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Flory theory of the unbinding transition

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Abstract. — The transition between bound and unbound surfactant bilayers, controlled by the strength of attractive van der Waals interactions, is described in a simple Flory-type picture. All the main features of the transition previously described only by functional renormalization group methods are recovered, including 1) second-order nature of the transition; 2) estimate of the critical strength of van der Waals interactions; 3) dependence of tricritical point on bilayer stiffness. Our Flory picture also reproduces known exponents for unbinding and wetting transitions in $d = 2$ dimensions.

Introduction.

Several years ago, Lipowsky and Leibler [1,2] (LL) produced an elegant and difficult theory of the unbinding of lyotropic lamellae under the action of steric repulsion, known as the Helfrich interaction [3]. Their work relied on functional renormalization group (FRG) and an approximate recursion relation, and their results appeared to admit no simpler description. They found a second-order transition between a state of “bound” lamellae and one of “unbound” lamellae, as a function of the Hamaker constant W (strength of the attractive van der Waals interaction between bilayer membranes). In the bound state, the bilayers only separate to a finite distance when exposed to large amounts of excess solvent; in the unbound state, the bilayer spacing is governed only by the amount of solvent present.

From their numerical FRG procedure LL found a mean bilayer spacing as a function of the control parameter (Hamaker constant) which diverged as the Hamaker constant approached a critical value from above: $\bar{l} \sim (W - W_c)^{-\psi}$, with $\psi = 1.00 \pm 0.03$ and W_c dependent upon nonuniversal parameters such as the range and strength of short-range repulsive potentials such as the hydration interaction $V_h(l)$, as well as the bilayer thickness δ (at which the form of the

van der Waals interaction crosses over from l^{-4} to l^{-2}). Typical values for these parameters and the resulting W_c are given in reference [1].

LL consider the behavior of a pair of impenetrable fluid bilayers with bending stiffness, interacting sterically and via direct hydration and van der Waals potentials. The bilayer positions are described by displacement variables $\{h_i(r)\}$ for the vertical displacement of the i th layer. The unbinding behavior of a stack of bilayers can be related to that of a single pair of bilayers by defining difference coordinates $\Delta h_i(r) = h_i(r) - h_{i-1}(r)$ giving the separation between adjacent bilayers, and then neglecting correlations between the $\Delta h_i(r)$ for different i . This evidently eliminates the possibility of describing collective modes (e.g., smectic undulations) in which many bilayers are displaced collectively, but still enables a study of unbinding driven by steric repulsion.

LL emphasize that superposition of the Helfrich or steric potential per unit area

$$V_s(l) = \frac{c_H T^2}{K(l - \delta)^2} \quad (1)$$

the hydration interaction

$$V_h(l) = A_h \exp(-l/\lambda_h) \quad , \quad (2)$$

and the van der Waals potential

$$V_W(l) = -\frac{W}{12\pi} \left[\frac{1}{l^2} - \frac{2}{(l + \delta)^2} + \frac{1}{(l + 2\delta)^2} \right] \quad (3)$$

$$\sim -\frac{W}{2\pi} \frac{\delta^2}{l^4} \quad , \quad l \gg \delta$$

in an attempt to produce an "effective potential" acting between the bilayers, gives an incorrect description of the transition. They observe that this potential $V_{\text{eff}}(l) = V_s(l) + V_W(l) + V_h(l)$ as a function of W has minima either at short distances (of order δ) or at infinite separation; thus if l were taken to be the order parameter in a form of mean-field approach, a first-order transition would be predicted (see Fig. 1).

Still, it is unsatisfying that no simple description of the transition should exist, as implied by reference [1]. In most common cases, mean-field treatments are adequate for predicting the approximate value of T_c (which after all is not universal). If anything, mean-field theories usually are overly optimistic about the existence of finite-temperature second-order transitions, since they neglect fluctuation effects which in various cases cause transitions either to be first order (Coleman-Weinberg mechanism [4], Brazovskii transition [5]) or to be suppressed to zero temperature (lower critical dimension effects).

1. A flory theory.

One recognizes that the volume fraction of bilayers ϕ , rather than the mean bilayer spacing \bar{l} , is a sensible choice for the order parameter (to begin with, it vanishes at the transition), by analogy to the elementary description of the ordinary liquid-gas transition. The theory of van der Waals gives a sensible description of the liquid-gas critical point, but not by adding an

