Heterogeneities in Polymerized Membranes

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A polymerized membrane composed of two different types of monomers is studied using Monte Carlo methods. An isolated heterogeneity in the flat phase with a longer average bond length than the surrounding lattice produces in-plane stresses that can be relieved by the lattice puckering up or down in the neighborhood of the heterogeneity. We treat the puckering direction as an Ising spin and investigate the connection between the Ising model and a heterogeneous polymerized membrane. The correlations between 'spins' suggest an antiferromagnetic interaction. Several arrangements for the two monomers, including a smaller sublattice and a line of heterogeneities, are investigated.

I. INTRODUCTION

Polymerized membranes, or tethered surfaces, are two-dimensional generalizations of linear polymer chains. They are characterized by long-range orientational order in the local membrane normals and quasi-long-range translational order, and are typically modeled as triangulated surfaces with fixed internal connectivity [1]. Unlike the linear polymer chain, which undergoes a self-avoiding random walk at distances longer than the persistence length, polymerized membranes exhibit a flat phase at low temperatures, which has attracted considerable theoretical interest [2] [3] [4].

Polymerized membranes provide a model for a number of systems in biology and materials science. The constraint that bonds between neighbors can never be broken is a reasonable approximation at experimentally relevant temperatures for many systems. For example, the spectrin skeletons of red blood cells form a triangulated network, with actin oligomers forming nodes and spectrin tetramers forming links. Experiments found critical exponents to be in good agreement with the flat phase predictions for this system [5]. Measurements of graphitic oxide sheets also agree with flat phase theory [6]. More recently, interest in polymerized membranes has focused on free-standing atomically thin materials, such as graphene and boron nitride [7].

In this paper, we will first summarize key results for homogeneous polymerized membranes, focusing on the flat phase. We will then discuss a framework for heterogeneous polymerized membranes, and present our simulation results regarding the interactions of heterogeneities.

II. EXISTENCE OF THE FLAT PHASE

The behavior of phantom polymerized membranes without bending rigidity and liquid membranes makes the existence of a flat phase in tethered surfaces surprising.

Membranes without bending rigidity must be phantom networks that allow self-intersection, because excluded volume effects generate bending rigidity. Forbidding self-intersection, even with zero imposed bending rigidity, prevents two neighboring normals from being antiparallel, giving a non-zero expectation value for an effective rigidity [4].

Properties of phantom membranes without bending rigidity can be studied using a Gaussian spring potential.

$$\beta H_{go} = \frac{1}{2} K \sum_{i,j} (\mathbf{r}_i - \mathbf{r}_j)^2. \tag{1}$$

The equilibrium bond length for this model is zero. This potential is not as unphysical as it might appear, as both rigid rod and hard sphere/string potentials converge to the Gaussian spring under Migdal-Kadanoff rescaling [8]. The spatial extent of the membrane is quantified by the radius of gyration, which can be derived in the Gaussian case in analogy with a network of resistors. Thus,

$$R_g^2 = \frac{1}{2N^2} \sum_{i,j} \langle (\mathbf{r}_i - \mathbf{r}_j)^2 \rangle = d\mathcal{R}, \tag{2}$$

where R_g is the radius of gyration, d is the spatial dimension that the D dimensional membrane is embedded in, and $\mathcal{R}$ is the network-averaged two-point resistance. Specializing to $d = 3$, $D = 2$, noting the form of a two-dimensional Coulomb potential, and coarse graining to a lattice, we find that

$$R_g^2 = \frac{3}{\pi K} \ln (L/a). \tag{3}$$

Therefore, if only a simple tethering potential with no bending rigidity is considered, there should be no flat phase. R_{go} for a flat phase would grow as L.

