Analyse Nucléaire Résonante par Diffusion Inélastique des Rayons X (NRAIXS) [8], à l'aide d'un spectromètre haute résolution capable de mesurer la DOS en unités absolues jusqu'à des fréquences d'environ 70 GHz. Une spectroscopie Raman complémentaire fournit une perspective macroscopique sur les anomalies vibrationnelles. Pour les échelles de temps plus longues, l'ISF est mesurée directement à l'aide de la *X-ray Photon Correlation Spectroscopy* (XPCS) [9], appliquée à l'étude des dynamiques de relaxation sous irradiation X et sous haute pression. Les expériences à haute pression sont complétées par de la nanocalorimétrie rapide *ex-situ*, ce qui permet de corréler directement la dynamique microscopique à la stabilité macroscopique et d'évaluer comment la densification module la stabilité du verre.

Structure de cette Thèse

Cette Thèse est organisée comme suit :

Le **premier chapitre** introduit l'état vitreux d'un point de vue macroscopique, puis passe à une description microscopique en discutant le cadre du paysage d'énergie potentielle et le rôle des fonctions de corrélation de densité telles que l'ISF. Les processus de relaxation dans les liquides surfondus et les verres sont présentés, suivis d'une discussion sur la *polyamorphie*, la coexistence de plusieurs formes amorphes partageant la même composition mais différant par leur structure et leurs propriétés thermodynamiques. Enfin, nous passons en revue les propriétés anormales des verres à basse température et les deux principaux modèles théoriques proposés pour les expliquer.

Le **deuxième chapitre** expose la motivation de ce travail. À partir de la phénoménologie de la stabilité des verres, nous décrivons comment elle peut être modulée, soit en utilisant différentes méthodes de préparation, telles que le trempe-fusion et le dépôt physique en phase vapeur, soit en appliquant des traitements externes comme l'irradiation lumineuse et les déformations mécaniques. Pour chaque approche, nous présentons l'état de l'art et mettons en évidence les questions ouvertes qui constituent la base de cette Thèse.

Le **troisième chapitre** détaille les méthodes expérimentales utilisées dans ce travail. Après une brève introduction aux processus de diffusion, nous décrivons en détail la technique NRAIXS pour la mesure de la densité

d'états vibrationnelle dans les verres ultra-stables et ordinaires, ainsi que la technique XPCS pour la mesure directe de la fonction de corrélation intermédiaire sous irradiation et haute pression. Pour les deux techniques, les fondements théoriques, les montages expérimentaux et les procédures d'analyse des données sont présentés. Les techniques complémentaires, telles que la spectroscopie Raman et la nanocalorimétrie rapide, sont également discutées.

Le **quatrième chapitre** présente les résultats relatifs à la dynamique vibrationnelle des verres ultra-stables et ordinaires. Après la description des échantillons étudiés, nous rapportons et analysons en détail les mesures de densité d'états vibrationnelle. Une procédure d'ajustement dédiée, développée dans ce travail, permet une comparaison directe avec les données de chaleur spécifique à basse température sur des échantillons équivalents. Les mesures Raman sont ensuite présentées, et les résultats sont discutés à la lumière des deux principaux modèles des anomalies des verres à basse température.

Le **cinquième chapitre** se concentre sur l'effet de l'irradiation lumineuse et de la compression sous haute pression sur la dynamique de relaxation structurale. Nous décrivons d'abord les échantillons étudiés, puis présentons les résultats de l'irradiation X, qui induit une transition de type *yielding* dont l'efficacité dépend de la composition du verre. Nous rapportons ensuite les résultats obtenus sous compression à haute pression, révélant une transition polyamorphe et une dépendance non monotone de la dynamique vis-à-vis de la pression. Les mesures de nanocalorimétrie rapide montrent que la densification conduit à une réjuvenation. Pour ces deux études de cas, les résultats sont interprétés et discutés dans le contexte de la littérature existante.

Le **sixième chapitre** résume les principales conclusions de ce travail et esquisse des perspectives pour approfondir la compréhension microscopique de la stabilité des verres.

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Résumé du Chapitre 1

Ce Chapitre propose une introduction théorique à la physique des verres et des liquides surrefondus, en mettant l'accent sur leurs propriétés structurales, thermodynamiques et dynamiques. La transition vitreuse est d'abord présentée comme un phénomène cinétique au cours duquel un liquide surfondu sort de l'équilibre et forme un solide amorphe. Les notions de viscosité, de fragilité cinétique et la classification d'Angell sont introduites afin de caractériser les formateurs de verre. Une perspective thermodynamique est ensuite développée à partir des considérations d'entropie et du cadre du paysage d'énergie potentielle (PEL), qui permet d'expliquer des phénomènes tels que le paradoxe de Kauzmann, le vieillissement physique et le rajeunissement. Le PEL fournit également un éclairage sur les comportements distincts des systèmes fragiles et forts, ainsi que sur les notions de stabilité cinétique et thermodynamique. Le Chapitre examine ensuite la structure et la dynamique microscopiques des systèmes désordonnés à travers les fonctions de corrélation, les observables de diffusion et le lien entre processus de relaxation et viscoélasticité. Une attention particulière est accordée à la hiérarchie des mécanismes de relaxation — vibrations rapides, relaxation β et relaxation α — ainsi qu'à leur relation avec les réarrangements coopératifs. Les transitions liquide-liquide et le polyamorphisme sont également discutés, en mettant en évidence l'existence possible de plusieurs états liquides aux structures distinctes. Enfin, les anomalies thermiques universelles des verres à basse température, telles que le boson peak et les états de tunneling, sont présentées à travers des modèles fondés sur la densité d'états vibrationnels.

Chapter 1

Theoretical introduction

This Chapter introduces the fundamental physics of glasses and supercooled liquids. It outlines the nature of the glass transition, the role of viscosity and fragility, and the thermodynamic perspective provided by the potential energy landscape. Structural and dynamical features are described through correlation functions, relaxation processes, and viscoelastic response. We also highlight phenomena such as liquid-liquid transitions, polyamorphism, and the universal low-temperature anomalies of glasses.

1.1 Supercooled liquids and the glass transition

Glasses are amorphous solids that lack long-range order, in contrast to crystals, which are characterised by a periodical and highly ordered lattice. The most common method to obtain a glass is to quench a material from its liquid state fast enough to avoid crystallisation [7, 10, 11].

Figure 1.1 depicts the temperature dependence of volume (or enthalpy) for a liquid at constant pressure. If the liquid is cooled down below its melting temperature T_m slowly enough, molecules have sufficient time to rearrange in an ordered way, creating a crystal. On the other hand, if the cooling rate is adequately high, the liquid enters a metastable phase, known as *supercooled liquid state*. As the temperature decreases, molecular motion slows down and the viscosity η of the liquid increases, such that the time required for the system to reach the equilibrium is longer and longer. At the glass transition temperature T_g , the viscosity becomes so large that the time for particles to reorganise is too long and molecules are trapped: the system falls out of equilibrium from the supercooled liquid state, becoming a glass [10]. The glass-transition temperature T_g is the temperature at which η reaches a value of 10^{12} Pa·s. At this point, the characteristic timescale

for molecular dynamics is about 100 s, and the system is no longer able to flow [11]: on the timescale of the experimental observation, the material can be considered a solid.

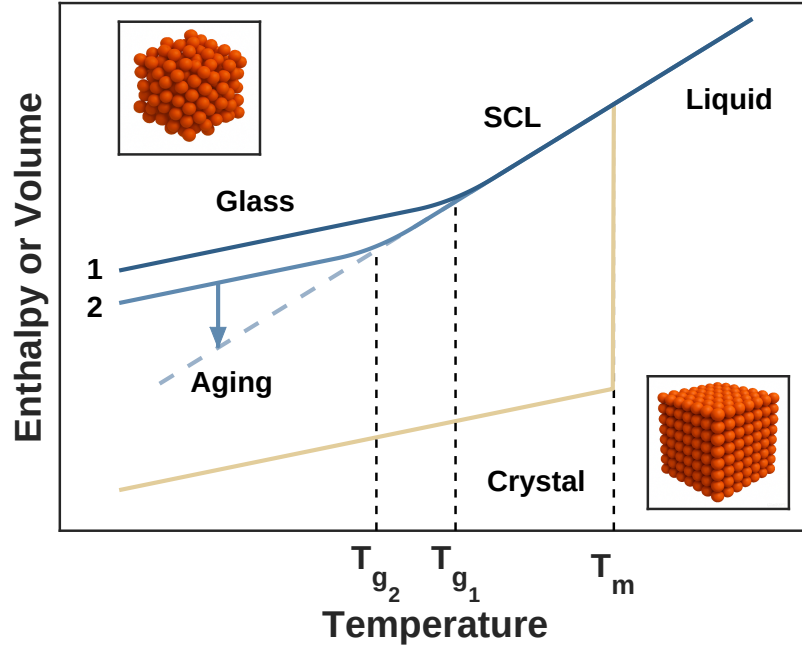


Figure 1.1: The enthalpy or the molar volume as a function of the temperature. Below the melting temperature, a liquid can undergo crystallisation (blue line) if it is cooled down slowly enough. Otherwise, the liquid becomes a supercooled liquid and at the glass transition temperature T_g , a glass is obtained (line 1). The slower the cooling, the denser the glass and the lower T_g (line 2). Through isothermal aging even denser glass can be generated (line 3). Furthermore, the typical particle configurations obtained from molecular dynamics simulations are illustrated for a glass, a supercooled liquid, and a crystal. Figure adapted from [10].

If the glass is maintained below T_g for a sufficiently long time, it undergoes *physical aging*, a slow densification toward the equilibrium supercooled liquid state, driven by the system's thermodynamic tendency to minimise free energy. This process is illustrated in Figure 1.1, line 3 (dashed yellow), and it may take geological timescales since the closer to the equilibrium state, the longer the time to rearrange is required [10].

It is crucial to highlight that the glass transition is not a first-order phase

transition. Unlike crystallisation, there is no discontinuity in volume or enthalpy at T_g . The glass transition is not even a second-order phase transition, since the transition depends on the thermal history of the system [7, 10, 11]. Slower cooling rates allow more molecular relaxation, since molecules have more time to rearrange before further cooling occurs, leading to denser glasses and lower T_g values, as also depicted in Figure 1.1. Moreover, a true phase transition occurs between equilibrium states, while glass formation marks the kinetic arrest of a system out of equilibrium.

Microscopically, glasses retain the disordered structure of the supercooled liquid, as shown from the particle configurations obtained from molecular dynamics simulations in Figure 1.1.

1.1.1 Kinetic fragility: temperature dependence of viscosity

As we have seen, viscosity η is a key macroscopic observable for describing supercooled liquids. The temperature dependence of η is a crucial factor used to classify these materials and is typically studied using the so-called *Angell plot*, where $\log_{10}(\eta)$ is plotted as a function of the inverse reduced temperature T_g/T [7, 11]. Based on the shape of $\eta(T)$ -curve, systems are classified as *strong* or *fragile* glass formers, terms that describe the sensitivity of the liquid to temperature changes [7, 11].

Strong liquids follow an Arrhenius law:

$$\eta = \eta_0 \exp\left(\frac{E}{k_B T}\right), \quad (1.1.1)$$

where η_0 is a phenomenological parameter and E is an effective activation energy. In the Angell plot, the $\eta(T)$ -curve of a strong system is a straight line, as illustrated in Figure 1.2. Usually, strong liquids are characterised by open networks and covalent bonds.

In contrast, fragile glass formers exhibit a super-Arrhenius increase in viscosity upon cooling (see Figure 1.2), which indicates that the activation energy increases on approaching T_g [7, 11]. The phenomenological equation describing a fragile glass-forming is the Vogel-Fulcher-Tammann:

$$\eta = \eta_0 \exp\left(\frac{DT_0}{T - T_0}\right), \quad (1.1.2)$$

where η_0 , D and T_0 are phenomenological parameters.

The degree of the fragility of a system can be quantified by the kinetic fragility m [11], which is the slope of $\log_{10}(\eta(T))$ in the limit of T approaching

T_g

$$m = \lim_{T \rightarrow T_g} \frac{\partial \log_{10}(\eta(T))}{\partial \frac{T_g}{T}} . \quad (1.1.3)$$

The fragility ranges from values of $m \sim 17$ for strong glass formers to $m \sim 150$ for very fragile ones.

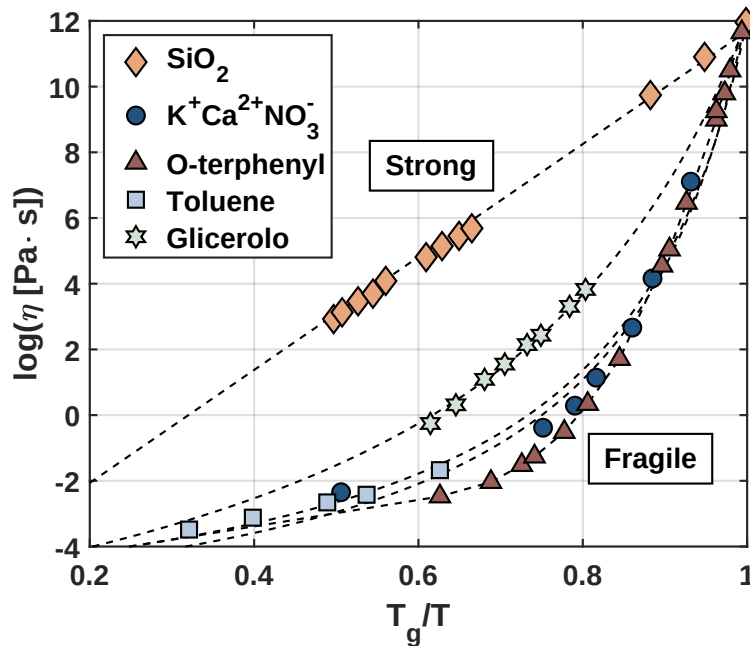


Figure 1.2: Arrhenius plot of viscosity for strong and fragile glass formers. Strong systems (e.g., SiO_2) exhibit linear behaviour, while fragile liquids (e.g., o-Terphenyl) show super-Arrhenius curves. Data taken from [7].

1.2 Potential energy landscape

While viscosity provides a macroscopic classification, a deeper understanding of the glass transition requires a more fundamental, thermodynamic perspective. This is provided by the concepts of entropy and the potential energy landscape (PEL).

Entropy S is a fundamental thermodynamic quantity that measures the number of microscopic configurations accessible to a system. In the case of liquids, the entropy is greater than that of the corresponding crystal at the same temperature, due to their higher degree of disorder. This difference is

quantified by the excess entropy [11]:

$$S_{\text{liq}}(T) = S_{\text{cry}}(T) + S_{\text{exc}}(T) , \quad (1.2.1)$$

where S_{liq} and S_{cry} are the entropies of the liquid and crystalline phases, respectively, and S_{exc} is the excess entropy.

As temperature decreases, $S_{\text{exc}}(T)$ decreases as well. However, below the glass transition temperature T_g , the system falls out of equilibrium, making it impossible to measure S_{exc} directly. By extrapolating S_{exc} to lower temperatures, it is observed to reach 0 linearly at a temperature T_K , known as the *Kauzmann temperature*. Below T_K , the extrapolated entropy of the liquid would be lower than that of the crystal, which appears as a paradox, since a crystal is a more ordered phase than a liquid. This scenario is referred to as the *entropy crisis* [7]. Nonetheless, there is no fundamental thermodynamic law preventing $S_{\text{liq}}(T)$ from becoming lower than $S_{\text{cry}}(T)$ [12].

To better understand these notions, it is helpful to introduce the concept of configurational entropy and the framework of the potential energy landscape (PEL). According to Boltzmann's formula:

$$S(N, V, E) = k_B \ln \Omega , \quad (1.2.2)$$

where k_B is Boltzmann's constant and Ω is the number of accessible microscopic configurations for a system with N particles, volume V , and energy E . Since $\Omega \geq 1$, entropy is always non-negative. In the limit of extremely slow cooling, the system may reach a unique low-energy configuration, causing the entropy to approach zero. To avoid the entropy crisis, it is hypothesised that the supercooled liquid undergoes a thermodynamic phase transition at T_K to an ideal glass, characterised by a single configurational state [7]. This can be represented in a qualitative way by the potential energy landscape, a topographic description of the glass transition [7]. First introduced by Goldstein in 1969, the PEL is the multidimensional hypersurface defined by the potential energy function $U(\mathbf{r}_1, \dots, \mathbf{r}_N)$ for N particles. While it resides in a $3N$ -dimensional configurational space, it is commonly visualised in two dimensions for clarity (see Fig. 1.3). The landscape is characterised by shallow valleys (*basins*) grouped into larger dales, known as *metabasins*. Thus, the key features of the PEL are local minima (*inherent structures*), saddle points, and barriers. Changes in the system density determine the deformation of the landscape, which for a system of N particles in a volume V is fixed. Each minimum corresponds to a metastable configuration, while the system's dynamics are governed by transitions between these basins.

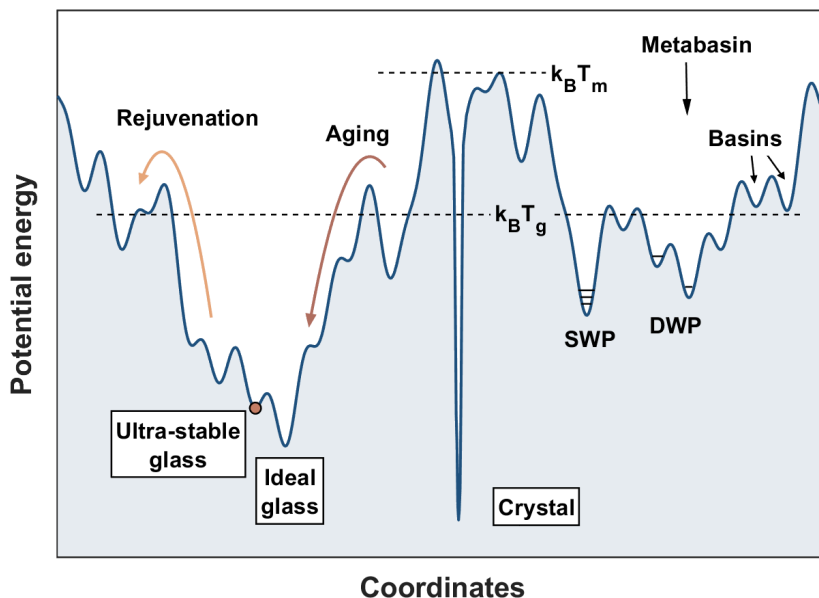


Figure 1.3: Schematic two-dimensional illustration of the potential energy landscape (PEL) for supercooled liquids and glasses. The x-axis represents configurational coordinates. Below the melting temperature T_m , the landscape features numerous valleys (basins), corresponding to metastable configurations. At high temperatures, the system samples the entire landscape. Below T_g , it becomes trapped in a local minimum. Deeper minima represent more stable glasses, with the hypothetical ideal glass occurring at T_K . Aging allows the system to reach lower minima, while rejuvenation moves it toward higher-energy configurations. Double-well and single-well potentials are also indicated (see Paragraph 1.6). Physical vapor deposition techniques enable preparation of glasses in deep regions of the PEL (see Paragraph 2.1.2). The crystalline state lies in the global minimum, representing the most thermodynamically stable configuration. Figure inspired from [2].

At high temperatures, the system has enough thermal energy to explore the full landscape, easily surmounting energy barriers, including those surrounding deep metabasins. As the temperature decreases and the system enters the supercooled liquid (SCL) regime, its dynamics slows down, and transitions between basins occur via thermally activated jumps. When $k_B T$ becomes comparable to the barrier heights of a metabasin, the system remains trapped there, losing ergodicity and entering the glassy state. If crystallisation is avoided, the system can only explore a limited region of the PEL on experimental timescales. At the Kauzmann temperature, it is spec-

ulated that the configurational entropy of the liquid vanishes and the system undergoes a thermodynamic phase transition: a unique configuration would be allowed, leading to the ideal glass state.

The PEL paradigm allows for a better understanding of the aging processes as well. In the glassy state, the system is out of equilibrium and it tries to reach a more stable configuration, i.e. deeper energy minima [13]. It is also possible to push a glass toward higher-energy configurations, a process known as *rejuvenation* (see Fig. 1.3), which is typically induced via mechanical deformation or rapid thermal cycling [14–21].

Furthermore, the shape of PEL can describe the two different families of glass formers: fragile systems are characterised by a landscape with numerous metabasins, in which the system gets easily stuck during the cooling, whereas strong liquids have a smoother landscape with fewer, deeper basins [7].

Finally, we introduce the concepts of kinetic and thermodynamic stabilities. The *kinetic stability* is related to the speed with which the system moves toward more stable configurations [22]. In a PEL description, the kinetic stability can be considered as the height of the barrier that the system has to surmount to reach a more equilibrated state [2]: lower barriers result in faster relaxation dynamics, whereas the higher the barriers, the more time to reach a more stable state is needed. *Thermodynamic stability*, on the other hand, is associated with the depth of the energy minima: deeper minima correspond to more stable configurations [2, 23]. Glasses formed with slower cooling rates are typically more thermodynamically stable, as they settle into deeper energy basins and exhibit lower T_g values.

1.3 Structure and dynamics of disordered systems

Having phenomenologically described the thermodynamics and dynamics of disordered systems (e.g., volume, enthalpy, viscosity vs. temperature) and introduced the potential energy landscape as a tool for visualising these properties, it is useful to introduce mathematical quantities to represent the dynamics at the microscopic level.

Let us consider a uniform system composed of N particles, with coordinates $\mathbf{q}^N = \mathbf{r}^N = (\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$. Their instantaneous spatial distribution is described by the microscopic particle density [24]:

$$\rho(\mathbf{r}, t) = \sum_{i=1}^N \delta[\mathbf{r} - \mathbf{r}_i(t)] \quad , \quad (1.3.1)$$

which counts the number of particles located in the neighbourhood of point $\mathbf{r}$ at time t . In reciprocal space, the density reads:

$$\rho(\mathbf{q}, t) = \sum_{i=1}^N e^{-i\mathbf{q} \cdot \mathbf{r}_i(t)} . \quad (1.3.2)$$

To study how particles move and correlate in space and time, one introduces the van Hove correlation function [24, 25]:

$$G(\mathbf{r}, t) = \frac{1}{N} \left\langle \sum_{i=1}^N \sum_{j=1}^N \delta[\mathbf{r} - \mathbf{r}_j(t) + \mathbf{r}_i(0)] \right\rangle . \quad (1.3.3)$$

This is a space-time correlation function that gives the probability of finding a particle j at position $\mathbf{r}_j(t)$ at time t , provided another particle i was at $\mathbf{r}_i(0)$ at the initial time. It can be rewritten in terms of density-density correlations:

$$\begin{aligned} G(\mathbf{r}, t) &= \frac{1}{N} \left\langle \sum_{i=1}^N \sum_{j=1}^N \int d\mathbf{r}' \delta[\mathbf{r}' + \mathbf{r} - \mathbf{r}_j(t)] \delta[\mathbf{r}' - \mathbf{r}_i(0)] \right\rangle \\ &= \frac{1}{N} \int \langle \rho(\mathbf{r}' + \mathbf{r}, t) \rho(\mathbf{r}', 0) \rangle d\mathbf{r}' \\ &= \frac{1}{\rho} \langle \rho(\mathbf{r}, t) \rho(\mathbf{0}, 0) \rangle , \end{aligned} \quad (1.3.4)$$

where ρ is the average particle density. Physically, $G(\mathbf{r}, t) d\mathbf{r}$ represents the probability of finding a particle in a volume element $d\mathbf{r}$ around $\mathbf{r}$ at time t , given that another particle was at the origin at $t = 0$ [24].

The van Hove function can be decomposed into two terms:

$$G(\mathbf{r}, t) = G_s(\mathbf{r}, t) + G_d(\mathbf{r}, t) , \quad (1.3.5)$$

where $G_s(\mathbf{r}, t)$ is the *self part* and $G_d(\mathbf{r}, t)$ the *distinct part*, defined respectively as:

$$G_s(\mathbf{r}, t) = \frac{1}{N} \left\langle \sum_{i=1}^N \delta[\mathbf{r} - \mathbf{r}_i(t) + \mathbf{r}_i(0)] \right\rangle , \quad (1.3.6)$$

$$G_d(\mathbf{r}, t) = \frac{1}{N} \left\langle \sum_{i=1}^N \sum_{j \neq i}^N \delta[\mathbf{r} - \mathbf{r}_j(t) + \mathbf{r}_i(0)] \right\rangle . \quad (1.3.7)$$

These two terms account for whether $i = j$ (self) or $i \neq j$ (distinct).

In the long-time limit ($t \rightarrow \infty$), both components become independent of position [24]:

$$\lim_{t \rightarrow \infty} G_s(\mathbf{r}, t) = \frac{1}{V} , \quad \lim_{t \rightarrow \infty} G_d(\mathbf{r}, t) = \rho , \quad (1.3.8)$$

where V is the volume of the system.

The Van Hove function $G(\mathbf{r}, t)$ contains both spatial and temporal information. For $t = 0$, it reduces to the instantaneous spatial distribution of particles, i.e. a static picture of their correlations

$$G(\mathbf{r}) = \frac{1}{\rho} \langle \rho(\mathbf{r}) \rho(\mathbf{0}) \rangle . \quad (1.3.9)$$

In the case of a homogeneous and isotropic system, this reduces to

$$G(\mathbf{r}) = \rho g(r) , \quad (1.3.10)$$

where $g(r)$ is the radial distribution function, or *pair distribution function*. In liquids and glasses, $g(r)$ exhibits a series of peaks, tends to unity at large r , and vanishes as $r \rightarrow 0$. Its shape encodes the structural organisation of the system, since the average number of particles located between r and $r + dr$ from a reference particle is given by $4\pi r^2 \rho g(r) dr$. The peaks in $g(r)$ correspond to successive “shells” of neighbours. The first peak describes the short-range order, characterising the local environment of nearest neighbours. Integrating over this peak yields the average coordination number [24]. At larger distances, up to 1-2 nm, $g(r)$ reflects the medium-range order (MRO), describing correlations extending beyond the first shell [26].

While real-space correlations provide a direct picture of atomic arrangements, scattering experiments probe dynamics in reciprocal space. For this reason, we introduce the correlation of Fourier-transformed density fluctuations [24]:

$$F(\mathbf{q}, t) = \frac{1}{N} \langle \rho(\mathbf{q}, t) \rho(-\mathbf{q}, 0) \rangle , \quad (1.3.11)$$

which is known as the *intermediate scattering function* (ISF). The ISF is related to the van Hove function by a spatial Fourier transform:

$$F(\mathbf{q}, t) = \int G(\mathbf{r}, t) e^{-i\mathbf{q} \cdot \mathbf{r}} d\mathbf{r} . \quad (1.3.12)$$

By tuning the momentum transfer $\mathbf{q}$ (set by the probe, e.g. X-rays or neutrons), one can select the length scale of density fluctuations being probed (see Sec. 3.3.1.2).

The time Fourier transform of the ISF yields the *dynamic structure factor*:

$$S(\mathbf{q}, \omega) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} F(\mathbf{q}, t) e^{i\omega t} dt . \quad (1.3.13)$$

Integration over frequency gives

$$\int_{-\infty}^{+\infty} S(\mathbf{q}, \omega) d\omega = F(\mathbf{q}, 0) = \frac{1}{N} \langle \rho(\mathbf{q}, 0) \rho(-\mathbf{q}, 0) \rangle , \quad (1.3.14)$$

which defines the *static structure factor*:

$$S(\mathbf{q}) = \frac{1}{N} \left\langle \sum_{i=1}^N \sum_{j=1}^N e^{i\mathbf{q} \cdot (\mathbf{r}_i - \mathbf{r}_j)} \right\rangle . \quad (1.3.15)$$

For a homogeneous system, this simplifies to

$$S(\mathbf{q}) = 1 + \rho \int (g(\mathbf{r}) - 1) e^{i\mathbf{q} \cdot \mathbf{r}} d\mathbf{r} . \quad (1.3.16)$$

The static structure factor thus reflects the degree of microscopic order. In crystals, $S(\mathbf{q})$ displays sharp Bragg peaks, evidencing long-range order. In liquids and glasses, the peaks are broader, signalling the absence of periodicity and the predominance of short- and medium-range correlations. In particular, the position of the first sharp diffraction peak (FSDP) is associated with the periodicity of the MRO.

Finally, the ISF is usually normalised to unity at $t = 0$ using $S(\mathbf{q})$:

$$F(\mathbf{q}, t) \rightarrow \frac{F(\mathbf{q}, t)}{S(\mathbf{q})} . \quad (1.3.17)$$

In liquids and glasses, $F(\mathbf{q}, t)$ is typically a decaying function of time, reflecting the progressive loss of correlation between microscopic configurations. The shape of this decay encodes the relevant dynamical mechanisms, ranging from short-time particle motions to the much slower structural rearrangements that dominate near the glass transition. Understanding this temporal behaviour of $F(\mathbf{q}, t)$ provides direct insight into the *relaxation processes*, which correspond to the microscopic dynamics of the system.

1.4 Relaxation processes

In this Section, we delve into a detailed discussion of relaxation processes, which are commonly investigated through the time dependence of the intermediate scattering function $F(\mathbf{q}, t)$ [27]. This function measures how similar the configuration of the system at a given time is to that at a later time t , with the wavevector $\mathbf{q}$ representing the inverse of the probed length scale. In

glass-forming systems, the decay of $F(\mathbf{q}, t)$ exhibits a non-trivial behaviour, reflecting a complex hierarchy of dynamical regimes.

In what follows, we focus on the structural (or α -) relaxation, which governs the long-time dynamics and is most directly linked to the glass transition. We will establish connections between microscopic relaxation and macroscopic viscoelasticity through the Maxwell relation, introduce phenomenological models to describe the decay of $F(\mathbf{q}, t)$, examine the q -dependence of the relevant dynamical parameters, and finally discuss the dynamical heterogeneities.

1.4.1 Relaxation processes in SCLs and glasses

In simple liquids, the intermediate scattering function $F(\mathbf{q}, t)$ typically exhibits a single exponential decay, reflecting the random, uncorrelated motion of particles in Brownian diffusion. In contrast, supercooled liquids (SCLs) and glasses show more complex dynamics, marked by multiple relaxation regimes (see Figure 1.4a)).

At very short timescales (picoseconds and sub-picoseconds), the dynamics are dominated by the *vibrational dynamics* of particles within their cages, formed by neighboring particles. These rapid, localized oscillations, often referred to as “rattling,” prevent free diffusion. As the temperature decreases, the amplitude of these motions diminishes, reflecting the increasing rigidity of the cage structure [28].

After these fast motions, the ISF enters a plateau region, followed by the onset of secondary relaxations, commonly known as β -relaxations. Among these, the Johari-Goldstein (JG) β -relaxation is particularly important and universal across all glass formers [29, 30]. In this regime, particles remain confined in their cages but exhibit slower, collective motions, leading to local structural rearrangements [7, 11, 29, 30]. β -relaxations typically occur on timescales between 10^{-6} and 10^{-3} [7, 11, 29, 30]. Within the potential energy landscape (PEL) framework, the JG β -relaxation corresponds to local jumps within a single metabasin.

At longer timescales, the system undergoes the final decay in $F(\mathbf{q}, t)$, known as α -relaxation or *structural relaxation* [27]. This process describes the escape of particles from their cages and transitions between different metabasins in the PEL. These rearrangements involve cooperative motion of many particles, overcoming significant energy barriers. Such events define *Cooperative Rearranging Regions* (CRRs), whose size and timescales increase markedly as the system approaches the glass transition [31]. Structural relaxation times can range from a few picoseconds in high-temperature liquids [32] to hundreds of seconds near the glass transition temperature T_g , and even

reach geological timescales in deeply glassy states. A schematic representation of the α -relaxation is reported in Figure 1.4b), where the insets illustrate the gradual loss of correlation between the instantaneous configurations of the system and the initial one.

The height of the plateau between the β - and α -relaxations is referred to as the *non-ergodicity factor*, f_q . It quantifies the extent to which the system is trapped in a non-ergodic state.

Figure 1.5 shows the temperature dependence of the characteristic decay times for both β - and α -relaxations in 1-propanol [33]. The two processes generally begin to decouple around $1.2 T_g$ [7, 34]. At lower temperatures, where the α -relaxation becomes experimentally inaccessible due to its extremely long timescale, the β -relaxation remains active, governing the residual microscopic dynamics [7, 34].

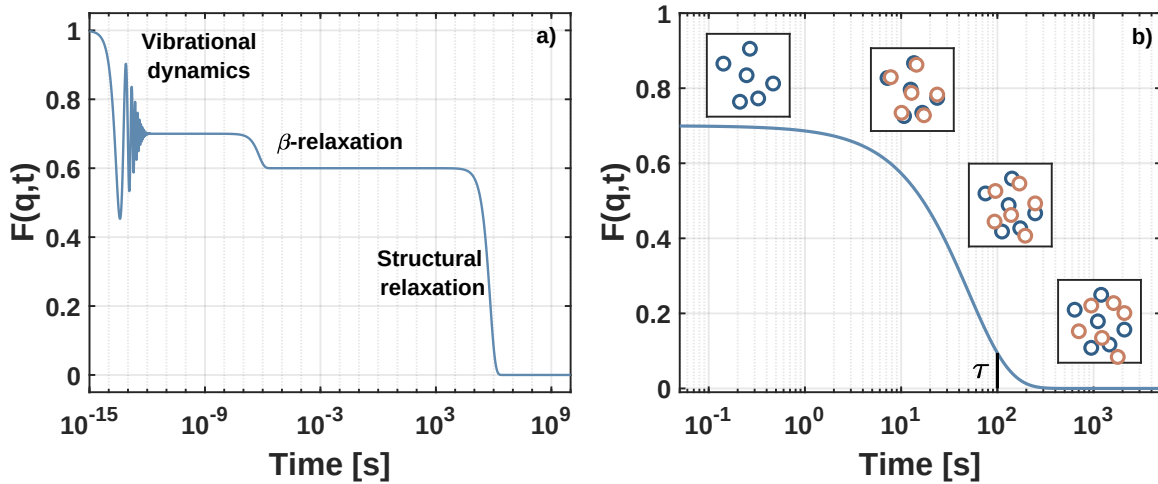


Figure 1.4: a) Sketch of the intermediate scattering function $F(\mathbf{q}, t)$ for a supercooled liquid close to its glass transition temperature. The main relaxation processes are shown. Adapted from [13]. b) Schematic representation of the intermediate scattering function $F(\mathbf{q}, t)$ in the α -relaxation regime. Insets depict the system's microscopic configuration over time, illustrating the gradual loss of structural correlation. Adapted from [35].

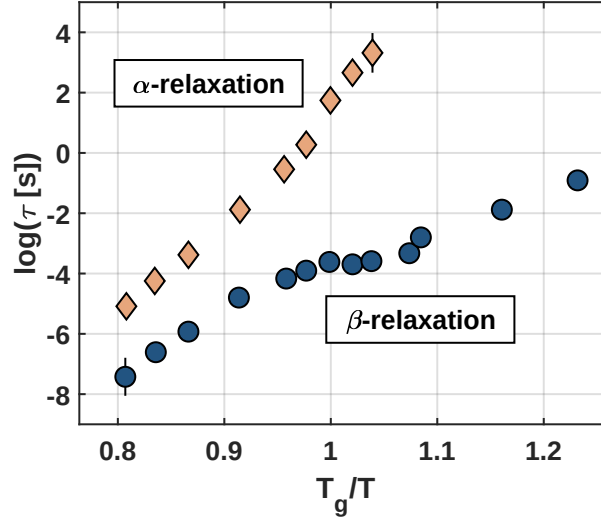


Figure 1.5: Temperature dependence of the characteristic decay times of β - and α -relaxations in 1-propanol. Data taken from [33].

1.4.2 The α -relaxation

The α -relaxation is the main relaxation process in supercooled liquids and plays a central role in the dynamic arrest that occurs at the glass transition. In fact, there is a connection between the microscopic dynamics and the macroscopic properties, described by Maxwell's viscoelastic model [10,11,30]. According to this framework, the structural relaxation time τ_α is related to the macroscopic viscosity η via:

$$\eta = G_\infty \tau_\alpha , \quad (1.4.1)$$

where G_∞ is the shear modulus of a material when it is subjected to an oscillatory shear deformation at infinitely high frequency, and typically is on the order of 10^9 Pa. As the system cools toward T_g , τ_α dramatically increases and reaches approximately 100 s at the glass transition. According to this theory, a viscoelastic material, liquid or solid, does not respond instantaneously to stresses but it will relax over time [36]. This relation forms the basis of theories such as the Adam-Gibbs model, which connects the growth of CRRs and the corresponding increase in τ_α to the decreasing configurational entropy near the glass transition [31].

The structural relaxation cannot be described by a simple exponential decay, but rather by the *Kohlrausch-Williams-Watts* (KWW) function [29] (see Figure 1.4a)):

$$F(\mathbf{q}, t) = f_q \exp \left[- \left(\frac{t}{\tau_q} \right)^{\beta_{KWW}} \right] , \quad (1.4.2)$$

where f_q is the non-ergodicity factor, τ_q the characteristic relaxation time, and β_{KWW} the shape parameter, which quantifies the deviation from a simple exponential behaviour. Usually, in the SCL, $\beta_{KWW} < 1$, indicating a stretched exponential relaxation. In this case, the decay is initially faster but develops a long-time tail, so that correlations persist much longer than in a simple exponential. In this sense, the relaxation is effectively “slower” (thus, stretched). As we will see below, β_{KWW} reflects the presence of a broad distribution of relaxation times, attributed to dynamic heterogeneity. The non-ergodicity factor f_q , as said, corresponds to the height of the long-time plateau of the intermediate scattering function that precedes the α -relaxation, and depends both on the amplitude of the atomic vibrations and the degree of disorder of the glass [27].

The KWW parameters, τ_q , β_{KWW} , and f_q , depend on several factors, including temperature, pressure, and the probed wavevector $\mathbf{q}$. For instance, in the case of simple Brownian diffusion, the relaxation time obeys the well-known scaling law [37]:

$$\tau_q = \frac{1}{Dq^2} , \quad (1.4.3)$$

where D is the diffusion coefficient and $q = |\mathbf{q}|$. Deviations from this q^{-2} scaling indicate *anomalous diffusion*. A weaker q -dependence (effective exponent $n < 2$ in $\tau_q \sim q^{-n}$) is characteristic of faster-than-diffusive, nearly ballistic dynamics, often reported in colloidal glasses and gels under internal stresses [38]. Conversely, a stronger q -dependence ($n > 2$) corresponds to *sub-diffusive* behavior, typical of systems with constrained dynamics, such as polymers or colloids approaching the glass transition [39, 40].

The Brownian scaling is valid in the low- q limit, i.e. in the hydrodynamic (macroscopic) regime. At intermediate q values, the relaxation time τ_q and, to a lesser extent, the stretching exponent β_{KWW} reflect the features of the static structure factor $S(\mathbf{q})$, giving rise to the phenomenon known as *De Gennes narrowing* [41–43]. This effect was first observed in quasi-elastic neutron scattering experiments, where the linewidth of the dynamic structure factor $S(\mathbf{q}, \omega)$, directly related to the decay of the intermediate scattering function

$F(\mathbf{q}, t)$ [44], was found to narrow at wavevectors corresponding to the first sharp diffraction peak (FSDP) of the liquid.

De Gennes showed that

$$\tau_q \sim \frac{S(q)}{Dq^2} , \quad (1.4.4)$$

which implies a slowing down of the dynamics at wavevectors near the FSDP of $S(\mathbf{q})$. This reflects that structurally favoured configurations are dynamically more stable. In other words, relaxation is slower over intermolecular distances because molecules must move into regions already occupied by nearby particles. The De Gennes narrowing has been observed in real liquids, SCL and some glasses [42, 43], and it is another manifestation of the interplay between structure and dynamics [41].

Dynamical heterogeneities

The origin of the nonexponential relaxation observed in supercooled liquids and glasses has been the subject of a long-standing debate. One possible interpretation is the homogeneous scenario, according to which the stretched character of the intermediate scattering function is an intrinsic property of the system. In this view, all regions of the material relax in the same non-exponential manner, and the local dynamics coincides with the ensemble-averaged one. The stretching is thus not the result of a spatial average over regions with different mobilities, but rather reflects the intrinsically disordered environment that each particle experiences at the microscopic level [45].

In contrast, the heterogeneous scenario attributes the nonexponential behaviour to a spatial distribution of relaxation times. In this picture, the Kohlrausch-Williams-Watts (KWW) function can be interpreted as a continuous superposition of exponential decays,

$$F(\mathbf{q}, t) = \int_0^{+\infty} G(\tau) e^{-t/\tau} d\tau , \quad (1.4.5)$$

where $G(\tau)$ is a distribution function of relaxation times. The shape parameter β_{KWW} quantifies the breadth of this distribution: smaller values indicate broader $G(\tau)$ and thus stronger dynamical heterogeneity [45]. This interpretation implies that supercooled liquids and glasses consist of regions that relax at different rates, forming transient nanometric clusters (2-3 nm) of slow or fast particles. Extensive simulations and experiments support this view, showing that the dynamical slowing down near the glass transition is accompanied by a growing correlation length over which local dynamics is

spatially correlated [34, 46–56]. Thus, while both scenarios have been considered, current evidence strongly favours the heterogeneous origin of the observed stretched relaxation.

The difficulty of directly probing microscopic dynamics has long sustained the homogeneous interpretation, since most experimental techniques measure ensemble-averaged quantities. Even at present, dynamical heterogeneities have been directly observed only in a limited set of systems, most notably colloidal suspensions or granular materials, where particle sizes are large enough to be imaged by microscopy [50, 52, 57]. However, both simulations [34, 46, 47] and experimental evidence from colloids and structural glasses [48–54] strongly support the presence of genuine dynamical heterogeneities as the glass transition is approached.

1.5 Polyamorphism

So far, we have focused on the universal phenomenology of amorphous systems. Glass-forming liquids can be classified as strong or fragile, depending on the temperature dependence of the viscosity η . However, certain systems exhibit anomalous changes in viscosity upon cooling, as shown in Figure 1.6, where a transition from fragile to strong behaviour (F-S) occurs. This fragile-to-strong (F-S) dynamical crossover has been reported in many systems, among which are silica, B_2O_3 , GeO_2 , chalcogenides, and metallic liquids [58–68].

In many cases, this crossover is linked to a transition between two liquid phases of the same composition, characterised by different local structures and thermodynamic properties [69, 70]. This phenomenon is known as a *liquid-liquid transition* (LLT) and can be induced by either temperature or pressure changes [69]. Across an LLT, anomalies appear in quantities such as the heat capacity, thermal expansion coefficient, and compressibility [60, 71–74]. In some cases, the LLT is sharp and discontinuous, exhibiting first-order behaviour with coexistence of two liquid phases of distinct structure [75] and density [76], as observed in phosphorus, silicon, and model systems of water [69]. In other systems, such as chalcogenide melts, LLTs of higher order have been reported. Depending on the material, the LLT may occur in the equilibrium liquid above the melting point [75–77], or in the metastable supercooled liquid [70, 78, 79]. In the latter case, its observation is particularly challenging because of the limited stability range between crystallisation at high T and vitrification at lower T [80].

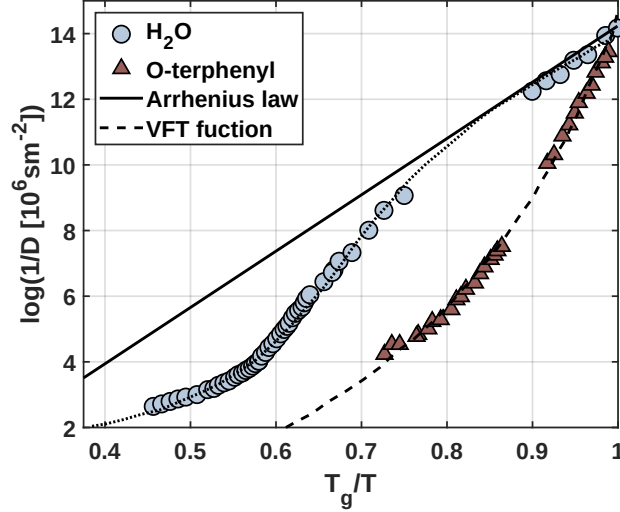


Figure 1.6: Angell plot of the inverse liquid diffusion coefficient D , related to viscosity, showing the fragile-to-strong dynamical crossover upon cooling. Data taken from [68].

A typical signature of an LLT is a crossover from a high-density liquid (HDL) to a low-density liquid (LDL) upon cooling. Above the transition, the density increases with decreasing T as expected; at the transition, density reaches a maximum, and below it, density decreases, leading to negative thermal expansion [69].

Experimentally, LLTs have been observed in numerous atomic systems, including S [77], Si [70], and P [75, 76], and suggested for Ge [70], Ga [81–84], Bi [85, 86], Sb, Ce [87], Te, and Se [70]. Oxides such as SiO_2 , GeO_2 , and B_2O_3 also display signatures of LLT [88]. Furthermore, LLTs are expected in several molecular liquids, including water, triphenyl phosphite (TPP) [89, 90], n-butanol [91], D-mannitol [92–94], trans-1,2-dichloroethylene [95–100], and molten sodium acetate trihydrate [101].

The solid counterpart of LLT is the *amorphous-amorphous transition* (AAT), or glass-glass transition (GGT), usually induced by pressure [102]. This phenomenon has been observed in water [103–105], silica, silicon, germanium, chalcogenides, molecular liquids, TPP, and even some metallic liquid glass formers [106–110]. Although LLT and AAT appear related, the connection is not obvious: LLT occurs thermodynamically between ergodic liquid states, whereas AAT occurs mechanically between non-ergodic amorphous states [70]. In AAT, increasing pressure drives a transformation from a low-density amorphous (LDA) to a high-density amorphous (HDA)

state [102]. Experimentally, AATs are detected through abrupt changes in structure under pressure. For example, Figure 1.7a) shows the static structure factor $S(q)$ of GeSe as a function of pressure: above ~ 3 GPa, the relative intensity of the first and second diffraction peaks changes markedly, a new high- q peak emerges, and the pre-peak disappears. These features signal an AAT, where the same composition adopts a different local structure.

LLT and AAT are thus two manifestations of the broader phenomenon of *polyamorphism*, i.e., the existence of multiple amorphous states of the same composition. This is schematically illustrated by the phase diagrams, as in Figure 1.7b): the LLT occurs in the supercooled liquid and involves a transition between HDL and LDL, while the AAT is pressure-driven and occurs between LDA and HDA.

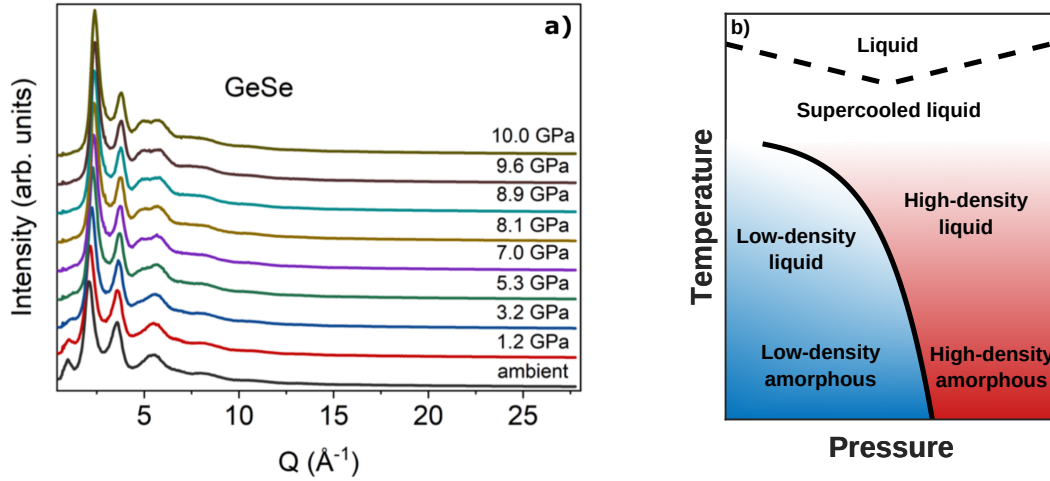


Figure 1.7: a) Evolution of the static structure factor $S(q)$ of GeSe with pressure. The structural changes above ~ 3 GPa indicate an amorphous-amorphous transition. Figure reproduced from *Fujita et al., Nature Communications (2023)* [102], licensed under CC BY 4.0. b) Schematic phase diagram of a system exhibiting both liquid-liquid and amorphous-amorphous transitions. In this example, the LLT occurs in the supercooled liquid phase and is characterised by a transition from high-density to low-density liquid, implying negative thermal expansion. Increasing pressure induces the AAT, transforming the system from low-density amorphous to high-density amorphous. Data from [111].

In the potential energy landscape framework, an LLT can be interpreted as a reorganisation of the system's accessible basins. At high temperatures, the system predominantly explores basins associated with an HDL. Upon

cooling, the system gradually shifts toward basins corresponding to an LDL. In this picture, the PEL may be seen as containing distinct “megabasins” corresponding to different local structures, separated by regions with few or no low-energy states. The LLT thus reflects a change in the population of basins explored by the system, which manifests as abrupt or anomalous changes in thermodynamic and dynamic properties [70, 112]. During the amorphous-amorphous transition, instead, the landscape undergoes a deformation in the depth and height of its basins [113].

1.6 Thermal properties at low temperatures

In the previous sections, we discussed how the primary structural relaxation process slows down upon cooling and eventually arrests at the glass transition temperature, as the system becomes trapped in a local minimum of the potential energy landscape. In contrast, secondary relaxation processes remain active even at lower temperatures. These involve local rearrangements within a metabasin and allow the glass to explore a set of nearly equivalent configurations separated by small energy barriers, fundamentally different from the crystalline state, which corresponds to a single global minimum. As a consequence, at temperatures below approximately 50 K, amorphous solids exhibit thermal, acoustic, and dielectric properties that deviate markedly from those of their crystalline counterparts, which are well described by Debye’s model [1, 114]. These anomalies are universally common to all glasses, in both qualitative and, often, quantitative ways.

In the following, we examine in detail the low-temperature behaviour of the specific heat in glasses. We introduce the vibrational density of states (DOS), the central quantity from which thermal properties are derived, and present the main theoretical models developed to explain the unique and unexpected low-temperature features observed in disordered solids, with particular focus on the Soft Potential Model (SPM) and the Heterogeneous Elasticity Theory (HET).

1.6.1 Anomalous thermal properties of glasses

Below 1-2 K, the specific heat C_p of glasses is much larger than that of the crystals, and it depends linearly on temperature, as it is possible to see from the reduced specific heat plot $C_p(T)/T^3$ in Figure 1.8a), where a divergence appears below 1 K. In the same temperature region, the thermal conductivity κ exhibits much lower values with respect to the crystalline counterparts and a quadratic dependence on T (Figure 1.8b)). Both behaviours are in contrast

to the $C_p(T) \propto T^3$ power law of crystals, well explained through Debye's theory.

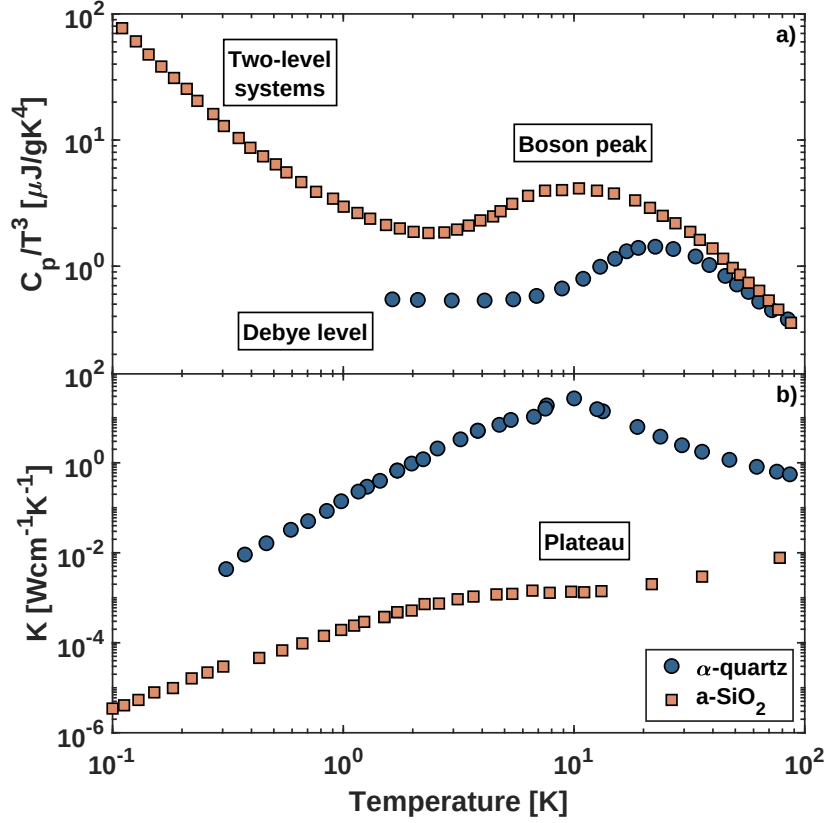


Figure 1.8: Low-temperature thermal properties of amorphous silica (a-Si). a) The specific heat plotted as $C_p(T)/T^3$ vs. temperature. Below ~ 1 K, the divergence reflects the linear temperature dependence of C_p on T followed by a shallow minimum. At ~ 10 K, the so-called boson peak appears as a broad maximum. b) Thermal conductivity as a function of temperature, showing an approximately linear behaviour below ~ 1 K, and a plateau near ~ 10 K. Data taken from Ref. [114–116].

Experimental measurements on acoustic properties proved that these anomalies are due to additional excitations to the Debye phonons. These *dynamical defects* are well represented by a phenomenological depiction known as the Standard Tunnelling Model (STM), which supposes the existence of one atom or groups of atoms that can sit roughly equally well in either of two energy minima of a double-well potential. These two minima are char-

acterised by a distance d and an energy difference of $2\Delta'$; in addition, they are separated by a potential barrier of height V_0 , as shown in Figure 1.9. The movement between these two level states (TLS) is described by the tunnelling effect, and this random distribution of tunnelling states provides the linear and the quadratic behaviours on T of the specific heat and the thermal conductivity, in non-crystalline solids. Furthermore, the Standard Tunnelling Model accurately represents the acoustic and dielectric properties of disordered solids at low temperatures. Despite the success of this model, the microscopic and structural origin of the TLS is still mysterious.

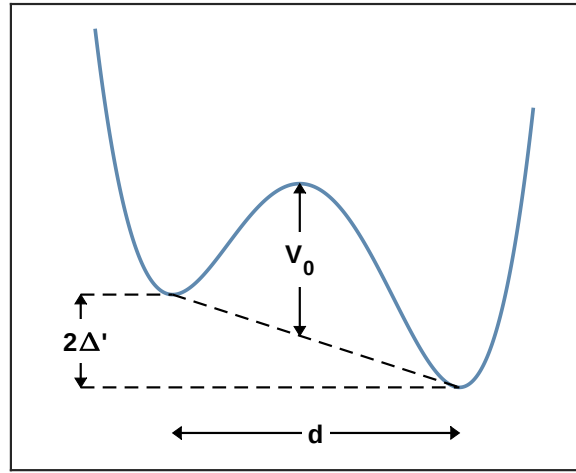


Figure 1.9: At low temperatures, the linear and the quadratic dependencies on temperature of the specific heat and the thermal conductivity are well depicted by the Standard Tunnelling Model. According to this phenomenological description, one atom or groups of atoms tunnel back and forth between the two energy minima of a double-well potential, where the two minima are separated by a distance of d and an energy difference of $2\Delta'$. The energy barrier between them is V_0 .

At about 3 – 10 K, the thermal properties of glasses show further anomalies, which cannot be described by the tunnelling effect between two-level states. In the specific heat over temperature cube, a broad peak arises in most glasses (Figure 1.8a)). It is related to the so-called *boson peak* (BP), which is evident in the reduced vibrational density of states $g(\omega)/\omega^2$ (see

Par. 1.6.2) around 1 THz [2]. In the same temperature region, the thermal conductivity is characterised by an astonishingly universal plateau (Figure 1.8b)), regardless of the glass material [117]. Several theories have been developed to explain the boson peak presence, among which are the Soft Potential Model (SPM) [118–120] and the Heterogeneous Elasticity Theory (HET) [121–124].

The SPM is based on the extension of the standard tunnelling model to higher temperatures and frequencies [125]: it assumes the presence in the glass of a distribution of soft anharmonic potentials, which give rise to two-level states and quasi-localised modes (QLM) [118–120]. The QLM dominate the DOS at and below the BP frequency, with a characteristic density that grows as the fourth power of frequency up to the BP maximum [126–131]. This model provides a unified framework that captures both the tunnelling states at very low temperatures and the vibrational excess at higher temperatures. In some implementations [132–134], the SPM allows for direct quantitative extraction of the various contributions to C_p and other thermal properties from experimental data, offering predictive power and fitting flexibility.

On the other hand, the Heterogeneous Elasticity Theory, developed by Schirmacher and co-workers [121, 135], attributes the boson peak and the thermal-conductivity plateau to spatial fluctuations of the elastic constants caused by the structural disorder. In particular, within mean-field approaches, random variations of the local shear modulus lead to an excess of low-frequency vibrational states, i.e. the boson peak, and limit the phonon mean free path, giving rise to the universal plateau in $\kappa(T)$ [121, 135]. Thus, unlike the SPM, HET explains these anomalies without invoking localized atomic defects. However, HET does not describe the lowest-temperature regime ($T \lesssim 1$ K), where TLS dominate, and instead assumes their presence following the Standard Tunnelling Model [136].

1.6.2 Vibrational density of states

Before proceeding with the main models developed to describe the anomalous thermal properties of glasses at low temperatures, it is useful to introduce the so-called vibrational density of states (DOS), from which the thermal observables are derived.

The vibrational density of states, $g(\omega)$, is a well-defined quantity both in crystals and in amorphous materials. It represents the number of available states for a system in the energy range $[\omega, \omega + d\omega]$

$$g(\omega) = \frac{\text{\#states in } [\omega, \omega + d\omega]}{d\omega} . \quad (1.6.1)$$

At sufficiently low frequency, the DOS in crystals is evaluated through the Debye model, which considers the molecular vibrations (phonons) of a lattice as $3N$ dependent harmonic oscillators. It is possible to prove that $g(\omega)$ in the Debye approximation is

$$g(\omega) = \frac{3}{\omega_D^3} \omega^2, \quad (1.6.2)$$

where ω_D is the Debye frequency and $3/\omega_D^3$ is the Debye level. From the Debye frequency is possible to define the Debye temperature θ_D

$$\theta_D = \frac{\hbar \omega_D}{k_B}. \quad (1.6.3)$$

The thermal properties of a solid can be computed from the DOS. Harmonic vibrational modes, such as phonons and quasi-localized modes, obey Bose-Einstein statistics:

$$n(\omega) = \frac{1}{\exp\left(\frac{\hbar \omega}{k_B T}\right) - 1}, \quad (1.6.4)$$

where k_B is the Boltzmann constant and $\hbar$ is the reduced Planck constant. The product between $g(\omega)$ and $n(\omega)$ is the number of occupied states at a given frequency. From this, thermodynamic quantities such as the internal energy U and specific heat C_p can be obtained:

$$\begin{aligned} U &= \int \hbar \omega \left(n(\omega) + \frac{1}{2} \right) g(\omega) d\omega \\ C_p &= \frac{\partial U}{\partial T} = \frac{\partial}{\partial T} \int \hbar \omega n(\omega) g(\omega) d\omega. \end{aligned} \quad (1.6.5)$$

For instance, in the low-temperature limit within the Debye approximation, the specific heat of crystals scales as

$$C_p = \left(\frac{12\pi^4 N k_B}{5\theta_D^3} \right) T^3, \quad (1.6.6)$$

where $g(\omega)$ has been normalized to $3N$ vibrational modes up to ω_D . This implies that the specific heat of ordered solids approaches the Debye level $C_D = \frac{12\pi^4 N k_B}{5\theta_D^3}$, where $\theta_D = \hbar \omega_D / k_B$ is the Debye temperature.

It is important to emphasise that equations (1.6.4) and (1.6.5) hold only within the harmonic approximation; they do not account for the contributions of two-level systems, which play a significant role in the low-temperature behaviour of glasses.

1.6.3 Models

In the following, we explore two key theoretical approaches developed to explain vibrational anomalies in glasses, such as the boson peak and low-temperature deviations from Debye behavior: the Soft-Potential Model, which attributes these features to quasi-localised low-energy excitations, and the Heterogeneous Elasticity Theory, which links them to spatial fluctuations in the elastic constants.

The Soft-Potential Model

For a long time, the low-temperature anomalies of glasses, i.e. the linear increase of the specific heat below 1-2 K attributed to two-level systems (TLS) and the boson peak (BP) observed as a broad maximum in C_p/T^3 above 1-2 K, were treated separately [137, 138]. The *Soft Potential Model* (SPM), introduced by the St. Petersburg group in the 1980s [137, 138] and further refined over the following decades [120, 132, 133, 139–143], represented the first serious attempt to unify these features within a single theoretical framework.

The central idea of the SPM is that, in addition to the standard acoustic phonons, glasses are characterised by a broad spectrum of quasi-localized low-energy excitations. These so-called *soft modes* span from strongly anharmonic TLS associated with double-well potentials (DWP) to nearly harmonic vibrational modes in single-well potentials (SWP) [141].

To properly construct a distribution of these excitations, consider a localised mode with a weak or negative restoring force. Because the mode is both soft and localized, the atomic displacements are large, and anharmonic terms in the potential must be included. In cases of negative curvature, anharmonicity is necessary to stabilise the system [141]. The resulting potential energy can be written as:

$$V(x) = W(D_1x + D_2x^2 + x^4), \quad (1.6.7)$$

where x is a dimensionless displacement of the soft mode, D_1 accounts for the potential asymmetry, while D_2 is related to the small positive or negative restoring force. Both D_1 and D_2 vary throughout the glass. The scale parameter W determines the characteristic energy of the soft mode and sets the crossover between tunnelling and vibrational behaviour.

The SPM is based on three key assumptions:

- (i) Soft modes can be characterised, on average, by a single energy scale W .

- (ii) The parameters D_1 and D_2 are randomly distributed near the origin of the $D_1 - D_2$ plane with a constant density $P(D_1, D_2) = P_s$
- (iii) The interaction between the soft modes and the sound waves is linear in both the displacement x of the mode and in the strain field of the sound wave

This model introduces three independent parameters: P_s , W and the coefficient of the interaction between soft modes and sound waves. Notably, the latter affects sound attenuation and thermal conductivity but does not influence the density of states (DOS) or the specific heat.

The first major success of the SPM is that it recovers the predictions of the standard tunnelling model at low temperatures [1] (see solid lines in Figure 1.8 in both the reduced specific heat and thermal conductivity). In particular, it accounts for the linear temperature dependence of the specific heat via the coefficient [141]:

$$C_{TLS} \sim \frac{10}{M_{at}} \frac{P_s}{W} k_B^2. \quad (1.6.8)$$

Moreover, the SPM describes the strong enhancement of the vibrational density of states at low frequencies, which culminates in the boson peak. This corresponds to the rise of $C_p(T)/T^3$ above its minimum at $T_{min} \simeq W/1.8k_B$, typically observed above 1-2 K. In this regime, the excess vibrational modes are attributed to soft quasi-harmonic excitations in SWPs. The density of these modes, in excess of the Debye contribution, scales with frequency as the fourth power of frequency:

$$g_s(\nu) = \frac{1}{24} \frac{P_s h}{W^5} (h\nu)^4. \quad (1.6.9)$$

In the quasiharmonic approximation, this leads to a low-temperature specific heat contribution:

$$C_{P,sm} \propto T^5 \quad (1.6.10)$$

However, since this prediction is based on an unlimited distribution of soft modes, $P(D_1, D_2) = P_s$, it cannot be valid indefinitely at higher frequencies. Specifically, it accounts only for the low-frequency tail of the boson peak, but not the peak maximum in $g(\omega)/\omega^2$. To address this, extensions of the model and alternative approaches have been proposed to more accurately describe the full vibrational density of states at higher frequencies [136].

Being $g_{sm}(\omega) \propto \omega^4$, it vanishes more rapidly than the Debye contribution ($\propto \omega^2$); thus, direct experimental detection of QLMs at low frequencies

is challenging. Moreover, their contribution to the quasi-elastic scattering signal can be obscured by the presence of anharmonic relaxations.

The existence of such soft modes is nonetheless supported by recent numerical simulations [126–128], which estimate that approximately 50% of the vibrational modes at frequencies around one-third of the boson peak maximum are quasilocalized [128]. Some simulations even suggest that soft harmonic modes may act as precursors to TLS [144].

The Heterogeneous-Elasticity Theory

A different approach to understand the vibrational density of states in glasses and strongly disordered solids in the boson peak region is provided by the *Heterogeneous Elasticity Theory* (HET). This theory is based on the model assumption that the structural disorder induces microscopic, random spatial fluctuations of the transverse elastic constant, i.e., the shear modulus [121]. These fluctuations are characterised by a finite correlation length ξ and are described statistically through their correlation function. The effect of this spatial elastic heterogeneity on the vibrational properties is treated using mean-field approximations, specifically the *self-consistent Born approximation* (SCBA), which allows for the calculation of effective, frequency-dependent elastic moduli and vibrational response functions averaged over disorder realizations [122–124, 145]. More recently, a variant based on the *coherent potential approximation* (CPA) has been proposed, which provides an improved description of glasses exhibiting stronger Boson peaks, such as SiO_2 [123, 124].

This framework sets the stage for the HET, which describes the terahertz-frequency vibrations of glasses within a harmonic approximation, where the vibrational modes are unrelated to low-temperature two-level system instabilities [123, 135], assumed to be present as additional excitations following the standard Tunnelling Model [123, 135]. The theory predicts the appearance of the boson peak as an excess in the DOS over the Debye ω^2 law, as well as the characteristic plateau observed in the thermal conductivity of glasses. The density of states is computed by means of a “generalised” Debye law [121], in which the first deviation from the Debye behaviour arises from the frequency-dependent dispersion and damping of sound waves, and it scales as ω^4 . Anharmonic processes can modify the sound dispersion and attenuation, thus giving rise to a temperature dependence of the DOS [146], while the eventual effect of secondary relaxation processes is not considered.

To provide a quantitative description, we now outline the Heterogeneous Elasticity Theory as formulated within the self-consistent Born approximation framework.

The elastic constants fluctuate spatially with a correlation length ξ , modelled as:

$$G(\mathbf{r}) = G_0 + \Delta G(\mathbf{r}),$$

where the fluctuations $\Delta G(\mathbf{r})$ are statistically characterized by the correlation function:

$$\begin{aligned} C_G(\mathbf{r}) &= \langle \Delta G^2 \rangle e^{-r/\xi}, \\ C_G(\mathbf{k}) &= \langle \Delta G^2 \rangle \frac{8\pi}{\xi} [k^2 + \xi^{-2}]^{-2}. \end{aligned} \quad (1.6.11)$$

The disorder-averaged vibrational properties are encoded in the self-energy $\Sigma(\omega) = \Sigma(q=0, \omega)$, which in SCBA satisfies the integral equation:

$$\Sigma(\omega) = \frac{\gamma}{2\varphi_3 \langle \Delta G^2 \rangle} \int_{|\mathbf{k}| < k_D} \left(\frac{d\mathbf{k}}{2\pi} \right)^3 C_G(k) [\chi_L(k, \omega) + \chi_T(k, \omega)], \quad (1.6.12)$$

where $\chi_L(k, \omega)$ and $\chi_T(k, \omega)$ are the longitudinal and transverse dynamical susceptibilities:

$$\begin{aligned} \chi_L(k, \omega) &= \frac{k^2}{-\omega^2 + k^2 (v_{L,0}^2 - 2\Sigma(\omega))}, \\ \chi_T(k, \omega) &= \frac{k^2}{-\omega^2 + k^2 (v_{T,0}^2 - \Sigma(\omega))}. \end{aligned} \quad (1.6.13)$$

The prefactor $\gamma = \langle \Delta G^2 \rangle \varphi_3 / v_{T,0}^4$ is the *disorder parameter*, quantifying the variance of local shear modulus fluctuations; $v_{L,0}$ and $v_{T,0}$ are the bare longitudinal and transverse sound velocities, and $\varphi_3 = \int_{|\mathbf{k}| < k_D} (d\mathbf{k}/2\pi)^3 C_G(\mathbf{k})$ normalizes the correlation function. The integration is cut off at the Debye wavevector k_D , which can be estimated from the mass density and average atomic weight of the material.

The vibrational density of states is then computed as:

$$g(\omega) = \frac{2\omega}{3\pi} \int_{|\mathbf{k}| < k_D} \left(\frac{d\mathbf{k}}{2\pi} \right)^3 \frac{1}{k^2} \text{Im} \{ \chi_L(k, \omega) + 2\chi_T(k, \omega) \}. \quad (1.6.14)$$

This generalised Debye approach, which shares similarities with random matrix theories [147, 148], enables an explicit connection between the boson peak excess and the frequency-dependent dispersion and damping of acoustic modes. In the low-frequency limit, the DOS reduces to the classical Debye form plus a correction associated with sound attenuation [121, 149]:

$$g(\nu) \sim \frac{3\nu^2}{\nu_D^3} + \frac{2v_D^2}{\pi\nu_D^2} \left(\frac{\Gamma_L}{v_L^2} + 2\frac{\Gamma_T}{v_T^2} \right), \quad (1.6.15)$$

where $v_{L,T}$ and $\Gamma_{L,T}$ are the sound velocities and attenuation (full width at half maximum) of longitudinal and transverse waves, respectively, and v_D is the Debye sound velocity. The sound attenuation in glasses typically follows a *Rayleigh scattering law*, $\Gamma_{L,T} \propto \nu^4$, at sufficiently low temperatures and frequencies [146, 150]. This means that the first deviation from the Debye prediction scales as $\propto \nu^4$.

An important characteristic scale emerging from HET is the *Ioffe-Regel frequency*, ω_{IR} , which marks the transition from propagating phonon-like excitations to diffusive vibrational modes. It is defined as the frequency at which the phonon mean free path becomes comparable to its wavelength, or equivalently, when the attenuation becomes comparable to the frequency:

$$\Gamma(\omega_{IR}) = \frac{\omega_{IR}}{\pi} . \quad (1.6.16)$$

In this regime, plane-wave descriptions break down due to strong elastic scattering, and ω_{IR} typically coincides with the boson peak frequency. Within the SCBA framework, ω_{IR} can be estimated from the computed attenuation functions $\Gamma_{L,T}(\omega)$ and is indicative of the vibrational crossover predicted by the theory [123].

Résumé du Chapitre 2

Ce Chapitre examine la manière dont la stabilité des verres peut être modulée à travers les méthodes de préparation et les interventions externes. Les concepts de stabilité cinétique et thermodynamique y sont définis et quantifiés à l'aide d'observables calorimétriques telles que la température fictive et la température d'apparition. Le rôle de l'histoire de préparation est mis en évidence, depuis la trempe conventionnelle à partir du liquide fondu jusqu'à des approches plus avancées comme le dépôt physique en phase vapeur, capable de produire des verres ultrastables aux propriétés remarquables. Les traitements post-formation, incluant le recuit, l'irradiation et la déformation mécanique, sont présentés comme autant de moyens d'augmenter ou de diminuer la stabilité en modifiant la position du système dans le paysage d'énergie potentielle. Ces différentes approches illustrent le caractère dynamique et modulable de l'état vitreux. Le Chapitre se conclut par l'énoncé de l'objectif spécifique de ce travail : étudier l'influence de la stabilité du verre sur les dynamiques microscopiques, au moyen de méthodes complémentaires couvrant des échelles de temps allant des vibrations picosecondes jusqu'à la relaxation structurale sur plusieurs centaines de secondes.

