Landau Theory of the Crumpling Transition

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An order-parameter theory of the crumpling transition in D-dimensional polymerized membranes embedded in d dimensions is developed. Within mean-field theory, we show how self-avoidance modifies the behavior at the second-order crumpling transition. Fluctuations drive the transition first order to lowest order in $\epsilon=4-D$, for $d<d_c\approx 219$.

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In contrast to linear polymers, surfaces can exhibit a rich variety of behavior, depending on rigidity, surface tension, and various microscopic constraints.[1] As collections of permanently joined particles, "tethered surfaces" exemplify a particularly simple universality class which is experimentally realizable in covalently bonded networks such as polymerized lipid bilayers, chalcogenide glasses, and gels.[2-6] Monte Carlo experiments[6] have shown that, unlike polymers which are always crumpled, tethered surfaces exhibit a remarkable finite-temperature transition[5] into an ordered or stretched phase at high rigidity or low temperature.

In this Letter we propose an order-parameter theory of the crumpling transition which gives mean-field predictions for the parameters measured in Ref. 6. The model reduces to shell theory[7] in a low-temperature flat phase and leads to a Gaussian crumpled surface[2] at high temperatures. How self-avoidance modifies this second-order crumpling transition is determined within the Flory approximation. This approximation should be sufficient for laboratory experiments on flexible membranes, except for very large surfaces close to the critical point. To lowest order in $\epsilon=4-D$, we show that critical fluctuations lead to a weakly first-order transition in D-dimensional membranes for embedding dimensions $d<d_c\approx 219$.

We focus on the quantity $\mathbf{r}(\mathbf{x})$, where $\mathbf{x}$ is an internal D-dimensional vector which labels the particles and $\mathbf{r}$ is an external d-dimensional position vector representing the embedding of the particles. In the simplest case, the internal connectivity of the particles corresponds to a D-dimensional lattice with nearest-neighbor interactions. A statistical description is developed by coarse graining of this lattice so that the vector $\mathbf{x}$ becomes a continuous variable which labels a "block" of lattice points.

Symmetries of the microscopic Hamiltonian delimit the form of the free-energy functional for the coarse-grained variable $\mathbf{r}(\mathbf{x})$. For a uniform network, overall translational invariance requires that this functional depends on gradients such as the coarse-grained tangent vectors $\mathbf{t}_\alpha=\partial\mathbf{r}(\mathbf{x})/\partial x_\alpha$, $\alpha=1,\ldots,D$. In the crumpled phase, these tangent vectors scale as $\mathbf{t}_\alpha\sim l^{\nu-1}$, and as ν is generically less than 1, they diminish under scaling. In the rigid phase, close to the transition $\mathbf{t}_\alpha$ are still small; hence an expansion in powers of $\mathbf{t}_\alpha$ and their derivatives is justified. In the simplest case of an isotropic network, overall rotational invariance leads to a "Landau-Ginzburg" expansion[3]

$$\beta F\{r_i(x_\alpha)\}=\int d^Dx\,[\tfrac{1}{2}\kappa(\partial_\alpha\partial_\alpha r_i)^2+\tfrac{1}{2}t(\partial_\alpha r_i)^2+u(\partial_\alpha r_i\,\partial_\beta r_i)^2+\tilde{v}(\partial_\alpha r_i\,\partial_\alpha r_i)^2]$$
$$+\tfrac{1}{2}b\int d^Dx\,d^Dx'\delta^d(\mathbf{r}(\mathbf{x})-\mathbf{r}(\mathbf{x}'))\quad(i-1,2,\ldots,d).\qquad(1)$$

The last term is a nonlocal excluded-volume term which represents the effects of self-avoidance at large length scales.[2-4] Self-avoiding interactions account for interparticle hard-core repulsions which mitigate collapse and also prevent the manifold from folding through itself to access unphysical configurations. The local terms represent elastic free energies: The coefficients t, u, and $\tilde{v}$ can be interpreted as harmonic and anharmonic stretching energies, while the coefficient κ is a measure of bending rigidity. Upon identifying the tangents $\mathbf{t}_\alpha=\partial_\alpha\mathbf{r}$ with a set of order parameters ϕ_α, an analogy with the usual ϕ^4 theories of critical phenomena[8] becomes apparent. Given the free energy (1), the probability for a configuration $\{\mathbf{r}(\mathbf{x})\}$ is proportional to the Boltzmann weight $e^{-\beta F}$, and the partition function is a functional integral over all surfaces $\{\mathbf{r}(\mathbf{x})\}$.

