Wetting on non-planar and heterogeneous substrates

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Abstract. We report results of wetting on non-planar and heterogeneous surfaces calculated from an effective interfacial Hamiltonian model. The lack of translational invariance along the substrate induces a series of structural changes of the interface such as unbending and a number of non-thermodynamic singularities and can modify the location of the wetting transition. We show that the order of the wetting transition in the planar homogeneous system strongly affects the behaviour of the non-planar and heterogeneous surfaces.

1. Introduction

The interaction of fluids with solid substrates is attracting new interest as experimental methods allow increasing control over the shape and chemical composition of solid surfaces [1]. The theoretical description of fluid adsorption necessarily involves breaking the fluid translational invariance due to the presence of a wall, representing the solid substrate. Due to the intrinsic difficulty of this, theoretical studies have concentrated mainly on planar and homogeneous substrates producing a deep understanding of the rich behaviour of those systems [2]. However, non-planar and chemically heterogeneous surfaces exhibit adsorption properties which differ from those of planar and homogeneous systems and require further study [3]. Here, we use an effective interfacial Hamiltonian model to examine the wetting properties of a corrugated substrate, and a planar substrate with a stripe of a material that is chemically different.

2. The model

For simplicity, we only break the symmetry along one of the directions of the wall and, therefore, one coordinate (x say) will describe any point on the surface. The free energy of an interfacial configuration is given by the standard effective Hamiltonian [2]

$$H[\ell] = \int \mathrm{d}x \left[\frac{\Sigma}{2} \left(\frac{\mathrm{d}\ell}{\mathrm{d}x} \right)^2 + \mathcal{W}(\ell; x) \right] \tag{1}$$

where $\ell(x)$ represents the height of the fluid interface, Σ is the interface stiffness and $\mathcal{W}(\ell; x)$ accounts for the (effective) interaction with the substrate. We can now anticipate that the new phenomena occurring for non-planar or heterogeneous systems take place due to the competition of the two terms in the Hamiltonian; whilst the first term forces the interface to minimize its extent, the second is constrained by the intermolecular forces between the particles. The character of these interactions is qualitatively captured by the following expression for the potential $\mathcal{W}$:

$$\mathcal{W}(\ell; x) = W_\gamma(\ell - \psi(x)) \qquad \text{for } x \in \Lambda_\gamma \tag{2}$$

where $\psi(x)$ is the height of the wall at the point x and W_γ is the effective binding potential of a fluid interface on a *planar* and *homogeneous* substrate (which extends along Λ_γ). A planar wall corresponds to $\psi(x) = 0$ whilst, for a chemically homogeneous wall, there is only one region Λ and consequently only one binding potential W. The approximation (2) is appropriate for walls whose non-planarity is not too severe (see later for further quantification).

Although effective binding potentials are well described in the literature [2], we want to outline some of their features for a subsequent discussion. In figure 1, two different types are plotted for different values of the temperature (at bulk liquid–vapour coexistence). For second-order wetting, (a), the potential has a single minimum, located at $\ell = \ell_\pi$, for $T < T_W$. The coverage of the planar system, ℓ_π, diverges at the wetting temperature T_W. In contrast, for first-order wetting, (b), the potential shows a minimum at $\ell = \ell_\pi$ and a maximum, the activation barrier, at $\ell = \ell_\star$. In this second case, the thickness of the adsorbed layer remains finite at the wetting temperature, coexisting with an infinitely thick layer, $W(\ell_\pi^W) = W(\infty) = 0$ (see figure 1). Furthermore, for a range of temperatures $T_W < T < T_S$, where T_S is the spinodal temperature, the first-order effective potential still shows a minimum which represents a thin layer metastable with respect to the infinitely thick one, $W(\ell_\pi) > W(\infty) = 0$.
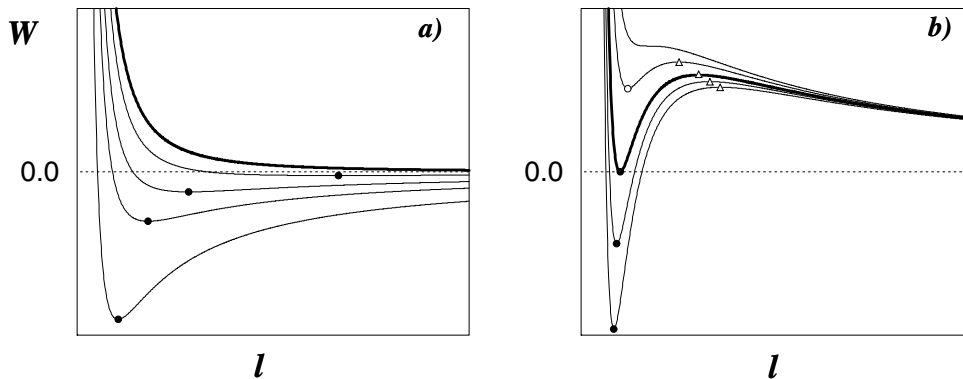

