

## Adsorption phenomena in amphiphilic systems

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The wetting behavior of a ternary mixture of oil, water, and amphiphile in the presence of a surface is studied. An interface model carefully derived from an underlying Ginzburg-Landau theory is introduced, which contains position dependent rigidity and stiffness coefficients. Using this model we predict a rich surface phase diagram containing thin-thick, first-order, and continuous wetting transitions. Application of the model to other interface behavior in these mixtures is also addressed. [S1063-651X(99)51209-9]

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A rich variety of structures may be observed when a small amount of amphiphile is added to a mixture of oil and water [1]. These include micellar solutions, the lamellar phase (a stack of monolayers separated by oil-rich or water-rich regions), and a microemulsion or middle phase characterized by a random array of monolayers. Due to this diverse range of phases and associated critical behavior these mixtures have attracted much attention in the statistical physics community [2–9]. Furthermore, thanks to a wide range of applications in the petroleum, paint, and pharmaceutical industries, such ternary systems are of importance to a broad audience of physicists and chemists.

More specifically, from the point of view of critical phenomena, any system containing three or more coexisting phases is of interest because of the possibility of wetting transitions in which a macroscopic layer of one phase may intrude at the interface between two other coexisting phases. In simple fluids, one typically considers the adsorption of one phase at a wall (which we view as a “spectator” phase), while a second phase is stable at large distances from the wall. In the context of amphiphilic systems the wetting of the oil-water interface by the microemulsion phase has been widely studied both analytically and experimentally. These studies have generally been carried out in the bulk so that the possibility of surface effects due to the presence of a wall or substrate have been largely ignored. One exception is the recent analysis of the wetting behavior of a wall-oil interface by the lamellar phase [10].

In this paper we instead study the possibility of wetting of the wall-microemulsion interface by either oil-rich or water-rich phases for systems at oil-water-microemulsion coexistence. We show that both first- and second-order phase transitions are possible for a given choice of surface enhancement, for example. The main tool we use in our analysis is an effective interface Hamiltonian, which is a functional of the thickness,  $l$ , of the adsorbed layer at the wall. In contrast to many earlier studies we make a careful derivation of the interface model, which results in the presence of position-dependent stiffness and rigidity coefficients highly analogous to recent discoveries of Fisher and Jin [11] for simple fluids. Later we discuss the importance of correctly incorporating the position dependence of the gradient terms for fluctuation effects.

To begin we describe the derivation of the effective model. Consider a semi-infinite geometry with a wall in the plane  $z=0$ , and use  $\mathbf{y}$  to denote the  $d-1$  dimensional vector displacement along this surface. Using this notation,  $l(\mathbf{y}) \geq 0$  represents the local separation of the unbinding interface from the wall. For our toy model we assume three phases (+, –, and middle) with symmetry between the + and – phases. We further assume that the middle phase is stable in the bulk (i.e., as  $z \rightarrow \infty$ ) and that the + phase is preferred at the wall. We base our derivation on a Ginzburg-Landau free-energy functional

$$\mathcal{H}[\phi] = \int d\mathbf{r} \{ \mathcal{L}_v[\phi, \nabla\phi, \nabla^2\phi] + \delta(z) \mathcal{L}_s[\phi, \nabla\phi] \}, \quad (1)$$

where  $\mathcal{L}_v = c(\nabla^2\phi)^2 + g(\phi)(\nabla\phi)^2 + f(\phi) - \mu\phi$  is the standard single order-parameter free-energy density for oil-water-amphiphile mixtures in the absence of a wall. In this formulation the amphiphile degrees of freedom are considered integrated out, but with their properties influencing  $c$ ,  $f$ , and  $g$ . For our study the chemical potential difference between oil and water,  $\mu$ , is zero, while the bulk free-energy density,  $f(\phi)$ , has three coexisting minima corresponding to the homogeneous +, –, and middle phases. From comparison with scattering experiments we know  $g(\phi)$  is negative in the middle (microemulsion) phase but is positive in the pure + and – phases. Finally,  $c$  is always positive, stabilizing the system, and for simplicity may be assumed constant. The wall enters through the surface density term  $\mathcal{L}_s = \mu_s\phi + \omega_s\phi^2 + g_s(\nabla\phi)^2$  characterized by three *surface parameters*. The local chemical potential,  $\mu_s$ , describes the preference of the wall for the + phase, while  $\omega_s$  is the surface enhancement. Finally, there is a gradient parameter,  $g_s$ , which has recently been associated with the local chemical potential of the amphiphile at the wall [10].

