

Crumpling Transition in Polymerized Membranes

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The effect of a finite bending rigidity κ' on flexible, polymerized surfaces without self-avoidance is studied via the Monte Carlo method. Unlike linear polymers or liquid membranes, these surfaces undergo a remarkable finite-temperature crumpling transition, with a diverging specific heat. For small $\kappa'/k_B T$, the surface is crumpled, and the radius of gyration R_G grows as $(\ln L)^{1/2}$, where L is the linear size of uncrumpled membrane. For large $\kappa'/k_B T$, we find that the surface remains flat, i.e., $R_G \sim L$. Our results strongly suggest a finite-temperature crumpling transition in polymerized self-avoiding membranes as well.

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Recent theoretical investigations have explored the properties of flexible sheet polymers ("tethered" surfaces) characterized by a fixed internal connectivity.¹ Tethered surfaces can be synthesized by polymerizing lipid monolayers or bilayers²; bilayers can be made more flexible via the addition of short-chain alcohols.³ There are fascinating accounts of cross-linked methyl methacrylate polymer assembled and then extracted from the surface of sodium montmorillonite clays.⁴ These materials are predicted to display a variety of interesting properties: For example, without self-avoidance, their radius of gyration R_G increases as $(\ln L)^{1/2}$, where L is the linear size of uncrumpled membrane, while the introduction of self-avoidance leads to $R_G \sim L^\nu$, with $\nu \approx \frac{4}{5}$. Implicit in this description is the idea of a surface which is crumpled on scales large compared with a finite persistence length $\xi(T)$. For linear polymer chains this length determines the effective monomer size, and is always finite, with an Arrhenius temperature dependence.⁵ Introducing bending or bending-and-twisting force constants along the chain only modifies the persistence length, with no effect on the asymptotic behavior.⁶

For membranes, the persistence length is basically a correlation length associated with order in the local normals to the surface.⁷ It is believed that the persistence length is also finite in membranes with *liquidlike* inplane order. Detailed renormalization-group calculations of the bending rigidity⁸ show that short-wavelength undulations soften the macroscopic rigidity and lead to a persistence length which diverges (exponentially) only at $T=0$. As emphasized by Polyakov,⁹ there is a useful analogy with two-dimensional models of Heisenberg ferromagnetism: The surface normals are like a (purely longitudinal) spin field, and a crumpled surface is like a Heisenberg paramagnet. The undulations which destroy long-range order in surface normals are similar to spin waves.

What happens when we combine bending rigidity with the fixed connectivity of a tethered surface? For small

rigidity one might expect an increase in the persistence length, but no change in the asymptotic behavior. Recently, however, it has been argued that a finite bending rigidity can qualitatively change the behavior of polymerized surfaces.¹⁰ The surface is assumed to be locally flat, and written with use of the Monge parametrization in terms of a normal displacement f , $\mathbf{r}(x_1, x_2) = (x_1, x_2, f(x_1, x_2))$. To lowest order in f and its gradients, the surface energy may be written¹¹

$$\mathcal{F} = \frac{1}{2} \bar{\kappa} \int d^2x (\nabla^2 f)^2 + \frac{1}{2} \int d^2x (2\mu u_{ij}^2 + \lambda u_{kk}^2), \quad (1)$$

where the strain matrix u_{ij} is related to f and the in-plane displacements u_i by $u_{ij} = \frac{1}{2} (\partial_i u_j + \partial_j u_i + \partial_i f \partial_j f)$, $\bar{\kappa}$ is the bending rigidity, and μ and λ are Lamé constants. At low temperatures, undulations are suppressed by the nonzero in-plane shear modulus. The renormalized rigidity increases with L , in a way which leads to long-range order in the normals. The equilibrium surface configurations are flat, in the sense that $R_G \sim L$. The authors of Ref. 10 suggest, but do not prove, the existence of a finite-temperature phase transition separating a low-temperature flat phase from the high-temperature crumpled one.

In this paper, we test this prediction via Monte Carlo simulations of tethered surfaces with a variable bending rigidity. We find strong evidence for a finite-temperature crumpling transition, characterized by a diverging specific heat and persistence length. Because these simulations were quite time consuming, most of our measurements were made on surfaces without self-avoidance. We argue, however, that the crumpling temperature found here is actually a lower bound on a similar transition in real, self-avoiding membranes. Self-avoidance, moreover, should be irrelevant in the high-rigidity uncrumpled phase studied here.