Chapter 2

Tuning the stability of glasses

Chapter 1 established the phenomenology of disordered systems, from the supercooled liquid state to the formation of a glass, highlighting the role of the glass transition temperature and the potential energy landscape. This Chapter builds on that foundation by exploring the practical and experimental aspects of glass stability. We will discuss various techniques, from conventional melt-quenching to physical vapor deposition and thermo-mechanical treatments, that can be used to navigate the PEL and systematically tune a glass's properties. Finally, we will use this comprehensive overview to define the specific aim of this Thesis and contextualise our contribution to the field.

2.1 Glassy stability

The stability of glasses is a central concept from both technological and fundamental perspectives. In materials science, glass stability generally refers to the resistance of a glass to crystallisation upon heating [151]: the higher the resistance, the greater the stability. Since glasses are non-equilibrium systems, their properties evolve over time, making the stability a crucial parameter for advanced technological applications [152]. For instance, in the electronics field, glass stability affects the performance of components ranging from phase-change memories to optical fibres and dielectric layers, where crystallisation can compromise reliability [69, 153–155]. In the pharmaceutical field, poorly soluble drugs are frequently formulated in an amorphous state to improve dissolution and bioavailability; however, their strong tendency to crystallise presents challenges for long-term preservation [156, 157]. Even in fundamental research, such as gravitational wave detection, highly stable glasses are required for the mirrors of interferometers to minimise noise and structural drift [158, 159].

To build a more comprehensive picture, it is useful to recall the distinction between kinetic and thermodynamic stability, introduced in Sec. 1.2. Kinetic stability reflects how slowly a glass relaxes toward equilibrium, that is, its resistance to structural aging or transformation back into the supercooled liquid [22]. Thermodynamic stability, on the other hand, refers to how low the glass lies in enthalpy relative to other amorphous states of the same composition [2, 23]. In terms of the PEL, a glass that is trapped in deeper basins with higher energy barriers is both thermodynamically and kinetically more stable.

These abstract concepts can be quantified using state variables, such as enthalpy, or material properties, like specific heat, as depicted in Figure 2.1. Consider first a conventional glass, obtained by cooling the liquid at a rate of -10 K/min [2] (blue solid line). Its glass transition temperature corresponds to the finite discontinuity in the heat capacity between the supercooled liquid and the glassy phases. If the glass undergoes a subsequent aging process (dashed light blue line), its effective T_g on cooling shifts to a lower temperature, indicating an enhanced stability. By reheating this new glass at $+10$ K/min (red solid line), the onset of devitrification (i.e. the return toward the supercooled liquid) will occur at the glass transition temperature of the initial glass. This characteristic temperature of devitrification is called *onset temperature* T_{on} , and, in a differential scanning calorimetry (DSC) trace, it is identified as the intersection between the extrapolated glass baseline and the transition peak. The enthalpy peak corresponds to the recovery of energy lost during aging [160]. The relative difference between the T_g of the aged glass and the onset temperature T_{on} provides a measure of kinetic stability. Generally speaking, a right shift of T_{on} relative to T_g corresponds to an increase of kinetic stability with respect to the conventional glass, while a left shift indicates a lower kinetic stability.

Thermodynamic stability is instead assessed by comparing the enthalpy or density of the glass with that of a conventional reference [2]. A convenient way to quantify this is through the *fictive temperature* T_f . By definition, T_f is the temperature at which state variables have the same value for the glass and for the extrapolated equilibrium liquid. For instance, as illustrated in the lower graph of Figure 2.1, it is where the extrapolated line of the liquid enthalpy intersects the glass curve. For a liquid-cooled glass, T_f corresponds to T_g , whereas for a more stable glass, T_f is significantly lower. Thus, the lower the fictive temperature, the greater the thermodynamic stability.

As said, glass stability is not a fixed property: it can evolve with time through aging or be actively tuned by external treatments. Preparation techniques determine the state of the system in the energy landscape [2].

Conventional melt-quenching at different cooling rates already allows some control over stability: faster cooling produces glasses with higher T_f and lower stability, while slower cooling yields more relaxed structures. Even more pronounced effects can be obtained via physical vapor deposition, which is capable of producing ultrastable glasses with such low fictive temperatures and high onset temperature values that are not achievable by conventional liquid quenching [2].

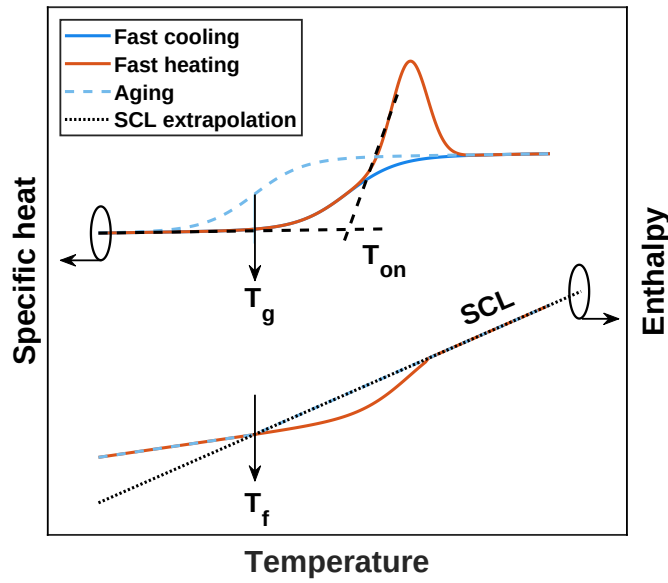


Figure 2.1: The upper curve depicts the typical specific heat of a liquid cooled with a fast cooling rate (solid blue line), that undergoes aging (light-blue dashed line). When the aged glass is heated up at the same fast rate (solid red line), it shows an overshoot due to the loss of enthalpy that occurred during the aging. T_{on} is the intersection between the extrapolations of the glass baseline and of the transition peak raise (dashed black lines). The lower curve is the enthalpy obtained by integrating the specific heat. The dotted black line is the extrapolation of the supercooled liquid (SCL) enthalpy line to lower temperatures. The fictive temperature is the intersection between the enthalpy of the cooled or heated glass and the extrapolation. Figure adapted from [2].

Stability can also be modified by thermo-mechanical treatments applied after the glass has formed [14]. Annealing below T_g promotes structural relaxation, lowers T_f , and enhances stability [2]. Conversely, irradiation or

mechanical deformation can increase the enthalpy of the system, rejuvenating the glass and effectively reducing its stability, shifting it to a higher-energy, shallower region of the PEL [4, 6, 14–21, 161]. These processes highlight the dynamic and tunable nature of the glassy state, which can be shifted toward either deeper or shallower regions of the energy landscape depending on external stimuli.

In the following sections, we will examine the most prominent techniques used to achieve this control, from conventional preparation routes like melt-quenching to advanced methods such as physical vapor deposition and thermo-mechanical treatments.

2.1.1 Melt-Quenching

Melt-quenching is the most common method for producing glasses. In this technique, a liquid is cooled rapidly enough to bypass crystallisation, forming an amorphous solid. The properties and stability of the resulting glass strongly depend on the cooling rate: rapid quenching traps the system in higher-energy configurations, resulting in glasses with higher enthalpy, lower density, and reduced kinetic stability, whereas slower cooling allows the system to explore deeper regions of the potential energy landscape, producing more stable glasses [2].

Melt-quenched glasses exhibit a high density of two-level systems and pronounced boson peaks at low temperature. However, controlled cooling or subsequent aging can partially enhance their thermodynamic and kinetic stability, making them useful benchmarks for studying how preparation history affects glass structure, dynamics, and low-temperature properties [2].

2.1.2 Physical vapor deposition

Physical vapor deposition (PVD) offers an alternative route to produce glasses, avoiding the crystallisation risk associated with melt-quenching. PVD is a set of techniques used for depositing thin films and coatings of metals, ceramics, glasses, and polymers on substrates [10]. In PVD processes, single atoms or molecules are evaporated from a solid or liquid source and carried to the substrate, over which a particle at a time, layer by layer, condensates [162]. The substrate is typically held at a fraction of the glass transition temperature ($T_{sub} \simeq 0.8 - 0.9 T_g$), providing a high mobility of molecules at the glass surface, which is estimated to be $\sim 10^9$ times greater than in the bulk. In this way, molecules can quickly sample the energy landscape and find the configuration closer to the equilibrium state before other incoming molecules bury them.

Physical vapor deposited glasses exhibit exceptionally low enthalpies and enhanced kinetic and thermodynamic stabilities, comparable to glasses cooled at extremely low rates or aged for thousands of years [2]. For this reason, these glasses are referred to as *ultra-stable glasses* (USG). Besides the enhanced stability, USG present a density 1-2% higher than that of the corresponding conventional liquid-cooled glasses [2].

Experiments show that USG can exhibit extremely low densities of two-level systems (TLS), or even a complete absence of them [3, 163], consistent with deep trapping in the PEL and suggesting their potential as “ideal” glasses, i.e. amorphous solids free of structural defects [10]. Figure 2.2 illustrates the reduced specific heat, $C_p(T)/T^3$, for indomethacin samples in different states. The crystalline sample (light data) follows Debye’s law. In contrast, the conventional glass (brown data) exhibits the typical TLS linear contribution at $T \lesssim 1 - 2$ K. Ultra-stable glasses (orange data) suppress this linear term, reflecting their exceptional stability. All glassy samples display a shallow boson peak around 4 K.

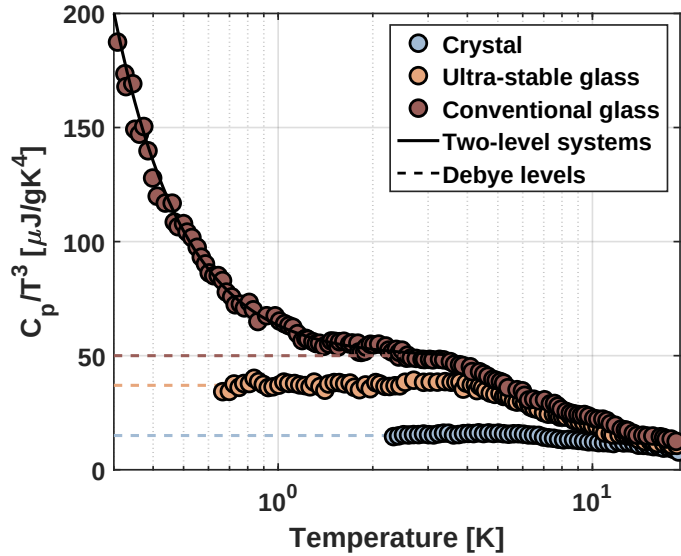


Figure 2.2: PVD produces glasses below T_g with enhanced density and stability. Left: schematic of deposition process. Right: reduced specific heat of indomethacin in various states. Crystals follow Debye’s law, conventional glasses exhibit TLS contributions, and ultra-stable glasses (USG-1 and USG-2) suppress TLS. The degraded USG recovers the linear term. All samples show a boson peak. Data taken from [117].

Despite these remarkable features, most vapor-deposited glasses exhibit

molecular packing anisotropy. Consequently, while USG resembles extremely aged or slowly cooled glasses in many respects, their properties may reflect unique configurations achieved through PVD rather than those accessible via conventional thermal histories [2].

It is important to note that the formation of USG via PVD is not universal for all materials, but is typically limited to polymers and organic molecules. Only in these systems is the surface mobility during deposition sufficiently high to enable efficient sampling of the energy landscape and the formation of low-enthalpy structures. In contrast, small inorganic molecules or network-forming oxides, such as SiO_2 , are not characterised by an adequate surface mobility under typical PVD conditions, and therefore do not form ultrastable glasses. Consequently, the exceptional properties of USG result not solely from the PVD technique, but from the combination of deposition method and material choice, which must provide favourable dynamical characteristics at the surface.

2.1.3 Annealing

In addition to preparation methods, the stability of glasses can be tuned through thermo-mechanical treatments applied to the formed glass [14]. One of the most common is annealing, in which a glass is heated to a temperature below its glass transition and maintained there for a controlled time. During annealing, atomic or molecular mobility is sufficient for structural relaxation to occur, enabling the glass to progressively explore deeper minima of the potential energy landscape without crystallising [2].

Annealing typically reduces the enthalpy and free volume of the glass, resulting in densification, lower fictive temperature, and greater kinetic and thermodynamic stability. This process is often interpreted as the glass approaching an equilibrium supercooled liquid state corresponding to the annealing temperature [2]. The effectiveness of annealing depends strongly on the treatment conditions, including the annealing temperature, duration, and applied stress. In some cases, mechanical loading during annealing can further accelerate relaxation processes and promote structural rearrangements [164].

Compared to ultra-stable glasses prepared via PVD, however, annealed glasses generally achieve more modest gains in stability, since equilibration is limited by the accessible timescales at temperatures below T_g [2].

2.1.4 Photo-induced transitions

Irradiation is another approach to modify the structure and stability of glasses [4,161,165]. Depending on the type and energy of the radiation, which can range from electrons and neutrons to X-rays and heavy ions, different microscopic mechanisms are activated [69]. These mechanisms include radiolysis, knock-on events and electronic rearrangements, which can significantly change the material's mechanical, structural, and dynamical properties [166].

At low to intermediate energies, ionizing radiation can lead to *radiolysis*, whereby an electron-hole pair is created upon radiation absorption, resulting in atomic displacement and the formation of a long-lived exciton. This gives rise to bond breaking and further displacement of atoms. At higher energies, irradiation can cause *knock-on events*, in which atoms are displaced from their equilibrium positions due to direct momentum transfer. Additionally, *electronic rearrangements* can occur, where changes in the local electronic structure modify bonding configurations without necessarily displacing atoms [166].

X-rays mainly induce radiolysis, and it has been proven in LiBO_2 by Martinelli *et al.* [165] that they can act like an external force, generating tiny defects that trigger hidden structural rearrangements, effectively pushing the material into a plastic, irreversible state at the microscopic scale. This process corresponds to a *yielding transition*, usually driven by application of stress or strain on the material. In materials science, yielding refers to the transition from an elastic response, where deformation is reversible, to a plastic state, where the material undergoes irreversible atomic rearrangements. In glasses, yielding is particularly subtle since plastic events appear at very small scales and are associated with localised atomic rearrangements known as shear transformation zones [165].

The thermodynamic, structural, and dynamical implications of this transition were subsequently explored in detail by Baglioni *et al.* [4], who investigated the photo-induced yielding transition on the chalcogenide glass GeSe_3 prepared by melt-quenching at different cooling rates. Their study demonstrated that intense X-ray irradiation invariably drives the glass into a unique yielded state, independently of its initial preparation history. The kinetics of the transition depend on the X-ray flux, but the final state is universal (see Fig. 2.3): rejuvenated, more disordered, and of higher enthalpy than annealed glasses, yet not extreme, resembling instead a glass quenched at a rate of 14000 K/s from $\sim 20\%$ above T_g . Remarkably, this state is stationary at room temperature: once established, it remains unchanged even if the beam is temporarily switched off. The initial state can only be recovered by heating the sample above T_g followed by quenching, which resets all the

radiation effects.

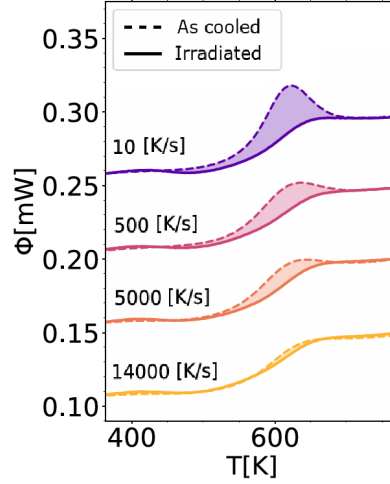


Figure 2.3: Fast differential scanning calorimetry traces of GeSe_3 glasses as quenched (dashed lines) and at yielding (full lines). The final rejuvenation effect of X-ray irradiation is the same on all GeSe_3 glasses, which were quenched at different cooling rates. All curves have been measured with a probing rate of 2000 K/s^{-1} . Legend modified. Adapted from J. Baglioni *et al.*, Rep. Prog. Phys. **87**, 120503 (2024). CC BY 4.0.

2.1.5 Mechanical deformations

The final approaches considered for tuning glass stability are mechanical deformations, achieved through treatments such as uniaxial compression, rolling, wire drawing, high-pressure torsion, and hydrostatic high-pressure compression [14]. In oxide glasses, studies are limited due to their intrinsic brittleness; nonetheless, investigations on hydrostatically densified SiO_2 have revealed a suppression of the boson peak and a reduction of the excess vibrational states above the Debye level, suggesting enhanced stability compared to the non-densified state [125].

Metallic glasses (MGs), in contrast, have been widely explored under mechanical treatments thanks to their ability to undergo plastic deformation [14]. Calorimetric measurements indicate that strong shear plastic deformations, including uniaxial compression, rolling, wire drawing, and high-pressure torsion, induce rejuvenation, typically accompanied by a reduction in mass density [14]. However, microscopic studies of the dynamics under such treatments are experimentally challenging and limited to recent *in-situ* investigations of hydrostatic compression in the GPa range [5, 6]. In the *in-*

situ approach, the studies are performed while the high-pressure compression is applied, allowing also the measurement of the elastic contribution of the deformation. In Ce-based MGs [5], hydrostatic compression is found to induce densification together with an amorphous-amorphous (polyamorphic) transition (Fig. 2.4b)). Concomitantly, the structural relaxation time first increases, consistent with aging during densification, but then decreases abruptly once the polyamorphic transition sets in (Fig. 2.4a)).

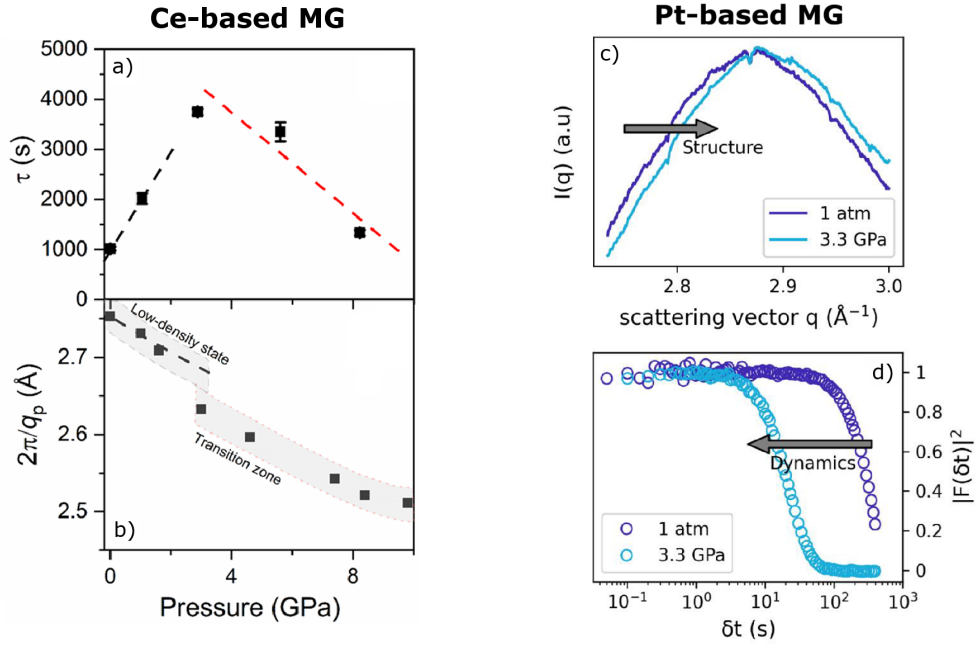


Figure 2.4: High-pressure hydrostatic compression on metallic glasses. *Left:* a) The Ce-based MG shows an unexpected non-monotonous dependence on pressure, with an acceleration in the structural relaxation time τ . This occurs in the region of the polyamorphic transition, well visible from the change of pressure dependence of the first sharp diffraction peak. Adapted from X. Zhang *et al.*, Proc. Natl. Acad. Sci. U.S.A. **120**, e2302281120 (2023). Licensed under CC BY-NC-ND 4.0. b). *Right:* The Pt-based MG shows a densification c) from ambient pressure to 3.3 GPa associated with an anomalous acceleration in the dynamics d). Reproduced from A. Cornet *et al.*, *Acta Materialia* 255, 119065 (2023), Fig. 1b–c, with permission from Elsevier.

A non-monotonous behaviour in the dynamics is observed also in a Pt-based MG under comparable pressures, even though no polyamorphic transition occurred in that system [6]. In particular, the relaxation time decreases

by nearly a factor of 15 between ambient pressure and 3.3 GPa (Fig. 2.4c-d)), followed by a further acceleration and a later deceleration. Such findings are counter-intuitive, as higher mass density is generally associated with greater stability and slower relaxation [6]. Nevertheless, rejuvenation upon densification is consistent with theoretical predictions of pressure-induced softening [167], as well as with experimental evidence of rejuvenation following triaxial compression in metallic glasses [168]. These results highlight that the relationship between glass stability and applied pressure is non-trivial.

2.2 Aim of this work

In the previous paragraphs, we reviewed how glass stability can be modified by a variety of preparation routes and thermo-mechanical treatments. Most of these studies, however, have focused on macroscopic observables, whereas a microscopic picture of stability, how it affects vibrational and structural dynamics across different timescales, remains largely unexplored.

The central aim of this Thesis is to investigate how glass stability influences the microscopic dynamics over the full dynamical range, from vibrations on the picosecond scale to structural relaxation on the timescale of 10-1000 seconds. To this end, we employ a combination of preparation methods and external treatments, with a particular focus on physical vapor deposition, X-ray irradiation, and hydrostatic high-pressure compression.

We address the picosecond vibrational dynamics by comparing ultra-stable and conventional glasses. In particular, we select the organic glasses, the prototypical system prepared by physical vapor deposition. These glasses are known to exhibit enhanced stability, as reflected by not only a large T_{on} right shift, but also by their calorimetric signatures at low temperature, with the suppression of TLS. Yet, the effect of this increased stability on the vibrational dynamics has not been established. Because direct measurements of the intermediate scattering function in the picosecond regime are extremely challenging, we investigate the problem in the frequency domain by probing the vibrational density of states. To this end, we combine Raman spectroscopy, which provides access to the boson peak and molecular vibrations, with a recently developed spectrographic approach to inelastic X-ray scattering with nuclear resonance analysis (NRAIXS) [169], which yield the DOS in absolute units down to 70 GHz. From the DOS we extract the specific heat and compare it with calorimetric data, thereby assessing the impact of stability on the low-frequency vibrational spectrum. In addition, comparing the DOS of USG with that of conventional glasses allows us to address fun-

damental open questions: are quasi-localized modes intrinsic to real glasses, or do they only appear in simulations because of finite-size effects and fast cooling? And how are they related to the presence of two-level systems and other anomalous low-temperature excitations?

Probing the effect of stability on the long-time structural relaxation of USG is experimentally demanding: the characteristic relaxation times reach $\sim 10^{14}$ s [2], far beyond experimental timescales, and the techniques required would irreversibly damage the samples. For this reason, the second part of this work focuses on glassy systems where relaxation dynamics can be directly probed (actually induced) in the accessible time window of 1-1000 s. To this end, we investigate the effect of stability under X-ray irradiation and hydrostatic high-pressure compression.

We have seen that X-rays can induce a yielding transition in glasses, effectively rejuvenating them [4]. However, systematic microscopic studies are currently limited to very few compositions. Here, we extend these investigations to two compositionally similar Ge-based structural glasses using X-ray Photon Correlation Spectroscopy (XPCS), measuring the ISF and, at the same time, quantifying how microscopic dynamics evolve during irradiation.

Finally, we explore how stability is affected by hydrostatic high-pressure compression. Previous studies on metallic glasses have revealed a surprising, non-monotonic dependence of relaxation time on pressure, including cases of dynamic acceleration upon densification [5, 6]. While this can be associated with an amorphous-amorphous transition, similar acceleration has also been observed in systems without polyamorphism, in agreement with theoretical predictions and experimental studies [6, 167, 168]. Since metallic glasses differ fundamentally from network-forming and polymeric glasses, extending such studies to more standard glass formers is crucial. For this reason, we selected Ge-based chalcogenide glasses, which are robust against X-ray damage and frequently display amorphous-amorphous transitions. By combining *in-situ* XPCS with high-pressure techniques, we directly probe the microscopic dynamics under compression, while complementary calorimetric measurements on densified samples (*ex-situ*) provide a macroscopic perspective on the permanent effects of densification.

In summary, this Thesis establishes a multi-scale, multi-technique investigation of how glass stability shapes microscopic dynamics. By studying vibrational excitations in organic USG and structural relaxation in irradiated and high-pressure compressed Ge-based glasses, we aim to bridge the gap between macroscopic stability properties and the underlying microscopic mechanisms.

Résumé du Chapitre 3

*Ce Chapitre présente le cadre théorique et expérimental des techniques employées pour sonder la dynamique vibrationnelle et les processus de relaxation dans les systèmes désordonnés. Il introduit les principales méthodes de diffusion, replacées dans le diagramme fréquence- q , ainsi qu'un rappel des principes de base de la diffusion. La Nuclear Resonant Analysis of Inelastic X-ray Scattering (NRAIXS) est ensuite décrite : cette méthode à haute résolution énergétique permet d'accéder aux propriétés vibrationnelles via la création et l'annihilation de phonons, liées à la densité d'états vibrationnels (DOS). Sont présentées les étapes d'extraction de la DOS à partir des spectres expérimentaux, en tenant compte de la convolution instrumentale et des corrections de Fourier. La mise en œuvre à la ligne ID14 de l'ESRF est détaillée, incluant la configuration en transmission, la détection au ^{57}Fe par photodiodes à avalanche et les mesures à basse température. Le Chapitre aborde ensuite la Photon Correlation Spectroscopy, l'origine physique des figures de speckle et leur lien avec la fonction de diffusion intermédiaire et les dynamiques de relaxation. Les avantages de l'approche multi-speckle et de la X-ray Photon Correlation Spectroscopy (XPCS), sondant les dynamiques atomiques, sont discutés. Sont ensuite présentés les détails expérimentaux de la XPCS : configuration de la ligne P10 de PETRA III (DESY, Hambourg), fonctionnement sous haute pression *in situ*, génération et mesure de la pression avec cellule à enclumes de diamant (DAC), ainsi que les protocoles développés pour étudier les effets du rayonnement X et de la pression. Enfin, sont décrites les méthodes d'analyse des données XPCS (masquage, calcul de $g_2(q, t)$, ajustement KWW, q -résolue, dépendance en dose, facteur de structure statique), ainsi que la spectroscopie Raman et micro-Raman et les techniques calorimétriques éclairant la stabilité vitreuse.*

Chapter 3

Experimental techniques

The intriguing features of glasses determine the presence of dynamical and vibrational phenomena that span many orders of magnitude in both length scale and frequency. As a result, no single probe can capture all relevant processes, and a comprehensive understanding requires the combined use of several complementary techniques.

Figure 3.1 provides an overview of a selection of such methods, positioned according to the characteristic frequencies they access and the length scales they probe. Along the horizontal axis, the characteristic wavelength of the probing radiation decreases, reflecting an increase in the characteristic size of the regions being explored. From bottom to top, the increasing frequency allows for probing faster and faster processes.

The two main techniques exploited in this Thesis are Inelastic X-ray scattering (IXS) and X-ray Photon Correlation Spectroscopy (XPCS), which, being based on X-rays, both cover the microscopic length scales. However, they cover distinct time scales. IXS allows for probing the fast vibrational processes, while XPCS is well-suited to capture the slow structural motion of disordered materials.

The Dynamical Light scattering extends the accessible range of XPCS to macroscopic length scales. On the other hand, scattering techniques as Raman and Brillouin Spectroscopy cover the same frequency range of IXS, but at macroscopic scales. Among these techniques based on visible light, only the Raman Spectroscopy will be employed in this Thesis.

Thus, to cover the macroscopic length scale to the microscopic one, from the fast processes to the slow ones, many different techniques must be used. However, a significant portion of the frequency-length-scale plane is still inaccessible to current experimental approaches. This gap underscores the ongoing challenge of bridging the microscopic vibrational regime with the macroscopic structural dynamics, a challenge that continues to drive the de-

velopment of novel experimental strategies.

In this Chapter, after a brief introduction to the characteristics of the scattering processes, we will explain in detail the experimental techniques employed in this work. We will extensively explore the IXS with Nuclear Resonant Analysis (NRAIXS) exploited to probe the vibrational dynamics of ultra-stable and conventional glasses. Then, XPCS, based on the coherent and elastic scattering, which is used to probe the slower relaxation processes, will be explained. Finally, Raman scattering and Differential Scanning Calorimetry, used to probe the macroscopic length scales, will be explained. Since calorimetry is not a scattering-based technique, it is not shown in the diagram of 3.1.

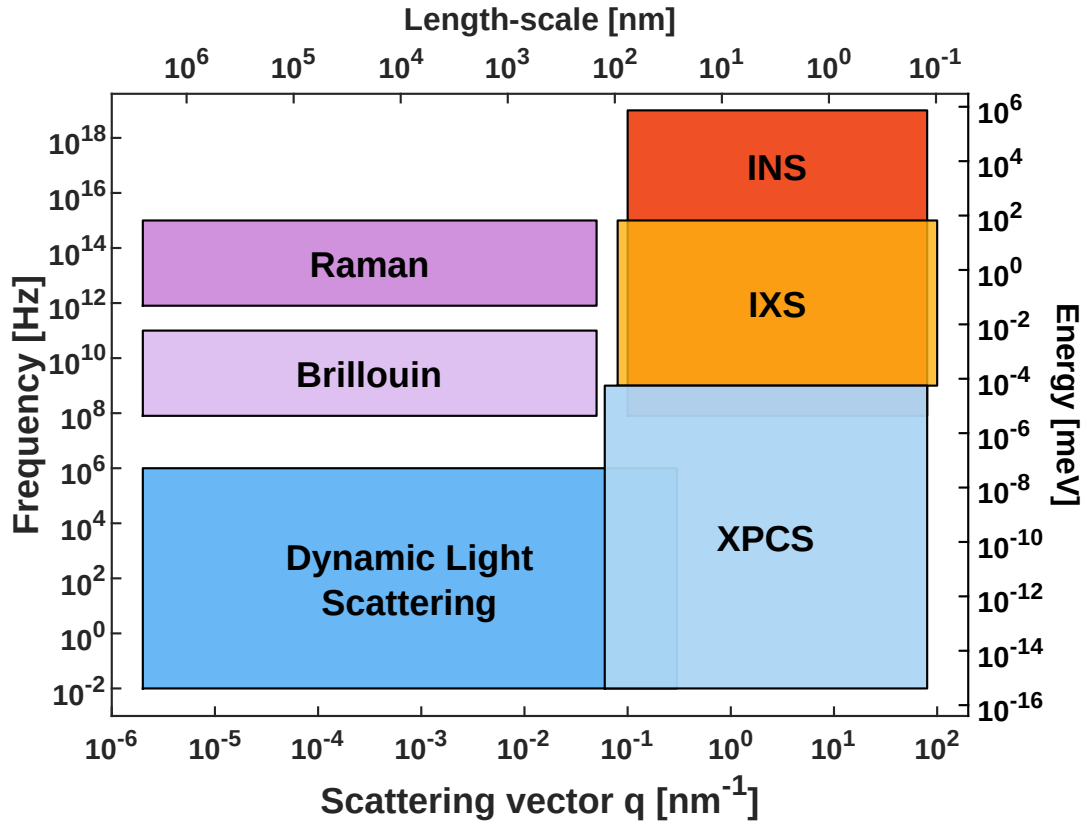


Figure 3.1: Energy-space range covered by different scattering techniques. Figure adapted from [9].

3.1 Scattering processes

Scattering processes consist of the deviation of an incident beam caused by its interaction with a target object. The incident probe can be electromagnetic radiation (e.g., X-rays or visible light), light particles such as electrons, or heavier neutral particles such as neutrons.

A generic scattering experiment is schematically illustrated in Fig. 3.2. The sample is illuminated by an incident beam characterised by a wavevector $\mathbf{k}_i$ and energy E_i . Upon interaction with the sample, the beam is scattered, with final wavevector $\mathbf{k}_f$ and energy E_f . The scattered beam is collected by a detector subtending a solid angle $d\Omega$ at a scattering angle θ with respect to the incident direction, at a distance R from the sample. The scattered beam is described by a wavevector $\mathbf{k}_f$ and energy E_f . The difference $\mathbf{k}_f - \mathbf{k}_i = \mathbf{q}$ defines the momentum transfer, while $E_i - E_f = \hbar\omega$ corresponds to the energy exchanged with the sample. If no energy is exchanged ($E_i = E_f$ or $|\mathbf{k}_f| = |\mathbf{k}_i|$), the process is termed *elastic scattering*; otherwise, it is called *inelastic scattering*.

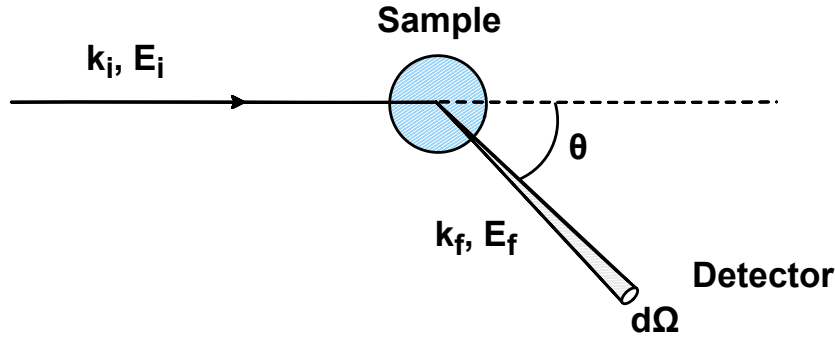


Figure 3.2: Schematic representation of a generic scattering experiment.

The efficiency of a scattering process is quantified by the *differential cross section*,

$$\frac{d\sigma}{d\Omega} = \frac{I_s}{\phi_0 \Delta\Omega} , \quad (3.1.1)$$

where ϕ_0 is the incident particle flux (number of particles per unit time and area) and I_s is the number of particles scattered by the sample and recorded by the detector per unit time within the solid angle $\Delta\Omega$ at distance R . The probability that an incident particle is scattered into a solid angle $d\Omega$ while exchanging an energy interval dE is described by the *double-differential cross section*, $\frac{d\sigma}{d\Omega dE}$.

Within a quantum mechanical framework, using Fermi's golden rule, and under the adiabatic approximation (in which nuclear motion is much slower than electronic motion), the double-differential cross section can be expressed in a compact formalism. For X-ray scattering, where the process originates from the weak interaction between photons and electrons, the result is:

$$\frac{d\sigma}{d\Omega dE} = \frac{k_f}{k_i} r_e^2 |\hat{\epsilon}_i \cdot \hat{\epsilon}_f|^2 S(\mathbf{q}, \omega) , \quad (3.1.2)$$

where k_i and k_f are the magnitudes of the incident and scattered wavevectors, $\hat{\epsilon}_i$ and $\hat{\epsilon}_f$ are the polarization unit vectors of the incident and scattered beams, and r_e is the classical electron radius (Thomson scattering length), a characteristic length scale that sets the strength of photon-electron scattering. The factor $r_e^2 |\hat{\epsilon}_i \cdot \hat{\epsilon}_f|^2$ represents the Thomson cross section for a single electron.

This expression shows that X-ray scattering experiments give direct access to the dynamic structure factor $S(\mathbf{q}, \omega)$, a fundamental quantity for investigating both the structural and dynamical properties of a system and introduced in Sec. 1.3.

3.2 Experimental techniques to probe the vibrational dynamics

This Section presents the theoretical and experimental framework for investigating vibrational dynamics. It first introduces Nuclear Resonant Analysis of Inelastic X-ray Scattering (NRAIXS), highlighting the principles of nuclear absorption, phonon processes, and their connection to the vibrational density of states (DOS). The methodology for DOS extraction and the experimental setup at ESRF are then outlined, together with key aspects of data treatment and analysis.

3.2.1 Theory of nuclear resonant analysis for inelastic X-ray scattering

The Mössbauer effect, or recoilless nuclear resonance fluorescence, is central to the Nuclear Resonant Analysis of Inelastic X-ray Scattering. This physical phenomenon, discovered by Rudolf Mössbauer in 1958, involves the resonant and recoilless emission and absorption of a γ -ray by a nucleus bound in a solid [170].

In general, when a free nucleus emits or absorbs a photon, it recoils to ensure both energy and momentum conservation. The energy of the emitted/absorbed photon in a nuclear transition of energy E_0 is $E_\gamma = E_0 \mp E_R$, where E_R is the recoil energy gain by the nucleus. Starting from the momentum conservation, it is possible to show that

$$E_R = \frac{E_\gamma^2}{2Mc^2} \quad , \quad (3.2.1)$$

where M is the nucleus mass and c is the speed of light in vacuum. Thus, the energy distributions of the emission and absorption processes are centred in $E_\gamma = E_0 \mp E_R$, respectively. Assuming Γ_0 to be the natural line-width of the nuclear transition, an emitted photon can be resonantly reabsorbed by another nucleus only if $2E_R < \Gamma_0$. The line-width Γ_0 is related to the lifetime τ_0 of the excited nuclear state according to Heisenberg's uncertainty principle

$$\tau_0 = \frac{\hbar}{\Gamma_0} \quad , \quad (3.2.2)$$

where $\hbar$ is the reduced Planck constant. Typical values for the lifetime of Mössbauer isotopes are between 10 ns and 1000 ns, which means that Γ_0 is of the order of $10^{-7} - 10^{-9}$ eV. The relative photon energies E_γ are about tens of keV; therefore, the recoil energy is not at all negligible. For instance, the first excited state of ^{57}Fe is $E_0 = 14.413$ keV, thus $E_R \simeq 2$ meV, which is much larger than its natural line-width $\Gamma_0 = 4.66$ neV [171]. As a result, nuclear resonance absorption can not occur for free nuclei.

On the other hand, bound nuclei within a solid recoil in a different way with respect to the previous case [172]: they are not free to recoil, since the binding energies are about a few eV. The absorption and the emission processes are provided by the lattice vibrations; there is a certain probability that 1, 2, ... n phonons are created, annihilated, or that no phonons are involved. In the last case, the crystal lattice recoils as a whole, which means that the mass term in (3.2.1) is of the entire lattice and that $E_R \rightarrow 0$. Therefore, nuclear resonance absorption is possible, since nuclear transition occurs with no recoil and $E_\gamma = E_0$. This fraction of recoil-free events of absorption/emission of photons is described by the Lamb-Mössbauer factor f_{LM} . Instead, for the events associated with the creation/annihilation of phonons, the recoil energy is of the atom/molecule involved in the inelastic scattering process.

3.2.1.1 Nuclear inelastic absorption/scattering

The absorption cross-section is a measure of the probability of an absorption process and is expressed in units of area. Singwi and Sjölander found a general formula for the γ -ray absorption cross-section per nucleus in the form of a time integral [173]. From that expression, the energy probability distribution of absorption $W(\mathcal{E})$ is found [8]

$$W(\mathcal{E}) = \int \frac{d\tau}{2\pi} \exp\left(-i\mathcal{E}\tau - \frac{\Gamma}{2}|\tau|\right) F(\mathbf{k}, \tau) , \quad (3.2.3)$$

where $\tau = t/\hbar$ and t is the time, Γ is the natural width of the excited nuclear state, $\mathcal{E}$ is the difference between the γ -ray energy and the resonance energy of the nuclear transition of ^{57}Fe ($\mathcal{E} = E_\gamma - 14.413 \text{ keV}$) and $\mathbf{k}$ is the wave vector of the incident γ -ray. $F(\mathbf{k}, \tau)$ is the time-dependent correlation function, strictly related to the Van Hove correlation function (1.3.3) introduced in Sec. 1.3,

$$F(\mathbf{k}, \tau) = \langle \exp(-i\mathbf{k}\mathbf{u}(0)) \exp(i\mathbf{k}\mathbf{u}(\tau)) \rangle . \quad (3.2.4)$$

It describes the temporal correlation between the displacement $\mathbf{u}$ of the nucleus at two different moments of time distance, t . This function can be extended for the general case of an anisotropic solid, as proved by Van Hove [8]

$$F(\mathbf{k}, \tau) = \exp(-Z(\mathbf{k})) \exp(M(\mathbf{k}, \tau)) , \quad (3.2.5)$$

where

$$M(\mathbf{k}, \tau) = E_R \sum_{\mathbf{q}, j} \frac{|\mathbf{s} \cdot \mathbf{e}_j(\mathbf{q})|^2}{\hbar\omega_j(\mathbf{q})} ((n_{\mathbf{q},j} + 1) \exp(i\hbar\omega_j(\mathbf{q})\tau) + n_{\mathbf{q},j} \exp(-i\hbar\omega_j(\mathbf{q})\tau)) \quad (3.2.6)$$

describes the creation and the annihilation of a phonon of frequency ω_j and

$$Z(\mathbf{k}) = M(\mathbf{k}, 0) = E_R \sum_{\mathbf{q}, j} \frac{|\mathbf{s} \cdot \mathbf{e}_j(\mathbf{q})|^2}{\hbar\omega_j(\mathbf{q})} (2n_{\mathbf{q},j} + 1) . \quad (3.2.7)$$

E_R is the recoil energy $E_R = \hbar^2 k^2 / 2M$, with M the nucleus mass and k the wave vector magnitude of the incident beam. $\omega_j(\mathbf{q})$ is the dispersion relation of phonons for the branch j , $\mathbf{e}_j(\mathbf{q})$ is the polarization vector of the vibrations in the mode $\{\mathbf{q}, j\}$ and $\mathbf{s} = \mathbf{k}/k$. In addition, $n_{\mathbf{q},j}$ is the Bose-Einstein distribution function

$$n_{\mathbf{q},j} = \frac{1}{\exp\left(\frac{\hbar\omega_j(\mathbf{q})}{k_b T}\right) - 1} \quad (3.2.8)$$

and $\exp(-Z(\mathbf{k})) \equiv f_{LM}(\mathbf{k})$ is the Lamb-Mössbauer factor introduced before. Thus, $F(\mathbf{k}, \tau)$ includes information about both recoilless nuclear absorption/emission and inelastic scattering due to phonons.

In order to evaluate the energy distribution $W(\mathcal{E})$ of equation (3.2.3), the exponential term $\exp(M(\mathbf{k}, \tau))$ is Taylor expanded as power series

$$W(\mathcal{E}) = \sum_{n=0}^{\infty} W_n(\mathcal{E}) , \quad (3.2.9)$$

where each term describes the creation and the annihilation of n phonons due to the absorption of a photon. The zeroth term of the expansion $W_0(\mathcal{E})$ is the elastic nuclear absorption, where no phonons are involved, and it has a Lorentzian form

$$W_0(\mathcal{E}) = \int \frac{d\tau}{2\pi} \exp\left(-i\mathcal{E}\tau - \frac{\Gamma}{2}|\tau|\right) f_{LM}(\mathbf{k}) = f_{LM}(\mathbf{k}) \frac{\Gamma}{2\pi(\mathcal{E}^2 + \Gamma^2/4)} . \quad (3.2.10)$$

The first term $W_1(\mathcal{E})$ is related to the single-phonon nuclear inelastic scattering

$$W_1(\mathcal{E}) = \int \frac{d\tau}{2\pi} \exp\left(-i\mathcal{E}\tau - \frac{\Gamma}{2}|\tau|\right) f_{LM}(\mathbf{k}) M(\mathbf{k}, \tau) . \quad (3.2.11)$$

The dependence on τ of $M(\mathbf{k}, \tau)$ is only inside an exponential factor, thus $W_1(\mathcal{E})$ is

$$W_1(\mathcal{E}) = E_R f_{LM}(\mathbf{k}) \sum_{\mathbf{q}, j} \frac{|\mathbf{s} \cdot \mathbf{e}_j(\mathbf{q})|^2}{\hbar\omega_j(\mathbf{q})} \times \left((n_{\mathbf{q},j} + 1) \frac{\Gamma}{2\pi((\mathcal{E} - \hbar\omega_j(\mathbf{q}))^2 + \Gamma^2/4)} + n_{\mathbf{q},j} \frac{\Gamma}{2\pi((\mathcal{E} + \hbar\omega_j(\mathbf{q}))^2 + \Gamma^2/4)} \right) . \quad (3.2.12)$$

In order to express $W_1(\mathcal{E})$ in terms of the density of states $g(\mathcal{E})$, the sum over $\mathbf{q}$ is substituted by an integral, according to

$$\sum_{\mathbf{q}} \rightarrow V_0 \int \frac{d\mathbf{q}}{(2\pi)^3} . \quad (3.2.13)$$

where V_0 is the volume of the unit cell. Moreover, the $\Gamma \rightarrow 0$ limit is considered, so that the Lorentzian function tends to the Dirac δ -function

$$\frac{\Gamma}{2\pi(\mathcal{E}^2 + \Gamma^2/4)} \xrightarrow{\Gamma \rightarrow 0} \delta(\mathcal{E}) . \quad (3.2.14)$$

$W_1(E)$ becomes

$$W_1(\mathcal{E}) = E_R f_{LM}(\mathbf{k}) \sum_j V_0 \int \frac{d\mathbf{q}}{(2\pi)^3} \frac{|\mathbf{s} \cdot \mathbf{e}_j(\mathbf{q})|^2}{\hbar\omega_j(\mathbf{q})} \times ((n_{\mathbf{q},j} + 1)\delta(\mathcal{E} - \hbar\omega_j(\mathbf{q})) + n_{\mathbf{q},j}\delta(\mathcal{E} + \hbar\omega_j(\mathbf{q}))) . \quad (3.2.15)$$

Now, the creation of a single-phonon (i.e. $\mathcal{E} = \hbar\omega_j(\mathbf{q})$) is taken into account. According to the delta distribution properties, it is true that

$$\int d\mathbf{q} f(\mathbf{q}) \delta(\mathcal{E} - \hbar\omega_j(\mathbf{q})) = \int_{\sigma_0} d\sigma(\mathbf{q}) \frac{f(\mathbf{q})}{|\nabla_{\mathbf{q}}(\hbar\omega_j(\mathbf{q}))|} , \quad (3.2.16)$$

where the integral on the right hand side is over σ_0 , the surface of constant energy $\mathcal{E} = \hbar\omega_j(\mathbf{q})$. Thus, all terms depending directly on $\hbar\omega_j(\mathbf{q})$ are constant over the integral and are evaluated in $\mathcal{E}$. $W_1(\mathcal{E})$ turns into

$$W_1(\mathcal{E}) = \frac{E_R}{E} f_{LM}(\mathbf{k}) (n(\mathcal{E}) + 1) \frac{V_0}{(2\pi)^3} \sum_j \int \frac{|\mathbf{s} \cdot \mathbf{e}_j(\mathbf{q})|^2}{|\nabla_{\mathbf{q}}(\hbar\omega_j(\mathbf{q}))|} d\sigma(\mathbf{q}) , \quad (3.2.17)$$

where the density of states arises

$$g(\mathcal{E}, \mathbf{s}) = \frac{V_0}{(2\pi)^3} \sum_j \int \frac{|\mathbf{s} \cdot \mathbf{e}_j(\mathbf{q})|^2}{|\nabla_{\mathbf{q}}(\hbar\omega_j(\mathbf{q}))|} d\sigma(\mathbf{q}) . \quad (3.2.18)$$

The term $n(\mathcal{E}) + 1$ is rewritten as

$$n(\mathcal{E}) + 1 = \frac{1}{1 - \exp\left(-\frac{\mathcal{E}}{k_b T}\right)} , \quad (3.2.19)$$

so that $W_1(\mathcal{E})$ can be expressed as

$$W_1(\mathcal{E}) = f_{LM}(\mathbf{k}) \frac{E_R g(|\mathcal{E}|, \mathbf{s})}{\mathcal{E} (1 - \exp(-\beta \mathcal{E}))} , \quad (3.2.20)$$

where $\beta = 1/k_b T$. Considering that the nuclear transition linewidth Γ is much smaller than the phonon energy, we introduce the term $S^{(n)}(\mathcal{E}, \mathbf{k})$ as follows

$$W^{(n)}(\mathcal{E}) = f_{LM}(\mathbf{k}) S^{(n)}(\mathcal{E}, \mathbf{k}) , \quad (3.2.21)$$

where

$$S^{(n)}(\mathcal{E}, \mathbf{k}) = \int \frac{d\tau}{2\pi} \exp(-i\mathcal{E}\tau) \frac{M(\mathbf{k}, \tau)^n}{n!} . \quad (3.2.22)$$

Manipulating this expression as

$$S^{(n)}(\mathcal{E}, \mathbf{k}) = \int \frac{d\tau}{2\pi} \exp(-i\mathcal{E}\tau) \frac{M(\mathbf{k}, \tau)}{n} \frac{M(\mathbf{k}, \tau)^{n-1}}{(n-1)!}, \quad (3.2.23)$$

one obtains the Fourier transform of the product between two functions, which is equal to the convolution between their Fourier transforms:

$$S^{(n)}(\mathcal{E}, \mathbf{k}) = \frac{1}{n} \int d\mathcal{E}' S^{(1)}(\mathcal{E}', \mathbf{k}) S^{(n-1)}(\mathcal{E} - \mathcal{E}', \mathbf{k}). \quad (3.2.24)$$

This recursive formula allows for the evaluation of multiphonon contributions starting from the single-phonon term.

Furthermore, from expression (3.2.21), we get

$$S^{(0)}(\mathcal{E}, \mathbf{k}) = \delta(\mathcal{E}) \quad , \quad S^{(1)}(E, \mathbf{k}) = \frac{E_R g(|\mathcal{E}|, \mathbf{s})}{\mathcal{E}(1 - \exp(-\beta\mathcal{E}))}. \quad (3.2.25)$$

Since $S^{(1)}(E, \mathbf{k})$ is Fourier Transform of $M(\mathbf{k}, \tau)$

$$S^{(1)}(\mathcal{E}, \mathbf{k}) = \int \frac{d\tau}{2\pi} \exp(-i\mathcal{E}\tau) M(\mathbf{k}, \tau) \quad (3.2.26)$$

and consequently

$$M(\mathbf{k}, \tau) = \int d\mathcal{E} \exp(i\mathcal{E}\tau) S^{(1)}(\mathcal{E}, \mathbf{k}), \quad (3.2.27)$$

it is possible to find the Lamb-Mössbauer factor

$$\begin{aligned} f_{LM}(\mathbf{k}) &= \exp(-M(\mathbf{k}, 0)) = \exp\left(\int d\mathcal{E} S^{(1)}(E, \mathbf{k})\right) \\ &= \exp\left(\int d\mathcal{E} \frac{E_R g(|\mathcal{E}|, \mathbf{s})}{\mathcal{E}(1 - \exp(-\beta\mathcal{E}))}\right). \end{aligned} \quad (3.2.28)$$

This description is developed considering that the sample is, at the same time, the energy analyser and the object whose vibrational properties are of interest. For instance, if we study the vibrational modes of ^{57}Fe , the sample itself is the energy analyser: one fraction of the scattering events is associated to the recoilless nuclear transition (so to f_{LM}), while the remaining part is related to the inelastic scattering of phonons (thus to E_R). This means that the photons are overall absorbed by the sample, such that the exchanged momentum of the nuclei $p = \hbar q$ is equal to the momentum of the

incident beam $p_\gamma = \hbar k$. For this reason, the recoil energy is expressed as $E_R = \hbar^2 k^2 / 2M$.

If the sample and the energy analyser do not coincide, as occurs in many experiments of this kind, the recoilless nuclear scattering is used to measure the inelastic signal given by the vibrational modes of the sample.

The result is that the recoil energy must be expressed with the general formula

$$E_R = \frac{\hbar^2 q^2}{2M}, \quad (3.2.29)$$

with q , the exchanged wavevector between the input beam and the phonons created or annihilated.

All the treatments previously described are general and apply to this case, since the incoherent approximation is guaranteed by the large magnitude of the exchanged momentum [174].

3.2.1.2 The method of DOS calculation

The approach explored so far assumes a perfectly monochromatic incident electromagnetic beam (X-ray). In practice, however, the beam exhibits a finite energy bandwidth, which can be described by an energy distribution $P(\mathcal{E})$. Before proceeding, the elastic contribution to the measured energy spectrum must be removed, since the theoretical framework does not account for a strong coherent elastic signal, which could otherwise produce an apparent faster decay of the synchrotron pulse [8]. The relevant quantity is therefore the inelastic component of the absorption probability distribution, $W_{inel}(\mathcal{E}) = W(\mathcal{E}) - W_0(\mathcal{E})$, which is not directly accessible experimentally but appears convoluted with the instrumental function $P(\mathcal{E})$. Thus, the measured energy spectrum, once the elastic contribution is subtracted, can be expressed as

$$\begin{aligned} I(\mathcal{E}, \mathbf{k}) &= I_0 \int d\mathcal{E}' P(\mathcal{E}') W_{inel}(\mathcal{E} - \mathcal{E}') \\ &= I_0 \int \frac{d\tau}{2\pi} \exp\left(-i\mathcal{E}\tau - \frac{\Gamma}{2}|\tau|\right) Q(\tau) f_{LM}(\mathbf{k}) [\exp(M(\mathbf{k}, \tau)) - 1] \end{aligned} \quad (3.2.30)$$

according to the convolution theorem for the inverse Fourier transform. Here, I_0 is a scaling factor, and $Q(\tau)$ is the inverse Fourier transform of $P(\mathcal{E})$. The goal is to isolate the term $M(\mathbf{k}, \tau)$, which is the inverse Fourier transform of $S^{(1)}(\mathcal{E}, \mathbf{k})$, directly related to the DOS as in Equation (3.2.25). Since the instrumental function is a peak around $\mathcal{E}$ of width roughly 0.2 meV (see next Sec. 3.2.2), the limit $\Gamma \rightarrow 0$ can be considered as done in the previous

Paragraph. Evaluating the inverse Fourier transform of $I(\mathcal{E}, \mathbf{k})$ and dividing the result by $I_0 Q(\tau) f_{LM}(\mathbf{k})$ yields

$$\frac{\mathcal{F}^{-1}(I(\mathcal{E}, \mathbf{k}))}{I_0 Q(\tau) f_{LM}(\mathbf{k})} = \frac{I_0 Q(\tau) f_{LM}(\mathbf{k}) [\exp(M(\mathbf{k}, \tau)) - 1]}{I_0 Q(\tau) f_{LM}(\mathbf{k})} = \exp(M(\mathbf{k}, \tau)) - 1 . \quad (3.2.31)$$

Therefore, $M(\mathbf{k}, \tau)$ is

$$M(\mathbf{k}, \tau) = \ln \left(\frac{\mathcal{F}^{-1}(I(\mathcal{E}, \mathbf{k}))}{I_0 Q(\tau) f_{LM}(\mathbf{k})} + 1 \right) \quad (3.2.32)$$

and the density of states is found

$$\begin{aligned} g(\mathcal{E}, \mathbf{s}) &= \frac{\mathcal{E}}{E_R} \mathcal{E} (1 - \exp(-\beta \mathcal{E})) S^{(1)}(\mathcal{E}, \mathbf{k}) \\ &= \frac{\mathcal{E}}{E_R} \mathcal{E} (1 - \exp(-\beta \mathcal{E})) \mathcal{F}(M(\mathbf{k}, \tau)) . \end{aligned} \quad (3.2.33)$$

To evaluate I_0 and $f_{LM}(\mathbf{k})$, the zero and the first moments of the experimental energy spectrum are considered, respectively

$$\langle \mathcal{E}^0 \rangle_I = \int d\mathcal{E} I(\mathcal{E}, \mathbf{k}) \quad \text{and} \quad \langle \mathcal{E}^1 \rangle_I = \int d\mathcal{E} I(\mathcal{E}, \mathbf{k}) \mathcal{E} . \quad (3.2.34)$$

It can be shown that (see Appendix A)

$$I_0 = \frac{\langle \mathcal{E}^1 \rangle_I - \langle \mathcal{E}^0 \rangle_I \langle \mathcal{E}^1 \rangle_P}{E_R} , \quad f_{LM}(\mathbf{k}) = 1 - \frac{\langle \mathcal{E}^0 \rangle_I}{I_0} . \quad (3.2.35)$$

Therefore, the only external parameter is E_R , because $Q(\tau)$ and the momenta of $I(\mathcal{E})$ and $P(\mathcal{E})$ are determined starting from the measured energy spectra and instrumental response.

Recoil energy

The recoil energy must be estimated, as it is the sole free parameter in the data analysis. It is given by the general expression introduced before

$$E_R = \frac{\hbar^2 q^2}{2M} .$$

To estimate the exchanged wavevector q , we consider that the exchanged energy $\mathcal{E}$ is of the order of meV, while the energy of the incident beam E_i and that of the scattered beam E_f are about tens of keV. This means that

$E_i \simeq E_f = 14.413$ keV and that $k_i \simeq k_f$ ($k = E/\hbar c$), which are the wavevectors moduli of the incident and the scattered beams, respectively. The exchanged wavevector is

$$\mathbf{q} = \mathbf{k}_i - \mathbf{k}_f \quad (3.2.36)$$

and, considering that $k_i \simeq k_f$, one obtains (see Figure 3.3)

$$q = |\mathbf{q}| = k_i \frac{\sin \theta}{\sin \alpha} = k_i \frac{\sin \theta}{\cos \frac{\theta}{2}} = 2k_i \sin \frac{\theta}{2} . \quad (3.2.37)$$

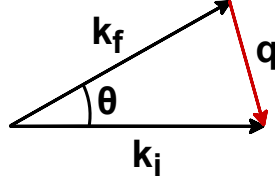


Figure 3.3: The exchanged wavevector $\mathbf{q}$ between the input beam of wavevector $\mathbf{k}_i$ and the sample; $\mathbf{k}_f$ is the output X-ray wave-vector. The approximation $k_i \simeq k_f$ is taken into account.

The angle θ varies in a range of $[0, \pi]$, since the detector is located such that it covers essentially a solid angle of 2π . Thus, we can average the value of q

$$q = \frac{1}{\pi} \int_0^\pi 2k_i \sin \frac{\theta}{2} = \frac{4}{\pi} k_i \simeq 9.3 \text{ \AA}^{-1} . \quad (3.2.38)$$

3.2.2 Experimental details of NRAIXS

The NRAIXS measurements presented in this Thesis were performed at the Nuclear Resonance beamline [169,175] ID18 (currently ID14) of the European Synchrotron Radiation Facility (ESRF) in Grenoble, France. The synchrotron X-ray beam passes through a recently developed spectrograph, achieving an energy resolution of $200 \mu\text{eV}$. The incident photon energy is tuned around the ^{57}Fe nuclear transition, and both the scattered radiation and the transmitted beam are detected. The detectors are large-area avalanche photodiodes covered with a ^{57}Fe foil, enabling the exploitation of the Mössbauer effect. This ensures that the output energy uncertainty is negligible compared to that of the incoming photons. Measurements can be performed at both room temperature and low temperatures.

3.2.2.1 ID14 beamline at the ESRF

The ID14 beamline is an undulator beamline consisting of a straight section equipped with three *revolver* undulators, each about 1.6 m long, with an interchangeable period of either 27 mm or 20 mm. The 27 mm undulators provide a broad hard X-ray energy range of 7.2–80 keV, while the 20 mm undulators are optimised for the ^{57}Fe nuclear transition at 14.413 keV [176], which is used in NRAIXS experiments.

The overall beamline layout and radiation path are shown in Fig. 3.4a). The X-rays produced in the undulators first pass through a high-heat-load monochromator (HHLM), designed to guarantee short- and long-term angular stability, high positioning accuracy, reliable energy definition, fixed exit geometry, matching between the source divergence and the monochromator angular acceptance, and preservation of the X-ray wave field propagation [177].

The HHLM is composed of two asymmetrically cut Si(111) crystals, designed to match the divergence of the beam up to 27 keV. The crystals are mounted on high-precision mechanics, enabling angular alignment with a resolution of 100 nrad and long-term stability better than 1 μrad per month. This configuration provides excellent energy stability of the monochromatised beam [177]. The HHLM operates under UHV conditions (10^{-8} mbar) and is nitrogen-cooled, preventing temperature drifts after ring refills.

After the HHLM, a first compound refractive lens (CRL_1) collimates the 14.413 keV beam, reducing its divergence from several μrad to about 1.7 μrad [178]. The beam then enters the spectrograph, which consists of three asymmetrically cut silicon crystals. The first crystal preserves the beam direction, while the second and third (using the (12 2 2) reflection) provide a high angular dispersion, reaching 28 $\mu\text{rad}/\text{meV}$ [179] (Fig. 3.4b)). This allows energy resolutions down to $\sim 120 \mu\text{eV}$.

A multilayer mirror (ML) ensures horizontal beam propagation and separates photons by energy, while a second compound refractive lens (CRL_2) focuses photons of different energies onto distinct vertical positions at an array of slits. This multi-slit configuration enables simultaneous measurement of several samples. A flux monitor placed before the samples measures the incident intensity using an ionising gas, allowing correction for storage-ring decay.

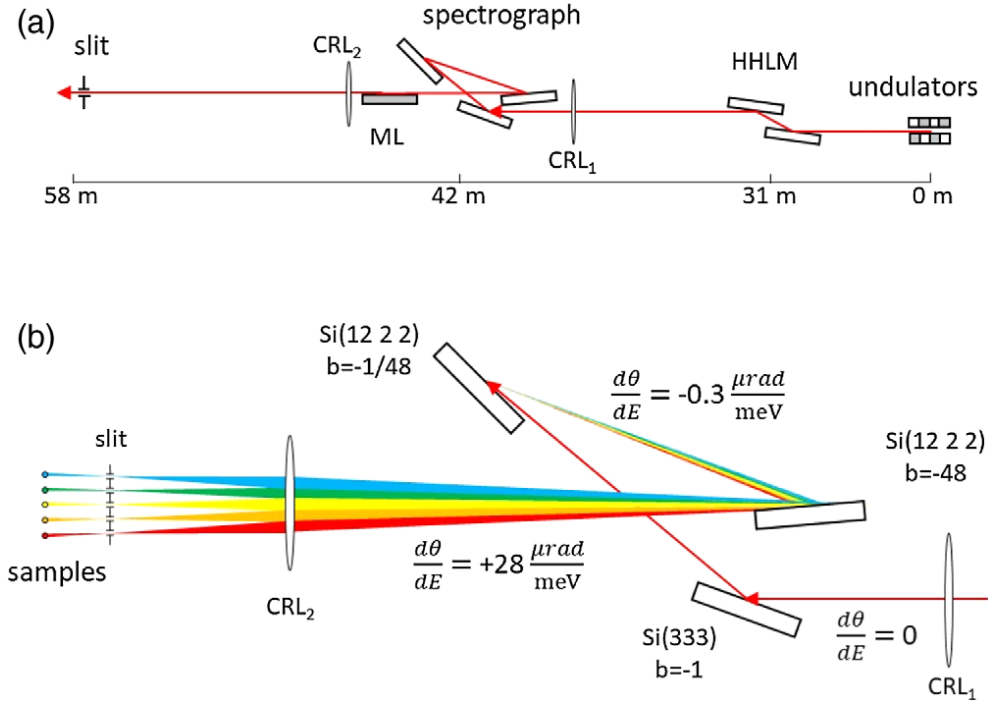


Figure 3.4: Experimental setup. a) Beamline layout and X-ray propagation, indicating the position of the high-heat-load monochromator (HHLM), two compound refractive lenses (CRL), a multilayer mirror (ML), and the spectrograph. b) Optical scheme of the spectrograph, consisting of three asymmetrically cut silicon crystals providing a total angular dispersion of $28 \mu\text{rad}/\text{meV}$. Each crystal is characterised by its Miller indices (hkl), asymmetry factor b , and angular dispersion $d\theta/dE$. Reprinted from Ref. [179], © 2019 American Physical Society, with permission.

The incident photon energy is varied within a narrow range ($\sim 15 \text{ meV}$) around the ^{57}Fe nuclear transition ($E_0 = 14.413 \text{ keV}$):

$$E_{\text{in}} = 14.413 \pm \mathcal{E} , \quad (3.2.39)$$

where $\mathcal{E}$ is the energy variation.

This configuration improves counting statistics and reduces acquisition time. However, since the beams emerging from the slits are vertically displaced, the samples must be tilted to compensate. The tilt angle θ corresponds to the grazing incidence angle of the beam on the sample. For samples deposited on substrates, θ must be chosen to maximise beam attenuation within the sample while minimising inelastic scattering from the substrate. The angle of incidence must remain below the substrate's critical

angle to ensure a shallow penetration depth. In this geometry, part of the radiation is scattered and collected by detectors positioned ~ 1 mm above each sample, covering nearly 2π of solid angle. As a result, the measured intensity can be considered independent of the momentum transfer q , since integration is effectively performed over a wide q -range ($q \simeq 0.7\text{--}14.6 \text{ \AA}^{-1}$). This ensures the validity of the incoherent approximation [174] and enables a proper determination of the vibrational density of states (VDOS). The reflected radiation is simultaneously measured by forward detectors, which record the instrumental function required for resolution deconvolution and elastic peak subtraction (see Sec. 3.2.3).

A limitation of this geometry is cross-talk between samples: scattered radiation from one sample may reach neighbouring ones, producing spurious peaks in the Stokes region. To avoid these artefacts, a transmission setup can be employed, allowing single-sample measurements.

Transmission configuration

In the transmission geometry, the incident X-ray beam crosses the sample as shown in Figure 3.5, ensuring the absence of any contribution from the substrate. Thus, the signal collected by the single detector placed above the sample results to be only from scattering by the sample. This detector is located 1 mm above the sample, providing the validity of the incoherent approximation and a correct DOS estimation. The detector in front of the beam measures the instrumental response in transmission, since the incident ray is attenuated only by the sample.

In the transmission geometry, the X-ray beam passes directly through the sample (Fig. 3.5), thereby eliminating substrate contributions. A single detector, located ~ 1 mm above the sample, collects the scattered radiation, ensuring the validity of the incoherent approximation. A forward detector simultaneously records the transmitted beam, providing the instrumental function in transmission.

In this setup, a single slit positioned after CRL₂ defines the beam aperture, which is optimised to maximise the scattered signal.

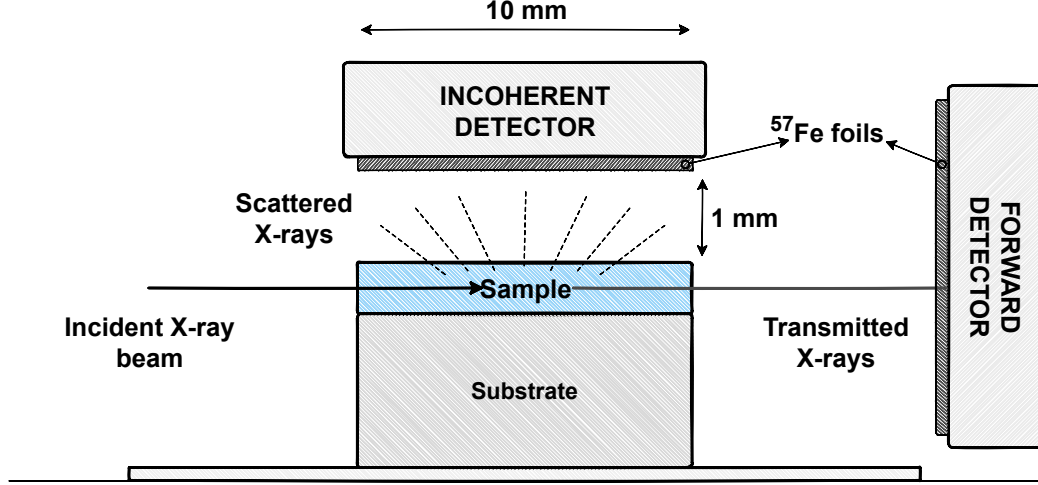


Figure 3.5: Transmission geometry. The X-ray beam, collimated by a slit, passes perpendicularly through the sample, ensuring irradiation of only the sample layer. The scattered radiation is detected by a sensor located 1 mm above the sample, while a forward detector records the transmitted beam to measure the instrumental response.

Low temperature measurement

The density of states (DOS) can also be measured at low temperatures. For these measurements, the sample is mounted inside a helium exchange-gas cryostat. In this setup, the sample chamber is filled with a small volume of helium gas, which is cooled by the cryostat.

The detectors and the Mössbauer effect

The detectors consist of a large-area avalanche photodiode (APD) covered by a $10\ \mu\text{m}$ thick ^{57}Fe foil. The avalanche photodiode is a highly sensitive semiconductor device that exploits the photoelectric effect to convert incoming electromagnetic radiation into an electric current [180].

The use of ^{57}Fe foils allows, in principle, measurements with an energy resolution on the order of neV. The detector operates based on the Mössbauer effect, also known as recoilless nuclear resonance fluorescence: a γ photon with energy matching the nuclear transition of the isotope is absorbed and re-emitted without energy loss, since the nucleus of the isotope does not suffer from recoil (see Section 3.2.1). This ensures that the photons emitted via nuclear absorption have a well-defined energy of $E_0 = 14.413\ \text{keV}$ for ^{57}Fe .

In addition, the bandwidth of nuclear transition of ^{57}Fe is $\Gamma_0 = 4.66$ neV, which means not only that the energy error is negligible with respect to the input uncertainty, but also that the photons are re-emitted with a delay of 141 ns, allowing to discriminate the nuclear transition from the fast radiation of picoseconds caused by the electronic transition. Therefore, photons with different energies hit the ^{57}Fe foil: those far from resonance interact with electronic transitions and are re-emitted within a few picoseconds, while photons precisely at $E_0 = 14.413$ keV excite the nuclear level and are re-emitted after the characteristic delay.

The APDs measure all the photons coming from the ^{57}Fe foil, resulting in a *prompt* signal due to electronic excitations occurring within the first 10 ns, and a *delay* signal from the nuclear transition in the subsequent time. The delay signal is of primary interest for data analysis, as it corresponds to photons scattered by the sample at the resonant energy $E_0 = 14.413$ keV. By knowing the input energy $E_{in} = 14.413 \pm \mathcal{E}$ keV, the energy exchange with phonons, $\mathcal{E}$, can be determined.

To isolate the nuclear fluorescence, the first 10 ns of data are discarded since the prompt electronic signal is several orders of magnitude more intense than the nuclear fluorescence, and its tails would otherwise obscure the delayed nuclear signal.

Extended spectrum

To accurately determine and properly normalise the density of states (see Section 3.2.3), an extended energy spectrum must be measured over a larger range of energies (up to ~ 400 meV). For this purpose, the spectrograph is replaced with a high-resolution monochromator (HRM) providing an energy resolution of approximately 1.8 meV. Since this measurement does not require ultra-high energy precision, using the HRM significantly reduces the total experimental time.

The HRM consists of four asymmetrically cut Si-crystals in an in-line configuration, where the input and the output beams are in the same direction as illustrated in Figure 3.6. The first pair of crystals collimates the incident beam, while the second pair selects the final bandwidth [13]. By setting the angles of the incident and exit beams relative to the crystal surface, the desired energy resolution can be achieved.

