Membranes with anchored polymers at the adsorption transition

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Abstract. – Polymers which are anchored to membranes exert bending moments onto these membranes. It is shown by general scaling arguments and explicit calculations for ideal chains i) that the polymer-induced "spontaneous" curvature $M_{\rm sp}$ has the scaling form $\Omega_{\rm sp}(\epsilon N^{\phi})/N^{\nu}$, where N and ϵ are the chain length and the distance from the adsorption-desorption transition, respectively, and ii) that $M_{\rm sp}$ changes its sign close to this transition. Thus, if the polymer and the membrane experience effectively attractive and repulsive interactions, the membrane is bent *towards* and *away from* the polymer, respectively.

Membranes consisting of layers of amphiphilic molecules are rather flexible and thus can be easily deformed (for recent reviews, see [1]). If such a membrane has two different sides or faces, it should prefer a curved rather than a planar state and, thus, should exhibit a spontaneous curvature. The latter quantity which has been introduced some time ago for monolayers [2] and bilayers [3] is both appealing from an intuitive point of view and is conjugate to the total mean curvature which is one of the basic measures of integral geometry [4], [5]. However, for a given physical system, the magnitude of the spontaneous curvature is rather difficult to estimate since it depends, in general, on many molecular parameters.

In this letter, we continue to explore the possibility to control the spontaneous curvature of a fluid membrane by decorating it with anchored polymers. Indeed, it has been previously shown that an anchored polymer which is repelled from the membrane surface exerts entropic or fluctuation-induced forces which act to bend the membrane *away* from it [6], [7]. It will be shown below that the opposite effect occurs if the membrane experiences *attractive* interactions with the polymer: the membrane now bends *towards* the polymer in order to maximize the number of contact points. In fact, in the limit of long chains, the sign of the polymer-induced curvature is found to change close to the adsorption-desorption transition. Therefore, anchored polymers close to such a transition provide a kind of "curvature switch".

We will focus on the dilute regime which consists of separate polymer "mushrooms" and "pancakes" for the desorbed and adsorbed state, respectively. This regime, which is governed

by the behavior of single chains, applies up to the overlap concentration at which the parallel extension of the anchored polymers becomes comparable to the separation of their anchors. For larger coverage, one has i) squeezed brushes for the strongly desorbed case as discussed in ref. [7], and ii) interpenetrating pancakes for the strongly adsorbed case as studied by mean-field theory in ref. [8]. The results of these latter studies are consistent with the general trend obtained below: the polymer-induced curvature is positive for desorption but negative for adsorption.

To proceed, let us consider a linear polymer chain which consists of N monomers (or statistical segments) of size $a_{\rm po}$ and which is anchored with one of its ends to the surface of a membrane. The forces between the anchored polymer and the surface are described by the interaction potential $V(\mathbf{r})$ which is the potential energy *per monomer* at position $\mathbf{r}$. Apart from the repulsive hard-wall potential arising from the impenetrable membrane surface, this interaction potential contains a short-ranged attractive part characterized by a potential well of depth $U < 0$ and range l_v. If the potential well is sufficiently attractive, the polymer will be adsorbed onto the membrane.

The adsorption of single chains onto *planar* surfaces has been studied in some detail, see, *e.g.*, ref. [9]-[12]. The adsorbed chain forms a pancake which is characterized by its thickness $L_\perp$ and its lateral extension $L_\parallel$ with $L_\parallel \gg L_\perp$ for large N. For an ideal chain, the free-energy difference $\delta\mathcal{F}_{\rm hs}$ between the adsorbed pancake and the unbound polymer state can be estimated as

$$\delta\mathcal{F}_{\rm hs}/L_\parallel^2 \simeq T/L_\perp^2 + (U/a_{\rm po}^2 + T/l_v^2)\mathcal{P}_{\rm b}, \tag{1}$$

where dimensionless coefficients of order one have been ignored (the subscript "hs" means "half space"). The first term in (1) gives the excess free energy arising from the entropy loss of the ideal chain. The second term gives the binding free energy within the short-ranged potential. The strength $U < 0$ is reduced by the entropic loss $\sim T/l_v^2$ within the potential well. The factor $\mathcal{P}_{\rm b}$, which describes the probability of a monomer to be bound inside this potential, can be obtained in a simple way, if one assumes that the adsorbed film has constant (monomer) density [9]. Indeed, the latter assumption implies that this probability is given by the partial volume $\simeq L_\parallel^2 l_v$ of the pancake, which is located within the potential well, divided by the total volume $\simeq L_\parallel^2 L_\perp$ of the pancake and, thus, by $\mathcal{P}_{\rm b} \simeq l_v/L_\perp$.

