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Adhesion theories : a didactic review about a century of progress

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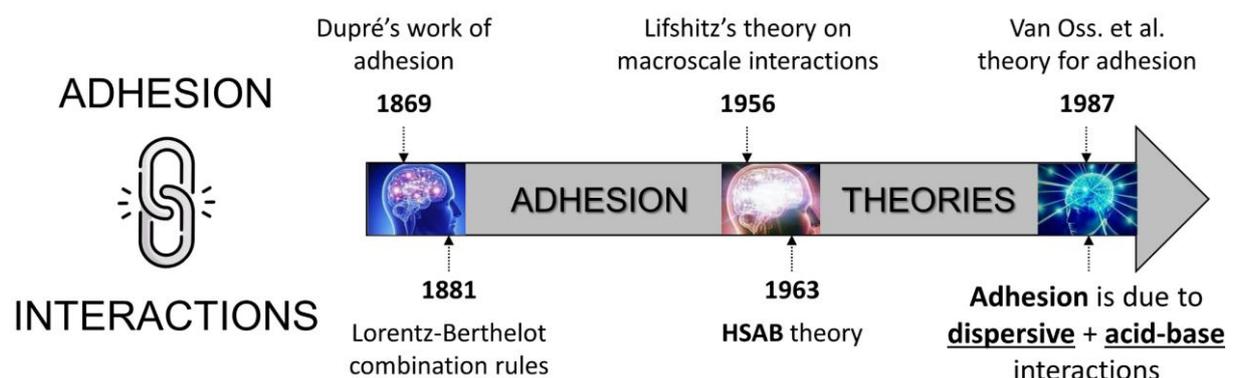
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Abstract : Adhesion results from the sum of different interactions and (in)compatibilities between two substrates described as adhesive to each other. This review aims to help neophytes to adhesion by answering an apparently simple question : what is adhesion and how does it work ?

In order to provide the reader with an overview of the complexity of the subject, adhesion is defined in the most digest possible way, by summarizing the main interactions involved and adhesion theories. The first section of this review defines the different interactions from the smallest scale at which they occur, and along this review to the larger scale at which adhesion phenomenon is observed, using illustrated examples. In a second section the main theories trying to explain adhesion, in a chronological order are reviewed.

Keywords : adhesion – interactions – interfaces – bonding – thermodynamics – superficial tension – interfacial tension

Graphical abstract :



Introduction

Adhesion is a physico-chemical process occurring between two substrates, bound together in such a way that their separation requires work. This work can be mechanical (traction, shear) or physicochemical (lubrication, dissolution). The interaction between the substrates can take place without any modification of the surfaces of the substrates, thus based on a mutual affinity of the surfaces brought into contact. But more generally, adhesion is generated by treating one or both surfaces in such a way as to promote inter-substrate interactions, using an additive (the adhesive) with a high affinity for both surfaces to be joined.

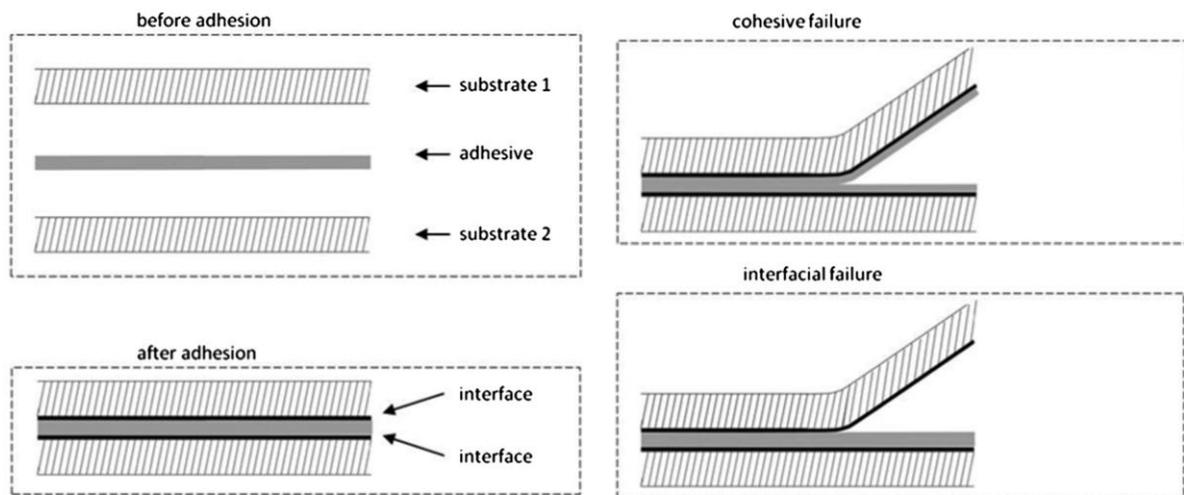


Figure 1 : Schematic representation of an adhesion process using an adhesive. Adapted from ¹ with permission from Elsevier.

The main property of the adhesive is its ability to support and diffuse the work induced by the application of a stress on the substrate by load transfer². The adhesive adds a third parameter to the system, which becomes a ternary system, and thus greatly increases the possibilities of variation of its mechanical properties. Hence it is possible to give the system elastic properties by using an elastomeric adhesive, or heat-dependent properties with a heat-sensitive adhesive, or even a mixture of both to obtain a material whose elastic properties depends on temperature. The range of possibilities is extremely wide and can be modified at several levels, from the design of the adhesive to its formulation and its processing environment. The choice of an adhesive formulation is usually ruled by two criteria : its specific affinity with the substrates involved (ex. wood glue) to avoid *interfacial failure* ; and its mechanical resistance adapted to the targeted application (ex. shear resistance, to avoid *cohesive failure*) (Figure 1).

To the best of our knowledge, the current literature lacks a review summarizing in both a concise and complete manner all the elements needed to understand the theoretical aspects of adhesion.

The present review of the fundamental literature on adhesion is thus composed of two sections. The first one aims at defining and clarifying the nature of the different forces at work at the molecular scale at the interface of an adhesive system. The second section of this review focusses on the bibliographic study of adhesion phenomena at the macroscopic scale.

I. Adhesion at the molecular level: molecular interactions

Adhesion is above all a matter of interaction between two substrates. Adhesion finds its origins at one of the smallest scales of matter : the atomic and subatomic scales. To understand adhesion issues at a macroscopic scale, it is crucial to bear in mind the nature and the order of magnitude of such interactions (Figure 2). This section aims to clearly and concisely define them, in order to relate them with the macroscopic point of view which will be exposed in the second part of this review.

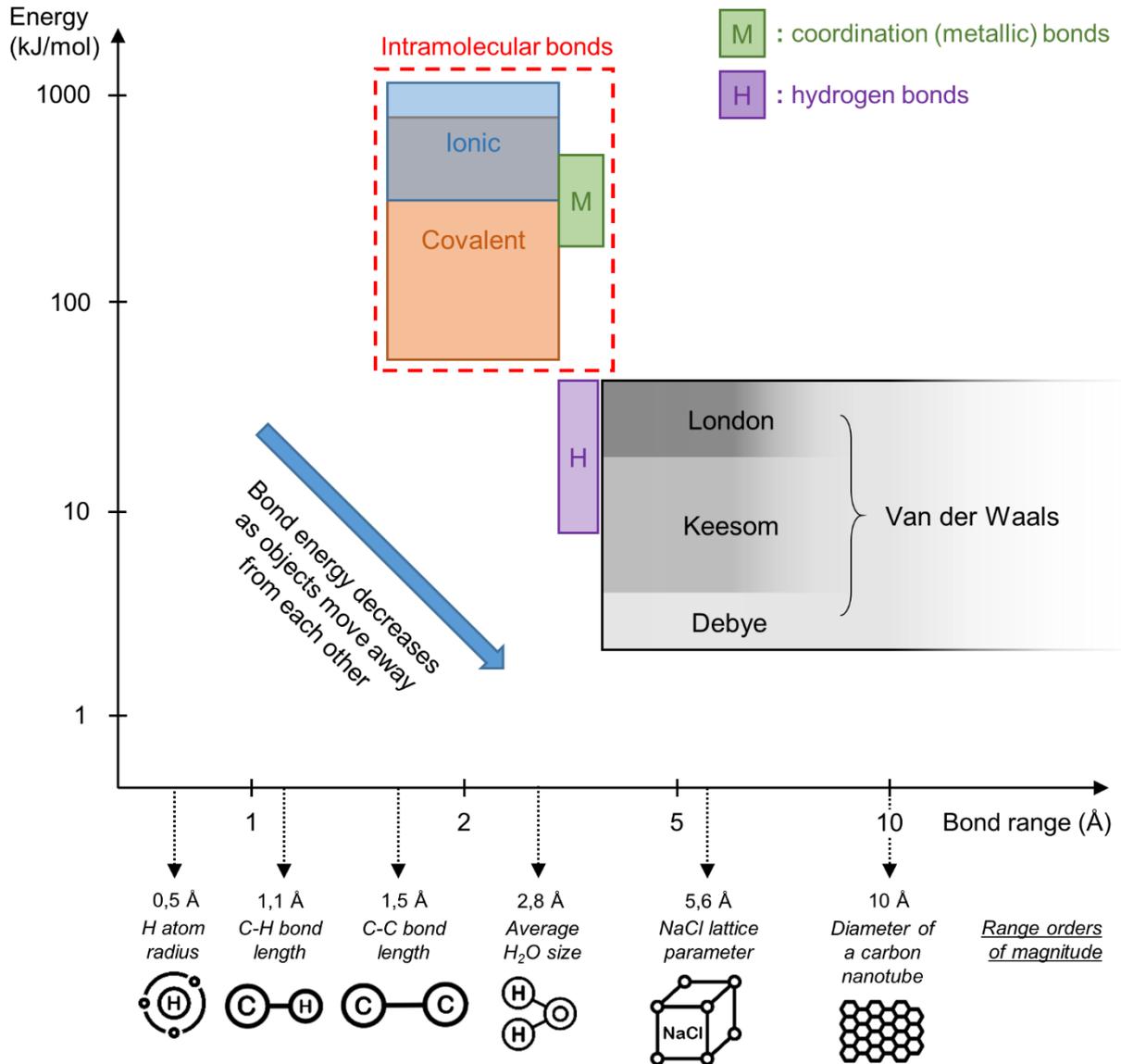


Figure 2 : Schematic representation of the energy and range of intra and intermolecular interactions. Personal representation, data from ³.

