

Scale-dependent rigidity of polymer-ornamented membranes

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Abstract. We study the fluctuation spectrum of fluid membranes carrying grafted polymers. Contrary to usual descriptions, we find that the modifications induced by the polymers cannot be reduced to the renormalization of the membrane bending rigidity. Instead we show that the ornamented membrane exhibits a scale-dependent elastic modulus that we evaluate. In ornamented lamellar stacks, we further compute the polymer contribution to the Caillé parameter characterizing the power law singularities of the Bragg peaks.

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The characterization of polymer-membrane interactions is a fundamental issue of colloidal science. In cosmetics, pharmaceuticals or detergency, many formulations are suspensions of self-assembled surfactant bilayers with polymers added for performance, processing, conditioning or delivery [1]. Likewise, lipid bilayers form the walls of living cells and liposomes, and host a great variety of macromolecules for coating protection, ion exchange and mechanical reinforcement [2]. In many instances, the polymers are end-tethered to the soft interfaces. Grafting is easily achieved experimentally by using polymer chains that carry hydrophobic groups. Typical examples are provided by the so-called PEG-lipids, hydrophilic chains of polyethylene glycol covalently linked to a double-tail phospholipid molecule. Recent studies have shown that polymers grafted to bilayers can induce gelation [3] or other phase changes [4,5] in liquid lamellar phases. They stabilize monodisperse vesicles [6], modify the properties of giant vesicles [7] and influence the geometry of monolamellar [8,9] and multilamellar [10] cylindrical vesicles. They also lead to drastic changes in the structure and phase behaviour of ternary amphiphilic systems [11].

As first explained by Canham and Helfrich, fluid membranes are fluctuating objects [12]. In thermal equilibrium, the surface assumes all the possible shapes allowed by the geometry with the associated Boltzmann probability $\mathcal{P} \sim \exp\{-\mathcal{H}_0/(k_B T)\}$. The Hamiltonian \mathcal{H}_0 is a quadratic function of c_1 and c_2 , the two principal curvatures at any given point of the surface,

$$\mathcal{H}_0 = \int dS \left\{ \frac{\kappa}{2} (c_1 + c_2 - 2c_0)^2 + \bar{\kappa} c_1 c_2 \right\}. \quad (1)$$

The spontaneous curvature c_0 vanishes for symmetric bilayers. The Gaussian rigidity $\bar{\kappa}$ plays an important role in the determination of the topology of the system, and the integral $\int dS \bar{\kappa} c_1 c_2$ does not depend on the particular shape of the membrane. The amplitude of the thermal fluctuations is controlled by the bending rigidity κ , that ranges from a few $k_B T$ to a few tens of $k_B T$. Conversely, the analysis of the height correlations in a membrane system allows for the determination of the constitutive rigidity. Many techniques were specifically developed to extract κ by comparing experiments and theoretical predictions for vesicles, lamellar stacks, bicontinuous phases and other geometries. These methods have so far been of limited application in polymer-membrane systems because of the lack of prediction for the fluctuation spectrum of bilayers in the presence of polymers. In this paper, we make a first step to bridge this gap by investigating the role of grafted chains on the fluctuation spectrum of fluid membranes. We first analyze the subtle interplay between *local* monomer concentration and surface curvature. We show that the chains induce additional height correlations that can be interpreted as the result of effective, scale-dependent elastic coefficients. For the specific case of an ornamented lamellar phase of membranes, we also determine the Caillé parameter that characterizes the power law singularities around the Bragg peaks.

