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Unbinding of Membranes

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I. INTRODUCTION

Ordered lamellar phases are formed in many-component systems containing amphiphilic molecules. In these phases, roughly parallel lamellae or membranes are separated by a fluid medium. Examples are (i) phospholipid bilayers separated by water, and (ii) swollen bilayers separated by oil (or water). In the latter case, the membranes consist of thin layers of water (or oil) sandwiched between two monolayers of surfactant. Recent swelling and dilution experiments have shown /1-4/ that the membrane spacing can become large compared to the membrane thickness. During such swelling or dilution experiments, the membranes undergo an unbinding process from a state where they are bound together to a state where they are completely separated.

The membrane separation is controlled by the intermembrane interactions. It is now generally accepted that one may distinguish two different types of interactions: (i) *direct* interactions between planar membranes which reflect the microscopic forces between the molecules /5,6/, and (ii) *fluctuation-induced* interactions arising from thermally excited undulations of the membranes as pointed out by Helfrich /7/. From a theoretical point of view, it is clearly desirable to obtain a *systematic* description for the *interplay* between these two types of interactions. This paper reviews some recent work in this direction /8,9/.

The next two sections contain a brief description of direct and fluctuation-induced interactions. Then, an effective Hamiltonian (or free energy functional) for the membrane configurations is introduced which serves as a starting point for a systematic theory, see Sec. IV. The statistical properties of this model can be investigated by a variety of theoretical methods. So far, the most powerful method is a functional renormalization group approach /8,10/ which is described in Sec. V. Then, two different types of unbinding transitions are discussed in Sec. VI and VII.

II. DIRECT INTERACTION BETWEEN PLANAR MEMBRANES

First, consider two *planar* membrane segments which are roughly parallel and, thus, have a constant separation, $\ell > 0$. The internal structure of the membranes will be ignored, i.e., they will be regarded as featureless sheets or drumheads of thickness δ. The direct interaction between these membranes has the generic form

$$V(\ell) = P\ell + V_m(\ell) \qquad (1)$$

for $\ell > 0$. The parameter P is (i) an external pressure /5/, or (ii) a Lagrange multiplier resulting from a constraint on the system /9/. The direct interaction, $V_m(\ell)$, for $P = 0$ arises from microscopic forces between molecules. In addition to these interactions which operate for $\ell > 0$, $V(\ell)$ also contains a *hard wall repulsion* given by

$$V_{HW}(\ell) = \infty \quad \text{for } \ell < 0$$
$$= 0 \quad \text{for } \ell > 0 \tag{2}$$

resulting from the steric hindrance of the membranes.

For two *neutral* or *uncharged* membranes, the interaction $V_m(\ell)$ is usually governed, for large ℓ, by van der Waals forces. As long as retardation effects can be ignored, one has $V_m(\ell) \simeq -W\delta^2/\ell^4$ for large ℓ where W is the Hamaker constant. Retarded van der Waals forces, on the other hand, will lead to $V_m(\ell) \simeq -1/\ell^5$ which is expected to apply for $\ell \geq 50$ nm /8/. Note that these effective van der Waals interactions between two identical membranes are always *attractive*. For small values of ℓ, two membranes separated by a water layer interact by repulsive short-ranged hydration forces /5,6/. For swollen bilayers separated by oil, one expects an additional attractive interaction as soon as the hydrocarbon chains of the surfactant molecules start to overlap. If the membranes are *charged*, they repel each other by electrostatic interactions. For ℓ large compared to the Debye length, λ_E, of the ionic solution, this electrostatic repulsion decays exponentially $\simeq \exp(-\ell/\lambda_E)$. If there are no ions between the membranes apart from counterions, λ_E is infinite (in practise, $\lambda_E \simeq 10^2 - 10^3$nm in water) and the electrostatic interactions lead to the Langmuir repulsion which behaves as $\simeq 1/\ell$ for large ℓ /6/.

The direct interactions described so far have been known for a long time. More recently, it has been argued that, for $\ell \simeq 1$-10 nm, the intermembrane interactions are more complex and not completely understood /11/. However, the process of unbinding studied here does not depend on the detailed form of the interaction $V(\ell)$ but only on its gross features. Furthermmore, the theoretical approach reviewed in this paper is quite general and can be applied to any form of $V(\ell)$. In fact, one important result of this approach is a *classification scheme* by which one can distinguish different classes of direct interactions, $V(\ell)$.

