Discontinuous unbinding transitions of flexible membranes

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Abstract. — The adhesion of membranes is often governed by an interaction potential which exhibits a potential barrier at intermediate membrane separations. At low temperatures, the membranes are trapped by the barrier. As the temperature is increased, thermally-excited shape fluctuations act to reduce the strength of this barrier until the membranes undergo an unbinding transition. This transition is discontinuous and continuous for strong and for weak potential barriers, respectively. Thus, the membranes can tunnel through weak barriers but remain trapped by strong ones. A simple criterion in terms of the parameters of the interaction potential is derived by which one can distinguish these two regimes.

1. Introduction: membranes *versus* strings.

The membranes considered here are lipid bilayers in water. Each bilayer consists of two monolayers which are arranged in such a way that the hydrocarbon chains of the lipids are in close contact whereas the hydrophilic head groups of the molecules point towards the water on both sides of the bilayer. Several preparation methods are available in order to obtain bilayers which contain essentially one type of lipid or a mixture of a few different lipid species. In addition, bilayers containing a large number of different lipids represent the basic structural element of all biomembranes [1].

Bilayer membranes often form bunches or stacks in which the membranes adhere to one another. Likewise, single membranes usually form closed vesicles which may adhere to other vesicles or to another surface such as the container wall. The adhesion of these membranes is governed by the interplay of direct interactions arising from the molecular forces and entropic or fluctuation-induced interactions arising from the thermally excited shape fluctuations of these membranes. On scales which are large compared to the bilayer thickness, which is 4-5 nm, typical shape fluctuations are bending modes [2, 3] which are directly visible in the light microscope.

The bending fluctuations act to renormalize the interaction of the membranes. This has been studied, in some detail, for interaction potentials which exhibit a single minimum or potential well. An example is provided by electrically neutral membranes. In this case, the direct interaction between rigid membranes consists of repulsive hydration and attractive van der Waals forces. With increasing temperature, the bending fluctuations may overcome the attractive van der Waals forces and lead to unbinding transitions between a bound state at low temperature and an unbound state at high temperature [4, 5]. These transitions have been experimentally observed for bunches of sugarlipid bilayers [6].

If the membranes carry electric charges, their direct interaction also depends on the electrostatic forces and may then exhibit an attractive potential well at small separations and a repulsive *potential barrier* at intermediate separations of the membranes. Such a form of the direct interaction is predicted by the classical theory of Derjaguin, Landau, Verwey and Overbeek [7, 8] and has been measured for two immobilized phospholipid bilayers with the surface force apparatus [9]. It is intuitively clear that the membranes may also undergo an unbinding transition in the presence of such a potential barrier. It is less obvious, however, if the transition through the barrier is *continuous* or *discontinuous*.

If one ignores the effect of the bending fluctuations, the potential barrier implies a discontinuous transition in which the mean separation of the membranes jumps from a small value as determined by the short-ranged potential well to infinity. In the presence of an external pressure, this leads to the coexistence of two different states of the membranes corresponding to two different separations and thus to the coexistence of two different lamellar phases [10].

However, the bending fluctuations of flexible membranes are expected to have a rather strong effect on the unbinding process. Indeed, it has been realized some time ago that, for fluid membranes, these shape fluctuations have scaling properties which are rather similar to those of 1-dimensional strings governed by a finite tension [11]. More recently, this analogy has been used in order to study the swelling behavior of bunches of fluid membranes and bundles of strings: the numerical work clearly shows that the critical behavior of these membrane bunches and string bundles is indeed quite analogous [12] as long as the interaction potential exhibits a single minimum (and thus no barrier).

For 1-dimensional strings in two dimensions, one has a complete classification of all universality classes for unbinding [13]. Here and below, I will focus on the *strong fluctuation regime*, i.e., on those interaction potentials which are sufficiently short-ranged and decay faster than $\sim 1/l^2$ for large separation l of the strings. In this case, the strings can *tunnel* through *any* potential barrier and the unbinding transition of these strings is always *continuous*.