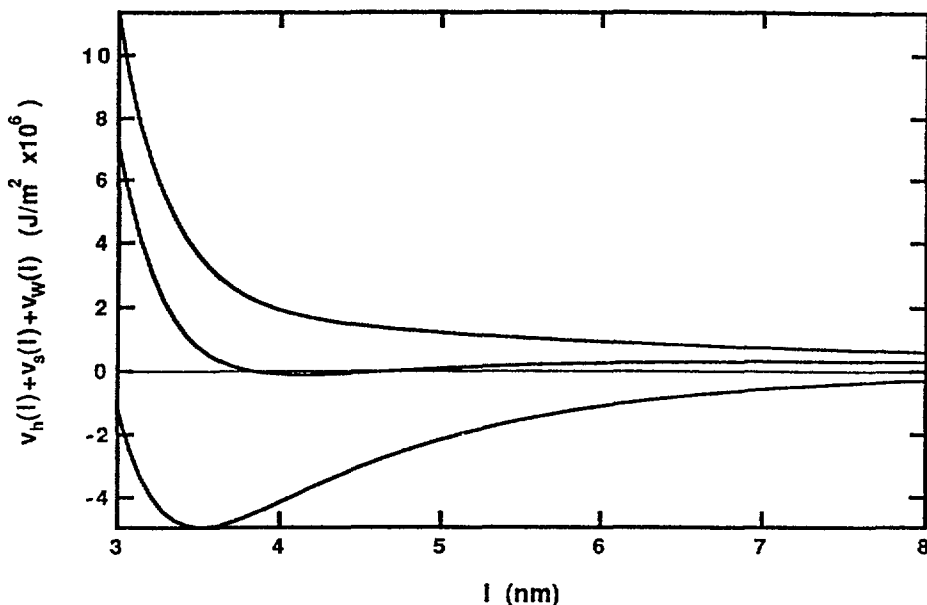


Fig. 1. — The sum of three contributions to the naive “effective potential” acting between bilayers (hydration, steric, and van der Waals) may have a minimum for finite bilayer spacing l if the van der Waals attraction is strong enough. Three curves shown correspond to Hamaker constant W equal to 2, 4, $6 \times 10^{-21} \text{ J/m}^2$.

ideal-gas estimate of the entropy of mixing (analogous to the entropically generated Helfrich term, in the case of the lamellae) to the interparticle interaction at the mean distance between particles. Rather, a virial expansion is invoked to include the perturbative effect of the small attractive interaction [6].

This approach is also used in the Flory-Huggins description of polymers in a good solvent: [7] the free energy is written as a sum of ideal lattice-gas entropies for the polymers $T\phi/N \log \phi$ and solvent $T(1-\phi) \log(1-\phi)$, plus a random-mixing estimate of the polymer-solvent enthalpic interactions $\chi\phi(1-\phi)$. When the polymer concentration ϕ is small, the last two terms may be expanded as $\frac{1}{2}(1-2\chi)\phi^2 + O(\phi^3)$; it is apparent that χ is nothing but the correction to the hard-sphere result for the virial coefficient of the monomers that make up the polymer chain.

This suggests a simple approach to constructing a theory for the unbinding transition of lamellae: we add the Helfrich estimate of the entropy of the stack neglecting all but hard-core interactions (i.e., the Helfrich potential), together with a term which represents the correction to the hard-wall virial coefficient of the bits of surface (of small size $\nu = a^2\delta$, say, where $a^2 = (K/T)\delta^2$ is the in-plane cutoff). Just as in the Flory-Huggins approach, the entropy term is computed in the absence of correlations induced by attractive interactions, and the correction to the virial coefficient is computed with complete neglect of the connectivity of the lamellae.

The above approach leads immediately to the following expression (a similar form is suggested in Ref. [8]; see below) for the free energy per unit volume of a lamellar stack of mean

spacing \bar{l} (and volume fraction $\phi = \delta/\bar{l}$, which must of course be positive):

$$f(\phi) = \frac{3\pi^2 T^2}{128K\delta^3} \phi^3 - T\chi\phi^2 \quad (4)$$

(We shall use the estimate $c_H = 3\pi^2/128$ from reference [3] for the Helfrich interaction, Eq. (1).) Here the coefficient χ is the correction to the hard-wall result for the virial coefficient. If the enthalpic interactions between patches of volume ν are sufficiently weak (discussed below), χ may be given as a function of the interactions by

$$\chi = -\frac{1}{2\nu^2} \int d^3r (1 - \exp[-\beta U_\nu(r)]) \quad , \quad (5)$$

where $U_\nu(r)$ is the interaction between bits of surface of volume ν , and the integral is limited to positions such that the surface bits do not overlap.

The free energy expression (4) evidently has a second-order transition between a bound-lamellae state at $\phi \neq 0$ for $\chi > 0$, which merges for $\chi = 0$ with the endpoint minimum $\phi = 0$ corresponding to unbound lamellae (see Fig. 2). We expect that χ will vanish linearly as the Hamaker constant W is varied about some critical value (the virial integral, Eq. (5), will have contributions from interactions other than van der Waals, in particular direct repulsive interactions). The corresponding phase diagram in the $\{\chi, \mu\}$ plane for this free energy

