# Unbinding and preunbinding in surfactant solutions

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We propose models for the first-order unbinding transition of lyotropic lamellae in surfactant solutions. The coupling between the surfactant volume fraction and the elastic degree of freedom is considered so that the net attractive interaction between the surfactant molecules is enhanced. The elastic degree of freedom can be either (i) a membrane elastic degree of freedom or (ii) a bulk elastic degree of freedom. The phase behaviors of these two models are analyzed. For both cases, the unbinding transition becomes first order when the coupling is strong enough. We determine the associated preunbinding line which separates two lamellar phases having different repeat distances. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2159475]

## I. INTRODUCTION

One of the simplest structures found in mixtures of water and surfactant is the lamellar phase in which the bilayers of amphiphile form roughly parallel layers separated by water. In some binary systems, it is known that the lamellar phase can be swollen almost without limit. For example, in the mixture of water and $C_{12}E_5$ (*n*-akylpolyglycolether), the repeat distance of the lamellar phase can exceed 3000 Å.[1] The amount of surfactant molecules in the unbound phase is less than 1%. The transition from the bound lamellar phase to the unbound phase is generally called the "unbinding transition."

The concept of the unbinding transition was theoretically introduced by Lipowsky and Leibler.[2] Whether this transition is second order or first order is a subtle problem (see also Sec. V). Using the functional-renormalization-group techniques, Lipowsky and Leibler showed that two membranes unbind continuously in the presence of thermal fluctuations. More precisely, the mean distance between the two membranes, $\ell$, diverges as $\ell \sim (T_u - T)^{-\psi}$ with $\psi \approx 1$ and $T_u$ is so called the unbinding temperature.[2]

For a bulk of lamellar phase, the volume fraction of surfactant, $\phi$, is inversely proportional to the mean distance $\ell$. If the above prediction by Lipowsky and Leibler for two membranes is applicable to the lamellar phase of an infinite number of membranes, the difference in volume fraction between the bound (lamellar) and the unbound phases should decrease linearly with $T_u - T$.[3,4] In other words, the lower boundary of the lamellar phase in the temperature-concentration plane should be a straight line of nonzero slope. Several mean-field theories for a lamellar phase were constructed in such a way to reproduce the exact results.[5–7]

Unfortunately, the critical behavior is not observed in the experimental phase diagram of surfactant solutions.[1] For example, the unbinding transition in the $C_{12}E_5$/water system is fairly abrupt because the lower boundary of the lamellar phase is almost horizontal.[3,4] This means that $\ell$ diverges discontinuously as the temperature is raised along the phase boundary, i.e., a first-order transition. Similar behavior of the

lamellar phase is observed for other types of nonionic surfactant such as $C_{16}E_6$ and $C_{16}E_7$.[8,9] We show in Fig. 1 the phase diagram of the $C_{16}E_7$/water binary system. (The lower boundary of the lamellar phase in this figure is the horizontal line at around 67 °C). These experimental results suggest that the unbinding transition in surfactant solutions may be generally *first order* rather than second order.

In the present paper, we propose a possible mechanism that leads to a discontinuous first-order unbinding transition in surfactant solutions. Based on the mean-field theory by Milner and Roux (MR),[6] we consider a phenomenological coupling between the surfactant concentration and the other elastic degree of freedom. Although the predictive power of the MR theory is relatively weak compared to the functional-renormalization-group theory, it provides us a useful model to incorporate other degrees of freedom in a simple manner. Two possibilities are considered; (i) a membrane elastic degree of freedom and (ii) a bulk elastic degree of freedom. For both cases, we assumed that the coupling affects the second virial coefficient in such a way to enhance the net attractive interaction. Analysis of our models shows that the unbinding transition is second order when the coupling is weak, while it becomes first order when the coupling is strong enough. We
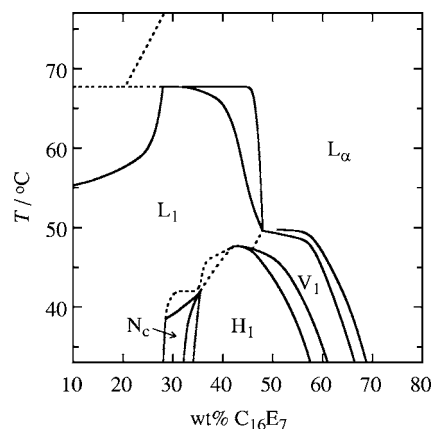


FIG. 1. Phase diagram of the $C_{16}E_7$/water system, redrawn from Fig. 1 in Ref. 9. $L_\alpha$, lamellar phase; $L_1$, isotropic micellar phase; $V_1$, cubic phase; $H_1$, hexagonal phase; and $N_c$, nematic phase.

