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Elastic property of bilayer membrane in copolymer–homopolymer mixtures

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Abstract. We study the domain morphology in a phase separated state of diblock copolymer–homopolymer mixtures. In the situation that one of the blocks of copolymers is incompatible with homopolymers, formation of a bilayer membrane of block copolymers is shown to be possible in the matrix of homopolymers. Starting with the free energy functional in terms of the local volume fractions of each monomer, we derive the bending and curvature rigidities in the Helfrich free energy for a membrane. It is found that the curvature modulus is negative only in a limited region of the parameters, where a closed shape of a membrane like a vesicle is possibly formed. We establish a method to calculate the rigidities without a molecular picture in a consistent way with the field theoretic model free energy. Stability of a bilayer membrane compared with micelles is also investigated.

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1 Introduction

A mixture of diblock copolymers and homopolymers exhibits fascinating phase separation. When one of the blocks is incompatible with homopolymers, the system undergoes macrophase separation at low temperatures segregating into copolymer–rich and homopolymer–rich domains. If there is a repulsive short range interaction between two blocks, microphase separation takes place in copolymer–rich domains. This double phase separation has indeed been observed experimentally [1,2].

In most of experiments [3], homopolymer is chosen to be chemically identical with one of the blocks and plays a role of a selective solvent because these experiments are motivated to study the influence of added homopolymers on the stability of microphase separated structures of pure copolymers. (See Ref. [4] for an exception.) Therefore the homopolymer volume fraction is chosen to be rather small. However, if the volume fraction of homopolymer is sufficiently large, one may expect essentially new morphologies. For instance, Hashimoto *et al.* [2,5] have observed onion–ring domains, assembly of rod–like domains. Vesicles of copolymers in a homopolymer–rich matrix have also been found recently [6,7]. These are not seen in a microphase separation of pure copolymers.

There are substantial number of theoretical studies of the equilibrium properties of copolymer–homopolymer mixtures [8–10]. Equilibrium phase diagram for the double phase separation has been obtained. In the case of small volume fraction of copolymers, Semenov investigated the formation of bilayer membranes and micelles in a homopolymer–rich matrix [11]. He considered a mixture of A–B type diblock copolymer and A–homopolymer employing some of his earlier results for pure diblock copolymers.

In a previous paper [12], Ito and one of the present authors have introduced a model equation for A–B type copolymer and C–homopolymer mixtures and have carried out computer simulations to explore the morphology and kinetics of domain growth in the course of the double phase separation. Remarkable findings are that a morphological change occurs in the microphase separated state by changing the interaction strength between B–blocks and C–homopolymers or the molecular weight of the copolymer and that the kinetics of domain coarsening is drastically affected by the morphology.

In the present paper, we shall investigate the equilibrium property of A–B copolymer and C–homopolymer mixtures based on the free energy functional introduced in reference [12]. We focus our attention on formation, stability and elasticity of bilayer membrane of copolymers. We assume that both polymer chains are flexible and there is a repulsive interaction between B–blocks and C-homopolymers as well as between A and B blocks. Thus one may expect a bilayer such that A blocks contact with C homopolymers at a sharp interface while the B blocks are in the middle part of the layer as shown in Figure 1a.

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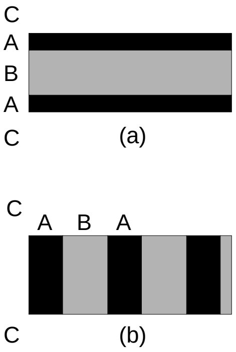

Fig. 1. (a) A bilayer membrane with B–domain in the middle and A–domains in the outer sides. (b) A "perpendicular morphology" of A and B domains in a copolymer–rich domain.

It is noted that the copolymer–homopolymer system considered here has a striking similarity with a water–surfactant system where a polar head of a surfactant molecule is attractive with water while a nonpolar tail is repulsive with water. As a result, micelles and bilayers of surfactant molecules are constituted in the water–rich matrix for suitable volume fractions of surfactants and temperature [13,14].

The elastic property of a membrane in the limit of an infinitesimally thin width is characterized by the Helfrich free energy density [15]

$$F_{\mathrm{mem}} = \sigma + 2\kappa H^2 + \bar{\kappa} K \tag{1}$$

where σ is an interfacial energy. The mean curvature H and the Gaussian curvature K are defined, respectively, by $H = (1/R_1 + 1/R_2)/2$ and $K = 1/(R_1 R_2)$ with the principal radii of curvatures R_1 and R_2. Our main concern is to derive the bending modulus κ and the curvature modulus $\bar{\kappa}$ as a function of the block ratio $f = N_{\mathrm{A}}/(N_{\mathrm{A}} + N_{\mathrm{B}})$ with N_{A} (N_{B}) the molecular weight of the A (B) block. We assume that both copolymer and homopolymer are monodisperse. Note that the spontaneous curvature is absent, by symmetry, in a copolymer bilayer [16,17]. In the case of surfactant mixtures, this is not generally the case [18].

