

Simulations of Fluid Self-Avoiding Membranes.

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Abstract. – A model for fluid flexible self-avoiding membranes is introduced and investigated by Monte Carlo methods. *Fluid* athermal membranes consisting of N monomers exhibit crumpled shapes and their mean square radii of gyration are $R^2 \sim N^{0.8}$. In contrast, *polymerized* self-avoiding membranes are flat and rough. The related anisotropy is characterized by the two larger eigenvalues of the inertia tensor, $\lambda_3 \sim \lambda_2 \sim N$, and by the smallest one, $\lambda_1 \sim N^{0.65}$. A free draining monomer of a fluid membrane exhibits a time-dependent displacement of $r^2(t) \sim t^{0.8}$, whereas approximately $r^2(t) \sim t^{0.4}$ for polymerized membranes.

Properties of flexible sheet polymer networks («tethered» surfaces) have been explored in recent theoretical investigations. Such «tethered membranes» are realized, *e.g.*, by polymerized Langmuir-Blodgett films and by cross-linked gels stabilized in a water-rich region between lipid bilayers. Polymerized membranes have a nonzero shear modulus in the plane and are said to be solidlike, whereas fluid membranes are not rigid in the plane and have zero in-plane shear modulus. Fluid isotropic membranes [1, 2] as well as polymerized membranes [3-7] have been predicted to exhibit a high-temperature crumpled phase similar to that of coiled polymers. This has been asserted for polymerized membranes by renormalization group arguments [8-10] and first pioneering Monte Carlo simulations [4, 11]. However, subsequent extensive molecular dynamics [12] and Monte Carlo simulations [13-15] did not reveal any evidence for a crumpled state of polymerized membranes imbedded in space dimensions $d = 3$, rather the membranes have been found to be essentially flat. For higher dimensions at least there should be a crumpling transition, but it has not yet been observed in simulations. The configurational properties of *fluid* self-avoiding membranes have not yet been examined by comparable models using simulations.

In the present letter 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, represents a distorted two-dimensional surface in three space dimensions on which the monomers should be able to diffuse freely

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among each other. Most of the membranes known in life sciences are fluid and hence investigations on fluid model membranes are of great importance.

Flexible fluidlike surfaces, but without self-avoidance («phantom membranes»), have been introduced [16-19] and studied by means of simulations [20-22] recently in the context of lattice field theory. Among others, one important question which has been addressed in those works is concerned with the value of the correlation length exponent ν . Semi-flexible phantom surfaces, *i.e.* surfaces with local bending energies, have been simulated as well ([23] and references therein).

The present investigations are the first which are concerned with a molecular model of a fluid membrane including self-avoidance. Our intention is to demonstrate the suitability of the fluid membrane model by its high-temperature configurational and dynamical properties in order to provide a sound basic model for future investigations on the thermodynamics of membranes. Furthermore, we are able to show that fluid self-avoiding surfaces exhibit a crumpled phase in contrast to polymerized self-avoiding surfaces.

The initial configuration of a tethered open membrane consists of N hard spheres of diameter σ connected to each other by tethers of maximum length $l_{\max} = \sqrt{2}$ according to a triangular lattice topology with free boundary. (Simulations of closed membranes with spherical topology («vesicles») will be published elsewhere.) A Monte Carlo step for polymerized membranes consists of randomly or sequentially choosing a grid point, which we call henceforth a monomer, and displacing it to a randomly selected nearby position. This trial is accepted if the finite extensibility of the tethers and the self-avoidance of the surface are still maintained. The former condition is taken into account in our model by the requirement that the length l of each of the new tethers, by which the moved monomer is connected to its neighbors, must be $l < l_{\max} = \sqrt{2}$. The self-avoidance is taken into account by attributing to each monomer a hard sphere of diameter $\sigma = 1.0$; then those attempted moves are rejected causing overlaps with other spheres. The crossing of tethers during a move is safely prohibited by our choice $\sigma/l_{\max} > \sqrt{3}/4$, similar as in the case of entangled linear polymer models [24]. As a technical remark, we note that we choose a maximum displacement of a monomer of 0.1σ , in order to have a success rate of about 0.6. The actual sampling of configurations is made at least every N Monte Carlo time steps (one Monte Carlo time step corresponds to N attempted moves). Since the expected correlation time between configurations is of the order of N^2 , the collected samples are not completely uncorrelated. This point will be considered in more details below discussing the dynamics of membranes. Equilibrium averages are taken over up to 10^4 configurations.

