Membrane curvature induced by polymers and colloids

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Abstract

Polymers and colloids change the 'spontaneous' curvature of flexible membranes such as lipid bilayers. Two general cases will be discussed: (i) The effect of single polymers or colloids which are *anchored* or *adsorbed* to the membranes and exert bending moments on the adjacent membrane segments; and (ii) the effect of unbalanced tensions in the two membrane/water interfaces which arise, e.g., from polymer brushes and from non-anchored polymers or colloids. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

All biomembranes consist of a bilayer of lipids and a large number of polymers which are attached to the membrane via hydrophobic anchors [1]. These molecules are usually connected to relatively stiff, rod-like filaments which belong to the cytoskeleton or to the extracellular matrix. Some fundamental aspects of these rather complex systems can be studied in model systems consisting of lipid bilayers and polymers.

In this review, we will focus on one such fundamental aspect: how is the 'spontaneous' curvature of the membranes affected by the polymers? Here and below, 'spontaneous' appears in quotes since this curvature arises from the interactions of the membrane with its surroundings. The concept of such a curvature has been introduced a long time ago for monolayers [2] and bilayers [3]. However, it has been usually treated as a phenomenological parameter since its magnitude depends, in general, on the details of the molecular structure. In contrast, the spontaneous curvature induced by the membrane/polymer interactions is usually governed by a *single* length scale such as

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the size of the polymer coil and thus exhibits simple scaling properties [4–6]. As explained below, similar scaling properties apply to membranes which interact with other colloidal particles.

The curvature effects discussed here should be accessible to experiments on vesicles. Indeed, it has been shown recently that one can deduce the 'spontaneous' curvature of the vesicle membrane from observations of the vesicle shapes [7,8]. Systematic studies in this direction are currently pursued in our laboratory.

The paper is organized as follows. First, we consider in Section 2 the dilute limit of single chains which are anchored or adsorbed onto the membranes. A more coarse–grained approach is described in Section 3, where the effects of the polymers and colloids are discussed in terms of unbalanced tensions for the two membrane/water interfaces. Finally, Section 4 contains some remarks about possible checkerboard states of the membranes induced by polymers or colloids.

2. Anchored polymers

To proceed, let us consider a membrane segment with a *single* polymer anchored or adsorbed to it. We will focus on linear polymer chains and distinguish several cases. For each case, we consider the free energy $\mathscr{F}_{po}$ of the attached polymer and its dependence on the mean curvature M of the membrane surface. In general,

$$\mathscr{F}_{po} \approx \mathscr{F}_0 + \mathscr{F}_1 LM \quad \text{for small } M, \tag{1}$$

where L is a characteristic length scale to be determined below.

For a tensionless membrane, the energy increase corresponding to the bending of the membrane is given by $\Delta\mathscr{E}_{me} = 2\kappa M^2 L^2$, where κ is the bending rigidity. If $\Delta\mathscr{E}_{me}$ is balanced against the polymer free energy $\mathscr{F}_{po}$ as given by Eq. (1), one obtains the 'spontaneous' mean curvature

$$M_{sp} = -\mathscr{F}_1/4\kappa L \tag{2}$$

for the membrane segment adjacent to the anchored polymer.

Anchored at one end. First, consider a single chain for which the anchor is located at one of its ends and for which the non-anchored polymer segments experience *repulsive* interactions with the membrane surface. Such a polymer forms a *mushroom*, see Fig. 1. The size of these mushrooms is comparable to the size of the free polymer, i.e., to $R_{po} \simeq a_{po}N^\nu$ with the persistence length a_{po} and the size exponent ν. The latter exponent is $\nu \simeq \frac{3}{5}$ for good solvents and $\nu = \frac{1}{2}$ for θ-solvents or ideal chains, see, e.g., Ref. [9].

The polymer size R_{po} represents the basic length scale L which enters in the curvature expansion, Eq. (1). In addition, the free energy $\mathscr{F}_1$ is found to be $\mathscr{F}_1 \simeq -T$. Therefore, the general relation, Eq. (2) leads to [4]

$$M_{sp} \sim +T/\kappa R_{po} \sim +T/\kappa a_{po}N^\nu \quad \text{for mushrooms,} \tag{3}$$
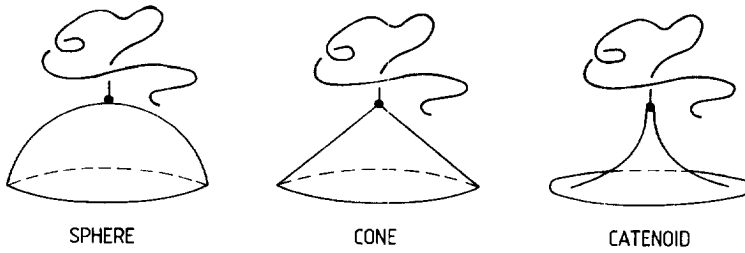
Fig. 1. Polymer mushrooms at the membrane segments of different shape.

where T is the temperature in energy units. The positive sign of M_{sp} in Eq. (3) implies that the membrane bends *away* from the polymer in order to increase the configurational entropy of the chain.