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also determine the associated preunbinding transition line which separates the two lamellar phases of different spacing.[10] In particular, the coupling to the bulk elastic degree of freedom leads to a three-phase coexistence.

In the next section, we briefly review the theories of unbinding transitions. We put an emphasis on the MR theory for a stack of lamellae in a surfactant solution, and confirm that it predicts a second-order unbinding transition. In Secs. III and IV, we extend the MR theory to take into account the above mentioned coupling mechanism. We show that our model exhibits a first-order unbinding transition when the coupling is strong enough. Finally, we give some discussions in the last section.

## II. UNBINDING TRANSITION

Fluid bilayer membranes experience steric repulsion arising from their reduced undulation entropy. The corresponding interaction energy per unit area of the membrane was considered by Helfrich,[11]

$$v_s(\ell) = \frac{b(k_B T)^2}{\kappa(\ell - \delta)^2}, \qquad (1)$$

where $k_B$ is the Boltzmann constant, $T$ the temperature, $\kappa$ the bending rigidity, $\delta$ the membrane thickness, and $\ell$ the average distance between bilayers. Note that $\ell - \delta$ represents the intermembrane distance within which membranes can fluctuate. The numerical prefactor $b$ was calculated to be $b = 3\pi^2/128$ in the original paper,[11] but subsequent various simulation studies revealed that the value of $b$ is smaller than the above one by a factor of 2.[12–14]

In general, the combination of the above steric repulsion and other direct microscopic interactions, such as long-ranged van der Waals attraction and short-ranged hydration repulsion, determines whether two membranes bind each other or unbind between them.[15] Lipowsky and Leibler pointed out that solving a simple superposition of Eq. (1) and other direct interactions at a mean-field level gives incorrect (first-order) description of the unbinding transition.[2] An appropriate treatment of this problem using a functional renormalization-group method predicted that the unbinding transition should be second order (*critical* unbinding transition).

Later, Milner and Roux proposed a theory for the unbinding transition in a bulk of the lamellar phase following the spirit of mean-field theory for polymers.[6] In their treatment, the Helfrich estimate of the entropy is taken into account accurately, whereas the other direct microscopic interactions are approximately incorporated as a correction to the hard-wall result for the second virial coefficient. The suggested free energy *per unit volume* of a lamellar stack is

$$\hat{g}_{MR}(\phi) = -k_B T \hat{\chi} \phi^2 + \frac{b(k_B T)^2}{\kappa \delta^3} \frac{\phi^3}{(1-\phi)^2} - \hat{\mu}\phi, \qquad (2)$$

where the membrane volume fraction $\phi = \delta/\ell \geq 0$ cannot be negative. In the above, $\hat{\chi}$ is the correction to the hard-wall result, and is calculated by
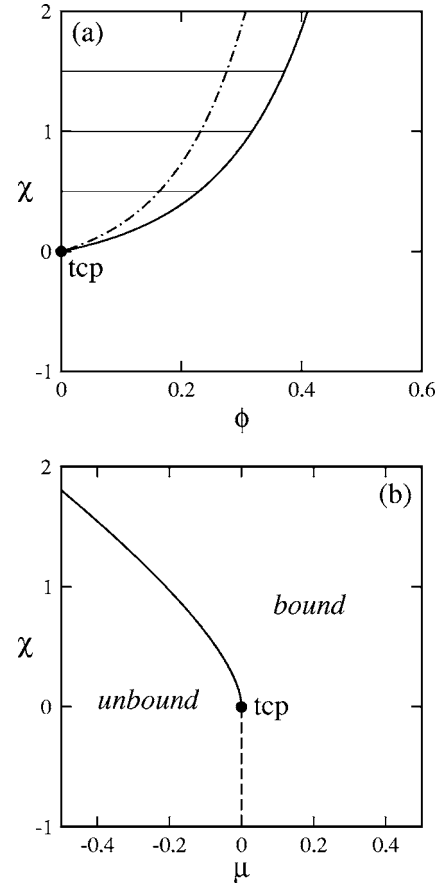


