Temperature-dependence of the static contact angle: a universal scaling law covering ideal cases, roughness effects and the transition to total wetting

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Abstract

In this work, a novel model that links the macroscopic contact angle, the system temperature and the surface tension is introduced. This model considers that the thermocapillary fluctuations on the droplet surface extend to the triple line and they interact with the solid substrate. The self-affine pinning of this triple line against a solid substrate is modelled with an homogeneous spatial distribution of potential wells. The introduction of a topological dimension in the equations yields a unified model that covers normal wetting (liquid droplets on smooth surfaces) but also Cassie-Baxter and Wenzel states on natural surfaces. The model also encompasses the transition to complete wetting.

1. Introduction

The physics of wetting is a topic of active research with an extremely broad range of practical applications. Daily applications cover the spreading of common liquids such as detergents on domestic surfaces, fungicides on plants or cosmetics on hair and skin. In the last two decades, a great deal of research has also been devoted to the modification of solid surfaces in order to produce surfaces displaying superhydrophobicity, superoleophobicity or superhydrophilicity.[1–4] These advanced surfaces often combine a chemical treatment and a roughness modification. These combinations of tailored geometry and chemical modifications spectacularly expand the functionalities of traditional coatings. As a result, novel coatings with specific anti-fingerprint, anti-fouling, non-wetting, non-adhesive or self-cleaning properties have become an industrial reality. All of the above-mentioned surfaces are exposed to a wide temperature range in working conditions. It is thus of importance to understand the impact of temperature variations on surface tensions and contact angles.

The surface tension and surface free energy of liquids and solids are not constant with temperature. Both of them are known to vary linearly with the temperature of the system.[5–10] The first theoretical studies devoted to the variation of surface tension of liquids as a function of temperature date back to the end of the 19th century and are attributed to Loránd Eötvös.[5,11] Eötvös understood the variation of surface tension with temperature in the light of van der Waals' equation of state and of the principle of corresponding states. He expressed this dependence in a surprisingly simple form:

$$\gamma_l . V_m^{2/3} = \kappa . (T_0 - T) \tag{1}$$

Where γ_l is the liquid surface tension, V_m is the molecular volume, κ is a constant, T_0 is a temperature close to the critical temperature of the liquid and T the temperature at which the experiment is performed.[5,12–14] While this mathematical

formulation is working strikingly well with the usual non-polar liquids, and to a lesser extent with polar liquids, the Eötvös κ constant is specific to each liquid.[5,8,12,13] The Eötvös law has been reinterpreted on theoretical grounds and proved a valid heuristic model when the vapor density is negligible compared with the liquid density.[12–14] A particular interpretation of this equation relies on Gibbs' free energy formulation ($\Delta G = \Delta H - T.\Delta S$). The constant κ is then understood as the entropy change when liquid molecules migrate from the core of the liquid to the surface.[12,13,15] These considerations help explaining why hydrogen-bonded "structured" liquids such as water or alcohols usually have a lower entropy change than non-polar liquids.[5,11–13] Early corrections of Eötvös' law were also proposed by Katayama, Ramsay and Shields to account for surface tension nonlinearities near T_c, but these corrections are of little use in narrow working ranges above the melting temperature and far from the critical temperature.[8,11,13] Aside the Eötvös model, other theoretical models also exist. For instance, a power-law model (sometimes named the Katayama-Guggenheim model) was also introduced by Ferguson and later backed up by Guggenheim's demonstration using the principle of corresponding states.[8,16,17] However, this model was restricted to non-polar liquids. The Flory, Orwoll and Vrijj equation of state theory can also be sued to predict surface tension from PVT data.[18–20] Nonetheless, this last approach requires specific equipment whereas Eötvös' law can be confirmed by surface tension measurements using the widely available pendant drop method.