So far, this model represents a polymerized surface. The fluidity is implemented in this model by a triangulation procedure (fig. 1) similar to techniques applied to fluid phantom

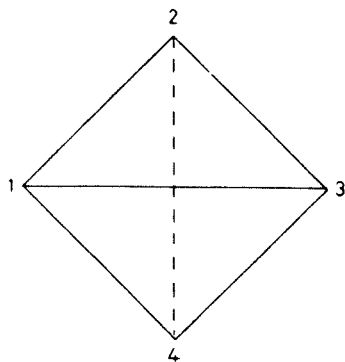


Fig. 1. – Scheme of triangulation procedure for fluid two-dimensional flexible surfaces in three space dimensions.

surfaces [16-19]. This procedure consists essentially in randomly deleting tethers and creating a new one with $\sigma < l < l_{\max}$ between previously unbounded monomers under the restriction that the surface is still well defined and covered by triangles. The simplest method of triangulation consists in choosing out of the N monomers on the surface, four monomers (labeled by 1, 2, 3 and 4) which are ringwise connected by four bonds representing a quadrangle (fig. 1). 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 in removing this bond and implementing a new one between monomers 2 and 4, which is accepted if $\sigma < l < l_{\max}$. Of course, the attempt must also be rejected if the number of tethers by which a monomer is connected to its neighbors is smaller than 3, because otherwise one would have either a dangling tether or a dangling triangle. It should be noted that bonds connected to monomers on the free boundary are treated by triangulation likewise. Thus by construction the surface still consists of triangles and still preserves its two-dimensional character in three space dimensions. The total number of tethers remains constant during the triangulation. This triangulation procedure is applied to N randomly selected bonds after each Monte Carlo step 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 mobile particle on the surface.

This view is supported by the time-dependent mean squared displacement of a labeled monomer relative to the motion of the center of mass,

$$r^2(t) = \langle [r_k(0) - r_{c.m.}(0) - r_k(t) + r_{c.m.}(t)]^2 \rangle, \quad (1)$$

where $r_k(t)$ and $r_{c.m.}(t)$ are the position vectors of the k -th monomer and the center of mass at time t , respectively. According to the data in fig. 2 for *fluid* membranes, the behavior of $r^2(t)$ is close to $\sim t^{0.8}$ and almost independent of the size N of the membranes. (Averages have been taken over six different monomer trajectories, and their deviations are in the order of the size of the symbols in fig. 2.) 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 [25], the displacements of a monomer trapped on a random surface can be understood as follows.

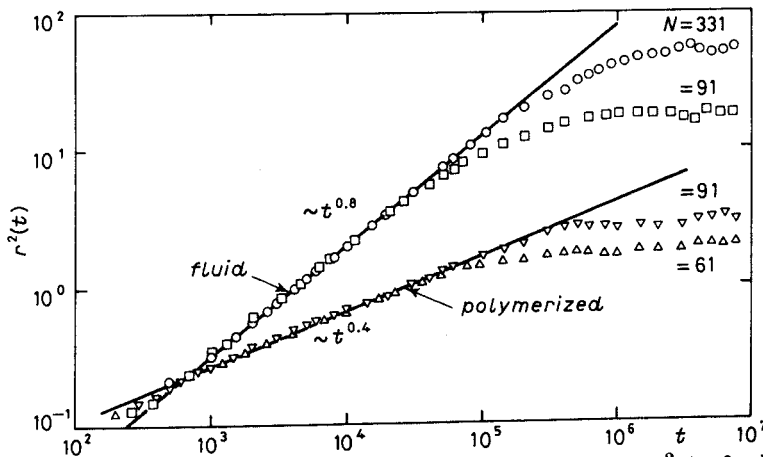


Fig. 2. – Log-log plot of the time-dependent mean-square displacements $r^2(t)$ of a labeled monomer relative to the center-of-mass displacements of *fluid* membranes (circles, squares) and of *polymerized* membranes (triangles) consisting of N monomers.

