

First-order unbinding and pre-unbinding in amphiphilic systems

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Abstract

We consider swollen lamellar phases in binary systems of amphiphile and solvent. We argue that the abrupt swelling of lamellar phases is the result of a first-order unbinding transition. Employing a self-consistent field theory to examine a similar system of homopolymer/diblock blends, we demonstrate that the unbinding here is indeed first-order by locating the associated line of pre-unbinding transitions. Along this line, two lamellar phases with different wavelengths coexist.

One of the most unusual features exhibited by some binary mixtures of amphiphile and water is the extent to which a phase of bilayers of the former can be swollen by the latter. For example[1], in the system of the n-akyl polyglycol ether $C_{12}E_5$ and water, the wavelength of the lamellar phase can exceed 300nm. It is surprising that the lamellar phase remains a distinct, ordered phase while consisting of 98.8 per cent water. A second surprising feature of this system is the abruptness of the transition to this swollen phase from one with a wavelength on the order of 7nm, a particularly small distance when it is compared to the 3.74nm thickness of the bilayer itself. A result of the abrupt transition is that the lower boundary of the lamellar phase in the temperature, concentration plane is almost horizontal. (See Fig. 1.)

As discussed below, analysis of the unbinding transition in this system is complicated by the fact that the role of fluctuations is essential; without them, the long-ranged van der Waals attraction between amphiphile bilayers would prevent any unbinding at all. Currently, the nature of the transition brought about by these fluctuations is not known[2, 3, 4]. Even the form of the appropriate Landau expansion in a single order parameter is not settled[5, 6, 7].

Because an understanding of the results of a mean-field analysis is a prerequisite for the solution of the full problem, we have examined this transition in a binary system which is well characterized employing a theory which is well understood. In particular, we have investigated a blend of diblock copolymer and homopolymer employing self-consistent field theory. That such systems can exhibit an unbinding transition within the purview of a mean-field theory was recently shown by Matsen[8, 9].

We considered an incompressible mixture of flexible, symmetric, AB diblock copolymers of polymerization index N and flexible A homopolymers of the same index. A and B monomers of equal statistical segment length, a , interact with a con-

tact potential whose strength is given by the Flory parameter χ , which is inversely proportional to temperature, T . We have employed self-consistent field theory in the grand canonical ensemble[8], and solved the self-consistent equations numerically after expanding them in a complete Fourier series[10] in one spatial coordinate. The phase diagram of this system is dominated by a disordered fluid phase, and a lamellar phase consisting of bilayers of copolymer with homopolymer between them. We find that for values of $1/(\chi N)$ less than $1/11.767$, the addition of A homopolymer, or equivalently the decrease in volume fraction ϕ of copolymer, has only a small effect on the period of the lamellar phase, and eventually brings about a first order transition between the lamellar phase of short wavelength and the disordered phase. There is a region of coexistence between these phases in the T, ϕ -plane. For $1/(\chi N)$ greater than $1/11.767$, however, addition of homopolymer swells the bilayers continuously producing a line of complete unbinding transitions[11] which extends to a Lifshitz critical point. The transition between these two behaviors is quite abrupt, just as was found by Matsen for a similar system of slightly asymmetric AB diblocks and A homopolymers of the same index of polymerization[9].

This description of the unbinding transition is incomplete, however. As one approaches the unbinding transition along the line of coexistence between lamellar and disordered phases, one should be able to distinguish between two possible scenarios. In the first, denoted critical unbinding[12], the distance between bilayers in the lamellar phase, ℓ increases continuously as the temperature approaches the unbinding temperature T_u . Because the volume fraction of copolymer is inversely related to the spacing ℓ , the difference between copolymer volume fractions in the disordered and lamellar phases vanishes continuously with temperature. In the second scenario, first-order unbinding, the distance between bilayers jumps discontinuously at the unbinding temperature T_u from some finite value to infinity. Consequently the difference between copolymer volume fractions in disordered and

lamellar phases vanishes discontinuously. If this is the case, we expect, in analogy to first-order wetting transitions [13], a line of first-order pre-unbinding transitions to emerge from this transition, i.e. a line which separates two lamellar phases of different spacing ℓ . It should end in a critical point. The first-order unbinding transition at T_u is a critical endpoint.

We have studied carefully the phase diagram in the vicinity of the unbinding temperature, considering disordered, lamellar, and hexagonal phases. The hexagonally perforated lamellar phase[8, 9] was not considered as it is not observed in the amphiphile, water system. We have located a pre-unbinding line. It follows that, for this polymer system, the unbinding transition is indeed first-order. This result has been checked by employing up to 40 basis functions, obtaining an accuracy of the free energy of one part in 10^8 . The phase diagram is shown in Fig. 2 in the $1/(\chi N)$, ϕ -plane. Like the pre-wetting line[14], the pre-unbinding line is quite short; it originates at the unbinding transition, $\chi N = 11.767$, and ends at the pre-unbinding critical point, $\chi N = 11.339$. At the former, the lamellar spacing of the bound phase is $\ell = 2.39aN^{1/2}$, while at the latter $\ell = 2.70aN^{1/2}$.