In order to derive an interface Hamiltonian from this model we follow the approach of Fisher and Jin [11] (FJ), and introduce a crossing constraint definition of the collective coordinate  $l$ . This involves finding the density profile  $\phi(\mathbf{y}, z)$ , which satisfies the constraint  $\phi(\mathbf{y}, z=l(\mathbf{y})) = \phi^X$  where  $\phi^X$  is a reference crossing value. We denote the constrained profile by  $\phi_{\Xi}(\mathbf{y}, z; l(\mathbf{y}))$ . In what follows we consider situations in which the order-parameter profile is oscillatory so that we typically choose  $\phi^X = 0$ . To ensure that the

interface location is uniquely defined we demand that  $l$  is the location where the profile *first* crosses the reference value. The key observation of FJ is that it is most convenient to expand about the *planar* constrained profile,  $\phi_\pi(z;l_\pi)$ , which satisfies  $\phi_\pi(z=l_\pi) = \phi^x \nabla \mathbf{y}$ . For the ternary amphiphilic system the constrained profiles are well defined and contain no singularities, this is in sharp contrast to the case of simple fluids where more care must be taken to control the profile smoothness [12]. Following this approach we derive an expansion for  $\phi_\Xi$  of the form  $\phi_\Xi(\mathbf{y}, z; l(\mathbf{y})) = \phi_\pi(z; l(\mathbf{y})) + B_1(z; l(\mathbf{y}))(\nabla^2 l) + B_2(z; l(\mathbf{y}))(\nabla l)^2 + \dots$  where the ellipsis represents higher order gradient terms that do not play a role in our analysis and the functions  $\phi_\pi$ ,  $B_1$ , and  $B_2$  satisfy simple differential equations [13].

We define our interface model  $\mathcal{H}_l[l]$  using the saddle-point identification  $\mathcal{H}_l[l(\mathbf{y})] \equiv \mathcal{H}[\phi_\Xi(\mathbf{r}; l(\mathbf{y}))]$ . In this way we derive the effective interface Hamiltonian

$$\mathcal{H}_l[l] = \int d\mathbf{y} \left\{ \frac{1}{2} \kappa(l) (\nabla^2 l)^2 + \frac{1}{2} \sigma(l) (\nabla l)^2 + W(l) \right\}. \quad (2)$$

Here  $W(l) = \int_0^\infty dz \{ \mathcal{L}_v[\phi_\pi, \partial \phi_\pi / \partial z, \partial^2 \phi_\pi / \partial z^2] + \delta(z) \mathcal{L}_s[\phi_\pi, \partial \phi_\pi / \partial z] \}$  is the interface potential which describes the interaction of the fluctuating interface with the wall. Further,  $\kappa(l) = \int_0^\infty dz \{ 2c(\partial \phi_\pi / \partial l)^2 + 2g(\phi_\pi)(\partial \phi_\pi / \partial l) B_1 + 8c(\partial^2 \phi_\pi / \partial z^2) B_2 \} + 2c(B_1(\partial^2 \phi_\pi / \partial z \partial l) - (\partial B_1 / \partial z)(\partial \phi_\pi / \partial l))|_{z=0}$  and  $\sigma(l) = \int_0^\infty dz \{ 4c(\partial^2 \phi_\pi / \partial z^2)(\partial^2 \phi_\pi / \partial l^2) + 2g(\phi_\pi)(\partial \phi_\pi / \partial l)^2 \} + 2g_s(\partial \phi_\pi / \partial l)^2|_{z=0}$  are position dependent *curvature* and *stiffness* coefficients, respectively. We note that similar models have recently been proposed by other authors [14] for free interfaces and, indeed for that case, our analysis is formally analogous to the eigenfunction approach of Gompper and Kraus at a Gaussian level. However, the method we have outlined here naturally allows the inclusion of walls, while accurately incorporating the corresponding boundary conditions. This is crucial for our study of wetting of the wall-middle phase interface by the + phase where, to begin, we use  $W(l)$  to determine the mean-field phase diagram. In particular we examine the form of the binding potential for given bulk and surface parameters, and observe whether the global minimum of the function is at a finite or infinite distance. In the first case we describe the interface as bound to the wall and hence there can be at most a thin (partial) wetting layer, while in the second case the interface is unbound and the wall is wet by the + phase.