Whereas it is really straight-forward to explain thermal surface tension variations, the variations of the contact angles with temperature are not that easy to explain. There exist several works in the literature dedicated to the variation of the static contact angle θ_s as a function of the temperature. As a general rule, the contact angle

is found to decrease with an increasing temperature; however, some rare systems show the opposite behavior.[21] Furthermore, the literature shows disagreements as to the type of equation linking θ_s and temperature. For instance, De Ruijter *et al.* measured a linear dependency of the contact angle θ_s on the temperature for the squalane/PET system.[22] Petke and Ray also found a linear relationship between temperature and contact angle for a range of liquids on polymer surfaces.[23] Other authors found a different result with a linear dependency of $\cos\theta_s$ on temperature.[24,25] Another more general view based on Gibbs adsorption isotherm and Polyani adsorption theory is that of a power-law dependency of $\cos\theta_s$ on T; this view has the advantage of including the linear dependency of some other systems in a relatively narrower temperature range.[26,27] Eventually, another work reports complex θ_s variations of *n*-decane on PTFE; the variations show singularities attributed to the various viscoelastic relaxations of PTFE in the studied temperature range.[28] Interestingly, the *dynamic* contact angle θ_d can be well described using Eyring's reaction rate theory.[22,24,29–31] In this theory, the rate of a liquid molecule jumping in or out of an active site located at the solid surface near the triple line determines the triple line speed. This view explicitly considers the temperature dependency of θ_d.

Regardless of the exact dependence of θ on temperature, a temperature-dependent wetting transition also exists.[7,32–36] This transition is sometimes abrupt and it marks the shift from a partial (or pseudo-partial) wetting characterized by a positive contact angle to a complete wetting where the liquid spreads spontaneously on the surface. The wetting transition framework can be subdivided in three different cases: the continuous long-range critical wetting that is activated by a sign change of the Hamaker constant, a discontinuous first-order transition implying a discontinuity in the first derivative of the surface free energy and the critical wetting near the critical

temperature of the liquid.[33,36,37] The wetting transition is never treated in a more general theoretical framework.

The present work is a different theoretical framework purported to the study of the temperature-dependence of the static contact angle. The effect of temperature was assessed in the light of the transition state theory. An alternative view is then proposed that correlates the amplitude of surface waves and the self-similar distortions of the triple line real surfaces modeled with a homogeneous distribution of potential wells.

2. Descriptive models: thermocapillary motion versus bound states

A description of the static contact angle as a function of temperature is introduced in this paragraph. This view is solely based on mechanistic considerations around the specific case of partial wetting of small monomolecular liquids; the cases of liquid macromolecules or colloids need to integrate obvious corrections such as collective displacement, interfacial repulsion or adsorption and specific Brownian motion. Thermal noise needs to be introduced first: it is well-known that the surface of liquids bears a certain roughness due to the existence of thermally excited capillary waves that introduce surface fluctuations.[38–41] The amplitude of these surface waves is proportional to:

$$\xi = \sqrt{\frac{k_B T}{\gamma_l}} \qquad (2)$$

Where k_B is the Boltzmann constant, T is the temperature and γ_l is the liquid surface tension. Consequently, ξ is the characteristic length (also known as the thermal length) of the problem and its theoretical value is in the order of 2-3 Å.[38,42,43] The measured root-mean-square amplitude of surface waves has been measured at ~5-7

Å for liquids such as alkanes or ethanol.[39,40] In recent works, it has been shown that the thermal fluctuations at the liquid-gas interface expand all the way to the triple line.[43]

The triple line has so far been described as a discontinuity anchored (or *pinned*) microscopically on a chemically heterogeneous surface; bound states of liquid molecules are due to the presence of periodically arranged potential wells (or *weak heterogeneities*) at the surface of the substrate.[7,44–46] Triple line pinning has a length scale is typically around 1 nm, which is in the same order of magnitude as ξ.[7,44,45] However, the competition between thermal fluctuations and liquid binding at the solid surface has never been used to provide useful scaling arguments related to the triple line description, to the best of our knowledge.

