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Complex wetting phenomena in liquid mixtures: frustrated-complete wetting and competing intermolecular forces

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Abstract

We give a phenomenological overview of recently discovered complex wetting states in simple liquid mixtures relevant to both fundamental research and industrial applications such as oil recovery. Alkanes on water show a sequence of two wetting transitions, from partial wetting to ‘frustrated-complete wetting’, and finally to complete wetting: a first-order thin–thick transition between a microscopic and a mesoscopic adsorbed alkane film is followed by a long-range critical wetting transition to a macroscopic wetting layer. The existence of the new ‘frustrated-complete wetting’ state follows from a competition between short-range and long-range components of the intermolecular forces, the latter opposing wetting. The effective long-range forces between interfaces consist of Debye dipolar and London dispersion contributions, which can also be in mutual competition. The London component is ultimately responsible for the frustration preventing complete wetting at ambient temperatures and pressures.

1. Perspective and motivation

From a fundamental scientific point of view as well as from the applied standpoint of technologies such as oil recovery, the wetting behaviour of organic liquids at interfaces is a focus of current interest. Recent experiments have revealed that, even for simple fluid mixtures, the paradigm of the isolated first-order wetting transition found for instance in cyclohexane/methanol binary liquid mixtures [1–3] is too simple to describe the observations. Besides first-order transitions, critical or continuous wetting transitions have also been found, of long-range [4] or short-range character [5]. Moreover, a sequence of first-order and critical wetting transitions has been observed, leading to the existence of an intermediate wetting state between the usual partial wetting and complete wetting regimes [6, 7]. For a recent review, see reference [8].

Our first concern in this paper is to describe the intermediate wetting state termed *frustrated-complete wetting* [9], discovered in alkanes adsorbed on water [4, 6, 7], and to discuss the connection between partial wetting in these systems and so-called *pseudo-partial wetting* predicted for a class of non-volatile liquids [10]. Secondly, we aim at elucidating the role of the so-called short-range and long-range forces in complex wetting states, and attempt to explain the observed behaviour in terms of a competition between these forces [11]. Finally, the long-range van der Waals forces themselves can be seen to be composed of two opposing contributions, in the frustrated-complete wetting state. The London dispersion forces and the Debye dipole–non-polar forces compete in a subtle manner in the vicinity of the long-range critical wetting transition of alkanes on water.

2. Frustrated-complete wetting

The state of frustrated-complete wetting has been discovered experimentally as a partial wetting state, intermediate between the usual partial wetting and the complete wetting state [4]. The context is a water surface in equilibrium with alkane vapour, and wetted by alkane liquid, also in equilibrium with the vapour. The usual state of partial wetting in such systems consists of macroscopic alkane liquid drops with finite contact angle, sitting on a (microscopically thin) adsorbed alkane liquid film. The ‘substrate’ is water. On the other hand, the state of complete wetting corresponds to a macroscopic alkane liquid layer, homogeneously spread over the water surface. The intermediate state of frustrated-complete wetting consists of a mesoscopic alkane film (of thickness much greater than a molecular diameter) on top of which drops with finite (but very small [7, 12]) contact angle can still form. This state is, strictly speaking, a partial wetting state, but in as far as the small spreading coefficient S (<0) and the small contact angle θ are concerned, the distinction between this state and complete wetting (for which $S = 0$ and $\theta = 0$) would be very difficult to discern experimentally.

In fact, the way in which frustrated-complete wetting was found is not through contact-angle or surface free-energy measurements, but by observing that the transition from partial to complete wetting in, for example, *n*-pentane on water does not take place in one step. Instead, two distinct transitions occur, well separated in temperature by several tens of kelvins, or, in alternate experiments, in pressure by several bars [7]. Not only is this system characterized by a sequence of wetting transitions, but it was also established experimentally that while one transition resembles the usual first-order wetting transition with hysteresis, the other is a continuous transition identified as the theoretically predicted but experimentally elusive critical wetting transition in systems with long-range forces.

