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Curvature Elasticity of an Adsorbed Polymer Layer

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Abstract. — We study theoretically the change of the curvature moduli of a surfactant membrane due to the adsorption of a polymer solution. Using a mean field theory of polymer adsorption, we study both cases of reversible and irreversible polymer adsorption in good and θ solvents. The curvature moduli of the adsorbed polymer layers are dominated by the short loops that the polymer forms on the membrane. The polymer contribution to the membrane bending modulus is always negative and the polymer contribution to the Gaussian curvature modulus is always positive.

1. Introduction

Surfactant molecules self-assemble in solution to form various kinds of aggregates and mesophases. One particular type of these aggregates is a fluid membrane which can be either a surfactant monolayer (at an interface between oil and water) [1, 2] or a surfactant bilayer (between oil and oil or water and water). Fluid membranes can either pile up in a lamellar smectic phase or fold to form vesicles. These phases are observed over a broad range of concentration in many synthetic surfactant systems. Fluid membranes also play a major role in biological systems (cell membranes).

The pioneering work of Helfrich [3, 4] has shown that in many instances, fluid membranes are not under tension and that their physical properties are dominated by the curvature elasticity of the membrane. The equilibrium shape of a vesicle is for example the shape that minimizes the curvature elasticity free energy. The curvature elasticity also controls the thermal undulation fluctuations of membranes; if the bending elasticity is weak, the undulation fluctuations are important and lead to strong repulsive interactions between membranes that can stabilize swollen lamellar phases with an interlamellar spacing that can be as large as several hundred angströms.

For weakly bent membranes, the curvature free energy can be expanded in powers of the local curvature. This leads to the so-called Helfrich free energy

$$\mathcal{F} = \int ds \left(\frac{1}{2} k_c (c_1 + c_2 - 2c_0)^2 + \bar{k}_c c_1 c_2 \right). \quad (1)$$

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The integral is carried out over the area of the membranes and c_1 and c_2 are the principal curvatures at each point. The curvature energy involves three intrinsic parameters of the membrane, the bending modulus k_c , the Gaussian curvature modulus \bar{k}_c and the spontaneous curvature c_0 . The free energies per unit area of a spherical and of a cylindrical vesicle of radius R are respectively $F_S = -4k_c c_0/R + (2k_c + \bar{k}_c)/R^2$ and $F_C = -2k_c c_0/R + k_c/2R^2$.

An important issue in surfactant physics is the monitoring of the two moduli k_c and \bar{k}_c . This can for example be done by changing the electrostatic charge of the membrane by mixing neutral and charged surfactants. The electrostatic contribution to the membrane curvature moduli has been studied theoretically quite extensively [5–7]. It depends on the membrane charge, on the ionic strength and also on the intermembrane distance in a lamellar phase. The electrostatic contribution to k_c is always positive, electrostatics makes the membrane stiffer. The electrostatic contribution to \bar{k}_c is negative and thus favors the formation of disconnected objects. An alternative way to change the curvature moduli is to adsorb or to graft a polymer on the surface of the membrane. Polymer grafting also leads to a stiffening of the membrane [8]. Polymer adsorption was first discussed by de Gennes [9] who constructed the scaling behavior of the polymer contribution to the moduli. His approach however does not give the sign of the polymer contribution. Brooks *et al.* [10] have used a mean field theory of polymer adsorption. In the case of reversible adsorption, they have obtained the surprising result that the adsorbed polymer decreases the modulus k_c and increases the Gaussian modulus \bar{k}_c .

In this paper, we extend the work of Brooks *et al.* Using the same mean field theory, we calculate analytically the polymer contribution to the curvature moduli in the case of strong reversible adsorption. We also study the curvature elasticity of an irreversibly adsorbed polymer layer both in good and θ solvents. In all cases, we find that the polymer contribution to the bending modulus is negative and thus that the adsorbed polymer layer makes the membrane less stiff.

The paper is organized as follows. In the next section, we study the curvature elasticity of a reversibly adsorbed polymer layer and in the following section the curvature elasticity of an irreversibly adsorbed polymer layer. The last section presents some concluding remarks and discusses some possible issues.