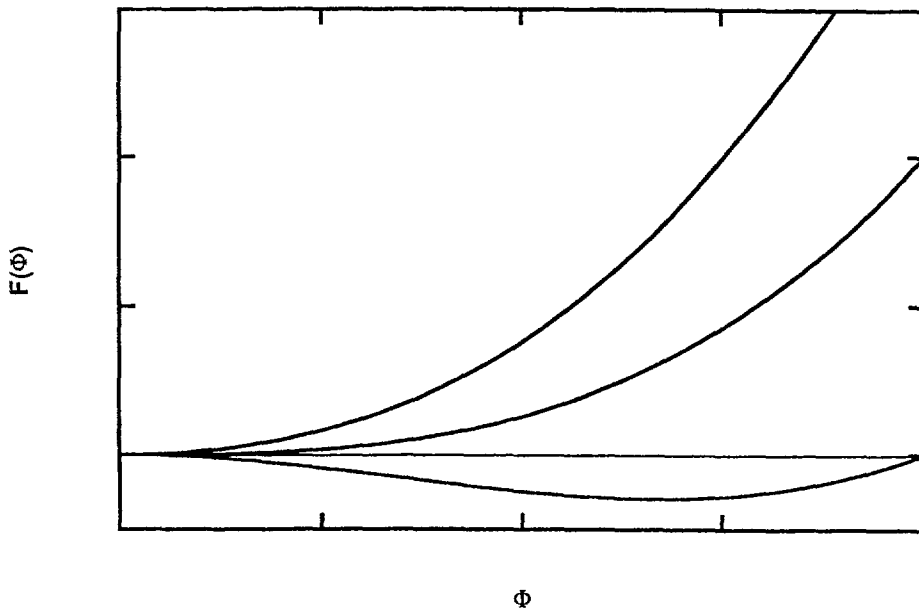


Fig. 2. — The free energy $F(\phi)$ is a sum of two terms: ideal steric repulsion ($\propto \phi^3$) and a random-mixing estimate of the perturbative effects of interactions ($\propto \phi^2$), which leads to a second-order transition as the coefficient of the ϕ^2 term is varied.

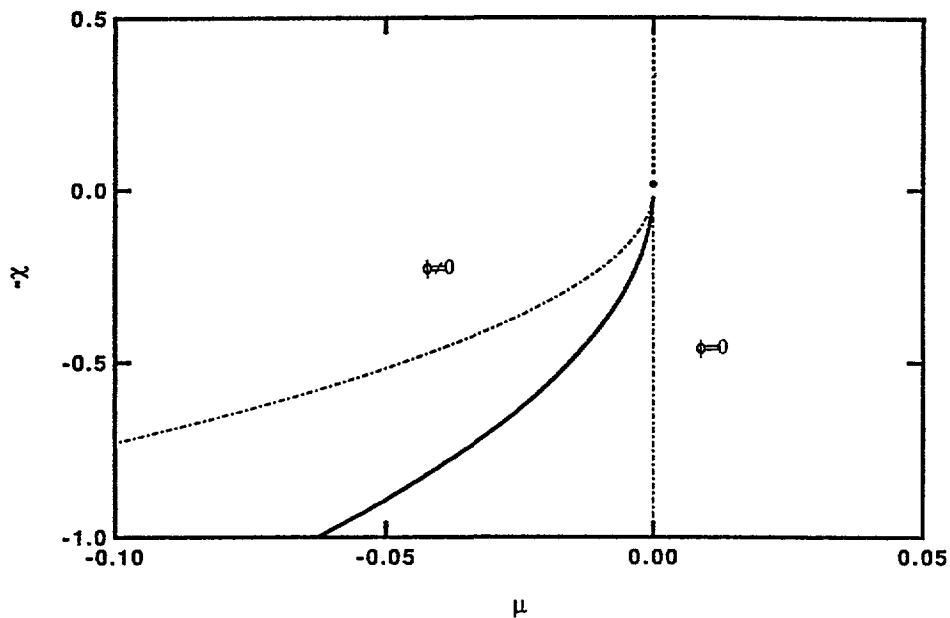


Fig. 3. — The phase diagram of a stack of lyotropic lamellae contains a first-order line separating bound ($\phi \neq 0$) from unbound ($\phi = 0$) lamellae, terminating in a tricritical point at $\chi = \mu = 0$. The corresponding spinodals are indicated by the dot-dashed curves. A line of complete-unbinding critical points extends away from the tricritical point for $\phi = 0, \chi < 0$.