The term frustrated-complete wetting was chosen [9] to describe this state with a thick, but still mesoscopic film, because calculations based on Dzyaloshinskii–Lifshitz–Pitaevski (DLP) theory, combined with the Cahn–Landau theory of wetting including van der Waals forces, showed that the long-range tail of the interaction free energy between interfaces (proportional to inverse film thickness squared) opposes the formation of a macroscopically thick wetting layer [4]. Thus ‘antagonistic’ [13] van der Waals forces prevent or ‘frustrate’ complete wetting, while the effect of all other force contributions combined would be to induce complete wetting. We will see further (section 4) that the van der Waals tails themselves also consist of ‘agonistic’ and antagonistic components, which we will identify.

We note that usual partial wetting and frustrated-complete wetting states have in common that they are *partial wetting* states, with drops or lenses with non-zero contact angle on top of an adsorbed liquid film. From an experimental point of view a sharp distinction between the two states can be made only at the first-order phase transition, at which the thin and the thick film coexist thermodynamically. On the other hand, the justification for using the

term ‘frustrated-complete wetting’ lies in the *separation of the microscopic and mesoscopic length scales*, which is possible for the specific systems studied experimentally, and which is most convincing close to complete wetting, in the vicinity of the long-range critical wetting transition, where the film thickness diverges due to a vanishing Hamaker constant.

In our context of wetting by volatile liquids the substrate is in equilibrium with the vapour phase of the adsorbate, and therefore there is always (at least) a thin adsorbed liquid film. In the framework of spreading of *non-volatile* liquids [14] there are similar states, but a somewhat different terminology has been employed, which can be related to ours. The ‘partial wetting’ state consists of a liquid drop on a ‘dry’ substrate. On the other hand, the ‘pseudo-partial wetting’ state [10] corresponds to a drop on a substrate which is ‘wetted’ by an adsorbed liquid film of finite thickness [10, 15]. Thus, *pseudo-partial wetting for non-volatile liquids is similar to partial wetting for volatile liquids*, since in both states there is a uniform adsorbed film on top of which drops with finite contact angle may occur. This is illustrated in figure 1.

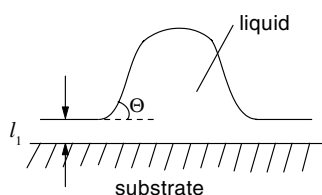


Figure 1. A sketch of a partial wetting configuration for a volatile liquid. The saturated vapour phase is assumed to surround the liquid drop. The thickness of the thin adsorbed liquid film is l_1 and the contact angle of the drop is θ . This configuration also corresponds to the pseudo-partial wetting phase of a non-volatile liquid, in which case there is no saturated vapour phase.

In closing this section we illustrate schematically in figure 2 the observed phase transition from the usual partial wetting state with a thin adsorbed film to the frustrated-complete wetting state. The transition zone profiles between the film and the liquid wedge are sketched for temperatures below, at, and above the first-order transition. The corresponding interface potentials, the minima of which indicate the equilibrium thicknesses of uniform films, are also shown.

3. Short-range forces versus long-range forces

Whether forces are considered to be of short range or long range depends on the context. In wetting research there is a general tendency to consider forces which decay exponentially with separation or which simply have a finite (microscopic) range to be of short range, and algebraically decaying interactions are termed long-range forces. The rationale behind this is that the usual van der Waals forces in fluids, which correspond to algebraically decaying intermolecular potentials proportional to r^{-6} , neglecting retardation, where r is the intermolecular distance, sum up to produce interaction potentials between interfaces decaying as l^{-2} , l being the interface separation. Therefore, a relatively rapidly decaying intermolecular potential produces a fairly long-ranged interface potential, which has important consequences for wetting phenomena.

For bulk critical phenomena it is well known that van der Waals forces belong to the class of the short-ranged models (Ising class), because the r^{-6} -decay of the interaction between molecules is faster than the threshold decay that would modify bulk critical behaviour [16]. For interfacial phenomena the situation is different. For example, the upper critical dimension above which the mean-field theory applies, and the system can be considered to feature (weak)

