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Molecular dynamics simulations of self-avoiding tethered membranes with attractive interactions: Search for a crumpled phase

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The equilibrium structure of closed self-avoiding tethered vesicles with attractive interactions is investigated by molecular dynamics simulations. The vesicles are constructed by connecting linear chains of $n=4$ or 8 monomers to form closed membranes with as many as 16 002 monomers. For $n=4$, the transition from a high-temperature flat phase to a low-temperature collapsed phase is discontinuous, with no evidence for an intermediate crumpled phase. However, for $n=8$ the transition is either continuous or very weakly first order. Assuming the transition is continuous, a scaling analysis suggests that at the transition there is an intermediate state which has a fractal dimension $d_f \simeq 2.4$, somewhat smaller than but close to the value predicted by the Flory theory for a crumpled membrane.

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The properties of two-dimensional tethered membranes embedded into three dimensions have been studied extensively since they were introduced by Kantor, Kardar, and Nelson [1]. These membranes appear in both a biological context, such as the red blood cell skeleton [2,3], and in a materials context, such as the two-dimensional polymer membranes recently synthesized by Stupp *et al.* [4] and the graphite oxide crystalline membranes studied by Wen *et al.* [5] and Spector *et al.* [6]. Kantor, Kardar, and Nelson [1] suggested, based on a simple Flory-level theory, that in the presence of only excluded volume interactions, a tethered membrane would crumple and that its size R_G would scale as $R_G^{d_f} \sim N$, where N is the number of monomers in the membrane and d_f is the fractal dimension. They found that for two-dimensional membranes embedded into three dimensions, $d_f = 2.5$. This conclusion was supported by renormalization group calculations [1,7,8] which suggested that the flat phase was unstable in $d=3$ and by Monte Carlo simulations on small systems [1]. Nelson and Peliti [9] found that at low temperatures a stable flat phase exists. However, more extensive computer simulations [10–19] on large systems have since shown convincingly that, in fact, in the presence of only excluded volume interactions, tethered membranes do not crumple but remain flat ($R_G^2 \sim N$). This lack of a crumpling transition in $d=3$ has been explained [14] in terms of an implicit bending rigidity which is induced by the self-avoidance requirement even when no such term is present in the microscopic Hamiltonian. Then, if bending rigidity is relevant, one cannot expect the Flory theory to work. An alternative explanation by Goulian [20], who used a Gaussian variational approximation, and Le Doussal [21], who did an expansion in large embedding space dimension d, is that the flat phase is stable for $d=3$ and two-dimensional membranes crumple only for $d>4$. This result is in agreement with earlier molecular dynamics simulations of Grest [18]. In a related calculation, Guitter and Palmeri [22] also using a variational approach found that the membrane can crumple only for $d>3$.

While it is now clear that two-dimensional tethered membranes with only excluded volume interactions remain flat, there have been some suggestions that the addition of attractive interactions may balance the implicit bending rigidity produced by the self-avoidance and produce a crumpled phase at intermediate temperatures. Abraham and Nelson [14] found in their molecular dynamics simulations that the introduction of attractive interactions between monomers leads to a collapsed membrane with fractal dimension 3 at sufficiently low temperature. Later Abraham and Kardar [23] found that for open membranes with attractive interactions, there is a well defined sequence of folding transitions with decreasing temperature. While they did not find any evidence for an intermediate crumpled phase, their scaling analysis, based on a Landau theory, suggested that such a state could exist. Following this work, Liu and Plischke [24] carried out Monte Carlo simulations for a similar model and found for small systems ($N \leq 817$) that the membranes did not undergo a series of folding transitions but instead between the high-temperature flat phase and the low-temperature collapsed phase there was an intermediate crumpled phase. This crumpled phase seemed to exist over a range of temperatures and was characterized by a fractal dimension $d_f \sim 2.5$. This interesting possibility of finally locating the elusive crumpled membrane phase led us to carry out extensive molecular dynamics simulations on tethered membranes with attractive interactions. To avoid the possibility of a folding transition, we studied a system of N monomers constructed from short, linear chains of length n of monomers which are connected to form a closed membrane [19]. This gives the model some local flexibility and reduces finite size effects since there is no free perimeter. In contrast to the findings of Liu and Plischke, our results do not support the existence of an intermediate range of temperatures where the membrane is crumpled. Instead, we find for short monomer chains, $n=4$, a first order transition from the high-temperature flat phase directly to the low-temperature collapsed phase. For longer polymer chains between the vertices, $n=8$, we find that the transition is either continuous or weakly first order; it is dif-