Instead, consider a model with no tethering potential that includes bending rigidity. This describes a liquid membrane. By analogy to liquid crystals, we define bending energy on a lattice

$$\beta H_b = -\kappa' \sum_{\langle i,j \rangle} \mathbf{n}_i \cdot \mathbf{n}_j. \tag{4}$$

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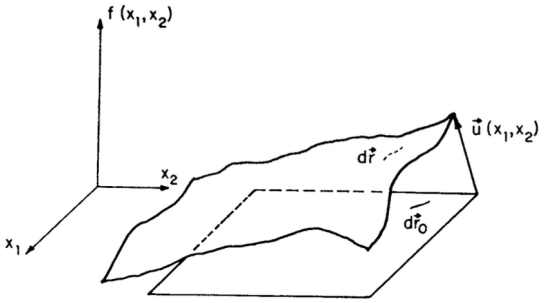

FIG. 1. Membrane coordinate system, from Ref. [1].

Taking only the leading order of the continuum limit of this equation and integrating by parts, the bending energy becomes

$$\beta H_b = \frac{1}{2}\kappa \int d^2x (\nabla^2 f)^2. \tag{5}$$

If a state in which the normals point on average along the $\hat{\mathbf{z}}$ axis is considered, the angle from $\hat{\mathbf{z}}$ can be denoted θ. The quadratic form of the Hamiltonian allows for the calculation of $\langle \theta(x,y)^2 \rangle$ by moving to Fourier space:

$$\langle \theta(x,y)^2 \rangle \approx \frac{k_B T}{\kappa} \ln (L/a). \tag{6}$$

The breakdown of orientational order is predicted by the logarithmic divergence.

In summary, for both bending rigidity alone and a simple tethering potential alone, a flat phase is not predicted at finite temperature. However, a flat phase is possible when these two potentials are combined. We first provide some intuition for how this phase can emerge, followed by the results for a quantitative renormalization treatment, based on Nelson et al. [1].

First, consider a membrane whose height can be described as a function of its x_1 and x_2 coordinates (see Figure 1). If the height is set to be zero at $T = 0$, when the membrane is perfectly flat, the fluctuations for $T > 0$ are given by

$$\vec{r}(x_1, x_2) = \begin{pmatrix} x_1 + u_1(x_1, x_2) \\ x_2 + u_2(x_1, x_2) \\ f(x_1, x_2) \end{pmatrix}. \tag{7}$$

By considering how line elements transform under deformations, the strain matrix is derived. To lowest order in gradients of u and f

$$u_{ij} = \frac{1}{2}[\partial_i u_j + \partial_j u_i + (\partial_i f)(\partial_j f)]. \tag{8}$$

Finally, after summing the stretching energy and previously derived bending energy, the free energy in terms of Lamé coefficients is [9]

$$\beta H = \frac{1}{2} \int d^2x [\kappa (\nabla^2 f)^2 + 2\mu u_{ij} u_{ij} + \lambda u_{ii} u_{kk}]. \tag{9}$$

Note that Equation 8 differs from the strain matrix for a two dimensional solid by the term $(\partial_i f)(\partial_j f)$. This term acts like a symmetric matrix vector potential, and introduces frustration into the system. Consider a vertical displacement field $f^*(x_1, x_2)$ with a low bending energy– this could be any low energy state for a liquid membrane. In order for f^* to represent a low energy configuration for the tethered membrane, there must be a u_{ij} such that $u_{ij}(f^*) = 0$. However, since $(\partial_i f)(\partial_j f)$ is a 2 x 2 symmetric matrix with three degrees of freedom, it is not generally possible to cancel all three components with only two scalar displacement fields u_1 and u_2. Therefore, many energetically favorable configurations of liquid membranes will be unfavorable for tethered membranes. This is a simple example of how bending and stretching energy can couple to change the ground states of the system. It is this interplay that is responsible for the emergence of the flat phase at non-zero bending rigidity.