In a mean-field description, ornamented membranes are assumed to have new parameters $\kappa_{\text{eff}} = \kappa + \Delta\kappa$ and $\bar{\kappa}_{\text{eff}} = \bar{\kappa} + \Delta\bar{\kappa}$ different from those of the bare membrane. We consider \mathcal{N} polymers grafted to each side of a membrane of area \mathcal{S} , the chains being free to diffuse along the

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membrane. The surface coverage $\sigma = \mathcal{N}/\mathcal{S}$ is low enough to avoid polymer-polymer interactions: $\sigma < \sigma^* \simeq R_F^{-2}$, with R_F the Flory radius of the chains. In this limit of small density, the excess surface energy is proportional to σ and one anticipates corrections of the order of $\Delta\kappa \sim \Delta\bar{\kappa} \sim k_B T (\sigma R_F^2)$ in both good and theta solvent. The effect of solvent quality and polymer architecture resides in the numerical prefactors of the variations. For Gaussian chains tethered by one extremity, the calculations can be carried out explicitly and one gets $\Delta\kappa = (1 + \frac{\pi}{2}) k_B T \sigma R_g^2$ and $\Delta\bar{\kappa} = -2k_B T \sigma R_g^2$ [13–16], with $R_g = (Na^2/6)^{1/2}$ the radius of gyration of a Gaussian chain of N monomers of size a . At the overlap concentration σ^* , the variations are of the order of the thermal energy $k_B T$. However, for most practical situations, the chains can freely move along the membrane surface: the degrees of freedom associated with the end positions are annealed, as opposed to the quenched results of references [13, 16]. A thorough study of the system reveals that averaging the free energy over the anchor position is not equivalent to averaging the partition function itself. As a consequence, the response to bending is lowered if one correctly accounts for the tendency of the chains to be at the top of the membrane undulation, leading to [17]

$$\Delta\kappa = k_B T \sigma R_g^2, \quad (2)$$

$$\Delta\bar{\kappa} = -2k_B T \sigma R_g^2. \quad (3)$$

The reduction of the effective modulus is due to the linear coupling between positions and spontaneous curvature and actually follows the general argument first recognized by Leibler [18], a consistency requirement for the low wave vector limit of the results discussed in this paper.

These mean-field results miss however a crucial feature, namely that the polymer-membrane interactions strongly depend on the length scale. We first consider the partition function \mathcal{Z}_N of a single Gaussian chain and construct a perturbative expansion in the limit of small surface deformations around the flat plane. In the absence of overhangs and inlets, the surface profile can be described by a single-valued function $h(\mathbf{r})$, where \mathbf{r} spans the reference plane. We expand \mathcal{Z}_N in a series $\mathcal{Z}_N^{(0)} + \mathcal{Z}_N^{(1)} + \mathcal{Z}_N^{(2)} + \dots$, where $\mathcal{Z}_N^{(i)}$ is of order h^i and $\mathcal{Z}_N^{(0)}(z) \approx z/(\sqrt{\pi}R_g)$ denotes the partition function of a chain tethered at a small distance z of a flat, impenetrable wall. It has been shown recently that the first-order term of the expansion is related to the pressure field applied by the grafted chain to the surface [19, 20]. At a distance $r = \sqrt{x^2 + y^2}$ from the grafting point, this entropic pressure decays with the scaling form $p(r) \sim k_B T r^{-3}$ ($a \ll r \ll R_g$) in both good and theta solvents, and then vanishes sharply beyond R_g [21].

We now evaluate the contribution of the tethered polymers to the fluctuation spectrum of the membrane. If one introduces the Fourier Transform (FT) of the height profile $\tilde{h}(\mathbf{q}) = \int d\mathbf{r} e^{-i\mathbf{q}\cdot\mathbf{r}} h(\mathbf{r})$, then the energy \mathcal{H}_0 of the pure membrane reads

$$\mathcal{H}_0 = \frac{1}{2} \int \frac{d\mathbf{q}}{(2\pi)^2} \tilde{h}(\mathbf{q}) \tilde{h}(-\mathbf{q}) \kappa q^4. \quad (4)$$

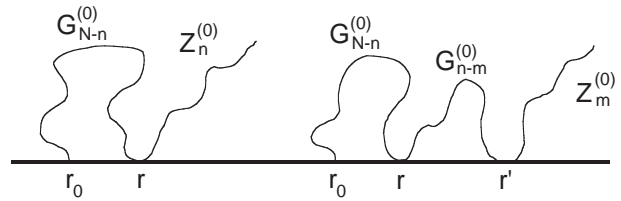


Fig. 1. Diagrammatic representation of the perturbative expansion of the Gaussian chain partition function at first order (left) and second order (right).

