From van der Waals equation to acid-base theory of surfaces: A chemical-mathematical journey

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Abstract   Although occasional observations concerning capillarity, adhesion and cohesion date back to antiquity, the proper scientific investigation of such phenomena began only in the early 19th century, with the fundamental contributions of T. Young and P.S. de Laplace, who provided the basic physical understanding and mathematical description of capillarity. The development of the molecular theory of matter led to the recognition of adhesion/cohesion as a macroscopic manifestation of intermolecular forces (van der Waals) and to their explanation in terms of the electromagnetic theory, with the introduction of the fundamental concepts of Keesom, Debye and London/dispersion interactions. The latter, in particular, relied also on the new ideas of quantum mechanics. Next was the attempt at calculating the adhesion forces between macroscopic bodies as a superposition of interactions between pairs of molecules (Hamaker). The quantum-mechanical approach had two important consequences: on the one hand, through quantum field theory, a completely new interpretation of dispersion forces (Casimir), that allowed to overcome the bimolecular approximation, resulted in the celebrated Lifshitz theory and made possible the first actual prediction of dispersion interactions between macroscopic bodies; on the other hand, through the concept of molecular orbital (particularly HOMO and LUMO), the idea that the ability of molecules to accept or donate electron density may provide an important contribution to intermolecular forces, thus introducing the concept of acid-base interactions. This brief review intends to discuss the main steps that led from van der Waals first insights on intermolecular interactions to the modern acid-base theory, which nowadays constitutes a fundamental paradigm to understand and describe adhesion phenomena.

Keywords   Lifshitz-van der Waals interactions, acid-base interactions, adhesion, cohesion

1. Introduction

Phenomena related to capillarity, cohesion and adhesion have been noticed since antiquity (Plautus, Aelianus, Aristotle) and in the Early Modern Period (Leonardo da Vinci, Galileo) [1,2]; the 18th century saw the first attempts to interpret the observed phenomena in terms of short-range forces among bodies and to provide a quantitative description of them (Clairaut, Segner, Monge) [3–5].

Only at the beginning of the 19th century science arrived at an appropriate mathematical description of the capillary phenomena (Young, Laplace), but on the basis of sole empirical evidence: the existence of a surface, or interfacial, tension between two fluid phases and of a contact angle (Young angle) among a liquid phase, a vapor phase and a solid surface. In spite of important and deep intuitions, the physical origin of the observed phenomena remained obscure because of the limited knowledge of the structure of matter: atom and molecule were still rather vague concepts, to some extent more philosophical than exactly scientific. It was then necessary to wait for Chemistry to provide the correct description of matter as composed of atoms and molecules (Dalton, Avogadro, Cannizzaro), thus opening the way to the interpretation of the forces responsible for capillarity, cohesion and adhesion as interactions between molecules.

The complexity of intermolecular forces in condensed phases precluded, however, any actual possibility to model quantitatively such interactions, an opportunity that was offered instead by the study of the physical properties of real gases, where interactions take place through wide empty spaces between molecules significantly far from each other. By the work of van der Waals the deviations in the behavior of the real gases from that of the ideal gases were ascribed to intermolecular forces. The way was thereby open, through the development of atomic theory, of electrodynamics and quantum mechanics, towards the modeling and fundamental understanding of the intermolecular forces, capillary phenomena and, finally, adhesion between different materials.

2. From T. Young to the microscopic description of molecular forces

The origins of the modern theory of molecular interactions can be traced to the intuitions and discoveries by Thomas Young and John Dalton, the scientistis who, at the beginning of the 19th century, laid the foundations of the theories that now are the basis of description of surface forces and so of the capillarity, cohesion and adhesion. The first one was a man of wide culture, a physician devoted to physics but with wide interests in humanities (Young proposed the early interpretation of Rosetta stone [6]) and the second was born in a very religious family of modest means; both reached the empyrean of modern science and it is impossible today to neglect their contribution to the development of the modern theory of matter and of the forces acting on it. Dalton became a member of the Royal Society only in 1822, while Young was a President of the Society well before; however Young

was fully aware of Dalton's work [7], and he also developed a theory on the origin of his famous eye defect [8].

However, for two centuries their discoveries and the problems they posed remained without a complete and coherent answer. Only today it is possible to look at the atomic and molecular theory and at the forces acting on atoms and molecules responsible for the phenomenon studied by Young, the surface tension, with the hope to arrive at a reasonable understanding. As commented elsewhere [9], however, even today there is no simple and complete theory of surface tension forces. The contact angle (CA), a quantity introduced essentially by Thomas Young, remains poorly listed or even not listed at all in handbooks [10].

The present paper is a short review to underline not all the history, but mainly the physics and the mathematical aspects of the theory of surface forces, giving rise to surface tension, cohesion and adhesion, and also the roles that the two main theories of the 20th century have played in the development of this topic: quantum mechanics and special relativity.

2.1 *The Young-Laplace tarpaulin*

In the paper by Thomas Young [11] the forces acting on the liquid drop are indirectly described through a well-known geometric shape, the so-called linteria curve, a name after the Latin word *linteum* meaning *linen cloth*, sometimes also substituted by the term *tarpaulin*, in analogy with the so-called *catenarian* curve. A flexible, infinitely thin, inextensible, and massless tarpaulin will take the profile of a rectangular tarpaulin attached to two horizontal bars, if filled with water up to the two bars and placed in a uniform gravitational field (with two side vertical planes limiting the flow of the liquid). The shape of the linteria can be defined very simply as a shape in which the curvature is proportional to the depth at each point, when the depth is measured as the height difference between the bar level and the position of a specific tarpaulin point.

The generalization of this condition to a 3D container corresponds to a liquid drop suspended from a planar horizontal surface.

In fact in this specific condition the pressure gap ΔP, i.e., the pressure difference across the surface, is proportional to the mean curvature H of the surface which is defined as twice the reciprocal of curvature radius, or more generally as the sum of the principal curvatures. Hence $\Delta P/H = const$, where the constant is precisely the surface tension attributed to the surface.

The proof of this result was the content of the paper by Laplace [12]. Young's idea of the forces in liquids came in fact from a generalization of a 3D tarpaulin.

The observations of capillary phenomena certainly provided the early basis for the analysis of the molecular forces. In a paper of 1816 [13] Young gave a numerical evaluation of the force and its range in connecting the particles of a fluid. His analysis was based on the ideas of Laplace [12], who had introduced two basic quantities: the first could be grossly defined as the force per unit area between two planar surfaces

in contact (L1) and the second as the work per unit area done in separating the two surfaces to infinite distances (L2). The latter is correlated to the idea of surface tension, it is precisely equal to twice the surface tension, while the former could be regarded as equivalent to an energy per unit volume or to the so-called internal pressure. This second interpretation, the internal pressure, was proposed a few years later, in 1825, by Dupré [14] on a thermodynamical ground, as the partial derivative of the internal energy U with respect to the volume V at a constant temperature T, so that $L1 = (\partial U / \partial V)_T$.

The ratio L2/L1 has the dimension of a length and could be considered the action range of the interparticle forces. We will return to this idea of Young in the next sections.

2.2   *The Dalton forces between atoms*

In the initial theory of Dalton there is no differences between atoms and molecules (which was made clear only after the work of two Italian chemists, A. Avogadro and especially S. Cannizzaro, who only in Karlsruhe Congress in 1860 made clear this fundamental difference).

For this reason, Dalton's conception of atomic/molecular forces was in fact unified. In a paper published in 1808 [15] he called gases *elastic fluids*, attributing to them a property which is typical of solids; moreover, he refused the idea of Claude Louis Berthollet that the forces among atoms depended on their mass, a hypothesis related to the existence of non-stoichiometric ratios among atoms (the so-called berthollide compounds); Dalton hypothesized also the existence of a repulsive force among atoms/molecules dependent on heat.

Contrary to the gases (elastic fluids), Dalton called liquids *inelastic fluids*; their different behaviour with respect to *elastic fluids* or gases is considered as dependent on no better defined "mechanical and chemical" actions.

From this point of view not much was changed in chemistry from the ingenious intuition of the famous alchemist I. Newton in his Principia [16], in 1725:

"And now we might add something concerning a certain most subtle Spirit, which pervades and lies hid in all gross bodies; by the force and action of which Spirit, the particles of bodies mutually attract one another at near distances, and cohere, if contiguous; and electric bodies operate to greater distances, as well repelling as attracting the neighbouring corpuscles; . . . . But these are things that cannot be explain'd in few words, nor are we furnish'd with that sufficiency of experiments which is required to an accurate determination and demonstration of the laws by which this electric and elastic Spirit operates."

2.3   *The equation of state of ideal gases*

The following step to be considered is the formulation of the equation of state of ideal gases, due to B.E.P. Clapeyron in 1834 [17]. In modern terms it is known

that the equation relies on some approximations: gases are described as consisting of material points, with no size and no interaction. The modern thermodynamic approach [18] classifies this equation as an "equation of state", or a homogeneous function of zero order in the extensive variables and written starting from the entropy representation.

In ref. [18] the thermodynamic basis of the approach is clearly stated, i.e. as a fundamental function of ideal gas in the entropy representation, S = S(U,V,n) with some integration constants: entropy S is expressed as a function of internal energy U, volume V and the number of moles n. In this form the function is homogeneous of first order in its extensive variables and has a general value, since it contains all the thermodynamical information about the gas. The common equation of state, written in the form P/T = nR/V to express the intensive quantity P/T in the entropy representation (i.e. the negative derivative of S with respect to V), is a homogeneous zero-order function. Similarly, the "internal energy function" should be written as 1/T = cRn/U in terms of the molar heat capacity c and provides another equation of state, i.e. another homogeneous function of zero-order in the entropy representation.

This very general approach, however, does not give insights in the details of gas behaviour and thermodynamic stability (phase transformations).

The existence of instability in gases and of phase transformations was investigated only in 1822 by Cagniard de la Tour [19] and the development of this topic needed considerable ingenious experimental work.

2.4   The van der Waals equation and van der Waals forces

In 1873 J.D. van der Waals proposed an important modification of ideal gas law in his PhD thesis whose Dutch title was *Over de Continuïteit van den Gas - en Vloeistoftoestand*, in English "On the continuity of the gaseous and liquid states" [20]; for the formulation of this law van der Waals was awarded the Noble Prize for physics in 1910. The original work was translated in English and at least cited and firstly commented on by J.C. Maxwell in 1874 in Nature [21]. Van der Waals equation of state for real gases is well known:

$$\left(P + \frac{an^2}{V^2} \right)(V - bn) = nRT$$

Besides the standard quantities of pressure P, volume V, absolute temperature T and number of moles *n*, along with the ideal gas constant R, van der Waals equation contains two absolutely new parameters. One is the covolume *b*, the molar volume occupied by the molecules or atoms in the gaseous phase, that must be subtracted from the total volume of the container to obtain the free volume available to the moving molecules. Van der Waals assumed such a volume to be equal

to 4 times the actual molar volume of the molecules, an assumption that Maxwell noticed to be made basically on an empirical ground, since molecules are not – we could say today – hard and rigid objects. For instance, the currently accepted value for the covolume of water is 30 cm³/mol, whereas the molar volume of liquid water is only 18 cm³/mol, because molecules in the liquid state are more "compressed" than in the gaseous state: molecules and atoms are soft objects and not hard spheres, whose volume may be modified by the forces acting on them.

But the most interesting parameter is the second one, *a*. It specifies how much the pressure of the gas must be numerically increased in order to reproduce the ideal behaviour. This means to assume that a sort of negative pressure acts between molecules, an inner pressure in the language of modern kinetic theory, that opposes the translational, or motional, pressure exerted by the gas on the external walls. Therefore, molecules interact via attractive forces that, although unable to keep them all together when they are in a gaseous state, however can reduce their capability for relative motion and diminish the pressure they can exert. From an experimental point of view the van der Waals parameters are related to the critical conditions, where van der Waals function P(V,T) at constant T has a point of inflection as a function of V, and defines the curve below which the gas phase comes in equilibrium with the liquid phase (Figure 1).

Van der Waals equation, as a smooth function, cannot rigorously account for the vapor-liquid phase transition, but it can be adapted to estimate the vapor pressure at which vapor condensation occurs at any given temperature below the critical value. Moreover, remarkably, van der Waals model succeeded in describing with a good accuracy the so-called Boyle points of real gases, i.e., the stationary points of the PV-versus-P isotherms (in the neighborhood of a Boyle point a real gas approximately shows an ideal behaviour, since for an ideal gas the PV isotherm is a constant function of P).

Although this point is not usually considered, it is important to stress that the van der Waals equation was not simply an attempt to express quantitatively the idea that attractive interactions occurred among molecules, but it also introduced, although perhaps not explicitly, the concept of repulsive molecular interactions: the definition of covolume involves the assumption that molecules can resist mutual interpenetration, so exhibiting some kind of repulsive force. Such a coexistence of attractive and repulsive forces in real gases can be easily checked on an experimental ground, comparing the ideal to the real behaviour of common gases, as shown in Figure 2.

