

Membrane curvature induced by polymer adsorption

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The phenomena resulting from interaction between polymers and membranes pose important problems for biological applications. Based on a scaling theory, we investigate the spontaneous curvature of a membrane induced by either flexible or semiflexible chain adsorption. Irrespective of chain stiffness, a weakly adsorbed polymer induces the membrane to bend away (to have a positive curvature) from the polymer mostly due to increase of the conformational entropy compared with that for a flat surface. On the other hand, a strongly adsorbed polymer induces the membrane to bend toward the polymer mostly due to decrease in the interaction energy, leading to a possibility of encapsulation of polymer by the membrane.

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I. INTRODUCTION

Polymers and membranes constitute two important ingredients of subcellular structures on mesoscopic length scales. It is remarkable that thermal fluctuation plays a significant role due to low dimensionality and flexibility in their primary structures. The conformational transitions are characteristics of soft matter that result from often-subtle interplay between interaction energy and entropy. A prominent example is the adsorption-desorption transition of a polymer near an attractive surface [1–3]. When the polymer is brought close to a membrane, the conformational fluctuation of the polymer is reduced due to the restriction of available space. The polymer thus adsorbs on the membrane if the attractive interaction dominates the entropic reduction due to the confinement, while it desorbs from the surface if the entropy dominates over the interaction.

The surface adsorption is influenced significantly by the chain stiffness typical of many biological macromolecules such as DNA, RNA, and actin filaments. The chain stiffness is described by a single length scale, the persistence length l , characteristic of segment orientational correlation. The chain persistence gives rise to the interesting features in polymer solutions, e.g., nematic liquid-crystalline (LC) ordering [4] in the bulk. In interaction with a surface, the persistence also brings about additional features of ordering transitions [5], the LC surface ordering in the adsorbed states, as studied in Ref. [6] using the Green's function theory and more simple scaling theory.

Like polymers, membranes themselves also exhibit various shape transitions such as budding and fusion in their fluid state [7]. The polymer association on membranes can have an influence on their stability and transitions [8]. The manner in which a polymer and a fluid membrane interact and affect the conformations of one another, poses a fundamental problem of biological relevance. While much attention has been paid to the flexible polymers interacting with rigid planar membranes, there are only a few studies [9–12] on shape changes and phase transitions of fluid membranes associated with the conformational fluctuations of the adsorbed polymers.

Recently, Hiegeist *et al.* [11] investigated the membrane

bending induced by adsorption transition of a flexible polymers. They studied the polymer free energy for small bending through a scaling argument as well as a calculation of partition function using the de Gennes' boundary condition. According to their result, in the adsorbed state the membrane bends toward the polymer (has negative spontaneous curvature) in order to have more surface contacts with the polymer. They considered that the polymer conformational entropy is independent of the bending, so that the interaction dominates in determining the bending direction. On the other hand, we have studied the conformations of a flexible polymer outside a curved surface based upon the grand canonical ensemble approach [12]. Our result for large curvature showed that for weak adsorption the conformational entropy of many loops increases for the positive curvature above that for a flat surface, giving rise to the possibility of polymer-induced membrane-budding transition. Compared with the above study of Hiegeist *et al.* [11], there are differences in the regimes of bending studied as well as in bending directions that resulted. Still a coherent understanding of the role of polymer adsorption on the determination of membrane bending, not only in its direction also in the magnitude, is lacking. Furthermore, the effects of polymer-adsorption strength and chain stiffness remain to be studied.

In this paper, we study the membrane spontaneous curvature induced by either flexible or semiflexible polymer adsorption. We base our arguments on a scaling theory, which retains the salient features of the physics involved. Considering first the persistence length smaller than any other length scales, we examine the case of a flexible chain and compare with the previous results [11,12] in order to clarify the competition between conformational entropy and interaction energy. Next, the case of a stiffer chain is studied, where we find the adsorption strength combined with the chain stiffness plays a dominant role in membrane bending.

