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The influence of substrate corrugation on wetting temperature

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Received 8 December 2000

Abstract

Wetting of periodically corrugated substrates is studied in the framework of the effective interface Hamiltonian approach applied to two non-smooth substrates with different convexity properties. We observe that first-order wetting of a planar substrate induces first-order wetting of a corrugated substrate. It is accompanied by a shift of the wetting temperature. The magnitude of this shift is discussed analytically and numerically as a function of parameters characterizing the corrugation when both the period and the amplitude of the corrugation change simultaneously leading to rescaling of the substrate. Critical wetting of the planar substrate induces critical wetting of the weakly corrugated substrate with no shift of the wetting temperature.

1. Introduction

Wetting phenomena taking place on planar and chemically homogeneous substrates are nowadays rather well understood and are described in many excellent reviews [1–6]. However, such perfect substrates are rare, while those encountered in practical applications are characterized by geometrical structure and/or chemical heterogeneity. Wetting of geometrically structured substrates has been the subject of recent theoretical research [7–33]. The results are often compared with those obtained for planar substrates which serve as the natural reference point. Another important class of substrates is formed by chemically heterogeneous systems which in addition may be geometrically structured [34–40].

In this paper we concentrate exclusively on geometrically structured and chemically homogeneous substrates. An important question related to wetting of such substrates is that of finding how corrugation affects wetting. There are two aspects of this question: the first is concerned with the order of the wetting transition on the corrugated substrate as compared to the planar substrate case; the second is related to the possible shift of the wetting temperature induced by corrugation. These questions have been investigated for smooth substrates often assumed to be translationally invariant in one direction, say the y -direction, and periodically corrugated in the x -direction. The two parameters that characterize their shapes were taken to be the amplitude and the period of corrugation. One of the interesting conclusions [20] obtained for such substrates is that for large enough corrugation amplitudes the continuous wetting transition on a planar substrate turns into first-order wetting on a corrugated substrate.

It is additionally accompanied by a shift of the wetting temperature. On the other hand, the first-order wetting on the planar substrate remained first order on a corrugated substrate and it was also accompanied by a shift of the wetting temperature.

In this paper we consider two different periodically corrugated substrates which are not smooth. They are described by functions parametrized by the period of the substrate and by the magnitude of the jump of the tangent to the substrate at certain points along the substrate. This system is analysed in such a way that the increase of the corrugation amplitude is necessarily accompanied by an increase of the length of the segment from which the periodic substrate is composed. This amounts to enlarging the single unit of the periodic system in both the x - and z -directions and we are interested in seeing how this way of modifying the substrate influences its wetting properties. This way of rescaling the substrate is certainly different from that of increasing the corrugation amplitude at fixed periodicity.

Our approach is of the mean-field type and is based on the effective interface Hamiltonian [41–43] which is known to successfully describe many aspects of wetting. On the other hand, the mean-field approach does not take into account the fluctuation effects which may influence the wetting scenario on planar substrates leading from critical to fluctuation-induced first-order wetting for 3D systems with short-range forces [41, 44]. This, however, requires taking into account the position-dependent interfacial stiffness coefficient which is one of the essential ingredients of renormalization group calculations. These fluctuation-related aspects of wetting are absent in our analysis.

The paper is organized as follows. In section 2 we specify the system, describe the substrate shapes and introduce the effective interface Hamiltonian. Mean-field analyses of wetting which employ appropriate parametrization of interfacial profiles are formulated. This leads to a system of equations for parameters characterizing the interfacial profiles and for the corresponding values of the free energy. In section 3 we discuss these equations, both numerically and analytically. The phase diagram is constructed. Special emphasis is put on the sign and magnitude of the shift of the wetting temperature with respect to the planar substrate case. Section 4 contains a summary of the results.