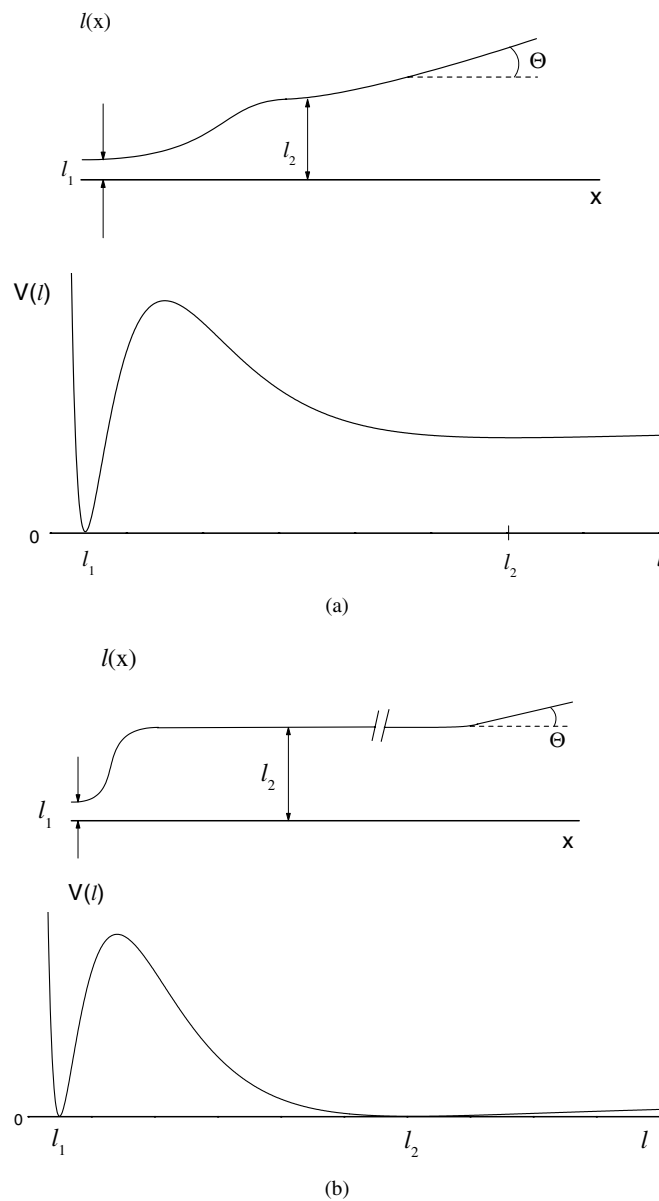


Figure 2. (a) A sketch of the film thickness profile $l(x)$, along the spatial coordinate x , of the transition zone between a thin adsorbed film of thickness l_1 and the liquid wedge which makes a contact angle θ with the horizontal substrate. The corresponding interface potential $V(l)$ features a global minimum at l_1 and a secondary minimum at l_2 . The relation between $V(l)$ and $l(x)$ is that $(dl/dx)^2$ is roughly proportional to $V(l)$. This case represents the partial wetting state below the transition to frustrated-complete wetting. (b) A sketch of the film thickness profile at the first-order transition between the thin film of thickness l_1 and the mesoscopic film of thickness l_2 . The break indicates that the mesoscopic plateau extends over an arbitrary lateral distance. Also shown is the transition zone between the mesoscopic film and the liquid wedge with small contact angle θ . The corresponding interface potential shows two equal minima. (c) A sketch of the film thickness profile in the frustrated-complete wetting state. The transition zone is between the mesoscopic film and the liquid wedge with very small contact angle. The corresponding interface potential features a global minimum at l_2 .

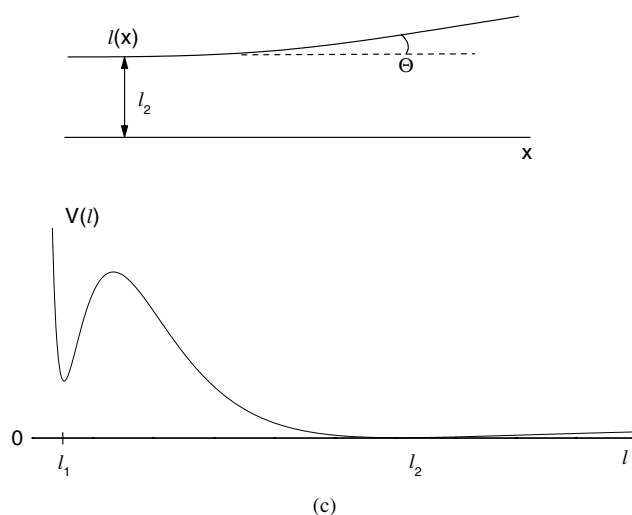


Figure 2. (Continued)

long-range forces, is

$$d_u = 3 - \frac{4}{\sigma + n} \quad (3.1)$$

where $\sigma = 3$ (4), for non-retarded (retarded) van der Waals forces and $n = 1, 2, \dots$ is the order of the wetting transition [17]. Clearly, $d_u < 3$, so algebraic decay does indeed guarantee mean-field behaviour and deserves the description ‘long ranged’.