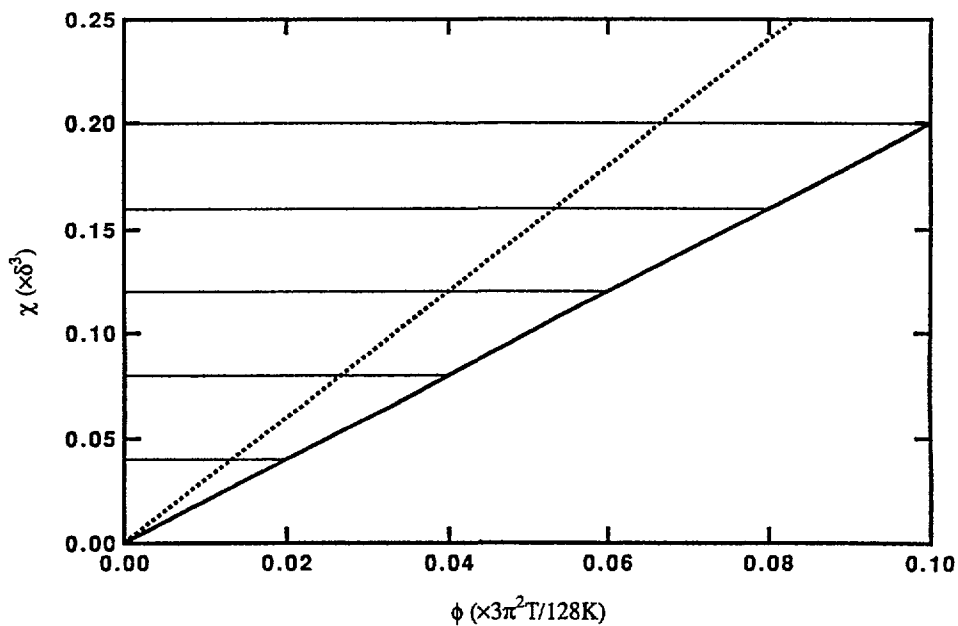


Fig. 4. — The phase diagram of a stack of lyotropic lamellae in the $\{\chi, \phi\}$ plane; the phase and spinodal boundaries are straight lines, and meet at the critical point $\chi = \phi = 0$.

$g(\chi, \mu) = f(\chi, \phi) - \mu\phi$ has a first-order line for $\chi > 0$ at $\mu = -3\chi^2/16$ separating bound and unbound lamellae. The first-order line ends at the tricritical point $\mu = \chi = 0$. A line of critical points, corresponding to the complete unbinding of the lamellae upon swelling with excess solvent, extends beyond the tricritical point for negative χ and $\mu = 0$. The spinodals in the region of parameter space corresponding to bound lamellae are at $\mu = -\chi^2/4$ and $\mu = 0$ (See Fig. 3). In the $\{\chi, \phi\}$ plane the phase boundary $\chi = 2\bar{\phi}$ and the spinodal $\chi = 3\bar{\phi}$ [$\bar{\phi} = 3\pi^2 T / (128K\delta^3)\phi$] meet at $\chi = \phi = 0$ (See Fig. 4).

The free energy density of equation (4) has the appearance of a Landau expansion, and ϕ the role of order parameter; ϕ vanishes at the second-order phase transition. Landau expansions are justified [9] by claiming that the free energy density ought to be analytic in the order parameter, and so expanded in a power series in the order parameter near the transition, where the order parameter is small. Expanding the free energy about $\phi = 0$ is not justified *a priori* in the present case since negative values of ϕ are not permitted; hence the phenomenological model is necessary for establishing the form of the free energy density.

Recall that the ϕ^3 term arises in the present model from the Helfrich interaction; note that such terms are in general to be expected if one accepts an expansion in powers of ϕ with no inversion symmetry. Ordinarily, a cubic term in a Landau expansion leads to a first-order transition; we evade this in the present case by the physical requirement $\phi \geq 0$.

Because of the unusual stabilizing term cubic in ϕ , the minimum of $f(\phi)$ at nonzero ϕ will approach $\phi = 0$ as $(W - W_c)$, rather than with the usual mean-field exponent $1/2$. Thus the mean bilayer spacing $\bar{l} = \delta/\phi$ will vary as $(W - W_c)^{-1}$; the exponent found by LL *via* their numerical RG procedure is indistinguishable from unity within their uncertainty. The unusual shape of the phase boundary (quadratic rather than linear approach to the critical point in the $\{\chi, \mu\}$ plane, see Fig. 3) has the same origin.

2. $d = 2$, other force laws.

We can make the customary generalization to $(d - 1)$ -dimensional interfaces in d dimensions, with a generalized dispersion relation for height variations $h(r)$ as a function of the transverse coordinates r , with the effective Hamiltonian

$$H = \int d^{d-1} q q^\rho |h_q|^2 \quad (6)$$

and extend the above simple Flory-type argument to derive strong-fluctuation regime exponents known for interfaces in $d = 2$ dimensions. Here ρ is an effective exponent describing the spectrum of height fluctuations; for bilayers controlled by bending stiffness, $\rho = 4$, whereas for interfaces under tension, $\rho = 2$.

The Hamiltonian, equation (6), leads to wandering exponent [10] $\zeta = (\rho + 1 - d)/2$, such that a patch of linear dimension L_{\parallel} has root-mean-square height excursions $L_{\perp} \sim \langle h^2(0) \rangle^{1/2} \sim L_{\parallel}^{\zeta}$.

The corresponding Helfrich-like interaction appears as a free energy per $(d - 1)$ -dimensional "area" $f \sim T/\xi_{\parallel}^{(d-1)}$, where $\bar{l} \sim \xi_{\parallel}^{\zeta}$ defines the in-plane correlation length ξ_{\parallel} in terms of the mean spacing between layers \bar{l} . Thus we have a Helfrich free energy per unit area $f \sim T/\bar{l}^{\tau}$, with $\tau = (d - 1)/\zeta$.

Here we have assumed a cost of order kT per collision between adjacent interfaces, independent of dimension d and dispersion exponent ρ . This is consistent with an estimate of that collision free energy based on the Hamiltonian, equation (6), and the lowest available mode of a patch of interface of area $\xi^{(d-1)}$, i.e., $\Delta F \sim \xi_{||}^{(d-1)}(\xi_{\perp}^2/\xi_{||}^{\rho}) \sim T$.

