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Wetting in the nanoscale: A continuum mechanics approach

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ABSTRACT

A continuum mechanics model has been developed to study the equilibrium shape of nanometric droplets on a planar solid substrate and how, in this scale, the contact angle depends on the drop size. The drop is modeled as a liquid volume enclosed in an inextensible membrane, subject to an isotropic tension (the surface tension) and to a field of surface forces including, in the proximity of the solid, the liquid-to-solid interactions, envisaged as a generic potential force per unit surface directed normally to the solid surface (i.e. vertically). The only conditions required to solve the problem are those of mechanical and thermodynamic equilibrium. The predictions of the model are discussed in comparison with data on nanodrops retrieved by a special AFM device for a number of different liquid–solid systems.

1. Introduction

All theories of ideal wetting issue from the Young Equation [1], which relates one observable geometric parameter (the contact angle θ) to three thermodynamic quantities (γ_{lv}, γ_{sl} and γ_{sv}) accounting for the interaction properties of the contacting phases and assumed to be isotropic and uniformly distributed throughout each phase.

One of the main problems with this equation is the parameter under-determination (γ_{sl} and γ_{sv} are normally unknown), which makes impossible, *de facto*, any experimental validation of the theory and prevents its use as a predictive figure. Other known difficulties concern the ideal conditions underlying its application, namely thermodynamic equilibrium and a perfectly smooth, planar and chemically homogeneous solid surface [2–7]. Recently, the evidence of a scale effect of wetting phenomena has shown up in the domain of micro and nanotechnologies and pushed the authors to ascribe these effects to various causes [8–13].

Many researchers have been working, in the latest decades, to tackle such problems, without giving up the Young Equation. Neumann and coworkers [14–16], who have been working on wetting problems for the latest 30 years, succeeded in reducing the number of unknowns, by showing that (Equation of State Theory), in nearly ideal conditions, for a given solid surface (i.e. with fixed γ_{sv}) $\gamma_{\mathrm{lv}}\cos\theta$ is only a function of γ_{lv} and therefore, on a phenomenological ground, γ_{sl} can be derived from a sort of state equation, which reads:

$$\gamma_{\mathrm{sl}} = \gamma_{\mathrm{lv}} + \gamma_{\mathrm{sv}} - 2\sqrt{\gamma_{\mathrm{lv}}\gamma_{\mathrm{sv}}}\exp\left[-\beta(\gamma_{\mathrm{lv}} - \gamma_{\mathrm{sv}})^2\right], \tag{1}$$

where β is a constant. Combining Eq. (1) with the Young Equation yields

$$\cos\theta = -1 + 2\sqrt{\frac{\gamma_{\mathrm{sv}}}{\gamma_{\mathrm{lv}}}}\exp\left[-\beta(\gamma_{\mathrm{lv}} - \gamma_{\mathrm{sv}})^2\right]. \tag{2}$$

Constants β and γ_{sv} can be determined, given a set of meaningful γ_{lv} and θ measured by evaluating several different liquids over the same solid surface, by an optimization procedure based upon a least-square technique [17–21]. A different approach, starting from a chemical background, leads to the "Acid–Base Theory" [22,23], that as originally proposed by Fowkes, states that

$$W_{\mathrm{adh}} = 2\sqrt{\gamma_{\mathrm{lv}}^{\mathrm{LW}}\gamma_{\mathrm{sv}}^{\mathrm{LW}}} + fN\left(-\Delta H^{\mathrm{AB}}\right), \tag{3}$$

where LW superscripts indicate the dispersive components, f is a parameter expressing the entropic component, N is the number of the acid–base interactions involved on the interface and ΔH^{AB} is the enthalpy calculated following the theory of Drago [23].

On this basis the problem to detect real contact angles is focused on the chemical nature of the evaluated liquid–solid system and special attention is paid to the contributes of dispersive Lifschitz–van der Waals, acid and basic components in the solid surface energy and the liquid surface tension. This theory is quite complex and we cannot but refer the reader to the original papers. Here we can point out that the Acid–Base Theory, like the Equation of State Theory mentioned above, aims to provide an explicit form of the solid–liquid energy γ_{sl}, by which it is possible to calculate the work of adhesion.

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Further developments of this Theory lead to the well-known Good–van Oss–Chaudury (GvOC) [24] and Della Volpe–Siboni and coworkers Theories [25–28]. Such approaches depend upon the contact angle data that one may collect by submitting the same solid surface to several liquids featured by different polar and dispersive characteristics. By the work of these authors it can be deduced that real γ_{sl} values can be obtained only when the corresponding liquid acidic, basic and dispersive components are evaluated in a representative scale, really able to provide the right values of each of them.

The high complexity of these two Theories gives room to some points not unanimously agreed by all researchers. The assumptions on which the Young Equation is based make the experimental measurement of the contact angle a tough task. To achieve the conditions of full thermodynamic equilibrium, that implies coexistence of mechanical and chemical equilibrium, is difficult in any real experiment. Moreover it is almost impossible to exclude any sort of contamination of the solid substrates by the surrounding atmosphere as well as any effect due to capillary spreading of the drop through the micro-roughness of a real surface. Many authors have shown that the synergy of these phenomena determines a considerable variation of the liquid–solid energetic equilibrium state and a very comprehensive study of these and other wetting features was published in 1985 by de Gennes [2]. Also precursors films, very thin liquid layers produced by fluid evaporation–condensation processes around the drop [29,30] may cause the drop to spread over a condensed liquid layer instead of a dry solid surface.