The thickness $L_\perp$ of the adsorbed polymer can now be obtained by minimization of $\delta\mathcal{F}_{\rm hs}$. It is convenient to introduce the dimensionless variable $u \equiv (l_v/a_{\rm po})^2 U/T$ which measures the overall strength of the attractive potential. The free energy $\delta\mathcal{F}_{\rm hs}$ has a minimum as a function of $L_\perp$ as long as $u < u_* \equiv -1$. The value of $L_\perp$ as determined from this minimum is given by $L_\perp = 2l_v/|\epsilon|$ with the critical parameter $\epsilon \equiv (u - u_*)/|u_*|$. Thus, in the limit of large N, the pancake thickness $L_\perp$ diverges as the transition point at $\epsilon = 0$ is approached from below.

It is not difficult to extend this scaling picture to curved surfaces if one assumes again i) that $L_\parallel \gg L_\perp$ and ii) that the monomer density within the pancake is constant. Similar assumptions have previously been used for polymer adsorption on colloidal particles [13]. For a spherical surface with mean curvature M and for $L_\perp > l_v$, one then obtains the probability

$$\mathcal{P}_{\rm b} \approx (l_v/L_\perp)(1 - (L_\perp - l_v)M) \quad \text{for} \quad L_\perp > l_v \tag{2}$$

to leading order in M. Note that $M = 1/R > 0$ and $M = -1/R < 0$, if the polymer is adsorbed *outside* and *inside* of the sphere, respectively.

Minimization of (1) with $\mathcal{P}_{\rm b}$ as given by (2) now leads to the excess free energy $\delta\mathcal{F}/L_\parallel^2 \approx \delta\mathcal{F}_{\rm hs}/L_\parallel^2 + T(2|\epsilon| - \epsilon^2)M/2l_v$ to leading order in M. In the large-scale limit with $L_\perp/l_v =$

$2/|\epsilon| \gg 1$, one then obtains

$$\Delta\mathcal{F}_{\mathrm{po}} \equiv \delta\mathcal{F} - \delta\mathcal{F}_{\mathrm{hs}} \approx 2T(L_\parallel^2/L_\perp)M \qquad \text{for small } M . \tag{3}$$

Since $\Delta\mathcal{F}_{\mathrm{po}} \sim M$, the adsorbed polymer prefers $M < 0$ and thus to be *inside* of the curved surface.

The form as given by (3) can be generalized if one assumes i) that $\Delta\mathcal{F}_{\mathrm{po}}$ has a well-defined limit for small potential range l_v and ii) that the microscopic length scale a_{po} enters $\Delta\mathcal{F}_{\mathrm{po}}$ only via the mesoscopic scales $L_\parallel$ and $L_\perp$. For a curved surface of mean curvature M and Gaussian curvature G, these assumptions lead to

$$\begin{aligned}
\Delta\mathcal{F}_{\mathrm{po}}/T &= f(L_\parallel/L_\perp, L_\parallel M, L_\parallel G) \\
&\approx f_1(L_\parallel/L_\perp)L_\parallel M + f_2(L_\parallel/L_\perp)(L_\parallel M)^2 + f_3(L_\parallel/L_\perp)L_\parallel^2 G ,
\end{aligned} \tag{4}$$

for small curvatures, which defines three scaling functions f_1, f_2, and f_3.

The length scales $L_\parallel$ and $L_\perp$, which appear in the small-curvature expansion in (4), are those corresponding to the planar surface with $M = 0$. These latter quantities scale as $L_{\parallel,\perp} = a_{\mathrm{po}}N^\nu\Omega_{\parallel,\perp}(\epsilon N^\phi)$ [10]. For ideal chains or chains in a θ-solvent, the size exponent ν and the crossover exponent ϕ which enter these scaling forms have the values $\nu = 1/2$ and $\phi = 1/2$, respectively. In addition, the scaling function $\Omega_\parallel = 1$ for ideal chains, since $L_\parallel = a_{\mathrm{po}}N^{1/2}$ for any value of ϵ. For self-avoiding chains, one has $\nu \simeq 3/5$ and $\phi \simeq 0.6$ [12].

