Bending elastic moduli of polymer grafted fluid membrane

Dept. of Polymer Science and Engineering, Yamagata University (*), JST CREST (†)
Takashi TANIGUCHI(*1) 1, Masataka SUGIMOTO(*) and Kiyohito KOYAMA(*1)

Introduction

A wide variety shape transformation of fluid membrane has been nicely described by the bending elastic model \[ E = \kappa \int_S (H - H_s)^2 dS + \kappa_G \int_S K dS \] (1) where \( H \) and \( K \) are the mean and Gaussian curvature of membrane, \( \kappa \) the bending elastic modulus, \( \kappa_G \) the Gaussian elastic modulus.

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 surfaces 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 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 membrane systems shown in Fig.2.

Figure 1: (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, \( S_A(S_B) \) (e) Conformational entropy of polymer chains grafted onto the curved membrane with \( H = 1/R \), \( S_A(S_B) \)

Figure 2: (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 both sides of the membrane, polymer chains are grafted with a coverage \( \sigma \). The
change of conformational entropy by a bending of membrane, $\Delta S^{(i)}$ is given by

$$\Delta S_i = S^{(i)}_0 - S^{(i)} = (\sigma_A \Delta S_A^{(i)} + \sigma_B \Delta S_B^{(i)}) A$$

$$= \frac{\Delta S_i'}{R} A + \frac{\Delta S_i''}{R^2} A + \cdots$$ (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 $H_{sp}^{(eff.)}$, the effective bending and Gaussian moduli ($\kappa^{(eff.)}$ and $\kappa_G^{(eff.)}$) found out to be

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

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

$$\kappa_G^{(eff.)} = \kappa_G - T(\Delta s_i'' - 4 \Delta s_i''').$$ (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 $\Delta s_i'$, $\Delta s_i''$ 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]

$$\frac{\partial G_n(r, r)}{\partial n} = \left(\frac{b^2}{6} - \frac{U(r)}{k_BT}\right) G_n(r, r)$$ (6)

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

$$G_n(r, r_0) = \delta(r - r_0) \quad \text{if} \quad n = 0$$ (8)

where $G_n(r, r_0)$ is a statistical weight of a chain that one end is located at the position $r$ and another end is at $r_0$. 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

$$S = k_B \ln W = k_B \ln \int G_N(r, r) dr.$$ (9)

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

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

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

$$\Delta s_B^{(1)} = k_B \ln \left[ \sum_{n=1}^{\infty} \frac{2 \sin n \pi b/R}{n \pi \text{erf}(b)(1 - b/R)} e^{-\frac{n^2}{4R^2}} \right]$$

$$= \Delta s_B^{(1)'} + \frac{\Delta s_B^{(1)''}}{R} + O(1/R^2).$$ (11)

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

$$\Delta s_A^{(2)} = k_B \ln \left[ \frac{1}{\text{erf}(b)} \int_0^\infty kdke^{-\frac{k^2}{6Nk^2}} \right]$$

$$\times \left[ \int_0^\infty e^{-\frac{k^2}{6Nk^2}} \int_R^\infty rdr K(r, R) \right]$$

$$= \frac{\Delta s_A^{(2)'} + \Delta s_A^{(2)''}}{R} + O(1/R^3)$$ (12)

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

$$\Delta s_B^{(2)} = k_B \ln \left[ \frac{2}{\text{erf}(b)} \sum_{n=1}^{\infty} J_0(knR) e^{-\frac{k^2}{6Nk^2}} \right]$$

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

where $kn$'s $(n = 1, 2, 3 \cdots)$ is determined by $J_0(knR) = 0$. We numerically estimated the values of $\Delta s_A^{(1)'}$, $\Delta s_A^{(1)''}$ for $NA = NB = 100$. Here we consider the most simplest case $(\sigma_A = \sigma_B = a)$. In this case, it should be noted that the effective spontaneous curvature $H_{sp}$ becomes zero. After numerical calculation, we obtained the following results:

$$\kappa^{(eff.)} = \kappa + 2.56 k_BT R_g^2 \sigma$$ (14)

$$\kappa_G^{(eff.)} = \kappa_G - 0.50 k_BT R_g^2 \sigma$$ (15)

3 Conclusion

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

Reference