The problem of the scale dependence appeared in the later years, i.e. whether the contact angle is influenced or not by the drop size or by the diameter of a capillary tube, has been reduced to the concept of triple-line tension [31–39], supported by Neumann's school as well as by many other researchers even if from different points of view. According to this concept, a surplus of thermodynamic energy is carried along the triple line in the form of a line tension. This is one of the most debated topics among researchers who study wetting problems. While few of them fully neglect these effects, there is an open debate in the rest of the scientific community about the sign and the intensity of this tension. Li and coworkers [9] developed the Modified Young Equation (4) by which it is possible, in a perfect liquid–solid system, to get the (always positive) line tension value τ by knowing the effective contact angle value θ, the contact angle corresponding to an infinitely large drop θ_∞ (equivalent to the classic Young contact angle) and the effective drop base radius a:

$$\cos\theta = \cos\theta_\infty - \frac{1}{a}\frac{\tau}{\gamma_{\mathrm{lv}}}. \tag{4}$$

These results, like those obtained by many other researchers [8–13], indicate a clear dependence of measured contact angles on the size of the evaluated drop. This fact is well known for drops lying in the range of micrometric size. Recently, however, it has become possible to investigate also drops and films at rest in the nanometric scale. This situation, emerging from the nanotech scenario, brings new problems in wetting studies. At a first glance it can be stated that nanodrops placed over inorganic solid surfaces, as those commonly adopted for nanoscale applications, lie in an environment much closer to the perfect one than those examined in macro or microscopic experiences. This is due to the fact that these solid substrates are nearly atomically perfect materials, like mica or silicon wafers for electronic use, liquids are generally extremely pure and the overall experimental setting requires extremely clean and neat working conditions. Moreover on this scale gravity effects are really unperceived. However, at the nanometric level, it is quite difficult to observe the geometry of drops in full detail, including their contact angles. No optical instruments can obviously detect objects smaller than visible light wavelength, while only ESEM or probe microscope techniques (like SPFM) provide a good insight of nanodrops [40–48].

In the present paper an approach to the wetting problem is attempted from the point of view of continuum mechanics. Following an old idea of surface thermodynamics, introduced by Gibbs and definitely assessed by Prigogine [49], the drop is modeled as a thin inextensible membrane, subject to an isotropic tension (the surface tension) and to a field of external forces applied to points of the surface per unit area. Far from the solid substrate these forces reduce to the pressure of the inside liquid (normal to the membrane) and the equilibrium condition is, trivially, the Laplace equation ($2\gamma_{\mathrm{lg}}/R = \Delta p$). In the proximity of the substrate the liquid molecules interact with the solid, through a generic potential force field directed normally to the solid substrate (i.e. vertically), a rapidly decreasing function of the vertical distance z from the solid surface. The range of these interactions is generally small in the order of nanometers, so that the validity of a continuum theory may appear to be questionable when applied to this region, the typical domain of discrete modelization theories, such as DFT (Density Function Theory) [50–52]. On the other hand, a continuum description is adopted, as a useful approximation, in many physical problems having to do with phenomena at the nanometric scale, such as the evaluation of stress and deformation fields around crystal dislocations and at the tips of microcracks [53,54]. The main assumption of the present model, amenable to the Gibbs–Prigogine concept of interface, consists in localizing at the liquid surface all the interactions the liquid exchanges with the solid substrate, which in this work will be considered ideally planar but, more generally, could be bounded by a surface of arbitrary shape. The nature of the potential force field needs not be specified but can be expected to be different in the case of wetting or non-wetting drops, namely if the interactions occur through a liquid or, respectively, a gaseous medium. Whichever its nature, the interaction force field will determine the shape of the membrane in the region near the triple line as quite different from a spherical shell and, simultaneously, will imply that the surface tension is not uniform in that domain. This effect works as a line tension at the triple line, but not exactly in the same way, as we shall see in the following. The problem consists, mathematically, in studying the conditions of mechanical and thermodynamic equilibrium for the membrane as defined above. The case of non-wetting liquids, corresponding to a completely closed membrane, with a contact angle higher than $\pi/2$ at the basis, is easier to understand and will be dealt with firstly, even though the examined experimental data concern only wetting liquids ($\theta < \pi/2$), for which supplementary hypotheses are required. The model provides a number of general results, which are: (i) a modified Young Equation relating the contact angle to the surface tension of the liquid (namely γ_{lv}), the molecular density at the liquid surface far from the contact and the value of the interaction potential at some limiting distance h from the solid surface; (ii) equations expressing both the molecular surface density and the surface tension as functions of the interaction potential; (iii) in a second-order approximation, a dependence of the contact angle on the drop size is predicted.

The nanometric level investigated with probe microscopes tools is particularly appropriate for a validation of this theory, for different reasons. First, the region where the drop shape is affected by the interaction force field has a size comparable with the drop size. Moreover, the imaging of the drop profile provided by the AFM probe is in reality just a scanning of forces acting in the proximity of the liquid surface. Finally, the dependence of the contact angle on the drop size can be followed on a wider size range, where the effect should appear with more evidence.

These aspects suggested to compare, for a number of different liquid–solid systems, the predictions of the theoretical model