For the adsorbed state with $\epsilon < 0$, the polymer pancake may be considered as a bound chain of blobs [14], [11]. Each blob with linear size $\simeq L_\perp$ contains $N_{\mathrm{bl}} \simeq (L_\perp/a_{\mathrm{po}})^{1/\nu}$ monomers. The blob chain undergoes a self-avoiding random walk in two dimensions which implies $L_\parallel \simeq L_\perp(N/N_{\mathrm{bl}})^{\nu_2} = L_\perp N^{\nu_2}(a_{\mathrm{po}}/L_\perp)^{\nu_2/\nu}$. The critical exponent ν_2 has the value $\nu_2 = 1/2$ and $\nu_2 = 3/4$ for ideal and self-avoiding chains, respectively.

If the scaling forms $L_{\parallel,\perp} = a_{\mathrm{po}}N^\nu\Omega_{\parallel,\perp}(\epsilon N^\phi)$ are inserted into (4), the excess free energy can be rewritten as

$$\Delta\mathcal{F}_{\mathrm{po}}/T \approx \Omega_1(y)L_\parallel M + \Omega_2(y)(L_\parallel M)^2 + \Omega_3(y)L_\parallel^2 G , \tag{5}$$

with $y \equiv \epsilon N^\phi$. In the following, we will focus on the properties of the scaling function Ω_1 which governs the polymer-induced spontaneous curvature.

For the adsorbed state with $\epsilon < 0$, the excess free energy $\Delta\mathcal{F}_{\mathrm{po}}$ must be extensive for large N, which implies $\Delta\mathcal{F}_{\mathrm{po}} \sim N \sim L_\parallel^{1/\nu_2}$. Using the scaling properties of ideal chains, one then recovers the functional dependence as given by (3), which implies that $\Omega_1(y) > 0$ for $y = \epsilon N^\phi < 0$. The desorbed polymer state, on the other hand, corresponds to $y = \epsilon N^\phi > 0$. It has previously been shown that $\Omega_1(y) < 0$ for the strongly desorbed state corresponding to large positive y [6], [7]. Therefore, the function $\Omega_1(y)$ must change its sign at a certain value $y = \epsilon N^\phi = y_0$.

The free-energy gain $\Delta\mathcal{F}_{\mathrm{po}}$ of the anchored polymer is balanced by the increase in the bending energy $\Delta\mathcal{E}_{\mathrm{me}}$ of the membrane segment affected by the polymer, which is given by $\Delta\mathcal{E}_{\mathrm{me}} = 2c_A\kappa(L_\parallel M)^2 + c_A\kappa_G L_\parallel^2 G$, since the area of this segment is $\mathcal{A} = c_A L_\parallel^2$ with c_A of order one. The total excess free energy of the membrane/polymer system is now given by $\Delta\mathcal{F} \equiv \Delta\mathcal{E}_{\mathrm{me}} + \Delta\mathcal{F}_{\mathrm{po}}$, which leads to the polymer-induced spontaneous curvature

$$M_{\mathrm{sp}} = -T\Omega_1(\epsilon N^\phi)/4c_A\kappa L_\parallel = -(T/4c_A\kappa)\Omega_{\mathrm{sp}}(\epsilon N^\phi)/a_{\mathrm{po}}N^\nu \tag{6}$$

with $\Omega_{\mathrm{sp}}(y) \equiv \Omega_1(y)/\Omega_\parallel(y)$. In this estimate, we have ignored the change of the bending rigidity κ arising from the Ω_2-term in (5). It is shown elsewhere that this change is of order T both for desorbed [7] and for adsorbed [15] chains.

