Stastical Mechanics and Crumpling of Tethered Manifolds

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I review several results on ideal and self-avoiding "tethered" D-dimensional surfaces of fixed connectivity embedded in d dimensions. I have focused on the insights gained from Flory theory as well as perturbative RG techniques in the calculation of the scaling of these surfaces' radius of gyration with intrinsic length, $R_G \sim L^\nu$.

I. INTRODUCTION

Polymers are ubiqutous in nature, as are their natural two-dimensional generalizations, membranes. Understanding the statistical mechanics of such objects provides crucial insight towards many chemical and biological systems, as well as into the engineering of broad varieties of applications. While there is still much to be understood, mathematical and physical techniques such as statistical analysis, field theory, Flory approximations, and perturbative RG have been successfully applied to study these systems as well as higher-dimensional generalizations.

II. D=1: POLYMERS

A. Ideal (Phantom) Polymer

Consider first the case of an "ideal" polymer, modeled by a d-dimensional random walk of N steps of size a. The end-to-end vector of such a walk is given by

$$\mathbf{r} = \sum_{i=1}^{N} \mathbf{a}_i \tag{1}$$

where each $\mathbf{a}_i$ is an independent vector of length a oriented along one of the $2d$ directions of the d-dimensional Cartesian coordinate system. Such a model allows for self-intersections and can theeqrefore be regarded a "phantom" walk. The $\mathbf{a}_i \to -\mathbf{a}_i$ symmetry inherent to such a walk allows to immediately conclude that $\langle r \rangle = 0$, and its Markovian nature allows us to easily compute the standard deviation of r, which is called the radius of gyration R_G:

$$R_G \equiv \sqrt{\langle r^2 \rangle} = N^{1/2}\sqrt{\langle |\mathbf{a_i}|^2 \rangle} = aN^{1/2} \equiv R_0. \tag{2}$$

Furthermore, by approximating the distribution in r as Gaussian, as is justified for $r \lesssim r_G$, we arrive at the weight

$$\mathcal{P}_N(r) \propto N^{-d/2} \exp\left[\frac{dr^2}{2Na^2}\right]. \tag{3}$$

It is important to note that many other more sophisticated microscopic theories (e.g. allowing for non-uniform step size, allowing for any step direction, etc.) all yield the same scaling exponent for R_G vs. N due to the central limit theorem, but will in general give different constant multiplicative factors as is typical for a universality class.

We can recast this theory in terms of a continuum model by coarse-graining the walk to a continuous function $\mathbf{r}(x)$, where x is a continuous variable representing the internal polymer coordinate. By treating (3) as the Boltzmann weight, the partition function then becomes

$$Z = \int \mathcal{D}\mathbf{r} \exp\left[-\frac{1}{2}K\int_0^L dx\, (\nabla \mathbf{r})^2\right] \tag{4}$$

where $L = Na$ is the internal length of the polymer, and K is a parameter dependent on the microscopic details (in this case $K = \frac{3T}{2Na^2}$) that encodes an entropy-induced elasticity.

The scaling of the radius of gyration with L can be calculated by integration of (4), and is

$$R_G \sim L^{1/2} \equiv L^\nu \tag{5}$$

in agreement with the discrete walk model.

Calculations of the critical exponent ν will be the main focus of this paper.

B. Self-Avoiding Polymer

To account for self-avoidance, the above theory must be modified. Specifically, one can add a non-local term to the Hamiltonian which reflects an energy cost for self-intersections,

$$-\beta H = -\frac{1}{2}K\int dx\, (\nabla \mathbf{r})^2 - v\int dx\, dx'\, \delta^d(\mathbf{r}(x) - \mathbf{r}(x')), \tag{6}$$

where v measures the "excluded volume." This is known as the Edwards model for self-avoiding polymers [1]. One can then employ approximation techniques to investigate how the scaling of R_G is modified by finite v.