To justify the existence of the flat phase rigorously, Nelson and Peliti [10] studied the renormalized bending constant. To lowest order in the stretching energy coefficient after integrating out the phonon degrees of freedom,

$$\kappa(\mathbf{q}) = \kappa + \frac{4\mu(\mu+\lambda)}{2\mu+\lambda} \int \frac{d^2k}{(2\pi)^2} \frac{[\hat{q}_i P_{ij}(\mathbf{k}) \hat{q}_j]^2}{\kappa |\mathbf{k}+\mathbf{q}|^4}, \tag{10}$$

where $P_{ij}(\mathbf{k})$ is the transverse projection operator. This integral diverges as q^{-2} for small q, with a positive coefficient. Therefore, the effective bending energy increases at long wavelengths as a result of the presence of stretching energy. By making a self-consistent approximation, the quantity $\langle \theta^2 \rangle$ that was found to grow logarithmically with system size for a fluid membrane can be re-examined. For the tethered surface, $\langle \theta^2 \rangle$ is now finite, indicating long-range order in the normals and the existence of a flat phase. This does not violate the Mermin-Wagner theorem because the membrane fluctuations produce long-range interactions, which are beyond the scope of the theorem.

While the flat phase is stable for low temperatures/high bending rigidity, the previous arguments for a non-rigid phantom membrane still hold at high temperatures/low bending rigidity. There exists a crumpling transition for phantom membranes with nonzero bending rigidity which can be observed by measuring the specific heat of the system. We show evidence for the conformational change using Monte Carlo simulations in Figure 2. There are many excellent references on this topic, which will not be discussed further here [1]. Furthermore, since we will restrict our attention to the flat phase in the work that follows, we will not consider self-avoidance explicitly.

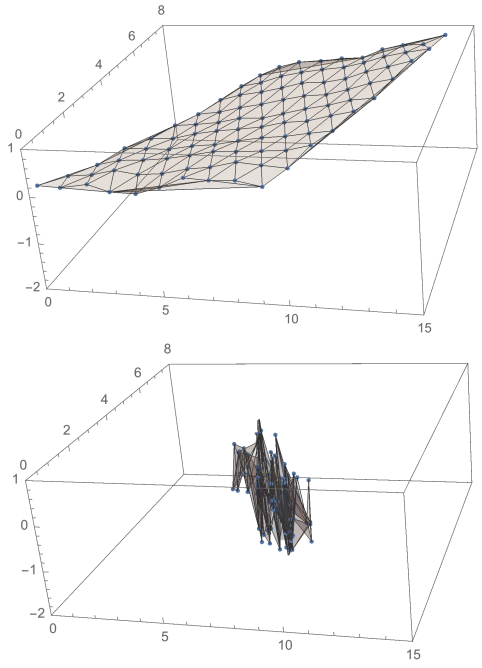

FIG. 2. Top: The flat phase at $\kappa' = 0.01$ for $L = 10$. Bottom: The crumpled phase at $\kappa' = 0.0001$ for $L = 10$.

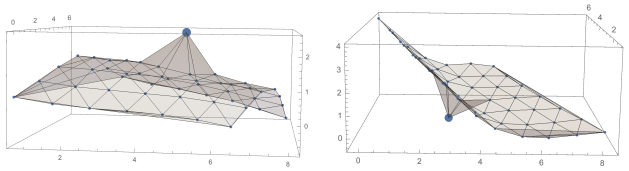

FIG. 3. A single heavy heterogeneity can relieve in-plane stresses by either puckering up or down, analogous to an Ising spin. Left: A "+1" heterogeneity. Right: A "-1" heterogeneity.

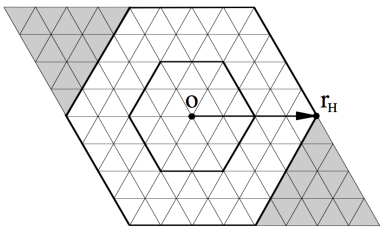

FIG. 4. Hexagon radius within a triangulated parallelogram domain, from Ref. [2].

III. HETEROGENEITIES

Heterogeneous polymerized membranes in the flat phase can be modeled with small modifications to the preceding theory. Much of the work on heterogeneities in polymerized membranes has focused on randomly placed heterogeneities, or defects, motivated by the desire to simulate more realistic systems for which random disorder is inevitable [11]. To the best of the author's knowledge, the case of a periodic sublattice of heterogeneities has not been methodically explored.