Note that with this definition there are inevitably situations where ‘short-ranged’ forces can in reality decay more slowly than ‘long-ranged’ ones over the experimentally relevant length scales, and vice versa. Two examples are ionic solutions [14] and type-I superconductors [18], where the decay lengths of the exponentially decaying interface potential, the Debye length, and the coherence length, respectively, can be as large as a micron.

Considering forces with algebraic decay one needs to consider whether the thermodynamic limit is still defined. Following the hierarchy down from bulk to surface, and ultimately to the thermodynamics of the contact line where three phases meet, one finds that the threshold decay for the existence of the thermodynamic limit becomes increasingly more difficult to satisfy. Bulk free energies are only well defined for intermolecular pair potentials decaying faster than r^{-3} , surface free energies require a decay faster than r^{-4} , and for line tensions the threshold is r^{-5} . For the line tension at a first-order wetting transition, the situation is even more sensitive. This quantity diverges already for van der Waals forces [19].

The most basic theory of wetting, Cahn–Landau theory, does not include long-range forces, and is therefore more appropriate for describing interface delocalization in Ising magnets or other short-range models than wetting phenomena in real fluids, which feature van der Waals forces. For describing these, the long-range forces must be incorporated, not only at the level of the surface field acting between substrate and adsorbate, but also in the adsorbate–adsorbate interaction. In general the inclusion of long-range forces leads to important (non-perturbative) effects. However, in special situations it can be done in a *perturbative* way, treating the system as one with short-range forces, to which weak but long-ranged tails of the intermolecular forces are added. This is the case, for example, when the leading amplitude of the effective substrate–adsorbate long-range interaction is vanishing, which happens for long-range critical wetting transitions.

This artificial but often very useful separation between short-range and long-range forces can most easily be understood at the level of the intermolecular pair potential, for which we assume a Lennard-Jones form. We then define a system with exclusively short-range forces as one in which the pair potential is cut off at a few multiples of the molecular diameter σ , as illustrated in figure 3. In molecular dynamics (MD) simulations this cut-off is often introduced to render the computations practicable. Typically one takes the cut-off at 2.5σ , as was done for instance in MD simulations of wetting and drying [20]. The basic bulk properties of the system are usually not affected by this. Phase equilibria between solid, liquid, and gas phases do not rely—at least not qualitatively—on the van der Waals tails. The effect of these tails is to strengthen the intermolecular attraction, which promotes condensation, so for example the bulk critical temperature is increased with respect to the truncated potential. However, at the level of interfacial and wetting phenomena the van der Waals tails can have important qualitative effects, as will now be discussed.

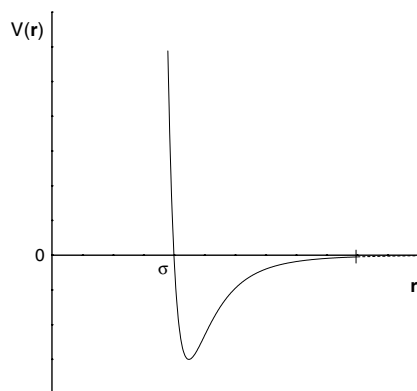


Figure 3. An intermolecular pair potential with a repulsive core and an attractive long-range tail. The cut-off between the short-range and long-range parts of the potential is where the solid line changes to a dotted one. The molecular diameter is σ .