FIG. 2. The phase diagrams of the Milner and Roux model as a function of (a) surfactant volume fraction $\phi$ and virial coefficient $\chi$, and (b) surfactant chemical-potential $\mu$ and virial coefficient $\chi$. The solid line is a first-order line, whereas the dashed line is a second-order one. The horizontal lines and the dot-dashed line in (a) are tielines and the spinodal line, respectively. The filled circle denotes the tricritical point (tcp).

$$\hat{\chi} = -\frac{1}{2\nu^2} \int d\mathbf{r}(1 - \exp[-U_\nu(\mathbf{r})/k_B T]), \qquad (3)$$

where $U_\nu(\mathbf{r})$ is the interaction between bits of membrane of volume $\nu$. All the direct microscopic (van der Waals, electrostatic, and hydration) interactions are taken into account through $U_\nu(\mathbf{r})$. The chemical potential, $\hat{\mu}$, is needed for the conservation of the membrane volume fraction $\phi$. The factor of $(1-\phi)^{-2}$ in the second term comes from the finite membrane thickness [see Eq. (1)].[16]

It is convenient to rescale all the energy densities by $2b(k_B T)^2/(\kappa\delta^3)$. Then Eq. (2) can be presented as

$$g_{MR}(\phi) = -\chi\phi^2 + \frac{\phi^3}{2(1-\phi)^2} - \mu\phi. \qquad (4)$$

The corresponding phase diagrams in the $(\chi, \phi)$ and $(\chi, \mu)$ planes are shown in Fig. 2. The volume fractions and chemical potentials for the binodal and the spinodal satisfy the relations[16]

$$\chi_{bin} = \frac{\phi_{bin}}{(1-\phi_{bin})^3}, \quad \mu_{bin} = -\frac{\phi_{bin}^2(1+\phi_{bin})}{2(1-\phi_{bin})^3}, \qquad (5)$$

and

$$\chi_{sp} = \frac{3\phi_{sp}}{2(1-\phi_{sp})^4}, \quad \mu_{sp} = \frac{\phi_{sp}^2(\phi_{sp}^2 - 4\phi_{sp} - 3)}{2(1-\phi_{sp})^4}, \quad (6)$$

respectively. When $\chi > 0$ the binodal line separates between the bound phase and the unbound phases where $\phi = 0$. For $\chi < 0$, on the other hand, the *complete* unbinding of the lamellae occurs at $\mu = 0$ upon swelling with excess water.[17] These first-order and second-order lines are continuously connected at the tricritical point (tcp). If we denote $\chi_u$ as the value of $\chi$ at which the lamellae first unbind as a single phase, we have here $\chi_u = \chi_{tcp} = 0$. As we go down in $\chi$ along the binodal line in Fig. 2(a) [more precisely, infinitesimally on the lamellar side of coexistence in Fig. 2(b)] and approach $\chi_u$ from above, the repeat distance $\ell$ increases *continuously*, and the critical unbinding transition takes place. This is consistent with the prediction by Lipowsky and Leibler.[2]

So far, the unbinding transition in a bulk of lamellar phase has been discussed within the MR theory. Next, we extend the MR theory by considering another degree of freedom which is coupled to the volume fraction of the surfactant. Two models are proposed, (i) the coupling to the membrane elastic degree of freedom (model A), and (ii) the coupling to the bulk elastic degree of freedom (model B).

## III. MODEL A

### A. Free energy

As an example of the membrane elastic degree of freedom, we consider the interfacial area $S$ per surfactant molecule. This quantity can fluctuate around the so-called saturated state $S = S^*$ at which the effective surface tension vanishes.[18] If we define the fluctuation of the area by $s = (S - S^*)/S^*$, the free energy *per surfactant molecule* is simply given by[19]

$$f_s(s) = \frac{A}{2} s^2, \quad (7)$$

where $A > 0$ has the dimension of energy.

