

Adhesion and Unbinding for Bunches of Fluid Membranes.

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Abstract. – The unbinding and adhesion of bunches of fluid membranes, interacting via attractive intermolecular forces, are considered. On the basis of scaling arguments it is argued that the nature of the unbinding transition should depend on both the number of membranes involved and the ratios of their rigidities. The results of extensive Monte Carlo simulations of three fluid membranes are presented. The data show that the unbinding of three membranes proceeds differently from the previously studied case of two membranes. At the transition the various length scales are found to diverge as power laws with exponents depending on the ratio of rigidities of the membranes. The conclusions drawn from the simulations are in qualitative agreement with the scaling picture.

Flexible membranes which interact via attractive intermolecular forces can undergo a transition between bound and unbound states as the temperature is increased. Such an unbinding (or adhesion) transition was first found from renormalization group (RG) calculations [1] and subsequently confirmed by Monte Carlo (MC) simulations [2]. It has also been observed experimentally for sugar-lipid membranes by optical microscopy [3, 4].

There is, however, one important difference between the theoretical and experimental results: all theoretical work done so far on the unbinding transition has been concerned with *two* membranes (or with a membrane attracted to another surface), while *six* to *eight* membranes were studied in the experiments. Therefore, before one can compare theory with experiment in a quantitative way, one has to address the question of whether the critical behaviour at the unbinding transition depends on the number of interacting membranes.

In this letter, we study the unbinding of *three* fluid membranes. First, we use the analogy between fluid membranes in $d = 2 + 1$ dimensions and domain walls in $d = 1 + 1$ to argue that the critical behaviour of three membranes should indeed be different from that of two membranes. This analogy is based on scaling arguments and does not allow one to determine the critical exponents. We then present the results of extensive Monte Carlo simulations which confirm the scaling arguments and give an estimate for these exponents.

It has been shown [5] that the renormalisation group flow equation for two fluid membranes in three dimensions is identical to that obtained for two domain walls interacting

via the same potential in two dimensions. Hence, one can infer the properties of the unbinding of two membranes by solving the simpler domain wall problem. It is not clear whether this analogy between p membranes in three dimensions and p domain walls or walks in two dimensions will be valid for arbitrary p . Already for $p = 3$, the domain wall problem itself becomes difficult and has not been solved exactly.

However, one may study a simplified model, the so-called necklace model, for three walls interacting via a contact potential [6, 7]. Recently, it has been found [8] that this necklace model for three walks leads to the same scenario for the unbinding transition as occurs if one considers two domain walls interacting via a short-range attractive potential plus an extra repulsion falling off as the inverse domain wall separation to the second power, *i.e.* $\sim 1/l^2$. Thus, the thermal fluctuations of the central domain wall produce a repulsive force $\sim 1/l^3$ on the two outer domain walls, as expected from simple scaling arguments. As one decreases the ratio of the surface tensions of the inner and outer domain walls, the thermal fluctuations of the central domain wall increase, so leading to an increased repulsive force on the outer walls.

In $d = 1 + 1$, the critical behaviour of two domain walls with stiffness κ and repulsive interactions $\approx W/l^2$ has been determined exactly and is found to depend on the dimensionless parameter $w \equiv 2\kappa W/T^2$ [9]. There is a whole line of unbinding transitions with w -dependent critical exponents. For $w > 0$, this line consists of two subregimes: i) in subregime (B) with $0 < w < w^{**} \equiv 3/4$, the unbinding transitions are continuous and the critical behaviour is governed by a single length scale; ii) in subregime (C) with $w > w^{**}$, the transitions are discontinuous but exhibit unusual scaling properties since the probability distribution for the domain wall separation l develops a power law tail at the transition [9, 5]. Such a nonuniversal behaviour is also found for the necklace model of three domain walls leading to exponents which depend on the surface tensions of the walls [8].

Now consider a stack of three fluid membranes with bending rigidities κ_1, κ_2 and $\kappa_3 = \kappa_1$ ⁽¹⁾. The analogy between membranes and domain walls now suggests that the central membrane leads to an effective repulsion $V^{(13)}(l) \approx c(q) T^2 / \kappa_2 l^2$, where $q \equiv \kappa_1 / \kappa_2$ and $c(q)$ is a dimensionless coefficient ⁽²⁾. The size of $c(q)$, which cannot be obtained from the above scaling arguments, should depend on the nature of the attractive forces and is expected to determine the nature of the unbinding transition: there is a characteristic value, $c = c^{**}$, such that the transition belongs to subregime (B) and (C) for $0 < c < c^{**}$ and $c > c^{**}$, respectively. In addition, the critical exponents are expected to depend on c and thus on q .

