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Polymers in Curved Boxes

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ABSTRACT: We apply results derived in other contexts for the spectrum of the Laplace operator in curved geometries to the study of an ideal polymer chain confined to a spherical annulus in arbitrary space dimension D and conclude that the free energy compared to its value for an uncurved box of the same thickness and volume is lower when $D < 3$, stays the same when $D = 3$, and is higher when $D > 3$. Thus, confining an ideal polymer chain to a cylindrical shell lowers the effective bending elasticity of the walls and might induce spontaneous symmetry breaking, i.e. bending. (Actually, the above mentioned results show that *any* shell in $D = 3$ induces this effect, except for a spherical shell.) We compute the contribution of this effect to the bending rigidities in the Helfrich free energy expression.

I. Introduction

Membrane-confined polymers are commonly found both in biological systems and in the laboratory. The physics of the membrane itself is mainly governed by elasticity. When a membrane is exposed to macromolecules, its bare elastic constants are renormalized. A specific case of this renormalization is computed in the present work: two membranes confining a polymer solution inside. The polymers avoid contact with the membrane but do not interact with each other. The inspiration for our work came from the theory of quantum mechanics in confined geometries, which we review below—we do not know of any current experiments on polymers on which we could test our results. As an aside we remark that our results are also relevant in determining the depletion force between two spherical shells with hard walls when there is a nonadsorbing polymer solution inside.

The quantum mechanics of particles confined to surfaces or surface layers embedded in a higher dimensional space, e.g. curves, tubular structures around curves, surfaces, or layers between two surfaces in three dimensions, has attracted attention from many authors in the past three decades. Recently, there has been considerable progress in rigorously and nonperturbatively analyzing the changes to the spectrum of the Laplacian in curved geometries in two dimensions—these have been motivated by applications in mesoscopic semiconductor physics.[1,2] There are also studies of the contribution of torsion to the bound state energies.[3,4] Until now the results for higher dimensional confinement are restricted to the perturbative regime.[5−10]

Below we summarize the main results of these studies, as they relate to the application of interest here. The next section reviews the relation between quantum mechanics and polymer physics in some detail. We compute the free energy in the geometries of interest in the third section. Most of the details of these calculations are left to an appendix. The final section computes the effective bending rigidities of a dilute polymer solution confined in a box with elastic walls and includes our concluding remarks.

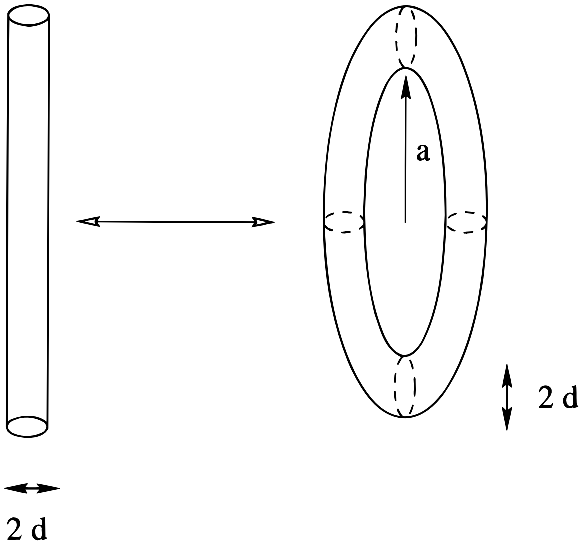

Figure 1. Twisting tube example: solid cylinder ↔ torus.

The correct quantization procedure for quantum particles confined to manifolds embedded in higher dimensional spaces turns out to be nontrivial.[5] Studies[6−12] which are perturbative in the curvature of the manifold conclude that confinement to a curved manifold results in an effective potential, which depends on both the manifold to which the particle is confined *and* the particular way this manifold is embedded in the higher dimensional space, i.e. on *both* the intrinsic *and* extrinsic curvatures of the manifold. This dependence on the extrinsic curvature means that one cannot arrive at the correct Schrödinger equation by just transforming the Laplacian to the coordinates of the confining manifold; this can be understood in the light of the uncertainty principle—the particle will know that there is an "outside", no matter how strongly it is confined.