Since the length scale $L_\parallel$ is always positive, the relation (6) implies that the polymer-induced spontaneous curvature changes its sign at $\epsilon N^\phi = y_0$ with $\Omega_1(y_0) = 0$. As shown below, $y_0 = 0$ for ideal chains if one considers the simplest model with a curvature-independent extrapolation length. Thus, in this case, the curvature switches directly at the adsorption transition. However, even for $y_0 \neq 0$, the curvature switch at $\epsilon = \epsilon_0 \equiv y_0/N^\phi$ will be close to the adsorption transition for long chains since ϵ_0 goes to zero for large N.

For the case of ideal chains with crossover exponent $\phi = 1/2$, the function $\Omega_{\rm sp}(y) = \Omega_1(y)$ with $y = \epsilon N^{1/2}$ can be derived explicitly as shown next. If an ideal chain is anchored at position $\mathbf{r}_{\rm an}$ and has its other end at position $\mathbf{r}$, the partition function is of the form $q^N Z(\mathbf{r}_{\rm an}|\mathbf{r}, N)$, where q describes the number of ways in which one may add a monomer to the chain ($q = 6$ for a simple cubic lattice). The reduced partition function Z satisfies the Schrödinger-type equation [16], [17]

$$\left[\frac{\partial}{\partial t} - \nabla_r^2 + V(\mathbf{r})/DT\right] Z(\mathbf{r}_{\rm an}|\mathbf{r}, t) = 0 \quad \text{for} \quad t > 0, \tag{7}$$

with $t \equiv Na_{\rm po}^2/q$, $D \equiv a_{\rm po}^2/q$, and the "initial condition" $Z(\mathbf{r}_{\rm an}|\mathbf{r}, t = 0) = \delta^{(3)}(\mathbf{r}_{\rm an} - \mathbf{r})$,.

In the presence of the membrane surface with area $\mathcal{A}$, the polymer can explore the volume $\mathcal{V}$. The short-ranged interaction potential $V(\mathbf{r})$ in front of the surface will be replaced by the boundary condition

$$\hat{n} \cdot \nabla_r Z(\mathbf{r}_{\rm an}|\mathbf{r}, t) = Z(\mathbf{r}_{\rm an}|\mathbf{r}, t)/l_{\rm ex} \tag{8}$$

for $\mathbf{r}$ at the surface where the normal vector $\hat{n}$ points *into* the volume $\mathcal{V}$. In general, the *extrapolation length* $l_{\rm ex}$ may depend on the curvature of the surface [18] and will then behave as $l_{\rm ex} \approx l_0(1 + l_1 M)$ for small M, where l_1 depends on the details of the molecular forces. For a planar surface, the inverse extrapolation length $1/l_0$ is proportional to the critical parameter ϵ which measures the distance from the adsorption transition of the ideal chain [12]; negative and positive values of $1/l_0$ correspond to adsorbed and desorbed chains, respectively.

In the following, we will focus on the statistical weight:

$$\mathcal{Z}(\mathbf{r}_{\rm an}|t) \equiv \int d\mathbf{r} \ Z(\mathbf{r}_{\rm an}|\mathbf{r}, t) \tag{9}$$

with $\mathcal{Z}(\mathbf{r}_{\rm an}|t = 0) = 1$. Direct integration of the differential equation (7) (with V replaced by the boundary condition (8)) leads to the relation

$$\mathcal{Z}(\mathbf{r}_{\rm an}|t) = 1 - (1/l_{\rm ex}) \oint_{\mathcal{A}} d\mathbf{r} \int_0^t dt' \ Z(\mathbf{r}_{\rm an}|\mathbf{r}, t'), \tag{10}$$

where $\oint d\mathbf{r}$ represents the integral over the membrane surface. This relation implies $\mathcal{Z}(\mathbf{r}_{\rm an}|t) = 1$ for $1/l_{\rm ex} = 0$ and *arbitrary* $t \geq 0$. Therefore, the excess free energies $\delta\mathcal{F} = -T \ln \mathcal{Z}$ and $\Delta\mathcal{F}_{\rm po} = \delta\mathcal{F} - \delta\mathcal{F}_{\rm hs}$ must vanish at $1/l_{\rm ex} = 0$ *irrespective* of the shape of the membrane surface. Since $\Delta\mathcal{F}_{\rm po}$ is identically zero for $1/l_{\rm ex} = 0$, all terms of the small-curvature expansions as given by (4) and (5) must also vanish.