Anchored at both ends. If the polymer chain is anchored at *both* ends, one has two competing effects [10,11]. When the two ends are close together, the polymer forms an anchored ring and the membrane again bends away from the chain. On the other hand, if both ends are far apart, the polymer is in a stretched state and then pulls on the membrane.

For ideal chains with $v = \frac{1}{2}$, these two competing effects cancel to leading order. Indeed, for a spherical surface, the curvature expansion of the polymer free energy leads to $\mathcal{F}_{po}^{ex} = \mathcal{F}_0$ for $M > 0$ and

$$\mathcal{F}_{po}^{in} \approx \mathcal{F}_0 - \mathcal{C}(\exp(-1/R_{po}^2 M^2)) \quad \text{for } M < 0; \tag{4}$$

for a cylindrical surface, one has

$$\mathcal{F}_{po} \approx \mathcal{F}_0 - cTR_{po}^2 M^2 \quad \text{for all } M. \tag{5}$$

Since $\mathcal{F}_{po}$ does not contain a term $\sim M$, ideal chains anchored with both ends do not induce a 'spontaneous' curvature in the usual sense. Because the leading term $\sim M^2$ in Eq. (5) is *negative*, a very flexible membrane with a relatively small bending rigidity κ could become unstable with respect to cylindrical deformations; in this case, the up–down symmetry would be broken spontaneously. It remains to be seen how this behavior is affected by self-avoidance.

Chains with several anchors. Next, consider an ideal chain with several anchors which partition the chain into m segments. Its partition function factorizes into a product of m partition functions, where each factor represents one chain segment. Those chain segments which are bounded by two anchors do not contribute to the 'spontaneous' curvature. Therefore, bending moments arise only from those ends which are not anchored. If both end segments are free and consist of N_1 and N_m monomers, respectively, they lead to

$$M_{sp} \simeq (T/\kappa)(R_1 + R_m)/R_{po}^2 \tag{6}$$

with $R_1 = a_{po}N_1^{1/2}$ and $R_m = a_{po}N_m^{1/2}$ for ideal chains.

Adsorbed chains. If the non-anchored segments of the chain experience *attractive* interactions with the membrane surface, the polymer will form an adsorbed *pancake*. Scaling arguments predict that the membrane now bends *towards* the polymer in order to maximize the number of contact points with the pancake. An expicit calculation for ideal chains shows, however, that the sign of M_{sp} may, in general, depend on microscopic parameters [6].

The attractive potential between the polymer and the surface is usually described by the so-called *extrapolation length* l_{ex}, see, e.g., Ref. [12]. In general, this length scale may depend on the curvature of the surface [13,6] and will then behave as $l_{ex} \approx l_0(1 + l_1 M)$ for small M. For a planar surface, the inverse extrapolation length $1/l_0$ measures the distance from the adsorption transition of the ideal chain; negative and positive values of $1/l_0$ correspond to adsorbed and desorbed chains, respectively.

For ideal chains, the free energy $\mathscr{F}_{po}$ can be calculated explicitly [6,14,15] and one finds (i) that the basic length scale L is provided by the lateral size $L_{\parallel} = a_{po}N^{1/2}$ of the pancake and (ii) that the free energy $\mathscr{F}_1 = T\Omega_1(y)$ with $y \simeq a_{po}N^{1/2}/l_0$. In the adsorbed regime away from the adsorption transition, one has

$$\mathscr{F}_1 \approx c\lambda Ta_{po}N^{1/2}/|l_0| \quad \text{with } \lambda \equiv 1 - l_1/l_0, \tag{7}$$

which depends on the parameter ratio l_1/l_0 [6]. This leads to

$$M_{sp} \simeq \lambda T/\kappa L_{-} \quad \text{for pancakes,} \tag{8}$$

where $L_{\perp} \simeq |l_0|$ decribes the thickness of the pancake.