Confinement to a curve in three dimensions generates a potential, which is attractive to the most highly curved regions, in the one-dimensional Schrödinger equation; this potential is proportional to the square of the local curvature of the curve.[11] If one considers a "thin tube" that is wound around a curve and has a constant cross-section (see Figure 1), to lowest order in the curvature one finds the same result: the energy change is proportional to the square of the curvature of the curve that the tube follows. The proportionality constant is inde-

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pendent of the shape of the cross-section, and also of the exact details of the confining potential (hard walls, etc.)[3,7,13]—this can be easily understood by dimensional analysis and scaling arguments and by using the result of ref 11. Confinement between two *equidistant* surfaces in a general dimension D results in a potential U, which (in the appropriate units, i.e. neglecting overall positive constants) is given to second order in the principal radii of curvatures R_i ($i = 1, 2, 3, ..., (D - 1)$), by[6]

$$U = -\frac{1}{4}\left(2\sum_i \frac{1}{R_i^{\,2}} - \left(\sum_i \frac{1}{R_i}\right)^2\right) \tag{1}$$

For a spherical shell embedded in D dimensions one sets $R_i = a$, for all i, where a is the radius of the shell, and, as first written down in ref 10, eq 1 reduces to $U = (D - 1)(D - 3)/a^2$. This is negative for $1 < D < 3$.

Of course, all of the above results apply to any physical system that contains the Laplacian in its equations of motion.

II. Connection to Polymer Physics

The particle-in-a-box problem of quantum mechanics is closely related to confined ideal polymers. A flexible polymer in solution is a random walk. In the case without excluded volume interactions this will be denoted as an "ideal chain"; i.e. ideal chains are allowed to self-intersect without raising their energy. An ideal polymer chain configuration may be mapped onto the motion of a quantum particle, where the probability distribution function is the analogue of the wave function, and the degree of polymerization (N) plays the role of imaginary time.[15] In this spirit we reduce the "ideal-chain-in-a-box" problem to a quantum "particle-in-a-box" problem.

We consider a random walk in space and work in the continuum description. Let $G(\vec{r},\vec{r}\,',N)$ be the probability for a walk of N steps to have its ends at $\vec{r}$ and $\vec{r}\,'$. The function G is defined to be 0 for $N < 0$, and it satisfies[15] the differential equation

$$\left(\frac{\partial}{\partial N} - \frac{l^2}{6}\nabla_{\vec{r}}^{\;2}\right)G(\vec{r},\vec{r}\,',N) = \delta(\vec{r} - \vec{r}\,')\delta(N) \tag{2}$$

Here l is the monomer length. Equation 2 describes diffusion once the boundary conditions are specified. We may also think about it as a Schrödinger equation, where N plays the role of imaginary time.

The partition function is just a sum over all configurations:

$$Z = (1/V)\int \mathrm{d}\vec{r}\ \mathrm{d}\vec{r}\,'\ G(\vec{r},\vec{r}\,',N) \tag{3}$$

The factor of $1/V$ keeps the volume fixed when the free energy is computed.

Here we comment on the exact problem that we are considering, and our choice of boundary conditions, when we compare the flat and curved boxes. Our main aim is to determine the effects of polymer confinement on the bending elasticities of the confining structure. Hence we would like to isolate the change in the free energy due to curvature *only*. Therefore we pick periodic boundary conditions in the transverse directions of the flat box. Also to the same end we conserve the volume of the box during bending; this, of course, will fix the radius of the curved box once the amount of material (the surface area of the flat box) is fixed. Assuming that the free energy per unit area for this system can be expanded in the curvature when this radius is large compared to the thickness of the box, one can compute the coefficients in this expansion to second order in the curvature. There are in general two bending elasticities to compute. These can be uniquely determined from the two equations one attains by considering the free energy of the sphere and the cylinder. We have in mind membranes which generally do not have free edges but end at the walls of a container or are closed vesicles. Then, e.g., for a container with repulsive walls, one has to take into account when computing the energy balance the fact that the eigenfunctions for the flat box vanish at the transverse edges. Also, the volume for the real system may *not* be conserved—this would bring translational entropy pieces into the energy balance in addition to the contributions we calculate in the present work.

