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Wetting on a cylindrical substrate off coexistence

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Abstract. We calculate a Landau mean-field phase diagram for the wetting transition on a cylindrical substrate as a function of the distance from coexistence. Although both the bulk field and the curvature cause the wetting layer to remain finite, they affect the wetting phase diagram in different ways.

Theoretical studies of wetting have concentrated on the growth of wetting layers upon planar substrates [1–5]. Lately, increasing attention has been devoted to curved substrates, particularly of cylindrical or spherical geometries [3–11], which are of both fundamental and practical interest, in such diverse applications as textile fibres, dyeing, lubricants, ink products, carbon fibres and oil recovery.

Recently a mean-field phase diagram was calculated for wetting on cylindrical substrates using a Landau-type continuum theory with short-range substrate-adsorbate forces [10, 11]. This study was restricted to coexistence. In this paper we extend this work by presenting results for wetting off-coexistence, on cylindrical substrates.

Typically a true wetting transition occurs for a semi-infinite two-phase fluid, say liquid/gas, bounded by a planar substrate. In such a system nothing prevents the liquid phase, which is favoured by the wall, from proliferating into the bulk. If, however, the adsorbate is not at two-phase coexistence then the wetting layer thickness remains finite. One speaks of a prewetting transition between a thin and a thick layer. The wetting transition on a cylinder could be argued to resemble the prewetting transition on a flat surface. An interface bound to a cylindrical or spherical substrate cannot expand to infinity, since the increase in its area would result in an unlimited positive contribution to the free energy.

We find that, although both a bulk field and curvature restrict the wetting layer to a finite thickness, they affect the wetting phase diagram in different ways. The re-entrant wetting transition found for substrates of curvature large compared to the correlation length [10] is quickly destroyed by the application of a bulk field.

Our starting point is the *Landau free-energy functional*

$$F[m] = \int \mathrm{d}^3 r [\tfrac{1}{2} c (\nabla m)^2 + f(m(\boldsymbol{r}))] + \int \mathrm{d}^2 r \gamma_{\mathrm{s}}(m_{\mathrm{s}}) \qquad (1)$$

of the order parameter $m(\boldsymbol{r})$. c is a constant. The first integral is taken over the volume containing the fluid and the second is taken over the interface of the fluid with the substrate. The bulk free energy density $f(m)$ is taken as usual to be

$$f(m) = a_0 - hm + a_2 m^2 + a_4 m^4 \qquad (2)$$

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where h is the bulk field. We make the choice of a bulk field disadvantaging the phase of positive $m(\boldsymbol{r})$, $h \leq 0$. It is convenient to choose $a_4 = 1$, $a_2 = 2(T - T_c)$ and $a_0(T, h)$ such that $\min\{f(m)\} = 0$. This amounts to subtracting the bulk free energy from the total free energy so that $F[m]$ is the *interfacial free energy*. The first integral in (1), say $F_d[m]$, is the contribution coming from the distortion in the profile m($\boldsymbol{r}$) due to the presence of the interface. The second integral, say $F_s[m_s]$, is the contribution coming from the direct contact with the substrate. The standard choice for the substrate-adsorbate surface free energy is

$$\gamma_s(m_s) = -h_s m_s - \tfrac{1}{2} g_s {m_s}^2 \tag{3}$$

where h_s is a surface field and g_s a surface coupling enhancement.

It is convenient to write $f(m)$ in the form

$$\begin{aligned} f(m) &= (m^2 - m_b^2)^2 - hm + \tilde{a}_0 \qquad T \leq T_c \\ f(m) &= (m^2 + m_b^2)^2 - hm + \tilde{a}_0 \qquad T \geq T_c \end{aligned} \tag{4}$$

where $m_b^2 = |T - T_c|$ and again $\tilde{a}_0$ is chosen such that $\min\{f(m)\} = 0$.