After the phenomenology of first-order wetting, prewetting, critical wetting, and tricritical wetting was established for systems with short-range forces [21], studies emerged of the effect of the van der Waals tails on wetting transitions¹. It was soon realized that for real fluids the interface potential $V(l)$ develops a slowly decaying tail, asymptotically varying as

$$V(l) - V(\infty) \sim Al^{-2} + Bl^{-3} + \dots \quad (3.2)$$

for large wetting layer thickness l . Here, we have defined $V(l)$ such that it takes the value zero at its minimum (see figure 2). The amplitude A is an effective Hamaker constant. We remark that our sign convention is *opposite* to that employed, for example, by Israelachvili [22]. For positive A ('agonistic case') the long-range forces tend to thicken the layer, while for negative A ('antagonistic case') they thin the film. In the former case only a first-order wetting transition can occur, in which a minimum of $V(l)$ at small l , governed by the short-range forces, exchanges stability with the minimum at very large l , controlled by the long-range forces. In the latter case there is no minimum at very large l . In conclusion, with the long-range tails re-attached to the potentials of the fluid, there is still room for first-order wetting but no longer for critical wetting, or so it seemed.

¹ For a brief overview of the relevant theoretical works on wetting in systems with long-range forces, we refer the reader to the introduction of reference [11].

Soon after this, however, theory predicted² that systems with long-range forces could in their own way display critical wetting, through a mechanism that is different from that exhibited by short-range forces. The Hamaker constant was found to be temperature dependent and it is conceivable that A changes sign, from negative to positive, in some system, while B remains positive. If this happens, and if for $A > 0$ the global minimum of $V(l)$ lies at very large (infinite) l , then a critical wetting transition occurs precisely when A vanishes. The equilibrium layer thickness diverges as $l_e \propto -B/A$ in this so-called long-range critical wetting phenomenon. Roughly ten years after the theory was expounded, a convincing experimental realization was found [4].

The state of frustrated-complete wetting is a special case of partial wetting, or, in the terminology of [10], of pseudo-partial wetting. In this state short-range forces favour complete wetting, but antagonistic long-range forces bring the layer thickness back to a mesoscopic rather than macroscopic value. What characterizes the observed frustrated-complete wetting specifically is that the minimum of the interface potential lies at a mesoscopic film thickness, governed by the balance between the leading term, proportional to A , and the next-to-leading term, proportional to B [4, 11], of an expansion of the interface potential in $1/l$.

Clearly, the possibility of a vanishing Hamaker constant at some temperature (or pressure) provides a means for the system to reach the complete wetting state through a continuous transition, without hysteresis. While this end of the frustrated-complete wetting range can be understood solely in terms of the Hamaker constant and the physics of the long-range forces, the other end of the range, towards partial wetting with only a microscopic film, involves both short-range and long-range forces.

To explain a possible phase transition from partial wetting with a microscopic film to frustrated-complete wetting, one can start from studying the physics of the short-range forces. In fact, the Cahn–Landau theory allows one to study the short-range forces in a zeroth-order approximation and to add the substrate–adsorbate long-range forces perturbatively to the surface free-energy functional, by virtue of their small amplitude and by making use of an auxiliary cut-off distance [11]. The result is that a first-order wetting transition in the system with short-range forces induces a first-order transition between partial and frustrated-complete wetting, when weak and antagonistic long-range forces are added. This first-order transition is between a microscopically thin and a mesoscopically thick film. On the other hand, if the system with short-range forces were to show only complete wetting or a critical wetting transition, then frustrated-complete wetting would not be preceded by a ‘thin–thick’ transition, and would be the only observable partial wetting state [23], but this is not the case in the experiments [4, 6, 7].

Since the first-order thin–thick transition is governed by both the short-range and the long-range forces, which determine the structure of the interface potential at small l , and the long-range critical wetting transition is solely controlled by the behaviour of the long-range tails, through the Hamaker constant, the two transitions appear to be independent. The first-order transition is brought about by the vanishing of the spreading coefficient S which expresses the surface free-energy balance between partial and complete wetting. The long-range forces can affect the spreading coefficient and the contact angle *quantitatively*, but they can modify *qualitatively* the layer thickness l in the mesoscopic to macroscopic range, by inducing an extra phase transition through a vanishing A . Are S and A related in our class of systems?

² For a brief overview of the relevant theoretical works on wetting in systems with long-range forces, we refer the reader to the introduction of reference [11].

