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Crumpling of fluid vesicles

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Models of athermal self-avoiding fluid and polymerized vesicles have been investigated by Monte Carlo simulations. There is no evidence for crumpling of polymerized vesicles, and the squared radius of gyration is proportional to the number of monomers on the surface, $R^2 \sim N$. Fluid vesicles, on the other hand, exhibit a crumpled shape and $R^2 \sim N^{0.8}$. We explain our model dynamics for fluid surfaces. The time-dependent mean-squared displacement $r^2(t)$ of a monomer on a fluid surface is $\sim t^{0.8}$, whereas $r^2(t) \sim \sqrt{t}$ for polymerized vesicles. The corresponding configurational correlation times are $\tau \sim N$ for fluid and $\tau \sim N^2$ for polymerized vesicles.

Fluid isotropic membranes[1,2] and polymerized membranes[3-7] have been predicted to exhibit a high-temperature crumpled phase. In fact, for polymerized self-avoiding membranes renormalization-group arguments[8-10] and pioneering Monte Carlo simulations[4,11] seemed to support evidence for a high-temperature crumpled phase, whereas subsequent extensive molecular dynamics simulations[12] and Monte Carlo simulations[13,14] have questioned the "crumpling" idea.

In the present Rapid Communication we report on Monte Carlo studies of a novel model membrane which has properties like *fluid* membranes. There the configurational arrangement of the constituents of the membrane, called monomers, represent a distorted two-dimensional surface in three space dimensions on which the monomers should be able to diffuse freely among each other. Most of the membranes known in life sciences are fluid and hence investigations on related phenomena are of great importance. However, their predicted configurational properties have not yet been examined by simulations.

Very recently an attempt to simulate fluid membranes has been reported.[15] There the focus was mainly to investigate the unbinding transition of semirigid fluid membranes rather than the configurational properties of a fluid membrane at high temperatures. Therefore a discretized model Hamiltonian with mean local curvature describing a smooth shape of a membrane has been used. The authors found that macroscopic properties of the membrane are strongly affected by shape fluctuations on microscopic length scales. Consequently, simulations of microscopic model membranes could be elucidating and hence would be of importance.

The present investigations are concerned with a microscopic model of a fluid self-avoiding membrane suitable for Monte Carlo and molecular-dynamics simulations and are concerned with membranes of spherically closed shape, i.e., vesicles. (The preference for investigations of fluid vesicles instead of fluid open membrane relies mainly on initial uncertainties with respect to the boundary effects of open membranes. Fluid open membranes are presently under investigation.)

Our intention is to demonstrate the suitability of the fluid-vesicle model by its high-temperature configurational and dynamical properties in order to provide a sound basic model for further investigations on the thermodynamics of vesicles.[16-18] Furthermore, we are able to show that fluid vesicles exhibit a crumpled phase in contrast to polymerized vesicles which is in agreement with previous results on open polymerized membranes.[12-14]

The initial configuration of a closed tethered membrane (vesicle) in three space dimensions is constructed on the surface of a sphere by Delaunay triangulation.[19] To insure that most of the points of the two-dimensional network have the same number of neighbors and the bonds have approximately the same length, one can use an icosahedron as the original network, and then adding more new points on each triangle to create larger networks. Subsequent rescaling of all bonds to the desired length is straight forward. Following this procedure one can generate vesicles consisting of $N = 10 \times 3^k + 2$ monomers with $k = 1,2,3,\ldots$. In the present simulations we studied up to $k = 4$. The number of triangles covering the surface is $2N - 4$.

A Monte Carlo step for polymerized membranes consists of randomly or sequentially choosing a monomer and displacing it to a randomly selected nearby position. The attempt is accepted if the new bonds of length l connecting the neighboring sites are within $\sigma < l < l_{\max}$, where σ represents the diameter of a hard sphere and $l_{\max}$ the maximum length of the tether (*hard-sphere-tether model*). The maximum displacement of a monomer is 0.1σ. For these models it is known[20] that if $\sigma / l_{\max} > \sqrt{3/4}$, self-interpenetration of the surface is prohibited. In the present simulations we used $\sigma = 1$, $l_{\max} = \sqrt{2}$. The corresponding polymer model ("bead-necklace chain") have been used extensively and successfully in Monte Carlo simulations of polymers.[20] The actual sampling of configurations is made every N^2 Monte Carlo steps. This time lapse can be considered approximately as an upper bound (apart from prefactors) for correlations between successive configurations. Averages are taken over up to 10^4 configurations.