Heterogeneities with a different average bond length from the rest of the lattice can be understood as a deformation of the preferred background metric. In-plane stresses can be relieved by movement of the membrane along the flat phase normal direction in a trade-off between bending and stretching energy [1].

For a heterogeneity that is 'heavy', i.e. has a longer average bond length than the surrounding lattice, the options at low temperatures are particularly simple. The heterogeneity will either pucker up or down, spontaneously breaking the symmetry of the flat phase. The heterogeneity is therefore Ising-like, and can be assigned a value $\pm$ 1 in the flat phase, as shown in Figure 3. Since two spatially separated heterogeneities can interact through the background lattice in this model, we can ask whether or not the puckers are well-described by an Ising interaction, and, if so, if the interaction is ferromagnetic or antiferromagnetic.

Understanding the interactions between periodic, isolated defects can aid in the understanding of more complicated systems of random defects.

IV. MODEL

The simulations consider a triangulated surface composed of L x L parallelograms with open boundary conditions, with L ranging from 9 to 25. As in Kantor [12], a discretized model of bending rigidity was used, similar to Equation 4, scaled so that the flat phase has zero bending energy, and a harmonic tethering potential with a monomer-type dependent bond length.

$$\mathcal{E} = -\frac{\kappa'}{2}\sum_{\langle l,m\rangle}(\mathbf{n}_l\cdot\mathbf{n}_m - 1) + \frac{k}{2}\sum_{\langle i,j\rangle}(|\mathbf{r}_i - \mathbf{r}_j| - a_{ij})^2. \quad (11)$$

The first sum considers the unit normals for neighboring triangles, and the second sum considers nearest-neighbor monomers.

Two monomers of type A have a bond length a_0, and a monomer of type A and a monomer of type B have a bond length $a_0 + v$. Monomer B is the 'heavy' monomer, so $v > 0$. In all of the simulations, B monomers are dispersed on a background lattice of A monomers such that there are no B-B bonds.

In order to isolate the interaction between heterogeneities in the flat phase, we must avoid curling of the membrane to relieve the in-plane stresses generated by the heavy monomers. Therefore, we follow the guidance of Bowick et al. [2] and place our heterogeneities within a hexagon of radius $r < L/4$ from the center to avoid boundary effects. This radius is defined in Figure 4.

To perform the simulation, a Monte Carlo method is used. At every time step, a lattice point is randomly se-

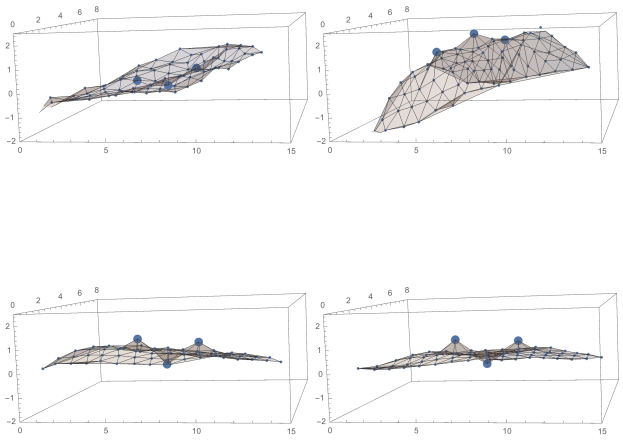

FIG. 5. Cooling of a line of heterogeneities, ending in an antiferromagnetic ground state. Top left: time=2×10^6. Top right: time=4×10^6. Bottom left: time=7×10^6. Bottom right: time=10^7.