This question has been addressed in general by Brochard-Wyart *et al* [10], who noted that a description of the interface potential $V(l)$ in terms of van der Waals forces alone leads to misleading relations between the Hamaker constant A and the spreading coefficient S . Many other force components may enter into $V(l)$ at small l . In fact, A and S are independent, *provided* that we consider a manifold of surfaces and of liquids with enough chemical variety. Léger and Joanny made a similar statement in their review [15], and remarked that S involves contributions both from the long-range tails of the potentials and from the short-range structure of the interaction. In most examples the physical origins of these two kinds of contribution are very different and S and $V(l)$ for large l may be considered as independent quantities.

The possible independence of S and A might lead one to speculate that the thin–thick transition and the long-range critical wetting transition could be brought close together, by varying the chemistry of the system. This would bring about novel phase diagrams, with critical-end-point scenarios for wetting, as was for example predicted for type-I superconductors [18]. However, in the experiments so far the two transitions appear coupled and the two transition lines, as functions of chemical composition, appear to run parallel. Two kinds of chemical variation have been explored so far. Firstly, the alkane chain length was varied, using pure compounds as well as mixtures and consequently equivalent carbon numbers [7]. In these experiments both temperature- and pressure-induced wetting sequences were found. Secondly—and this is how the first wetting sequence was discovered—*n*-hexane was adsorbed on brine and the wetting transitions were studied varying the salt concentration. From these experiments, the conclusion is that S and A are coupled, and a partial theoretical explanation for this has been proposed [24].

The separation that we have made theoretically, between short-range and long-range forces, was also performed in a recent density-functional theory study of long-range critical wetting [25]. In that approach explicit calculations of the substrate–liquid and substrate–gas density profiles were carried out for alkanes on water, and these were used to evaluate the asymptotic expansion for the interface potential. For a narrow range of system parameters, the sequence of two wetting transitions could be reproduced, thus corroborating the Cahn–Landau theory and the experimental results.

The density-functional computations show that, as regards the location of the first-order wetting transitions, significant shifts are observed upon inclusion of the long-range tails of the potentials. This is not a surprise, since the amplitude of the substrate–adsorbate long-range forces is not small in the vicinity of the first-order transition, but only near the long-range critical wetting transition. The perturbative approach adopted in [11], adequate for demonstrating the occurrence of an intermediate regime between the first-order and the continuous transitions, is not suitable for locating the first-order transition accurately in temperature.

In closing this section we comment briefly on the phenomenon of *short-range critical wetting*. From the point of view of real fluids, the theory of wetting in systems with short-range forces was considered to be at most a reasonable first approximation and the subtle physics associated with the short-range critical wetting transition was thought to be reserved for Ising models. Sophisticated renormalization group theory and extensive Monte Carlo simulations have produced a wealth of results and controversies [26], none of which was thought to be relevant for van der Waals fluids.

This situation has changed drastically since the observation of several signatures of short-range critical wetting in some mixtures of alkanes and methanol with wetting temperatures close to the bulk consolute point T_c [5]. In these systems agonistic long-range forces are present, and consequently only first-order wetting can occur, in the strict theoretical sense. However, in the observed range of wetting layer thicknesses, the asymptotic regime where the

long-range forces dominate is not reached, and the physics of short-range forces, which leads to critical wetting near T_c , prevails. Remarkably, both experiment and computer simulation indicate that mean-field theory is valid for short-range critical wetting, while renormalization group predictions are very different [26]. We conclude that the mean-field theory is a very useful approach for wetting phenomena in liquid mixtures, being naturally suitable for long-range forces (since $d_u < 3$), and being in practice adequate for describing the physics of short-range forces to the extent that the experiments can resolve it.

4. Debye dipole–non-polar forces versus London dispersion forces

When non-polar alkanes are adsorbed on dipolar water, the effective interaction between the alkane liquid/vapour interface and the water surface at large distance (typically several hundred Å) arises from the London dispersion forces (induced-dipole/induced-dipole) and the Debye forces (dipole/non-polar) between molecules. Both contributions decay as r^{-6} for large intermolecular separation, neglecting retardation effects. Indeed, the effective interaction between the two interfaces bounding the wetting layer arises from the underlying substrate–adsorbate and adsorbate–adsorbate intermolecular forces. If the substrate (the water phase) is inert, which we assume since hardly any water molecules are present in the alkane phases (liquid or vapour) and vice versa, the substrate–substrate interactions do not contribute to the thickness dependence of the surface free energy of the wetting film. This is why the Keesom energy, which stems from dipole–dipole forces between freely rotating water molecules, can be neglected in this discussion.

