Polymer induced phase coexistence in systems of lamellar phases

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The effect of adding nonadsorbing polymer to a lamellar phase of surfactant bilayers is studied theoretically. We find that the polymer produces coexistence between two lamellar phases of different layer spacings. The coexistence region is a closed loop, as in the experiments of Ficheux et al. [J. de Physique II 5 823 (1995)]. Within our model the coexistence is driven by depletion.

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I. INTRODUCTION

Many surfactants in solution form bilayers, i.e., two back-to-back layers of surfactant molecules with their alkane-like tails in the centre and only their hydrophilic headgroups in contact with the surrounding water [1]. These bilayers have been extensively studied both because of their diverse behaviour [2] and because they serve as simplified model systems for cell membranes [3]. In solution, bilayers form a stack of parallel layers: a lamellar phase. Here, we study theoretically the effect of adding non-adsorbing polymer to an unbound lamellar phase [4–6]. In particular, we attempt to understand some recent experimental results [4,6]. A schematic of the system is shown in Fig. 1. An unbound lamellar phase is one in which the interactions between the bilayers are purely repulsive, leading to a depletion in the density of polymer segments near the surface of a bilayer [7–9]. Thus the polymer induces an attraction between the bilayers. The attraction leads to phase separation: two lamellar phases with different spacings between the bilayers coexist.

II. MODEL AND THEORY

The lamellar plus polymer phase is described starting from the free energy of a pure lamellar phase which is well known, see Refs. [1,2,4]. Then semidilute polymer solutions are discussed and the confining effect of the bilayers on a semidilute polymer solution is estimated. The confinement free energy of the polymer solution between the bilayers is then added to the free energy due to the direct interaction between the bilayers to produce a final free energy. This free energy is used to calculate the phase behaviour of the bilayers plus polymer system.

A. The interactions between the bilayers

We treat the lamellar phase as a stack of uniformly-spaced rigid plates; thus we can define a separation $d$ between consecutive plates in the stack. This is the spacing between the surfaces of consecutive plates; the mesoscopic period is $d + d_0$, where $d_0$ is the (assumed constant) thickness of a bilayer. Of course, the bilayers are not completely rigid but they bend on length scales that are much larger than $d$ or the size of a polymer coil [2]. We neglect any interactions between nonadjacent plates.

In the absence of polymer the free energy $F$ of a stack of $n$ layers, each of area $A$, is taken to be

$$ F = \frac{A_e}{d} + A_h \exp(-d/\lambda_h), $$

(1)

The first of the two terms of Eq. (1) is the contribution of electrostatic interactions and is long ranged while the second term is due to the so-called hydration forces [1,2,3,4]. The hydration interaction is much shorter ranged than the electrostatic interaction, its range is of the order of 1nm. We will not derive Eq. (1) here, it is a quite standard expression for the interaction of a pair of charged bilayers separated by water. The electrostatic term is derived from the Poisson-Boltzmann equation for two charged plates separated by a gas of the counterions [3,4] without added salt to screen the electrostatic interactions between the bilayers. Moderate screening has been found not to change the phase behaviour we predict. $A_e$ is a positive constant that is proportional to the surface charge density on the plates. The second term in Eq. (1) is essentially an empirical description of the strong repulsion between two bilayers less than about 1nm apart. This repulsion is, to a good approximation, exponential. Although it is strong, $A_h \gg A_e/d$ for $d = 1$nm, this repulsion is much shorter ranged than the electrostatic interaction; $\lambda_h$ is small $\approx 0.2$–0.35nm [2,3,4]. Equation (1) does not include the contribution to the interlayer interaction of the Helfrich or undulation forces [3,4] because these are dominated by the electrostatic repulsions [3] if, as here, the electrostatic repulsions are not screened.
B. The polymer–bilayer interactions

