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Absence of first-order unbinding transitions of fluid and polymerized membranes

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Unbinding transitions of fluid and polymerized membranes are studied by renormalization-group (RG) methods. *Two different* RG schemes are used and found to give rather consistent results. The fixed-point structure of both RG's exhibits a complex behavior as a function of the decay exponent τ for the fluctuation-induced interaction of the membranes. For $\tau > \tau_{S2}$, interacting membranes can undergo first-order transitions even in the strong-fluctuation regime. Our estimates for τ_{S2} imply, however, that both fluid and polymerized membranes unbind in a continuous way in the *absence* of lateral tension.

Membranes such as, e.g., lipid bilayers, experience a variety of interactions arising from intermolecular forces.[1] These *direct* interactions can be measured when the membranes are immobilized on mica surfaces.[2] In this way, rather detailed information has been obtained for direct interactions resulting from van der Waals, electrostatics, or structural forces.

In solution, membranes undergo thermally excited shape fluctuations on many length scales. These undulations renormalize the direct interaction and increase its repulsive part.[3] In fact, sufficiently strong fluctuations overcome the attractive part of the direct interaction and lead to nontrivial unbinding transitions.[4] Such transitions were first predicted theoretically on the basis of renormalization-group (RG) calculations both for fluid[4,5] and for polymerized (or tethered or crystalline)[5] membranes. For fluid membranes, the existence of these transitions has been confirmed by experiments on digalactosyl diclyceride membranes[6] and by Monte Carlo simulations.[7] In this case, both experiments and simulations indicate that the transition is continuous and, thus, of *second order.*

Unbinding phenomena can also be studied for lyotropic liquid crystals, i.e., for lamellar phases (i) in two-component systems of water and lipid, and (ii) in microemulsions of three or more components.[8] For dipalmitoyl phosphatidylcholine bilayers, an unbinding transition may have been observed with decreasing salinity,[1,4] but its precise nature has not been determined so far. In some mixtures, two coexisting lamellar phases have been observed[9] which implies a first-order transition from a small to a large (but finite) separation of the membranes. This seems to indicate that unbinding transitions could also be of *first order.*

The shape fluctuations of a *single* membrane lead to a characteristic membrane roughness: A membrane segment of lateral size $L_\parallel$ has a typical fluctuation amplitude $L_\perp \sim L_\parallel^\zeta$.[10] The roughness exponent ζ depends on the internal membrane structure and, in addition, on the lateral tension. Fluid membranes are characterized by $\zeta = 1$,[3,4,11] while polymerized membranes have $\zeta < 1$.[5,12] In the latter case, recent Monte Carlo simulations indicate $\zeta \simeq 0.6$.[13] Lateral tension, on the other hand, strongly reduces the undulations[14] which are then characterized by $\zeta = 0(\sqrt{\log})$.

Now consider two interacting membranes at separation l. Their steric hindrance leads to an overall loss of entropy which can be regarded as an effective fluctuation-induced repulsion, $V_{\rm fl}(l) \sim 1/l^\tau$ with decay exponent $\tau = 2/\zeta$.[5,10] Using the aforementioned values for ζ, one obtains $\tau = 2$ and $\tau \simeq 3.3$ for tensionless fluid and polymerized membranes, respectively, while lateral tension implies $\tau = \infty$. Other values for τ are conceivable and could arise, e.g., from long-range forces within the membrane.

In this paper, we study the nature of unbinding transitions as a function of τ. We find that (i) both fluid and polymerized membranes always undergo *second-order* unbinding transitions in the absence of lateral tension (when their bound state is governed by van der Waals forces); (ii) in the presence of lateral tension, unbinding transitions are typically first order; and (iii) membranes under tension may also undergo first-order transitions between two different bound states.

Our results are based on RG transformations for the membrane interaction. In principle, one can formulate *exact* RG transformations[15,16] which are, however, rather difficult to study for general τ. Therefore, one has to simplify these transformations by using appropriate approximation schemes. Below, we will use and compare *two different* approximations which are based on a *hard*-cutoff[17,18] and on a *soft*-cutoff[15,19] procedure, respectively.

