Reduced Persistence Length and Fluctuation-Induced Interactions of Directed Semiflexible Polymers on Fluctuating surfaces

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Abstract

We consider directed semiflexible polymers embedded in a fluctuating surface which is governed by either surface tension or bending rigidity. The attractive interactions induced by the fluctuations of the surface reduce the rigidity of the polymers. In particular, it is shown that for arbitrarily stiff parallel polymers, there is a characteristic separation below which they prefer to bend rather than stay linear. The out-of-plane fluctuations of the polymer, screen out the long-range fluctuation-induced forces, resulting in only a short-ranged effective attraction.

87.20, 82.65D, 34.20
Fluid membranes with linear inclusions have shown a variety of interesting phenomenon. These inclusions can be incorporated by a polymerization of membranes containing unsaturated amphiphiles using UV irradiation [1]. Also, some (partially) hydrophobic polymers that are water soluble can become immersed or multiply anchored to the interior of a bilayer due to hydrophobic attractions [1]. Thermal fluctuations, or the elastic structure of the membrane, in conjunction with the constraint that inclusions are attached to the surface, affect structural properties of the polymers. For example, it has been shown that [2], depending on the value of rigidity parameters, elastic properties of the membrane may stabilize or destabilize the straight configuration of semiflexible polymers. Thermal fluctuations have been shown to induce an effective nematic-like orientational interaction between different segments of a polymer [3]. Polymers in turn, restricts membrane fluctuations and alter its behavior. It was found that cross-linked polymerization could promote wrinkling of the membranes [4], while linear polymerization causes the membrane to bulge and bud [5].

The long distance orientational interaction between rod-like inclusions due to thermal surface fluctuations were examined in Ref. [6]. There, it was assumed that the rods are much more rigid than the ambient membrane. In the limit that the separation $R$ between rods is much greater than their length $L$, the interaction falls off as $k_B T (L/R)^4$; similar to the attractive interaction between disk-like inclusions [7]. It was also shown that the interactions have the non-trivial orientational dependence of squared dipolar interactions for inclusions on a film, and squared quadrupolar interactions on a membrane. For parallel rods at close separation, $R \ll L$, the behavior is similar to the Casimir interaction between parallel plates [8], resulting in an interaction proportional to $k_B T (L/R)$.

If the distances between the external objects, as well as their characteristic sizes, are larger than the membrane thickness, one can forget about the microscopic details of the membrane. In this limit, the membrane is well-described by the elastic Hamiltonian [9],

$$\mathcal{H}_{CH} = \int dS \left[ \sigma + \frac{\kappa}{2} H^2 + \bar{\kappa} K \right],$$

(1)

where $dS$ is the surface area element, and $H, K$ are the mean and Gaussian curvatures.
respectively. The elastic properties of the surface are described by the tension $\sigma$, and the bending rigidities $\kappa$ and $\bar{\kappa}$. A finite surface tension is the most important coupling in Eq. (1) and dominates the bending terms at long wavelengths. This is the case for films on a frame, interfaces at short distances, and possibly closed membranes in the presence of osmotic pressure differences between their interior and exterior. On the other hand, for closed bilayers in the absence of osmotic stress, as well as for microemulsions, the surface tension is effectively zero \cite{10–12}. In these cases, the energy cost of fluctuations is controlled by the rigidity terms. For simplicity we shall refer to surface tension dominated surfaces as films, and to rigidity controlled ones as membranes as in Ref. \cite{6}.

