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1989 J. Phys. A: Math. Gen. 22 L1069

(http://iopscience.iop.org/0305-4470/22/22/004)

J. Phys. A: Math. Gen. **22** (1989) L1069-L1074. Printed in the UK

LETTER TO THE EDITOR

Wetting between concentric spheres

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Received 24 August 1989

Abstract. Results are presented for the mean-field phase diagram of a system at bulk coexistence contained between two concentric spheres as a function of the sphere radii, the temperature and the interactions with the surface. As with the wetting of a spherical substrate, re-entrant transitions are found. The relevance of the results to the wetting of an array of spheres is emphasised.

The wetting transition on planar surfaces is now well understood [1] but very little attention has been paid to curved substrates [2-7]. Therefore our aim in this letter is to present results for the density profile of a system at bulk coexistence, contained between concentric spheres, as a function of its interactions with the substrates.

Starting from a Landau form for the free energy, we obtain the critical surface which separates the two-phase region, where there is a first-order transition between two different density profiles, and the one-phase region, where the profile varies continuously. We are able to do this analytically for the case where the surface fields on the inner and outer spheres, H_1 and H_2, are equal. Numerical results are presented for $H_1 \neq H_2$.

This work extends a recent study of wetting on a spherical substrate which uncovered new and unexpected features [6, 7]. In particular, there were found to be two distinct regions of first-order transitions; $r/\xi \gtrsim 1$ and $r/\xi \lesssim 1$ where r is the sphere radius and ξ the bulk correlation length. Similar behaviour is found for the case considered here. We also emphasise the relation of this problem to the wetting of an array of spheres, which is likely to be an easier geometry to handle experimentally.

Consider two concentric spheres of inner and outer radii r_1 and r_2 respectively, with a fluid contained between them. A standard form for the Landau free energy functional is

$$F[m(r)] = 4\pi \int_{r_1}^{r_2} r^2 \, \mathrm{d}r \left[\frac{c}{2} \left(\frac{\mathrm{d}m}{\mathrm{d}r} \right)^2 + f[m(r)] \right] + 4\pi r_1^2 \gamma_1[m(r_1)] + 4\pi r_2^2 \gamma_2[m(r_2)] \tag{1}$$

where $m(r)$ is the order parameter profile. We consider the case where $f[m(r)]$ corresponds to two-phase coexistence in the infinite system

$$f[m(r)] = a_0 + a_2 m^2 + a_4 m^4 \tag{2}$$

where $a_4 = 1$, $a_2 = 2(T - T_c)$ and a_0 is chosen such that $\min\{f[m(r)]\} = 0$. Then (2) can be written in terms of the bulk order parameter, m_b,

$$f[m(r)] = (m^2 - m_b^2)^2 \tag{3}$$

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for $T \leqslant T_c$, the critical temperature. γ_i, the local surface energy per unit area, is taken to be

$$\gamma_i[m(r_i)] = -h_i[m(r_i)] - \tfrac{1}{2}g_i[m(r_i)]^2 \qquad i = 1, 2 \tag{4}$$

where h_i is a surface field and g_i a surface-coupling enhancement.

It is convenient to define the reduced variables

$$\rho = \frac{r}{r_1} \qquad d = \frac{r_2}{r_1} \qquad x(\rho) = \frac{m(r)}{m_b} \tag{5}$$

in terms of which (1) becomes

$$\Gamma[x(\rho)] = \int_1^d \rho^2 \, d\rho \left[\frac{1}{2}\left(\frac{dx}{d\rho}\right)^2 + \tfrac{1}{4}\alpha^2(x^2-1)^2\right] - H_1 x_1 - \tfrac{1}{2}G_1 x_1^2 - d^2(H_d x_d + \tfrac{1}{2}G_d x_d^2) \tag{6}$$

where we have used x_1 and x_d as shorthand for $x(\rho = 1)$ and $x(\rho = d)$ respectively and

$$\Gamma[x(\rho)] = \frac{F[m(r)]}{4\pi c r_1 m_b^2} \qquad H_i = \frac{r_1 h_i}{c m_b} \qquad G_i = \frac{r_1 g_i}{c} \qquad i = 1, d \tag{7}$$

$$\alpha^2 = \frac{4 r_1^2 m_b^2}{c} \equiv \left(\frac{r_1}{\xi}\right)^2 \tag{8}$$

in terms of the bulk correlation length

$$\xi = c^{1/2}/2m_b. \tag{9}$$

Extremisation of (6) leads to the Euler–Lagrange equation

$$\frac{d^2x}{d\rho^2} + \frac{2}{\rho}\frac{dx}{d\rho} = \alpha^2 x(x^2-1) \tag{10}$$

together with the boundary conditions

$$\left[\frac{dx}{d\rho}\right]_1 = -H_1 - G_1 x_1 \tag{11}$$

$$\left[\frac{dx}{d\rho}\right]_d = H_d + G_d x_d. \tag{12}$$

The solutions of (10) may be found numerically for a given α and d by fixing the values of H_i and G_i on one surface, say the inner sphere, and iterating to obtain the outer surface density and its derivative

$$x_d = F_1(H_1, G_1, x_1) \qquad \left[\frac{dx}{d\rho}\right]_d \equiv \dot{x}_d = F_2(H_1, G_1, x_1). \tag{13}$$

Elimination of x_1 between these equations defines the curve which relates $\dot{x}_d$ to x_d for a given H_1 and G_1. Examples of these are given in figure 1. Solutions then correspond to the intersection of this curve with the straight line defined by (12).