Contrary to the previous mean-field results, we assert here that the presence of the chains entails non-local contributions to the elastic description of the membrane. This can be shown by extending the perturbative scheme up to second order in h , a calculation that we perform analytically for a Gaussian chain. In this case, the single-chain partition function obeys the Edwards equation [22]

$$\left(\frac{\partial}{\partial n} - \frac{a^2}{6} \nabla^2 \right) \mathcal{Z}_n(\mathbf{r}, z) = 0, \quad (5)$$

where (\mathbf{r}, z) is the position of the constrained extremity. The linearity of equation (5) implies that each term of the development obeys an Edwards equation. The solution of the successive orders are coupled through the (Dirichlet) boundary condition on the wall $\mathcal{Z}_n(\mathbf{r}, h(\mathbf{r})) = 0$. The solution of equation (5) obeying the impenetrability condition is then determined recursively, and is given to each order by [23]

$$\mathcal{Z}_N^{(i)}(\mathbf{r}, z) = \frac{a^2}{6} \int_0^N dn \int d\mathbf{r}' \frac{\partial G_{N-n}^{(0)}(\mathbf{r}, z; \mathbf{r}', 0)}{\partial z'} \mathcal{Z}_n^{(i)}(\mathbf{r}', 0), \quad (6)$$

where the Green function $G_N^{(0)}$ of equation (5) satisfies the Dirichlet condition on the horizontal plane [21]. This solution corresponds to a “loop expansion” of \mathcal{Z}_N : the term of order i enumerates the conformations that encounter the surface i times, as depicted in Figure 1. Finally, the statistical weight \mathcal{Z}_N is averaged for all possible positions of the anchoring point along the surface.

In general, the membrane carries a finite polymer concentration σ . We neglect, for the sake of simplicity, the interactions between the chains, whose origin is twofold: in addition to the usual steric repulsions, the mean deformation resulting from the polymer pressure gives rise to attractive, deformation-sharing interactions [21]. However, the latter do not modify the fluctuation spectrum of the membrane. Our results are thus exact in the low-density limit $\sigma R_g^2 \ll 1$, where direct polymer interactions can be neglected. Assuming \mathcal{N} chains on each side of the membrane, the total partition function of the system is given by the path integral

$$\begin{aligned} \mathcal{Z} &= \frac{1}{(\mathcal{N}!)^2} \int \mathcal{D}[h] e^{-\beta\mathcal{H}_0} \left(\frac{1}{\mathcal{S}} \int d\mathbf{r} \mathcal{Z}_N \right)^{2\mathcal{N}} \\ &= \frac{1}{(\mathcal{N}!)^2} \int \mathcal{D}[h] e^{-\beta\mathcal{H}_{\text{eff}}}, \end{aligned} \quad (7)$$

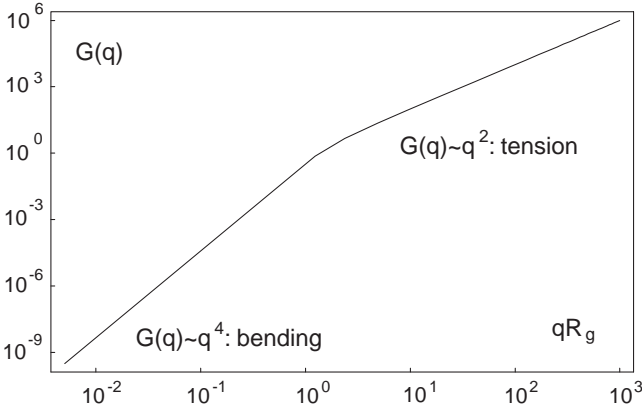


Fig. 2. Non-local polymer contribution to the fluctuation spectrum of a membrane. At the natural length scale R_g , the function $G(q)$ crosses over from a bending-like behaviour to a tension-like behaviour.