2. Curvature Elasticity of a Reversibly Adsorbed Polymer Layer

We consider a membrane with a vanishing spontaneous curvature immersed in a polymer solution which reversibly adsorbs on the membrane. The bulk polymer solution of concentration c_b imposes the chemical potential of the polymer adsorbed on the membrane. For simplicity we consider here the adsorbed polymer layer only on one side of the membrane and determine the two curvature moduli and the spontaneous curvature of the membrane with the adsorbed polymer. If the polymer adsorbs on both sides of the membrane, the polymer contribution to the moduli is clearly twice bigger and the spontaneous curvature exactly vanishes for symmetry reasons. The polymer contribution to the curvature elasticity is obtained by studying first a cylindrical membrane of radius R , then a spherical membrane and by calculating the free energies per unit area in these two geometries.

An adsorbed polymer layer has a double layer structure and is composed of two sublayers, an inner layer where the polymer essentially forms loops on the adsorbing surface and an outer layer formed by the tails of the adsorbed chains [11]. We find below that the curvature elasticity is dominated by the short distances in the vicinity of the membrane *i.e.* by the short loops. It is thus sufficient to consider the loops on the surface and to ignore the tail sections of the chains. This is done by using the classical mean field theory based on the so-called ground state dominance approximation [12]. The free energy of the adsorbed polymer solution (at fixed

chemical potential) in this approximation is written as a functional of the order parameter ψ which is related to the local concentration c by $c = \psi^2$

$$\mathcal{F}_P/kT = -Ac_s/d + \int d\mathbf{r} ((\nabla\psi)^2 + G(\psi)). \quad (2)$$

The first term is the direct attractive interaction between the polymer and the surface, A being the total area of the membrane; the extrapolation length d measures the adsorption strength and decreases when the adsorption gets stronger. In principle, the extrapolation length can depend on the local curvature of the surface, we ignore this dependence by considering an infinitely short range interaction between the monomers and the surface. The gradient term is related to the connectivity of the polymer chain, we choose here as the unit length $a/6^{1/2}$ where a is the monomer size. The last term describes the interactions between monomers and depends on the solvent quality; the precise form of the interaction free energy does not need to be specified at this point; the relevant thermodynamic potential is the grand canonical free energy at constant chemical potential, the interaction free energy is thus minimal and vanishes when the concentration has the bulk value. The equilibrium monomer concentration profile is obtained by minimization of this free energy

$$\nabla^2\psi = \frac{1}{2} \frac{\partial G}{\partial \psi} \quad (3)$$

with the boundary condition $\mathbf{n}\nabla\psi = -\psi/d$ where \mathbf{n} is the unit vector normal to the membrane.

We first study the adsorption of the polymer on a cylindrical membrane of radius R and expand the free energy in powers of the curvature $1/R$. The order parameter is expanded as $\psi = \psi_0 + \psi_1/R$. It only varies with the radial coordinate $r = R + z$. The order parameters ψ_0 and ψ_1 satisfy then the equations

$$\frac{\partial^2\psi_0}{\partial z^2} = \frac{1}{2} \frac{\partial G}{\partial \psi_0} \quad (4)$$

$$\frac{\partial^2\psi_1}{\partial z^2} + \frac{\partial\psi_0}{\partial z} = \frac{\psi_1}{2} \frac{\partial^2 G}{\partial \psi_0^2}. \quad (5)$$

Using these equations and the fact that for a flat membrane the free energy is minimal when the order parameter is ψ_0 , we can express the polymer free energy up to second order in curvature as a function of ψ_0 and ψ_1 only. The first order term gives the spontaneous curvature induced by the polymer layer and the second order term the adsorbed layer contribution to the bending modulus δk_c . We find

$$k_c c_0 = -kT \int_0^\infty z dz G(\psi_0), \quad \delta k_c = -2kT \int_0^\infty dz \psi_1 \frac{\partial \psi_0}{\partial z}. \quad (6)$$

The spontaneous curvature can thus be calculated as a moment of the interaction free energy in a flat geometry quite similarly to the mechanical model of membranes proposed by Helfrich [2, 3]. The calculation of the bending modulus requires the expansion of the order parameter to first order in curvature. The Gaussian curvature modulus can be obtained by considering a spherical membrane and comparing the free energy to that of a cylindrical membrane of the same radius. It can also be expressed as a moment of the interaction free energy in the flat geometry

$$\delta \bar{k}_c = 2kT \int_0^\infty z^2 dz G(\psi_0). \quad (7)$$

The interaction free energy is always positive and whatever its precise expression the polymer contribution to the Gaussian curvature modulus has a positive value.