Therefore, the sign of the 'spontaneous' curvature is *negative* for $l_1/l_0 < 1$ but *positive* for $l_1/l_0 > 1$, and the membrane bends *towards* and *away* from the polymer in these two cases, respectively. For a contact potential, one expects $l_1/l_0 = 0$ and the membrane bends *towards* the polymer [6]. It is conceivable, however, that sufficiently long-ranged forces lead to $l_1/l_0 > 1$ and, thus, to the opposite curvature. Such a non-universal behavior could also apply to adsorption layers consisting of many polymer chains. In the latter case, it has been proposed by de Gennes [16] that the membrane bends *away* from the adsorption layer whereas Brooks et al. [17] found from a self-consistent calculation that the membrane bends *towards* the adsorbed polymers.

Collapsed chains and colloidal particles. So far, we have assumed that the anchored polymers are swollen, i.e., that they are in good or θ solvent. A somewhat different situation is encountered for collapsed chains, i.e., for chains in bad solvent.

To a first approximation, a collapsed chain behaves like a fluid droplet characterized by a finite surface tension and will thus attain a near-spherical state with radius R_{po}. If such a droplet is anchored to the membrane, the configurational entropy of its desorbed state will be determined, to a large extent, by the structure of the anchor. In the adsorbed state, on the other hand, the tensionless membrane will try to encapsulate the droplet.

Thus, consider a state in which the droplet is completely contained in a spherical membrane bud. The adhesive energy of this state is given by $W4\pi R_{po}^2$, where $W < 0$

is the adhesive energy per unit area of the two surfaces. The bending energy of the membrane bud is $8\pi\kappa$. Therefore, encapsulation is energetically favored as soon as

$$R_{po} \gtrsim R_* \equiv \sqrt{2\kappa/|W|}\,. \tag{9}$$

The same behavior applies to colloidal particles which have a near-spherical shape and a radius which exceeds R_*.

3. Unbalanced interfacial tensions

Let us now consider a situation in which the membrane is exposed to many polymers or colloids and let us assume that the interaction between the membrane surface and these particles can be described by a change in the interfacial tension of the two membrane/water interfaces. We will also assume that there is no tendency for phase separation which implies that the interfacial tensions are uniform along the membrane. As soon as the corresponding interfacial tensions are different, they will induce a 'spontaneous' curvature of the layer as envisaged in the classical work of Bancroft and Tucker [2].

If the neutral surface of the membrane has area A and mean curvature M, the areas A^{in} and A^{ex} of its interior and its exterior interface are given by $A^{ex} \approx (1 + l_{me}M)A$ and $A^{in} \approx (1 - l_{me}M)A$, respectively, where l_{me} denotes the membrane thickness. In addition, the interfacial tensions, Σ^{in} and Σ^{ex}, of these two lipid/water interfaces will depend on M, and one has

$$\Sigma \approx \Sigma_0 + \Sigma_1 LM \quad \text{for small } M, \tag{10}$$

where L is again an appropriate length scale which will be specified further below. If one now compares the flat and the curved state, one obtains the excess free energy

$$\Delta\Sigma \approx [l_{me}(\Sigma_0^{ex} - \Sigma_0^{in}) + L^{ex}\Sigma_1^{ex} - L^{in}\Sigma_1^{in}]M \tag{11}$$

of the curved state up to first order in M.

If the excess free energy $\Delta\Sigma$ is balanced against the bending energy $2\kappa M^2 A$, one obtains the tension-induced curvature

$$M_{sp} = [l_{me}(\Sigma_0^{in} - \Sigma_0^{ex}) + L^{in}\Sigma_1^{in} - L^{ex}\Sigma_1^{ex}]/4\kappa. \tag{12}$$

In general, the bending rigidity κ also contains contributions arising from the second-order terms of $\Delta\Sigma$ but this will not be discussed here. If Σ_0 and Σ_1 have different signs, the 'spontaneous' curvature as given by Eq. (12) may be positive or negative.

Several cases will now be considered for which the curvature expansion, Eq. (10), has been explicitly performed.