At high temperatures we expect a crumpled phase where t is positive for entropic reasons.[2] At low temperatures, however, the microscopic surface tangents tend to

align in order to minimize the microscopic bending energy, driving the manifold to form a flat phase described by a negative value of t. For $t<0$, the manifold is stabilized by the anharmonic terms, provided that $u>0$ and $v=\tilde{v}+u/D>0$. We anticipate a continuous transition between these phases when $t\equiv a(T-T_c^0)\approx 0$.

As an illustration, we first discuss the mean-field solution in the absence of self-avoidance using the *Ansatz* $\mathbf{r}(x_\alpha)=\zeta x_\alpha \mathbf{e}_\alpha$, where the $\{\mathbf{e}_\alpha\}$ are a set of orthogonal unit vectors specifying the orientation of the manifold in $\mathbb{R}_d$, and the x_α range from 0 to L. The prefactor ζ, which was studied numerically in Ref. 6 for $D=2$, $d=3$, is an order parameter which measures the shrinkage of the manifold in the flat phase due to undulations, and vanishes for $t>0$. Minimization of Eq. (1) for $t<0$ leads to $\zeta=\frac{1}{2}(-t/Dv)^{1/2}$, which shows that the radius of gyration scales as $R_G=\zeta L\sim |t|^{1/2}L$ when the crumpling transition is approached from below. Fluctuations within the ordered phase can be studied by the introduction of in-plane phonon modes u_α ($\alpha=1,\ldots,D$) and out-of-plane undulations h_β ($\beta=D+1,\ldots,d$) and our setting

$$\mathbf{r}(x_\alpha)=\zeta[(x_\alpha+u_\alpha)\mathbf{e}_\alpha+h_\beta\mathbf{e}_\beta], \tag{2}$$

where the orthonormal vectors $\{\mathbf{e}_\beta\}$ are orthogonal to the $\{\mathbf{e}_\alpha\}$. To leading order in gradients of the u_α and h_β, the free energy (1) reduces to a generalization of the deformation energy of a flat plate,[7]

$$\beta F=\int d^Dx[\tfrac{1}{2}\kappa(\nabla^2 h_\beta)^2+\mu u_{ij}^2+\tfrac{1}{2}\lambda u_{kk}^2], \tag{3}$$

where the strain matrix is $u_{ij}=\frac{1}{2}[\partial_i u_j+\partial_j u_i+\partial_i h_\beta \partial_j h_\beta]$ and the elastic constants are $\mu=4u\zeta^4$ and $\lambda=8\tilde{v}\zeta^4$. This model could, in principle, be applied to linear polymers ($D=1$) with very large rigidities, although (because of undulation modes) all polymers with short-range interactions eventually crumple as $L\to\infty$.[9] The $d=3$, $D=2$, version of this low-temperature model was studied in Ref. 5, where it was shown that the renormalized bending rigidity grows at large distances and stabilizes the stretched phase against undulations. Note that the elastic constants in this treatment are predicted to vanish like $(T_c-T)^2$ near the crumpling transition. Mean-field theory leads in the usual way to a discontinuity in the specific heat at $t=0$ and a tangent-tangent correlation length $\xi\sim|t|^{-1/2}$ close to T_c. Above T_c, $R_G\sim L^{1-D/2}$, while precisely at T_c, $R_G\sim L^{\nu_c}$ with $\nu_c=1-D/4$. Although the Monte Carlo data on $D=2$ tethered surfaces in $d=3$ dimensions without self-avoidance are not yet good enough to obtain precise exponents, all measured quantities in Ref. 6 behave qualitatively as predicted above. Differences, such as the apparently *diverging* specific heat and somewhat larger exponent ν_c are probably due to critical fluctuations, which will be discussed later.