A. Short distance interactions: interatomic (chemical) bonds

1. Covalent bonding

Covalent bonds are interactions that involve the pooling of electrons between the valence shells of 2 non-metal atoms. This pooling occurs by overlapping two atomic orbitals, each with a valence electron, and results in the formation of a highly energetic interatomic bond. For this overlap to occur, both atoms must be close to each other by an order of magnitude comparable to their atomic radius, and they must each have an orbital compatible with the sharing of a pair of electrons.

It is possible to divide covalent bonds into two distinct categories: some of the bonds can under certain conditions be described as "purely" covalent; bonds that do not meet these conditions are then said to be "ionocovalent" or "partially ionic". By definition, a purely covalent bond is one that has a zero ionicity factor (f_i in eq. 1), according to the original definition of the ionicity factor proposed by Pauling^{3,4} :

$$f_i = 1 - \exp\left[-\frac{1}{4}(\chi_A - \chi_B)^2\right] \quad (1)$$

where χ_A and χ_B are the respective electronegativities of atoms A and B according to the Pauling scale.

As an example, the Li-F bond is 92% ionic; the H-Cl bond is 18% ionic; and the C-H bond is only 3% ionic.

2. Ionic bonding and coulombic forces

Ionic bonds are the result of a mutual attraction force of electrostatic nature between two atoms of opposite charges. This electrostatic attraction force is called the Coulomb force (F in eq. 2), it is non-directional (because the electrostatic charge of the ion is distributed uniformly in all directions at a given distance), and its intensity is expressed according to Coulomb's law³ :

$$F = \frac{Q_1 Q_2}{4\pi\epsilon_0\epsilon r} = \frac{Z_1 Z_2 e^2}{4\pi\epsilon_0\epsilon r} \quad (2)$$

where Q_1 and Q_2 are the respective electric charges of two atoms 1 and 2 ; Z_1 and Z_2 the respective valence number of atoms 1 and 2 ; e the elementary electronic charge constant ($e = 1.602 \times 10^{-19} \text{ C}$) ; ϵ_0 the permittivity constant of the vacuum ($\epsilon_0 = 8.9 \times 10^{-12} \text{ C}^2\text{N}^{-1}\text{m}^{-2}$) ; ϵ the relative permittivity of the medium and r the distance between both ionic charges.

The notion of coulombic forces also covers the interactions between ions - permanent dipoles and ions - induced dipoles, which nature is the same as ionic bonds, although of lower intensity.

3. Special case: the coordination (covalent) bonds

Coordination (covalent) bonds are quite special bonds. They are different from classical covalent bonds, which involve the sharing by 2 atoms of their valence electrons to form a shared pair. In a coordination bond, the electron pair is provided by only one atom. The electron-deficient atom is called a "Lewis acid", and the atom that provides the doublet to the bond is called a "Lewis base". In the relatively common case where the Lewis acid is a metal, the bond is also called a metallic or metal-ligand bond.

The nature of the coordination bond is much closer to a covalent bond, because the interaction involves a non-bonding electron pair that is shared, and not the transfer of one or more electrons from a surplus atom to a deficit atom as in the case of an ionic bond. It is worth to precise that the electron "transfer" is meant in terms of probability, as electrons must not be considered as individuals but as a density of probability on each atom they belong to.

The covalent character of the coordination bond is also marked by the existence of a dipole moment within the bond, which makes it directional and selective, unlike the ionic bond.

B. Long distance interactions: physical (intermolecular) bonds

1. Van der Waals interactions

The name "Van der Waals forces", "Van der Waals interactions" or "Van der Waals bonds" generally stands for a type of electrodynamic interaction at long distances ($> 5 \text{ \AA}$) and low energy. Unlike the bonds discussed above, they do not involve the displacement, exchange or pooling of electrons. Indeed, these interactions are rather due to the exchange of virtual particles (quantum fluctuations) between the atoms, by analogy with the Casimir effect observed in the framework of the theory of quantum electrodynamics by the eponymous researcher⁵⁻⁸.

The Van der Waals interaction can be broken down into 3 different forces of cumulative intensity according to the Van der Waals equation of state:

- Permanent dipole - permanent dipole interactions (*Keesom* or orientation forces). The dipole-dipole interaction is much weaker in intensity than an ion-dipole interaction because it takes place between partial charges (dipole moments);
- Permanent dipole - induced dipole interactions (*Debye* or induction forces). The intensity of the latter is nearly always weaker than the Keesom forces;
- Induced dipole - induced dipole interactions (*London* forces or dispersion forces).

The particularity of the London forces is that they occur independently of the polarity of the molecules, and that they are therefore observable between two compounds without permanent polarization. They arise from the fact that an electron cloud has a very low probability of being uniformly distributed in space at a given time, and that at any time it is therefore likely to be polarized. The subsequent leads to an inductive polarization of the electron clouds of the molecules surrounding it, propagating like an electromagnetic wave. Instead of the intuitive thought that these forces are the weakest of the Van der Waals interactions, quantum computation has shown that the London dispersion forces are by far the most important contribution to the intensity of the attractive forces of the Van der Waals interaction⁹ (Table 1).

Their range can reach ten nanometers or more, and their intensity does not usually follow a simple power law for more complex molecules or compounds³.

Molecules	d_w (Å)	% Keesom	% Debye	% London	U_w (kT/molecule)
Ne	3.1	0	0	100	0.11
Ar	3.7	0	0	100	0.22
Xe	4.3	0	0	100	0.38
CO	4.0	0.006	0.0003	99.99	0.26
CH ₄	4.0	0	0	100	0.60
HCl	3.6	9	5	86	1.38
HBr	3.8	2	2	96	1.53
HI	4.2	0.1	0.5	99.4	1.64
CH ₃ Cl	4.3	24	8	68	1.60
NH ₃	3.2	34	9	57	2.51
H ₂ O	2.8	69	7	24	7.0

Table 1: Comparative proportion of the three terms of the attractive Van der Waals interaction for different molecules. d_w is the maximum range of the attractive interaction, and U_w is the calculated total energy of the interaction (at 298 K, $1kT/\text{molecule} = 2.478 \text{ kJ/mol}$). Adapted with permission from⁹.

At distances greater than 10 nm, a delay effect of the London forces must be taken into account, highlighted by Casimir and Polder^{3,10}. This delay effect arises from the fact that a finite time is required for an electromagnetic wave to propagate in the medium where the particles are located. If this time can be considered as long, the electromagnetic field of the electron receiving these waves could be in a less favorable position (as for antiphase signals, resulting in destructive interference) for the attractive interaction than for a short time. This delay effect can be considered as leading to an even stronger decrease in the intensity of the London forces with distance, the corresponding term then varying in r^{-7} at distances > 10 nm instead of r^{-6} at distances < 10 nm³.

As mentioned above, the Keesom and Debye forces are sometimes referred to as "dipole-dipole interactions" and "dipole-induced dipole interactions" respectively. In this case, London forces are sometimes referred to as "Van der Waals forces" by misuse of language, even in the recent literature, which can lead to confusion. Several references^{9,11,12} point out that the Keesom, Debye and London forces are components of the potential energy equation of the Van der Waals forces. The term "Van der Waals forces" should therefore systematically include the Keesom and Debye "dipole-dipole" and "dipole-induced dipole" interactions, unless it is explicitly stated which component is involved (e.g. *London-Van der Waals forces*).

Interestingly, it has been shown that the mechanical properties of non-crosslinked polymers, such as amorphous polyethylene, are governed by the strength of London-Van der Waals interactions between polymer chains. This observation corroborates the regularly stated principle that the mechanical strength of a material depends directly on the strength of the weakest cohesive bonds within the material^{3,13}.

2. Special case: the hydrogen bond

Hydrogen bonding is an intermolecular electrostatic interaction, and thus falls into the category of coulombic forces. However, its unusually high binding energy makes it necessary to classify it in a separate category, especially since hydrogen bonding does not involve any exchange of electrons, like Van der Waals interactions. It is a bond that can be described as hybrid, at the border between ionic bonding (electrostatic forces), covalent bonding (directional and selective interaction) and Van der Waals bonding (Keesom's permanent dipole - permanent dipole interaction).

The formation of a hydrogen bond occurs when two dipoles, each consisting of a strongly electronegative atom (F, O, N, Cl) linked to a hydrogen atom by a covalent bond, are approached at a very tiny distance. This distance, which corresponds to the maximum range of the interaction, is necessary for the interaction energy to be greater than kT , the energy brought to the system by the sole contribution of the temperature¹² (Table 1).

The strength of the hydrogen bond depends on the electronegativity of the strongly electronegative atom. Its characteristic binding energy is intermediate between that of covalent bonds (200-800 kJ/mol) and that of Keesom-Van der Waals dipole-dipole interactions (4-21 kJ/mol) (Figure 2). This particular energy is attributed to the very small size of the hydrogen atom ($r = 0.03$ nm), which allows the formed dipoles to gather close enough to create an unusually strong electromagnetic field¹². This oriented magnetic field allows one to observe a surprising cohesion in media where the molecules are small enough, such as H₂O, NH₃ and HF among others. Nevertheless, it is important to bear in mind that the nature of this bond is nothing more than a directional and particularly strong dipole-dipole interaction.