We consider a two-dimensional (2D) triangular array of atoms with positions $\{\mathbf{r}_i\}$, embedded in three dimensions. The energy assigned to a particular configuration

of particles is

$$\mathcal{E} = -\kappa' \sum_{\langle \alpha, \beta \rangle} (\mathbf{n}_\alpha \cdot \mathbf{n}_\beta - 1) + \sum_{\langle i, j \rangle} V(|\mathbf{r}_i - \mathbf{r}_j|). \quad (2)$$

The first sum is over pairs $\langle \alpha, \beta \rangle$ of unit normals $\{\mathbf{n}_\alpha\}$ erected perpendicular to each elementary triangle in the surface (see Fig. 1). In a real lipid membrane, these normals would be aligned along the long axis of the lipid molecules. The bending rigidity κ' plays the role of a "Heisenberg exchange coupling" between neighboring normals. With use of the Monge form of the normal, $\mathbf{n} \approx (\partial_1 f, \partial_2 f, 1)$, it is straightforward to check that this contribution to the energy reduces to the first term of Eq. (1) in the continuum limit, with $\tilde{\kappa} \propto \kappa'$, plus boundary terms. The second summation in Eq. (2) is over neighboring pairs of atoms $\langle i, j \rangle$ in the array interacting via a tethering potential $V(r)$, which vanishes for $1 < r < \sqrt{3}$, and is infinite otherwise.¹

If the array is confined to a plane, it will behave like a 2D isotropic solid with entropy-induced elastic constants μ and λ which are strictly proportional to temperature. Thus, this contribution corresponds to the nonlinear stretching energy displayed in the continuum model of Eq. (2). Our choice of surfaces with entropic in-plane elasticity was made for computational convenience; the long-wavelength elastic properties should be similar to real polymerized amphiphiles, whose elasticity arises from a combination of van der Waals and covalent forces. According to Ref. 10, the dimensionless nonlinear coupling between surface undulations in this model is proportional to $K_0 = 4a^2\mu(\mu + \lambda)/k_B T(2\mu + \lambda)$, where a is the 2D equilibrium lattice constant. We have measured¹² μ and λ in a simulation of a tethered surface confined to a plane, and find $K_0 \approx 20$, so that nonlinearities should have a strong effect on the bending undulations characteristic of a purely liquid membrane.

Our simulations were carried out by first excising from a triangular lattice a hexagon with diameter L atoms across ($L = 3, 5, 7, 11$, and 15) and then equilibrating it

by use of the Monte Carlo, or Brownian-dynamics, method, as in Ref. 1: We randomly chose an atom and attempted to move it by $s=0.2$ in a randomly chosen direction. The probabilistic decision, whether to allow the move, was made by comparing the initial and final energies of the system. During a single "Monte Carlo time unit," on the average, one attempt of position change is made for each atom. Temperature is measured by the reciprocal of the dimensionless rigidity, $\kappa \equiv \kappa'/k_B T$. For $\kappa=0$, the equilibrium time (or the time between two statistically independent configurations) is given by¹ the Rouse relaxation time $\tau_0 \approx N/s^2$, where $N = (3L^2 + 1)/4$ is the number of atoms in the surface. The total simulation time t for each κ was $300\tau_0$ for $L \leq 11$, and $500\tau_0$ ¹³ for $L = 15$. Such simulation times produce good statistical averages for small κ ; the surface is crumpled in this case, as evident from Fig. 1.

For large κ the surface appears to be flat (see Fig. 1). The relaxation time τ_f of a flat surface can be found by consideration of the lowest vibrational mode of a stiff membrane. The flexural modes of membranes are very soft,¹¹ leading to large relaxation times¹⁴ $\tau_f \approx 0.036N^2/\kappa s^2 \approx 0.036N\tau_0/\kappa$. Thus even for $L = 15$ (with $\kappa \sim 1$) we still have $t \approx 100\tau_f$ and good equilibration.

The above estimates of relaxation times may not be valid close to the transition point, where one expects critical slowing down. It is reasonable to assume that even close to the transition point this time will not exceed the reptation time¹ of the surface. Since our t is always larger than or equal to this time, we may presume that we always have a well-equilibrated system, although the statistics may be poor near the transition point.

To check whether the crumpled and flat behaviors depicted in Fig. 1 indeed reflect two different asymptotic regimes, we measured R_G for various values of L and κ , and attempted to determine the asymptotic values of the persistence length ξ defined via $R_G \equiv \xi(\ln L)^{1/2}$ ($T > T_c$), and obtained from our simulations by extrapolating $\xi(\kappa, 1/L)$ to $1/L = 0$. For small κ (high temperatures), ξ becomes independent of L (after an initial crossover), while for large κ it seems to diverge with increasing L . The extrapolated values of ξ are depicted in Fig. 2.