As the polymer is nonadsorbing the bilayer–polymer interaction is assumed to be a simple excluded volume interaction, i.e., each bilayer excludes polymer segments from a planar volume. The polymer will be in the semidilute regime, we therefore use a simple scaling description of the structure and thermodynamics of the polymer solution \(10\). The size of an isolated polymer coil of \(N\) segments each of length \(a\), is measured by its radius of gyration \(R_G\) which is given by \(R_G \sim a N^{3/5}\), in a good solvent \(10\). The concentration of the polymer is specified by its volume fraction \(\phi_b\). The subscript \(b\) is to remind us that it is the volume fraction of the polymer far from the surface of a bilayer. Near the surface of a bilayer the polymer’s density drops below \(\phi_b\). The average volume fraction of polymer in the surfactant plus polymer system is not equal to \(\phi_b\); it will be less. The correlations (fluctuations) in an isolated polymer coil extend across the entire coil; the correlation length \(\xi\) is thus \(\xi \sim R_G\). In a bulk solution of polymer, when the polymer coils begin to overlap, interactions between different chains reduce the correlation length \(\xi\) \(10\). The overlap volume fraction \(\phi_b^*\) is \(\phi_b^* \sim N^{-1/5}\). This volume fraction is the boundary between the dilute and semidilute regimes; below \(\phi_b^*\) the interactions between chains can be treated as a perturbation but above \(\phi_b^*\) the interaction between a pair of chains is \(\gg k_BT\), where \(k_B\) is Boltzmann’s constant and \(T\) is the temperature. So, \(\xi = R_G\) in the dilute regime, and

\[
\xi \sim a \phi_b^{-3/4}\ 
\text{in the semidilute regime. (2)}
\]

We require the form of the osmotic pressure of a polymer solution, it is

\[
\frac{\Pi}{k_BT} \sim \left(\frac{a}{\xi}\right)^3 \sim \phi_b^{9/4}\ 
\text{in the semidilute regime. (3)}
\]

The Helmholtz free energy of a polymer solution \(F_p\) is also required. We can obtain the density dependent part of the free energy, which is all that is required for determining phase coexistence, from the thermodynamic relation \(\Pi = -\partial F_p/\partial V\), where \(V\) is the volume of the solution. The volume derivative may be transformed into a density derivative. Then the integration of \(\Pi\) as a function of density leads to

\[
\frac{F_p a^3}{k_BT} \sim \text{const.} + \phi_b^{9/4}\ 
\text{. (4)}
\]

Finally, the polymer’s chemical potential \(\mu_p\) is obtained from \(\mu_p = F_p a^3/(V \phi_b) + \Pi a^3/\phi\)

\[
\frac{\mu_p}{k_BT} \sim \text{const.} + \phi_b^{5/4}\ 
\text{. (5)}
\]

All of the above is for a bulk polymer solution, i.e., a solution just of polymer. In the presence of bilayers the solution is no longer uniform, the polymer density at a point will depend on the distance from the bilayers above and below the point. However, at distances \(\gg \xi\) from any bilayer, the polymer density will reach a constant value.

We model the bilayer–polymer interaction as a hard wall–polymer interaction \(11\); there is no adsorption. The correlation length \(\xi\) is a measure of the distance over which correlations decay. Therefore, if we introduce a single bilayer, modelled as a hard sheet, into a polymer solution it perturbs the solution above and below its surface out to a distance of order \(\xi\). This is a much longer ranged perturbation than in a simple liquid where the density of the fluid returns to its bulk value in a distance of a few times \(a\). Within \(\xi\) of the surface the conformational freedom of the polymer chains is reduced by the presence of the surface, reducing their entropy and hence their density near the surfaces of the bilayers \(11\). The introduction of the bilayer has changed the free energy of the polymer solution by introducing two polymer–wall ‘interfaces’ (they are not true interfaces as they do not separate two coexisting bulk phases). This layer of reduced density is often called a depletion layer \(11\). We require the difference \(\gamma\), between the free energy of unit area of the layer which is depleted in polymer and the free energy of unit area of a layer of the same width of the bulk fluid. It is, essentially, the free energy of a hard wall–polymer interface. The picture is of a layer of thickness \(\xi\) in which the density drops from its bulk value \(\phi_b\) to a much lower value. The excess free energy of the depletion layer is then approximately equal to the amount of work done in squeezing out the polymer from a slab of unit area and width \(\xi\) \(10\). Thus,

\[
\gamma \sim \Pi \xi\ 
\text{. (6)}
\]

This is the surface tension of one wall–polymer solution interface. In a system of bilayers and polymer we can use this expression provided both \(\Pi\) and \(\xi\) correspond to those values in a bulk solution at the density of the polymer solution far, \(\gg \xi\), from the surface of any bilayer. This can perhaps be made more clear if we consider that the surfactant plus polymer system is in equilibrium with a pure polymer solution across a semi-permeable membrane permeable to the polymer but not to the surfactant. Then the volume fraction of the pure polymer solution in equilibrium with our bilayers plus polymer solution, is the volume fraction at which the \(\Pi\) and \(\xi\) of Eq. \((6)\) should be evaluated.