Ajdari and Leibler [16] and Wang [17] have studied independently the elastic property of a bilayer membrane in A–B copolymer and A homopolymer mixtures. These authors have employed the method of the grafted chain picture which was introduced for a monolayer membrane [19,20]. In the Ajdari–Leibler theory [16], the free energy of a membrane has been defined per unit area. On the other hand, Wang [17] has used the free energy per chain allowing the change of the number of copolymer molecules in a membrane upon bending [21].

Our approach is a density functional method in terms of the local volume fractions of monomers [22]. Since the model is not specific to polymeric systems, the present theory to derive the Helfrich free energy has a wider applicability. In the present paper we assume that the number of copolymer chains is unchanged for a gently curved membrane. However, the theory can be extended, without any difficulty, to the case considered by Wang.

A bilayer membrane contains three characteristic lengths, the interface width ξ, the membrane width w and the typical radius of curvature R. The Helfrich free energy density (1) is defined in the limit $\xi \ll w \ll R$. As mentioned above, we assume that ξ is infinitesimal in the strong segregation limit. Since a bilayer has an internal structure we have to keep w finite in the calculation of the membrane free energy and then take a limit $w/R \to 0$. However there is a conceptual problem how to choose uniquely the radius of curvature due to the finiteness of w. In other words, we need to make a unique reduction of degrees of freedom associated with three domains as in Figure 1a to obtain (1) which is expressed only in terms of one degree of freedom.

In the previous studies of a monolayer membrane [19,20] and a bilayer membrane [16], the membrane free energy is defined per area of copolymer chain so that expressions of the rigidity moduli independent of the choice of curvature are obtained. One could also define the free energy per chain in the present theory. However, since our model is field theoretic, relying on the chain picture is not internally consistent. Furthermore, formation of bilayer is not necessarily restricted to polymeric materials. Hence one needs to establish a method of deriving the Helfrich free energy without using the chain degrees of freedom. We shall provide an answer to this problem.

Since a copolymer–homopolymer mixture contains a fairly large number of parameters, we specify the conditions in the present study. We consider the strong segregation limit for both micro– and macro–phase separations. This means that the interfacial width is much smaller than the bilayer thickness. The molecular weight of homopolymers is large enough so that the homopolymers cannot enter into the A–rich domains. In other words, we assume a dry brush of A–blocks. The repulsive interaction between the B–blocks and the C–homopolymers is assumed to be sufficiently strong so that there is always an A–domain between B–and C–domains. This condition excludes the possibility of a "perpendicular morphology" of domains as in Figure 1b. Finally we do not consider, for simplicity, the interaction between bilayers and/or micelles.

The organization of the paper is as follows: in Section 2, we explain our free energy functional. The free energy of a bilayer with a cylindrical geometry is calculated in Section 3 whereas that of a spherical vesicle is given in Section 4. In Section 5, we evaluate the elastic rigidities in the Helfrich Hamiltonian as a function of the block ratio and the interfacial energies between A blocks and C homopolymers as well as A and B blocks. The results are compared with those obtained by Ajdari and Leibler [16]. In Section 6, we examine the free energy increase for weak deformations around a flat bilayer membrane. Comparing this with those of cylindrical and spherical vesicles, we show how to identify the elastic moduli uniquely without the molecular picture. When the block ratio is close to unity, formation of micelles with a core of B blocks is not excluded. Therefore we examine, in Section 7, the relative stability of a flat bilayer compared with spherical and worm–like (cylindrical) micelles. The results obtained are discussed in Section 8. Some technical details used in Sections 3 and 4 are summarized in the Appendix.

2 Model free energy

We start with the free energy functional for a mixture of A–B diblock copolymers and C homopolymers, which is written in terms of the local volume fractions $\phi_{\mathrm{A}}(\mathbf{r})$, $\phi_{\mathrm{B}}(\mathbf{r})$ and $\phi_{\mathrm{C}}(\mathbf{r})$. One of the most important properties of a copolymer system is the osmotic incompressibility due to chain connectivity. This gives rise to a Coulomb type long range interaction between the local volume fractions [22]. Thus the free energy functional consists of two parts:

$$F = F_{\mathrm{S}} + F_{\mathrm{L}}. \tag{2}$$

The short range part F_{S} takes the following form

$$F_{\mathrm{S}} = \int \mathrm{d}\mathbf{r} \left\{ \frac{1}{2}(\nabla\phi_{\mathrm{A}})^2 + \frac{1}{2}(\nabla\phi_{\mathrm{B}})^2 + \frac{1}{2}(\nabla\phi_{\mathrm{C}})^2 + W(\phi) \right\}. \tag{3}$$

The local part $W(\phi)$ is modeled, for instance, by a Flory–Huggins form

$$W(\phi) = \sum_{i=\mathrm{A,\,B,\,C}} \frac{\phi_i}{N_i} \ln \phi_i + \frac{1}{2}\sum_{i,j} u_{ij}\phi_i\phi_j - \mu(\phi_{\mathrm{A}} + \phi_{\mathrm{B}} - \phi_{\mathrm{C}}) \tag{4}$$

where N_i (i = A, B, C) is the molecular weight of an i–polymer and u_{ij} is the interaction constant between i and j polymers. The constant μ in the last term stands for the chemical potential difference between the copolymer and the homopolymer. Since we are not concerned with macrophase separation, hereafter we will not consider the last term in (4).

