Wetting at Non-Planar Substrates: Unbending & Unbinding

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Abstract

We consider fluid wetting on a corrugated substrate using effective interfacial Hamiltonian theory and show that breaking the translational invariance along the wall can induce an unbending phase transition in addition to unbinding. Both first order and second order unbending transitions can occur at and out of coexistence. Results for systems with short-ranged and long-ranged forces establish that the unbending critical point is characterised by hyperuniversal scaling behaviour. We show that, at bulk coexistence, the adsorption at the unbending critical point is a universal multiple of the adsorption for the correspondent planar system.

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Recently, the subject of fluid adsorption and wetting on structured (non-planar) and heterogeneous substrates has began to receive considerable attention [1]. This work is not only a natural extension of studies of wetting on idealised planar surfaces [2] but it is also of more fundamental interest since the broken translational invariance along the wall necessarily leads to competition between surface tension and direct molecular effects. Thus, we may anticipate that new interesting phenomena (phase transitions, scaling, universality) will emerge which do not occur for planar systems. In this letter, we report results of extensive numerical calculations, supported by approximate non-perturbative analysis and scaling theory, of wetting on a periodic (corrugated) substrate. These reveal that novel first and second order transitions can take place, directly related to the inhomogeneity along the wall. For long-ranged forces, the phase transition, referred as unbending, only occurs for sufficiently large wall corrugations (beyond the range of previously employed perturbative methods [3]), dependent on the wave vector of the corrugation. In contrast, for short-ranged forces, the critical threshold is wave vector independent and rather weak. There are three aspects of our work that we emphasize in particular. Firstly, the unbending transition precedes a wetting (unbinding) transition occurring at a higher temperature (and at bulk two-phase coexistence). For second order unbinding transitions, on which we concentrate, the location of the wetting transition is unaffected by wall corrugation. Secondly, the location of the unbending line and critical point, as well as the interface structure, only depend on the amplitude and period of the wall corrugation function through hyperuniversal scaling variables analogous to that encountered in the theory of finite-size effects at bulk critical points [4]. As a consequence, the unbending critical point is associated with non-trivial universal amplitude ratios which relate the adsorptions in the non-planar and correspondent planar system. Finally, unbending is directly related to nonlinear bifurcation phenomena occurring in dynamical systems, a subject whose mathematical aspects continue to attract attention [5].

To begin, we describe the results of a specific mean-field (MF) model of unbending and unbinding which also serves to illustrate important scaling properties which we shall later
put in a more general context. For simplicity, we assume that the wall has a corrugated sinusoidal shape \( \psi(x) = a \cos(qx) \), which breaks the translational invariance in one direction only. Following the work of earlier authors [1,3], we take as our starting point the (reduced) standard effective interfacial model

\[
H[\ell] = \frac{1}{L} \int_L dx \left[ \frac{\Sigma}{2} \left( \frac{\partial \ell}{\partial x} \right)^2 + W(\ell - \psi) \right]
\]

(1)

restricted to the space of periodic solutions which is sufficient for our description of equilibrium phenomena. Here, \( \Sigma \) is the surface stiffness, \( W \) is the binding potential and \( \ell(x) \) is the collective coordinate measuring the height of the interface relative to the mean position of the wall whose period \( L \) satisfies \( q = 2\pi/L \). We also restrict ourselves to a MF description in which the equilibrium profiles \( \ell_\nu \) are obtained by minimising Eq. (1). The importance of fluctuation effects will be discussed later in the context of scaling theory [6]. We start by considering systems with short-ranged forces at bulk two-phase coexistence and write [2]

\[
W(\ell) = -\Delta T e^{-\ell} + \beta e^{-2\ell};
\]

(2)

so that both the film thickness \( \ell \) and corrugation amplitude \( a \) are measured in units of the bulk correlation length. With this potential (and positive \( \beta \)) the planar system undergoes a second-order unbinding transition at \( \Delta T \equiv T_w - T = 0 \) such that the MF interface thickness and the transverse correlation length diverge at that critical point as \( \ell_\pi \sim -\log(\Delta T) \) and \( \xi_\parallel \sim \Delta T^{-1} \), corresponding to standard wetting critical exponents \( \beta_S = 0 \) (log) and \( \nu_\parallel = 1 \) respectively [2].