To compute the partition function we use the method of eigenfunctions and levels of the Schrödinger equation. This is an "effective Hamiltonian" method where one integrates out certain configurations of the polymer chain and labels the coarse-grained modes by discrete "levels". Thus we write $Z = \sum_n e^{-\epsilon_n/k_BT}$, where the sum is over the levels and ϵ_n's are the eigenvalues of the effective Hamiltonian that describes the system in terms of these levels only. For the remainder of this paper, in order to simplify the notation, we measure all energies in the units of Nk_BT and all lengths in the units of $(l/\sqrt{6})$ (except in the final results). It becomes clear what these levels are from the eigenfunction expansion[16] for the propagator of the chain: $G(\vec{r},\vec{r}\,',N) = \sum_n \Psi_n^*(\vec{r})\Psi_n(\vec{r}\,')e^{-NE_n}\Theta(N)$. Here $\Theta(N)$ is the step function assuring that $G = 0$ for $N < 0$, and the $\Psi_n(\vec{r})$'s are normalized solutions to $\nabla^2\Psi(\vec{r}) = -E\Psi(\vec{r})$. It is easy to verify that this expansion indeed solves eq 2 (recall: $(\partial/\partial N)\Theta(N) = \delta(N)$). The boundary conditions are $\Psi(\vec{r}) = 0$ at the walls which are at $|\vec{r}| = a$ and $|\vec{r}| = a + d$. This is a slab of thickness d in one dimension, and a spherical shell of radius a and thickness d in any dimension D.

Using this eigenfunction expansion in the partition function expression, eq 3, we find

$$Z = (1/V)\sum_n e^{-NE_n}\int \mathrm{d}\vec{r}\ \Psi_n^*(\vec{r})\int \mathrm{d}\vec{r}\,'\ \Psi_n(\vec{r}\,') = (1/V)\sum_n e^{-NE_n}\left|\int \mathrm{d}\vec{r}\ \Psi_n(\vec{r})\right|^2 \tag{4}$$

We see that in the geometry of interest all states except the spherically symmetric ones disappear from the sum in eq 4, even though they do contribute to the propagator. (In $D = 1$, the sinusoidal solutions with an even number of peaks disappear). Hence

$$Z = (1/V)\sum_{n=1}^{\infty} e^{-NE_n(a,d)}\left|\int \mathrm{d}r\ r^{(D-1)}R_n(r)\right|^2 \tag{5}$$

where n labels the distinct s-wave levels, $R_n(r)$ is the normalized radial wavefunction, and we explicitly indicate the dependence of the energies on a and d. Defining

$$B_n(a,\,d) \equiv \frac{\left|\int \mathrm{d}r\ r^{(D-1)}R_n(r)\right|^2}{\frac{S_{D-1}}{D}((a + d)^D - a^D)} \tag{6}$$

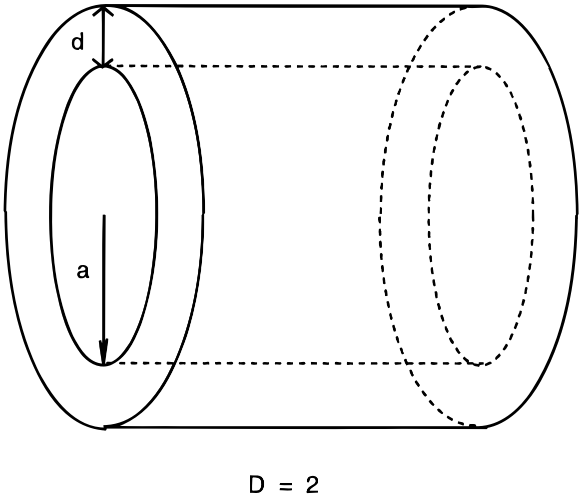

Figure 2. $D = 2$ annulus.