Finally, although it is regularly described as an intermolecular bond as in water, the medium at the origin of its discovery, the hydrogen bond can also be observed intramolecularly in the case of very large molecules like proteins, and is at the origin of the helical forms of such molecules (we speak then of *intramolecular hydrogen bridging*).

For more details on the different molecular interactions, in particular on their respective energies and ranges, and the corresponding mathematical expressions, the reader can consult the very extensive works on the subject proposed by Israelachvili¹² (in English) and Gerschel⁹ (in French), as well as the chapters of Gutowski and Lee in Lee's book about adhesion fundamentals³.

C. Hamaker's microscopic approach and the beginnings of a macroscopic vision

Once all these interactions described and defined, it is important to understand how the history of adhesion science came back from a microscopical approach to a macroscopic point of view towards adhesion concerns.

The German physicist Fritz London proposed in 1930¹⁴ the first theory that aims to describe and explain the attraction between two noble gases observed by Berthelot in 1898¹⁵, which will be detailed further in this review.

As early as 1937 and following London's work, Hamaker develops equations to characterize numerically the interactions between two systems, by approximating the additivity of the interaction forces. He finds that in all his equations, covering various system geometries, a common factor A systematically recurs. He calls this factor *Hamaker's constant*, noted A and expressed as follows:

$$A = r^2 \rho_1 \rho_2 B_{1,2} \quad (3)$$

where r is the distance between both geometries of the system, ρ_1 and ρ_2 the numbers of atoms/molecules per unit volume in geometries 1 and 2, and $B_{1,2}$ a coefficient in r^{-6} related to the expression of the London forces. Subsequently, $B_{1,2}$ has been modified to take into account the entire Van der Waals interactions and not only the contribution of the dispersive forces³.

Thanks to this expression of the Hamaker constant, scientists are now for the first time able to calculate the interfacial forces between two different geometries, by summing up the interactions at the microscopic scale. The 3 typical cases of application are the sphere-sphere, sphere-plane and plane-plane geometries. This expression has also been extended later to take into account the delay effect of the London dispersive forces¹⁶.

Hamaker's work thus lays the foundation for Lifshitz's theory of macroscale interactions, which will be presented later in this article as the first steps of adhesion science towards a macroscopic approach which has been proven to be way more accurate and experimentally verified.

II. Adhesion at the macroscopic level

Following a macroscopic approach of adhesion, it is necessary for the adhesive-substrate system to meet certain criteria in order to be in favorable conditions to the creation of such interactions. The fundamental criterion is the distance between both materials, which must necessarily be extremely small for surface interactions. However, the surface of most substrates is very irregular on the distance scale at which intermolecular interactions begin to appear (Figure 2).

For this reason, adhesives are generally formulated to exhibit viscoelastic material properties. Viscoelastic materials are modeled in rheology as a combination of the behaviors of a perfect elastic solid (modeled by a *Hooke spring*) and a Newtonian viscous liquid (modeled by a *purely viscous damper*)^{17,18}.

The elasticity modeled by the spring allows the adhesive to resist deformation of the substrate, by absorbing the energy of the strain stress within the material until it is released. If the adhesive is not elastic enough, this energy may dissipate directly at the adhesive-substrate interface, potentially leading to the failure of interfacial bonds.

On the other hand, the viscous character modeled by the damper allows by definition the adhesive to have properties close to those of a liquid, i.e. to be able to flow and adapt to the surface which it is in contact with. These flowing properties are crucial in order to obtain the most intimate interfacial contact between adhesive and substrate, so that the distances between them approach the distances at which molecular interactions occur (Figure 2).

In order to allow such intimate contact between adhesive and substrate, three main parameters are important to consider: tribology, surface energies and wetting of the adhesive and substrate. While the first is mainly related to the superficial macrostructure of the substrate, both surface energies and wetting deal with the physical and chemical compatibilities between the surfaces involved. Each of these concepts is discussed in the different parts of this section. It should be noted that the content of this section is not exhaustive and is only intended to give the reader an overview of the main theories on the vast and complex subject of adhesion.

A. Adhesion and tribology: mechanical anchoring approach

In theory, if two complementary surfaces at any point are brought close enough to each other, and the surface tension of both surfaces is low enough to allow this approach, they will then come into intimate contact (see II. B. *Adhesion and surface tension: thermodynamic approach*). One would then observe a bonding of both materials sufficient to provide the system with a greatly improved mechanical strength, due to the stress transfer that would take place at the interface. A good example is the protective tempered glass for smartphones, which nowadays no longer uses adhesives. They are usually brought with both a protective plastic film, for the inner side of the protective glass ; and a cleaning kit for smartphone screen. Once the smartphone perfectly clean, the protective glass can be applied on the screen, and they will stick together as long as irregularities does not appear at the interface (e.g. most of the time the protective glass breaking).

But most of the time in other cases of adhesion needs, a clean and smooth surface cannot be obtained, for either practical or technical concerns. Adhesives have been invented to pass away through this obstacle, ensuring adhesion between rough surfaces.

The so-called *mechanical anchoring* approach is the oldest theory (1925) that has attempted to explain an adhesion phenomenon¹⁹⁻²¹. It is easily conceptualized by imagining a system where the substrate is a lock and the adhesive is a master key. A concrete example is that of wood glue, which takes advantage of the surface irregularity of this material to benefit from an effect known as *mechanical anchoring* or, more precisely, from the *imbrication* of the glue in the asperities of the wood. Indeed, once the glue is hardened by solvent evaporation and/or chemical cross-linking *in situ*, it adheres to the wood like a key turned a quarter turn in a lock. A crucial condition for this type of adhesion to show up is the roughness of the substrate : the rougher the surface, the stronger the adhesion. Adhesion strength of the system is also strongly related to the surface area covered by the adhesive, as it will be explained later in this document.

Since it is difficult to isolate this mechanical anchoring effect in systematic tests, a regular debate within the adhesion science community is to define the part of mechanical anchoring in the explanation of the adhesion phenomenon. Some researchers tend to defend a major contribution of this effect, while others qualify it as negligible compared to the thermodynamic aspects and the good wetting of the substrate by the adhesive (aspects that will be studied in the rest of this section). Other researchers tend to marginalize this anchoring effect, justifying improved adhesion by a simple increase in the specific surface area available for the creation of interactions at the molecular scale²².

Writing about technical aspects and characterization of surfaces, a specific field is dedicated to the study of surfaces: *tribology*. From the ancient greek *tribo*, "friction" and *-logia* "science, study", it is the name given to the science that studies the interface between two particular materials, of which a whole branch is dedicated to the study of the skin-material interface. Even if a large part of the studies on this subject is dealing with the study of dynamic systems, i.e. the study of friction at the adhesive-substrate interface, some works regularly use the estimation of an *adhesion force* for static systems. We can therefore expect a strong support of the theory of mechanical anchorage by this field of study, which is manifested by numerous studies of mathematical formalization of this theory.

Actually, no proper mathematical formalization capable of explaining the origin of the adhesion phenomenon has been identified in the literature²³⁻²⁷. Instead, the adhesion force is regularly estimated by means of approximations derived from a thermodynamic approach to adhesion, which will be explained later in this article (see II. B. *Adhesion and surface tension: thermodynamic approach*). It has been recognized that tribology is traditionally a field of study focused on a very macroscopic approach to the problem of adhesion²⁸. This tradition tends to become more and more obsolete with the increasing improvement of technologies over the last three decades, which have shown that the phenomena observed on a macroscopic scale are often governed by laws operating on much smaller scales that traditional tribology approach does not take into account²⁸.

To this day, the theory of mechanical anchorage is no longer considered as a theory to explain the phenomenon of adhesion. It was made obsolete 25 years after its proposal by the pioneering works of Zisman^{29,30}, then Good and Girifalco³¹⁻³³, on the theory of an adsorption governed by the laws of thermodynamics rather than those of mechanics. As for tribology, it tends to integrate more and more an understanding at the microscopic scale of its observations, and some works show that both approaches are perfectly compatible and complementary³⁴. The Johnson-Kendall-Roberts (JKR) theory³⁵ which extends the Hertz theory³⁶ on the contact of two elastic bodies (which constitutes the foundation of contact mechanics) should also be mentioned. In their work later enriched by D. Maugis³⁷ the authors showed that the contact zone between two elastic bodies under zero load is finite and caused by attraction forces, and that these attraction forces depend on the surface energies and geometries of the two bodies.

B. Adhesion and surface tension: thermodynamic approach

This section aims to expose the most advanced and widely accepted theory to characterize and explain adhesion in both theoretical systems and practical applications. Hereby are described the main theories following the so-called “*thermodynamic approach*”, in chronological order. It is important to bear in mind that every equation mentioned in this section is still used nowadays. Usually the simplest expressions are commonly used in quite simple issues, or qualitative measurements ; meanwhile the more complex ones are preferred for theoretical advanced systems or very specific applications.

1. Clarification of language in this document

At the surface of any body, a number of unsaturated bonds exists, and gives the constituent elements of the surface a different state of energy and cohesive stresses than the constituent elements inside the body. The elements constituting this surface are called *surface phase* and their properties are different from the internal constitutive elements which are called *bulk phase*.¹⁶ Two of these surface properties of bodies are studied in this part: the surface tension σ and the surface energy density γ . It is important to define them for reasons of clarity of the rest of this review.

