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Capillary condensation and prewetting between spheres

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Abstract. We use an interface potential approach to consider the adsorption of a fluid with long-range interactions onto a substrate of two adjacent spheres. The interplay between prewetting-like thin–thick transitions and capillary condensation is discussed.

Wetting and capillary condensation are key areas in the study of fluids within porous media [1–3]. These phenomena are well understood in simple geometries where a fluid is confined within planar substrates [4]. However, in porous media, the role of more complicated substrate geometries is expected to be important. Therefore we have recently presented results for capillary condensation between spherical substrates [5]. Here we extend this work to discuss the effect of discontinuous wetting behaviour on the bridging transition that occurs between two adjacent spheres.

Consider a planar substrate immersed in a fluid close to two-phase coexistence. The chemical potential relative to its value at coexistence, $\Delta\mu$, is chosen such that the gas phase is preferred. The substrate–fluid interaction is defined so that the substrate attracts the fluid atoms. Hence a layer of liquid forms on the substrate. At coexistence, $\Delta\mu = 0$, the liquid layer can either be finite or infinite with the transition between the two cases termed ‘wetting’. The wetting transition can either be first order or continuous. Off coexistence, $\Delta\mu \neq 0$, the formation of an infinite wetting layer is suppressed and a first-order wetting transition is replaced by a thin–thick transition called ‘prewetting’.

The main difference for a spherical substrate [6, 7] is that the area of the liquid–gas interface and hence the associated free energy increases with distance from the substrate. This precludes the interface unbinding to infinity. The wetting transition is replaced, even at coexistence, with a thin–thick transition reminiscent of prewetting.

Consider now two spherical substrates of equal radius r_0 with centres separated by a distance D . This geometry allows a second interface transition, capillary condensation [4]. The liquid–gas interface can either adopt the topology shown in figure 1(a), where it forms a closed loop around each sphere individually, a situation favoured by the chemical potential contribution to the free energy, or that in figure 1(b) where there is a bridge of liquid between the spheres which may reduce the area of the interface. In previous work [5] we used an interface potential approach to study such a bridging transition. We found that it is first order as expected and presented results for the dependence of the phase boundary on $\Delta\mu$, r_0 , and D . However, we restricted ourselves to a thin wetting layer. Our aim here is to present

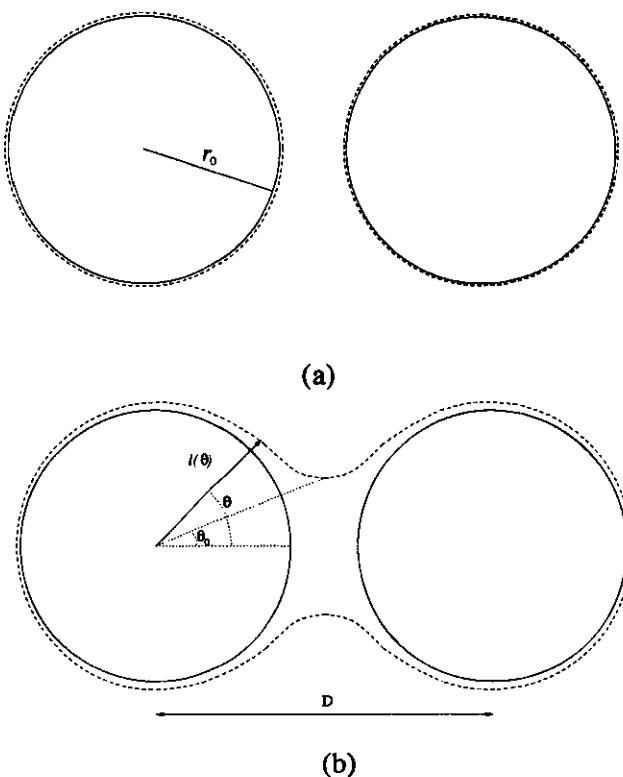


Figure 1. Two neighbouring spheres of radius r_0 and separation D . The liquid layers remain separated (a) until $\Delta\mu$ is sufficiently small to allow the formation of a liquid bridge between the two spheres (b).

the phase diagram in a space that also allows thin–thick wetting transitions for each sphere.

We work within the approximation where there is an interface at a position $l(\theta)$, where l is the distance of the interface from the centre of the nearest sphere and the angle θ is measured from the line joining the centres of the spheres (see figure 1). The interface extends to a minimum angle θ_0 , which is non-zero only for a bridged system. In terms of $l(\theta)$ the interfacial free energy is taken to be

$$\Omega[l(\theta)] = 4\pi \int_{\theta_0}^{\pi} \sin \theta d\theta \left(\sigma l \sqrt{l^2 + l_\theta^2} \right) + \widetilde{\Delta\mu} \left\{ 4\pi \int_{\theta_0}^{\pi} (l^3 \sin \theta / 3) d\theta + 2\pi (D^3 \tan^2 \theta_0 / 24 - 4r_0^3 / 3) \right\} + \omega[l(\theta)] \quad (1)$$

where the subscript θ indicates differentiation with respect to the polar angle.