As mentioned in reference [5], functional renormalization group (RG) calculations originally indicated that fluid membranes can also tunnel through a potential barrier provided this barrier is sufficiently small. This latter result was obtained by explicit RG transformations of the interaction potential for rescaling factor $b = 2$. In addition, a systematic study of the RG transformation in the infinitesimal rescaling limit seemed to imply that fluid membranes can also tunnel through any such barrier [14, 15]. However, this is not consistent with the simple stability arguments described below which predict discontinuous transitions for sufficiently strong potential barriers. These arguments have been recently confirmed by extensive Monte Carlo simulations as will be described elsewhere [16].

One should note that the membranes considered here consist of molecules which are essentially insoluble in water. For example, when phospholipids with two identical chains containing $2N_c$ carbon atoms are dissolved in water at room temperature, the mole fraction of these molecules is $\sim \exp[-1.7N_c]$ [17]. For $N_c = 16$ as applicable to DPPC (dipalmitoyl phosphatidyl choline), this implies that there is, on average, less than one lipid molecule per 10 μm^3 water. Therefore, the exchange of lipid molecules between the bilayer membrane and the water is very
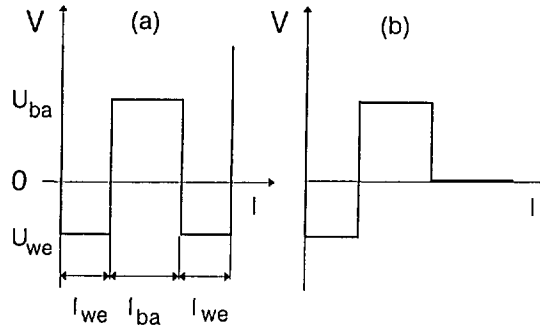
Fig. 1. — Direct interactions $V(l)$ with a potential barrier: (a) symmetric potential consisting of two wells with depth $|U_{we}|$ and range l_{we} separated by the barrier of height U_{ba} and thickness l_{ba}; and (b) asymmetric potential consisting of one well between the hard wall at $l = 0$ and the barrier.

slow, and the corresponding times scales are very long compared to the typical time scales which are relevant for the phenomena considered here. In such a situation, one may assume that the membrane has a constant number of molecules.

2. Symmetric double-well potential.

To proceed, consider two fluid membranes with identical bending rigidity κ_1 which interact via the potential $V(l)$ and experience the external pressure P. The separation l of these membranes is governed by the effective Hamiltonian [4]

$$\mathcal{H}\{l\} = \int d^2x \left\{ Pl + V(l) + \frac{1}{2}\kappa(\nabla^2 l)^2 \right\} \tag{1}$$

with the reduced bending rigidity $\kappa = \kappa_1/2$. Such a model is also appropriate for two adjacent membranes within a bunch or stack of many membranes, see section 4 below [18].

It is instructive to consider first a *symmetric* double-well potential $V(l)$ with two degenerate minima at finite values of l as shown in figure 1a. This potential exhibits two attractive square wells of depth $|U_{we}|$ and range l_{we} separated by a short-ranged potential barrier of height U_{ba} and thickness l_{ba}.

Let us assume that the membrane is confined within one of these wells and let us see if such a state is stable with respect to thermal excitations in which a membrane segment is displaced into the other potential well. Such a conformation corresponds to an *island* bounded by an edge where the edge goes through the potential barrier. This line of reasoning is analogous to the so-called Peierls argument for phase transitions in bulk systems [19]. It has been previously applied by us to a smooth double well potential as mentioned at the end of reference [14] but we did not consider its consequences for the nature of the unbinding transition. Similar arguments have been recently used for wetting transitions in d dimensions [20].