Polymer brushes. If the coverage of the membrane by anchored polymers is larger than the overlap coverage, one enters the brush regime [5,18,19]. The properties of such a brush depend on the reduced coverage $\bar{\Gamma} = (a_{po}/\xi_{an})^2$, where ξ_{an} is the mean

anchor separation (which is taken to be curvature independent here). In this case, the basic length scale L which enters in Eq. (10) is given by the brush height h_0. Within the usual blob picture, one finds

$$L = h_0 = N \bar{\Gamma}^{(1-v)/2v} a_{po}. \tag{13}$$

In addition, the interfacial tensions in Eq. (10) are

$$\Sigma_0 = (T/a_{po}^2)N \bar{\Gamma}^{1+1/2v} \quad \text{and} \quad \Sigma_1 = -\Sigma_0/2v. \tag{14}$$

Since $\Sigma_1 \simeq -\Sigma_0$, even the asymmetric case, in which only one side of the membrane is covered by a brush, can lead to a positive or a negative 'spontaneous' curvature depending on the relative size of the membrane thickness l_{me} and the brush height h_0. For $h_0 \gg l_{me}$, the terms arising from Σ_1 dominate and $M_{sp} > 0$ corresponding to a membrane which bends away from the brush [5].

Non-anchored polymers and colloids. The excess free energy arising from a dilute solution of non-anchored polymers has been calculated in Ref. [14]. The corresponding curvature expansion leads to $L = R_{po}$ and to the interfacial tensions

$$\Sigma_0 = Tn2R_{po}/\sqrt{\pi} \quad \text{and} \quad \Sigma_1 = \sqrt{\pi}\Sigma_0/2 \tag{15}$$

for n polymers per unit volume. If the polymers are only on the exterior side, e.g., one has

$$M_{sp} = -(T/2\sqrt{\pi}\kappa)n^{ex}R_{po}^{ex}(l_{me} + \sqrt{\pi}R_{po}^{ex}/2) \tag{16}$$

and the membrane bends *towards* the polymer solution.

Essentially, the same behavior also applies to dilute solutions of spherical colloids with radius R_{co}. Indeed, all formulas remain valid (apart from numerical coefficients of order one) if the size R_{po} of the polymer coils is replaced by the size R_{co} of the colloids. If the colloids are thin rods, the curvature expansion of the interfacial tension leads to $\Sigma_0 > 0$ but $\Sigma_1 = 0$ [20] and the only contribution to the 'spontaneous' curvature arises from the membrane thickness.

Electrolytes. Another case for which the curvature expansion, Eq. (10), has been considered are bilayers in electrolytes. In this case, the basic length scale is provided by the Debye–Hückel screening length l_{DH}. Using the results of Refs. [21–23], one obtains the interfacial tensions

$$\Sigma_0 = Q^2 l_{DH}/2\varepsilon \quad \text{and} \quad \Sigma_1 = -\Sigma_0, \tag{17}$$

where Q and ε are the surface charge per unit area and the static dielectric constant, respectively, in SI units. Since $\Sigma_1 = -\Sigma_0$, the 'spontaneous' curvature M_{sp} can again be positive or negative and it is small if $l_{DH} \simeq l_{me}$.
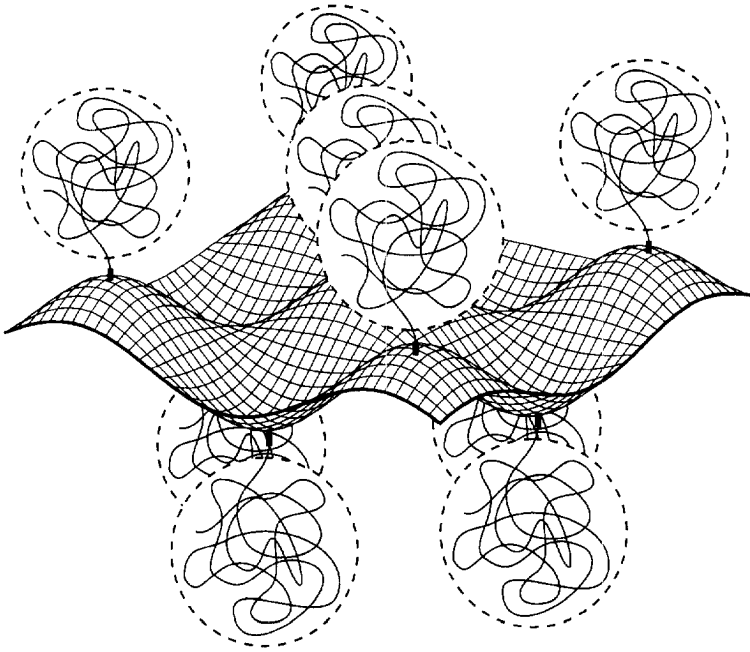
Fig. 2. Checkerboard array of mushrooms.