At low temperatures, it is convenient to define a parameter ζ , via $R_G \equiv \zeta L$ ($T < T_c$), which measures the shrinkage of a macroscopically flat surface due to undulations. We measured ζ by extrapolating $\zeta(\kappa, 1/L)$ to the limit $1/L = 0$. Large fluctuations in surface normals will produce small values of ζ : In fluid membranes, we would always expect that $\zeta = 0$, because in crumpled surfaces, $R_G \sim L^\nu$, with $\nu < 1$. As shown in Fig. 2, ζ in fact remains finite for tethered surfaces, and vanishes at a finite value of κ . From our results for ξ and ζ , we conclude there is a continuous finite-temperature phase transition at $\kappa_c = 0.46 \pm 0.03$.

An additional confirmation of the two distinct regimes indicated in Fig. 2 can be obtained from the measurement of the mean ratio A between the smallest and the

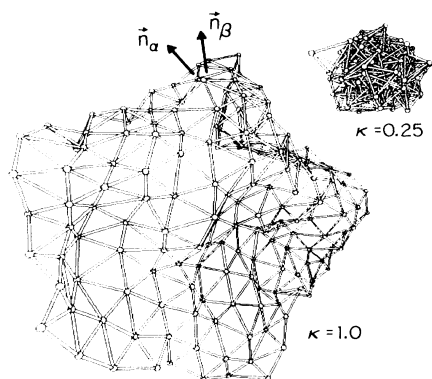


FIG. 1. Shape of the surface for two different values of κ . For clarity, atoms are shown at $\frac{1}{2}$ of their true hard-sphere radius. Unit normals \mathbf{n} to two elementary triangles are shown.

largest principal moments of inertia, which is a quantitative measure of asphericity. For a fixed L the asphericity is a monotonically decreasing function of κ . However, the increase in L affects differently the low- and high-temperature regions: For $\kappa > \kappa_c$, A decreases with increasing L , i.e., the surfaces becomes more flat, while for $\kappa < \kappa_c$ the surfaces becomes more spherical (A increases) with increasing L .¹⁴ For large κ , this implies a renormalized rigidity which increases with L as suggested in Ref. 10.

The presence of the phase transition is also clearly seen in the specific heat, which has been found from energy fluctuations in the surface. The specific heat (per atom) C has a well pronounced peak, which increases with L , as depicted in Fig. 3. For $\kappa=0$, the fluctuations are purely entropic, and $C=0$. (We suppress the trivial kinetic part $\frac{1}{2}k_B$ of the specific heat.) For sufficiently large κ , one can neglect the coupling between the transverse fluctuations, and obtain $C=\frac{1}{2}k_B$, in accordance with Dulong-Petit law. (The in-plane oscillations do not contribute to the specific heat because the elastic constants are proportional to temperature.) In the absence of a phase transition one might expect a smooth interpretation of C as κ changes from 0 to ∞ . Figure 3, on the other hand, shows a pronounced peak, which sharpens for large L . The peak maximum for large L is close to the value κ_c determined from Fig. 2.

The transition we observe seems very nearly second order, and we can severely limit the size of any possible first-order transition: Following the method of Dasgupta and Halperin,¹⁵ we find that the jump of the entropy at the transition point cannot exceed 0.08, which is smaller than any other parameter in the problem.

We have also examined correlations in the layer nor-

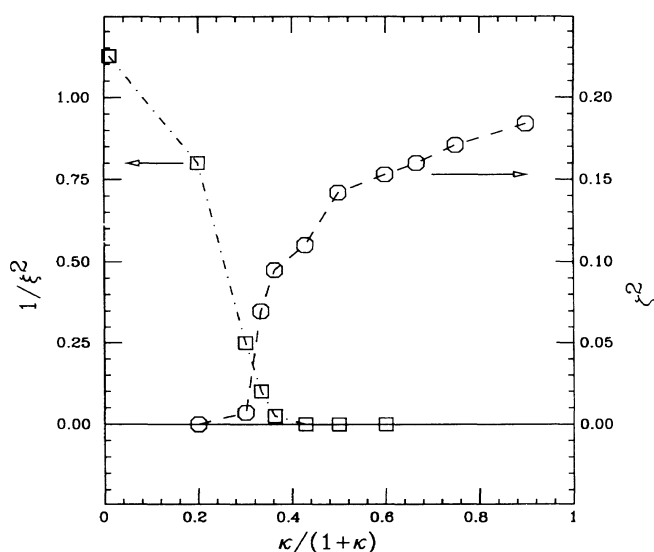


FIG. 2. Extrapolated values of ξ and ζ (see text) vs $\kappa = \kappa'/k_B T$.