The possibility of laboratory experiments on crumpled surfaces requires that we also understand self-avoiding interactions. The Landau expansion (1) allows us to treat such effects (within mean-field theory) with the Flory approximation.[9] For a network of size R_G, the Flory estimates for the individual terms of (1) are summarized by

$$2\beta F/D\approx \kappa R_G^2 L^{D-4}+tR_G^2L^{D-2}+DvR_G^4L^{D-4}+bR_G^{-d}L^{2D}/D. \tag{4}$$

With these estimates, it is straightforward to show that self-avoidance is irrelevant for $t<0$, where $R_G\sim|t|^{1/2}L$. For $t>0$, the anharmonic terms u and v are asymptotically irrelevant, and balancing of the entropic and self-avoiding energies leads to $R_G\sim t^{-\omega}L^{\nu_F}$ where $\omega=1/(d+2)$, and $\nu_F=(D+2)/(d+2)$ is the Flory exponent for self-avoiding manifolds. At $t=0$, $R\sim L^{\nu_c}$ where $\nu_c=(D+4)/(d+4)$. The behavior of R_G near the crumpling transition for $D=2$, $d=3$ is sketched in Fig. 1.

It is interesting to note that the distinct scaling forms in the vicinity of $t\sim 0$ (including finite-size effects) can be combined into a single homogeneous function $R_G\sim L^{\nu_c}\Psi(tL^y)$, where $\Psi(0)=\text{const}$, $\Psi(x)\to|x|^{\phi_\pm}$ for $x\to\pm\infty$, $y=2(d-D)/(d+4)$, and $\phi_-=\frac{1}{2}$ and $\phi_+=-1/(d+2)$. The theories in the $t>0$ and $t<0$ regimes are very different, so that, in principle, two different crossover exponents y_- and y_+ cannot be ruled out. Within mean-field theory, however, this does not occur, and we conjecture that it is always true. Note that the exponents y_+ and y_- are the inverse of the exponents w_1 and w_2 defined in a related scaling analysis in Ref. 6.

Similar homogeneous scaling functions, with the same exponent y, can be constructed for other variables such as the free energy and heat capacity. In particular, as we approach the transition from the crumpled side, the specific heat per particle scales anomalously, $C\sim t^{-\alpha}L^{-k}$ with $\alpha=(d+4)/(d+2)$ and $k=2(d-D)/(d+2)$. This result applies only for $t>t_x\sim L^{-y}$. It would be interesting if the prediction $C\sim t^{-7/5}L^{-2/5}$

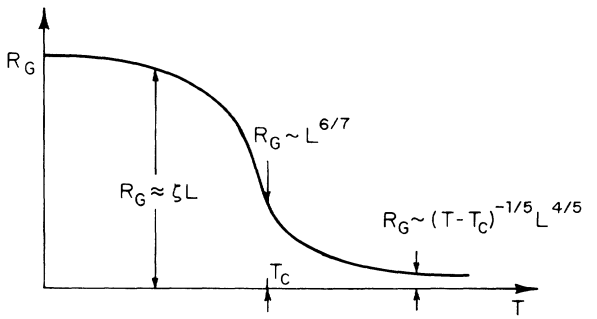

FIG. 1. Radius of gyration of a polymerized membrane with linear dimension L as a function of temperature.

could be observed experimentally in a dilute solution of tethered surfaces.

A systematic perturbative analysis of self-avoidance in the crumpled phase has recently been developed.[3,4] Upon inclusion of fluctuations, the radius of gyration takes the form $R \sim t^{-\omega} L^{\nu}$ with ν calculated via an $\tilde{\epsilon}=4D-d(2-D)$ expansion. Furthermore, since there is a general scaling form[2,3] $R_G^2 \sim L^{(2-D)} t^{-1} f(bt^{d/2} L^{\tilde{\epsilon}/2})$, where $f(x) \sim x^{2(2\nu+D-2)/\tilde{\epsilon}}$ for large x, ω and ν are not independent: $\omega=(2D-d\nu)/\tilde{\epsilon}$. For $\nu=\nu_F=(D+2)/(d+2)$, we recover the Flory result, $\omega=1/(d+2)$. This $\tilde{\epsilon}$ expansion does not include anharmonic strain energies close to the transition, which are, however, irrelevant for $t > t_x$.