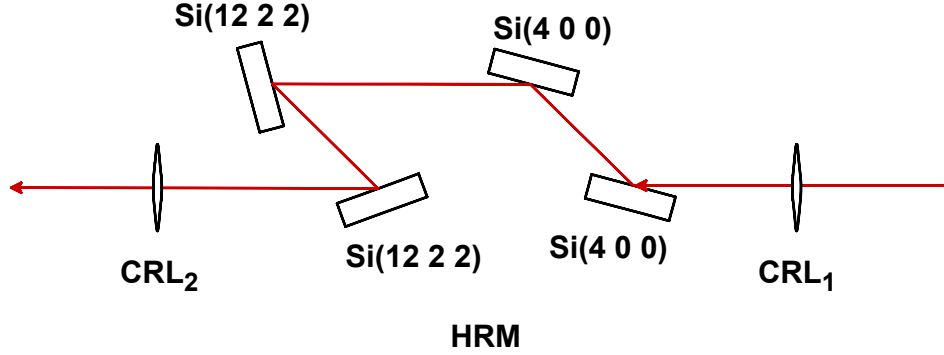


Figure 3.6: Schematic of the high-resolution monochromator (HRM) used to measure the extended energy spectrum. The four asymmetrically cut silicon crystals enable an energy resolution of 1.8 meV by collimating and selecting the bandwidth of the beam.

Measuring the background

To properly analyse the energy spectrum, it is essential to measure the background signal detected by the avalanche photodiodes. This background may be due to cosmic rays, electronic noise, or photons that bounce around. To estimate it, the input beam energy is set to -100 meV, far from the resonant energy of ^{57}Fe , and the number of photons in the delay signal is recorded over 500 seconds.

Additionally, the prompt signal, which essentially captures all incoming photons, is measured at both -100 meV and 0 meV. This allows rescaling the background counts obtained at -100 meV to match the measurement conditions of the energy spectra, where the effective detected energy transfer $\mathcal{E}$ is always around 0 meV due to the Mössbauer effect.

Ideally, the sample should be removed to avoid scattering contributions when measuring the background on both forward and upper detectors. However, to maintain consistent conditions with the spectral measurements, the sample is left in place and the background is measured at -100 meV, where scattering is negligible since the anti-Stokes region exhibits very low vibrational intensity. Moreover, in the low-energy boson peak region (below 2 meV), the signal is way larger than the background. This approach affects the high-energy region more significantly; however, that region is primarily used for DOS normalisation.

3.2.2.2 Static structure factor measurements

During the experiment, the static structure factor $S(q)$ of the samples can be monitored by exploiting the θ - 2θ (Bragg-Brentano) geometry. The detector placed above the sample is removed, and the forward detector is used to record the scattered intensity while varying the exchanged wavevector q . The output beam is selected by a slit 1.64 mm wide, located at a distance $l = 295.2$ mm from the sample, as depicted in Figure 3.7. Both the forward detector and the slit are moved vertically along the z -axis to scan different values of q .

From the expression for the exchanged wavevector derived in Par. 3.2.1.2, the measured intensity can be expressed in terms of the exchanged wavevector q :

$$\theta = \tan^{-1} \left(\frac{z}{l} \right) \quad \longrightarrow \quad q = 2k_i \sin \frac{\theta}{2} . \quad (3.2.40)$$

It should be noted that this setup does not constitute a full diffractometer, resulting in relatively low input resolution.

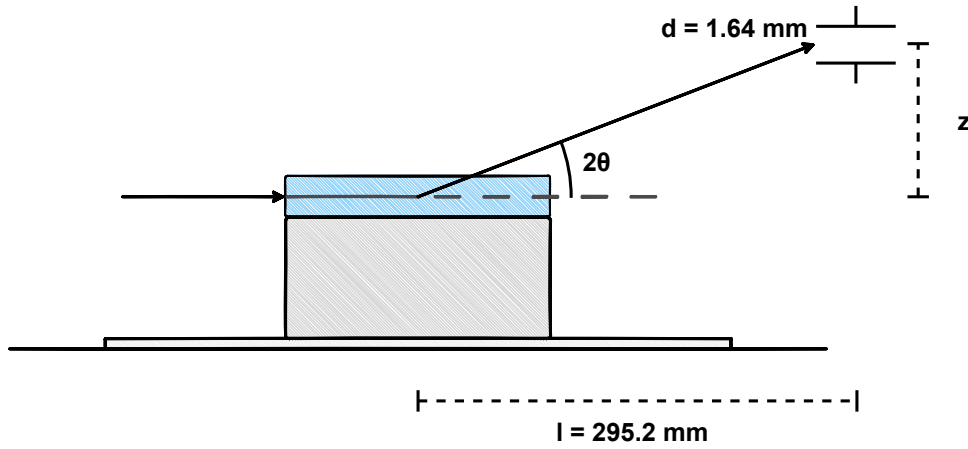


Figure 3.7: Setup for static structure factor measurements. The slit selecting the scattered intensity is positioned 295.2 mm from the sample. By varying the vertical positions of the slit and the detector, the scattered intensity as a function of the exchanged wavevector q is measured.

3.2.3 Data analysis of NRAIXS

The computer realisation of what is explained in Sec. 3.2.1 is operated employing a program developed by Khon and Chumakov [8], which was kindly provided at our disposal.

Sum and binning of the data

First of all, the data from all measured scans are summed for both the total scattered signal (I_{tot}) and the instrumental function (IF). In this way, distinctive DOS curves are obtained thanks to a gain in statistics. In the subsequent step, data are binned from groups of channels to one channel due to the following reason: a computer program can not operate a Fourier transform on raw data, since the noises presence leads to statistical deviation in experimental data, which may result in false peaks or the hiding of real small peaks in the density of states. An example of raw data and their subsequent binning is reported in Figure 3.8a) and 3.8b), respectively.

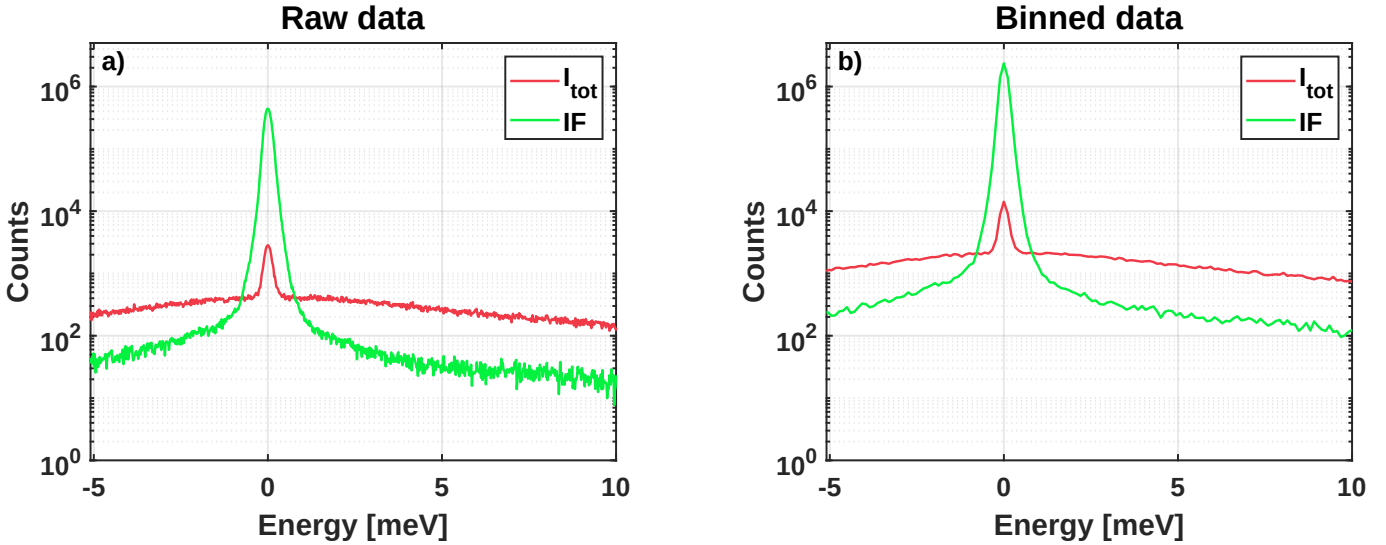


Figure 3.8: From raw to binned data. a) Data from multiple scans are summed to increase statistics. b) Data are binned in a channel of a specific energy width. The red curves are the total scattered signal collected with the detector located above the sample, while the green lines are the instrumental function measured by the forward detector.

Subtraction of the central peak

To correctly operate the analysis procedures, it is necessary to subtract the elastic contribution from the total scattered signal $I_{tot}(\mathcal{E})$ to obtain the intensity due to inelastic scattering only, $I(\mathcal{E})$. Firstly, the background is removed from both $I_{tot}(\mathcal{E})$ and the instrumental function $P(\mathcal{E})$. After that, the energy range within which the subtraction is operated is fixed (here, as an example, $[-3, 3]$ meV): beyond it, the instrumental response is set to zero. The central peak is characterised by two boundaries, $\mathcal{E}_1 = -|\mathcal{E}_1|$ and $\mathcal{E}_2$, which the intensities I_1 and I_2 correspond to. Besides the elastic contribution, the central peak contains the inelastic scattering as well, which can be approximated by a linear function near $\mathcal{E} = 0$ passing through $\mathcal{E}_1$ and $\mathcal{E}_2$

$$I_{in}(\mathcal{E}) = \left(\frac{I_2 - I_1}{\mathcal{E}_2 - \mathcal{E}_1} \right) (\mathcal{E} - \mathcal{E}_2) + I_2 . \quad (3.2.41)$$

At this point, it is possible to subtract the central peak, according to

$$I(\mathcal{E}) = I_{tot}(\mathcal{E}) - \alpha P(\mathcal{E}) , \quad (3.2.42)$$

where α is a re-scaling factor, since the instrumental function is characterised by a larger signal than $I_{tot}(\mathcal{E})$, as represented from plots in Figure 3.8. To find α , the condition $I(0) = I_{in}(0)$ is imposed

$$\alpha = \frac{I_{tot}(0) - I_{in}(0)}{P(0)} , \quad (3.2.43)$$

where $I_{in}(0)$ results to be

$$I_{in}(0) = - \left(\frac{I_2 - I_1}{\mathcal{E}_2 - \mathcal{E}_1} \right) \mathcal{E}_2 + I_2 . \quad (3.2.44)$$

The graph of Figure 3.9 proves that here the elastic contribution is relevant in an energy range of $[-1, 1]$ meV, while outside this region it is compatible with the statistical errors; this means that the $[-3, 3]$ meV range is reasonable.

The subtraction of the measured $I_{tot}(\mathcal{E})$ and $P(\mathcal{E})$ brings to significant fluctuation. For this reason, the central part of both the scattered signal and the instrumental response is approximated by a third-degree polynomial:

$$y(x) = a(x - x_1)^3 + b(x - x_1)^2 + c(x - x_1) + d . \quad (3.2.45)$$

The coefficients are obtained from the conditions of continuity and derivability with the true spectra in $x_1 = \mathcal{E}_1$ and $x_2 = \mathcal{E}_2$

$$\begin{aligned} a &= \frac{x_{21}G - 2F}{x_{21}^3} , & b &= \frac{3F - x_{21}G}{x_{21}^2} , \\ c &= y'(x_1) , & d &= y(x_1) , \end{aligned} \quad (3.2.46)$$

where

$$\begin{aligned} F &= y(x_2) - y(x_1) - x_{21}y'(x_1) \\ G &= y'(x_2) - y'(x_1) \\ x_{21} &= x_2 - x_1 \end{aligned} \quad (3.2.47)$$

The subtraction is performed iteratively, following steps that may or may not be applied. First, a subtraction can be carried out with an energy shift of the elastic peak, using guessed values for $\mathcal{E}_1$ and $\mathcal{E}_2$. Subsequently, a subtraction with peak broadening can be applied. The choice between energy shifting and broadening is made to minimise residual fluctuations. Figure 3.10a) shows an example of subtraction of peaks with an energy shift; in Figure 3.10b), a subtraction with a peak broadening is presented, where the broadening is exaggerated to highlight the effect of the central peak removal.

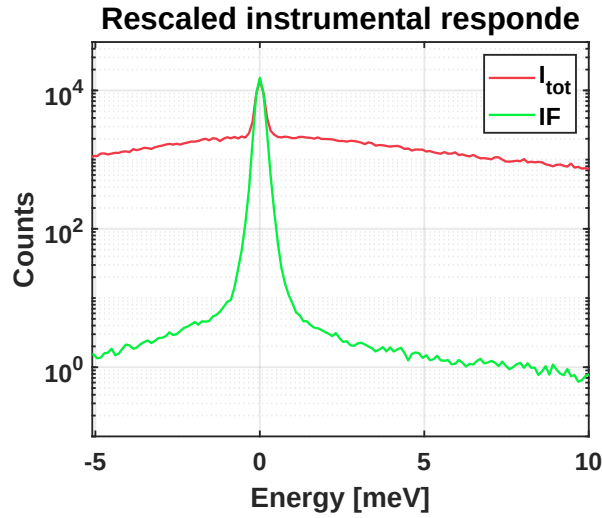


Figure 3.9: The rescaling of the instrumental function. Before subtracting the elastic peak from the total scattered intensity, $P(\mathcal{E})$ must be re-scaled with a factor α . The elastic contribution to I_{tot} is negligible outside the $[-3, 3]$ meV range.

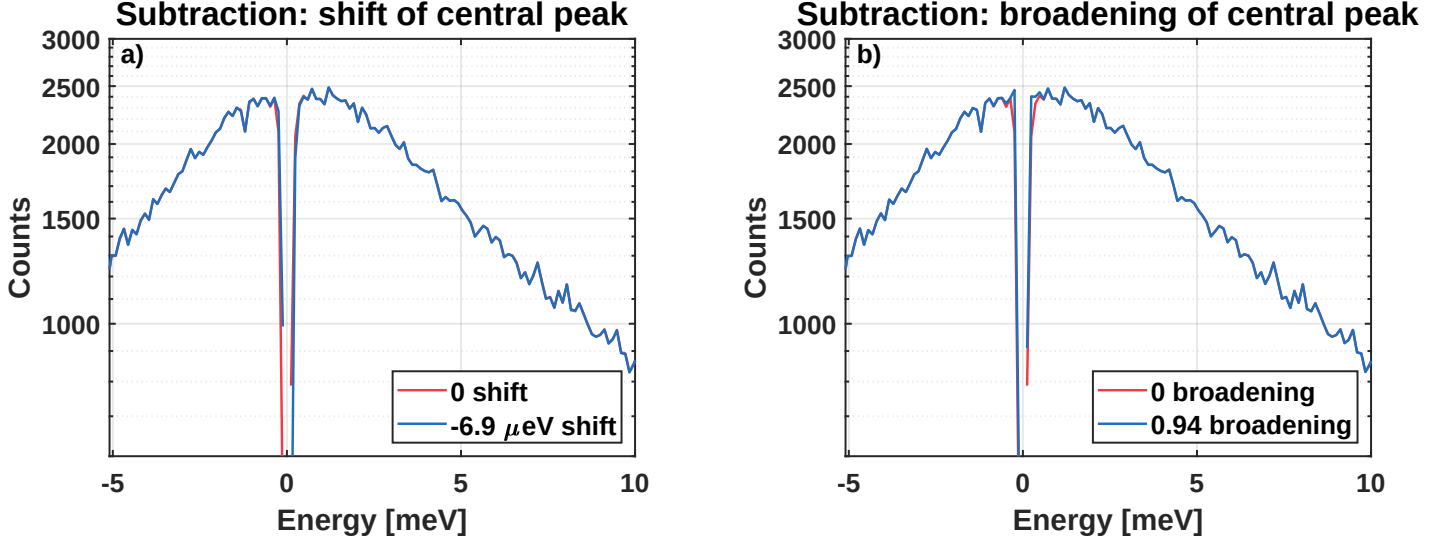


Figure 3.10: Subtraction procedure. a) The effects of the subtraction of the central peak with an energy shift of $-6.9 \mu\text{e}$ (blue line) and with no shift (red line) are compared. b) Comparison between the central part removal with a peak broadening of a factor 0.94 (blue line) and that without any broadening. The energy shift and the broadening are operated only if the fluctuations are minimised during the subtraction.

Once the peak is subtracted, the inelastic contribution $I(\mathcal{E})$ is linearly approximated between two final values of $\mathcal{E}_1$ and $\mathcal{E}_2$, chosen between the points closer to $\mathcal{E} = 0$, such that $I(\mathcal{E}_1) \simeq I_{tot}(\mathcal{E}_1)$ and $I(\mathcal{E}_2) \simeq I_{tot}(\mathcal{E}_2)$. The example here reported is shown in the plot in Figure 3.11a), where $\mathcal{E}_1 = 0.59 \text{ meV}$ and $\mathcal{E}_2 = 0.60 \text{ meV}$.

Finally, the entire procedure is verified by the comparison between the Stokes and the Anti-Stokes sides, according to the detailed balance

$$I^{AS}(-\mathcal{E}) = e^{-\frac{\mathcal{E}}{k_B T}} I^S(\mathcal{E}) . \quad (3.2.48)$$

See Figure 3.11b).

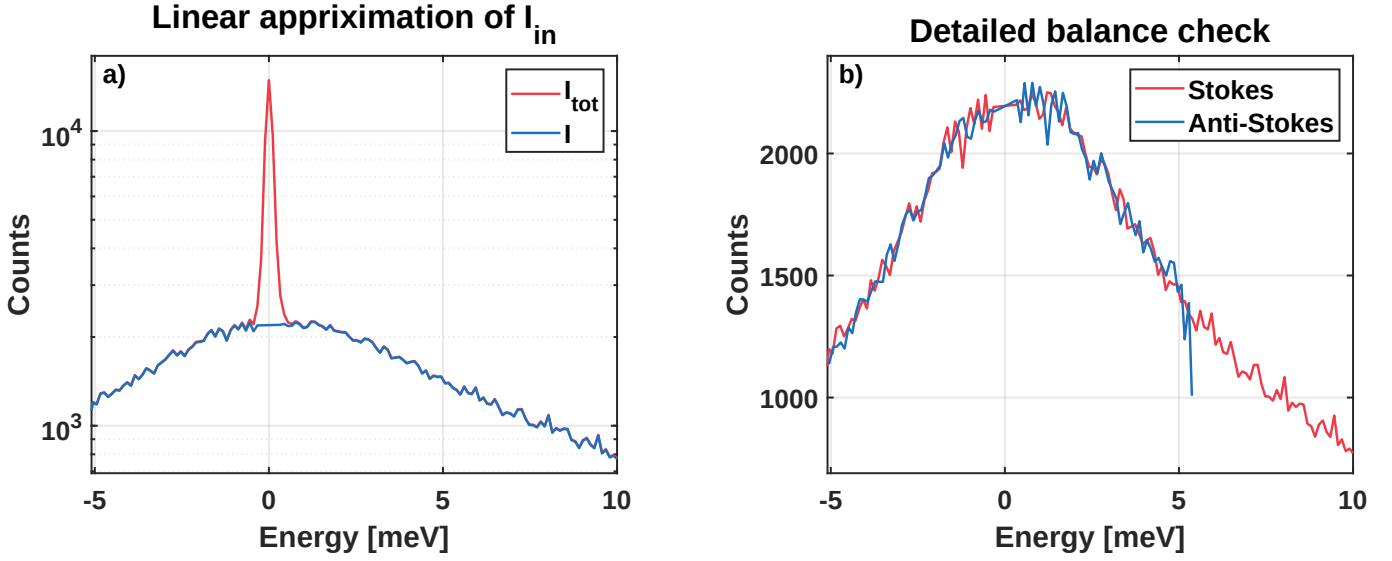


Figure 3.11: Final steps of the subtraction procedure. a) After the subtraction, the inelastic contribution to the central peak is approximated to a linear function according to Equation (3.2.41). b) The procedure of elastic peak subtraction is verified by comparing the Stokes side with the Anti-Stokes one; if they correspond, then the procedure can be considered reliable.

Extension of the graph

To properly evaluate the density of states, thus to operate Fourier transforms, it is essential to lengthen the high-resolution (HR) energy spectra by attaching the extended spectrum. To do that, the extended spectrum has to be rescaled to the height of the high-resolution one. The two spectra are then attached, removing the more external and noisy points of the HR spectrum (Figure 3.12a)). Moreover, the instrumental function of the HR spectrum is extended to zero in the same energy interval, to have the same number of points as the entire new spectrum. After that, the entire spectrum is further expanded using the detailed balance principle (Figure 3.12b)).

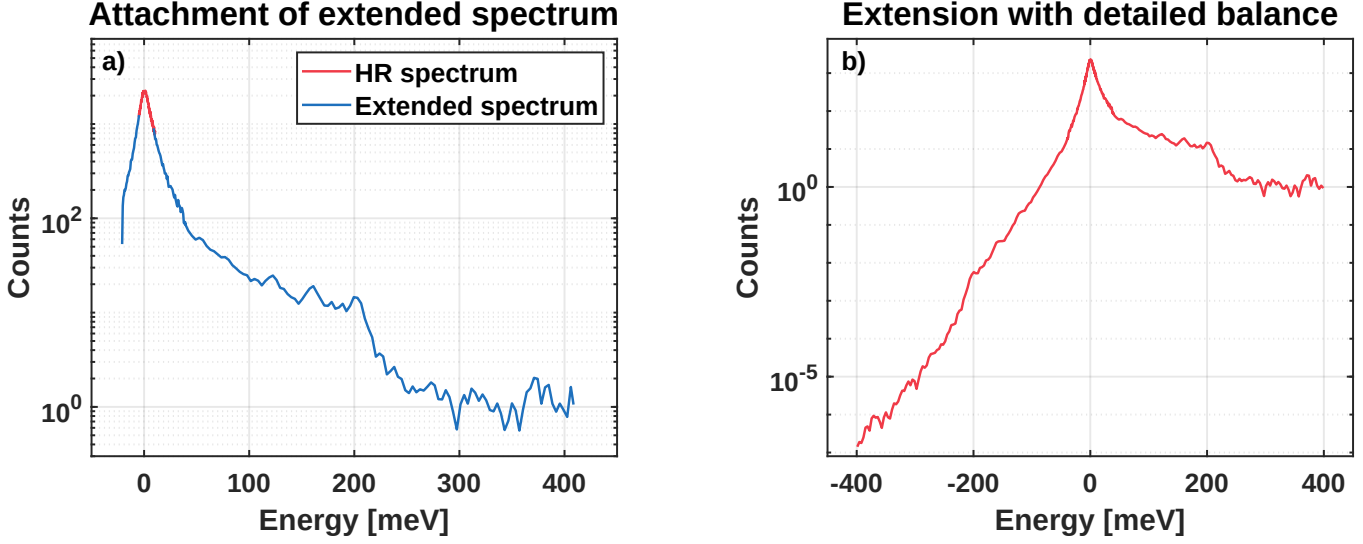


Figure 3.12: Extension of the high-resolution spectrum with the extended one. To better evaluate the Fourier transforms used for the DOS calculation, the HR spectra must be expanded to a large energy range. To this, the extended spectrum is re-scaled and attached to the high resolution one (HR) a); the result is further extended, exploiting the detailed principle b).

Calculation of DOS

To find the density of states, a simultaneous deconvolution of the multi-phonon contribution and the instrumental response is required. Hence, the Anti-Fourier transforms of $I(\mathcal{E})$ and $P(\mathcal{E})$ are operated

$$Q(\tau) = \int d\mathcal{E} \exp(i\mathcal{E}\tau) P(\mathcal{E}) , \quad \mathcal{F}^{-1}(I(\mathcal{E})) = \int d\mathcal{E} \exp(i\mathcal{E}\tau) I(\mathcal{E}) . \quad (3.2.49)$$

However, a computer program cannot directly calculate the ratio of Equation (3.2.31), since the tails of $Q(\tau)$ are equal to zero. Thus, $1/Q(\tau)$ is replaced by

$$\frac{1}{Q_0(\tau)} = \frac{1 + P_{\text{if}}}{Q(\tau) + P_{\text{if}}} , \quad (3.2.50)$$

where P_{if} is a parameter of the program. It is possible to observe that if one sets $P_{\text{if}} = 0.1$, the instrumental function is almost completely deconvoluted; on the other hand, if $P_{\text{if}} = 100$, the instrumental response is not deconvoluted, because $Q_0(\tau) \simeq 1$. The Fourier transforms are calculated using the Fast

Fourier Transformation (FFT), and the number of channels must be $N = 2^n$, with n an integer. The energy range within the Anti-Fourier transforms are calculated is set to $[-256, 256]$ meV.

To find the scaling factor I_0 , the value of the energy recoil E_R must be fixed. A first estimation of its values can be performed by Eq.(3.2.29). Later, its value must be tuned to obtain a 0 meV^{-1} baseline of the peaks in the DOS at high energies.

At this point, the density of states can be calculated by fixing the energy interval $[0, E_d]$, within which the DOS is determined, and the total number of points N_d that make it up. Usually, the energy distance between two adjacent points is set to 0.1 meV ; therefore, $N_d = 10E_d$. The density of states $g(\mathcal{E})$ is always normalised to 1.

The DOS calculated from this procedure is a generalised one ($\tilde{g}(\mathcal{E})$) since the measured spectra are the sum of the contributions from atoms with very different masses, each weighted by unequal coefficients, which take into account the different atomic cross-sections as well [181]. To obtain the true DOS, $g(\mathcal{E})$, the generalised one $\tilde{g}(\mathcal{E})$ is divided by a correction function $C(\mathcal{E})$. If the correction function for the samples is unknown, it can be constructed as follows. In the range of the optical modes (above $\sim 30 \text{ meV}$), a constant value of $C(\mathcal{E}) = 0.9$ can be fixed. In the range of the acoustical modes (below $\sim 30 \text{ meV}$), a parabolic function $C(\mathcal{E}) = a\mathcal{E}^2 + b$ is used. The parameter a of the parabola is determined by a scaling coefficient η based on the relation [181]:

$$\lim_{\mathcal{E} \rightarrow 0} \frac{\tilde{g}(\mathcal{E})}{\mathcal{E}^2} = \eta \lim_{\mathcal{E} \rightarrow 0} \frac{g(\mathcal{E})}{\mathcal{E}^2} \quad (3.2.51)$$

and

$$\eta \simeq \frac{\langle m^2 \rangle}{\langle m \rangle^2} \quad , \quad (3.2.52)$$

where m is the atomic mass. The parameter b instead is set to ensure the continuity between the parabolic function and the constant value of 0.9 at the transition energy from acoustic to optical modes $\mathcal{E}_a = 30 \text{ meV}$. An example of a correction function is shown in Figure 3.13. The choice of $C(\mathcal{E})$'s functional form and the transition frequency $\mathcal{E}_a$ is guided by previously evaluated $C(\mathcal{E})$ functions for other systems (see Fig. S9 of [182]). The specific form of $C(\mathcal{E})$ has little impact on the main results.

Finally, the DOS is obtained. In Figure 3.14, the DOS of the ultra-stable TPD glass measured at 300 K is shown, where the peaks are the vibrational modes of the system. Some of them will also be present in Raman spectra, while the remaining will be non-Raman-active peaks.

Usually, the density of vibrational states is plotted as the reduced density of vibrational states $g(\mathcal{E})/\mathcal{E}^2$ (see Figure 3.15).

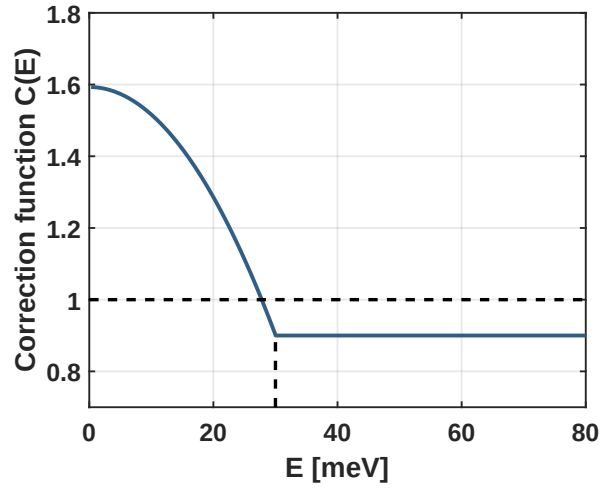


Figure 3.13: A plausible shape for the correction function.

The reliability of the DOS data can be tested by evaluating the specific heat from the DOS according to (1.6.5) and comparing the results with the experimental data. Further details are found in Par. 4.2.3.

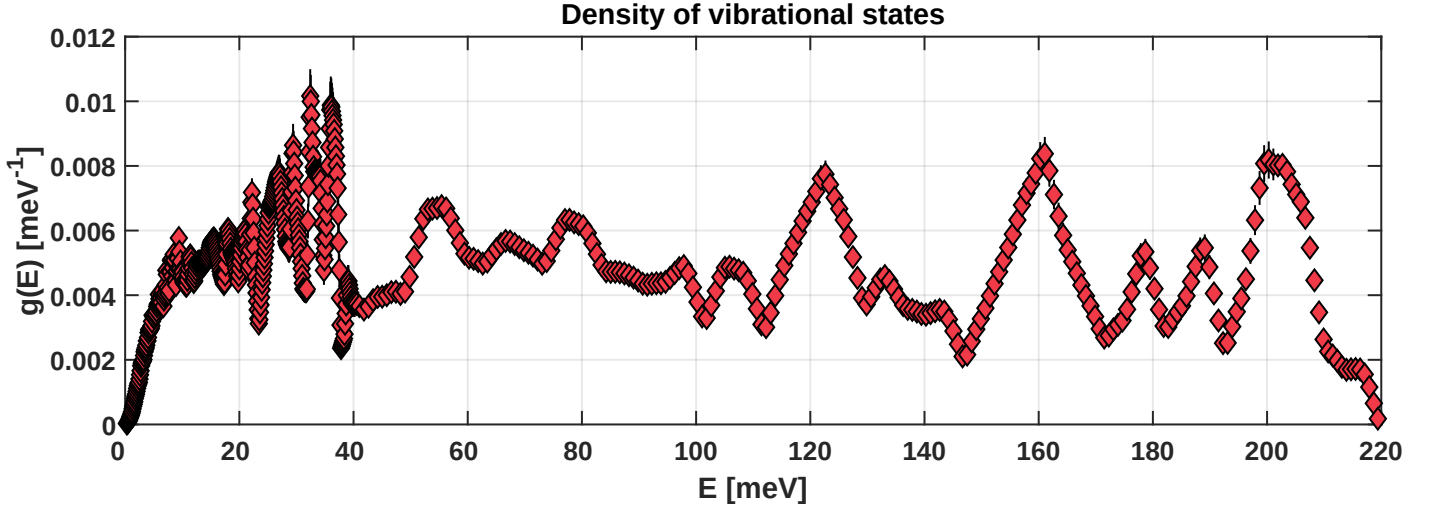


Figure 3.14: Density of vibrational states of the ultra-stable TPD glass measured at 300 K, obtained from the data-reduction procedure. Peaks correspond to characteristic vibrational modes of the glass.

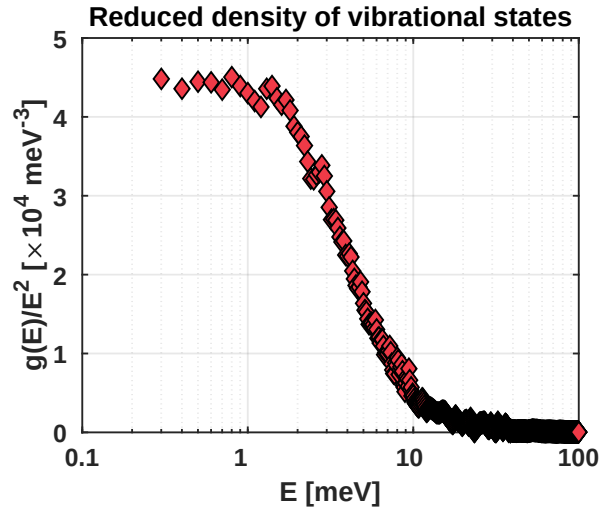


Figure 3.15: The reduced density of vibrational states of the ultra-stable TPD glass measured at 300 K. It is found by dividing the $g(\mathcal{E})$ for $\mathcal{E}^2$.

3.3 Experimental approaches to study relaxation processes

This Section presents experimental methods to study relaxation processes in disordered systems. It first introduces photon correlation spectroscopy (PCS), where speckle patterns and their fluctuations are used to extract microscopic dynamical information. Limitations of single-speckle analysis are addressed, with the multi-speckle approach enabling studies of non-ergodic and slowly evolving systems. A central focus is X-ray Photon Correlation Spectroscopy (XPCS), which extends PCS to atomic scales while facing challenges such as partial coherence, detector limits, and beam-induced motion. The experimental setups for standard XPCS and *in-situ* high-pressure XPCS are then explained. The Section also details data analysis procedures, including correlation function computation and modelling, complemented by q -resolved studies and static structure factor extraction.

3.3.1 Theory of photon correlation spectroscopy

Before exploring the methods used to extract dynamical information from scattered radiation, it is essential to understand the nature of the scattered intensity itself. When a coherent beam interacts with a disordered system, it gives rise to a fluctuating interference pattern known as a speckle pattern. These temporal and spatial intensity fluctuations contain detailed information about the microscopic dynamics of the material. The following sections begin by discussing the physical origin and statistical properties of speckle patterns, which form the basis of photon correlation spectroscopy. We then describe how these fluctuations can be analysed to access the intermediate scattering function, and how the multi-speckle approach extends the technique to non-ergodic or slowly evolving systems. The discussion then focuses on the case of X-ray Photon Correlation Spectroscopy (XPCS), including the challenges and opportunities posed by the use of partially coherent X-ray beams. Finally, we address the dual role of XPCS as both a probe and a perturbing agent, highlighting how the coherent X-ray beam can itself induce dynamics in the system under study.

3.3.1.1 From speckle patterns to dynamic correlations

When a coherent electromagnetic beam impinges on an amorphous system, the scattered intensity forms a random diffraction pattern, known as a *speckle pattern* [183, 184]. This pattern arises from the interference of scattered

waves with different phases, generated by independent, dynamically evolving regions within the scattering volume. Because the internal structure of the sample fluctuates over time, the speckle pattern exhibits corresponding temporal fluctuations, encoding information about the system's dynamics. The first observations of speckle patterns emerged with the advent of lasers [37, 185, 186]. Figure 3.16 shows a typical speckle pattern generated by laser scattering from an amorphous system.

In the following, we discuss how dynamical information can be extracted from these fluctuating speckle patterns, leading to the intermediate scattering function introduced in Section 1.4. We also highlight how the multi-speckle approach generalizes the technique to non-ergodic systems or systems with slow dynamics, where the waiting time to achieve sufficient statistics increases substantially. Before addressing these advanced topics, we briefly review the statistical properties of speckles.

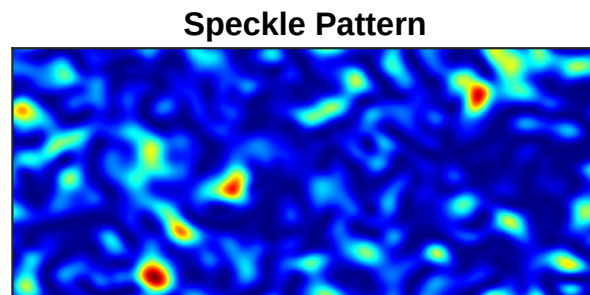


Figure 3.16: A typical speckle pattern generated by laser scattering from an amorphous system.

Speckle statistics

It can be shown [185] that the intensity distribution of a speckle pattern generated by fully coherent radiation follows negative exponential statistics, provided that the scattering amplitudes and phases are statistically independent, and the phases are uniformly distributed over 2π (i.e., the scatterers are completely random). The probability distribution $P(I)$ of the intensity I is then given by

$$P(I) = \frac{1}{\langle I \rangle} \exp \left(-\frac{I}{\langle I \rangle} \right), \quad (3.3.1)$$

where $\langle I \rangle$ denotes the mean intensity. The corresponding standard deviation is

$$\sigma = \sqrt{\langle I^2 \rangle - \langle I \rangle^2} = \langle I \rangle. \quad (3.3.2)$$

The ratio $A = \sigma^2 / \langle I \rangle^2 = 1$ quantifies the speckle contrast, which reaches unity (100%) under fully coherent illumination.

In practice, speckle patterns are recorded by 2D pixel detectors, with resolution limited by the pixel size. The photon statistics can be analyzed by grouping pixels that correspond to the same momentum transfer Q , effectively averaging over an ensemble of equivalent speckles.

If the observed intensity pattern results from the incoherent sum of M independent speckle patterns, the intensity distribution generalizes to the gamma distribution [185]:

$$P_M(I) = \frac{M^M I^{M-1}}{\langle I \rangle^M \Gamma(M)} \exp\left(-\frac{MI}{\langle I \rangle}\right), \quad (3.3.3)$$

where $\Gamma(M)$ is the gamma function. This distribution has the same mean $\langle I \rangle$ but a reduced variance $\sigma^2 = \langle I \rangle^2 / M$, implying $A = 1/M$. This model accurately describes partially coherent speckle patterns with good photon counting statistics.

Physically, M can be approximated as the ratio of the scattering volume to the coherence volume V_c . The limiting case of perfect contrast ($A = 1$) corresponds to a scattering volume equal to V_c . Contrast reduction ($M > 1$) can also arise from detector effects, such as pixel sizes larger than the speckle size, causing speckle pattern smearing. Thus, M accounts for coherence losses both from the incident beam and the detection system.

In the regime of weak speckle patterns dominated by photon counting noise (with discrete photon numbers $k = 0, 1, 2, \dots$ per pixel), the gamma distribution must be convolved with the Poisson distribution:

$$P(k) = \frac{\langle k \rangle^k e^{-\langle k \rangle}}{k!}. \quad (3.3.4)$$

This convolution yields the Poisson-gamma distribution (also known as the negative binomial distribution) for integer k :

$$P_P^M(k) = \frac{\Gamma(k+M)}{\Gamma(M)\Gamma(k+1)} \left(\frac{M}{M+\langle k \rangle}\right)^M \left(\frac{\langle k \rangle}{M+\langle k \rangle}\right)^k. \quad (3.3.5)$$

For low photon counts and weak contrast (large M), distinguishing Poisson-gamma statistics from pure Poisson noise is challenging. Nevertheless, Eq.

(3.3.5) has been successfully applied to quantify coherence in weak speckle patterns [187], provided the images are carefully post-processed to assign correct photon numbers to each pixel.

Finally, the speckle size itself plays a central role in determining the detected contrast. The linear speckle size at the detector plane, sometimes referred to as the transverse coherence length, is given by [37]:

$$\sigma_S \sim \frac{\lambda D}{d}, \quad (3.3.6)$$

where λ is the X-ray wavelength, D is the sample-detector distance, and d is the beam source size. To maximise the detected contrast, the detector pixel size must be matched to σ_S : if pixels are significantly larger than the speckle size, several speckles are averaged within one pixel, thereby reducing the measured visibility.

From speckle patterns to the intermediate scattering function

As introduced, the interference of scattered waves from independent, fluctuating regions within the material produces a time-dependent speckle pattern. Monitoring the temporal evolution of the intensity fluctuations at a fixed momentum transfer q provides insight into the density dynamics inside the sample.

Figure 3.17 illustrates an example of the intensity $I(q, t)$ (blue solid line, left y-axis) measured over time at fixed q , together with its time average $\langle I(q, t) \rangle$ (orange dashed line, right y-axis).

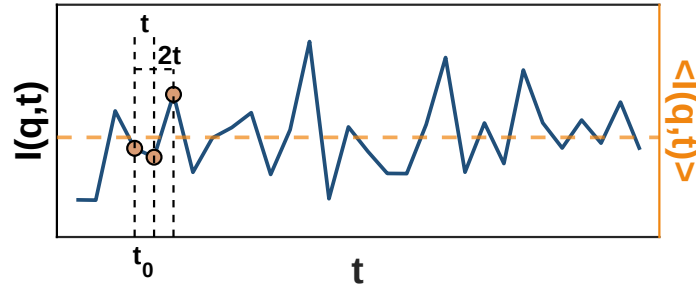


Figure 3.17: Temporal fluctuations of the scattered intensity $I(q, t)$ at fixed momentum transfer q (blue solid line) and its time average (orange dashed line).

Dynamical information is extracted via the intensity autocorrelation function, which quantifies the correlation between intensity values at times separated by a lag t [37, 188]:

$$g_2(q, t) = \frac{\langle I(q, t_0) I(q, t_0 + t) \rangle_{t_0}}{\langle I(q, t_0) \rangle_{t_0}^2}. \quad (3.3.7)$$

This second-order coherence function represents the probability that, given an intensity I_0 at time t_0 , the intensity at $t_0 + t$ remains correlated. Known as the homodyne autocorrelation function, $g_2(q, t)$ involves intensity correlations (thus a 4-field) rather than electric field correlations, which define the heterodyne detection scheme [37].

The first-order degree of coherence (2-fields correlation function) is

$$g_1(q, t) = \frac{\langle E(q, t_0) E^*(q, t_0 + t) \rangle_{t_0}}{\langle |E(q, t_0)| \rangle_{t_0}^2} = F(q, t), \quad (3.3.8)$$

where $F(q, t)$ is the *intermediate scattering function* introduced in Section 1.4.

Under the Gaussian field approximation [189], the Siegert relation connects g_2 and g_1 :

$$g_2(q, t) = 1 + A |g_1(q, t)|^2, \quad (3.3.9)$$

where A is the experimental contrast, accounting for coherence loss caused by experimental conditions. Therefore, measuring $g_2(q, t)$ enables the extraction of the ISF, which reveals the sample's relaxation dynamics. The Siegert relation is valid when the scattered field exhibits Gaussian statistics, typically satisfied when the speckle pattern arises from the interference of many independent scatterers. In addition, stationarity of the process is required so that correlation functions depend only on the time delay. In particular, ergodicity is necessary to ensure that temporal averages are equivalent to ensemble averages.

The homodyne detection scheme offers a simpler experimental configuration than heterodyne detection, since only the intensity fluctuations of a single speckle (recorded by a point-like detector) are needed. In a fully developed speckle pattern, all speckles are statistically equivalent; thus, the temporal intensity fluctuations of one speckle contain the same dynamical information as the entire ensemble. Unlike heterodyne setups, no reference beam or phase information is required. The intensity autocorrelation can be computed in hardware or software to obtain g_2 and thus the ISF.

A central assumption of homodyne detection is ergodicity, i.e. the equivalence of time and ensemble averages. Since Eq. (3.3.7) is evaluated from time averages of the intensity fluctuations of a single speckle, this approach is best suited for stationary systems with sufficiently fast dynamics. For slow dynamics, however, acquisition times required to obtain reliable statistics

become prohibitively long. Moreover, in non-ergodic systems (e.g. aging or out-of-equilibrium materials), the time-averaged $g_2(q, t)$ from a single speckle no longer reflects the true ensemble dynamics, because the system explores only a limited portion of phase space during the measurement.

To address these limitations, the multi-speckle approach was developed [38]. By recording many speckles simultaneously with a 2D detector, statistical sampling is greatly improved, enabling the study of slowly evolving and non-ergodic systems. This method will be discussed in detail in the following Section.

Finally, note that speckle contrast A is optimised when the speckle size matches the detector pixel size or the point-like detector area.

Multi-speckle approach and two-times correlation function

As anticipated, the multi-speckle technique generalises the autocorrelation function (3.3.7) to non-ergodic or slowly evolving systems, for which achieving sufficient statistics via single-speckle time averaging is impractical and the Siegert relation no longer holds [38].

Using a 2D detector, multiple speckles at the same q -value are measured simultaneously over time. The degree of correlation between two intensity frames recorded at times t_1 and t_2 is given by the two-times correlation function (TTCF):

$$C_q(t_1, t_2) = \frac{\langle I_p(t_1) I_p(t_2) \rangle_p}{\langle I_p(t_1) \rangle_p \langle I_p(t_2) \rangle_p}, \quad (3.3.10)$$

where $I_p(t)$ is the intensity at pixel p and time t , and $\langle \dots \rangle_p$ denotes averaging over pixels at fixed q . Repeating for all pairs (t_1, t_2) generates the TTCF matrix.

Figure 3.18a) shows an example TTCF. The main diagonal ($t_1 = t_2$) corresponds to the autocorrelation of each frame with itself. Off-diagonal elements represent correlations between frames separated by $|t_2 - t_1|$.

Fixing either t_1 or t_2 yields the standard autocorrelation function g_2 , corresponding to vertical or horizontal slices of the TTCF matrix. Alternatively, expressing the TTCF in terms of waiting time $t_w = \frac{t_1 + t_2}{2}$ and delay time $t = |t_2 - t_1|$ (see Figure 3.18a) axes) maps the time evolution of the microscopic dynamics. For instance, if the width of the main diagonal increases with t_w , it indicates a slowing down of the dynamics.

Due to noise, extracting a single g_2 curve from the TTCF can be noisy. To improve statistics, one averages over a time window Δt :

$$g_2(q, t) = \langle C_q(t_w, t_w + t) \rangle, \quad (3.3.11)$$

where $\langle \dots \rangle$ denotes averaging over t_w . For stationary systems, this averaging enhances statistics compared to single-speckle measurements of equal duration. For non-stationary dynamics, however, it reduces the time resolution of the TTCF. Nevertheless, if the dynamics evolves slowly within the averaging window, Eq. (3.3.11) remains an effective method to monitor the temporal evolution of the system. This is illustrated in Fig. 3.18b), where g_2 curves were computed by averaging over different time windows Δt ($[0; 600]$ s, $[200; 800]$ s, $[400; 1000]$ s, respectively from the darker blue to the lighter one), revealing the evolution of dynamics. The t_w in the legend of Figure 3.18b) are the middle points of the time windows Δt .

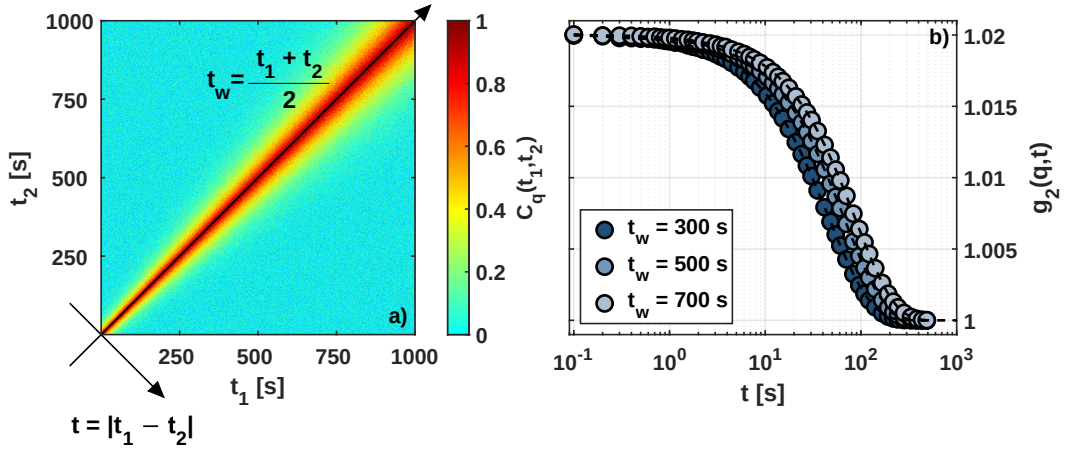


Figure 3.18: a) Example two-times correlation function (TTCF) showing the evolution of dynamics with waiting time t_w and delay time t . b) Corresponding averaged autocorrelation functions $g_2(q, t)$ computed over different time windows, illustrating dynamics slowing down.

3.3.1.2 X-ray Photon Correlation Spectroscopy

The principles outlined above apply to any coherent electromagnetic radiation. The probing wavelength λ determines the length scales accessible via the exchanged wavevector

$$q = \frac{4\pi n}{\lambda} \sin(\theta/2), \quad (3.3.12)$$

where θ is the scattering angle and n the refractive index. Shorter wavelengths enable probing larger q values and correspondingly smaller length

scales.

Visible light (wavelengths 380–750 nm) probes up to a few tens of μm^{-1} , corresponding to length scales of hundreds of nanometers. The smallest q accessible experimentally is on the order of 10^{-8} nm^{-1} . This range is typical for Dynamic Light Scattering (DLS), or Visible Photon Correlation Spectroscopy, illustrated as the blue box in Figure 3.1. To investigate smaller length scales, the wavelength must be reduced into the X-ray regime.

X-rays combine interatomic wavelengths with weak interaction cross sections, minimal multiple scattering, and negligible refraction ($n \approx 1$), providing advantages over visible light. X-ray Photon Correlation Spectroscopy (XPCS) extends photon correlation techniques down to a few Ångströms, accessing atomic length scales and q values up to 10^{-4} nm^{-1} in small-angle geometries, overlapping with Dynamic Light Scattering [9]. Figure 3.1 illustrates XPCS as the green box. Both techniques cover frequencies from 10^{-4} to 10^6 rad/s , enabling studies of slow dynamics. Other complementary techniques like Raman and Inelastic X-ray Scattering, discussed in previous chapters, are also depicted in the scheme, showing how they probe, instead, faster relaxations [9, 190].

Despite these advantages, X-rays present challenges. They can induce sample damage, necessitating sample replacement or flux reduction. Furthermore, as discussed next, X-ray coherence is lower than that of lasers, requiring intense fluxes from synchrotron sources [191].

Partially coherent X-rays

A crucial requirement for XPCS is the use of a coherent X-ray beam. Coherence determines the ability of scattered waves to interfere constructively or destructively, which is essential for extracting dynamical information [192]. While it is convenient to idealise the incident X-ray beam as a perfect, infinite plane wave with complete spatial and temporal coherence, real experimental beams deviate significantly from this ideal, especially when using synchrotron or laboratory-based X-ray sources. Unlike optical lasers, where stimulated emission produces highly monochromatic, phase-correlated beams with long coherence lengths, most X-ray sources, including synchrotron radiation, are based on spontaneous emission processes, resulting in inherently limited coherence both in space and time [192].

A real X-ray beam deviates from an ideal plane wave primarily in two ways: it is not strictly monochromatic, and it does not propagate along a perfectly defined direction. Consequently, its coherence properties are characterised by two transverse coherence lengths (horizontal and vertical) and one longitudinal coherence length [193]. The longitudinal coherence length, L_L ,

can be derived by considering two plane waves A and B with slightly different wavelengths λ and $\lambda - \Delta\lambda$, propagating in exactly the same direction (see Fig. 3.19a). These waves are in phase at a reference point P, and L_L defines the distance along the propagation direction after which they become completely out of phase. After travelling that distance twice, they return to being in phase. If this distance corresponds to N wavelengths of the first wave and $N + 1$ wavelengths of the second, we have $2L_L = N\lambda = (N + 1)(\lambda - \Delta\lambda)$. Rearranging and solving under the approximation that $\Delta\lambda \ll \lambda$ gives $N \approx \frac{\lambda}{\Delta\lambda}$, leading to the expression for the longitudinal coherence length [193]:

$$L_L \approx \frac{\lambda^2}{2\Delta\lambda} . \quad (3.3.13)$$

Similarly, the transverse coherence length, L_T , is obtained by considering two waves with the same wavelength but slightly different propagation directions, deviated by an angle $\Delta\theta$ (Fig. 3.19b). These waves are in phase at a common point, and L_T represents the distance along the wavefront where they remain phase-correlated. This leads to [193] $L_T = \frac{\lambda}{2\Delta\theta}$.

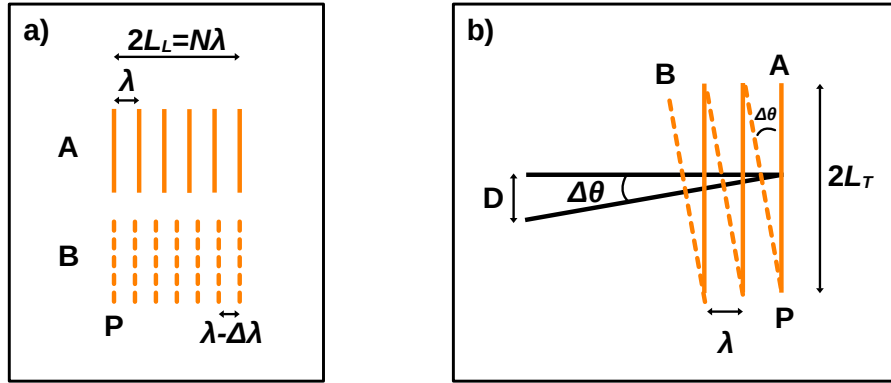


Figure 3.19: Longitudinal and transverse coherence lengths. a) Two plane waves with slightly different wavelengths propagate in the same direction, shown vertically displaced for clarity. After travelling a distance equal to the longitudinal coherence length L_L , the two waves are out of phase. b) Two plane waves with identical wavelengths originate from the edges of a finite-sized source with dimension D , displaying the concept of transverse coherence.

The angle $\Delta\theta$ is often determined by the source size D and the distance to the observation point R , yielding [193]:

$$L_T \approx \frac{\lambda R}{2D} . \quad (3.3.14)$$

A schematic illustration of these configurations, showing propagating waves used to determine both longitudinal and transverse coherence lengths, is presented in Figure 3.19.

In practical terms, the achievable coherence lengths depend on both the source characteristics and the beamline optics. For example, at a third-generation synchrotron, typical vertical source sizes are around $100 \mu\text{m}$, and with experimental stations located approximately 20 m downstream, the vertical transverse coherence length for $1 \text{ \AA}$ wavelength X-rays is roughly $10 \mu\text{m}$. The longitudinal coherence length depends on the monochromaticity of the beam, often determined by the monochromator. A Si(111) monochromator, providing $\Delta\lambda/\lambda \approx 10^{-5}$, yields a longitudinal coherence length of about $5 \mu\text{m}$ for $1 \text{ \AA}$ wavelength X-rays, comparable to the transverse coherence length.

An important quantity that distinguishes highly coherent laser sources from partially coherent X-ray sources is the degeneracy parameter N_c , representing the number of photons contained within the coherence volume V_c , defined by the product of the two transverse and the longitudinal coherence lengths [192]. In optical lasers, N_c can reach values of $10^7 - 10^8$, whereas synchrotron X-ray undulator sources typically achieve N_c values between $10^{-3} - 10^{-2}$, explaining the significantly lower coherent photon flux available for X-ray experiments compared to optical systems. Despite this limitation, coherent X-ray scattering experiments remain feasible by tailoring the beam aperture to match the transverse coherence lengths and selecting an appropriate spectral bandwidth to maximise L_L . The coherent photon flux scales with the brilliance B of the source, following [194, 195]:

$$I_c \approx \frac{B\lambda^2}{4} , \quad (3.3.15)$$

where B represents the photon emission rate per source area, solid angle, bandwidth, and time.

Furthermore, to ensure observable interference effects in a scattering experiment, the maximum path length difference (PLD) of radiation reaching the detector must not exceed the longitudinal coherence length; otherwise, the superposition of scattered waves becomes incoherent, and interference is lost. In typical transmission geometry, this condition can be expressed as [194, 195]:

$$h \sin^2(2\theta)/2 + d \sin(\theta) \lesssim L_L , \quad (3.3.16)$$

where h is the sample thickness, d is the beam size, and θ is the scattering angle. With L_L on the order of $1 \mu\text{m}$ (for Si(111) monochromated X-rays), this condition is satisfied for scattering angles up to $2\theta \approx 45^\circ$ for an 8 keV beam, assuming the detector is positioned far from the sample with respect to h and d .

Finally, the finite coherence length imposes an upper limit on the separation of objects if they are to produce measurable interference. For instance, in the case of two electrons, if the projection of their separation along the scattering vector $\mathbf{q}$ is significantly greater than the coherence length, the total scattered intensity is simply the sum of the individual contributions, rather than the squared modulus of the coherent sum of amplitudes [193]. Thus, precise control over the coherence properties of the X-ray beam is crucial for the success of interference-based measurements such as XPCS.

The finite coherence length of the X-ray beam also imposes constraints on the experimental geometry and sample characteristics. For instance, in Wide Angle X-ray Scattering (WAXS) configurations, the speckle size is typically smaller due to the larger scattering angles involved, which can reduce the speckle contrast if the detector pixel size is not sufficiently small or if the sample thickness causes excessive averaging over scattering volumes. Thicker samples tend to degrade the speckle contrast because the scattering originates from regions that exceed the longitudinal coherence length, effectively summing incoherent contributions. Therefore, optimising sample thickness and detector resolution is crucial to maximise the speckle contrast and the sensitivity of XPCS measurements [195]. As a practical guideline, for typical XPCS experiments at ambient conditions with a beam size of $\sim 3 \mu\text{m}$ and $L_L \sim 1 \mu\text{m}$, an optimal sample thickness is about $5 \mu\text{m}$, which balances coherence requirements with sufficient transmission. Furthermore, to ensure that the speckle size matches the detector resolution (pixel size $\sim 75 \mu\text{m}$), the sample-detector distance must be adjusted accordingly; for an 8 keV beam, this typically requires distances on the order of 2 m.

In summary, while X-ray sources provide only partially coherent beams, careful experimental design (matching beam coherence properties, sample thickness and X-ray absorption, and detector characteristics) enables effective coherent scattering experiments that extract dynamical information at atomic and nanometric length scales.

Signal-to-noise ratio in XPCS

In X-ray Photon Correlation Spectroscopy, the signal-to-noise ratio (SNR) of the intensity autocorrelation function $g_2(q, t)$ is a critical parameter, particularly when working in low-intensity regimes. For multi-speckle XPCS experiments using area detectors, the SNR can be expressed as follows [192]:

$$\text{SNR} = I_0 \left(\frac{a}{R} \right)^2 \sqrt{N} \sqrt{T} \sqrt{dt} \frac{A}{\sqrt{A+1}} \quad (3.3.17)$$

where I_0 is the total scattered intensity, a is the pixel size, R the distance between the sample and the detector, N is the total number of pixels of the detector, T the total acquisition time, and dt is the exposure time per single frame. One of the major consequences of this expression is that by increasing the beam intensity by one order of magnitude, the exposure time dt can be decreased by a factor of 100, accessing faster time decorrelations without losing in SNR quality.

The SNR also increases with larger detector areas or smaller sample-detector distances. However, in both cases, the q -range covered by the detector increases, lowering the accessible wavevector range.

XPCS as a pump and probe technique

XPCS not only probes atomic-scale dynamics within disordered materials, but also acts as a pump technique, where the high flux of coherent X-rays can actively influence the dynamics of the sample during measurement. This phenomenon, known as *beam-induced dynamics*, was first reported by Ruta *et al.* [166] in vitreous silica and germania. They showed that X-ray irradiation generated atomic motion via a radiolysis process. An example is reported in Fig. 3.20, where the relaxation dynamics of silica exhibits a speed up systematically with increasing X-ray flux. This probe and pump feature of XPCS leads to a huge advantage: those intrinsic properties, such as the relaxation time, that would be experimentally inaccessible, become reachable thanks to the induced effect of X-rays.

Subsequent studies have demonstrated that beam-induced dynamics is widespread across various glassy and amorphous materials, including borate glasses [161, 196–198], sodium silicates [161], lithium-borates [198], and chalcogenide glasses [4, 199]. In addition, investigations on oxide glass LiBO_3 [165] and chalcogenide glass GeSe_3 [4] revealed that beyond a certain absorbed X-ray dose, the system reaches a photo-induced steady state characterised by a yield-like response (see Par. 2.1.4). The threshold dose depends strongly on the material's chemical and structural properties.

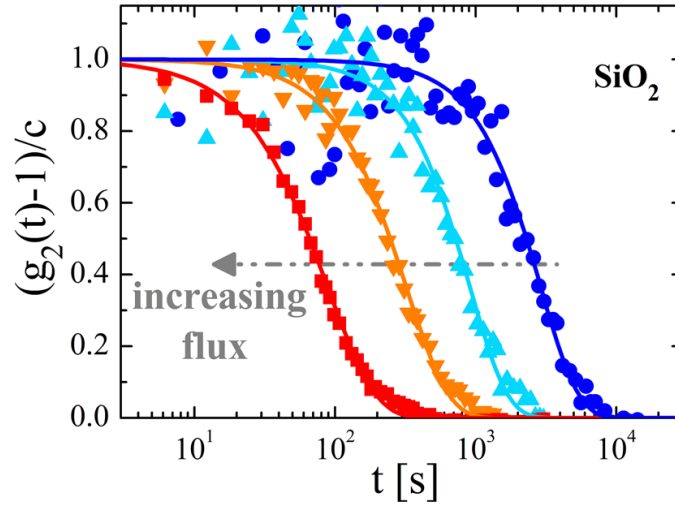


Figure 3.20: Beam-induced dynamics in vitreous silica. Intensity autocorrelation functions $g_2(q, t)$ measured at $T = 295$ K and at the wave vector corresponding to the first sharp diffraction peak, for different incident X-ray fluxes. From left to right, the probing flux increases, leading to a systematic acceleration of the relaxation dynamics. This illustrates the pump-probe nature of XPCS: while the correlation function probes atomic motion, the beam itself acts as a pump that can trigger or speed up relaxation processes. Reproduced from B. Ruta *et al.*, Sci. Rep. **7**, 3962 (2017). Licensed under CC BY 4.0.

As said, the interplay between probing and perturbing the system enriches the information obtainable by XPCS, allowing simultaneous studies of spontaneous and X-ray driven dynamics: even when the X-ray beam induces motion within the system, the resulting dynamics are not arbitrary, they often reflect the underlying relaxation mechanisms and dynamical properties of the material itself. Consequently, XPCS is a uniquely powerful tool to investigate how complex materials respond dynamically to external stimuli, including temperature, pressure, and irradiation [4], that would be otherwise experimentally unreachable.

Nevertheless, it is essential to acknowledge that beam-induced effects can complicate data interpretation and sometimes obscure intrinsic dynamics. Careful control of experimental parameters, such as beam flux and exposure time, is crucial for distinguishing between intrinsic relaxation processes and radiation-induced dynamics. Thus, to extract meaningful physical insights, especially when studying how dynamics evolve under, for instance, temperature or pressure, it is crucial to assess whether the beam-induced effects

and the external changes act independently. A careful and systematic data analysis is thus required to ensure that the observed changes in dynamics genuinely originate from the external control parameters, and are not inadvertently driven or modulated by the X-ray beam itself. This remains one of the key challenges and active research directions within the XPCS community.

3.3.2 Experimental details of XPCS

3.3.2.1 P10 beamline at PETRA III

The XPCS experiments presented in this work were conducted at the Coherence Beamline P10 at Petra III, DESY synchrotron (Hamburg, Germany), a third-generation synchrotron radiation light source. Figure 3.21 provides a simplified schematic of the P10 beamline, highlighting its main components. Further details can be found in [200].

The “pink” beam, generated by a 5 m long U32 undulator in an energy range between 5 keV and 20 keV, is monochromatised by a high-heat load monochromator (HHLM) located at ~ 38 m from the source, in the Optical Hutch (OH). The HHLM is liquid-nitrogen-cooled and equipped with a Si(111) crystal pair and a Si(111) channel-cut crystal, offering excellent angular stability and energy resolution.

Following monochromatization, the beam enters the first experimental hutch (EH1), positioned 67-79 m from the source. EH1 is designed to perform XPCS and Coherent Diffractive Imaging (CDI) experiments for soft matter in USAXS geometry, which requires long sample-detector distances, and Rheology measurements. Within EH1, a set of Si-based absorber foils is installed to tune the X-ray flux incident on the sample. These attenuators are crucial to study the effect of the X-ray beam on the dynamics of the samples. The second experimental hutch EH2, situated 83-95 m from the X-ray source, is devoted to standard CDI and XPCS setups, and to the Göttingen Instrument for Nano-Imaging with X-Rays (GINI-X) setup.

In EH2, the X-ray beam is focused near the sample stage using compound refractive lenses (CRLs). Depending on the experimental requirements, the sample may be mounted in a vacuum chamber, equipped with a resistive heater and a temperature controller, or enclosed within a diamond anvil cell (DAC). For further details, see Paragraphs 3.3.2.2 and 3.3.2.3.

The scattering signal is then collected through a vacuum pipe and detected by a 2D single photon detector Eiger4M (DECTRIS), located at ~ 1.83 m from the sample. The Eiger4M is a Si-based detector characterised by 2070×2167 pixels, each $75 \times 75 \mu\text{m}^2$, and supports frame rates up to 750 Hz.

It is mounted on a circular rail, allowing changing of the scattering angle for XPCS scans, as well as for static measurements of the intensity profile $I(q)$.

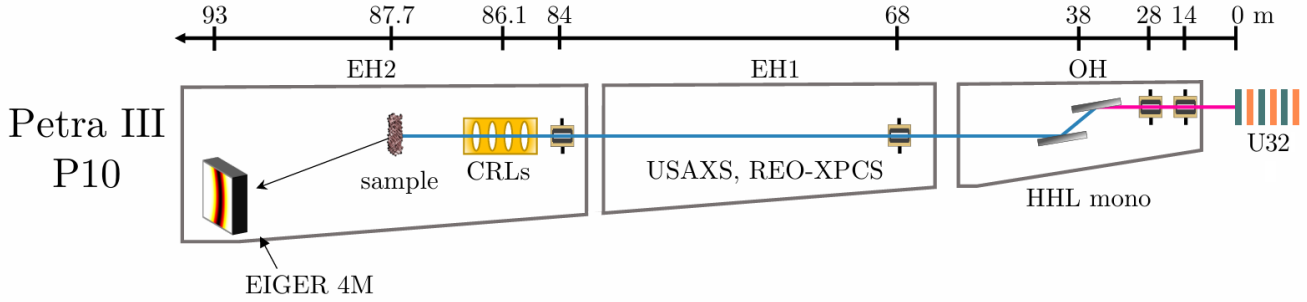


Figure 3.21: Sketch of P10 beamline at PetraIII at DESY (Hamburg, Germany). The pink beam generated by the undulator is monochromatized and focused onto the sample using a combination of slits and mirrors (not shown). The scattered intensity is recorded with a pixelated single-photon counting detector. For clarity, only a few key beamline components are illustrated. A detailed description and the complete layout can be found in [200]. Sketch reprinted from [201].

3.3.2.2 Beam-induced experiment

To characterise the influence of the X-ray beam on the sample dynamics, long XPCS scans are carried out at systematically varied beam intensities. The incident photon flux is adjusted by means of Si-based absorber foils, thereby allowing a controlled modulation of the deposited radiation dose. If the dynamics is beam-driven, it is expected to slow down as the intensity decreases; hence, lower fluxes must necessarily be probed with proportionally longer scans to capture the complete temporal evolution of the system. All relevant experimental parameters, such as beam flux, spot size, and energy, must therefore be carefully recorded, and they are reported in the corresponding Results Sections 5.2 and 5.3.

To minimise cumulative irradiation effects and thus ensure an accurate characterisation of the intrinsic beam influence, each XPCS scan must be performed on a fresh, previously unexposed region of the sample. The beam spot size is of the order of a few micrometres, and its effect can extend up to $\sim 10 \mu\text{m}$, while the total sample area in standard XPCS setups typically spans about $2 \times 4 \text{ mm}^2$. In this way, a sufficiently large number of independent positions can be accessed within a single specimen, enabling multiple scans without overlap or cross-contamination of irradiation effects. In specific configurations, however, such as in in-situ high-pressure setups (see next

section), the available sample size is limited to approximately $90 \times 90 \mu\text{m}^2$ due to experimental constraints, making measurements on fresh spots considerably more challenging.

To investigate the photo-induced effects at different temperatures, the sample is mounted between two copper plates forming a so-called “hot finger” configuration. This geometry ensures good thermal contact and enables precise, localised temperature control. The temperature is monitored by three thermocouples placed at different positions, while stability is maintained by a resistive heater regulated through a Lakeshore controller. All measurements are performed under vacuum, thereby preventing oxidation and ensuring that the observed dynamics reflect the intrinsic behaviour of the material rather than extrinsic surface effects.

To assess whether irradiation damage is reversible or permanent, dedicated control protocols are implemented. In these tests, an initial XPCS scan is recorded on a given spot, after which the beam is switched off for a defined dark period. The same spot is then re-exposed for a second scan. By comparing the two measurements, it becomes possible to establish whether the dynamics returns to its original state (indicating reversibility), remains altered (indicating permanent damage), or continues to evolve even in the absence of irradiation (indicating a beam-triggered but self-sustained or thermally activated process). In this way, one can disentangle transient, irreversible, and latent effects of the beam.

Finally, the dependence of the beam effect on the scattering vector q was explored by changing the detector angle, which allowed us to monitor potential q -dependent features in the induced dynamics.

3.3.2.3 In-situ high pressure experiment

To investigate the evolution of atomic motion under varying pressure conditions, the *in-situ* High-Pressure (HP) X-ray Photon Correlation Spectroscopy setup is employed. This configuration combines a diamond anvil cell (DAC) capable of generating static high pressures with a conventional XPCS measurement system, as described previously and illustrated in Figure 3.22. A key advantage of this setup is the simultaneous acquisition of both structural and dynamical information: structural changes are inferred from the integrated detector intensity, while dynamical behaviour is extracted from the time-dependent speckle fluctuations (see Sec. 3.3.3).

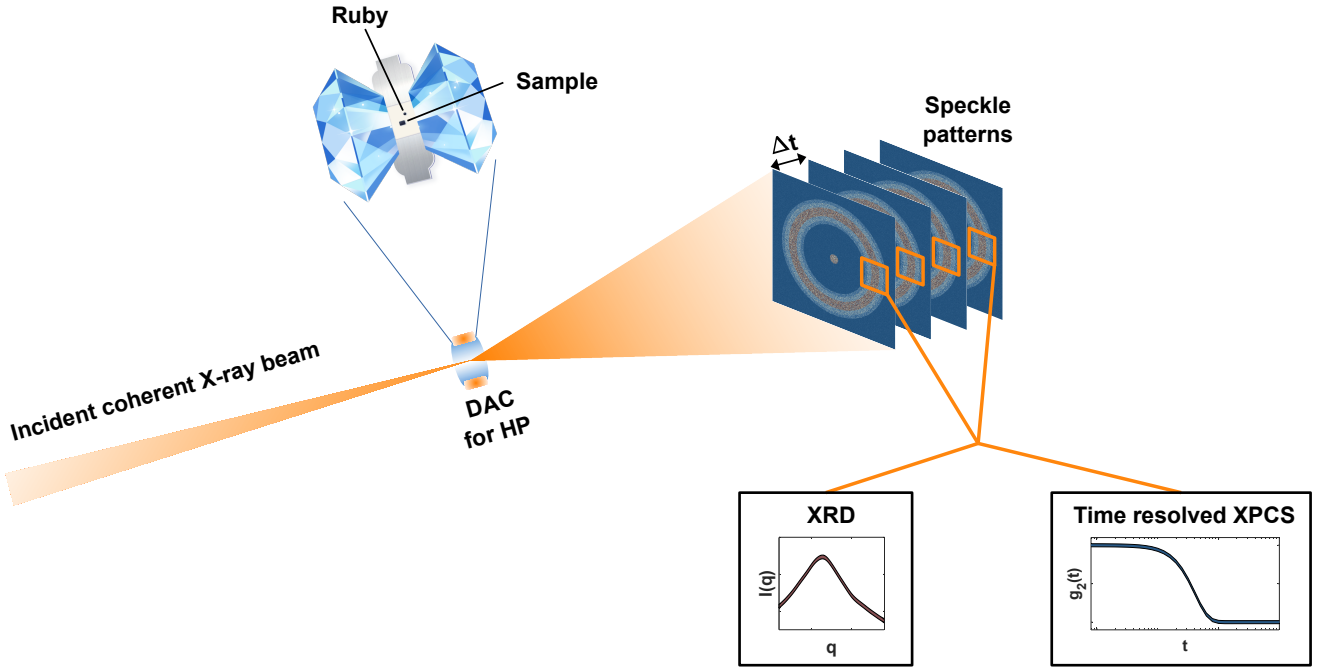


Figure 3.22: Sketch of in-situ High Pressure XPCS setup. A coherent X-ray beam is directed at the sample, kept under high pressure applied via a diamond anvil cell. Pressure is monitored using ruby fluorescence. Scattered X-rays are recorded by a detector (orange square), acquiring frames at intervals of Δt . The time-averaged intensity along detector columns yields the XRD pattern, while the temporal autocorrelation of individual pixels reveals the sample's microscopic dynamics. The speckle pattern shown is a representative example from small-angle XPCS; it does not correspond to the wide-angle geometry used in HP-XPCS experiments.