In principle, the shape of $V_m(\ell)$ could be determined by experiments since, for planar membranes, the pressure P is given by

$$P = P(\ell) = -\partial V_m/\partial \ell. \tag{3}$$

Thus, one could calculate $V_m(\ell)$ from the measured values of $P(\ell)$. Indeed, such a procedure has often been used for bilayers in water /5/. One must realize, however, that real membranes are, in general, not planar but deformed as a result of thermal fluctuations. In such a situation, the measurement of $P(\ell)$ will determine an *effective* interaction which is already renormalized by membrane fluctuations. On the other hand, force measurements in the absence of thermal fluctuations are possible when the membranes are attached to mica surfaces /6,11/.

III. FLUCTUATION-INDUCED INTERACTIONS

Some years ago, Helfrich pointed out /7/ that thermal fluctuations lead to an effective *repulsive* interaction between membranes. For spatial dimensionality d=3, he predicted that these undulations together with a hard-wall interaction as in (2) lead to the fluctuation-induced interaction/7/

$$V_{FL}(\ell) \simeq (k_BT)^2/\kappa\ell^2, \tag{4}$$

where κ is the rigidity constant. Recent experiments indicate that this parameter is roughly given by $\kappa \simeq 10^{-12}$erg for lipid bilayers /1,12/ and by $\kappa \simeq 10^{-14}$erg for swollen bilayers in quasi-ternary systems /2-4/.

It is instructive to rederive the effective repulsion as given by (4) from scaling arguments /8/. First, assume that the membranes are completely separated. Then, each membrane is governed by the effective Hamiltonian (or free energy functional) /13,14/

$$H_0\{\ell\} = \int d^{d-1}x \ \frac{1}{2} \ \kappa \ (\nabla^2\ell)^2, \tag{5}$$

where $\ell=\ell(\underset{\sim}{x})$ measures the distance of the membrane from a reference plane with coordinate $\underset{\sim}{x}=(x_1,...,x_{d-1})$. Here it is assumed that the spontaneous curvature of the membranes is negligible. Likewise, higher order terms arising from the mean curvature are omitted which is justified as long as $(\nabla\ell)^2 << 1$. Now, it follows from (5) that a membrane segment of longitudinal dimension, $L_{\parallel}$, will typically make a transverse excursion, $L_{\perp} \sim L_{\parallel}{}^{\zeta}$, with the spatial anisotropy exponent /8/

$$\zeta = (5-d)/2 \qquad \text{for } d < d_0 \equiv 5. \tag{6}$$

On the other hand, if the membranes are bound together, the transverse excursions are limited and the largest humps have a typical size, $\xi_{\perp}$. Then, scaling arguments show that these largest humps or fluctuations have a longitudinal extension, $\xi_{\parallel}$,with /8/

$$\xi_{\perp} \approx (\mathscr{C}_{\infty} \ k_BT/\kappa)^{1/2} \ \xi_{\parallel}{}^{\zeta}, \tag{7}$$

where $\mathscr{C}_{\infty}\sim O(1)$ is related to the difference correlation function. For the Gaussian model in d = 3, one has $\mathscr{C}_{\infty}\simeq 0.125$. Similar ideas have been presented by Sornette /15/.

The largest humps or fluctuations of the confined membrane lead to an increase of the free energy per unit area as given by /8/

$$V_{FL}(\xi_{\perp}) \approx c_V \ k_BT \ (k_BT/\kappa)^{\tau/2} \ \xi_{\perp}{}^{-\tau} \tag{8}$$

for d<5 with $c_V\sim O(1)$ and decay exponent

$$\tau = 2(d-1)/(5-d) \quad . \tag{9}$$

For d=3, the Helfrich interaction (4) is recovered provided one assumes that $\ell \sim \xi_\perp$. This relation is indeed valid for a hard wall repulsion, i.e., for $V(\ell)=V_{HW}(\ell)$ as given by (2) but does not hold in general: sufficiently long-ranged interactions $V_m(\ell)$ lead to $\xi_\perp << \ell$, /8,9/.