We characterize the polymer attraction per segment with the membrane surface by the range b and the strength U (>0). We neglect the intersegment interactions (such as excluded volume effect) other than incorporated by chain connectivity. There is another length scale ξ characteristic of segmental density change perpendicular to the surface, the so-called polymer thickness of adsorption (Fig. 1).

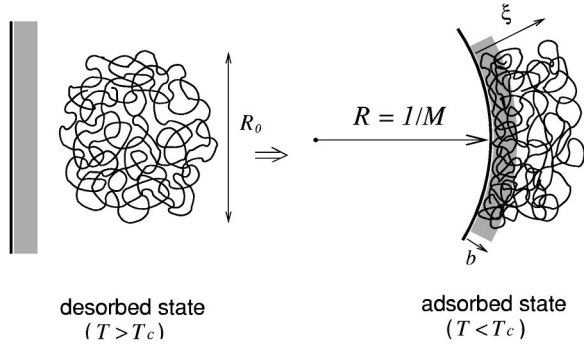


FIG. 1. A schematic figure of membrane bending induced by polymer adsorption. The thick-solid line indicates the membrane surface and the shaded region indicates the interaction range b of attractive potential. The ξ is polymer thickness of adsorption. As a polymer adsorbs on area $A \sim R_0^2$, a membrane bends to minimize total free energy, yielding a positive curvature ($M = 1/R$) in this case.

II. MEMBRANE BENDING INDUCED BY FLEXIBLE CHAIN ADSORPTION

Let us begin with a brief review on the scaling theory for weak adsorption of a long flexible polymer with a segmental number N ($N \gg 1$) onto a planar surface [3,6,11]. The persistence length l is now the Kuhn's segmental length. The free energy F of adsorption is

$$F = E - T(S_b + S_\xi). \quad (1)$$

The first term is the attraction energy acquired by adsorption, $E = -UN_b$. The N_b is the number of segments bound within the attraction range,

$$N_b \approx \frac{V_b}{V_\xi} N \approx \frac{b}{\xi} N. \quad (2)$$

Here $V_b = Ab$ and $V_\xi = A\xi$ are the volumes occupied by the polymer within the range b and ξ from the surface, respectively, and A is the polymer-covered area on the surface (Fig. 1). The entropy change S_ξ incurred by confining the polymer to the thickness ξ is

$$S_\xi \sim -\left(\frac{V_0}{V_\xi}\right)^2 \sim -\left(\frac{R_0}{\xi}\right)^2 \sim -N\left(\frac{l}{\xi}\right)^2, \quad (3)$$

in dimension of k_B (we put $k_B = 1$) as is well-known. Here $V_0 \sim R_0^3$ is the volume of polymers occupied in free space with the mean end-to-end distance, $R_0 = lN^{1/2}$. Noting that $A \sim R_0^2$ and S_ξ should be proportional to N [3], Eq. (3) is obtained. Extending the argument with replacement of N and ξ by N_b and b , respectively, the entropy change S_b arising from the segments bound within the range b is obtained as

$$S_b \sim -N_b \left(\frac{l}{b}\right)^2. \quad (4)$$

Taking all terms together, we rewrite the free energy as,

$$\frac{F}{TN} \sim -\epsilon \left(\frac{l}{b}\right)^2 \frac{b}{\xi} + \left(\frac{l}{\xi}\right)^2, \quad (5)$$

where

$$\begin{aligned} \epsilon &\sim \left(\frac{b}{l}\right)^2 U \left(\frac{1}{T} - \frac{1}{T_c}\right) \\ &\sim \left(\frac{T_c}{T} - 1\right) \equiv \tau, \end{aligned} \quad (6)$$

with $T_c \sim (b/l)^2 U$. When $T < T_c$ ($\epsilon > 0$), the polymer is in an adsorbed state with the negative free-energy minimum at $\xi \sim 2b/\epsilon$. The ϵ is a measure of adsorption strength for the flexible chain. The weakly adsorbed state is characterized by $\epsilon \ll 1$ and $\xi \gg b$.