Both RG transformations act as nonlinear maps in the function space of interactions. In order to understand this action, we could iterate the transformations and study the resulting RG flow.[17] Such an approach is, however, quite tedious and typically requires a large number of iterations. Instead, we will perform a *global* analysis of the fixed-point structure for both RG's which allows us to study the order of the unbinding transitions in a systematic way.

The local separation of the two interacting membranes will be denoted by $z(\mathbf{x})$ where $\mathbf{x} = (x_1, x_2)$ is a parallel coordinate. For thermally excited undulations, the bending free energy per unit area is given by $\frac{1}{2} K (\nabla^n z)^2$, where K is an effective bending rigidity and $n = 1 + \zeta$. The mem-

brane configurations are then governed by the effective Hamiltonian

$$H(z)=\int d^2x[\tfrac{1}{2}K(\nabla^n z)^2+V(z)]\,. \tag{1}$$

The second term represents the direct interactions of the membranes and contains a hard wall at $z=0$ since the membranes cannot penetrate each other.

Our first RG method[17] represents an extension of Wilson's approximate recursion relations[19] and is based on a hard-cutoff (HC) procedure. For infinitesimal rescaling factor $b\rightarrow 1+\Delta s$, this functional RG leads to the flow equation[17]

$$\frac{\partial U}{\partial s}=\zeta\left[\tau U+y\frac{\partial U}{\partial y}+\ln\left[1+\frac{\partial^2 U}{\partial y^2}\right]\right], \tag{2}$$

with $\tau=2/\zeta$ and dimensionless variables $y\sim z$ and $U\sim V$.

Another approximate RG can be constructed by using a smooth-cutoff procedure,[15,19] which leads to the flow equation

$$\frac{\partial U}{\partial s}=\zeta\left[\tau U+y\frac{\partial U}{\partial y}+\frac{\partial^2 U}{\partial y^2}-\left[\frac{\partial U}{\partial y}\right]^2\right]. \tag{3}$$

First we study the fixed points, $U^*(y)$ with $\partial U^*/\partial s=0$. In the HC case, they satisfy

$$\tau U^*+y\frac{\partial U^*}{\partial y}+\ln\left[1+\frac{\partial^2 U^*}{\partial y^2}\right]=0\,, \tag{4}$$

and in the soft-cutoff (SC) case, we have

$$\tau U^*+y\frac{\partial U^*}{\partial y}+\frac{\partial^2 U^*}{\partial y^2}-\left[\frac{\partial U^*}{\partial y}\right]^2=0\,. \tag{5}$$

Therefore, the rescaled fixed points depend only on one parameter, namely τ.

The fixed-point Eqs. (4) and (5) must be supplemented by appropriate boundary conditions. For unbinding transitions, one wants to include a hard wall at $y=0$ and a tail which decays to zero for large y. These boundary conditions lead to a whole line of fixed points $U^*(y)=U^*(y\,|\,\sigma)$ with $\sigma>0$. For the HC case, the asymptotic behavior of these fixed points is given by[5]

$$U^*(y)\approx\sigma/y^\tau+[(\tau+2)/\tau]\ln y \tag{6}$$

for small y, and by

$$U^*(y)\approx\rho_L(\sigma)/y^\tau+\rho_S(\sigma)y^{\tau-1}\exp(-y^2/2) \tag{7}$$

for large y. For the SC case, asymptotic analysis of (5) leads to

$$U^*(y)\approx\ln(\sigma/y)+\tfrac{1}{6}y^2\{1-\tau[\ln(\sigma/y)+\tfrac{5}{6}]\} \tag{8}$$

for small y, and the same asymptotic behavior as in (7) for large y.

The function $\rho_L(\sigma)$ for the power-law tail of the fixed points can be obtained by numerical integration of (4) and (5) using (6) and (8) as initial conditions. For small τ, the function $\rho_L(\sigma)$ is convex downwards with a unique minimum at σ_{E1},[5,16] and has two zeros at $\sigma=\sigma_{S0}$ and $\sigma=\sigma_{S1}$, which correspond to short-ranged fixed points with a Gaussian tail; see (7). Such a convex downwards piece of $\rho_L(\sigma)$ persists to larger values of τ. However, as τ is increased, the function $\rho_L=\rho_L(\sigma)$ develops more structure.