2. Description of the system

We consider substrates which are translationally invariant in the y -direction and periodically corrugated in the x -direction with period $2a$. Correspondingly, only periodic interfacial configurations with the periodicity of the substrate are taken into account and it suffices to concentrate on a single segment of the substrate, say $x \in [-a, a]$. Our discussion is limited to two special kinds of such periodic substrates which are described by the functions $z = b_1(x) = |x| \cot \varphi - x^2 \cot \varphi / 2a$ and $z = b_2(x) = x^2 \cot \varphi / 2a$, respectively; see figure 1. Each of these functions is parametrized by two parameters: the size of the segment $2a$, and the angle φ which is related to the non-analyticity of substrate's shape either at the segment's centre (for the first substrate) or at its end-points (for the second substrate). More precisely, $\Delta b_1 = b_1(0^+) - b_1(0^-) = 2 \cot \varphi$ and $\Delta b_2 = b_2(a^+) - b_2(a^-) = -2 \cot \varphi$. Note that the parameter $\cot \varphi$ characterizes also the magnitude of the average inclination of the substrate over half of the segment. For $\cot \varphi \rightarrow 0$ one recovers in both cases the planar substrate limit. In the following analysis we consider substrates whose shapes do not depart too much from the planar configuration, i.e. we consider $\cot \varphi \ll 1$. This restriction excludes the possibility of taking the limit of large corrugation amplitude at fixed periodicity considered previously in the literature [20].

The two substrates differ in their convexity properties and we would like to see how these geometric properties influence wetting. The thermodynamic conditions of the system

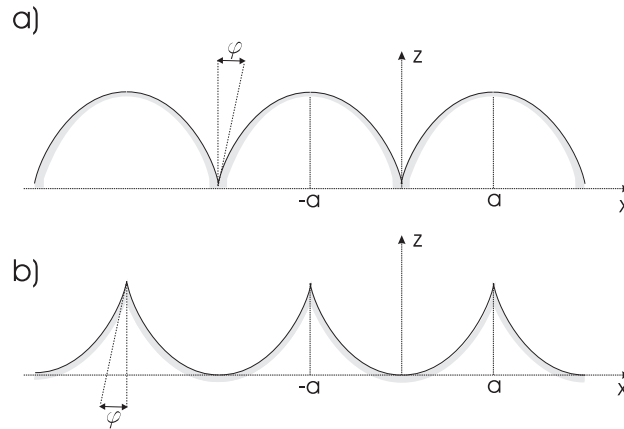


Figure 1. A schematic plot of the substrate shapes considered in this paper. The length of the periodically repeated segment is $2a$. The parameter $\cot \varphi$ characterizes the discontinuity of the tangent to the substrate at $x = 0$ for the b_1 -substrate (a) and at $x = \pm a$ for the b_2 -substrate (b).

are chosen along the coexistence line of two bulk phases denoted as α and β such that far away from the substrate the system is in phase α while a layer of quasi- β -phase is adsorbed on the substrate. The α - β interface is located at $z = f(x)$ and its distance from the substrate is denoted by $l(x) = f(x) - b(x)$. At this stage of the analysis the cases $b = b_1$ and $b = b_2$ do not need to be considered separately and the substrate shape is denoted just by $b(x)$. One wants to know how the position of the interface depends on temperature, and specifically one wants to locate the temperature at which the interface detaches from the substrate, i.e. the wetting temperature of the corrugated substrate.

Our analysis is based on the effective interface Hamiltonian

$$\mathcal{H}[f] = \int_{-a}^a dx \left\{ \frac{\sigma_{\alpha\beta}}{2} \left(\frac{df(x)}{dx} \right)^2 + \omega(l(x)) \right\} \quad (1)$$

where $\sigma_{\alpha\beta}$ denotes the α - β interfacial tension and $\omega(l)$ is the effective interface potential. More precisely, the effective Hamiltonian in equation (1) describes the relative cost in free energy of having the interface at position $z = f(x)$ compared to the situation in which the interface is removed infinitely far away from the substrate, i.e. $\mathcal{H}[f = \infty] = 0$. The effective potential $\omega(l)$ in (1) describes the interaction between the α - β interface and the substrate and is taken to be of the same form as for the planar substrate case. Note that the range of applicability of the above Hamiltonian is limited to small inclinations of the substrate with respect to the reference plane, i.e. for $\cot \varphi \ll 1$. Otherwise it would require modifications. One of them would amount to replacing the effective potential $\omega(l)$ by $\sqrt{[1 + b'(x)^2]} \omega(l)$. The constraint $\cot \varphi \ll 1$ which reflects the range of applicability of the description based on the effective Hamiltonian in equation (1) also limits the possible types of rescaling of the substrate mentioned before.