Similarly, if one has $p > 3$ membranes, one also expects an effective repulsive potential $\sim 1/l^2$ to be felt by the outermost membranes. The strength of this potential should increase with p , there being a characteristic value, $p = p^{**}$, such that for $p < p^{**}$ one is in subregime (B) and for $p > p^{**}$ one is in subregime (C). In addition, the above scaling arguments can be directly extended to polymerized (or other types of) membranes ⁽³⁾. In all cases, these two different subregimes should be present depending on the elastic moduli and on the interaction parameters.

Let us now define the problem more precisely. The Hamiltonian for three fluid

⁽¹⁾ The 3-membrane bunch considered here is invariant under the exchange of the two outer membranes. This symmetry ensures that all three membranes unbind simultaneously. In the absence of this symmetry, a 3-membrane bunch could also undergo a sequence of two unbinding transitions.

⁽²⁾ A flexible membrane between two rigid walls at fixed separation l has been previously considered by Helfrich [10]. Starting from such a geometry, the general conclusion $V^{(13)}(l) \sim 1/l^2$ can also be reached, see [11].

⁽³⁾ For a recent view, see [12]. For membranes with roughness exponent ζ , the effective interaction $V^{(13)}(l) \sim 1/l^\tau$ with $\tau = 2/\zeta$.

membranes with coordinates $l_a(\mathbf{x})$ and bending rigidities κ_a ($\alpha = 1, 2, 3$), interacting via a potential V can be written as

$$\mathcal{H}\{l_1, l_2, l_3\}/T = \int d^2x \left[\frac{1}{2T} \sum_a \kappa_a (\nabla^2 l_a)^2 + \frac{V(l_2 - l_1)}{T} + \frac{V(l_3 - l_2)}{T} \right], \tag{1}$$

where T is the temperature. A microscopic cut-off a , of the order of the membrane thickness, is implicitly assumed in this continuum model. To ensure that all three membranes unbind simultaneously, we shall only consider the case $\kappa_1 = q\kappa_2 = \kappa_3 = \kappa$. We shall also limit ourselves to interactions of a square-well form:

$$V(l) = \begin{cases} \infty & \text{for } l < 0 \\ -U & \text{for } 0 < l < l_0 \\ 0 & \text{for } l_0 < l. \end{cases} \tag{2}$$

The problem can be simplified by making an orthogonal transformation to extract a centre-of-mass coordinate, which diffuses freely, see [8]. One is then left with the effective Hamiltonian

$$\mathcal{H}\{y_1, y_2\}/T = \int d^2x \left[\frac{\kappa}{2T} (\nabla^2 y_1)^2 + \frac{\kappa}{2T} (\nabla^2 y_2)^2 + \hat{V}(y_1, y_2) \right], \tag{3}$$

where

$$\hat{V}(y_1, y_2) = \frac{1}{T} V(\sqrt{1+q}y_1) + \frac{1}{T} V\left(\frac{\sqrt{1+2q}y_2 - qy_1}{\sqrt{1+q}}\right). \tag{4}$$

To be able to perform a MC simulation of this problem, the spatial coordinate \mathbf{x} is discretised as a square lattice of size $N \times N$, with sites $\{\mathbf{x}_i\}$ and lattice constant a , as was done in [2]. The configuration of the three membranes is then represented by the set $\{y_{1i}, y_{2i}\}$ and the Hamiltonian takes the form

$$\mathcal{H}\{z_{1i}, z_{2i}\}/T = \sum_i \left[\frac{\kappa}{2T} (\nabla_a^2 z_{1i})^2 + \frac{\kappa}{2T} (\nabla_a^2 z_{2i})^2 + \hat{U}(z_{1i}, z_{2i}) \right], \tag{5}$$

where we have used the dimensionless variables $z_{ai} \equiv y_{ai}/a$ and $\hat{U}(z_{1i}, z_{2i}) \equiv a^2 \hat{V}(az_{1i}, az_{2i})$, so that

$$\hat{U}(z_{1i}, z_{2i}) = \begin{cases} \infty & \text{for } z < 0 \\ -a^2 U/T = -u & \text{for } 0 < z < z_0 \\ 0 & \text{for } z_0 < z. \end{cases} \tag{6}$$

∇_a^2 is the discrete Laplacian and $z_0 \equiv l_0/a$. (Apart from q and κ , this problem depends only on the dimensionless parameter $(\kappa/T)^{1/2} z_0$.)