Let's start the demonstration based on the application of the theory of absolute reaction rates, in a spirit similar to that developed in the pioneering work of Blake and Haynes(1969).[30,47,47,48] If one imagines that a liquid molecule at the triple line jumps forward and is adsorbed, the rate constant can be expressed as :

$$k_{ads} = \tau \frac{F_{ads}^{\ddagger}}{F_{norm}} \frac{k_B T}{h} e^{\frac{-E_{ads}}{k_B T}} \tag{3}$$

Where τ is the transmission coefficient, also known as the steric factor; it allows for all the collisions not be effective when the energy requirements are satisfied. $F_{ads}^{\ddagger}$ is the partition function for the activated site and F_{norm} is the partition function for the normal state.[49] Naturally, h is the Planck constant. The same formula can be written for desorption, when an adsorbed liquid molecule moves backwards from the gas phase to the liquid one:

$$k_{des} = \tau \frac{F^{\ddagger}_{des}}{F_{norm}} \frac{k_B T}{h} e^{\frac{-E_{des}}{k_B T}} \qquad (4)$$

The transmission coefficient remains the same due to symmetry considerations. As proposed by Blake, the net rate of exchange is zero at equilibrium, thus:

$$k_{des} = k_{ads} \qquad (5)$$

Therefore:

$$\frac{F^{\ddagger}_{ads}}{F^{\ddagger}_{des}} = e^{\frac{-(E_{ads}-E_{des})}{k_B T}} \qquad (6)$$

This result was originally proposed by Blake and Haynes.[30] The term $E_{ads}\text{-}E_{des}$ will simply be called activation energy $E^{\ddagger}$ in the rest of the article This energy is also the energy that is required to maintain the presence of a liquid front near a statistically defined triple line at the equilibrium temperature, balancing thermocapillary effects with fast adsorption-desorption phenomena. The main hypothesis of this work is that the triple line is stochastically jumping forward and backward with an amplitude equal to that of thermocapillary waves, *i.e.* ξ. This energy can thus be expressed as:

$$E^{\ddagger} \sim -S.\xi^2 \qquad (8)$$

Where S is the spreading parameter, corresponding to the free energy difference between a dry solid and the same solid covered by a liquid:[7,50]

$$S = \gamma_{sv} - (\gamma_{sl} + \gamma_l) \qquad (9)$$

It is known that $S > 0$ corresponds to the total wetting case and $S < 0$ corresponds to the partial wetting case. Using the law of Young-Dupré, it is possible to express S as a function of the contact angle θ:[7,44]

$$S = \gamma_l(\cos\theta - 1) \qquad (10)$$

Which brings a macroscopic parameter that is measurable (θ) in an equation otherwise built on microscopic considerations:

$$\frac{F^{\ddagger}_{ads}}{F^{\ddagger}_{des}} = e^{\frac{\gamma_l(\cos\theta - 1).\xi^2}{k_B T}} = e^{\cos\theta - 1} \qquad (11)$$

Now, in the equilibrium state, one can consider that ratio of partition functions is the ratio of a capillary wave amplitude divided by a cutoff length $< d >$. This characteristic distance ($< d >$) can be understood as the correlation distance between adsorption sites (or wells of potential) on the surface. This concept was developed and successfully used by others in the so-called *weak pinning* framework in order to explain contact angle hysteresis.[44,46] Therefore :

$$\frac{F_{ads}^{\ddagger}}{F_{des}^{\ddagger}} \sim \left(\frac{\xi}{\langle d \rangle}\right)^{f} \tag{12}$$

Where f is the fractal dimension of the problem: $1 \leq f < 2$ for a linear "normal" triple line and $2 \leq f < 3$ for a planar triple line, *i.e.* a Cassie-Baxter state with entrapped gas between the solid surface and the liquid. On the opposite, if "hemiwicking" takes place (Wenzel state), $f < 1$ since the liquid is channeled through the surface grooves ahead of the triple line, thereby decreasing the fraction of triple line in contact with the solid. In this equation, the parameters f and $< d >$ need to be determined for each {solid ; liquid} pair since each liquid will uniquely "probe" a given solid due the specificities of their chemical interplay (Van der Waals forces, hydrogen bonds, electrostatic forces, π-interactions, etc), steric effects and the energy landscape of the solid surface. Therefore, a very simple equation is produced that describes the variations of contact angle with temperature:

$$\left(\frac{\xi}{\langle d \rangle}\right)^{f} \sim e^{\cos\theta - 1} \tag{13}$$