The equilibrium configuration \bar{f} of the interface minimizes $\mathcal{H}[f]$ and is obtained as the solution of the equation

$$\sigma_{\alpha\beta} \frac{d^2 \bar{f}}{dx^2} = \omega'(\bar{l}) \quad (2)$$

with the boundary conditions $\bar{f}'(0) = \bar{f}'(a) = 0$. For each substrate analysed, equation (2)

can be rewritten in the following form:

$$\sigma_{\alpha\beta} \frac{d^2 \bar{l}}{dx^2} = \tilde{\omega}(\bar{l}) \quad (3)$$

where

$$\tilde{\omega}(l) = \omega(l) \pm l \sigma_{\alpha\beta} \cot \varphi / a. \quad (4)$$

The upper sign corresponds to substrate b_1 and the lower sign corresponds to substrate b_2 . In this way the structure of the substrate is encoded in the modified effective potential $\tilde{\omega}(l)$. In equation (3) the modified effective potential $\tilde{\omega}(l)$ plays the role reserved for the potential $\omega(l)$ in the case of the planar substrate. This rather simple encoding is possible only for substrate shapes described by polynomials of second order. For other substrates, equation (3) would contain x -dependent terms and its analysis would be much more complicated. Using the language of mechanics, one would then have to analyse a non-conservative system. The same difficulties are brought about by including the corrugation effects into the potential term in equation (1) as mentioned just after equation (1). Note that although the modified potential $\tilde{\omega}$ looks like that corresponding to a system which is out of bulk coexistence, this similarity is superficial and of no practical help. The corresponding boundary conditions take the form $\bar{l}'(0^+) = -\cot \varphi$, $\bar{l}'(a^-) = 0$ for the b_1 -substrate and $\bar{l}'(0^+) = 0$, $\bar{l}'(a^-) = -\cot \varphi$ for the b_2 -substrate.

Further analysis can be simplified by transforming equation (3). This has to be done separately for each substrate. Below, we sketch this transformation for the case of the b_1 -substrate while the corresponding results for the b_2 -substrate are just quoted at the end of this section.

Integrating (3) one obtains

$$\frac{\sigma_{\alpha\beta}}{2} \left[\left(\frac{d\bar{l}}{dx} \right)^2 - \left(\frac{d\bar{l}}{dx} \right)^2 \Big|_{x=0} \right] = \tilde{\omega}(\bar{l}) - \tilde{\omega}(\bar{l}_1) \quad (5)$$

where $\bar{l}_1 = \bar{l}(0)$ and $\bar{l}_2 = \bar{l}(a)$. From this equation and the corresponding boundary conditions, one concludes that

$$\tilde{\omega}(\bar{l}_1) = \tilde{\omega}(\bar{l}_2) + \frac{\sigma_{\alpha\beta}}{2} \cot^2 \varphi. \quad (6)$$

This equation has to be supplemented by the constraint

$$a = \sqrt{\frac{\sigma_{\alpha\beta}}{2}} \int_{\bar{l}_2}^{\bar{l}_1} \frac{dl}{\sqrt{\tilde{\omega}(l) - \tilde{\omega}(\bar{l}_2)}} \quad (7)$$

which reflects the periodicity of the substrate. In this way the solutions of equation (3) are parametrized with the help of two parameters \bar{l}_1 and \bar{l}_2 which fulfil equations (6), (7). Finally it is the value of the Hamiltonian in equation (1) corresponding to different solutions of equations (6), (7) which selects the equilibrium interface configuration. This Hamiltonian can be rewritten in the following form:

$$\mathcal{H}[\bar{l}] = \sqrt{8\sigma_{\alpha\beta}} \int_{\bar{l}_2}^{\bar{l}_1} dl \left[\sqrt{\tilde{\omega}(l) - \tilde{\omega}(\bar{l}_2)} - \sqrt{\frac{\sigma_{\alpha\beta}}{2}} \cot \varphi \right] + 2a\omega(\bar{l}_2) + \frac{\sigma_{\alpha\beta}}{3} a \cot^2 \varphi. \quad (8)$$