In order to get a quantitative value of the moduli, we now specialize to the case of a polymer solution in a good solvent. In the mean field approximation, the interaction free energy is proportional to the square of the local concentration and the grand canonical free energy can be written as $G(\psi) = \frac{1}{2}v(c - c_b)^2 = \frac{1}{2}v(\psi^2 - \psi_b^2)^2$ where we have introduced the bulk order parameter $c_b = \psi_b^2$. In a good solvent, the excluded volume parameter v is positive. Although the mean field approximation neglects the excluded volume correlations which are known to play an important role, it is expected to give a good qualitative description of the adsorption and to be accurate in the so-called marginal solvent limit [13]. The natural unit length for the adsorption problem is then the bulk correlation length $\xi_b = (2/vc_b)^{1/2}$. It is convenient to use the dimensionless order parameters $\psi_0 = \phi_0\psi_b$ and $\psi_1 = \phi_1\xi_b\psi_b$ and the dimensionless length $y = (z + d)/\xi_b$. The order parameter in the flat geometry is

$$\psi_0 = \coth y. \quad (8)$$

This leads to the classical concentration profile for a polymer solution in the vicinity of a flat adsorbing surface $c(z) = c_b \coth[(z + d)/\xi_b]$.

The adsorption is weak if the extrapolation length d is larger than the correlation length ξ_b . For a flat membrane, the polymer concentration or the order parameter ψ_0 then essentially decay exponentially from the surface. In this limit, the perturbation to the order parameter ψ_1 is easily calculated from equation (5) and then the curvature moduli from (6, 7). The results are identical to those found in reference [10] and in particular the polymer contribution to the bending modulus is negative.

The strong adsorption limit where $d < \xi_b$ seems more relevant experimentally. The change in the order parameter due to the curvature can also be calculated explicitly from equation (5). Only the short distance expansion $y \ll 1$ is needed to determine the bending modulus

$$\phi_1(y) = -\frac{1}{6} \left(\frac{\tilde{d}^2}{y^2} + 1 \right) \quad (9)$$

where $\tilde{d} = d/\xi_b$ is the dimensionless extrapolation length. The two curvature moduli are then calculated as

$$\delta \bar{k}_c = \frac{1}{27} \frac{kT a^4}{vd}, \quad \delta k_c = -\frac{2}{81} \frac{kT a^4}{vd}. \quad (10)$$

We have reestablished here the homogeneity of the formula. In agreement with the results of [10] we find that in this limit of reversible adsorption, the polymer contribution to the bending modulus is negative and the polymer contribution to the Gaussian curvature modulus is positive. The dependence on the various parameters is the same as in [10] and the prefactors are very close to those determined numerically in this work.

3. Curvature Elasticity of an Irreversibly Adsorbed Polymer Layer

In many experiments, the time required for an adsorbed polymer layer to reach equilibrium with a bulk solution is prohibitively large and the adsorption is irreversible. A reasonable approximation is then to assume that the total adsorbed polymer amount remains constant when the membrane bends but that the chain conformations inside the adsorbed layer reequilibrate freely. In the following, we suppose that the polymer has been adsorbed from a dilute solution on a flat membrane with a surface excess (quantity of polymer per unit area) Γ and that the

solution has been replaced by pure solvent. The curvature moduli are calculated at constant value of Γ .

The free energy of the adsorbed polymer layer still has the form of equation (2) but $G(\psi)$ is simply the interaction free energy of the polymer solution. In order to determine the polymer concentration profile, one must minimize the free energy with the constraint that the adsorbed polymer amount is constant. This can be done by introducing a Lagrange multiplier μ that plays the role of an effective chemical potential.