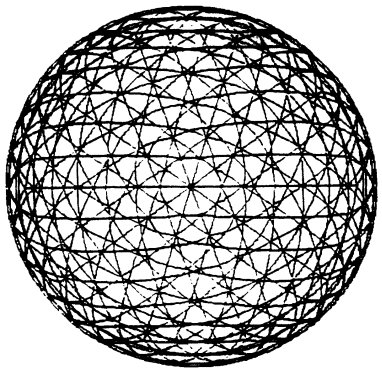

FIG. 1. Illustration of the initial state for a membrane of size $N=9002$ with $n=8$ additional monomers between each vertex. This system contains 1080 edges and 720 triangular faces. Note that the bond lengths are not exactly the same, as the points have been projected onto the surface of a sphere. If all bond lengths were equal, the membrane would have the shape of an icosahedron.

ficult from the present simulations to distinguish. However, assuming that the transition is continuous, we can carry out a scaling analysis, similar to that for a Θ point for linear chains. At the critical temperature, this analysis suggests that the membrane has a fractal dimension $d_f \simeq 2.4$, slightly less than but quite close to the Flory theory prediction for a crumpled membrane. Our results for smaller systems are consistent with those of Liu and Plischke [24], in that they also suggest a possible range of intermediate temperatures where the membranes appear to be crumpled with $d_f \simeq 2.5$. However, because we were able to simulate significantly larger systems than they could, we were able to show that there is in fact no intermediate regime.

Molecular dynamics simulations were performed on the model for closed membranes used previously by us [19] to model the red blood cell skeleton in a good solvent [3]. Each membrane consists of a two-dimensional triangular array of N monomers of mass m connected to form a closed vesicle, as shown in Fig. 1. This was done by constructing an icosahedron with n_V monomers per edge. An additional n monomers connected linearly were then added between each node. All but 12 of the vertices are sixfold coordinated. The remaining 12 are fivefold coordinated, which is necessary to close the vesicle. The total number of monomers $N=10n_V^2(1+3n)+2$ with $30n_V^2$ edges of length $L_0=n_V(n+1)$ and $20n_V^2$ faces. For the present studies, we used $n=4$ with $1172 \leq N \leq 15\,732$ and $n=8$ with $1002 \leq N \leq 16\,002$. All monomers interact through a shifted Lennard-Jones potential which is terminated at separations greater than 2.5σ, where σ is the Lennard-Jones unit of length and corresponds to the separation where the interaction is zero. For monomers which are tethered (nearest neighbors) there is an additional attractive interaction as described elsewhere [18]. No explicit bending terms are included. By changing the temperature T, one effectively changes the solvent quality. For high T, the attractive part of the interaction is irrelevant and the membrane is in its "flat" state, in which the mean squared radius of gyration $\langle R_G^2 \rangle$ scales as N. Since the membrane is closed, the flat phase is actually a spherical shell. As T decreases, the attractive part

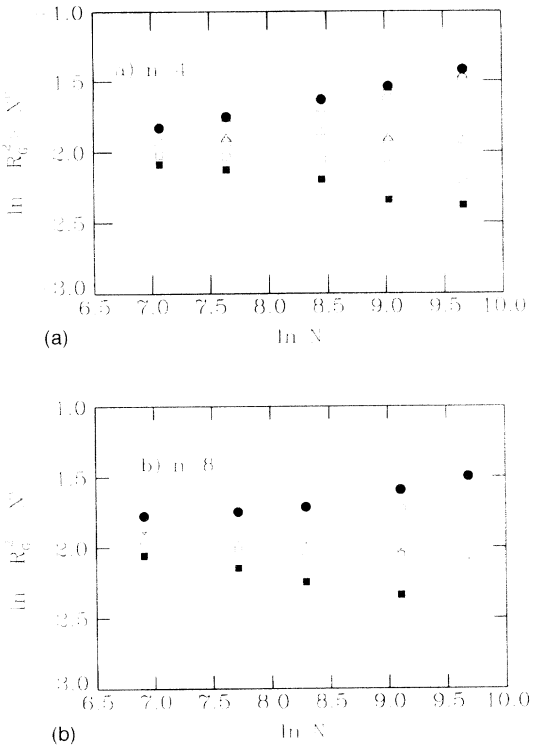

FIG. 2. Mean square radius of gyration $\langle R_G^2 \rangle / N^{\nu}$ ($\nu=0.8$) versus N for (a) $n=4$ and (b) $n=8$ for a variety of temperatures, $k_BT/\epsilon=3.5$ (●), 3.25 (Δ), 3.0 (○), 2.75 (×), 2.5 (□), and 2.0 (■).

of the interaction begins to play a role. For low T, the membrane collapses into a compact phase characterized by $\langle R_G^2 \rangle \sim N^{2/3}$. The interesting question is what happens in between these two phases.

