Bending elastic moduli of polymer grafted fluid membrane

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脂質二重膜の両面に、高分子がグラフトすることより膜は堅くなるだろうか、それとも軟らかくなるだろうか? この問題はグラフトする高分子鎖が理想鎖の場合でさえ、内外の高分子鎖の配位の増減が直観的には求まらないため簡単ではない。この研究では、円筒と球の内側と外側の表面にグラフトした高分子鎖の配位エントロピーを計算し、膜の弾性率がどのように変化するかを求めた。その結果、理想鎖の場合には曲げ弾性は増加し、ガウス弾性率は減少することが分かった。

1 Introduction

A wide variety shape transformation of fluid membrane has been nicely described by the bending elastic model [1], where the free energy E of a fluid membrane $\mathcal{S}$ is written as

$$E = \kappa \int_S (H - H_s)^2 dS + \kappa_G \int_S K dS \quad (1)$$

where H and K are the mean and Gaussian curvature of membrane, κ the bending elastic modulus, κ_G the Gaussian elastic modulus.

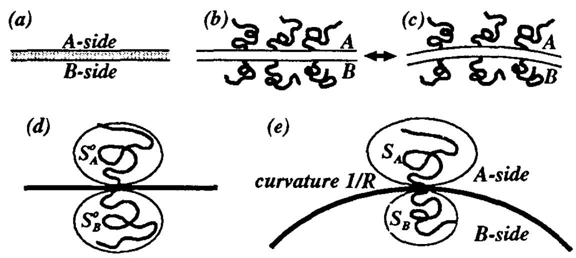

Figure1: (a) fluid membrane, (b) polymer grafted flat membrane, (c) curved membrane of (b) (Top line). (d) Conformational entropy of polymer chains grafted onto the A(B)-side, $S^o_A(S^o_B)$ (e) Conformational entropy of polymer chains grafted onto the curved membrane with $H = 1/R$, $S_A(S_B)$

When polymers with a length aN are grafted homogeneously onto the both sides of a membrane, how are the bending moduli changed by the effect of polymers? This question is not trial even when the polymer chains are ideal ones, since it is not easy to evaluate whether the total value of conformational entropy of polymer chains attached onto inner and outer surface increases or not when the membrane is slightly curved. The aim of the present work is to evaluate the change of bending moduli by attached polymer chains onto the both sides of a membrane.

2 Bending elastic moduli of polymer grafted membrane

In order to estimate an effective bending moduli, we shall consider the following membranes systems shown in Fig.2.

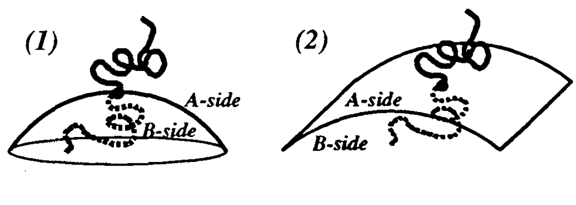

Figure2: (1) Two polymer chains grafted onto the both sides of a spherical surface with curvatures $H = 1/R, K = 1/R^2$. (2) Two polymer chains grafted onto the both sides of a cylindrical surface with curvatures $H = 1/R, K = 0$.

Onto the both sides of the membrane, polymer chains are grafted with a coverage σ. The

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change of conformational entropy by a bending of membrane, $\Delta S^{(i)}$ is given by

$$\Delta S_i = S^{(i)} - S_o^{(i)} = (\sigma_A \Delta s_A^{(i)} + \sigma_B \Delta s_B^{(i)})A = \frac{\Delta s_i'}{R} A + \frac{\Delta s_i''}{R^2} A + \cdots \quad (2)$$

where the subscript (i) denotes the case (1) or (2) in Fig.2. After calculations for cases (1) and (2), the effective spontaneous curvature $H_{sp}^{(\mathrm{eff.})}$, the effective bending and Gaussian moduli ($\kappa^{(\mathrm{eff.})}$ and $\kappa_G^{(\mathrm{eff.})}$) found out to be

$$H_{\mathrm{sp}}^{(\mathrm{eff.})} = H_{\mathrm{sp}} + \frac{T\Delta s_1'}{\kappa}, \quad \Delta s_1' = \Delta s_2' \quad (3)$$

$$\kappa^{(\mathrm{eff.})} = \kappa - 8T\Delta s_2'' \quad (4)$$

$$\kappa_G^{(\mathrm{eff.})} = \kappa_G - T(\Delta s_1'' - 4\Delta s_2''). \quad (5)$$

From Eq.(4), the membrane becomes more rigid if the number of conformation in case (2) decreases. In this way, the effective spontaneous curvature and elastic moduli are modified according to the change of conformational entropy. In order to obtain the effective moduli and spontaneous curvature, all we have to do is to evaluate the change of conformational entropy $\Delta s_A^{(i)}$, $\Delta s_B^{(i)}$ for each case (1) and (2).