Similar analysis leads in the case of the b_2 -substrate to the following set of equations:

$$\tilde{\omega}(\bar{l}_1) = \tilde{\omega}(\bar{l}_2) - \frac{\sigma_{\alpha\beta}}{2} \cot^2 \varphi \quad (9)$$

$$a = \sqrt{\frac{\sigma_{\alpha\beta}}{2}} \int_{\bar{l}_2}^{\bar{l}_1} \frac{dl}{\sqrt{\tilde{\omega}(l) - \tilde{\omega}(\bar{l}_1)}} \quad (10)$$

$$\mathcal{H}(\bar{l}_1) = \sqrt{8\sigma_{\alpha\beta}} \int_{\bar{l}_2}^{\bar{l}_1} dl \left[\sqrt{\tilde{\omega}(l) - \tilde{\omega}(\bar{l}_1)} - \sqrt{\frac{\sigma_{\alpha\beta}}{2}} \cot \varphi \right] + 2a\omega(\bar{l}_1) + \frac{\sigma_{\alpha\beta}}{3} a \cot^2 \varphi. \quad (11)$$

Each set of equations, i.e. equations (6)–(8) or equations (9)–(11), has to be supplemented with the specific form of the effective interface potential $\omega(l)$. It corresponds either to a first-order or to a critical wetting transition on a planar substrate. Then equations (6), (7) (or equations (9), (10)) are solved and the parameters \bar{l}_1 , \bar{l}_2 are determined. Each solution corresponds to a certain interfacial configuration and the equilibrium configuration is chosen as the one with the smallest value of the free energy in equation (8) or equation (11). This procedure is then repeated for various temperatures and various values of the parameters a and $\cot \varphi$. In this way the mean-field phase diagram is constructed.

Alternatively one may analyse this problem with the help of two auxiliary functions $\mathcal{F}(l_2)$ and $\mathcal{A}(l_2)$ defined (for the b_1 -substrate) in the following way:

$$\mathcal{F}(l_2) = \sqrt{8\sigma_{\alpha\beta}} \int_{l_2}^{l_1} dl \left[\sqrt{\tilde{\omega}(l) - \tilde{\omega}(l_2)} - \sqrt{\frac{\sigma_{\alpha\beta}}{2}} \cot \varphi \right] + 2a\omega(l_2) + \frac{\sigma_{\alpha\beta}}{3} a \cot^2 \varphi \quad (12)$$

$$\mathcal{A}(l_2) = \sqrt{\frac{\sigma_{\alpha\beta}}{2}} \int_{l_2}^{l_1} \frac{dl}{\sqrt{\tilde{\omega}(l) - \tilde{\omega}(l_2)}} \quad (13)$$

where the parameter l_1 is determined as a function of l_2 by solving

$$\tilde{\omega}(l_1) = \tilde{\omega}(l_2) + \frac{\sigma_{\alpha\beta}}{2} \cot^2 \varphi. \quad (14)$$

Note that $\mathcal{A}(\bar{l}_2) = a$ is the necessary condition for a local minimum of $\mathcal{F}(\bar{l}_2)$. Straightforward calculation shows that

$$\frac{d\mathcal{F}(l_2)}{dl_2} = 2\tilde{\omega}'(l_2) [a - \mathcal{A}(l_2)]. \quad (15)$$

Thus, alternatively to previous procedures, the equilibrium configurations and the sought-for phase diagram may be obtained as solutions minimizing $\mathcal{F}(l_2)$, i.e. solutions of the equation $\mathcal{A}(\bar{l}_2) = a$. A similar set of equations holds also for the second substrate. This turns out to be a very effective way of obtaining the phase diagram and we employ it in our analysis.

3. Phase diagram

3.1. The first-order transition

We begin with the effective interface potential $\omega(l)$ which corresponds to the first-order wetting on a flat substrate. It is chosen in the following dimensionless form [27, 41, 43]:

$$\omega(l)/\sigma_{\alpha\beta} = At \exp(-l/\xi_\beta) + B[1 - Ct^2 l/\xi_\beta] \exp(-2l/\xi_\beta) \quad (16)$$

which corresponds to a system with short-range forces [27, 41]. The parameter t is taken as $t = (T_0 - T)/T_0$, where T_0 is larger than the first-order wetting temperature T_w^π for a flat substrate and depends on the parameters A , B and C . The parameter ξ_β denotes the bulk correlation length in phase β . The calculations are done for $A = 2$, $B = 1/3$, $C = 10$. For this choice, $T_0 = 1.451T_w^\pi$.

For each substrate the procedure described at the end of section 2 can be implemented only numerically. The resulting phase diagram is shown in figure 2.