The proposed scaled free energy *per unit volume* of the system is

$$g_A(\phi, s) = -\chi\phi^2 + \frac{\phi^3}{2(1-\phi)^2} - \mu\phi - \gamma\phi^2 s + \frac{a}{2}\phi s^2, \quad (8)$$

with the constraint $\phi \geq 0$ as before and $a = (A/S^*\delta) \times [\kappa\delta^3/2b(k_BT)^2]$. The first three terms depend only on $\phi$, and are identical to the right-hand side of Eq. (4). The term $-\gamma\phi^2 s$ represents a phenomenological coupling between $\phi$ and $s$ with a dimensionless coefficient $\gamma > 0$. It is assumed here that the area fluctuation affects the bare virial coefficient so that the binary interaction between the surfactant molecules is shifted. Note that $\chi_{eff} = \chi + \gamma s$ can be regarded as an effective virial coefficient of the system. Moreover, a constant shift in $s$ can always be adsorbed by redefining $\chi$. A lower-order coupling term such as $\phi s$ simply renormalizes $\chi$ after the minimization with respect to $s$, and is neglected here. A somewhat similar coupling was proposed in Ref. 20 where the unbinding of a *single* mixed membrane was discussed.

Minimizing the free energy in Eq. (8) with respect to $s$ gives

$$s = \frac{\gamma}{a}\phi. \quad (9)$$

By substituting back this relation into Eq. (8), the free energy as a function of $\phi$ only becomes

$$g_A(\phi) = -\chi\phi^2 + \frac{\phi^3}{2(1-\phi)^2} - \frac{\gamma^2}{2a}\phi^3 - \mu\phi. \quad (10)$$

We then minimize $g_A(\phi)$ with respect to $\phi$ to get the equation of state. The two-phase region is obtained by the standard Maxwell construction.

The variable $s$ can represent other physical quantities. For example, $s$ can be the nematic order parameter magnitude of the surfactant molecules. In liquid-crystal systems, the microscopic interaction between two rodlike molecules depends not only on their relative distance but also on their relative orientation. Maier and Saupe considered that the interaction potential is lowered as the molecules align each other when they are located at a fixed distance.[21] Such an effect would lead to a virial coefficient which depends on the orientational order, as expressed in Eq. (8). In the lyotropic systems, however, the orientational order should vanish when $\phi \rightarrow 0$, and the last term in Eq. (8) is necessary. In fact, a linear relation between the orientational order parameter $s$ and the volume fraction $\phi$ [see Eq. (9)] has been indicated in some NMR studies of nonionic surfactant solutions.[22,23]

### B. Phase behavior

Here we discuss how the shape of the phase diagrams changes as the value of the coupling strength $\gamma^2/a$ is changed. (We do not change $\gamma$ and $a$ independently.) Depending on the coupling strength, there are two different types of phase behavior; (i) weak coupling regime ($\gamma^2/a < 1$) and (ii) strong coupling regime ($\gamma^2/a > 1$). The corresponding phase diagrams are shown in Figs. 3 and 4 for $\gamma^2/a = 0.5$ and 5, respectively.

In the weak coupling case $\gamma^2/a < 1$ (see Fig. 3), the phase behavior is basically unchanged compared to that of the MR model (see Fig. 2). Here the binodal and the spinodal are given by

$$\chi_{bin} = \frac{\phi_{bin}}{(1-\phi_{bin})^3} - \frac{\gamma^2}{a}\phi_{bin},$$

$$\mu_{bin} = -\frac{\phi_{bin}^2(1+\phi_{bin})}{2(1-\phi_{bin})^3} + \frac{\gamma^2}{2a}\phi_{bin}^2, \quad (11)$$

and

$$\chi_{sp} = \frac{3\phi_{sp}}{2(1-\phi_{sp})^4} - \frac{3\gamma^2}{2a}\phi_{sp},$$

$$\mu_{sp} = \frac{\phi_{sp}^2(\phi_{sp}^2 - 4\phi_{sp} - 3)}{2(1-\phi_{sp})^4} + \frac{3\gamma^2}{2a}\phi_{sp}^2, \quad (12)$$