The the surface energy density energy γ is a parameter that is expressed in J.m^{-2} . It characterizes the excess of free energy of the constituent elements of a surface, compared to that which they would have if they were in the bulk phase of the body. On the other hand, the *surface energy* noted E_S (in Joule) is defined by the product of γ with the surface covered by the interface of area S and is expressed as follows:

$$E_S = \gamma * S \quad \equiv \quad \gamma = \frac{E_S}{S} \quad (4)$$

It is therefore important not to confuse surface energy E_S , expressing the excess of free energy of a given surface; and surface energy density γ , expressing the excess of free energy by surface unit. As exposed in the previous expression, both parameters are closely related to the surface area of the system involved, highlighting the strong dependence of adhesion to the surface area.

In this review, the notion of surface energy E_S will not be used, the use of the expression "surface energy" by convenience will thus systematically refer to the notion of surface energy density γ .

The surface tension, noted σ and expressed in N.m^{-1} , characterizes the disturbance of the internal cohesive stress between the different elements of the surface phase, compared to the internal cohesive stress of the elements of the volume phase. In a liquid, the surface tension is the interfacial tangential force, caused by cohesive interactions in the liquid, that resists external force. It can also be expressed as an energy (in J.m^{-2} , as proven by dimensional analysis) and is then noted γ and identified as the surface energy density defined above.

Finally, by "surface" we mean an interface between an object and the surrounding atmosphere, thus an object-air interface. In the case of an object-object interface, for example the interface formed by the application of a liquid on a solid surface, we will rather speak of "interfacial" energies and tensions.

Adhesion is a very wide and complex concern, which comprehension has considerably increased in the two past centuries. In this section is proposed a review of the historical literature about the birth of the most accepted theoretical foundations of adhesion science : the thermodynamic approach.

2. Genesis of the concepts of interfacial tension and adhesion work

In 1805, Thomas Young became interested in the cohesion of fluids and proposed a relationship that is still the basis of the science of surface and interfacial tensions³⁸ :

$$\gamma_S = \gamma_{SL} + \gamma_L \cos \theta \quad (5)$$

where θ represents the contact angle of a drop of liquid at equilibrium on a solid surface, perfectly nondeformable, isotropic, smooth and homogeneous.³⁹ γ_S , γ_{SL} and γ_L represent the surface tensions at the solid/air, solid/liquid and liquid/air interfaces respectively. This equation has been the subject of many studies because it is the first equation to propose a way to estimate the value of the surface energy of a solid, γ_S , to which the wetting properties of the solid are closely related.⁴⁰

In 1869, Athanase Dupré and his son Paul defined an expression for the thermodynamic work of adhesion W_a (*work of adhesion*) needed for the rupture of a solid-liquid interface, which is expressed according to the equation⁴¹ :

$$W_a = \gamma_S + \gamma_L - \gamma_{SL} \quad (6)$$

By combining this expression with Young's equation, they propose a simple expression for W_a : known as Young-Dupré's law, it allows to evaluate experimentally the adhesion force of a liquid on a solid in air, and is expressed as follows:

$$W_a = \gamma_L(1 + \cos \theta) \quad (7)$$

In this expression, γ_L is a constant whose values are known and referenced in the literature for common liquids; and θ is a parameter that can be measured by reproducing Young's experiment.

However, this equation effectively describes the work required to lift off a liquid sessile drop from a solid surface without any change in shape. One can wonder whether such work reflects any real situation. Indeed a sessile drop is generally generated by deposition of a spherical droplet onto the solid surface, a process that definitely involves a change in shape. M. E. Shrader convincingly revised and criticized this expression of work of adhesion in 1995.⁴² Nevertheless, in practice neither the Young-Dupré Equation, nor the revised versions proposed by Shrader⁴² or Harkins⁴³ accurately represent the work of adhesion. Indeed, they do not take into account potential topological irregularity of the test surfaces,, reactions between the liquid and solid or change in the viscosity of the sessile drop, for example. All these equations still remain useful for qualitative comparisons.

Since these first steps in the mathematical formalization of the adhesion phenomenon by a thermodynamic approach, researchers have tried to find new models that are experimentally verified in numerous particular cases, with the aim of developing a universal model. For this purpose, 3 main approaches have been proposed. They differ mainly by the number of components in their mathematical expression, which allows to take into account more complex interactions between the adhesive and the substrate if applicable.

3. One-component approach: Zisman's theory

The simplest approach was proposed by Zisman and Fox in 1950, who proposed a concept of *critical surface tension*, γ_C .^{29,30}

This is an empirical method to determine the *wettability* of a solid (see II. Adhesion at the macroscopic level.), by establishing that the surface energy of a solid γ_S is equal to the surface tension of a liquid that would perfectly wet the solid in question ($\theta = 0$).

A series of liquids is applied to the solid surface and their contact angle measured, then plotted against the known surface tension of the liquids (Figure 3).

Liquids with a surface tension γ_L lower than γ_C do wet the solid, and are represented on a straight line, while liquids for which $\gamma_{LV} > \gamma_C$ deviate from the straight line and are considered non-wetting. This simple approach only divides solids according to their "wettability" by certain liquids, and has multiple flaws.⁴⁴ The main issue with Zisman's approach is that polar liquids deviate from the linear relationship, due to specific interactions

with the solid surface that are not accounted for in this method (Figure 4). Therefore, this approach is only used for very apolar surfaces, using exclusively apolar liquids. PTFE is a very useful apolar substrate to investigate the wetting behavior of liquids. For example, the work of Jańczuk and Zdziennicka on PTFE further demonstrated that the values of solid surface free energy determined directly and indirectly by using the contact angle data can be caused by the presence of the liquid vapor in air and by different structures of the liquid and/or solid at the solid–liquid interface in comparison with that at the liquid–air one.⁴⁵

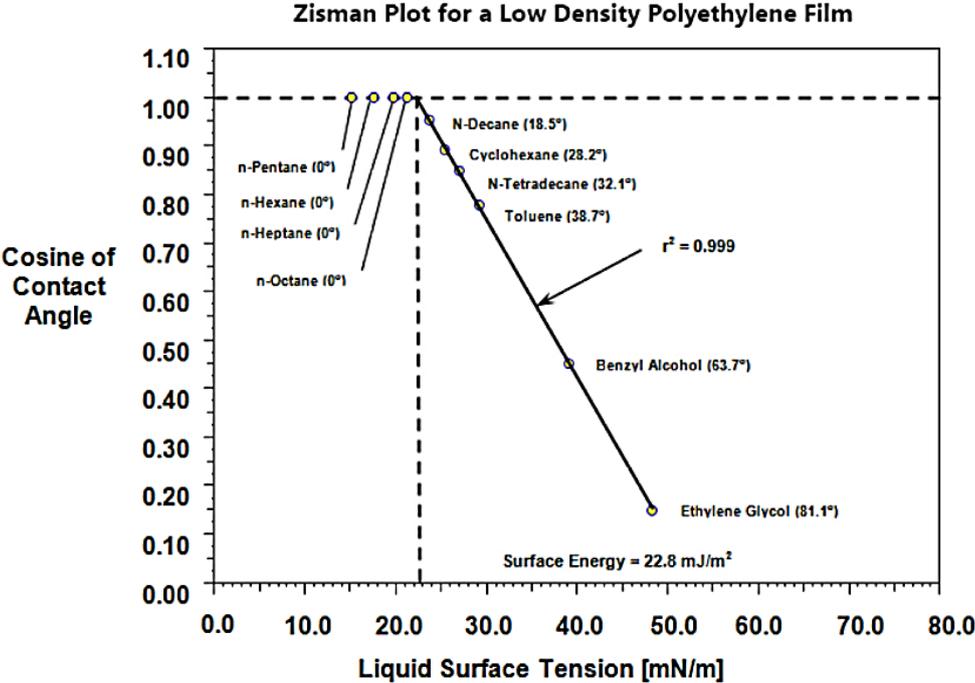


Figure 3 : Graphical plot of the determination of γ_{SV} by the Zisman method on a PELD film⁴⁴

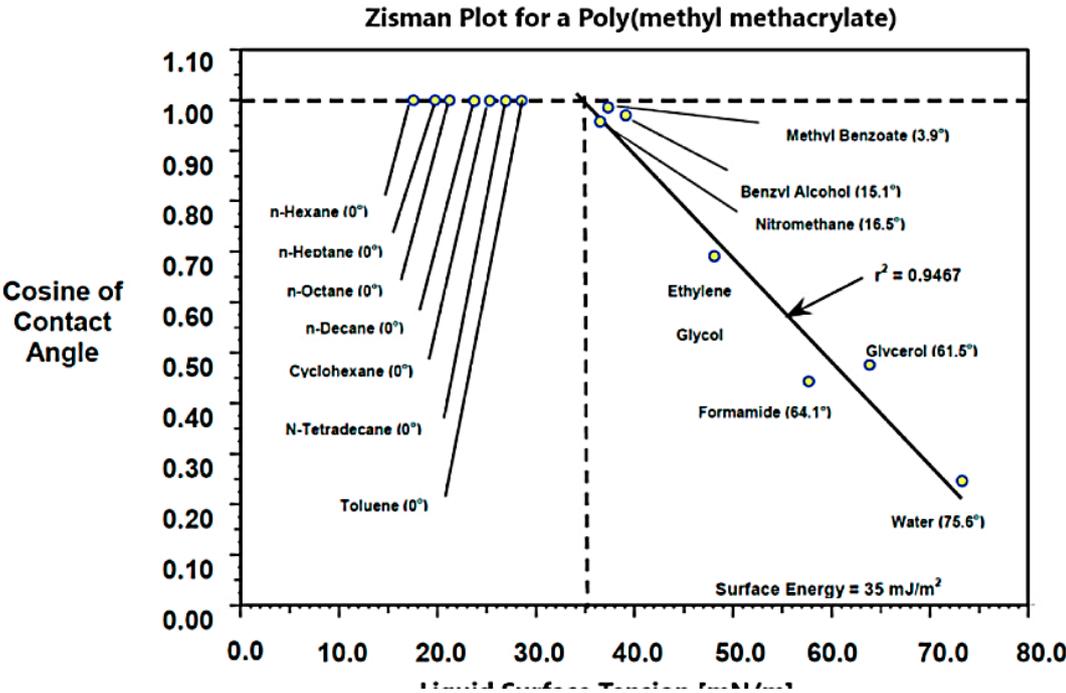


Figure 4 : Graphical plot of the determination of γ_{SV} by the Zisman method on a PMMA surface⁴⁴

4. Two-component approach : Fowkes' theory, origin and improvements

As discussed in the previous paragraph, Zisman's theory has a major flaw which is characterized by a deviation from the linearity relation when polar liquids are tested. This deviation is explained by particular interactions between the polar liquid and the surface, which are not considered in this determination method.