Several points of intersection can exist corresponding to maxima and stable and metastable minima of the free energy. We are interested in finding where different solutions exchange roles as the global minimum as a function of, say, H_d and G_d, as this corresponds to a first-order transition between different order parameter profiles.

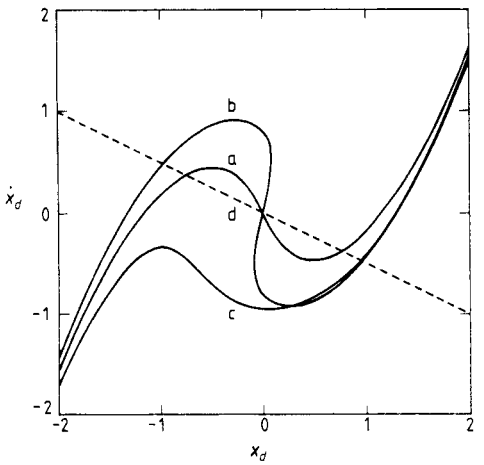

Figure 1. Trajectories, $\dot{x}_d(x_d)$, which satisfy equations (10) and (11) for $\alpha = 1$, $d = 2$ and: a, $H_1 = 0$, $G_1 = 1$; b, $H_1 = 0$, $G_1 = 2$; c, $H_1 = 2$, $G_1 = 1$. Shown as a broken line is $\dot{x}_d = G_d x_d + H_d$ for $H_d = 0$, $G_d = -0.5$ (see (12)). Where this intersects the curves the free energy (6) is extremised for the given surface fields.

To this end it is helpful to note that the free energy difference between solutions corresponding to outer surface densities x_d and x'_d can be written in the form

$$\Gamma(x'_d) - \Gamma(x_d) = \int_{x_d}^{x'_d} (\dot{x}_d(t) - H_d - G_d t)\, \mathrm{d}t \tag{14}$$

where the integral is taken along the curve $\dot{x}_d(x_d)$. This equation is just an equal areas rule which indicates that the transition occurs when the total area enclosed by the curve $\dot{x}_d(x_d)$ above and below the line (12) is zero.

We first consider the nature of the transition if H_1 and G_1 are fixed and H_d is allowed to vary. Recall that this corresponds to vertical displacements of lines such as curve d of figure 1, the slopes of which are determined by G_d. Consideration of the geometry of the curves $\dot{x}_d(x_d)$, examples of which are shown in curves a–c of figure 1, together with the equal areas rule, (14), now determines the phase diagram. For trajectories with a finite minimum gradient, $G_{\min}$ say, if $G_d < G_{\min}$ the profile will vary continuously, whereas for $G_d > G_{\min}$ a first-order jump between two different density profiles will occur. Thus we can define a critical surface given by $G_d = G_{\min}$. Note that 'rotated' trajectories, where $G_{\min}$ is $-\infty$, such as curve b in figure 1, always lie within the two-phase region.

The critical surface for the special case $H_1 = H_2$ can be obtained analytically because symmetry considerations demand that a transition is only possible for $H_1 = H_2 = 0$. The minimum gradient occurs at $x_d = 0$ and can be obtained from linearising (10) and solving it exactly. This gives a critical surface

$$G_d = \alpha\left(\frac{1 - G_1 - \alpha \tan(d-1)\alpha}{\alpha + (1 - G_1)\tan(d-1)\alpha}\right) - \frac{1}{d} \tag{15}$$

dividing the space (α, G_1, G_d) into a one-phase and a two-phase region as shown in figure 2. Note that the transition in the two-phase region is between symmetric profiles $\pm x(\rho)$.

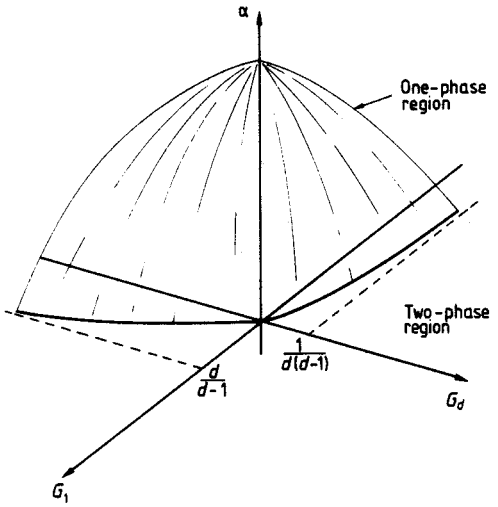

Figure 2. Schematic representation of the critical surface for $H_1 = H_d$. The two-phase region lies in front of the surface and the one-phase region behind it. By symmetry, any transition takes place at $H_1 = H_d = 0$.