Figure 1. Effective binding potentials for (a) second-order and (b) first-order wetting transitions in planar homogeneous systems. The minimum of the potential ($\bullet$) represents the equilibrium configuration. At the wetting temperature (thick line), that configuration has zero energy. Note the activation barrier ($\triangle$) and the existence of metastable states ($\bigcirc$) in the first-order potential.

3. Results

We restrict ourselves to a mean-field description of the system and, to calculate the equilibrium profile, we minimize the Hamiltonian (1), which is equivalent to solving the Euler–Lagrange equation:

$$\frac{d^2\ell}{dx^2} = W_\gamma'(\ell - \psi(x)) \qquad \text{for } x \in \Lambda_\gamma. \tag{3}$$

The results depend sensitively on the character of the wetting transition on the planar substrate and, therefore, we present some representative results for non-planar surfaces according to the order of the wetting transition on the planar substrate.

3.1. Non-planar walls

3.1.1. Second-order wetting binding potentials. First, we consider a homogeneous corrugated wall, with $\psi(x) = a\cos(2\pi x/L)$, where a represents the corrugation amplitude and L the period of the corrugation. We assume that the wavelength $L \gg a$ so that the corrugation is relatively weak. In this limit, scaling properties emerge which are correctly captured by the assumption of a vertical height interaction in the effective binding potential (see (2)). Details of this problem for a second-order binding potential have been given elsewhere [4] but we report the results here for the sake of comparison. In this case, the interface undergoes a first-order *unbending* transition at a temperature T *below* the wetting transition T_W provided the corrugation exceeds a certain threshold (see figure 2 (left)). At low temperatures, the interface closely follows the corrugations, so the interface and wall have a similar shape. Above the transition temperature, however, the interface is significantly flatter (unbent). The difference between these coexisting states reduces with the corrugation and it disappears at a critical point ($\bullet$). As pointed out, this transition takes place due to the competition of the two terms of the Hamiltonian (1). Whilst the system minimizes the functional at low temperatures by following the shape of the surface (with a large negative contribution of the second term of the Hamiltonian), the unbent configuration reduces the energy by decreasing the (positive) contribution of the first term. Interestingly, the period of the corrugation does not change the structure of the surface phase diagram but acts as a scaling parameter [4]. Within this model, neither the location (at $T = T_W$) nor the character of the wetting (unbinding) transition is modified.
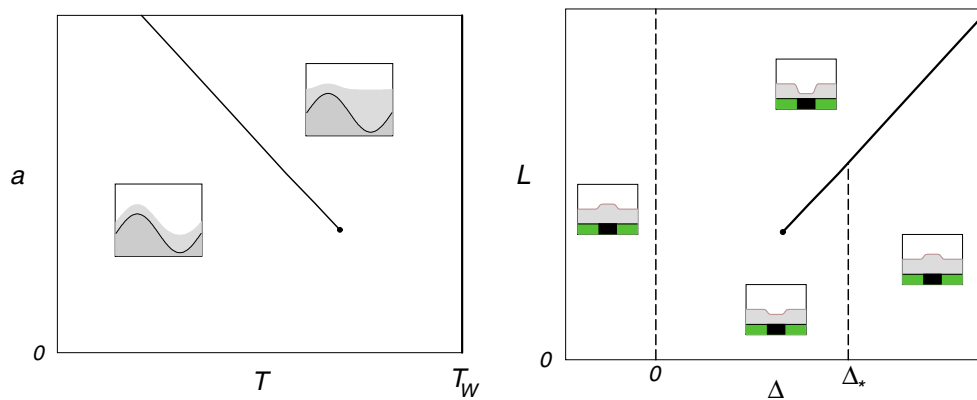