If one considers only the energy of the membrane confined in the well, the barrier height is given by $U_{ba} + |U_{we}|$. However, the membrane also suffers a loss of entropy by the confinement which implies an excess free energy per unit area or a fluctuation-induced interaction V_{fl} of the membrane. For fluid membranes confined to a potential well of width l_{we}, this excess free energy density is given by $V_{fl}(l_{we}) \sim T^2/\kappa l_{we}^2$ which depends on the temperature T and on the bending rigidity κ [3]. Therefore, the free energy density of the confined membrane is

$-|U_{\text{we}}| + cT^2/\kappa l_{\text{we}}^2$, and the effective barrier height is given by $U_{\text{ba}}^{\text{eff}} = U_{\text{ba}} + |U_{\text{we}}| - cT^2/\kappa l_{\text{we}}^2$ where c is a dimensionless coefficient.

The edge of the island consists of membrane segments which go through the potential barrier of thickness l_{ba}. Within the barrier, the potential is constant and membrane fluctuations of wavelength $\xi_\parallel$ have an amplitude $\xi_\perp \sim (T/\kappa)^{1/2} \xi_\parallel$ as appropriate for fluid membranes. Using this scaling relation, the edge of the island has an effective width $a_{e\perp} \sim (\kappa/T)^{1/2} l_{\text{ba}}$. The edge energy per unit length which will be denoted by σ_{o} can then be estimated as $\sigma_{\text{o}} \simeq U_{\text{ba}}^{\text{eff}} a_{e\perp}$. The quantity σ_{o} represents the line tension on small scales. This implies that the small-scale cutoff $a_{e\parallel}$ parallel to the edge scales as $a_{e\parallel} \simeq (\sigma_{\text{o}}/T)a_{e\perp}^2$.

For a displaced membrane segment or island of linear size $L_\parallel$, one has the edge energy $\sim \sigma_{\text{o}} L_\parallel$ and the edge entropy $\sim \ln(3) L_\parallel/a_{\parallel e}$ arising from the different shapes of the edge. In the latter estimate, the edge is viewed as a random walk with three possibilites at each step. This leads to the excess free energy of the edge as given by

$$\Delta F_e = [c_1 \sigma_{\text{o}} - c_2 T \ln(3)/a_{e\parallel}] L_\parallel \qquad (2)$$

with dimensionless coefficients c_1 and c_2. The expression within the square brackets represents an estimate for the line tension σ on large scales. This line tension is positive for low temperatures $T < T_{\text{ba}}$ where T_{ba} satisfies the implicit relations

$$T_{\text{ba}} \sim a_{e\parallel} \sigma_{\text{o}} \qquad \text{or} \qquad T_{\text{ba}} \sim (\kappa U_{\text{ba}}^{\text{eff}} l_{\text{ba}}^2)^{1/2} \qquad (3)$$

as follows from the above expressions for σ_{o} and $a_{e\parallel}$. For $T < T_{\text{ba}}$, the membrane fluctuations experience an effective barrier, the line tension is positive on large scales, and the original state should be stable. For $T > T_{\text{ba}}$, on the other hand, the edge entropy wins and the membrane feels no effective barrier.

The temperature T_{ba} represents an estimate for the critical temperature T_c of this system. For $T < T_c$, the membrane stays in one of the two wells and thus exhibits two coexisting states with two different mean values $\langle l \rangle$ of its displacement field. This implies that, for $T < T_c$, the membrane *cannot tunnel* through the intermediate potential barrier and thus will undergo a *discontinuous transition* between the two states as one varies an external field which breaks the symmetry between these states. This coexistence curve for $T < T_c$ ends in a critical point at $T = T_c$ where the system attains a unique thermodynamic state.

As mentioned, this stability argument is analogous to the so-called Peierls argument for phase transitions in bulk systems. It is well-known in this latter context that this argument is reliable as far as the existence of the coexistence curve at low temperatures is concerned but that it does not necessarily predict the correct behavior close to the critical point.