The Hamaker constant A for the interaction of two media (the water phase, ‘1’, and the alkane vapour, ‘2’) across a third medium (the alkane liquid, ‘3’) can be calculated conveniently using a continuum theory of interacting dielectric media. According to the DLP theory [22], A can be decomposed into a static or zero-frequency term, which reads

$$A_{\nu=0} = -\frac{3}{4}kT \frac{(\epsilon_1 - \epsilon_3)(\epsilon_2 - \epsilon_3)}{(\epsilon_1 + \epsilon_3)(\epsilon_2 + \epsilon_3)} \quad (4.1)$$

where ϵ_i denotes the (relative) static dielectric constant ϵ_r of medium i . This contribution includes the Debye interaction, and since it is a static quantity, it does not undergo retardation effects. The finite-frequency or dynamic term contains the dispersion forces and reads, approximately,

$$A_{\nu>0} \approx -\frac{3h\nu_I}{8\sqrt{2}} \frac{(n_1^2 - n_3^2)(n_2^2 - n_3^2)}{s_{13}s_{23}(s_{13} + s_{23})} \quad (4.2)$$

where n_i is the refractive index of phase i and $s_{ij} = (n_i^2 + n_j^2)^{1/2}$. For obtaining this result, a simple oscillator model with one eigenfrequency has been assumed for calculating the dielectric constant, and ν_I is a typical ionization frequency in the UV range ($h\nu_I \approx 10$ eV). This dispersion term does undergo retardation, and is weakened, as soon as the wetting layer thickness (medium 3) exceeds several hundred Å. The total Hamaker constant equals

$$A = A_{\nu=0} + A_{\nu>0}. \quad (4.3)$$

Let us now define what the sign of the Hamaker constant would be in the ‘simplest’ case. Under normal gravity, the phases are ordered in space, from bottom to top, according to decreasing density. This is also the case in our system, consisting of water, alkane liquid, and alkane vapour phases, the corresponding labels being 1, 3, and 2. The simplest approximation would then be to assume that the static dielectric constants as well as the refractive indices are increasing functions of density, so that $\epsilon_1 > \epsilon_3 > \epsilon_2$ and $n_1 > n_3 > n_2$. The validity of this

approximation is probably restricted to fluid mixtures of *similar* molecules, e.g., all non-polar, the density being the only relevant parameter for distinguishing the phases. In this case one easily verifies that both contributions to A are positive, resulting in a repulsive force which tends to thicken the wetting layer.

Alkane molecules and water molecules are quite dissimilar. The static dielectric constant of water is much larger than that of the alkane phases. As it happens, the ordering of the static dielectric constants, which for water, pentane, and vapour are 80, 1.84, and 1, respectively, does obey the simple inequality, but the ordering of the refractive indices at ambient temperature does not. The refractive index of liquid pentane at room temperature, 1.349, is slightly *higher* than that of water, 1.333, in spite of the lower density. This results in a negative dynamic contribution to A . In order to see which contribution prevails, we evaluate the two terms and study their dependence on temperature.

The static term, which cannot exceed $3kT/4$, is about $0.21kT$ for our system and its explicit temperature dependence is given by the proportionality to kT , indicating that this contribution is of entropic origin. The dynamic term, which has an implicit T -dependence, equals about $-0.0008h\nu_l$ at ambient temperature, or, equivalently, $-0.33kT_a$, with $T_a = 300$ K, which opposes and outweighs the static contribution. Therefore, at room temperature the attraction between the interfaces bounding the wetting layer, originating from the London forces, prevails.