where the factor $1/\mathcal{N}!$ reflects the fact that particles are indistinguishable. The properties of the decorated surface are described by the new Hamiltonian $\mathcal{H}_{\text{eff}} = \mathcal{H}_0 + \Delta\mathcal{H}$, with

$$\Delta\mathcal{H} = \frac{1}{2} \int \frac{d\mathbf{q}}{(2\pi)^2} \tilde{h}(\mathbf{q}) \tilde{h}(-\mathbf{q}) G(\mathbf{q}) . \quad (8)$$

The algebra will be detailed elsewhere [17], and we now discuss the results. Integrating out the degrees of freedom of the grafted chains generates the additional contribution

$$G(\mathbf{q}) = \frac{2k_B T \sigma}{R_g^2} \left\{ e^{-q^2 R_g^2} - 1 + q^2 R_g^2 \right\} . \quad (9)$$

The correlation function $G(\mathbf{q})$ is displayed in Figure 2. At length scales larger than the polymer size $qR_g \ll 1$, one can extract a correction to the bending rigidity that reads $\Delta\kappa = \lim_{q \rightarrow 0} [q^{-4} G(\mathbf{q})] = k_B T \sigma R_g^2$. We retrieve in this limit the mean-field correction (2), as expected. Interestingly, the polymer-membrane interactions also induce a tension-like term at short distances: $G(\mathbf{q}) \simeq 2k_B T \sigma q^2$ for $qR_g \gg 1$. The correlations between chain and membrane conformations are stronger inside the polymer mushroom: as a consequence, the fluctuations of the surface are smoothed out at length scales smaller than the polymer size. The coefficient of this effective surface tension corresponds to the two-dimensional perfect gas pressure (recall that *both sides* are ornamented with \mathcal{N} chains). Note that our results contrast with the usual interfacial behaviour, where tension is dominant at large scales whereas bending effects appear only at shorter scales. We should emphasize that the results presented here do not depend on the nature of the interface: they can be used to study a wide class of surfaces, provided that grafting of macromolecules is feasible.

We now apply our predictions to the lyotropic phase L_α . This phase consists in a stack of regularly spaced membranes, that form a quasi-crystalline structure in one direction while retaining their fluid properties in the perpendicular plane. In pure water, the smectic order is generally stabilized by long-range electrostatic interactions. At

high salt concentration or for neutral surfactant molecules, the stability of the phase arises from the entropic repulsions between fluctuating membranes: we will refer to this system as to the Helfrich system. In a continuum elastic theory, the multilayer membrane system is described by the displacement field $u(\mathbf{r})$ in the z -direction normal to the layers. The standard theory of a pure L_α phase is based on the smectic energy density [24]

$$\frac{F}{V} = \frac{1}{2} B \left(\frac{\partial u}{\partial z} \right)^2 + \frac{1}{2} K (\nabla_\perp^2 u)^2 , \quad (10)$$

the subscript \perp referring to the coordinates along the layers. K is the smectic curvature modulus and is directly related to the membrane bending rigidity through the relation $K = \kappa/d$, with d the average layer spacing. The smectic compressibility modulus B reflects the inter-lamellar interactions, and is given in a Helfrich system by $B = 9\pi^2 (k_B T)^2 / (64\kappa d^3)$.

The lyotropic phase is a good candidate to probe experimentally the fine modifications to the properties of the pure phase induced by the addition of macromolecules [25, 26]. X-ray or neutron scattering experiments allow to measure the exponent η that characterizes the power law singularities around the Bragg peak: $I(q) \sim |q - q_0|^{-1+\eta}$, with $q_0 = 2\pi/d$ [27]. The “strength” of the smectic order varies conversely to η . For pure membrane systems, the FT of the average height fluctuations is $\langle |u(\mathbf{q})|^2 \rangle = V k_B T / (B q_z^2 + K q_\perp^4)$, which leads to the classical prediction first derived by Caillé [28]:

$$\eta = q_0^2 \frac{k_B T}{8\pi \sqrt{KB}} . \quad (11)$$

Likewise, a decorated membrane has, according to equation (9), a scale-dependent bending rigidity $\kappa(\mathbf{q}) = \kappa(1 + \alpha g_D(q^2 R_g^2))$, where we define the dimensionless parameter $\alpha = \frac{k_B T}{\kappa} \sigma R_g^2$, and $g_D(x) = \frac{2}{x^2} (e^{-x} - 1 + x)$ is the Debye function [29]. This is certainly the most fundamental step for forecasting the properties of membrane-polymer complexes, but one should keep in mind that some macromolecular interactions such as repulsion between different membranes of the lamellar stack cannot be reduced only to the modification of the single membrane parameters. Notwithstanding this point, the height fluctuations are now given by