Suppose that the membrane is flexible enough to undergo bending with a curvature $M = 1/R$ on the polymer adsorbed area (Fig. 1). Assuming that the ϵ does not have it, the curvature dependence in the free energy of the adsorbed polymer comes from two factors. The first one is [11,13]

$$\frac{N_b}{N} \approx \frac{V_b}{V_\xi} = \frac{(R+b)^3 - R^3}{(R+\xi)^3 - R^3} \approx \frac{b}{\xi} [1 - (\xi - b)M], \quad (7)$$

which departs from Eq. (2) by the linear order in M considering small curvature, $M\xi \ll 1$ and $Mb \ll 1$. (It should be noted that ξ and b can nevertheless be large within these constraints.) The second curvature dependence arises in S_ξ given by Eq. (3). We first note that

$$V_\xi = \frac{A}{3R^2} [(R+\xi)^3 - R^3] \approx A\xi(1 + M\xi). \quad (8)$$

From the recent calculation of Mondescu and Muthukumar [14], the mean-squared end-to-end distance on a sphere is affected with the curvature by the leading order of $(MR_0)^2$. Accordingly, $A \sim R_0^2 [1 + \mathcal{O}(MR_0)^2]$, and we find that, to the linear order in M ,

$$S_\xi \sim -N \left(\frac{l}{\xi}\right)^2 (1 - 2M\xi). \quad (9)$$

In sum,

$$\frac{F}{TN} \sim -\epsilon \left(\frac{l}{b}\right)^2 \frac{b}{\xi} [1 - (\xi - b)M] + \left(\frac{l}{\xi}\right)^2 (1 - 2M\xi). \quad (10)$$

For the equilibrium polymer thickness

$$\xi \sim \frac{b}{\epsilon + (\epsilon + 2)Mb}, \quad (11)$$

the free energy is at its minimum,

$$\frac{F(M)}{TN} \sim \left(\frac{l}{b}\right)^2 \left[-\frac{\epsilon^2}{4} - \frac{\epsilon^2}{2} Mb \right]. \quad (12)$$

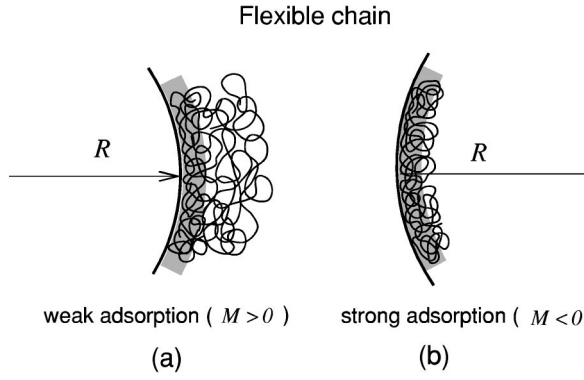


FIG. 2. Schematic picture of membrane bending through the interaction with a flexible polymer. (a) Weak adsorption of a flexible polymer induces a positive spontaneous curvature. (b) A strongly-adsorbed flexible polymer makes the membrane curved toward the polymer, yielding a negative curvature.

Combining this with the membrane bending energy, the total free energy is

$$\mathcal{F}(M) = F(M) + 2\kappa AM^2, \quad (13)$$

where κ is the bending rigidity of magnitude, $1 \sim 100T$. Further minimizing the free energy leads to the thermodynamically stable spontaneous curvature of the membrane,

$$M_{sp} \sim \frac{TNl^2}{\kappa A} \frac{\epsilon^2}{b} \sim \frac{T\epsilon^2}{\kappa b} > 0. \quad (14)$$

The induced curvature has the positive sign, meaning that the membrane bends away from the weakly adsorbed polymer as depicted in Fig. 2(a).

To make quantitative contacts with real systems, we provide an order of magnitude estimate by inserting typical values for the physical parameters. Throughout this paper, we consider the membrane to be flexible so that $\kappa \sim 10T$ where T is a physiological temperature. For the case of weak adsorption in which $\epsilon \sim \tau \equiv T_c/T - 1$ can be taken as order of 0.1, Eqs. (11) and (14) give the estimates $\xi \sim 10b$ and $R = 1/M \sim 10^3b$. It implies that for an attraction range of $b \sim 1$ nm, R can have the order of magnitude of $1 \mu\text{m}$. As the range of interaction increases to a large value with ϵ fixed (e.g., poorly screened electrostatic interaction, where $b = \text{Debye length}$ approaching about $1 \mu\text{m}$), the induced radius R can be imperceptibly large.