Now we estimate the contribution of an attractive short-ranged interaction by a virial estimate. Near unbinding, when \bar{l} is large, we assert that the distance between interfaces undergoes large fluctuations about the mean spacing, and the probability of close approach per $(d - 1)$ -dimensional area is $1/\bar{l}$.

This viewpoint requires for consistency that the actual microscopic interaction $V(l)$ falls off faster for large l than the Helfrich interaction. This defines the strong fluctuation (SFL) regime [1,11]. For short-range forces we are always in the SFL regime as long as $\tau < \infty$, i.e., as long as $\zeta > 0$.

Then the free energy per area is estimated as the sum of these two terms,

$$f = -t/\bar{l} + 1/\bar{l}^{\tau} \quad , \tag{7}$$

with t a control parameter describing the strength of the virial coefficient (average over the direct interaction $V(l)$). The form (7) is not in general suggestive of a Landau expansion, since τ is not in general an integer; hence we retain l as a variable. (Note that for interfaces with tension, i.e., directed random walks ($\rho = 2$) in $d = 2$ dimensions, we recover the form of Eq. (4).)

We have upon balancing the two terms a power law for the divergence of \bar{l} ,

$$\bar{l} \sim t^{-1/(\tau-1)} \sim t^{-\zeta/(d-1-\zeta)} \tag{8}$$

For $d = 2$ dimensions, where analytical results exist [10,11] this agrees exactly with known results for unbinding transitions of thermally wandering interfaces in the SFL regime: reference [11] gives $\bar{l} \sim t^{-\nu_{\perp}}$ and $\xi_{||} \sim t^{-\nu_{||}}$ with $\nu_{\perp} = \zeta\nu_{||} = \zeta/(1 - \zeta)$. Because the Helfrich term may be written $T/\xi_{||}^{(d-1)}$ for interfaces thermally wandering with adjustable dispersion relation as we have considered, hyperscaling is obeyed: $2 - \alpha = (d - 1)\nu_{||}$, where $\xi_{||} \sim t^{-\nu_{||}}$, and $\nu_{||} = 1/(d - 1 - \zeta)$ from equation (8).

Lipowsky has argued [12] on the basis of FRG recursion relations that the unbinding exponent ψ for fluid membranes in $d = 3$ dimensions (for which $\tau = 2$) is exactly $\psi = 1$. His recursion relation depends only on the Helfrich exponent τ and not separately on d ; hence ψ must be the same as the known result $\psi = 1$ for interfaces with tension in $d = 2$ (for which $\tau = 2$ also). The present simple approach is obviously consistent with this argument; the Flory-type free energy of equation (7) depends only on τ .

The agreement between unbinding exponents obtained by the above simple Flory-type argument and exact results for unbinding in $d = 2$ dimensions, encourages the application to $d = 3$ dimensions where analytical results are absent.

Our simple argument signals new behavior when the Helfrich term diverges at *small* l less strongly than the virial term, i.e., when $\tau < 1$. Then, an attractive term estimated by a uniform-density approximation is not stabilized by the Helfrich term. This suggests either a

first-order collapse to a very dense state ($l \ll 1$, $\phi \sim 1$) or the breakdown of a uniform-density picture. This occurs when $\zeta > (d-1)$, or $\rho > 3(d-1)$; for $\rho = 4$ (bending stiffness), the borderline value of d is $d = 7/3$, so that semiflexible chains in $d = 2$ dimensions with short-range attractions are not described by the above argument. Recent work on semiflexible chains in $d = 2$ dimensions suggests that unbinding is effectively discontinuous, consistent with our simple picture [13,14].

We note finally that in adopting a Gaussian description of the height fluctuations in equation (6), we cannot describe the crossover between effective values of ρ as a function of layer spacing, as is expected for example in the case of semiflexible chains, which cross over to Gaussian and then to self-avoiding chains as the layer spacing is increased [13,14].

3. Independent units and hard cores.

We now address the question of the reasonableness of our approximation; in particular, we examine the evaluation of the virial coefficient in the presence of strong interactions at short range. Our goal is to decide 1) what should be the size of an independently moving "unit" of surface, corresponding to a monomer in the Flory-Huggins theory of polymer melts, and 2) how to handle the strong short-range repulsion within our picture. The discussion in this section is cast in the language of bilayers with bending stiffness in $d = 3$ dimensions.

Upon reflection it may seem unreasonable to adopt as the independent unit a microscopic piece of surface, of size $a^2\delta$, as analogous to a monomer in the Flory theory for polymer solutions. Elements of the fluid surface are much more correlated in their positions than the gas molecules or even the monomers of polymer chains that inspired the present approach. One might say that when the mean bilayer separation is \bar{l} , only patches with dimensions of order the correlation length $\xi(\bar{l}) \sim \sqrt{K/T\bar{l}}$ may be regarded as having independent positions along the z -axis. The interaction potential between two such patches at a distance r is then $W\delta^2\xi^4/r^6$ for $r \gg \xi$.

What happens to equation (5) when the size of the independent unit is changed? If the units interact weakly enough beyond the hard-wall excluded volume interaction so that the Boltzmann factor may be expanded,

$$\chi \approx -\frac{\beta}{2\nu^2} \int d^3r U_\nu(r) \quad , \quad (9)$$

then χ is *independent* of the volume ν of the unit (e.g., for van der Waals attractions, $U_\nu(r) = \nu^2 W/r^6$ is proportional to ν^2).