In order to facilitate quantitative calculations we must further specify the functions  $f(\phi)$  and  $g(\phi)$  appearing in the Ginzburg-Landau model. For analytic purposes it is convenient to use a piecewise parabolic model, however, we note that, in general, quantitatively similar results are anticipated if a  $\phi^6$  model is used instead [15]. Hence we have

$$f(\phi) = \begin{cases} \omega_+(\phi - \phi_{0,+})^2, & \phi > \phi_{0,+} \\ \omega_m \phi^2 + f_0, & \phi_{0,-} < \phi < \phi_{0,+} \\ \omega_-(\phi - \phi_{0,-})^2, & \phi < \phi_{0,-}, \end{cases} \quad (3)$$

where  $\phi_{0,+}$  and  $\phi_{0,-}$  are chosen to ensure that  $f$  is continuous, and we require  $f_0 = 0$  for three-phase coexistence. In this model  $g(\phi)$  is assumed piecewise constant [1], with

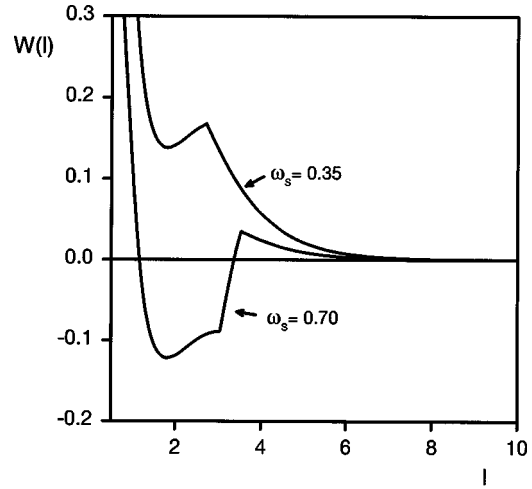


FIG. 1. Binding potentials for bound ( $\omega_s = 0.70$ ) and unbound ( $\omega_s = 0.35$ ) interfaces with surface parameters  $g_s = 1$  and  $\mu_s = -2$ . The potentials are calculated in the symmetric piecewise parabolic model with parameters  $c = 1$ ,  $\omega_+ = 4$ ,  $\omega_m = 1$ ,  $g_+ = 4.5$ , and  $g_m = -1$ .

$g(\phi > \phi_{0,+}) = g_+$ ,  $g(\phi_{0,-} < \phi < \phi_{0,+}) = g_m$ , and  $g(\phi < \phi_{0,-}) = g_-$ . For simplicity we consider only symmetric systems where  $\phi_+ = -\phi_- = 1$ ,  $\omega_+ = \omega_-$ , and  $g_+ = g_-$ . In what follows we have fixed the parameter values as  $c = 1$ ,  $\omega_+ = 4$ ,  $\omega_m = 1$ ,  $g_+ = 4.5$ , and  $g_m = -1$ .

Using this model we predict that wetting occurs in our system. For example, when  $g_s = 1$  and  $\mu_s = -2$ , we find a first-order wetting transition as we reduce  $\omega_s$  from a large positive value. Typical binding potentials on each side of this transition are shown in Fig. 1; for  $\omega_s > 0.527$  the potential has its global minimum at  $l \approx 1.8$ , while for  $\omega_s < 0.527$  the global minimum is at infinity, but a local minimum remains at  $l \approx 1.8$  until  $\omega_s = -0.161$ . This point may be identified as a metastable limit beyond which the only minimum of the potential is at infinity. A similar limit exists at  $\omega_s = 1$  when the extremum at infinity changes nature from a minimum to a maximum. Some explanation of the kinks visible in the interface potential is appropriate at this point. These arise because the width of the interface is not fully determined within the piecewise parabolic model and must be found from further minimization [1]. The optimal width varies with  $l$  and displays discontinuities for small  $l$  when the crossing criterion is accurately applied. These problems can be avoided by the use of smooth free-energy densities  $f(\phi)$  and  $g(\phi)$ .