First, at a certain value $\tau=\tau_2$, it exhibits a point of inflection with zero slope at $\sigma=\sigma_{E2}$ with $\sigma_{E2}<\sigma_{S1}$; see Fig. 1. This point of inflection bifurcates, for $\tau>\tau_2$, into an additional minimum and maximum of $\rho_L(\sigma)$ at $\sigma=\sigma_{E\bar{2}}$ and σ_{E2}. The new minimum at $\sigma=\sigma_{E\bar{2}}$ moves down with increasing τ and starts to intersect the σ axis at $\tau=\tau_{S2}>\tau_2$; compare Table I. As τ is increased even further, another point of inflection with zero slope appears for $\tau=\tau_3$, which lies between the minimum and the maximum of the previous bifurcation. This inflection point develops into another pair of extrema of $\rho_L(\sigma)$ which are located at $\sigma=\sigma_{E\bar{3}}$ and σ_{E3}; see Fig. 2.

Now, consider the eigenperturbations, $f_\lambda(y)$, at the fixed points $U^*(y)$ governed by

$$-\left[\tau-\frac{\lambda}{\zeta}\right]f_\lambda+y\frac{\partial f_\lambda}{\partial y}+\left[1+\frac{\partial^2 U^*}{\partial y^2}\right]^{-1}\frac{\partial^2 f_\lambda}{\partial y^2}=0 \tag{9}$$

for the HC case and by

$$\left[\tau-\frac{\lambda}{\zeta}\right]f_\lambda+y\frac{\partial f_\lambda}{\partial y}-2\frac{\partial U^*}{\partial y}\frac{\partial f_\lambda}{\partial y}+\frac{\partial^2 f_\lambda}{\partial y^2}=0 \tag{10}$$

for the SC case. For the HC case, f_λ behaves as[5] $f_\lambda\sim 1/y^{\tau-\lambda/\zeta}$ for small y and as

$$f_\lambda(y)\approx C/y^{\tau-\lambda/\zeta}+Dy^{\tau-1-\lambda/\zeta}\exp(-y^2/2) \tag{11}$$

for large y. For the SC case, we find $f_\lambda(y)\approx 1-(\tau-\lambda/\zeta)y^2/6$ for small y and the same asymptotic behavior as in (11) for large y.

Relevant perturbations with a power-law tail $C/y^{\tau-\lambda/\zeta}$ would dominate the tail of U^*.[5] Therefore, we use the boundary condition $C=C(\lambda/\zeta,\sigma)=0$ both for the HC and for the SC case. This condition selects a *discrete but infinite* set of *short*-ranged eigenperturbations. For

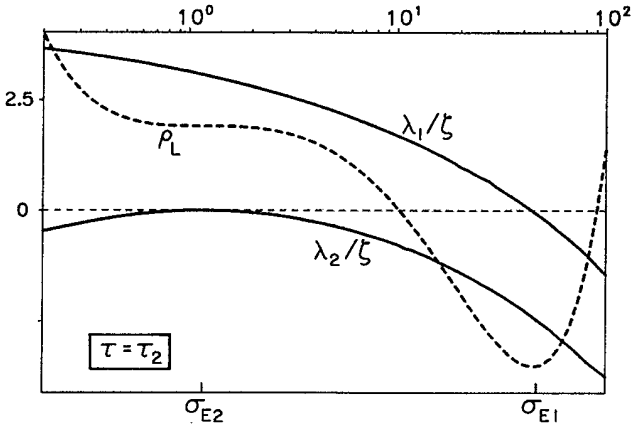

FIG. 1. Functional form of $\rho_L(\sigma)$ (dashed curve) and of the eigenvalues $\lambda_j(\sigma)$ for $\tau=\tau_2$ as obtained from the HC scheme. At $\sigma=\sigma_{E2}$, $\rho_L(\sigma)$ exhibits a point of inflection with zero slope and $\lambda_2(\sigma)$ touches the σ axis.

