

## Stacks and bunches of fluid membranes

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**Abstract.** Fluid membranes such as lipid bilayers often form oriented stacks or bunches. Within these bunches, the direct molecular forces are renormalized by thermally excited shape fluctuations. For purely repulsive forces between the membranes, this renormalization depends only weakly on the number  $N$  of the membranes within the bunch. In the presence of attractive forces, these bunches undergo continuous unbinding transitions. For freely suspended bunches, all membranes unbind simultaneously at a unique  $N$ -independent temperature  $T_*^s$ , but the effective critical behaviour depends on  $N$  over many length scales. For bunches that adhere to another surface, the membranes can peel off one after another in a sequence of transitions that occur in a finite temperature range above  $T_*^s$ .

### 1. Introduction

The interaction of fluid bilayers and other flexible membranes is determined by the renormalization of molecular forces by thermally excited shape fluctuations. On length scales large compared to the membrane thickness, these shape fluctuations are believed to be bending undulations. The renormalization effect of these undulations is well understood in the case of *two* interacting membranes [1]. However, many experimental systems contain whole stacks or bunches of membranes which exhibit a more complex behaviour.

Indeed, lipid bilayers in solution often form stacks or bunches (or multilayers or lamellar states) in which several membranes are, on average, parallel to each other. Large oriented stacks corresponding to lyotropic liquid crystals have long been studied by x-ray and neutron scattering methods [2–4]. On the other hand, bunches containing only a relatively small number of membranes are also accessible to experiment: freely suspended bunches can be directly observed in a light microscope [5, 6], whereas multilayers attached to a fluid–vapour interface can be investigated by surface reflectivity measurements [7]. Likewise, stacks of bilayers spread on a solid substrate such as a glass slide are often used in order to prepare lipid vesicles [8].

In this paper, recent theoretical work on membrane bunches is briefly reviewed. The basic theoretical model that contains both the interaction energies arising from molecular forces and the elastic energies of bending undulations is defined in section 2, which also serves to introduce the notation. This model can be studied within a simple two-membrane approximation, see section 3, which is presumably exact for the balance between purely repulsive interactions and the external pressure  $P$  in the limit of small  $P$ . Attractive forces between the membranes lead to continuous unbinding transitions for freely suspended bunches, see section 4, and for bunches which adhere to another surface, see section 5.

## 2. Model for bunches of membranes

Consider a bunch of  $(N + 1)$  fluid membranes labelled by  $n = 0, 1, \dots, N$  which are, on average, parallel to a reference plane. The distance of membrane  $n$  from this reference plane is denoted by the height variable  $h_n$ . The membranes have bending rigidities  $\kappa_n$  and experience the external pressure  $P$ . The interaction potential of membrane  $n$  with membrane  $(n - 1)$  is denoted by  $V_n$ . Their configurational energy (or effective Hamiltonian) is then given by

$$\mathcal{H}(\underline{h}) = \int d^2x \left( \sum_{n=1}^N V_n(h_n - h_{n-1}) + P \sum_{n=1}^N (h_n - h_{n-1}) + \frac{1}{2} \sum_{n=0}^N \kappa_n (\nabla^2 h_n)^2 \right). \quad (1)$$

Even though the membrane positions within the stack are described by  $(N + 1)$  fields  $h_n$ , only  $N$  of these variables are coupled by the direct interactions  $V_n$  since the 'centre-of-mass' coordinate decouples from the  $N$  separation variables  $l_n \equiv h_n - h_{n-1}$  with  $n \geq 1$ . Note that the pressure term is equal to  $P(h_N - h_0)$ .

The mean separation of the membranes within the stack is determined by the mutual interactions and forces. In the absence of shape fluctuations, the balance of forces within the stack implies  $P = -\partial V_n(l_n)/\partial l_n$  for  $l_n = \ell_n$ . In the presence of shape fluctuations, the direct interaction  $V_n(l)$  becomes renormalized into  $V_n^R(l)$ , and  $P = -\partial V_n^R(l_n)/\partial l_n$  for  $l_n = \ell_n$ .