In this paper we examine the effect of surface fluctuations of adsorbed directed semiflexible polymers. The directed semiflexible polymer is represented by a two dimensional position vector $\vec{r}(t)$ that indicates the transverse position of the polymer at point $t$ along its backbone; its elastic energy is then described by the Hamiltonian \cite{13}

$$\mathcal{H}_{DP} = \frac{\kappa_p}{2} \int dt \left( \frac{d^2 \vec{r}(t)}{dt^2} \right)^2$$

$$= \frac{\kappa_p}{2} \int \frac{dq}{2\pi} q^4 \left( |\vec{r}_{||,1}(q)|^2 + |\vec{r}_{\perp,1}(q)|^2 \right).$$

Such a polymer is rigid only at distances less than a bare persistence length $\ell^0_p \sim \kappa_p/(k_B T)$. Upon adsorption on a fluctuating surface, the induced interactions soften the rigidity of the polymer. While the reduction in persistence length $\ell_p$ is not appreciable for a polymer adsorbed on a film, there is a logarithmic reduction (see below) upon adsorption on a membrane. The softening is more dramatic for two parallel rods, which due to their mutual attraction want to bend towards each other. This leads to an instability in the modes describing their relative in-plane fluctuations. (Modes where the polymers fluctuate in parallel are stable). The stiffness of the polymer is able to prevent such instabilities only if the length of the polymer is less than a characteristic size

$$L_p(R) \sim \ell^0_p \left( \frac{R}{\ell^0_p} \right)^{3/4},$$

which is much lower than $\ell^0_p$. 3
The *out of plane* fluctuations of the semiflexible polymers have a dramatic effect on their “Casimir” attraction. Consider two polymers adsorbed on the surface which are, on average, parallel to each other at separations $a \ll R < L$, where $a$ is a microscopic length scale such as membrane thickness. The membrane and polymers have thermal fluctuations but are constrained to remain attached at all times. In the absence of *out of plane* polymer fluctuations, there is a fluctuation-induced interaction that falls off as $k_B T (L/R)$. The *out of plane* fluctuations actually screen out this interaction, resulting in a short-ranged attraction. The precise form of the interaction (presented in Eq.(15) below) is not particularly illuminating. We have instead approximately fitted the variations of the free energy to a form

$$\frac{F^\perp(R)}{L} = -\frac{A}{2\pi R} \exp \left[ -b \left( \frac{R}{\lambda} \right)^{\alpha} \right],$$

where $A_F = \pi^2/12$, $A_M = 2.90514$, $b_F = 3.32$, $b_M = 4.17$, $\alpha_F = 0.679$ and $\alpha_M = 0.397$ are numerical constants corresponding to the cases of films and membranes respectively. The “screening” lengths that determine the range of the interactions are defined as $\lambda_F = (\kappa_p/\sigma)^{1/3}$ for films and $\lambda_M = \kappa_p/\kappa$ for membranes.

To perform the calculations we start with a thermally fluctuating planar membrane subject to the Hamiltonian in Eq.(9). For the membrane case, we assume that its size is well below the persistence length $\xi_p$. In this limit, the membrane experiences only small fluctuations about a flat state. We may then parametrize the membrane surface with a height function $h(r)$, and approximate the full coordinate-invariant Hamiltonian in Eq.(1) by the Gaussian form $H_M = \kappa/2 \int d^2r (\nabla^2 h(r))^2$. For the case of films, the corresponding Gaussian approximation can be written as $H_F = \sigma/2 \int d^2r (\nabla h(r))^2$, which is valid in the limit where $\sigma a^2/k_B T \gg 1$, where $a$ is a microscopic length. We also parametrize the polymers as $R_\alpha(t) = (r_\alpha(t), r_{\perp,\alpha}(t))$ where the “perpendicular” axis is the same as the height function, while $r$ stands for the in plane coordinates. In calculating fluctuation induced interactions, we assume that the relaxation of surface modes takes place much faster than that of the polymers. We thus assume fixed (quenched) configurations for the polymers, and integrate over the constrained surface fluctuations, following Ref. [8].
\[ \exp(-\beta \mathcal{H}_{\text{eff}}) = \frac{1}{Z_0} \int \mathcal{D}h(r) \prod_{\alpha=1}^{2} \delta \{ h(r_{\alpha}(t_{\alpha})) - r_{\perp,\alpha}(t_{\alpha}) \} e^{-\beta \mathcal{H}} \]