So far, this model represents a polymerized vesicle and corresponding models for open polymerized membranes have been investigated.[11-14] In the present hard-sphere-tether model the fluidity is introduced by a triangulation procedure. This procedure consists essentially of deleting a bond connecting two monomers and creating a new bond with $\sigma < l < l_{\max}$ between two monomers different from the previous one under the restriction that the surface is still well defined and covered by triangles. The simplest method to achieve this consists of choosing out of the N monomers on the surface, four monomers (labeled by 1, 2, 3, and 4) which are ring-wise connected by four bonds representing a quadrangle. Since by construction the surface must always be covered by triangles, two of the monomers, say 1 and 3, are connected in addition by a bond. A triangulation attempt consists of removing this bond and implementing a new one between monomers 2 and 4, which is accepted if $\sigma < l < l_{\max}$. Thus the surface still consists of triangles and still preserves its two-dimensional character in three space dimensions. This procedure is applied to N randomly selected bonds after each Monte Carlo step (i.e., N attempts) of monomer displacements. It is clear that this procedure provides a possibility for a given monomer to escape after several bond removals from its original neighborhood of monomers, and hence representing a "fluid" particle.

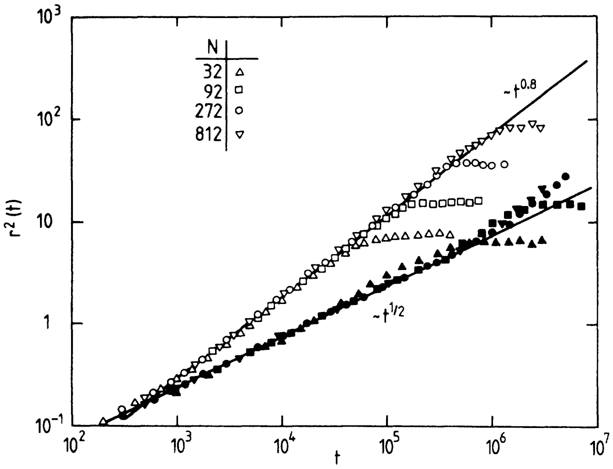

FIG. 1. Log-log plot of the time-dependent mean-squared displacements $r^2(t)$ of a labeled monomer relative to the center-of-mass displacements on *fluid* vesicles (open symbols) and on *polymerized* vesicles (solid symbols) consisting of N monomers.

In fact, this view is supported by the time-dependent mean-squared displacement of a labeled monomer relative to the motion of the center of mass, $r^2(t) = \langle [\mathbf{r}_k(0) - \mathbf{r}_{\text{c.m.}}(0) - \mathbf{r}_k(t) + \mathbf{r}_{\text{c.m.}}(t)]^2 \rangle$, where $\mathbf{r}_k(t)$ and $\mathbf{r}_{\text{c.m.}}(t)$ are the position vectors of the kth monomer and the center of mass at time t, respectively.

According to the data in Fig. 1 for fluid vesicles (open symbols), the behavior of $r^2(t)$ is close to $\sim t^{0.8}$ and almost independent of the size N of the vesicles. (Averages have been taken over six different monomer trajectories, and their deviations are in the order of the size of the symbols in Fig. 1.) This seems to support the idea of a monomer moving freely among others, similar to particles in a fluid, but here confined to a rough surface in three space dimensions. Following similar arguments as for the restricted motion of a polymer chain trapped in a random tube,[21] the displacements of a monomer trapped on a random surface can be understood and one obtains $r^2(t) \sim t^\nu$, where ν is the correlation length exponent: In a surface-fixed coordinate system the monomer performs isotropic linear displacements $L^2 \sim t$, where $L^2 \sim N$. Since the surface is $R^2 \sim L^{2\nu}$, where R is the radius of gyration, the monomer moves in the laboratory system according to $r^2(t) \sim t^\nu$. For times larger than τ_2 (their estimates are given in Table I), $r^2(t)$ is approximately a constant and $r^2(\infty) \approx 2R^2 \sim N^\nu$. One of our main results is that R exhibits properties in agreement with the predicted[1,2,8] crumpled phase, i.e., $R \sim N^{0.4}$ (Table I). This is supported by estimates of the volumes of the vesicles as well, which exhibit $V \sim N^{1.2}$ (Table I). Estimates of the longest relaxation time τ_2 seem to exhibit $\tau_2 \sim N$ (Table I) and are consistent then with the time dependence of the monomer displacement $r^2(t) \sim t^{0.8}$ for $t < \tau_2$ and $r^2(t) \sim N^{0.8}$ for $t > \tau_2$. For comparison, we have estimated the configurational correlation time τ from the correlation function of the square radius of gyration $R^2(t)$ at time t,

$$\tau = \int_0^\infty dt \langle R^2(0) R^2(t) \rangle - \langle R^2 \rangle^2] / [\langle R^4 \rangle - \langle R^2 \rangle^2] \,.$$

We found almost exponential relaxation and $\tau \approx \tau_2$, indicating that the longest relaxation time of a fluid vesicle is related to its configurational relaxation.