Thus far, we have neglected critical fluctuations. As the crumpling temperature is approached from the flat phase, self-avoiding effects are always irrelevant for $L \to \infty$. A simple application of the Ginzburg criterion shows that mean-field theory for Eq. (1) breaks down for $t^2(\kappa/-t)^{D-2}/8Dv \lesssim 1$. Provided the transition remains continuous, the analogy with ϕ^4 theory for $T < T_c$ suggests that $\zeta = R_G/L \sim t^{\beta}$ with a nontrivial β, which can be calculated perturbatively in $\epsilon=4-D$ and $1/n=1/d$ expansions.[8] We have also just demonstrated that $R_G \sim t^{-\omega} t^{\nu}$ for $T > T_c$. Assuming that R_G still assumes the scaling form $R_G \approx L^{\nu_c} \Psi(tL^{y})$ with a common value of y for $t > 0$ and $t < 0$, we find $\nu_c=(\omega+\beta\nu)/(\omega+\beta)$. The relation $\omega=(2D-d\nu)\tilde{\epsilon}$ then allows ν_c to be expressed entirely in terms of ν and β. Use of the Flory estimate $\nu=\frac{4}{5}$ and the assumption that β decreases with fluctuations to a typical ϕ^4 value of $\beta \approx \frac{1}{3}$ gives $\nu_c=\frac{7}{8}$ for $D=2$, $d=3$, which is greater than the mean-field Flory estimate $\nu_c=\frac{6}{7}$ displayed in Fig. 1.

Having justified neglecting the self-avoiding term, we can treat critical fluctuations by an $\epsilon=4-D$ expansion. To lowest order in ϵ, the recursion relations for u and $v=\tilde{v}+u/D$ read

$$du/dl=\epsilon u - K_4[\tfrac{4}{3} v^2 + 6uv + (\tfrac{65}{12} + \tfrac{1}{3} d)u^2], \quad (5a)$$

$$dv/dl=\epsilon v - K_4[(4d+5)v^2 + \tfrac{21}{2} uv + \tfrac{21}{16} u^2], \quad (5b)$$

where $K_4=1/2\pi^2$ and we have used units such that $\kappa=1$. These equations have no stable fixed points for d less than $d_c=219$, and lead instead to a first-order transition. Such predictions are not always reliable for $\epsilon \sim 1$ in conventional critical phenomena,[10] and so we cannot be certain of what happens for the interesting case $\epsilon=2$, $d=3$. A weak fluctuation-driven first-order phase transition certainly cannot be ruled out in the simulations of Ref. 6. For $d > d_c$ the exponents at the transition are readily determined from the recursion relation for t,

$$dt/dl=2t+K_4[\tfrac{9}{2} u + 2(2d+1)v]/(1+t). \quad (6)$$

In the limit $d \to \infty$, exact saddle-point techniques show an isomorphism to the limit $n \to \infty$ of O(n) $|\phi|^4$ models. In this limit, we find, for example, a continuous transition with a specific heat singularity $C \sim |t|^{(4-D)/(D-2)}$ and a diverging persistence length $\xi \sim |t|^{-1/(D-2)}$. In contrast to the case $d=3$,[5] a $D=2$ surface is always crumpled in the limit $d \to \infty$, while a more-dimensional manifold exhibits a finite-temperature rigid phase. While this manuscript was in preparation we learned of interesting work by David and Guitter,[11] who solve a model similar to ours, but with infinite bare elastic constants. These authors show that a finite-temperature crumpling transition is recovered for $D=2$ within a $1/d$ expansion for $d < \infty$. In other related work, Aronovitz and Lubensky[12] have studied the singular renormalization of κ, μ, and λ in the low-temperature phase described by (3) to lowest order in $\epsilon=4-D$.

In summary, we developed a unified theory of regular tethered networks in d dimensions, encompassing polymers $D=1$, surfaces $D=2$, and gels $D=3$ as special cases. The theory includes harmonic and anharmonic stretching energies and bending energies, as well as nonlocal self-avoiding interactions. Checking the proposed scaling forms for singular behavior around the crumpling transition is an important challenge, both experimentally and theoretically, for the future.

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