\[ = \frac{1}{Z_0} \int \mathcal{D}h(r) \prod_{\alpha=1}^{2} \mathcal{D}\psi_{\alpha}(t_{\alpha}) \exp \left\{ -\beta \mathcal{H} + i \sum_{\alpha=1}^{2} \int dt_{\alpha} \psi_{\alpha}(t_{\alpha}) [h(r_{\alpha}(t_{\alpha})) - r_{\perp,\alpha}(t_{\alpha})] \right\} \]

\[ = \int \prod_{\alpha=1}^{2} \mathcal{D}\psi_{\alpha}(t_{\alpha}) e^{-\mathcal{H}_1}, \]

where \( \mathcal{H} \) can be either \( \mathcal{H}_F \) or \( \mathcal{H}_M \), and

\[ \mathcal{H}_1 \equiv \frac{1}{2} \Psi^T \mathbf{M} \Psi + i \Psi^T r_{\perp} \]

\[ = \frac{1}{2} \sum_{\alpha,\beta=1}^{2} \int dt_{\alpha} dt_{\beta} \psi_{\alpha}(t_{\alpha}) G(r_{\alpha}(t_{\alpha}) - r_{\beta}(t_{\beta})) \psi_{\beta}(t_{\beta}) + i \sum_{\alpha=1}^{2} \int dt_{\alpha} \psi_{\alpha}(t_{\alpha}) r_{\perp,\alpha}(t_{\alpha}), \]

and the expressions for \( G(r - r') \) read

\[ G_F(r - r') = \frac{k_B T}{\sigma} \left( \frac{1}{-\nabla^2} \right)_{rr'}, \]

\[ G_M(r - r') = \frac{k_B T}{\kappa} \left( \frac{1}{\nabla^4} \right)_{rr'}, \]

corresponding to films and membranes respectively. Hence, the resulting expression reads

\[ \beta \mathcal{H}_{\text{eff}} = \frac{1}{2} \ln \det \{ \mathbf{M}[r_{\alpha}(t_{\alpha})] \} + \frac{1}{2} \sum_{\alpha,\beta=1}^{2} \int dt_{\alpha} dt_{\beta} r_{\perp,\alpha}(t_{\alpha}) \mathbf{M}^{-1}(t_{\alpha}, t_{\beta}) r_{\perp,\beta}(t_{\beta}). \]

To calculate \( \ln \det \{ \mathbf{M} \} \) we parametrize the in-plane coordinates of the polymers as \( r_{1}(t) = (t, r_{\perp,1}(t)) \) and \( r_{2}(t) = (t, R + r_{\perp,2}(t)) \), and follow closely the method of Ref. [8]. We obtain

\[ \beta \mathcal{H}_{\text{eff}} = \frac{L}{2} \int \frac{dq}{2\pi} \ln(N(q)) - \frac{1}{2} \int \frac{dq}{2\pi} A(q) \left( |r_{\perp,1}(q)|^2 + |r_{\perp,2}(q)|^2 \right) \]

\[ + \frac{1}{2} \int \frac{dq}{2\pi} B(q) \left( r_{\perp,1}(q)r_{\perp,2}(-q) + r_{\perp,1}(-q)r_{\perp,2}(q) \right) \]

\[ + \frac{1}{2} \int \frac{dq}{2\pi} G(q, 0) \left( |r_{\perp,1}(q)|^2 + |r_{\perp,2}(q)|^2 \right) \]

\[ - \frac{1}{2} \int \frac{dq}{2\pi} G(q, R) \left( r_{\perp,1}(q)r_{\perp,2}(-q) + r_{\perp,1}(-q)r_{\perp,2}(q) \right) + O(r^3), \]