From 1962 to 1964, Fowkes published a series of papers⁴⁶⁻⁴⁹ on a theory taking into account for the first time the contribution of London dispersion forces to the surface energy term γ_{SV} . This theory is accepted as the most widely used in the field of interfacial tension studies. But to fully understand Fowkes' approach on the subject, a step back in time is needed.

In 1881, the famous Dutch physicist H. A. Lorentz proposed the first mathematical expression of the energy of interaction between two different atoms that were not chemically linked (which would only be called "London forces" a century and a half later, following the work of the eponymous researcher). He expresses this force called the *attraction constant* and noted A_{ab} as an arithmetic average of the cohesion constants of two compounds *a* and *b* according to the equation⁵⁰ :

$$A_{ab} = \frac{A_{aa} + A_{bb}}{2} \quad (8)$$

where A_{aa} is the cohesion constant between 2 molecules A, A_{bb} the cohesion constant between 2 molecules B and A_{ab} the attraction constant between molecules A and B.

Lorentz's theory is based on Dalton's postulate in 1805 who was the first to attribute a spherical shape to the atom. It is only verified for "hard sphere" type systems and therefore does not consider the ductile character of electron clouds in the case of induced dipole - induced dipole interactions of the London forces.

In 1898, the French chemist Marcellin Berthelot theorized a relation according to which the attraction constant between two molecules A and B would be more reliably represented by the result of the geometric mean of their respective cohesion constants¹⁵ :

$$A_{ab} = \sqrt{A_{aa}A_{bb}} \quad (9)$$

This relationship derives from the work of Van der Waals himself, who introduced the term A_{ab} in his expression of the dispersive forces of Van der Waals⁵¹ (which became the London Forces), without however proposing an expression, which he reproached Berthelot for in a note to the Académie des Sciences⁵². Berthelot retorted that his expression, although not verified experimentally, perfectly satisfied the numerical verifications that he had carried out, even on gases with unconventional behaviour¹⁵.

These two theories, better known as the Lorentz-Berthelot combination rules, are used by default in almost all simulation programs to model molecular interactions. However, they are not without flaws and their relevance has been regularly questioned⁵³⁻⁵⁵.

Half a century later, in 1950, Zisman's theory was proposed, based on the analogy between the surface energy of a solid and the surface energy of a liquid wetting it perfectly (see 3. *One-component approach: Zisman's theory*).

In 1957, Good and Girifalco proposed a "Theory for the estimation of surface and interfacial energies"³¹⁻³³. This work is one of the most important milestones in the history of the thermodynamic approach to adhesion. Good and Girifalco were indeed the first to link Berthelot's equation (9), on molecular interactions, with the pioneering work of Hildebrand and Scott on the solubility of non-electrolyte compounds, which gave rise to the Hildebrand solubility parameter⁵⁶.

They write the following relation which will be named the Good and Girifalco equation³¹ :

$$\gamma_{SL} = \gamma_S + \gamma_L - 2\Phi\sqrt{\gamma_S\gamma_L} \quad (10)$$

where γ_S , γ_L are the free surface energies of a solid and a liquid respectively; and γ_{SL} the energy of an interface formed by the same solid and liquid in contact. The interaction parameter Φ is a constant specific to the solid-liquid system implemented, which is the first to account for specific interactions between both surfaces.

Indeed, Good and Girifalco deduce from their results 3 possible interpretations to the values of Φ obtained experimentally:

- $\Phi = 1$: The cohesive forces of the liquid and the solid, as well as the attractive forces at the interface are of the same nature. For example, a drop of aliphatic hydrocarbon on a polyethylene film (Figure 3): the forces at the interface are mostly of the dispersive type (London-Van der Waals forces), due to the absence of heterogeneous chemical grouping. We observe a perfect wetting of the surface ($\theta = 0$).
- $\Phi < 1$: The cohesive forces of the liquid and the solid are of non-complementary nature. For example, an interface consisting of a drop of ethylene glycol (very polar) applied to a hydrophobic surface such as a PE film (Figure 3: the forces on the surface of the PE film are mainly dispersive, whereas the ethylene glycol seeks to create highly polarized hydrogen bonds. We observe a moderate wetting of the surface ($\theta > 0$).
- $\Phi > 1$: Specific interactions appear due to heterogeneous and complementary chemical functions. For example, a drop of ethylene glycol on a PMMA film (Figure 4): the corresponding point does not align correctly with the linear regression obtained by the Zisman method, showing specific interactions between the 2 phases.

This interaction parameter Φ is very well characterized and exploited in much greater depth in the original work of Good and Girifalco.³¹⁻³³ They thus laid the foundations of a subject of study that would interest many researchers thereafter: the question of the nature of these specific interactions, and all the parameters that govern their appearance or not between two surfaces.

Following this work, Fowkes proposed, in 1962, to express γ representing the total surface tension of a surface, as the sum of two distinct terms according to the equation 11:

$$\gamma = \gamma^d + \gamma^p \quad (11)$$

where γ^d called the "dispersive component", represents the part of interfacial forces induced by the London-Van der Waals forces; and γ^p the "polar" component representing the contribution of all other non-dispersive forces. He originally studied a liquid-liquid system, where the forces at the interface between liquids 1 and 2 are only due to dispersive forces (London-VdW). The attractive forces at the interface are then opposed only to the respective cohesive forces of the liquids, and we find the postulate formulated by Berthelot and taken up by Hildebrand and then London, opposing forces of attraction and cohesion (Figure 5).

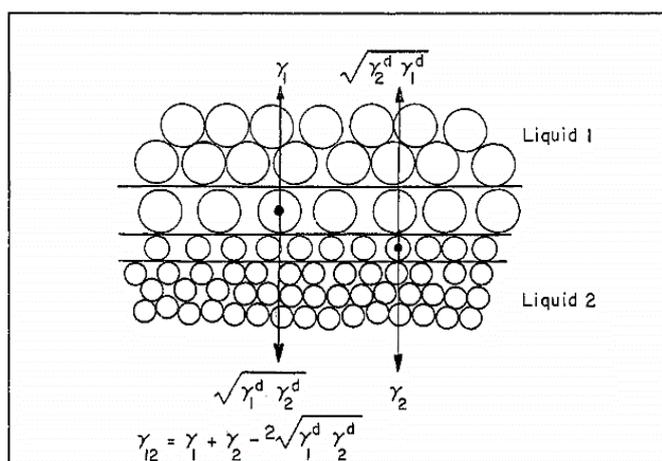


Figure 5: Schematic representation of a liquid-liquid interface where interfacial tension resides. Reprinted with permission from⁴⁷. Copyright © 1963, American Chemical Society.

From this representation, Fowkes deduced a mathematical expression for the interfacial tension between 1 and 2 :

$$\gamma_{12} = \gamma_1 + \gamma_2 - 2\sqrt{\gamma_1^d \gamma_2^d} \quad (12)$$

This expression, transposed to a solid-liquid system, leads to the Fowkes equation:

$$\gamma_{SL} = \gamma_S + \gamma_L - 2\sqrt{\gamma_S^d \gamma_L^d} \quad (13)$$

Fowkes thus proposes an expression close to that of Good and Girifalco, with one fundamental modification: the absence of the interaction parameter Φ . This is because it is considered equal to 1 by Fowkes (presence only of attractive forces of the dispersive type at the interface). However, it has been shown that this parameter is not always negligible, and this approximation can sometimes induce important deviations in the results obtained with the Fowkes equation (see 6. *A different thermodynamic approach: the equation of state of the interfacial tension*).

In the absence of Φ the Fowkes equation can be substituted in Young's equation (5), which then allows to express for the first time the dispersive component of an interfacial tension, as a function of a measurable contact angle and the known tension γ_L :

$$\gamma_L(1 + \cos \theta) = 2\sqrt{\gamma_S^d \gamma_L^d} \quad (14)$$

Fowkes has extensively verified this relationship through multiple experimental works published over several years, reported in a whole book chapter^{39,57}.