Given a two-dimensional coordinate system $\{s_1, s_2\}$ on the surface, where $s_1(x, y, z)$ and $s_2(x, y, z)$ are unit tangent vectors at the points (x, y, z) in the absolute coordinate systems, then, a monomer k at time $t=0$ with coordinate $L_k(s_1, s_2; t)$ performs within the time interval t isotropic mean-square displacements $L^2(t)$ measured along the contour of the surface according to $\langle (L_k(0) - L_k(t))^2 \rangle \equiv L^2(t) \sim t$. Since in the absolute coordinate system the corresponding distance r is given by $r \sim L^\nu$, the monomer performs mean-square displacements, measured in the absolute coordinate system, according to

$$r^2(t) \sim t^\nu, \quad (2)$$

where $\nu \approx 0.8$ as discussed below. For very long times, $r^2(t)$ approaches a constant value

$$r^2(\infty) \sim R^2 \quad (t > \tau_2), \quad (3)$$

reflecting simply the fact that the monomer displacement measured relative to the centre-of-mass motion is bounded by the finite size of the membrane. The corresponding crossover time defines the longest relaxation time τ_2 of the membrane and their estimated values as given in table I for various sizes N of membranes. A rough estimate gives $\tau_2 \sim N^{1.4 \pm 0.4}$. This latter result is not quite consistent with (2) and (3) which yield $\tau_2 \sim N$. We suspect that our estimates of τ_2 as given in table I are too crude in order to give a clear indication.

TABLE I. – Mean-squared radius of gyration R^2 , eigenvalues λ_k of the inertia tensor, and longest relaxation time τ_2 for fluid membranes. The number in brackets denotes the estimated statistical error for the last digit.

N	R^2	λ_3	$\tau_2 N^{-1} \cdot 10^{-4}$	λ_1/λ_3	λ_2/λ_3
37	5.78(5)	3.95(3)	0.94(3)	0.16(8)	0.37(17)
61	8.78(5)	5.81(3)	1.1(3)	0.16(5)	0.38(14)
91	12.6(6)	8.31(5)	2.0(5)	0.18(9)	0.41(19)
127	15.5(8)	9.21(5)	2.5(4)	0.21(9)	0.51(18)
169	20.1(8)	12.5(5)	2.4(4)	0.21(9)	0.45(18)
217	27.0(8)	17.3(6)	2.7(6)	0.20(11)	0.43(17)
271	31.4(7)	18.7(7)	2.9(7)	0.21(15)	0.53(19)
331	33.8(9)	21.7(8)	3.0(8)	0.23(16)	0.58(16)
397	39.6(9)	25.6(8)	3.7(9)	0.22(20)	0.56(16)

One of our main results is that fluid membranes are crumpled, *i.e.* the mean-square radius of gyration exhibits $R^2 \sim N^\nu$ with $\nu = 0.8 \pm 0.03$, which is depicted in fig. 3 and table I. There we have also included estimates of the largest eigenvalue λ_3 of the inertia tensor which is related to the radius of gyration by

$$R^2 = \lambda_3 + \lambda_2 + \lambda_1. \quad (4)$$

From table I, where we present estimates of the two remaining eigenvalues λ_2 and λ_1 , it can be seen that these eigenvalues are comparable to the largest one, and complete our observation $R^2 \sim \lambda_k \sim N^{0.8}$.

