Shape Fluctuations of a Droplet

Containing a Polymer

Mark Goulian* and Scott T. Milner

Exxon Research and Engineering Company

Annandale, New Jersey 08801

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Abstract

We consider the problem of an ideal polymer confined in a droplet. When the droplet radius is smaller than the (unconfined) polymer radius of gyration, the polymer entropy will depend on the droplet shape. We compute the resulting surface free energy. Using parameters appropriate for polymers confined in microemulsions, we find that the polymer and bending surface energies are comparable for the lowest modes. Finally, we argue that chain self-avoidance will decrease the strength of the polymer contribution to the surface energy.

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*Address after Aug. 31: Center for Studies in Physics and Biology, The Rockefeller University, 1230 York Avenue, New York, NY 10021.
The Hamiltonian governing surface shapes usually follows from considerations of two-dimensional elasticity and geometry. Thus, fluid surfaces such as bilayers, emulsions and microemulsions are well-described by surface tension and curvature elasticity, while solid membranes also depend on in-plane shear and compression moduli [1]. In general, however, one must also take into account the response of the surrounding three-dimensional medium. (For convenience we speak of only one medium although in general the surface may separate two different materials.) The medium is characterized by a length, $\xi$, which describes the distance over which disturbances are screened in the bulk. If we consider only surface perturbations with wavelengths larger than $\xi$, the bulk will contribute to the surface elastic constants but the form of the Hamiltonian will be as described above. For perturbations with wavelengths below $\xi$, on the other hand, the bulk response gives rise to new terms in the surface Hamiltonian.

As an illustration, consider a surface bounding an elastic solid with modulus $B$. In this case, $\xi$ is infinite. The contribution to the surface energy from the bulk elasticity can be estimated by dimensional analysis for surface perturbations with wavelengths much less than the size of the system. If we allow a surface tension, $\mu$, and bending rigidity, $\kappa$, then the energy per area of a surface displacement $u(q) \exp(iqr)$ must take the form:

$$\text{Energy/Area} \sim (Bq + \mu q^2 + \kappa q^4) |u(q)|^2.$$  

(1)

Thus, for sufficiently small $q$, the bulk elasticity dominates.

In this paper we consider an approximately spherical surface (droplet) enclosing a single polymer. We are interested in the limit in which the radius of the droplet is smaller than the radius of gyration of the unconfined polymer. We were motivated by recent work in which individual polymers have been confined within microemulsion droplets [2], [3]. In order to make the problem tractable, we consider ideal polymers, i.e. we neglectoidance. We will return to this point at the end.

The droplet is assumed to be incompressible, with volume $V = 4\pi R^3/3$. Points on the droplet surface, $S$, are parametrized in terms of the radial displacement from the sphere
with radius $R$:

$$R_S(\theta, \phi) = (R + u(\theta, \phi))\hat{r}.$$  \hspace{1cm} (2)

Incompressibility implies:

$$\int d\Omega \frac{1}{3} R_S(\theta, \phi)^3 = \frac{4}{3} \pi R^3.$$  \hspace{1cm} (3)

After expanding $u$ in normalized spherical harmonics \[6\],

$$u(\theta, \phi) = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} u_{lm} Y_{lm}(\theta, \phi),$$  \hspace{1cm} (4)

we enforce the constraint Eq. (3) by solving for $u_{00}$:

$$u_{00} = -\frac{1}{2R\sqrt{\pi}} \sum_{lm} |u_{lm}|^2 + O(u_{lm}^3).$$  \hspace{1cm} (5)

The surface free energy of the droplet has the form $\mathcal{F} = \mathcal{F}_b + \mathcal{F}_p$, where $\mathcal{F}_p$ is the free energy of the confined polymer and $\mathcal{F}_b$ is the bending energy of the droplet surface (c.f. \[4\]):

$$\mathcal{F}_b = \frac{\kappa}{2} \sum_{l>0, m} \frac{|u_{lm}|^2}{R^2} (l + 2)(l - 1)(l(l + 1) - 4w + 2w^2).$$  \hspace{1cm} (6)

$\kappa$ is the bending rigidity and $w$ is the ratio of $R$ to the spontaneous curvature radius. For simplicity, we have ignored surface tension, although it may easily be included. $\mathcal{F}_p$ is the free energy of the confined polymer.