respectively. We immediately see that these relations reduce to Eqs. (5) and (6) in the limit of $\gamma^2/a \rightarrow 0$. The binodal
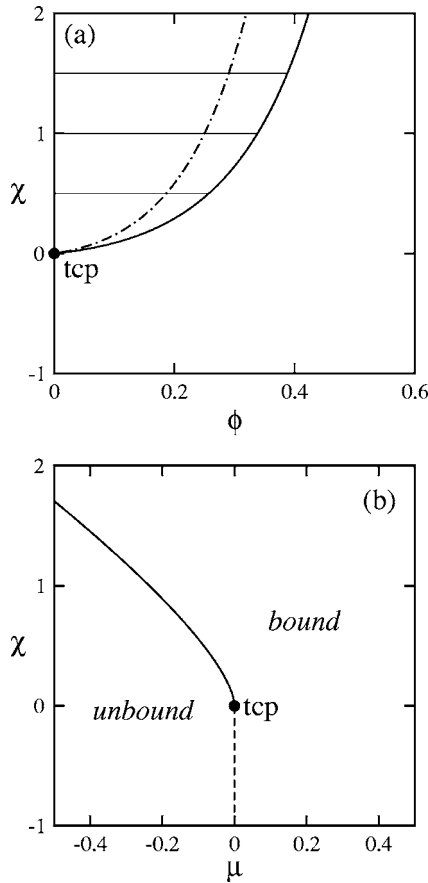
FIG. 3. The phase diagrams for $\gamma^2/a=0.5$ in model A as a function of (a) surfactant volume fraction $\phi$ and virial coefficient $\chi$, and (b) surfactant chemical-potential $\mu$ and virial coefficient $\chi$. The same notation of different lines is used as in Fig. 2. The filled circle denotes the tricritical point (tcp).

separates between the lamellar phase and the excess water. The tricritical point appears at $\chi_{\text{tcp}}=0$ which again coincides with the unbinding transition point; i.e., $\chi_u=\chi_{\text{tcp}}=0$. It should be noted, however, that the two-phase region in Fig. 3(a) is wider compared to that in Fig. 2(a). This is due to the enhanced attractive interaction between the surfactant molecules.

In the strong coupling regime $\gamma^2/a>1$ (see Fig. 4), there exists a first-order line separating two lamellar phases of different spacing $\ell$. This first-order line corresponds to the pre-unbinding line and ends at an ordinary critical point (cp). The locus of the critical point can be calculated from the conditions that both the second and the third derivatives of $g_A(\phi)$ vanish; $g_A''(\phi)=g_A'''(\phi)=0$. This yields

$$\chi_{\text{cp}}=-\frac{6\phi_{\text{cp}}^2}{(1-\phi_{\text{cp}})^5}, \quad \frac{\gamma^2}{a}=\frac{1+3\phi_{\text{cp}}}{(1-\phi_{\text{cp}})^5}. \tag{13}$$

In Fig. 5, we have plotted $\chi_{\text{cp}}$ as a function of $\gamma^2/a$.

As shown in Fig. 4(b), the second-order line ends at the critical end point (cep) on the first-order line. It is important to note that the value of $\chi$ at the critical end point is negative; $\chi_{\text{cep}}<0$. Since $\chi_u=\chi_{\text{cep}}$ in the strong coupling regime, the unbinding transition point is determined by the conditions $f_A(\phi)=f_A'(\phi)=0$, where $f_A(\phi)=g_A(\phi)+\mu\phi$. Then we have
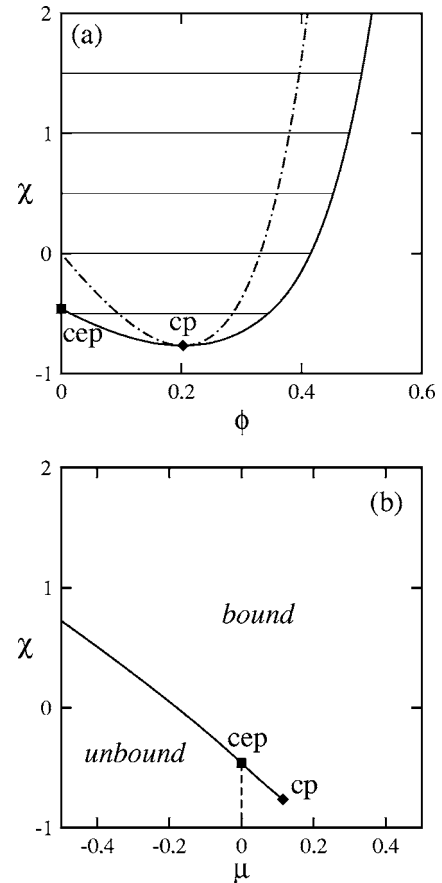