where the kernels are defined as

\[ A(q) = \int \frac{dp}{2\pi} \frac{G(p, 0)}{N(p)} \left. \frac{\partial^2 G(p + q, R)}{\partial R^2} \right|_{R=0} \]

\[ + \int \frac{dp}{2\pi} \left( \frac{\partial G(p, R)}{\partial R} \right)^2 \left( \frac{G(p, 0)G(p + q, 0) + G(p, R)G(p + q, R)}{N(p)N(p + q)} \right), \]
and

\[ B(q) = \int \frac{dp}{2\pi} \frac{G(p,R)}{N(p)} \frac{\partial^2 G(p+q,R)}{\partial R^2} \]

\[ + \int \frac{dp}{2\pi} \frac{\partial G(p,R)}{\partial R} \frac{\partial G(p+q,R)}{\partial R} \left( \frac{G(p,0)G(p+q,0) + G(p,R)G(p+q,R)}{N(p)N(p+q)} \right) , \]

with

\[ G(p,R) = \int dt \ e^{ipt} G(t,R), \]

\[ N(p) = (G(p,0))^2 - (G(p,R))^2. \]

The Fourier transformed Green’s functions for films and membranes are respectively

\[ G_F(p,R) = \frac{k_B T}{\sigma} \frac{e^{-|p|R}}{2 |p|} \]

\[ G_M(p,R) = \frac{k_B T}{\kappa} \frac{1}{4 |p|^3} \left( 1 + |p| R \right) e^{-|p|R} . \]

On the slower time scales after surface modes have come to equilibrium, fluctuations of the semiflexible polymers are governed by the Hamiltonian \( \mathcal{H}_{\text{tot}} = \mathcal{H}_{DP} + \mathcal{H}_{\text{eff}} \) (see Eqs.(2) and (10)). In the linearized theory, the modes parallel and perpendicular to the surface are independent. We shall first describe the behavior of a single polymer, obtained from the limit \( R \to \infty \), with \( B(q) = G(q,R) = 0 \). The out of plane modes of the semiflexible polymer turn out to be stable.

More care is necessary for the in plane fluctuations. Close examination of the kernels \( A(q) \) and \( B(q) \) shows that they have a very well-behaved expansion in powers of \( qR \). So in the long wavelength limit, we can keep only the first few terms in the expansion. As \( R \to \infty \), i.e. for a single polymer, \( B_F(q) = B_M(q) = 0 \), \( A_F(q) = (1/6\pi)q^3 \) and \( A_M(q) = (1/\pi)[\ln(L/a) - 1]q^3 \). In this case, the in-plane modes have eigenvalues equal to \( (\kappa_p/k_BT)q^4 - (1/6\pi)q^3 \) for the case of films and \( (\kappa_p/k_BT)q^4 - (1/\pi)[\ln(L/a) - 1]q^3 \) for membranes. To prevent instability, all eigenvalues must remain positive. This places restrictions on the length of the polymer, leading to new persistence lengths. One can easily see that for films the persistence length doesn’t differ from that of the non-embedded polymer namely, \( \ell_p^F \sim \ell_p^0 \). However, for the
membrane case the persistence length is logarithmically decreased namely, \( \ell_p^M \left[ \ln(\ell_p^M/a) - 1 \right] \sim \ell_p^0. \)