As for the quantitative description of molecular forces, the first proposal was perhaps due to Mie and Grüneisen (1903–1912), a purely empirical model based on thermodynamic considerations and consisting in a pairwise interaction potential of the form $Ar^{-n}-Br^{-m}$, expressed in terms of the intermolecular distance r and suitable positive parameters A,B,n,m. In these approaches of Mie [22] and Grüneisen [23,24] pressure is considered as a linear function of internal energy. Yet today a Grüneisen parameter expresses the effect that change in the volume of
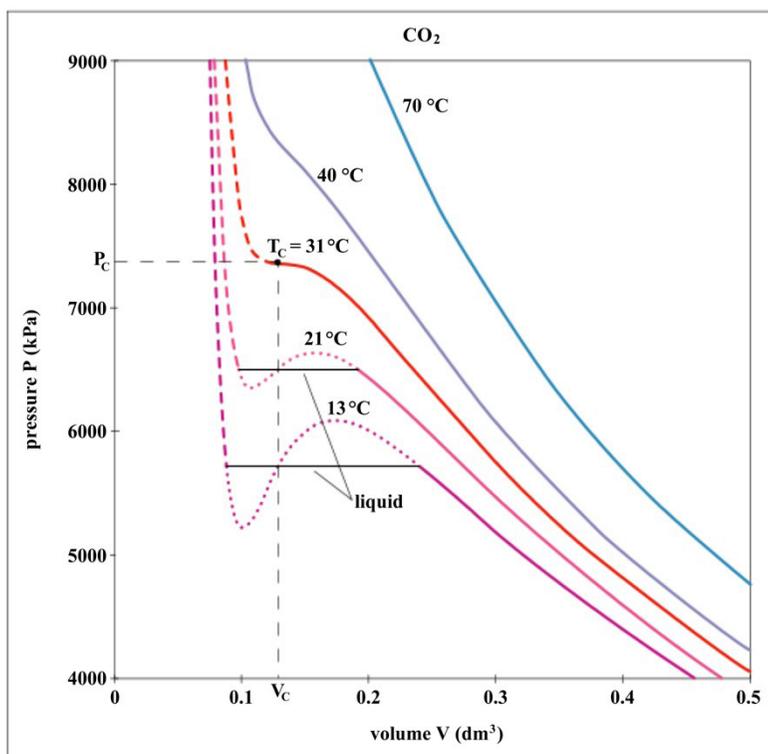
Figure 1 Comparison between the typical appearance of real gas isotherms (in the case of carbon dioxide) and that predicted according to van der Waals model. The non-monotonic sections of the dashed curves show the deviations between the model and the experimental data and correspond to vapor condensation. T_c and P_c denote the critical values of temperature and pressure, respectively.

a crystal lattice has on its vibrational properties and, as a consequence, the effect that change in temperature has on the size or dynamics of the crystal lattice. Mie developed an intermolecular potential for deriving high-temperature equations of state of solids, while Grüneisen extended Mie's model to temperatures below the Debye temperature, at which quantum effects become important.

The theoretical interpretation of the van der Waals forces required the recognition of the role played by the electrical dipoles of molecules, a development that lasted some decades. In spite of a certain level of ambiguity in the literature, now one can define van der Waals forces as all the forces related to dipolar interactions, dependent on both permanent dipoles (as in the case of water or carbon monoxide molecules) or induced dipoles (as in the case of helium atoms subjected to an electric field of whatever origin). Thus, the set of van der Waals (or dispersion) forces will include all the possible combinations of dipolar interactions: dipole-induced
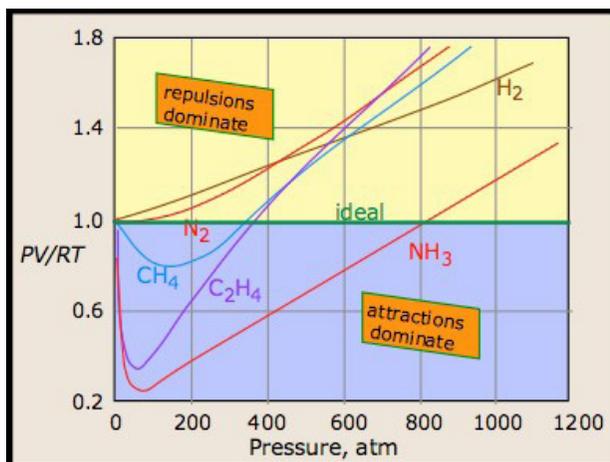
Figure 2 Graph of the ratio PV/RT versus the pressure P for one mole of some simple gases. The ideal behaviour should correspond to the horizontal straight line PV/RT = 1. Above this straight line repulsive forces between molecules are expected to dominate, whereas below the same line molecular attraction prevails. http://chemwiki.ucdavis.edu/

dipole (Debye forces, 1920–1921) [25,26], (permanent) dipole-dipole (Keesom forces, 1921–1922) [27–29], and induced dipole-induced dipole (London forces, 1937) [30]. For all of these contributions, the interaction energies between atoms due to van der Waals forces vary as the inverse of the sixth power of the distance r : $V = -B/r^6$, where B is a constant. Noticeably, Lennard-Jones proposal (1928) [31] of the "12-6" potential energy $V = A/r^{12} - B/r^6$ came well after Debye and Keesom results, and just before London's quantum mechanical analysis of induced dipole-induced dipole interactions. Lennard-Jones potential energy (Figure 3) encompasses the attractive contribution of van der Waals interactions, but it also provides a description of the short-range repulsive interactions, although on a purely empirical basis.

London forces are calculated by using a quantum-mechanical approach (1937), but by considering larger distances compared to the molecular sizes [32] and neglecting the effect of the finite-speed propagation of electromagnetic fields; the electromagnetic interaction between molecules is treated as instantaneous. It must be remembered that London claims his theory satisfies the superposition principle, but actually this is not the case for condensed phases, where interatomic or intermolecular distances are comparable with the size of interacting atoms or molecules: London dispersion forces are not additive [33]. We will come back to this important point in the last section, discussing the macroscopic mechanical properties of solids.

In 1948 H.B.G. Casimir and D. Polder [34] proposed a more accurate description of dispersion forces, valid also for larger distances than those considered in London's model, where allowance is made for the retardation of electromagnetic potentials due to finiteness of light speed. Their conclusions confirm London's

$$V(r) = 4\varepsilon \left(\frac{\sigma^{12}}{r^{12}} - \frac{\sigma^{6}}{r^{6}} \right)$$
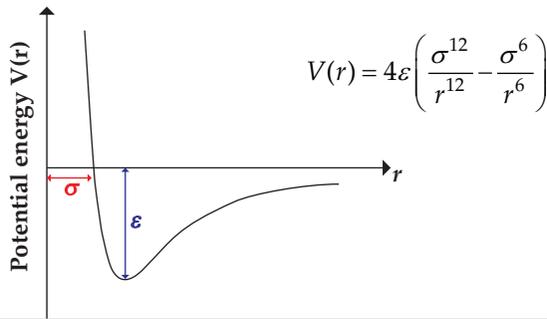
Figure 3 Graph and mathematical definition of the "12-6" Lennard-Jones potential energy. The parameter ε is an energy, representing the "depth" of the "energy well". The larger the depth ε, the stronger the interaction between the particles. The second parameter σ is defined as the value of the interaction distance r at which the potential energy vanishes.

result in the limit of short distances, but they predict a more rapid decrease $V = -B/r^7$ of interaction energy at larger distances, due to the retardation effects.

Casimir and Polder addressed also the problem of quantifying the interaction energy between a neutral atom and a conducting wall, obtaining a result which for short distances is still in agreement with the prediction of London's approach to the same problem, i.e., an interaction energy proportional to $1/r^3$, but which introduces a weaker asymptotic trend of order $1/r^4$ at larger distances, due again to retarded electromagnetic potentials.

According to a common belief, although not supported by written documents, N. Bohr suggested to Casimir the idea that London's dispersion forces could be interpreted in terms of zero-point energy of the electromagnetic field between the interacting atoms (or the neutral atom and the conducting wall). It is noticeable that in the original work by London the idea of zero-point energy was already present, but in a different sense; it was considered as related to the motion of electrons within an atom, related to the quantum mechanical principle of indetermination. The step forward made by Casimir was to shift the attention from the zero-point energy of the electrons within the atoms to the zero-point energy of the quantum electromagnetic field around the interacting atoms [35], and then wonder whether such an approach could be applied to macroscopic bodies.

These ideas led to Casimir's pioneering work (1948) on what is now known as the "Casimir effect", the prediction of an attractive force between two planar conducting parallel plates placed at a very short distance (some nanometers) from each other.

2.5 Details on the Casimir effect

In [36] Casimir addressed the problem of the interaction between two conducting parallel plates placed at a very short distance from each other and being
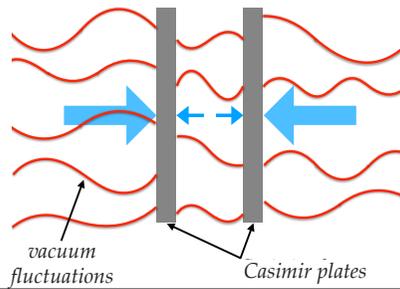
Figure 4 Schematic illustrating the origin of Casimir effect, due to the different zero-point energy of the quantum electro-magnetic field between the two close, parallel conducting plates compared to the field outside.

electrically neutral. Although one may classically expect no interaction at all, due to the absence of net electrical charges on the plates, Casimir had the idea to consider, in analogy with his previous treatment of the retarded dispersion forces between a pair of molecules, the fluctuating zero-point quantum electromagnetic field which is present in the space between the plates according to quantum field theory (Figure 4). Significantly, in spite of some formal problems that have been solved by more recent and rigorous treatments (i.e., formally infinite additive terms that are independent of the plate distance and ignored as physically irrelevant), the energy per unit area associated with such a zero-point electromagnetic field between the plates turned out to be dependent on the distance a according to the formula:

$$E = -\frac{\pi^2}{720a^3}\hbar c$$

thereby corresponding to an interplate force per unit area given by:

$$\boldsymbol{F} = -\frac{dE}{da} = -\frac{\pi^2}{240a^4}\hbar c,$$

where c is the speed of light in vacuum and $\hbar = h/2\pi$. The quantum nature of the interaction is attested by the Planck constant h that appears in the relationship as a factor, so that the force vanishes when h tends to zero in the classical limit. The physical interpretation is well-known and pertains to the odd behaviour of vacuum according to the quantum vision: vacuum is not really empty but due to zero-point energy, or uncertainty principle, it consists of a constantly changing "foam" of virtual photons and particle-antiparticle pairs that continuously appear and disappear. Although almost an amphibian between being and not being, such a "quantum vacuum" depends on the boundaries of the bodies it surrounds and is

able to exert a pressure on them. When the distance between the plates in Casimir's system varies, the properties of the in-between vacuum change, thus resulting in a variation of the "vacuum energy" and a net pressure on the plates. At a distance of some nanometers the pressure may be of order 1 atm.

From an experimental point of view the Casimir effect is difficult to be measured accurately, but the measurement has been repeatedly carried out and the results are in perfect agreement with the theory. Measurements were performed in 1997 by S.K. Larmoreaux at Los Alamos National Laboratory [37] and by U. Mohideen and A. Roy at the University of California, Riverside [38], by using a metal plate and a spherical surface of large radius. In 2001 an Italian group (G. Bressi, G. Carugno, R. Onofrio and G. Ruoso) [39] performed the first measurement between resonators, using parallel plates.

In a book [40] devoted to the Casimir effect, K.A. Milton writes: "*It might seem to the reader that the Casimir effect is an esoteric aspect of quantum mechanics of interest only to specialists. That this is not the case should be apparent from the duality of this effect with van der Waals forces between molecules. The structure of gross matter is therefore intimately tied to the Casimir effect.*". In other words, what chemists have always called "London-van der Waals forces" are actually intimately related to the quantum-mechanical nature of matter and electromagnetic radiation and should more appropriately be named Casimir-Polder forces.

3. Intermolecular forces: the macroscopic point of view

It has been previously seen how van der Waals forces between molecules in real gases can be described within the realm of quantum theory and taking into account the retardation effects in electromagnetic interactions due to the finite propagation speed of electromagnetic fields. The conclusion was that van der Waals forces could be defined as Casimir-Polder forces and that their behaviour had much to do with the deepest nature of matter, space and time (quantum mechanics and zero-point energy).

In this section a different point of view will be presented: the macroscopic one. Instead of describing the forces between two atoms or molecules, the analysis will be focused on the interaction of macroscopic bodies, an aspect which has a huge importance for practical purposes, particularly in the study of adhesion. Notice that Casimir had already adopted this point of view by describing his effect, but in the present discussion the original, unretarded London-van der Waals interactions will be considered and the macroscopic confirmation of such forces investigated.

To this end, the first important concept to be introduced is that of the internal pressure P_i. The internal pressure is already present in the van der Waals equation for real gases and corresponds to the term an^2/V^2; this pressure P_i must be added to the pressure P exerted on the walls of the vessel, the "external" pressure which can be measured experimentally, in order to obtain the so-called "motional", or "translational", or "thermal" pressure P_t. The last one is inherently of thermal

origin, being due to the motion of the atoms or molecules. In other words, the pressure acting on the wall is partially reduced by the internal pressure:

$$P = P_t - P_i.$$

Notice that in the case of an ideal gas there is no need to distinguish between its external and translational pressure, since $P_i = 0$ by definition. By considering 1 mol of water vapor at standard conditions and using a tabulated value [41] of $a = 553.7$ kPa L^2/mol^2, since the occupied volume is $V = 22.4$ L the result is $P_i = 1100$ Pa, i. e. about 1% of the total pressure (1 atm = 101235 Pa). The extension of the same estimates to a condensed phase, e.g., to the case of liquid water or ice, requires an appropriate and formal definition of the internal pressure. In terms of the internal energy U, volume V and absolute temperature T, the internal pressure is defined as:

$$P_i = \left(\frac{\partial U}{\partial V} \right)_T$$

and using the first law of thermodynamics $T\, dS = dU + P\, dV$, possibly along with Maxwell's identities, it can be rewritten into the equivalent form:

$$P_i = T \left(\frac{\partial P}{\partial T} \right)_V - P.$$

This quantity can be found tabulated in the literature [42] and for most liquids its value is around 0.2–0.7 GPa, about 1 billion times higher than that of real gases. This provides a very interesting remark, illustrated in Figures 5(a) and 5(b) which are inspired by a classical textbook on kinetic theory [43].