1. *Flory Theory*

The Flory approximation states that the entropic term should contribute to the free energy an amount $F_{el} \simeq$

$\frac{1}{2}KR_G^2/L$, while the self-interaction term should contribute $F_{sa} \simeq vL^2/R_G^d$. This can be understood in terms of a mean-field approximation by noting the approximate scalings $\mathbf{r} \sim R_G$, $\nabla \sim 1/L$, and $\int dx \sim L$. Then, minimizing the total free energy $F = F_{el} + F_{sa}$ with respect to the radius of gyration yields

$$R_G \sim (v/K)^{1/(d+2)} L^{\nu_F}, \quad \nu_F = \frac{3}{d+2}. \tag{7}$$

It is worth noting that for $d = 4$, the ideal exponent of $\nu = 1/2$ is recovered. For $d > 4$, one might suspect a smaller critical exponent, however in reality the self-avoiding term becomes sub-dominant and the polymer returns to the ideal scaling with small corrections. To see this, note that the radius of gyration of the self-avoiding polymer must be greater than that of the ideal polymer, $R_G > R_0$. Thus the energy due to self-interactions is at most $F_{sa\,max} \approx vL^2/(R_0)^d \sim L^{(2-d/2)}$, which will be small compared to the elastic energy for large L when $d > 4$. Therefore above four dimensions one expects the polymer's scaling exponents to be that of the ideal case for large L.

2. Perturbative RG

The preceding discussion, as well as experiments in $d \leq 3$, motivate a direct RG treatment in dimensions $d = 4 - \epsilon$. Such a calculation was first carried out by des Cloizeaux [2] to second order in ϵ, with the result

$$\nu = \frac{1}{2}\left[1 + \frac{\epsilon}{8} + \frac{\epsilon^2}{256} + \ldots\right]. \tag{8}$$

3. Isomorphism to Spin Models

It is also worth noting that the Laplace transform of the two point distribution function $\langle \mathbf{r} - (\mathbf{r}(L) - \mathbf{r}(0))\rangle$ is exactly the correlation function for an $n = 0$ component spin model. Therefore the result (8) can also be derived via Wilsonian RG [3].

III. D=2: TETHERED SURFACES

One can generalize the notion of a polymer to a two-dimensional surface of fixed connectivity, also known as a tethered surface or membrane. This is to be contrasted with "liquid" membranes, where mobile disclinations in the network may exist, which are not discussed here.

A. Phantom Surface

A example microscopic model of such a surface includes particles with nearest-neighbor interactions,

$$-\beta H = \sum_{\langle \mathbf{x},\mathbf{x}'\rangle} V(|\mathbf{r}(\mathbf{x}) - \mathbf{r}(\mathbf{x}')|). \tag{9}$$

For a Gaussian potential $V(r) = \frac{1}{2}K_0 r^2$, this model is exactly solvable and yields

$$R_G \sim (\ln(L))^{1/2} \tag{10}$$

in contrast with the $D = 1$ result.

Such a local model describes an entropy-induced elastic membrane without self-avoidance, and is therefore a model for a "phantom" surface. For other potentials $V(r)$, one can apply a Migdal-Kadanoff bond-moving approximation, which renormalizes V to analyze the large-length-scale behavior [4]. Under such a procedure, the Gaussian potential is invariant, and many other potentials converge to a Gaussian. The number of iterations necessary for convergence defines a persistence length for non-Gaussian potentials.

A non-Gaussian model amenable to numerical simulations involves hard spheres connected by strings of fixed length. For example, $V(r) = 0$ for $1 < r < \sqrt{3}$ and ∞ otherwise would describe spheres of unit diameter connected by strings of length $\sqrt{3}$. Monte-Carlo simulations of such surfaces at finite temperature numerically confirms the scaling in (10).