Two phases represented on this diagram correspond to finite and to infinite thickness of the adsorbed β -like layer; we call them the non-wet and wet phase, respectively. In the wet phase both \bar{l}_1 and \bar{l}_2 are infinite. In the non-wet phase the layer thickness varies between finite

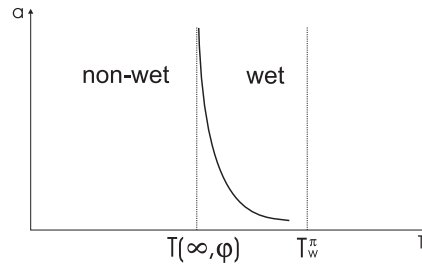


Figure 2. A schematic phase diagram for the first-order wetting transition in the variables temperature T and periodicity a for $\cot \varphi \ll 1$. The coexistence curves evaluated for the two cases practically coincide and are denoted by a single thick line. For $a/\xi_\beta \rightarrow \infty$ —which corresponds to enlarging the periodic unit—the coexistence lines approach the asymptote $T = T(\infty, \varphi)$ which is shifted from the planar substrate wetting temperature T_w^π by a distance proportional to $\cot^2 \varphi$. For small values of a , both coexistence curves tend to T_w^π .

\bar{l}_2 and \bar{l}_1 which both depend on t and a . The transition between these two phases is first order. Thus for the effective potential $\omega(l)$ given in equation (16), one observes—for both types of substrate—no change of the order of the wetting transition as compared to the planar substrate case. This first-order transition takes place upon crossing the coexistence line $T = T_w^i(a, \varphi)$, $i = 1, 2$, whose forms are identical (up to numerical accuracy) for the two substrates. In each case, $T_w^i(a, \varphi) < T_w^\pi$, which means that wetting of a corrugated substrate takes place at an absolute temperature which is lower than the wetting temperature of the planar substrate. This fact can be qualitatively understood by examining the effective interface Hamiltonian in equation (1). At the first-order transition point the free energy of the finite, non-planar configuration of the interface is equal to the free energy of the infinite solution, which is zero. For the finite solution the positive contribution corresponding to the gradient squared term has to be balanced by a negative contribution from the interface potential $\omega(l)$. This negative contribution from the interface potential is possible only for $T < T_w^\pi$. In the appendix we present analytical arguments showing that for the b_1 -substrate one should expect the same order of wetting transition as for the planar substrate.

In the limit $a/\xi_\beta \rightarrow \infty$, the two coexistence lines approach the same asymptote $T = T(\infty, \varphi)$. Its position depends on the angle φ and in the limit $\varphi = \pi/2$ it coincides with the wetting point of the planar substrate, i.e. $T(\infty, \varphi) \rightarrow T_w^\pi$ for $\cot \varphi \rightarrow 0$. Of course, this behaviour of the coexistence line is expected, because for $\varphi = \pi/2$ both substrates become planar, i.e. $b_1(x) = b_2(x) = 0$.

The asymptotic behaviour of the coexistence line can be—for both substrates—derived analytically in the limit of large a and small $\cot \varphi$. Since the derivations are very similar for the two substrates, we present that for the b_1 -substrate and then just quote and comment on the results for the other substrate.

We know from numerical analysis that in the case of large a and small $\cot \varphi$ the equilibrium values of \bar{l}_1 and \bar{l}_2 in the non-wet situation at a given temperature are close to each other and close to the corresponding value of the width l_π of the wetting layer on the planar substrate. The width l_π is determined as a solution of the equation $\omega'(l_\pi) = 0$. We also note that $\omega''(l_\pi) > 0$ and that, upon approaching the wetting temperature of the planar substrate, $\omega(l_\pi) \rightarrow 0$ from below. The quantity $\omega''(l_\pi)$ can be conveniently rewritten as $\omega''(l_\pi) = \sigma_{\alpha\beta} \xi_\parallel^{-2}$ and the correlation length ξ_\parallel sets the length scale in the consideration below. For the case of first-order wetting this quantity remains finite, unlike in the second-order wetting case where it becomes infinite at the transition point.