The energy range covered by the P10 beamline is from 5.0 keV to 10.0 keV. To optimise transmission through the DAC, high energy values are preferred. For instance, at 8 keV, a 1 mm-thick diamond exhibits only 22% transmission, whereas at 15 keV, this value increases to approximately 79%.

In the following sections, we describe the working principles of the DAC, the pressure-transmitting medium (PTM), pressure measurement via ruby fluorescence, and the experimental protocols employed to characterise the effect of hydrostatic compressions on the glass stability at the microscopic level.

Diamond anvil cell and gasket

Today, several devices are available to generate high-pressure environments, and the choice of the cell generally depends on the experimental setup, the probe used, and the pressure and sample volume requirements. For instance, the *diamond anvil cell* (DAC) is widely used in X-ray experiments due to its ability to reach extremely high static pressures within a small sample chamber. Other designs, such as large-volume presses or multi-anvil cells, are often preferred for neutron experiments or when larger sample volumes are required. The development of DAC technology has significantly advanced high-pressure research, enabling numerous scientific discoveries. Despite its compact size and straightforward design, the DAC can achieve pressures as high as 500 GPa.

A typical DAC consists of two high-quality, single-crystal diamonds with flat tips that act as anvils. These diamonds are mounted on two separate components of the device, known as the *piston* and the *cylinder*. The sample is placed between the flat diamond faces and compressed as the piston is driven toward the cylinder. The cylinder serves to align and stabilise the piston, ensuring that the diamond anvils remain perfectly aligned and parallel. The flat tips of the diamonds, known as *culets*, typically have dimensions in the range of hundreds of micrometres, and the smaller the culets, the higher pressures can be reached.

A *gasket*, usually made of a thin metal disk, is inserted between the anvils. It is first pre-indented by pressing the culets together, and then a small hole is drilled at the centre to define the *sample chamber*. In our experiments, we used stainless steel gaskets, which are well-suited for the targeted pressures and room temperature conditions. The sample and a *pressure transmitting medium* (PTM) are placed inside this chamber to obtain an isotropic (hydrostatic) pressure distribution.

In this work, the experiments were conducted using membrane-type DACs. In such devices, the pressure on the sliding piston is controlled by a thin metallic membrane mounted above it and held in place by a threaded cover on the base cylinder. A gas-driven pressure controller adjusts the volume inside the membrane, which causes it to expand. This expansion applies force to the piston, compressing the diamonds and, in turn, the sample. The pressure driver remains connected throughout the experiment to compensate for any potential gas leakage, ensuring constant pressure conditions. Although the membrane is actuated with a relatively low gas pressure (tens of millibars), this is sufficient to generate several GPa of pressure on the sample.

A schematic illustration of the DAC working principle is provided in Figure 3.23a), while Figure 3.23b) presents a diagram of a membrane DAC.

Additional technical details on membrane DACs are available in Ref. [202].

When the sample is compressed, the resulting pressure distribution is inherently uniaxial, with gradients that peak at the centre. Embedding the sample in a PTM helps to achieve a more isotropic (hydrostatic) pressure distribution, minimising shear stresses. Typical gaskets have diameters of ~ 1 cm and thicknesses of ~ 210 μm , although these values vary depending on specific experimental requirements.

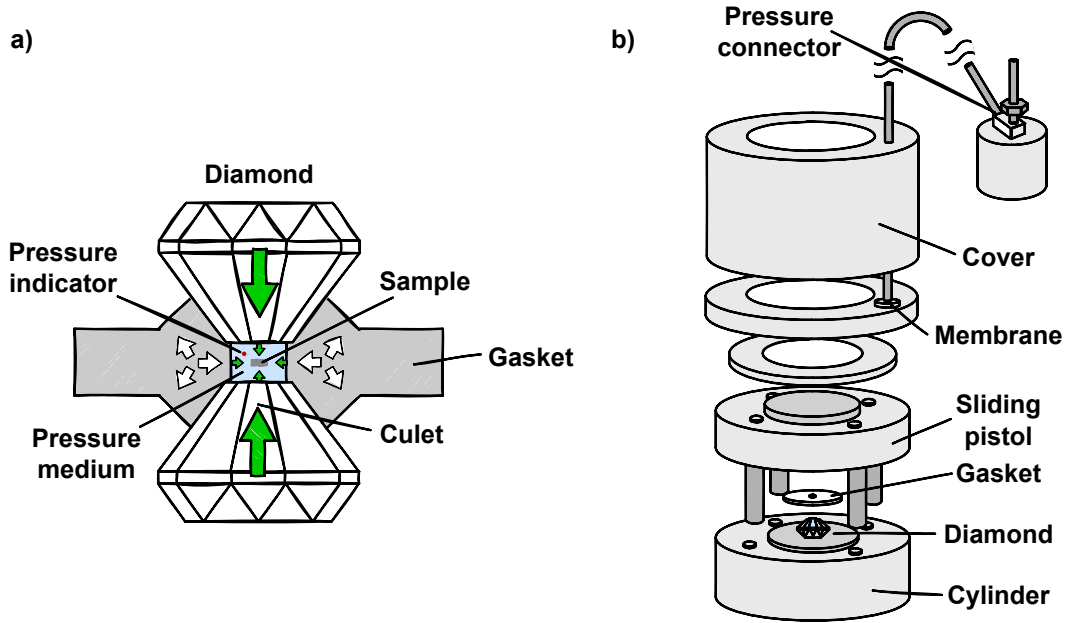


Figure 3.23: a) Schematic of diamond anvil cell working principle, inspired from [203]. b) Sketch of membrane-type DAC used in the experiment.

Pressure transmitting medium

The pressure applied by the uniaxial compression of the diamond anvils is transmitted to the sample through a pressure-transmitting medium, which plays a crucial role in ensuring hydrostatic or quasi-hydrostatic conditions within the sample chamber. If the PTM solidifies at high pressure, the pressure distribution becomes anisotropic, and hydrostatic conditions are compromised. This can significantly affect the sample environment and lead to artefacts or altered dynamics in the measured data.

Therefore, the choice of PTM must fulfil several criteria: it should remain hydrostatic (or quasi-hydrostatic) over the desired pressure range, it must not chemically react with the sample, and it should not interfere with the

measurement techniques being employed. Typical PTMs include liquids, such as methanol, ethanol, or their mixtures, and inert gases like helium, neon, nitrogen, or argon. In our experiments, a 4:1 methanol-ethanol mixture was used, as it provides quasi-hydrostatic conditions up to approximately 10.5 GPa [204].

This highlights how the choice of PTM is a key parameter in high-pressure XPCS experiments. It directly influences the quality and reliability of the measurements by controlling the homogeneity of the pressure environment around the sample.

Fluorescence ruby for pressure measurement

Pressure monitoring is carried out using a portable Pressure by Ruby Luminescence (PRL) spectrometer mounted on a motorised stage. The system includes a laser for excitation of the ruby fluorescence (${}^2E \rightarrow {}^4A_2$ transition), a camera, and illumination optics to enable *in-situ* imaging.

The ruby fluorescence method exploits the pressure dependence of the R1 and R2 emission lines, typically centred around 692.8 nm and 694.25 nm at ambient conditions. As pressure increases, the lines shift and merge. An initial pressure estimate is provided by the Betsa software, while a more accurate value is obtained by post-processing the R1 line shift using the following calibration formula [205]:

$$P \text{ [GPa]} = 1.87(\pm 0.01) \times 10^3 \left(\frac{\Delta\lambda}{\lambda_0} \right) \left(1 + 5.63(\pm 0.03) \frac{\Delta\lambda}{\lambda_0} \right), \quad (3.3.18)$$

where λ_0 is the R1 line position at ambient pressure (694.25 nm), and $\Delta\lambda$ is the shift under pressure. The typical precision of this method is around 0.01 GPa [205].

As an example, Figure 3.24 shows a ruby fluorescence spectrum recorded at 0.9 GPa, illustrating the R1 and R2 line positions used for pressure determination.

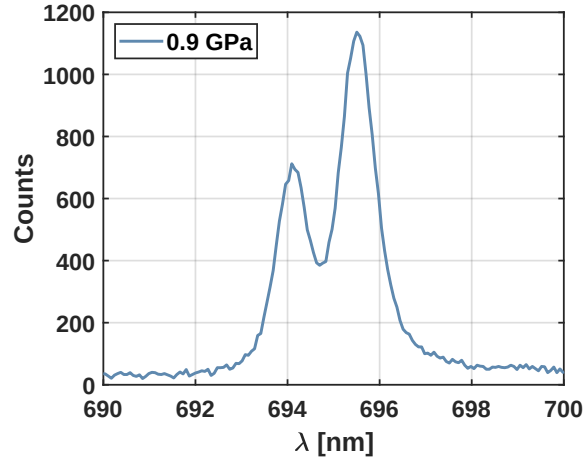


Figure 3.24: Representative ruby fluorescence spectrum recorded during pressure monitoring.

Experimental methods and HP-XPCS protocol

The DAC loading procedure involves a sequence of precise steps. First, the gasket is pre-indented to approximately $80\ \mu\text{m}$ in thickness, using wax as a support to hold it in place. The deformation is carefully monitored with a digital indicator placed on the diamond surface. Once the desired thickness is reached, a hole with a diameter of $300\ \mu\text{m}$ is drilled at the centre of the indentation using a high-power laser. The gasket is then cleaned in an ultrasonic bath to remove any residual metallic dust or imperfections that could compromise hydrostatic conditions. The sample is subsequently prepared by cutting it into small pieces, typically ranging from 50 to $80\ \mu\text{m}$ in size, using a confocal microscope for precise handling. These pieces, along with two ruby spheres for pressure measurement, are placed inside the gasket hole. Finally, the cell is loaded with the pressure-transmitting medium, and a preliminary pressure is applied by increasing the membrane pressure, typically to around $40\ \text{mbar}$, corresponding to an internal DAC pressure of approximately $0.4\ \text{GPa}$.

A photo of the DAC after loading is shown in Figure 3.25, where the samples and the two rubies are visible. The sample consists of a small fragment of a $\text{Ge}_{15}\text{Te}_{85}$ flake, and several irradiated spots can be observed on its surface.

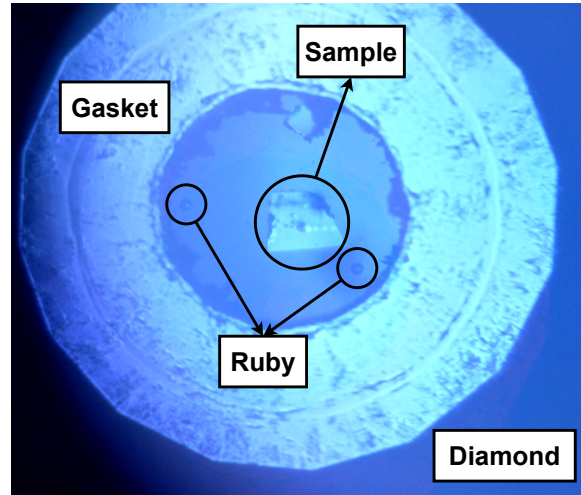


Figure 3.25: Image of the DAC after sample mounting. The $\text{Ge}_{15}\text{Te}_{85}$ fragment is positioned in the sample chamber together with two ruby spheres used for pressure calibration. The irradiated regions on the sample surface are also visible.

During the XPCS measurements, a dedicated protocol is implemented to ensure isobaric conditions throughout the data acquisition. After each pressure increment, a waiting period of approximately 20 minutes is observed to allow for pressure stabilisation before starting the scans. Firstly, it is important to disentangle the beam-induced effects of XPCS from those of the high-pressure compressions; therefore, at each pressure point, the internal dynamics of the sample is measured using three different beam flux levels, 64%, 41%, and 25% of the full beam intensity. Once the irradiation effect at HP is characterised, measurements using a single beam flux value can be performed.

Furthermore, since the sample's response to pressure evolves gradually in time, it is important to ensure that XPCS scans always start at the same elapsed time after each pressure change.

Figure 3.26a) shows an example of the applied time-pressure protocol, while Fig. 3.26b) illustrates the protocol used at 4 GPa during the first beam-time. In this case, the acquisition times of the three XPCS scans performed at different beam fluxes must be adjusted to account for the beam-induced effect, whereby halving the beam intensity approximately doubles the timescale of the induced dynamics. To ensure that the entire decorrelation of the dynamics is captured, scans at lower fluxes are therefore extended accordingly.

Lastly, it is important to emphasise that XPCS is highly sensitive to pressure drifts. To mitigate pressure overshooting and drifts, the membrane pressure must be carefully reduced after each pressure change. The strategy adopted is described in detail in Ref. [206].

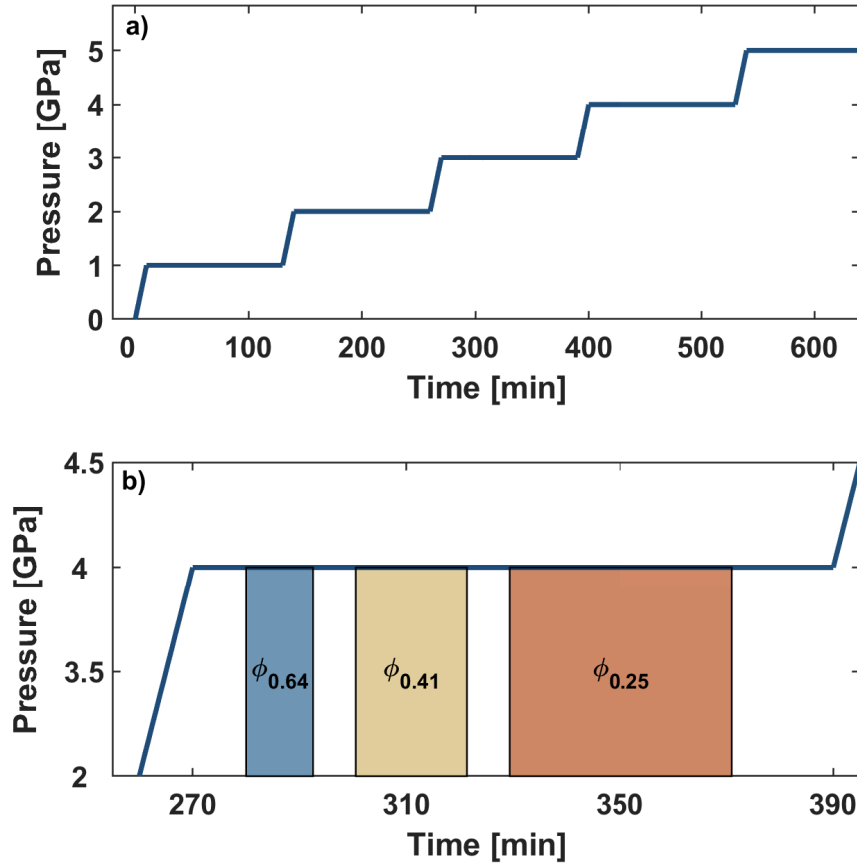


Figure 3.26: a) Example of the time-pressure protocol used to stabilise the sample after each pressure increment. b) Specific measurement protocol at, for instance, 4 GPa during the first beamtime, showing the sequence of XPCS scans performed at different beam fluxes (64%, 41%, and 25% of the full intensity). The acquisition times are adjusted to capture the full decorrelation of the dynamics at each flux level.

3.3.3 Data analysis of XPCS

The analysis of the XPCS data is performed using a MATLAB routine derived from the P10 beamline software and further developed by the SDSC

group in Trento.

The analysis begins by processing the 2D images acquired by the Eiger4M detector. This involves masking all pixels that do not carry reliable information from the sample. For instance, hot and cold pixels are excluded, as are those located at the edges of the detector modules, which produce artefacts due to modular discontinuities. These masked regions appear as horizontal and vertical lines in Figure 3.27, which shows a representative detector frame. At the P10 beamline, the scattered X-ray signal travels through a vacuum tube before reaching the detector (see Paragraph 3.3.2.1). This tube partially obscures the detector area, resulting in the characteristic elliptical shape of the scattering signal. The pixels covered by this shadow, as well as those bordering the shadow's edge, are also masked.

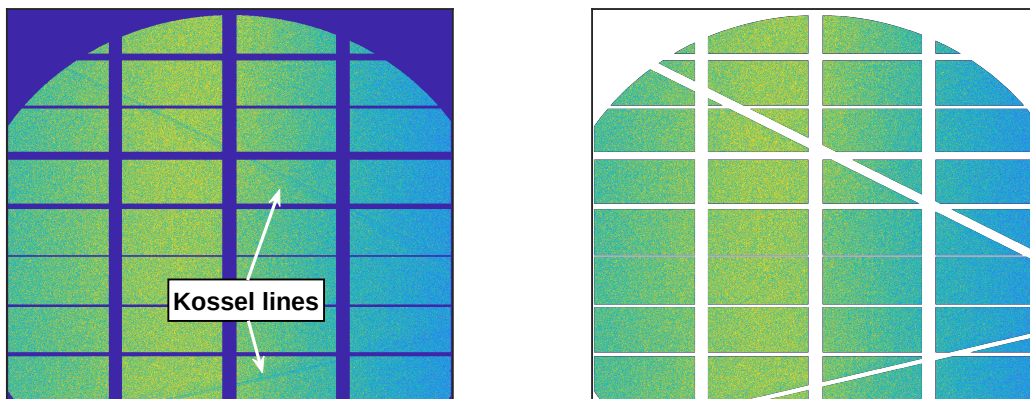


Figure 3.27: Example of masked Eiger4M detector frame. Masked regions include hot/cold pixels, module edges, pseudo-Kossel lines, and detector shadow from the vacuum flight tube.

When using a DAC, additional features such as pseudo-Kossel lines may appear in the diffraction pattern (Figure 3.27), originating from the diamonds under high pressure [207]. These lines introduce incoherent, static contributions to the signal and are therefore masked during data treatment. In some cases, local crystallisation may occur due to exposure to the X-ray beam, elevated temperature, or pressure variations. This manifests as sharp Bragg peaks in the diffraction pattern. Nevertheless, if the crystalline contributions are small enough, by carefully masking them, the dynamics of the underlying amorphous matrix can still be reliably extracted.

Once the masking is complete, the two-time correlation function (TTCF) is computed as defined in Equation (3.3.10). From this, the intensity autocor-

relation function $g_2(q, t)$ is calculated via time averaging (Equation (3.3.11)). In the following, the Kohlrausch-Williams-Watts (KWW) model to extract dynamical parameters will be explained, and how they can be studied to investigate how the sample dynamics evolves with absorbed dose and as a function of the scattering vector q . Additionally, how one can extract the static structure factor $S(q)$ and how to track the sample's scattered intensity $I(t)$ will be explored.

Kohlraush-Williams-Watts function

As discussed in Paragraph 1.4, the intermediate scattering function $F(q, t)$ can be modelled using the Kohlrausch-Williams-Watts (KWW) function [208]. The corresponding intensity autocorrelation function $g_2(q, t)$ takes the form [209]:

$$g_2(q, t) = y_0 + C e^{-2(\frac{t}{\tau})^\beta}, \quad (3.3.19)$$

where $C = C_e |f_q|^2$, with f_q being the non-ergodicity factor and C_e the experimental contrast. The parameter τ is the characteristic relaxation time of the dynamics, while β describes the shape of the decay. A value of $\beta < 1$ indicates a stretched exponential decay, typical of glassy or disordered systems, whereas $\beta > 1$ corresponds to a compressed decay. The baseline offset y_0 accounts for any incoherent background in the signal.

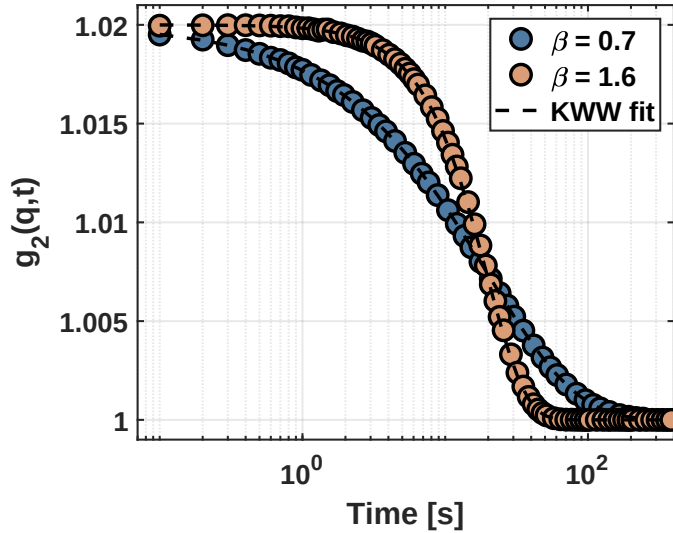


Figure 3.28: Representative examples of $g_2(q, t)$ fitted with different β values using the KWW model.

Each parameter depends on external variables such as the scattering vector q , temperature T , absorbed dose D , and pressure P .

When dynamics are induced by the X-ray beam, it is often useful to express τ in terms of the absorbed dose D_τ needed to drive the observed relaxation. This dose is calculated as:

$$D_\tau = \frac{\epsilon}{m} F \tau, \quad (3.3.20)$$

where ϵ is the X-ray energy, F is the absorbed flux, and m is the mass within the scattering volume V_s . The absorbed flux is defined as $F = \phi(1 - T_r)$, where ϕ is the incident beam flux and T_r is the transmission of the sample

$$T_r = \exp(-L/\mu), \quad (3.3.21)$$

with L being the sample thickness and μ the attenuation length of the sample at a specific X-ray energy. The mass $m = \rho V_s$, with ρ being the atomic mass density, $V_s = AL$, where A is the beam spot area and L is the sample thickness. In the case of *in-situ* high-pressure XPCS, both ρ and μ evolve with pressure, and their variation must be taken into account when evaluating the D_τ .

Analysis in time and in dose

As said, the dynamics of a system is encoded in the two-time correlation function, where non-stationary behaviour manifests as changes of the intensity correlations along the diagonal of the matrix (Figure 3.29). To quantify temporal evolutions, one computes the intensity autocorrelation function $g_2(q, t)$ over finite time windows Δt , by averaging the TTCF over selected submatrices (black squares in Figure 3.29a)). Each resulting $g_2(q, t)$ curve characterises the decay of correlations at a given waiting time t_w , defined as the midpoint of Δt . Examples of $g_2(q, t)$ functions computed at different t_w are shown in Figure 3.18a).

This time-windowed approach is particularly well-suited to follow slowly evolving systems, such as those undergoing aging, since it captures the dynamics locally in time. However, its accuracy decreases when Δt becomes too small: if the chosen interval is shorter than the system's characteristic relaxation time, the $g_2(q, t)$ does not fully decorrelate within the window, leading to less reliable fits.

In such cases, an alternative strategy consists of taking vertical or horizontal cuts of the TTCF, as proposed in [210] and illustrated in Figure 3.29b). By averaging along columns (or rows), one can recover the full decorrelation

of the signal and obtain meaningful $g_2(q, t)$ curves even for strongly out-of-equilibrium systems.

In beam-induced dynamics, it is often insightful to analyse the evolution as a function of absorbed dose. The total dose absorbed over a time window Δt is given by:

$$D = \frac{\epsilon}{m} F \Delta t , \quad (3.3.22)$$

with all quantities defined as in Equation (3.3.20).

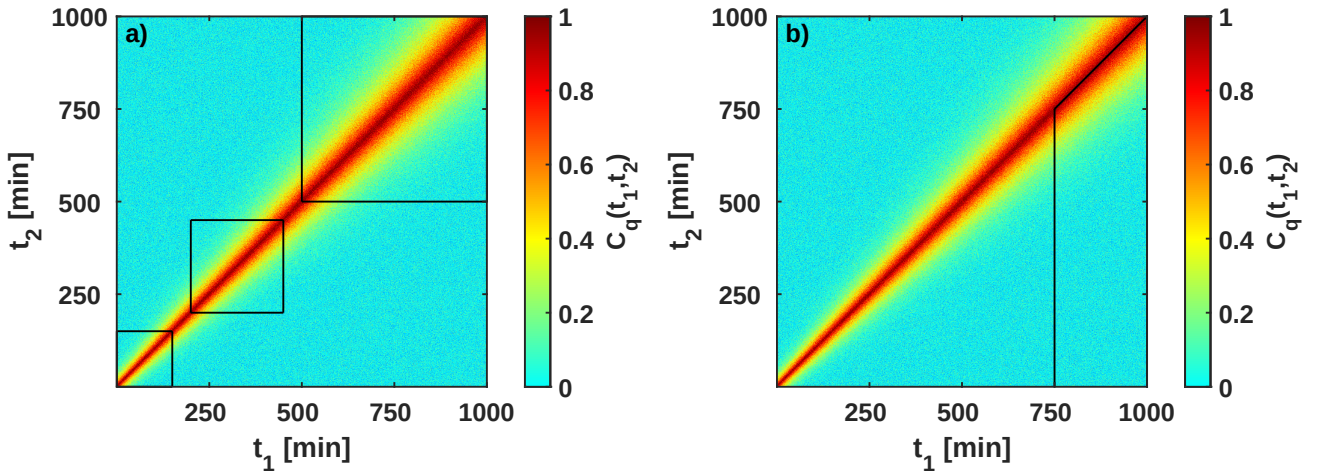


Figure 3.29: Two-time correlation map showing a dynamics that evolves over time. a) Black squares indicate the submatrices used to compute the $g_2(t)$ within finite time windows Δt . b) Alternative averaging method along TTCF columns (or rows), applied when full decorrelation is not reached within a single window.

Analysis in q

The detector area covers a scattering angle of about 5 degrees, since its distance from the sample is ~ 1.83 m and it is characterised by a 2070-pixel width (with $75 \mu\text{m}$ pixel size). To resolve the q -dependence of the dynamics more finely, the detector area can be divided into azimuthal slices, as illustrated in Figure 3.30. While this approach improves angular resolution, it

reduces the number of pixels per region and thus decreases statistical quality.

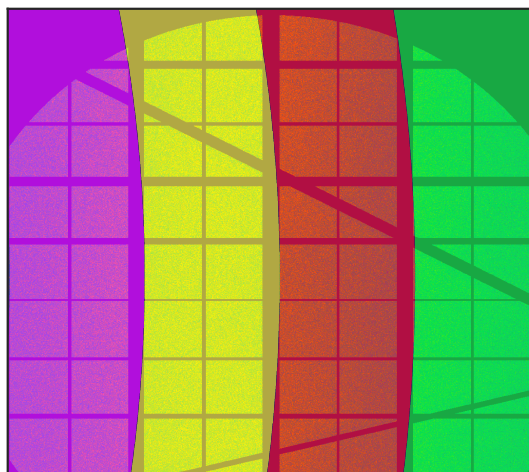


Figure 3.30: Division of the detector area into angular slices for improved q -resolution in the analysis of $g_2(q, t)$.

Static structure factor and averaged scattered intensity

From the 2D diffraction patterns collected by the detector, the static structure factor $I(q)$ can be obtained by radially averaging the intensity. Knowing the pixel size and detector-sample distance, a conversion from scattering angle to the scattering vector q can be done. If the scattered intensity does not evolve over time, $I(q)$ can be averaged over the full duration of the measurement to improve signal quality. An example is shown in Figure 3.31a). Although the accessible q -range and resolution are limited compared to conventional XRD, this approach is still sensitive to significant structural changes.

In addition, by averaging the intensity over the entire active area of the detector for each frame, one obtains the total scattered intensity as a function of time $I(t)$ (Figure 3.31b), which can also be plotted versus absorbed dose according to (3.3.20).

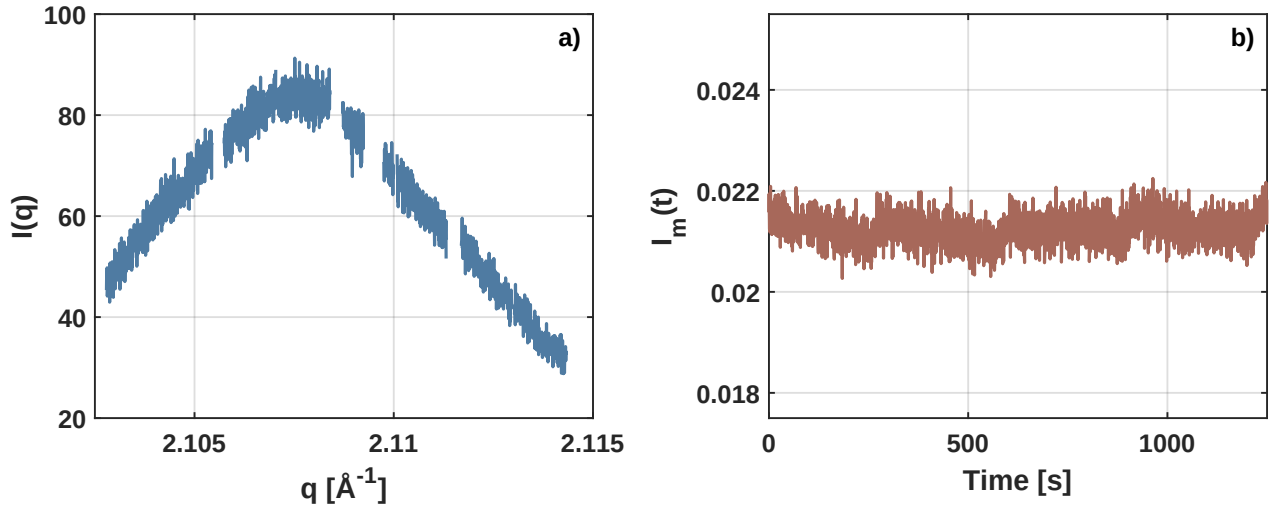


Figure 3.31: a) Static structure factor $I(q)$ extracted from the detector. b) Time evolution of total scattered intensity $I(t)$. Both quantities are measured on a sample of $\text{Ge}_{15}\text{Te}_{85}$ at 2.7 GPa.

3.4 Raman scattering

Raman scattering is the inelastic scattering of photons by matter, typically induced by visible laser light. The process involves energy exchange between the photon and molecular vibrations, providing insight into the sample's atomic dynamics. Most photons are elastically scattered (Rayleigh scattering), but a fraction undergoes a frequency shift, the Raman shift, within about $5\div 3500\text{ cm}^{-1}$ from the laser line.

Molecular vibrations are quantised, and Raman transitions occur via a virtual electronic state. If the scattered photon loses (gains) energy, the process is called Stokes (Anti-Stokes) scattering; elastic scattering corresponds to Rayleigh. Stokes peaks are generally stronger because lower vibrational levels are more populated, as dictated by the Bose-Einstein distribution. The Stokes/Anti-Stokes intensity ratio follows

$$\frac{I_S}{I_{AS}} = \left(\frac{\omega_l - \omega}{\omega_l + \omega} \right)^4 \exp \frac{\hbar\omega}{k_B T} \quad , \quad (3.4.1)$$

where ω_l is the laser frequency k_B is the Boltzmann constant and T is the sample temperature. This relation reflects the principle of detailed balance, which states that at thermodynamic equilibrium, each microscopic process is balanced by its reverse.

Raman processes can occur only if there is a change in the molecular polarizability α , which is generally a tensor quantity. Thus, a normal mode can be Raman-active or silent. In crystals, selection rules determine which vibrational modes are allowed, typically producing sharp spectral peaks. In contrast, glasses present a breakdown of the selection rules and exhibit broad, continuous spectra. This difference originates from two intrinsic characteristics of amorphous solids: the electrical disorder, arising from the random local coupling between atomic displacements and the induced polarizability; and mechanical disorder, due to the loss of translational symmetry, which distorts vibrational eigenmodes so that they no longer resemble plane waves [211].

As a result of both types of disorder, the entire vibrational density of states (DOS), $g(\omega)$, contributes to the Raman signal. The Raman intensity can therefore be written as

$$I^R(\omega) = C(\omega)g(\omega)\frac{1 + n(\omega)}{\omega} \quad (3.4.2)$$

where $n(\omega)$ is the Bose-Einstein occupation number, and $C(\omega)$ is a material-dependent coupling coefficient describing how the molecular electron clouds interact with the electric field of the incident light. Because $C(\omega)$ is generally

unknown and varies with frequency, Raman spectroscopy cannot yield the DOS unambiguously. A direct and model-independent determination of $g(\omega)$ instead requires inelastic X-ray or neutron scattering experiments, in which the coupling factor is absent [211].

3.4.1 Micro-Raman Spectroscopy

Raman micro-spectroscopy is a technique that allows for performing Raman measurements on microscopic samples or localised areas of interest of larger samples. The experimental measuring apparatus consists of a Raman detector integrated with an optical microscope, which enables focusing the laser on samples. The main benefit of this technique is the opportunity to study spectra without requiring a large amount of material. Furthermore, being faster than standard Raman spectroscopy, it becomes suitable for analysing samples whose spectra and responses are unknown. Deterioration in time due to air exposure and due to the laser power can be checked.

The spectra obtained through Micro-Raman spectroscopy can be used as a reference in Raman measurements whenever the samples are thin and composed of substrates. In the standard Raman setups, it is not possible to focus precisely on a specific spot of the sample, risking shining on the substrate as well. A comparison between spectra measured with the two techniques ensures the actual probed system is the sample and not the substrate.

Setup - Measurement procedures

The Raman microscope consists of a laser source of three different wavelengths (532 nm, 632.8 nm, 785 nm), which can be filtered in an adjustable way, to reduce the power on the sample. A system of lenses, whose magnification, numerical aperture and focal length can be set, focuses the laser beam on a specific area of the sample. A monochromator separates the wavelength of the scattered light in a back-scattering configuration: it is possible to set the diffraction grating step to choose the most suitable resolution.

A CCD detects and counts emitted photons in a frequency range of 700 cm^{-1} , in contrast to the standard Raman spectroscope, which measures one frequency at a time; furthermore, the CCD is cooled to increase the signal-to-noise ratio. At the CCD camera input, there is a filter which cuts all the frequencies under 100 cm^{-1} to avoid damage due to elastic scattering.

Finally, the experimental apparatus is equipped with a moving stage, where the sample is placed, and it can be translated in any direction. Through a microscope, the movements of the stage can be followed, the suitable location of the sample can be chosen, and the laser can be better focused. The

microscope has the same focal length, but different magnifications (x4, x10, x50, x100).

Finally, the polarisation of the laser can be set either unpolarised, vertical or horizontal. At the output, two different polarisations (vertical and horizontal) can be selected.

An implemented software allows setting the main measurement parameters, and it displays and saves the measured data.

3.4.2 Raman Spectroscopy

Setup - Measurement procedures

Standard Raman spectroscopy can be used to investigate the low-wavenumber vibrational spectra of the samples at both room temperature and low temperatures. When working with thin films only a few tens of microns thick and deposited on substrates, as in the present study, special care must be taken to minimise spurious contributions from the substrate. To address this, the 90° scattering geometry is exploited.

In this geometry, the samples are illuminated by a laser beam with power on the order of mW, modulated using a diaphragm. The beam hits the sample surface at an angle close to 90° , effectively avoiding any scattering related to the substrate. The scattered light is collected and focused through a lens into a U-1000 double monochromator (Figure 3.32). The U-1000 consists of two 1800 grooves/mm diffraction gratings whose synchronised rotation disperses the incoming light. The use of a double monochromator provides a greater dynamic range than a single-stage design [212]. Its optical layout is shown in Figure 3.33.

The spectrometer disperses the scattered beam into many wavenumbers, allowing for the analysis of the light intensity as a function of the wavelength. At the spectrometer output, a photomultiplier converts the optical signal into an electrical current with a gain of 10^6 : for each detected photon, 10^6 electrons are produced. To avoid damage from the intense laser line, absorption filters at the corresponding wavelength of the laser are placed at the spectrometer entrance. Since only inelastic scattering is of interest, this does not affect the Raman measurements.

Apertures at the spectrometer input, output, and within the monochromator stages allow adjustment of both intensity and spectral resolution. Through software at our disposal, the measurements can be optimised by setting the integration time, the wavenumber range of measurement and the wavenumber step. Moreover, the software allows for setting the polarisation

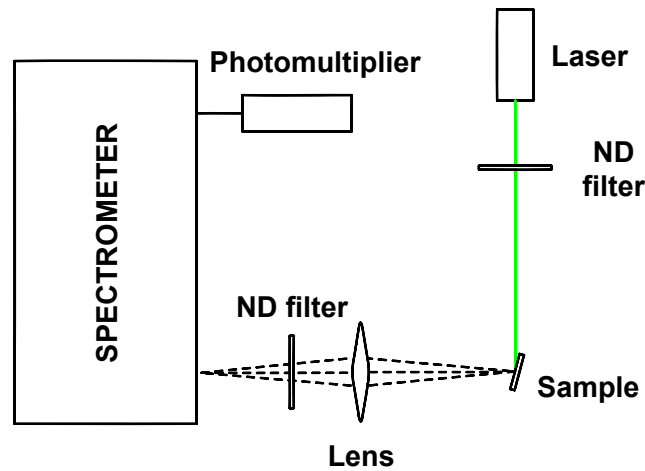


Figure 3.32: Experimental Raman setup. The 90° scattering geometry enables thin-film measurements by aligning the laser onto the sample at a nearly perpendicular incident angle, thereby avoiding scattering from the substrate. The scattered light is focused via a lens into the double monochromator (U-1000), which decomposes the beam so that a photomultiplier can measure the intensity as a function of wavelength. Optical filters at the corresponding wavelength of the laser protect the detector from the strong elastic signal.

of the output beam, which can be vertical or unpolarised.

The measurements at room temperature can be conducted with the samples held in air. In the low-temperature measurements, the sample is mounted on a cold finger using thermally conductive silicone paste, placed under vacuum inside a cryostat, and cooled with liquid nitrogen. A thermocouple in direct contact with the cold finger is used to monitor the temperature.

This setup allows for high-resolution spectra measurements at low wavenumbers. However, to correctly perform the data analysis (see next Paragraph), it is essential to measure spectra over wide wavenumber ranges. Wide-range spectra can also be used to check whether the laser has been correctly aligned on the sample by comparing them with those measured by Micro-Raman spectroscopy, where the laser can instead be finely focused on the sample.

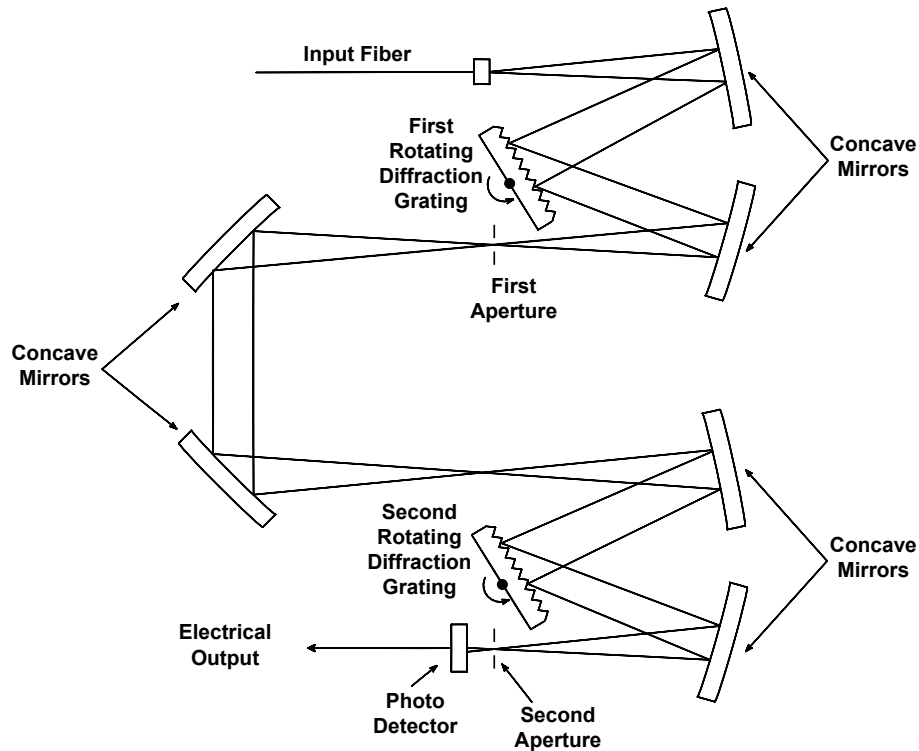


Figure 3.33: Optical layout of the U-1000 spectrometer. The scattered beam enters the U-1000 spectrometer and is reflected by a concave mirror to a first rotating diffraction grating, which disperses the light. The dispersed beam crosses a first aperture and, through a system of concave mirrors, it hits a second rotating diffraction grating. The light is reflected by a final concave mirror into a second aperture outside the spectrometer. Reprinted from [212].

Data analysis

The goal of the Raman scattering measurements in this Thesis is to observe and characterise the boson peak in the reduced vibrational density of states, $g(\omega)/\omega^2$, at low wavelengths. Achieving this requires a careful and systematic data reduction procedure.

First, all spectra are shifted by the laser frequency to convert the spectrometer output, originally expressed in absolute frequency ω_0 , into the Raman shift ω . The wide-range spectra are then used to estimate the background: data points in the plateau regions are selected and fitted with a power-law function. The resulting spectra are subsequently corrected for the instrumental response, previously measured using silicon dioxide reference samples. The quality of the background subtraction is verified by applying the Stokes-anti-Stokes relation (Eq. (3.4.1)): the Stokes side is multiplied by the corresponding Boltzmann factor and compared to the anti-Stokes side. Good overlap between the two confirms the correctness of the background removal. Figure 3.34 shows an example for a sample of an ultrastable glass of TPD: the fitted background (top), the instrumental response (bottom left), and the Stokes-anti-Stokes comparison (bottom right).

To properly treat the high-resolution spectra measured in the restricted wavenumber range, the background function from the wide-range measurement is subtracted directly, since the limited range does not allow a reliable in situ background estimate. To ensure proper subtraction, the wide-range spectra are rescaled to match the intensity of the restricted-range data (Figure 3.35). After subtraction, the spectra are corrected for the instrumental function and multiplied by the Boltzmann factor to compare Stokes and anti-Stokes sides. To enable consistent comparison between different samples, the spectra are normalised to a specific peak.

As said, the Raman scattered intensity $I_R(\omega)$, in the low frequency region, is related to the density of states $g(\omega)$ by [213]:

$$J_R(\omega) \equiv \frac{I_R(\omega)}{\omega(1 + n(\omega))} \propto C(\omega) \frac{g(\omega)}{\omega^2} , \quad (3.4.3)$$

where $J_R(\omega)$ is known as reduced Raman spectrum. Here, $C(\omega)$ is a function which depends on the material polarizability and is usually unknown.

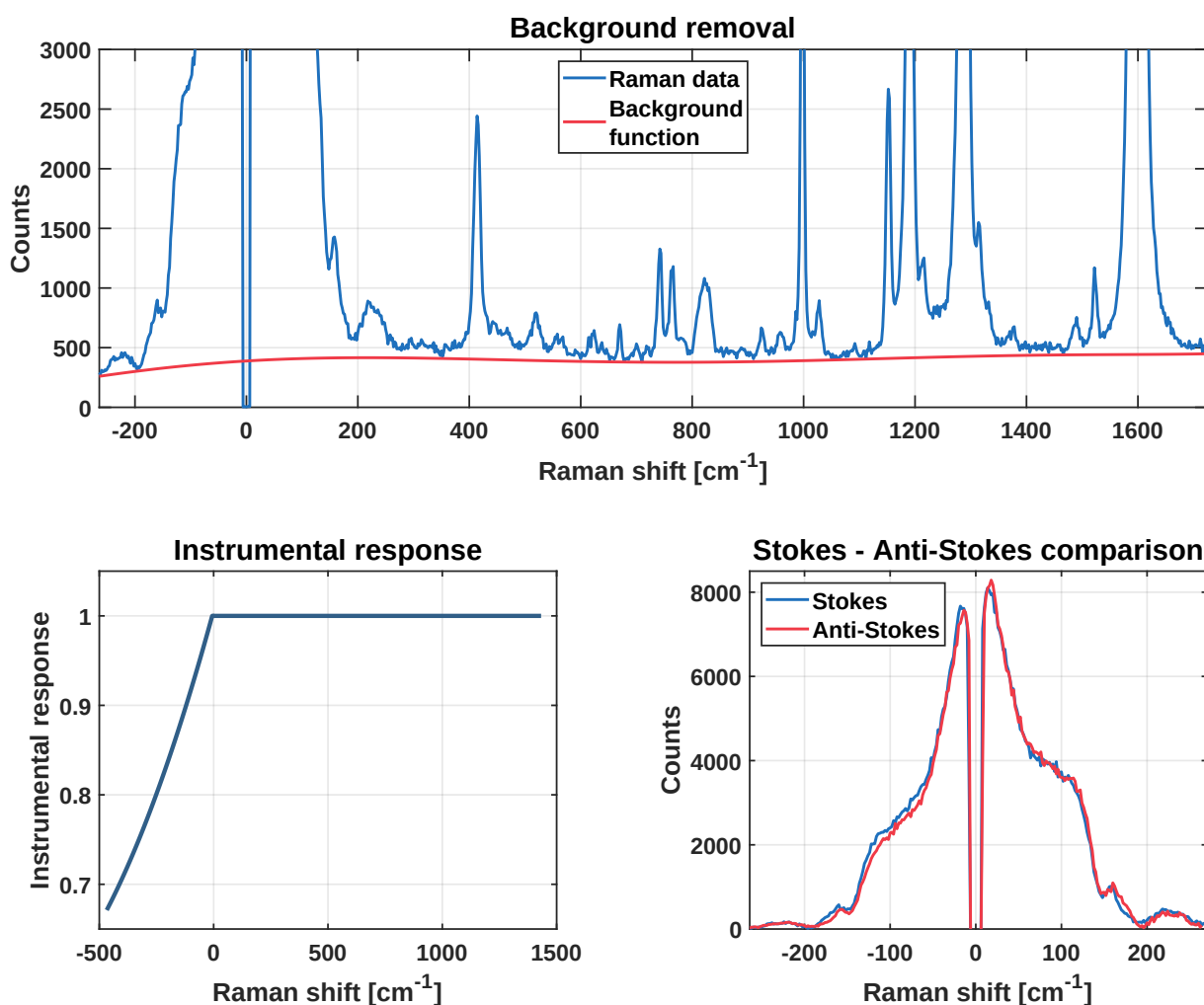


Figure 3.34: The data reduction of Raman measurements of the ultra-stable TPD glass at 298 K. On top, the background function is estimated by fitting the minima of the spectrum to a power law, and it is subtracted from the Raman data. The result is multiplied by the instrumental response plotted in the bottom left; finally, the spectrum is multiplied by the exponential term of equation (3.4.1) and flipped around zero cm^{-1} , to check the goodness of the background estimation by comparing Stokes and Anti-Stokes sides.

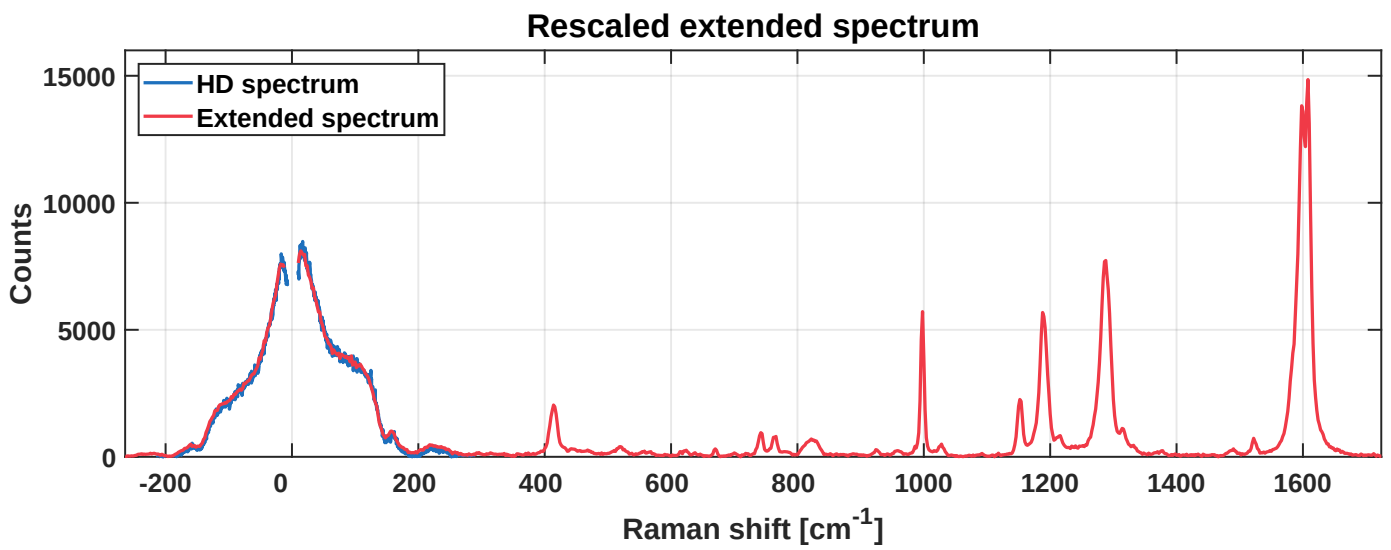


Figure 3.35: Rescaling of the extended spectrum over the high-resolution one for the ultra-stable TPD glass at 298 K. To properly remove the background function from the spectra measured in a restricted wavenumber range (HD spectrum), it is necessary to rescale the extended spectrum over the HD spectrum. In this way, the background function found for the large spectrum is correctly subtracted from the restricted spectrum.

3.5 Calorimetry

Differential Scanning Calorimetry (DSC) is the most widely used thermal analysis technique for investigating the thermodynamic and kinetic properties of materials, with applications ranging from fundamental research to industrial quality control [214]. In glass science in particular, DSC has established itself as an indispensable tool for characterising phase transitions, structural relaxation, and the evolution of material properties under heating, cooling, or annealing. The method relies on monitoring the heat flow difference between a sample and a reference as a function of time and temperature, thereby quantifying the energy absorbed or released during physical transformations and chemical reactions [215]. While conventional DSC is highly sensitive to energetic events, its relatively slow scanning rates, typically 1-40 K/min, limit its ability to capture subtle signals, such as those from metastable phase transitions [216], or localized atomic/molecular rearrangements [217], which may be suppressed at low temperature scanning rates [218]. In addition, conventional DSC usually requires milligram-scale samples and cannot measure microgram-scale specimens. To overcome these limitations, extremely fast calorimetric techniques were developed, leading to the advent of flash nanocalorimetry (Flash DSC) [219–226]. Based on chip-calorimeter technology [220, 221], Flash DSC enables heating and cooling rates several orders of magnitude higher than standard instruments and can measure microgram-scale specimens, allowing access to previously inaccessible time and temperature regimes and thereby offering new insights into the stability, relaxation, and phase transformations of glassy materials.

In the following, I provide a brief description of the experimental approach adopted in this work. The sample densifications, the measurements and data analysis were carried out by Dr Jie Shen, a postdoctoral researcher in our group at the Institut Néel in Grenoble, with my participation during the densifications and measurement campaigns.

Setup - Measurements

Fast scanning calorimetry is performed using a Flash DSC instrument (Mettler-Toledo FDSC 2+), shown in Figure 3.36. This chip-based calorimeter employs dynamic power compensation, which allows operation across a broad range of scanning rates, from very low to ultrahigh values. Heating/cooling rates of up to 40,000 K/s can be achieved, over a temperature window from -95°C to 1000°C, suitable for the investigation of organic and metallic glasses.



Figure 3.36: Photograph of the Mettler-Toledo Flash DSC 2+ instrument used for fast scanning calorimetry measurements [227].

In this configuration, a small sample ($\sim \mu\text{m}^2$) is placed on the sensor surface, with a thin layer of bonding material (e.g., silicone oil) applied between them to ensure good thermal contact. The Flash DSC employs a MEMS-based twin sensor, consisting of two identical silicon-nitride/oxide membranes suspended within a ceramic frame. Each membrane has a length of 1.6 mm, a thickness of 1 μm , and a central sample area of 0.5 mm coated with aluminium to ensure homogeneous temperature distribution. The sample and reference sides of the sensor each include two thermal resistance heaters, while the sample temperature is monitored by a thermopile of eight p-n polysilicon thermocouples acting as a heat sink. For the present measurements, a heating rate of 500 K/s was chosen to optimise the balance between signal-to-noise ratio and thermal lag. The investigated temperature range covers the devitrification and crystallisation of the samples (298–623 K). To prevent sample detachment due to residual stresses, silicone oil (polydimethylsiloxane) was applied as a contact medium at the sensor stage before sample placement. The silicone oil also improves thermal contact, which cannot be achieved by slightly melting the sample as is commonly done; otherwise, the effects of treatments on the samples (such as densification) would be lost. To ensure reproducibility and minimise statistical error, each measurement was repeated with different sample masses, up to three times.

Data analysis

The raw heat-flow signal obtained from the Flash-DSC is first corrected to remove the instrumental contribution. To achieve this, the glassy region of

each curve is fitted with a third-order polynomial, as illustrated in Fig. 3.37, and the resulting fit is subtracted from the original data. This procedure ensures a flat baseline across both the glassy and supercooled-liquid regions, thereby enabling reliable comparison between scans. The correction accounts for the intrinsic baseline of the Flash-DSC sensor and for the thermal contribution of the silicone-oil contact medium, which is, however, negligible in the temperature range of interest. For quantitative comparison among different measurements, all heat-flow curves are normalised by sample mass, so that the signals in the supercooled-liquid region overlap.

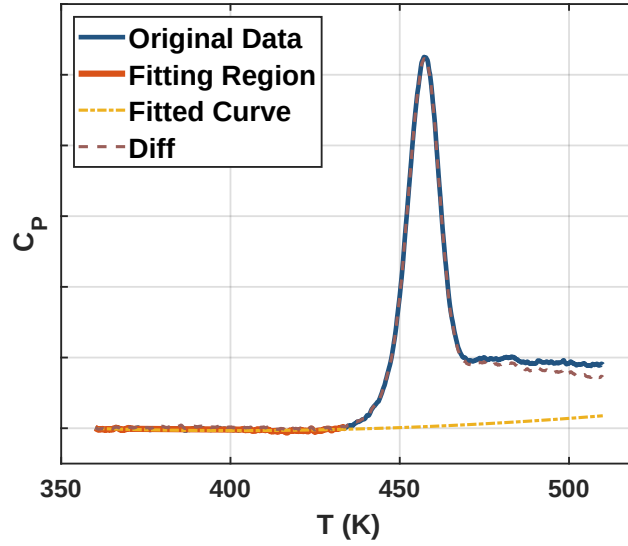


Figure 3.37: Baseline correction of a representative Flash-DSC heat-flow curve for densified $\text{Ge}_{15}\text{Te}_{85}$ measured at 1.1 GPa. The glassy region (red line) of the raw data (blue) is fitted with a third-order polynomial (dashed-dotted yellow line), which is then subtracted to obtain a flat baseline across the glass and supercooled-liquid regions (dashed brown line).

The thermodynamic state of each sample can be further characterised by determining the fictive temperature, T_f , using the area-matching method introduced by Moynihan [228]. The fictive temperature corresponds to the temperature at which a glass of a given structure would be in thermodynamic equilibrium with its supercooled liquid [229]. According to the Moynihan method, it can be obtained by imposing that

$$\int_{T_f}^{T'} (C_{p,l} - C_{p,g}) dT = \int_{T_d}^{T'} (C_p - C_{p,g}) dT , \quad (3.5.1)$$

where $C_{p,g}$ is the glass heat capacity extrapolated from the data below the glass transition, $C_{l,g}$ is the equilibrium liquid heat capacity fitted from the data, T_d marks the onset of deviation of the experimental heat capacity C_p from the glass baseline, and T' is any temperature above the glass transition region [218].

This procedure is depicted in Fig. 3.38: panel a) illustrates the case of an endothermic event, corresponding to devitrification, while panel b) shows an exothermic event preceding the devitrification. The glassy and liquid baselines of the data (brown curves) are first approximated by linear fits (dashed and dotted lines, respectively). Starting from an initial guess of T_f , the two integrals in Eq. (3.5.1) are computed: the left-hand side corresponds to the yellow area A_1 , and the right-hand side to the blue area A_2 . The overlapping region appears in green. The final T_f value is obtained iteratively by adjusting T_f until the two areas match.

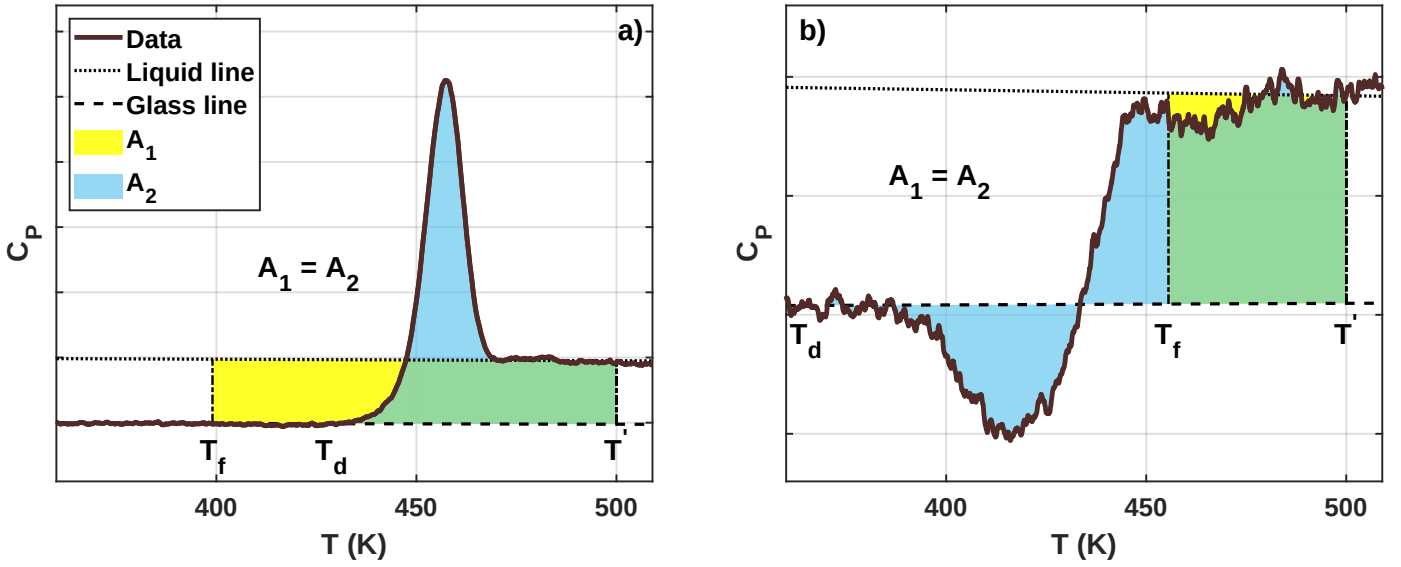


Figure 3.38: Schematic illustration of the Moynihan area-matching method used to determine the fictive temperature T_f for a) an endothermic event and b) an exothermic event. The brown curves show the heat capacity C_p of densified $\text{Ge}_{15}\text{Te}_{85}$ samples measured at different pressures. The dashed line represents the glass line, while the dotted line denotes the extrapolated supercooled-liquid line. The fictive temperature T_f is defined as the temperature at which the area enclosed between the liquid and the glass lines (A_1 , yellow) calculated between T_f and T' equals the area between the experimental curve and the glass baseline (A_2 , blue) evaluated between T_d and T' .

Résumé du Chapitre 4

Ce Chapitre présente une étude comparative de la dynamique vibrationnelle dans des verres ordinaires et ultra-stables de TPD, un semi-conducteur organique. Des mesures de diffusion inélastique nucléaire résonante des rayons X (NRAIXS) à l'ESRF ont permis d'obtenir la densité d'états vibrationnels (DOS) à 295 K et 150 K. La DOS réduite a révélé une suppression marquée du pic de boson dans les verres ultra-stables (USG) par rapport aux verres ordinaires (OG), en accord avec les données calorimétriques. Les écarts dépendant de la température à très basse fréquence ont mis en évidence des contributions anharmoniques et relaxatoires, nécessitant une extrapolation au-delà de l'approximation harmonique pour décrire la capacité calorifique à basse température. Les fits des données calorimétriques à partir de la DOS ont confirmé une contribution réduite des systèmes à deux niveaux dans les USG et ont montré que la stabilité affecte principalement le pic de boson tout en laissant inchangés les modes vibrationnels de plus basse fréquence. La spectroscopie micro-Raman n'a révélé aucune différence spectrale entre les USG et les OG au niveau moléculaire. Les spectres Raman à basse fréquence ont en outre corroboré les résultats de la NRAIXS : le pic de boson est plus faible dans les USG, avec de légers déplacements induits par la température et une suppression des queues anharmoniques. Enfin, nous avons comparé les résultats expérimentaux avec deux cadres théoriques, le modèle des potentiels souples et la théorie de l'élasticité hétérogène. Nous montrons que la présence des modes quasi-localisés n'est pas strictement nécessaire pour décrire la densité mesurée des vibrations à basse fréquence.

Chapter 4

Vibrational dynamics of ultra-stable and conventional TPD glasses

This Chapter investigates the vibrational dynamics of ordinary and ultra-stable glasses of TPD, using NRAIXS and Raman spectroscopy. The data reveal a pronounced reduction of the boson peak in ultra-stable glasses, as well as the two-level systems, while the low-frequency vibrational spectrum appears almost unaffected by the glass stability. Micro-Raman spectroscopy was employed to characterise the spectra at the molecular level. Finally, the results are compared with the Soft Potential Model and Heterogeneous Elasticity Theory to interpret the effects of glass stability on terahertz vibrations.

4.1 Samples

To investigate how vibrational dynamics differs between ordinary glasses and their vapor-deposited counterparts, we focused on the prototypical class of ultra-stable organic molecular glasses. Among these, indomethacin [3] and TPD [163] have been extensively studied, both being known for exhibiting an exceptionally low density of two-level systems. In this work, we selected TPD due to its higher resistance to X-ray radiation compared to indomethacin.

TPD (N,N'-Bis(3-methylphenyl)-N,N'-diphenylbenzidine) is an organic semiconductor with chemical formula $C_{38}H_{32}N_2$, whose molecular structure is shown on the left in Fig. 4.1. The samples were prepared by collaborators at the Universitat Autònoma de Barcelona. Films of $\sim 60 \mu\text{m}$ thickness were grown by PVD onto $1 \times 1 \text{ cm}^2$ Si substrates inside a high-vacuum chamber

(base pressure 1×10^{-8} Torr). During deposition, the substrate was held at 283 K ($0.85 T_g$) to produce the ultra-stable glass and at the glass transition temperature $T_g = 333$ K to prepare the ordinary glass.

Differential scanning calorimetry measurements yielded an onset temperature $T_{\text{on}} = 363.3$ K for the USG. The DSC analysis was performed by heating the as-deposited sample at $+10$ K/min and subsequently cooling at -10 K/min, following the protocol in Ref. [2]. The corresponding calorimetric trace is presented in Fig. 4.1 (right).

Low-temperature specific heat measurements on equivalent samples, performed by collaborators at the Universidad Autónoma de Madrid [163], revealed an almost complete suppression of the TLS contribution in the USG.

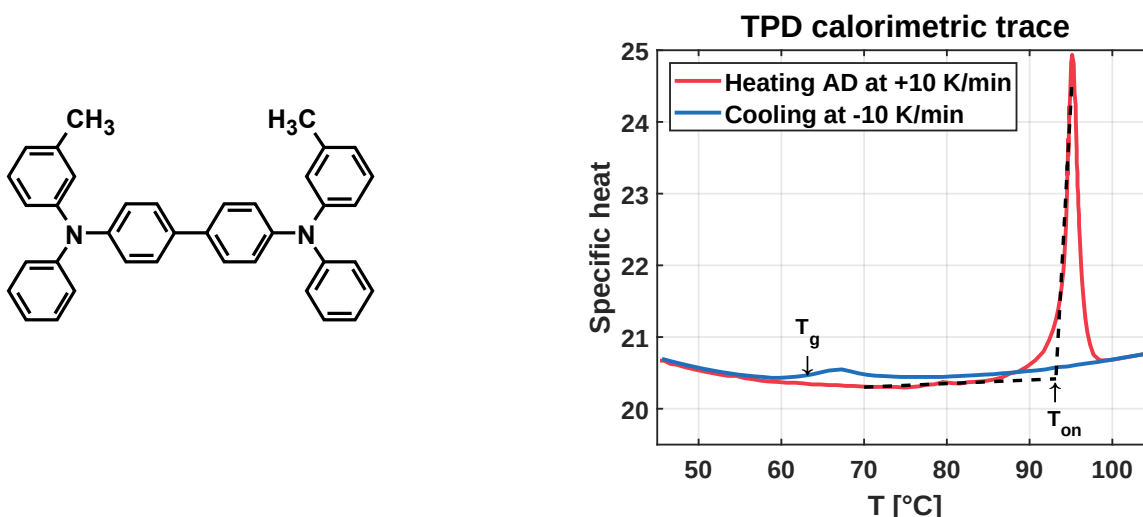


Figure 4.1: *Left:* Molecular structure of TPD ($\text{C}_{38}\text{H}_{32}\text{N}_2$) organic glass. Reprinted from [230]. *Right:* DSC trace of ultra-stable TPD. The USG was deposited at $0.85 T_g$ and then heated at $+10$ K/min (red). The sample was subsequently cooled at -10 K/min (blue). T_{on} is determined from the intersection between the extrapolated glass baseline and the transition peak. T_g is identified as the inflexion point of the specific heat curve.

The vibrational dynamics of both USG and OG samples were investigated using three complementary techniques: NRAIXS, Micro-Raman spectroscopy, and standard Raman spectroscopy. These methods are presented in detail in Chapter 3; here, each of the following sections begins with a description of the specific measurement conditions.

4.2 NRAIXS results

NRAIXS measurements were carried out during two beamtimes at the ESRF, ID18 beamline (now ID14). In the first session, both USG and OG samples were studied at 295 K, while in the second, the USG was additionally investigated at 150 K to assess temperature dependence and anharmonic effects below 0.8 meV.

An X-ray beam, with a focal spot of $\sim 35 \mu\text{m}$, was scanned in 0.02 meV steps across the ^{57}Fe nuclear transition over the interval $[-5, 10]$ meV, with 2 s integration per point. The energy resolution was $\sim 180 \mu\text{eV}$ in the first experiment and $120 \mu\text{eV}$ in the second. At 295 K, 65 scans of USG (~ 27 h) and 33 of OG (~ 14 h) were recorded; at 150 K, 168 scans (~ 70 h) were accumulated to ensure adequate statistics. During the first beamtime, an additional wide-range spectrum, required for DOS normalisation, was collected over the range $[-20, 410]$ meV for the USG sample at 295 K, using the high-resolution monochromator (HRM, ~ 1.8 meV) (Sec. 3.2.3). Due to time constraints, this was not repeated for OG or at 150 K. As corroborated by Raman results, the high-energy DOS (> 10 meV) is nearly identical for both glasses and independent of temperature. Background levels were periodically checked. The static structure factor $S(q)$ was also verified through θ - 2θ scans to exclude crystallisation.

The DOS was obtained after deconvolution of the instrumental response and removal of multi-phonon contributions, with the recoil energy E_R fixed as described in Eq. 3.2.29. From the mean atomic mass of TPD, $M_m = \frac{32M_C + 38M_H + 2M_N}{72} = 7.176$ g/mol, an initial estimate of $E_R \simeq 25$ meV (~ 6.1 GHz) was derived, then refined by requiring the DOS baseline to approach zero at high energy. Final values are listed in Table 4.1. The larger E_R at 150 K is attributed to the cryostat geometry, which slightly increases the detector-sample distance and thus reduces contributions from small scattering angles.

	E_R [meV]	E_R [THz]
USG - 300 K	10.7	2.59
OG - 300 K	10.1	2.44
USG - 150 K	18.6	4.50

Table 4.1: Recoil energy values used to compute the DOS of USG and OG at 300 K, and USG at 150 K.

The true vibrational density of states $g(E)$ was obtained by dividing the

generalised DOS by the correction function $C(E)$, with $\eta \simeq 1.59$ for TPD (see Equations (3.2.51) and (3.2.52)).

4.2.1 Static structure factor

The static structure factor $S(q)$ of both ultra-stable and ordinary glasses was measured in θ - 2θ geometry (Par. 3.2.2.2) to verify the absence of crystallisation. Figure 4.2 shows the corresponding diffraction curves: no sharp Bragg peaks are observed, confirming the amorphous character of the samples. The number and shape of the peaks are consistent with independent measurements performed at the Universidad Aut3noma de Barcelona. A slightly more pronounced pre-peak around $q \simeq 4 \text{ nm}^{-1}$ is observed for the ultra-stable glass, consistent with the structural anisotropy of TPD grown by physical vapour deposition [231].

We remark that the setup is not optimised for diffraction, resulting in relatively low q resolution.

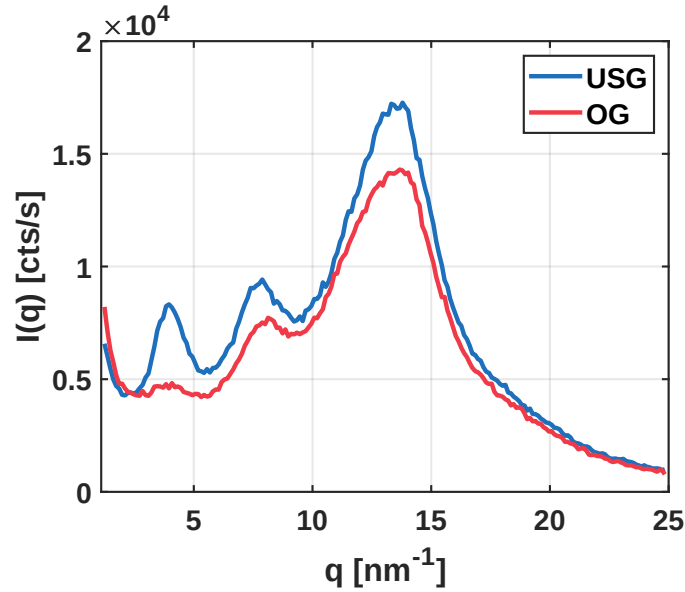


Figure 4.2: The intensity measured in the θ - 2θ geometry. The broad peak structure confirms that both the ultra-stable glass (USG) and the conventional glass (OG) remain amorphous.

4.2.2 Reduced density of vibrational states

Although all experimental parameters and analysis steps were expressed in energy units, the vibrational density of states is presented in frequency, the standard convention in the field ($1 \text{ meV} = 0.242 \text{ THz}$). From the processed spectra, the DOS was obtained in absolute units and is shown in Fig. 4.3 as the reduced form $g(\nu)/\nu^2$. Panel a) corresponds to USG and panel b) to OG. To emphasise the low-frequency regime, the axis is plotted on a logarithmic scale. Data are reliable down to $\sim 0.07 \text{ THz}$, corresponding to about twice the full width at half maximum of the instrumental resolution.

The boson peak appears at about 0.3 THz in both samples. The direct comparison between USG and OG highlights a key result: the intensity of the BP is strongly reduced in the ultra-stable glass. This observation is consistent with calorimetric data on the specific heat of the same materials [163], and it demonstrates the remarkable sensitivity of the BP to the thermodynamic stability of the glass.