For some choices of surface parameters we see very different behavior where the location of the global minimum of  $W(l)$  diverges continuously as we approach the transition boundary, corresponding to a continuous wetting transition. In general, for a given choice of surface parameter  $g_s$ , we find first-order transitions for smaller values of  $|\mu_s|$  and continuous transitions for larger  $|\mu_s|$ . Recall that we only consider negative  $\mu_s$  values here as appropriate for wetting by the + phase, however, due to the symmetry of our system we predict analogous behavior for positive  $\mu_s$  with the - phase wetting the wall-middle phase interface. The surface phase diagram for the  $g_s = 1$  case is given in Fig. 2, showing first-order (FW) and continuous wetting transition phase boundaries. The two lines meet at a tricritical point (TCP),

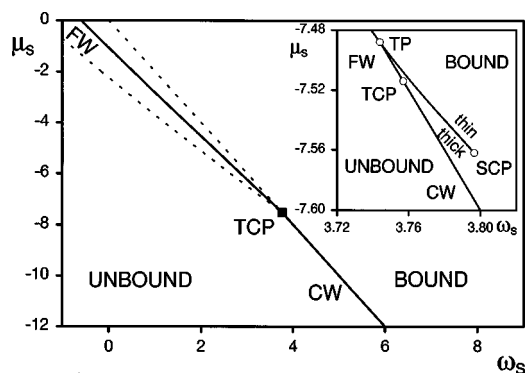


FIG. 2. Mean-field surface phase diagram for the case  $g_s = 1$ , calculated within the symmetric piecewise parabolic model with parameters  $c = 1$ ,  $\omega_+ = 4$ ,  $\omega_m = 1$ ,  $g_+ = 4.5$ , and  $g_m = -1$ . First-order (FW) and continuous (CW) wetting phase boundaries are shown by solid lines; the two regimes are separated by a tricritical point (TCP). In the vicinity of TCP a thin-thick transition can occur (see inset). The thin-thick transition boundary begins at a triple point (TP) on the FW line and terminates at a surface critical point (SCP). The dashed lines denote the metastable limits discussed in the main text.

which is also the terminus for the two metastable limits (dashed lines) discussed above. In the vicinity of the TCP, we further find a (first-order) thin-thick transition, which may precede the wetting transition (see inset of Fig. 2). The corresponding thin-thick transition line extends from a triple point on the FW line and terminates at a surface critical point where the layer thicknesses on each side of the transition become the same. We stress that the thin-thick transition is not an artifact of the crossing criterion definition of  $l$  but can be understood in terms of oscillations in the binding potential. These are on the scale of  $10^{-5}$  and hence are not visible in Fig. 1, however, close to TCP, both the depth of the minimum at finite  $l$  and the height of the potential barrier are of this order and the oscillations become important. In principle, further layering transitions may also be expected although we have been unable to locate such transitions due to the very small energy differences involved.

We have made the arbitrary choice of  $g_s = 1$  since we do not know *a priori* what is a reasonable value for this parameter. Repeating our analysis for other values of  $g_s$  (including  $g_s \leq 0$ ) results in a qualitatively identical picture. The main quantitative difference is that we find a larger region of the first-order wetting transition when we use smaller, or negative, values of  $g_s$  (that is, the FW transition line extends over a wider range of  $\mu_s$  values than shown in Fig. 2). Hence we find transitions occurring for positive and negative values of all three surface parameters and consequently believe this wetting transition should be accessible in experimental systems. To that end we propose an experimental study of a ternary system containing nonionic amphiphiles, such as the  $n$ -alkyl polyglycol ethers, in the presence of a substrate pretreated to favor the + phase [16]. The temperature–amphiphile-concentration phase diagram of such mixtures is well understood [1] so it is straightforward to prepare the system in the middle phase, while the appearance of the lamellar phase is prevented by the strength of the amphiphiles. Thus initially only a finite layer of the favored + phase will be adsorbed at the substrate, and will manifest

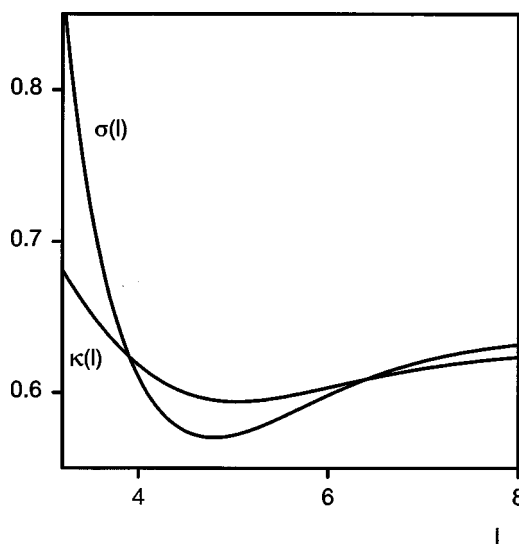


FIG. 3. Stiffness,  $\sigma$ , and rigidity,  $\kappa$ , calculated in the symmetric piecewise parabolic model with parameters  $c = 1$ ,  $\omega_+ = 4$ ,  $\omega_m = 1$ ,  $g_+ = 4.5$ , and  $g_m = -1$ , and surface parameters  $g_s = 1$ ,  $\mu_s = -2$ , and  $\omega_s = 0.45$ .