Each bilayer creates two polymer depletion layers. If the bilayers are sufficiently far apart, \(d \gg \xi\), then these layers are independent and we have \(2n\) depletion layers, each of which contributes an amount to the free energy given by Eq. \((6)\). However, as the bilayer separation \(d\) is reduced to \(\sim \xi\) the depletion layers of adjacent bilayers overlap. When the layers overlap, the volume occupied by these layers is less and therefore the total free energy associated with these layers decreases. It is this reduction
in free energy which, we suggest, is responsible for creating coexistence between two bilayer phases with different bilayer spacings.

A difficulty now arises: the analysis which led to our estimate of \( \gamma \) in Eq. (1) was purely qualitative, whereas we now require a definite expression for how the free energy of two depletion layers changes as they coalesce. The definite expression is required to calculate a theoretical phase diagram in order to compare with experimental phase behaviour. The free energy of a pair of depletion layers \( \gamma_2(d) \), must be \( 2\gamma \) if there are far apart, \( d \gg \xi \). Within the scaling approach there is only one relevant length scale: \( \xi \). Thus, \( \gamma_2 \) is of the form

\[
\gamma_2(d) = 2\Pi \xi f(d/\xi); \quad (7)
\]

that is, we are assuming that the density dependence is only through \( \xi \). The functional form of \( f(d/\xi) \) is the same at all densities. When \( d \ll \xi \) the polymer density between the two bilayers will be much less than in the bulk at the same chemical potential. But if the polymer density between the plates is negligible then the pressure exerted by the polymer inside the plates is negligible and the pressure due to the polymer solution is the negative of the pressure of the bulk polymer solution, independent of the separation \( d \). If the polymer contribution to the pressure is a constant then its contribution to the free energy must be \( \Pi d \), which forces \( f(d/\xi) = d/(2\xi) \), for \( d \ll \xi \). In the other limit, \( d \gg \xi \) \( \gamma_2 = 2\gamma \) and so \( f(d/\xi) = 1 \). A function which satisfies both these requirements is \( f(z) = \tanh(z/2) \). This is merely an ad hoc function which is consistent with the little we definitely know about the free energy of a polymer solution in a slit [12]. Brooks and Cates [10] have taken a different approach to the same problem. They obtain a free energy expression valid for all values of \( d \) by forcing the different scaling theory free energies [2] in the different scaling regimes to match. Polymer induced coexistence occurs for \( d/\xi \sim 1 \) and so it is for these values of \( d/\xi \) that \( f(z) \) is required. However, scaling theory is unable to predict the form of the free energy when the parameter \( d/\xi \) is of order unity. So, where we find coexistence, there is no reason to expect the free energy expression of Brooks and Cates to be any more accurate than the much simpler interpolation formula given here. They found coexisting lamellar phases, as we will do, but they did not find reentrance. In order to find reentrance it is necessary to explicitly include the contribution of hydration forces, which Brooks and Cates did not do.

For the bilayer plus polymer solution system we use the variables \( d \) and \( \mu_p \), as these are most convenient. A thermodynamic potential \( \Gamma/(nA) \) for a pair of adjacent interacting bilayers is then obtained by adding the Helmholtz free energy due to the repulsions between the bilayers \( F/(nA) \), to the grand potential of the polymer between the bilayers, where the grand potential includes an interfacial term, \( \gamma_2 \). We treat the slit between a pair of bilayers as a thermodynamic phase. The grand potential of the polymer in the slit is then, by definition [12],

\[
\Gamma = -2\Pi d + \gamma_2 A, \quad \text{as the volume of the phase is } Ad.
\]

As we are fixing the chemical potential not the density of the polymer the bulk part of the contribution of the polymer is not its Helmholtz free energy but \(-IV\). So, from Eqs. (6) and (7)

\[
\frac{\Gamma}{nA} = \frac{F}{nA} - \Pi d + 2\Pi \xi f(d/\xi) \quad (8)
\]

The right hand side of Eq. (8) is \( \Gamma \) per slit. The three terms are the direct repulsion between the two bilayers, the bulk part of the grand potential of the ‘phase’ between the slits and the interfacial part of the grand potential of this ‘phase’. Equation (8) is correct in the two limits of pure bilayers and pure polymer, and the third term is a crude approximation to the additional cost of the polymer–bilayer depletion layer. In the derivation of Eq. (8) we have implicitly treated the bilayers plus polymer mixture not as a mixture but as a polymer solution between a stack of hard walls. Because of this assumption II is unaltered by phase separation and is the same in the coexisting phases. It is not the pressure of the bilayer plus polymer system.