TABLE I. Numerical results for the characteristic τ values τ_2, τ_{S2}, τ_3, and τ_{S3}, and for the critical exponent $\psi=\zeta/\lambda_1(\sigma_{S1})$ as obtained from the hard-cutoff (HC) and the soft-cutoff (SC) scheme.

	τ	ψ	$\tau=\tau_2$	ψ	$\tau=\tau_{S2}$	ψ	τ	ψ	$\tau=\tau_3$	ψ	$\tau=\tau_{S3}$	ψ	τ	ψ
HC	2	1.06	4.175	0.71	4.797	0.66	5	0.65	6.615	0.58	7.342	0.52	8	0.49
SC	2	1.12	4.077	0.69	4.491	0.66	5	0.62	6.113	0.56	6.613	0.53	8	0.48

$\sigma>\sigma_{E1}$, all of these perturbations are irrelevant. As σ is decreased, a relevant perturbation with eigenvalue $\lambda_1>0$ first appears at $\sigma=\sigma_{E1}$, i.e., at the minimum of $\rho_L(\sigma)$. For $\tau<\tau_2$, no other short-ranged perturbation is relevant for any value of σ. For $\tau=\tau_2$, the second short-ranged perturbation with eigenvalue $\lambda_2=\lambda_2(\sigma)$ touches the σ axis at $\sigma=\sigma_{E2}$; see Fig. 1. For $\tau>\tau_2$, λ_2 becomes relevant in the intermediate σ regime $\sigma_{E\bar{2}}<\sigma<\sigma_{E2}$. For $\tau=\tau_3$, a third eigenvalue, $\lambda_3=\lambda_3(\sigma)$ touches the σ axis and becomes relevant for $\tau>\tau_3$; see Fig. 2. Since there is an infinite sequence of short-ranged eigenperturbations, this type of bifurcation will go on indefinitely as τ is increased towards infinity.

The generic structure of the RG flow for $\tau_{S2}<\tau<\tau_3$ is displayed in Fig. 3. The parameter ρ_L governs the power-law tail of the direct interaction while the coordinates ρ_1 and ρ_2 represent the two short-ranged perturbations with eigenvalues λ_1 and λ_2. This three-dimensional (3D) parameter space contains a 2D separatrix between bound and unbound states (see Fig. 3) with a line of tricritical transitions which separates a (shaded) region of *first-order* transitions from an (unshaded) region of *second-order* transitions.

The RG flow within the 3D parameter space is confined to planes of constant ρ_L; see Fig. 3. For $\rho_L\neq 0$, this flow describes the renormalization of those direct interactions, $V(z)$, which decay as $V(z)\sim 1/z^\tau$ for large separation z. For $\rho_L=0$, on the other hand, the RG flow governs all *sufficiently short-ranged* interactions with $V(z)\ll 1/z^\tau$ for large z. The latter interactions form the *strong-fluctuation* (SFL) *regime*.[10] Inspection of Fig. 3 shows that the plane defined by $\rho_L=0$ has four intersections with the line of fixed points. Thus, the SFL regime is governed, for $\tau_{S2}<\tau<\tau_{S3}$, by four *short*-ranged fixed points with $\rho_L=0$; compare Eq. (7).[20]

The numerical results of the two RGs are compared in Table I. The exponent $\psi=\psi(\sigma_{S1})=\zeta/\lambda_1(\sigma_{S1})$ as displayed in Table I belongs to the short-ranged fixed point $U^*(y\,|\,\sigma_{S1})$ for critical unbinding within the SFL regime. It is interesting to note that $\psi(\sigma_{S1})$ decreases monotonically as a function of τ; see Table I. On the other hand, $\tau\psi(\sigma_{S1})$ increases monotonically with τ which implies the specific-heat exponent $\alpha=2-\tau\psi(\sigma_{S1})\leq 0$ for $\tau\geq 2$. The usual Harris criterion then indicates that frozen disorder within the direct interaction $V(z)$ is irrelevant and does not affect the critical behavior for $\sigma=\sigma_{S1}$. However, this is not generally valid for $\sigma<\sigma_{S1}$ since α approaches the limiting value $\alpha=1$ for small values of σ.