In Figure 5(a) the internal and translational pressures are compared for a real gas. The external pressure P is smaller than the translational pressure P_t because the latter is slightly reduced by the internal pressure P_i. However, both P_t and P_i are small. In the case of a liquid or solid, Figure 5(b), the situation appears completely different in the sense that both P_t and P_i are large; the molecular interactions are so strong that they can prevent the surface particles from effectively hitting the medium (gas) in contact with the liquid. P_i almost completely balances P_t, although the final difference is again P as before. The final values of the experimental P are the same, but they are the result of two very unlike differences, i.e., between two small pressures in the case of gases, and between two large pressures for condensed phases.

The internal pressure P_i has a good linear correlation with other quantities, particularly with the surface tension σ of liquids, as shown in Figure 6.

Such an occurrence is not surprising, since the internal pressure alters the structure of the liquid surface, which has no molecules outside able to counterbalance
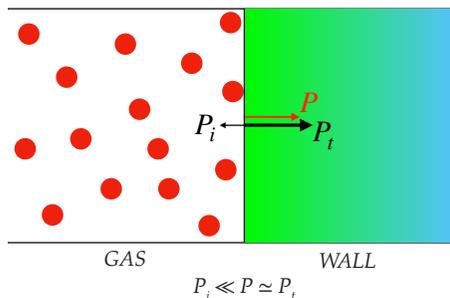
Figure 5(a) Pressures acting in a gas
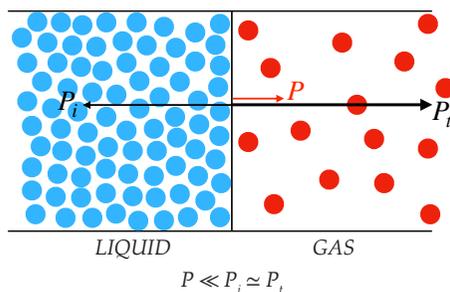
Figure 5(b) Pressures acting in a liquid (or solid)

the action of the internal pressure, thus resulting in a sort of surface "membrane" (the liquid-vapor interface) responsible for the effect of surface tension (Figure 7). Such a membrane had already been hypothesized by T. Young in 1804.

It is the same that appears visible when a water measurer (*Hydrometra stagnorum*, hydrometra is the Latin word for water measurer) or a pond strider (*Gerridae*) "skates" on the water surface (Figure 8).

Another interesting consequence of the internal pressure concerns water, for which P_i is about 0.17 GPa. Looking at the phase diagram of water (Figure 9), one can see that at a pressure of 0.170 GPa and a temperature below 0°C up to about −20°C, water is liquid (see the blue beak-shaped protrusion in the diagram, among ices I, III, V).

This suggests an important consequence: the internal pressure exerted by the bulk on the surface strongly changes the structure of water. Ice, whose density is smaller than that of liquid water, does not resist such a strong pressure and partially melts, taking a molecular configuration characterized by a larger density, as shown in the picture of Figure 10, obtained by numerical calculations of molecular dynamics [44] and confirmed by various experimental measurements. In particular, when hydrogen bonds are broken at an interface, water molecules are forced to adopt configurations that are not as energetically favorable as those deep within
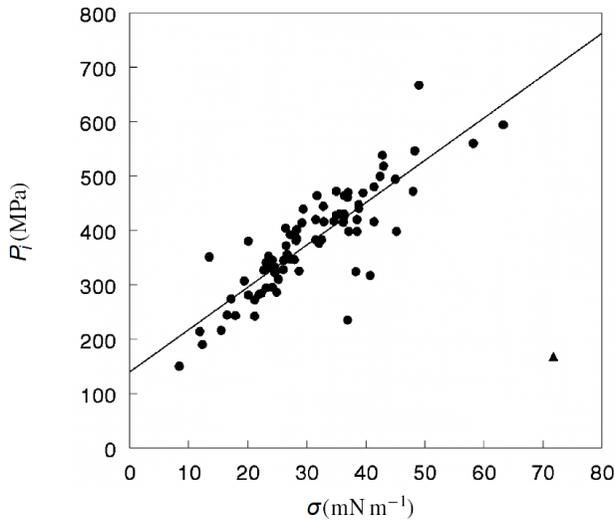
Figure 6 Internal pressure versus surface tension for some liquids. The straight-line shows the linear correlation between data. Water is represented by the triangle and appears as an evident outlier, significantly far from the linear straight-line correlation. Reprinted with permission from [42]. Copyright (2013) American Chemical Society.
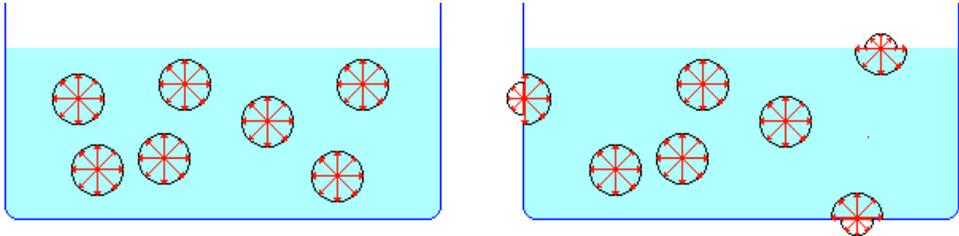

Figure 7 Onset of surface tension due to unbalanced intermolecular forces at the liquid-vapor interface. The intermolecular forces are also responsible for internal pressure.

the bulk of the material. At the interface between ice and its vapor, this can result in the top layers of ice becoming disordered. Such a disorder makes it possible for water at the surface to flow, much like a liquid, accounting for why ice is slippery. At a temperature between 0°C and about −30°C [45,46] the surface of ice and snow presents a thin layer of water in a state between liquid and solid, commonly referred to as a premelting layer. The premelting layer does not behave exactly like supercooled liquid water, so it is also referred to as a quasi-liquid layer. The thickness of such a layer is variable and increases with the increase of temperature; this

Figure 8 A *Gerridae* "skating" on top of water by using surface tension.
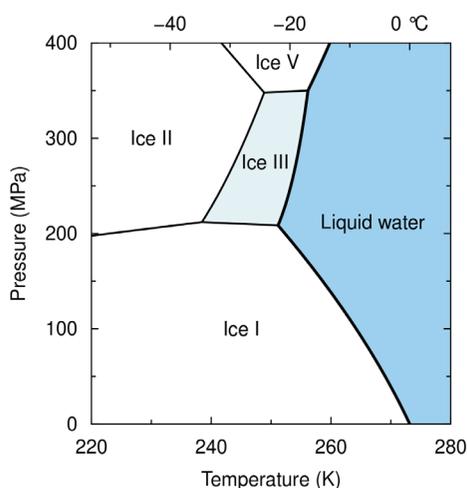

Figure 9 The phase diagram of water in the neighborhood of Ice III phase.

layer, whose existence does not depend on the external load (pressure) exterted on ice or snow, is precisely what makes skiing, ice-skating or curling possible. When it disappears, below about −30°C, the friction coefficient of ice abruptly increases and skiing becomes very difficult, or even impossible.

The common interpretation that skiing and ice-skating are possible owing to the weight of the skier or skater would only work at a temperature slightly below 0°C, but not lesser, because in that condition nobody weighs enough to exert the pressure needed to melt ice. For a skater 80 kg heavy on a pair of skates with a 5 cm² blade each (25 cm long × 0.5 cm thick), the mean pressure would be only about 800 N/0.001 m² = 0.8 MPa. The decrease of the fusion temperature of ice related to the increase of pressure can be estimated by Clausius-Clapeyron equation:
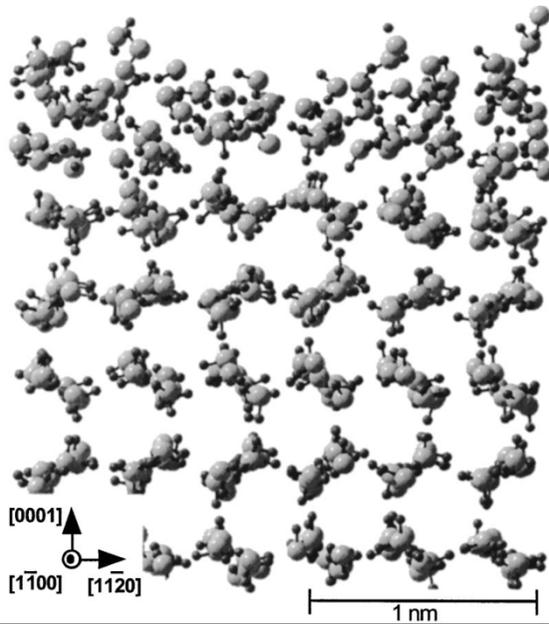
Figure 10 Melting layer on ice Ih surface shown by molecular-dynamics calculation. The large gray and the small black circes denote oxygen and hydrogen atoms, respectively, while the thin lines represent the covalent bonds. The free surface of ice corresponds to the top of the picture. Reproduced from [44], with the permission of AIP Publishing.

$$\frac{dT}{dP} = \frac{T \Delta V}{\lambda}$$

which gives:

$$\Delta T = \frac{T \Delta V}{\lambda} \Delta P$$

in terms of the specific latent heat of fusion $\lambda = 3.33 \cdot 10^5$ J/kg of ice, the reference temperature T = 273 K and the specific volume variation from ice to liquid water $\Delta V = -0.0905$ L/kg, resulting in:

$$\Delta T = -0.059°C.$$

Therefore a skater is unlikely to cause any melting of an ice rink. The idea that the surface of ice could have a "liquid water" film had already been suggested by M. Faraday [47] by a very elegant experiment where two ice spheres were led to stick by a simple contact, using the phenomenon of regelation.
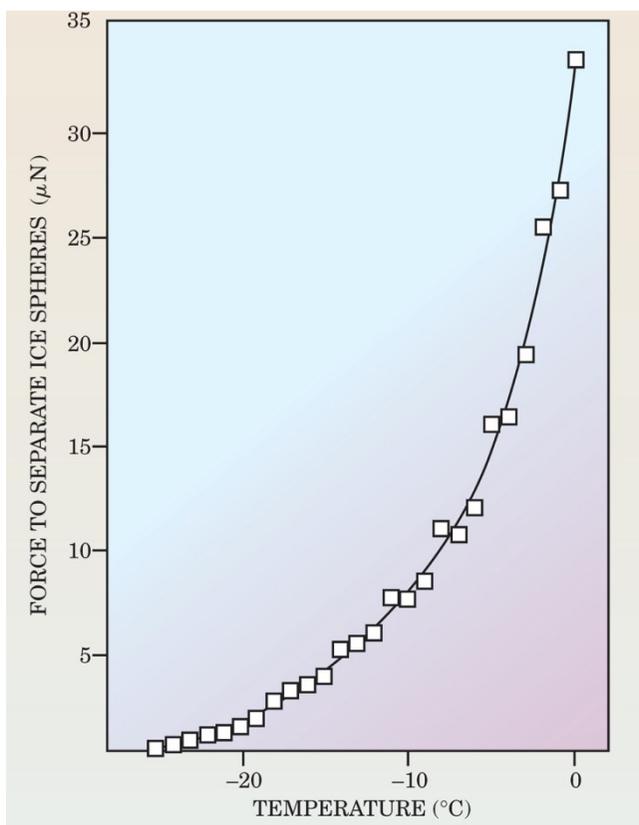
Figure 11 The graph summarizes the results by Hosler and coworkers, who measured the force needed to pull apart a pair of equal ice spheres in contact with each other and in equilibrium. The increase of force as the temperature increased provided an indication that higher temperatures, although still well below the fusion temperature of ice, promote the formation of increasingly thick layers of semiliquid water on the surface of each sphere, so affecting the adhesion between the two surfaces. Data adapted from ref. [51], with permission. Published (1957) by the American Meteorological Society.

This observation was the topic of a discussion [48] among Faraday, the physicist and engineer J. Thomson (brother of W. Thomson, Lord Kelvin), who did not believe the result was correct, and even W. Gibbs, who in contrast agreed with Faraday. Since then the effect has been confirmed many times, for instance by Nakaya and Matsumoto who repeated Faraday's experiment in 1954 [49], or by Hosler and coworkers [50,51], see Figure 11. Alternative experimental methods, like X-ray scattering, have also provided further support to this conclusion by

measuring the correlation length of surface molecules being significantly larger than that for bulk ice molecules [52,53].

Moreover, a similar effect, that could be named "surface melting", is observed also in other materials and gives rise to intrinsically slippery surfaces [54].

Although Figure 6 shows a good linear correlation between internal pressure and surface tension, it also makes evident a significant outlier: water, whose surface tension appears clearly larger than the internal pressure compared to most of liquids. In this respect the behaviour of water is similar to that of other liquids where the role played by hydrogen bonds is significant, thus providing an indication that some important aspect is still missing. This remark was made some years ago by H.S. Frank [55]; water and more generally all the molecules far from an "ideal", simple spherical shape, correspond to systems where part of the free energy is related to "not apparent" degrees of freedom. By using the above definition of the internal pressure as an estimate of intermolecular forces, water seems to have intermolecular forces weaker than, e.g., pentane, a conclusion which appears really odd. Molecules such as hydrocarbons, without strong specific interactions, would have the same internal pressure as water and thereby the same interaction forces. Such a result is doubtful and suspect.