For \( a \neq 0 \), the MF configuration(s) are the solutions of the Euler-Lagrange equation

\[
\Sigma \ell''_\nu(x) = W'(\ell_\nu - \psi),
\]

(3)

solved subject to periodic boundary conditions and where the prime denotes differentiation w.r.t. the argument. This deceptively simple looking nonlinear equation can show multiple solutions and bifurcations corresponding to different possible phases for the equilibrium interface configuration. Whilst a full analytic solution is not possible, it is straightforward
to show that the solutions exhibit an important scaling property which allows us to collapse results obtained for different periods $L=2\pi/q$ onto a universal surface phase diagram. To see this, we introduce the new variables $\eta \equiv \ell - \psi - \ell \pi$ and $t \equiv q x$ so that (3) becomes

$$\ddot{\eta} = \Delta \tilde{T}^2 (e^{-\eta} - e^{-2\eta}) + a \cos t,$$

which is the equation of a forced inverted nonlinear oscillator. Here the overdot corresponds to differentiation w.r.t. $t$ whilst the temperature, stiffness and substrate periodicity are combined in the rescaled temperature variable $\Delta \tilde{T} \equiv \Delta T / q \sqrt{2 \beta \Sigma}$. Consequently, any new phase transition induced by the corrugation amplitude $a$ is not affected by the value of the wall periodicity $q$ which only acts to rescale the temperature deviation from $T_w$. In Fig. 1, we show plots of the mean interface thickness $\ell_0$, defined as the average $\langle \ell(x) \rangle_x$, as a function of $\Delta \tilde{T}$ for various $a$, obtained by numerically minimising Eq. (1). It can be seen that, whilst the location of the unbinding transition is unaffected by the wall corrugation, a new phase transition occurs for corrugation amplitudes $a > a_c \approx 2.914$ and $\Delta \tilde{T} > \Delta \tilde{T}_c \approx 2.12$.

The surface phase diagram is shown in Fig. 2 and exhibits the termination of the first-order phase boundary at an unbending critical point as well as representative shapes of the coexisting interfacial phases at the transition. Again, we emphasize the universal value of the critical corrugation amplitudes $a_c$ (which is independent of $q$) whilst the temperature shift from $T_w$ satisfies $\Delta T_c(q) \propto q$.

Before we discuss further scaling properties that emerge from the exact minimization of (1), we describe an approximate treatment of the model which recovers the unbending transition and yields relatively good values for the critical point. To this end, we suppose that the interface configuration, and consequently the free-energy, can be parametrized by two variables by restricting ourselves to profiles of the form $\ell(x) \approx \ell_0 + (1 - \epsilon) \psi(x)$. Thus, $\ell_0$ is the average interface displacement whilst $\epsilon$ measures the extent of interfacial corrugation. The bounding value $\epsilon = 1$ corresponds to a completely flat configuration whereas $\epsilon = 0$ refers to a configuration with identical corrugation to the wall. Substituting this parametrized profile shape into the Hamiltonian, Eq. (1), and minimising w.r.t. $\ell_0$, we are led to the
following approximate expression for the dependence of the free-energy \( F \) on the interface corrugation parameter \( \epsilon \),

\[
\frac{2}{\Sigma q^2} F(\epsilon) = \frac{a^2}{2} (1 - \epsilon)^2 - \Delta \tilde{T} \frac{I_0'(\epsilon a)}{I_0(2\epsilon a)}
\]  

(5)

where \( I_0 \) denotes the modified Bessel function of zero-order. The two terms on the r.h.s. represent the competition between the surface tension and binding potential effects which are each minimized separately by \( \epsilon = 1 \) (flat interface) and \( \epsilon = 0 \) (corrugated interface) respectively. Plots of \( F(\epsilon) \) for various \( a \) moving along the unbending line are shown in Fig. 3 and illustrate the possibility of phase coexistence between bent and rather flat states for sufficiently large \( a \). The locus of the unbending transition in the surface phase diagram obtained in this approximate manner is shown as the dashed line in Fig. 2 and agrees reasonably well with the exact numerical result. Note that the solutions will only depend on \( \Delta \tilde{T} \) and \( a \), as in the exact solution. This method also has a distinct advantage over previously adopted perturbative treatments [3] (involving an expansion about the planar system) which, whilst not without merit, cannot handle the occurrence of distinct branches (i.e. a bifurcation) in the free-energy [4]. We also note that the location of the unbending critical point within this approximate non-perturbative method can be determined with an elegant graphical construction [8].