mals. For $\kappa > \kappa_c$, we find that $\langle \mathbf{n}(\mathbf{x}) \cdot \mathbf{n}(\mathbf{0}) \rangle$ falls off very slowly, i.e., the normals have a strong positive correlation over the entire system, consistent with long-range order as $x \rightarrow \infty$, where x is measured in Cartesian coordinate system (x_1, x_2) attached to the fluctuating surface. At small κ , we expect that the probability of a particular surface configuration in the continuum limit is proportional to

$$\exp \left(-\frac{1}{2} K \int d^2x |d\mathbf{r}(x_1, x_2)/d\mathbf{x}|^2 + \dots \right),$$

where $K \approx 0.67$ for $\kappa=0$. In such a model, one expects that correlations in the normal

$$\mathbf{n}(\mathbf{x}) \propto (d\mathbf{r}/dx_1) \times (d\mathbf{r}/dx_2)$$

decay rapidly to zero. Our simulations for small κ are consistent with exponential decay, dropping to zero within, e.g., two to three lattice spacings, for $\kappa=0.25$.

To make contact with real polymer surfaces,^{2,3} we must discuss effects of distant self-avoidance. The critical temperature found here is clearly a *lower* bound on the critical temperature with self-avoidance, since excluded volume interactions can only flatten the surface. Self-avoidance effects should be negligible in the low-temperature flat phase, although they will certainly swell the high-temperature crumpled one.¹ We have calculated the normal-normal correlation functions with self-avoidance in the high-temperature limit $\kappa=0$. These correlations decay appreciably within three to five lattice spacings, suggesting a high-temperature crumpled phase as well as a low-temperature flat one. One expects, however, that the power-law density-density correlation

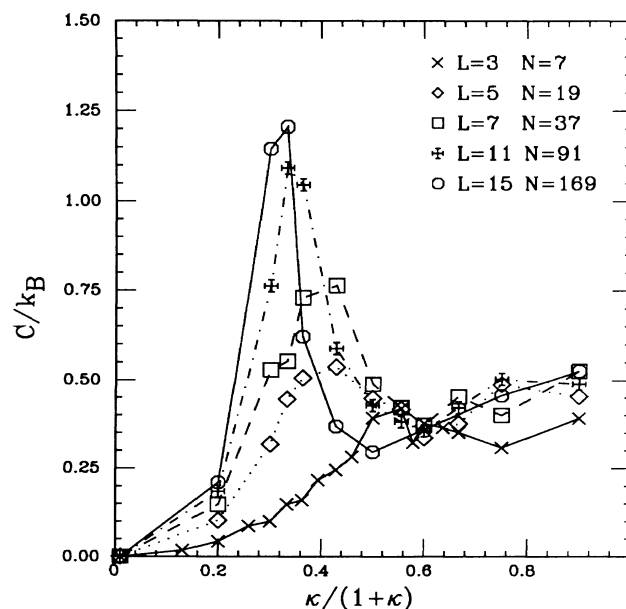


FIG. 3. Specific heat (per atom) C as a function of κ for surfaces of different sizes L .

functions associated with self-avoidance will lead to *algebraic*, rather exponential, decay of the normal-normal correlations in the crumpled phase.

At the transition, one might expect the radius of gyration of tethered surface without self-avoidance to grow like $R_G \sim L^{\nu'}$. A rough attempt to extract ν' from our data give $\nu' = 0.78 \pm 0.10$. We may treat the excluded-volume interaction as a small perturbation and calculate its scaling at the critical point which has been obtained for the phantom surface. From the simulation we estimate that the number of overlaps between the atoms at the transition point increases as L^ω , with $\omega = 3.6 \pm 0.3$. The relevance of the excluded-volume interaction is determined by $L^\omega/R_G^3 \sim L^\gamma$, where $\gamma = \omega - 3\nu'$. According to our estimates γ is positive, indicating that the importance of the excluded volume will increase, as one goes to larger length scales. This result suggests a new critical behavior at the transition for self-avoiding surfaces.

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