For an ideal polymer of $N$ segments, $\mathcal{F}_p$ may be expressed in terms of the statistical weight $G_N(r_0, r_1)$, which is the number of walks that start at $r_0$ and end at $r_1$ after $N$ steps:

$$\mathcal{F}_p = -k_B T \log \left[ \int_V d^3r_0 \int_V d^3r_1 G_N(r_0, r_1) \right].$$  \hspace{1cm} (7)

$G_N(r_0, r_1)$ satisfies the diffusion equation (c.f. \[5\])

$$\frac{\partial}{\partial N} G_N(r_0, r_1) = \frac{b^2}{6} \nabla_{r_1}^2 G_N(r_0, r_1),$$  \hspace{1cm} (8)

where $b$ is the effective bond length. The radius of gyration of the polymer, $R_g$, is related to $N$ by $R_g^2 = Nb^2/6$. For either $r_0$ or $r_1$ on the boundary of the droplet, $S$, $G_N(r_0, r_1)$ vanishes. In terms of orthonormal eigenfunctions $\psi_i$ of the Laplacian, satisfying
∇²ψᵢ = −kᵢ²ψᵢ  \quad \psiᵢ(r)|_{r \in S} = 0, \quad (9)

we have the expansion

\[ G_N(r₀, r₁) = \sum \psiᵢ(\bar{r}) \psiᵢ(r₁) \exp(−kᵢ²R₂^2). \quad (10) \]

Since S is a perturbation of a sphere of radius R, Eq. (2), the eigenvalues \( k_i^2 \) are proportional to \( 1/R^2 \). In the limit \( R \gg R_g \), \( G_N(r₀, r₁) \) falls off rapidly for \( |r₀ − r₁| \gg R_g \), and Eq. (7) reduces to the translational free energy of the polymer, as expected: \( F_p \approx −k_B T \log(V) \).

For \( R_g > R \), the sum in Eq. (10) can be approximated by keeping only the lowest eigenvalue \( k₀^2 \) (ground-state dominance [5]). Within this approximation, the free energy is given by

\[ F_p = k_B T \frac{π}{R_g} R_2^2 k₀^2 − 2k_B T \log(c₀) + O\left(e^{−R_g^2 (k₁^2 − k₀^2)}\right) \]

\[ c₀ ≡ \int_V d³r \psi₀(r). \quad (11) \]

The first term on the right-hand side of Eq. (11) is the leading term (in \( R/R_g \)). We have also included the first correction (the second term in Eq. (11)) because it may be calculated with little extra work (see appendix). Note that the remaining higher order corrections are exponentially suppressed. Thus, for a confined chain, the shape dependence of \( F_p \) is determined by the shift in \( k₀^2 \) and \( ψ₀ \) for perturbations of the form Eq. (2).

As a simple application of the above formula, we first compute the free energy of the polymer as a function of the droplet radius. We therefore take \( R_S = R \) and the eigenvalues in Eq. (4) reduce to \( (nπ/R)^2 \), \( n = 1, \ldots \). Thus, for \( R < R_g \), the free energy is given by

\[ F_p ≈ k_B T \frac{π}{R_g^2} \frac{R_2^2}{R^2}. \quad (12) \]

It is tempting to view the interior of the droplet as an elastic solid with bulk modulus \( B \). To estimate \( B \), we relax the requirement of incompressibility and compute the change in free energy under a uniform change in the radius of the droplet. We thus take \( R \to R − u \) and expand Eq. (12) in the strain \( u/R \); the term linear in \( u/R \) simply reflects the fact that we are perturbing about a compressed chain. Dividing by the droplet volume gives a bulk modulus...
of order $B \sim k_B T R_g^2 / R^5$. We can now use the result from the introduction to estimate $\mathcal{F}_p$ for surface disturbances with wavelength much smaller than $R$. This corresponds to a mode $u_{lm}$ with wavevector $q \sim l/R, l \gg 1$. From the argument in the introduction we then find

$$\mathcal{F}_p \approx k_B T l \frac{R_g^2 u_{lm}^2}{R^2}.$$

(13)

As we shall see below, $\mathcal{F}_p$ does indeed take this form in the limit of large $l$. However, it is in the low $q$ modes where the contribution from the polymer is expected to be important (compared with the contribution from the bending energy). This corresponds to small $l$ (i.e. wavelengths comparable to $R$) and requires a more careful analysis, which we now present.

As described above, we must find the ground state of Eq. (9). The general problem of the change in the spectrum of the Laplacian under a boundary perturbation was considered some time ago and appears in a number of contexts, such as acoustics in or around irregular regions, cavity resonators, and the Wigner-Seitz approximation for electrons in a crystal (see [7] and references therein). The early work on this problem focused on the solution to first order in the perturbation. Unfortunately, we require the result to second order (i.e. $O(u_{lm}^2)$), which is substantially more difficult to determine. In [7] a general formula is given for the change in the eigenvalues to second order, however the final formula appears to be incorrect. Therefore, in the appendix we calculate the ground-state eigenvalue and integral of the ground-state wavefunction for a perturbation of the form Eq. (2).