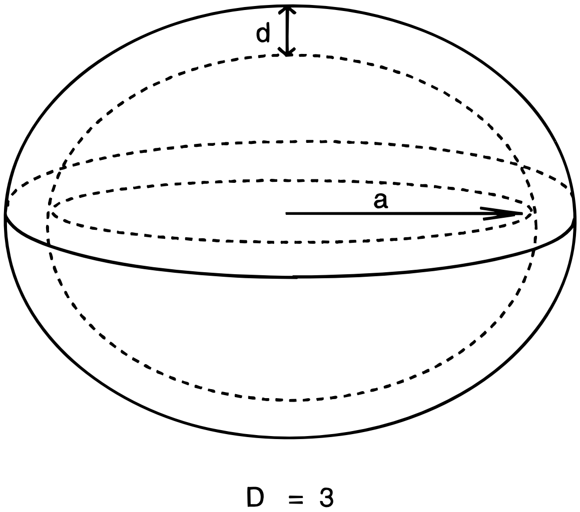

Figure 3. $D = 3$ annulus.

where S_{D-1} is the surface area of the unit sphere in D dimensions, we can write for the free energy

$$F = -k_B TM \log(\sum_{n=1}^{\infty} e^{-(E_n(a,d)Nl^2/6)} B_n(a, d)) \qquad (7)$$

where M is the number of chains (each containing N links) in the box.

We now proceed with the analysis of the above expression.

III. Free Energy for Polymers in Boxes

We consider a spherical annulus of large radius and small thickness in an arbitrary dimension D. The walls are taken to be repulsive for the polymer. Physical interest lies in $D = 2$ (Figure 2), which is a cylindrical shell in three dimensions, and $D = 3$ (Figure 3), a spherical shell in three dimensions. [The length along the axis of the cylinder is taken to be large compared to the other dimensions and therefore does not play an essential role here.]

The Laplacian in D dimensions is $\nabla^2 = d^2/dr^2 + (D - 1)/r(d/dr) - \vec{L}^2/r^2$. Here $\vec{L}$ is the angular momentum operator in D dimensions. After standard manipulations we find the following quantization condition in terms of dimensionless variables:

$$J_{\xi}\left[(\tilde{E})^{1/2}\frac{1}{\epsilon}\right]N_{\xi}\left[(\tilde{E})^{1/2}\left(1 + \frac{1}{\epsilon}\right)\right] - J_{\xi}\left[(\tilde{E})^{1/2}\left(1 + \frac{1}{\epsilon}\right)\right]N_{\xi}\left[(\tilde{E})^{1/2}\frac{1}{\epsilon}\right] = 0 \qquad (8)$$

where $\tilde{E} \equiv Ed^2$, $\xi^2 \equiv \nu^2 + (D - 2)^2/4$, $\epsilon \equiv (d/a)$, and ν^2 is an eigenvalue of the $SO(D)$ symmetric Casimir operator, and the functions J and N are the standard Bessel functions. [SO(D) is the rotation group in D dimensions.] As explained earlier, the spherical symmetry of the geometries considered causes all but the $\nu = 0$ states to drop out of the partition function. Defining $\mu = 4\xi^2$ (for $\nu = 0$), $\mu = (D - 2)^2$, and labeling these s-wave states by $n = 1, 2, ...$, one can now proceed with a perturbative analysis by expanding eq 8 in powers of $\epsilon = d/a$, which results in

$$d^2E_n(a,d) = (n\pi)^2 + \frac{(D - 1)(D - 3)}{4}\left[\left(\frac{d}{a}\right)^2 - \left(\frac{d}{a}\right)^3 + \left(\frac{d}{a}\right)^4\left(1 - \frac{3}{8n^2\pi^2}\right) + ...\right] \qquad (9)$$

This is the same perturbative result cited above. We see that the curvature lowers the spherically symmetric energy spectrum for $1 < D < 3$, does not affect it when $D = 1$ (trivial) or $D = 3$, and increases it everywhere else. Notice that the perturbation series stops for $D = 1$ and $D = 3$. Also notice that the perturbative effect is the same for all modes up to fourth order. This simplifies treating the full free energy of the polymer, eq 7. This treatment requires an expression for $B_n(a,d)$, the computation of which is difficult in general, but we were able to find an exact expression in $D = 3$, and a perturbative one in $D = 2$. We now summarize our results. Details are left to the appendix.