Now, the interesting phenomenon which takes place in this system as a function of temperature is that the refractive index of pentane decreases fairly rapidly, and a matching of refractive indices between pentane and water occurs at $T \approx 70$ °C. Above this temperature the denser phase (water) has the larger refractive index and we retrieve the previously defined ‘simplest’ situation with a positive dynamic Hamaker constant. Already at $T \approx 53$ °C, the total Hamaker constant changes sign, so the net long-range forces become agonistic. This temperature gives the location of the long-range critical wetting transition. Figure 4 shows the temperature dependence of the Hamaker constant and its contributions. Incidentally, as

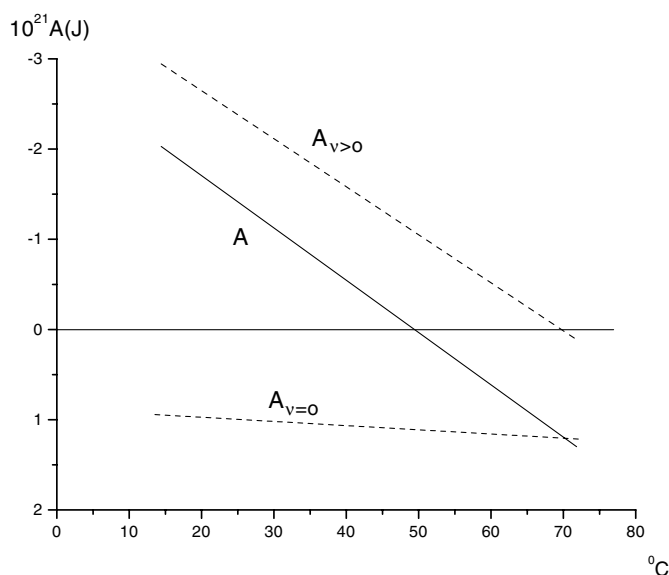


Figure 4. A sketch of the Hamaker constant and its static and dynamic contributions as functions of temperature in the vicinity of the long-range critical wetting transition of pentane on water, after reference [4].

one can see from this figure, and as was pointed out by Thanh-Khac Pham and Hirasaki [27], a reasonable approximation to the critical wetting temperature is the temperature for which $A_{v>0}$ passes through zero. Thus, the simple criterion of refractive index matching slightly overestimates the actual wetting temperature.

In conclusion, we have seen that the London dispersion forces are responsible for the frustration effect, which prevents the wetting layer from thickening to macroscopic dimensions. When the temperature is increased, due to incipient refractive index matching of pentane and water, the agonistic Debye forces prevail and the frustration is relieved. Note that retardation effects have been ignored in this discussion, because they are negligible in the experimentally observed range of layer thicknesses, not exceeding several hundred Å. The term Bl^{-3} in the interface potential (3.2) does not represent retardation, but arises from the finite thickness of the substrate–adsorbate interface on a microscopic scale [28].

5. Conclusion and outlook

In this paper we have taken a close look at complex wetting states which were observed experimentally in alkanes adsorbed on water, a system relevant for both fundamental and applied research. We have paid special attention to the so-called frustrated-complete wetting regime, originating from short-range forces tending to thicken the wetting film, and long-range forces which oppose the formation of a macroscopic layer. This wetting state is a special case of partial wetting, or, depending on the context, of pseudo-partial wetting, pertaining to, respectively, volatile or non-volatile liquid drops sited on surfaces wetted by a thin adsorbed film.

At low temperatures the experimentally observed frustrated-complete wetting regime starts at a first-order thin–thick transition from a microscopic to a mesoscopic film. This transition between two partial wetting states is governed by the physics of both the short-range and the long-range force components of the intermolecular interactions. The short-range forces are by definition those that remain when the intermolecular pair potentials are truncated at a few molecular diameters. The higher-temperature end of the frustrated-complete wetting regime is a long-range critical wetting transition, the physics of which is controlled by the behaviour of the Hamaker constant as a function of temperature. Although the two transitions of the wetting sequence appear to originate from different mechanisms, the transitions have been observed to move in parallel as a function of, for instance, the salinity of the water phase, or the chain length of the alkane molecules.

The long-range forces that frustrate the thickening of the wetting layer to macroscopic dimensions can themselves be seen to be composed of two competing contributions. The Debye interactions, arising between the dipolar water molecules and the non-polar alkane molecules, lead to a static part of the Hamaker constant which favours wetting. The London dispersion forces, however, prevent wetting due to a frequency-dependent part of the Hamaker constant which is opposite to and stronger than the static term at room temperature. As the temperature is increased, incipient refractive index matching of water and alkane causes the total Hamaker constant to change sign, relieving the frustration and inducing a continuous phase transition, without hysteresis, to the complete wetting state. Retardation effects can be ignored in the experimentally observed range of layer thicknesses.

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