The interaction $v(z)$ between a unit area of surface and a bilayer a distance z away is given by the integral of U_ν over the area of the bilayer, $v(z) = (\delta/\nu)^2 \int d^2r U_\nu(r; z)$. In terms of $v(z)$ we may write equation (9) as

$$\chi = -\beta/(2\delta^2) \int dz v(z) \quad (10)$$

This amounts to saying that the average contribution of the van der Waals interaction to the free energy can be computed by randomly placing other bilayers along the z -axis with average

spacing \bar{l} ; in the limit of large \bar{l} , the resulting term in the free energy per volume must go as $1/\bar{l}^2$ and hence ϕ^2 , as long as the integral converges. It is physically reasonable that as $\phi \rightarrow 0$ under the influence of the Helfrich interaction, the distance between adjacent bilayers will fluctuate strongly about the mean spacing; indeed, equation (10) is a sensible starting point for computing the perturbative effects on the free energy of a weak direct interaction.

To find out if it is reasonable to expand the Boltzmann factor, consider the van der Waals interaction between two patches on neighboring bilayers with area of order the correlation area ξ^2 separated along the z -axis by a distance l . For large separations l this interaction decays as $W\delta^2\xi^4l^{-6}$ and is thus small. When two bilayers approach closely, we should ask not about the interaction energy of patches of area ξ^2 but about patches of the local correlation area $\xi(l)^2$, where l is the local distance of close approach (i.e., the separation in z between the patches). This interaction energy is $\xi(l)^2V(l)$ and goes as $\xi(l)^2W\delta^2/l^4 \sim (K/T)W\delta^2/l^2$, where we have assumed l is larger than the layer thickness δ . We see that the interaction energy becomes comparable to kT at a separation $l \sim \sqrt{(KW/T^2)\delta}$. This turns out to be comparable to δ at the transition, where W_c is roughly of order T^2/K (see Eqs. (11) and (12) below); thus, the Boltzmann factor may be expanded except at separations where strong repulsive short-ranged interactions will be important (see below).

We have so far avoided the question of repulsive interactions between the bilayers, by incorporating their effect into the ideal Helfrich calculation. Note that the correction term in δ/l from the Helfrich interaction, equation (1), leads to a term in the free energy $f_H(l) \sim T^2/K(\delta/\phi - \delta)^3 = T^2/(K\delta^3)\phi^3(1 + 3\phi + O(\phi^2))$. Apparently, a hard wall of finite thickness produces a coefficient in the free energy of order ϕ^4 (rather than a virial-type term of order ϕ^2); such a term does not affect the nature or location of the critical point at $\phi = 0$. What is the distinction between the weak van der Waals attraction and the hard-wall repulsion which leads to different powers of ϕ in the free energy?

The distinction rests in whether or not the interaction of units of size $\xi(l)$ at a distance l is weak or strong compared to T . For strong short-range repulsive interactions, the interaction of patches of surface upon close approach becomes arbitrarily large. Then the issue of the appropriate size of an independent unit is relevant. A sensible way to deal with this question for a short-range repulsive potential $V_h(l)$ is to choose a distance of closest approach l_c such that $\xi(l_c)^2V_h(l_c)$ is of order T ; the potential is then modeled as a hard wall at l_c and a weak potential — the sum of the van der Waals attraction and the weak tail of the hydration repulsion — for which the Boltzmann factor may indeed be expanded [15]. Then the issue of the size of the independent unit is avoided, as discussed above.

Intuitively, it is reasonable that a strong short-range repulsion does not contribute to the virial term ($O(\phi^2)$ in Eq. (4)), but only leads to an increase in the apparent thickness of the bilayers. As a consequence, previous studies of the phase behavior of systems containing self-assembled surfactant layers (e.g., microemulsions) need not be modified to take account of such a virial term, assuming that the surfactant layers in such cases do not have significant attractions.

In general, we should expect a nonzero critical value of W at which $\chi = 0$, since there is some weak repulsive contribution to χ as well as the contribution from attractions. Reference [1] gives the hydration interaction as $V_h(l) = A_h \exp(-l/l_h)$ with typical values $A_h = 0.2 \text{ J/m}^2$ and $\lambda_h = 0.3 \text{ nm}$; a range of bending constants K is quoted for lecithin-type bilayers, from $(1 - 20) \times 10^{-19} \text{ J}$ ($20 - 400T$); the bilayer thickness is $\delta = 4 \text{ nm}$. The separation at which the

hydration interaction of a correlation area $\xi^2 = (K/T)l^2$ is T , is given by

$$\frac{l^*}{\lambda_h} = \log \left[\frac{A_h \lambda_h^2 K}{T} \left(\frac{l^*}{\lambda_h} \right)^2 \right] \quad (11)$$

For the above parameters, $A_h \lambda_h^2 / T = 4$, and so l^* ranges from $8.7\lambda_h = 2.6$ nm for $K = 20T$, up to $12.4\lambda_h = 3.7$ nm for $K = 400T$. (A stiffer bilayer has a larger correlation area at a given spacing, hence a larger l^* .)