In order to solve equations (6), (7) one expands $\tilde{\omega}(\bar{l}_i)$, $i = 1, 2$, around l_π up to the second-order terms in $\bar{l}_i - l_\pi$. For small values of the difference $\bar{l}_1 - \bar{l}_2$, the integral on the right-hand side of equation (7)—although diverging in the limit $a \rightarrow \infty$ —can be evaluated by expanding the argument of the square root in the denominator around l_π up to the second-order terms and then integrating. In this way one obtains the following solution:

$$(\bar{l}_1 - \bar{l}_2)/\xi_{\parallel} = \cot \varphi \left[1 - \exp(-a/\xi_{\parallel})/2 + \dots \right] \quad (17)$$

$$(\bar{l}_2 - \bar{l}_\pi)/\xi_{\parallel} = -\cot \varphi \left[\xi_{\parallel}/a - \exp(-a/\xi_{\parallel})/2 \dots \right] \quad (18)$$

where dots denote terms which are higher order in $\cot \varphi$, ξ_{\parallel}/a , or in $\exp(-a/\xi_{\parallel})$. Note that in the limit $a = \infty$ one obtains $\bar{l}_2 = l_\pi$ and $\bar{l}_1 \neq \bar{l}_2$. Only after taking the limit $\cot \varphi = 0$ does one get $\bar{l}_1 = \bar{l}_2 = l_\pi$. In order to find the first-order wetting temperature, the expressions in equations (17), (18) are substituted into equation (8) and the corresponding value of the free energy is set equal to the value of the free energy corresponding to the wetting configuration. This is equal to zero—see equation (1) and the following remarks. In this way one obtains the following equation:

$$\omega(l_\pi)/\sigma_{\alpha\beta} = -\frac{1}{6} \cot^2 \varphi \left[1 - 3\frac{\xi_{\parallel}}{a} + \dots \right]. \quad (19)$$

Note that $\omega(l_\pi)$ in the above equation depends on temperature both explicitly—see equation (16)—and implicitly via l_π . After expanding $\omega(l_\pi)$ around T_w^π one obtains, to leading order in ξ_{\parallel}/a ,

$$T_w^1(a, \varphi) = T_w^\pi - \frac{\sigma_{\alpha\beta}}{6|\omega_t|} \cot^2 \varphi \left[1 - 3\frac{\xi_{\parallel}}{a} + \dots \right] \quad (20)$$

where dots denote higher-order terms, as before. The symbol ω_t denotes the partial derivative of ω with respect to t evaluated at the planar substrate wetting temperature; note that $\omega_t < 0$. An identical expression for the asymptotic behaviour of the coexistence line is obtained also for the second substrate. Thus, to leading order, the asymptotic behaviours of the two coexistence lines are the same, which is also confirmed by numerical results. We note that the shift of the asymptotic temperature $T_w(\infty, \varphi)$ (the same for both substrates) with respect to the corresponding planar substrate wetting temperature T_w^π is proportional to $\cot^2 \varphi$. The same kind of behaviour is observed for the shift of the filling temperature in an infinite wedge with opening angle 2φ [26, 27] with respect to the corresponding planar substrate wetting temperature T_w^π . In the opposite limit $a/\xi_\beta \rightarrow 0$, our numerical results show that $T_w^i(a, \varphi) \rightarrow T_w^\pi$. Again it can be checked analytically for both substrates that in this limit $T_w^\pi - T_w^i(a, \varphi) \sim a^2 \cot^2 \varphi$. These properties of $T_w^i(a, \varphi)$ are depicted in figure 2.

3.2. The continuous transition

In the case of the critical wetting transition on a planar substrate, the effective potential $\omega(l)$ has the following dimensionless form:

$$\omega(l)/\sigma_{\alpha\beta} = At \exp(-l/\xi_\beta) + B \exp(-2l/\xi_\beta) \quad (21)$$

where t denotes the dimensionless deviation from the planar substrate wetting temperature, i.e. $t = (T_w^\pi - T)/T_w^\pi$, and the parameters A and B are taken as $A = -1$, $B = 1$. The effective potential $\omega(l)$ in equation (21) corresponds to a system with short-range forces [41, 43]. This potential is inserted into equations (6)–(8) which are then analysed numerically for different values of the parameters t , a and $\cot \varphi$, similarly to in the preceding subsection. This analysis shows that depending on the values of t and a , the system is either in the non-wet or in the wet phase and the transition between these two phases is continuous. The numerically determined

transition line turns out to be very simple: independently of the values of the parameters a and φ (provided that $\cot \varphi \ll 1$), it coincides with T_w^π . Thus, in contrast to the results obtained above for the first-order transition, we observe no shift of the continuous transition with respect to the planar substrate case. This is true for both kinds of substrate. Our results do not confirm the conclusions reported in [20], where it is shown that for large enough corrugation amplitudes the continuous transition on a planar substrate turns into the first-order transition. This however should not be considered as a contradiction. Our method of analysis remains valid only for small substrate corrugation and thus the parameter $\cot \varphi$ must be kept small. This precludes the possibility of analysing systems with increasing corrugation amplitude at fixed periodicity.