For this reason, the internal pressure of a liquid could be estimated in a different way, by means of another quantity: the density of cohesion energy, i.e., the enthalpy of vaporization per unit volume, which has precisely the same physical dimensions of a pressure. The comparison of the two estimates was made for instance by Marcus for various liquids [42]. It turns out that for "normal" liquids, that is to say liquids without hydrogen bonds, the two quantities take very similar values, but this is not the case for liquids with hydrogen bonds: these bonds cannot be described as van der Waals interactions and have different effects.

For water the cohesion energy per unit volume is about 2.3 GPa in the liquid state, whereas the internal pressure as calculated by the alternative definition was only 0.17 GPa; that of ice would be only slightly larger, just above 2.5 GPa. Therefore, this would be the order of magnitude of the pressure exerted at the interface, which would justify a very peculiar behaviour of water. In the phase diagram one may expect a behaviour of water surface closer to that of other ice phases instead of a disordered, quasi-liquid state. One may simply think that the molecular bombardment at the surface, due to internal pressure, prevents the effective formation of hydrogen bonds and reduces the intermolecular forces to the simpler state of van der Waals interactions.

4. Microscopic description of the interactions between macroscopic bodies

After London's work in 1937 [30] it was commonly believed that a satisfactory description of van der Waals interactions was available. The time was ripe to try an estimate of interactions between macroscopic bodies placed at a very small

distance from each other. And indeed, the first attempt was already made in 1937 [56] by H.C. Hamaker, a Dutch physicist working at the Philips Laboratories of Eindhoven (the same institution where H.B.G. Casimir worked too). Hamaker's basic hypotheses were two: (1) an interaction energy of the form $W(r) = -C/r^6$ for two particles at a distance r and (2) additivity of the interactions. Of course, Hamaker's approach was "pre-Casimir" and thereby suffered from ignoring the retardation effects in the calculation of the pairwise interaction energy; but this was neither the only nor the main problem. In fact, the assumption of pairwise additivity is as crucial in the calculation as basically unsatisfactory from a physical point of view.

Additivity requires that in the interaction between two molecules the electrical dipole orientation (in the case of permanent dipoles) or the molecular polarization (in the case of induced dipoles) is not significantly affected by the neighboring molecules, an assumption that may be rather accurate for low-density materials like dilute gases or vapors, but it appears hardly acceptable for condensed phases (such as liquids or solids).

As an illustration, Figure 12 explains the failure of the pairwise approximation to dipole-dipole interaction for condensed phases.

Unlike dilute gases, dipoles are very close and not freely rotating in a higher-density condensed phase (the mean distance among molecules in condensed phases is approximately ten times less than in gases), so that the minimum energy of the system corresponds to a complex configuration of dipoles that cannot be identified with a minimum energy of a simple pairwise interaction. The actual geometrical structure of the molecules may also play a relevant role because of the closer approach of dipoles. Moreover, particularly when the strength of the dipole moments is significant, thermal motion may not be very effective in randomizing the dipole orientations. As a conclusion, additivity certainly constitutes an oversimplification of the problem.
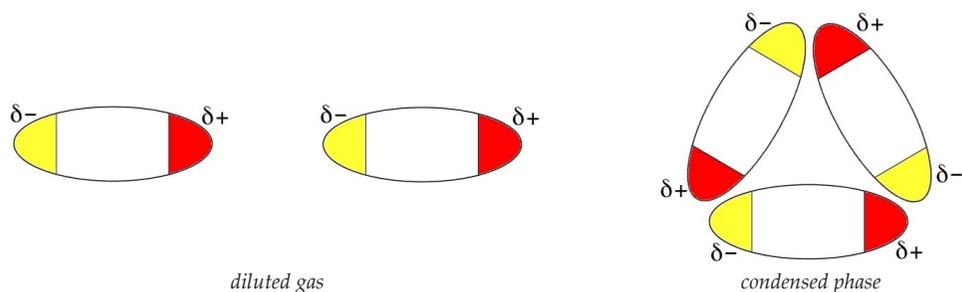
Figure 12 Schematic explaining the reason why the pairwise approximation to dipole-dipole interaction turns out to be satisfactory for dilute gases, but fails in the case of condensed phases.

In spite of the previous difficulties, the Hamaker calculation of the interaction energy can be carried out for various geometries. Table 1 shows some examples. In all formulas the interaction energy and force are expressed in terms of a characteristic constant that depends on the kind of atoms or small molecules comprising the two interacting bodies. In the simplest case of the direct pairwise atom-atom (or molecule-molecule) interaction the constant is a "van der Waals coefficient" C, that under quite general assumptions can be derived from the experimental parameters a and b of van der Waals real gas equation [57]:

$$C = 1.05 \cdot 10^{-76} \cdot ab \ Jm^6.$$

In contrast, for macroscopic bodies the central role is played by the "Hamaker constant" A, defined as:

$$A = \pi^2 C \rho_1 \rho_2$$

in terms of the previous C and the number densities per unit volume ρ_1 and ρ_2 of the two bodies.

The value of the Hamaker constant is similar even for very different materials and is of order 10^{-19} J, with typical values between 0.4 and 4×10^{-19} J, as noticed in [59] (see Table 2), also when the bodies consist of molecules with great differences in polarizability and size. Far from being a simple coincidence, this is because the constant C in the intermolecular pair potential according to London's theory is approximately proportional to the square of the polarizability α, which is in turn roughly proportional to the volume v of a molecule; since the number density ρ is proportional to $1/v$, the Hamaker constant A is not expected to vary too much.

Nevertheless, as already pointed out, the above calculations rely on the additivity assumption that is certainly flawed on a physical ground and therefore represents a crude approximation. This fundamental problem was fully overcome by Lifshitz theory in 1956, by means of a completely different approach.

Hamaker uses another basic condition in addition to the non-delayed method of electrostatics, it uses the so-called torque additivity method. What is it about?

The interactions between all the particles of one body and the other are considered one pair at a time and are added or integrated with each other; this seems obvious and is certainly the simplest from the mathematical point of view; obviously it should be divided by two because each interaction is considered twice; but that is not the point.

This point of view assumes that each pair of atoms or molecules is actually capable of reaching the MINIMUM of potential energy; this makes sense for cases in which the particles are sufficiently distant as in gases, and therefore free to move; but it does NOT make sense in cases where the particles are very close as in solids and liquids; in this second case the minimum is not a pair but a multibody and does not have a simple expression.

Table 1 Van der Waals interactions between macroscopic bodies in the Hamaker's approximation (pairwise additivity of molecular interactions with unretarded electromagnetic potentials). Formulas from [58].

Geometry of interacting bodies whose surfaces are D apart	Van der Waals interaction	
	Energy W	Force −dW/dD
Two atoms or small molecules of size a at a distance $D \gg a$	$-C/D^6$	$-6C/D^7$
Two spheres or large molecules of radii R_1 and R_2 at a distance $D \ll R_1, R_2$	$-\dfrac{A}{6D}\left(\dfrac{R_1 R_2}{R_1 + R_2}\right)$	$-\dfrac{A}{6D^2}\left(\dfrac{R_1 R_2}{R_1 + R_2}\right)$
Sphere or large molecule of radius $R \gg D$ near a large flat surface	$-AR/6D$	$-AR/6D^2$
Two large parallel flat surfaces of sizes $a_1, a_2 \gg D$ (per unit area)	$-A/12\pi D^2$	$-A/6\pi D^3$
Two parallel cylinders or rods of radii $R_1, R_2 \gg D$ (per unit length)	$-\dfrac{A}{12\sqrt{2}D^{3/2}}\left(\dfrac{R_1 R_2}{R_1 + R_2}\right)^{1/2}$	$-\dfrac{A}{8\sqrt{2}D^{5/2}}\left(\dfrac{R_1 R_2}{R_1 + R_2}\right)^{1/2}$
Cylinder or rod of radius $R \gg D$ near a flat surface (per unit length)	$-\dfrac{A}{12\sqrt{2}D^{3/2}}\sqrt{R}$	$-\dfrac{A}{8\sqrt{2}D^{5/2}}\sqrt{R}$
Two cylinders or rods of radii $R_1, R_2 \gg D$ crossed at 90°	$-\dfrac{A}{6D}\sqrt{R_1 R_2}$	$-\dfrac{A}{6D^2}\sqrt{R_1 R_2}$

Table 2 Hamaker constants as calculated by assuming pairwise additivity.

Medium	VDW Constant, C (10^{-79} Jm^6)	Density of Atoms, ρ (10^{28} m^{-3})	Hamaker Constant, $A = \pi^2 C \rho^2$ (10^{-19} J)
Hydrocarbon	50	3.3	0.5
CCl$_4$	1500	0.6	0.5
H$_2$O	140	3.3	1.5

VDW = Van der Waals

In the condensed phase, the procedure chosen by Hamaker gives excessive importance to polar interactions because they are calculated with the additive method; such interactions cannot reach the minimum value for each pair but rather a single global minimum that cannot be calculated in a trivial way. The common diatribe about polar/non-polar in the condensed phase is based on the results obtained from the Hamaker approach which in fact is a rough approximation, applicable only in the gas phase; but that has remained in our jargon, unreasonably.

Two questions with short answers may be useful to analyse:

1. What is the strength of the van der Waals forces evaluated by this method? For two planar contact surfaces (0.2 nm apart) a typical value is:

$$P = A/6\pi D^3 \approx 7 \times 10^8 \ \text{Nm}^{-2} \approx 7000 \ \text{atm}$$

The pressure that keeps them together is enormous, even if it rapidly decreases with distance; at 10 nm it becomes only 0.05 atm, but it is still measurable.

2. Why if something breaks we are not able to re-join it perfectly just by putting the parts back together? Well, we are immersed in an ocean of humid and dirty air that immediately intrudes between the detached parts, modifying the surfaces and contaminating them; furthermore, unless they are really flat, the surfaces of contact between the parts will never fit perfectly together.

4.1   Lifshitz theory

At the time of the publication of Lifshitz paper [60] the science situation was very different from today; the Soviet Union school of physics was largely considered as a very advanced one and the arms race was the reason for great attention to the Soviet scientific results. As an example, Lifshitz cited a book by Rytov [61], book that today can be easily found in the literature as a free pdf. But in the introduction of its English translation one may read:

ACKNOWLEDGMENTS

The key sentence is: "there is considerable current interest in the topics treated by Rytov and a comparable English text is lacking"; therefore, this document was both very interesting and contemporarily "classified"; this could explain the difficulty with which the Rytov and Lifshitz ideas entered the physical chemistry of the time.

The reason for the interest of US Air Force and US Atomic Commission for the Rytov book was probably related to the strong electromagnetic pulse generated by atomic explosion in high atmosphere, whose existence and importance was recognized only after the Yucca experiments and then after the Starfish Prime experiment, carried out respectively in 1958 and 1962 on Yucca mountain and at 400 km height on Johnston Atol (USA). The translation of the book was completed in 1959.

Sergei Mikhailovich Rytov was a mathematical physicist and one of the most prominent physicists of the 20th century; born in 1908, in 1937 he proposed an efficient method for the analysis of the structure of waves in a non-homogeneous medium (Rytov method) - a powerful tool for the study of wave propagation. Sergei Mikhailovich Rytov is the author of the most general phenomenological theory of molecular light scattering, which includes an analysis of the Mandelstam-Brillouin radiation spectra and depolarization as well as the scattering spectrum described by thermal fluctuations. This theory is confirmed by numerous experiments and is a reference in the field. In his work, he also gave a rigorous solution to the problem of the reflection of electromagnetic waves coming from a layer of material exhibiting a negative dielectric constant; he explored the question of the relationship between the Poynting vector, the group velocity vector and the energy density in the propagation of electromagnetic waves in anisotropic media.

| phase 1 | phase 3 (vacuum) | phase 2 |
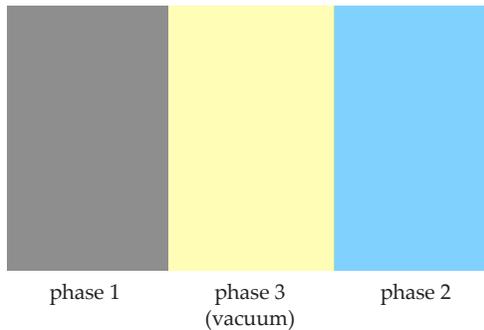
Figure 13 Schematic depicting Lifshitz interaction model between two large bodies. The interacting bodies are represented as indefinitely extended homogeneous phases (phase 1 and phase 2), separated by two parallel planes at a fixed distance from each other. The intermediate region may be occupied by another medium (phase 3), or simply by empty space (vacuum).

The "Rytov method" is extremely general and could be applied to material waves in hydrodynamics as well as to electromagnetic waves as it is in our case.

The scheme of Lifshitz approach is as follows (see Figure 13):

1. the interaction between two bodies 1 and 2 separated by a phase 3, in which a fluctuating electromagnetic field acts, is computed by determining the energy of the fluctuating electromagnetic field, followed by calculation of the forces resulting from such a field.
2. after that a series of cases, as small separations and different temperatures, are considered.
3. short considerations on experimental comparison are finally made using the experiments by Deriagin and Abrikosova [62,63]. We prefer to refer here to another paper published in Scientific American [64] which is easier to find as well as reporting a more accurate comparison of theory and experiment.