The conformation of polymer chain with a length aN can be calculated by the Edwards equation and the next boundary condition [2]

$$\frac{\partial G_n(r_o, r)}{\partial n} = \Big(\frac{b^2}{6}\nabla^2 - \frac{U(\boldsymbol{r})}{k_B T}\Big) G_n(\boldsymbol{r}_o, \boldsymbol{r}) \quad (6)$$

$$G_n(\boldsymbol{r}_o, \boldsymbol{r}) = 0 \qquad \text{if } \boldsymbol{r} \in \partial D \quad (7)$$

$$G_n(\boldsymbol{r}_o, \boldsymbol{r}) = \delta(\boldsymbol{r} - \boldsymbol{r}_o) \qquad \text{if } n = 0 \quad (8)$$

where $G_n(\boldsymbol{r}, \boldsymbol{r}_o)$ is a statistical weight of a chain that one end is located at the position $\boldsymbol{r}$ and another end is at $\boldsymbol{r}_o$. In this article, since we show the result for the case of ideal polymer chain, hereafter we neglect the potential term U. After obtaining G_N, the entropy S can be calculated by

$$S = k_B \ln W = k_B \ln \int G_N(\boldsymbol{r}_o, \boldsymbol{r}) d\boldsymbol{r}. \quad (9)$$

In case (1) and A-side of Fig.2, the change of entropy can be obtained analytically and given by the following equation

$$\Delta s_A^{(1)'} = \frac{\sqrt{\pi}}{2} k_B R_g \sigma_A, \ \Delta s_A^{(1)''} = -\frac{\pi}{8} k_B R_g^2 \sigma_A. \quad (10)$$

On the other hand, the change of entropy $\Delta s_B^{(1)}$ in case (1) and B-side of Fig.2 is

$$\Delta s_B^{(1)} = k_B \ln \Big[\sum_{n=1}^{\infty} \frac{2 \sin n\pi\tilde{b}/\tilde{R}}{n\pi \mathrm{erf}(\tilde{b})(1 - \tilde{b}/\tilde{R})} e^{-\frac{\pi^2 n^2}{4\tilde{R}^2}} \Big] = \frac{\Delta s_B^{(1)'}}{\hat{R}} + \frac{\Delta s_B^{(1)''}}{\hat{R}^2} + \mathcal{O}(1/R^3). \quad (11)$$

For case (2A), we also derived analytical expression for conformational entropy

$$\Delta s_A^{(2)} = k_B \ln \Big[\frac{1}{\mathrm{erf}(\hat{b})} \int_0^{\infty} k dk e^{-\frac{a^2}{6} N k^2} \times \frac{K(r_o, R)}{[J_0(kR)]^2 + [N_0(kR)]^2} \int_R^{\infty} r dr K(r, R) \Big] = \frac{\Delta s_A^{(2)'}}{\hat{R}} + \frac{\Delta s_A^{(2)''}}{\hat{R}^2} + \mathcal{O}(1/R^3) \quad (12)$$

where $K(r, R) \equiv J_0(kr)N_0(kR) - J_0(kR)N_0(kr)$, and J_0 is $0th$ Bessel function, and N_0 are $2nd$ kind $0th$ Bessel function. For case (2B),

$$\Delta s_B^{(2)} = k_B \ln \Big[\frac{2}{\mathrm{erf}(\hat{b})} \sum_{s=1}^{\infty} \frac{J_0(k_n r_0)}{k_n R J_1(k_n R)} e^{-\frac{a^2}{6} N k_n^2} \Big]$$

$$\Delta s_B^{(2)} = \frac{\Delta s_B^{(2)'}}{\hat{R}} + \frac{\Delta s_B^{(2)''}}{\hat{R}^2} + \mathcal{O}(1/R^3) \quad (13)$$

where k_n's ($n = 1, 2, 3 \cdots$) is determined by $J_0(k_n R) = 0$. We numerically estimated the values of $\Delta s_{A(B)}^{(1,2)'}$ and $\Delta s_{A(B)}^{(1,2)''}$ for $N_A = N_B = 100$. Here we consider the most simplest case $(\sigma \equiv)\sigma_A = \sigma_B$. In this case, it should be noted that the effective spontaneous curvature H_{sp} becomes zero. After numerical calculation, we obtained the following results:

$$\kappa^{(\mathrm{eff.})} = \kappa + 2.56 k_B T R_g^2 \sigma \quad (14)$$

$$\kappa_G^{(\mathrm{eff.})} = \kappa_G - 0.50 k_B T R_g^2 \sigma \quad (15)$$

3 Conclusion

We found that (i) the bending modulus κ is effectively increased, and (ii) the Gaussian elastic modulus is decreased, by grafting polymer chains onto both sides of membrane.

Reference

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