

Glassy State of Polymerized Membranes.

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Abstract. - Spatial conformations of a model polymerized membrane (tethered surface) with a quenched in-plane disorder have been studied using Monte Carlo methods. As the temperature decreases the membrane first undergoes a transition from a crumpled to fluctuating flat state. Specific heat singularity is detected at the transition point. Further decrease of the temperature freezes the transverse fluctuations, but does not cause the membrane to approach a flat state. On the contrary, the deviation from a flat configuration increases, and the membrane settles into a partially folded ground state.

Polymerized membranes, or tethered surfaces [1] are the two-dimensional analogues [2] of linear polymers [3]. At low temperature T a membrane with bending rigidity is asymptotically flat, and its radius of gyration (root-mean-squared size) R_g increases as the linear dimension (internal size) L of the surface. As the temperature increases the membranes undergo (in the absence of self-avoiding interactions) a crumpling transition [4] between the flat phase and a crumpled linear-polymer-like high-temperature phase in which [1] $R_g \sim \sqrt{\ln L}$. During the last five years a significant attention has been directed to the properties of the flat phase [5] and to the properties of the transition itself [4, 6]. A significant effort has also been directed towards understanding the properties of self-avoiding membranes, both homogeneous [7] and disordered [8].

Homogeneous two-dimensional *rigid* sheets imbedded in three dimensions are flat at $T = 0$. However, the introduction of quenched in-plane disorder [9] may significantly modify the situation: consider a membrane at $T = 0$ in which part of the monomers have been replaced by monomers of different, say larger, size. Such impurities will introduce in-plane stress which can be partially relaxed by popping the monomer «up» or «down» relatively to the plane of the membrane. Such movement, however, cannot completely relax the stress since the bending rigidity resists the removal of the monomer from the plane. For a single impurity the «up» and «down» positions of the monomer are energetically equivalent. However, in the presence of a finite concentration of such impurities the interaction between them leads to a situation somewhat resembling a two-dimensional Ising model (the «spin» corresponding to the direction of the deviation of the impurity from the surrounding membrane) with random strength (antiferromagnetic) interactions. Such a system has many local energy minima, and at low T one may expect to encounter a glasslike behaviour. At this

point, however, the features of the low-temperature states are not known. Details of the phase diagram in the temperature-randomness plane are not known, either. It is even not clear whether the ground state is asymptotically flat or crumpled.

In this work I present the results of a first attempt to investigate *numerically* the features of a rigid model membrane with a strong in-plane disorder. The results provide information regarding the possible features of the phase diagram. A Monte Carlo (MC) equilibration of two-dimensional surfaces is usually extremely slow, and in the present case the problem is further aggravated by the multiple minima in the low-temperature free-energy landscape. Since this is a first MC investigation of such a system, no attempt has been made to determine the entire phase diagram. Rather, an extremely slow cooling was performed for a single (large) value of the randomness parameter. The results show that the low- T phase is *not* crumpled, and that the phase transition persists even for strong disorder.

In the continuum limit the flat phase of a polymerized two-dimensional membrane is characterized by its bending constant κ and by the in-plane elastic constants, *e.g.* the Lamé constants λ and μ . The simplest way to introduce disorder is by replacing the local preferred flat metric $\delta_{\alpha\beta}$, by varying metric $\delta_{\alpha\beta}[1 + \delta c(\mathbf{x})]$, where $\alpha, \beta = 1, 2$ are the internal coordinate indices, while $\delta c(\mathbf{x})$ describes random dilations and compressions. ($\langle \delta c \rangle = 0$, $\langle \delta c^2 \rangle = \sigma^2$, where $\langle \rangle$ denotes the average over the membrane.) Nelson and Radzihovsky [9] predicted that the flat configuration will be destabilized by disorder for temperature lower than $T_s = (16\mu/k_B)((\mu + \lambda)/(2\mu + \lambda))^2 \sigma$. They suggested that the instability may either represent the appearance of low-temperature glassy state, or re-entrant transition into a crumpled state similar to the high-temperature configurations. At high temperatures randomness acts as an effective increase in temperature, thus leading to a decrease of the crumpling transition temperature T_c . For small σ we may expect the transition from a crumpled to a flat phase followed by transition to the glassy state as the temperature decreases. Increase in σ leads to increase in T_s and decrease in T_c . Thus, it is possible that at high σ the flat phase region disappears altogether. In such a case, we might observe a directed transition from a crumpled to a glassy state. However, if the nature of the low-temperature phase is identical to that of the crumpled phase, then for high σ the phase transition should disappear completely.