This critical behavior has been recently studied by Monte Carlo simulations [16]. The Monte Carlo data give strong evidence that this critical point belongs to the same universality class as the critical point of the 2-dimensional Ising model. This is quite plausible since the same type of thermal excitations, namely the islands considered above, restore the symmetry both for the membrane in the double well potential and for the Ising model. Note that the line tension in the 2-dimensional Ising model vanishes as $\sigma \sim |T - T_c|$ [21] which is, in fact, the behavior as predicted from (2) with $T_c \equiv T_{\text{ab}}$.

For comparison, let us apply the same kind of reasoning to a 1-dimensional string which moves in a double-well potential in two dimensions. In this latter case, the excitations from one potential well to the other well correspond to kinks of the string. The excess energy of such a kink is $\sim \sigma_{\text{o}}$ and its excess entropy is $\sim \ln(L_\parallel)$ which leads to the excess free energy $\Delta F_k = c_1 \sigma - c_2 T \ln(L_\parallel)$ per kink. For finite $T > 0$, the entropy term always dominates, and this argument leads to the correct prediction that the string always tunnels through the potential barrier.

3. Unbinding through a potential barrier.

Next, consider membranes which interact *via* the potential as shown in figure 1b. This potential is given by

$$V(l) \quad \begin{aligned} &= \infty & &\text{for} \quad l < 0 \\ &= -|U_{\text{we}}| & &\text{for} \quad 0 < l < l_{we} \\ &= U_{\text{ba}} & &\text{for} \quad l_{\text{we}} < l < l_{\text{we}} + l_{\text{ba}} \\ &= 0 & &\text{for} \quad l_{\text{we}} + l_{\text{ba}} < l \end{aligned} \tag{4}$$

and is appropriate for the unbinding from a potential well in the presence of a potential barrier.

Assume that the membrane is originally confined within the potential well. A segment of linear size $L_{\parallel}$ then has the free energy $\Delta F_0 \simeq (-|U_{\text{we}}| + c_3 T^2/\kappa l_{\text{we}}^2)L_{\parallel}^2$ where the second term again represents the loss of entropy. If this segment is thermally excited to overcome the potential barrier, it will form a "hump" with free energy $\Delta F_1 \simeq \Delta F_{\text{e}} + c_4 T$ where the first term represents the edge free energy as given by (1), and the second term corresponds to the entropy loss of the $L_{\parallel}$–hump which lies in front of the potential barrier (where $V(l) = 0$).

The excess free energy of the hump is given by $\Delta F \equiv \Delta F_1 - \Delta F_0$ and thus by

$$\Delta F = (|U_{\text{we}}| - c_3 T^2/\kappa l_{\text{we}}^2)L_{\parallel}^2 + [c_1 \sigma_{\text{o}} - c_2 T \ln(3)/a_{\parallel\text{e}}]L_{\parallel} + c_4 T \tag{5}$$

Within this approximation, the unbinding transition occurs when the coefficient of the $L_{\parallel}^2$–term vanishes. In this case, the free energy of the membrane confined in the potential well is equal to the free energy of the unbound membrane which lies outside of the potential. This leads to the characteristic temperature

$$T_{\text{we}} \sim (\kappa |U_{\text{we}}| l_{\text{we}}^2)^{1/2} \tag{6}$$

which represents an estimate for the unbinding temperature $T = T_{\text{u}}$.

In order to determine the character of this unbinding transition, one must now ask if the membrane still feels an effective barrier at $T = T_{\text{we}}$, i.e., if the line tension σ of the island excitations is still positive at this temperature. At the latter temperature, the effective barrier height $U_{\text{ba}}^{\text{eff}} = U_{\text{ba}}$ since there is no loss of entropy for the unbound state of the membrane. It then follows from (3) that the temperature T_{ba} is given by $T_{\text{ba}} \sim (\kappa U_{\text{ba}} l_{\text{ba}}^2)^{1/2}$ For $T < T_{\text{ba}}$, the membrane cannot tunnel through the barrier.