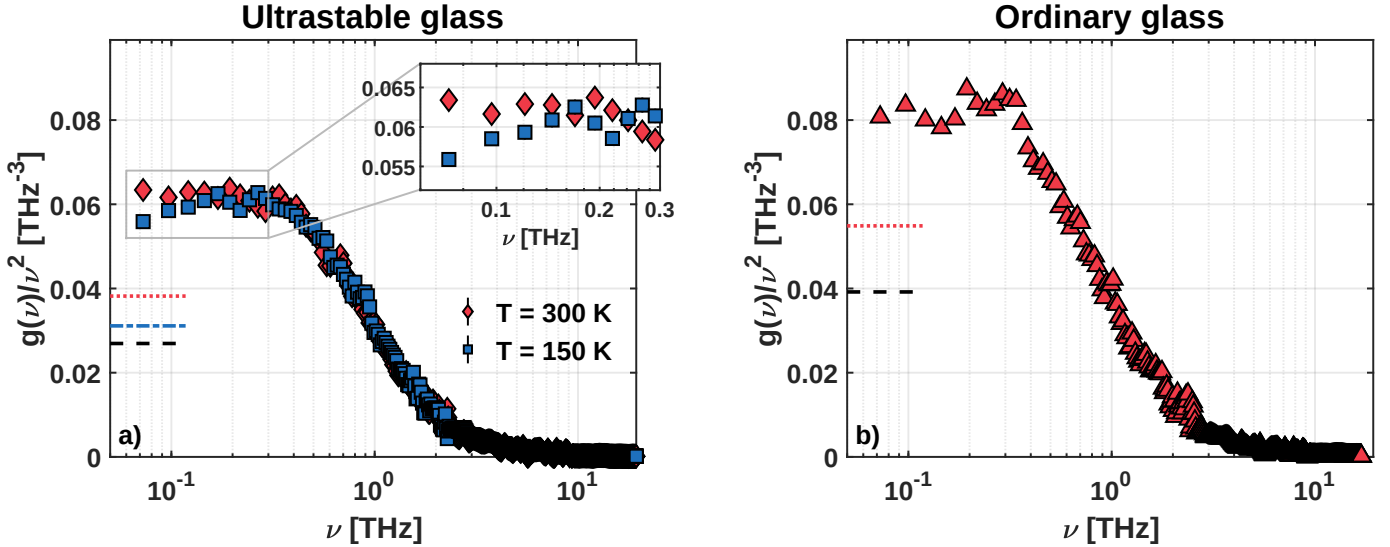


Figure 4.3: Reduced density of vibrational states. a): ultra-stable glass measured at 300 K (red diamonds) and at 150 K (blue squares); b): ordinary glass at 300 K (red triangles). The horizontal lines indicate the Debye levels estimated from the elastic moduli (Brillouin spectroscopy) at 300 K (red dotted), at 150 K (blue dot-dashed), and in the limit $T \rightarrow 0 \text{ K}$ (black dashed) [163]. The inset of panel a) expands the low-frequency region, where a difference between the two temperatures becomes visible below $\sim 0.15 \text{ THz}$.

A closer examination of the reduced DOS reveals further features. At room temperature, both glasses show an almost flat behaviour between 0.07 and 0.3 THz. These values are about 50% higher than the Debye levels calculated from the elastic moduli measured by Brillouin spectroscopy [163], indicated by the horizontal lines in Fig. 4.3.

In the USG, the lowest frequencies display a temperature dependence: as seen in the inset of panel a), the 150 K and 300 K spectra start to diverge below ~ 0.15 THz. This indicates that in this frequency region, anharmonic or relaxational contributions become relevant. The harmonic approximation, which predicts a temperature-independent DOS, is, thus, no longer valid in this regime, although it holds true at higher frequencies or sufficiently low temperatures.

To interpret this behaviour, we decompose the DOS into vibrational and relaxational contributions:

$$g(\nu, T) = g_{rel}(\nu, T) + g_{vib}(\nu, T). \quad (4.2.1)$$

Here, g_{rel} is associated with thermally activated jumps in asymmetric double-well potentials [232–235]. At low enough temperatures, where the BP appears in C_p/T^3 , this relaxational part vanishes and g_{vib} dominates. However, even g_{vib} can exhibit a temperature dependence through anharmonic effects, which are observed in both glasses and crystals [146, 236].

In the very low-temperature limit, where both relaxation and anharmonicity can be neglected, the DOS well below the BP maximum can be expressed as:

$$\lim_{T \rightarrow 0K} g(\nu, T) = g_{vib}(\nu, 0) \sim \frac{3}{\nu_D^3} \nu^2 + A_{ex} \nu^4 \equiv g_{LF}(\nu), \quad (4.2.2)$$

where ν_D is the Debye frequency, and A_{ex} quantifies the leading correction to the Debye prediction (“ex” stands for “excess”). This quartic contribution may arise from distinct physical mechanisms:

- (i) presence of quasi-localized modes with a density $g_{QLM} \propto \nu^4$ [130, 237, 238];
- (ii) Rayleigh scattering of acoustic phonons, which introduces a ν^4 dependence in the sound attenuation and hence in the DOS [121, 146];
- (iii) deviations from Debye behaviour also appear in crystals when approaching the first van Hove singularity, producing again a ν^4 correction.

The parameters ν_D and A_{ex} , which define $g_{LF}(\nu)$, can be evaluated through their effect on the low-temperature specific heat, as discussed in the following.

4.2.3 Low temperature specific heat

To validate the DOS results, we estimate the specific heat from the measured spectra and compare it with calorimetric experiments on equivalent samples. Calorimetric measurements were performed at the Universidad Autónoma de Madrid using ^3He and ^4He cryostats and the thermal relaxation method. The samples were mounted on sapphire substrates within the calorimetric cell, as described in Ref. [163].

In Par. 1.6.2, we showed how the specific heat can be derived from the DOS in the harmonic approximation. For clarity, we rewrite the expressions in terms of the specific heat per unit mass:

$$C_p(T) = \frac{3}{M_{at}} \int d\nu g(\nu) \frac{\partial n(T, \nu)}{\partial T} h\nu, \quad (4.2.3)$$

where M_{at} is the atomic mass, h is Planck's constant, and $n(T, \nu)$ is the Bose population factor for phonons,

$$n(T, \nu) = \frac{1}{e^{\frac{h\nu}{k_B T}} - 1}. \quad (4.2.4)$$

The DOS is normalized such that $\int_0^\infty g(\nu) d\nu = 1$.

A first calculation of C_p using the measured DOS is shown in Figure 4.4. Here, the DOS is assumed to be temperature-independent and extrapolated towards zero frequency by extending the lowest measured values horizontally (panel a). The calculated specific heat curves, shown in panel b), deviate significantly from the experimental data, especially at low temperatures. This discrepancy highlights the limitations of the harmonic approximation when applied to DOS spectra measured at finite temperature. As already emphasised in Fig.4.3, the USG displays a clear temperature dependence of the reduced DOS below 0.15 THz, precisely in the range controlling the low- T specific heat ($T < 10$ K). Neglecting this effect in the calculation inevitably leads to the observed discrepancy. In other words, the failure of this first attempt originates directly from using a DOS measured at finite temperature, where anharmonic effects modify the low-frequency dynamics. Similarly, the finite-temperature deviation from the Debye level cannot be ignored, contrary to assumptions sometimes made in the literature [239, 240].

A more reliable approach is to replace the low-frequency part of the measured DOS with an extrapolation consistent with the expected low-temperature behaviour. Following Eq. (4.2.2), the reduced DOS at low frequencies can be written as a parabola:

$$\frac{g_{LF}(\nu)}{\nu^2} = \frac{3}{\nu_D^3} + A_{ex}\nu^2, \quad (4.2.5)$$

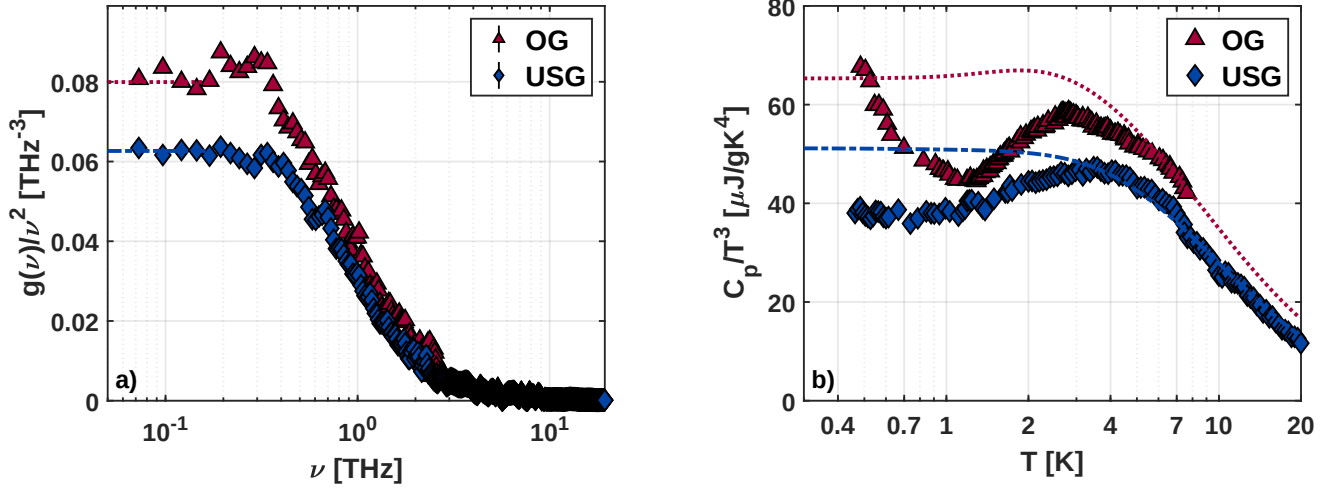


Figure 4.4: Specific heat calculation assuming the measured DOS to be harmonic. a): reduced DOS of the OG (red triangles) and USG (blue diamonds) at room temperature. The extrapolation towards zero frequency is done by assuming a constant value (lines). b): specific heat divided by the cube of temperature of the OG and USG. The calculated curves (lines) are obtained from Eq. (4.2.3) with the measured DOS. The mismatch with experimental calorimetric data (symbols) shows that the harmonic approximation with temperature-independent DOS is not valid at low temperatures.

The transition between the experimental DOS and the parabolic extrapolation occurs at a frequency ν_0 , defined by the continuity condition:

$$\frac{g_{exp}(\nu_0)}{\nu_0^2} = \frac{3}{\nu_D^3} + A_{ex}\nu_0^2. \quad (4.2.6)$$

Figures 4.5a-c) illustrate this procedure for USG (300 K and 150 K) and OG (300 K). Below ν_0 (left of the dashed line), the experimental DOS is replaced by the parabolic extrapolation (solid line). For reference, Debye levels from Brillouin spectroscopy are also shown.

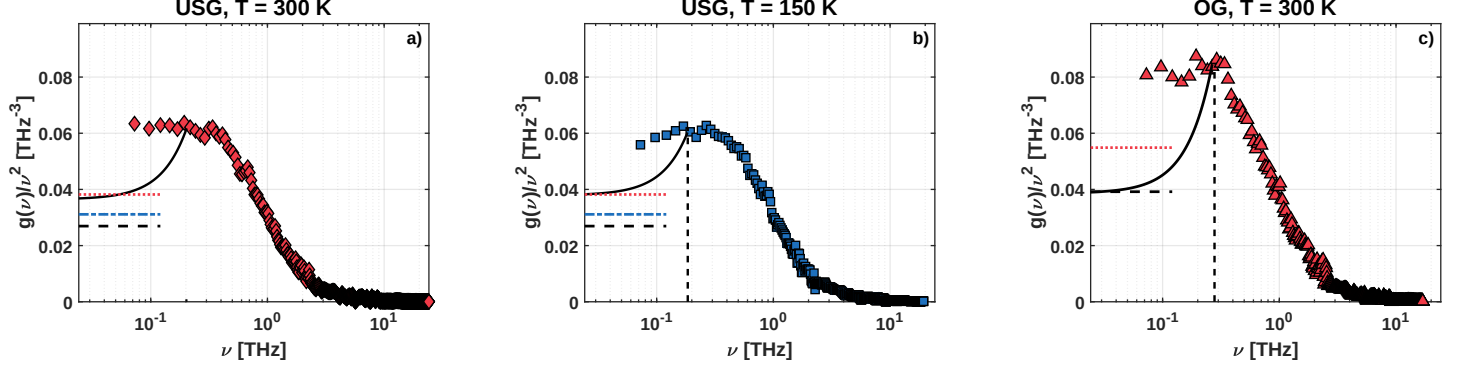


Figure 4.5: Low-frequency extrapolation of the reduced DOS. a): USG at 300 K, b): OG at 300 K, c): USG at 150 K. The parabolic extrapolation (black solid lines) replaces the experimental DOS below the frequency ν_0 (vertical dashed lines). The horizontal lines mark the Debye levels estimated from Brillouin spectroscopy at 300 K (red), 150 K (blue), and $T \rightarrow 0$ K (black).

With this corrected DOS, the specific heat can finally be evaluated. In addition to the harmonic vibrational term, one must include the contribution of two-level systems, which produces a linear term at the lowest temperatures of C_p . The full expression becomes:

$$\begin{aligned}
 C_p(T) &= \frac{3}{M_{at}} \int d\nu g(\nu) \frac{\partial n(T, \nu)}{\partial T} h\nu + C_{TLS}T \\
 &= \frac{3}{M_{at}} \left(\int_0^{\nu_0} d\nu g_{LF}(\nu) \frac{\partial n(T, \nu)}{\partial T} h\nu + \int_{\nu_0}^{\infty} d\nu g_{exp}(\nu) \frac{\partial n(T, \nu)}{\partial T} h\nu \right) + C_{TLS}T,
 \end{aligned}
 \tag{4.2.7}$$

where ν_0 , ν_D , and C_{TLS} are free parameters to be determined by fitting the calorimetric data. Since Eq. (4.2.6) links ν_0 , ν_D , and A_{ex} , one can equivalently choose A_{ex} as the fitting parameter. The best-fit values of ν_D , A_{ex} (and ν_0), and C_{TLS} are reported in Table 4.2, together with the corresponding Debye frequencies measured independently by Brillouin light scattering.

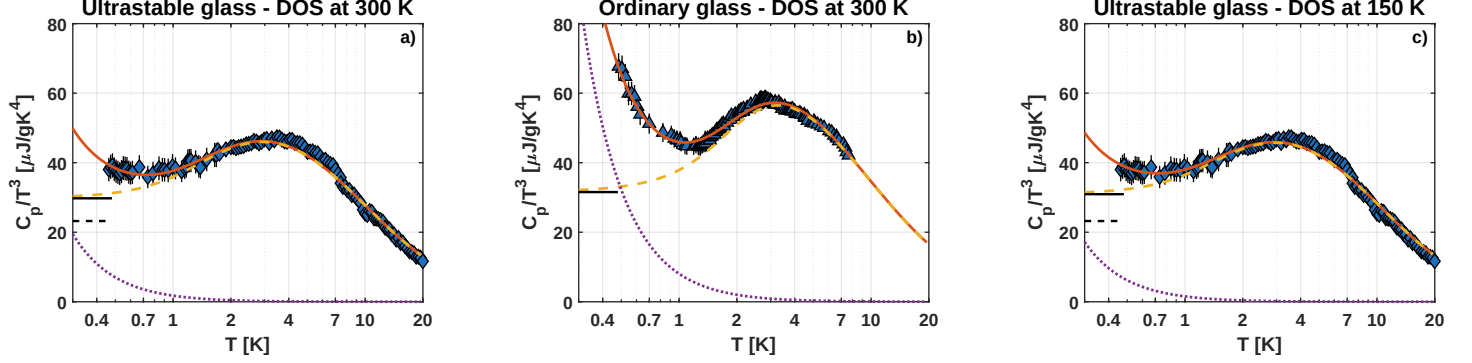


Figure 4.6: The specific heat over T^3 and the fit for the three cases. a): USG at 300 K, b): OG at 300 K, c): USG at 150 K. The red solid lines represent the full fit including the TLS contribution, the yellow dashed lines show the purely harmonic part, and the violet dotted lines indicate the TLS term. Black lines mark the Debye levels: solid from the fit, dashed from Brillouin spectroscopy. The good agreement validates the DOS analysis.

	ν_D [THz]	C_D^{DOS} [$\mu\text{J/gK}^4$]	ν_0 [THz]	A_{ex} [THz $^{-5}$]	C_{TLS} [$\mu\text{J/gK}^2$]	ν_D^{BLS} [THz]	C_D^{BLS} [$\mu\text{J/gK}^4$]
USG - 300 K	4.29 ± 0.08	31 ± 2	0.20 ± 0.01	0.66 ± 0.06	1.5 ± 0.6	4.73 ± 0.06	23 ± 1
OG - 300 K	4.27 ± 0.06	32 ± 1	0.279 ± 0.005	0.65 ± 0.03	8.1 ± 0.6	4.25 ± 0.05	32 ± 1
USG - 150 K	4.29 ± 0.08	31 ± 2	0.19 ± 0.01	0.66 ± 0.06	1.5 ± 0.6	4.73 ± 0.06	23 ± 1

Table 4.2: Best fitting parameters and comparison with Brillouin spectroscopy data. The ν_D , A_{ex} (ν_0) and C_{TLS} are determined by fitting Eq. (4.2.7) to the specific heat data of the two glasses. The corresponding Debye level in the specific heat, C_D^{DOS} , found with Eq. (4.2.10), is also displayed. The last two columns report the Debye frequency and the Debye level determined from the elastic moduli measured with Brillouin spectroscopy [163].

The calculated (red lines) and experimental specific heats agree very well in all three cases. For the OG, the fitted Debye frequency ν_D coincides with that from Brillouin scattering (ν_D^{BLS}), supporting both the robustness of our approach and the use of Eq. (4.2.2). In the case of the ultra-stable glass, however, the fitted Debye frequency is lower than the Brillouin estimate (see Table 4.2). This difference likely reflects the anisotropic molecular orientation induced during vapour deposition at $0.85T_g$. Since Brillouin measurements probe sound waves with a wavevector parallel to the substrate, they

overestimate the averaged sound velocity, giving an apparently lower Debye level—lower even than the crystalline case (Tables 4.2–4.3).

The fits also confirm a strong reduction of C_{TLS}/T^3 (violet dotted lines in Figs. 4.6a–c) when moving from OG to USG, although the TLS contribution does not vanish completely.

Having established reliable Debye levels, we can now plot the DOS in Debye units (Fig. 4.7). The figure clearly shows that glass stability strongly reduces the boson peak: its intensity decreases by almost a factor of two when going from OG to USG, consistent with numerical studies of vapor-deposited glasses [241] and experiments on stable polymer spheres [242]. By contrast, the very low-frequency portion of $g(\nu, 0)$ (shaded region) remains essentially unchanged with stability. This robustness reflects the fact that our estimate of the low- T DOS is anchored to specific heat data, as detailed above. It suggests that stability and TLS density do not significantly affect the harmonic vibrational spectrum at the lowest frequencies, far below the BP.

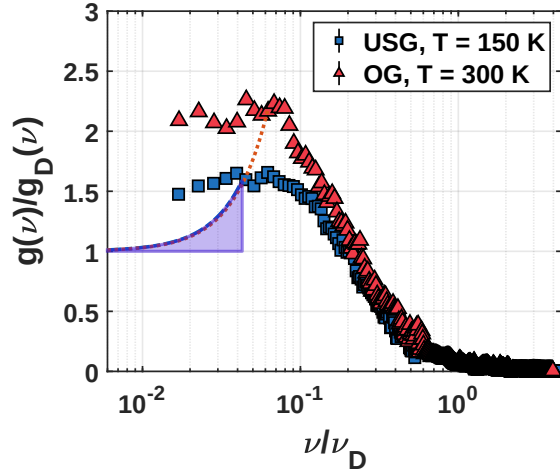


Figure 4.7: The reduced density of states in Debye units for the OG measured at 300 K (red triangles) and the USG measured at 150 K (blue squares). The frequency is reported in units of the Debye frequency, ν_D , and $g(\nu)$ is divided by the Debye DOS, $g_D(\nu) = 3\nu^2/\nu_D$. The low frequency estimate of the harmonic DOS based on Eq. (4.2.2) is shown as a dotted red line for the OG and a dash-dotted blue line for the USG. The shaded violet region indicates the contribution of the excess modes, $A_{ex}\nu^4$ in Eq. (4.2.2), to the reduced harmonic DOS, highlighting the fact that this contribution is insensitive to the glass stability.

To analyse this behaviour further, we approximate the low- T specific heat by neglecting the high-frequency DOS contribution:

$$C_p(T) \sim C_{TLS}T + \frac{3}{M_{at}} \int_0^\infty d\nu g_{LF}(\nu) \frac{\partial n(T, \nu)}{\partial T} h\nu = C_{TLS}T + C_D T^3 + C_{ex} T^5, \quad (4.2.8)$$

where C_D and C_{ex} are related to ν_D and A_{ex} via:

$$C_D = \frac{12\pi^4}{5} \frac{k_B}{M_{at}} \left(\frac{k_B}{h} \right)^3 \frac{1}{\nu_D^3}, \quad (4.2.9)$$

$$C_{ex} = \frac{16\pi^6}{7} \frac{k_B}{M_{at}} \left(\frac{k_B}{h} \right)^5 A_{ex}. \quad (4.2.10)$$

The values for C_D and C_{ex} of the OG and the USG at 150 K are summarised in Table 4.3. Equivalent parameters for the crystal can be obtained by directly fitting Eq. (4.2.8) to C_p/T^3 , with $C_{TLS} = 0$. The results are reported in Table 4.3, and the corresponding fit is shown in Fig. 4.8a) (green line). Interestingly, the A_{ex} (C_{ex}) parameter for the crystal is almost an order of magnitude smaller than that of the glasses, indicating that A_{ex} is strongly affected by disorder, while being essentially insensitive to glass stability.

	ν_D [THz]	A_{ex} [THz ⁻⁵]	C_D^{DOS} [μJ/gK ⁴]	C_{ex} [μJ/gK ⁴]
USG - 150 K	4.29 ± 0.08	0.66 ± 0.06	31 ± 2	6.6 ± 0.6
OG - 300 K	4.27 ± 0.06	0.65 ± 0.03	32 ± 1	6.5 ± 0.3
Crystal	4.421 ± 0.004	0.66 ± 0.06	28.35 ± 0.08	1.11 ± 0.04

Table 4.3: Best fitting parameters of the glasses and the crystal. The first two columns of the table report the values of the Debye level ν_D and of the A_{ex} . The second two columns are the same parameters expressed as the Debye level in the specific heat, C_D^{DOS} , and the coefficient of the T^5 term in the specific heat, C_{ex} . The parameters ν_D and A_{ex} for the crystal are estimated by fitting Eq. (4.2.8) to the crystal specific heat at low temperature, considering that in the crystal there are no TLS.

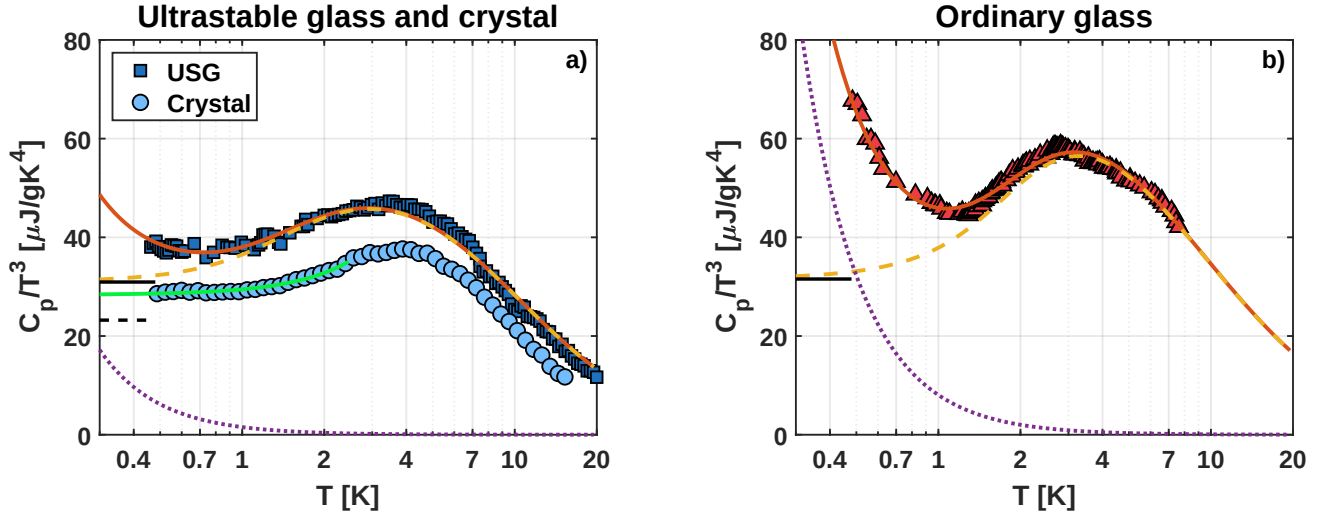


Figure 4.8: The specific heat over T^3 . The calculated C_p (red solid line) compared to the experimental ones for the USG (blue squares) in a) and for the OG (red triangles) in b). The harmonic contribution (yellow dashed line) and the TLS contribution (violet dotted line) are shown as well. The Debye level found with the fitting procedure is plotted as a black horizontal line. A significant discrepancy with the $T \rightarrow 0$ K estimate from the elastic moduli (black dashed line) is found for the USG, while the two values coincide for the OG. The specific heat of the crystal is also shown for comparison (light-blue circles) in panel a) together with the fit to a parabola at low temperatures (green line), as discussed in the text. The specific heat data are from Ref. [163].

4.3 Micro-Raman results

Micro-Raman spectroscopy was used to characterise and compare the molecular vibrational spectra of USG and OG in large frequency ranges. Moreover, the spatial variations, visible under the microscope, on the TPD surface morphology were explored.

All measurements employed a 532 nm laser, 1200 cm^{-1} grating step, 1% laser power (~ 1 mW), 5 s acquisition, 5 accumulations, and a spectral range of [100, 3350] cm^{-1} . Focusing was done with a 100 $\times$ lens at 0.01% power.

First, tests for laser-induced degradation and temporal deterioration were performed by repeatedly probing the same spot of the samples. Multiple positions were then studied to characterise surface heterogeneity. Different samples of both USG and OG were measured to investigate spectral variations due to the specific sample. Measurements in vertical and horizontal polarisations were also performed on the USG.

The spectra collected from different regions and different samples are normalised to the maximum peak at approximately 1291.5 cm^{-1} . No variation either over time or across sample areas is observed. Furthermore, spectra from different ultrastable samples exhibit excellent overlap, as illustrated in the top panel of Figure 4.9, indicating high sample uniformity.

The bottom panel of Figure 4.9 compares the Raman spectrum of an ultrastable sample with that of an ordinary one. No significant differences are observed, confirming that, at the molecular vibrational level, both types of glass share the same structural features.

Usually, spectra exhibiting sharp peaks are associated with crystalline structures. Therefore, to better understand the vibrational properties of the TPD glasses, we focus on a single spectrum, we divide it into three spectral regions, 0-900 cm^{-1} , 900-1800 cm^{-1} , and 1800-3600 cm^{-1} , and we label the main peaks (Figure 4.10). We associate the peaks with molecular vibrations within the TPD molecule, referring to the tabulated values in the Sigma-Aldrich database [243], obtained from measurements of infrared spectroscopy. Structural interpretation requires knowledge of the chemical bonds and atomic species in the TPD molecule, as shown in Figure 4.1. The molecule includes C-H and C-N single bonds, C=C double bonds within aromatic rings, and characteristic hydrocarbon groups. Nitrogen atoms bonded to aromatic rings classify TPD as an aromatic amine. The double bonds within the closed rings of carbon atoms are related to the conjugated and cyclic alkenes compound class. The observed Raman peaks correspond to various vibrational modes, including C-H and C=C stretching, bending, and,

at lower frequencies, frustrated ring rotations. Peak assignments are summarised in Table 4.4.

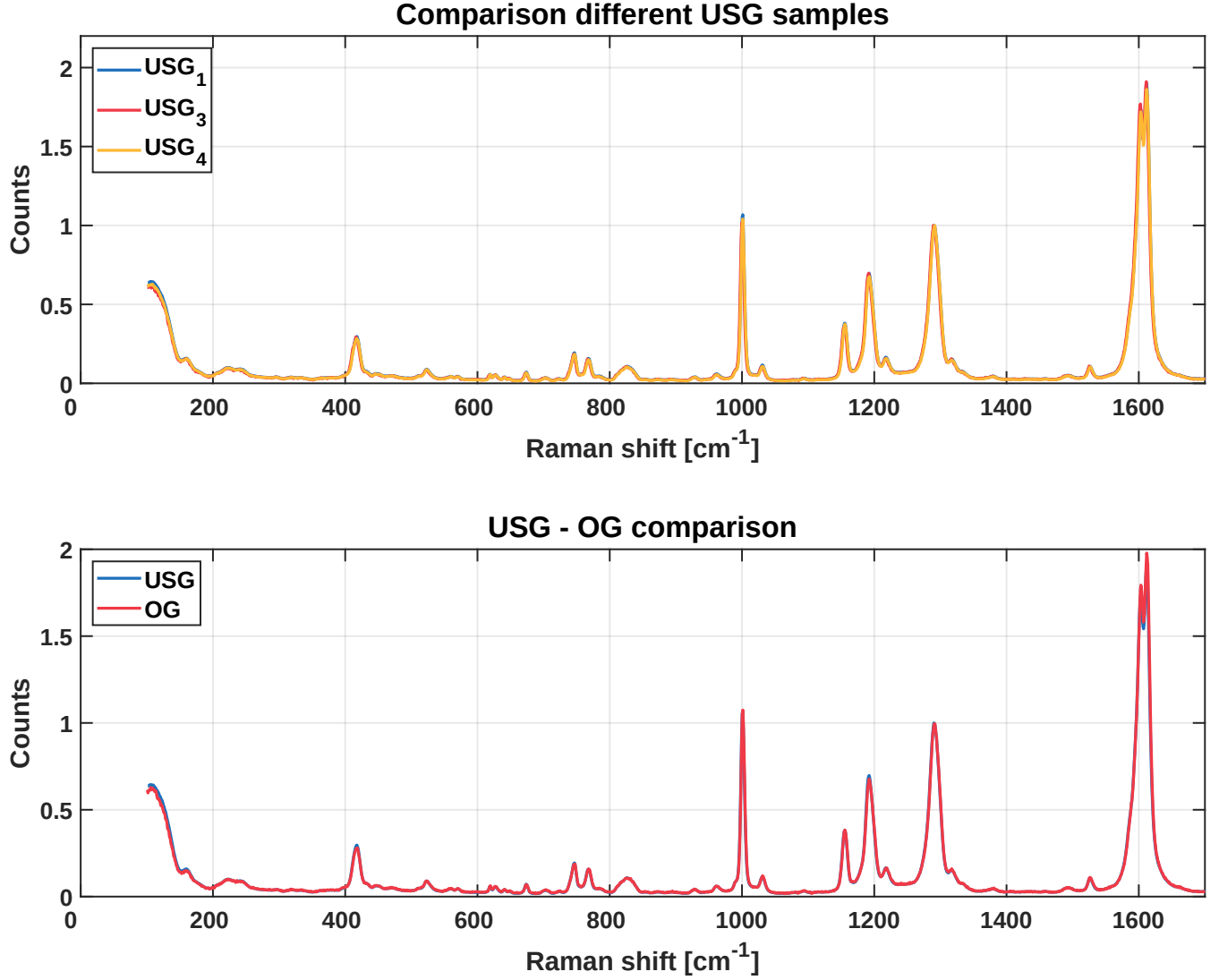


Figure 4.9: Top: Micro-Raman spectra of three different TPD ultrastable glass samples, normalized to the 1291.5 cm⁻¹ peak. All spectra display identical peak positions and relative intensities. Bottom: Comparison between ultrastable and conventional TPD glasses reveals no appreciable spectral differences. The low-wavenumber limit of 100 cm⁻¹ is due to a CCD filter.

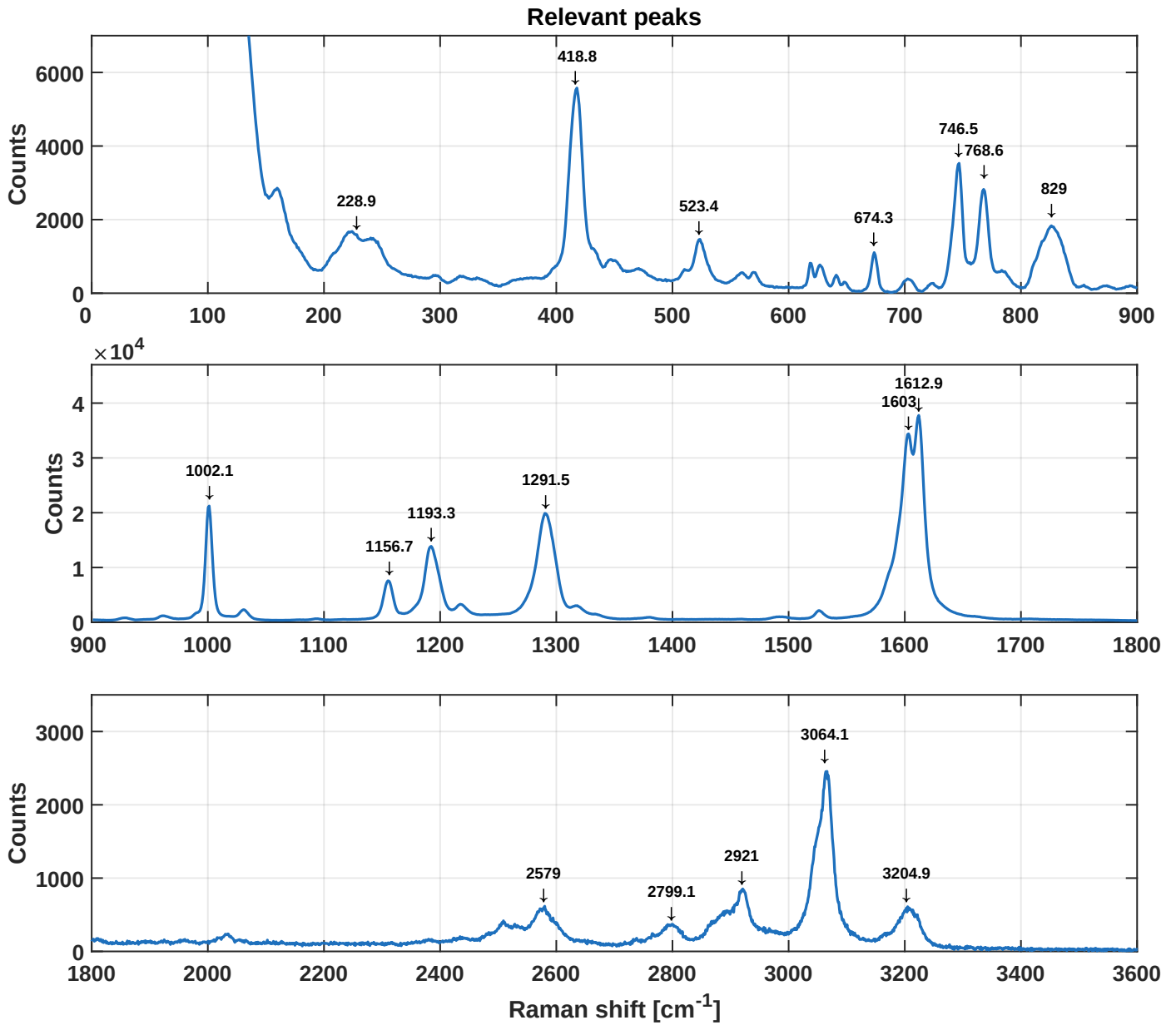


Figure 4.10: Micro-Raman spectrum of an ultrastable TPD glass, divided into three regions: 0-900 cm^{-1} , 900-1800 cm^{-1} , and 1800-3600 cm^{-1} . The main peak positions are marked in cm^{-1} .

Table 4.4: The peaks measured through Micro-Raman spectroscopy and the associated molecular vibrations from IR spectroscopy (Sigma-Aldrich database [243]).

Peak [cm^{-1}]	Group	Peak [cm^{-1}]	Group
228.9	Frustrated rotations between different	1193.3	C-N stretching
418.8	structures: ring/ring,	1291.5	C-N stretching
523.4	ring/N or ring+CH ₃ /N	1603	C=C stretching
674.3	C=C bending	1612.9	C=C stretching
746.5	C-H bending	2579	overtone of 1291.5 cm^{-1} C-N stretching
768.6	C-H bending	2799.1	C-H stretching
829	C=C or C-H bending	2921	C-H stretching
1002.1	C=C bending	3064.1	C-H stretching
1156.7	C-N stretching	3204.9	overtone of 1612.9 cm^{-1} C-N stretching

The effect of polarisation on the Raman spectra is shown in Appendix B Figure B.1, where measurements were taken without polarisation, with vertical polarisation, and with horizontal polarisation. All spectra are normalised to the 1291.5 cm^{-1} peak. Notable differences appear at 523.4 cm^{-1} , 746.5 cm^{-1} , 768.6 cm^{-1} , 1002.1 cm^{-1} , and in the relative intensities of the double peak near 1608 cm^{-1} . Variations are also evident in the low-frequency region ($< 200 \text{ cm}^{-1}$). The pronounced polarisation dependence of the 523.4 cm^{-1} peak originates from the silicon substrate.

Conventional TPD samples show at the microscope clear crystalline nuclei, as reported in Appendix B Figure B.2. These nuclei form after prolonged

exposure to humidity. Raman spectra measured on such nuclei display the same peak positions but with altered relative intensities and increased amplitude compared to spectra taken in nucleus-free regions (Figure B.3, bottom panel). In contrast, Raman spectra from non-crystalline regions of different conventional samples remain consistent (Figure B.3, top panel).

4.4 Raman results

Raman spectroscopy in 90° scattering geometry was employed to probe the low-wavenumber vibrational spectra, with particular focus on the boson peak near $\sim 15 \text{ cm}^{-1}$. Measurements were performed on USG at 298 K and 145 K, and on OG at room temperature. A 532 nm laser (18786.5 cm^{-1} , $\sim 30 \text{ mW}$) was used. Wide-range spectra (-260 to 1700 cm^{-1}) were first collected and compared with micro-Raman data to confirm the probed region (Fig. B.4). Repeated scans over this range excluded laser-induced degradation. High-resolution spectra ($\sim 2.5 \text{ cm}^{-1}$) in the range -260 to 260 cm^{-1} were then acquired to resolve the boson peak. Data were processed as described in Sec. 3.4.2 to obtain the reduced vibrational density of states $g(\omega)/\omega^2$. For the low-temperature measurement, the thermocouple indicated $T = 89 \text{ K}$. However, applying this value to Stokes-anti-Stokes scaling did not yield spectral overlap, due to a thermal gradient between the cryostat cold finger and the sample (cooled only by contact). The best overlap was achieved for $(145 \pm 3) \text{ K}$, which we adopt as the effective sample temperature.

To enable comparison between different samples and temperatures, restricted spectra were normalised to the peak near $\sim 1200 \text{ cm}^{-1}$ using the wide-range data. The reduced Raman spectrum is given by

$$J_R(\omega) \equiv \frac{I_R(\omega)}{\omega(1 + n(\omega))} \propto C(\omega) \frac{g(\omega)}{\omega^2},$$

and is shown in Fig. 4.11(a-b) for USG (blue) and OG (red). The spectra extend down to 5.6 cm^{-1} ($\simeq 0.17 \text{ THz}$) for USG and 6.4 cm^{-1} ($\simeq 0.19 \text{ THz}$) for OG. In both cases, the boson peak is clearly visible.

Panels (c-d) of Fig. 4.11 compare USG at 298 K and 145 K. At low temperature, the boson peak is slightly shifted to higher frequency ($\sim 7\%$) and reduced in intensity ($\sim 7\%$), while the very low-frequency part of $J_R(\omega)$ is suppressed by $\sim 20\%$. The upturn observed below $\sim 7 \text{ cm}^{-1}$, present at both temperatures, is attributed to anharmonic contributions that diminish upon cooling [244].

The boson peak was fitted using a log-normal distribution,

$$f(x) = h_{BP} \exp \left(-\frac{(\log x - \log \omega_{BP})^2}{\Gamma_{BP}^2} \right), \quad (4.4.1)$$

where h_{BP} is the peak height, ω_{BP} its position, and Γ_{BP} its width. The results are summarised in Table 4.5, with peak positions reported in both cm^{-1} and THz. Fitted curves are displayed in Fig. 4.11(b-d), with the logarithmic x-axis emphasising the low-wavenumber regime.

Table 4.5: Boson peaks positions, in cm^{-1} and meV, and heights of ultrastable and conventional glasses.

	ω_{BP} [cm^{-1}]	ν_{BP} [THz]	h_{BP} [a.u.]
USG (298 K)	17.1 ± 0.3	0.51 ± 0.01	5.56 ± 0.05
OG (298 K)	13.4 ± 0.3	0.40 ± 0.01	8.37 ± 0.05
USG (145 K)	18.5 ± 0.3	0.56 ± 0.01	5.30 ± 0.04

The key result is that the boson peak in the ultra-stable glass is systematically weaker than in the ordinary glass. This trend is consistent with low-temperature specific heat data [163] and NRAIXS results on equivalent TPD samples. The larger difference observed in Raman spectra is likely overestimated due to uncertainties in background subtraction at very low wavenumbers. A modelling approach presented below confirms that this discrepancy is indeed artefactual.

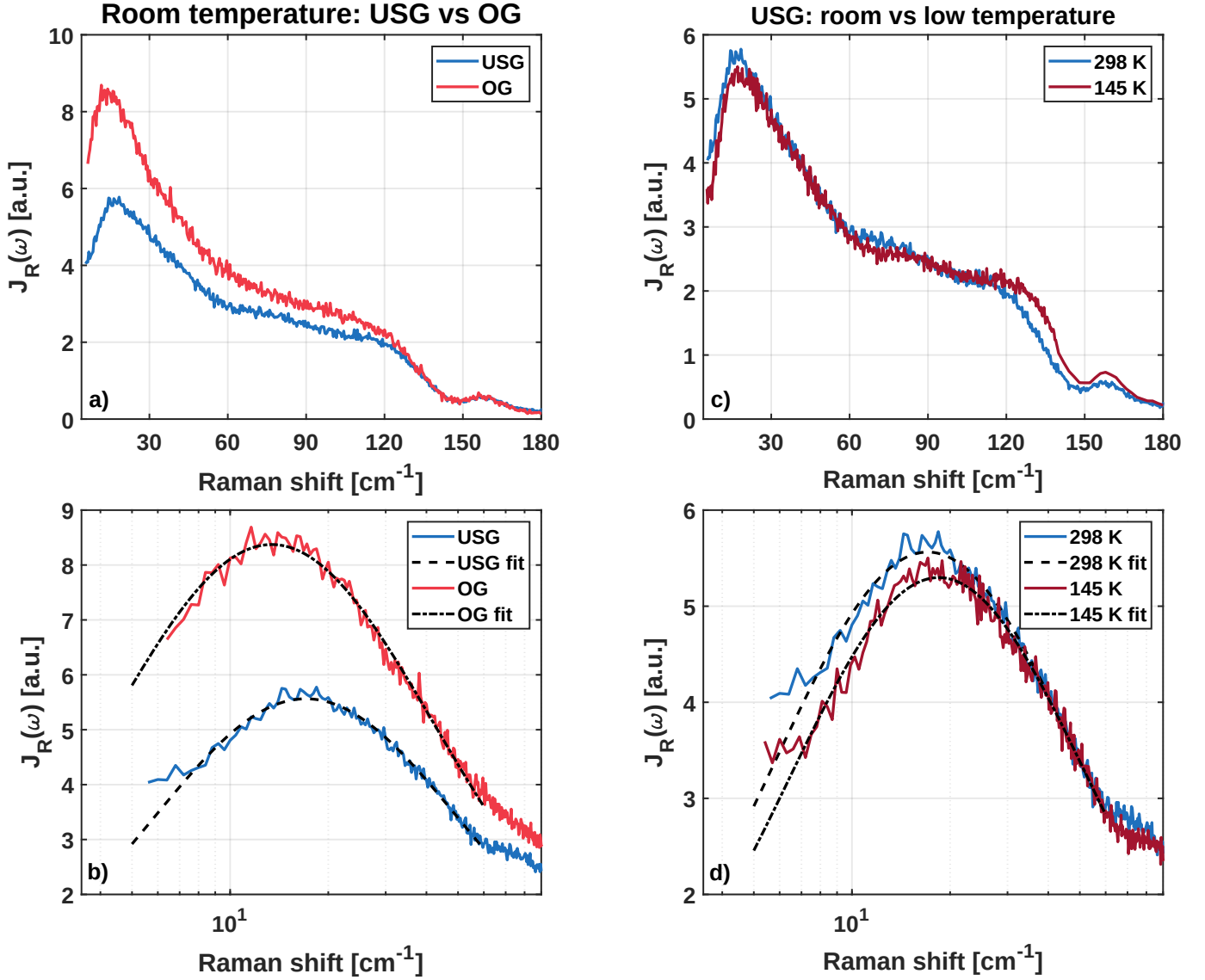


Figure 4.11: Reduced Raman spectra $J_R(\omega)$. (a-b) Comparison between USG (blue) and OG (red) at room temperature, both showing a boson peak around 15 cm^{-1} , with OG displaying a higher intensity. (c-d) USG at 298 K (blue) and 145 K (dark red). At low temperature, the boson peak is shifted to a higher frequency and reduced in intensity. Fitted log-normal curves are superimposed in (b-d). The logarithmic frequency scale emphasises the low-wavenumber regime.

4.5 Discussion

We now compare the measured data with the predictions of the soft potential model (SPM) [118–120] and of the heterogeneous elasticity theory (HET) [121–124], two well-established but competing descriptions of the terahertz vibrations in glasses. The models are presented in detail in Sec. 1.6.3.

The Soft Potential Model

The Soft Potential Model [118–120, 136, 237] extends the tunnelling model to higher temperatures and frequencies, providing a unified framework for two-level systems and the boson peak. It postulates a distribution of soft anharmonic potentials that produce TLS at low energies and quasi-localized modes at higher energies, the latter having a density that scales as ω^4 up to the BP maximum, in agreement with numerical simulations [126–131]. The model is characterised by three parameters: the density of soft modes P_s , a crossover frequency W/h separating TLS from QLM, and a coupling coefficient C relevant for sound attenuation and thermal transport but not for DOS or specific heat.

At frequencies below W/h , the SPM predicts a density of tunnelling states proportional to P_s/W (Eq. (1.6.8)):

$$C_{TLS} \sim \frac{10}{M_{at}} \frac{P_s}{W} k_B^2 .$$

At higher frequencies, it predicts harmonic vibrations, with an excess density of QLM given by (Eq. (1.6.9)):

$$g_s(\nu) = \frac{1}{24} \frac{P_s h}{W^5} (h\nu)^4 .$$

From the measured values of C_{TLS} and A_{ex} , we estimate P_s and W for OG and USG. The results, summarized in Table 4.6, indicate that USG presents significantly fewer soft modes ($P_s \sim 0.17 \times 10^{-6}$ states/atom) than OG ($P_s \sim 1.25 \times 10^{-6}$), with corresponding crossover frequencies $W/h \sim 25$ GHz (USG) and 38 GHz (OG). Thus, the TLS-QLM crossover lies below the frequency window accessible to our inelastic scattering experiments. In this sense, the SPM adapts well to our observations: glass stability strongly reduces the TLS density but leaves the QLM density essentially unchanged.

In addition, the SPM predicts a relaxational contribution to the vibrational DOS, which can be approximated as [233]:

$$g_{rel}(\nu, T) = \frac{1}{3} \frac{P_s h}{W^2} h\nu \left(\frac{k_B T}{W} \right)^{3/4} \ln^{-1/4} \left(\frac{1}{2\pi\nu\tau_0} \right), \quad (4.5.1)$$

Table 4.6: Soft potential model parameters for the USG and the OG.

	P_s [state/atoms] $\times 10^{-6}$	W/h [GHz]
USG	0.17 ± 0.09	25 ± 3
OG	1.25 ± 0.07	38.1 ± 0.6

with $\tau_0 \sim 0.1$ ps. This contribution scales approximately as ν^{-1} in the reduced DOS at finite temperature, since the logarithmic correction is nearly constant in the relevant frequency range. Using the parameters P_s and W , the reduced DOS is obtained by summing $g_s(\nu)$ and $g_{rel}(\nu, T)$. The results, shown as dashed lines in Fig. 4.12, demonstrate that the SPM overestimates the relaxational component by about a factor of two. This is not unexpected, since the relaxational model is designed for kHz-MHz frequencies and tends to overestimate damping at higher frequencies [245].

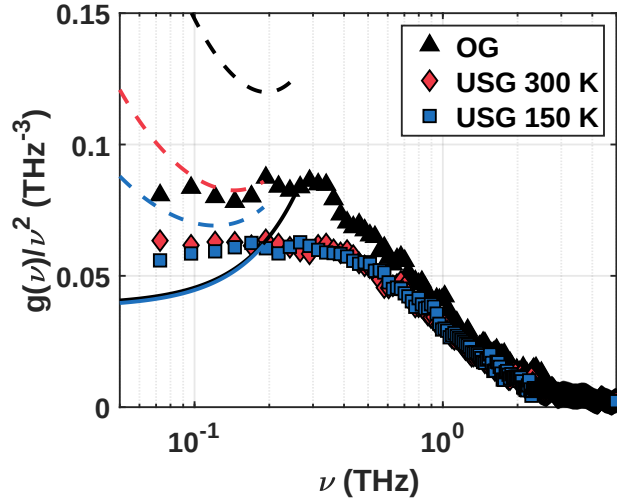


Figure 4.12: SPM prediction for the relaxational contribution to the DOS. Reduced DOS of the OG and USG with symbols as in the legend. The continuous lines are our estimate of the low-frequency harmonic DOS (black line for the OG, blue for the USG). The dashed lines are the SPM estimates of the low-frequency part of the DOS, including both the harmonic contribution of eq. (1.6.9) and the relaxational part of eq. (4.5.1). The blue line is calculated at 150 K with the SPM parameters of the USG, the red line at 300 K for the USG and the black line at 300 K for the OG.

Lastly, we focus on the vibrational modes at higher frequencies. The original SPM accounts for deviations from the Debye level but not for the BP maximum itself. Later extensions [120] introduced additional contributions to describe the BP excess, but these do not include non-localised vibrational modes such as propagating sound waves or high-frequency vibrations. As a result, direct comparison with our experimental DOS requires assumptions that are difficult to justify [233]. In this respect, the SPM remains inadequate to explain the strong sensitivity of the BP to glass stability.

The Heterogeneous Elasticity Theory

We now turn to the heterogeneous elasticity theory [121–124], which attributes the boson peak to microscopic spatial fluctuations of the local shear modulus (see Sec. 1.6.3 for details). Unlike the soft potential model, the HET provides a purely harmonic description of terahertz vibrations, independent of tunnelling states or low-energy instabilities. The vibrational density of states is obtained through a “generalised” Debye law [121], in which the first deviation from the Debye level, giving rise to the coefficient A_{ex} in Eq. (4.2.2), is linked to the dispersion and damping of acoustic modes:

$$g(\omega) = \frac{2\omega}{3\pi} \int_{|\mathbf{k}| < k_D} \left(\frac{d\mathbf{k}}{2\pi} \right)^3 \frac{1}{k^2} \text{Im}\{\chi_L(k, \omega) + 2\chi_T(k, \omega)\}.$$

Anharmonic effects may further modify sound dispersion and attenuation, leading to a temperature dependence of the DOS [146], while secondary relaxation processes are not explicitly considered.

In the weak-disorder limit, the model depends on a single free parameter, γ , which characterises the variance of the local shear modulus fluctuations. To evaluate the DOS, the Debye wavevector k_D and the zero-temperature longitudinal and transverse sound velocities ($v_{L,0}$, $v_{T,0}$) are required for both glasses. The Debye wavevector is calculated using the sample mass densities ($\rho_{USG} = 1.116 \text{ g/cm}^3$, $\rho_{OG} = 1.1 \text{ g/cm}^3$) and the mean atomic weight of the TPD molecule ($\simeq 7.18 \text{ g/mol}$). $v_{L,0}$ and $v_{T,0}$ are, instead, obtained starting from Brillouin scattering data [163]: since we want to reproduce the Debye level estimate through our fitting procedure, a slight adjustment (1-2%) of the extrapolated velocities is required for the OG sample, while for the USG one a change of $\sim 11\%$ is needed. The resulting parameter values are listed in Table 4.7.

Figure 4.13 compares the HET predictions with the experimental data. The model reproduces the BP positions in both the reduced DOS (panels

Table 4.7: HET parameters for the USG and OG glasses.

	$v_{L,0}$ [m/s]	$v_{T,0}$ [m/s]	k_D [Å ⁻¹]	γ
USG	2771	1357	1.77	0.404
OG	2933	1351	1.76	0.413

a-b)) and in the specific heat (panel c)), as expected. The BP height of the OG is well described, while for the USG, the model clearly overestimates it. According to the HET, the BP height should reach about twice the Debye level, consistent with the OG but in clear contrast with the unusually weak BP of the USG.

At higher frequencies, the model overestimates the DOS and, correspondingly, the specific heat above the BP temperature. This limitation is most likely due to the constraint of the generalised Debye law, which confines all vibrational modes below the Debye frequency ν_D , whereas the maximum vibrational frequency in TPD is about one order of magnitude higher (see Fig. 3.14 for the full spectrum, where 200 meV $\sim$ 48 THz). Additionally, the low-temperature specific heat of the USG does not align with the C_p/T^3 plateau.

It is important to note that the sound velocities listed in Table 4.7 are taken from Brillouin measurements and tuned to obtain the same value of the Debye frequency found with our fitting procedure. Nevertheless, the difference between the USG and OG curves in Fig. 4.13a-b) depends almost exclusively on γ , and only weakly on the sound velocities. In the HET framework, the sound velocities determine the Debye level, but not the relative excess above it.

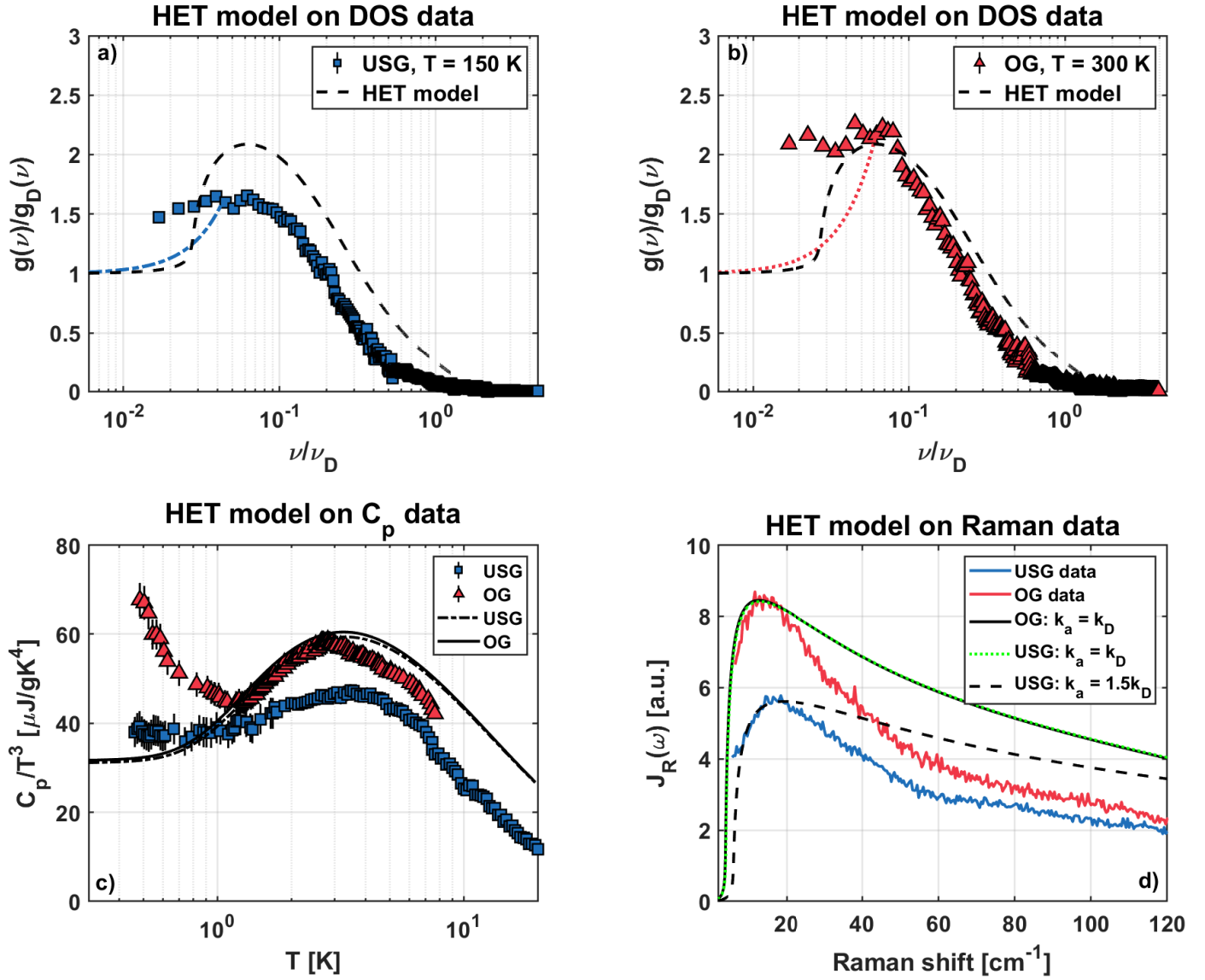


Figure 4.13: The comparison of experimental data and the HET. a-b) The DOS $g(\nu)$ normalised to the Debye contribution $g_D(\nu) = 3\nu^2/\nu_D^3$ compared to the curve obtained applying the HET, normalised by the DL found from k_D , $\nu_{L,0}$ and $\nu_{T,0}$. Panel a): USG. Panel b): OG. c) The specific heat measurement [163] of equivalent TPD USG and OG samples are shown in blue squares and red triangles. The models are plotted as dot-dashed and solid black lines. d) The models for the reduced Raman spectra $J_R(\omega)$ of the USG and the OG are respectively plotted in dotted and solid black lines, with the Pockels wavevector cutoff k_a equal to the Debye wavevector k_D . The boson peak position is well described for both glasses, while the relative boson peak height of USG is better described with $k_a = 1.5k_D$ (dotted green line).

The generalised Debye law underlying the HET, and similar random-matrix-based approaches [147, 148], also provides a general expression for the sound attenuation contribution to the DOS. In the low-frequency limit, it reduces to [121, 149]:

$$g(\nu) \sim \frac{3\nu^2}{\nu_D^3} + \frac{2v_D^2}{\pi\nu_D^2} \left[\frac{\Gamma_L}{v_L^2} + 2\frac{\Gamma_T}{v_T^2} \right], \quad (4.5.2)$$

where $v_{L,T}$ and $\Gamma_{L,T}$ are the sound velocities and linewidths of longitudinal (L) and transverse (T) waves, and v_D is the Debye velocity. At low temperatures and frequencies, the attenuation follows the Rayleigh law, $\Gamma_{L,T} \propto \nu^4$ [146, 150], so that Eq. (4.5.2) reduces to Eq. (4.2.2) with $A_{ex} \propto A_R$. Assuming comparable damping of L and T modes, and attributing the BP solely to acoustic attenuation (i.e., neglecting QLM), we estimate the Ioffe-Regel frequency (Eq. (1.6.16)) as $\nu_{IR} \sim 0.36$ THz for both OG and USG, remarkably close to the BP frequency, as observed in many glasses [246].

Finally, we extend the model to Raman scattering, following Ref. [124]. Here, the local elasto-optic (Pockels) constants, $a(\mathbf{r}) = a_0 + \Delta a(\mathbf{r})$, fluctuate over a correlation length ξ_a . This is introduced through a cutoff k_a in the integration of the susceptibilities:

$$\chi_{L,T}^a(\omega) = \frac{3}{k_a^3} \int_0^{k_a} dk k^2 \chi_{L,T}(k, \omega). \quad (4.5.3)$$

The reduced Raman intensity then follows as

$$J_R(\omega) \propto \frac{2 \operatorname{Im}\{\chi_L^a(\omega)\} + 3 \operatorname{Im}\{\chi_T^a(\omega)\}}{\omega}. \quad (4.5.4)$$

As a first approximation, the Raman cutoff was set equal to the Debye wavevector. The resulting models (dashed-dotted and solid black lines) of the reduced Raman intensity are shown in Fig. 4.13d). While the BP positions are well reproduced for both glasses, the relative peak heights are overestimated in the USG case, as expected. A better agreement with the experimental Raman data is obtained by setting the Pockels cutoff to $k_a = 1.5k_D$ (dotted green line). As in the DOS and specific heat, the HET does not capture the high-frequency side of the boson peak in the Raman spectra.

4.6 Conclusions

The comparison between the ordinary glass and the ultra-stable glass shows two key results. First, the deviation of the DOS from the Debye prediction is nearly unaffected by glass stability, in sharp contrast with recent numerical simulations [149, 247, 248]. Second, the intensity of the boson peak decreases strongly as stability increases.

These findings can be interpreted within two alternative scenarios. In the first picture, the deviation from Debye behaviour is attributed to quasi-localised modes, regarded as the high-frequency harmonic counterparts of the two-level excitations. The crossover between the two types of excitations occurs at a stability-dependent frequency, which may reflect differences in the underlying energy landscape. In this view, QLM accumulate near the BP maximum, but the soft potential model does not explain why the BP intensity is so sensitive to stability.

In the second picture, the deviation from the Debye level is instead explained by the damping of acoustic phonons, without invoking QLM. Within this framework, the Ioffe-Regel limit falls very close to the BP frequency, consistent with earlier results on other glasses [246].

The apparent disagreement between our experiments and simulations regarding the stability dependence of low-frequency vibrations could stem from several factors: (i) the simplified interatomic potentials employed in simulations; (ii) the different levels of stability achievable numerically compared to experimental OG and USG; or (iii) the possibility that QLM are artifacts of the simulations. Our results can, in fact, be fully interpreted without QLM if the deviation from Debye behaviour is attributed solely to the rapid frequency dependence of sound attenuation.

A decisive test would be a direct measurement of sound damping as a function of glass stability, in the frequency range dominated by Rayleigh scattering. Techniques enabling such measurements in thin films have recently been demonstrated for vitreous silica [249, 250]. Combining Rayleigh-scattering data with measurements of the low-frequency DOS tail would provide a powerful route to resolve the nature of low-frequency vibrations in glasses.

Résumé du Chapitre 5

Ce Chapitre présente l'étude des réponses structurales, dynamiques et thermodynamiques des verres $\text{Ge}_{15}\text{Te}_{85}$ et $\text{Ge}_{15}\text{Sb}_{85}$ face à l'irradiation par rayons X, ainsi qu'une analyse spécifique du comportement du verre $\text{Ge}_{15}\text{Te}_{85}$ sous compression à haute pression. Le travail compare le matériau à changement de phase (PCM) $\text{Ge}_{15}\text{Sb}_{85}$ au verre non-PCM $\text{Ge}_{15}\text{Te}_{85}$. Les expériences de XPCS montrent que, dans les deux verres, la dynamique atomique est induite et contrôlée par le faisceau de rayons X, sans dégradation structurale notable. Cependant, leurs réponses diffèrent : le PCM affiche une dynamique stationnaire et un fluage photo-induit quasi instantané, tandis que $\text{Ge}_{15}\text{Te}_{85}$ présente, à $0.7T_g$, une dynamique dépendante du temps d'attente et non de la dose, indiquant un relâchement de contraintes intrinsèques réversible. À $0.8T_g$, le comportement devient purement photo-induit. La plus grande sensibilité du PCM au fluage résulte de sa structure moins rigide et de la mobilité locale liée à la relaxation β . La seconde partie est consacrée à la réponse de $\text{Ge}_{15}\text{Te}_{85}$ à la compression haute pression. Les mesures XPCS in situ révèlent une dynamique toujours induite par le faisceau, mais stabilisée par la pression, qui bloque le fluage. Une transition amorphe-amorphe (AAT) apparaît vers 4 GPa, marquant le passage d'une phase à basse à une phase à haute densité. Les mesures calorimétriques ex situ confirment une régénération du verre vers un état d'enthalpie plus élevée, liée à l'augmentation du désordre chimique. Pour les deux études, des discussions approfondies sont développées afin d'expliquer les résultats observés et de relier les réponses dynamiques aux caractéristiques structurales des verres. L'ensemble montre que la réponse dynamique et la propension au fluage dépendent étroitement de la composition et de la topologie du réseau vitreux.

Chapter 5

Mechanical and photo-induced relaxation dynamics in hard glasses

In this Chapter, we investigate the structural, dynamical, and thermodynamic responses of $\text{Ge}_{15}\text{Te}_{85}$ and $\text{Ge}_{15}\text{Sb}_{85}$ glasses to X-ray irradiation, along with the high-pressure behaviour of $\text{Ge}_{15}\text{Te}_{85}$. XPCS measurements reveal that the X-ray beam drives atomic dynamics in both glasses, yet their responses differ markedly: the $\text{Ge}_{15}\text{Sb}_{85}$ exhibits stationary dynamics and quasi-instantaneous photo-induced yielding transition, whereas $\text{Ge}_{15}\text{Te}_{85}$ shows a pronounced aging accompanied by a crossover of the relaxation function from compressed to stretched exponential behaviour, with the onset of a yielding-like transition that, however, is not fully reached. Under compression, $\text{Ge}_{15}\text{Te}_{85}$ undergoes an amorphous-to-amorphous transition near 4 GPa, whose dynamics evolves non-monotonically. Calorimetry reveals enthalpy rejuvenation linked to increased chemical disorder. For each study, our results are compared with previous literature to interpret the observed behaviours and to relate the dynamic responses to the structural features of the glasses.

5.1 Samples

As introduced in Chapter 2, this work focuses on Ge-based glasses to explore the effects of photo-induced processes and mechanical treatments on the stability and relaxation dynamics. The stability of a glass and its relaxation spectrum can be tuned not only by means of specific sample preparation techniques as vapor deposition, but also by applying external parameters, such as X-rays, pressure, or temperature, to drive the material through different

metastable states. In particular, we will focus on two main classes of Ge-based materials: phase-change materials (PCMs) and non-PCMs. Despite their similar chemical compositions, they exhibit remarkably different physical properties. Moreover, there are no studies at the microscopic dynamical level on PCMs, and very few on conventional Ge-based non-PCMs [4, 199]. For this reason, we selected the PCM alloy $\text{Ge}_{15}\text{Sb}_{85}$ and the non-PCM alloy $\text{Ge}_{15}\text{Te}_{85}$ for a systematic comparison.

PCMs such as $\text{Ge}_{15}\text{Sb}_{85}$, $\text{Ge}_2\text{Sb}_2\text{Te}_5$, GeTe , and Ag-In-doped Sb_2Te are functional materials of great technological relevance for electronic and optical switching devices [79, 251]. They can be rapidly and reversibly switched between amorphous and crystalline states by Joule heating or optical pulses. The pronounced contrast in their electrical and optical properties enables applications ranging from data storage to beam manipulation in photonic devices. Although both PCMs and conventional Ge-based non-PCMs (e.g. $\text{Ge}_{15}\text{Te}_{85}$, GeSe , GeSe_2) are usually classified as covalent glasses, they differ substantially in key aspects such as liquid fragility, structural relaxation, crystallisation kinetics, and glass-forming ability [79, 251]. PCMs crystallise more readily, a behaviour that has been attributed to their higher liquid fragility, whereas non-PCMs are generally better glass formers.

$\text{Ge}_{15}\text{Sb}_{85}$ is a metallic-like alloy classified as a PCM due to its ultrafast and reversible amorphous–crystalline transformation, a property essential for non-volatile memory devices [79, 252, 253]. In contrast, $\text{Ge}_{15}\text{Te}_{85}$ is a conventional chalcogenide glass, well-known for its high amorphous stability and slow crystallisation kinetics, and has been extensively investigated in both the liquid and glassy states [102, 252, 254–261]. However, microscopic dynamical investigations are still missing. This composition is also of technological interest as a selector material, thanks to its high crystallisation temperature, rapid threshold switching, and low threshold voltage [258].

From a dynamical perspective, recent studies have revealed that PCMs, including $\text{Ge}_{15}\text{Sb}_{85}$, exhibit a pronounced secondary β -relaxation in the glassy state, occurring at timescales faster than the main α -relaxation. This feature indicates the presence of local fast atomic motions and loosely bonded regions in the material [262]. By contrast, replacing Sb with Te in $\text{Ge}_{15}\text{Te}_{85}$ suppresses the β -relaxation, resulting in a rigid bonding network with negligible local dynamics. This striking difference in relaxation behaviour correlates with the contrasting glass-forming ability, thermal stability, and crystallisation kinetics of the two alloys [262]. While $\text{Ge}_{15}\text{Te}_{85}$ is a good glass former with a stable supercooled liquid region, $\text{Ge}_{15}\text{Sb}_{85}$ crystallises readily upon approaching its glass transition temperature.

Another interesting feature of both PCM and conventional chalcogenide-

based non-PCM alloys is the common presence of liquid-liquid transitions in their molten state, which suggests the possibility of a corresponding amorphous-amorphous transition in the glassy state. For some compositions (e.g. GeTe, GeSe), pressure-induced amorphous-amorphous transitions have indeed been reported. This makes Ge-based glasses attractive candidates for investigating how stability is influenced not only by X-ray irradiation but also by hydrostatic compression at high pressures.

To pursue this high-pressure study, we selected $\text{Ge}_{15}\text{Te}_{85}$, the same composition used in the irradiation experiments. This choice ensures a consistent comparison: it allows us to explore stability under two distinct perturbations (irradiation and pressure) while also disentangling beam-induced from pressure-induced effects, since both studies are conducted using X-rays.

The microscopic investigation under high pressure is carried out with *in-situ* HP-XPCS, and is complemented by a macroscopic study on *ex-situ* densified samples using Flash DSC. In both irradiation and compression experiments, thin flakes are used for XPCS measurements, while calorimetric studies are performed on densified samples obtained from bulk pieces. Despite the different sample forms (flakes vs. bulk), the structural, dynamical, and thermodynamic results are consistent. The following paragraphs describe the synthesis and characterisation procedures.

As-deposited samples

For XPCS experiments under both ambient and high-pressure conditions, thin, homogeneous samples with a thickness of a few micrometres are required. To this end, glassy $\text{Ge}_{15}\text{Sb}_{85}$ and $\text{Ge}_{15}\text{Te}_{85}$ films were prepared by collaborators at the University of Aarhus using magnetron sputtering. Stoichiometric targets, synthesised following the procedure described in Ref. [252], were deposited onto 4-inch Si (100) wafers under DC sputtering (10 W), with an Ar flow of 10 sccm at 5×10^{-3} mbar. A steep-edge profilometer was used to determine the deposition rates of the target compositions and thus calibrate the sputtering time required to obtain layers of thickness $L = 3\text{--}8 \mu\text{m}$, comparable to the absorption length μ of the samples.