Combining the results of the appendix with the constraint Eq. (5) gives:

$$k_0^2 = \frac{\pi^2}{R^2} \left[ 1 + \sum_{l>0,m} \left( \frac{l+2}{2\pi} - \frac{f_l}{2} \right) \frac{|u_{lm}|^2}{R^2} + O(u_{lm}^3) \right].$$

(14)

$$c_0 = 2 \sqrt{\frac{2}{\pi}} R^{3/2} \left[ 1 + \sum_{l>0,m} \left( 2(l+2)f_l - \pi f_l^2 - 3(l+2)^2 \right) \frac{|u_{lm}|^2}{R^2} + O(u_{lm}^3) \right],$$

where $f_l \equiv j_{l+1}(\pi) / j_l(\pi)$ and $j_l$ is the spherical Bessel function of order $l$. Note that the $u_{1m}$-dependent terms in the volume preserving perturbation Eqs. (4,5) correspond to infinitesimal translations, which should not change the spectrum of the Laplacian. One may readily check that indeed the order $u_{1m}^2$ terms in Eqs. (4-5) vanish.
Substituting the above results into Eq. (11), and dropping an additive constant that is independent of \( u_{lm} \), we find for the polymer contribution to the droplet free energy:

\[
\mathcal{F}_p = \frac{k_B T}{2} \sum_{l>0,m} \frac{|u_{lm}|^2}{R^2} \Gamma_l + \ldots
\]  

(15)

\[
\Gamma_l \equiv \left[ \frac{R_g^2}{R^2} \pi (l + 2 - \pi f_l) + \frac{\pi}{4} f_l^2 - \frac{l + 2}{2} f_l + \frac{3l + 6}{4\pi} \right].
\]

In the limit of large \( l \), \( \Gamma_l \) has the behavior

\[
\Gamma_l \sim l \pi \left( \frac{R_g^2}{R^2} + \frac{3}{4} \right).
\]  

(16)

We thus recover the form predicted from simple elasticity Eq. (13).

As discussed above, the \( l = 0 \) mode is constrained by incompressibility and the \( l = 1 \) modes correspond to translations (which implies \( \Gamma_1 = 0 \)). Therefore, the leading contribution in the small-\( l \) or long-wavelength limit comes from \( l = 2 \):

\[
\Gamma_2 = \frac{R_g^2}{R^2} \pi (\pi^2 - 3) + \frac{(\pi^2 - 9)(\pi^2 + 3)}{36\pi} \approx 7.2 \frac{R_g^2}{R^2} + 0.1.
\]  

(17)

We thus find that for \( R_g > R \), the surface free energy picks up a contribution from the polymer which does not appear to have a simple interpretation in terms of surface elasticity and geometry. Furthermore, for the lowest modes, this contribution to the surface energy can be quite important. For the experiments in [3], \( R_g/R \approx 4 \), \( \kappa \approx 2k_B T \), and \( w \approx 2 \). With these values, the ratio of the \( (l = 2) \) polymer contribution to the free energy to the bending contribution is \( \mathcal{F}_p|_{l=2}/\mathcal{F}_b|_{l=2} \approx 2.4 \); the contributions from bending energy and the polymer are comparable.

In the calculations above we have neglected self-avoidance. However, in the limit of very high compressions self-avoidance will certainly be important. \( R \) is bounded from below by \( R_m \), the radius for which the polymer volume fraction is equal to one. Near this limit, we expect the interior of the droplet to be similar to a melt. The screening length \( \xi [5] \) is then microscopic and the polymer free energy is insensitive to the shape of the droplet: \( \Gamma_l \approx 0 \). Therefore, for the polymer to make a significant contribution to the surface free energy, the droplet radius must be in the range \( R_m < R < R_g \). However, even for droplets within this
range, self avoidance will be important for the lowest modes. A simple scaling estimate of $\xi$ gives

$$\xi \approx R \left( \frac{R}{R_g} \right)^{1/(3\nu-1)},$$

where $R_g \sim N^\nu$. For a chain in a good solvent, $\nu \approx 3/5$, and in a theta solvent, $\nu = 1/2$. Thus, even for a modest compression of the polymer ($R \lesssim R_g$), the screening length is comparable to $R$ ($\xi \lesssim R$) and the lowest modes of the droplet are just at the wavelengths where screening becomes important. While this results in a suppression of the free energy of the lowest modes, we cannot gauge the size of the effect. In particular, we do not know whether this suppression is strong enough to significantly reduce the polymer contribution to the surface energy relative to the bending energy.