Other theories were established by different researchers a few years later, following a similar approach to that employed by Fowkes. Zettlemoyer in 1969 took up Fowkes' postulate, applying an arithmetic mean instead of the geometric mean initially postulated, as in the Lorentz equation (8)⁵⁸:

$$\gamma_{SL} = \gamma_S + \gamma_L - (\gamma_S^d + \gamma_L^d) \quad (15)$$

At the same time, another more advanced theory was proposed. Owens, Wendt, Rabel and Kaeble propose to incorporate in the Fowkes equation a component γ_S^h related to hydrogen bonds. Called "*geometric mean approach*" by its creators, it is expressed as follows⁵⁹ :

$$\gamma_{SL} = \gamma_S + \gamma_L - 2\sqrt{\gamma_S^d \gamma_L^d} - 2\sqrt{\gamma_S^h \gamma_L^h} \quad (16)$$

In 1971, Wu took up Fowkes' work and decided to apply a harmonic mean instead of the geometric mean used by Fowkes^{60,61}. He incorporated into this harmonic mean a component γ_S^p representing the non-London forces that Fowkes ignored in his original postulate (13). He thus follows a similar approach to that of Owens et al., with the difference that his component of non-dispersive forces extends to all polarized dipole-dipole interactions and not only to hydrogen bonds. The Wu equation is expressed as:

$$\gamma_{SL} = \gamma_S + \gamma_L - 4 \left[\frac{\gamma_S^d \gamma_L^d}{\gamma_S^d + \gamma_L^d} + \frac{\gamma_S^p \gamma_L^p}{\gamma_S^p + \gamma_L^p} \right] \quad (17)$$

The different expressions presented here are only a summary of the most common theories following a two-component approach: dispersive (London-VdW) and polar (non-London). It should be noted that they should only be considered as theoretical models, and thus their experimental verification will depend on the system to which one will try to apply them. However, as they rely on different mathematical operations, in certain cases an expression among the others may be more successful⁵⁸.

5. Three-component approach: LW-AB theory of Van Oss et al.

Following the theory of the microscopic approach developed by Hamaker in 1937 (see C. Hamaker's microscopic approach and the beginnings of a macroscopic vision), a more advanced theory on intermolecular bonds was proposed in 1956. This was the work of the Soviet physicist E.M. Lifshitz, who proposed a new vision of the forces of attraction between two solids, no longer at a microscopic scale but at a macroscopic scale⁶². In this approach, atoms and molecules are considered as massive dipoles that emit a fluctuating electromagnetic field, and the distance between two bodies adhering to each other is considered to be very small compared to the interatomic distance inside the bodies. For the calculation of the interaction force, the individual atomic structure of the bodies is then ignored : only the properties of the massive bodies are involved¹⁶. The theory is very complete and sophisticated, it considers the contribution of non-retarded and retarded forces, and is applicable to any material, at any temperature.

Lifshitz's theory of macroscopic forces allows adhesion researchers to re-evaluate past work with a new perspective on the nature of the interactions described. Therefore, Van Oss, Chaudhury and Good suggested in 1985 to re-examine the nature of the forces responsible for the strong adhesion experimentally observed between certain biopolymers (albumin and human immunoglobulin) and solid polymers with low surface energy (PTFE, PS). They re-examined, according to Lifshitz's theory, the role of London forces and hydrogen bonds in these adhesive systems, whose adhesion was previously described as due to "hydrophobic interactions"⁶³.

The work of Van Oss, Chaudhury, and Good establishes that these "hydrophobic interactions" cannot be responsible for the strong adhesion of these biopolymers to low surface energy polymers, since these hydrophobic interactions are "repulsive in nature". Therefore, Van Oss et al. first introduce a new term γ^{SR} for *short-range interaction*, to account for the contribution of short-range interactions in the biopolymer-PTFE system, opposed to long-range London forces^{64,65}.

Subsequently, Van Oss et al. expanded on this work by proposing a much more advanced definition of the term γ^{SR} . In a review of their work published in 1987⁶⁶, they propose to rename these *short-range interactions* as *Lewis acid-base interactions*, noted γ^{AB} and clearly redefine in 3 distinct categories the interactions included in the name "*polar interactions*" :

1. Dipolar compounds, i.e. those with a permanent and significant dipole moment in their molecular structure;
2. Hydrogen bond promoting compounds, according to the Brønsted-Lowry theory of acids and bases:
 - a. Compounds that are simultaneously proton donors (acids) and acceptors (bases), e.g. the water molecule, which will be referred to as bipolar. It is specified that the donor and acceptor characters are not necessarily of equal strength;
 - b. Acidic compounds, much more donor than acceptor, e.g. CHCl_3 ;
 - c. Basic compounds, much more acceptors than donors, e.g. ketones;
3. Electroactive compounds according to the Lewis acid and base theory, i.e. electron acceptor and donor compounds respectively:
 - a. Compounds that are simultaneously electron donors and electron acceptors, which will be qualified as bipolar in the same way as category 2.a., because (in general) the Lewis theory encompasses the Brønsted-Lowry theory ;
 - b. Acidic compounds, much more electron acceptors than donors;
 - c. Basic compounds, much more electron donors than acceptors.

As a result, they propose to incorporate two new terms into the Fowkes equation:

- A term γ^- which represents the contribution of the acidic character of the interactions (categories 2b and 3b);
- A term γ^+ which represents the contribution of the basic character of the interactions (categories 2c and 3c).

According to Van Oss et al. and the theory of solution thermodynamics of Drago et al.⁶⁷, γ^{AB} can then be expressed as the geometric mean of these two terms according to the expression :

$$\gamma^{AB} = 2\sqrt{\gamma^+\gamma^-} \quad (18)$$

They also bring some precisions on particular cases to the theory previously stated. For example, the case of benzene, which has a zero-dipole moment, cannot be considered as polar in the sense of dipole. On the other hand, it has been shown that its π electronic structure can act as an electron donor by being involved in hydrogen bonds with hydroxyl groups of various compounds, as well as with the proton of chloroform⁶⁸. Thus, hydrogen bonds between an acid proton and a group with π electrons induce a certain basicity of these π electrons, which is not necessarily found in all Lewis acids⁶⁶.

This new theory is also based on the thesis work of Chaudhury, who showed that according to the Lifshitz theory, the contributions to the surface energy of the London, Keesom and Debye interactions could be grouped into a single term, under the name of Lifshitz-Van der Waals (LW) interactions⁶⁹. These LW interactions represent the summation at macroscale of the Van der Waals forces, and their contribution to the surface energy is expressed as:

$$\gamma^{LW} = \gamma^{Keesom} + \gamma^{Debye} + \gamma^{London} \quad (19)$$

Van Oss et al. then combined the expressions of Drago and Chaudhury and proposed a new expression for the interfacial energy γ_{SL} , which is the basis of the three-component thermodynamic approach that is now considered as the most faithful to experimental observations in systems involving interactions other than London dispersive forces^{44,63}:

$$\gamma_{SL} = \left(\sqrt{\gamma_S^{LW}} - \sqrt{\gamma_L^{LW}} \right)^2 + 2 \left(\sqrt{\gamma_S^+} - \sqrt{\gamma_L^+} \right) \left(\sqrt{\gamma_S^-} - \sqrt{\gamma_L^-} \right) \quad (20)$$

Combining this expression with Young's equation (5) gives an expression for the experimental determination of the work of adhesion⁶³:

$$W_a = \gamma_L(1 + \cos \theta) = 2 \left(\sqrt{\gamma_S^{LW}\gamma_L^{LW}} + \sqrt{\gamma_S^+\gamma_L^-} + \sqrt{\gamma_S^-\gamma_L^+} \right) \quad (21)$$

This expression highlights for the first time the distinct contribution of acidic substrate - basic adhesive, basic substrate - acidic adhesive interactions, as well as the Keesom, Debye, and London forces.

It is interesting to relate this expression to the work of Fowkes, who worked at the same time as Van Oss et al. on a theory of the contribution of acid-base interactions in the forces causing adhesion, according to Chaudhury⁷⁰. One of Fowkes' tests regularly reported in the literature is one that depicts the adhesion strength of a basic polymer, polymethyl methacrylate (PMMA), on an acidic silica surface (Figure 6).

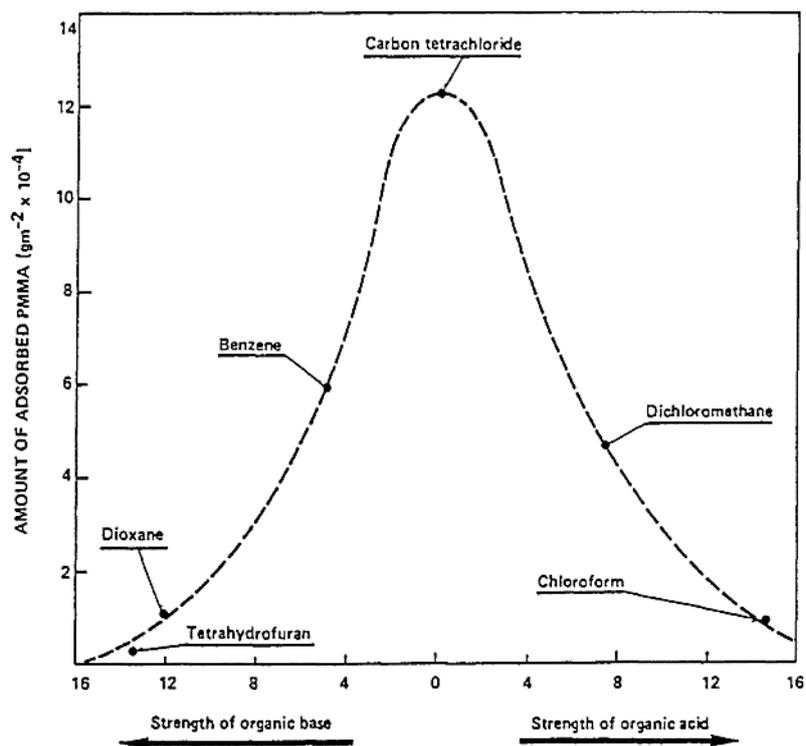


Figure 6 : Amount of PMMA adsorbed on a silica plate, depending on the acid-base character of the solvent used. Reprinted from ⁷⁰, with permission from Elsevier.