The resulting amorphous films were then detached from the Si substrates and collected as flakes. The nominal compositions were verified by X-ray fluorescence (Rigaku NEX CG) within an experimental uncertainty of $\sim 3\%$, both at the target stage and after deposition. The main properties of the two samples are reported in Table 5.1 [79, 257, 262].

	T_g [K]	FSDP [nm ⁻¹]	ρ [g/cm ³]	L [μ m]	μ [μ m]
Ge ₁₅ Sb ₈₅	500	20.5	5.323	3	8.5
Ge ₁₅ Te ₈₅	412	19.6	5.53	8	6.9

Table 5.1: Calorimetric glass transition temperature T_g , wavevector of the first sharp diffraction peak (FSDP) maximum, mass density ρ , sample thickness, and X-ray attenuation length at 8.0 keV and 8.1 keV, energies used in the XPCS experiments for Ge₁₅Te₈₅ and Ge₁₅Sb₈₅ [79, 257, 262].

Densified samples

Since *in-situ* high-pressure (HP) Flash nano-calorimetry is not experimentally feasible, the samples were densified *ex-situ*. For this purpose, fragments of bulk material were compressed in a diamond anvil cell equipped with 600 μ m culets and a 400 μ m gasket hole. The samples were held under hydrostatic conditions, using silicone oil as a pressure-transmitting medium, for 10 minutes at ambient temperature. This procedure enables densification under pressures of several gigapascals [263].

The bulk amorphous Ge₁₅Te₈₅ used for this study was synthesised by melting high-purity Ge and Te (99.999-99.9999 at.%) in an evacuated and sealed silica tube. The mixture was heated to 800°C in a rocking furnace and held for 8 hours to ensure complete homogenisation, followed by rapid quenching in ice water to obtain the amorphous Ge₁₅Te₈₅ alloy.

5.2 Photo-induced yielding

In this Section, we characterise the influence of X-ray irradiation on the stability of these two compositionally similar alloys, $\text{Ge}_{15}\text{Sb}_{85}$ and $\text{Ge}_{15}\text{Te}_{85}$, in the vicinity of their glass transition temperature T_g .

XPCS experiments were carried out during two separate beamtimes at the beamline P10 of PETRA III synchrotron in Hamburg, Germany. In the first experiment, we measured the $\text{Ge}_{15}\text{Te}_{85}$ composition. An X-ray beam of 8 keV was focused onto a spot size of full width at half maximum (FWHM) of $2.8 \times 2.2 \mu\text{m}^2$ (H $\times$ V) with a photon flux of $\phi_0 \sim 4.5 \times 10^{10}$ ph/s, whereas in the second experiment, we measured the $\text{Ge}_{15}\text{Sb}_{85}$ using a beam energy of 8.1 keV, with a spot size of $3.4 \times 2.0 \mu\text{m}^2$ and a photon flux of $\phi_0 \sim 8 \times 10^{10}$ ph/s. The measurements were performed at a wave vector q corresponding to the position of the maximum of the first sharp diffraction peak for both compositions. $\text{Ge}_{15}\text{Te}_{85}$ was studied at temperatures $T = [295, 325]$ K (corresponding to $T \simeq [0.7, 0.8]T_g$, see values in Table 5.1), while $\text{Ge}_{15}\text{Sb}_{85}$ was measured at $T = [295, 350, 400]$ K ($T \simeq [0.6, 0.7, 0.8]T_g$). Additionally, the $\text{Ge}_{15}\text{Te}_{85}$ composition was investigated as a function of the scattering vector q in a range $[2.18; 27.37] \text{ nm}^{-1}$ at 295 K.

To explore the effect of the X-rays on the dynamics, the full beam intensity ϕ_0 was attenuated through Si attenuators (att). The fractions of the transmitted beam intensity (i.e. the transmission T_a) and the relative beam fluxes ϕ used in the experiments are summarised in Table 5.2. To avoid cumulative irradiation effects, each XPCS scan was performed in a fresh spot.

$\text{Ge}_{15}\text{Sb}_{85}$			$\text{Ge}_{15}\text{Te}_{85}$		
	T_a	ϕ [$\times 10^{10}$ ph/s]		T_a	ϕ [$\times 10^{10}$ ph/s]
att = 0	100%	8	att = 0	100%	4.5
att = 2	45%	3.58	att = 2	44%	1.96
att = 4	22%	1.73	att = 3	28%	1.26
att = 6	10%	0.77	att = 4	20%	0.91
att = 8	5%	0.40	att = 6	9%	0.39

Table 5.2: Transmission percentages for the silicon attenuators used in the XPCS experiments for each material.

5.2.1 Results

Consistent with previous studies on other Ge-based glasses [4, 199], our results show that the probed atomic motion is induced by X-ray irradiation also in $\text{Ge}_{15}\text{Sb}_{85}$ and $\text{Ge}_{15}\text{Te}_{85}$. This effect is present at all investigated temperatures.

At the probed q , no appreciable structural damage is detected. Figure 5.1 reports the average scattered intensity per frame, normalised to the incident beam intensity and vertically shifted for clarity, as a function of absorbed dose. The absence of significant variations during the XPCS measurements indicates that the scattered intensity remains stable over time. This stability can be interpreted in two ways. First, the amorphous structure may indeed remain unaffected during the X-ray exposure within the probed timescale, meaning that the observed dynamical changes are not linked to any degradation of the glass network. Alternatively, structural modifications could still occur but be undetectable in the average intensity, either because they fall below our sensitivity or take place outside the explored q range. The latter scenario would be consistent with reports of subtle, beam-induced changes in other glassy systems [4, 165].

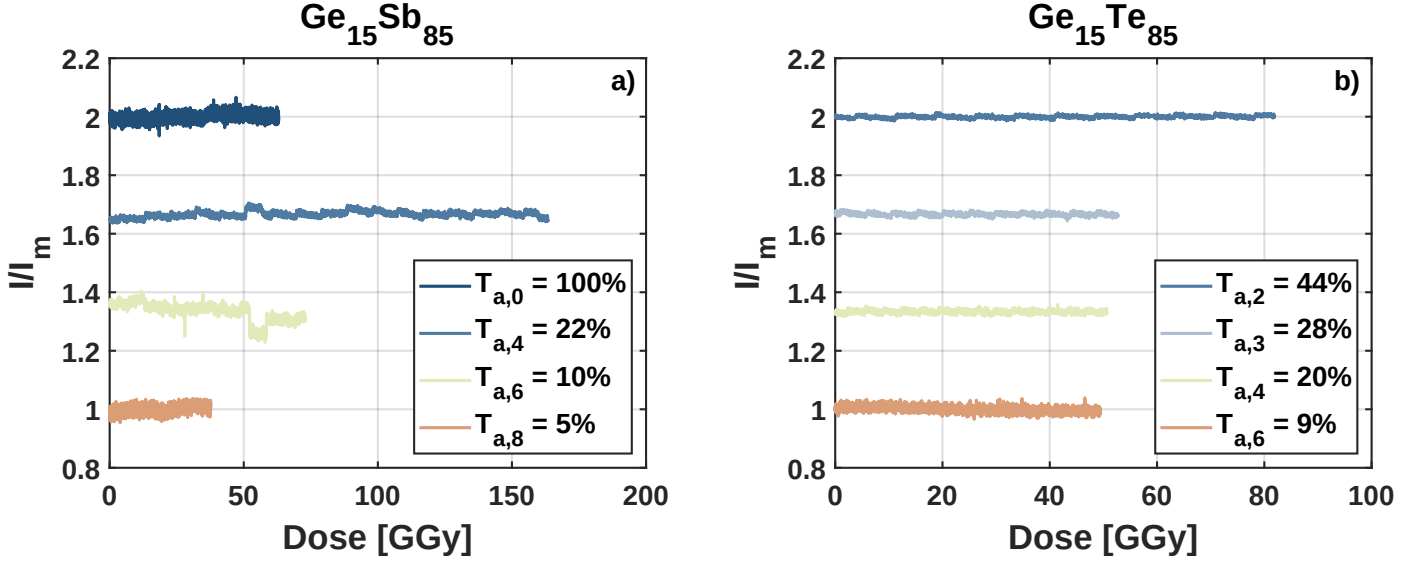


Figure 5.1: The average scattered intensity collected by the detector for each frame, normalised to the relative beam intensity at various attenuation levels. As time passes, no appreciable structural damage is occurring.

As said, both samples exhibit atomic motion tuned by the X-ray beam.

This behaviour is illustrated in Fig. 5.2, which shows representative XPCS auto-correlation functions measured at $T = 0.7T_g$ for different X-ray fluxes. In both $\text{Ge}_{15}\text{Sb}_{85}$ (panel a)) and $\text{Ge}_{15}\text{Te}_{85}$ (panel b)), the curves display a characteristic long-time decay that reflects the timescale of the underlying dynamics. A clear trend emerges: as the X-ray flux is reduced, the decay gradually shifts to longer times, revealing that the pace of the dynamics can be controlled by tuning the beam intensity. The black dashed lines in the figure represent fits to the experimental data using Eq. (1.4.2), which provides a reliable description of the observed relaxation. To ensure consistency between data collected at different X-ray fluxes, we analysed the $g_2(t)$ functions at a fixed absorbed dose of 38 GGy for each composition.

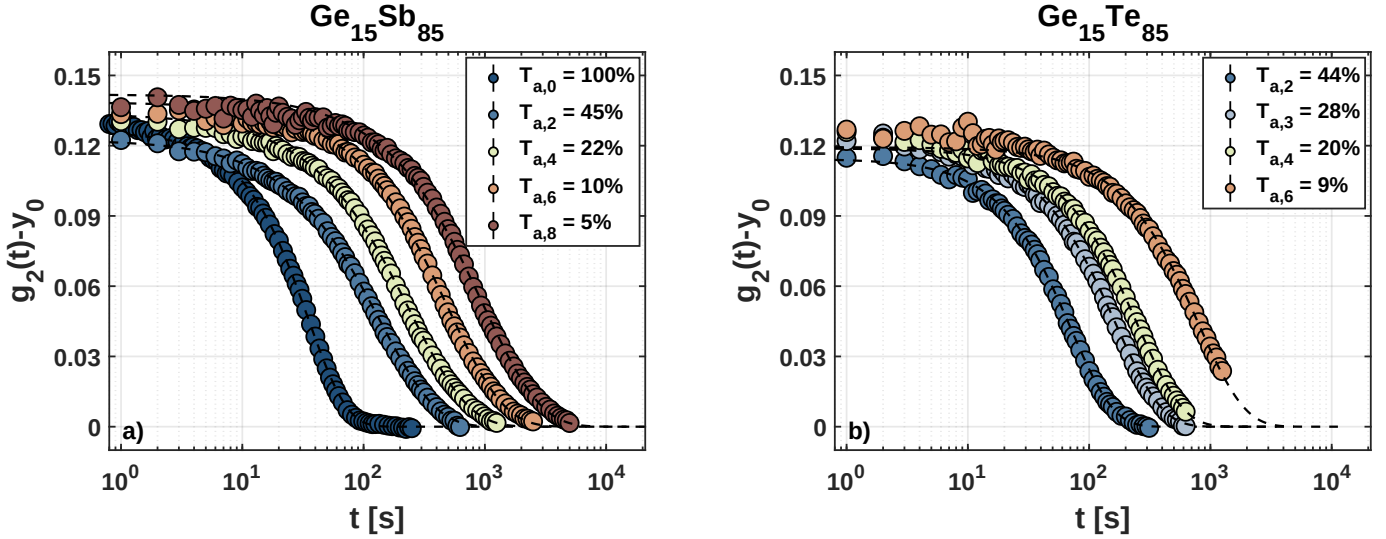


Figure 5.2: Auto-correlation functions of the intensity fluctuations measured with XPCS at $0.7T_g$ in **a)** $\text{Ge}_{15}\text{Sb}_{85}$ and **b)** $\text{Ge}_{15}\text{Te}_{85}$ at varying beam attenuations. The curves of each sample are obtained by ensuring a total absorbed dose of 38 GGy for both samples. The dashed black lines represent the best fits to the KWW model. Each curve has been measured on a fresh sample position.

Although the dynamics of both glasses depends on the X-ray flux, their responses to beam exposure differ markedly. This contrast is most evident in the temporal evolution of their relaxation processes at fixed beam intensity, as shown in Fig. 5.3. To obtain the curves, we averaged the TTCFs using Eq. (3.3.11) over time windows Δt , centred at waiting times $t_w = \Delta t(n+1/2)$ with $n \in [0, 3]$. The chosen windows were $\Delta t = 900$ s for $\text{Ge}_{15}\text{Sb}_{85}$ and

$\Delta t = 700$ s for $\text{Ge}_{15}\text{Te}_{85}$, where t_w represents the time elapsed since the beginning of each measurement.

For $\text{Ge}_{15}\text{Sb}_{85}$, the $g_2(t)$ curves acquired at different waiting times overlap onto one another (Fig. 5.3a), indicating stationary dynamics. This stationarity is also reflected in the TTCF (Fig. 5.3c), where a uniform intensity is observed along the main diagonal. By contrast, $\text{Ge}_{15}\text{Te}_{85}$ displays a progressive slowing down of the dynamics. The $g_2(t)$ curves shift systematically toward longer decay times as t_w increases from 350 s to 2450 s (Fig. 5.3b), and the corresponding TTCF (Fig. 5.3d) shows a clear broadening of the diagonal, consistent with the observed slowing behaviour.

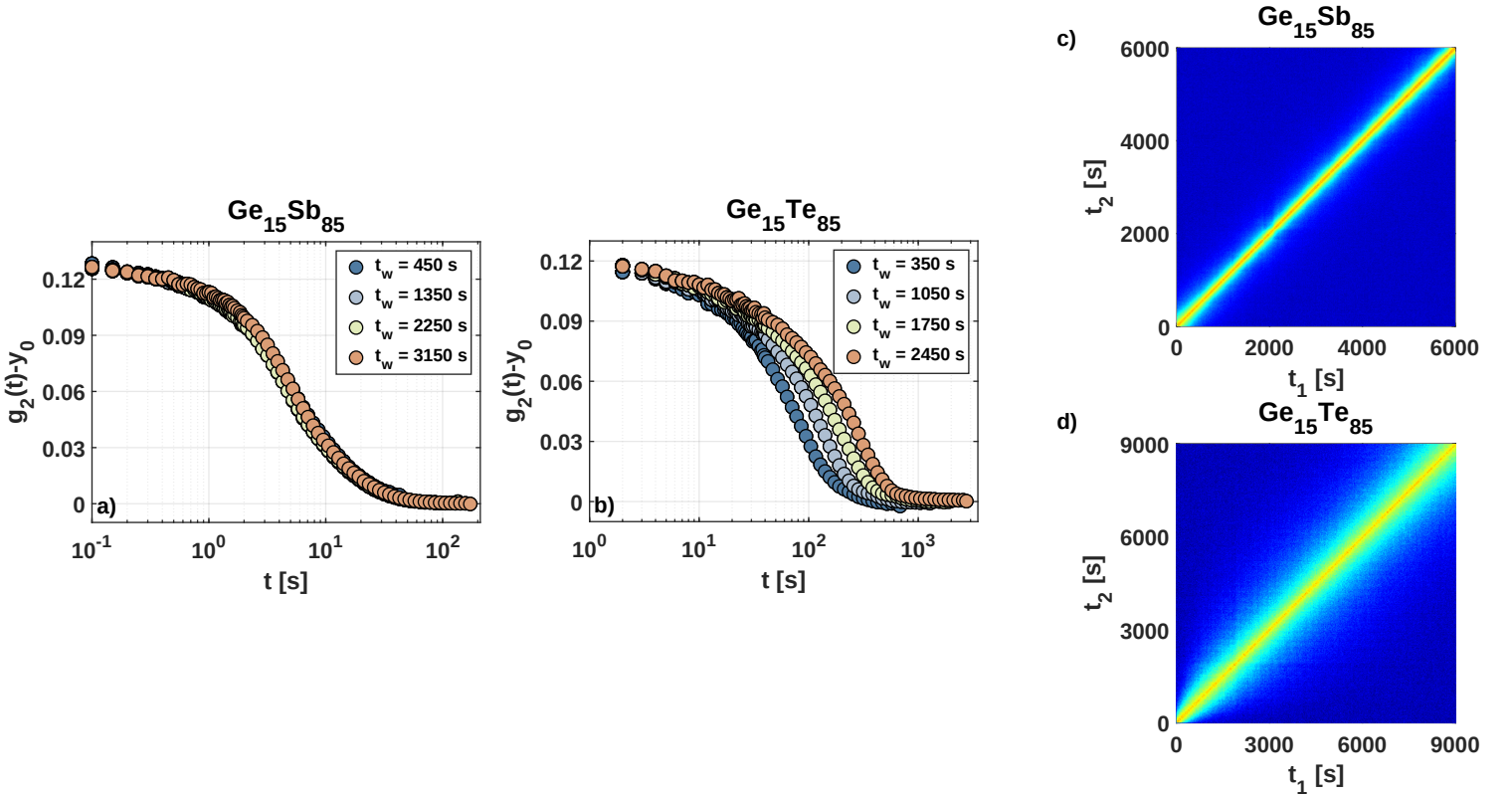


Figure 5.3: Temporal evolution of the dynamics at $0.7T_g$ for a fixed flux of the X-ray beam of 3.58×10^{10} ph/s in $\text{Ge}_{15}\text{Sb}_{85}$ a) and of 1.96×10^{10} ph/s in $\text{Ge}_{15}\text{Te}_{85}$ b). The dynamics remains stationary within the probed time window for the $\text{Ge}_{15}\text{Sb}_{85}$ a), while physical aging in the $\text{Ge}_{15}\text{Te}_{85}$ is signalled by the shift of the curves toward longer times with increasingly t_w b). Two-times correlation functions measured in $\text{Ge}_{15}\text{Sb}_{85}$ c) and $\text{Ge}_{15}\text{Te}_{85}$ d) showing stable dynamics and aging, respectively.

The progressive slowing down of the dynamics is a well-known phenomenon in glasses held near T_g , commonly referred to as physical aging [264]. As explained in Chapter 1, being out-of-equilibrium systems, glasses gradually evolve toward more energetically favourable configurations, which manifests as an increase in their relaxation times. Under normal conditions, this process is thermally driven, as the system slowly explores its energy landscape. In this case, however, the observed slowing down is not purely spontaneous: it is actively induced by the X-ray beam. The beam not only probes and stimulates atomic dynamics but also drives a temporal evolution of the system itself. This behaviour may arise from stress release triggered by irradiation or from local annealing processes initiated by the beam, mechanisms that will be examined in more detail later in this section.

The contrasting temporal evolutions observed in the two compositions indicate the presence of distinct responses to the accumulated dose D . As introduced in Par. 3.3.3, this aspect can be better analysed by expressing the relaxation time τ , obtained from XPCS measurements and KWW fits (3.3.19), in terms of the absorbed dose D_τ required to generate the observed dynamics:

$$D_\tau = \frac{\epsilon}{m} \phi_0 T_a (1 - T_r) \tau .$$

This formulation incorporates the interaction between the material and the X-rays. For a process governed entirely by irradiation [166], τ is expected to scale inversely with the incident flux ϕ : reducing the beam flux by half ($T_a = 50\%$) should double τ . In this scenario, the dynamics depends solely on the absorbed dose and remains independent of flux variations. Expressing the results in terms of D_τ thus enables direct comparison of relaxation dynamics across different sample compositions and experimental conditions. To study the distinct responses of $\text{Ge}_{15}\text{Sb}_{85}$ and $\text{Ge}_{15}\text{Te}_{85}$, Figs. 5.4-5.5 and 5.6-5.9 present the absorbed dose in relaxation time D_τ and the KWW exponent β as functions of the accumulated dose D for different attenuator transmissions $T_{a,i}$. This representation highlights the dependence of the dynamical parameters on dose and provides insight into the underlying mechanisms, helping to distinguish between purely beam-induced dynamics and those influenced by additional processes.

We first focus on the dynamical behaviour of $\text{Ge}_{15}\text{Sb}_{85}$. Figures 5.4-5.5 present the dependence of the XPCS parameters τ (in terms of D_τ) and β on the accumulated dose D at two temperatures, $0.7T_g$ and $0.8T_g$. Panels a) show the absorbed dose D_τ accumulated within a relaxation time τ , while panels b) report the evolution of the stretching parameter β . Different symbols and colours correspond to different beam fluxes.

The dynamics is clearly beam-induced: for almost all datasets, D_τ is

independent of the beam flux, implying that the decorrelation time τ scales inversely with flux. Overall, the data from different fluxes collapse well in all panels, indicating consistent behaviour. One exception is the dataset represented by blue circles at $0.7T_g$, corresponding to the full beam on the sample. These points exhibit a lower D_τ and a higher β , likely due to local beam-induced heating that slightly increases the effective temperature of the probed region.

Excluding this outlier, the remaining data suggest that the system is in a yielded state throughout the measurement: D_τ remains nearly constant with accumulated dose, and β stays close to one, similar to observations in LiBO_3 [165] and GeSe_3 [4].

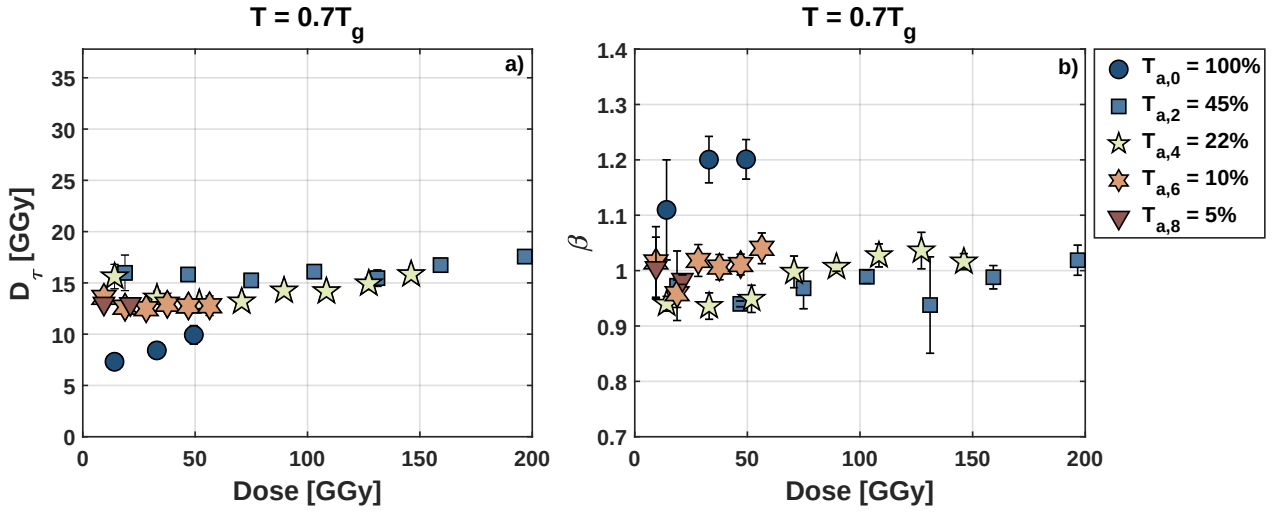


Figure 5.4: Evolution of the dynamics in $\text{Ge}_{15}\text{Sb}_{85}$ as a function of the absorbed dose at $0.7T_g$. The D_τ and the β tend to collapse into a master curve when plotted versus Dose. Both parameters are almost independent of the applied dose.

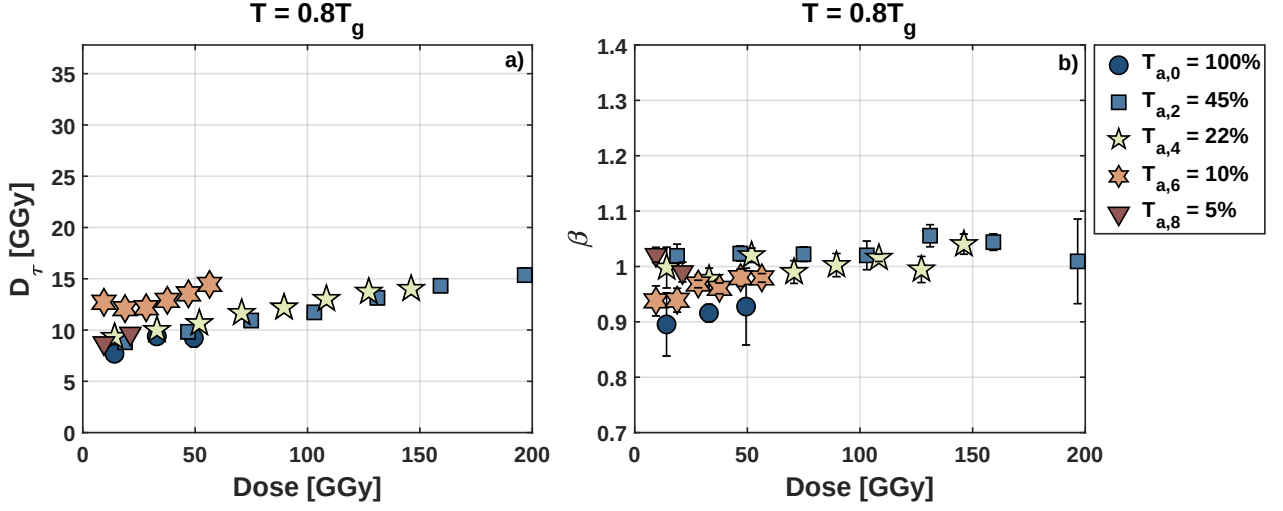


Figure 5.5: Evolution of the dynamics in $\text{Ge}_{15}\text{Sb}_{85}$ as a function of the absorbed dose at $0.8T_g$. The D_τ and the β tend to collapse into a master curve when plotted versus Dose. Both parameters are almost independent of the applied dose.

We now turn to the dynamical behaviour of $\text{Ge}_{15}\text{Te}_{85}$. As discussed earlier, if the dynamics is purely beam-induced, the relevant parameters, such as the absorbed dose per XPCS relaxation time, D_τ , and the stretching parameter β , would collapse onto universal curves when plotted as a function of the accumulated dose D . For $\text{Ge}_{15}\text{Te}_{85}$ at $0.7T_g$, however, this scaling is not observed (Fig. 5.6). While the X-ray beam clearly drives the dynamics, both D_τ and β show significant variations with the incident flux when plotted against D . This means that the absorbed dose alone does not fully capture the evolution of the system, suggesting the presence of additional mechanisms influencing the dynamics.

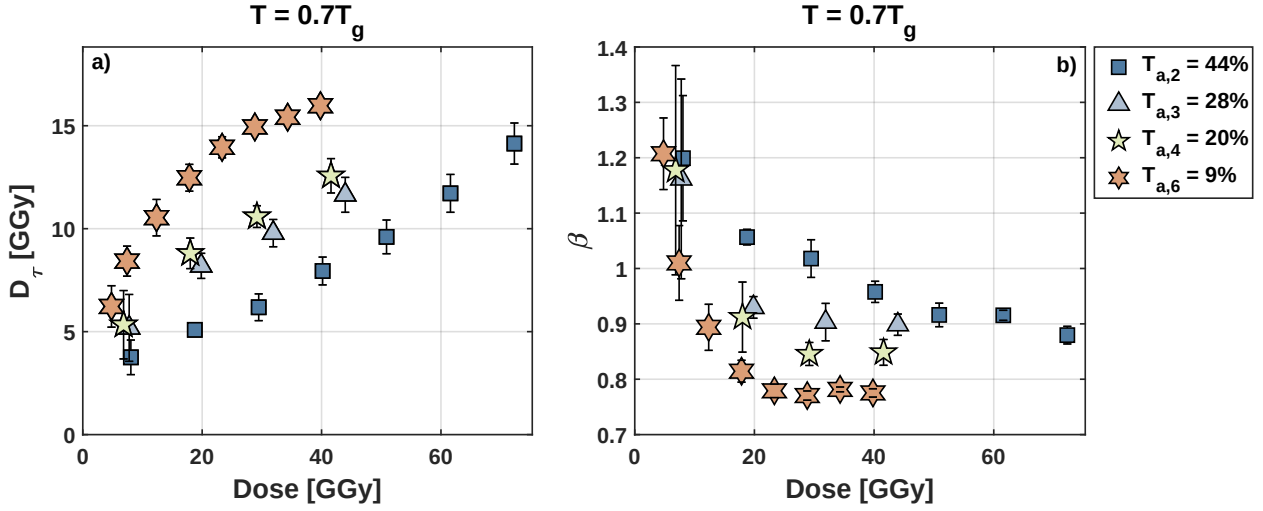


Figure 5.6: Dynamics evolution at $T = 0.7T_g$ of $\text{Ge}_{15}\text{Te}_{85}$. a) D_τ and b) β fail to collapse into a master curve when plotted versus D .

To further elucidate this behaviour, we plot D_τ and β as functions of the experimental waiting time t_w , defined as the time elapsed since the start of X-ray exposure. Remarkably, when expressed in terms of t_w , the data from all fluxes collapse onto master curves (Fig. 5.7a-b), revealing a universal, time-dependent evolution of the dynamics. To our knowledge, such a collapse with respect to waiting time, rather than absorbed dose, has not been previously reported in studies of beam-induced dynamics. This observation suggests that, while X-ray irradiation initiates atomic motion, the subsequent evolution at $0.7T_g$ is primarily governed by the material's intrinsic relaxation processes, with timescales set by the system itself rather than the accumulated dose. This behaviour can be rationalised by noting that $0.7T_g$ corresponds to room temperature for $\text{Ge}_{15}\text{Te}_{85}$. The sample likely retains residual stresses from its preparation, which are gradually released under X-ray exposure. Stress relaxation thus drives the evolution of the dynamics, dominating over the purely beam-induced contribution.

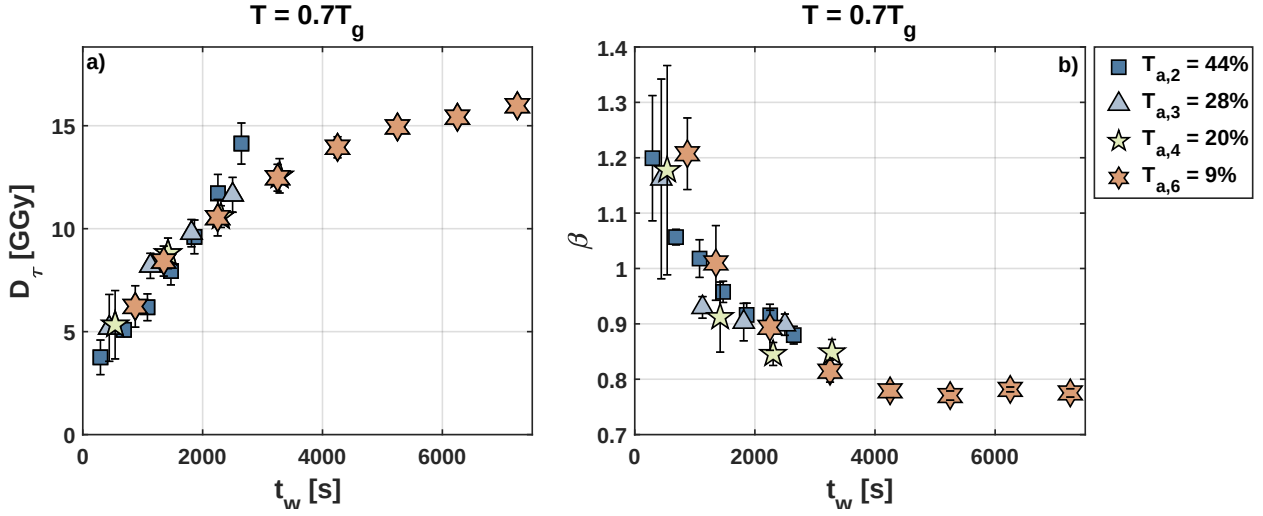


Figure 5.7: **a-b)** Evolution of the dynamics in $\text{Ge}_{15}\text{Te}_{85}$ as a function of the waiting time t_w , at $0.7T_g$. D_τ and β collapse into a master curve when plotted versus t_w , suggesting the dynamics is primarily influenced by intrinsic relaxations active in the material.

Further evidence for this interpretation comes from “beam-off” experiments (Fig. 5.8), in which the X-ray beam was interrupted for extended periods. For short interruptions (10 minutes), stress relaxation continues, suggesting that intrinsic structural relaxation processes, once initiated by the beam, persist even in its absence. In contrast, for longer interruptions (1 hour), both D_τ and β gradually revert toward their initial values, indicating a recovery of the original state when irradiation is halted. This reversible response upon switching off the beam has not been observed in previously reported non-stationary beam-induced dynamics and provides strong evidence that the observed changes do not correspond to permanent structural damage within the experimental dose range.

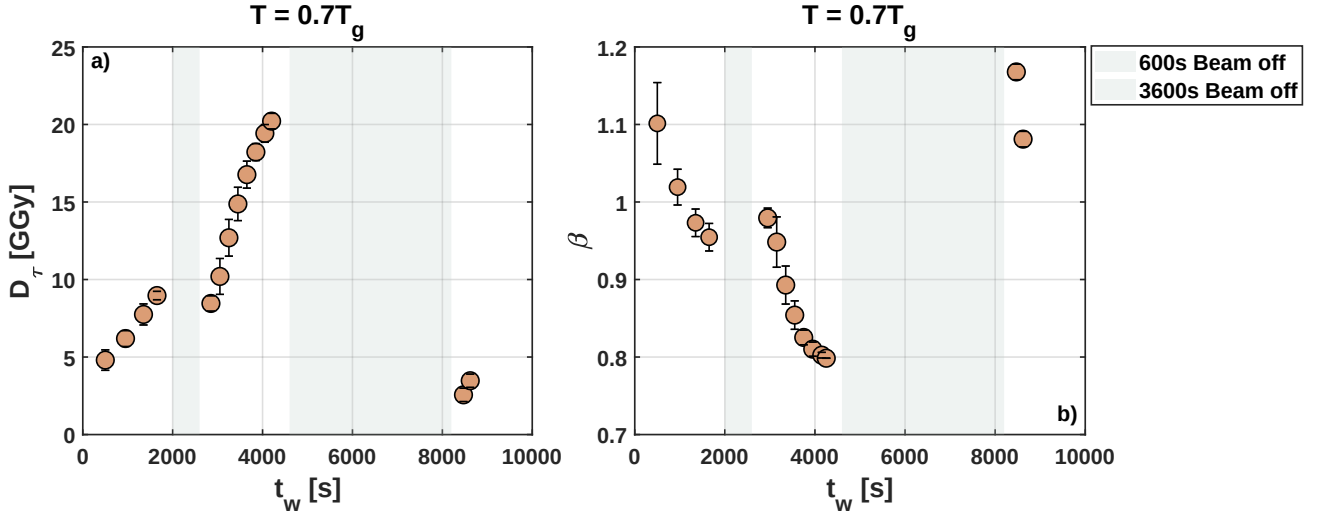


Figure 5.8: The temporal evolution of the dynamical parameters in “beam-off” experiments, measured at $T_a = 44\%$. While the sample is irradiated by the beam, the system evolves. If the beam is turned off for a short time period, the D_τ and β parameters suggest restoring their initial values, meaning that the effect of the beam persists. For longer interruptions, both D_τ and β tend to completely recover the initial state.

This hypothesis of room-temperature stress release is further supported by measurements at $0.8T_g$, where both D_τ and β exhibit universal scaling with the absorbed dose D , independent of the incident flux (Fig. 5.9a-d). At this higher temperature, the dynamics is governed solely by the X-ray beam and can therefore be considered purely beam-induced. Remarkably, a modest 10% increase in temperature is sufficient to suppress the stress-driven contributions observed at $0.7T_g$, placing the system entirely under the control of irradiation-driven dynamics.

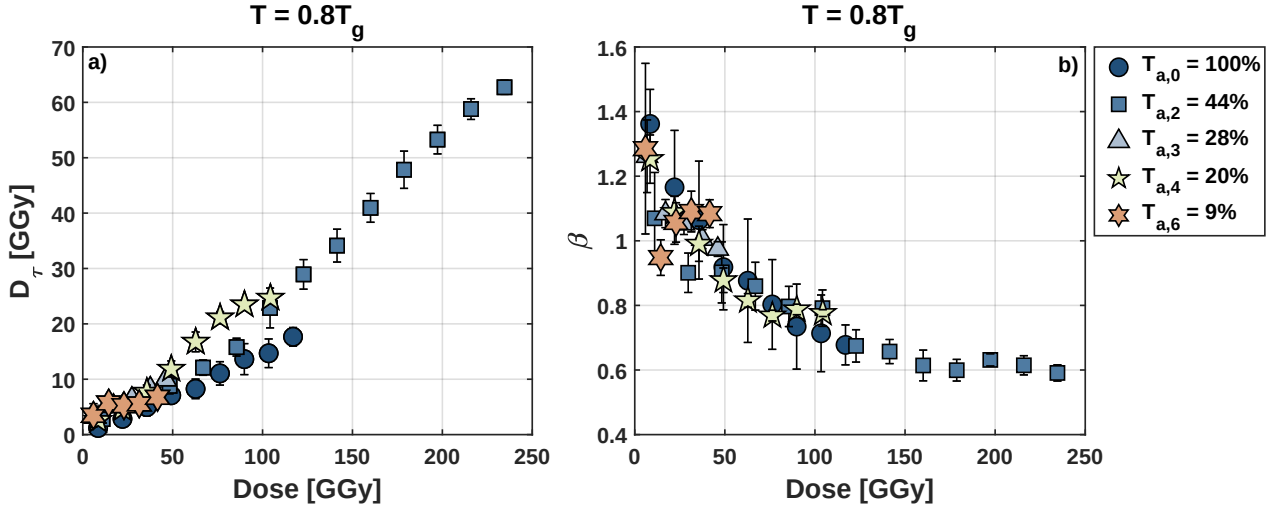


Figure 5.9: At $0.8T_g$, D_τ and β collapse in a master curve by plotting them versus the Dose. a-c) As the waiting time or the deposited dose increases, the dynamics slows down, suggesting a final plateau. b-d) With increasing the absorbed dose, the shape parameter β decreases from $\beta > 1$, signature of compressed correlation functions, to $\beta < 1$, typical of stretched exponential decays.

Next, we examine how the dynamical parameters of the two compositions depend on the absorbed dose D (or on the waiting time t_w) at both $0.7T_g$ and $0.8T_g$, referring to Figs. 5.4-5.5 and 5.6-5.9 for $\text{Ge}_{15}\text{Sb}_{85}$ and $\text{Ge}_{15}\text{Te}_{85}$, respectively.

As anticipated, $\text{Ge}_{15}\text{Sb}_{85}$ exhibits stationary dynamics with a KWW exponent $\beta \lesssim 1$ at both temperatures. These features correspond to a local, photo-induced yielding of the glass by the X-rays, in line with previous studies on other chalcogenide and oxide glasses [4, 165, 199]. For the chalcogenide glass GeSe_3 , this X-ray-induced yielding occurs within approximately 100 s of exposure at ambient temperature [4]. In contrast, $\text{Ge}_{15}\text{Sb}_{85}$ reaches a stationary state within just 1 s of exposure at the probed temperatures of 350 K and 400 K ($0.7T_g$ and $0.8T_g$, respectively). This faster timescale likely reflects the larger thermal fluctuations at these temperatures, which facilitate local yielding at lower doses.

Consistent with previous works, we also observe a transient state with weak aging at $0.6T_g$ in $\text{Ge}_{15}\text{Sb}_{85}$, accompanied by a transition of the KWW exponent β from compressed (≥ 1) to stretched (≤ 1), reaching a stationary regime around 40 GGy (Fig. 5.10). As discussed in Ref. [165], these are characteristic signatures of an X-ray-induced yielding transition.

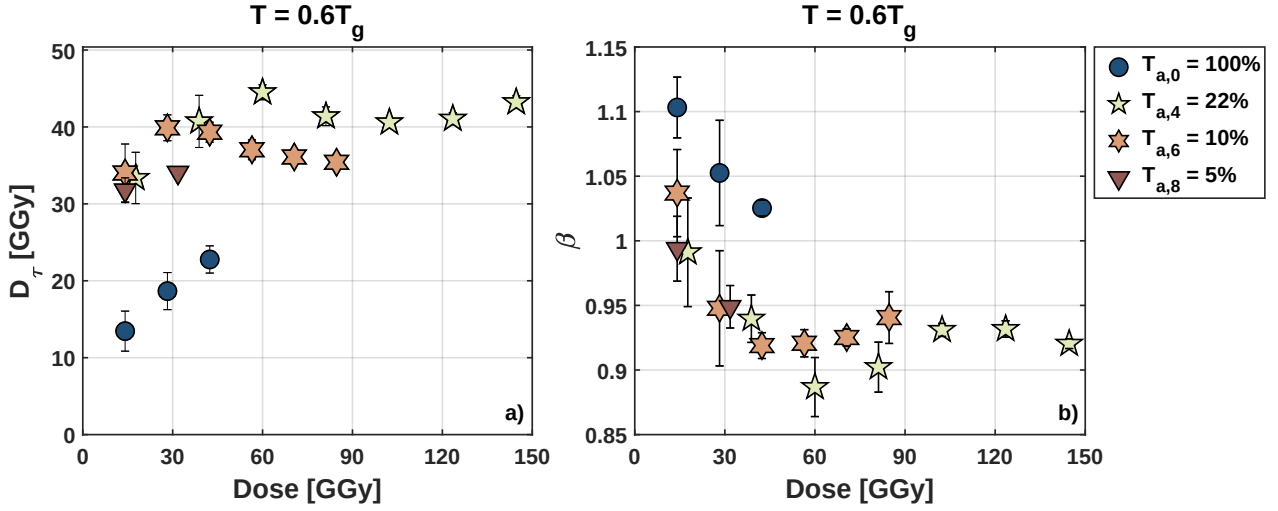


Figure 5.10: Dynamics evolution at $T = 0.6T_g$ of $\text{Ge}_{15}\text{Sb}_{85}$. **a)** the relaxation time τ shows a constant behaviour, except for very high beam intensities. **b)** β decreases from ~ 1.1 to ~ 0.9 .

In contrast, $\text{Ge}_{15}\text{Te}_{85}$ shows a pronounced dependence on both waiting time and absorbed dose at both temperatures, as illustrated in Fig. 5.75.65.9. Neither the absorbed dose associated with the relaxation time, D_τ , nor the KWW exponent β fully reaches a plateau. Only D_τ measured at $T_{a,6}$ and β at $T_a \geq 28\%$ at $0.7T_g$ hint at an approach toward a stationary regime. To determine whether this behaviour corresponds to the onset of a photo-induced yielding transition, we examined the wave-vector q dependence of the dynamics, and hence of D_τ and β , as a function of increasing absorbed dose (Fig. 5.11). According to Ref. [165], the transition to local yielding should be accompanied by a crossover from a $1/q$ dependence of τ and an almost q -independent evolution of β toward a more liquid-like behaviour.

At low q , the log-log representation of D_τ versus q (Figure 5.11a) reveals a linear trend, consistent with a power-law relationship between relaxation time and wavevector. By analysing this dependence in the range $[2-7] \text{ nm}^{-1}$, one can probe the nature of the particle dynamics and its evolution with absorbed dose. The behaviour is captured by the scaling law $D_\tau(q) = (bq^\alpha)^{-1}$, with the exponent α characterising the type motion. The fit gives $\alpha = 1.7 \pm 0.4$, which remains essentially unchanged with dose (see inset of Figure 5.11a). This value is significantly larger than that reported for LiBO_2 glass, where α decreases from ~ 1.1 to ~ 0.3 with increasing dose. In that system, the trend was interpreted as a transition in the nature of the collective motion: from ballistic-like dynamics at low dose towards a regime where defect creation and annihilation balance each other, reminiscent of a steady-state condition

observed in liquids [165]. By contrast, in $\text{Ge}_{15}\text{Te}_{85}$ the larger value of α suggests diffusive motion at low q , with negligible dependence on dose. Nevertheless, additional measurements at lower q values, well separated from structural features, are required to unambiguously confirm this behaviour.

At high q (above 7 nm^{-1}), D_τ increases overall with dose D , while the KWW exponent β decreases. Across all doses, D_τ exhibits a pronounced peak at $\sim 10.5 \text{ nm}^{-1}$, which coincides with the pre-peak of the static structure factor $S(q)$ [257]. At higher doses, an additional peak emerges at $\sim 19.6 \text{ nm}^{-1}$, corresponding to the first sharp diffraction peak (FSDP). A similar trend is observed in the behaviour of β , which develops features reflecting the evolution of $S(q)$, weak at low doses but increasingly evident at higher doses. The parallel between the q -dependence of τ and β and that of $S(q)$ is reminiscent of the phenomenon of *de Gennes narrowing*. Originally observed in neutron scattering experiments on liquids [41], this effect refers to the narrowing of the quasi-elastic peak at q values corresponding to the FSDP of $S(q)$. As said in Par. 1.4.2, the structural configurations that dominate the static correlations are also the most dynamically stable. In $\text{Ge}_{15}\text{Te}_{85}$, the observed q -dependence of D_τ and β therefore suggests that the irradiated sample volume exhibits liquid-like dynamics and undergoes local yielding, in close analogy to what was reported for LiBO_2 . This interpretation is further supported by the evolution of β : it decreases from values larger than 1, characteristic of stress-driven dynamics in glasses well below T_g [265], to values smaller than 1, which are the hallmark of liquid-like heterogeneous relaxation [266, 267].

Notably, in LiBO_2 , de Gennes narrowing is absent at low doses (below 0.5 GGy) for both τ and β [165]. In contrast, in the case of $\text{Ge}_{15}\text{Te}_{85}$ the effect is already visible at the lowest probed doses (below 7 GGy), manifesting as a clear dynamical signature at the pre-peak of $S(q)$ around $\sim 10.5 \text{ nm}^{-1}$. At these low doses, only the pre-peak feature is observed in the q -dependence of D_τ , whereas at higher doses the signature of the main peak at $\sim 19.6 \text{ nm}^{-1}$ emerges as well. The fact that such a pronounced dynamical response can be associated with the relatively weak structural pre-peaks is a hallmark of glass-forming liquids. This behaviour has been widely linked to the role of dynamic heterogeneity, which governs relaxation at both the single-particle and collective level [268, 269].

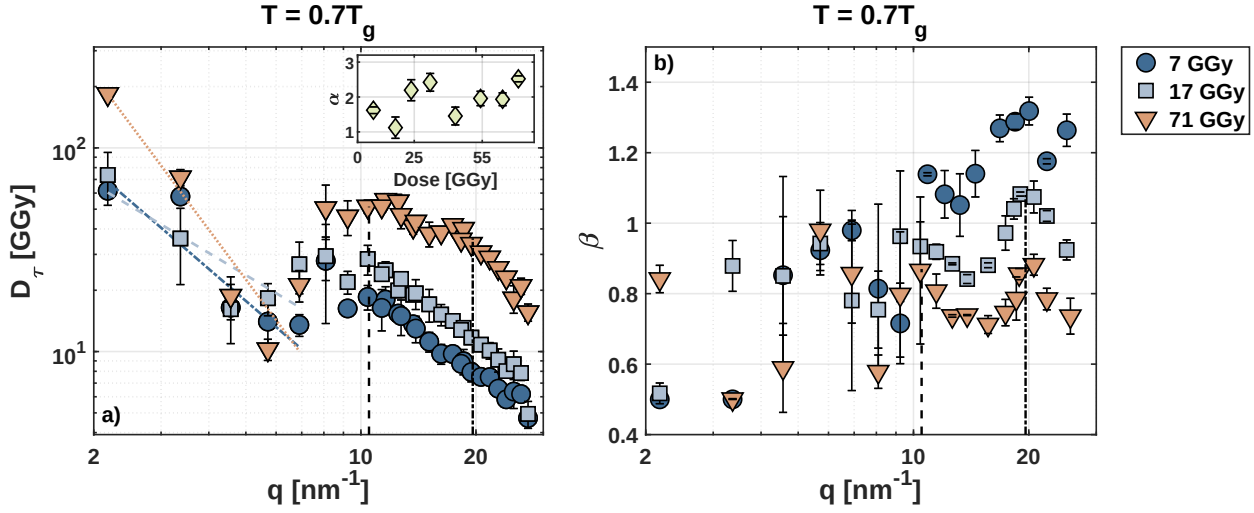


Figure 5.11: Wave vector dependence of D_τ a) and β b) at $0.7T_g$ of $\text{Ge}_{15}\text{Te}_{85}$ for three selected doses: $D = 7$ GGy (blue circles), $D = 17$ GGy (light-blue squares) and $D = 74$ GGy (orange triangles). The vertical dashed and dashed-dotted black lines represent, respectively, the position of the pre-peak and the main peak. a) The inset shows the dependence on the dose of the power-law exponent α describing the linear dependence of τ at low q -values.

5.2.2 Discussion

Our results reveal a strong correlation between the local atomic structure and the dynamical response to intense X-ray fluxes in two compositionally similar glasses, $\text{Ge}_{15}\text{Sb}_{85}$ and $\text{Ge}_{15}\text{Te}_{85}$. In line with previous findings in oxides and chalcogenides [4, 165, 199], the irradiation can drive both systems into a locally yielded state, where the amorphous matrix displays liquid-like features within the probed volume. The propensity of this phenomenon, however, is not universal but depends sensitively on the chemical identity and structural characteristics of the glass.

In the phase-change material $\text{Ge}_{15}\text{Sb}_{85}$, the data reveal an almost instantaneous photo-induced yielding transition at $0.7T_g$ and $0.8T_g$. At room temperature, by contrast, the transition requires ~ 400 s of continuous irradiation to occur (see Fig. 5.10), highlighting the role of thermal motion in accelerating the process. This behaviour echoes the case of GeSe_3 [4], where yielding sets in after only ~ 100 s at ambient temperature. The faster response in GeSe_3 is likely linked to the lighter atomic mass of Se compared to Sb, a hypothesis corroborated by relaxation times of $\tau \sim 2$ s in GeSe_3 versus $\tau \sim 100$ s in $\text{Ge}_{15}\text{Sb}_{85}$ for comparable doses. Raising the temperature

of $\text{Ge}_{15}\text{Sb}_{85}$ to 350 K ($0.7T_g$) enhances atomic mobility and allows the system to reach the yielded state almost immediately. In striking contrast, $\text{Ge}_{15}\text{Te}_{85}$ never fully reaches the yielded state within the experimental time window, neither at $0.7T_g$ (room temperature) nor at $0.8T_g$. The higher atomic mass of Te reduces mobility and increases resistance to X-ray-induced structural rearrangements, thereby hindering a complete transition. This interpretation is consistent with the absence of visible changes in the first sharp diffraction peak, which in GeSe_3 displays clear signatures of irradiation-induced reorganisation. Moreover, $\text{Ge}_{15}\text{Te}_{85}$ exhibits recovery effects once the beam is switched off: the system progressively relaxes back toward its initial dynamical state, with the extent of recovery increasing with the off-time (see Fig. 5.8a-b). In GeSe_3 , by contrast, once the yielded state is reached, the dynamics remain stable even in the absence of irradiation. These distinct behaviours cannot be rationalised solely in terms of bonding type, since both GeSe_3 and $\text{Ge}_{15}\text{Te}_{85}$ are covalent glasses with good glass-forming ability and slow crystallisation kinetics. The comparison instead points to a more intricate interplay of factors, including atomic mass, network topology, and local structural heterogeneity, which must be considered to fully capture the mechanisms governing the onset and nature of yielding under X-ray irradiation.

The faster photo-induced atomic motion in the PCM $\text{Ge}_{15}\text{Sb}_{85}$ and its higher sensitivity to X-ray-induced yielding are likely the consequence of its locally loosely bonded microscopic structure, together with the presence of a pronounced secondary β -relaxation that promotes local mobility at the atomic scale [262]. Such mobility is further supported by the observation that the dynamics does not scale strictly with the absorbed dose D , reinforcing the idea that an intrinsic dynamical process is already active at the probed temperatures. By contrast, the more rigid, covalently bonded network of $\text{Ge}_{15}\text{Te}_{85}$ is far less prone to changes of the local atomic environment. This rigidity translates into longer relaxation times at the atomic scale and a response dominated by intrinsic dynamics at ambient temperatures. At this temperature, the scaling law is not fulfilled, most likely due to additional stresses related to sample preparation that contribute to the irradiation-induced yielding transition.

Interestingly, $\text{Ge}_{15}\text{Te}_{85}$ exhibits a dependence on absorbed dose that mirrors the behaviour reported for the oxide glass LiBO_2 [165]. In both systems, increasing the dose drives a transition of the KWW β shape parameter from a compressed ($\beta \geq 1$) to a stretched ($\beta \leq 1$) regime. This crossover is accompanied by the emergence of a liquid-like q -dependence of the dynamics at high doses. As previously argued [165], such behaviour can be attributed to a transition from a purely beam-induced, stress-driven motion toward a

local yielding process under X-ray irradiation.

It is, however, important to emphasise the key differences between LiBO_2 and $\text{Ge}_{15}\text{Te}_{85}$. A crucial factor governing the beam-induced dynamics is the X-ray absorption. $\text{Ge}_{15}\text{Te}_{85}$ consists of heavier atoms, which absorb X-rays much more efficiently than the lighter constituents of LiBO_2 . This disparity is reflected in the experimental conditions: the thickness of the $\text{Ge}_{15}\text{Te}_{85}$ samples was comparable to their attenuation length at 8 keV ($\sim 8 \mu\text{m}$), ensuring substantial absorption, whereas the LiBO_2 samples were significantly thinner ($125 \mu\text{m}$) relative to their attenuation length at 8.4 keV ($680 \mu\text{m}$). Consequently, the accessible dose range in $\text{Ge}_{15}\text{Te}_{85}$ reached tens of GGy, while in LiBO_2 it remained within only a few GGy. Remarkably, despite this order-of-magnitude difference in absorbed dose, both systems exhibit a similar evolution of the KWW β parameter and of $\tau(q)$ as a function of dose. This observation suggests that atomic rearrangements in $\text{Ge}_{15}\text{Te}_{85}$ require the generation of a substantially higher number of electron-hole pairs, likely a direct consequence of its heavier atomic composition. Consistently, the dynamics in $\text{Ge}_{15}\text{Te}_{85}$ is markedly slower (hundreds of seconds) compared to that in LiBO_2 ($\sim 20 \text{ s}$), despite the much higher absorbed dose.

In conclusion, both systems are influenced by X-ray irradiation, yet their responses diverge significantly. $\text{Ge}_{15}\text{Sb}_{85}$ undergoes a rapid transition to a stationary yielding regime within the exposure time, marked by a KWW parameter $\beta \lesssim 1$. $\text{Ge}_{15}\text{Te}_{85}$, by contrast, exhibits a pronounced dose-dependent evolution: aging effects and a progressive crossover of β from compressed ($\beta > 1$) to stretched ($\beta < 1$). This transition is consistent with the emergence of liquid-like collective motion, as evidenced by the de Gennes narrowing observed in the q -dependence of the dynamics. Unlike $\text{Ge}_{15}\text{Sb}_{85}$, however, $\text{Ge}_{15}\text{Te}_{85}$ does not reach a stationary regime within experimental timescales, indicating that local yielding requires thousands of seconds. Its resistance to photo-induced yielding is in line with its heavier atomic constituents, which enhance structural rigidity and therefore require significantly higher deposited doses to trigger local transformations. These findings further align with its higher amorphous thermal stability and slow crystallisation kinetics [258], in sharp contrast to $\text{Ge}_{15}\text{Sb}_{85}$, which crystallises rapidly and exhibits weaker covalent bonding [252].

Overall, our results demonstrate that neither chemical composition alone nor bonding character alone can account for the X-ray-induced response of the non-PCM $\text{Ge}_{15}\text{Te}_{85}$ and the PCM $\text{Ge}_{15}\text{Sb}_{85}$. Instead, the dynamics emerge from the complex interplay between irradiation-driven effects and intrinsic relaxation pathways. Finally, we note that such beam-induced dynamics may provide a novel avenue for probing β -relaxations in PCMs below T_g . Previous studies have already shown that PCMs such as $\text{Ge}_2\text{Sb}_2\text{Te}_5$,

GeTe, and (Ag,In)-doped Sb₂Te (AIST) exhibit pronounced excess wings in the loss modulus associated with β -relaxations, in stark contrast to chalcogenide non-PCMs where such wings are vanishingly small [270].

Beyond the microscopic dynamics, an important open question concerns the impact of X-ray irradiation on the thermodynamic stability of the probed glasses. For GeSe₃, Baglioni *et al.* [4] demonstrated that irradiation drives the system into a rejuvenated state of higher enthalpy, resembling a rapidly quenched glass, and that this state is stationary at room temperature. A comparable study on Ge-based alloys would require implementing Flash-DSC directly at the beamline to enable simultaneous XPCS and calorimetric measurements. Such an implementation would demand several experimental campaigns to optimise the set-up and therefore goes beyond the scope of the present Thesis. As a result, we cannot directly determine whether similar macroscopic rejuvenation occurs in Ge₁₅Sb₈₅ or Ge₁₅Te₈₅. Nevertheless, the dynamical results reported here provide indirect hints.

For Ge₁₅Sb₈₅, the rapid and irreversible transition into a stationary yielded regime suggests that irradiation likely decreases the stability, in analogy with GeSe₃, by populating higher-energy configurations that remain trapped even when the beam is switched off. By contrast, Ge₁₅Te₈₅ exhibits clear recovery effects once irradiation ceases, with the system progressively reverting toward its original dynamical state. This behaviour indicates that, unlike in GeSe₃ or Ge₁₅Sb₈₅, irradiation does not irreversibly rejuvenate the glass but instead induces a transient without fully changing the system. The lack of a stationary yielded state in Ge₁₅Te₈₅ thus points to a fundamental resistance to beam-driven rejuvenation, consistent with its heavier atomic constituents and intrinsically higher stability.

5.3 Mechanical driven relaxation dynamics in $\text{Ge}_{15}\text{Te}_{85}$

Having established the response of Ge-based glasses to X-ray irradiation, we can now select a well-defined irradiation dose and thus a specific initial state of the glass, and use XPCS to probe how its atomic dynamics and stability evolve under an additional external stimulus: hydrostatic compression. For this purpose, we report here the results of high-pressure compression experiments on $\text{Ge}_{15}\text{Te}_{85}$. We first present how pressure affects the structure and microscopic dynamics, as revealed by *in-situ* high-pressure XPCS measurements, followed by a discussion of the complementary calorimetric results obtained on densified bulk samples using fast nano-calorimetry. Together, these findings provide a comprehensive picture of how compression influences the stability and relaxation behaviour of $\text{Ge}_{15}\text{Te}_{85}$.

5.3.1 In-situ experiments

High-pressure XPCS measurements on $\text{Ge}_{15}\text{Te}_{85}$ were performed during two independent beamtime sessions at P10 beamline in DESY, exploiting a 15 keV coherent beam.

The first experiment covered the 0-10 GPa range and was primarily devoted to investigating the effect of the X-ray beam on the dynamics under pressure using a dedicated protocol. As learnt from the previous Section, at ambient pressure, $\text{Ge}_{15}\text{Te}_{85}$ displays beam-induced dynamics that tends to drive the glass towards a yielding state, although the transition is not reached within experimental timescales. It was therefore crucial to examine systematically how hydrostatic compression influences this beam-driven response. To do so, three different incident fluxes were used at each pressure, obtained with Si attenuators (64%, 41%, and 25% of full intensity). The incident beam was focused to $2.1 \times 1.1 \mu\text{m}^2$, with a photon flux of $\phi_0 \sim 4.1 \times 10^{10}$ ph/s.

We report here the evolution of the relaxation time τ and the shape parameter β as a function of the absorbed dose (Eq. (5.3.2)) at a representative pressure of 2.7 GPa. Figure 5.12 shows the dose-dependent normalised relaxation time D_τ (calculated from Eq. (5.3.3)) together with β . The sample exhibits aging, while β remains essentially constant without any systematic trend. When plotted against dose, the D_τ curves collapse onto a single master curve, confirming that the observed dynamics are predominantly beam-induced. The small deviations from perfect overlap in D_τ can be attributed to a slow intrinsic pressure effect: once the pressure is stabilised, the sample undergoes a modest amount of pressure-driven aging, much smaller than that

induced by the beam. This interpretation is consistent with the observation that D_τ values measured at 64% transmission are systematically lower than those at 41%, which in turn are lower than those at 25%.

The central question for high-pressure dynamics is whether the glass undergoes a photo-induced yielding transition under compression, similar to that observed at ambient pressure. Such a transition would manifest as both aging and a crossover of β from values > 1 to < 1 . Here, however, while aging is observed, β remains essentially constant and well above unity. This suggests that high pressure locks the sample in the dynamical regime observed at low doses at ambient pressure, preventing the beam from driving it into a yielding-like state.

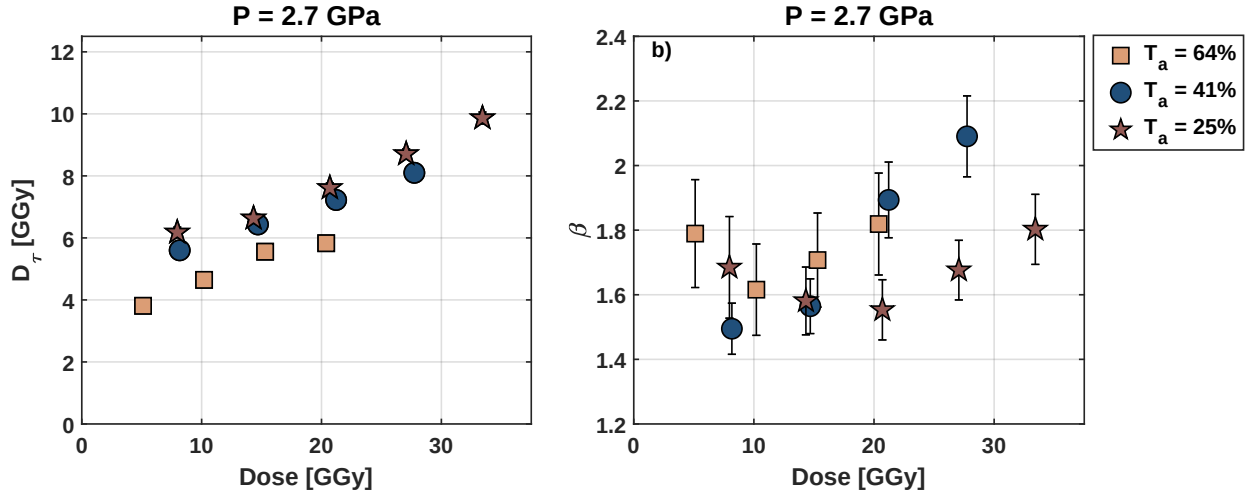


Figure 5.12: Dose dependence of D_τ and β at 2.7 GPa.

Thanks to these results, a second experiment was carried out to extend the accessible pressure range up to 15 GPa. In this case, the beam was slightly tighter ($1.8 \times 1.1 \mu\text{m}^2$) with a flux of $\phi_0 \sim 2.4 \times 10^{10}$ ph/s. All measurements were performed at a single flux level (73% of full intensity), corresponding to the same effective flux as the 41% transmission used in the first experiment.

In both sessions, the detector was aligned on the first sharp diffraction peak of the sample, and each XPCS run was performed on a fresh, previously unexposed spot to avoid cumulative radiation effects. Figure 3.25 shows a photograph of the sample mounted in the DAC, where the X-ray-irradiated spots are visible.

Structural evolution

A key advantage of the XPCS setup is the simultaneous access to both structural and dynamical information under varying external parameters. In particular, structural information can be obtained from the q -dependent scattered intensity, $I(q)$, integrated over the detector (see Sec. 3.3.3). Figure 5.13 shows $I(q)$ at selected pressures. With increasing pressure, the FSDP progressively shifts to higher q , evidencing densification. Moreover, the peak narrows and intensifies, indicating an enhancement of medium-range order. Because the XPCS detector covers a narrow q window ($\sim 0.011 \text{ \AA}^{-1}$), much smaller than the full FSDP width, it records only the top part of the peak. This limited window does not compromise the analysis, as many XRD studies likewise focus on the peak maximum.

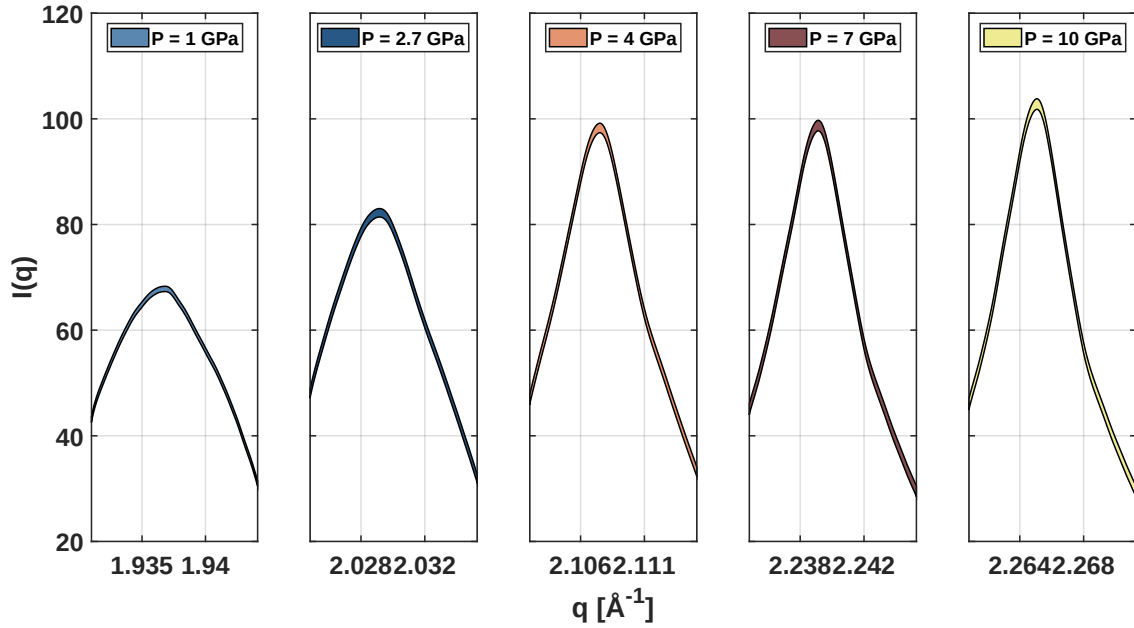


Figure 5.13: Structural evolution under pressure. Selected portions of the FSDP measured by the XPCS detector. Increasing pressure leads to peak narrowing, intensification, and a shift to higher q , consistent with densification and enhanced medium-range order.

To quantify this evolution, the upper 30% of the FSDP was fitted with a Gaussian function centred at q_{max} and with width Γ . Since q_{max} reflects the characteristic periodicity of the MRO, it can be used to estimate the relative atomic volume through the relation $V(P)/V(P_0) = (q_{\text{max}}(P_0)/q_{\text{max}}(P))^3$. This approach has been widely validated in oxide, metallic, and chalcogenide

glasses, and is here extended to $\text{Ge}_{15}\text{Te}_{85}$. Given that the XPCS setup is not optimised for precise q calibration as in standard XRD, absolute comparisons of V and Γ between different beamtimes are not possible. Instead, we normalised both quantities to their respective values at $P_0 \simeq 10$ GPa. The resulting trends, shown in Fig. 5.14, reveal two distinct regimes: below ~ 4 GPa, V/V_0 and Γ decrease steeply with pressure, whereas above this threshold the slopes are much weaker. This crossover is a hallmark of a polyamorphic transition between low-density (LDA) and high-density (HDA) amorphous states, consistent with previous reports on other Ge-based glasses [102].

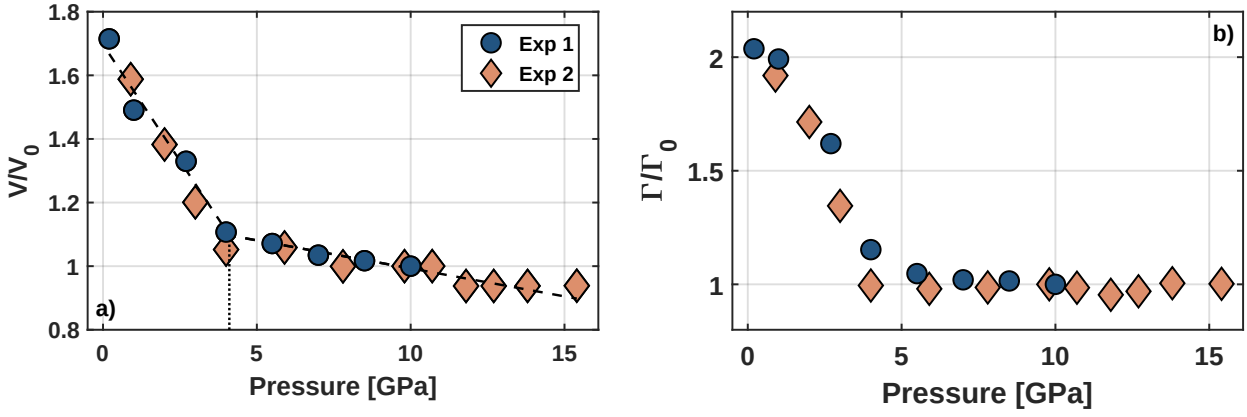


Figure 5.14: a) Normalised volume ratio V/V_0 and b) FSDP width Γ/Γ_0 as functions of pressure. Both parameters exhibit two distinct regimes, consistent with a polyamorphic transition. The transition pressure $P_{AA} = (4.2 \pm 0.8)$ GPa (dotted line in b)) is determined from the intersection of the linear fits (dashed lines).

We determine the pressure P_{AA} at which the transition occurs from the volume ratio. Linear fits to the low- and high-pressure regimes (dashed lines in Fig. 5.14a) intersect at $P_{AA} = (4.1 \pm 0.8)$ GPa. From the slope, we also extracted the compressibility k via

$$\frac{V(P)}{V_0} = 1 - k(P - P_0). \quad (5.3.1)$$

We find $k = (0.09 \pm 0.01)$ GPa^{-1} in the LDA phase and $k = (0.010 \pm 0.001)$ GPa^{-1} in the HDA phase, a nearly ninefold reduction that highlights the magnitude of the structural rearrangement across the transition. Similar values were also found in a similar composition GeTe [102]. Interestingly, the

increase in Te content shifts the transition to larger pressures with respect to the GeTe glass.

The data shown in Fig. 5.13 and the blue circles in Fig. 5.14 correspond to measurements acquired at an effective beam flux of 41%, which we present as a representative dataset because its structural response is indistinguishable from that obtained at the other fluxes. To confirm that the beam intensity does not affect the structural evolution, Fig. 5.15 compares the FSDP position q_{max} , the peak height I_{max} normalised for the attenuators transmission T_a , and the width Γ for all three flux levels used in the first experiment (orange squares: 64%; blue circles: 41%; brown stars: 25%). All three parameters follow the same pressure dependence within experimental uncertainties, demonstrating that the structural trends discussed above are intrinsic and independent of the incident flux.