Even for the higher modes, for which screening is unimportant (i.e. $l > R/\xi$), there will be corrections due to self-avoidance. We can again use a scaling argument to estimate the free energy of a polymer in a spherical droplet (with $R < R_g$):

$$\mathcal{F}_p \approx k_B T \left( \frac{R_g}{R} \right)^{1/\nu}. \quad (19)$$

Ignoring numerical factors, the above estimate is smaller than the ideal polymer result, Eq. (12), by a factor of $(R_g/R)^{2-1/\nu}$. Following the arguments leading to Eq. (13), we then expect the large-$l$ behavior of $\Gamma_l$ to be smaller by a factor of $(R_g/R)^{1/3}$ for a polymer in a good solvent; there is no correction for a polymer in a theta solvent.

To summarize, we have determined the contribution to the surface free energy arising from confining an ideal polymer within a droplet. Not surprisingly, this contribution does not have a simple interpretation in terms of two-dimensional elasticity and geometry. Using parameters appropriate for polymers confined in microemulsions [3], we find that the bending and polymer terms in the surface energy are comparable for the lowest modes. Scaling arguments suggest that chain self-avoidance will tend to decrease the magnitude of the polymer contribution.

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In this appendix we find the ground-state eigenvalue and integral of the ground-state eigenfunction to second order in the perturbation of the shape of the boundary, Eq. (2). In [7] a formula for the eigenvalues of the Laplacian to second order in a boundary perturbation is given for the case of Dirichlet boundary conditions (Eq. (9.2.71) of [7]). We have not been able to reproduce the derivation of this formula. Furthermore, when one applies the formula of [7] to the simple case of a spherical boundary with a perturbation of the radius, $R \rightarrow R - \delta R$, it does not give the correct result. However, by a similar procedure to that described in [7], we can derive the correct formula for general perturbations of a sphere.

We follow the notation in [7] and denote the perturbed volume by $V$ and the boundary by $S$. $S$ is a perturbation of $S_0$, which is a sphere of radius $R$. For the purposes of the derivation, however, we must formally consider perturbations that are entirely contained within the unperturbed surface. We therefore consider a second sphere $S'$ with a slightly larger radius than $S_0$, such that $S$ is entirely contained in $S'$ (Fig. 1); the volume contained in $S'$ is $V'$. We will compute the spectrum for the Laplacian on $V$ in terms of the spectrum on $V'$. The surface $S$ is thus given by:

$$r_S = (R' + v(\theta, \phi))\hat{r} \quad v(\theta, \phi) \leq 0,$$

where in terms of the perturbation $u(\theta, \phi)$ (Eq. (2))

$$v(\theta, \phi) = u(\theta, \phi) - a \quad R' = R + a \quad a \equiv \max_{\theta, \phi} u(\theta, \phi).$$

We wish to determine the ground-state eigenfunction and eigenvalue on $V$:

$$(\nabla^2 + k^2)\psi = 0 \quad \psi(r)|_{r \in S} = 0,$$

in terms of the orthonormal eigenfunctions and eigenvalues on $V'$:

$$(\nabla^2 + k_{nl}^2)\phi_{nlm} = 0 \quad \phi_{nlm}(r)|_{r \in S'} = 0.$$
Since $S'$ is a sphere of radius $R'$, Eq. (A4) is easily solved:

$$
\phi_{nlm}(r) = \sqrt{\frac{2}{R'^3}} \frac{j_l(k_{nl}r)}{j_{l+1}(k_{nl}R')} Y_{lm}(\theta, \phi)
$$

$$
k_{nl} = \frac{x_{nl}}{R'}
$$

(A5)

where $l = 0, 1, \ldots, m = -l, \ldots, l$, $n = 1, 2, \ldots$, $j_l(x)$ is the spherical Bessel function of order $l$ and $x_{nl}$ is the $n$th root of $j_l(x)$ [6]. To leading order we have $\psi(r) = \phi_{100}(r) + O(v)$ and $k^2 = k_{10}^2 + O(v)$. A simple application of Green’s theorem gives:

$$
(k^2 - k_{10}^2) \int_V d^3r \ \phi_{100}(r) \psi(r) = - \int_S d^2r \ \phi_{100}(r) \left( \frac{\partial \psi(r)}{\partial n} \right),
$$

(A6)

where we have used the fact that $\psi(r)$ vanishes on $S$; $\partial/\partial n$ denotes the outward normal derivative at the boundary. As in [7], we solve this integral equation iteratively in powers of $v$; the right-hand side is $O(v)$, since $\phi_{100}(r)$ vanishes on $S'$.