FIG. 4. The phase diagrams for $\gamma^2/a=5$ in model A. The same notation of different lines is used as in Fig. 2. The filled square and diamond indicate the critical end point (cep) and critical point (cp), respectively.

$$\chi_u=-\frac{\phi_u^2}{(1-\phi_u)^3}, \quad \frac{\gamma^2}{a}=\frac{1+\phi_u}{(1-\phi_u)^3}. \tag{14}$$

The behavior of $\chi_u$ as a function of $\gamma^2/a$ is also plotted in Fig. 5.

## IV. MODEL B

### A. Free energy

In the model B, we consider the bulk elastic degree of freedom $\sigma$. The suggested free energy *per unit volume* of the system is
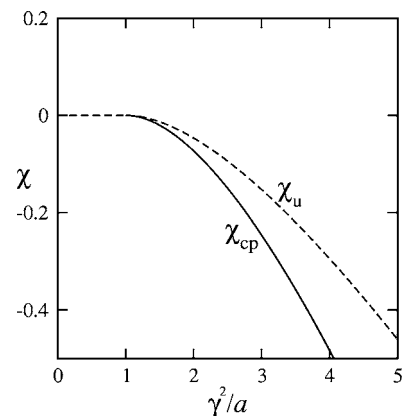


FIG. 5. The values of $\chi$ at the critical point $\chi_{\text{cp}}$ (solid line) and the unbinding transition point $\chi_u$ (dashed line) as a function of the coupling strength $\gamma^2/a$ for model A.

$$g_B(\phi,\sigma) = -\chi\phi^2 + \frac{\phi^3}{2(1-\phi)^2} - \mu\phi - \lambda\phi^2\sigma + \frac{c}{2}\sigma^2, \quad (15)$$

where $\lambda$ is a new dimensionless coupling constant and $c > 0$. The physical meaning of the coupling term $-\lambda\phi^2\sigma$ is similar to that in Eq. (8). The only difference compared to Eq. (8) is that the last term $c\sigma^2/2$ does not vanish in the limit of $\phi \to 0$. This is the reason why $\sigma$ is called the bulk elastic degree of freedom. Such a variable could play a role, for example, when not only the surfactant molecules but also the solvent molecules can sustain a local orientational order throughout the system. Although the above model may not directly describe the binary surfactant solutions, it is worth considering because of the conceptual difference and significance.

By minimizing Eq. (15) first with respect to $\sigma$, we obtain

$$\sigma = \frac{\lambda}{c}\phi^2. \quad (16)$$

Then the minimized free energy becomes

$$g_B(\phi) = -\chi\phi^2 + \frac{\phi^3}{2(1-\phi)^2} - \frac{\lambda^2}{2c}\phi^4 - \mu\phi. \quad (17)$$

which contains a quartic term in $\phi$ with a negative coefficient. This should be contrasted with the cubic term in Eq. (10), and leads to a somewhat different phase behavior.

## B. Phase behavior

For the model B, there are three different regimes; (i) weak coupling regime $(\lambda^2/c < 5.36)$, (ii) intermediate coupling regime $(5.36 < \lambda^2/c < 6.75)$, and (iii) strong coupling regime $(\lambda^2/c > 6.75)$.