Coexistence can be found from the common tangent condition. This leads to the requirement that at coexistence the two phases have equal values of \( \partial[\Gamma/(nA)]/\partial d \) and \( \Gamma/(nA) - \Pi = 0 \) for the polymer is not its Helmholtz free energy but \( \gamma_2 A \). For the purposes of calculation we express them in reduced units. These units are defined using the length of a polymer segment \( a \) as our length scale and as our energy scale we use \( k_B T \). Then \( A_c, A_h, \lambda_h \) and \( R_G \) are expressed in units of \( k_B T/a, k_B T/a^2 \), and \( a \), respectively. We take \( k_B T = 4 \times 10^{-21} \text{J} \) and \( a = 0.3 \text{nm} \); the first is approximately its value at room temperature and the second is reasonable for a flexible polymer. We set \( A_c = 0.5 k_B T/a \), \( A_h = 50 k_B T/a^2 \), \( \lambda_h = a \) and \( R_G = 10a \). These values correspond to \( A_c = 6.67 \times 10^{-12} \text{J m}^{-1}, A_h = 2.22 \text{J m}^{-2} \), \( \lambda = 0.3 \text{nm} \) and \( R_G = 3 \text{nm} \). Ficheux et al. report an \( R_G = 2.9 \text{nm} \) [11]. A hydration decay length of \( 0.3 \text{nm} \) is approximately what has been found in a number of experiments [11,13]. Our value of \( A_h \) is comparable to the estimate given by Roux and Safinya of \( 2 \text{J m}^{-2} \) [13] and our \( A_c \) is comparable to the \( 4.49 \times 10^{-12} \text{J m}^{-1} \) obtained from (the dominant term in) the solution of the Poisson-Boltzmann equation [11].

Using this set of parameters, we have calculated the phase diagram of a stack of bilayers in the presence of a
polymer solution; the $\Pi-d$ plane of the diagram is shown in Fig. 2. There is a closed region of phase coexistence, as in the experiment of Ficheux et al.; it is bounded at high and low polymer pressures by two critical points. Note, however, that Ficheux et al do not rule out the possibility of the polymer adsorbing onto the bilayers. If too little or too much polymer is added no phase coexistence is found. The presence of a closed loop of phase separation is distinctly unusual. We will show why theory predicts it in the hope that our theory provides a reasonable description of the experiment of Ficheux et al.. It is worth noticing that the closed loop is entirely within the semidilute regime. The dashed curve in Fig. 2 shows $2\xi$ which only reaches its $2R_G$, indicating the crossover to the dilute regime, at values of $\Pi$ below those of the phase coexistence loop.

In the absence of polymer, the free energy $\Pi$, and the pressure, of a stack of bilayers is a monotonically decreasing function of $d$. The plates repel each other at all separations due to the repulsive electrostatic and hydration interactions. In the presence of polymer, there is an additional term in the thermodynamic potential $\frac{\Pi}{d}$, from the depletion layers. It is the overlap of these layers that is driving phase separation. For a stack with $d$ a few times $\xi$, the depletion layers contribute nearly $2\gamma$ per bilayer. However, if this phase separates into two phases: one with a large $d$ and one with a $d \lesssim 2\xi$, then the total free energy of the polymer decreases because of the reduced total volume of the solution within $\xi$ of a bilayer surface. Thus the total contribution of the depletion layers to the free energy is reduced, at a cost in free energy due to the bilayer–bilayer interactions. As the parts of the free energy from bilayer–bilayer interactions increase more rapidly than linearly, the phase separation necessarily increases this part of the free energy.

The total free energy available from overlapping the polymer depletion layers is of the order of $\Pi \xi$. Thus, phase separation will only occur if this is sufficient to overcome the repulsion of the bilayers. Of course, this repulsion decreases as $d$ increases; so if $\xi$ is large the polymer depletion layers overlap when the bilayers are far apart and repel each other only weakly. Conversely, if $\xi$ is small the repulsions are strong. The polymer solution can only overcome the bilayer repulsions and produce two bilayer phases if both $\Pi$ and $\xi$ are sufficiently large. In the semidilute regime $\xi$ decreases as $\Pi$ increases and so the two requirements are, to an extent, antagonistic. They are only satisfied for a range of $\Pi$.