The substrate we consider is a cylinder of radius r_1 and length L. Introducing the scaled variables

$$\rho = r/r_1 \qquad x(\rho) = m(r)/m_b \tag{5}$$

the scaled free energy per unit area of the substrate is

$$\Gamma[x] \equiv \frac{1}{2\pi L c m_b^2} F[m] = \Gamma_d[x] + \Gamma_s(x_s) \tag{6}$$

where

$$\Gamma_d[x] = \int_1^\infty \rho \mathrm{d}\rho \left[\frac{1}{2} \left(\frac{\mathrm{d}x}{\mathrm{d}\rho} \right)^2 + f(x(\rho)) \right] \tag{7}$$

and

$$\Gamma_s(x_s) = -H_s x_s - \tfrac{1}{2} G_s x_s^2. \tag{8}$$

In terms of the scaled variables the bulk free energy density becomes

$$\begin{aligned} f(x) &= \tfrac{1}{4}\Omega(x^2 - 1)^2 - Hx + A_0 \qquad T < T_c \\ f(x) &= \tfrac{1}{4}\Omega(x^2 + 1)^2 - Hx + A_0 \qquad T > T_c \end{aligned} \tag{9}$$

where A_0 is chosen such that $\min\{f(x)\} = 0$. We have introduced the scaled fields

$$H = \frac{h r_1^2}{c m_b} = \frac{h}{(|T - T_c|)^{1/2}} \left(\frac{r_1}{\sqrt{c}} \right)^2 \tag{10}$$

$$H_s = \frac{h_s r_1}{c m_b} = \frac{h_s}{(|T - T_c|)^{1/2}} \left(\frac{r_1}{c} \right) \tag{11}$$

$$G_s = g r_1 / c \tag{12}$$

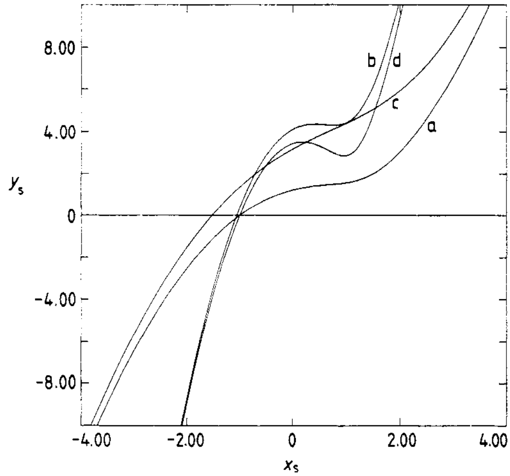

Figure 1. Curves $y_s(x_s)$ of boundary conditions on a cylindrical substrate for $T < T_c$ and (*a*) $\Omega = 1, H = 0$; (*b*) $\Omega = 1, H = -2$; (*c*) $\Omega = 16, H = 0$; (*d*) $\Omega = 16, H = -2$. The points of intersection of a given curve $y_s(x_s)$ with the straight line $y_s = H_s + G_s x_s$ correspond to the profiles extremizing the free energy $\Gamma[x]$.

and defined the important dimensionless parameter

$$\Omega = \frac{4m_b^2 r_1^2}{c} = 4|T - T_c|\left(\frac{r_1}{\sqrt{c}}\right)^2 = \left(\frac{r_1}{\xi}\right)^2 \tag{13}$$

which compares the cylinder radius to the bulk correlation length $\xi = \sqrt{c}/2(|T - T_c|)^{1/2}$.

Minimizing the scaled surface free energy (6) leads to the Euler–Lagrange equation

$$\frac{d^2x}{d\rho^2} + \frac{1}{\rho}\frac{dx}{d\rho} = f'(x) \tag{14}$$

together with the boundary conditions

$$\left.\frac{dx}{d\rho}\right|_s = -H_s - G_s x_s \tag{15}$$

and

$$x \to x_\infty \qquad \text{as} \quad \rho \to \infty$$

where x_∞ is the global minimum of $f(x)$ given by the minimum root of

$$\begin{aligned} &x^3 - x - (H/\Omega) = 0 \qquad T < T_c \\ &x^3 + x - (H/\Omega) = 0 \qquad T > T_c \end{aligned} \tag{16}$$

which corresponds to the stable value of the mean-field magnetization.

The apparently simple nonlinear differential equation (14) defies an analytical solution. We will therefore resort to numerical integration. Letting $y \equiv -dx/d\rho \equiv -\dot{x}$ we can rewrite (14) as a system of two equations

$$\dot{x} = -y \qquad \dot{y} = -y/\rho - f'(x). \tag{17}$$

For a given value of x_s we integrate this system once, requiring that the trajectory $y(x)$ in the phase plane (x, y) passes through $(x_\infty, 0)$, in accordance with (16). Repeating this process for a given set of x_s values, we obtain a curve in the (x_s, y_s) plane. Examples of the curve $y_s(x_s)$ are shown in figure 1 for different values of Ω and H.