We have carried out MC simulations of the effective Hamiltonian (5) with the Metropolis algorithm using a Cray X-MP 416. Square lattices of size $N = 20, 41$ and 80 were used and the runs were typically of the order of 10^6 MC steps per site. The mean membrane separations, $\langle l \rangle$, were measured by calculating $\langle l_{21} \rangle \equiv \sqrt{1+q} \langle z_1 \rangle a$ and $\langle l_{32} \rangle \equiv (\sqrt{1+2q} \cdot \langle z_2 \rangle - q \langle z_1 \rangle) a / \sqrt{1+q}$, where $\langle \dots \rangle$ represents an ensemble average. The behaviour of the perpendicular correlation length ξ_{\perp} was determined by evaluating

$$\hat{\xi}_{\perp} / a = \sqrt{\langle l_{21}^2 \rangle - \langle l_{21} \rangle^2} = \sqrt{\langle l_{32}^2 \rangle - \langle l_{32} \rangle^2}. \tag{7}$$

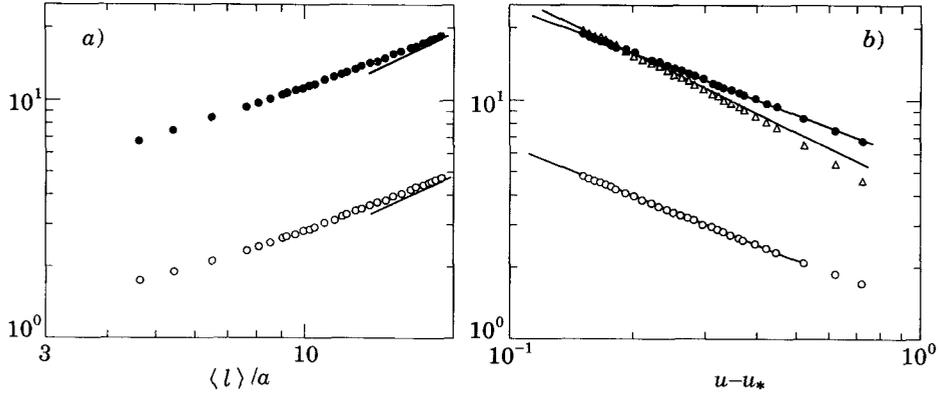


Fig. 1. - *a*) Log-log plot of the parallel and perpendicular correlation lengths, $\hat{\xi}_{\parallel}$ (\circ) and $\hat{\xi}_{\perp}$ (\bullet) against the mean membrane separation, $\langle l \rangle$, for $q = 1$ and $\kappa/T = 1.367 \cdot 10^{-3}$. The solid lines have unit slope. *b*) Log-log plot of the three lengths $\hat{\xi}_{\parallel}$ (\circ), $\hat{\xi}_{\perp}$ (\bullet) and $\langle l \rangle$ (Δ) against the deviation of the potential well depth from its transition value, $u_* = 2.48$, for $q = 1$ and $\kappa/T = 1.367 \cdot 10^{-3}$. The solid lines show the fits obtained and are $\log(\hat{\xi}_{\parallel}/a) = 0.13 - 0.65 \log(u - 2.48)$, $\log(\hat{\xi}_{\perp}/a) = 0.74 - 0.69 \log(u - 2.46)$, and $\log(\langle l \rangle/a) = 0.63 - 0.80 \log(u - 2.48)$.

Assuming one is in a regime in which the fluctuations may be regarded as Gaussian, one can show that the parallel correlation length $\xi_{\parallel} \sim \hat{\xi}_{\parallel} \equiv a \exp[2\pi\kappa\langle(\nabla l_a)^2\rangle/T]$, see [2]. So, we also determined $\langle(\nabla l_{21})^2\rangle$ and $\langle(\nabla l_{32})^2\rangle$ to examine the behaviour of ξ_{\parallel} . Notice that if one happens to be in subregime (C), in which scaling is not governed by a single length scale, this method of assessing ξ_{\parallel} may fail. To observe the unbinding transition, we fixed the values of κ , q and the potential well width, $z_0 = 1$, and varied the depth of the potential well u , decreasing it towards the critical value u_* .