IV. EFFECTIVE HAMILTONIAN FOR INTERACTING MEMBRANES

So far, two types of interactions have been considered: (i) direct interactions between planar membranes, i.e., in the absence of thermal fluctuations, and (ii) fluctuation-induced interactions where the explicit form of the direct interaction $V(\ell)$ has been ignored. Now, an effective Hamiltonian, $\mathcal{H}(\ell)$, will be introduced in order to study the interplay between these two interactions in a systematic way.

First, the local distance of two membranes from a reference plane is denoted by $\ell_1(\underset{\sim}{x})$ and $\ell_2(\underset{\sim}{x})$ with $\underset{\sim}{x}=(x_1,\ldots,x_{d-1})$ as before. Now, deformations of these membranes are governed by $\mathcal{H}_o\{\ell_1\}+\mathcal{H}_o\{\ell_2\}$ where the effective Hamiltonian $\mathcal{H}_o$ has been defined in (5). Furthermore, the direct interaction beween the deformed membranes is taken to be $V[\ell_1(\underset{\sim}{x})-\ell_2(\underset{\sim}{x})]$. It is then convenient to introduce new variables, $\ell=\ell_1-\ell_2$ and $\ell_o=(\ell_1+\ell_2)/2$. Then, the effective Hamiltonian separates into two terms, $\mathcal{H}_o\{\ell_o\} + \mathcal{H}\{\ell\}$, with $\mathcal{H}_o$ as given by (5) and /8,9/

$$\mathcal{H}\{\ell\} = \int d^{d-1}x \ \{ \ \tfrac{1}{2} \ \kappa \ (\nabla^2\ell)^2 + V[\ell(\underset{\sim}{x})] \ \} \ . \qquad (10)$$

This expression implicitly contains a small-distance cutoff, $1/\Lambda \simeq \delta$, where δ is the membrane thickness. The Hamiltonian as given by (10) governs the unbinding process of the membranes. Obviously, it contains both an elastic free energy as in (5) associated with membrane deformations and an interaction free energy which is given in terms of $V(\ell)$. Now, one can use the general rules of statistical mechanics in order to calculate thermodynamic quantities and expectation values of ℓ via the Boltzmann factor, $\exp[-\mathcal{H}/k_BT]$.

V. FUNCTIONAL RENORMALIZATION

The effective Hamiltonian (10) resembles the interface models studied in the context of wetting phenomena, see, e.g., Refs.16-18. Such models have been studied by a variety of field-theoretic methods. Not surprisingly, the same methods can be used in the present context. Here, I will describe a functional renormalization group (RG) approach /10,8/ which has been found to be most widely applicable.

This functional RG which represents an extension of Wilson's approximate recursion relation /19/ preserves the form of the effective Hamiltonian (10): it acts as a nonlinear map in the function space of direct interactions, $V(\ell)$, while the elastic term, $(\nabla^2\ell)^2$,remains unchanged. This implies that the rigidity, κ, stays finite at the unbinding transition or, in field-theoretic language, that the variable ℓ does not acquire an anomalous dimension. This is indeed valid for the effective Hamiltonian as given by (10) as one can show by scaling arguments /8/ and within the loop expansion /9/.

In order to write the recursion relation for the RG in a transparent way, let us introduce the free energy density scale

$$v \equiv k_BT \int_{\Lambda/b}^{\Lambda} d^{d-1}p \ / \ (2\pi)^{d-1} \tag{11}$$

and the length scale, $a_\perp$, defined by

$$a_\perp^2 \equiv (k_BT/\kappa) \int_{\Lambda/b}^{\Lambda} d^{d-1}p \ / \ (2\pi)^{d-1} \ p^4, \tag{12}$$

where $\Lambda \simeq 1/\delta$ is the high-momentum cutoff and $b>1$ is the usual spatial rescaling factor. The length scale $a_\perp$ can be regarded as the roughness of the membranes arising from small-scale excitations with wavenumber $\Lambda/b \lesssim p \lesssim \Lambda$. Then, the initial interaction $V^{(0)}(\ell) \equiv V(\ell)$ is renormalized by successive applications of