Figure 2. A schematic phase diagram of the structure of an adsorbed layer of liquid on a homogeneous corrugated wall (left) and on a planar substrate with a stripe of a material that is chemically different (right). Bold lines represent expected phase transitions. For the heterogeneous wall, the dashed lines illustrate non-thermodynamic singularities where the interface shows a qualitative change of shape in which a trough becomes a crest and vice versa.

3.1.2. First-order wetting binding potentials. If the binding potential is first order, the surface phase diagram is richer and the effect of the corrugation is triple. First, an *unbending* transition can also take place as the above-mentioned competition between the two terms of the Hamiltonian is still present. However, first-order effective potentials have an activation barrier which allows the interface to adopt a variety of shapes to minimize the energy. These shapes can

be characterized by the number of minima of the interface $\ell(x)$ and the change of this number gives rise to a number of non-thermodynamic singularities. These singularities have been studied for a corrugated wall in a related system (in the context of confinement) [5]. Figure 3 (left) shows schematically the possible configurations of the interface. Note that, in this case, the interface shape can deviate significantly from the wall shape and adopt configurations which are not found with a second-order effective potential. The third effect of the corrugation on this type of surface comes from the fact that the energy of the unbound state (i.e., the wet configuration, $\ell = \infty$) is always zero. Therefore, the wettability is favoured by any positive contribution to the Hamiltonian and the wetting temperature is reduced. This effect is absent in the second-order wetting potential because the interface always finds a configuration whose positive contribution (first term of the Hamiltonian) is lower than the negative (second term) and the balance remains negative for any corrugation. The presence of the activation barrier makes this compromise impossible and the wetting transition takes place at a *lower* temperature in the corrugated system than in the planar one, although the nature of the transition is still first order. Figure 3 (right) shows a typical variation of the wetting temperature as a function of the corrugation amplitude (in units of that of the planar system). The periodicity of the corrugation, as in the previous case, only acts as a scaling parameter (this is a property of the Hamiltonian (1)). Note that the temperature drops as a function of the corrugation amplitude, a, but it presents a minima for $a \sim 1.5$ (in units of liquid bulk correlation length). For larger values of a, the tendency is inverted and the wetting temperature increases slightly and tends to a certain constant value. This behaviour can be traced back to the varying shape that the interface can adopt to minimize the energy [6]. As a result of this non-monotonic variation of the wetting temperature with corrugation, the shape of the interface at the wetting transition itself shows similar sensitivity [6].
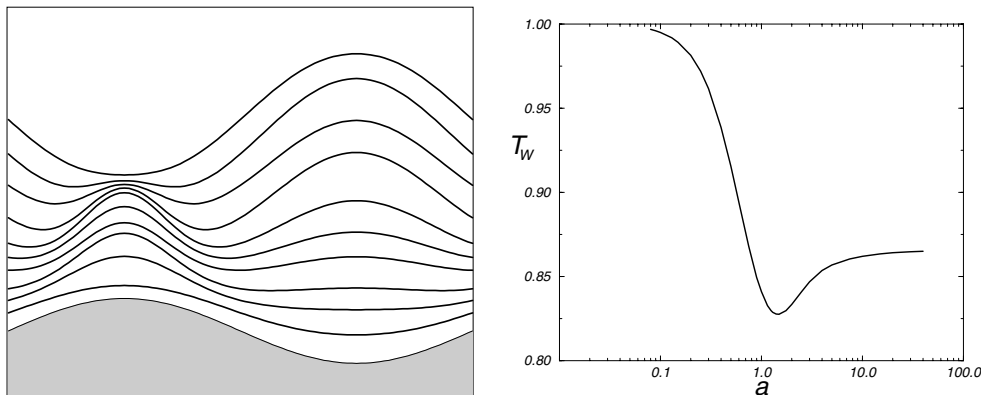