4. Checkerboard states

Two mushrooms or pancakes which are anchored to two different sides of the membrane want to *avoid* each other: If we force two such polymers to be directly opposite to each other, we loose the free energy $2\Delta\mathscr{F}$ where $\Delta\mathscr{F} \sim \kappa M_{sp}^2 \mathscr{A}_{do}$ is the free energy gained for each curved membrane domain and $\mathscr{A}_{do}$ is the domain area. For mushrooms and pancakes, one has $\Delta\mathscr{F} \sim T^2/\kappa$ and $\Delta\mathscr{F} \sim (T^2/\kappa)(R_{po}/L_\perp)^2$, respectively. In general, the domains may also arise from colloidal particles attached to the membrane or from lateral phase separation within the membrane.

If the coverage $\bar{\Gamma}$ is of the order of half the overlap coverage, the domains on different sides of the membrane can still avoid each other if they attain a checkerboard array and the membrane aquires a corresponding curvature modulation as displayed in Fig. 2. In such a situation, the membrane domains with $M_{sp} \neq 0$ are connected by intermediate membrane segments which consist essentially of saddle points and thus cost no bending energy (such a curvature modulation has been previously discussed in different contexts [24–26]).

The free-energy difference between the checkerboard state and the flat state is $\Delta\mathscr{F}$ per domain. Such a situation resembles an antiferromagnet with nearest-neighbor coupling constant $J \simeq -\Delta\mathscr{F}$, which undergoes a phase transition to an ordered state at $J = J_c \simeq -0.5\,T$. Thus, for $\Delta\mathscr{F} \gtrsim 0.5\,T$, the system may exhibit ordered checkerboard states [27].

References

[1] R. Lipowsky, E. Sackmann (Eds.), Structure and Dynamics of Membranes, Handbook of Biological Physics, vol. 1, Elsevier, Amsterdam, 1995.

[2] W. Bancroft, C. Tucker, J. Phys. Chem. 31 (1927) 1681.

[3] W. Helfrich, Z. Natur. 28 C (1973) 693.

[4] R. Lipowsky, Europhys. Lett. 30 (1995) 197.

[5] C. Hiergeist, R. Lipowsky, J. Phys. (France) 6 (1996) 1465.

[6] C. Hiergeist, V. Indrani, R. Lipowsky, Europhys. Lett. 36 (1996) 491.

[7] H.-G. Döbereiner, Ph.D. Thesis, Simon Fraser University, 1995.

[8] H.-G. Döbereiner, E. Evans, M. Krans, U. Seifert, M. Wortis, Phys. Rev. E 55 (1997) 4458.

[9] P.-G. de Gennes, Scaling Concepts in Polymer Physics, Cornell University Press, Ithaca, 1979.

[10] C. Hiergeist, Ph.D. Thesis, University of Potsdam, 1997.

[11] C. Hiergeist, R. Lipowsky, in preparation.

[12] E. Eisenriegler, Polymers Near Surfaces, World Scientific, Singapore, 1993.

[13] R. Ball, M. Blunt, W. Barford, J. Phys. A 22 (1989) 2587.

[14] E. Eisenriegler, A. Hanke, S. Dietrich, Phys. Rev. E 54 (1996) 1134.

[15] V. Indrani, R. Lipowsky, in preparation.

[16] P.-G. de Gennes, J. Phys. Chem. 94 (1990) 8407.

[17] J. Brooks, C. Marques, M. Cates, J. Phys. II (France) 1 (1991) 673.

[18] S. Milner, M. Cates, Macromolecules 21 (1988) 2610.

[19] K. Hristova, D. Needham, J. Colloid Interface Sci. 168 (1994) 302.

[20] K. Yaman, P. Pincus, C. Marques, preprint.

[21] M. Winterhalter, W. Helfrich, J. Phys. Chem. 92 (1988) 6865.

[22] H.N.W. Lekkerkerker, Physica A 159 (1989) 319.

[23] B. Duplantier, Physica A 168 (1990) 179.

[24] M. Kleman, C. Williams, M. Costello, T. Gulik-Krzywicki, Phil. Mag. 35 (1977) 33.

[25] A.G. Petrov, M.D. Mitov, A. Derzhanski, Phys. Lett. A 65 (1978) 374.

[26] R. Goetz, W. Helfrich, J. Phys. II (France) 6 (1996) 215.

[27] R. Lipowsky, H. Döbereiner, C. Hiergeist, V. Indrani, Mater. Res. Soc. Symp. Proc., vol. 463, Pittsburgh, 1997, p. 81.