In subregime (B) our scaling arguments imply that all the lengths scale in the same way, diverging as

$$\langle l \rangle \sim |u - u_*|^{-\psi}, \quad \xi_{\perp} \sim |u - u_*|^{-\nu_{\perp}} \quad \text{and} \quad \xi_{\parallel} \sim |u - u_*|^{-\nu_{\parallel}} \quad (8)$$

with $1/2 \leq \psi = \nu_{\perp} = \nu_{\parallel} \leq 1$. In subregime (C) these quantities should no longer scale in the same way. ξ_{\perp} and $\langle l \rangle$ may have discontinuities at the transition, and if not, one finds that $\psi < \nu_{\perp} < 1/2$. The parallel correlation length always diverges as a power law at the transition with an exponent $\nu_{\parallel} = 1/2$ in this regime.

The first set of MC simulations were carried out taking all three membranes to have equal rigidities, *i.e.* $q = 1$. The data for rigidity modulus $\kappa/T = 1.367 \cdot 10^{-3}$ are shown in fig. 1. Figure 1*a*) shows the behaviour of the correlation lengths $\hat{\xi}_{\parallel}$ and $\hat{\xi}_{\perp}$ *vs.* the mean membrane separation $\langle l \rangle$. One observes that on the log-log plot the data tend towards a line with slope 1 as one approaches the transition, indicating that the three lengths scale in the same way as appropriate to subregime (B)⁽⁴⁾. To attempt to determine the exponents ν_{\parallel} and ν_{\perp} , the data

⁽⁴⁾ We have also studied higher moments, $\langle l^n \rangle$ and found that $\langle l^n \rangle \sim \langle l \rangle^n$ as appropriate for subregime (B). This is not to be expected from the analogy with the necklace model for three identical domain walls. Indeed, the latter model corresponds to $w = -35/4$, see [13], which belongs to subregime (C) and leads to discontinuous behaviour of $\langle l \rangle$ and ξ_{\perp} and to moments $\langle l^n \rangle$ which do not scale with a single length scale.

were fitted to the forms

$$\hat{\xi}_{\parallel}/a = A(u - u_*)^{-\nu_{\parallel}} \quad \hat{\xi}_{\perp}/a = B(u - u_*)^{-\nu_{\perp}} \quad (9)$$

with A , B , u_* , ν_{\parallel} and ν_{\perp} as fit parameters, using the Levenberg-Marquardt method for a three-parameter fit [14]. To examine the effects of the finite size of the system, many data points were checked using different system sizes. Also, to try to determine the onset of scaling we used consecutive slope methods to test for curvature in the data. Fits thus obtained are shown together with the data in fig. 1b). We estimate that $\nu_{\parallel} = 0.65 \pm 0.03$ and $\nu_{\perp} = 0.69 \pm 0.12$. Assuming the transition to occur at the value u_* obtained from fitting the two correlation lengths we then fitted our data for $\langle l \rangle$ to the form $\langle l \rangle/a = C(u - u_*)^{-\psi}$. In this way we find that $\psi = 0.8 \pm 0.1$. The data and a fit for the mean membrane separation are also shown in fig. 1b). The fact that the mean membrane separation appears to scale with a larger exponent than the two correlation lengths may be due to the presence of crossover effects in our data for $\langle l \rangle$. One would need to approach the transition much more closely to be sure of eliminating this problem. Even though our estimate for the critical exponents has relatively large errors, we can definitely conclude that these exponents are smaller than the values $\nu_{\parallel} = \nu_{\perp} = \psi = 1$ which apply to the unbinding transition of two membranes [1, 2, 5].

Simulations carried out at a different value of κ/T (to be presented elsewhere) give results in complete agreement with those above, within our error bars. For $\kappa/T = 3.4175 \cdot 10^{-3}$ we find $\nu_{\parallel} = 0.67 \pm 0.03$, $\nu_{\perp} = 0.66 \pm 0.08$ and $\psi = 0.8 \pm 0.1$. This is consistent with there being no dependence of the exponents on κ/T for a given q .