B. Self-Avoiding Surface

To account for self-avoidance, one can again introduce a non-local term into the continuum Hamiltonian, which penalizes self-intersection:

$$-\beta H = -\frac{1}{2}K \int d^2\mathbf{x}\, (\nabla \mathbf{r})^2 - v \int d^2\mathbf{x}\, d^2\mathbf{x}'\, \delta^d(\mathbf{r}(\mathbf{x}) - \mathbf{r}(\mathbf{x}')). \tag{11}$$

As was the case for $D = 1$, correlation functions can be computed perturbatively in v from (11) by applying a Flory-type approximation or RG techniques. The latter will be discussed in the context of the more general case in section IV.

1. Flory Theory

Applying a similar approximation as in section II B 1, we can estimate the contribution to the free energy from entropy-induced elasticity as $F_{el} \approx \frac{1}{2}KR_G^2$, and the contribution from self-interaction as $F_{sa} \approx vL^4/R_G^d$. Minimizing the sum of these terms then yields

$$R_G \sim (v/K)^{1/(d+2)} L^{\nu_F}, \quad \nu_F = \frac{4}{d+2}. \tag{12}$$

For $d = 3$, the Flory approximation predicts a scaling exponent of $\nu_F = 0.8$, which agrees with MC simulations performed on the aforementioned hard-sphere model.

In contrast with the $D = 1$ case, this result shows that the phantom scaling ($\nu = 0$) is not reproduced at any finite d, but requires $d \to \infty$. This is related to the fact that the Hausdorff dimension of the phantom surface is infinite [5], and is also reflected by a diverging correction to R_G when calculated perturbatively from (11) as $L \to \infty$ [6, 7].

C. Rigidity and the Crumpling Transition

In addition to elasticity, 2-dimensional membranes can also exhibit bending rigidity, which induces an energy cost proportional to the curvature of the surface. This rigidity leads to a new "flat" phase at low temperature, in which $R_G \sim L$.

Such a phase can be studied numerically by MC simulation of the surface energy given by

$$\mathcal{F} = \frac{1}{2}\kappa \int d^2\mathbf{x}(\nabla^2 f)^2 + 2\mu u_{ij}^2 + \lambda u_{kk}^2 \tag{13}$$

where f describes the normal displacement of the surface from a flat sheet, i.e. $\mathbf{r}(\mathbf{x}) = (\mathbf{x_1}, \mathbf{x_2}, \mathbf{f}(\mathbf{x_1}, \mathbf{x_2}))$, κ is the bending rigidity, μ and λ are the Lamé coefficients, and u_{ij} is the strain matrix. In this model self-avoidance, which should be irrelevant in the flat phase, is neglected. Such numerical study reveals a flat phase where $R_G = \zeta L$ at high values of κ, with ζ, which measures the shrinkage of R_G in the flat phase due to undulations, approaching zero as $\kappa \to \kappa_c = .46 \pm 0.03$ from above. This indicates a transition from the flat phase to the crumpled phase, where $R_G \sim L^\nu$ with $\nu < 1$[8].

IV. GENERAL D

In order to systematically study the scaling behavior and phase transitions of tethered surfaces, one can further generalize the object of study to D-dimensional manifolds embedded in d-dimensional space. In doing so one hopes to achieve results in agreement with simulations and experiments for $D = 1$ polymers, $D = 2$ membranes, and $D = 3$ gels, as well as provide a method for systematically treating contribution from the self-avoiding interaction, which as mentioned in section III B diverges for $D = 2$.

A. ϵ Expansions

Consder the D-dimensional generalization of (11), given by

$$-\beta H = -\frac{1}{2}K \int d^D\mathbf{x}\ (\nabla \mathbf{r})^2 - v \int d^D\mathbf{x}\ d^D\mathbf{x}'\ \delta^d(\mathbf{r}(\mathbf{x}) - \mathbf{r}(\mathbf{x}')). \tag{14}$$

Dimensional analysis of the elastic term reveals that $[r] \sim [x]^{1-D/2}$, revealing the fractal dimension of an ideal manifold to be $d_f^0 = 2D/(2-D)$. Such an ideal manifold only self-intersects when embedded in a dimension $d < 2d_f^0$, yielding the critical dimensionality $d^*(D) = 2d_f^0 = 4D/(2-D)$ which in the (d, D) plane delineates the separation between self-avoiding and ideal behavior. Note that we recover the critical dimensions $d^*(1) = 4$, $d^*(2) \to \infty$ discussed previously.