The profiles that extremize the free energy correspond to the points of intersection of the curve of boundary conditions $y_s(x_s)$ with the straight line $y_s(x_s) = H_s + G_s x_s$. Depending on the values of the ratio H/Ω, which affects the shape of $y_s(x_s)$, and of H_s and G_s, which affect the position of the straight line, there can either be one or three points of intersection. If the curve $y_s(x_s)$ and the straight line $H_s + G_s x_s$ intersect only once then any change in the profile must be continuous. If they intersect three times then the transition involves a jump between two distinct profiles when they exchange roles as the global minimum of the free energy; this is clearly a first-order transition. An equal-areas rule enables us to study graphically the latter type of transition; it also tells us that the intersection in the middle corresponds to a maximum of the free energy which can be discarded.

The equal-areas rule follows from considering the surface free energy functional $\Gamma[x]$ for profiles satisfying the bulk equation and the boundary condition (16), as a function of x_s, say $\tilde{\Gamma}(x_s) = \tilde{\Gamma}_d(x_s) + \Gamma_s(x_s)$, which is to be compared with (6). Requiring that $d\tilde{\Gamma}(x_s)/dx_s = 0$, and using the boundary condition at the substrate, (15), we see that $d\tilde{\Gamma}_d(x_s)/dx_s$ and $y_s(x_s)$ are identical functions of x_s. This implies

$$\tilde{\Gamma}[x_s''] - \tilde{\Gamma}[x_s'] = \int_{x_s'}^{x_s''} [y_s(x_s) - (H_s + G_s x_s)]dx_s. \tag{18}$$

Drawing the straight line $y_s = H_s + G_s x_s$ across the curve $y_s(x_s)$, it follows that a first-order transition occurs when the two enclosed areas become equal.

Our aim is to calculate the phase boundary which separates the two phase region, where there is a discontinuous transition between a thin and a thick wetting layer, from the one phase region, where the change in the profile is continuous. If the value of G_s exceeds the value of the slope of the curve $y_s(x_s)$ at its point of minimum slope, that is its point of inflexion, then the line $y_s(x_s) = H_s + G_s x_s$ will cut equal areas from the curve $y_s(x_s)$ for some H_s and a first-order transition will occur. Hence the phase boundary follows from a determination of the minimum slope of $y_s(x_s)$.

We now present phase diagrams for wetting on a cylindrical substrate off coexistence. We shall also display results for the wetting of a planar substrate off coexistence as we are interested in comparing the effects of curvature and a bulk field, both of which limit the thickness of the wetting layer. In figure 2 we show the most direct comparison to the results Indekeu *et al* [10] obtained for the zero field case. The phase boundary is plotted in the variables $\Omega^{1/2} = r_1/\xi$ versus G_s for different values of the ratio $h(r_1/\sqrt{c})^3$. In the case $H = 0$, for a fixed small positive coupling enhancement G_s, the first-order transition appears, disappears and reappears. As H is increased the most striking feature is that the re-entrance is destroyed very quickly, i.e. by $h(r_1/\sqrt{c})^3 = -0.01$.

In figure 3, for comparison, we plot $1/\xi$ versus $G_s = g/c$ for a planar substrate in a bulk field [1, 2, 12–14], $h/c^{3/2} = -1$. The bulk field *does not* introduce re-entrance. Note that the variables used in figure 3 are not the obvious scaling variables for the mean field theory of wetting on a planar substrate in a field. For a planar substrate, in zero bulk field, the phase boundary is made up of two straight segments [11], which pass through the origin of the $(G_s, 1/\xi)$ plane, one for $T < T_c$, of slope $-1/\sqrt{2}$, and one for $T > T_c$, of slope 1 . For $h \neq 0$ the phase boundary retains this shape only if the ratio H/Ω is kept constant, as can be shown analytically. Keeping H/Ω constant implies that $h \sim |T - T_c|^{3/2} \sim 1/\xi^3$. Therefore one is led to introduce a scaling factor $\lambda \equiv |h|^{-1/3}$ and plot a phase diagram using the variables λG_s and λ/ξ [15]. The phase