I considered a two-dimensional triangular array of monomers («atoms») with positions $\{\mathbf{r}_i\}$, embedded in a three-dimensional space. In the simulation a hexagonal sheet (15 monomers across) excised from the triangular lattice has been used. The connectivity of the system was fixed by keeping nearest-neighbour atoms on the lattice connected by harmonic springs, while the energy assigned to a particular configuration of the membrane was

$$\mathcal{E} = -\kappa' \sum_{(l,m)} (\mathbf{n}_l \cdot \mathbf{n}_m - 1) + \frac{1}{2} k \sum_{(i,j)} (|\mathbf{r}_i - \mathbf{r}_j| - a_{ij})^2.$$

The first sum is performed over all pairs of neighbouring triangles and \mathbf{n} denotes a unit normal to a triangle, while the second sum is performed over all neighbouring atoms. The force constant k of the springs connecting the nearest neighbours is the same everywhere, however the equilibrium distance («bond length») a_{ij} between the neighbouring atoms varies among the atom pairs but is kept frozen during the simulation. The bond lengths have been chosen by the following procedure: every atom i was independently assigned a random number $p_i = \pm 1$, representing «big»/«small» atoms, respectively. The bond length between atom i and (neighbouring) atom j was set as $a_{ij} = 1 + (p_i + p_j)v$. Thus the bond length between two big atoms was $1 + 2v$, the bond length between two small atoms was $1 - 2v$, while the distance between a big and a small atom was 1. Such choice maintains an average

bond length $a = 1$. In the simulation I used $v = 0.4$ which is close to the maximal contrast between the long and the short bonds as allowed by the algorithm. To increase the influence of this disorder I used $k = \varepsilon_0/a^2$ and $\kappa' = 0.1\varepsilon_0$, where ε_0 is an arbitrary energy unit, *i.e.* stiff springs and weak bending resistance. The disorder variable for such large v can be estimated as $\sigma \sim 0.5$ leading to an extremely high value of $T_g \sim 3\varepsilon_0/k_B$. As will be seen, this estimate is way above the crumpling transition temperature T_c in the MC study. Therefore, the present simulation probes the strong randomness regime of the phase diagram, where the disappearance of the flat phase or complete disappearance of the phase transition may be expected. No excluded-volume interactions have been included in this simulation.

An elementary move in such MC simulation consists of randomly choosing an atom and attempting to move it by an amount sa in a randomly chosen direction ($s \ll 1$). The resulting configuration is accepted or rejected in accordance to its Boltzmann weight. During one MC time unit an attempt is made to move every atom of the surface. In a single MC time unit the centre of mass of the surface diffuses a typical distance of sa/\sqrt{N} where $N = 169$ is the number of atoms in the simulation. Thus, during the time $\tau_0 = N/(sa)^2$ it diffuses a distance of order of unit length. Frequently, a reasonable estimate of the equilibration time τ is obtained by calculating the time required for a polymeric object to diffuse its own radius of gyration R_g . In the crumpled phase [1] $R_g^2 \approx a^2 \ln N$, and therefore $\tau_{\text{crump}} \approx \tau_0$. In the flat phase $R_g^2 \approx a^2 N$, and we may expect $\tau_{\text{flat}} \approx N\tau_0$. These estimates are *not* exact: at the crumpling transition we may expect a critical slow-down of the relaxation, while at very low temperatures the relaxation may slow down due to the «glassy energy landscape» of the membrane. An important factor for searching for the ground state in a random structure is a slow cooling rate. The simulation began at high temperature T , which was decreased from time to time by a factor 1.1. At each fixed T a long simulation has been performed. Both at high and low temperatures the length of such equilibration exceeded τ_{crump} , and τ_{flat} , respectively, by two orders of magnitude. These cooling rates and equilibration times have been chosen when it became clear that further slowing-down of the cooling does not modify the state at which the system arrives at the end of the process, *i.e.* repeated cooling brought the system to *the same state*. Such slow cooling rate resulted in extremely high computer time consumption: investigation of a single quench (including the repeated cooling) consumed 80 *days* CPU time on Sun4 minicomputer. An increase in the cooling rates results in the system arriving at *local* energy minima, which change every time the cooling is repeated. The geometrical nature of those local minima is very different from the shape of the absolute minimum: the local-minimum states are extremely crumpled and self-entangled. It should be noted that the borderline between «high» and «low» temperatures is somewhere around $T \sim \kappa = 0.1$.