In the weak coupling regime $\lambda^2/c < 5.36$, the phase diagrams are similar to those obtained for the weak coupling regime in the model A (see Fig. 3). The binodal and the spinodal are now given by

$$\chi_{bin} = \frac{\phi_{bin}}{(1-\phi_{bin})^3} - \frac{3\lambda^2}{2c}\phi_{bin}^2,$$

$$\mu_{bin} = -\frac{\phi_{bin}^2(1+\phi_{bin})}{2(1-\phi_{bin})^3} + \frac{\lambda^2}{c}\phi_{bin}^3, \quad (18)$$

and

$$\chi_{sp} = \frac{3\phi_{sp}}{2(1-\phi_{sp})^4} - \frac{3\lambda^2}{c}\phi_{sp}^2,$$

$$\mu_{sp} = \frac{\phi_{sp}^2(\phi_{sp}^2 - 4\phi_{sp} - 3)}{2(1-\phi_{sp})^4} + \frac{4\lambda^2}{c}\phi_{sp}^3, \quad (19)$$

respectively.

In the intermediate coupling regime $5.36 < \lambda^2/c < 6.75$, the phase behavior turns out to be qualitatively different, as shown in Fig. 6 for $\lambda^2/c = 6$. In this regime, a lamellar-lamellar coexisting region starts to appear. In addition, there is another coexistence region between the lamellar phase with a larger spacing (smaller $\phi$) and the excess water phase. As seen in Fig. 6(b), the corresponding first-order line, ends
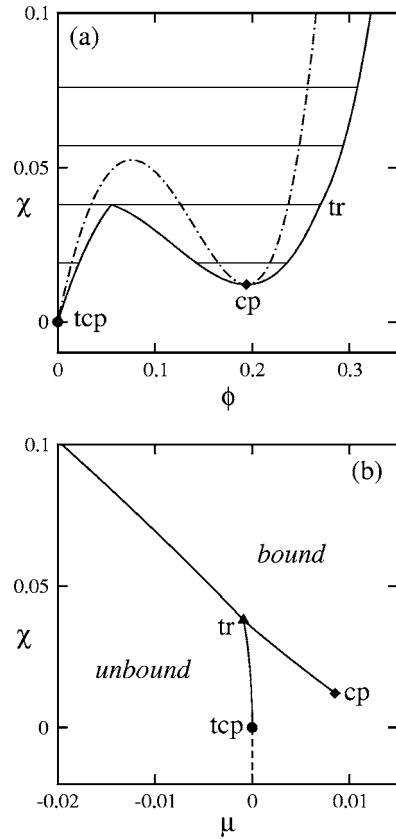


FIG. 6. The phase diagrams for $\lambda^2/c = 6$ in model B. The same notation of different lines is used as in Fig. 2. The filled circle, triangle, diamond indicate the tricritical point (tcp), triple point (tr), critical point (cp), respectively.

at a tricritical point $(\chi_{tcp} = \mu_{tcp} = 0)$ from which a second-order line emerges. Hence the unbinding transition takes place at $\chi_u = \chi_{tcp} = 0$ in this regime. As $\chi$ is increased, we reach a triple point (tr) at which the two lamellar phases and the unbound phase coexist. Above the triple point, the first-order line separates between the lamellar phase and the excess water. The locus of the critical point which appears for $\lambda^2/c > 5.36$ is

$$\chi_{cp} = \frac{3\phi_{cp}(1-5\phi_{cp})}{4(1-\phi_{cp})^5}, \quad \frac{\lambda^2}{c} = \frac{1+3\phi_{cp}}{4\phi_{cp}(1-\phi_{cp})^5}. \quad (20)$$

In Fig. 7, we have plotted $\chi_{cp}$ as a function of $\lambda^2/c$. We see that $\chi_{cp}$ is a decreasing function of $\lambda^2/c$, and is limited to $\chi_{cp} < 0.068$.

In the strong coupling regime $\lambda^2/c > 6.75$, the phase diagrams are similar to Fig. 4 of model A. The unbinding transition point is given by

$$\chi_u = \frac{\phi_u(1-3\phi_u)}{4(1-\phi_u)^3}, \quad \frac{\lambda^2}{c} = \frac{1+\phi_u}{2\phi_u(1-\phi_u)^3}. \quad (21)$$

The behavior of $\chi_u$ as a function of $\lambda^2/c$ is plotted in Fig. 7 as well.