4. Conclusions

We have analysed the wetting of two corrugated and non-smooth substrates. Each of them was translationally invariant in the y -direction and periodic with period $2a$ in the x -direction. Within each segment $x \in [-a, a]$, each substrate was described by a second-order polynomial in x . One of them was concave and the other was convex. Functions describing the substrates were—in addition to a —parametrized by $\cot \varphi$ measuring the discontinuity of the tangent to the substrate either at the centre of this segment or at its ends. The parameter $\cot \varphi$ also measured the deviation of the substrate from planarity. The interfacial configurations were assumed to have the periodicity of the substrate and so one could analyse just a single segment of the substrate. Our mean-field analysis was based on the effective interface Hamiltonian. The interfacial configurations were parametrized by two parameters relating to the width of the adsorbed layer at the centre of the segment and the width at the end of the segment. In addition to considering two types of substrate, we also considered effective potentials corresponding either to first-order or to continuous wetting on a planar substrate. The effective potentials which we have chosen were of rather general type and are frequently used in the literature. Thus we had to consider four cases depending on the type of substrate and the type of potential. In each of these four cases the set of equations leading to the equilibrium configuration was analysed numerically for different values of the temperature and different values of the parameters a and $\cot \varphi$.

We conclude that within the range of parameters considered, the order of the wetting transition does not change on going from a planar to a corrugated substrate. In the case of continuous wetting, the value of the wetting temperature does not change as compared to the planar substrate case. This is not true for the first-order transition. In this case the wetting temperature is shifted towards smaller values. The shift from the planar substrate wetting temperature depends on both substrate parameters, i.e. on a and $\cot \varphi$, and is (up to numerical accuracy) the same for the two substrates. At fixed value of $\cot \varphi$, this shift increases monotonically with a . The asymptotic behaviour of the first-order wetting temperature is such that for $a/\xi_\beta \rightarrow \infty$ it tends to a certain $\cot \varphi$ -dependent value and its distance from this value decreases proportionally to $1/a$. On the other hand, for $a/\xi_\beta \rightarrow 0$ the difference between the wetting temperature of the corrugated substrate and the planar substrate wetting temperature is decreasing proportionally to $a^2 \cot^2 \varphi$. Our results do not indicate any very substantial influence of substrate convexity on the wetting behaviour. Such an influence has been observed within the macroscopic description of adsorption on corrugated substrates with different convexity properties [23]. We think that the mesoscopic description adopted in this paper may also detect such an influence provided that the effective interface Hamiltonian takes a more complete account of the substrate corrugation than the one employed in the present analysis. This, however, requires a systematic derivation of such an effective Hamiltonian from a more fundamental theory of adsorption on a corrugated substrate.

It should be stressed that, although the effective potentials employed in our analysis are of general type, the substrates are rather specific, described by second-order polynomials, and are non-smooth. Thus an open question remains as regards to what extent these results remain valid for other types of substrate and what the generic properties of substrates are that determine whether the possible change of order of the wetting transition as compared to the planar case occurs.

Acknowledgment

The support by the Foundation for German–Polish Collaboration under Grant No 3269/97/LN is acknowledged.

Appendix

In this appendix we argue that the order of the wetting transition taking place on the b_1 -substrate is the same as that of the one occurring on the corresponding planar substrate. The argument does not apply to the case of the b_2 -substrate.

In our analysis we employ equations (12)–(15). It follows from equation (15) that the equilibrium interface configuration fulfils the condition $\mathcal{A}(l_2) = a$. Accordingly, this equation will be used to find the equilibrium interface configuration and to see how it evolves upon increasing the temperature.