The maximum adsorption of PMMA on silica is observed when the solvent used has the most neutral acid-base character in the solvent series. On the other hand, the adsorption decreases when the solvent has a more marked acid-base character, which is attributed by Fowkes to a competition effect between the solvent and the polymer (basic solvents) or between the solvent and the silica (acid solvents).

Similar results are found in a second example by Fowkes consisting of spreading a PMMA film (basic) on a glass plate with basic character (20% sodium oxide 80% silica)⁷⁰. The film showed poor adhesion under these conditions and was easily removed. In contrast, if the same glass was pre-treated with hydrochloric acid, the surface was converted to acidic silica and the PMMA film subsequently applied under the same conditions showed very strong adhesion to the substrate.

Fowkes carried out numerous other experimental works tending to corroborate the theory of the contribution of interfacial acid-base interactions to the phenomenon of adhesion, the results of which he reported in a review on the subject⁷¹.

However, it is important to bear in mind that all these approaches, via an equation of state or not, even if they can sometimes agree very well with the experimental results, remain approximations that will not always be valid⁷². The reader is referred for more information to the discussions of Israelashvili on the notions of correctness and accuracy of theories based on Lorentz-Berthelot combination rules^{73,74}.

The chronological sequence described in this section is summarized for an easier overview in Figure 7.

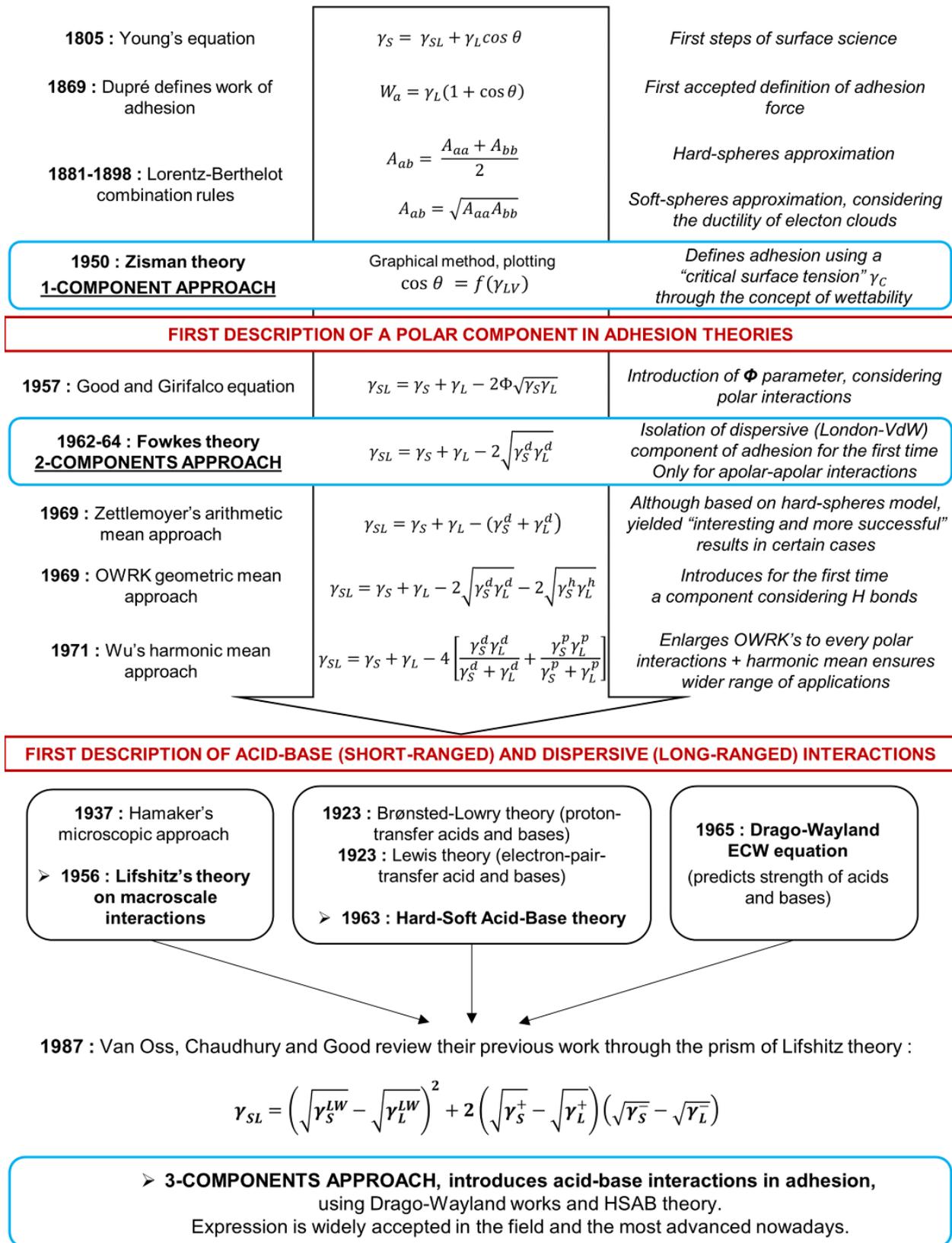


Figure 7 : Evolution of the historical progress of adhesion theories.

6. A different thermodynamic approach: the equation of state of the interfacial tension

Following the work of Good and Girifalco³¹ (see Eq. (10)), and in parallel with the work of Fowkes on the two-component approach, a theory emerges under another approach. Ward and Neumann^{75,76} propose a new mathematical conception of the notion of surface tension, according to which γ_{SL} would depend only on γ_S and γ_L . This theory is then based on the postulate that a relation such as $\gamma_{SL} = f(\gamma_S, \gamma_L)$ exists and governs the thermodynamic behavior of the system⁵⁶. It is opposed to the approaches presented previously, in the sense that γ_{SL} does not depend only on γ_S and γ_L but also on parameters related to the different specific intermolecular interactions between both surfaces.

This relation $\gamma_{SL} = f(\gamma_S, \gamma_L)$ has been named "*equation of state of the interfacial tension*". The conformity of this equation to the principles of thermodynamics has been demonstrated several times⁷⁶⁻⁷⁸ based on the phase rule or Gibbs-Duhem rule, which describes the variance of a thermodynamic system at equilibrium. The first expression of this equation was established empirically from experimental data and on the basis of the expression of the interaction parameter Φ of Good and Girifalco³¹:

$$\Phi = \frac{\gamma_S + \gamma_L - \gamma_{SL}}{2\sqrt{\gamma_S\gamma_L}} \quad (22)$$

The first equation of state for interfacial tension is expressed as:

$$\gamma_{SL} = \frac{(\sqrt{\gamma_S} - \sqrt{\gamma_L})^2}{1 - 0.015\sqrt{\gamma_S\gamma_L}} \quad (23)$$

Subsequently, two major modifications of the interfacial tension equation of state have occurred. The first major redesign was proposed by Li and Neumann, who questioned their theory in 1990. This rethinking followed the work of Maitland et al.⁷⁹ who, based on London's theory of dispersion forces, proposed an adjustment to Berthelot's combination rule, which had been observed to tend to overestimate the strength of interactions between two dissimilar molecules⁶³. This adjustment is expressed:

$$\varepsilon_{ij} = (1 - k_{ij})\sqrt{\varepsilon_{ii}\varepsilon_{jj}} \quad (24)$$

where ε_{ij} is the interaction energy parameter between two dissimilar molecules i and j ; ε_{ii} et ε_{jj} the interaction energy parameters between two identical molecules i and j ; and k_{ij} an empirical parameter quantifying the deviation of the Berthelot model in interactions between dissimilar molecules.

Based on this adjustment by Maitland et al., Li and Neumann introduce a new combination rule⁷⁸:

$$\varepsilon_{ij} = \sqrt{\varepsilon_{ii}\varepsilon_{jj}} e^{-\alpha(\varepsilon_{ii}-\varepsilon_{jj})^2} \quad (25)$$

where α is an empirical parameter.

From this new combination rule, and by empirically determining α , they then publish a second major modification of the expression for the interfacial tension equation of state:

$$\gamma_{SL} = \gamma_S + \gamma_L - 2\sqrt{\gamma_S\gamma_L} e^{-0.0001247(\gamma_S-\gamma_L)^2} \quad (26)$$

Since the creation of this approach to surface tension by an equation of state in 1974, many other revisions of the equation of state have been proposed⁸⁰⁻⁸³. Most of them have aimed at proposing new versions that are in better agreement with experimental observations. In particular, the empirically determined constant quantities have been regularly modified because of the perpetual improvement of the precision of measuring instruments during the last decades. Other thermodynamic approaches to adhesion that have met with less success have also been proposed, including the work of Lyklema who proposes a theory that takes into account the influence of temperature on the accuracy of surface energy values (difference between surface energy and surface *free* energy)⁸⁴⁻⁸⁶.

C. Adhesion and wetting: macroscopic approach and interfacial tension

Wetting is the name given to a parameter describing the affinity of a liquid applied to the surface of a solid. A liquid with a high affinity to a solid is said to wet it well, i.e. it spreads well on the substrate. Wetting is commonly characterized by the contact angle formed at the triple interface between a drop of liquid, deposited on a solid, in equilibrium with an ambient gas phase (usually air).

The wetting of surfaces in an adhesive system therefore refers to the proper spreading of the adhesive on the substrate. Thus, the viscous nature of the adhesive is a fundamental characteristic that enables it to overcome the surface roughness of the substrate in order to achieve adhesion, provided that the adhesive spread is thick enough.