Any point on the line described by $d^*(D)$ thus provides a valid expansion point for a perturbative RG treatment of self-avoidance. For example, one can work in $d = 3$ dimensions and let $\epsilon = D - \frac{6}{7}$. Then $\epsilon = \frac{1}{7}$ corresponds to self-avoiding polymers, and $\epsilon = \frac{8}{7}$ to self-avoiding surfaces.

In such a perturbative RG study, the most important divergences result from the relevance of v as

$$\epsilon \equiv 4D - (2-D)d \tag{15}$$

tends to zero. For this ϵ, the result for the modification of the exponent ν is [9]

$$\nu = \frac{2-D}{2} + \frac{2-D^*}{8(D^* + 2\mathcal{C}(D^*))}\epsilon + \mathcal{O}(\epsilon^2) \tag{16}$$

where

$$\mathcal{C}(D) = \frac{\pi^{1/2}\Gamma(2/(2-D)}{2^{2D/(2-D)}\Gamma((2+D)/2(2-D))}. \tag{17}$$

While this discussion omits the details of the calculation behind this result, it is worth noting that the RG treatment in this case requires the propagator lines in Feynman diagrams to be replaced by propagator manifolds, with distinct rules and organizations that generalize traditional techniques in field theory.

B. Landau Theory of Crumpling

In order to study the crumpling transition in rigid D-dimensional membranes, one can generalize (10) and (14) to a model which includes rigidity, elasticity, and self-avoidance. Such a model can be realized via a "Landau-Ginzburg" expansion in powers of the tangent vectors $\mathbf{t}_\alpha = \partial\mathbf{r}(\mathbf{x})/\partial\mathbf{x}_\alpha$ and their derivatives which preserves isotropy and translational invariance: [10]

$$\beta F = \int d^D\mathbf{x}\left[\frac{1}{2}\kappa(\partial_\alpha\partial_\alpha r_i)^2 + \frac{1}{2}t(\partial_\alpha r_i)^2 + u(\partial_\alpha r_i\partial_\beta r_i)^2 + \tilde{v}(\partial_\alpha r_i\partial_\alpha r_i)^2\right] + \frac{1}{2}b\int d^D\mathbf{x}d^D\mathbf{x}'\delta^d(\mathbf{r}(\mathbf{x}) - \mathbf{r}(\mathbf{x}')). \quad (18)$$

Such an expansion is valid in the crumpled phase where $\mathbf{t}_\alpha \sim L^{\nu-1}$ with $\nu < 1$, as well as close to the transition. Note that b encodes the excluded volume due to non-local self-avoidance.

1. Ideal Manifold

When the tangents are idendified with a set of order parameters $t_\alpha = \partial_\alpha\mathbf{r} = \phi_\alpha$, a clear analogy with ϕ^4 theory can be made for (18) in the $b = 0$ (ideal) case. One can then import the results of ϕ^4 theory to make conclusions about the phase space of t_α. Specifically, for $t < 0$ the manifold is stabilized by the anharmonic u and $\tilde{v}$ terms, provided that $u > 0$ and $v = \tilde{v} + u/D > 0$. This ordered phase corresponds to a flat manifold. For $t > 0$, we expect a disordered phase, which corresponds to a crumpled manifold. Thus this theory suggests a phase transition at $t \approx 0$, in agreement with one's expectation from considering competing entropic and bending contributions to the free energy.