We consider now a cylindrical membrane. The equations for the order parameter at zeroth and first order in curvature are

$$\frac{\partial^2 \psi_0}{\partial z^2} = \frac{1}{2} \frac{\partial G}{\partial \psi_0} + \epsilon \psi_0 \quad (11)$$

$$\frac{\partial^2 \psi_1}{\partial z^2} + \frac{\partial \psi_0}{\partial z} = \frac{\psi_1}{2} \frac{\partial^2 G}{\partial \psi_0^2} + \epsilon \psi_1 - \mu_1 \psi_0. \quad (12)$$

Where as for the order parameter, we have expanded the Lagrange multiplier in powers of the curvature $\mu = -\epsilon + \mu_1/R$. The chemical potential of the solution where the adsorbed layer was formed is $\mu_0 = -\epsilon$ and the value of ϵ (> 0) fixes the adsorbed polymer amount. As in the reversible adsorption case, the polymer free energy can be expressed up to second order in curvature as a function of ψ_0 and ψ_1 only. The Lagrange multiplier μ_1 is determined by imposing the conservation of the adsorbed polymer mass. Up to first order in the curvature this can be written as

$$\int_0^\infty z dz \psi_0^2 = -2 \int_0^\infty dz \psi_0 \psi_1. \quad (13)$$

The curvature moduli are obtained from the coefficients of the expansion of the free energy in powers of the curvature for a cylindrical and then for a spherical membrane. The Gaussian curvature modulus and the spontaneous curvature are given by the same laws (14, 7) as for the reversible case where $G(\psi_0)$ is replaced by an effective free energy $G + \epsilon \psi_0^2$ (G being the appropriate interaction energy for the irreversible adsorption problem); they can thus be calculated from the order parameter profile in the flat geometry. The bending modulus is given by

$$\delta k_c = -2kT \int_0^\infty dz \psi_1 \frac{\partial \psi_0}{\partial z} - kT \mu_1 \int_0^\infty z dz \psi_0^2. \quad (14)$$

We first consider a polymer in a good solvent. The interaction free energy is $G = \frac{1}{2} v c^2 = \frac{1}{2} v \psi^4$. The natural length scale of the problem is the adsorbed layer thickness $\xi = \epsilon^{-1/2}$, the dimensionless length is defined as $y = (z + d)/\xi$; we also consider the strong adsorption limit where $d < \xi$. We introduce an order parameter scale $\bar{\psi} = (2\epsilon/v)^{1/2}$ and define the dimensionless order parameters as $\psi_0 = \bar{\psi} \phi$ and $\psi_1 = \xi \bar{\psi} \phi_1$. The effective chemical potential is written as $\mu_1 = \epsilon^{1/2} \bar{\mu}_1$. The equations for the order parameters can be solved exactly. The order parameter profile for the adsorption on a flat membrane is

$$\phi_0 = 1/\sinh y. \quad (15)$$

The first correction to the order parameter due to the curvature is

$$\begin{aligned} \phi_1 = & \frac{\alpha \cosh y}{\sinh^2 y} + \frac{\bar{\mu}_1}{2} \left(\frac{y \cosh y}{\sinh^2 y} - \frac{1}{\sinh y} \right) \\ & - \frac{\cosh y}{3 \sinh^2 y} \left(\frac{\cosh 2y - \sinh 2y - 1}{4} - \tanh y + \frac{3y}{2} \right) \end{aligned} \quad (16)$$

where $\alpha = -\frac{\tilde{d}^2}{6} + \frac{\tilde{\mu}_1 \tilde{d}^3}{3}$. The conservation of the adsorbed polymer amount gives the effective chemical potential as

$$\tilde{\mu}_1 = -\frac{4}{3} \log(1/\tilde{d}) \quad (17)$$

where as above $\tilde{d} = d/\xi$. The bending modulus of an adsorbed polymer layer is then calculated as

$$\delta k_c = -\frac{2}{81} \frac{kT a^4}{v d} \left(1 - 2\tilde{d} \log^2(1/\tilde{d})\right). \quad (18)$$

Up to leading order in \tilde{d} , the bending modulus of an irreversibly adsorbed polymer layer is thus equal to that of a reversibly adsorbed polymer layer. The correction is positive as can be expected (the irreversibly adsorbed layer is obviously stiffer) but this correction is subdominant and the polymer contribution to the bending modulus is negative.