On the other hand, the time-dependent displacements of a labeled monomer on a *polymerized* surface (i.e., network), which is according to Fig. 1 $r^2(t) \sim t^{1/2}$, can be understood within the well-known framework of polymer dy-

TABLE I. Mean-squared radius of gyration R^2, average volume V, and longest relaxation time τ_2 for *fluid* vesicles. λ_1, λ_2, and λ_3 are the three axes of inertia, where λ_3 is the largest one. The number in brackets denotes the estimated statistical error for the last digit.

N	32	92	272	812
R^2	3.3(1)	7.8(2)	18(1)	44(2)
$R^2N^{-0.8}$	0.206(7)	0.209(6)	0.203(9)	0.207(9)
V	10.1(2)	40(2)	150(10)	590(60)
$VN^{-1.2}$	0.158(3)	0.176(9)	0.180(12)	0.19(2)
$\tau_2 N^{-1} \times 10^{-3}$	1.2(2)	1.3(1)	1.3(2)	1.3(2)
λ_1/λ_3	0.38(2)	0.37(3)	0.33(4)	0.37(4)
λ_2/λ_3	0.60(3)	0.66(6)	0.57(5)	0.6(1)

TABLE II. Same quantities as in Table I, but here for *polymerized* vesicles. τ is the configurational correlation time.

N	32	92	272	812
R^2	2.85(3)	7.30(5)	20.7(2)	61.2(8)
$R^2N^{-1.0}$	0.089(1)	0.079(1)	0.076(1)	0.075(1)
V	15.1(2)	73.8(6)	372(3)	1920(13)
$VN^{-1.5}$	0.084(1)	0.084(1)	0.083(1)	0.083(1)
τ	$2.2(2)\times10^2$	$1.2(2)\times10^3$	$1.1(3)\times10^4$	$8(2)\times10^4$
τN^{-2}	0.21(2)	0.14(2)	0.15(4)	0.12(3)
τ_2	$6(1)\times10^5$	$3(1)\times10^6$	...	...
λ_1/λ_3	0.78(1)	0.81(1)	0.85(1)	0.87(1)
λ_2/λ_3	0.89(1)	0.90(1)	0.92(1)	0.95(1)

namics[22] and has been shown[11] to be related to the Rouse model where $r^2(t)\sim t^{\nu/\nu+1}$, $\tau\sim N^{\nu+1}$, and $r^2(t)\sim R^2\sim N^{\nu}$ for $t\geq\tau$. Since in the case of polymerized vesicles $\nu\simeq1$, according to R^2 and V in Table II, the dynamical and the static data are consistent and support previous observations[12–14] that polymerized membranes are most likely *not* to be crumpled. A direct estimate of the longest relaxation time τ_2 for polymerized vesicles from the data depicted in Fig. 1 is possible only for smaller vesicles, $N=32$ and 92. It is interesting to note that the corresponding times τ_2 for fluid vesicles (cf. Fig. 1) are shorter by an order of magnitude; this is also of practical importance. Estimates of configurational correlation times τ, which are presented in Table II, show that for polymerized vesicles $\tau_2\gg\tau$, which indicates that the longest relaxation time τ_2 is probably not related to the configurational correlation time τ, at least not as defined by the correlation function of the radius of gyration as given above.

Since the Monte Carlo runs for $N=272$ and 812 were not long enough in order to observe $r^2(t)\rightarrow$ const for $t>\tau_2$, there is still an uncertainty in these cases about the equilibration and to what extent the static quantities are affected thereby. Therefore comparison has been made to the smaller vesicles, which show that time averages of R and V do not change significantly their value as long as $t\gg\tau$, even if $t<\tau_2$. Monte Carlo runs up to $t>\tau_2$ for the larger polymerized vesicles are presently out of our capabilities. Applications of sublattice techniques as used in previous calculations[14] would considerably improve the simulations, but would not provide reasonable informations about $r^2(t)$ and τ_2. However, this and related problems to polymerized membranes are not within the main scope of the present paper and do not affect our basic conclusions about fluid vesicles.

It should be noted that for fluid as well as for polymerized vesicles the center-of-mass diffusion is approximately given by $r^2_{\mathrm{c.m.}}(t)\simeq1.1\times10^{-3}l^2N^{-1}t$. Ratios of the axes of inertia are given in Tables I and II, where λ_1 and λ_3 are the smallest and the largest axis, respectively. The ratios for polymerized vesicles suggested shapes close to sphericity, whereas fluid vesicles seem to have marked ellipsoidal shapes.

Finally, it should be emphasized that exponents given in the present paper for various static and dynamic quantities are not to be considered as almost exact (of course, this is left to more rigorous analytical calculations), rather the intention was to provide evidence for the different physical concepts propounded in the literature by distinguishing clearly between "flat" phases ($\nu\simeq1$) and crumpled phases ($\nu\simeq0.8$). Therefore we have renounced to present "best fitted" exponents in Table I and II. The question how accurate the Flory exponent[8] $\nu=0.8$ describes fluid membranes, must be left to further investigations.

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