For the case of two polymers (or finite \( R \)) one finds \( A(q) = B(q) = (A/\pi)/R^3 \) to the leading order, where \( A \) is defined as in Eq.(4) for films and membranes (the \( R \) independent terms already considered above are neglected here). The normal modes of in-plane oscillations describe either the parallel motion of the polymers with eigenvalue \((\kappa_p/k_B T)q^4 - A(q) + B(q)\), or their relative motion with eigenvalue \((\kappa_p/k_B T)q^4 - A(q) - B(q)\) (see Eq.(10)). One can see that to the leading order, the parallel modes are stable (and this indeed holds to any order), while the relative distance modes may be unstable. This new instability introduces a new characteristic length for the combined system of two semiflexible polymers adsorbed on a fluctuating surface, defined in Eq.(\( \Xi \)). As one can immediately see, this \( L_p \) is considerably smaller than the persistence length of a single polymer. Since it is a function of the separation of the polymers, one can estimate the closest separation that two rigid rods can have, in order not to completely lose their rigidity. Assume that the rods are very rigid while they are free \((L \ll \ell_p^0)\), then the critical “rigidity-blurring” separation occurs when \( L \sim L_p \) which reads \( R_c \sim L(L/\ell_p^0)^{1/3} \). For example for relatively rigid rods with \( L/\ell_p^0 \sim 10^{-3} \), the critical separation is only about \( R_c/L \sim 1/10 \). Since the unstable modes are the relative distance modes, this result give us the following picture. The rods move towards each other due to the attractions and when the get closer than \( R_c \), they start to bulge out. If there exist some short distance anchoring interaction between the polymers, they would bend towards each other to form bound states (like a necklace). However, if short distance interactions are repulsive, they would bounce back against each other and stretch out from either side.

In the absence of polymer fluctuations \( r_\parallel = r_\perp = 0 \), the interaction between rods in given by the first term in Eq.(\( \Xi \)) and decays as \( L/R \). Assuming that the lengths \( L \) and \( R \) are selected such that the stability conditions given above are satisfied, a new net fluctuation-induced interaction between semiflexible polymers is obtained by integrating over both \( r_\parallel \) and \( r_\perp \) in Eq.(\( \Xi \)), keeping the center of mass distance fixed at \( R \). However, integration over \( r_\parallel \) in this case will depend on the low momentum cut-off and we don’t consider that
contribution here, since it doesn’t have any particular effect, other than introducing some small corrections to the long range “Casimir” interaction. The contribution of out of plane modes to the resulting constrained free energy is given by

\[ F_\perp L(R) = \frac{k_B T}{2} \int \frac{dq}{2\pi} \ln \left[ \left( \frac{\kappa_p}{k_B T} \right)^2 q^8 + 2 \frac{\kappa_p}{k_B T} q^4 \frac{G(q,0)}{N(q)} + \frac{1}{N(q)} \right]. \]  

(15)

It is interesting to note that the above expression cancels the the long-range “Casimir” interaction from \( \ln N(q) \) in Eq.(10), and the remaining expression do not result in a long-ranged interaction anymore. So as soon as the rods have a finite rigidity, no matter how large, and they are allowed to have out-of plane fluctuations, the interaction will be “screened”. However, the “screening length” is defined by the rigidity and for separations that are much smaller than this “screening length”, one may neglect this effect.

Plugging in the explicit expressions for the Green’s functions from Eqs.(14) and (13), we obtain \( F_F^\perp \) and \( F_M^\perp \) in terms of integrals that do not have analytic expressions. Since those forms are not very illuminating, we give the best fit for the result in terms of exponentials of power laws. These result are quoted in Eq.(4) for both films and membranes and Fig. 1 compare the fits and the interactions. It is important to note that the integral expressions are non-analytical at \( R = 0 \) as it reveals when one tries to make a taylor expansion. That’s why fitting is done with non-analytical powers. This is also checked against the stability of the fit.

In conclusion, we have shown that the rigidity of semiflexible polymers is lowered upon adsorption to a fluctuating surface. The effect is enhanced when two such polymers are brought in close proximity. The out of plane fluctuations of the polymer, in turn, soften the boundary conditions that give rise to long-ranged “Casimir” attraction. After they are integrated out, the attraction between two parallel polymers becomes short-ranged.

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FIGURES

FIG. 1. Dimensionless energy $f = F^\perp/F_C$ plotted versus the dimensionless separation $x = R/\lambda$, where $F_C$ is the long-ranged Casimir interaction. The solid curves represent the best fit to the exact data point obtained from numerical integration.