In the absence of an external pressure, real membranes are bound by attractive van der Waals forces.[1] The corresponding direct interaction decays as $\sim 1/z^4$ for large separation z and thus belongs to the SFL regime both for fluid membranes with $\tau=2$ and for polymerized mem-

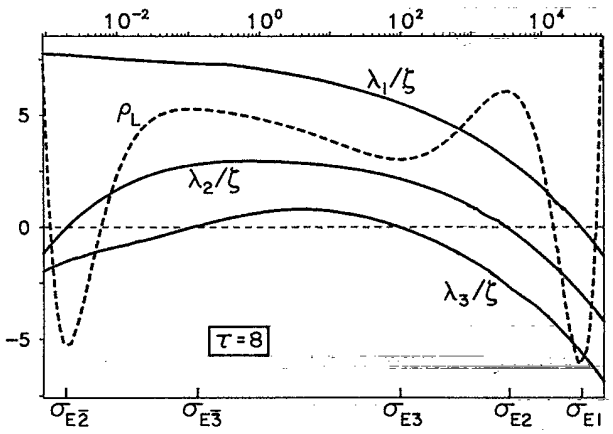

FIG. 2. Functional form of $\rho_L(\sigma)$ (dashed curve) and of the eigenvalues $\lambda_j(\sigma)$ for $\tau=8$ (HC scheme). Note that the extrema of $\rho_L(\sigma)$ correspond to zeros of the eigenvalues.

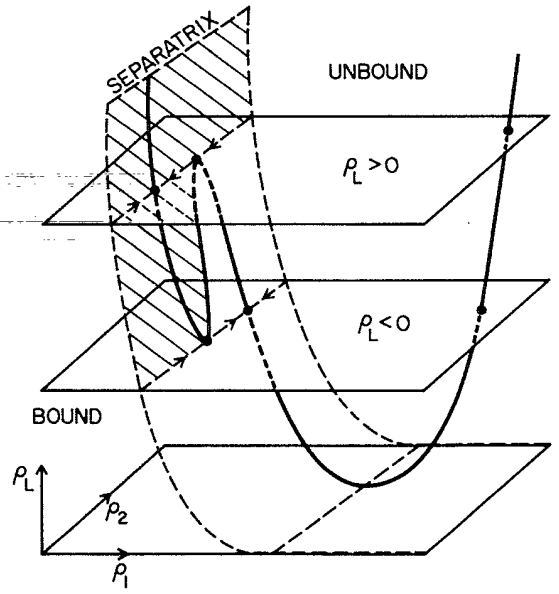

FIG. 3. Fixed-point structure and RG flow for $\tau_{S2}<\tau<\tau_3$. The line of fixed points (solid curve) governs (i) unbound states, and (ii) the separatrix for unbinding transitions. The separatrix contains a line of tricritical points which separates a shaded region of first-order transitions from an unshaded region of second-order critical transitions.

branes with $\tau \simeq 3.3$. If these τ values satisfy $\tau < \tau_{S2}$, all unbinding transitions are governed by the short-ranged fixed point $U^*(y \mid \sigma = \sigma_{S1})$ and, thus, must be of *second-order.*

It follows from Table I that the two RG's lead to $\tau_{S2} = 4.6 \pm 0.2$. A more conservative estimate is obtained when the approximate ψ values for $\tau = 2$ are compared with the presumably exact value $\psi = 1$. Then, the HC and SC scheme lead to $\tau_{S2} = 4.8 \pm 0.3$ and $\tau_{S2} = 4.5 \pm 0.4$, respectively. All estimates are thus consistent with the bound $\tau_{S2} \gtrsim 4$, and we conclude that both fluid and polymerized membranes always unbind in a continuous way (within the SFL regime).