It is clear from the first page of the paper that Lifshitz's approach is both classical and quantum: classical because it uses Maxwell's equations, quantum because in the same equations allowance is made for the fluctuation term of the electromagnetic field, which is described by Rytov's theory and has a quantum nature. This can be seen from the expression for the correlations (1.2) and (1.4) of the paper, where Planck's constant appears. Only in the empty space between the two media the fluctuation field K is zero, and therefore the equations are those of Maxwell as well. On the other hand, the final expression for the force depends on $h/2\pi$, thus it is clear that the quantum aspect plays a fundamental role.

It is precisely in the expression for those correlations that the link between the fluctuation field and the macroscopic properties, measurable, of the continuous medium (complex dielectric constant as a function of the monochromatic

electromagnetic wave frequency) emerges. Such a link constitutes the reason for which Lifshitz's theory is so famous. But without Rytov's theory it would not be possible to calculate the interaction energy in terms of the dielectric constant. As well summarized by Lifshitz:

> *"We can however approach this problem in purely macroscopic fashion (since the distance between the bodies is assumed to be large compared to interatomic distances). From this point of view, the interaction of the objects is regarded as occurring through the medium of the fluctuating electromagnetic field which is always present in the interior of any absorbing medium, and also extends beyond its boundaries, - partially in the form of travelling waves radiated by the body, partially in the form of standing waves which are damped exponentially as we move away from the surface of the body. It must be emphasized that this field does not vanish even at absolute zero, at which point it is associated with the zero point vibrations of the radiation field."*

There are a series of conditions and results which appear extremely important for our purposes:

a. The calculation is based on the properties of macroscopic matter and the properties (and even the existence!) of single molecules are not considered at all. There is ONLY one assumption which refers to molecules; the theory is valid if the distance between the bodies is larger than the molecule's size.

b. Two closely spaced bodies are considered and the electromagnetic field produced in the narrow gap between them and in the space around them by the fluctuations in the various regions of the material is calculated. From the difference between the field strength in the gap and in the surrounding space the force can be obtained.

c. The fluctuations, expressed using the Rytov formulas, contain the Planck quantum constant and are valid at all temperatures, also at absolute zero. They use the dielectric permeabilities of the macroscopic bodies, which is an experimental property.

d. The effect of the temperature is indirect: with the temperature variation the absorption spectrum of each phase varies (because the quantum state of its electrons varies) and consequently there is a temperature effect.

e. The calculated interactions are not additive, as illustrated in Figure 14. This is really a fundamental feature of Lifshitz approach.

f. Given the non-additivity of forces it is impossible to describe mathematically the macroscopic situation by a microscopic, two-molecule model approach, but the converse can be done. The attraction between a pair of isolated molecules comes out of the Lifshitz theory as a special limiting case.
To examine this point in more detail, look also at the way the author shows that his theory reproduces the London result, the paragraph after equation (3.1) in Lifshitz paper.
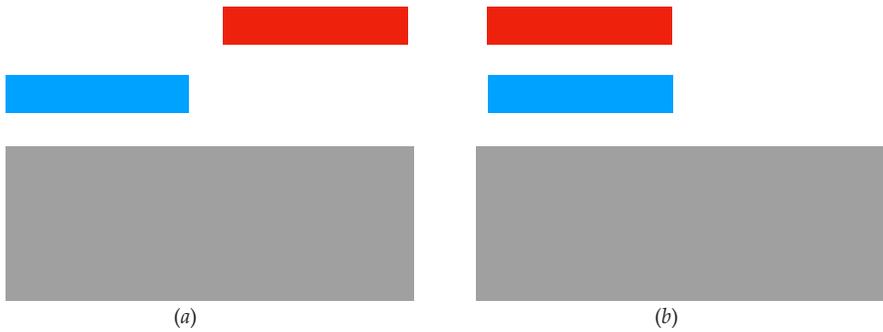
Figure 14 The overall interaction of three bodies is not additive in Lifshitz theory, so that the situations illustrated in (a) and (b) are not equivalent.

He practically says, even if he does not report the details of the calculations and the task is not trivial at all, that when the two interacting media are very rarefied (gases), if the two-body approximation and the London model of interaction between the two are applied to neutral atoms, by integrating the contributions of the interaction (atom of medium 1) - (atom of medium 2) on the half-space of the first material and on the half-space of the second one obtains his formula (within the limit of dielectric constants close to 1, that of vacuum). Therefore, it is a double check: not only that London's formula is in agreement with Lifshitz theory, but also that for rarefied materials the sum of the two-body interactions is physically acceptable.

This implies that the interaction between condensed materials at very short distances may reserve some surprises, since in that case the two-body approximation is not satisfactory and may predict forces which deviate significantly from the experimental results.

The final comparison between Lifshitz theory and Deriagin experiment is evidenced in Figure 15 and Figure 16, from which it appears that there is an extremely good agreement.

A very important point is the method used to replace the additivity approach so critical in Hamaker. This is the image method applied to the electric field and therefore an electrostatics method, in which the electric field is conceived in a stationary way, without considering the fact that the field is transmitted (with all its possible time variations) at the speed of light. To analyze these cases, the so-called Poisson equation is applied, the basis of electrostatics, which corresponds to saying that the Laplacian of that certain field is equal to the charge density divided by the dielectric constant and changed in sign:

$$\nabla^2 \phi = -\frac{\rho}{\varepsilon_0}.$$
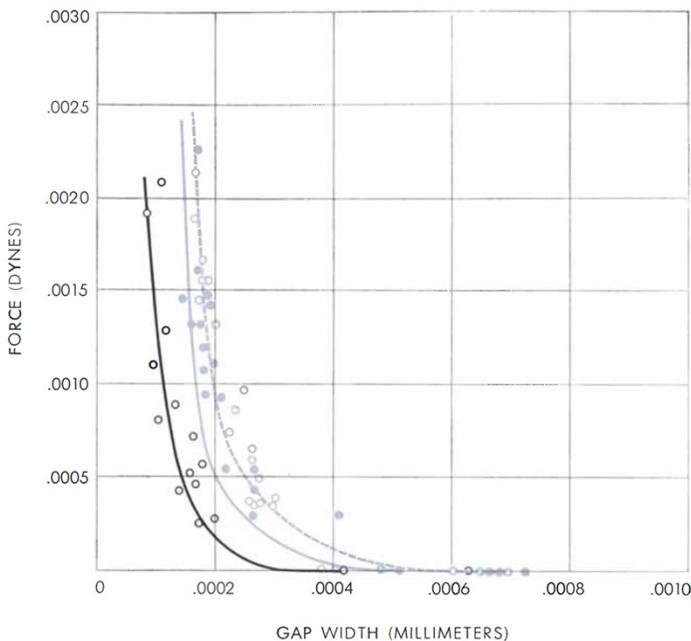
Figure 15 The force of attraction measured between a flat plate and a spherical lens 10 cm in radius, as a function of the mutual distance between the bodies. The points represent the experimental values, while the curves correspond to the predictions of Lifshitz theory. Data for quartz bodies are in black; for thallium halide, in solid gray; for a quartz and a chromium body, in broken gray line and open dots. From [64] with permission of Scientific American.

The symbol ϕ stands for the potential of the electric field (energy per unit of charge) and is valid for a point charge but also for a charge distribution in space, such as that of a molecule (in this case it is also a complex function). What is the practical meaning of the Laplacian? It is the average of the vector values leaving a point. There is a graphic way to see the Laplacian: let us consider the potential as the function describing the levels of gray distribution of an image, the one on the left of Figure 17.

The Laplacian is the image on the right, obtained by replacing a "transformed" value at each point of the image by means of a matrix operation pixel by pixel that provides the sum of the second derivatives calculated at that point; it can be shown that such a kind of "finite-differences" Laplacian operator is described by the following matrix:

$$\begin{bmatrix} 1 & 1 & 1 \\ 1 & -8 & 1 \\ 1 & 1 & 1 \end{bmatrix}.$$
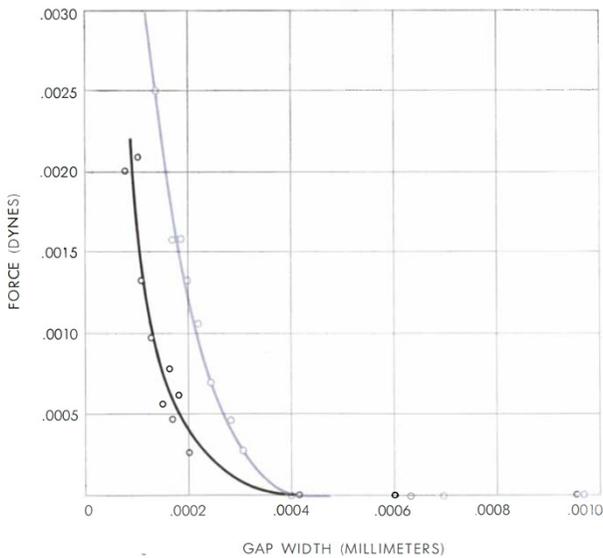
Figure 16 The same as in Figure 15, but for a 10-cm quartz sphere (in black) and for a 26-cm sphere (in gray). From [64] with permission of Scientific American.

If the point of interest is the one in the center and you give it a weight –8, then you give weight 1 to those just above, below, backwards and forwards (the nearest neighbors), and for each point of interest compute the sum of these weights multiplied by levels of gray of the matrix points and divided by a constant factor h^2, the square of the space step h. The result is the image on the right that represents the sum of the second derivatives with respect to the horizontal and vertical coordinate at each point, essentially highlighting the contours of the image, in this case the profiles of the houses and the landscape.

Therefore, if you have a 2D potential field represented by the image on the left, its Laplacian provides the profiles described on the right that identify the areas of maximum variation of the variation (the derivative of the derivative, the second derivative), the areas of maximum contrast of the image that you identify by eye as profiles of objects.

Lifshitz aim was to calculate the forces of interaction between the particles of his system of atoms and molecules of macroscopic dimensions, but he did not have the potential of the field that interested him. He had only the distribution of charges, nuclei and electrons, i.e., he had his own transform, his own Laplacian and wanted to find the potential function, from which then to calculate the forces (remember that the force is the derivative, with changed sign, of the potential with respect to the distance, a sort of rate at which the potential changes, with changed sign). Therefore he wanted to go "backwards" from the right image to the left one. How do you go about solving this "inverse" problem in a general way?
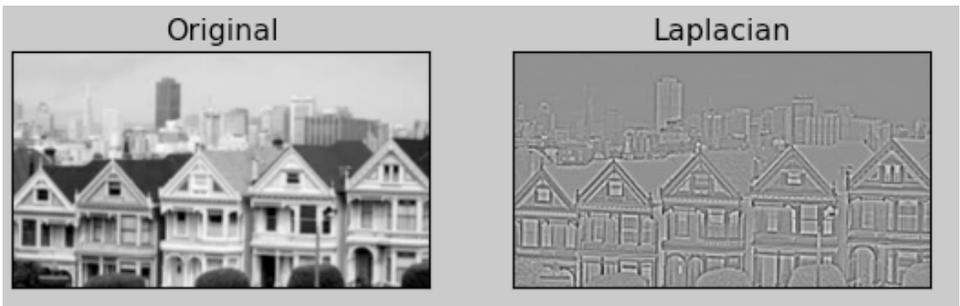
Figure 17 The potential ϕ represented as the levels of gray of a b/w image (left) and the corresponding Laplacian as calculated by a standard finite-difference method (right).

The charge image method is a possible solution, based on the properties of the Poisson equation, known since the 19th century.

The basic concept is the uniqueness theorem: there is only one acceptable solution to the potential problem for each case (boundary conditions) considered. In some cases the solution is simple, in others it is not at all. But it may happen that problems, whose solution is difficult, have an equation and a set of boundary conditions identical, at least in a region of the space, to those for which a simple solution is available. Therefore, <u>by the uniqueness theorem</u> we can use the same simple solution to solve the difficult problem at least in that region of space.

To simply show the principles of the image method one can use an example due to Feynman in his famous physics book [65] (for an illustration see Figure 18).

Look at the top of the image. We have an infinite conducting plane placed in space, (for simplicity we can connect it to earth (so its potential is zero) and, at a finite distance from this, a positive electric charge. What will be the potential in all the space on the top? We do not have a clear solution. We can guess two or three hypotheses:

– the positive charge induces a negative charge on the conductor, with non-uniform distribution (it will probably be greater close to the point charge and less as one moves further along the conductor); this charge in turn generates a potential in space; but until we know the charge distribution we cannot determine how the potential behaves;
– the potential along the conducting plane is zero because it is placed on the ground;
– the potential at infinity with respect to the charges is zero.