$$V^{(N+1)}(\ell) = \mathfrak{R}[V^{(N)}(\ell)] \tag{13}$$

where /8,20/

$$\mathfrak{R}[V(\ell)] \equiv -vb^{d-1} \ln\{ \int_{-\infty}^{+\infty} dz \ \exp[-\tfrac{1}{2}(z/a_\perp)^2 - G(\ell,z)]/[2\pi a_\perp^2]^{1/2} \} \tag{14}$$

with

$$G(\ell,z) \equiv [V(b^\zeta\ell - z) + V(b^\zeta\ell + z)] \ / \ 2v \tag{15}$$

and $\zeta=(5-d)/2$ as in (6). In the infinitesimal rescaling limit $b=\exp(\delta t)$ with $\delta t \to 0$, one obtains the nonlinear flow equation given by

$$dV/dt = (d-1)V + \zeta\ell\partial V/\partial\ell + \tfrac{1}{2}B \ \ln[1+(A^2/B)\partial^2V/\partial\ell^2] \tag{16}$$

with cutoff-dependent scale parameters A and B.

These recursion relations are very similar to the nonlinear recursion relation used in the context of wetting /10/. Indeed, these two RG's differ only (i) in the spatial anisotropy exponent, ζ, which determines the rescaling factor of ℓ; and (ii) in the choice for the length scale $a_\perp$ which ensures that this RG is exact to linear order in V for all values of b and d. Therefore, most features of the functional RG found for wetting/10/ have immediate analogies for the RG used here for membranes.

By definition, a RG fixed point, V^*, satisfies $\mathfrak{R}[V^*(\ell)]=V^*(\ell)$. This relation is trivially fulfilled for the Gaussian fixed point $V_G^*=0$. Furthermore, numerical iterations of the recursion relation as given by (13)-(15) reveal two nontrivial fixed points, $V_o^*(\ell)$ and $V_c^*(\ell)$, for $d<d_o=5$. In $d=d_o=5$, these two fixed points do not bifurcate from the Gaussian fixed point, $V_G^*=0$, but rather from an unusual line of drifting fixed points as will be described elsewhere /21/, see also /10/.

Within the subspace of direct interactions, $V_m(\ell)$, which satisfy

$$V_m(\ell) \ll 1/\ell^\tau \quad \text{for large } \ell \quad , \tag{17}$$

with $\tau = 2(d-1)/(5-d)$, there is no relevant perturbation at the fixed point $V_o^*(\ell)$. Therefore, this fixed point has a large domain of attraction. In particular, a hard wall repulsion, $V_{HW}(\ell)$, as given by (2) is mapped onto V_o^*. Therefore V_o^* may be called the "hard wall fixed point". In contrast, there is one relevant perturbation at the other fixed point, $V_c^*(\ell)$, which governs the critical effects at a critical unbinding transition /8/. These features apply to general $d < 5$. In the remaining sections, I will discuss the physical case of 3-dimensional systems.

VI. COMPLETE VERSUS INCOMPLETE UNBINDING

Consider two membranes which are in a bound state as the result of an external pressure or constraint corresponding to $P > 0$. As $P \to 0$, the mean separation, $\bar{\ell}$, of the membranes can (i) attain a finite limit, or (ii) become arbitrarily large. These two cases correspond to *incomplete* and *complete* unbinding, respectively. It is intuitively clear that the behavior of the membranes for $P \to 0$ will, in general, depend on their direct interaction, $V_m(\ell)$. If this interaction is *repulsive*, i.e., $V_m(\ell) \approx V_R(\ell) \geq 0$ for large ℓ, the membranes will completely unbind as $P \to 0$. Such a situation occurs, for example, for the Langmuir repulsion $V_m(\ell) \sim 1/\ell$ arising from the pressure of counterions. On the other hand, the direct interaction can also be *attractive* for large ℓ. Then, one may write

$$V_m(\ell) \approx V_A(\ell) + V_R(\ell) \tag{18}$$

with $|V_A(\ell)| \gg V_R(\ell)$ for large ℓ where $V_A(\ell)$ and $V_R(\ell)$ represent the attractive and the repulsive part of the interaction. In this case, the membranes can *not* unbind completely if $V_A(\ell)$ is sufficiently long-ranged and satisfies $|V_A(\ell)| \gg 1/\ell^2$ for large ℓ (in d=3). For real systems, the attraction comes from van der Waals forces which lead to $V_A(\ell) \sim 1/\ell^4$ or $\sim 1/\ell^5$ for large ℓ as mentioned. Thus, one has

$$|V_A(\ell)| \ll 1/\ell^2 \text{ for large } \ell . \tag{19}$$

In the latter case, the membranes can unbind completely or incompletely depending on the *strength* of the attractive interaction, $V_A(\ell)$ /8/. What happens can be determined within the functional RG approach described in Sec. V. Indeed, this RG provides a *simple criterion for complete unbinding*: the membranes unbind completely whenever they interact by a direct interaction, $V_m(\ell)$, which is mapped onto the hard wall fixed point , V_o^*.