As a specific example, let us consider a polyelectrolyte and an oppositely charged membrane mutually interacting electrostatically. In the presence of background ionic solutions, the electrostatic interaction is exponentially screened with the b represented by Debye screening length depending upon monovalent ion concentration. For a fixed physiological temperature, we choose $b \approx 6$ nm corresponding to 5 mM of 1:1 electrolytes, such as NaCl [15]. On the other hand, the interaction strength U depends on not only the line charge density α of polyelectrolyte but also the membrane surface potential ψ_0 , which is determined by surface charge density and salt concentration. For most practical situations [16], one can assume the constant surface potential as $\psi_0 \approx$

$-100 \text{ mV} \approx -4T/e$ and the interaction strength thus depends solely on the fractional charge per segment α (degree of dissociation of the segments) [2]. For the flexible chain (e.g., $l \leq 1$ nm), one can consider the weak-adsorption state by choosing $U \approx 0.03T$ (corresponding to $\alpha \approx 0.008e$; very weakly charged polyelectrolyte). Equation (14) then gives the induced radius of curved surface as $R = 1/M \sim 6 \mu\text{m}$. Note that the adsorbed layer thickness ξ is given as 120 nm and therefore original assumption of $M\xi \ll 1$ and $Mb \ll 1$ is easily satisfied.

As mentioned earlier, an important feature to determine conformations of soft matter is the competition between the entropy associated with thermal fluctuation and the direct interaction. On the membrane with the positive curvature, the space accessible to polymer conformation (entropy) increases compared with that on flat surface while the number of segments bound inside the attraction range decreases. For the weak-to-moderate adsorption of flexible polymer where there are a lot of loop conformations, the conformational entropy gain dominates over the cost of bending energy for free-energy minimization, leading to the positive curvature. This result is consistent with our previous study [12] on the polymer conformation over the surface with large curvature.

On the other hand, Hiergeist *et al.* showed that the negative curvature is driven, on the basis of a scaling theory, and a partition function calculation using the de-Gennes' boundary condition that specifies the decay of segmental density on surface over the characteristic length called the extrapolation length [11]. They considered the curvature dependence in N_b/N only while neglecting the curvature effect in the confinement entropy [Eq. (9)]. In their calculation of partition function, they did not correspondingly take into account the curvature independence of the extrapolation length l_{ex} which is nothing other than the minus polymer thickness $l_{ex} = -\xi$. Incorporating the curvature dependence as shown in Eq. (11),

$$l_{ex} \sim -\frac{b}{\epsilon} \left(1 - \frac{\epsilon + 2}{\epsilon} Mb \right), \quad (15)$$

into their free energy of adsorption, we find that the free energy is in agreement with ours in the curvature dependence. This is a convincing evidence for the essential validity of our scaling argument.

As the adsorption strength ϵ increases, the ξ decreases and the adsorbed layer tends to have a pancakelike conformation. In the strong adsorption, where most of the segments lie within the attraction range with little amount of chain loops beyond it, the polymer thickness assumes a fixed magnitude $\xi = b(1 + \delta)$ with δ being a small positive parameter, rather than variationally determined by free-energy minimization. In this case the polymer free energy is given by

$$F \sim -NT\epsilon \left(\frac{l}{b} \right)^2 \frac{b}{\xi} (1 - bM\delta). \quad (16)$$

The minimization of the total free energy incorporated with the membrane bending energy of $2\kappa AM^2$ leads to the equilibrium spontaneous curvature given by the negative value