The first term in equation (1) is the free energy of the interface itself, the surface area of the interface multiplied by the liquid–gas surface tension σ . The second contribution to the free energy results from adsorbing a given volume of the thermodynamically unfavourable liquid phase. The difference in number densities between the two phases has been subsumed into the chemical potential

$$\widetilde{\Delta\mu} = (\rho_l - \rho_g) \Delta\mu. \quad (2)$$

The final term is due to interactions between fluid and substrate atoms. It can be expressed as an integration over the gas volume of the sum of the disjoining pressures due to each sphere. If the distances from the centres of the two spheres are r and r'

$$\omega[l(\theta)] = 4\pi \int_{\theta_0}^{\pi} \sin \theta \, d\theta \int_{l(\theta)}^{l_{\max}(\theta)} r^2 \, dr (\Pi(r) + \Pi(r')). \quad (3)$$

The upper limit $l_{\max}(\theta)$ restricts the integration to the half-space occupied by one sphere

$$l_{\max}(\theta) = \begin{cases} D/2 \cos \theta & \theta < \pi/2 \\ \infty & \theta > \pi/2. \end{cases} \quad (4)$$

For the case of a potential that falls away with distance as $1/r^p$ the disjoining pressure of a single spherical substrate is [6]

$$\Pi(r) = W_p \left((p-4) \left\{ \frac{1}{(r-r_0)^{p-3}} - \frac{1}{(r+r_0)^{p-3}} \right\} - \frac{(p-3)}{r} \left\{ \frac{1}{(r-r_0)^{p-4}} - \frac{1}{(r+r_0)^{p-4}} \right\} \right). \quad (5)$$

The interfacial free energy (1) may be derived from a density functional theory by making a 'sharp kink' approximation, and ignoring higher derivatives of l [3]. We work under the assumption that the width of the liquid-gas interface is small compared to the thickness of the adsorbed film.

Minimizing the free energy (1) with respect to $l(\theta)$ yields the equation of motion of the interface

$$l_{\theta\theta} - 3l_{\theta}^2/l - 2l + \cot \theta \{ l_{\theta} (l^2 + l_{\theta}^2) / l^2 \} + (\Pi(l) + \Pi(l') - \widetilde{\Delta\mu}) (l^2 + l_{\theta}^2)^{3/2} / \sigma l = 0 \quad (6)$$

where l' is the distance of the interface from the centre of the second sphere. The boundary conditions are imposed by symmetry:

$$l_{\theta} = \begin{cases} 0 & \theta = 0 \\ 0 & \theta = \pi \end{cases} \quad (7)$$

for separated solutions and

$$l_{\theta} = \begin{cases} -D/2 \sin \theta & \theta = \theta_0 \\ 0 & \theta = \pi \end{cases} \quad (8)$$

for bridged solutions.

To model a first-order wetting transition, the potential $\omega[l]$ must have two local minima separated by a barrier. This can be modelled by taking the disjoining pressure to be the sum of three terms corresponding to different values of p , and choosing the amplitude W_p to be sufficiently negative for the middle p (all other W_p positive). The values of p taken in this work are 6 (non-retarded van der Waals), 7 and 8. Note

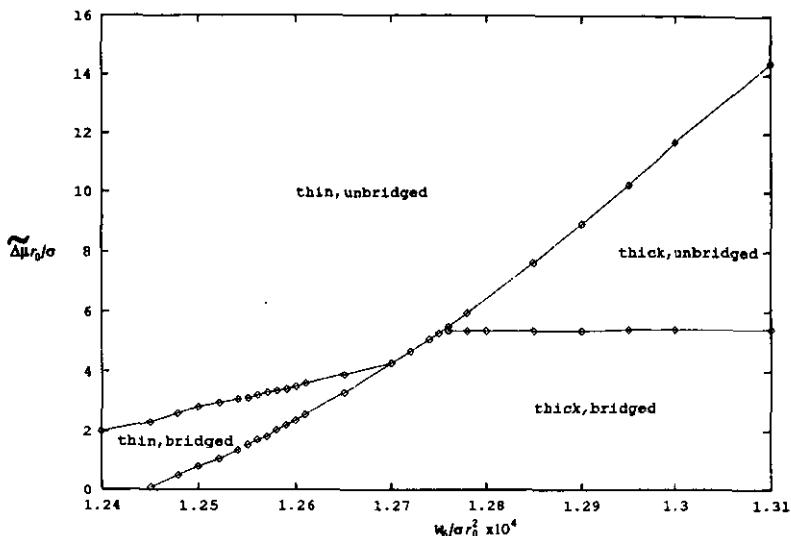


Figure 2. Wetting phase diagram for two neighbouring spheres, $W_7/\sigma r_0^3 = -1.0 \times 10^{-6}$, $W_8/\sigma r_0^4 = 2.045 \times 10^{-9}$ and $D/r_0 = 2.2$.

that dividing both sides of (1) by σr_0^2 , the free energy can be expressed in terms of the dimensionless variables l/r_0 , $\Delta\mu r_0/\sigma$, D/r_0 and $W_p/\sigma r_0^{(p-4)}$.