We may solve the problem by applying the image method i.e., we can use the uniqueness of the solution. Let us imagine placing a second charge equal to the first but opposite (it is the image or imaginary charge); let us place it at the same
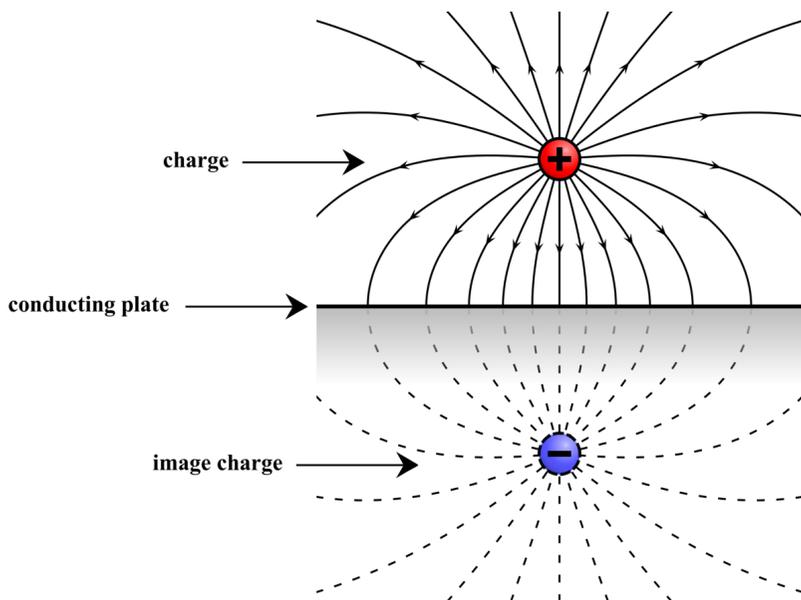
Figure 18 The method of images in electrostatics used to determine the potential generated by a positive point charge in the vicinity of an infinite conducing plate.

distance from the plane and in a symmetrical position with respect to it, as shown in the figure, so on the plane the potential will be zero.

This will give us the same boundary conditions as in the top half-space, but also new conditions in the bottom half-space; the valid solution on the top will be the same in the two cases. Mathematics, by means of the uniqueness theorem, allows us to get this result.

This method of the image charge, i.e., of the charge that looks like a reflection of the real charge to the opposite side of the plane, can be used in many other cases and allows Lifshitz to calculate what he needs.

Israelachvili's book [66] contains the essentials of Hamaker's and Lifshitz's ideas, explained in a lucid way and with several exercises and examples. It has to be noted that the book does not contain any reference to acid-base theory, which will be analysed in the following section and represents the "state-of-the-art" of adhesion theory.

5. The acid-base interactions and acid-base theory

Lifshitz approach to the determination of molecular interactions between macroscopic bodies, although very general and powerful, has an important limitation: the calculated interactions do not take into account the structure of the molecular orbitals, but only some macroscopic, electromagnetic properties of the molecules.

The interacting body is described as a continuum material, endowed with some quantum properties (e.g., the zero-point energy); the electromagnetic interaction is retarded and the assumption of pairwise molecular interaction is not required, thus removing a crucial flaw of Hamaker's treatment. Nevertheless, the quantum-mechanical details related to the structure of molecular orbitals, along with any other microscopic feature, are not considered. The discrete nature of matter is actually ignored.

That some important contribution to the intermolecular interactions was missing was already suggested by the occurrence of considerable outliers in the otherwise good linear correlation between surface tension and internal pressure of liquids, outliers corresponding to molecules (like water) that are known to have significant hydrogen bonds (Figure 6). The difference between the internal pressure and the enthalpy of vaporization per unit volume, in the case of water, has already been stressed previously; the disruption of all the possible intermolecular interactions in the case of the enthalpy of vaporization demonstrated an attractive contribution that the internal pressure alone was not able to justify. And such an occurrence was found to be critical in the case of liquids with hydrogen bonding. Hydrogen bonds cannot be classified as "dispersion" molecular interactions, described by London's, Hamaker's or Lifshitz's analysis; they are something else, intimately connected with the microscopic quantum-mechanical structure of matter.

The modern interpretation [67–69] of hydrogen bonding relies on the concept of charge-transfer interaction, or interaction between frontier orbitals. Such a concept is very powerful and able to provide a unified description of molecules and materials, through which properties like the valence and conduction bands in conductors, semiconductors and insulators, the frontier orbitals of molecules, or the Fermi energy in solids appear as particular cases of a general theory.

Arriving at this last step of our analysis we need to give an explicit definition of adhesion in chemical terms; and probably the most important point is that adhesion constitutes however a kind of chemical reaction although no new chemical bond in classical terms is formed. Even in the case of reversible and weak interactions the adhesion is a chemical reaction which implies the modification of the electron distribution in the most sensitive part of the molecules. This part is represented by the so-called "frontier orbitals", as defined in his seminal book by I. Fleming [70].

While in the analysis of a typical chemical reaction the perturbative approach does not appear very useful, because while the original system changes it cannot be applied and is limited to the early beginning of the process. In the case of adhesion, where the reaction is intrinsically weak, the perturbative approach is successful.

The frontier orbitals are the so-called HOMO (Highest Occupied Molecular Orbital) and LUMO (Lowest Unoccupied Molecular Orbital), functions pertaining respectively to the highest occupied molecular orbital and to the lowest unoccupied one. Generally, the HOMO has an energy value which is well lower than that of the corresponding LUMO and the two orbitals are on different molecules.

There is a general equation to express the energy variation due to the interaction process [71]:

$$\Delta E = -\underbrace{\sum_{a,b}(q_a + q_b)\beta_{ab}S_{ab}}_{\text{first term}} + \underbrace{\sum_{k<h}\frac{Q_kQ_h}{\varepsilon R_{kh}}}_{\text{second term}}$$

$$+ \underbrace{\left(\sum_r^{occ.}\sum_s^{unocc.} - \sum_s^{occ.}\sum_r^{unocc.} \frac{2(\sum_{a,b}c_{ra}c_{sb}\beta_{ab})^2}{E_r - E_s} \right)}_{\text{third term}}$$

where:

q_a and q_b are the electron populations of orbitals a and b, respectively

β_{ab} and S_{ab} denote the resonance and overlap integrals for the interaction orbitals a and b, respectively

Q_k and Q_h are the total electrical charges on atoms k and h, respectively

ε is the local relative permittivity (dielectric constant)

R_{kh} stands for the distance between the (nuclei of) atoms k and h

c_{ra} is the coefficient of atomic orbital a in the linear combination defining the molecular orbital r (r refers to the molecular orbitals of one molecule, while s refers to those of the other)

E_r denotes the energy of the molecular orbital r

the upper limits *occ.* and *unocc.* specify that the summations must be carried out on the occupied and unoccupied orbitals of the two molecules, respectively.

The first term describes a purely electrostatic interaction, by taking into account the electric charge distribution in the occupied orbitals of the two molecules; the second term is purely electrostatic too and considers only the positions of the atoms (nuclei) in each molecule; the third term is related to the interaction between occupied and unoccupied orbitals of the two molecules (and it is apparent that HOMO and LUMO, on having the closest energies, provide the largest contribution).

Therefore, the main contributions to the interaction of two colliding molecules are the following:

1. the repulsion between the occupied orbitals of one molecule and the occupied orbitals of the other molecule;
2. the attraction between any positive charge of one molecule and any negative charge of the other (or repulsion for any positive);
3. the interaction between the occupied orbitals of one molecule (particularly the HOMO) and the unoccupied orbitals of the other (especially LUMO).

From these "practical" rules it becomes clear that electrical charges (even coming from dipoles) which exist on the molecules may influence the interaction, but also that these "polar" interactions are not alone and may be overcome by the direct orbital interactions related to the specific shape and symmetry of the orbitals. So, finally, after many years of investigations, the importance of quantum mechanical interactions depending on the details of the molecular structure appears decisive also to adhesion.

Values of HOMO and LUMO energies of common molecules are collected and freely available as in the case of PITT quantum repository data base [72] (a data base managed by the Department of Chemistry at the University of Pittsburgh, https://pqr.pitt.edu/). As an example, the 60 liquids used in the development of acid-base theory and whose acid-base parameters are given in the seminal book of van Oss [73] are shown in the Figure 19.

How is it possible to apply this description? And is it useful and complete? We may start from the basic idea of this interaction expressed in Figure 20.
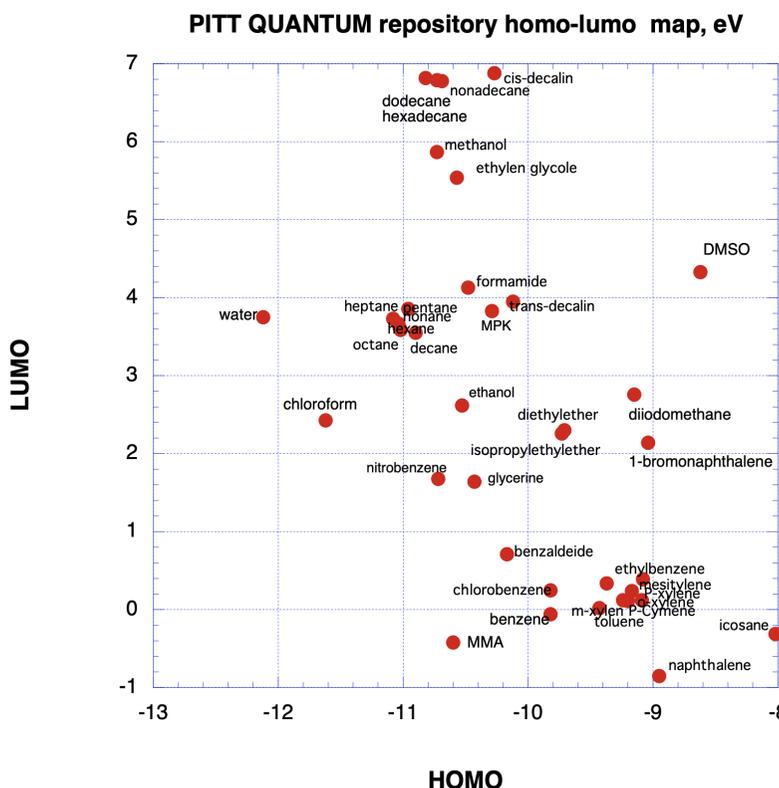
Figure 19 LUMO versus HOMO energies (eV) for various common liquids. Data from [72]. For the numerical data see the Appendix.
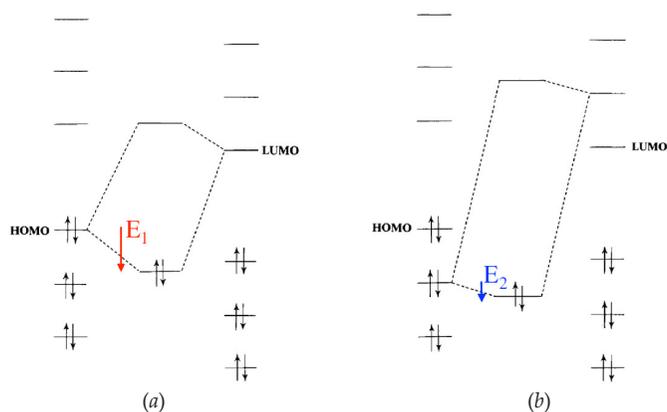
Figure 20 Effect of the interaction of the HOMO of one molecule with the LUMO of another (left). Comparison with the case of the interaction between a lower filled MO of a molecule and a higher unoccupied MO of another molecule (right). Reprinted with permission from [70]. Copyright John Wiley & Sons Inc.

When two orbitals interact they are modified and form two new orbitals as shown in the plot; the new orbital energies depend on the initial orbital energies, their HOMO-LUMO energy difference and degree of interaction (symmetry and overlapping).

When two orbitals of similar initial energy interact strongly, they may form classic bonding or nonbonding orbitals; in the present case the interaction is weaker and so the bond energy, if favourable, is weaker. This basic datum explains the basic weakness of these interactions but also their being common and widespread.

To show that the specificity of the molecules may help to understand their behaviour, we may compare a set of common molecules and their specific interactions. Three interesting molecules are water, chloroform and dimethyl sulfoxide (DMSO).

The starting point is that these three molecules are polar but while water-DMSO and chloroform-DMSO mix well, water and chloroform do not mix at all and often chloroform is even defined as a "non-polar" molecule.

This definition is strictly wrong because the value of the dipole moment is high or significant and this is true for all three liquids. In fact, water and chloroform are only slightly different in polarity (water 1.86D and chloroform 1.04D), while in comparison DMSO has 3.94D. What is the reason why two polar molecules behave so differently with DMSO and between them?

One can note empirically that chloroform is a weak Brönsted acid, stronger than water, and it may even corrode steel tubes when used in HPLC devices. It is also a weak Lewis acid and can form donating-only hydrogen bonds. On the contrary, DMSO is an aprotic liquid and can be considered as a Lewis base; it may form accepting-only hydrogen bonds.

A suggestion comes also from the spectroscopic analysis of their interface found in literature [74] using vibrational sum-frequency spectroscopy:

"The spectral analysis, aided by isotopic dilution studies, shows that the moderate polarity of the chloroform phase results in a mixed interfacial region with stronger organic–water bonding and fewer bonding interactions between adjacent water molecules than was previously found for studies of non- polar organic liquid–water interfaces. Even with the more mixed interfacial region and stronger organic–water interactions, interfacial water retains a significant amount of orientational ordering."

In contrast, DMSO-water interactions are very strong and their solutions are widely used in biology to preserve proteins; at low concentration of DMSO, single H-bonded molecules prevail [75]. In other words, the interaction among these molecules appears to be dominated by Lewis acid-base interactions and by the formation of H-bonds, not by polarity!

Moreover, it appears that water prefers to interact with predominantly Lewis bases (electron donors as DMSO) than with predominantly Lewis acids (electron acceptors as chloroform); and this may suggest that water is a predominant Lewis acid than Lewis base as the authors suggested some years ago [76].