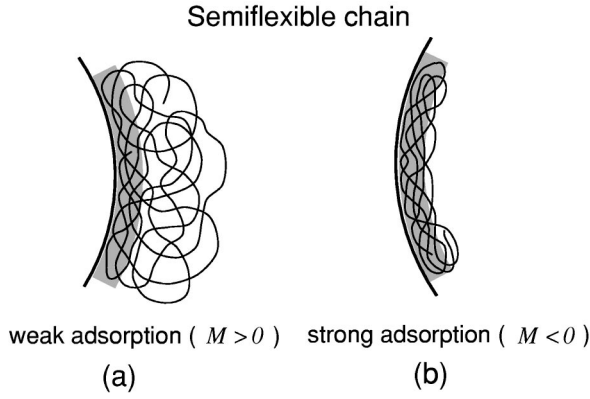


FIG. 3. Schematic picture of the membrane bending through the interaction with a semiflexible polymer. (a) Positive spontaneous curvature due to the weak adsorption of stiff chain. (b) Negative curvature due to the strongly adsorbed stiff chain.

$$M_{sp} \sim -\frac{TN}{\kappa A} \left(\frac{l}{b}\right)^2 \epsilon b \delta \sim -\frac{T\epsilon}{\kappa b} \delta < 0. \quad (17)$$

As the most segments have surface-bound conformation, it is energetically favorable for the membrane to bend toward the polymer by maximizing the surface contacts contrary to the foregoing case [Fig 2(b)]. The adsorption energy dominates over the entropy.

For an order of magnitude estimation, consider a strong adsorption where $\epsilon \sim \tau = 10$ and $\delta = 0.1$. Equation (17) yields $R = -1/M \sim 10b$. The bending radius is smaller than that estimated for the weak adsorption. For an attraction range with $b \sim 1$ nm, $R \sim 10$ nm. The increase of b with ϵ fixed can enhance the bending radius to a micron size. Again, for a specific numerical estimate in the case of electrostatic interaction, we consider the same surface potential ψ_0 , as well as ionic concentration (implying $b \approx 6$ nm) as before. Selecting $U \approx 0.3T$ ($\alpha \approx 0.08e$, implying the increased-fractional charge per segment) for representative values of strong adsorption, one also obtains the induced radius $R = -1/M \sim 60$ nm.

III. MEMBRANE BENDING INDUCED BY STIFF POLYMER ADSORPTION

Now let us consider the case with stiff chain of the persistence length l larger than the range of attractive interaction b . The segments within the attraction range will tend to align along the surface [Fig. 3(a)]. Therefore, the persistence length has no influence on the entropy reduction within the range [6],

$$S_b \sim -N_b, \quad (18)$$

while it affects the lateral dimension of adsorbed polymer ($A \sim R_0^2 \sim Nl^2$) as in the case of flexible chain. Hence the free-energy change in weakly adsorbed states with liquid-crystalline type surface ordering is the same as Eq. (10) in form where

$$\epsilon \sim \left(\frac{b}{l}\right)^2 U \left(\frac{1}{T} - \frac{1}{T_c}\right) \sim \left(\frac{b}{l}\right)^2 \left(\frac{T_c}{T} - 1\right) = \left(\frac{b}{l}\right)^2 \tau \quad (19)$$

with a transition temperature $T_c \sim U$. For strong adsorption of stiff chains with ξ approaching b , there exists a possibility of liquid-crystalline surface ordering for most of the segments with little chance to form loops into the bulk phase [Fig. 3(b)]. The scaling function for the free-energy change is then obtained as the Eq. (16) with ϵ defined as Eq. (19) above. As mentioned before, in the case of strong adsorption, ξ is not a variable determined through free-energy minimization but bounded as $b(1 + \delta)$.

Considering the membrane bending energy together with the polymer free energy, the equilibrium spontaneous curvature is given by Eq. (14) and (17) for the weak and strong adsorption, respectively, but with a difference in the expression of the adsorption strength ϵ as mentioned above. Equations (14) and (17) then predict that, with both the attraction strength and range fixed, a stiffer semiflexible chain tends to induce less membrane bending (with a positive and a negative curvature, respectively) for weak and strong adsorption.