The main features of the phase diagram can be easily detected by an observation of the temperature-dependence of the spatial conformations of the membranes, as depicted in fig. 1: for high temperatures ($T \gg ka^2 = 1$, in ε_0/k_B units) the springs connecting the neighbouring atoms are unable to maintain their equilibrium bond length and the membrane looks like a crumpled tangle of atoms with a variety of bond lengths. This effect is an artifact of the model which maintains strict harmonicity of the springs, even for distortions exceeding their equilibrium length. In real systems the increase in the fluctuations of the bond length would be checked by anharmonic effects, while at very high T the bonds would simply break. For $0.2 < T < 1$, the fluctuations of the bond lengths are small, while the surface is strongly crumpled. This is a typical configuration of the crumpled phase (in the absence of self-avoiding interactions). For T close to the crumpling transition temperature T_c the surface starts unfolding; its R_g become of order of L with fluctuations approximately of the same order. Such fluctuations indicate the presence of the phase transition. At somewhat lower T the membrane is almost flat except for transverse fluctuations. Finally, at $T \approx 0$ the

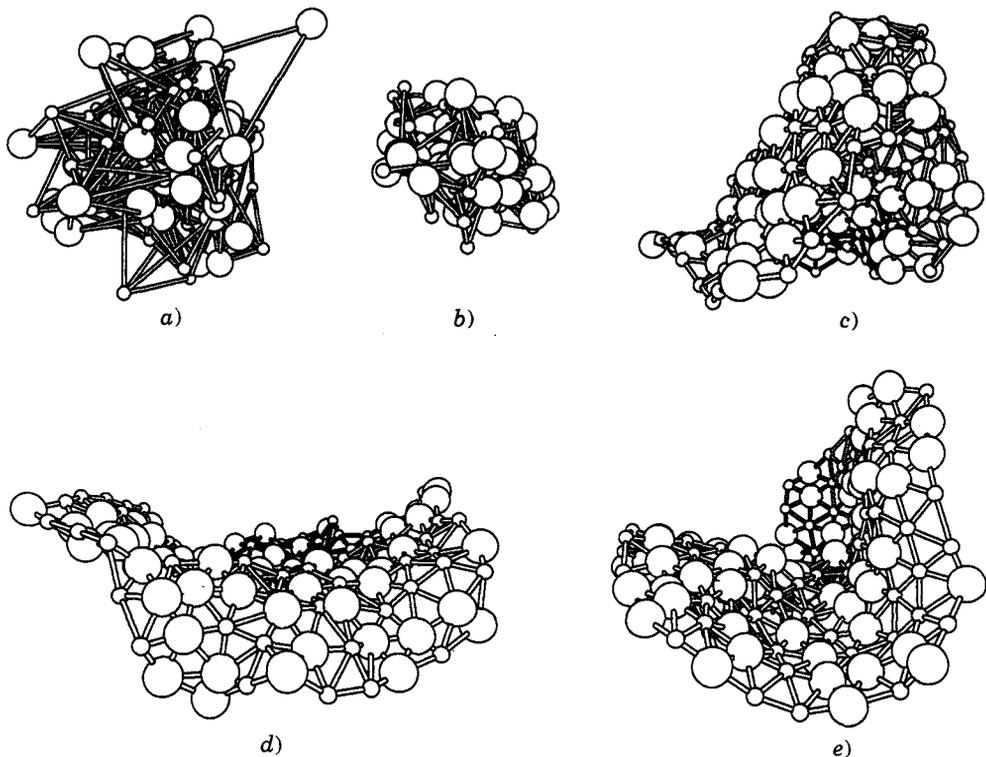


Fig. 1. - Typical spatial conformations of the two-dimensional membrane *a*) at very high temperature ($T = 2$) in ε_0/k_B units, *b*) in the crumpled phase ($T = 0.8$), *c*) very close to the crumpling-transition point ($T = 0.2$), *d*) in the low-temperature phase close to the crumpling transition ($T = 0.1$), and *e*) at the ground state ($T = 0$).

surface freezes into a time-independent ground state. Notice that this state is more folded than the typical state in the fluctuating flat configuration.