## V. DISCUSSION

A few points merit further discussion. There are some other possibilities which may cause the unbinding transition to become a first-order one.[15] First, Lipowsky argued that,
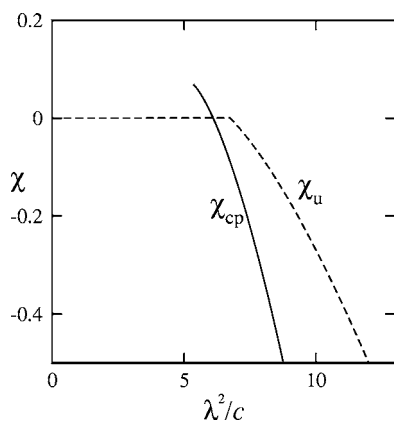
FIG. 7. The values of $\chi$ at the critical point $\chi_{cp}$ (solid line) and the unbinding transition point $\chi_u$ (dashed line) as a function of the coupling strength $\lambda^2/c$ for model B.

even in the presence of fluctuations, the unbinding transition of two membranes can be first order when the interaction potential exhibits a sufficiently high potential barrier.[24] We encounter such a potential barrier when the membranes carry electric charges. In this case, the direct interaction exhibits an attractive potential well at small separations and a repulsive potential barrier at intermediate separations. For non-ionic surfactant systems, however, the direct interaction potential exhibits only a single minimum resulting from a repulsive hydration and an attractive van der Waals interaction.

Second, Lipowsky discussed that, for a stack of $N$ membranes, the amplitude of the critical singularities have a strong $N$ dependence so that the critical region for the second-order transitions become very small.[25] As a result, the unbinding transition may be very abrupt in the large $N$ limit. This conjecture could explain, at least in part, the discontinuous nature of the unbinding transition in the surfactant systems. However, the quantitative phase behavior for an infinite stack has not yet been considered prior to our work.

Next, we refer to some other works which are related to the present paper. Some years ago, a direct observation of a discontinuous unbinding transition was reported for hydrated multilamellar phospholipid membranes.[26] Using x-ray reflectivity techniques, they measured the repeat distance as well as the fluctuation spectra. But since they did not observe an increase in the repeat distance as the temperature is raised, they concluded that the steric repulsion was not responsible for the unbinding. Later the same systems were reinvestigated by another group using grazing angle neutron-scattering techniques.[27] In contrast with the previous experiment, they detected the increase of the repeat distance, which was attributed to the enhancement of thermal fluctuations. On the other hand, they did not observe the unbinding transition, and even questioned the results of Ref. 26. At the moment, it is not clear whether multilamellar phospholipid membranes exhibit the unbinding transition or not. However, we expect that the coupling between the local lipid concentration and the elastic degree of freedom will drive the unbinding transition to be first order.

From theoretical viewpoints, Matsen showed that a blend of asymmetric diblock copolymers and homopolymers exhibits an unbinding transition by using a self-consistent-field theory.[28,29] With the use of the same method, Janert and Schick investigated a mixture of symmetric diblock copolymers and homopolymers which have identical chain lengths.[3] They demonstrated that the unbinding in this system is first order, and located the preunbinding transition line. In their later work, the channel of unbinding is shown to close as soon as the homopolymer is made slightly larger than the block.[4] It should be noted, however, that these calculations do not include the attractive long-ranged van der Waals interaction, nor do they include the effect of fluctuations.

In this paper, we did not consider the presence of the isotropic micellar phase, and argued only the phase separation between the bound and unbound phases. However, in the experimental phase diagram shown in Fig. 1, the micellar phase (denoted by $L_1$) exists in the lower surfactant concentration region. This micellar phase not only coexists with the lamellar phase (denoted by $L_\alpha$), but also exhibits the phase separation between a dilute and a dense micellar phases. In order to explain all of these phase behaviors, one has to take into account the free energy of the micellar phase and compare it with that of the lamellar phase. Such an analysis as well as other extensions of the present study are currently under progress.

In summary, we have proposed a phenomenological model which exhibits a first-order unbinding transition of lamellae in surfactant solutions. The main idea is to take into account the coupling effect between the surfactant volume fraction and the other elastic degree of freedom. For the latter, we considered two cases, (i) a membrane elastic degree of freedom or (ii) a bulk elastic degree of freedom. For both models, the unbinding transition becomes discontinuous when the coupling is strong enough. We also determined the associated preunbinding line which separates the two lamellar phases having different repeat distances.

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