## 3. Two-membrane approximation

First, let us focus on one pair of nearest-neighbour membranes within the stack with  $n = a$  and  $n = a + 1 \equiv b$ . These two membranes interact with each other and with the two adjacent membranes with  $n = a - 1 \equiv \alpha$  and  $n = b + 1 \equiv \beta$ . Within the two-membrane approximation considered here, which is of the mean-field type, the two membranes with  $n = \alpha$  and  $n = \beta$  are now replaced by rigid walls with positions  $\langle h_\alpha \rangle = \langle h_a \rangle - \ell_a$  and  $\langle h_\beta \rangle = \langle h_b \rangle + \ell_\beta$ , respectively. In addition, the two-membrane interactions  $V_a(h_a - h_\alpha)$  and  $V_b(h_b - h_b)$  are approximated by the renormalized interactions  $V_a^R(h_a - \langle h_\alpha \rangle)$  and by  $V_b^R(\langle h_\beta \rangle - h_b)$ , respectively. If one now expands these interaction energies in powers of  $h_a - \langle h_a \rangle$  and  $h_b - \langle h_b \rangle$ , one obtains

$$V_a^R(h_a - \langle h_\alpha \rangle) + V_b^R(\langle h_\beta \rangle - h_b) \approx V_a^R(\ell_a) + V_b^R(\ell_\beta) - P\ell_b + P(h_b - h_a) \quad (2)$$

for small fluctuation amplitudes. If the last term is combined with all other terms of the energy (1) that depend explicitly on  $h_a$  and  $h_b$ , one obtains the effective Hamiltonian for the membrane pair with  $n = a$  and  $n = b$  which interact via the two-membrane interaction  $V_b(h_b - h_a)$  and are subject to the external pressure  $P$ . Therefore, within this approximation, the renormalized potential of two membranes within the bunch is identical with the renormalized potential of two isolated membranes [9, 10].

The simplest pair potential is the hard-wall interaction defined by  $V(l) = \infty$  for  $l < 0$  and  $V(l) = 0$  for  $l > 0$ . For two identical membranes with bending rigidities  $\kappa$ , this potential is renormalized, in the limit of small  $P$ , into  $V^R(l) \approx 2c_v T^2/\kappa l^2$  with  $2c_v = 0.115 \pm 0.005$  (as follows from figure 1 of [11]). Recent Monte Carlo simulations of bunches of three and four membranes interacting with hard-wall potentials have shown that the same value for  $2c_v$  also applies to these bunches [12]. This value for  $2c_v$  is very close to  $3\pi^2/256$ , which is exactly half the value originally proposed by Helfrich [13].

Thus, for the hard-wall interaction, the two-membrane approximation becomes presumably exact as the membranes unbind: each pair of neighbouring membranes behaves asymptotically as if it were unaffected by the presence of the other membranes within the stack. Scaling and renormalization group arguments imply that this asymptotic separability is valid as long as the two-membrane interactions are purely repulsive (and one does not include next-nearest neighbour interactions or  $n$ -membrane interactions with  $n > 2$ ). It is not obvious, however, that this separability also applies in the presence of *attractive* forces between the membranes.

#### 4. Cohesion of freely suspended bunches

Now, consider the case of three identical membranes with bending rigidities  $\kappa_n = \kappa$  and with direct interactions  $V_n(l) = V(l)$  which contain an attractive part. At zero external pressure, the membranes form a bound and an unbound state at low and at high temperatures, respectively. Because the energy of the three membranes is invariant under an exchange of the two outer membranes, all three membranes must unbind *simultaneously* at the unbinding temperature  $T = T_*^s(3)$  (where the superscript  $s$  indicates that the bunch is symmetric).

The model (1) for three membranes has been studied by extensive Monte Carlo simulations [14, 15]. For  $P = 0$ , the membranes undergo a continuous unbinding transition, but the critical behaviour was found to be different from the case of two membranes over the accessible range of length scales. The best fit for the mean separation  $\ell$  leads to the power law  $\ell \sim 1/|T - T_*^s(3)|^\psi$  with the effective critical exponent  $\psi = 0.91 \pm 0.04$ , which differs from the presumably exact value  $\psi = 1$  for two membranes. The critical unbinding temperature  $T_*^s(3)$ , on the other hand, was found to be identical with the corresponding temperature  $T_*^s(2)$  for two membranes [15]. Very similar results were found from numerical iterations of the transfer matrix for bundles of one-dimensional strings: the transition temperature  $T_*^s$  was found to be identical for  $N = 2, 3$  and 4 strings (within the numerical accuracy) but the effective critical exponents were again  $N$ -dependent over the accessible range of scales [16].