The sequence of pictures in fig. 1 should be compared with the T -dependence of the specific heat depicted in fig. 2. The specific heat has been calculated from the energy fluctuations, and the graph represents only the potential-energy part of the specific heat; the temperature-independent kinetic part has been omitted. For $T \gg 1$ the specific heat per atom C saturates. In the depicted range there is still some temperature dependence of C . We notice only one singularity at $T_c \approx 0.15$ signalling the crumpling transition. No singularities can be detected at lower temperatures. This fact is not surprising if there is a transition to a glassy state. At $T < 0.05$ the specific heat no longer depends on the temperature, but the motion of the system becomes so slow, that the measurement of C is no longer reliable. Values of C have been measured both during the «cooling» of the system and during its «heating», and they agree within statistical errors. For comparison, C of a homogeneous system is also presented. The statistical errors prevent an exact determination of the position of the specific-heat peak. However, it is clear that there is no indication that the extreme randomness reduces T_c . This result is inconsistent with the expectation that T_c decreases with increasing σ , unless the decrease is much smaller than can be expected from simple arguments.

Some indication of the presence of glassy state can be found by examining the eigenvalue

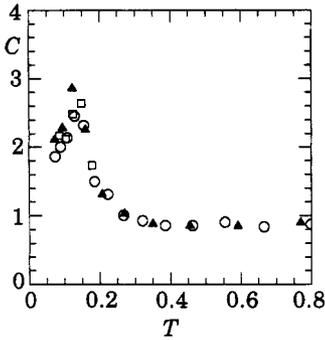


Fig. 2.

Fig. 2. - Specific heat per atom C (in k_B units) as a function of temperature (in ε_0/k_B units). The trivial-temperature-independent kinetic part has been excluded. Open circles and squares represent C measured during the cooling and heating of the surface, respectively. For comparison, C of a homogeneous membrane is shown by full triangles.

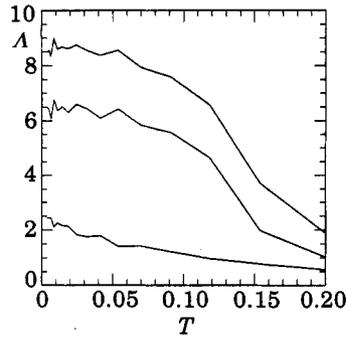


Fig. 3.

Fig. 3. - Temperature (in ε_0/k_B units) dependence of the three (ordered) eigenvalues Λ (in a^2 units) of the shape tensor S of the membrane.

of the shape tensor $S_{\alpha\beta} \equiv (1/N) \sum_i r_{i\alpha} r_{i\beta} - (1/N^2) \sum_{i,j} r_{i\alpha} r_{j\beta}$, where the summations are performed over all atoms, while the Greek indices indicate the Cartesian directions. Figure 3 depicts the T -dependence of the eigenvalues Λ_i of S . These eigenvalues characterize the mean largest, intermediate, and smallest squared dimensions of the object. For $T > T_c$, all eigenvalues are small. Below T_c the membrane becomes «flat» and the two largest eigenvalues of S approach their maximal possible values. Further decrease in T should gradually decrease the smallest Λ , due to the decrease of the transverse thermal fluctuations. In fig. 3 we observe an opposite effect, *i.e.* an increase in the smallest Λ with decreasing T . Part of this increase (in the range $0.05 < T < 0.2$) may be an effect related to the smearing of the phase transition due to the finite size of the membrane. However, for $T < 0.05$ it seems to be a real effect of the membrane freezing into relatively wrinkled ground state. Indeed in the low-temperature picture in fig. 1 we can see that the two ends of the membrane are rotated by almost 90 degrees.

In this work I attempted to establish the main geometrical features of the spatial conformations of membranes with strong in-plane disorder. The crumpling transition temperature seems very insensitive to the presence of the disorder. The results indicate that the low-temperature glassy phase is very different from the crumpled high-temperature phase, and therefore at least one phase transition should be present even for very high disorder. The ground state of the system is surprisingly smooth, although it is *not* «flat», *i.e.* its overall bend is of the order of the system size. The surfaces have not been sufficiently large to show a clear difference between the low-temperature glassy state and the intermediate-temperature flat state. (Since only one disordered quenched configuration has been used, no attempt has been made to evaluate the standard glassy-state order parameters.) It is quite obvious that in order to resolve those differences, one needs to increase the linear dimensions of the surface by a significant factor, perhaps even by an order of magnitude. Such an increase, however, presently does not seem to be possible, due to the enormity of the relaxation times: I estimate that an increase of L by a factor of 5 will prolong the simulation by at least four orders of magnitude. Since the present simulation required

several months of CPU time, the prospects of a further progress using MC methods are definitely limited. On the other hand, real polymerized membranes are frequently disordered. Due to excluded-volume effects, they probably do not have any crumpling transitions. Self-avoidance, however, should not influence the presence of the glassy phase, which does not self-intersect even in the absence of excluded-volume interactions. Therefore, the transition between the flat and the glassy low-temperature state could in principle be measured experimentally.

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