If the rigidity of the central membranes is decreased relative to one of the outer membranes, *i.e.* $q > 1$, one expects that the fluctuation-induced repulsion between the inner and outer membranes will be increased in magnitude. Any deviations from the two-membrane case should then be amplified. (Notice that $q = 0$ corresponds to the case of two membranes, as then the central membrane acts as a solid wall.) We therefore also studied the case $q = 4$. The data for $\kappa/T = 5.468 \cdot 10^{-3}$ are shown in fig. 2. A log-log plot of $\hat{\xi}_{\parallel}$ and $\hat{\xi}_{\perp}$ against $\langle l \rangle$ is given in fig. 2a). The data were fitted as described above to give us the estimates that $\nu_{\parallel} = 0.61 \pm 0.04$, $\nu_{\perp} = 0.58 \pm 0.07$ and $\psi = 0.73 \pm 0.10$. We repeated the

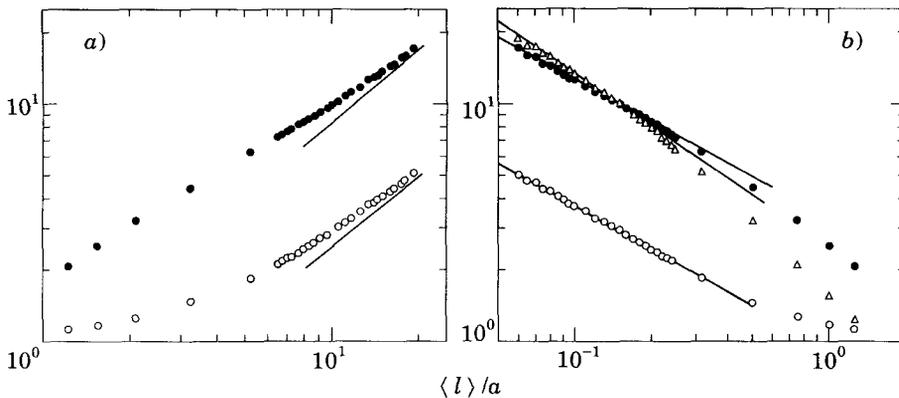


Fig. 2. - a) Log-log plot of the parallel and perpendicular correlation lengths, $\hat{\xi}_{\parallel}$ (\circ) and $\hat{\xi}_{\perp}$ (\bullet) against the mean membrane separation, $\langle l \rangle$, for $q = 4$ and $\kappa/T = 5.468 \cdot 10^{-3}$. The solid lines have unit slope. b) Log-log plot of the three lengths $\hat{\xi}_{\parallel}$ (\circ), $\hat{\xi}_{\perp}$ (\bullet) and $\langle l \rangle$ (\triangle) against the deviation of the potential well depth from its transition value, $u_* = 2.25$, for $q = 4$ and $\kappa/T = 5.468 \cdot 10^{-3}$. The solid lines show the fits obtained and are $\log(\hat{\xi}_{\parallel}/a) = -0.04 - 0.61 \log(u - 2.25)$, $\log(\hat{\xi}_{\perp}/a) = 0.52 - 0.58 \log(u - 2.26)$, and $\log(\langle l \rangle/a) = 0.40 - 0.73 \log(u - 2.25)$.

simulations at a smaller value of $\kappa/T = 1.367 \cdot 10^{-3}$. For these data it was not clear, from plotting the correlation lengths against the mean membrane separation, whether all lengths scaled in the same way and we obtained lower estimates for the exponents: $\nu_{\parallel} = 0.4 \pm 0.1$ and $\nu_{\perp} = 0.4 \pm 0.1$.

From our data it is difficult to determine whether the case $q = 4$ is consistent with still being in subregime (B), with $\nu_{\parallel} = \nu_{\perp} = \psi$ less than their $q = 1$ value, or is consistent with having moved into subregime (C), where the various lengths scale in different ways, or does not agree at all with the scenario derived from scaling. An accurate determination of the exponents in subregime (C) may prove to be a hard task, due to the presence of many critical points (at which, in turn, higher cumulants of the membrane separation become discontinuous at the transition) and associated crossover behaviour. Although the quality of our data does not allow us to draw quantitative conclusions, the qualitative picture is clear: when the ratio of outer to inner membrane rigidities, q , is increased the exponents at the unbinding transition decrease.

To summarize, one can conclude from our simulations that the unbinding of three fluid membranes does proceed in a different manner from that of two membranes. Our results are qualitatively in agreement with the scenario obtained from using scaling ideas and the analogy between membranes and domain walls, in that: i) the exponents for all cases investigated do not coincide with the values $\nu_{\parallel} = \nu_{\perp} = \psi = 1$ as appropriate for the unbinding of two membranes; ii) for three membranes of equal rigidities ($q = 1$), all lengths appear to scale in the same way, with an exponent between 1/2 and 1, consistent with subregime (B) and the exponents obtained are independent of the rigidity κ/T ; iii) for $q = 4$, the exponents are further reduced from their values for the $q = 1$ case, consistent with nonuniversal exponents, decreasing as the ratio q increases.

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