Originally, we thought that the observed  $N$ -dependence of the critical behaviour could be understood in terms of an effective repulsion between the two outer membranes that arises from the loss of entropy of the confined membrane in the middle. Such a mechanism is present in the so-called necklace model for interacting strings [17]. However, the necklace model predicts a discontinuous unbinding transition for three identical strings, whereas the transfer matrix results clearly showed that the transition is continuous [16].

On the other hand, continuous transitions but with  $N$ -independent critical exponents were subsequently found (i) within two mean-field theories [18, 19], (ii) from a mapping of the string problem to a quantum spin chain [20], and (iii) in the limit of attractive potentials with an infinitesimally small potential range [21]. Thus, it is likely that the critical exponent for the asymptotic behaviour is  $\psi = 1$  for all  $N$ , but that the approach to asymptotia exhibits an intermediate scaling regime with an effective  $N$ -dependent exponent  $\psi < 1$ . It has been recently argued that such a crossover arises if one considers the renormalization of more general models with 3-membrane interactions [22]. Thus, the asymptotic critical behaviour will be difficult to see in real systems, whereas the intermediate scaling regime observed in the simulations should also be accessible to experiments.

The fact that the unbinding temperature  $T_*^s$  does not depend on  $N$  can be understood within the following scaling theory. Locally, three membranes (or strings) which interact via square well potentials can attain three different types of configurations. (i) All three

membranes are 'locally free' if their separation exceeds the range of the interaction potential. (ii) Two of the three membranes form a bound pair, whereas the third one is 'locally free'. (iii) All three membranes form a bound triplet. The probabilities for these three different local configurations will be denoted by  $\mathcal{P}_0$ ,  $\mathcal{P}_2$ , and  $\mathcal{P}_3$ , respectively. In configuration (i), the membranes still have a finite separation and then suffer a loss of entropy. The loss of entropy per unit area will be denoted by  $\Delta F_0$  for each separation variable. On the other hand, the excess free energy per unit area for a bound pair and a bound triplet will be denoted by  $\Delta F_2$  and  $\Delta F_3$ , respectively. For interactions between nearest-neighbour pairs of membranes, one has  $\Delta F_3 \simeq 2\Delta F_2$ . Thus, the excess free energy per unit area of the bunch can be estimated as

$$\Delta F \simeq 2\Delta F_0\mathcal{P}_0 + (\Delta F_2 + \Delta F_0)\mathcal{P}_2 + 2\Delta F_2\mathcal{P}_3. \quad (3)$$

If the unbinding transition is continuous, the probabilities  $\mathcal{P}_2$  and  $\mathcal{P}_3$  must vanish in a continuous way, whereas  $\mathcal{P}_0 \approx 1$  as the transition is approached. In addition, the scaling properties at such a transition will be governed by the single length scale  $\xi_\perp$  which determines the roughness of the separation variables  $l_1$  and  $l_2$ .

So far, these arguments are rather general and apply to any kind of shape fluctuations. If the membranes undergo bending undulations, the entropy loss per unit area of 'locally free' membrane segments is given by  $\Delta F_0 \sim T^2/\kappa\xi_\perp^2$  [13]. In order to determine  $\xi_\perp$  from the free energy  $\Delta F$  as given by (3), one has to know how the probabilities  $\mathcal{P}_2$  and  $\mathcal{P}_3$  depend on this length scale.