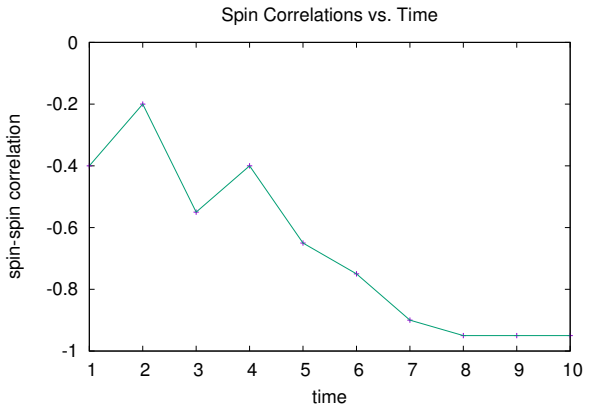

FIG. 6. Spin correlations as a function of simulation time/temperature. Time is measured in units of 10^6 simulation steps. Convergence to -1 at long times suggest an antiferromagnetic interaction.

lected to move to a random position within a cube of side $2s$ centered on the original position. If the move results in a lower energy, it is accepted. If it results in a higher energy, it is accepted with a probability proportional to its Boltzmann weight. The cube parameter s is tuned so that approximately 50% of the moves are accepted, ensuring that phase space is being sampled efficiently.

In order to reach the ground state, we start at a temperature below the crumpling transition temperature that still shows strong fluctuations, and decrease the temperature periodically by a factor of 1.002 until a lower bound is reached. The rate of temperature decrease must be very slow. If the system is cooled too rapidly, domains of order will form, and the system will be unable to attain the ground state within a reasonable simulation time. A typical time series is shown in Figure 5. As in Kantor [12], κ' is set to $0.1\epsilon_0$ and k is ϵ_0/a_0^2, where ϵ_0 is an arbitrary energy scale. The difference in bond length, v, is varied between $0.4a_0$ and $0.6a_0$.

V. RESULTS

In order to classify the interactions between Ising-like heterogeneities, we set up systems in which ferromagnetism, antiferromagnetism, and disorder can be distinguished in the flat phase. Based on the speculations in Kantor [12] and physical intuition, antiferromagnetic order is expected. However, since the background lattice is triangular, the heterogeneity sublattice must be selected with care. One obvious choice is a line of heterogeneities, for which the ground state is alternating up and down spins.

A line of three heterogeneities on a lattice $L = 9$ reached an antiferromagnetic ground state in 19 of 20 simulations. This is convincing evidence that the heterogeneities have an antiferromagnetic interaction. The trial that did not achieve an antiferromagnetic ground state had a higher energy than the other trials, and may have had insufficient equilibration time or overly rapid cooling.

In order to quantify the approach to the ordered state, the sample averaged nearest-neighbor spin-spin correlation was calculated and averaged over the 20 samples at 10 equal times during the simulation. For the case of three spins, this is particularly simple. Ferromagnetic alignment is assigned a value of 1, antiferromagnetic alignment is assigned -1, and the pattern (+ + -) or (- - +) is assigned 0. In most cases, it was unambiguous whether or not a heterogeneity was spin up or spin down, although the spin assignment ignores some of the subtleties of the system, including how far the heterogeneity protrudes from the background membrane and a case in which a transition from, for example (+ - +) to (- + -) occurs.

Figure 6 shows the correlation quantity. It is clear that the average value converges to -1 (antiferromagnetic order) over the timescale of the simulation. It is interesting to note that ferromagnetism appears most likely to occur at intermediate temperatures. This can be understood by examining Figure 5. At intermediate temperatures, the membrane can relieve the stresses caused by the heterogeneities with a global deformation and ferromagnetic order. At lower temperatures, this configuration is more highly penalized.

A longer line of heterogeneities (five) required a substantially larger lattice ($L = 23$) in order to satisfy the Bowick constraint, and simulations were too lengthy to generate meaningful statistics at sufficiently slow cooling rates. The simulations that were run to completion for this set of parameters did not achieve the antiferromag-

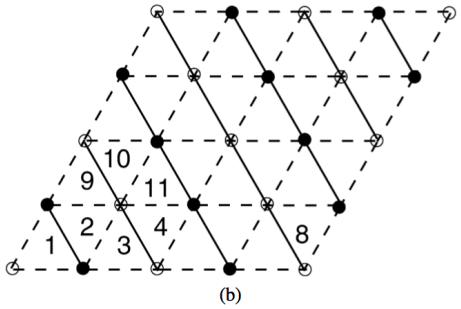

FIG. 7. Ground state of an Ising antiferromagnet on a triangulated parallelogram, from Ref. [13]. Dashed lines are favorable interactions and solid lines are unfavorable. The numbers refer to the procedure used in the article to demonstrate that this is the lowest energy configuration.