Figure 3. The effect of corrugation on the wetting properties of an interface which (in the planar case) undergoes a first-order wetting transition: the left-hand diagram illustrates schematically how the interface moves away from the wall, on increasing the temperature (at fixed corrugation), and adopts a number of distinct shapes which differ from that of the wall (lowest line). The wetting temperature is also reduced by corrugation (right). See the text for details.

3.2. Heterogeneous walls

We now focus our attention on (planar) heterogeneous walls. As mentioned, we study an infinite homogeneous and planar substrate (called 2) with a stripe of constant width L of a chemically different material (called 1), represented by two different effective potentials. This geometry

allows us to concentrate just on the structural changes of the interface due to the heterogeneity, since the infinite substrate 2 governs the wetting behaviour of the whole system [7]. The influence of heterogeneity on the wetting properties of a substrate (for instance, due to a periodic array of stripes) is a more complex problem which requires the prior understanding of this simpler system. Without loss of generality, we can consider that homogeneous substrates 1 and 2 undergo first- and second-order wetting transitions respectively. The structure of the phase diagram of this system does not depend on the order of the wetting transition of the infinite system. In fact it depends mainly on two quantities only: the stripe width, L, and the *mismatch* between the effective potentials of the two substrates (at fixed temperature), i.e., the difference between the thickness of the adsorbed layers in the infinitely homogeneous systems, $\Delta \equiv \ell_\pi^{(2)} - \ell_\pi^{(1)}$. Figure 2 (right) shows a schematic phase diagram as a function of these variables. As expected, the interface is flat if the mismatch is zero ($\Delta = 0$, — — —). For small values of Δ, positive or negative, the thickness of the interface above the heterogeneity roughly behaves as in the infinite system. For narrow stripes ($L \sim 0$), however, we found that the interface also flattens when Δ reaches the value $\Delta_\star \equiv \ell_\star^{(1)} - \ell_\pi^{(1)}$ (— — —). At that point, the minimum of potential 2 matches the *maximum* of potential 1, $\ell_\pi^{(2)} = \ell_\star^{(1)}$. Surprisingly, the flat configuration is stable even though it would be unstable for an infinite system. Nevertheless, if the stripe width exceeds a certain value, the flat configuration becomes metastable with respect to a non-flat one. This is due to the crossing of a line of generalized *unbending* transitions (——) which arises from the ubiquitous balance between the two terms in Hamiltonian (1). This line ends at a critical point (Δ_c, L_c) (●). Note that the configurations along the coexistence line correspond to those of an unbending transition as mentioned above if $\Delta_c < \Delta < \Delta_\star$ but, for $\Delta > \Delta_\star$, the coexisting states are interfaces bent in opposite directions. This second part of the line has its origin in the existence of an activation barrier of the effective potential of the heterogeneity. At this point, we note that the structure of the phase diagram when the stripe effective potential is second order (no activation barrier) can be intuitively obtained from that in figure 2 (right) by considering $\Delta_\star \to \infty$, thus recovering a usual unbending transition.

As a last remark, we want to discuss the twofold role of the temperature in this description. On the one hand, the phase diagram deforms (although the general features are conserved). On the other, the value of Δ varies. We can anticipate that from these two competing tendencies the phase diagram can show a complex behaviour including re-entrant phases [6].

Acknowledgment

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