Now, assume that $V_m(\ell)$ leads to complete unbinding. Then, the mean separation, $\bar{\ell}$, behaves as

$$\bar{\ell} \sim 1/P^\psi \quad \text{as} \quad P \to 0. \tag{20}$$

The critical exponent, ψ, is correctly given by mean-field (MF) theory as long as $V_m(\ell) = V_R(\ell) >> 1/\ell^2$ (in d=3). This applies, for instance, to the Langmuir repulsion which leads to /9/

$$\psi = 1/2 \qquad \text{for } d = 3 \quad . \tag{21}$$

Within MF theory, the exponent ψ reflects the nature of the underlying microscopic forces. On the other hand, for sufficiently short-ranged interactions with $|V_m(\ell)| << 1/\ell^2$ for large ℓ, one finds the *universal* value /8,9/

$$\psi = 1/3 \qquad \text{for } d = 3 \ . \tag{22}$$

Thus, there are two scaling regimes for complete unbinding /9,18/: (i) a MF regime, and (ii) a weak-fluctuation (WFL) regime which is characterized by nonclassical critical exponents while the phase boundary is still given by P=0 as in MF theory.

These scaling regimes can be distinguished experimentally via the behavior of the scattering intensity, I, of X-rays which exhibit Laudau-Peierls singularities:

$$I(q_z) \sim (q_z - q_m)^{-(2-X_m)} \quad ,$$

where $q_m = 2\pi m/\bar{\ell}$ and q_z is the momentum transfer perpendicular to the membranes /3,4,9/. In the WFL-regime, the exponent X_m is independent of $\bar{\ell}$ for large $\bar{\ell}$. In contrast, it depends explicitly on $\bar{\ell}$ within the MF regime: e.g., one finds $X_m \sim 1/\bar{\ell}^{1/2}$ in the presence of the Langmuir repulsion /9/. This qualitatively different behavior has indeed been observed in recent high-resolution X-ray experiments /22/.

VII. CRITICAL UNBINDING TRANSITION

Now, assume that P=0 and consider again a direct interaction $V_m(\ell) = V_A(\ell) + V_R(\ell)$ with $|V_A(\ell)| << 1/\ell^2$ for large ℓ as in (19). The parameters of such an interaction span a low-dimensional space. Within this parameter space, there is a region where the membranes are completely separated and another region where they are bound together /8/. Obviously, these two regions must be separated by a phase boundary. In fact, it turns out /8/ that the transition along this phase boundary is typically a second order transition at which the mean separation, $\bar{\ell}$, of the membranes diverges in a continuous manner. Thus, the parameter space contains a manifold of critical unbinding points. The critical behavior along this manifold which depends on two different scaling fields has been described in Ref. 8 and will be discussed in more detail in Ref. 21. Recent experiments on a quasi-ternary mixture indicate that such a critical unbinding transition can be studied experimentally by changing the membrane thickness, δ /23/.

VIII. SUMMARY AND OUTLOOK

In summary, the interplay between direct and fluctuation-induced interactions leads to critical phenomena associated with the unbinding of amphiphilic membranes. We have theoretically studied these critical effects both for complete unbinding, see Sec.VI, and for unbinding critical points, see Sec.VII. Our theoretical results are confirmed by recent experiments.

The theory for unbinding of membranes is far from complete. Some interesting problems which we currently investigate are: (i) the marginal case with $V_m(\ell) \sim -1/\ell^2$ which should lead to an unbinding transition of infinite order, (ii) tricritical unbinding transitions which should be governed by yet another fixed point, compare /10/, and (iii) the influence of higher order gradient terms arising from the mean curvature.

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