Therefore, the membrane will undergo a discontinuous unbinding transition from the potential well to infinity *provided* $T_{\text{we}} < T_{\text{ba}}$. For $T_{\text{we}} > T_{\text{ba}}$, on the other hand, there is no effective barrier at $T = T_{\text{we}}$ which implies that the unbinding transition will be continuous. If one expresses T_{ba} and T_{we} in terms of the potential parameters *via* (3) and (6), one finds that the unbinding transition should be *discontinous* for relatively strong potential barriers with

$$U_{\text{ba}} l_{\text{ba}}^2 \gg |U_{\text{we}}| l_{\text{we}}^2 \tag{7}$$

but should be *continuous* for relatively weak potential barriers with $U_{\text{ba}} l_{\text{ba}}^2 \ll |U_{\text{we}}| l_{\text{we}}^2$.

If the unbinding transition through the barrier is continuous, it should belong to the same universality class as the unbinding transition in the complete absence of a barrier. This expectation is confirmed by the results of functional renormalization. In this latter approach, the unbinding transition in the absence of a barrier is governed by a critical fixed point potential which has a single minimum (and thus no barrier) [4]. When the renormalization group (RG) transformation (with rescaling factor $b = 2$) is applied to interaction potentials with a weak barrier, one finds indeed that such a barrier is reduced under successive iterations of the RG transformation and that these potentials are also mapped to the vicinity of the critical

fixed point. At these continuous unbinding transitions, the mean separation $\langle l \rangle$ diverges as $\langle l \rangle \sim 1/|T - T_{\mathrm{u}}|^{\psi}$ where the critical exponent ψ has the presumably exact value $\psi = 1$ [11].

On the other hand, if the transition through the barrier is discontinuous, the membrane can be trapped in the bound state even if this state is only metastable. In such a situation, the first term of the excess free energy ΔF as given by (5) is negative, and ΔF exhibits a maximum as a function of the hump size $L_{\parallel}$ which corresponds to the critical droplet for the nucleation process. The decay of such metastable states has been recently observed in Monte Carlo simulations [16] and the measured decay times are consistent with classical nucleation theory [22].

It is straightforward to generalize the above criterion to other types of membranes. In general, shape fluctuations with wavelength $\xi_{\parallel}$ are characterized by the roughness $\xi_{\perp} \sim (T/K)^{1/2} \, \xi_{\parallel}^{\zeta}$ where K represents a scale-independent elastic modulus. One example is provided by polymerized membranes which have a roughness exponent ζ with $1/2 \leq \zeta < 1$ [23, 24]. The best analytical estimate seems to be $\zeta \simeq 0.59$ [25]. If such a membrane is confined within a potential well of width l, its loss of entropy leads to the fluctuation-induced interaction $V_{\mathrm{fl}}(l) \sim T^{1+1/\zeta}/K^{1/\zeta} l^{2/\zeta}$ [11]. Repeating the above arguments, one now finds that the criterion for a discontinuous transition has the more general form $U_{\mathrm{ba}} l_{\mathrm{ba}}^{2/\zeta} \gg |U_{\mathrm{we}}| l_{\mathrm{we}}^{2/\zeta}$.

Note that these discontinuous transitions for strong barriers must be separated from the continuous transitions for weak barriers by a multicritical point at $U_{\mathrm{ba}} l_{\mathrm{ba}}^{2/\zeta} = c_{\mathrm{mc}} |U_{\mathrm{we}}| l_{\mathrm{we}}^{2/\zeta}$. At this multicritical point, the membranes should still undergo a continuous transition but the corresponding exponents should differ from those for interaction potentials without a barrier (or with a weak barrier). These critical exponents have not been determined so far but the exponent ψ for the mean separation should satisfy the inequalities $1/2 \leq \psi \leq 1$.

In the framework of the functional RG, the multicritical unbinding transition should be governed by another multicritical fixed point. Such a fixed point has, however, not been found for the membranes considered here which are characterized by a roughness exponent $\zeta \geq 1/2$ [14, 15]. Therefore, the functional RG approach predicts that these membranes do not exhibit any discontinuous unbinding transitions. In view of the simple and general arguments described above, this must be considered as a deficiency of the RG approach which remains to be clarified.