As mentioned, membranes with lateral tension are marginally rough and then governed by $\tau = \infty$ which obviously is larger than $\tau = \tau_{S2}$. Therefore, such membranes could undergo first-order transitions even in the SFL regime. In fact, the van der Waals attraction now belongs to the weak-fluctuation regime which exhibits first-order transitions as follows from a superposition of the direct interaction $V(z)$ and the fluctuation-induced interaction $V_{\text{fl}}(z) \sim \exp(-z/z_0)$.[10]

Finally, let us assume that the membranes experience an interaction $V(z)$ which exhibits two minima at two finite values of z. Such a situation can be described by $V(z) \approx H(z - z_0) + c_2(z - z_0)^2 + c_4(z - z_0)^4$ for small $z - z_0$. Within mean-field theory, this interaction implies first-order transitions between *two different bound states* for $H = 0$ and $c_2 \sim T - T_c < 0$, and a critical point at $c_2 \sim T - T_c = 0$. Close to T_c, the mean separation $\langle z \rangle$ behaves as $\langle z \rangle - z_0 \sim (T_c - T)^{\beta}$ with the mean-field exponent $\beta = \frac{1}{2}$.

Membrane fluctuations affect the critical behavior just described. In the presence of lateral tension, these fluctuations are governed by an elastic term $\sim (\nabla z)^2$, and one is led to study a model which is in the same universality class as the 2D Ising model. This implies a downward shift of T_c and the nonclassical value $\beta = \frac{1}{8}$. For tensionless membranes, the fluctuation effects are even more pronounced but a Peierls-type argument indicates that T_c is still finite which implies the bound $\beta \leq \frac{1}{8}$.

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[1]For a review, see R. P. Rand, Annu. Rev. Biophys. Bioeng. **10**, 277 (1981).

[2]See, e.g., J. N. Israelachvili, *Intermolecular and Surface Forces* (Academic, Orlando, FL, 1985).

[3]W. Helfrich, Z. Naturforsch. **33a**, 305 (1978).

[4]R. Lipowsky and S. Leibler, Phys. Rev. Lett. **56**, 2541 (1986); **59**, 1983 (E) (1987).

[5]R. Lipowsky, Europhys. Lett. **7**, 255 (1988); Phys. Rev. Lett. **62**, 704 (1989).

[6]M. Mutz and W. Helfrich, Phys. Rev. Lett. **62**, 2881 (1989).

[7]R. Lipowsky and B. Zielinska, Phys. Rev. Lett. **62**, 1572 (1989).

[8]See, e.g., *Physics of Amphiphilic Layers,* edited by J. Meunier, D. Langevin, and N. Boccara, Springer Proceedings in Physics Vol. 21 (Springer-Verlag, Berlin, 1987).

[9]See, e.g., H. Wennerström, in *Physics of Amphiphilic Layers* (Ref. 8), p. 171.

[10]For a review, see R. Lipowsky, in *Random Fluctuations and Growth,* edited by H. E. Stanley and N. Ostrowsky (Kluwer, Dordrecht, 1988).

[11]We tacitly assume here that the persistence length of the fluid membrane is much larger than the membrane size.

[12]D. R. Nelson and L. Peliti, J. Phys. (Paris) **48**, 1085 (1987).

[13]S. Leibler and A. Maggs, Phys. Rev. Lett. **63**, 406 (1989).

[14]W. Helfrich and R. M. Servuss, Nuovo Cimento D **3**, 137 (1984).

[15]K. G. Wilson and J. B. Kogut, Phys. Rep. **12C**, 75 (1974); F. J. Wegner, in *Phase Transitions and Critical Phenomena,* edited by L. Domb and M. S. Green (Academic, New York, 1976), Vol. 6.

[16]F. Jülicher, R. Lipowsky, and H. Müller-Krumbhaar, Europhys. Lett. (to be published) have studied an exact RG for $\tau = 2$.

[17]R. Lipowsky and M. E. Fisher, Phys. Rev. Lett. **57**, 2411 (1986); Phys. Rev. B **36**, 2126 (1987).

[18]K. G. Wilson, Phys. Rev. B **4**, 3184 (1971).

[19]S. Scheidl, Ph.D. thesis, Universität München, 1989 (unpublished).

[20]The fixed points with $\rho_L = 0$ have been independently studied by F. David and S. Leibler (unpublished).