We have also studied the bending modulus of an irreversibly adsorbed polymer layer in a θ solvent. In a θ solvent, the second virial coefficient vanishes and one must expand the free energy to third order in concentration $G = \frac{1}{6} w^2 c^3 = \frac{1}{6} w^2 \psi^6$. The procedure is the same as in a good solvent. The natural unit length is $\xi = \epsilon^{-1/2}$ and the natural order parameter unit is $\bar{\psi} = (6\epsilon/w^2)^{1/4}$. Using the same notations as above in a good solvent the order parameter profile for the adsorption on a flat surface is

$$\phi_0 = 1/\sinh^{1/2}(2y). \quad (19)$$

The first curvature correction can also be calculated explicitly, and in the vicinity of the surface, $\phi_1 = -\frac{y^{1/2}}{2^{1/2}8} - \frac{3\tilde{d}^2}{2^{1/2}8y^{3/2}}$. The polymer contribution to the bending modulus is still dominated by the first term in equation (14)

$$\delta k_c = -\frac{1}{96} \frac{kT a^3}{w} \log(1/\tilde{d}). \quad (20)$$

At leading order in \tilde{d} , the polymer contribution to the bending modulus is negative and as in a good solvent, the first correction is positive and of order $(kT a^3/w)$.

4. Concluding Remarks

The main result of this paper is that, in agreement with the previous work, in all the cases that we were able to study, the contribution of an adsorbed polymer layer to the bending modulus of a membrane is negative and the contribution to the Gaussian curvature modulus is positive.

The Gaussian curvature modulus is given by a moment of the pressure distribution in a flat layer and thus its calculation does not require the determination of the adsorbed polymer concentration profile in a curved geometry. In the mean field theory that we use, the sign of this modulus is independent of the explicit form of the free energy and the polymer contribution to the Gaussian curvature modulus is always positive. Quite similarly to the mechanical model proposed by Helfrich, the determination of the bending modulus requires the expansion of the concentration profile to first order in curvature. The adsorbed polymer always makes the membrane less stiff in both cases of reversible and irreversible adsorption.

We have considered here that in an irreversibly adsorbed layer, the total adsorbed polymer amount is constant and that the chain conformation in the layer can reequilibrate freely. The irreversibility can however be stronger, for example, the number of monomers in contact with the surface or the loop distribution can be frozen. We, of course, expect that the membrane is stiffer (and that δk_c increases) if the constraint imposed by the irreversibility gets stronger.

The polymer contribution to the modulus can eventually become positive as for a polymer brush. Many authors have in particular modelled adsorbed polymer layers in terms of pseudo-brushes which are polydisperse grafted polymer layers with a fixed distribution of chain or loop sizes *i.e.* a fixed number of grafting points. It is reasonable to assume that for a polydisperse polymer brush, the polymer contribution to the bending modulus is positive. The difference with the adsorbed polymer layer where the surface concentration is free to reequilibrate upon bending is thus due to the redistribution of the short loops that lead to the negative contribution to the bending modulus.

In all the examples that we have studied, the moduli are dominated by the short distances *i.e.* by the short loops that the polymer makes on the surface. We have thus considered only loops and ignored the tail contributions to the polymer concentration profiles. The tail contribution to the modulus could be included in equation (6) but this contribution remains small. When the tails are taken into account, the large distance cutoff is not the size of the layer ξ but the crossover length between the loops and tail regions z^* .

The major assumption made in this work is the use of the mean field theory. This is a reasonable assumption for a polymer in a θ solvent where our results are reliable but this is not a good approximation in a good solvent where the concentration fluctuations are known to be relevant. We do not know of any study of the curvature moduli of adsorbed polymer layers that treat correctly the excluded volume correlations. Brooks *et al.* have used a so-called Widom approximation which is a rescaled mean field theory that produces the correct scaling exponents [14]. This approximation leads qualitatively to the same predictions as the mean field theory but it is rather uncontrolled and although it produces clearly the right scaling behavior of the moduli, it is not clear whether the amplitudes and thus the sign of the moduli are reliable.

We also have treated the polymer layer using the continuous theory which is appropriate to semi-dilute solutions. This theory may not be too accurate in the vicinity of the adsorbing surface where the polymer concentration is high and where the molecular details may become important. This could strongly affect the values of the bending moduli.

Finally it would be interesting to compare directly our results to experiments. The numerical prefactors given by the mean field theory are however very small and the polymer contribution to the moduli always seems smaller than kT .

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