The equations of motion were integrated with a velocity-Verlet algorithm [25], with a time step $\Delta t=(0.006\text{–}0.008)\tau$. The higher T, the smaller Δt. Here $\tau=\sigma(m/\epsilon)^{1/2}$, where ϵ is the Lennard-Jones unit of energy. Since for this model the Θ point for a linear polymer chain is $(3.0\pm0.1)\epsilon/k_B$ [26], we first scanned T from $4.0\epsilon/k_B$ to $2.0\epsilon/k_B$ for small N to locate the approximate transition region. We found that the transition was in fact close to the Θ temperature of a linear chain. We then carried out long runs $(2\text{–}5)\times10^5\Delta t$ after equilibrium was reached for a variety of T and N. Because of the relatively dense packing of these membranes, reaching equilibrium was a very slow process. For our largest system, more than 3×10^5 time steps were often needed just to reach equilibrium after changing T. On our Cray XMP or Silicon Graphics Challenge computers, several of these equilibrations runs took more than 100 hours of CPU time each. Most of the results were obtained on cooling from the previous higher temperature state. However, in the vicinity of the transition, additional runs were made on heating from lower temperature.

In the crumpled phase, should it exist, the mean squared radius of gyration is expected to scale as $\langle R_G^2 \rangle / N^{\nu}$, where $\nu=2/d_f$. In the Flory theory, $\nu=\frac{4}{5}$. In the collapsed phase, $\nu=\frac{2}{3}$ and in the flat phase, $\nu=1.0$. By plotting $\langle R_G^2 \rangle / N^{\nu}$ ver-

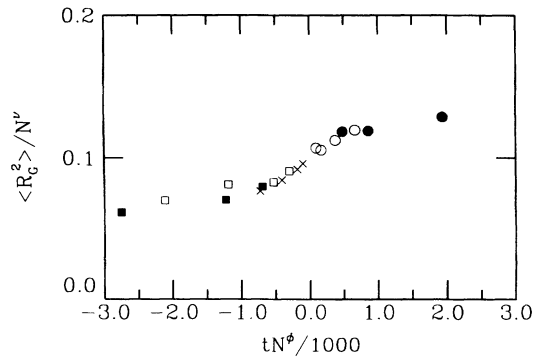

FIG. 3. Scaling plot of $\langle R_G^2 \rangle / N^\nu$ versus tN^ϕ for $n=8$, where $\nu=0.85$, $\phi=1.0$, and $T_c=2.89\epsilon/k_B$. Here $t=(T-T_c)/T_c$ and the symbols are the same as in Fig. 2.

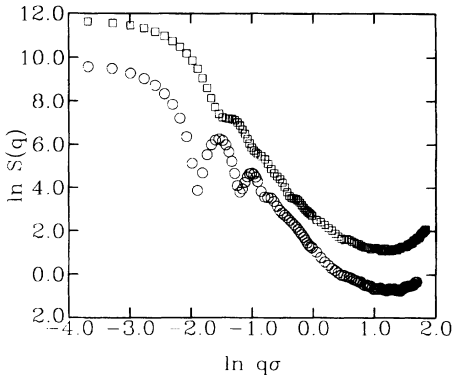

FIG. 5. Static structure factor $S(q)$ for the $N=16\,002$ ($n=8$) membranes for $k_BT/\epsilon=3.0$ (○) and 2.5 (□). Data for $T=2.5\epsilon/k_B$ shifted vertically for clarity.