A mean-field solution can be found using the ansatz $\mathbf{r}(\mathbf{x}_\alpha) = \zeta\mathbf{x}_\alpha\mathbf{e}_\alpha$, with $\{\mathbf{e}_\alpha\}$ a set of orthogonal unit vectors. Applying the saddle-point approximation to (18) then yields

$$\zeta \propto \begin{cases} (-t/Dv)^{1/2} & \text{for } t < 0 \\ 0 & \text{for } t > 0 \end{cases} \quad (19)$$

Therefore the radius of gyration scales with t as $R_G = \zeta L \sim |t|^{1/2}L$ as the crumpling transition is approached from below.

Fluctuations about the flat ansatz can then be studied by introducing in-plane stretching modes u_α ($\alpha = 1,\ldots,D$) and out-of-plane undulations h_β ($\beta = D-1,\ldots,d$), so that $\mathbf{r}(x_\alpha) = \zeta[(x_\alpha + u_\alpha)\mathbf{e}_\alpha + h_\beta\mathbf{e}_\beta]$. Upon substituting this parameterization into (18) to leading order in the gradients of u_α and h_β, one arrives at a generalization of the flat plate energy (13), with $f = h_\beta$, $u_{ij} = \frac{1}{2}[\partial_i u_j + \partial_j u_i + \partial_i h_\beta\partial_j h_\beta]$, $\mu = 4u\zeta^4$, and $\lambda = 8\tilde{v}\zeta^4$. Accounting for such fluctuations then results in a discontinuity in the specific heat at $t = 0$, as well as a tangent-tangent correlation length $\xi \sim |t|^{-1/2}$ near $t = 0$. For $t > 0$, $R_G \sim L^{1-D/2}$ and at $t = 0$, $R_G \sim L^\nu$ with $\nu = 1 - D/4$. Note that this result differs from those of section 12, presumably due to critical fluctuations.

2. Self-Avoiding Manifold

When self-interactions are included, one can again apply the Flory approximation to estimate the correction to ν in the crumpled phase. As in sections II B 1 and III B 1, we can estimate the contributions to the free energy from each term in the LG expansion as

$$2\beta F/D \approx \kappa R_G^2 L^{D-4} + tR_G^2 L^{D-2} + DvR_G^4 L^{D-4} + bR_G^{-d}L^{2D}/D \quad (20)$$

which reveals, as expected, that self-avoidance is irrelevant for $t < 0$ since $R_G \sim |t|^{1/2}L$. For $t > 0$, the anharmonic terms u and v are irrelevant as $L \to \infty$, and minimizing the sum of the remaining entropic and self-avoiding terms yields

$$R_G \sim t^{-\omega}L^{\nu_F}, \;\; \omega = 1/(d+2), \;\; \nu_F = (D+2)/(d+4). \quad (21)$$

In addition, a perturbative RG approach for large d can be carried out for the self-avoiding Landau-Ginzburg model through a $1/d$ expansion [11].

V. CURVED SURFACES

In contrast with a flat plate, the curvature of a spherical membrane causes coupling between in-plane stretching modes and out-of-plane undulations. As a result, thermal fluctuations produce a radius-dependent effective inward pressure. Perturbative RG techniques can be used [12] to show that large spherical shells are crushed due to this thermal pressure. Such a calculation reveals spontaneous buckling of spherical shells above the maximum radius

$$R_{max} \approx 160\frac{\kappa_0}{T}\sqrt{\frac{\kappa_0}{Y_0}} \quad (22)$$

where κ_0 is the bare rigidity and Y_0 is the bare Young's modulus of the surface.

Spherical membranes are ubiquitous in biological systems, however in these system osmotic pressure can stabilize the membrane against thermal buckling.

VI. CONCLUSION

In this paper I have attempted to highlight several results regarding the statistical mechanics of tethered surfaces and the buckling transition to create what I hope is a useful starting point for others with some background in statistical mechanics and RG techniques that are interested in learning more about this field. Closely related areas of research not discussed in this paper include the statistical mechanics of liquid hexatic membranes [13, 14], as well as membrane dynamics [7] and models for membrane/interface growth [15]. For the sake of brevity I have omitted or only summarized most calculational details, but I encourage readers to consult the given references to learn more about their methods and results.

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