A. Three Dimensions. Defining Z_0 as the partition function of the flat box and $k \equiv (Nl^2\pi^2/6d^2)$, we find the exact result for the partition function:

$$Z/Z_0 = 1 + g(\epsilon)(1 - 3f(k)) \qquad (10)$$

where the functions f and g are defined in the appendix. One can expand the above expressions in two limits: when the typical polymer dimension, $R_g \equiv \sqrt{N}l$, is smaller or larger than the box width, d. The latter is the so-called ground state dominance regime (GSD) (here $k > 1$); the former we will denote by “the colloid limit” (CL), since in this limit the coils look like small balls (here $k < 1$). In GSD, the corrections due to B_n are negligible, and we find that the free energy does not have any corrections due to curvature. In CL we find

$$\Delta F = k_B TM\frac{1}{12}\left(\frac{d}{a}\right)^2\left(\frac{8}{\pi^{1/2}}\sqrt{\frac{Nl^2}{6d^2}} - \frac{4(3\pi - 8)}{\pi}\frac{Nl^2}{6d^2} - \frac{16(3\pi - 8)}{\pi^{3/2}}\left(\frac{Nl^2}{6d^2}\right)^{3/2} + ...\right)$$

B. Two Dimensions. In this case we find (to lowest order in ϵ)

$$Z/Z_0 = e^{+k\epsilon^2/4\pi^2}\left(1 - \frac{\epsilon^2}{16}\left(1 - f(k) - \frac{8}{\pi^2}h(k)\right) + ...\right) \qquad (11)$$

where f is the same function as for three dimensions and h is defined in the appendix. This, in GSD, leads to

$$\Delta F = -k_B TMN\frac{1}{24}\frac{l^2}{a^2}$$

In CL there are no terms of order $\sqrt{k}$ and two terms of order k which cancel each other exactly, and the expansion starts at third order (this is similar to what happens for small hard spheres, i.e. colloids; there one finds that there is no shift in the free energy in two dimensions and a positive shift in three dimensions[17]):

$$\Delta F = -k_B TM\frac{1}{18\sqrt{6\pi}}\left(\frac{d}{a}\right)^2\left(\frac{Nl^2}{d^2}\right)^{3/2} + ...$$

In the strong confinement (GSD) regime it does not matter to which chain the monomers belong (the shift in the energy is proportionl to the total number of monomers, MN); in the CL regime we have an ideal gas of M objects.

We comment on some issues before computing effective bending rigidities using the above results: In the nonperturbative regime we solved the eigenvalue equation, eq 8, numerically for the ground states in $D = 2$, 4, and 5, for $2 < a/d < 50$. The large a/d behavior of the solutions (see the curves plotted in Figure 4) are exactly as predicted by eq 9. [This is not obvious from the plot given here.] Notice that they are all converging to the flat case value of π^2 for very small curvature. As the curvature increases, the behavior changes its functional form and becomes much sharper than just a quadratic deviation. One can follow these curves farther toward infinite curvature and see that they tend to a constant value that depends on the dimensionality. This pattern is also valid for $n \neq 1$, $\nu = 0$ (s-wave), states.

For surfaces in three dimensions eq 1 reduces to $U = -(1/4)(1/R_1 - 1/R_2)^2$. The effect of this potential, even after integration over the entire surface, is always attractive except in two cases where it has no effect at all, the flat surface and the sphere. Notice also that in $D = 2$ one always gets an attractive potential if the confining curves are not perfectly flat. Thus in two dimensions (physically we think about generalized cylinders living in three dimensions), the free energy is reduced by any curvature, regardless of the shape of the boundaries. Although we are not considering large curvatures here, it is worthwhile to mention that the literature cited in the Introduction proves that in one- and two-dimensional structures (tubes and strips), the ground state energy of the Laplace operator decreases due to curvature, and there is a bound state localized in the regions of curvature. This is a nonperturbative statement, and it makes very weak assumptions about the detailed geometry. This is important because it implies that in these systems (at least in GSD), the polymer would localize in regions where there is curvature. One explicit example of this is the numerical solution of the Schrödinger equation in oval-shaped rings.[14] In fact, this may be the easiest way of looking for the effects we derive in this work, since for reasonable values of the degree of polymerization and the radius of curvature one finds that the free energy shift for the cylindrical shell translates to a density fluctuation of ∼5% in a race-track type of geometry.