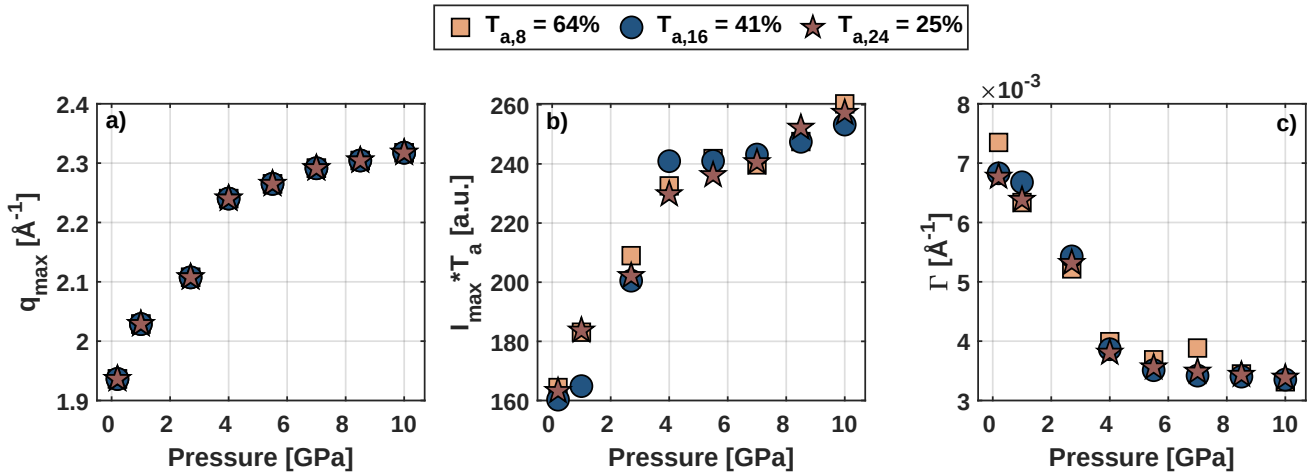


Figure 5.15: Pressure evolution of structural parameters extracted from the FSDP at different beam intensities T_a .

The $I(q)$ curves discussed above represent time averages over all frames in a given XPCS scan. This averaging is justified by the absence of systematic time dependence in the total scattered intensity, suggesting either that no significant structural rearrangements occurred during acquisition at the probed q -values. To gain further insight, we now turn to the temporal evolution of the microscopic dynamics across the polyamorphic transition.

Dynamical evolution

To explore the temporal evolution of the dynamics across the polyamorphic transition, we examined the two-time correlation functions at selected pressures ($P = 2.7, 4.0$, and 5.5 GPa) from the first experiment, measured at all three flux levels. In Fig. 5.16, the x -axis represents the laboratory time, i.e. the elapsed time since the target pressure was reached, while the y -axis corresponds to the delay time (see Sec. 3.3.1.1). To allow direct comparison across different fluxes, the delay times are normalised by the corresponding attenuator transmission T_a .

Below and above P_{AA} , the TTCFs display a generally continuous temporal evolution with a gradual tendency to aging. At $P = 4.0$ GPa, near the transition, the TTCFs exhibit abrupt changes. The dynamics is initially very fast, likely due to rapid structural rearrangements triggered by the amorphous-amorphous transition. After about 90 minutes, this fast relaxation ceases, and the dynamics slows abruptly, followed by weaker intermittent activity. This discontinuous behaviour at the dynamical level, in the absence of detectable structural changes in $I(q)$, demonstrates the enhanced sensitivity of density fluctuations beyond what is accessible from average structure alone. At 5.5 GPa, the dynamics becomes significantly slower and nearly stationary, consistent with the system having reached the HDA state. Nevertheless, small fluctuations over the average dynamics remain visible, even at other pressures. These features likely originate from changes in the stress field induced by tiny structural rearrangements in the amorphous structure. Superimposed on this pressure-dependent behaviour, we also observe a slightly faster relaxation at the onset of each new measurement, suggesting a minor additional contribution induced by the X-ray beam itself, which triggers a stress-release at ambient temperature, as previously observed even in the absence of pressure. This effect, however, is negligible with respect to the one inferred by pressure.

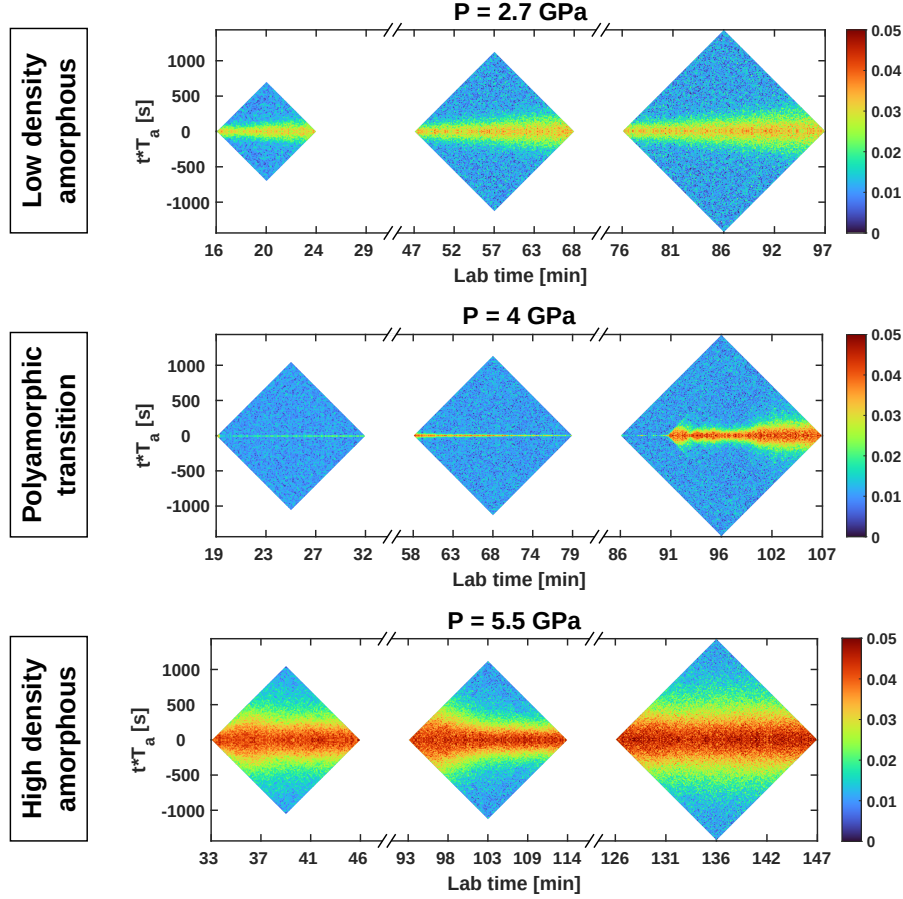


Figure 5.16: Temporal evolution of the atomic motion near the polyamorphic transition. TTCFs are shown for scans at 2.7 GPa (low-density glass), 4 GPa (transition region), and 5.5 GPa (high-density glass). At 2.7 GPa, the dynamics remains nearly stable. At 4 GPa, it is accelerated and evolves with time, then abruptly slows down after ~ 91 minutes, marking the end of the transition. At 5.5 GPa, the dynamics is significantly slowed and nearly stable, indicating the system is beyond the transition. Along the y-axis, each TTCF is normalised by the corresponding attenuator transmission for consistent comparison.

We now turn to investigate how the dynamics evolves with pressure over the entire pressure range covered in the experiments. To consistently compare dynamics across different pressures and fluxes, we extracted the autocorrel-

ation functions $g_2(t)$ from the TTCFs using exposure times Δt adjusted so that the absorbed dose D is the same in all cases:

$$D = \frac{\varepsilon}{m} \phi_0 T_a (1 - T_r) \Delta t, \quad (5.3.2)$$

where m is the sample mass within the scattering volume, and $T_r = \exp(-L/\mu)$ is the sample transmission, with L the thickness and μ the absorption length. Clearly, m depends on the density, as well as μ . In fact, the higher ρ , the more efficient the X-ray absorption. Density variations are estimated from the structural volume ratio V/V_0 , shown in Fig. 5.14a). A common dose was chosen to optimise the signal-to-noise ratio of the second experiment, ensuring comparability with the first experiment at $T_a = 41\%$.

The resulting $g_2(t)$ functions are shown in Fig. 5.17. Four regimes can be identified: a) below P_{AA} , b) between P_{AA} and 8.5 GPa, c) from 8.5 to 11.8 GPa, and d) above 11.8 GPa. The dynamics slows progressively up to ~ 10 GPa, then accelerates between 10 and 12 GPa. This is unexpected, since there is no visible structural signature in $I(q)$. Beyond 12 GPa, the dynamics slows again as pressure increases further.

The evolution of the contrast parameter of the $g_2(t)$ functions mirrors the structural changes. A pronounced increase in contrast up to ~ 4 GPa, followed by a weaker growth at higher pressures, reflects the ordering at the level of the medium-range order, which is associated with an increase in scattering intensity (see Fig. 5.14). Since the background remains constant, the signal-to-noise ratio improves with pressure, driving the contrast behaviour [271].

The $g_2(t)$ functions are fitted with the Kohlrausch-Williams-Watts function to extract the relaxation time τ and stretching exponent β . To account for the induced nature of the dynamics and enable comparison between different experiments, τ is expressed in terms of the absorbed dose D_τ required to induce the observed dynamics:

$$D_\tau = \frac{\varepsilon}{m} \phi_0 T_a (1 - T_r) \tau. \quad (5.3.3)$$

As in Eq. (5.3.2), this expression incorporates the density dependence of m and T_r . Figure 5.18a) shows D_τ as a function of pressure for both experiments (blue circles: first beamtime, $T_a = 41\%$; orange diamonds: second beamtime). It is important to note that with this representation, the change in dynamics is reduced, having already been normalised by the increase in density. Despite some discrepancies in the absolute values, the same trend is reproduced: a slowing of the dynamics up to ~ 10 GPa, followed by an acceleration between 10 and 12 GPa, and a final slowdown above ~ 12 GPa. The

quantitative differences likely stem from the different waiting times between pressure changes and XPCS scans under study: about 50 minutes in the first experiment and 20 minutes in the second. Since pressure effects are not instantaneous and aging may also contribute, the longer waiting time plausibly explains the systematic shift of D_τ towards larger values in the first data-set. An additional source of difference could also arise from small pressure variations between the two experiments (considering that we have pressure fluctuations of ~ 0.1 GPa)

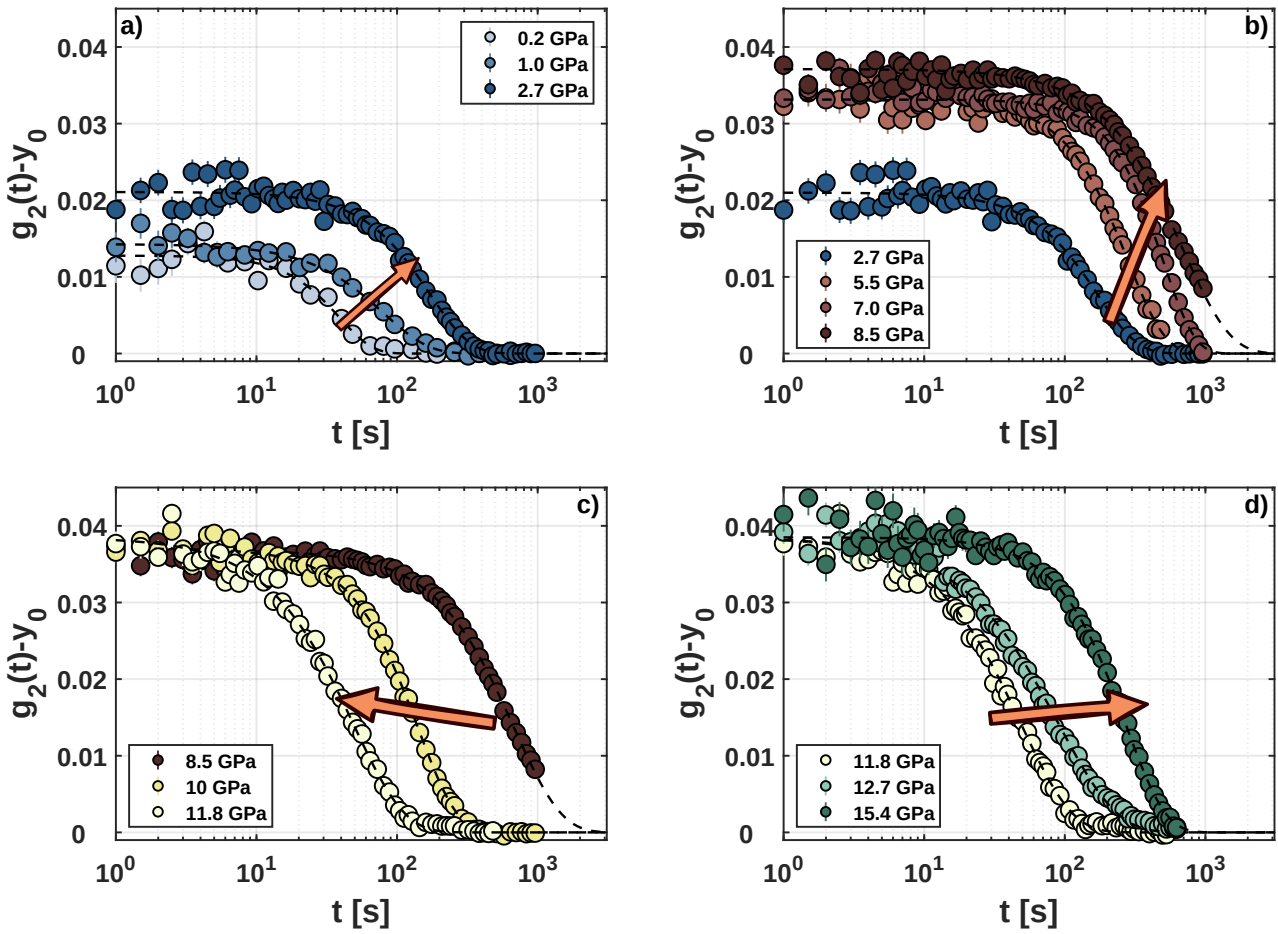


Figure 5.17: Autocorrelation functions $g_2(t)$ at different pressure ranges. a) Below the polymorphic transition, b) 4–8.5 GPa, c) 8.5–11.8 GPa, d) above 11.8 GPa. The dynamics slows up to ~ 10 GPa, accelerates between 10 and 12 GPa, and then slows again at higher pressures.

To correlate dynamics and structure, D_τ is compared with $q_0/q_{\max}$, shown in Fig. 5.18b). The acceleration of dynamics occurs roughly 5 GPa above P_{AA} , indicating that the influence of the amorphous-amorphous transition extends over a broader pressure range than revealed by structural probes alone. The data suggest that the transition is only completed at ~ 12 GPa, where the dynamics finally slows down, as expected by the increased density.

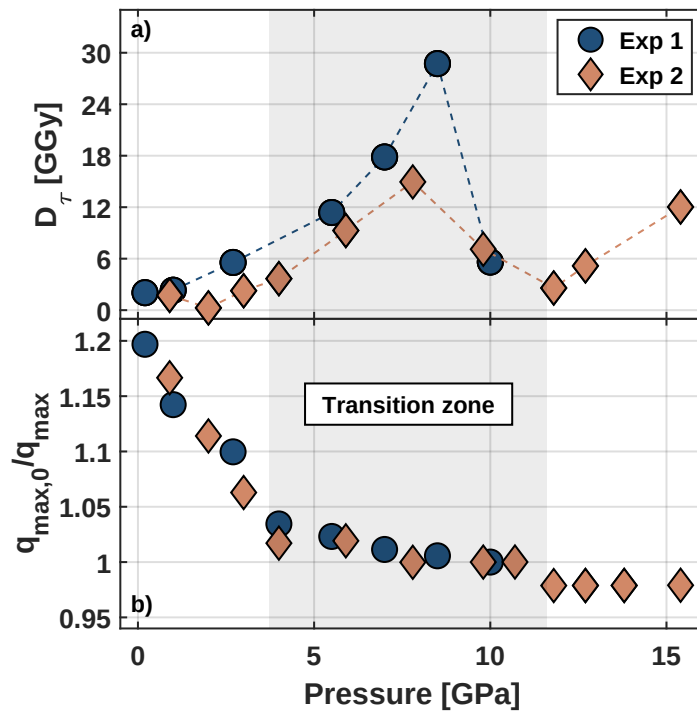


Figure 5.18: a) D_τ as a function of pressure, showing a slowdown up to ~ 10 GPa, an acceleration between 10–12 GPa, and a final slowdown above 12 GPa. b) The structural parameter $q_0/q_{\max}$ vs P. The dynamical acceleration occurs about 5 GPa above P_{AA} , suggesting that the transition extends over a broader pressure range than visible from structure alone.

Finally, the stretching exponent β provides additional insight. As shown in Fig. 5.19, β is ~ 1.6 below 10 GPa and increases to ~ 1.8 above this threshold. Although the presence of large fluctuations in the values, particularly at low pressures, the growth of β reflects enhanced internal stresses and the presence of more localised plastic regions, contributing to increased rigid-

ity in the high-pressure phase. The observed variations in β , even with high-quality $g_2(t)$ data, reflect the discontinuities seen in the TTCFs (Fig. 5.16): local stress rearrangements modify the shape of the decorrelation curves along the TTCFs, resulting in non-unique instantaneous values of β . Even though β is generally less robust than τ , a direct comparison of normalised $g_2(t)$ curves at 3 and 11.8 GPa illustrates the effect clearly: at higher pressures, the curves are more compressed.

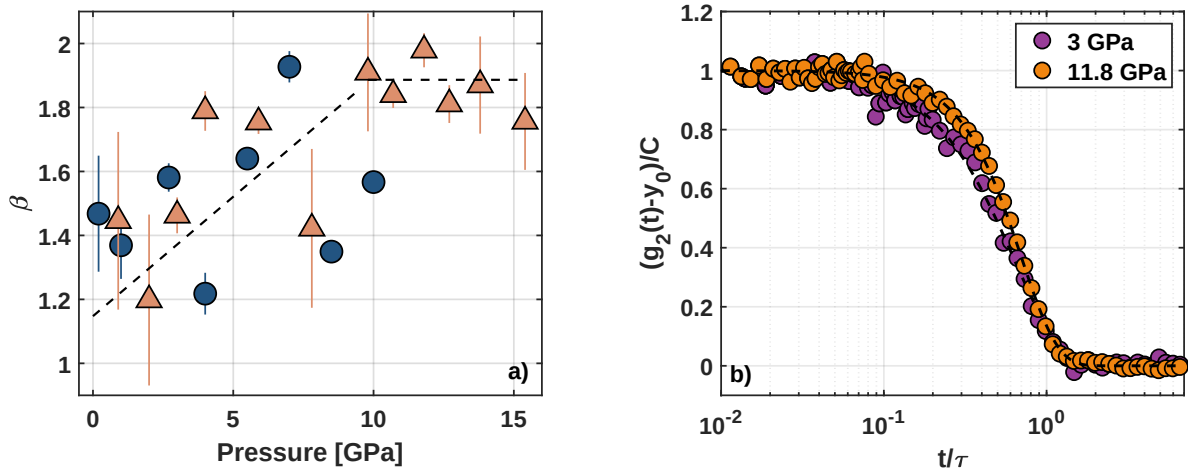


Figure 5.19: Stretching exponent β as a function of pressure. Below 10 GPa, $\beta \sim 1.6$, while above 10 GPa it increases to ~ 1.8 , indicating enhanced rigidity and a more compressed relaxation behaviour in the HDA phase.

5.3.2 Ex-situ experiment

To complement the *in-situ* XPCS study and gain a more comprehensive picture of the high-pressure effects in $\text{Ge}_{15}\text{Te}_{85}$, we performed fast differential scanning calorimetry measurements. Since *in-situ* calorimetry at high pressures is not feasible, the measurements were carried out *ex-situ*: samples were densified at different pressures P_d in a DAC for 10 minutes at room temperature and then recovered for analysis. As discussed in Sec. 3.5, this procedure allows us to study the effect of permanent densification related to anelastic contributions. All FDSC scans were carried out between 298 and 623 K at a rapid heating rate of 500 K/s.

Following the data-reduction procedure described in Sec. 3.5, Fig. 5.20 displays a representative heat-flow (HF) trace for a sample densified at 1.1 GPa over the entire temperature range. Two main thermal events are apparent:

an endothermic feature between 400 and 490 K, attributed to devitrification, the release of enthalpy stored in the glassy structure, and a subsequent sharp exothermic peak between 520 and 620 K, associated with the cold crystallisation of the sample upon further heating.

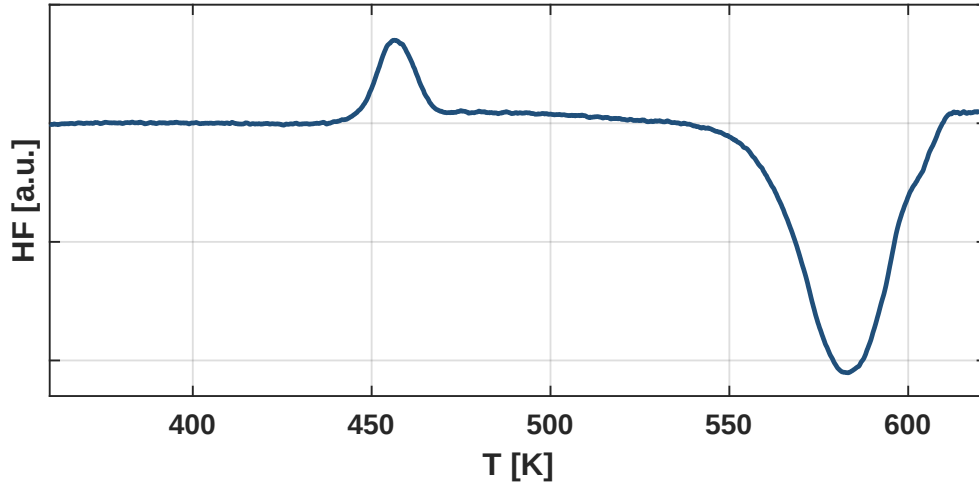


Figure 5.20: Representative heat flow (HF) curve for a sample densified at 1.1 GPa and measured with a heating rate of 500 K/s. The low-temperature endothermic feature corresponds to devitrification, while the high-temperature exothermic peak arises from crystallisation.

To ensure reproducibility and reduce statistical uncertainties, each measurement was repeated on two to three pieces of the same sample. An example of repeated HF curves for a sample densified at 1.1 GPa is shown in Fig. 5.21, illustrating an overlap between the scans sufficient to confirm the reliability of the procedure.

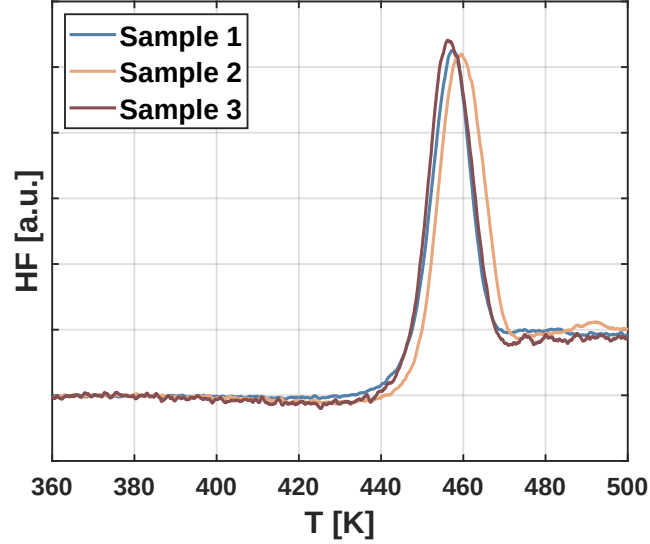


Figure 5.21: Reproducibility for FDSC measurements at $P_d = 1.1$ GPa, showing consistent HF curves across different pieces of the densified sample.

Focusing on the devitrification region, Fig. 5.22a) compares the HF curves of samples densified at increasing densification pressures P_d . A clear evolution emerges: the endothermic devitrification peak, initially dominant at low P_d , gradually diminishes in intensity with increasing pressure and eventually disappears. Simultaneously, an exothermic feature develops at lower temperatures. This crossover indicates a profound change in the glassy state: as the densification pressure increases, the enthalpy recovery upon heating is progressively suppressed and ultimately turns into an energy release. In thermodynamic terms, the glass becomes increasingly *rejuvenated* and the degree of rejuvenation grows systematically with P_d .

A closer comparison between the ambient-pressure curve and that of the sample densified at 1.1 GPa highlights marked differences in the shape and position of the peaks. At ambient pressure, the endothermic peak appears at lower temperatures and exhibits a steeper rise than at 1.1 GPa. This behaviour can be rationalised by the pressure-induced change in the kinetic fragility of the glass: compression drives the system from a more fragile state at ambient pressure toward a stronger glassy state. Fragile glasses respond more abruptly to temperature variations, leading to sharper enthalpy peaks and devitrification at lower temperatures. In contrast, stronger glasses display a more gradual response and higher onset temperatures for devitrification, consistent with the densification process.

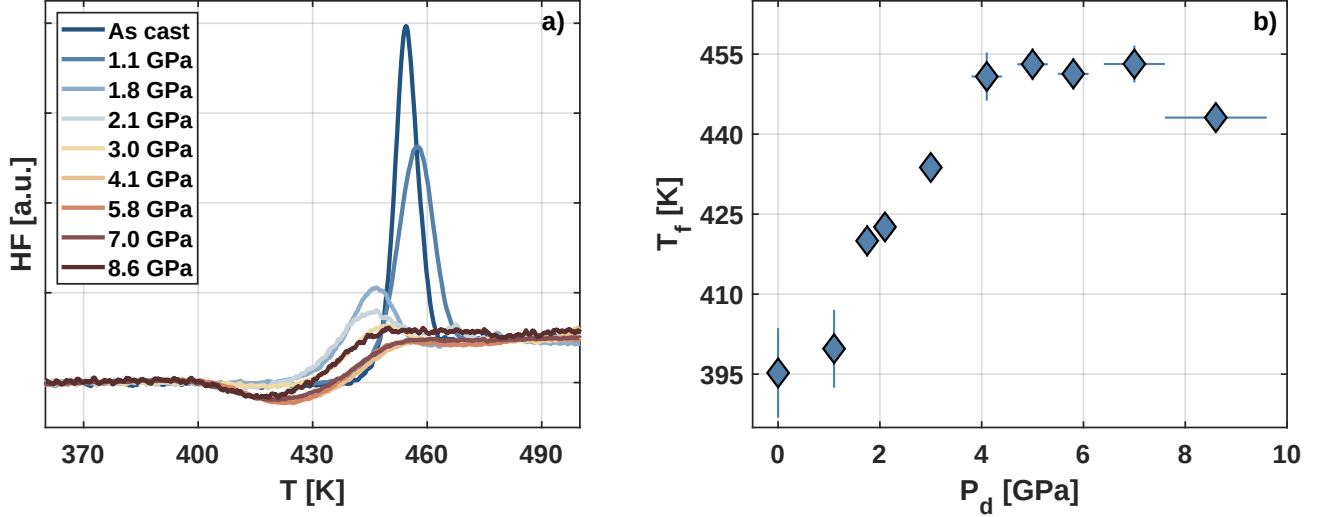


Figure 5.22: a) HF curves in the devitrification region for samples densified at various P_d , showing the suppression of the endothermic recovery peak and the emergence of an exothermic feature at higher pressures. The data are measured with a probing rate of 500 K/s. b) Fictive temperature T_f as a function of P_d , determined via the Moynihan method. Error bars represent the standard deviation from repeated measurements on different pieces of the same sample.

To quantify this rejuvenation effect, we determined the fictive temperature T_f of each sample using the Moynihan method (Sec. 3.5). The results, summarised in Fig. 5.22b), show that T_f rises steeply up to ~ 4 GPa before reaching a more gradual plateau at higher pressures. Remarkably, this trend parallels the structural evolution captured during *in-situ* HP measurements (Fig. 5.14), including the signatures of the pressure-induced amorphous-amorphous transition. Remarkably, the transition occurs at the same pressure across the dynamical, structural, and calorimetric perspectives, even though the latter is measured *ex-situ*. The agreement between calorimetric and scattering measurements highlights two key points: (i) the structural changes induced by compression are largely irreversible and persist after pressure release, and (ii) these changes occur rapidly, within just 10 minutes of densification, much faster than the characteristic timescales used to perform XPCS measurements.

An intriguing observation is a decrease of T_f at $P_d = 8.6$ GPa, suggesting a partial loss of rejuvenation. This behaviour resembles the non-monotonic pressure dependence of the dynamics, where acceleration begins near 10 GPa. Further *ex-situ* calorimetric measurements at higher pressures are needed to

confirm or refute this trend.

At first glance, the association of increased rejuvenation with slower dynamics might appear paradoxical, as rejuvenated glasses typically exhibit faster relaxation. However, as reported in other glass-forming systems [263], isothermal compression shifts T_g to higher temperatures, effectively pushing the system deeper into the glassy state and thus decelerating the relaxation at elevated pressures. In this sense, the densified sample is still thermodynamically “younger” (more rejuvenated) than its non-densified counterpart.

Finally, we note that the uncertainties in T_f increase significantly at high P_d . This is due to the solidification of the silicone oil pressure-transmitting medium above ~ 5.5 GPa, which causes a progressive loss of the hydrostatic condition. The onset of shear stresses leads to non-uniform pressure distributions within the DAC. To account for this, multiple ruby spheres were placed at different locations in the sample chamber, and the pressure was determined through each ruby. At low pressures, the rubies reported nearly identical values, yielding small uncertainties. At higher pressures, however, shear resulted in considerable pressure variation across the chamber, leading to a larger pressure variance.

It is therefore possible that the high-pressure trend of T_f , including the decrease near 8.6 GPa, might partly reflect the loss of hydrostaticity. Nevertheless, since shear typically promotes additional rejuvenation, the observed decrease in T_f is most likely intrinsic to the sample rather than an artefact of non-hydrostatic conditions.

5.3.3 Discussion

Our results on $\text{Ge}_{15}\text{Te}_{85}$ reveal a clear amorphous-amorphous transition (AAT) occurring at $P_{\text{AA}} = (4.2 \pm 0.8)$ GPa, as evidenced by the structural analysis. An unexpected dynamical behaviour accompanies this transition: the relaxation time τ first increases up to ~ 10 GPa, then decreases sharply between 10 and 12 GPa, before increasing again at higher pressures. In parallel, the stretching exponent β increases above 10 GPa, signalling enhanced internal stresses. Ex-situ calorimetry on densified samples independently confirms the occurrence of the AAT, showing that the effect is permanent and associated with a progressive rejuvenation of the glass.

To interpret these findings, it is useful to compare our results with those of similar chalcogenide glasses. In-situ XRD studies by Fujita *et al.* [102] demonstrated an AAT in the covalent GeSe (~ 3.7 GPa) and in the phase-change material GeTe (~ 1.8 GPa). In both cases, the transition leads to a high-density amorphous state with increased symmetry, reduced compressibility, and a more metallic-like character, closely resembling what we observe

in $\text{Ge}_{15}\text{Te}_{85}$. Structurally, the AAT has been linked to the breakdown of Peierls-like distortions (PLDs), distorted octahedral units characterised by alternating short and long bonds. In the amorphous state, these distortions give rise to a quasi-periodic medium-range order. The transition corresponds to the gradual disappearance of PLDs, accompanied by a reduction of tetrahedral units in favour of more symmetric octahedral environments. The higher P_{AA} of GeSe compared to GeTe is consistent with its stronger covalency, which requires greater pressure to overcome the PLDs. Since $\text{Ge}_{15}\text{Te}_{85}$ is known to exhibit PLDs in the liquid state at ambient pressure [257], it is reasonable to assume that they also persist in the glass and that their progressive suppression under compression drives the observed AAT, as in GeSe and GeTe.

However, combined density-functional simulations and high-energy X-ray and neutron diffraction measurements by Kalikka *et al.* [272] indicate that the structure of $\text{Ge}_{15}\text{Te}_{85}$ is more complex. The local environment of Ge at ambient conditions is heterogeneous, comprising both tetrahedral GeTe_4 units (four-fold coordinated) and defective octahedral motifs in which one or more bonds are missing. At ambient pressure, these defective octahedral motifs are Peierls-like distorted, with alternating long and short bonds. This coexistence suggests that the suppression of PLDs alone cannot fully explain the pressure-induced transformations in $\text{Ge}_{15}\text{Te}_{85}$. Insight comes from a recent X-ray absorption spectroscopy (XAS) study by Mijit *et al.* [273] on GeSe_2 up to 160 GPa, which shows a tetrahedral-to-octahedral transition. This finding implies that the high-pressure response of $\text{Ge}_{15}\text{Te}_{85}$ could involve a mixed mechanism, combining the tetrahedral-to-octahedral transition typical of GeSe_2 with the suppression of PLDs dominant in GeTe.

The anomalous behaviour of τ and the rejuvenation upon densification cannot, however, be explained solely by structural arguments. The XAS study of GeSe_2 provides important clues, since it not only reveals local structural rearrangements but also changes in the nature of the chemical bonding. In GeSe_2 , the AAT begins around 10 GPa, while the transformation to the high-density amorphous phase extends up to 30 GPa and full stabilisation is only reached near 120 GPa. In the low-density amorphous region (<10 GPa), the structure remains mostly tetrahedral. In the transition region (10-30 GPa), medium-range order progressively decreases, accompanied by an increase in disorder. Between 30 and 80 GPa, the system approaches the HDA state, with a significant increase in “wrong” homopolar bonds (Ge-Ge and Se-Se), which are unfavourable in simple tetrahedral glasses, where ideally only heteropolar bonds should be present. Their appearance enhances the so-called chemical disorder, as atoms occupy non-ideal sites or form bonds with atoms of the same species. This mixed bonding topology raises the in-

ternal energy of the system. Above 120 GPa, GeSe_2 reaches a fully stabilised octahedral structure.

The study of GeSe_2 clearly indicates that the transition from LDA to HDA is not abrupt but gradual, extending over nearly 20 GPa, and requires pressures up to 80 GPa to be completed and up to 120 GPa to achieve full stabilisation. A similar scenario may also apply to related systems such as GeTe , GeSe , and $\text{Ge}_{15}\text{Te}_{85}$. The absence of comparable structural observations in these glasses is most likely due to the limited pressure ranges explored so far, which did not exceed 15 GPa. In contrast, the dynamics, being more sensitive than the structure, reveals that the effect of the AAT extends over a much broader pressure range: in $\text{Ge}_{15}\text{Te}_{85}$ the acceleration of τ begins about 5 GPa after P_{AA} . The observed non-monotonicity can be rationalised in terms of increasing chemical disorder. As pressure rises, the formation of wrong homopolar bonds is probable, placing the system in a higher-energy state where structural relaxation is facilitated and dynamics accelerates. This interpretation is supported by the higher values of β observed above 10 GPa, consistent with enhanced internal stress. A growing chemical disorder with increasing pressure would also account for the rejuvenation observed in densified samples: the proliferation of wrong bonds raises the internal energy and shifts the glass to a less stable state. Moreover, it provides a natural explanation for why the fictive temperature T_f follows a pressure dependence that mirrors the structural evolution. Unfortunately, calorimetric measurements at densification pressures above 10 GPa are currently lacking due to experimental challenges, such as good HP control and difficulty in recovering the sample after densification in the DAC. Extending the study to at least 15 GPa is crucial, since the value of T_f measured at ~ 9 GPa suggests a decreasing trend. While this could be attributed to noise, it may also indicate that T_f mimics the non-monotonic evolution of τ .

Similar non-monotonic behaviour of $\tau(P)$ has also been observed in a Ce-based metallic glass via in-situ HP-XPCS (Chapter 2), although limited statistics preclude determining whether the onset coincides with P_{AA} or occurs above it. By contrast, in the Pt-based metallic glass [6], no AAT has been detected: only a dynamical anomaly is present, and its trend is reversed compared to $\text{Ge}_{15}\text{Te}_{85}$ and the Ce-based system. This highlights that the non-monotonic behaviour of τ does not always correlate with a structural AAT and that its exact manifestation can vary between systems. The rejuvenation we observe in $\text{Ge}_{15}\text{Te}_{85}$, however, parallels that in Ce-based metallic glasses, reinforcing the view that such dynamical anomalies are not confined to metallic systems but represent a more general response of glasses under high-pressure compression.

In summary, the combined structural, dynamical, and calorimetric evidence suggests that the AAT in $\text{Ge}_{15}\text{Te}_{85}$ could involve both a tetrahedral-to-octahedral transition, as in GeSe_2 , and the suppression of Peierls-like distortions in octahedral environments, as in GeTe . The anomalous dynamics and rejuvenation effects indicate an additional role of chemical disorder arising from pressure-induced homopolar bonding. The transition, therefore, extends over a much broader pressure range than revealed by structure alone and likely requires pressures beyond those explored so far for full completion.

Altogether, these findings suggest that the AAT in $\text{Ge}_{15}\text{Te}_{85}$ is a gradual, multi-stage process extending well beyond the structural signature at ~ 4 GPa, with its completion that may require pressures well above those currently explored (> 15 GPa). Future calorimetric experiments at higher densification pressures will be essential to confirm the proposed link between the fictive temperature and the non-monotonic evolution of the relaxation dynamics. An intriguing open question concerns the long-time behaviour of the dynamics under constant pressure: for instance, if the system were held at ~ 11 GPa for an extended period, would it progressively evolve towards a more stable configuration and thereby suppress the anomalous acceleration of τ observed at higher pressures, or would the same non-monotonic behaviour persist regardless of equilibration time?

5.4 Conclusions

Our investigations of $\text{Ge}_{15}\text{Sb}_{85}$ and $\text{Ge}_{15}\text{Te}_{85}$ under X-ray irradiation and of $\text{Ge}_{15}\text{Te}_{85}$ under high-pressure compression demonstrate that the stability of these chalcogenide glasses exerts a decisive influence on their microscopic dynamics.

Under irradiation, we found that $\text{Ge}_{15}\text{Sb}_{85}$ readily undergoes a photo-induced yielding transition, reaching a stationary liquid-like regime almost instantaneously once the temperature approaches a fraction of T_g . This behaviour reflects its less rigid structure, where loose bonding and an active secondary relaxation promote local mobility, making the glass more susceptible to changes. By contrast, $\text{Ge}_{15}\text{Te}_{85}$ shows remarkable resistance to irradiation: its dynamics evolves much more slowly and displays clear recovery once the beam is removed, all pointing to a higher intrinsic resistance that prevents a permanent transition to a yielding state. The comparison between these two compositionally similar but structurally distinct glasses highlights the delicate interplay between atomic mass, network topology, and intrinsic relaxation channels in determining how stability mediates beam-driven dynamics.

When probing $\text{Ge}_{15}\text{Te}_{85}$ under compression, however, the picture changes: the glass undergoes an amorphous-amorphous transition near 4 GPa, accompanied by a non-monotonic evolution of the relaxation time and calorimetric signatures of rejuvenation. These findings indicate that pressure not only suppresses Peierls-like distortions but also promotes a gradual tetrahedral-to-octahedral transition, together driving the system toward more symmetric coordination environments. At the same time, compression introduces chemical disorder through the formation of homopolar bonds, which elevates the internal energy and shifts the glass into a less stable state, thereby accelerating its dynamics despite the overall densification. The observation that compression can rejuvenate even the intrinsically more rigid $\text{Ge}_{15}\text{Te}_{85}$ demonstrates that the route by which stability is perturbed, via both structural reorganisation and bond rearrangements, is as important as the underlying structural rigidity of the glass itself.

Altogether, our results show that changing the stability of chalcogenide glasses has a profound impact on their microscopic dynamics, but the outcome depends on both the material and the perturbation pathway. X-ray irradiation strongly affects systems such as $\text{Ge}_{15}\text{Sb}_{85}$, leading to irreversible yielding, while leaving more robust systems like $\text{Ge}_{15}\text{Te}_{85}$ largely unaffected. In contrast, high-pressure compression can induce rejuvenation even in stronger glasses, with chemical disorder acting as the driving mechan-

ism. These complementary approaches demonstrate that the dynamics of disordered materials emerge from a subtle balance of intrinsic structure and external perturbations, and that stability, not merely composition, sets the stage for how glasses respond to irradiation or pressure.

Chapter 6

Conclusions

The stability of a glass reflects how deeply the system is trapped within its Potential Energy Landscape (PEL) and can be tuned both by preparation conditions and by external treatments such as irradiation or pressure. The results presented in this Thesis show how these parameters act in distinct ways, affecting vibrational and relaxational properties.

To study the dependence of the vibrational properties on the glass stability, I have compared the vibrational density of state of a standard glass with that of an ultrastable glass of the same composition produced by physical vapour deposition. Measurements of the vibrational density of states (DOS) down to 0.07 THz using Nuclear Resonance Analysis of Inelastic X-ray Scattering revealed in the ultrastable glass a boson peak near 0.3 THz with reduced intensity compared to ordinary glasses, confirming the strong dependence of the BP on stability. Reconstruction of the harmonic DOS below the boson peak and comparison of the calculated specific heat to experimental C_p data demonstrated that the harmonic excess over the Debye prediction remains essentially unchanged between ordinary and ultrastable glasses, yet is nearly an order of magnitude larger than in crystalline TPD, showing that this vibrational contribution is controlled primarily by structural disorder rather than by stability. In contrast, two-level systems are strongly suppressed in ultrastable glasses, highlighting that increased stability reduces defects associated with the double-well potential in the PEL.

To investigate how stability influences relaxation dynamics, I adopted two complementary approaches. First, I examined the effect of X-ray irradiation on the stability of two similar Ge-based compositions, $\text{Ge}_{15}\text{Sb}_{85}$ and $\text{Ge}_{15}\text{Te}_{85}$. The substitution of Sb by Te produces a stronger glassy matrix and suppresses a secondary β -relaxation process. Second, I kept the irradiation dose fixed in $\text{Ge}_{15}\text{Te}_{85}$ and studied how its structure and dynamics respond to high-pressure compression, linking these changes to the variations

in thermodynamic stability.

Irradiation experiments with X-ray Photon Correlation Spectroscopy (XPCS) on $\text{Ge}_{15}\text{Sb}_{85}$ and $\text{Ge}_{15}\text{Te}_{85}$ glasses hint that irradiation drives both systems towards rejuvenation, but through markedly different pathways. In $\text{Ge}_{15}\text{Sb}_{85}$, the dynamics is stationary, stretched and almost entirely dose-induced, leading to a complete and rapid local yielding. In contrast, in $\text{Ge}_{15}\text{Te}_{85}$ the relaxation dynamics is characterised by a strong aging and a crossover from compressed to stretched dynamics, and the irradiation induces rejuvenation only partially and more slowly, reflecting its higher mass and structural rigidity.

Finally, as said, compression at high pressures offers a complementary route to manipulate glass stability. High-pressure XPCS on $\text{Ge}_{15}\text{Te}_{85}$ revealed that pressure enhances density and medium-range order, eventually driving an amorphous-amorphous transition (LDA-HDA) starting around 4 GPa. The corresponding dynamics does not evolve monotonically: relaxation first slows down, then unexpectedly accelerates between 10 and 12 GPa, before slowing again at higher pressures. This anomalous acceleration points to the emergence of homopolar bonds and chemical disorder, which destabilise the local structure by increasing the internal energy and facilitating rearrangements. *Ex-situ* calorimetry proved that these structural changes are mostly permanent and also induce thermodynamic rejuvenation, despite the pronounced densification and structural ordering. Such counter-intuitive pressure responses have also been reported in metallic glasses using both macroscopic and microscopic techniques [6, 168, 263], where they have been linked to the appearance of a secondary local minimum in the PEL at intermediate pressures [167]. Our results show that a similar phenomenology can probably be extended also to chalcogenide glasses. Our data show that pressure promotes overall rejuvenation, but its effect on microscopic dynamics is non-trivial, reflecting a complex interplay between densification, bonding, and disorder.

Overall, these findings demonstrate that glass stability governs microscopic vibrational and relaxational dynamics through intertwined effects of composition, density, packing, disorder, and bonding. Preparation protocols that enhance stability determine the initial depth in the PEL, suppressing tunnelling states and reducing the boson peak, while irradiation injects energy that drives the system toward shallower basins, and pressure reshapes the PEL by altering basin topology and energy barriers. Stability thus emerges as a multifaceted property, governed by the PEL's topology, with different parameters selectively influencing vibrational anomalies, tunnelling defects, and structural dynamics.

6.1 Future perspectives

The work presented in this Thesis provides new insights into the role of glass stability at both vibrational and relaxational dynamical scales. The results open several promising directions for further research, spanning both fundamental and methodological aspects.

Our findings show that the deviation of the DOS from the Debye level is essentially insensitive to stability, whereas the boson peak intensity is strongly suppressed in the ultrastable glass. This contrasts with recent simulations predicting a stability dependence of low-frequency vibrations and leaves open the long-standing debate on whether the excess modes originate from quasi-localised vibrations or from acoustic-phonon damping near the Ioffe-Regel limit. Future work should focus on directly probing the stability dependence of sound attenuation in the Rayleigh-scattering regime, now accessible in thin films, and on correlating these measurements with the low-frequency DOS tail. Additional NRAIXS measurements at lower temperatures could provide direct access to the first deviation from the Debye level, but under the assumption of exclusively harmonic origin. Such combined experiments would help clarify the microscopic origin of the boson-peak anomaly and reconcile experimental and numerical results. Finally, it would be interesting to investigate the role of anisotropy in both the boson-peak intensity and the Debye level by performing measurements on ultrastable glasses deposited at different temperatures below T_g , thus tuning the structural anisotropy.

Regarding relaxation dynamics, the interplay between atomic composition, bonding nature, and response under extreme conditions opens further questions. A natural extension concerns the effect of the X-ray irradiation on glasses. Our study demonstrated that the response to irradiation depends strongly on the material. Future work could systematically investigate a broader range of glass compositions to disentangle the respective roles of bonding type, atomic mass, network topology, and local heterogeneity. Combining XPCS with complementary approaches, such as dynamical simulations under irradiation, would be especially valuable for clarifying the microscopic rearrangements responsible for the observed differences. In addition, combined calorimetry and XPCS experiments under identical conditions could establish a direct correlation between glass stability, stored enthalpy, and irradiation effects. Such measurements would make it possible to determine whether X-ray-induced rejuvenation can be systematically mapped onto conventional thermal rejuvenation and aging processes. Finally, it would be worth testing whether prolonged X-ray exposure could drive $\text{Ge}_{15}\text{Te}_{85}$ into a

permanently yielded state.

Our high-pressure studies revealed a non-monotonic evolution of the relaxation time across the LDA-HDA transition, suggesting a complex interplay between densification, medium-range ordering, and bond reconfiguration. This calls for systematic HP-XPCS investigations over extended pressure ranges, possibly combined with high-resolution EXAFS or Raman spectroscopy, to track local structural and chemical transformations and their correlation with dynamic slowdowns or speed-ups. Further measurements during decompression could provide insight into the non-monotonicity of the dynamics as a function of pressure. Since calorimetric data showed that the effect of pressure is largely permanent, no non-monotonic behaviour would be expected upon decompression because the transition has already occurred at higher pressures. Should the non-monotonicity reappear, it could point to additional mechanisms beyond the LDA-HDA transformation. It would also be interesting to investigate how the non-monotonic behaviour evolves if compression is applied for very long periods at pressures below those where this anomaly emerges. If the system is held at a given pressure for a long time, would it gradually settle into a more stable configuration, suppressing the non-monotonic behaviour, or would the non-monotonic behaviour persist, independently of equilibration time? Extending these studies to other glass compositions under similar conditions could provide further insight into the generality of this behaviour.

Finally, the potential technological relevance of these studies should not be overlooked. Understanding how external fields such as X-rays and pressure affect the relaxation dynamics of PCMs and non-PCMs could provide useful guidelines for tailoring stability and switching properties in memory applications. For instance, controlled irradiation or pressure treatment could become novel routes to tune the structural state of a PCM, offering alternative methods of cycling beyond conventional thermal protocols.

Overall, this work opens new avenues for understanding and controlling the complex dynamics of glasses, providing a foundation for both fundamental insights and practical strategies to manipulate stability and relaxation in functional materials.

Conclusions

La stabilité d'un verre reflète la profondeur avec laquelle le système est piégé dans son *Paysage d'Énergie Potentielle* (PEP, ou PEL en anglais) et peut être modulée à la fois par les conditions de préparation et par des traitements externes tels que l'irradiation ou la pression. Les résultats présentés dans cette Thèse montrent comment ces paramètres agissent de manière distincte, en affectant les propriétés vibrationnelles et relaxationnelles.

Pour étudier la dépendance des propriétés vibrationnelles à la stabilité du verre, j'ai comparé la densité d'états vibrationnelle d'un verre standard à celle d'un verre ultrastable de même composition, produit par dépôt physique en phase vapeur (*Physical Vapor Deposition*, PVD). Les mesures de la densité d'états vibrationnelle (DOS) jusqu'à 0,07 THz, réalisées par analyse nucléaire résonante de la diffusion inélastique des rayons X (NRAIXS), ont révélé dans le verre ultrastable un *boson peak* près de 0,3 THz d'intensité réduite par rapport aux verres ordinaires, confirmant la forte dépendance du *boson peak* à la stabilité. La reconstruction de la DOS harmonique sous le *boson peak* et la comparaison de la capacité calorifique calculée avec les données expérimentales de C_p ont montré que l'excès harmonique par rapport à la prédiction de Debye reste essentiellement inchangé entre les verres ordinaires et ultrastables, mais demeure presque un ordre de grandeur plus élevé que dans le TPD cristallin, indiquant que cette contribution vibrationnelle est principalement contrôlée par le désordre structurel plutôt que par la stabilité. En revanche, les systèmes à deux niveaux (TLS) sont fortement supprimés dans les verres ultrastables, soulignant qu'une stabilité accrue réduit les défauts associés aux potentiels à double puits dans le PEP.

Pour explorer l'influence de la stabilité sur la dynamique de relaxation, j'ai adopté deux approches complémentaires. D'abord, j'ai examiné l'effet de l'irradiation X sur la stabilité de deux compositions à base de germanium similaires, $\text{Ge}_{15}\text{Sb}_{85}$ et $\text{Ge}_{15}\text{Te}_{85}$. Le remplacement du Sb par le Te produit une matrice vitreuse plus rigide et supprime un processus de relaxation secondaire de type β . Ensuite, j'ai maintenu la dose d'irradiation fixe dans $\text{Ge}_{15}\text{Te}_{85}$ et étudié la réponse de sa structure et de sa dynamique à la compression sous

haute pression, reliant ces changements aux variations de stabilité thermodynamique.

Les expériences d'irradiation menées par *X-ray Photon Correlation Spectroscopy* (XPCS) sur les verres $\text{Ge}_{15}\text{Sb}_{85}$ et $\text{Ge}_{15}\text{Te}_{85}$ suggèrent que l'irradiation conduit les deux systèmes vers la réjuvenation, mais selon des voies très différentes. Dans $\text{Ge}_{15}\text{Sb}_{85}$, la dynamique est stationnaire, étirée et presque entièrement induite par la dose, conduisant à un *yielding* local complet et rapide. En revanche, dans $\text{Ge}_{15}\text{Te}_{85}$, la dynamique de relaxation est caractérisée par un fort vieillissement et un passage progressif d'une dynamique comprimée à une dynamique étirée ; l'irradiation n'y induit qu'une réjuvenation partielle et plus lente, reflétant sa masse plus élevée et sa rigidité structurale accrue.

Enfin, comme mentionné, la compression à haute pression constitue une voie complémentaire pour moduler la stabilité vitreuse. Les expériences de XPCS sous haute pression sur $\text{Ge}_{15}\text{Te}_{85}$ ont montré que la pression augmente la densité et l'ordre à moyenne distance, entraînant finalement une transition amorphe-amorphe (LDA-HDA) à partir d'environ 4 GPa. La dynamique correspondante n'évolue pas de manière monotone : la relaxation ralentit d'abord, puis s'accélère de façon inattendue entre 10 et 12 GPa, avant de ralentir de nouveau à des pressions plus élevées. Cette accélération anormale suggère l'apparition de liaisons homopolaires et d'un désordre chimique, qui déstabilisent la structure locale en augmentant l'énergie interne et en facilitant les réarrangements. La calorimétrie *ex-situ* a montré que ces changements structuraux sont en grande partie permanents et induisent également une réjuvenation thermodynamique, malgré la densification prononcée et le renforcement de l'ordre structural. De telles réponses contre-intuitives à la pression ont également été rapportées dans les verres métalliques par des techniques macroscopiques et microscopiques [6, 168, 263], où elles ont été attribuées à l'apparition d'un minimum local secondaire dans le PEP à des pressions intermédiaires [167]. Nos résultats montrent qu'une phénoménologie similaire peut probablement être étendue aux verres chalcogénures. Nos données indiquent que la pression favorise globalement la réjuvenation, mais son effet sur la dynamique microscopique est non trivial, reflétant une interaction complexe entre densification, liaisons et désordre.

Dans l'ensemble, ces résultats démontrent que la stabilité vitreuse gouverne les dynamiques vibrationnelles et relaxationnelles microscopiques à travers des effets entrelacés de composition, densité, compacité, désordre et nature des liaisons. Les protocoles de préparation qui augmentent la stabilité déterminent la profondeur initiale dans le PEP, supprimant les états de tunnel et réduisant le *boson peak*, tandis que l'irradiation injecte de l'énergie qui entraîne le système vers des bassins plus superficiels, et que la pression recon-

figure le PEP en modifiant la topologie des bassins et les barrières d'énergie. La stabilité apparaît ainsi comme une propriété multifacette, gouvernée par la topologie du PEP, différents paramètres influençant sélectivement les anomalies vibrationnelles, les défauts de tunnel et la dynamique structurale.

6.2 Perspectives futures

Le travail présenté dans cette Thèse apporte de nouveaux éclairages sur le rôle de la stabilité vitreuse aux échelles dynamiques vibrationnelles et relaxationnelles. Les résultats ouvrent plusieurs pistes prometteuses pour des recherches ultérieures, tant sur le plan fondamental que méthodologique.

Nos résultats montrent que l'écart de la DOS par rapport au niveau de Debye est essentiellement insensible à la stabilité, alors que l'intensité du *boson peak* est fortement supprimée dans le verre ultrastable. Cela contraste avec des simulations récentes prédisant une dépendance de la stabilité pour les vibrations à basse fréquence et laisse ouverte la question, débattue depuis longtemps, de savoir si les modes excédentaires proviennent de vibrations quasi-localisées ou de l'amortissement des phonons acoustiques près de la limite d'Ioffe–Regel. Les travaux futurs devraient se concentrer sur la mesure directe de la dépendance de l'atténuation sonore à la stabilité dans le régime de diffusion de Rayleigh, désormais accessible dans les films minces, et sur la corrélation de ces mesures avec la queue basse fréquence de la DOS. Des mesures NRAIX supplémentaires à plus basse température pourraient fournir un accès direct à la première déviation par rapport au niveau de Debye, mais sous l'hypothèse d'une origine exclusivement harmonique. De telles expériences combinées contribueraient à clarifier l'origine microscopique de l'anomalie du *boson peak* et à rapprocher les résultats expérimentaux et numériques. Enfin, il serait intéressant d'étudier le rôle de l'anisotropie dans l'intensité du *boson peak* et le niveau de Debye en effectuant des mesures sur des verres ultrastables déposés à différentes températures en dessous de T_g , afin de moduler l'anisotropie structurale.

Concernant la dynamique de relaxation, l'interaction entre composition atomique, nature des liaisons et réponse sous conditions extrêmes soulève d'autres questions. Une extension naturelle concerne l'effet de l'irradiation X sur les verres. Notre étude a montré que la réponse à l'irradiation dépend fortement du matériau. De futurs travaux pourraient étudier systématiquement un éventail plus large de compositions vitreuses pour démêler les rôles respectifs du type de liaison, de la masse atomique, de la topologie du réseau et de l'hétérogénéité locale. L'association de la XPCS à des approches complémentaires, telles que des simulations dynamiques sous irradiation, serait

particulièrement précieuse pour clarifier les réarrangements microscopiques responsables des différences observées. De plus, des expériences combinées de calorimétrie et de XPCS dans des conditions identiques pourraient établir une corrélation directe entre la stabilité vitreuse, l'enthalpie stockée et les effets de l'irradiation. Ces mesures permettraient de déterminer si la réjuvenation induite par les rayons X peut être systématiquement reliée aux processus conventionnels de réjuvenation et de vieillissement thermiques. Enfin, il serait pertinent de tester si une exposition prolongée aux rayons X pourrait amener $\text{Ge}_{15}\text{Te}_{85}$ dans un état de *yielding* permanent.

Nos études à haute pression ont révélé une évolution non monotone du temps de relaxation au travers de la transition LDA-HDA, suggérant une interaction complexe entre densification, organisation à moyenne distance et reconfiguration des liaisons. Cela appelle à des investigations systématiques par HP-XPCS sur des plages de pression plus étendues, éventuellement combinées à des mesures EXAFS haute résolution ou à la spectroscopie Raman, afin de suivre les transformations structurales et chimiques locales et leur corrélation avec les ralentissements ou accélérations dynamiques. Des mesures supplémentaires lors de la décompression pourraient apporter un éclairage sur la non-monotonie de la dynamique en fonction de la pression. Étant donné que les données calorimétriques ont montré que l'effet de la pression est en grande partie permanent, aucun comportement non monotone ne serait attendu lors de la décompression, car la transition s'est déjà produite à haute pression. Si la non-monotonie réapparaissait, cela pourrait révéler des mécanismes supplémentaires au-delà de la transformation LDA-HDA. Il serait également intéressant d'examiner comment le comportement non monotone évolue si la compression est appliquée pendant de longues périodes à des pressions inférieures à celles où cette anomalie émerge. Si le système est maintenu à une pression donnée pendant longtemps, se stabiliserait-il progressivement dans une configuration plus stable, supprimant le comportement non monotone, ou celui-ci persisterait-il indépendamment du temps d'équilibration ? Étendre ces études à d'autres compositions vitreuses dans des conditions similaires pourrait apporter un éclairage supplémentaire sur le caractère général de ce comportement.

Enfin, la pertinence technologique potentielle de ces études ne doit pas être négligée. Comprendre comment des champs externes tels que les rayons X et la pression influencent la dynamique de relaxation des matériaux à changement de phase (PCM) et des non-PCM pourrait fournir des indications utiles pour ajuster la stabilité et les propriétés de commutation dans les applications de mémoire. Par exemple, une irradiation ou un traitement sous pression contrôlés pourraient devenir de nouvelles voies pour ajuster l'état structural d'un PCM, offrant des méthodes alternatives de cyclage au-delà

des protocoles thermiques conventionnels.

Dans l'ensemble, ce travail ouvre de nouvelles perspectives pour la compréhension et le contrôle de la dynamique complexe des verres, fournissant une base à la fois pour des avancées fondamentales et pour des stratégies pratiques visant à manipuler la stabilité et la relaxation dans les matériaux fonctionnels.

Appendix A

In order to prove the expressions for I_0 and $f(\mathbf{k})$ in Eq. (3.2.35), the zeroth and the first momenta for the probability of absorption $W(\mathcal{E})$ are evaluated. The integration by parts of $W(\mathcal{E})$ is

$$W(\mathcal{E}) = \int \frac{d\tau}{2\pi} \exp(-i\mathcal{E}\tau) \phi(\tau) = \frac{1}{i\mathcal{E}} \int \frac{d\tau}{2\pi} \exp(-i\mathcal{E}\tau) \frac{d\phi(\tau)}{d\tau} , \quad (\text{A.1})$$

where

$$\phi(\tau) = \exp\left(-\frac{\Gamma}{2}|\tau|\right) F(\mathbf{k}, \tau) , \quad (\text{A.2})$$

since both $\phi(\tau)$ and its derivative go to zero for $|\tau| \rightarrow 0$. The zeroth momentum of $W(\mathcal{E})$ is

$$\begin{aligned} \langle \mathcal{E}^0 \rangle_W &= \int d\mathcal{E} W(\mathcal{E}) = \int \int d\mathcal{E} \frac{d\tau}{2\pi} \exp(-i\mathcal{E}\tau) \phi(\tau) = \\ &= \int d\tau \delta(\tau) \phi(\tau) = \phi(0) = 1 \times \exp(-M(\mathbf{k}, 0)) \exp(M(\mathbf{k}, 0)) = 1 , \end{aligned} \quad (\text{A.3})$$

which proves the right normalization for a probability distribution. The first momentum is

$$\begin{aligned} \langle \mathcal{E}^1 \rangle_W &= \int d\mathcal{E} W(\mathcal{E}) \mathcal{E} = \int \int d\mathcal{E} \frac{d\tau}{2\pi} \exp(-i\mathcal{E}\tau) \phi(\tau) \mathcal{E} = \\ &= \int \int d\mathcal{E} \frac{1}{i\mathcal{E}} \frac{d\tau}{2\pi} \exp(-i\mathcal{E}\tau) \frac{d\phi(\tau)}{d\tau} \mathcal{E} \\ &= \int d\tau \delta(\tau) \frac{d\phi(\tau)}{i d\tau} = \frac{d\phi(\tau)}{i d\tau} \Big|_{\tau=0} = \frac{dM(\mathbf{k}, \tau)}{i d\tau} \Big|_{\tau=0} . \end{aligned} \quad (\text{A.4})$$

Deriving equation (3.2.6), one obtains

$$\begin{aligned} \frac{dM(\mathbf{k}, \tau)}{i d\tau} \Big|_{\tau=0} &= \frac{E_R}{iN} \sum_{\mathbf{q}, j} \frac{|\mathbf{s} \cdot \mathbf{e}_j(\mathbf{q})|^2}{\hbar\omega_j(\mathbf{q})} \\ &\quad \times ((n_{\mathbf{q}, j} + 1) i\hbar\omega_j(\mathbf{q}) \exp(i\hbar\omega_j(\mathbf{q})\tau) - n_{\mathbf{q}, j} i\hbar\omega_j(\mathbf{q}) \exp(-i\hbar\omega_j(\mathbf{q})\tau)) \Big|_{\tau=0} = \\ &= \frac{E_R}{N} \sum_{\mathbf{q}, j} |\mathbf{s} \cdot \mathbf{e}_j(\mathbf{q})|^2 = E_R \end{aligned} \quad (\text{A.5})$$

Keeping in mind that $W_{inel}(\mathcal{E}) = W(\mathcal{E}) - W_0(\mathcal{E})$ and $W_0(\mathcal{E}) = f_{LM}(\mathbf{k})\delta(\mathcal{E})$ for $\Gamma \rightarrow 0$, one can calculate the zeroth and the first momenta of $I(\mathcal{E})$. The

zeroth momentum is

$$\begin{aligned}
\langle \mathcal{E}^0 \rangle_I &= \int d\mathcal{E} I(\mathcal{E}, \mathbf{k}) = I_0 \int \int d\mathcal{E} d\mathcal{E}' P(\mathcal{E}') W_{inel}(\mathcal{E} - \mathcal{E}') \\
&= I_0 \int d\mathcal{E}' P(\mathcal{E}') \int d\mathcal{E} (W(\mathcal{E} - \mathcal{E}') - W_0(\mathcal{E} - \mathcal{E}')) \\
&= I_0 \int d\mathcal{E}' P(\mathcal{E}') \left(1 - \int d\mathcal{E} f_{LM}(\mathbf{k}) \delta(\mathcal{E} - \mathcal{E}') \right) \\
&= I_0 \int d\mathcal{E}' P(\mathcal{E}') (1 - f_{LM}(\mathbf{k})) = I_0 (1 - f_{LM}(\mathbf{k})) ,
\end{aligned} \tag{A.6}$$

where $\langle \mathcal{E}^0 \rangle_P = Q(0) = \int d\mathcal{E} P(\mathcal{E}) = 1$ is used, since the instrumental function is normalized to 1. The first momentum is

$$\begin{aligned}
\langle \mathcal{E}^1 \rangle_I &= \int d\mathcal{E} I(\mathcal{E}, \mathbf{k}) \mathcal{E} = I_0 \int \int d\mathcal{E} d\mathcal{E}' P(\mathcal{E}') W_{inel}(\mathcal{E} - \mathcal{E}') \mathcal{E} \\
&= I_0 \int d\mathcal{E}' P(\mathcal{E}') \int d\mathcal{E} (W(\mathcal{E} - \mathcal{E}') - W_0(\mathcal{E} - \mathcal{E}')) \mathcal{E} \\
&= I_0 \int d\mathcal{E}' P(\mathcal{E}') \left(\int d\mathcal{E} W(\mathcal{E} - \mathcal{E}') \mathcal{E} - f_{LM}(\mathbf{q}) \mathcal{E}' \right) \\
&= I_0 \int d\mathcal{E}' P(\mathcal{E}') \left(\int d\tilde{\mathcal{E}} W(\tilde{\mathcal{E}})(\tilde{\mathcal{E}} + \mathcal{E}') - f_{LM}(\mathbf{q}) \mathcal{E}' \right) \\
&= I_0 \int d\mathcal{E}' P(\mathcal{E}') (E_R + \mathcal{E}' - f_{LM}(\mathbf{q}) \mathcal{E}') = I_0 (E_R + \langle \mathcal{E}^1 \rangle_P (1 - f_{LM}(\mathbf{q}))) .
\end{aligned} \tag{A.7}$$

Solving the system

$$\begin{cases} \langle \mathcal{E}^0 \rangle_I = I_0 (1 - f_{LM}(\mathbf{k})) \\ \langle \mathcal{E}^1 \rangle_I = I_0 (E_R + \langle \mathcal{E}^1 \rangle_P (1 - f_{LM}(\mathbf{q}))) \end{cases} \tag{A.8}$$

one can easily find the expressions for I_0 and $f(\mathbf{k})$.

Appendix B

We present here the Micro-Raman spectra used to characterise the effect of different laser polarisations. Figure B.1 displays spectra acquired without polarisation, with vertical polarisation, and with horizontal polarisation, all normalised to the 1291.5 cm^{-1} peak. Pronounced differences are observed

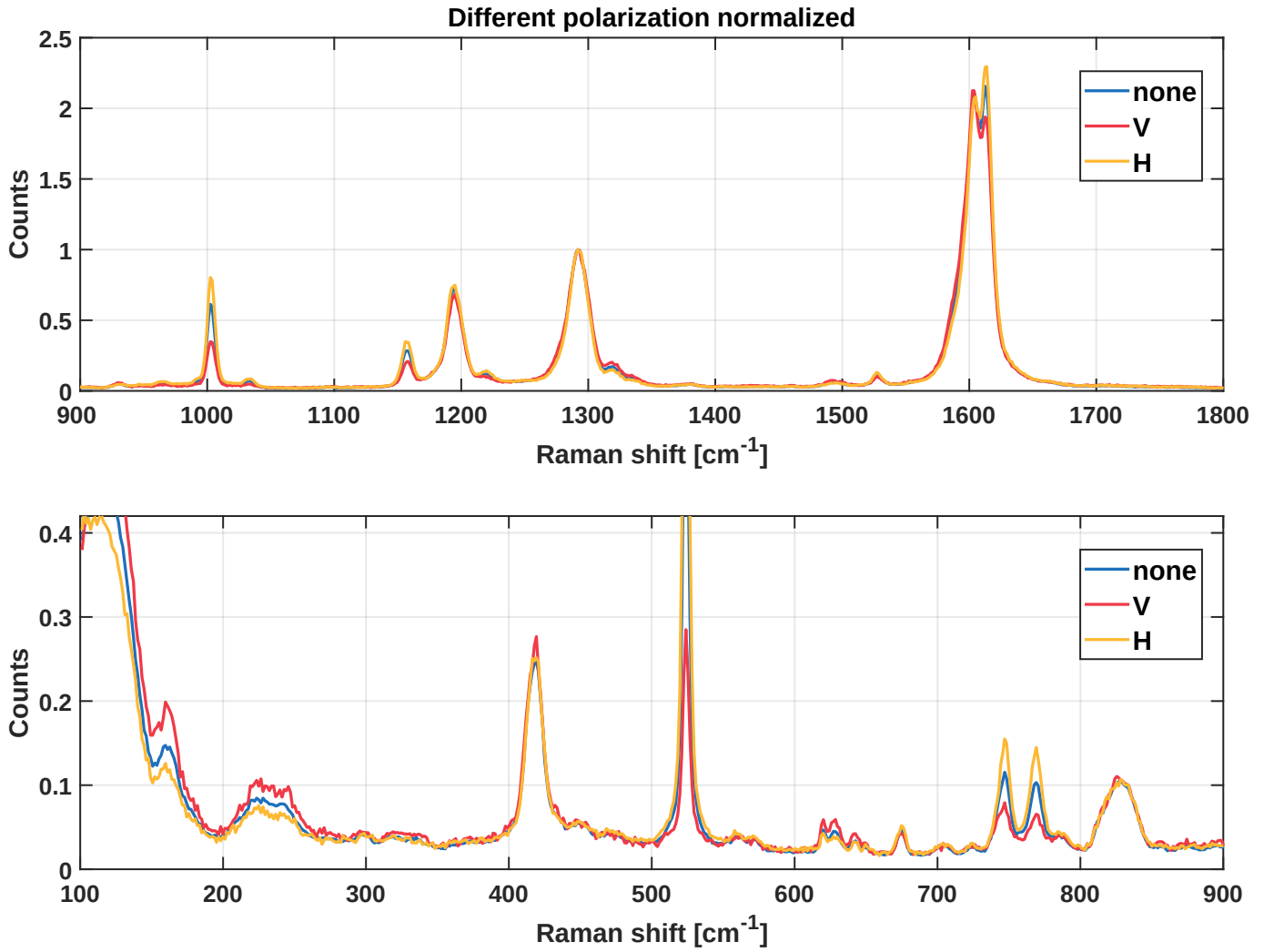


Figure B.1: Micro-Raman spectra acquired with no polarisation (blue), vertical polarisation (red), and horizontal polarisation (yellow). Peaks at 746.5 , 768.6 , 1002.1 , and 1612.9 cm^{-1} exhibit polarisation-dependent variations in intensity.

at 523.4 cm^{-1} , 746.5 cm^{-1} , 768.6 cm^{-1} , 1002.1 cm^{-1} , and in the relative intensities of the double peak near 1608 cm^{-1} . Variations also appear in the low-frequency region ($< 200\text{ cm}^{-1}$). The strong polarisation dependence of the 523.4 cm^{-1} peak originates from the silicon substrate.

In ordinary TPD samples, optical microscopy reveals visible crystalline nuclei (Figure B.2). Raman spectra measured on these nuclei show the same peak positions as non-crystalline regions but with altered relative intensities and increased amplitude (Figure B.3, bottom panel). In contrast, spectra from non-crystalline regions of different conventional samples remain consistent (Figure B.3, top panel).

The comparison between the spectra measured with Micro-Raman spectroscopy and with standard Raman spectroscopy shows a good overlap, ensuring the reliability of the standard Raman measurements.

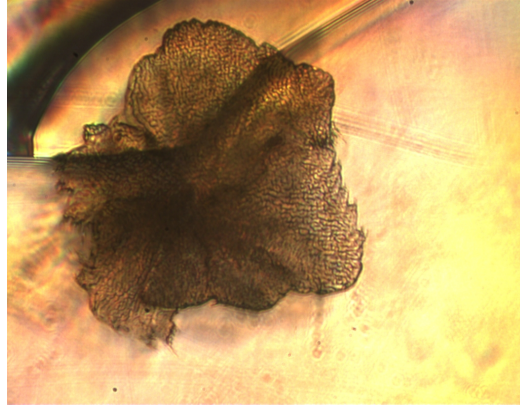


Figure B.2: A microscopic picture of the TPD conventional glass. It presents a clear crystalline nucleus.

