An elegant advance in the physics of wetting

VIEWPOINT

An elegant advance in the physics of wetting

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Abstract
The non-local interfacial Hamiltonian for short-ranged models of wetting phenomena proposed by Parry and co-authors is discussed in the context of the history of wetting transitions.

Equation (1) of the paper by Parry *et al* in this issue [1] is a strong contender for an important new physical equation that illustrates Dirac's assertion that the best physics is likely to be the most beautiful:

$$W = a_1 \quad + b_1 \quad + \cdots. \tag{1}$$

This is a new equation for the binding potential of the interface Hamiltonian that describes interfacial phase transitions known as wetting transitions. Astoundingly, the coefficients a_1, b_1, etc, are independent of the geometry of the substrate, indicated by the non-planar nature of the wavy lines denoting the boundaries of the adsorbed film, so this equation can equally be applied to the wetting of spheres and cylinders, and structured substrates such as grooves, edges, and cones. Before attempting to summarize the physics on the right-hand side of this *wetting equation* let us first recap some of the history of wetting.

Wetting denotes a wide range of fundamentally and technologically important situations in which a bulk fluid approaches two-phase coexistence in the presence of a substrate wall (or spectator phase) such that the incipient bulk phase first appears at the substrate. For example, figure 1 shows an adsorption isotherm depicting the amount of liquid adsorbed from gas as a function of chemical potential or, alternatively, representing the stability of liquid films that have been deposited at a chosen thickness. The shape of this isotherm is appropriate to a first-order wetting transition. If one chooses a specific chemical potential (vertical dashed line) then the horizontal displacement to the point on the adsorption isotherm defines the *disjoining pressure* $\Pi(\ell)$ of the film at thickness ℓ. The binding potential (interface potential) $W(\ell)$ then follows from the relation $\Pi(\ell) = -\partial W(\ell)/\partial \ell$. These are mean-field quantities, at this level, because we have implicitly neglected capillary-wave fluctuations of the upper surface of the adsorbed film away from planar symmetry. From the figure it follows that the mean-field binding potential possesses two minima, which would be of equal depth if and only if the shaded areas were equal. Thus we have arrived at a standard mean-field description of a first-order phase transition, with an associated Maxwell construction. The figure has assumed that the system is at saturation (the dashed line is the chemical potential at bulk liquid–vapour
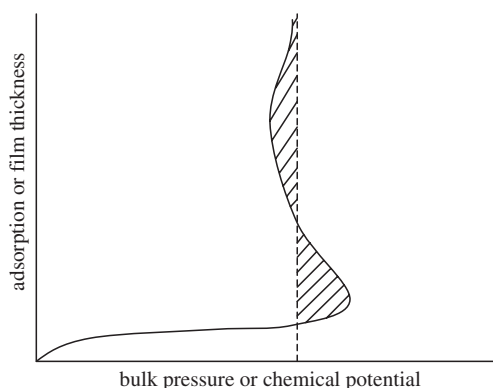
Figure 1. An adsorption isotherm displaying a first-order wetting transition.

coexistence), which defines the wetting transition at coexistence. Lying off coexistence (move the dashed line to the left) is the thin–thick transition. It is also possible that the van der Waals loop might vanish over some part of the bulk coexistence curve, leading to a continuous wetting transition, so-called *critical wetting* because it is an example of interfacial critical phenomena. So far, we have only discussed the knowledge possessed by the Russian School of Frumkin and Derjaguin, in the 1930s [2]. This early work relied on London dispersion theory to estimate the nature of the disjoining pressure. Two decades later Lifshitz and co-workers extended Lifshitz's theory of dispersion interactions to directly calculate the normal component of the pressure tensor at the substrate, which is the disjoining pressure defined from statistical mechanics [3]. This work became a cornerstone of modern colloid and interface science, but physicists were slow to grasp the fundamental relevance to interfacial phase transitions. This had to wait until 1977, with a paper by Cahn [4] that implied the ubiquitous presence of wetting transitions in nature (the important albeit flawed Cahn argument) and a density functional treatment by Ebner and Saam [5] that was ahead of its time. Soon it was realized that the full wetting phase diagram requires an additional thermodynamic field, to represent the attraction of the substrate to the film molecules [6]. In this extended picture, it is obvious that if one starts, say, in the partial wetting regime, equivalent to excess adsorption forming drops with a non-zero Young's contact angle, and then increases the substrate field one must eventually encounter a wetting transition to a macroscopically thick film (contact angle of zero). For theoretical physicists, the main excitement was generated by short-ranged models of critical wetting. Since for short-ranged models the upper critical dimension is precisely $d = 3$ (lower if dispersion forces are included [7]) it was possible to work out a complex scenario involving multiple regimes of non-universal exponents [8] that should be amenable to simulation and carefully constructed experiments. At this stage the story should have had a happy ending, but the party was spoilt by null results obtained from Ising model simulations [9] and this topic has remained stalled for about two decades, until now, with the discovery of the wetting equation of Parry *et al*.