For a spherical surface segment with mean curvature M, one can explicitly calculate the statistical weight $\mathcal{Z}$ for a polymer anchored at distance $l_{\rm an}$ from this surface. Extending the results of ref. [19], one then arrives, in the limit of small $l_{\rm an}$, at the closed expression

$$\mathcal{Z}(l_{\rm an} = 0|t) = A_1 + A_2 \ \exp[t(M + 1/l_{\rm ex})^2] \ \text{erfc}[\sqrt{t}(M + 1/l_{\rm ex})] \tag{11}$$

with $A_1 \equiv M/(M + 1/l_{\rm ex})$, $A_2 \equiv 1/(1 + Ml_{\rm ex})$, and the complementary error function $\text{erfc}(y)$. It now follows that $\Delta\mathcal{F}_{\rm po} = -T \ln(\mathcal{Z}/\mathcal{Z}_{\rm hs}) \approx T\Omega_1(\sqrt{t}/l_0)L_\parallel M$ for small M with

$L_\parallel = \sqrt{qt} = a_{\mathrm{po}} N^{1/2}$ and the scaling function

$$\Omega_1(y) = \left[1 - 2\lambda y^2 + \frac{-1 + 2\lambda y/\sqrt{\pi}}{\exp[y^2]\mathrm{erfc}(y)} \right] / \sqrt{q}y \,, \tag{12}$$

which depends on the scaling variable $y \equiv \sqrt{t}/l_0 = a_{\mathrm{po}} N^{1/2}/\sqrt{q}l_0 \sim \epsilon N^{1/2}$ and on the parameter $\lambda \equiv 1 - l_1/l_0$. In the limit of small l_1, in which the extrapolation length becomes curvature-independent, the function $\Omega_1(y)$ vanishes at $y = y_0 = 0$, and one has $\Omega_1(y) > 0$ and $\Omega_1(y) < 0$ for the adsorbed and desorbed state, respectively.

If the anchor of the polymer represents a strong perturbation of the local membrane structure, the membrane segment which is affected by the polymer may be deformed into a shape with a point-like defect. One possibility is that the membrane segment forms a cone-like shape with the polymer anchored to the apex of the cone. The surface of the cone is defined by the angle ψ_{co} which measures the deflection from the planar surface. For $\psi_{\mathrm{co}} < 0$ and $\psi_{\mathrm{co}} > 0$, the polymer is anchored inside and outside of the cone, respectively. For this geometry, one obtains the excess free energy

$$\Delta\mathcal{F}_{\mathrm{po}}/T \approx (2/\sqrt{\pi q}) \left(\frac{\cos\psi_{\mathrm{co}}}{1 + \sin\psi_{\mathrm{co}}} - 1 \right) a_{\mathrm{po}} N^{1/2}/l_{\mathrm{ex}} \tag{13}$$

up to first order in $1/l_{\mathrm{ex}}$. Since the prefactor is proportional to $-\psi_{\mathrm{co}}$ for small ψ_{co}, one finds again that the anchored polymer prefers to sit inside and outside of the cone if it is adsorbed and desorbed, respectively.

In summary, we have shown that the curvature induced by anchored polymers changes its sign close to the adsorption-desorption transition and exhibits a scaling form as derived from rather general arguments and explicitly calculated for ideal chains. The anchored polymers also induce contributions to the bending rigidities of the membrane as determined in ref. [7] for the desorbed case. Close to the adsorption transition, these excess rigidities again scale with the chain length N and with the distance from the transition, as will be discussed elsewhere [15].

After the completion of this work, we received a preprint by Eisenriegler, Hanke and Dietrich [20] about polymers interacting with spherical and rod-like particles: for ideal chains, these authors derive a statistical weight, which is equivalent to (11), and obtain results for generalized cylinder surfaces, which are consistent with our general relation (10). These authors also find that a flexible surface in contact with a dilute solution of *non*-anchored polymers prefers to bend *towards* the solution if the surface *repels* the polymers. This disagrees with the results of Podgornik [21] who found, for reasons we do not understand, that the surface bends *away* from the non-attached polymers. Another issue addressed in [20] is the adsorption transition on cylindrical surfaces, a situation which is equivalent to the one studied in ref. [22].

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