The virial integral is evaluated by equation (10) with $v(z) = V_h(z) + V_w(z)$, with a lower limit $z = l^*$; we find a critical Hamaker constant

$$W_c = \frac{12\pi\lambda_h T^2}{l^* K} \left[1 - \frac{2l^*}{l^* + \delta} + \frac{l^*}{l^* + 2\delta} \right]^{-1} \quad (12)$$

For $K = 20T$ we find $W_c = 2 \times 10^{-21}$ J ($\approx 0.5T$), comparable to the value of 5.8×10^{-22} J obtained by LL.

As l^* varies only logarithmically with K , we see that the critical Hamaker constant W_c varies roughly inversely with K . For $K = 400T$, the range of the effective hard-wall potential increases to 3.7 nm, and W_c decreases to 10^{-22} J. (LL obtain 5.6×10^{-23} J for these values of parameters.)

The exact value is not particularly sensitive to the procedure for choosing the range of the effective hard-wall potential. If the definition of the correlation area contains a coefficient a ($\xi^2 = a(K/T)l^2$) and the hydration interaction at the effective hard-wall cutoff is taken to be bT , the resulting equation (11) for l^* will contain a factor of a/b inside the logarithm, resulting in a small change in l^* . Of course, the location of the critical point may also be shifted by fluctuation corrections. Note also that the results of reference [1] are somewhat sensitive to the details of the numerical procedure [8].

4. Previous approaches.

Two other authors have presented approaches to the unbinding transitions alternative to that of reference [1]. Helfrich [8] proposed a model similar to ours. He considered a weak, short-ranged attractive potential of depth U and width d between a pair of adjacent bilayers. He supposes that one bilayer is weakly bound to the next, with a spread w in position along the z -axis; w would presumably be of order the mean bilayer spacing \bar{l} in a stack of such bilayers.

The sum of free energies due to Helfrich repulsion and the mean energy in the weak attractive well for the pair is then (omitting coefficients) $f = T^2/(Kw^2) - Ud/w$. For a stack, the free energy per volume is then f/w with $\phi = 1/w$; this is similar to equation (4), but has $\phi_c = 0$ — any attractive potential binds the bilayers. Helfrich attempts to take some correlations into account by saying that when a bilayer is within the range of the attraction, the entropy per area is further reduced beyond the $T^2/(Kw^2)$ estimate by some phenomenological amount B ; then U is replaced by $U - B$, and $U_c = B$.

This model differs from the present calculation in the following respects: 1) The potential is explicitly taken to be weak, attractive and short-ranged, which eliminates the need to separate

the strong short-ranged part into an effective hard core before evaluating the perturbative effect of the attractive potential on the free energy. 2) The proposed origin in reference [3] of the nonzero value of binding strength is not that there are both attractive and repulsive direct interactions in the system. The proposal of reference [3] is essentially that a further entropic penalty must be paid for close approaches. Equivalently, the distribution $P(z)$ of the positions along the z -axis of a point on the bilayer should be smaller near the wall. The difficulty of properly accounting for the effects of correlations in computing the virial coefficient are discussed below.

Wennerstrom [16] has recently considered the phase behavior of a stack of bilayers, in which he essentially adds together the effective Helfrich potential and the direct interactions together with a chemical potential term. (We believe this approach to be incorrect, as argued in Sect. 1 and reference [1]). Reference [16] finds a first-order transition between bilayers bound at a distance of order δ and essentially unbound bilayers, until the chemical potential is turned up so high that even in the "unbound" state, bilayers are forced into the system at a spacing of order δ . Then a critical point appears, but with $\phi_c \sim 1/\delta$ and conventional mean-field exponents. As discussed in reference [1] and in the Introduction, this is not an appropriate model for critical unbinding; indeed, there is an apparent contradiction between the assumption that the bilayers maintain a well-defined separation \bar{l} (for purposes of estimating the direct interactions), and that the Helfrich interaction is responsible for repulsion between bilayers.

5. Difficulty of refining flory theory.

One might think that a way to improve the description of the transition would be to use not a random-mixing estimate for the location of the bilayers along z , but rather include the effects of correlations induced by the Helfrich interaction. Such improvements to Flory-type theories are characteristically difficult to implement, as we now describe.

The correlations between the positions of neighboring surfaces may be expressed for present purposes in terms of the distribution function $P(h)$ for the z -coordinate h of a point on a bilayer between rigid walls. The Helfrich calculation of fluctuation-induced repulsions in effect approximates $P(h)$ in the absence of attractive interactions as a Gaussian, but this does not describe the way in which $P(h)$ must vanish as the bilayer approaches a wall. More detailed calculations [17] suggest that $P(h)$ in the absence of attractive interactions with the walls is a universal function, with a broad maximum between the walls, and vanishing near the walls as $(h \pm d)^c$ with $c \approx 4.5$.

The suggested improvement in estimating χ is then

$$\chi = -\frac{1}{2} \int_0^d dz P(z)v(z) \quad , \quad (13)$$

with $P(z)$ no longer assumed constant.