We start with critical wetting on a planar substrate. In this case the effective potential $\omega(l)$ is given in equation (21) and the integral on the right-hand side of equation (13) can be rewritten in the following way:

$$\mathcal{A}(l_2) = \sqrt{\frac{\sigma_{\alpha\beta}}{2}} \int_{\tilde{\omega}_2}^{\tilde{\omega}_1} d\tilde{\omega} \frac{l'(\tilde{\omega})}{\sqrt{\tilde{\omega} - \tilde{\omega}_2}} \quad (\text{A.1})$$

where $\tilde{\omega}_i = \tilde{\omega}(l_i)$, $i = 1, 2$, and $\tilde{\omega}_1 = \tilde{\omega}_2 + \sigma_{\alpha\beta}/2 \cot^2 \varphi$. This change of variables in the integral is legitimate because we consider cases where $l_2 > l_0$, where l_0 corresponds to the minimum of $\tilde{\omega}(l)$. In this range, $\tilde{\omega}(l)$ is an increasing function of l . The inverse function $l(\tilde{\omega})$ exists and its derivative is present in equation (A.1). We note that $\mathcal{A}(l_2) \rightarrow \infty$ for $l_2 \rightarrow l_0$ and $\mathcal{A}(l_2) \rightarrow a$ for $l_2 \rightarrow \infty$. In order to find the behaviour of $\mathcal{A}(l_2)$ for intermediate values of l_2 , it is helpful to analyse the derivative $\mathcal{A}'(l_2)$:

$$\frac{d\mathcal{A}(l_2)}{dl_2} = \tilde{\omega}'(l_2) \sqrt{\frac{\sigma_{\alpha\beta}}{2}} \int_{\tilde{\omega}_2}^{\tilde{\omega}_1} d\tilde{\omega} \frac{l''(\tilde{\omega})}{\sqrt{\tilde{\omega} - \tilde{\omega}_2}}. \quad (\text{A.2})$$

The sign of the second derivative $l''(\tilde{\omega})$ depends on the value of l ; it is negative for $l_0 \leq l < l_{inf}$ and positive for $l > l_{inf}$, where l_{inf} denotes the inflection point of $\tilde{\omega}(l)$, i.e. $\tilde{\omega}''(l_{inf}) = 0$. On the other hand, the derivative $\tilde{\omega}'(l)$ is positive for $l > l_0$. The above facts lead to the conclusion that $\mathcal{A}(l_2)$ is a non-monotonic function of l_2 and has a single minimum. It is presented schematically in figure A1. We see that there is only single finite value of l_2 , say \bar{l}_2 , at which $\mathcal{A}(\bar{l}_2) = a$. This value grows continuously to ∞ for $T \rightarrow T_w^\pi$. The corresponding free energy is always smaller than the free energy of the infinite, i.e. the wetting, solution.

Similar analysis can be performed for the effective potential $\omega(l)$ corresponding to the first-order wetting on a planar substrate; see equation (16). In this case the potential $\tilde{\omega}(l)$ has—depending on the values of the temperature and the parameters a and $\cot \varphi$ —either one or two minima and it always has two inflection points, similarly to $\omega(l)$. The plot of $\mathcal{A}(l_2)$

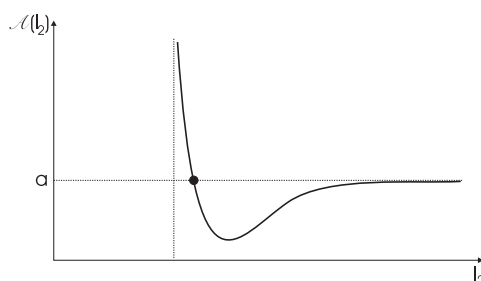


Figure A1. A schematic plot of the function $\mathcal{A}(l_2)$ in the case of a critical wetting transition on a planar substrate. The point at which $\mathcal{A} = a$ is denoted by a thick dot and corresponds to an equilibrium finite value of the parameter l_2 characterizing the thickness of the adsorbed layer. Upon increasing the temperature towards the planar substrate wetting temperature, this point is continuously shifted towards ∞ .

consists of three branches corresponding to different ranges of l_2 -values. Similarly to before, one is interested in values of l_2 for which $\mathcal{A}(l_2) = a$. Such values of l_2 corresponding to the first two branches remain finite independently of the temperature. The third branch corresponds to the largest values of l_2 and for these values $\mathcal{A}(l_2)$ is a monotonically decreasing function; the condition $\mathcal{A}(l_2) = a$ is fulfilled only by $l_2 = \infty$. Thus there is no possibility of continuous increase of the finite solution of equation $\mathcal{A}(l_2) = a$ to ∞ upon increasing the temperature. Thus the transition must be first order and corresponds to a discontinuity of l_2 .

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