We consider now the same phenomena for systems with long-ranged (dispersion) forces. For this case, we use the binding potential [2]

\[
W(\ell) = -\frac{\Delta T}{\ell^2} + \frac{\beta}{\ell^3}
\]

(6)

which again describes a continuous unbinding transition in the planar system as \( T \to T_w \) [2]. For this system, the film thickness and transverse correlation length diverge as \( \ell_\pi \sim \Delta T^{-1} \) and \( \xi_\parallel \sim \Delta T^{-5/2} \), corresponding to critical exponents \( \beta_5 = 1 \) and \( \nu_\parallel = 5/2 \) respectively [2].

Turning to the non-planar geometry, we make the judicial change of variables \( \eta \equiv (\ell - \psi)/\ell_\pi \) and \( t \equiv q x \) which again reduces the Euler-Lagrange equation (3) to that of a forced inverted nonlinear oscillator:
\[ \dot{\eta} = \Delta \tilde{T}^2 \left( \frac{1}{\eta^3} - \frac{1}{\eta^1} \right) + \tilde{a} \cos t. \]  

(7)

Once more, the two scaling variables \( \Delta \tilde{T} \equiv 2 \Delta T / \Sigma q^2 \xi^4 \) and \( \tilde{a} \equiv a / \ell_\pi \) determine the multiplicity of solutions and hence the surface phase diagram.

Plots of the mean interface position \( \ell_0 \) vs. \( \Delta \tilde{T} \) for different \( a \) obtained from the numerical minimization of Eq. (4) are, in essence, the same as that shown in Fig. 1 for short-ranged forces and, therefore, are not presented here. The numerical values for the scaled variables at the unbending critical point are \( \tilde{a}_c \approx 2.061 \) and \( \Delta \tilde{T} \approx 8.66 \) which imply a wave-vector dependence \( a_c(q) \propto q^{-2/5} \) and \( \Delta T_c(q) \propto q^{2/5} \) for the critical corrugation amplitude and temperature shift, respectively.

The MF results described above suggest that the location of the unbending critical point can be understood using scaling theory. To this end, we suppose that, in the planar system, the excess free-energy per unit area contains a singular contribution \( F_\pi^{\text{sing}} \sim \Delta T^{2-\alpha_S} \) (with \( \alpha_S = 0 \) and \( -1 \) for the model potential (2) and (6), respectively [2]). In the non-planar system, we conjecture that the corresponding quantity is described by the scaling function

\[ \Delta F_\nu^{\text{sing}} = \Delta T^{2-\alpha_S} \ W \left( a \Delta T^{\beta_S}, q \Delta T^{-\nu_\parallel} \right) \]

(8)

where \( W(x,y) \) is the scaling function whose variables correspond to the hyperuniversal combination of length-scales \( a / \ell_\pi \) and \( q \xi_\parallel \) [4]. Since the singularity in the free-energy at the unbending critical point occurs for \( \Delta T \neq 0 \), we are immediately led to the prediction for the critical corrugation amplitude and temperature

\[ a_c(q) \propto q^{-\beta_S/\nu_\parallel} ; \quad \Delta T_c(q) \propto q^{1/\nu_\parallel} \]

(9)

consistent with our explicit results, provided that for short-ranged forces we interpret \( \beta_S / \nu_\parallel \) as zero and not logarithmic. We believe that the existence of a finite critical threshold even in the \( q \to 0 \) limit is a surprising finding of our work. These scaling ideas can be extended to the interface structure at the unbending critical point where the hyperuniversal nature of the scaling variables \( x \) and \( y \) play an important role. Here, we concentrate on systems with
long-ranged forces for which $\beta_S \neq 0$ where the definition of universal critical amplitudes is more straightforward. We suppose that, in the vicinity of the unbending critical point, the mean interface thickness in the non-planar system is described by the scaling law

$$\ell_0 = \ell_\pi \Lambda \left( \frac{a}{\ell_\pi}, q \xi_\parallel \right)$$  \hspace{1cm} (10)

where $\Lambda(x, y)$ is a universal scaling function. As a consequence, precisely at the unbending critical point, the mean film thickness $\ell_0^c$ is a universal multiple of the corresponding planar adsorption (at the same temperature). Thus, we define the universal critical amplitude ratio

$$R \equiv \frac{\ell_0^c}{\ell_\pi} \text{ at } a = a_c(q), \Delta T = \Delta T_c(q)$$ \hspace{1cm} (11)