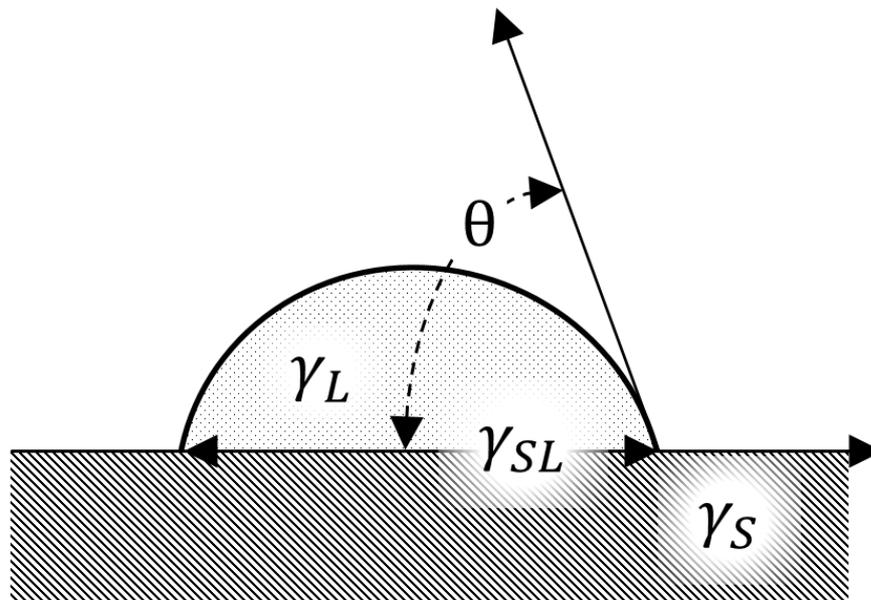


Figure 8 : Representation of a liquid drop of surface energy γ_L on a solid substrate of energy γ_S forming an interface of energy γ_{SL} with a contact angle θ .

Ideally, the proper spreading of the adhesive should also allow, under adequate spreading conditions, to remove or at least help to remove as much as possible the air (and contaminants if any: dust, grease...) that would be at the interface and could prevent the surfaces from coming into intimate contact, some adhesives being sometimes specifically formulated for this purpose⁸⁷.

The good spreading observed when a liquid has a strong affinity with a solid is mathematically translated by a parameter named *spreading parameter*, noted S :

$$S = \gamma_S - (\gamma_{SL} + \gamma_L) \quad (27)$$

When $S \geq 0$, the total wetting of the solid surface by the liquid, which spreads spontaneously, is observed. The contact angle is zero ($\theta = 0$) and the final equilibrium state in the presence of an infinite reservoir of liquid should be a monomolecular film of liquid separating the substrate from the ambient air⁸⁸. However, this monomolecular film hypothesis has been contradicted by De Gennes, who instead predicts that the liquid becomes more of a relatively thick (≈ 10 nm) "pancake" shape at the equilibrium, with the thickness depending on S . The structure in the vicinity of the edges of the pancake may be complex and depends on the chemical composition of the equilibrium phases and the different interactions present⁸⁹.

If $S < 0$ the wetting is said to be *partial* and the liquid drop does not spread completely on the substrate ($\theta > 0$). The case of partial wetting has been extensively studied by Zisman et al.⁹⁰ and this phenomenon is at the origin of his first theory which tried to explain the adhesion phenomenon by a thermodynamic approach.

The drop takes the form of a hemisphere filled with liquid, and the contact angle on the substrate is described by Young's equation presented previously ($\gamma_S = \gamma_{SL} + \gamma_L \cos \theta$, Eq. 5). However, γ_S and γ_L are defined values specifically to the liquid and the solid studied, whereas γ_{SL} depends on the unique solid-liquid couple. S thus depends directly on the interfacial energy γ_{SL} , which directly reflects the affinity of a liquid for a given solid. The wetting behavior,⁹¹ and thus the contact angle can be further described by the Cassie equation which describes the wetting of a liquid on an heterogeneous surface. For a bicomponent solid surface, for example, Cassie equation is written as (eq. 28):

$$\cos \theta_c = \sigma_1 \cos \theta_1 + \sigma_2 \cos \theta_2 \quad (6)$$

where θ_1 and θ_2 are the contact angles for components 1 with fractional surface area σ_1 and 2 with fractional surface area σ_2 . This model is commonly applied to describe incomplete wetting of rough surfaces (ie. that traps air gaps between the liquid and solid. If the liquid then wets the rough surfaces, the Wenzel model (Eq. 29) should then be used.

$$\cos \theta_w = r \cos \theta_y \quad (6)$$

where θ_w is the apparent contact angle, θ_y the Young contact angle for an ideal surface, and r the roughness ratio defined as the ratio of the true area of the solid surface to its apparent area.

Curiously, it is common to find that interfacial energy tends to take a back seat in studies dealing with adhesion concerns. It is briefly stated in several of these studies that, "for optimal adhesion, the interfacial tension should be as low as possible" without further consideration⁹². Applicative studies on this subject regularly tend to focus on the value of the thermodynamic work of adhesion of Dupré W_a (often roughly called "adhesion energy"), by adapting the formulation of a liquid coating to increase γ_L and thus W_a , rather than working on the decrease of the interfacial tension γ_{SL} . This can be explained by the simplicity for an industrial company to evaluate γ_L of a formulation for example (a simple tensiometer is enough⁴⁴, see (7)), rather than γ_{SL} which requires advanced techniques such as spatially resolved ellipsometry, or grazing incidence X-ray reflectivity, which are not even always suitable for the interface under study¹⁶.

However, the reduction of this interfacial tension is crucial for the good performance of the adhesive. Indeed, even if both parameters γ_{SL} and W_a are mathematically linked, they represent different parameters which difference is important to understand. As a reminder, the thermodynamic work of adhesion defined by Dupré is expressed as a function of γ_{SL} as follows:

$$W_a = \gamma_S + \gamma_L - \gamma_{SL} \quad (6)$$

This expression tells us that during the formation of an adhesion phenomenon, one sacrifices a solid surface of energy γ_S and a liquid surface of energy γ_L , to form an interface of energy γ_{SL} . W_a is therefore a parameter that allows us to estimate whether this sacrifice is thermodynamically favorable.

The interfacial energy γ_{SL} is therefore a property of the newly formed interface. It represents a sort of "incompatibility" factor between both surfaces on the thermodynamic level, once the interface is formed. It thus translates the thermodynamic propensity to the rupture of the interface, as a factor of "fragility" of the interface.

To illustrate this with a practical example, KRÜSS GmbH provides a pertinent document reporting a case they encountered in their activity⁹². A customer of them were facing issues on the sealing of cardboard packages used to pack biscuits, cereals etc. This type of boxes is usually sealed using hot melt adhesives, formulated specifically to allow both a sealing resistant to storage in dirty environments; and a clean and easy opening by the customer. They observed that in a particularly warm and wet storage environment, the sealing of a significant number of boxes was failing before its delivery, despite their R&D efforts to set up a formulation optimized to enhance adhesion forces. KRÜSS went to help them, by running a complete characterization of the system, by measuring its adhesion energy and interfacial tension, among others. They reported to have solved this issue by looking at it from another point of view : they changed the formulation of the adhesive by increasing its polarity, to fit more with the relatively high polarity of the cardboard surface. They demonstrated not only that it did not affect the adhesion energy, but the interfacial tension significantly decreased, therefore promoting interactions at the adhesive/cardboard interface, rather than the adhesive/water

interface. These efforts resulted in a rate of sealing failure almost divided by 10 in wet environments, ensuring the full satisfaction of their customer.

Therefore, even if the adhesion energy measurement seems at first sight a good prediction to estimate the life span of the coating on its substrate, it does not give direct information on the stability and the thermodynamic strength of the interface. Thus, it is not advised to formulate a coating based exclusively on measurements of the work of adhesion obtained once the interface is formed, because this parameter does not necessarily predict the good resistance of the coating to the external aggressions encountered during the application tests.

These problematics of contact between a liquid and a solid were encountered as early as the 18th century, with concerns about the rise of liquids in thermometers¹⁶. Many other aspects of the wetting phenomenon are still subject to study today, particularly phenomena of deviation from thermodynamic equilibrium such as hysteresis in static wetting. This article does not deal with dynamic wetting observations, which will probably require a few more years of research to be understood and clearly defined. Currently, physicists routinely use the simplified image of the motion of a tracked vehicle to illustrate dynamic wetting.

Conclusion

In this review the different interactions involved in adhesive systems have been described and explained. Ranging from covalent bonds to Van der Waals interactions, light has been shed onto a complex balance of interrelated forces, distributed on a wide spectrum of scales and technically proven as responsible for adhesion. The short-ranged interactions (covalent and ionic) generally stand for the main contribution to the global cohesion of adhesive systems, but in certain cases when the surfaces are sufficiently distant, Lifshitz-Van der Waals interactions can overcome the short-range forces.

In practice, it is generally accepted that adhesion is a complex and circumstantial balance of all the forces presented above. Furthermore, if one can indeed consider that most adhesive interfaces involve bonding mechanisms, which are themselves complex and at varying distances, the consideration of possible mechanical anchoring effects and the compatibility of the surfaces described by the wetting parameters must never be neglected²¹.

Nowadays adhesion mechanics are more and more genuinely exploited by industrials to develop new ground-breaking technologies. The megatrends mostly include biomimetic-formulated adhesive solutions : mussel-inspired adhesives^{93,94}, octopus-like adhesives^{95,96}, or the particular case of synthetic gecko setae⁹⁷⁻¹⁰⁹, explored for their capacity to strongly and reversibly adhere to a tremendously wide range of surfaces, relying exclusively on Van der Waals forces. However, the latter was very recently proven to be inaccurate : using interface-sensitive spectroscopy, Singla et. al. showed evidence of acid-base interaction in gecko setae¹¹⁰. The gecko effect is notably important for the development of dry adhesives.

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