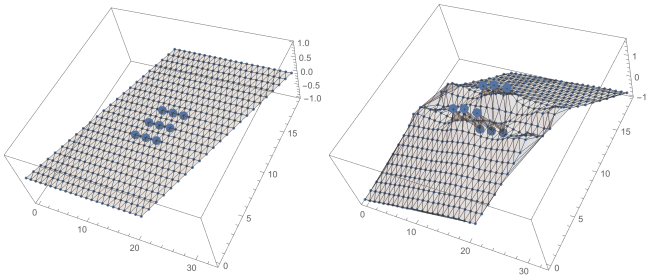

FIG. 8. Left: Initial condition of a parallelogram of heterogeneities, $L_{het} = 3$. Right: The system after cooling down and equilibrating. It does not attain the antiferromagnetic ground state.

netic ground state. It is likely that the cooling rate was too rapid or the equilibration time was insufficient. Three heterogeneities at a greater separation distance were also simulated on an $L = 23$ lattice. These heterogeneities did reach the antiferromagnetic ground state.

Moving to a two-dimensional sublattice, the ground states for an antiferromagnet on a triangular lattice can be constructed by considering the frustrated triangular cells within the lattice. The lowest possible energy for each of these cells has two satisfied bonds and one unsatisfied bond. Arranging these minimally frustrated subunits in order to minimize the number of unsatisfied bonds for the entire lattice gives the ground state configuration, which is in general highly degenerate. However, Millane et al. [13] found that a finite triangulated parallelogram has a ground state with only two possible configurations, as shown in Figure 7. We therefore arrange our heterogeneities in a parallelogram and seek this state.

Two parallelograms of heterogeneities were simulated, one with $L_{het} = 3$ in a background lattice of $L = 23$ (Figure 9) and one with $L_{het} = 4$ in a background lattice of $L = 25$ (Figure 8). Both reached a state that differed from the expected ordered state for a triangulated parallelogram with an antiferromagnetic Ising model. This could be the result of a number of sources of error. However, it is also possible that the ground state in Figure 7 is not the ground state for our system, due to the desire of the lattice surrounding the heterogeneities to be as flat as possible.

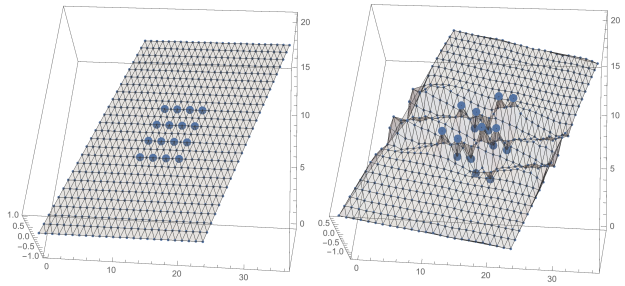

FIG. 9. Left: Initial condition of a parallelogram of heterogeneities, $L_{het} = 4$. Right: The system after cooling down and equilibrating. It does not attain the antiferromagnetic ground state.

VI. CONCLUSION

The results presented here suggest that heterogeneities in the flat phase of a polymerized membrane behave like antiferromagnetic Ising spins. The interaction between heterogeneities is quantified for a line of heavy monomers. Further studies are required to determine how accurate the analogy between the two models is. Our inability to reproduce the expected ground state for a two dimensional lattice of heterogeneities could be the result of a systematic error, such as overly rapid cooling of the system or boundary effects, or it could be the case that the specifics of the system add additional constraints to the model that change the ground state.

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