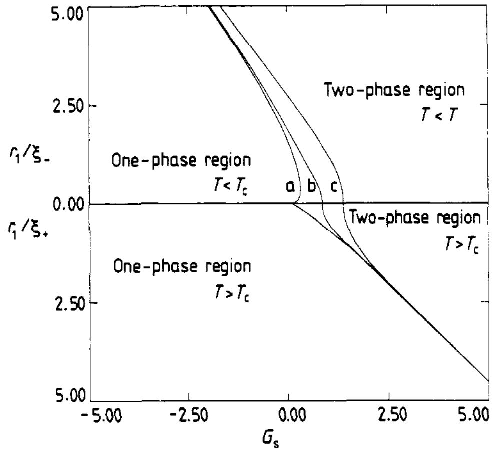

Figure 2. Phase diagram for wetting on a cylindrical substrate. For $T < T_c$, the correlation length ξ is denoted by ξ_-, and for $T > T_c$, by ξ_+. The critical line separates the one-phase region from the two-phase region for (a) $h = 0$ and for fixed values of h, r_1 and c satisfying (b) $h(r_1/\sqrt{c})^3 = -0.1$, (c) $h(r_1/\sqrt{c})^3 = -1$; note that $H = (2h/\sqrt{\Omega})(r_1/\sqrt{c})^3$.

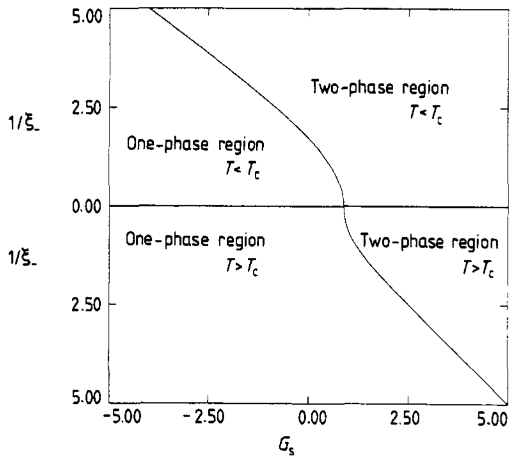

Figure 3. Phase diagram for wetting on a planar substrate in a field. This diagram is valid for fixed values of h and c such that $h/(\sqrt{c})^3 = -1$; H varies according to $H = (2h/\sqrt{\Omega})(1/\sqrt{c})^3$. Note that as $\Omega^{1/2} = 1/\xi \to \infty$, $H \to 0$ and the slope of the phase boundary tends toward $-1/\sqrt{2}$ for $T < T_c$ and 1 for $T > T_c$.

boundary is now explicitly independent of h. Provided that we fix $c = 1$ the resulting graph is identical to that in figure 3 for all $h < 0$.

Our results show that although bulk field and curvature both suppress an infinite wetting layer they affect the wetting phase diagram in different ways. A re-entrant two-phase region in the $(r_1/\xi, G_s)$ space seems peculiar to wetting on a curved substrate very close to coexistence. Whether this is an artefact of the mean field approximation used [16] or has deeper physical significance remains an open question.

We should also expect the nature of the phase transition to be different in the case of curvature and a bulk field. In the former case the interface is of finite size and hence the first-order transitions will be rounded and the critical line will show a finite-size shift and rounding. This effect has been discussed by Upton *et al.* They argue that the transition is not destroyed by finite-size rounding but a full theory of the effect has not yet been presented. The prewetting critical point on a planar substrate is, however, known to be a sharp phase transition in the two-dimensional Ising universality class [2, 17].

This study of wetting on curved substrates off coexistence was partly motivated by the experimental situation. Experiments on the adsorption of ^{4}He films on the surface of graphite fibers have been reported [18]. Several experiments on the stability of silica microspheres immersed in an homogeneous two-component fluid have also been conducted recently [19, 20]. Gurfein *et al* [19] observed a reversible flocculation as a function of temperature near the coexistence curve. They argued that this could be caused either by a pure surface transition, that is prewetting, or by capillary condensation [21]. The theory presented here may be able to shed some light on the origin of the flocculation curve. This work is in progress and will be reported elsewhere.

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