IV. Effect on κ and $\bar{\kappa}$

We conclude by calculating the contribution of this effect to the effective bending curvature elasticity of an ideal polymer confined to a fluid bilayer membrane. Let f_c be the curvature free energy per area. Up to quadratic order in the principal radii $1/R_1$ and $1/R_2$, f_c can be written in terms of the mean and Gaussian curvatures of the surface. In terms of the principal radii, the mean curvature is $H = (1/2)(1/R_1 + 1/R_2)$ and the Gaussian curvature is $K = (1/R_1)(1/R_2)$. A general form of f_c to this order is given by[18] $f_c = 2\kappa(H - c_0)^2 + \bar{\kappa}K$, where κ and $\bar{\kappa}$ are constants usually denoted by "bending rigidities". The spontaneous curvature of the surface, c_0, is taken as zero for the rest of this discussion, because the film is assumed symmetric with respect to its midplane.

To examine the effects of polymer confinement on κ and $\bar{\kappa}$, we first consider a vesicle (a spherical shell in $D = 3$) with a small curvature, i.e. a shell of radius a, with a finite thickness d, where $d \ll a$. For a sphere both principal radii are equal to a, and we find $f_c = (1/2)\kappa(2/a)^2 + \bar{\kappa}(1/a)^2$. Next consider a cylindrical shell ($D = 2$); now $R_1 = a$, but $R_2 = \infty$. Thus, $f_c = (1/2)(\kappa/a^2)$. Defining $\Phi_M = M/V = M/(Sd) + O(\epsilon)$, S being the surface area, and using the results for ΔF for the sphere and the cylinder, we conclude that

$$\delta\kappa = (k_B T)(\Phi_M d^3)\left(\frac{1}{8}\left(1 - f(k) - \frac{8}{\pi^2}h(k)\right) - \frac{k}{2\pi^2}\right) \quad (12)$$

$$\delta\bar{\kappa} = (k_B T)(\Phi_M d^3)\left(-\frac{1}{6} + \frac{2}{\pi^2}h(k)\right) \quad (13)$$

where $\delta\kappa$ and $\delta\bar{\kappa}$ are the changes in the bending rigidities. These expressions can be expanded in GSD and CL to give

$$\delta\kappa = -(k_B T)(\Phi_M l^3)\begin{cases} N\frac{1}{12}\left(\frac{d}{l}\right) & k > 1 \\ N^{3/2}\frac{1}{9\sqrt{6\pi}} + ... & k < 1 \end{cases} \quad (14)$$

$$\delta\bar{\kappa} = +(k_B T)(\Phi_M l^3) \times$$
$$\begin{cases} N\frac{1}{6}\left(\frac{d}{l}\right) & k > 1 \\ \sqrt{N}\frac{1}{3}\sqrt{\frac{2}{3\pi}}\left(\frac{d}{l}\right)^2 - N\frac{3\pi - 8}{18\pi}\left(\frac{d}{l}\right) - & \\ \quad N^{3/2}\frac{1}{9}\left((3\pi - 8)\sqrt{\frac{2}{3\pi^3}} - \sqrt{\frac{2}{3\pi}}\right) + ... & k < 1 \end{cases} \quad (15)$$