sus N on a log-log plot for these three values of ν, it is not difficult to distinguish the three phases. In Fig. 2, we show our results for $\nu=0.8$ for the two values of n studied. Note that for high T, $\langle R_B^2 \rangle / N^{0.8}$ clearly increases with increasing N, while for low T, $\langle R_B^2 \rangle / N^{0.8}$ decreases. In the intermediate range, there is strong hysteresis for $n=4$. In this regime, both the low T collapsed phase and the high T flat phase were stable as far as we could tell from the length of runs carried out. For $n=4$, both states were stable at $T=3.25\epsilon/k_B$ for $N \geq 2082$, while for $T=3.0\epsilon/k_B$, a similar result was observed for $N \geq 8322$, suggesting a first order transition. For $n=8$, the transition is continuous or nearly so. Though the relaxation times to go from a high-temperature flat phase to the low-temperature collapsed phase in the vicinity of the transition were very long, no hysteresis was observed for this case. At $T=2.75\epsilon/k_B$, for example, it took more than $3\times10^5\Delta t$ for the configuration to go from an initial flat state to a collapsed one for $N=9002$. For 16 002, the time was so long that we could not follow the transformation completely. Further analysis of the low-temperature data for both cases indicates that the membranes are collapsed and $\nu=0.67\pm0.02$. For higher temperatures the data are consistent with $\nu=1$, though the best fit to the data for the range N studied is somewhat smaller, 0.95. This is surely a finite size effect and has been observed in previous simulations of excluded volume membranes. These results suggest a first order transition at approximately $3.25\epsilon/k_B$ for $n=4$ and a continuous or weakly first order transition for $T_c \approx (2.85\text{–}2.90)\ \epsilon/k_B$ for $n=8$. However, due to the strong hysteresis for $n=4$, an exact determination of the transition temperature in this case is not possible.

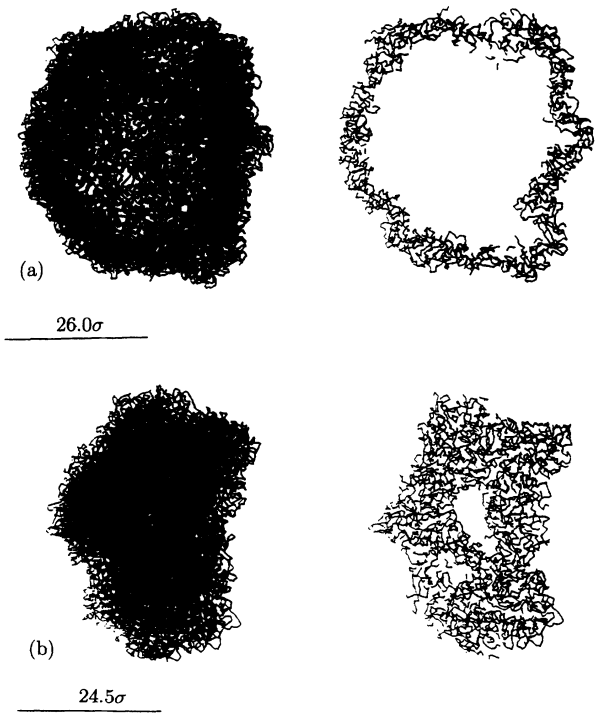

FIG. 4. A typical configuration and a cross section through the center of the membrane for a closed self-avoiding tethered membrane with $N=16\,002$ monomers for (a) $T=3.0\epsilon/k_B$, which is in the high-temperature flat phase, and (b) $T=2.5\epsilon/k_B$, which is in the collapsed phase.

To try to help determine whether the transition for $n=8$ is continuous or not, we did a scaling analysis of the data, in analogy to that done for the Θ point for linear chains. In that case, the Θ temperature is a tricritical point separating the self-avoiding random walk, high T phase, and the collapsed, low T phase. In the vicinity of the Θ temperature, $\langle R_G^2 \rangle$ can be written in a scaling form. Adapting the same general form, we scaled the data in Fig. 2(b) as

$$\langle R_G^2 \rangle = N^\nu f(tN^\phi), \tag{1}$$

where $t=(T-T_c)/T_c$. This scaling form has three unknowns, the two exponents ν and ϕ and the critical temperature T_c. Here ν is for the intermediate phase. While T_c and ν are both bounded in a relatively narrow range, nothing is known about the crossover exponent ϕ. The scaling function $f(x)$ is such that $f(x) \sim x^{(1-\nu)/\phi}$ for $t>0$, $f(x)=1$ for $t=0$, and $f(x) \sim x^{(2/3-\nu)/\phi}$ for $t<0$. In Fig. 3, we show a scaling plot of $\langle R_G^2 \rangle / N^\nu$, with $\nu=0.85$ and $\phi=1.0$. Note that the data scale reasonably well and are consistent with a continuous transition. From a number of such plots, we find that the data scale reasonably well for $\nu=0.85\pm0.02$ and $\phi=1.00\pm0.05$, though not with $\nu=0.80$. The data seem to

support the point of view that this system has a critical point at which the implicit bending rigidity coming from the excluded volume interactions is balanced by the attractive interactions, giving rise to a crumpled state with d_f very close to 2.4. Of course this analysis does not rule out a weak first order transition.