The difficulty is that for consistency, $P(z)$ must be calculated in the presence of attractive interactions. Far from the unbinding transition, $P(z)$ may contain strong correlations, but near the transition $P(z)$ should become quite uniform. A simple example (see below) illustrates the dependence of $P(z)$ on the strength of the attractions.

Calculations of $P(z)$ including the effect of attractive interactions are not available at present. If we try to use results for $P(z)$ in the absence of attractive interactions in equation (13) to describe the unbinding transition, trouble ensues. The expression for χ will no longer be independent of d in the large- d limit; in fact, $\chi(d) \sim d^{-4}$ if $v(z) \sim z^{-4}$ for large z (as is evident upon scaling $z = z'd$ and noting that the integral converges for small z). This leads to a ϕ^5 term in the free energy — instead of the ϕ^2 term obtained with a roughly constant $P(z)$ — and totally ruins the simple critical point we obtained earlier. The gross cancellation of errors in the Flory-type description is upset by an improvement in only one feature of the calculation (computing χ including some effects of correlations *via* $P(h)$) while another feature remains primitive (computing $P(h)$ without including the effect of attractive interactions).

We may gain some insight into the results of a consistent calculation of $P(h)$ in the presence of attractive interactions by considering a much simpler analogous problem: a long, flexible polymer chain confined between impenetrable walls at $z = \pm L$, with an attraction of short range a and variable strength U . For a non-self-interacting chain as we are considering, the polymer configuration in the directions parallel to the walls does not matter; the phantom polymer confined between walls is equivalent to a directed polymer in $d = 2$ dimensions. De Gennes [18] has described the effect of the short-range attraction on the equation for the dominant ground-state wavefunction $\psi(z)$ (the lowest eigenmode in an expansion of the propagator of the polymer chain; the monomer density is proportional to $|\psi(x)|^2$). The attraction results in a boundary condition of the form $d\psi/dz \pm \kappa(U)\psi = 0$ at $z = \pm L$. Here $\kappa(U)$ is a decreasing function of the attraction strength U . For a *repulsive* short-ranged interaction with the impenetrable walls, by contrast, the ground-state wavefunction and hence the monomer density are essentially unchanged; the wall is already avoided by the polymer, so a short-range repulsion has little effect beyond thickening the walls, as anticipated in the previous section.

As U increases, the wavefunction (which for no attraction is $\cos(\pi z/2L)$, vanishing at the walls) becomes a progressively flatter section $\cos(\alpha\pi z/2L)$ ($\alpha < 1$) of a cosine, and nonzero at the walls. The repulsion between the walls caused by the confinement of the polymer (analogous to the Helfrich interaction) becomes progressively weaker. For a critical value of U (of order T , independent of L) $\kappa(U) = 0$, and the wavefunction is flat. For still larger U , the wavefunction is largest at the two walls, and the polymer chain mediates an attraction between the walls.

From this analogy, we draw two conclusions: first, it is consistent with our simple picture of unbinding transitions that the monomer density becomes flat near the transition between the attractive and repulsive cases; second, a finite attraction (of order T per monomer) is required to reach the transition, even though we have no explicit repulsive interaction (in agreement with the suggestion of reference [8]).

6. Conclusions.

We have presented a simple Flory-type theory of the critical unbinding of a stack of lamellae as the strength of the attractive van der Waals interactions is varied. Our physically transparent description reproduces all the main features of the transition previously described only by functional renormalization group calculations of Lipowsky and Leibler, including: 1) a second-order transition, with the volume fraction of the bound state vanishing as $(W - W_c)$; 2) a value of W_c in the range of $10^{-21} - 10^{-22}$ J/m² for parameters corresponding to lethicin bilayers; 3) a trend toward lower values of W_c for stiffer bilayers. Our simple picture also reproduces exact

unbinding exponents for $d = 2$ dimensional systems in the strong-fluctuation (SFL) regime, in which direct attractions are of short range relative to Helfrich repulsion.

With a simple theory of the unbinding transition in hand, we can make some experimental predictions away from the critical point. Relating the free energy equation (4) to that of a smectic-A lamellar phase, we can compute the smectic compressional modulus following reference [3], but now including the effects of direct interactions.

The modulus at constant chemical potential \bar{B} , which can be directly measured in dynamic light-scattering experiments [19,20] and is obtained from the thermodynamic derivative $\bar{B} = d^2\partial^2g/\partial d^2|_{\mu}$ as

$$\bar{B} = \frac{9\pi^2 T^2}{64Kd^3} - \frac{2T\chi}{d^2} ; \quad (14)$$

hence the modulus will be smaller in the presence of attractive interactions ($\chi > 0$) for a given layer spacing d . As a consequence, measurements of the Landau-Peierls exponent η [21,22] or of hydrodynamic modes [19] should be affected by the presence of attractive interactions.

As a final note, we remark that the separation of a stack of bilayers to infinite separation has been shown to be interrupted by a transition to an isotropic "sponge" phase, in which the simple topology of a stack of bilayers is replaced by a locally smooth but randomly connected interface [23,24]. This possibility is not contained in the simple model presented here, nor in the calculations of reference [1], both of which tacitly assume a stack of bilayers at all separations.

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