In this context Fukui showed [77] that the most important interaction between two molecules is that involving the HOMO and LUMO orbitals, i.e., the Highest Occupied and the Lowest Unoccupied Molecular Orbitals of the interacting molecules. The former is the occupied molecular orbital with the highest energy, whereas the latter corresponds to the empty molecular orbital of lowest energy; collectively, they are commonly known as frontier orbitals. An alternative way to look at the HOMO-LUMO interaction of two molecules is to consider it as the interaction between a donor and an acceptor of electron density, or as a Lewis interaction in a generalized sense, not necessarily confined to non-bonding electron pairs (although lone electron pairs are certainly favored). All the other possible interactions among occupied and unoccupied orbitals play a minor role and only affect the energetics of the transition states.

It is noticeable that in the case of semiconductors and insulators the HOMO corresponds to the upper energy level of the valence band, while the LUMO can be identified with the lower energy level of the conduction band. Similarly, definitions such as the Fermi level, the ionization energy or the electron affinity can be related, in a quantitative way, to the energies of the same frontier orbitals. As an example, the Fermi level is the arithmetic mean of the HOMO and LUMO energies.

Some molecular interactions, like the hydrogen bonds, can be regarded as HOMO-LUMO interactions and therefore as generalized acid-base interactions between a base (the donor oxygen of a molecule) and an acid (the acceptor hydrogen of the other molecule). In very general terms the interaction between any kinds
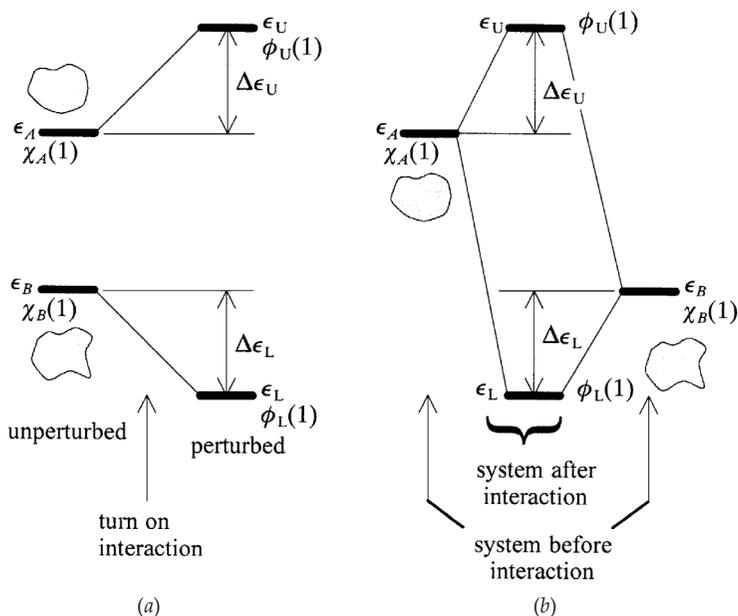
Figure 21 Schematic illustrating the interaction between two molecules in terms of per-turbation of molecular orbitals. (a) Perturbative view of the interaction of two orbitals. (b) Standard diagram representing the same interaction. Reprinted with permission from [78]. Copyright John Wiley & Sons Inc.

of molecular orbitals (not necessarily HOMO or LUMO) can be illustrated by the schematic of Figure 21 [78].

The basic idea is that the interaction between atoms or molecules, of quantum-mechanical nature, can be described as an interaction of their orbitals, by means of suitable linear combinations of atomic or molecular orbitals, no matter whether they are actually occupied, only partially occupied or empty, thus resulting in interaction orbitals with different energies with respect to the original ones. In particular, the interaction between two orbitals each belonging to a different atom or molecule will give rise to two new orbitals, one with an energy lower than that of the original ones, and one with a higher energy, as shown in Figure 21. If the two orbitals are unoccupied the interaction will produce a new potentially electron-acceptor orbital with a lower energy, i.e., an acceptor site with a Lewis acidic behaviour with an energy lower than before. It could be that there is no electron available to occupy it, but the orbital is present (the orbital function is defined). What happens in the case of a HOMO, endowed with a pair of electrons, and an empty LUMO? The situation is illustrated in Figure 20: a new set of molecular orbitals is produced, one of which has a lower energy. The energy decrease of this new "interaction" orbital depends on the closeness of the energies of the
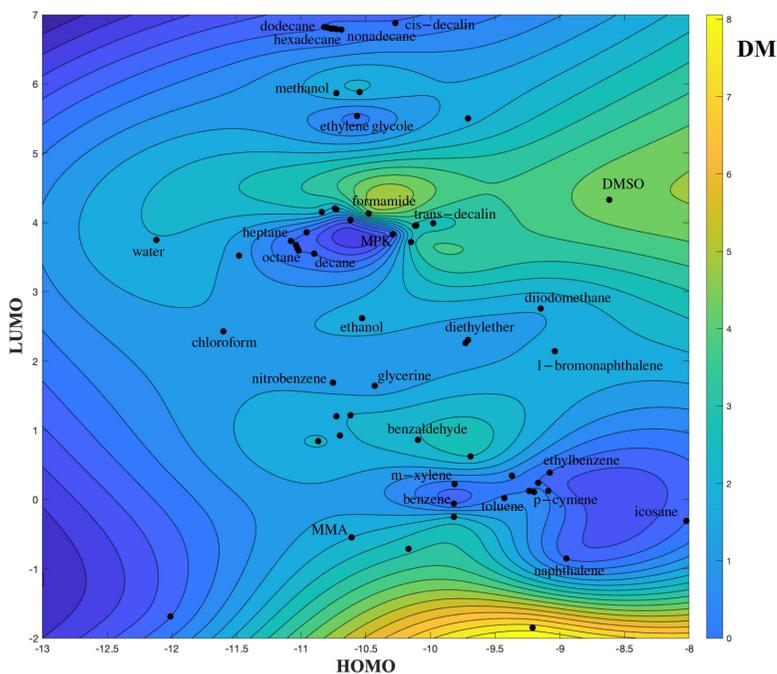
Figure 22 HOMO energy (eV), LUMO energy (eV) and electric dipole moment (D) of 59 chemical compounds. Deepest blue areas are an artifact of the graphical tool for the contour plot generation. Data from PITT quantum repository [72].

two orbitals before the interaction; as a rule, the closer the energies, the larger the decrease. Wide lists of HOMO and LUMO energies are available for many molecules in the literature and on the WEB [72].

But things are not so simple, in the sense that two molecules with similar HOMO and LUMO energies do not necessarily have the same chemical properties, or at least a similar behaviour. An illustration of this claim is provided by the contour plot in Figure 22, where HOMO and LUMO energies are plotted for some common liquids. Compounds corresponding to points close to each other should show the same properties, but this is not the case, or at least not always. For the benzene derivatives, in the lower right corner of the diagram, the condition seems to be approximately satisfied. In contrast, the linear hydrocarbons appear organized in various, well-separated groups throughout the HOMO-LUMO diagram, whereas in the center of the picture one can see, in very close positions, some hydrocarbons, the methyl propyl ketone (MPK), the formamide and the trans-decalin, which exhibit a significantly different chemical behaviour. It is apparent that HOMO and LUMO energies are not sufficient to characterize the electron-acceptor or the electron-donor properties of molecules. Some further information is needed.

Such a further information is not even the electrical dipole moment of the molecule, as shown by a representation of HOMO-LUMO energies and electrical dipole moments for 59 chemical compounds (named in van Oss book and for which acid-base components of surface tension have been listed) in contour plot part of Figure 22.

In the Appendix, Table 3 collects all the numerical data corresponding to this image.

In this respect an important point to stress is that the role played by the permanent electrical dipole moment of molecules in chemical reactivity (and also in adhesion phenomena) is often overestimated. An example of the excessive relevance attributed to permanent dipole moment is precisely the hydrogen bond, that is often classified (and not only in educational textbooks) as a particular form of essentially electrostatic bond between electrical dipoles, occurring under suitable conditions [67]. Actually, this is not the case: hydrogen bond must be thought as a very special example of acid-base interaction, related to acceptance and donation of electron density, as recently claimed by a formal recommendation by IUPAC[67–69]. As an example of the difference between a prevalently electrostatic interaction and hydrogen bond it has to be noted that there are some hydrogen bonds defined as *anti-electrostatic hydrogen bonding interactions* between ions with the same electric charge (e.g: fluoride and bicarbonate ions, see [79]). In a 2014 paper Weinhold writes [67]:

> "Both direct and statistical lines of evidence point to the essential resonance covalency of H-bonding interactions, rather than the statistically insignificant "dipole–dipole" character that is persistently advocated in current textbooks. The revised conception of H-bonding is both supported by modern quantum chemical technology and consistent with the pre-quantal insights of G. N. Lewis and other bonding pioneers."

The crucial information actually needed to describe the acid-base properties, according to Functional Density Theory (FDT), is the "Fukui density function", which describes the variation of the local electron density ρ when the number N of electrons in the molecule varies because of either an electrophilic attack:

$$f^- = \rho(N) - \rho(N-1)$$

or a nucleophilic attack:

$$f^+ = \rho(N+1) - \rho(N).$$

Such a function is not tabulated, but it can be calculated by *ab initio* methods; it specifies the sites where the electrophilic or nucleophilic reactivity of the molecules may more easily result in a reaction. In the case of adhesion, the reaction consists in the formation of weak reversible bonds, whose origin is precisely due

to this kind of interaction, in addition to the ubiquitous Lifshitz-van der Waals contribution.

The acid-base theory of adhesion, however, did not recognize this aspect at its very beginning, or did it only on a purely semi-empirical ground. According to the theory, developed by van Oss, Chaudhury and Good [80], two main contributions determine the adhesion between two phases:

– the Lifshitz-van der Waals interactions, due to the retarded electromagnetic forces previously discussed;
– the generalized Lewis interactions, related to the electron density accepted or donated between HOMO and LUMO of the molecules involved.

In the acid-base theory the surface tension of a phase s is written in the following form:

$$\gamma_s^{Tot} = \gamma_s^{LW} + 2\sqrt{\gamma_s^+ \gamma_s^-},$$

where the superscripts LW, + and − refer to the Lifshitz-van der Waals, acidic and basic "components" of the phase, respectively; γ_s^{LW} expresses the ability of the phase to produce dispersion interactions, while γ_s^+ is related to the capability of accepting electron density in LUMO and similarly γ_s^- to that of donating electron density in HOMO. The use of the geometric mean of the acidic and basic components to quantify the acid-base contribution to surface tension is clearly an approximation.

The work of adhesion between two different phases, denoted by l and s, is written instead as:

$$W_{adh} = 2\left(\sqrt{\gamma_l^{LW} \gamma_s^{LW}} + \sqrt{\gamma_l^+ \gamma_s^-} + \sqrt{\gamma_l^- \gamma_s^+} \right),$$

where the geometric mean rule is adopted as a common method of approximation used in many other cases in physical chemistry, and the subscripts l and s refer to the corresponding phases.

It is apparent that the dispersion, Lifshitz-van der Waals interactions are treated in terms of the geometric mean of the relative components. The same holds true for the acid-base interactions, but with an important difference, i.e., on a complementary ground: the geometric mean is calculated between the basic component of one phase (acting as donor of electron density) and the acidic component of the other (acceptor of electron density), and vice versa, finally adding the two partial contributions. It is noticeable that both the acidic and basic components of one chemical species are not necessarily different from zero. For instance, in the case of a hydrocarbon and water, the hydrocarbon will neither be able to accept from nor to donate electron density to water, and therefore the only Lifshitz-van der Waals interactions will be effective. In contrast, when both phases are able to

accept and donate, the acid-base contribution to the work of adhesion will be significant. Obviously, the same will hold true in the limiting case where one phase is only able to donate (its acidic component vanishes) and the other can only accept electron density (the relative basic component is zero).

An aspect of the utmost importance to stress is that the adhesion of water to other condensed phases is not due to its own permanent electrical dipole moment, but mainly relies on acid-base interactions (HOMO-LUMO, hydrogen bonds), along with dispersion forces, so that the common use of the term "polar" to explain the adhesion property of water must be regarded as flawed. More generally, the contribution of "polar" (Keesom and Debye) forces to adhesion in condensed phases is typically rather small [81, 82].

At the moment the acid-base theory is developed on a semiempirical ground; the correlation between van Oss-Chaudhury-Good approach and that of Fukui functions has only been conjectured and analyzed to some extent in the literature [83], but the application of *ab initio* calculations to acid-base interactions is still a task to be tackled.

6. A short note on macroscopic mechanical properties

Comparing the development of fracture mechanics and adhesion it appears that no significant theory on fracture was available until 1898, when Kirsch [84] solved the problem of an infinite plate with a circular hole for a tension strip. Only 15 years later Inglis (1913) solved the same problem with an elliptical hole [85]. And only in 1921 Griffith, an English engineer and father of modern theories on fracture mechanics, finally introduced a correlation between the thermodynamics and the mechanics of fracture, pushing the adhesion from empiricism to science [86]. His point of view was, however, purely macroscopic.

Therefore it appears self-evident that: (1) the understanding of macroscopic solid behaviour was largely empirical until 1920 and (2) while the theories on gas behaviour became extremely complex and were developed at a microscopic level through the machinery of quantum mechanics and relativity, the application of the new physical theories to solids and adhesion has developed only after a long "digestion". This may justify the difficulty in arriving at a common point of view accepted by chemists, physicists and engineers. And that is also why in the present paper the adhesion theories commonly found in engineering treatises are only briefly discussed.