For $H_1 \neq 0$ the phase boundary must be calculated numerically, as the minimum gradient of $\dot{x}_d(x_d)$ no longer occurs at the origin (see curve c in figure 1). We find that the one-phase region extends to larger values of α as $|H_1|$ increases. In the limit $\alpha \to 0$ the critical surface is independent of H_1.

To explore the phase space further we have also considered fixing the boundary conditions on the outer sphere, H_d and G_d, and looking at the nature of the transition as H_1 is varied. Again there is an extension of the one-phase region as $|H_1|$ increases from zero. For larger H_d an interesting new feature appears: a plot of the critical surface in the (α^2, G_1) plane starts to show re-entrant behaviour as H_d increases. Hence there can be two distinct regions of first-order transitions for a given H_d, G_d and d as shown in figure 3. Profiles corresponding to the points (a) and (b) in figure 3 are shown in figures 4(a) and (b). Similar re-entrant behaviour was seen in the wetting transitions on a spherical substrate [6, 7]. A full physical explanation is still lacking.

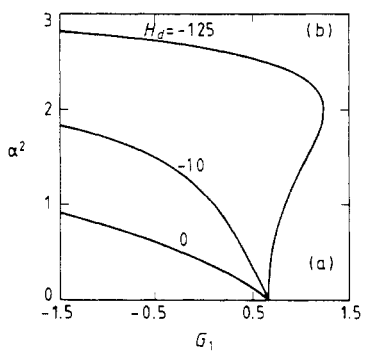

Figure 3. Cross sections of the critical surface showing the re-entrance of the two-phase region. The curves were obtained for $G_d = -0.25$ and $d = 2$.

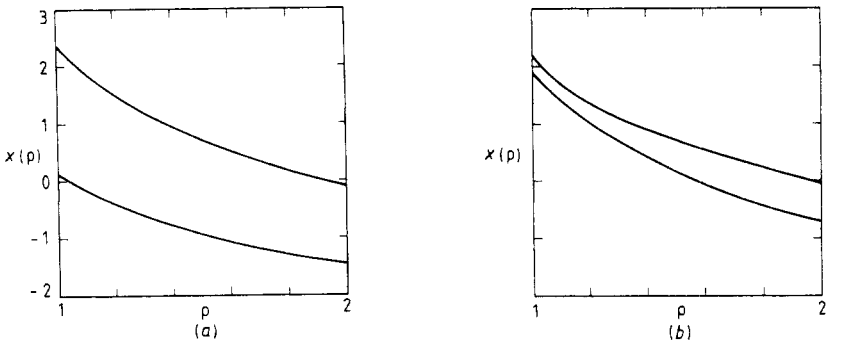

Figure 4. Density profiles at coexistence obtained at the points $H_d = -1.25$, $G_d = -0.25$, $G_1 = 1$, $d = 2$ and (*a*) $\alpha^2 = 0.4$; (*b*) $\alpha^2 = 2.8$, corresponding to points (a) and (b) in figure 3.

The qualitative dependence of the critical surface on the sphere separation can be obtained by noting that as d increases $G_{\min}$ becomes more negative. Hence the extent of the one-phase region is reduced. As d increases the trajectories $\dot{x}_d(x_d)$ can spiral round, allowing for several metastable and unstable solutions which correspond to density profiles which can oscillate.

It may be useful to bear our results in mind when considering the experimentally more accessible problem of the wetting of a regular array of identical spheres in a fluid at bulk coexistence. Because of the periodic nature of the problem the geometry is equivalent to a sphere centred within a cube with the normal derivative of the density profile constrained to be zero on the surface of the cube. One might expect the solutions of this problem to be similar to those for the concentric sphere geometry considered here with $H_d = G_d = 0$. For these boundary conditions it follows immediately from (15) that the critical surface is given by

$$G_1 = \frac{\alpha(1-d)+(1+\alpha^2 d)\tan(d-1)\alpha}{\tan(d-1)\alpha - \alpha d} \tag{16}$$

with the first-order transition being between profiles symmetric about $x(\rho) = 0$.

Several other avenues for future work are opened up by the results presented in this letter. In particular, the system considered is finite in all dimensions. Hence any transition will be rounded [8]. The extent of the rounding has been discussed in [7], where it is suggested that for the wetting of a single sphere at least, the transition will still be observable, but more work is needed. Another effect of the finite size is that the surface fields will move the system away from coexistence [9]. Therefore the addition of a bulk field is needed to study the phase diagram more completely. Such a field also allows us to investigate the competition between capillary condensation [10] and the re-entrant transition. This work is in progress and will be reported elsewhere.

We should like to thank J O Indekeu, P Sen and P J Upton for helpful comments.

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