We have not considered any interactions between monomers. We expect that interactions between chains in a concentrated solution would screen out the effect of the walls over a very short distance and hence weaken this curvature effect. We are currently studying this situation. But our results may hold qualitatively for concentrations below the overlap concentration, Φ^*_M. To be consistent with our analysis we use Gaussian exponents to estimate Φ^*_M: In GSD we require $N\Phi^*_M = N/R_F{}^2d = 1/(l^2d)$. Thus $\Phi^*_M = 1/(Nl^2d)$. In CL the walks are three dimensional and we require $N\Phi^*_M = N/R_F{}^3 = 1/\sqrt{N}l^3$. Thus $\Phi^*_M = 1/(N^{(3/2)}l^3)$. This leads to

$$\frac{\delta\kappa}{(k_B T)} = -\begin{cases} \frac{1}{12} & k > 1 \\ \sim 0.026 & k < 1 \end{cases} \quad (16)$$

$$\frac{\delta\bar{\kappa}}{(k_B T)} = +\begin{cases} \frac{1}{6} & k > 1 \\ 0.06\frac{1}{N}\left(\frac{d}{l}\right)^2 & k < 1 \end{cases} \quad (17)$$

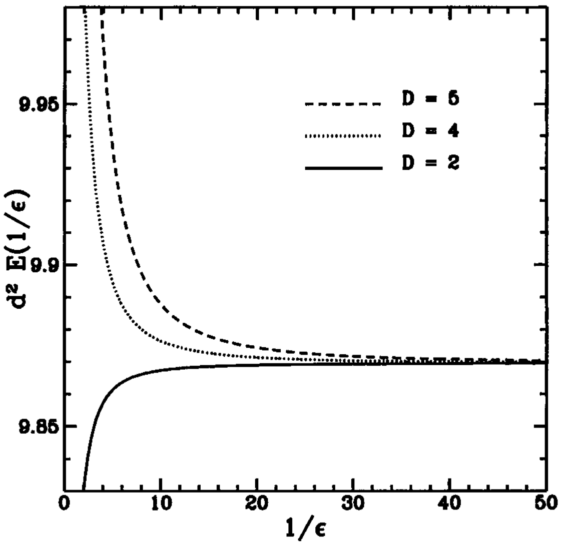

Figure 4. Numerical solution for $\tilde{E}(1/\epsilon)$, in two, four, and five dimensions.

Edwards' theory assumes slow variations of the propagator[16] and is therefore valid over large length scales compared to the lattice spacing, l, and moderately large number of steps, N. (Aside: We also need $d \ll a$, in order to use our perturbative result.) Notice that for $k < 1$ we have $(1/N)(d/l)^2 > 1$—which can be achieved, e.g., with $N \sim 100$ and $d/l \sim 20$; then this term gives a factor of 4. Estimating the bare rigidities of the box to be of the order of k_BT, we see that the effect is about 1% for κ and 5% for $\bar{\kappa}$.

We emphasize that the major result of this article is that polymer confinement might reduce κ and thereby induce spontaneous curvature in the system, such as transitions from lamellar to bicontinuous phases or tubules, etc., provided that the effect persists after the inclusion of self-avoidance, i.e. monomer—monomer interactions, in the analysis. We expect that this would be the case below the overlap threshold, but future work should address this issue in detail. We note here that, since there are two length scales in the problem, one cannot solve the self-avoiding walk problem by simple scaling arguments.

After one understands the role of interactions, one could also consider the case of a polymer with a finite persistence length. We expect that in the regime where the radius of curvature is much larger than the persistence length, the result will approach the one for the totally flexible polymer case treated in the present article (modulo interactions). But when the two lengths are comparable, the aversity of rigid polymers to bending should modify the effect computed here.

Note Added in Proof. As we were preparing to publish, we received a preprint by E. Eisenriegler, A. Hanke, and S. Dietrich, in which the authors also compute bending rigidities of systems with chains near a repulsive surface.

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Appendix A: Details of the Free Energy Computation

We employ eq 6 in three dimensions, which involves integrals that are trivial to do, and we find for B_n the following expression:

$$B_n(a, d) = \frac{8}{n^2\pi^2}\begin{cases} 1 + g(\epsilon) & n = \text{odd} \\ -3g(\epsilon) & n = \text{even} \end{cases} \tag{A1}$$

where $g(\epsilon) = -(1/4)[\epsilon^3/((1 + \epsilon)^3 - 1)]$. Using this in eq 4 results in eq 10, where f is defined as follows:

$$f(k) \equiv \frac{\sum^{(e)} \dfrac{e^{-kn^2}}{n^2}}{\sum^{(o)} \dfrac{e^{-kn^2}}{n^2}} \tag{A2}$$