At a continuous transition, the probability distribution  $\mathcal{P}(l_1, l_2)$  for the two separation variables  $l_1$  and  $l_2$  will exhibit the general scaling form

$$\mathcal{P}(l_1, l_2) \approx (a_\perp/\xi_\perp)^2 \Omega(l_1/\xi_\perp, l_2/\xi_\perp)$$

where  $a_\perp$  is the range of the square well potential. If the scaling function  $\Omega(s_1, s_2)$  is finite for small arguments  $s_1$  and  $s_2$ , one has  $\mathcal{P}_2 \sim (a_\perp/\xi_\perp)$  and  $\mathcal{P}_3 \sim (a_\perp/\xi_\perp)^2 \sim \mathcal{P}_2^2$ . In general, one should have  $\mathcal{P}_3 \ll \mathcal{P}_2$  as long as one considers only two-membrane forces which act between nearest-neighbour pairs of membranes.

The behaviour of  $\xi_\perp$  can now be determined by minimizing the excess free energy  $\Delta F$  with respect to  $\xi_\perp$ . The unbinding transition occurs when  $\Delta F_2$  vanishes. Therefore, the transition of three membranes occurs at the same temperature  $T_*$  as the transition of two. For a square well potential of depth  $|U|$ , one has  $\Delta F_2 \simeq -|U| + cT^2/\kappa a_\perp^2$ , where the first and the second term represent the interaction energy and the entropy loss within the square well, respectively. Thus, one has  $T_*^s \simeq \sqrt{\kappa|U|a_\perp^2/c}$ .

The minimization of  $\Delta F$  leads to a continuous unbinding transition at  $T = T_*^s$  with  $\xi_\perp \sim 1/|T_*^s - T|^\psi$ . The critical exponent  $\psi$  has the universal value  $\psi = 1$  if the probability for bound pairs behaves as  $\mathcal{P}_2 \sim (a_\perp/\xi_\perp)$ . On the other hand, if the probability distribution  $\mathcal{P}(l_1, l_2)$  were singular for small arguments, one would have  $\mathcal{P}_2 \sim (a_\perp/\xi_\perp)^{1-b}$ . This would lead to the same unbinding temperature  $T_*^s$  but to the changed critical exponent  $\psi = 1/(1+b)$ .

The scaling arguments just described can be directly extended to symmetric bunches containing an arbitrary number of membranes. One again finds the  $N$ -independent unbinding temperature  $T_*^s$ , whereas the critical behaviour of  $\xi_\perp$  depends on the behaviour of the probability distribution for small values of the separation variables. Furthermore, the behaviour discussed here is not restricted to the case of square well potentials but also applies to realistic van der Waals interactions and all other interactions within the 'strong-fluctuation regime' [1].

## 5. Adhesion to another surface

Finally, consider a bunch of  $N$  identical membranes with bending rigidity  $\kappa$  which adheres to a solid substrate (or another interface). This represents the limiting case of model (1) in which the bottom membrane with  $n = 0$  has infinite rigidity. In general, the interaction  $V_1(l) = V_s(l)$  between the substrate and the membrane with  $n = 1$  will differ from the mutual interaction  $V(l)$  between two membranes of the bunch.

If the interaction potential  $V_s$  is relatively weak compared to the mutual interaction potential  $V$ , the separation of the two outer membranes of the bunch will stay finite while the whole bunch unbinds from the substrate at a critical temperature  $T_*^a < T_*^s$  [21]. On the other hand, if  $V_s$  is comparable with or stronger than  $V$ , the stack undergoes a sequence of unbinding transitions at successive temperatures  $T_*^a(n)$  with  $T_*^s \leq T_*^a(n) \leq T_*^a(1)$  [15]. At all of these transitions, the critical behaviour is universal and the critical exponent  $\psi = 1$ .

For large  $n$ , the unbinding temperatures  $T_*^a(n)$  attain the limiting value  $T_*^s$ . In this limit, one expects  $T_*^a(n) - T_*^s \sim 1/n^\lambda$ . Extrapolation of the numerical data obtained for  $n \leq 3$  gives the rough estimate  $\lambda \simeq 2$  [15]. On the other hand, the analytical solution for strings leads to  $\lambda = 1$  [21]. For a large stack at  $T = T_*^s$ , the membrane density at distance  $z$  from the substrate should exhibit a power-law tail for large  $z$  as has been calculated for bundles of strings [21].

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