The characteristic features of the phase diagram can be obtained without solution of the full mean field theory by considering a Landau expansion of the free energy. By analogy with wetting transitions in systems with short ranged forces[13], we assume an expansion of the form:

$$F = F(0) + a(T) \exp(-\ell/D) + b \exp(-2\ell/D) + c \exp(-3\ell/D) + \dots, \quad (1)$$

where ℓ is the lamellar spacing and D is some length scale, characterizing the width of each bilayer. For this form of the free energy with b negative and c positive, one finds a first-order unbinding transition at the temperature T_u given implicitly by $a(T_u) = b^2/4c$. At this point, the lamellar spacing jumps from $\ell_0 = D \log(2c/b)$, its value in the bound phase, to infinity. For $T > T_u$, there is a complete unbinding in which, for sufficiently small chemical potential μ , the lamellar spacing diverges

according to $\ell \sim D \log(1/\mu)$, with μ measured from the transition. Near the line of complete unbinding but within the lamellar phase, one encounters the pre-unbinding line at which lamellar phases with long and short periods coexist. As the transition temperature T_u is approached from above along the pre-unbinding line, the lamellar spacing diverges as $\ell \sim -D \log(T - T_u)$, leading to a horizontal lower boundary of the lamellar phase. All these predictions are in agreement with the results of the full self-consistent field theory.

Of course, a critical unbinding transition is also possible and would occur if $a(T)$ in Eq. 1 were to change sign at T_u , with b and c positive. If T_u were approached from below on the coexistence line between the lamellar and the disordered phase, the lamellar spacing would diverge as $\ell \sim D \log(2b/|a|)$ with $a \sim T - T_u$. Equivalently, $T - T_u \sim -\exp(-\ell/D)$, so that the lower boundary of the lamellar phase would be flat as it unbinds.

Our calculation does not include the attractive long-ranged van der Waals interaction which exists between bilayers of amphiphile, nor does it include the effect of fluctuations. It is well known that these fluctuations produce a repulsive interactions between bilayers[15] which decreases as ℓ^{-2} . At large separations, this repulsion will dominate the van der Waals attraction, which decreases as ℓ^{-4} for large separations, and can bring about an unbinding transition. Whether it is a continuous or first-order one is not known. The effect of fluctuations on the unbinding of two membranes was considered by Lipowsky and Leibler[12] who analyzed an effective interface Hamiltonian by a functional renormalization group transformation. They found that the transition was continuous with $\ell \propto (T_u - T)^{-\psi}$, and $\psi = 1$. Because the density of amphiphile, ϕ , is proportional to ℓ^{-1} , this result for the unbinding of two membranes, if applicable to the lamellar phase of an infinite number of membranes, would imply that the difference in density between the disordered and lamellar phases would decrease linearly with $T_u - T$. The lower boundary of

the lamellar phase would be a straight line of non-zero slope. This is not the case in the experimental results of Fig.1. More recently, Lipowsky[4] has argued that for sufficiently strong attractive potentials, the unbinding transition of two membranes can be first-order even in the presence of fluctuations. The effect of fluctuations on a stack of three membranes was examined by Netz and Lipowsky[3] employing Monte Carlo simulation. They found a value of $\psi \approx 0.91$ which, if applicable to the lamellar phase, would produce a lower boundary of the lamellar phase which becomes flat very near the critical point. There are no comparable results for an infinite stack, as in a lamellar phase.

A further effect of fluctuations is that they are expected to prevent the lamellar phase from unbinding completely[16]. This is because the orientational order of the lamellar phase can no longer be sustained when the distance between lamellae becomes of the order of the persistence length of the bilayers. At this point a first-order transition to a disordered, but structured phase occurs, which is commonly referred to as the L_3 or sponge phase. This converts the first-order unbinding transition from a critical endpoint to a triple point. Here the disordered phase coexists with two bound lamellar phases; one of short period, and the other of long period, of the order of the persistence length.

Finally, our calculation ignores the stabilization of the disordered phase by the formation of micelles. The additional entropy provided by the formation of these structures enlarges the region of stability of the disordered phase, as can be seen by comparing the experimental phase diagram of Fig. 1 with our calculated Fig. 2. Because the phase diagram results from a comparison of the free energies of all phases, it is conceivable that the entire pre-unbinding line is pre-empted by the disordered phase. Even were this so, an upward curvature in the lower phase boundary of the lamellar phase would be a remnant of the pre-unbinding line. But the outlook may be more positive. The fact that the pre-wetting line has

been observed[14] in spite of similar difficulties as to its short length, and that coexistence of lamellar phases has been observed[17] encourages us to hope that the pre-unbinding line can also be detected.

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Figure Captions

Fig. 1 Phase diagram of water $C_{12}E_5$ system. The lamellar phase is denoted L_α , while isotropic disordered phases are denoted L_1 , L_2 , and L_3 . The L_1 phase is a micellar fluid, L_3 is the sponge phase. Regions without labels are of two-phase coexistence. (After Ref. 1)

Fig. 2 Phase diagram of the AB-copolymer, A-homopolymer system. The possible occurrence of a hexagonally perforated lamellar phase is ignored. Line of complete unbinding is shown dashed and ends at a Lifshitz point, marked with a diamond. Beyond it is a line of second order transitions from the disordered phase, D , to the lamellar phase, L_α . The coexistence region between two lamellar phases ends at a critical point, also denoted by a diamond. Regions without labels are of two-phase coexistence.