itself, for example, in the scattering intensity of x rays [17]. The predicted wetting transition can now be induced by approaching the three phase coexistence region (in practice this may be achieved by decreasing the amphiphile concentration at fixed temperature) and will result in a growth of the layer thickness. In such systems the presence of van der Waals forces is sure to influence the phase behavior we have predicted above. The magnitude of the fluid-fluid forces is anticipated to be rather small because the densities of all three phases are very close to one another. Hence we only consider the inclusion of a long-range substrate potential, which effectively adds a term of the form  $a/l^2$  to the interface potential. The Hamaker constant,  $a$ , is proportional to the difference in densities of the wetting phase and the bulk phase. Hence if we assume that the adsorbed phase is the oil-rich one, then  $a < 0$  and the unbinding transition is suppressed. However, if the adsorbed phase is the water-rich one then  $a > 0$  and the unbinding transition remains, although only first-order transitions will now be observed. Consequently, we predict first-order wetting transitions should be experimentally observable in the proposed system provided that the substrate is treated, such that the (denser) water-rich phase is preferred.

For completeness we show examples of the gradient terms  $\sigma(l)$  and  $\kappa(l)$  in Fig. 3. As  $l \rightarrow \infty$ , these functions tend to constants,  $\sigma_\infty$  and  $\kappa_\infty$ , representative of a free + phase-middle phase interface. Distortions of the interface due to the presence of the wall account for the position dependence at smaller  $l$ , where both functions dip below their bulk values [18]. This position dependence is important for analyzing the effect of fluctuations on the predicted wetting behavior because, upon applying functional renormalization group (RG) techniques to the model (2), we find the flow equation for the binding potential depends nontrivially on the functions  $\Delta\sigma(l) \equiv \sigma(l) - \sigma_\infty$  and  $\Delta\kappa(l) \equiv \kappa(l) - \kappa_\infty$ . Solving the RG equations is beyond the scope of this paper, but we anticipate that the wetting transition remains and is probably always first order in character; hence the mean-field continuous tran-

sition is driven fluctuation induced first order [11,13].

Furthermore, the importance of these terms extends far beyond the specific system considered in this paper. The Hamiltonian model (2) is valid for any situation where there are interactions between interfaces in a ternary amphiphilic system. Hence two fluctuating lamellae separated by a distance  $l(\mathbf{y})$  should be modeled using the same Hamiltonian. (It is not justified to assume that the rigidity and stiffness may be considered constant.) So, for example, even if a single lamellae may be modeled as a tensionless interface ( $\sigma_\infty = 0$ ), an important position-dependent stiffness contribution remains when a stack of such lamellae is studied. Further, our model may be used to explain small-angle x-ray scattering measurements, of the effective compressibility in an asymmetric lamellar stack, which show clear discrepancies with corresponding theoretical predictions [19]. The compressibility can be directly associated with the effective rigidity of the stack. If we use Eq. (2) to model interactions between each pair of layers in the stack, we find an overall effective rigidity which is a function of, e.g.,  $l_1$  and  $l_2$ , the thicknesses of the oil and water layers, respectively. This position-dependent function must be used in place of the assumed constant within the theory in order to compare with the experiments. This conclusion is supported by a recent Monte Carlo study of a three layer stack by Netz [20], which

found that the effective rigidity is precisely a function of  $l_1/l_2$ .

In conclusion, we have introduced a technique for accurately deriving an effective interface model suitable for studies of unbinding effects in ternary amphiphilic systems. The model is applicable to situations in which two fluctuating interfaces are interacting (such as in the lamellar phase) and to study unbinding and adsorption effects, where external walls or surfaces are present. In contrast to standard phenomenological approaches the model contains position-dependent stiffness and rigidity terms, which are essential to capture some of the essential physics found in these complex mixtures (e.g., the effective compressibility in an asymmetric lamellar stack). We have applied our model to study the possibility of wetting of the wall-microemulsion interface by the water-rich phase, as might be appropriate in the analysis of confined microemulsions. We predict a rich mean-field surface phase diagram containing thin-thick transitions and both continuous and first-order wetting transitions.

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