The pressures due to the electrostatic and hydration interactions are $A_e/d^2$ and $(A_h/\lambda_h)\exp(-d/\lambda_h)$, respectively. In order for the polymer to control the phase behaviour the osmotic pressure of the polymer must be greater than both of these, at the separations at which the polymer depletion layers begin to overlap. So, we have two inequalities which must be satisfied in order for there to be phase separation,

$$\Pi > A_e/\xi^2. \quad (9)$$

and

$$\Pi > \frac{A_h}{\lambda_h} e^{-\xi/\lambda_h}. \quad (10)$$

Both of these inequalities only give the correct order of magnitudes. The correlation length $\xi$ varies with $\Pi$ as $\xi = a(\Pi/T)^{-1/3}$. Using this relation we see that the right hand side of Eq. (10) varies as $\Pi^{2/3}$, more slowly than the left hand side. Thus Eq. (10) provides a lower bound to the polymer osmotic pressure required to induce phase coexistence. For values of $\Pi$ above this bound the overlap of the interfaces releases enough free energy to overcome the electrostatic repulsions. Now, consider Eq. (10). If we express $\xi$ in Eq. (10) in terms of $\Pi$ we see that the right hand side of Eq. (10) increases with $\Pi$ as $\exp(-\Pi^{-1/3})$. This increase is more rapid than linear and so Eq. (10) provides an upper bound to the polymer osmotic pressure required to induce phase coexistence. The presence of these lower and upper bounds — due to the long and short ranged parts of the bilayer repulsions, respectively — leads straightforwardly to a closed loop coexistence region. There is slight subtlety in that the loop is $d \approx 15$ which is $5\lambda_h$. The hydration repulsion is able to have an effect at such long range because the electrostatic repulsions and polymer induced attractions are delicately balanced in the coexistence region. Analogous behaviour has been predicted by Gast et al. when polymer is added to a suspension of charged spherical particles. There, as here, the decreasing range of the polymer induced attraction can cause reentrant miscibility. When the spheres repel each other with a long ranged electrostatic repulsion then the range of the polymer induced attraction between the spheres must have a longer ranged than this repulsion.

As polymer is added the dielectric constant of the solution between the bilayers decreases; decreasing the repulsive electrostatic interactions. Our neglect of this effect may cause us to underestimate the size of the coexistence loop but incorporating a polymer concentration dependent $A_e$ will not change the qualitative phase behaviour.

**IV. CONCLUSION**

Our theoretical model yields a closed-loop phase-coexistence region in the phase diagram. The model is a simple, additive, combination of a standard model for the interaction between charged bilayers and a crude scaling form for the free energy of a polymer solution in a slit. It provides a description of the behaviour of a mixture of surfactant bilayers and semidilute nonadsorbing polymer on a length scale of 1–10nm; the length scale on which the entropy of the polymer solution and the repulsive bilayer–bilayer interactions are competing. Thus, we provide an explanation of the phase behaviour in terms of behaviour at mesoscopic length scales. The model shows...
qualitatively the same behaviour as found in experiment [6], without any fitting. This encourages us to believe that our theory describes correctly the mechanism behind the experimental observations.

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FIG. 1. Schematic of a pair of bilayers with a polymer solution between them. The thick curves denote the surfaces of the bilayers and the polymer is represented by the entangled thinner curves. $d$ is the spacing between the bilayers and $\xi$ is the polymer correlation length. Note the low density of polymer near the surfaces of the bilayers: the depletion layer.
**FIG. 2.** The phase diagram of a bilayer plus polymer solution system, as calculated from the thermodynamic potential \(\Pi\), with the parameter values given in the text. \(\Pi\) is the osmotic pressure of the polymer and \(d\) is the spacing between the surfactant bilayers. The solid curve separates the one and two-phase regions and the dashed curve is \(2\xi\) as a function of the osmotic pressure of the polymer \(\Pi\). As \(\Pi\) decreases \(\xi\) increases until it reaches the radius of gyration, equal to \(2d\) here, whereupon it remains constant. The thin horizontal lines are tie lines.