In Fig. 4, a typical configuration for our largest membrane, $N=16\,002$, for $n=8$ is shown for two values of T, one above T_c and the other below. Also shown is a cross section through the center of the membrane. Note that the configuration for $T=3.0\epsilon/k_B$, which is the flat phase, is a spherical shell. This configuration is very similar to that obtained earlier by us [19] in a very good solvent (a purely repulsive interaction), except that the thickness of the shell is somewhat larger and more dense. This is in contrast with the configuration at $T=2.5\epsilon/k_B$, which is in the collapsed phase. This configuration is much more homogeneous in density, though there remains a region in the interior which is monomer free. At even lower temperatures, this shell fills in completely. While the configurations for the two temperatures are markedly different, the static structure functions $S(q)$ over much of the range of wave vector q are not. $S(q)$ is defined by

$$S(q)=\frac{1}{N}\left\langle \sum_{i,j} e^{i\mathbf{q}\cdot(\mathbf{r}_i-\mathbf{r}_j)} \right\rangle, \tag{2}$$

where the angle brackets represent a configurational average taken every $2000\Delta t$ and averaged over 20 random orientations for each $q=|\mathbf{q}|$. Since both membranes are nearly spherical, there is extra structure for small q, not seen in open membranes. For large q, $S(q)\sim q^{-3}$ as one would expect for a collapsed membrane. As seen in Fig. 5, even though $T=3.0\epsilon/k_B$ is in the flat phase, the high q range of $S(q)$ it is not very different from that for $T=2.5$. This should not be too surprising since in this high range of q, $S(q)$ is dominated by correlations at short distance and is strongly influenced by the dense region around the shell. The expected scaling $S(q)\sim q^{-2}$ for a flat phase is obscured by the oscillations coming from the low q oscillations. Similar results were found for these membranes in a very good solvent (purely repulsive interactions) in Ref. [19].

In summary, we have shown that attractive interactions between monomers in a two-dimensional tethered membrane give rise either to a first order phase transformation from the high T flat phase and the low T collapsed phase for short polymer chains between the vertices ($n=4$) or to possibly a continuous transition for longer strands ($n=8$), the difference being in the local flexibility of the membrane. For the tethered membrane model studied here, in which a closed vesicle is constructed from short linear chain segments, the sequence of folding transitions observed by Abraham and Kardar [23] for an open membrane with $n=0$ does not occur. The introduction of linear chain segments between the vertices allows one to study the transition from the flat phase to the collapsed phase directly. The first order transition for $n=4$ is consistent with these earlier results of Abraham and Kardar, in that the transition from the flat to the folded state was also discontinuous. For small n, the introduction of holes in the membrane gives the membrane enough local flexibility to avoid the folding transitions but not enough to make the transition continuous. For large n, the attractive interactions more exactly balance the inherent bending rigidity, giving rise to either a continuous or weakly first order transition. To distinguish these two possibilities, simulations on systems with both large N and n, which are not feasible at this time, are necessary.

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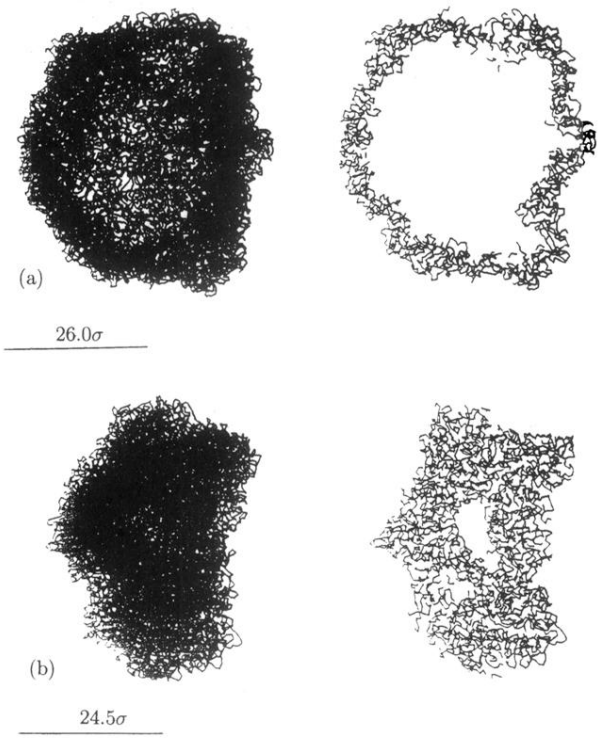

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