4. Coexistence of two lamellar phases.

Bilayer membranes in solution often form stacks or bunches (or multilayers or lamellar states) in which several membranes adhere to each other. Oriented stacks containing a large number of such membranes correspond to lyotropic liquid crystals and have been studied for a long time by X-ray scattering methods, see e.g. [26]. On the other hand, bunches containing only a relatively small number of membranes are also accessible to experiments: freely suspended bunches can be directly observed in the light microscope [6] whereas multilayers attached to an interface can be investigated by surface reflectivity measurements [27, 28]. Likewise, stacks of bilayers spread on a solid substrate such as a glass slide are often used in order to prepare lipid vesicles.

The simplest theoretical description is obtained if one focusses on one membrane within the stack and replaces the two nearest neighbor membranes by two rigid walls. Such a one-membrane approximation was used by Helfrich in order to estimate the loss of entropy of the membrane confined in the stack [3]. As mentioned by de Gennes and Taupin [29], this approximation represents the analogue of the Einstein model for lattice vibrations or phonons in solids.

In the one-membrane approximation, all fluctuations in which two neighboring membranes

are displaced in the same direction are suppressed. In the context of phonons, this is a well-known defect of the Einstein model: it gives an approximate description of optical phonons in which neighboring atoms move against each other but fails to describe acoustical phonons in which neighboring atoms move in phase. However, the latter modes are most easily excited since they become soft in the limit of long wavelengths.

In order to overcome the limitations of the one-membrane approximation, one may focus on a *pair* of nearest-neighbor membranes within the stack [4, 5]. These two membranes are taken to interact with each other and with the two adjacent membranes which are now replaced by rigid walls. This leads to an effective Hamiltonian for the local separation l of the membrane pair which has the same form as given by (1) as has been explicitly derived in reference [18]. Thus, within this two-membrane approximation, the renormalized potential of two membranes within the stack is identical with the renormalized potential of two isolated membranes.

In many cases, the membrane separations in the stack are constrained by the overall composition of the lipid water system. Such a situation corresponds to an effective pressure P which pushes the membranes closer together. In the presence of a finite pressure $P \geq 0$, the membrane separation is determined by $-\partial V_{\text{eff}}(l)/\partial l = P$ where $V_{\text{eff}}(l)$ represents the fully renormalized interaction. As explained in the previous section, $V_{\text{eff}}(l)$ still has a potential barrier and thus two local minima at finite and at infinite l, respectively, if the unrenormalized interaction $V(l)$ exhibits a sufficiently strong barrier.

For zero pressure, the equation $-\partial V_{\text{eff}}(l)/\partial l = P = 0$ has two solutions at small and at infinite $\langle l \rangle$ corresponding to the two coexisting states at the discontinuous unbinding transition. For small but nonzero P, one still has two solutions corresponding to the coexistence of two states with small and with large $\langle l \rangle$, respectively. This coexistence line will end up in a critical point which must belong to the same universality class as the critical point of the symmetric double well potential studied above. As mentioned, the Monte Carlo simulations of reference [16] give strong evidence that this is the universality class of the 2-dimensional Ising model.

The coexistence of two lamellar phases has been experimentally observed in several mixtures of amphiphilic molecules and solvent, see reference [10]. In general, different amphiphiles such as double-chained lipids and single-chained surfactants can have rather different solubilities which can lead to very different time scales for the exchange of molecules between the membranes and the solution. The theory described above is applicable to these systems as long as the typical shape fluctuations are bending modes and are not governed by the adsorption or desorption of the amphiphilic molecules from the solution or from the membrane. This should apply to lipid bilayers but may be more questionable for surfactant membranes.

In summary, simple scaling arguments predict that membranes can form two coexisting lamellar phases provided their direct interaction exhibits a strong potential barrier which satisfies the criterion as given by (7). On the other hand, flexible membranes are also predicted to tunnel through weak barriers; therefore, interactions with weak barriers do not lead to the coexistence of two lamellar states.

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