Or:

$$f . ln\left(\frac{\xi}{\langle d \rangle}\right) = \cos\theta - 1 \tag{14}$$

One notices that the transition to complete wetting ($\theta = 0$) matches to $\xi = < d >$, meaning that the critical wetting temperature corresponds capillary waves with an amplitude equal to the correlation distance between adsorption sites. In energy

terms, this can be understood as modification of the energy landscape to the point where the activation energy between two states disappears at a critical temperature, *i.e.* the activated state and the initial state have the same energy. The overall slope is always negative (as expected for an infinite spreading in the complete wetting case) and the energy landscape still bears $<d>$-periodic variations corresponding to the remaining presence of adsorption sites. A schematic is given in Figure 1. This model is also congruent with that of Prevost *et al.* which states that the triple line advances through thermally-activated jumps.[51]
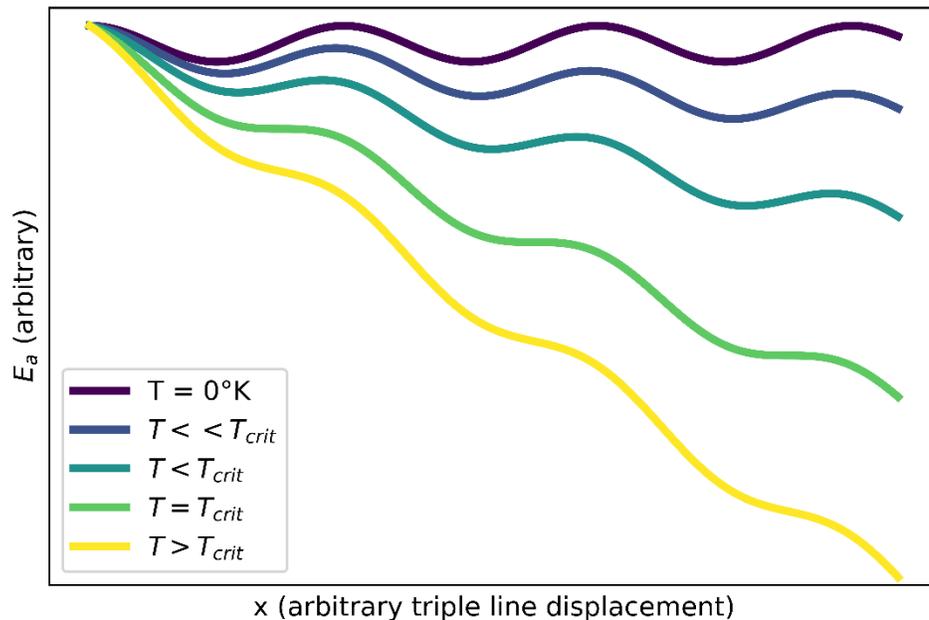

Figure 1. Conceptual view of the energy landscape involved at different temperatures

3. Conclusions

An alternative wetting model is proposed based on the transition state theory. This model encompasses regular wetting but also wetting on natural surfaces, *i.e.* Cassie-

Baxter or Wenzel states, and the transition to complete wetting. A hypothesis is made: the surface wave amplitude is "tuned" to a triple distortion amplitude characteristic of a set of correlated random heterogeneities. These heterogeneities are interpreted as wells of potentials. Under this hypothesis, a good description of the static contact angle variations with temperature can be provided for polar and dispersive liquids on a large set of materials representing real surfaces, using only two understandable variables, a fractal dimension f and a cutoff length $< d >$. This theory doesn't at present cover the case of macromolecular liquids, polymer solutions or suspensions. However, it shows that the static contact angle is the result of thermally activated jumps and it seems to hold for a very wide range of contact angles. Experiments were conducted on a set of six solid surfaces (PTFE, glass, stainless steel, brass, zirconia and alumina) and using six liquids with a wide range of polarities with temperatures varying from 25 to 240°C. These results were confronted to the proposed equation (Eq. 14) by fitting f and $< d >$ for each {liquid ; solid} pair and plotting $-f.\ln(\xi/\langle d \rangle)$ versus $1-\cos\theta$. The agreement between the model and the experiments was excellent ($R^2 > 0.96$). These experimental results will be presented in a subsequent publication.

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