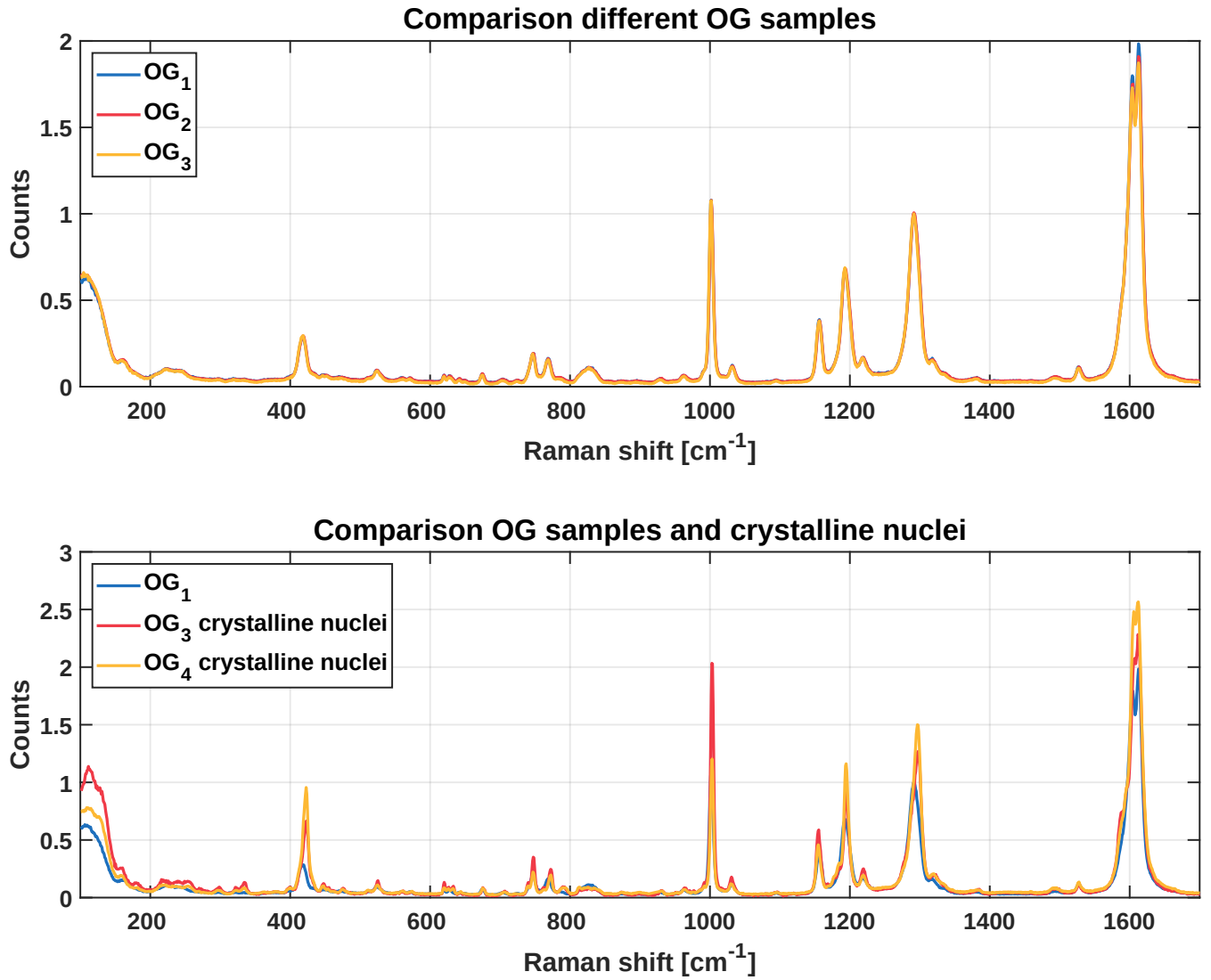


Figure B.3: Top: Raman spectra from three different conventional TPD glasses recorded in regions free of crystalline nuclei show identical peak positions and relative intensities. Bottom: Spectra from different crystalline nuclei exhibit variable relative peak intensities, while peak positions remain constant.

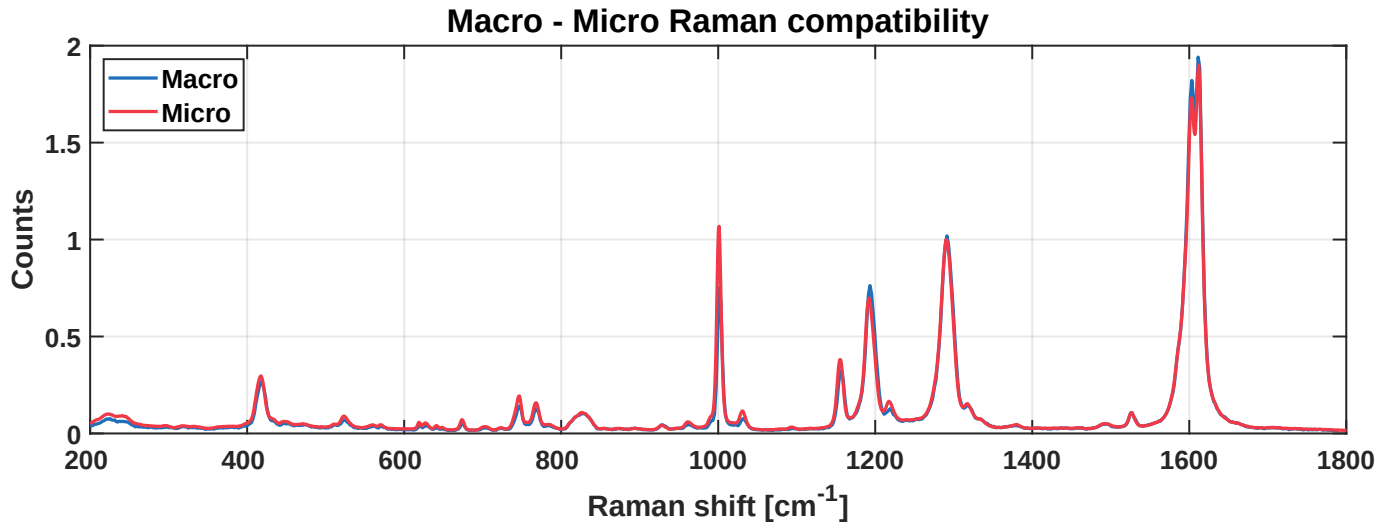


Figure B.4: Compatibility between the spectra measured with standard Macro-Raman spectroscopy (blue data) and those measured with Micro-Raman spectroscopy (red data).

Bibliography

- [1] W. Andrew Phillips. *Amorphous solids: low-temperature properties*. Springer Berlin, 1981.
- [2] C. Rodriguez-Tinoco, M. Gonzalez-Silveira, M. A. Ramos, and J. Rodriguez-Viejo. Ultrastable glasses: new perspectives for an old problem. *La Rivista del Nuovo Cimento*, 45(5):325–406, May 2022.
- [3] Tomás Pérez-Castañeda, Cristian Rodríguez-Tinoco, Javier Rodríguez-Viejo, and Miguel A. Ramos. Suppression of tunneling two-level systems in ultrastable glasses of indomethacin. *Proceedings of the National Academy of Sciences*, 111(31):11275–11280, aug 2014.
- [4] Jacopo Baglioni, Alessandro Martinelli, Peihao Sun, Francesco Dallari, Fabian Westermeier, Michael Sprung, Gerhard Grübel, and Giulio Monaco. Uniqueness of glasses prepared via x-ray induced yielding. *Reports on Progress in Physics*, 87(12):120503, nov 2024.
- [5] Xin Zhang, Hongbo Lou, Beatrice Ruta, Yuriy Chushkin, Federico Zontone, Shubin Li, Dazhe Xu, Tao Liang, Zhidan Zeng, Ho kwang Mao, and Qiaoshi Zeng. Pressure-induced nonmonotonic cross-over of steady relaxation dynamics in a metallic glass. *Proceedings of the National Academy of Sciences*, 120(24):e2302281120, 2023.
- [6] Antoine Cornet, Gaston Garbarino, Federico Zontone, Yuriy Chushkin, Jeroen Jacobs, Eloi Pineda, Thierry Deschamps, Shubin Li, Alberto Ronca, Jie Shen, Guillaume Morard, Nico Neuber, Maximilian Frey, Ralf Busch, Isabella Gallino, Mohamed Mezouar, Gavin Vaughan, and Beatrice Ruta. Denser glasses relax faster: Enhanced atomic mobility and anomalous particle displacement under in-situ high pressure compression of metallic glasses. *Acta Materialia*, 255:119065, 2023.
- [7] Pablo G. Debenedetti and Frank H. Stillinger. Supercooled liquids and the glass transition. *Nature*, 410(6825):259–267, Mar 2001.

- [8] V. Kohn and A. Chumakov. Dos: Evaluation of phonon density of states from nuclear resonant inelastic absorption. *Hyperfine Interact*, 125:205, 03 2000.
- [9] G. Grübel and F. Zontone. Correlation spectroscopy with coherent x-rays. *Journal of Alloys and Compounds*, 362:3–11, 2004.
- [10] Ludovic Berthier and Mark D. Ediger. Facets of glass physics. *Physics Today*, 69(1):40–46, jan 2016.
- [11] C. A. Angell. Formation of glasses from liquids and biopolymers. *Science*, 267(5206):1924–1935, 1995.
- [12] K. L. Kearns, S. F. Swallen, M. D. Ediger, Tian Wu, Ye Sun, and Lian Yu. Hiking down the energy landscape: Progress toward the kauzmann temperature via vapor deposition. *The Journal of Physical Chemistry B*, 112(16):4934–4942, 2008.
- [13] Giulio Monaco and Federico Caporaletti. *Atomic dynamics in glass-forming liquids during the Johari-Goldstein relaxation*. PhD thesis, Università di Trento, 04 2020.
- [14] Yonghao Sun, Amadeu Concustell, and A. Greer. Thermomechanical processing of metallic glasses: Extending the range of the glassy state. *Nature Reviews Materials*, 1, 06 2016.
- [15] J. Pan, Y. X. Wang, Q. Guo, D. Zhang, A. L. Greer, and Y. Li. Extreme rejuvenation and softening in a bulk metallic glass. *Nature Communications*, 9(1):560, Feb 2018.
- [16] J. Pan, Yu. P. Ivanov, W. H. Zhou, Y. Li, and A. L. Greer. Strain-hardening and suppression of shear-banding in rejuvenated bulk metallic glass. *Nature*, 578(7796):559–562, Feb 2020.
- [17] S. V. Ketov, Y. H. Sun, S. Nachum, Z. Lu, A. Checchi, A. R. Beraldin, H. Y. Bai, W. H. Wang, D. V. Louzguine-Luzgin, M. A. Carpenter, and A. L. Greer. Rejuvenation of metallic glasses by non-affine thermal strain. *Nature*, 524(7564):200–203, Aug 2015.
- [18] Takeshi Egami, Yang Tong, and Wojciech Dmowski. Deformation in metallic glasses studied by synchrotron x-ray diffraction. *Metals*, 6(1), 2016.

- [19] Y. Tong, W. Dmowski, H. Bei, Y. Yokoyama, and T. Egami. Mechanical rejuvenation in bulk metallic glass induced by thermo-mechanical creep. *Acta Materialia*, 148:384–390, 2018.
- [20] G. Ding, C. Li, A. Zacccone, W. H. Wang, H. C. Lei, F. Jiang, Z. Ling, and M. Q. Jiang. Ultrafast extreme rejuvenation of metallic glasses by shock compression. *Science Advances*, 5(8):eaaw6249, 2019.
- [21] Chaoyi Liu and Yue Fan. Emergent fractal energy landscape as the origin of stress-accelerated dynamics in amorphous solids. *Phys. Rev. Lett.*, 127:215502, Nov 2021.
- [22] Day Anthony. *Kinetic Stability*. School of Crystallography, Birkbeck University, 1996.
- [23] ScienceDirect Topics. Thermodynamic stability – an overview. <https://www.sciencedirect.com/topics/engineering/thermodynamic-stability>, 2025.
- [24] J.-P. Hansen and I. R. McDonald. *Theory of Simple Liquids*. Academic Press, London, 2nd edition, 1986.
- [25] Léon Van Hove. Correlations in space and time and born approximation scattering in systems of interacting particles. *Physical Review*, 95(1):249–262, July 1954.
- [26] Y.Q. Cheng and E. Ma. Atomic-level structure and structure–property relationship in metallic glasses. *Progress in Materials Science*, 56(4):379–473, 2011.
- [27] Liesbeth M. C. Janssen. Mode-coupling theory of the glass transition: A primer. *Frontiers in Physics*, 6, 2018.
- [28] Alexei Sokolov and Vladimir Novikov. Fast relaxation in disordered systems: From a double well to a cage. *Philosophical Magazine - PHILOS MAG*, 84:1355–1360, 05 2004.
- [29] G. P. Johari and M. Goldstein. Viscous liquids and the glass transition. ii. secondary relaxations in glasses of rigid molecules. *The Journal of Chemical Physics*, 53(6):2372–2388, 1970.
- [30] K. L. Ngai. *Relaxation and Diffusion in Complex Systems*. Springer Science & Business Media, New York, NY, 1st edition, 2011.

- [31] Gerold Adam and Julian H. Gibbs. On the temperature dependence of cooperative relaxation properties in glass-forming liquids. *The Journal of Chemical Physics*, 43(1):139–146, July 1965.
- [32] C. Masciovecchio, S. C. Santucci, A. Gessini, S. Di Fonzo, G. Ruocco, and F. Sette. Structural relaxation in liquid water by inelastic uv scattering. *Physical Review Letters*, 92(25):255507, June 2004.
- [33] Jan Gabriel, Florian Pabst, and Thomas Blochowicz. Debye process and β -relaxation in 1-propanol probed by dielectric spectroscopy and depolarized dynamic light scattering. *The Journal of Physical Chemistry B*, 121(37):8847–8853, 2017.
- [34] Ludovic Berthier and Giulio Biroli. Theoretical perspective on the glass transition and amorphous materials. *Reviews of Modern Physics*, 83(2):587–645, June 2011.
- [35] Francesco Dallari. *Slow dynamics in colloids and network glasses close to the structural arrest: the Stress-relaxation as a root to equilibrium*. PhD thesis, Università degli Studi di Trento, 2018. PhD thesis.
- [36] Marc André Meyers and Krishan Kumar Chawla. *Mechanical Behavior of Materials*. Cambridge University Press, Cambridge, UK, 2nd edition, 2008.
- [37] Bruce J. Berne and Robert Pecora. *Dynamic Light Scattering: With Applications to Chemistry, Biology, and Physics*. Courier Dover Publications, Garden City, NY, reprint of 1976 edition edition, 2000.
- [38] A. Duri, H. Bissig, V. Trappe, and L. Cipelletti. Time-resolved-correlation measurements of temporally heterogeneous dynamics. *Physical Review E*, 72(5):051401, November 2005.
- [39] J. Colmenero, A. Alegría, A. Arbe, and B. Frick. Correlation between non-debye behavior and q behavior of the α relaxation in glass-forming polymeric systems. *Physical Review Letters*, 69(3):478–481, 1992.
- [40] Arantxa Arbe and Juan Colmenero. *The Scaling of Relaxation Processes*, volume 9 of *Advances in Dielectrics*. Springer, Cham, Switzerland, 2018.
- [41] P.G. De Gennes. Liquid dynamics and inelastic scattering of neutrons. *Physica*, 25(7):825–839, 1959.

- [42] A. Tölle, H. Schober, J. Wuttke, and F. Fujara. Coherent dynamic structure factor of ortho-terphenyl around the mode coupling crossover temperature t_c . *Physical Review E*, 56(1):809–815, 1997.
- [43] A. Tölle. Neutron scattering studies of the model glass former ortho-terphenyl. *Reports on Progress in Physics*, 64(11):1473–1535, 2001.
- [44] Oleg Sobolev. De gennes narrowing and hard-sphere approach. *The Journal of Physical Chemistry B*, 120(37):9969–9977, 2016.
- [45] Andrea Cavagna. Supercooled liquids for pedestrians. *Physics Reports*, 476(4–6):51–124, 2009.
- [46] Claudio Donati, Sharon C. Glotzer, Peter H. Poole, Walter Kob, and Steven J. Plimpton. Spatial correlations of mobility and immobility in a glass-forming lennard-jones liquid. *Physical Review E*, 60(3):3107–3119, 1999.
- [47] Ludovic Berthier. Time and length scales in supercooled liquids. *Physical Review E*, 69(2):020201(R), 2004.
- [48] M. Vogel and E. Rössler. Exchange processes in disordered systems studied by solid state 2d nmr. *The Journal of Physical Chemistry*, 102(11):2102–2106, 1996.
- [49] U. Tracht, M. Wilhelm, A. Heuer, H. Feng, K. Schmidt-Rohr, and H. W. Spiess. Length scale of dynamic heterogeneities at the glass transition determined by multidimensional nuclear magnetic resonance. *Physical Review Letters*, 81(13):2727–2730, 1998.
- [50] A. S. Keys, A. R. Abate, S. C. Glotzer, and D. J. Durian. Measurement of growing dynamical length scales and prediction of the jamming transition in a granular material. *Nature Physics*, 3(4):260–264, 2007.
- [51] R. Zondervan, F. Kulzer, G. C. G. Berkhout, and M. Orrit. Local viscosity of supercooled glycerol near t_g probed by rotational diffusion of ensembles and single dye molecules. *Proceedings of the National Academy of Sciences of the United States of America*, 104(31):12628–12633, 2007.
- [52] Z. Zhang, P. J. Yunker, P. Habdas, and A. G. Yodh. Cooperative rearrangement regions and dynamical heterogeneities in colloidal glasses with attractive versus repulsive interactions. *Physical Review Letters*, 107(20):208303, 2011.

- [53] M. D. Ediger and P. Harrowell. Perspective: Supercooled liquids and glasses. *The Journal of Chemical Physics*, 137(8):080901, 2012.
- [54] P. Zhang, J. J. Maldonis, Z. Liu, J. Schroers, and P. M. Voyles. Spatially heterogeneous dynamics in a metallic glass forming liquid imaged by electron correlation microscopy. *Nature Communications*, 9:1129, 2018.
- [55] Ludovic Berthier, Giulio Biroli, Jean-Philippe Bouchaud, Luca Cipelletti, Dalle El Masri, Dominique L’Hôte, François Ladieu, and Marco Pierno. Direct experimental evidence of a growing length scale accompanying the glass transition. *Science*, 310(5755):1797–1800, 2005.
- [56] Céline Dalle-Ferrier, Cécile Thibierge, Christiane Alba-Simionesco, Ludovic Berthier, Giulio Biroli, Jean-Philippe Bouchaud, François Ladieu, Dominique L’Hôte, and Gilles Tarjus. Spatial correlations in the dynamics of glass-forming liquids: Experimental determination of their temperature dependence. *Physical Review E*, 76(4):041510, 2007.
- [57] Eric R. Weeks, John C. Crocker, Andrew C. Levitt, Andrew Schofield, and David A. Weitz. Three-dimensional direct imaging of structural relaxation near the colloidal glass transition. *Science*, 287(5453):627–631, 2000.
- [58] K. Ito, C. T. Moynihan, and C. A. Angell. Thermodynamic determination of fragility in liquids and a fragile-to-strong liquid transition in water. *Nature*, 398:492–495, 1999.
- [59] S. Wei, F. Yang, J. Bednarcik, I. Kaban, O. Shuleshova, A. Meyer, et al. Liquid-liquid transition in a strong bulk metallic glass-forming liquid. *Nature Communications*, 4:3083, 2013.
- [60] P. Lucas. Fragile-to-strong transitions in glass forming liquids. *Journal of Non-Crystalline Solids: X*, 4:100034, 2019.
- [61] S. Stølen, T. Grande, and H.-B. Johnsen. Fragility transition in gse_{2-} se liquids. *Physical Chemistry Chemical Physics*, 4:3396–3399, 2002.
- [62] M. Stolpe, I. Jonas, S. Wei, Z. Evenson, W. Hembree, F. Yang, et al. Structural changes during a liquid-liquid transition in the deeply undercooled $\text{Zr}_{58.5}\text{Cu}_{15.6}\text{Ni}_{12.8}\text{Al}_{10.3}\text{Nb}_{2.8}$ bulk metallic glass forming melt. *Physical Review B*, 93:014201, 2016.

- [63] S. Hechler, B. Ruta, M. Stolpe, E. Pineda, Z. Evenson, O. Gross, et al. Microscopic evidence of the connection between liquid-liquid transition and dynamical crossover in an ultraviscous metallic glass former. *Physical Review Materials*, 2:085603, 2018.
- [64] I. Gallino, D. Cangialosi, Z. Evenson, L. Schmitt, S. Hechler, M. Stolpe, et al. Hierarchical aging pathways and reversible fragile-to-strong transition upon annealing of a metallic glass former. *Acta Materialia*, 144:400–410, 2018.
- [65] C. Way, P. Wadhwa, and R. Busch. The influence of shear rate and temperature on the viscosity and fragility of the $\text{Zr}_{41.2}\text{Ti}_{13.8}\text{Cu}_{12.5}\text{Ni}_{10.0}\text{Be}_{22.5}$ metallic-glass-forming liquid. *Acta Materialia*, 55:2977–2983, 2007.
- [66] C. Zhang, L. Hu, Y. Yue, and J. C. Mauro. Fragile-to-strong transition in metallic glass-forming liquids. *Journal of Chemical Physics*, 133:014508, 2010.
- [67] H. Liu, W. Chen, R. Pan, Z. Shan, A. Qiao, J. W. E. Drewitt, et al. From molten calcium aluminates through phase transitions to cement phases. *Advanced Science*, 7:1902209, 2020.
- [68] Rui Shi, John Russo, and Hajime Tanaka. Origin of the emergent fragile-to-strong transition in supercooled water. *Proceedings of the National Academy of Sciences*, 115(38):9444–9449, 2018.
- [69] Pierre Lucas, Shuai Wei, and C. Austen Angell. Liquid-liquid phase transitions in glass-forming systems and their implications for memory technology. *International Journal of Applied Glass Science*, 11(2):236–244, 2020.
- [70] Hajime Tanaka. Liquid–liquid transition and polyamorphism. *The Journal of Chemical Physics*, 153(13):130901, 10 2020.
- [71] Wei Xu, Magdalena T. Sandor, Yao Yu, Hai-Bo Ke, Hua-Ping Zhang, Mao-Zhi Li, Wei-Hua Wang, Lin Liu, and Yue Wu. Evidence of liquid–liquid transition in glass-forming $\text{La}_{50}\text{Al}_{35}\text{Ni}_{15}$ melt above liquidus temperature. *Nature Communications*, 6:7696, 2015.
- [72] Mika Kobayashi and Hajime Tanaka. The reversibility and first-order nature of liquid–liquid transition in a molecular liquid. *Nature Communications*, 7:13438, 2016.

- [73] Ken ichiro Murata and Hajime Tanaka. Liquid–liquid transition without macroscopic phase separation in a water–glycerol mixture. *Nature Materials*, 11:436–443, 2012.
- [74] Shuang Wei, Pierre Lucas, and C. Austen Angell. Phase change alloy viscosities down to T_g using adam–gibbs-equation fittings to excess entropy data: A fragile-to-strong transition. *Journal of Applied Physics*, 118(3):034903, 2015.
- [75] Y. Katayama, T. Mizutani, W. Utsumi, O. Shimomura, M. Yamakata, and K.-I. Funakoshi. A first-order liquid–liquid phase transition in phosphorus. *Nature*, 403:170–173, 2000.
- [76] Y. Katayama, Y. Inamura, T. Mizutani, M. Yamakata, W. Utsumi, and O. Shimomura. Macroscopic separation of dense fluid phase and liquid phase of phosphorus. *Science*, 306(5697):848–851, 2004.
- [77] L. Henry, M. Mezouar, G. Garbarino, D. Sifré, G. Weck, and F. Datchi. Liquid–liquid transition and critical point in sulfur. *Nature*, 584:382–386, 2020.
- [78] S. Wei, G. J. Coleman, P. Lucas, and C. A. Angell. Glass transitions, semiconductor-metal transitions, and fragilities in ge-v-te ($v = \text{as, sb}$) liquid alloys: the difference one element can make. *Phys. Rev. Appl.*, 7:034035, 2017.
- [79] S. Wei, P. Lucas, and C. A. Angell. Phase-change materials: the view from the liquid phase and the metallicity parameter. *MRS Bull.*, 44:691–698, 2019.
- [80] P. H. Poole, T. Grande, C. A. Angell, and P. F. McMillan. Polymorphic phase transitions in liquids and glasses. *Science*, 275:322, 1997.
- [81] C. Tien, E. V. Charnaya, W. Wang, Y. A. Kumzerov, and D. Michel. Possible liquid-liquid transition of gallium confined in opal. *Phys. Rev. B*, 74:024116, 2006.
- [82] R. Li, L. Li, T. Yu, L. Wang, J. Chen, Y. Wang, Z. Cai, J. Chen, M. L. Rivers, and H. Liu. Study of liquid gallium as a function of pressure and temperature using synchrotron x-ray microtomography and x-ray diffraction. *Appl. Phys. Lett.*, 105:041906, 2014.
- [83] D. A. Carvajal Jara, M. Fontana Michelon, A. Antonelli, and M. de Koning. Theoretical evidence for a first-order liquid-liquid phase transition in gallium. *J. Chem. Phys.*, 130:221101, 2009.

- [84] R. Li, G. Sun, and L. Xu. Anomalous properties and the liquid-liquid phase transition in gallium. *J. Chem. Phys.*, 145:054506, 2016.
- [85] A. G. Umnov, V. V. Brazhkin, S. V. Popova, and R. N. Voloshin. Pressure temperature diagram of liquid bismuth. *J. Phys.: Condens. Matter*, 4:1427, 1992.
- [86] Y. Greenberg, E. Yahel, E. N. Caspi, C. Benmore, B. Beuneu, M. P. Dariel, and G. Makov. Evidence for a temperature-driven structural transformation in liquid bismuth. *Europhys. Lett.*, 86:36004, 2009.
- [87] A. Cadien, Q. Hu, Y. Meng, Y. Cheng, M. Chen, J. Shu, H. Mao, and H. Sheng. First-order liquid-liquid phase transition in cerium. *Phys. Rev. Lett.*, 110:125503, 2013.
- [88] V. V. Brazhkin and A. G. Lyapin. High-pressure phase transformations in liquids and amorphous solids. *J. Phys.: Condens. Matter*, 15:6059–6084, 2003.
- [89] H. Tanaka, R. Kurita, and H. Matakai. Liquid-liquid transition in the molecular liquid triphenyl phosphite. *Phys. Rev. Lett.*, 92:025701, 2004.
- [90] R. Kurita and H. Tanaka. Critical-like phenomena associated with liquid-liquid transition in a molecular liquid. *Science*, 306:845–848, 2004.
- [91] R. Kurita and H. Tanaka. On the abundance and general nature of the liquid-liquid phase transition in molecular systems. *J. Phys.: Condens. Matter*, 17:L293–L302, 2005.
- [92] M. Zhu, J.-Q. Wang, J. H. Perepezko, and L. Yu. Possible existence of two amorphous phases of d-mannitol related by a first-order transition. *J. Chem. Phys.*, 142:244504, 2015.
- [93] M. Zhu and L. Yu. Polyamorphism of d-mannitol. *J. Chem. Phys.*, 146:244503, 2017.
- [94] W. Tang and J. H. Perepezko. Polyamorphism and liquid-liquid transformations in d-mannitol. *J. Chem. Phys.*, 149:074505, 2018.
- [95] S. Kawanishi, T. Sasuga, and M. Takehisa. Existence of novel liquid phases of trans-1,2-dichloroethylene at high pressure. *J. Phys. Soc. Jpn.*, 50:3080–3084, 1981.

- [96] S. Kawanishi, T. Sasuga, and M. Takehisa. A novel liquid state of trans-1,2-dichloroethylene. *J. Phys. Soc. Jpn.*, 51:1579–1583, 1982.
- [97] S. Rzoska, J. Ziolo, A. Drozd-Rzoska, J. L. Tamarit, and N. Veglio. New evidence for a liquid–liquid transition in a one-component liquid. *J. Phys.: Condens. Matter*, 20:244124, 2008.
- [98] K. Merkel, A. Kocot, R. Wrzalik, and J. Ziolo. Origin of the liquid–liquid phase transition for trans-1,2-dichloroethylene observed by ir spectroscopy. *J. Chem. Phys.*, 129:074503, 2008.
- [99] D. A. Turton, D. F. Martin, and K. Wynne. Optical kerr-effect study of trans- and cis-1,2-dichloroethene: Liquid–liquid transition or super-arrhenius relaxation. *Phys. Chem. Chem. Phys.*, 12:4191–4200, 2010.
- [100] M. Rovira-Esteva, N. A. Murugan, L. C. Pardo, S. Busch, J. L. Tamarit, G. J. Cuello, and F. J. Bermejo. Differences in first neighbor orientation behind the anomalies in the low and high density trans-1,2-dichloroethene liquid. *J. Chem. Phys.*, 136:124514, 2012.
- [101] Xun Liu, Shiyu Liu, Enyi Chen, Liang Peng, and Yao Yu. First-order liquid–liquid transition without density discontinuity in molten sodium acetate trihydrate and its influence on crystallization. *Journal of Physical Chemistry Letters*, 10(15):4285–4290, 2019.
- [102] Tomoki Fujita, Yuhan Chen, Yoshio Kono, Seiya Takahashi, Hidetaka Kasai, Davide Campi, Marco Bernasconi, Koji Ohara, Hirokatsu Yumoto, Takahisa Koyama, Hiroshi Yamazaki, Yasunori Senba, Haruhiko Ohashi, Ichiro Inoue, Yujiro Hayashi, Makina Yabashi, Eiji Nishibori, Riccardo Mazzarello, and Shuai Wei. Pressure-induced reversal of peierls-like distortions elicits the polyamorphic transition in gete and gese. *Nature Communications*, 14, 12 2023.
- [103] O. Mishima, L. D. Calvert, and E. Whalley. "melting ice i at 77 k and 10 kbar: A new method of making amorphous solids". *Nature*, 310:393–395, 1984.
- [104] O. Mishima. Reversible first-order transition between two h2o amorphs at ~ 0.2 gpa and ~ 135 k. *J. Chem. Phys.*, 100:5910, 1994.
- [105] O. Mishima. Relationship between melting and amorphization of ice. *Nature*, 384:546–549, 1996.

-
- [106] H. W. Sheng and et al. Polyamorphism in a metallic glass. *Nat. Mater.*, 6:192–197, 2007.
- [107] C. Sonnevile and et al. Polyamorphic transitions in silica glass. *J. Non-Cryst. Solids*, 382:133–136, 2013.
- [108] D. Daisenberger and et al. High-pressure x-ray scattering and computer simulation studies of density-induced polyamorphism in silicon. *Phys. Rev. B*, 75:224118, 2007.
- [109] F. Walton and et al. Polyamorphism mirrors polymorphism in the liquid–liquid transition of a molecular liquid. *J. Am. Chem. Soc.*, 142:7591–7597, 2020.
- [110] E. Principi and et al. Polyamorphic transition of germanium under pressure. *Phys. Rev. B*, 69:201201, 2004.
- [111] National Institute for Materials Science. Experimental evidence of two liquid waters: Direct observation of reversible liquid–liquid transition in a trehalose aqueous solution, Feb 2022.
- [112] C. A. Angell, K. L. Ngai, G. B. McKenna, P. F. McMillan, and S. W. Martin. Relaxation in glass-forming liquids and amorphous solids. *Journal of Applied Physics*, 88(6):3113–3157, 2000.
- [113] M. Courtois, A. Berthelot, A. Cornet, S. Le Floch, C. Martinet, and T. Deschamps. Pressure-induced amorphous–amorphous transition in pre-densified silica glass: an experimental exploration of the potential energy landscape. *Scientific Reports*, 15(1):6719, 2025.
- [114] R. C. Zeller and R. O. Pohl. Thermal conductivity and specific heat of noncrystalline solids. *Physical Review B*, 4(6):2029–2041, 1971.
- [115] M. T. Loonen, R. C. Dynes, V. Narayanamurti, and J. P. Garino. Measurements of the time-dependent specific heat of amorphous materials. *Phys. Rev. B*, 25:1161–1173, Jan 1982.
- [116] David G. Cahill and Robert O. Pohl. Thermal conductivity of amorphous solids above the plateau. *Annual Review of Physical Chemistry*, 39:93–121, 1988.
- [117] T. Pérez-Castañeda *et al.* Slow dynamics in glasses: Evidence for a nearly universal two-level system density. *Proc. Natl. Acad. Sci. U.S.A.*, **111**:11275–11280, 2014.

- [118] V. G. Karpov, M. I. Klinger, and F. N. Ignatiev. Theory of the low-temperature anomalies in the thermal properties of amorphous structures. *Sov. Phys. JETP*, 57(2):439, 1983.
- [119] U. Buchenau, Yu. M. Galperin, V. L. Gurevich, and H. R. Schober. Anharmonic potentials and vibrational localization in glasses. *Phys. Rev. B*, 43:5039–5045, Feb 1991.
- [120] D. A. Parshin, H. R. Schober, and V. L. Gurevich. Vibrational instability, two-level systems, and the boson peak in glasses. *Phys. Rev. B*, 76:064206, Aug 2007.
- [121] W. Schirmacher, G. Ruocco, and T. Scopigno. Acoustic attenuation in glasses and its relation with the boson peak. *Phys. Rev. Lett.*, 98:025501, Jan 2007.
- [122] Walter Schirmacher, C. Tomaras, B. Schmid, Giacomo Baldi, G. Viliani, G. Ruocco, and Tullio Scopigno. Sound attenuation and anharmonic damping in solids with correlated disorder. *Condensed Matter Physics*, 13, 01 2010.
- [123] Walter Schirmacher, Tullio Scopigno, and Giancarlo Ruocco. Theory of vibrational anomalies in glasses. *Journal of Non-Crystalline Solids*, 407:133–140, 2015. 7th IDMRCS: Relaxation in Complex Systems.
- [124] Zhiwen Pan, Omar Benzine, Shigeki Sawamura, Rene Limbach, Akio Koike, Thomas D. Bennett, Gerhard Wilde, Walter Schirmacher, and Lothar Wondraczek. Disorder classification of the vibrational spectra of modern glasses. *Phys. Rev. B*, 104:134106, Oct 2021.
- [125] G. Baldi, A. Fontana, and G. Monaco. Vibrational dynamics of non-crystalline solids, 2020.
- [126] Edan Lerner, Gustavo Düring, and Eran Bouchbinder. Statistics and properties of low-frequency vibrational modes in structural glasses. *Phys. Rev. Lett.*, 117:035501, Jul 2016.
- [127] Luca Angelani, Matteo Paoluzzi, Giorgio Parisi, and Giancarlo Ruocco. Probing the non-debye low-frequency excitations in glasses through random pinning. *Proceedings of the National Academy of Sciences*, 115(35):8700–8704, 2018.
- [128] Hideyuki Mizuno, Hayato Shiba, and Atsushi Ikeda. Continuum limit of the vibrational properties of amorphous solids. *Proceedings of the National Academy of Sciences*, 114(46):E9767–E9774, 2017.

- [129] N. S. Shcheblanov, M. E. Povarnitsyn, J. D. Wiles, S. R. Elliott, and S. N. Taraskin. Phonon traces in glassy vibrations. *Physical Review B*, 102(2):024202, jul 2020.
- [130] David Richard, Karina González-López, Geert Kapteijns, Robert Pater, Talya Vaknin, Eran Bouchbinder, and Edan Lerner. Universality of the nonphononic vibrational spectrum across different classes of computer glasses. *Phys. Rev. Lett.*, 125:085502, Aug 2020.
- [131] Edan Lerner and Eran Bouchbinder. Boson-peak vibrational modes in glasses feature hybridized phononic and quasilocalized excitations. *The Journal of Chemical Physics*, 158(19):194503, 05 2023.
- [132] M. A. Ramos and U. Buchenau. Low-temperature thermal conductivity of glasses within the soft-potential model. *Physical Review B*, 55:5749–5754, 1997.
- [133] M. A. Ramos and U. Buchenau. Beyond the standard tunneling model: The soft-potential model. In P. Esquinazi, editor, *Tunneling Systems in Amorphous and Crystalline Solids*, pages 528–569. Springer, New York, 1998.
- [134] M. A. Ramos. Are the calorimetric and elastic debye temperatures of glasses really different? *Philosophical Magazine*, 84:1313–1321, 2004.
- [135] W. Schirmacher. Thermal conductivity of glassy materials and the “boson peak”. *Europhysics Letters*, 73:892–898, 2006.
- [136] Miguel A. Ramos. *Low-Temperature Specific Heat of Glasses and Disordered Crystals*, chapter 2, pages 21–67. World Scientific (Europe), 2022.
- [137] V. G. Karpov, M. I. Klinger, and F. N. Ignatiev. Atomic tunneling states and low-temperature anomalies of thermal properties in amorphous materials. *Solid State Communications*, 44:333–337, 1982.
- [138] M. A. Il’in, V. G. Karpov, and D. A. Parshin. Parameters of soft potentials in glasses. *Soviet Physics JETP*, 65:165–174, 1987. Originally published in *Zh. Eksp. Teor. Fiz.* 92, 291–305 (1987).
- [139] U. Buchenau, Yu. M. Galperin, V. L. Gurevich, D. A. Parshin, M. A. Ramos, and H. R. Schober. Interaction of soft modes and sound waves in glasses. *Physical Review B*, 46:2798–2808, 1992.

- [140] L. Gil, M. A. Ramos, A. Bringer, and U. Buchenau. Low temperature specific heat and thermal conductivity of glasses. *Physical Review Letters*, 70:182–185, 1993.
- [141] M. A. Ramos, L. Gil, A. Bringer, and U. Buchenau. The density of tunneling and vibrational states of glasses within the soft-potential model. *Physica Status Solidi (a)*, 135:477–492, 1993.
- [142] D. A. Parshin. Model of soft atomic potentials and universality of low-temperature properties of glasses. *Physics of the Solid State*, 36:991–1024, 1994.
- [143] V. L. Gurevich, D. A. Parshin, and H. R. Schober. Anharmonicity, vibrational instability, and the boson peak in glasses. *Physical Review B*, 67:094203, 2003.
- [144] Dmytro Khomenko, David R. Reichman, and Francesco Zamponi. Relationship between two-level systems and quasilocalized normal modes in glasses. *Physical Review Materials*, 5(5), may 2021.
- [145] B. Schmid and W. Schirmacher. Raman scattering and the low-frequency vibrational spectrum of glasses. *Physical Review Letters*, 100(13):137402, 2008.
- [146] G. Baldi, V. M. Giordano, B. Ruta, R. Dal Maschio, A. Fontana, and G. Monaco. Anharmonic damping of terahertz acoustic waves in a network glass and its effect on the density of vibrational states. *Phys. Rev. Lett.*, 112:125502, Mar 2014.
- [147] T. S. Grigera, V. Martín-Mayor, G. Parisi, and P. Verrocchio. Phonon interpretation of the ‘boson peak’ in supercooled liquids. *Nature*, 422(6929):289–292, mar 2003.
- [148] Florian Vogel and Matthias Fuchs. Vibrational phenomena in glasses at low temperatures captured by field theory of disordered harmonic oscillators. *Phys. Rev. Lett.*, 130:236101, Jun 2023.
- [149] Elijah Flenner and Grzegorz Szamel. Defects, Sound Damping, and the Boson Peak in Amorphous Solids. *The Journal of Physical Chemistry B*, 129(6):1855–1863, feb 2025.
- [150] G. Baldi, V. M. Giordano, G. Monaco, and B. Ruta. Sound attenuation at terahertz frequencies and the boson peak of vitreous silica. *Phys. Rev. Lett.*, 104:195501, May 2010.

- [151] G. Iezzi, A. L. Elbrecht, M. Davis, F. Vetere, V. Misiti, S. Mollo, and A. Cavallo. Glass stability (gs) of chemically complex (natural) sub-alkaline glasses, 2018.
- [152] Birte Riechers, Lisa A. Roed, Saeed Mehri, Trond S. Ingebrigtsen, Tina Hecksher, Jeppe C. Dyre, and Kristine Niss. Predicting nonlinear physical aging of glasses from equilibrium relaxation via the material time. *Science Advances*, 8(11):eabl9809, 2022.
- [153] Anastasia A. Yakusheva. Devitrification kinetics and optical stability of optical fibers at high temperatures. Master’s thesis, Virginia Tech, 2018.
- [154] Shu-En Wei, Yitao Wang, Heng Yao, Maxime Cavillon, Bertrand Pommellec, Gang-Ding Peng, and Matthieu Lancry. Thermal stability of type ii modifications by ir femtosecond laser in silica-based glasses. *Sensors*, 20(3):762, 2020.
- [155] Florian Calzavara et al. Resolved-detrimental surface crystallization in yttrium lanthanum gallate glasses for optical fiber applications. *Journal of the American Ceramic Society*, 106(10):5754–5765, 2023.
- [156] B. C. Hancock and M. Parks. What is the true solubility advantage for amorphous pharmaceuticals? *Pharmaceutical Research*, 17(4):397–404, 2000.
- [157] L. Yu. Amorphous pharmaceutical solids: preparation, characterization and stabilization. *Advanced Drug Delivery Reviews*, 48(1):27–42, 2001.
- [158] LIGO Collaboration. Mirror substrates for ligo: Fused silica low-loss glass to minimize thermal noise. *Precision Optical Metrology – Syracuse University*, n.d. LIGO’s test mass mirrors are thick cylinders ... of fused silica, an extremely pure form of glass ... where low thermal noise is a requirement.
- [159] G. M. Harry et al. Development of mirror coatings for gravitational-wave detectors. *Philosophical Transactions of the Royal Society A*, 2017. Thermal noise in mirror coatings limits detector sensitivity by translating to surface motion.
- [160] Qiuju Zheng, Yanfei Zhang, Maziar Montazerian, Özgür Gulbiten, John C. Mauro, Edgar D. Zanolto, and Yuanzheng Yue. Understanding glass through differential scanning calorimetry. *Chemical Reviews*, 119(13):7848–7939, July 2019.

-
- [161] E. Alfinelli, F. Caporaletti, F. Dallari, A. Martinelli, G. Monaco, B. Ruta, M. Sprung, M. Zanatta, and G. Baldi. Amorphous-amorphous transformation induced in glasses by intense x-ray beams. *Phys. Rev. B*, 107:054202, Feb 2023.
- [162] Wikipedia contributors. Physical vapor deposition — Wikipedia, the free encyclopedia. https://en.wikipedia.org/w/index.php?title=Physical_vapor_deposition&oldid=1105727974, 2022.
- [163] Manuel Moratalla, Marta Rodríguez-López, Cristian Rodríguez-Tinoco, Javier Rodríguez-Viejo, Rafael J. Jiménez-Riobóo, and Miguel A. Ramos. Depletion of two-level systems in highly stable glasses with different molecular ordering. *Communications Physics*, 6(1):274, sep 2023.
- [164] Nikolai V. Priezjev. Aging and rejuvenation during elastostatic loading of amorphous alloys. *arXiv preprint arXiv:1905.00761*, 2019.
- [165] Alessandro Martinelli, Federico Caporaletti, Francesco Dallari, Michael Sprung, Fabian Westermeier, Giacomo Baldi, and Giulio Monaco. Reaching the yield point of a glass during x-ray irradiation. *Phys. Rev. X*, 13:041031, Nov 2023.
- [166] B. Ruta, F. Zontone, Y. Chushkin, G. Baldi, G. Pintori, G. Monaco, B. Rufflé, and W. Kob. Hard x-rays as pump and probe of atomic motion in oxide glasses. *Scientific Reports*, 7(1):3962, Jun 2017.
- [167] Anh D. Phan, Alessio Zaccone, Vu D. Lam, and Katsunori Wakabayashi. Theory of pressure-induced rejuvenation and strain hardening in metallic glasses. *Phys. Rev. Lett.*, 126:025502, 2021.
- [168] J. Pan, Y. X. Wang, Q. Guo, D. Zhang, and A. L. Greer. Extreme rejuvenation and softening in a bulk metallic glass. *Nature Communications*, 9:560, 2018.
- [169] A. I. Chumakov, A. Q. R. Baron, R. Rüffer, H. Grünsteudel, H. F. Grünsteudel, and A. Meyer. Nuclear resonance energy analysis of inelastic x-ray scattering. *Phys. Rev. Lett.*, 76:4258–4261, May 1996.
- [170] Wikipedia contributors. Mössbauer effect — Wikipedia, the free encyclopedia. https://en.wikipedia.org/w/index.php?title=M%C3%B6ssbauer_effect&oldid=1097496607, 2022.

- [171] R. Röhlberger. *Nuclear Condensed Matter Physics with Synchrotron Radiation. Basic Principles, Methodology and Applications*. Springer-Verlag Berlin Heidelberg, 2004.
- [172] H. Frauenfelder. The Mössbauer Effect, A Review with a Collection of Reprints. *Nuclear Physics*, New York, (1962).
- [173] K. S. Singwi and A. Sjölander. Resonance absorption of nuclear gamma rays and the dynamics of atomic motions. *Phys. Rev.*, 120:1093–1102, Nov 1960.
- [174] Alexey Bosak and Michael Krisch. Phonon density of states probed by inelastic x-ray scattering. *Phys. Rev. B*, 72:224305, Dec 2005.
- [175] Rudolf Ruffer and Aleksandr I. Chumakov. Nuclear Resonance Beamline at ESRF. *Hyperfine Interactions*, 97(1):589–604, Dec 1996.
- [176] ID18 stuff. X-ray source. https://www.esrf.fr/home/UsersAndScience/Experiments/MEx/ID18/beamline_layout/optics/xsource.html, 2022.
- [177] ID18 stuff. Elements of the beamline: high-heat-load monochromator. https://www.esrf.fr/home/UsersAndScience/Experiments/MEx/ID18/beamline_layout/optics/HHLM.html, 2022.
- [178] ID18 stuff. Elements of the beamline: compound refractive lenses. https://www.esrf.fr/home/UsersAndScience/Experiments/MEx/ID18/beamline_layout/optics/CL.html, 2022.
- [179] Aleksandr I. Chumakov, Yuri Shvyd'ko, Ilya Sergueev, Dimitrios Bessas, and Rudolf Ruffer. Hard-x-ray spectroscopy with a spectrographic approach. *Phys. Rev. Lett.*, 123:097402, Aug 2019.
- [180] Wikipedia contributors. Avalanche photodiode — Wikipedia, the free encyclopedia, 2022. [Online; accessed 20-August-2022].
- [181] A. I. Chumakov, A. Bosak, and R. Ruffer. Contribution of acoustic modes to the density of vibrational states measured by inelastic scattering techniques. *Phys. Rev. B*, 80:094303, Sep 2009.
- [182] A. I. Chumakov, G. Monaco, A. Fontana, A. Bosak, R. P. Hermann, D. Bessas, B. Wehinger, W. A. Crichton, M. Krisch, R. Ruffer, G. Baldi, G. Carini Jr., G. Carini, G. D'Angelo, E. Gilioli, G. Trippodo, M. Zanatta, B. Winkler, V. Milman, K. Refson, M. T. Dove,

- N. Dubrovinskaia, L. Dubrovinsky, R. Keding, and Y. Z. Yue. Role of disorder in the thermodynamics and atomic dynamics of glasses. *Phys. Rev. Lett.*, 112:025502, Jan 2014.
- [183] J. D. Rigden and E. I. Gordon. The granularity of scattered optical maser light. *Proc. IRE*, 50:2367–2368, 1962.
- [184] Jr. K. F. Ludwig. Comment on “speckle in the diffraction patterns of hendricks–teller and icosahedral glass models”. *Physical Review Letters*, 61(13):1526, September 1988.
- [185] J. W. Goodman. Statistical properties of laser speckle patterns. In J. C. Dainty, editor, *Laser Speckle and Related Phenomena*, volume 9 of *Topics in Applied Physics*, pages 9–74. Springer-Verlag, Berlin, 1984.
- [186] P. Lehmann. Surface-roughness measurement based on the intensity correlation function of scattered light under speckle-pattern illumination. *Applied Optics*, 38(7):1144–1152, March 1999.
- [187] S. O. Hruszkewycz, M. Sutton, P. H. Fuoss, B. Adams, S. Rosenkranz, Jr. K. F. Ludwig, W. Roseker, D. Fritz, M. Cammarata, D. Zhu, S. Lee, H. Lemke, C. Gutt, A. Robert, G. Grübel, and G. B. Stephenson. High contrast x-ray speckle from atomic-scale order in liquids and glasses. *Physical Review Letters*, 109(18):185502, November 2012.
- [188] Redouane Borsali and Robert Pecora, editors. *Soft-Matter Characterization*. Springer, Dordrecht, 1st edition, 2008.
- [189] A. Siegert. On the fluctuations in signals returned by many independently moving scatterers. Technical report, Radiation Laboratory, Massachusetts Institute of Technology, 1943.
- [190] J. Carnis, W. Cha, J. Wingert, J. Kang, Z. Jiang, S. Song, M. Sikorski, A. Robert, C. Gutt, S.-W. Chen, Y. Dai, Y. Ma, H. Guo, L. B. Lurio, O. Shpyrko, S. Narayanan, M. Cui, I. Kosif, T. Emrick, T. P. Russell, H. C. Lee, C.-J. Yu, G. Grübel, S. K. Sinha, and H. Kim. Demonstration of feasibility of x-ray free electron laser studies of dynamics of nanoparticles in entangled polymer melts. *Scientific Reports*, 4(1):6017, August 2014.
- [191] B. Ruta, A. M. Puertas, G. Baldi, A. R. Ni, C. R. S. Carvalho, G. Monaco, W. H. Wang, M. P. Eastwood, J. C. Dyre, M. Laurati, and T. Scopigno. Wave vector dependence of the dynamics in supercooled metallic liquids. *Physical Review Letters*, 125(5):055701, 2020.

- [192] Anders Madsen, Andrei Fluerașu, and Beatrice Ruta. Structural dynamics of materials probed by x-ray photon correlation spectroscopy. In *Synchrotron Light Sources and Free-Electron Lasers: Accelerator Physics, Instrumentation and Science Applications*, pages 1–21. Springer International Publishing, 2015.
- [193] Jens Als-Nielsen. *Elements of Modern X-Ray Physics*, volume 55. Wiley, 01 2002.
- [194] G. Grübel and D. L. Abernathy. Coherent x-rays and their applications. In *Proceedings of SPIE*, volume 3154, pages 103–112, 1997.
- [195] G. Grübel, A. Madsen, and A. Robert. X-ray photon correlation spectroscopy (xpcs). In R. Borsali and R. Pecora, editors, *Soft-Matter Characterization*, pages 935–995. Springer, New York, 2008.
- [196] G. Pintori, G. Baldi, B. Ruta, and G. Monaco. Relaxation dynamics induced in glasses by absorption of hard x-ray photons. *Phys. Rev. B*, 99:224206, Jun 2019.
- [197] Katharina Holzweber, Christoph Tietz, Tobias Michael Fritz, Bogdan Sepiol, and Michael Leitner. Beam-induced atomic motion in alkali borate glasses. *Phys. Rev. B*, 100:214305, Dec 2019.
- [198] Dallari, Pintori, Baldi, Martinelli, Ruta, Sprung, and Monaco. X-rays induced atomic dynamics in a lithium-borate glass. *Condensed Matter Physics*, 22(4):43606, November 2019.
- [199] Jianheng Li, Meera Madhavi, Spencer Jeppson, Louie Zhong, Eric M. Dufresne, Bruce Aitken, Sabyasachi Sen, and Roopali Kukreja. Observation of collective molecular dynamics in a chalcogenide glass: Results from x-ray photon correlation spectroscopy. *The Journal of Physical Chemistry B*, 126(28):5320–5325, 2022. PMID: 35730616.
- [200] Deutsches Elektronen-Synchrotron (DESY). Coherence beamline p10 coherence applications — petra iii. https://photon-science.desy.de/facilities/petra_iii/beamlines/p10_coherence_applications/index_eng.html, 2025. Accessed: 2025-07-28.
- [201] Alessandro Martinelli. *Density relaxations across the glass-transition under equilibrium and non-equilibrium conditions*. PhD thesis, Università degli Studi di Trento, Trento, Italy, April 2021.

- [202] J. C. Chervin, C. Jung, and B. Canny. High pressure as a tool to study structural properties of thiolate heme proteins. *Review of Scientific Instruments*, 66(2):2595–2598, 1995.
- [203] Naemi Waesermann. *Structural transformations in complex perovskite-type relaxor and relaxor-based ferroelectrics at high pressures and temperatures*. Phd thesis, University of Hamburg, 2012. Accessed: 2025-09-15.
- [204] S Klotz, J-C Chervin, P Munsch, and G Le Marchand. Hydrostatic limits of 11 pressure transmitting media. *Journal of Physics D: Applied Physics*, 42(7):075413, mar 2009.
- [205] Guoyin Shen, Yanbin Wang, Agnes Dewaele, Christine Wu, Dayne E. Fratanduono, Jon Eggert, Stefan Klotz, Kamil F. Dziubek, Paul Loubeyre, Oleg V. Fat’yanov, Paul D. Asimow, Tsutomu Mashimo, and Renata M. M. Wentzcovitch. Toward an international practical pressure scale: A proposal for an ipps ruby gauge (ipps-ruby2020). *High Pressure Research*, 40(3):299–314, 2020.
- [206] A. Cornet, A. Ronca, J. Shen, F. Zontone, Y. Chushkin, M. Cammarata, G. Garbarino, M. Sprung, F. Westermeier, T. Deschamps, and B. Ruta. High pressure x-ray photon correlation spectroscopy at fourth-generation synchrotron sources. *Journal of Synchrotron Radiation*, 31(3):527–539, May 2024.
- [207] M. Okada and H. Iwasaki. X-ray diamond anvil cell and pseudo-kossel line pattern. *physica status solidi (a)*, 58(2):623–628, 1980.
- [208] J. C. Phillips. Stretched exponential relaxation in molecular and electronic glasses. *Reports on Progress in Physics*, 59(9):1133, 1996.
- [209] Gerhard Grübel and Federico Zontone. Correlation spectroscopy with coherent x-rays. *Journal of Alloys and Compounds*, 362(1):3–11, 2004. Proceedings of the Sixth International School and Symposium on Synchrotron Radiation in Natural Science (ISSRNS).
- [210] A Duri and L Cipelletti. Length scale dependence of dynamical heterogeneity in a colloidal fractal gel. *Europhysics Letters (EPL)*, 76(5):972–978, December 2006.
- [211] J. Jäckle. Low frequency raman scattering in glasses. In W. Andrew Phillips, editor, *Amorphous Solids: Low-Temperature Properties*, pages 135–160. Springer Berlin Heidelberg, Berlin, Heidelberg, 1981.

- [212] Single monochromator vs double monochromator. <https://www.rfwireless-world.com/Terminology/Single-Monochromator-vs-Double-Monochromator.html>. Accessed: 2022-09-19.
- [213] A. Fontana, R. Dell'Anna, M. Montagna, F. Rossi, G. Viliani, G. Ruocco, M. Sampoli, U. Buchenau, and A. Wischnewski. The raman coupling function in amorphous silica and the nature of the long-wavelength excitations in disordered systems. *Europhysics Letters*, 47(1):56–61, 1999.
- [214] J. O. Hill. *For Better Thermal Analysis and Calorimetry*. International Confederation for Thermal Analysis and Calorimetry, Leeds, UK, 3rd edition, 1991.
- [215] R. Pignatello. *Drug-Biomembrane Interaction Studies*. Woodhead Publishing Limited, Cambridge, UK, 2013.
- [216] J. E. K. Schawe and J. F. Löffler. Kinetics and thermodynamics of crystallization in deeply undercooled metallic melts. *Acta Materialia*, 226:117630, 2022.
- [217] M. Gao and J. H. Perepezko. Separating β relaxation from α relaxation in fragile metallic glasses based on ultrafast flash differential scanning calorimetry. *Phys. Rev. Mater.*, 4:025602, Feb 2020.
- [218] Qiuju Zheng, Yanfei Zhang, Maziar Montazerian, Ozgur Gulbiten, John C. Mauro, Edgar D. Zanzotto, and Yuanzheng Yue. Understanding glass through differential scanning calorimetry. *Chemical Reviews*, 119(13):7848–7939, July 2019.
- [219] M. F. J. Pijpers, V. B. F. Mathot, B. Goderis, R. L. Scherrenberg, and E. W. van der Vegte. High-speed calorimetry for the study of the kinetics of (de)vitrification, crystallization, and melting of macromolecules. *Macromolecules*, 35:3601–3613, 2002.
- [220] M. Y. Efremov, J. T. Warren, E. A. Olson, M. Zhang, A. T. Kwan, and L. H. Allen. Thin-film differential scanning calorimetry: A new probe for assignment of the glass transition of ultrathin polymer films. *Macromolecules*, 35:1481–1483, 2002.
- [221] A. A. Minakov, S. A. Adamovsky, and C. Schick. Non-adiabatic thin-film (chip) nanocalorimetry. *Thermochimica Acta*, 432:177–185, 2005.

- [222] D. Mileva, R. Androsch, E. Zhuravlev, and C. Schick. Critical rate of cooling for suppression of crystallization in random copolymers of propylene with ethylene and 1-butene. *Thermochimica Acta*, 492:67–72, 2009.
- [223] R. T. Tol, A. A. Minakov, S. A. Adamovsky, V. B. F. Mathot, and C. Schick. Metastability of polymer crystallites formed at low temperature studied by ultra fast calorimetry: Polyamide 6 confined in sub-micrometer droplets vs. bulk pa6. *Polymer*, 47:2172–2178, 2006.
- [224] C. Schick. Differential scanning calorimetry (dsc) of semicrystalline polymers. *Analytical and Bioanalytical Chemistry*, 395:1589–1611, 2009.
- [225] Marta González-Silveira et al. Thin-film differential scanning nanocalorimetry: Heat capacity analysis. *The Journal of Physical Chemistry B*, 116(9):2812–2817, 2012.
- [226] Marta González-Silveira et al. In situ nanocalorimetry of thin glassy organic films. *Journal of Non-Crystalline Solids*, 407:1–5, 2015.
- [227] Mettler Toledo / TA Instruments. Flash dsc 2+ – ta instruments / thermal analysis system. https://www.mt.com/ca/fr/home/products/Laboratory_Analytics_Browse/TA_Family_Browse/ta-instruments/thermal-analysis-system-Flash-DSC-2-plus.html, 2025. Accessed: 2025-09-25.
- [228] C. T. Moynihan, P. B. Macedo, C. J. Montrose, P. K. Gupta, M. A. DeBolt, J. F. Dill, B. E. Dom, P. W. Drake, A. J. Easteal, P. B. Elterman, R. P. Moeller, H. Sasabe, and J. A. Wilder. Structural relaxation in vitreous materials. *Annals of the New York Academy of Sciences*, 279:15–35, 1976.
- [229] Christoph Schick and V. B. F. Mathot. *Fast Scanning Calorimetry*. Advanced Topics in Science and Technology in China. Springer, Cham, Switzerland, 2016.
- [230] Joan Ràfols-Ribé, Ana Vila-Costa, Cristian Rodríguez-Tinoco, Aitor F. Lopeandía, Javier Rodríguez-Viejo, and Marta Gonzalez-Silveira. Kinetic arrest of front transformation to gain access to the bulk glass transition in ultrathin films of vapour-deposited glasses. *Phys. Chem. Chem. Phys.*, 20:29989–29995, 2018.

- [231] Ankit Gujral, Kathryn O'Hara, Michael Toney, Michael Chabiny, and M. Ediger. Structural characterization of vapor-deposited glasses of an organic hole transport material with x-ray scattering. *Chemistry of Materials*, 27:150413092114002, 04 2015.
- [232] U. Buchenau, H. M. Zhou, N. Nucker, K. S. Gilroy, and W. A. Phillips. Structural relaxation in vitreous silica. *Phys. Rev. Lett.*, 60:1318–1321, Mar 1988.
- [233] U. Buchenau, A. Wischnewski, M. Ohl, and E. Fabiani. Neutron scattering evidence on the nature of the boson peak. *Journal of Physics: Condensed Matter*, 19(20):205106, may 2007.
- [234] S. Caponi, A. Fontana, F. Rossi, G. Baldi, and E. Fabiani. Effect of temperature on the vibrational density of states in vitreous SiO₂: A Raman study. *Phys. Rev. B*, 76:092201, Sep 2007.
- [235] B. Rufflé, D. A. Parshin, E. Courtens, and R. Vacher. Boson peak and its relation to acoustic attenuation in glasses. *Phys. Rev. Lett.*, 100:015501, Jan 2008.
- [236] Qingyong Ren, Mayanak K Gupta, Min Jin, Jingxuan Ding, Jiangtao Wu, Zhiwei Chen, Siqi Lin, Oscar Fabelo, Jose Alberto Rodríguez-Velamazán, Maiko Kofu, Kenji Nakajima, Marcell Wolf, Fengfeng Zhu, Jianli Wang, Zhenxiang Cheng, Guohua Wang, Xin Tong, Yanzhong Pei, Olivier Delaire, and Jie Ma. Extreme phonon anharmonicity underpins superionic diffusion and ultralow thermal conductivity in argyrodite Ag₈SnSe₆. *Nature Materials*, 22(8):999–1006, aug 2023.
- [237] U. Buchenau. *The Soft-Potential Model and Its Extensions*, chapter 8, pages 299–330. World Scientific (Europe), 2022.
- [238] Ding Xu, Shiyun Zhang, Hua Tong, Lijin Wang, and Ning Xu. Low-frequency vibrational density of states of ordinary and ultra-stable glasses. *Nature Communications*, 15(1):1424, feb 2024.
- [239] Avraham Moriel, Edan Lerner, and Eran Bouchbinder. Boson peak in the vibrational spectra of glasses. *Physical Review Research*, 6(2):023053, apr 2024.
- [240] Avraham Moriel, Edan Lerner, and Eran Bouchbinder. Experimental evidence for the ω^4 tail of the nonphononic spectra of glasses. *Journal of Applied Physics*, 136(22):225105, dec 2024.

- [241] Sadanand Singh, M. D. Ediger, and Juan J. de Pablo. Ultrastable glasses from in silico vapour deposition. *Nature Materials*, 12(2):139–144, feb 2013.
- [242] Xavier Monnier, Juan Colmenero, Marcel Wolf, and Daniele Cangialosi. Reaching the ideal glass in polymer spheres: Thermodynamics and vibrational density of states. *Phys. Rev. Lett.*, 126:118004, Mar 2021.
- [243] Sigma-Aldrich. Ir spectrum table and chart. <https://www.sigmaaldrich.com/IT/it/technical-documents/technical-article/analytical-chemistry/photometry-and-reflectometry/ir-spectrum-table>, 2022.
- [244] J. Wiedersich, S. V. Adichtchev, and E. Rössler. Spectral shape of relaxations in silica glass. *Physical Review Letters*, 84:2718–2721, 2000.
- [245] U. Buchenau, G. D’Angelo, G. Carini, X. Liu, and M.A. Ramos. Sound absorption in glasses. *Reviews in Physics*, 9(April):100078, dec 2022.
- [246] B. Rufflé, G. Guimbretière, E. Courtens, R. Vacher, and G. Monaco. Glass-specific behavior in the damping of acousticlike vibrations. *Phys. Rev. Lett.*, 96:045502, Jan 2006.
- [247] Lijin Wang, Andrea Ninarello, Pengfei Guan, Ludovic Berthier, Grzegorz Szamel, and Elijah Flenner. Low-frequency vibrational modes of stable glasses. *Nature Communications*, 10(1):26, jan 2019.
- [248] Elijah Flenner and Grzegorz Szamel. The origin of sound damping in amorphous solids: Defects and beyond. *Science Advances*, 11(15):eadu6097, 2025.
- [249] Danny Fainozzi, Federico Caporaletti, Flavio Capotondi, Dario De Angelis, Ryan A. Duncan, Laura Foglia, Alessandro Martinelli, Riccardo Mincigrucci, Keith A. Nelson, Emanuele Pedersoli, Marco Zanatta, Alexei A. Maznev, Giulio Monaco, Filippo Bencivenga, and Giacomo Baldi. Temperature effects on the nanoscale thermoelastic response of a sio2 membrane. *APL Materials*, 12(5):051122, 05 2024.
- [250] Peng-Jui Wang, Agnès Huynh, Jinn-Kong Sheu, Xavier Lafosse, Aristide Lemaître, Benoit Rufflé, René Vacher, Bernard Perrin, Chi-Kuang Sun, and Marie Foret. Quartic scaling of sound attenuation with frequency in vitreous silica. *Phys. Rev. Lett.*, 134:196101, May 2025.

- [251] Piarristeguy, Andrea, Noé, Pierre, and Hippert, Françoise. Verres de chalcogénures pour le stockage de l'information. *Reflets phys.*, 74:58–63, 2022.
- [252] Jens Moesgaard, Tomoki Fujita, and Shuai Wei. Unveiling the boson peaks in amorphous phase-change materials. *Journal of Physics: Condensed Matter*, 37(2):025101, oct 2024.
- [253] Jean Yves Raty, Wei Zhang, Jennifer Luckas, Chao Chen, Riccardo Mazzarello, Christophe Bichara, and Matthias Wuttig. Aging mechanisms in amorphous phase-change materials. *Nature Communications*, 6(1):7467, Jun 2015.
- [254] M. Chen, K. A. Rubin, and R. W. Barton. Compound materials for reversible, phase-change optical data storage. *Applied Physics Letters*, 49(9):502–504, 09 1986.
- [255] Shuai Wei, Pierre Lucas, and Charles Angell. Phase change alloy viscosities down to tg using adam-gibbs-equation fittings to excess entropy data: A fragile-to-strong transition. *Journal of Applied Physics*, 118:034903, 07 2015.
- [256] Hans Weber, Jiri Orava, Ivan Kaban, Julian Pries, and A. Lindsay Greer. Correlating ultrafast calorimetry, viscosity, and structural measurements in liquid gete and $\text{ge}_{15}\text{te}_{85}$. *Phys. Rev. Mater.*, 2:093405, Sep 2018.
- [257] Shuai Wei, Moritz Stolpe, Oliver Gross, William Hembree, Simon Hechler, Jozef Bednarcik, Ralf Busch, and Pierre Lucas. Structural evolution on medium-range-order during the fragile-strong transition in $\text{ge}_{15}\text{te}_{85}$. *Acta Materialia*, 129:259–267, 2017.
- [258] Rathinavelu Sengottaiyan, Nishant Saxena, Krishna Dayal Shukla, and Anbarasu Manivannan. Temperature dependent structural evolution and crystallization properties of thin $\text{ge}_{15}\text{te}_{85}$ film revealed by in situ resistance, x-ray diffraction and scanning electron microscopic studies. *Journal of Physics D: Applied Physics*, 53(2):025108, oct 2019.
- [259] Pierre Lucas, Shuai Wei, and Charles Angell. Liquid-liquid phase transitions in glass-forming systems and their implications for memory technology. *International Journal of Applied Glass Science*, 11, 02 2020.

- [260] Julian Pries, Shuai Wei, Felix Hoff, Pierre Lucas, and Matthias Wuttig. Control of effective cooling rate upon magnetron sputter deposition of glassy ge15te85. *Scripta Materialia*, 178:223–226, 2020.
- [261] Julian Pries, Yuan Yu, Peter Kerres, Maria Häser, Simon Steinberg, Fabian Gladisch, Shuai Wei, Pierre Lucas, and Matthias Wuttig. Approaching the glass transition temperature of gete by crystallizing ge15te85. *physica status solidi (RRL) – Rapid Research Letters*, 15(3):2000478, 2021.
- [262] Yudong Cheng, Qun Yang, Jiangjing Wang, Theodoros Dimitriadis, Mathias Schumacher, Huiru Zhang, Maximilian J. Müller, Narges Amini, Fan Yang, Alexander Schoekel, Julian Pries, Riccardo Mazzarello, Matthias Wuttig, Hai-Bin Yu, and Shuai Wei. Highly tunable β -relaxation enables the tailoring of crystallization in phase-change materials. *Nature Communications*, 13(1):7352, Nov 2022.
- [263] Jie Shen, Antoine Cornet, Alberto Ronca, Eloi Pineda, Fan Yang, Jean-Luc Garden, Gael Moiroux, Gavin Vaughan, Marco di Michiel, Gaston Garbarino, Fabian Westermeier, Céline Goujon, Murielle Legendre, Jiliang Liu, Daniele Cangialosi, and Beatrice Ruta. Revealing the role played by α - and β -relaxation in hydrostatically compressed metallic glasses. *Science Advances*, 11(1), 2025.
- [264] Zach Evenson, Beatrice Ruta, Simon Hechler, M. Stolpe, Eloi Pineda, Isabella Gallino, and Ralf Busch. X-ray photon correlation spectroscopy reveals intermittent aging dynamics in a metallic glass. *Physical Review Letters*, 115:175701, 10 2015.
- [265] Maximilian Frey, Nico Neuber, Sascha Riegler, Antoine Cornet, Yuriy Chushkin, Federico Zontone, Lucas Ruschel, Bastian Adam, Mehran Nabahat, Fan Yang, Jie Shen, Fabian Westermeier, Michael Sprung, Daniele Cangialosi, Valerio Di Lisio, Isabella Gallino, Ralf Busch, Beatrice Ruta, and Eloi Pineda. Liquid-like versus stress-driven dynamics in a metallic glass former observed by temperature scanning x-ray photon correlation spectroscopy. *Nature Communications*, 16, 05 2025.
- [266] B. Ruta, S. Hechler, N. Neuber, D. Orsi, L. Cristofolini, O. Gross, B. Bochtler, M. Frey, A. Kuball, S. S. Riegler, M. Stolpe, Z. Evenson, C. Gutt, F. Westermeier, R. Busch, and I. Gallino. Wave-vector dependence of the dynamics in supercooled metallic liquids. *Phys. Rev. Lett.*, 125:055701, Jul 2020.

- [267] Nico Neuber, Oliver Gross, Maximilian Frey, Benedikt Bochtler, Alexander Kuball, Simon Hechler, Fan Yang, Eloi Pineda, Fabian Westermeyer, Michael Sprung, Isabella Gallino, Ralf Busch, and Beatrice Ruta. Disentangling structural and kinetic components of the α -relaxation in supercooled metallic liquids, 2022.
- [268] Vladimir Novikov, K Schweizer, and Alexei Sokolov. Coherent neutron scattering and collective dynamics on mesoscale. *The Journal of chemical physics*, 138:164508, 04 2013.
- [269] Beatrice Ruta, Giacomo Baldi, Y Chushkin, Benoit Rufflé, Luigi Cristofolini, A Fontana, Marco Zanatta, and Francesco Nazzani. Revealing the fast atomic motion of network glasses. *Nature communications*, 5:3939, 05 2014.
- [270] Si-Xu Peng, Yudong Cheng, Julian Pries, Shuai Wei, Hai-Bin Yu, and Matthias Wuttig. Uncovering β -relaxations in amorphous phase-change materials. *Science Advances*, 6(2):eaay6726, 2020.
- [271] William Chèvremon, Thomas Zinn, and Theyencheri Narayanan. Improvement of ultra-small-angle xpcs with the extremely brilliant source. *Journal of Synchrotron Radiation*, 31(1):65–76, 2024.
- [272] J Kalikka, J Akola, R O Jones, S Kohara, and T Usuki. Amorphous ge15te85: density functional, high-energy x-ray and neutron diffraction study. *Journal of Physics: Condensed Matter*, 24(1):015802, dec 2011.
- [273] Emin Mijit, Murat Durandurdu, João Elias F. S. Rodrigues, Angela Trapananti, S. Javad Rezvani, Angelika Dorothea Rosa, Olivier Mathon, Tetsuo Irifune, and Andrea Di Cicco. Structural and electronic transformations of GeSe₂ glass under high pressures studied by x-ray absorption spectroscopy. *Proceedings of the National Academy of Sciences*, 121(14):e2318978121, 2024.