Of course, it is of interest to compare the properties for *fluid* membranes as given above, to those of *polymerized* membranes. This is discussed below. The largest eigenvalues λ_3 of polymerized membranes are depicted in fig. 4 and indicate that the membranes are essentially flat, *i.e.* $\lambda_3 \sim \lambda_2 \sim N^{0.97 \pm 0.03}$ (since λ_2 is comparable to λ_3 , the former has been

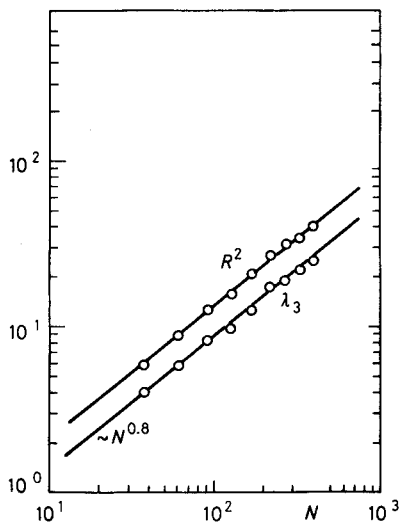


Fig. 3.

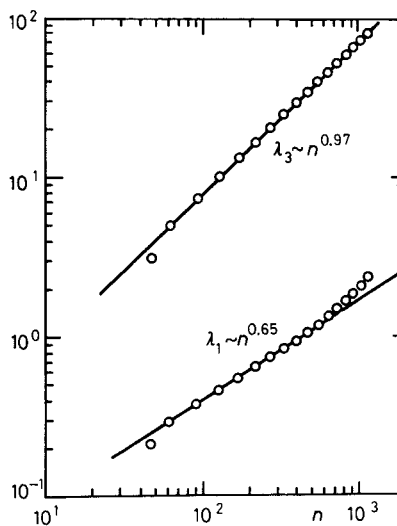


Fig. 4.

Fig. 3. – Log-log plot of the mean-squared radius of gyration R^2 and largest eigenvalue λ_3 of the inertia tensor for *fluid* membranes for various sizes N .

Fig. 4. – Log-log plot of the largest eigenvalue λ_3 and the smallest one λ_1 of the inertia tensor of a *polymerized* membrane *vs.* the number of monomers n of patches inside the membrane of size $N = 1141$.

omitted in fig. 4). This confirms previous findings [12-15]. The smallest eigenvalue characterizing the roughness of the membrane increases according to $\lambda_1 \sim N^\zeta$ with $\zeta = 0.65 \pm 0.02$ (fig. 4), which is consistent with other Monte Carlo results [15, 26]. As a technical remark, it should be noted that estimates of λ_k as depicted in fig. 4 have been obtained from a single large membrane of size $N = 1141$. There one defines inside the membrane patches consisting of $n < N$ monomers, from which the exponent can be estimated according to $\lambda_k \sim n^\nu$. The time-dependent displacements of a labeled monomer on a *polymerized* membrane is much smaller (fig. 2) than that of a monomer of a fluid membrane. This can be understood within the well-known framework of polymer dynamics [27] and has been shown [11] to be related to the Rouse model where $r^2(t) \sim t^{\nu/(\nu+1)}$, $\tau_2 \sim N^{\nu+1}$, and $r^2(\infty) \sim R^2 \sim N^\nu$ for $t \geq \tau_2$. Using the correlation exponent $\nu \approx 1$ of the largest eigenvalue, which yields $r^2(t) \sim t^{1/2}$, gives a poor agreement with the observation $r^2(t) \sim t^{0.40 \pm 0.05}$ in fig. 2. Assuming that the smallest eigenvalue with $\lambda_1 \sim N^{0.65}$ dominates the monomer displacements, one has $r^2(t) \sim t^{0.4}$, which is in better agreement with the Monte Carlo result. Whether this is just fortuitous or not deserves further investigations. The upward bending of $\lambda_1(n)$ for $n > 10^3$, as shown in fig. 4, is probably related to an effect from the free boundary of the open membrane, because similar phenomena are observed for smaller membranes too, if n approaches N .

It should be noted that for fluid as well as for polymerized membranes the center of mass diffusion exhibits, as expected, the free draining behavior, $r_{c.m.}^2(t) \sim l^2 N^{-1} t$.

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