All the phenomena considered in engineering treatises (interlocking, diffusion, wetting, even electrostatics) as possible mechanisms of adhesion are in the best case valid only in specific situations. What remains in all cases is that elementary forces among atoms and molecules have a valid and wide support from quantum mechanics and relativity, as explained in the present paper. In this regard, an observation about interlocking may help. Interlocking is basically due to the mutual repulsion of electron clouds and accounts for the impenetrability of
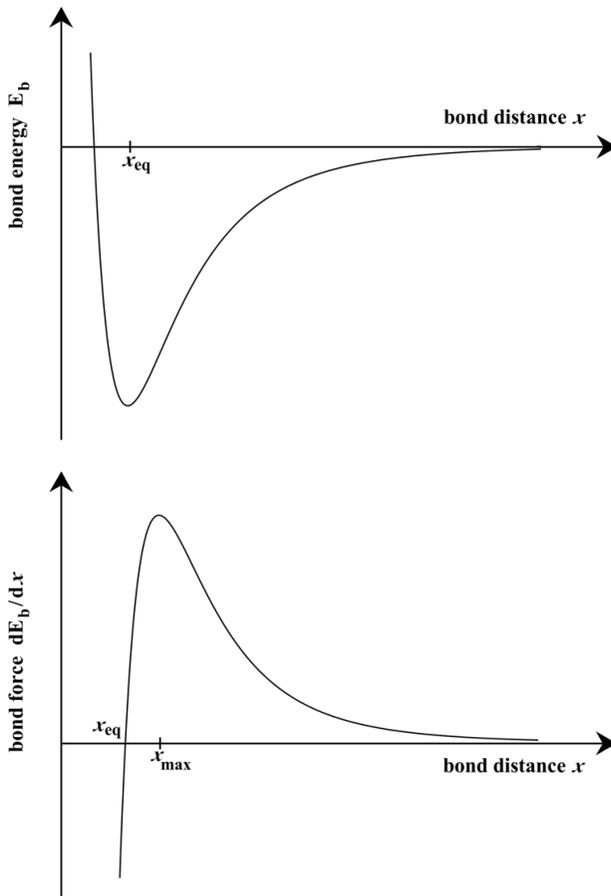
Figure 23 A typical graph of bond energy versus bond distance in a crystal (top). The derivative provides the bond force, repulsive if negative (bottom). The equilibrium distance x_{eq} occurs where the derivative of the bond energy with respect to the bond distance vanishes (the bond energy has a minimum). The maximum attractive force corresponds to the inflection point x_{max} of the upper graph, where the second derivative of the bond energy is zero. It represents the force needed to tear the atoms apart and defines the theoretical strength.

material bodies, since repulsion forces in Lennard-Jones model are stronger than attractive ones, as is clear from the trend of potential versus the intermolecular distance. No other "theory" is really necessary at a fundamental level.

The correlation between the microscopic and the macroscopic properties of a solid is not simple but some hints can be introduced. Theoretical physics helps to go deeper in this topic [87–89].

The depth of the energy curve is of the order of few eV and the bond distance is of the order of a couple of angstroms; from these values it is possible to estimate the force which will tear the atoms apart and defines the *theoretical strength*, as shown in Figure 23. For an energy depth of -1 eV the maximum force which breaks the bond is the derivative of the curve at the inflection point and corresponds to about 1 nN. Given the area to which this force is applied (about 3Å square) one can estimate the stress $\sigma = F/A = 16\,GPa = 160$ tonnes per square cm. This number has the correct order of magnitude and the exact results may depend on the choice of the energy depth curve: how many eV? For example, for steel 0.5 GPa, for carbon fibers 7–8 GPa, for a 2D graphene layer, the strongest material we know, is between an "intrinsic" value of 130 GPa [90] and a practical value of 60 GPa [91], thus perfectly aligned with the previous estimate. This very interesting agreement is valid essentially for materials without defects. In 1921, Griffith published a seminal study on the fracture of brittle materials establishing the relationship between the change in potential energy with crack growth and the free energy of the newly created surface [86]. Griffith deduced also that the **actual** breaking strength of the brittle material was governed by the sizes of defects and flaws within the material, rather than the intrinsic strength of its atomic bonds. Griffith wrote that *"in the limit, in fact, a fiber consisting of a single line of molecules must possess the theoretical molecular tensile strength,"* the maximum stress that can be supported by the material calling it "the intrinsic strength". He estimated the intrinsic tensile strength by measuring the quantity with fibers of progressively smaller diameters, finally extrapolating the results to an atomic radius. Today it is possible to work directly on atomic sized materials as it is the case in the cited papers.

Pay attention, however, that these evaluations are correlated with strong chemical bonds, not with the typical weak bonds present in adhesion interactions, which are at least one order of magnitude weaker.

It is also important to remember that it was early realized that the interactions in solid phases should not be approximated to be pair-wise additive – especially for metals, as discussed also in the present review. This is a so widely accepted concept that you may even find it stated on Wikipedia!

Finally, notice that the prediction of these properties from the basic chemical interactions is made difficult by the existence of material defects (lattice vacancies, dislocations, grain boundaries, microcracks, voids, chemical impurities). As a rule, defects in the material result in weaker mechanical properties of the real material than those predicted by the chemical interaction models. A better agreement can be obtained for very small samples (small fibers, nanoparticles), as already noted by Griffith in glass fibers of different sizes and more recently for some nanomaterials and nanocomposites (Veprek and Argon, [87]), where defects are easier to remove.

Nevertheless, the fracture processes, occurring when the cohesion of the material fails, are intimately related to the interactions within the solid, particularly to the long-range attractive ones.

7. Summary

This long journey started with van der Waals forces in the gas phase and arrived at the modern acid-base theory of solid surfaces.

We took advantage of the topic to review many of the modern theories underlying the chemistry and forces between molecules and atoms. We hope we have not bored you, repeating with a limited mathematical depth some basic concepts of relativity or quantum mechanics.

We have tried to manage the essential mathematical part, in a way which could be appreciated also by the non-specialist.

What is interesting is that the history of adhesion theories has been strongly influenced by the development of the two most basic and prominent theories of physics: relativity and quantum mechanics.

It is certainly very impressive that such a common phenomenon as adhesion, nowadays with its numerous practical effects (capillarity, surface tension, skiing, liquid miscibility, etc) may be such useful training ground to discuss the consequences of the most modern approaches to physics and chemistry even in significant details.

The difficulty of theoretical calculation may explain why there is no completely unified and thus satisfactory theory of the forces acting between macroscopic bodies.

The main difficulties are:

–   the retardation effect investigated by Casimir and Polder for non-macroscopic bodies
–   the pairwise additivity analysis performed by Hamaker for macroscopic bodies
–   the quantum mechanical approach for macroscopic bodies developed by the Russian school (Lifshitz, Deriagin) which overcomes pair-additivity but neglects the retardation effect and the existence of molecules with related orbital interactions and non-van der Waals (non-dispersion) interactions.

As a consequence, the most complete discussion is a semiempirical approach, i.e., the acid-base theory by van Oss, Chaudhury and Good, which recovers all the force components, avoids the pair additivity risk with its excessive consideration of "polar" forces, but is not based on a fully theoretical model able to include both retardation and quantum mechanics at least at a mesoscopic scale.

The only way to obtain a complete calculation of adhesion forces is to evaluate for each case the retarded Casimir-Polder (not yet van der Waals) forces AND evaluate the Fukui surfaces for HOMO-LUMO orbital interactions. This has not yet been accomplished in a systematic way, but may be performed by a case-by-case analysis or possibly achieved by some semiempirical approach (as is the case of the acid-base theory).

The adhesion forces are a FULLY quantum-relativistic effect and cannot be approximated at a simpler, classical or semiclassical level without neglecting some fundamental aspect.

Finally, we know today that the two basic theories of Physics: Quantum Mechanics and Relativity, are not in agreement; given their role in adhesion science it may be that also the theoretical approach to adhesion will be modified in the future, when probably a wider and unified theory will be introduced in Physics and Chemistry.

List of symbols

P:	pressure
ΔP:	pressure difference across a surface
H:	mean curvature of a surface (sum of the principal curvatures)
U:	internal energy of a phase
V:	volume of a phase
T:	absolute temperature
L1:	first Laplace's parameter, grossly corresponding to $(\partial U / \partial V)_T$
L2:	second Laplace's parameter, corresponding to twice the surface tension of a liquid
S:	entropy of a phase
n:	number of moles of a phase
R:	gas constant
c:	molar heat capacity of an ideal gas
a:	van der Waals parameter for pressure correction
b:	van der Waals' covolume
V:	intermolecular potential energy
r:	intermolecular distance
A,B,m,n:	parameters of Grüneisen's interaction energy model
ε, σ:	parameters in 12-6 Lennard-Jones potential energy
E:	energy per unit area between plates in Casimir's theory
F:	force per unit area between plates in Casimir's theory
a:	interplate distance in Casimir's theory
h:	Planck constant
$\hbar$:	$h/2\pi$ (h bar)
P_i:	internal pressure of a phase
P_{i_t}:	translational, or thermal, pressure of a phase
σ:	surface tension
λ:	specific latent heat of fusion of a solid (ice)
ΔV:	specific volume variation from ice to liquid water
W:	potential energy of interaction between macroscopic bodies
ϕ:	electrostatic potential
ρ:	electric charge density
ε_0:	dielectric constant in vacuo (or vacuum permittivity)
ΔE:	energy variation due to the interaction of two molecules in Klopmann's theory (see the text for Klopmann formula and the symbols therein)

$X_A(1)$, $X_B(1)$:	molecular orbitals of two molecules without interaction
$\phi_U(1)$, $\phi_L(1)$:	molecular orbitals of two molecules with interaction
f^-:	Fukui density function for electrophilic attack
f^+:	Fukui density function for nucleophilic attack
ρ:	electron density function in Fukui theory
γ_S^{LW}:	dispersion component of a phase s (possibly a solid) in vOCG theory
γ_S^+:	acidic component of a phase s (possibly a solid) in vOCG theory
γ_S^-:	basic component of a phase s (possibly a solid) in vOCG theory
γ_l^{LW}:	dispersion component of a phase l (possibly a liquid) in vOCG theory
γ_l^+:	acidic component of a phase l (possibly a liquid) in vOCG theory
γ_S^-:	basic component of a phase l (possibly a liquid) in vOCG theory
γ_S^{Tot}:	surface free energy (or surface tension) of phase s
W_{adh}:	work of adhesion between two phases
E_b:	intermolecular bond energy in a condensed phase

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Appendix:

Table 3 Values of HOMO, LUMO and dipole moment (DM) of 59 molecules from PITT
data base [72].

Molecule	HOMO (eV)	LUMO (eV)	DM (Debye)
Water	−12.12	3.75	2.13
Glycerol	−10.43	1.64	1.34
Formamide	−10.48	4.13	3.91
Methylene iodide	−9.15	2.76	1.70
Ethylene glycol	−10.57	5.54	0.44
1-Bromonaphthalene	−9.040	2.14	1.88
DMSO	−8.62	4.33	4.61
Nitrobenzene	−9.21	−1.85	7.79
Benzaldehyde	−10.17	−0.71	3.08
Chlorobenzene	−9.82	−0.25	2.11
Naphthalene	−8.95	−0.85	0
Cis-Decalin	−10.27	6.88	0.07
o-Xylene	−9.20	0.11	1.03
Trans-Decalin	−10.29	3.83	0
Ethyl benzene	−9.37	0.34	0.69
m-Xylene	−9.24	0.12	0.64
Icosane	−8.02	−0.31	0
Benzene	−9.82	−0.060	0
Mesitylene	−9.17	0.24	0.10
Nonadecane	−10.69	6.78	0.060
Toluene	−9.43	0.020	0.65
p-Xylene	−9.08	0.39	0
p-Cymene	−9.09	0.12	0.18
Ethyl nonanoate	−10.73	4.19	1.97
N-octanol	−10.55	5.88	2.12
Hexadecane	−10.73	6.79	0.01
Tetrahydrofuran	−9.71	5.5	1.98
Chloroform	−11.60	2.43	1.54

(*Continued*)

Table 3 (Continued)

Molecule	HOMO (eV)	LUMO (eV)	DM (Debye)
Pentadecane	−10.75	6.80	0.07
Ethyl octanoate	−10.73	1.20	2.030
CCl$_4$	−12.01	−1.69	0
Heptaldehyde	−10.15	3.72	2.86
Methyl hexyl ketone	−10.11	3.95	3.10
Tetradecane	−10.77	6.80	0.01
Ethyl hydrogen carbonate	−11.48	3.52	1.36
Methyl amyl ketone	−10.11	3.95	3.17
Tridecane	−10.80	6.81	0.060
Ethyl hexanoate	−10.74	4.20	2.040
Ethyl propyl ketone	−9.980	3.99	2.99
Dodecane	−10.82	6.82	0.020
Cyclohexane	−10.62	4.03	0
Butyl acetate	−10.84	4.15	2.20
Isoamyl n-butyrate	−10.70	0.92	2.10
Methyl butyl ketone	−10.11	3.95	3.11
Undecane			0
Methyl ethyl ketone	−10.11	3.96	3.14
2-Amino-2-ethylbutanoic acid	−9.69	0.62	2.67
Ethyl acetate	−10.87	0.84	2.19
Decane	−10.90	3.55	0
Ethyl isovalerate	−10.62	1.22	2.15
Nonane	−10.96	3.86	0.07
Methanol	−10.73	5.87	1.94
Ethanol	−10.53	2.62	1.81
Methyl propyl ketone	−10.12	3.95	3.20
Octane	−11.02	3.59	0
Heptane	−11.030	3.62	0
Hexane	−11.040	3.67	0
Isopropyl ethyl ether	−9.71	2.30	1.27
Ethyl ether	−9.73	2.26	1.29