For weak adsorption of a semiflexible chain with $\tau = 0.1$ and $l/b \sim 1$ [6] (indicating $\epsilon \sim 0.1$), Eqs. (11) and (14) predict $\xi \sim 10b$ and $R \sim 10^3b$. Taking the same value of l/b for a strong adsorption with $\tau = 10$ ($\epsilon \sim 10$) and $\delta = 0.1$, Eq. (17) predicts $R = -1/M \sim 10b$. The bending radius just obtained are comparable to those for the flexible chain, due to the fixed values of ϵ , in either case of weak or strong adsorption. It should be born in mind, however, that the interaction strength U must be significantly larger for the semiflexible polymer to have the similar bending. As can be seen from Eqs. (6) and (19), U should be larger by two-orders of magnitude for the increase of l by ten times to keep the adsorption strength ϵ fixed. For example, when a semiflexible polymer like a spectrin ($l \approx 10$ nm) [17] is adsorbed on a membrane with $b \approx 6$ nm and $U \approx 1.3T$ for a weak adsorption ($\epsilon \sim 0.1$), and $U \approx 20T$ for a strong adsorption ($\epsilon \sim 10$), respectively. These interaction strengths are significantly larger than those for a flexible chain with $l \leq 1$ nm, i.e., $U \approx 0.03T$ ($\epsilon \sim 0.1$) and $U \approx 0.3T$ ($\epsilon \sim 10$) in the previous section.

It is noted that the negative curvature obtained for the strongly adsorbed case is not limited to a small value so the interaction may lead to encapsulation of the polymer by the membrane (Fig. 4), which, for semiflexible polymer, may have relevance to the biological phenomena such as endocytosis. For the complete vesiculation, the induced curvature should be of order of the inverse of polymer macroscopic dimension, $M_{sp} \sim R_0^{-1}$, because the polymer covered area does not change very much from the initial value $A \sim R_0^2$. Supposing $\xi \sim b$, this condition reduces to $l \sim (T/\kappa) \tau N^{1/2} b \delta$, which means that complete encapsulation takes place when very stiff chain (large l) is strongly adsorbed (large τ) on the flexible membrane (small κ). It should be also noted that the strong adsorption of semiflexible polymer needs molecular binding energy (e.g., $U \approx 20T$) mentioned above. Our analysis thus implies that the vesicle encapsulation, leading to a possibility of endocy-

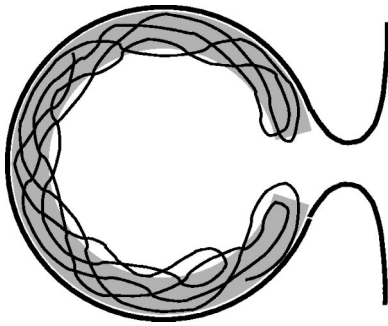


FIG. 4. A stage preceding complete vesiculation due to the strong adsorption of a stiff polymer. Since the polymer covered area ($A \sim R_0^2$) does not change appreciably during the bending, the induced radius should be of order of the polymer radius of gyration, $R \sim R_0$.

toxis, can be generated by rather strong and specific chemical bonds such as lock and key molecules [18].

IV. SUMMARY AND DISCUSSION

In summary, we have studied the spontaneous membrane curvature induced by polymer adsorption. It is found that the polymer and membrane, soft matter as they are, affect the conformations of one another through their interactions. The presence of an attractive interaction makes the polymer chain

with finite stiffness bend along the surface. Through the interplay between interaction energy and conformational entropy, spontaneous membrane curvature is induced, with a different sign depending upon the adsorption strength. A simple scaling theory facilitates understanding the basic physics of the interplay. Estimates based on the scaling theory prediction are biologically relevant, inviting further exploration.

For complete adsorption of a semiflexible polymer, where δ is negligibly small, the membrane would exhibit little bending in our model because only the segments outside the range are susceptible to the entropic effects the curvature yields. We did not consider, in this paper, the phase transitions of lipid molecules and the consequent increase of membrane elasticity [19] due to the complete adsorption. Recently, there have been several interesting reports on the structural reorganization of membrane polymer mixtures: for example, DNA-cationic lipid complexes exhibit various phases [20]. Depending upon constituent properties of complexes, adsorbed polymer may induce significant structural changes of membranes, which is beyond the scope of present theory.

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