which we have numerically determined as $R \approx 1.321$ (independent of $q$) calculated using our MF theory with the binding potential (6). Note that the definition of $R$ is equivalent to the ratio of adsorptions in the non-planar and planar systems. Other universal critical amplitudes can also be defined. For example, at the unbinding critical point, the shift in the mean interface height relative to the planar system satisfies

$$R' \equiv \frac{\ell_0^c - \ell_\pi(\Delta T_c)}{a_c(q)}$$ \hspace{1cm} (12)

with $R'$ also independent of $q$. The advantage of this definition is that it is also appropriate for systems in which $\beta_S = 0$ (log). We have numerically determined that $R' = 0.640$ and 0.156 for the potentials (2) and (6) respectively.

To finish our article, we make two pertinent remarks. Firstly, we have established that for $a > a_c$ the first order unbending transition also occurs out of the two-phase coexistence for sufficiently small bulk ordering field $\bar{h}$. The result of our numerical calculations for short-ranged forces including an additional $\bar{h}\ell$ term in the binding potential are shown in Fig. 4. The existence of an unbending line extending out of bulk two-phase coexistence is analogous to prewetting at (planar) first-order phase transitions. Secondly, we have established that unbending also occurs for first order wetting transitions in non-planar systems although the scaling behaviour is less obvious. A section of the surface phase diagram in the $(T, \bar{h})$ plane
thus shows both prewetting and unbending lines. While this first appears similar to prefilling on a wedge, there are profound and subtle differences between unbending and prefilling relating to the order of these transitions and their relation with wetting. In summary, we have shown that for non-planar systems an additional interfacial phase transition is associated with unbinding. The critical point of the unbending transition exhibits novel scaling and observable universal critical properties. Further work should concentrate on more general wall shapes, calculations with more microscopic models and also aim to establish whether the values of the universal critical amplitudes presented here are substantially affected by including fluctuation effects beyond mean-field level. At present, simulation studies seem best equipped to answer this latter question although renormalization group analysis may be possible.

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[6] We anticipate that similar results to those described here will emerge from studies of improved non-local hamiltonians. For instance, C. Bauer, S. Dietrich (to be published).

[7] Predictions, based on low-order perturbation expansions of the free energy in terms of $a$ and $q$ (see [3](c)), that the second order wetting transition becomes first order for sufficiently large $a$ are not correct. Systematic inclusion of higher order terms shows that the series expansion diverges as $\Delta T \to 0$, which is indicative of a spinodal point associated with the unbending transition $\delta$.

[8] C. Rascón, A.O. Parry, A. Sartori (in preparation).
For systems with short-ranged forces, where $\beta_S = 0$, the appropriate dimensionless measure of $a$ is in units of the bulk correlation length.
FIG. 1. Film thickness $\Delta \tilde{\tau}$ vs. $\Delta \tilde{T}$ for different values of $a$ from the numerical minimization of Eq. (1). From below, $a/\sqrt{2} = 0.00, 0.50, 1.00, 1.50, 1.75, 1.90, 2.0605, 2.10, 2.15, 2.20, 2.25, 2.30$. All distances are measured in units of the bulk correlation length.
FIG. 2. Section of the surface phase diagram at bulk coexistence showing the unbending coexistence line which finishes at the critical point $\Delta \tilde{T} \approx 2.12$ and $a_c \approx 2.914$. The solid line represents the results of minimizing Eq. (1). The dashed line is the result of the variational approximate solution (see text). The vertical line $\Delta \tilde{T} = 0$ represents the second order unbinding transition. Schematic representation of the interfacial configuration on either side of the unbending line are also shown.
FIG. 3. Free Energy from the expression (5) for different values of $a$ at the transition temperatures (See Fig. 2). From above, $a = 5.0, 4.0, 3.5, 3.0, 2.75$ and $2.46866$. The last value is the critical value $a_c$ within the present approximation.
FIG. 4. Phase diagram of the unbending transition in a system of short ranged forces for different values of $a/\sqrt{2} = 2.5, 3.0, 4.0$ and 5.0, from numerical minimization of Eq. (1) (continuous lines, left to right). The circle represents the unbending critical point for $a_c \approx 2.914$. The loci of critical points obtained from the approximate model is represented as a broken line. The triangle locates the critical wetting temperature.