where the symbol $\sum^{(e)}$ denotes a sum over all positive even n (n = 2, 4, 6, ...) and $\sum^{(o)}$ is over all positive odd n (n = 1, 3, 5, ...). As emphasized in the text, eq 10 is exact with the function f defined as above. This function can be expanded for large arguments (GSD regime) as

$$f(k) = \frac{1}{4}e^{-3k}(1 + O(e^{-8k})) \tag{A3}$$

For small arguments one can also expand f with a little more work. First we define the function $A(t) \equiv \sum_{n=-\infty}^{\infty} e^{-tn^2}$. This function has the following property:

$$A(t) = \sqrt{\frac{\pi}{t}}A\left(\frac{\pi^2}{t}\right) \tag{A4}$$

Now we define $E(k) \equiv \sum^{(e)} e^{-kn^2}/n^2$ and $O(k) \equiv \sum^{(o)} e^{-kn^2}/n^2$. Then $f(k) = E(k)/O(k)$. (Aside: $(8/\pi^2)$ $O(k)$ is the partition function for the flat strip.) One can easily verify that $E(0) = \pi^2/24$ and $O(0) = \pi^2/8$. Also, $\partial E(k)/\partial k = (1/2)(A(4k) - 1)$ and $\partial O(k)/\partial k = -(1/2)(A(k) - A(4k))$. Using eq A4, and the fact that $A(t) = 1 + O(e^{-t})$, when k is large, one finds that $\int_0^k dt\ A(t) = \int_0^k dt\ A(4t) = 2\sqrt{\pi k} + O(e^{-\pi^2/k})$, when k is small. This allows an expansion of f:

$$f(k) = \frac{1}{3}\frac{1 - 12\pi^{-2}(\sqrt{\pi k} - k)}{1 - 4\pi^{-2}\sqrt{\pi k}} + O(e^{-1/k}) \tag{A5}$$

This function crosses over to $(1/4)e^{-3k}$ at $k \sim 0.3$.

Notice that these expressions satisfy the consistency checks: $\epsilon = 0 \Rightarrow B_n(d) = 8/(n^2\pi^2)$, if n is odd, and $B_n = 0$, if n is even. Also, $k = 0 \Rightarrow \Delta F = 0$.

In two dimensions the integrals are also exactly doable but the final expression for B_n is now much more complicated—we do not bother including this here. It can, however, be expanded in ϵ to yield:

$$B_n(a, d) = \frac{8}{n^2\pi^2}\begin{cases} 1 - \dfrac{1}{16}\epsilon^2 + \dfrac{1}{2\pi^2n^2}\epsilon^2 + \ldots & n = \text{odd} \\ \dfrac{1}{16}\epsilon^2 + \ldots & n = \text{even} \end{cases} \tag{A6}$$

Now, when one is not in GSD, one in principle needs to worry about the terms that depend on n in the expansion of the energy spectrum, eq 9. But when the argument of the terms in question is larger than 1, we are deep into the GSD regime, whereas when it is smaller than 1 these terms can be expanded in ϵ, giving only ϵ^4 corrections. Thus, they can in practice be ignored when computing bending rigidities. Defining

$$h(k) \equiv \frac{\sum^{(o)} \frac{e^{-kn^2}}{n^4}}{\sum^{(o)} \frac{e^{-kn^2}}{n^2}} \qquad \text{(A7)}$$

we find for the partition function the result in eq 11. Noticing that $-\partial h(k)/\partial k = O(k)$ and $h(0) = \pi^2/12$, one can expand h using the expressions derived above:

$$h(k) = \frac{\pi^2}{12}\frac{1 - 12\pi^{-2}k + 32\pi^{-7/2}k^{3/2}}{1 - 4\pi^{-3/2}\sqrt{k}} + O(e^{-1/k}) \qquad \text{(A8)}$$

Again, these expressions satisfy the above-mentioned consistency checks. These expansions for f and h are in excellent agreement with numerical results for $0 < k < 1/\pi$. The results for the bending rigidities follow from these expansions.

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