The non-linear differential equation (6) was solved using a relaxation method. In general four solutions exist, which are either bridged or separated, and with a thin or thick liquid layer absorbed onto the sphere surfaces. By numerically evaluating the free energy of each solution a phase diagram can be produced, as shown in figure 2. The value taken for the sphere separation D/r_0 is 2.2, and the constants $W_p/\sigma r_0^{(p-4)}$ were -1.0×10^{-6} and 2.045×10^{-9} for $p = 7$ and 8, respectively.

If the first term in the potential W_6 is sufficiently large, and the field $\Delta\mu$ is not too large, liquid bridges will have formed between the spheres and the coating on the spheres away from the bridges will be thick. As the chemical potential is increased, both the bridge and the thick film become less favourable, and there will be (first-order) transitions to an unbridged state and to a state with a thin adsorbed film. As can be seen in figure 2, these transitions can occur independently or simultaneously.

The line of thin-thick transitions closely follows the corresponding line of transitions for a single sphere. Larger differences would be expected only when the thickness of the thick film is comparable to or larger than the sphere separation D , a physically unrealistic situation.

On the thin film side of the thin-thick transition line, the line of bridging transitions has a stronger dependence on the strength of the Van der Waals interactions than on the thick film side, because the change in the contribution to the free energy from these forces caused by the transition is larger in the former case. As W_6 tends to zero the thin film becomes more favourable, and, depending on the values of W_7 and W_8 , the spheres may remain unbridged at coexistence.

The bridging transition is more sensitive to the sphere separation than the thin-thick transition. In the limit $D/r_0 \gg 2.0$ bridging will actually increase the surface area of the system unless the liquid layer adsorbed onto the sphere surfaces is

comparable in size to D . Thus for bridging to be favourable, the surface tension σ must be small so that the film thickness can increase on approach to coexistence. In the opposing limit, $D/r_0 \rightarrow 2$, the bridging transition mimics capillary condensation in a system of parallel plates with a separation $D - 2r_0$.

When the system is in the thin, bridged phase, the interface must pass over the barrier in the interaction $\omega[l]$ with the substrate. There is a competition between the surface tension, which favours a slowly varying interface, and the potential barrier which it would be advantageous to pass over as quickly as possible. The behaviour of $l(\theta)$ is not a sharp jump, but a very rapid change, as shown in figure 3, akin to the rapid growth in the thickness of a wetting film around the contact line on a planar surface at a first-order wetting transition [8]. The effect of the barrier is slightly to increase the free energy of the thin, bridged phase relative to the thick, bridged phase, and this creates the gap in the phase diagram between the thin, bridged to thin, unbridged and the thick, bridged to thick, unbridged phase boundaries.

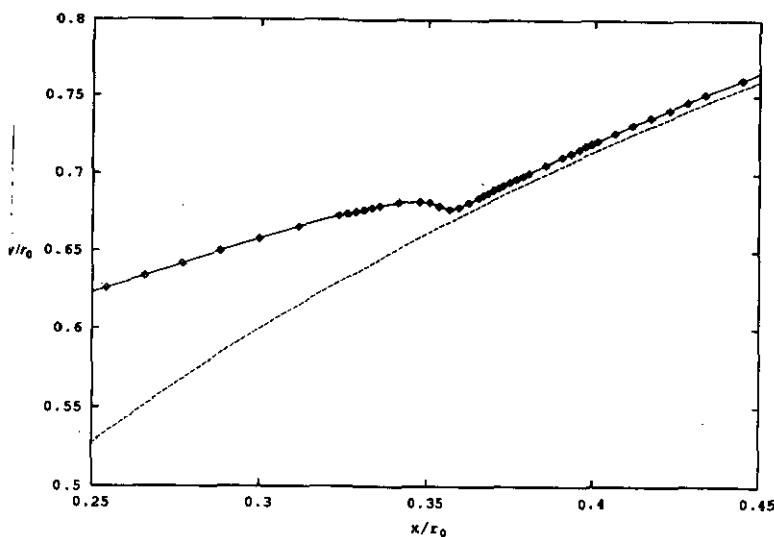


Figure 3. Interface profile for a thin, bridged system. The graph axes are the coordinates (in units of r_0) in a Cartesian system centred at the midpoint between the two spheres, with the x axis passing through the centres of both spheres. $\Delta\mu r_0/\sigma = 1.0$ and $W_6/\sigma r_0^2 = 1.25 \times 10^{-4}$; $W_7/\sigma r_0^3$, $W_8/\sigma r_0^4$ and D/r_0 take the same values as in figure 2. The dashed line marks the substrate surface.

In this paper we have obtained the phase diagram for wetting on two spheres. A novel feature is the juxtaposition of prewetting and capillary condensation. Both have previously been suggested as possible mechanisms for the flocculation of colloids [9], and it is interesting to find that in some cases they are expected to occur simultaneously! However, neither mechanism can explain the observation of aggregation on both sides of the consolute (critical) point.

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