At the lowest order, we substitute $\phi_{100}(r)$ for $\psi(r)$ in Eq. (A6), express the integrals over $V$ and $S$ in terms of the nearby $V'$ and $S'$, and expand in $v$ to give

$$
k^2 - k_{10}^2 = \frac{2}{2R' \sqrt{\pi}} k_{10} \sum_{lm} k_{nl} v_{lm} + O(v^2),
$$

(A7)

where $v_{lm}$ are defined by expanding $v(\theta, \phi)$ in spherical harmonics:

$$
v(\theta, \phi) = \sum_{lm} v_{lm} Y_{lm}(\theta, \phi).
$$

(A8)

By a further application of Green’s theorem, and again using Eq. (A6), the ground-state eigenfunction may be written as (see [7])

$$
\psi(r) = \phi_{100}(r) + \frac{k_{10}}{2R' \sqrt{\pi}} \sum_{nlm} k_{nl} v_{lm} \frac{k^2_{nl} - k_{10}^2}{k_{nl}^2 - k_{10}^2} \phi_{nlm}(r) + O(v^2).
$$

(A9)

The prime on the sum in Eq. (A9) indicates that the state $(n = 1, \ l = m = 0)$ is excluded. In order to compute $k^2$ to second order in $v$, we would like to substitute the above expression for $\psi(r)$ into Eq. (A6). Unfortunately, the sum over $n$ in Eq. (A9) converges quite slowly.
\((k_{nl} \sim n \text{ for large } n)\) and we cannot move the derivative in Eq. (A6) past this sum. In order to improve the convergence, we sum the leading large-\(n\) behavior in Eq. (A9) using

\[
\sum_{nlm} v_{lm} \frac{\phi_{nlm}(r)}{k_{nl}} = \sum_{lm} v_{lm} Y_{lm} \left( \frac{r}{R'} \right)^l,
\]

which follows from the identity (for \(r < 1\)) [8]:

\[
\sum_{n=1}^{\infty} j_l(x_{nl}r) = \frac{r^l}{2}.
\]

After summing the large-\(n\) behavior, Eq. (A9) gives:

\[
\psi(r) = \phi_{100}(r) + \frac{k_{10}}{\sqrt{\pi} R'} \left[ \sum_{nlm} v_{lm} \frac{k_{10}^2}{k_{nl}(k_{nl}^2 - k_{10}^2)} \phi_{nlm}(r) \right. \\
+ \sum_{lm} v_{lm} Y_{lm}(\theta, \phi) \frac{r}{\sqrt{2R'}} \left( \frac{r}{R'} \right)^l - v_{00} \frac{\phi_{100}(r)}{k_{10}} \left] + O(v^2). \right.
\]

This expression converges sufficiently rapidly that it may be substituted into Eq. (A6).

We evaluate the resulting sums over \(x_{nl}\) by contour integration [8] and then use Eq. (A2) to express the perturbation in terms of \(u\). The final result for the ground state eigenvalue is:

\[
k^2 = \frac{\pi^2}{R^2} \left[ 1 - \frac{u_{00}}{\sqrt{\pi} R} + \frac{3}{4\pi} u_{00}^2 + 2\pi \sum_{l>0,m} \frac{|u_{lm}|^2}{R^2} (l + 1 - \pi f_l) \right] + O(u^3),
\]

where \(f_l \equiv j_{l+1}(\pi)/j_l(\pi)\).

By a similar iteration, again using Eq. (A10) to improve convergence, we find for the integral of the normalized ground-state eigenfunction:

\[
\frac{\int_V d^3r \psi(r)}{\int_V d^3r \psi(r)^2} = 2 \sqrt{\frac{2}{\pi}} R^{3/2} \left[ 1 + \frac{3}{4\sqrt{\pi}} \frac{u_{00}}{R} + \frac{3}{32\pi} \frac{u_{00}^2}{R^2} \right. \\
+ \frac{1}{8} \sum_{l>0,m} \left( 2(l + 2)f_l - \pi f_l^2 - 3 \frac{(l + 1)}{\pi} \right) \frac{|u_{lm}|^2}{R^2} + O(u_{lm}^3) \right].
\]

\(^1\)We note that the identity Eq. (A10) is a counterexample to a claimed general result used in [7] to improve the convergence of sums arising in boundary perturbations (see p. 1044 of [7]).
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FIGURES

FIG. 1. The surface of the droplet, $S$, is a perturbation of a sphere $S_0$. $S$ may be viewed as a perturbation of a slightly larger sphere, $S'$, which contains $S$. 