The difficulty with the approach by theoretical physicists concerned the reduction in the degrees of freedom necessary to make analytic progress. For a start, molecular degrees of freedom belonging to a fully realistic Hamiltonian are integrated out, to yield what is known as a Landau–Ginzburg–Wilson (LGW) 'model', defined as a functional of a fluctuating three-dimensional density profile. This aspect is not in doubt at a qualitative level (for short-ranged models); instead, the problem lies with the fact that the LGW functional is too complicated to deal with. Physicists sought to transform to a lower level of description, identical to the

binding potential picture of Frumkin–Derjaguin apart from the addition of a standard term to account for capillary wave fluctuations. Added together, these two simplified functionals of the film thickness define the interface Hamiltonian. One attempt to identify the error in the critical wetting interface Hamiltonian was based on renormalizing the prefactor of the capillary wave term [10], but this created even worse problems by denying the very existence of critical wetting. Now the wetting equation appears to have come to the rescue, so what is the important physics contained in the wetting equation?

The qualitatively different physics arises because the binding potential is now non-local. This property is represented in the wetting equation by the thick lines joining filled circles placed at either side of the adsorbed film. Each filled circle denotes that one must integrate over the entire surface on which it lies. The higher-order terms involve increasing numbers of zig-zag lines and if summed up would generate the hard-wall repulsion of the underlying substrate. However, if this aspect is put in by hand one should be able to simply use the two leading-order terms depicted, to describe critical wetting correctly. The assertion of Parry *et al* is that the previous problems have arisen because when reducing the LGW functional to an interface Hamiltonian one must be careful to keep the non-local nature of the binding potential. The problems with [10] are now avoided and the difficulties with simulation [9] are attributed to a crossover regime requiring significantly larger system sizes. The beautifully simple structure of the non-local binding potential is either an added bonus or a sign that the authors have to be correct, depending on your philosophical approach to physics. The pictorial representation of the wetting equation is natural to physicists because they have often preferred to view wetting transitions in terms of fluid-mediated interactions across the film, as expressed in language such as *interface delocalization transitions*. The black lines joining the filled circles represent this interaction between the surfaces. For a standard LGW model this turns out to be the well-known Yukawa correlation function of the *bulk* phase, a very general fluid mediated interaction for short-ranged models that was already known to van der Waals and rediscovered in various guises ever since [11]. Hence, the diagrammatic expansion is amenable to analytic evaluation for basic models. Although the diagrammatic expansion is formally exact, one might have anticipated that the important physical interaction is actually long-wavelength capillary wave fluctuations leading to collisions between the interfaces, rather than straight tubes. Interestingly, though, simulations of Ising models typically yield tube-like fluctuations, essentially as drawn in the wetting equation, so one could quite physically interpret the higher-order diagrams in terms of reflections of these tubes at the surfaces. In fact, this physical picture bears a strong resemblance to the shooting algorithm of transition path sampling, developed by Chandler and co-workers [12]. Also of relevance here is the fact that wetting transitions are strongly constrained by an extensive body of exact results or sum rules [13]. Some of these sum rules display an identical structure; i.e. they equate statistical-thermodynamic quantities to surface integrals over pair distribution functions with coordinates lying on opposite sides of the film. One such example is the sum rule for the derivative of the disjoining pressure of a fluid adsorbed in a planar pore, with respect to the pore width. Another aspect of the wetting equation worth stressing is the remarkably general nature of the equation. Its pictorial representation already indicates that one can use it in any circumstance in which an incipient phase β is appearing at an interface between a spectator phase γ and the bulk phase α. Furthermore, the coefficients of the diagrams are independent of geometry, except perhaps from the restriction that interface configurations do not contain overhangs. In fact, Parry *et al* anticipate that important results will soon follow for adsorption at non-planar and structured substrates. Some of these situations will be far more easy to study experimentally [14] than critical wetting, and yet will be directly related mathematically through the wetting equation. Experimental nanoscience may therefore have some important contributions to make to fundamental interfacial physics.

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