$$\begin{aligned} \langle |u(\mathbf{q})|^2 \rangle_{\text{pol}} &= \frac{V k_B T}{B q_z^2 + K q_\perp^4 (1 + \alpha g_D(q_\perp^2 R_g^2))} \\ &\simeq \langle |u(\mathbf{q})|^2 \rangle - \\ &\alpha \frac{V k_B T}{(B q_z^2 + K q_\perp^4)^2} K q_\perp^4 g_D(q_\perp^2 R_g^2) . \end{aligned} \quad (12)$$

at lowest order in α . It ensues that the q_\perp corrections lead to the same power law divergence of the scattering intensity with new exponent

$$\eta_{\text{pol}} = \eta \left(1 - \frac{k_B T}{2\kappa} \sigma R_g^2 \right) . \quad (13)$$

The low- q part of $G(\mathbf{q})$ (*i.e.*, the correction to κ) actually provides the main contribution to the integrals leading to (13). Providing that the interlamellar distance is not affected, the tethered chains stiffen the lamellar order, that leads to a sharpening of the Bragg peak. A decrease of η with polymer concentration is indeed observed in numerous experiments —see, for instance, [3,5]. However, the measured variation of η is much sharper than the predicted linear behaviour at low coverage. As explained above, the chains are also likely to induce non-trivial variations of the compressibility B . A simple explanation of these modifications has been proposed by Castro-Roman *et al.* [5]: a reduction in η would be due to the polymer layer that effectively increases the membrane thickness. Within this picture, however, it is still difficult to explain why the membrane thickness varies so sharply with polymer coverage. Our study suggests that this could be caused by a non-homogeneous chain distribution, arising from the coupling between position and curvature. This naturally leads to a higher density of polymers in curved regions, which also correspond to the contact zones between the fluctuating bilayers. The concentration at which η is significantly modified should then be as lower as the coverage needed to roughly have one polymer by membrane contact point, *i.e.* $\sigma \sim 1/d^2$. Since the size of the polymer is smaller than the interlamellar distance, this coverage is a factor $R_g^2/d^2 \ll 1$ smaller than the overlapping coverage. Note that the diffusion time of a polymer chain over a distance d is a factor R_g/d smaller than the Zimm time of a typical membrane fluctuation, there are thus no kinetic reasons restricting the mobile grafted polymers to be always at the intermembrane contact points.

In conclusion, we have developed a local description of the fluctuation spectrum of fluid membranes ornamented with grafted polymers. Contrary to current mean-field predictions, we find that the effect of the grafted chains cannot be reduced to an effective increase of the membrane bending rigidity. Instead, we show that the elastic coefficient is a scale-dependent quantity. On scales much larger than the polymer size, the bending rigidity is indeed renormalized. This low- q correction is the dominant contribution to the so-called Caillé exponent measured by X-ray experiments in L_α phases. On scales smaller than the polymer size, polymer-membrane interactions smooth the fluctuations, leading to a tension-like contribution to the correlation function. Our results were obtained for Gaussian chains, a good representation for polymers in θ solvents. It is not clear at this point whether or not this description is robust with respect to the introduction of monomer-monomer excluded-volume interactions. In particular, the “tension” regime that develops at short length scales might exhibit a different, non-trivial form. Indeed, the Debye function g_D is known to scale as $g_D \sim q^{-1/\nu}$, with $\nu = 1/2$ in theta solvent and $\nu \simeq 3/5$ in good-solvent conditions. If the relation $G \propto q^4 g_D$ still holds for chains with excluded volume, one should then expect $G(\mathbf{q})$ to behave like $G(\mathbf{q}) \sim q^{7/3}$ for large wave vectors \mathbf{q} . Work on this issue is currently under progress.

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