Equation (4) is valid for ternary blends and an approximation for copolymers [23]. When the repulsive interaction between A blocks and C homopolymers is weak, or the molecular weight of the homopolymer is not sufficiently large, the local volume fraction changes gradually in each domain. In this case the concentration profile depends explicitly on the short range part of the free energy. However, we consider the strong segregation limit where the local volume fractions are assumed to take a step-function form at the interfaces. In this situation we believe that the results obtained below are insensitive to the form of the local interaction $W(\phi)$ and the short range part F_{S}.

The long range part F_{L} is given by

$$F_{\mathrm{L}} = \frac{1}{2}\sum_{i,j=\mathrm{A,\,B}} \alpha_{ij} \int \mathrm{d}\mathbf{r} \int \mathrm{d}\mathbf{r}'\ G(\mathbf{r},\mathbf{r}')\ \{\phi_i(\mathbf{r}) - \bar{\phi}_i\} \times \{\phi_j(\mathbf{r}') - \bar{\phi}_j\} \tag{5}$$

where

$$-\nabla^2 G(\mathbf{r},\mathbf{r}') = \delta(\mathbf{r}-\mathbf{r}') \tag{6}$$

and $\bar{\phi}_i$ is the spatial average of ϕ_i. The coupling constants α_{ij} are given by $\alpha_{\mathrm{AA}} = 6/N_{\mathrm{A}}^2$, $\alpha_{\mathrm{BB}} = 6/N_{\mathrm{B}}^2$ and $\alpha_{\mathrm{AB}} = \alpha_{\mathrm{BA}} = -6/(N_{\mathrm{A}}N_{\mathrm{B}})$. The Kuhn statistical length of both copolymer and homopolymer has been put to be unity. The form of F_{L} can be obtained from a microscopic model such as the Edwards Hamiltonian for copolymer–homopolymer mixtures and using the random phase approximation by generalizing the method in reference [22] to copolymer–homopolymer mixtures. In deriving F_{L}, we have used the incompressibility $\phi_{\mathrm{A}}(\mathbf{r}) + \phi_{\mathrm{B}}(\mathbf{r}) + \phi_{\mathrm{C}}(\mathbf{r}) = 1$ to eliminate $\phi_{\mathrm{C}}(\mathbf{r})$.

Note that the 2×2 matrix α_{ij} has a zero eigenvalue, which is associated with macrophase separation, so that F_{L} becomes simpler after diagonalizing the matrix α_{ij}.

$$F_{\mathrm{L}} = \frac{\alpha}{2} \int \mathrm{d}\mathbf{r} \int \mathrm{d}\mathbf{r}'\ G(\mathbf{r},\mathbf{r}')\phi'(\mathbf{r})\phi'(\mathbf{r}') \tag{7}$$

where ϕ' and α are given, respectively, by

$$\phi' = \frac{1}{\sqrt{N_{\mathrm{A}}^2 + N_{\mathrm{B}}^2}}(N_{\mathrm{B}}\phi_{\mathrm{A}} - N_{\mathrm{A}}\phi_{\mathrm{B}}) \tag{8}$$

$$\alpha = \alpha_{\mathrm{AA}} + \alpha_{\mathrm{BB}}. \tag{9}$$

Note here that $\bar{\phi}' = 0$ which is called a neutrality condition is automatically satisfied since $N_{\mathrm{B}}\bar{\phi}_{\mathrm{A}} - N_{\mathrm{A}}\bar{\phi}_{\mathrm{B}} \propto N(N_{\mathrm{B}}f - N_{\mathrm{A}}(1-f)) = 0$ with $N = N_{\mathrm{A}} + N_{\mathrm{B}}$. The eigen function of the zero mode is given by

$$\psi' = \frac{1}{\sqrt{N_{\mathrm{A}}^2 + N_{\mathrm{B}}^2}}(N_{\mathrm{A}}\phi_{\mathrm{A}} + N_{\mathrm{B}}\phi_{\mathrm{B}}). \tag{10}$$

In the strong segregation limit, ϕ_i is equal to either 0 or 1. Therefore the value of ϕ' is given in an A domain by

$$\phi' \equiv A = \frac{N_{\mathrm{B}}}{\sqrt{N_{\mathrm{A}}^2 + N_{\mathrm{B}}^2}} \tag{11}$$

and in a B domain by

$$\phi' \equiv -B = -\frac{N_{\mathrm{A}}}{\sqrt{N_{\mathrm{A}}^2 + N_{\mathrm{B}}^2}}\,\cdot \tag{12}$$

In C domains, ϕ' is identically equal to zero in the strong segregation limit.

Our aim is to investigate the existence and the stability of a bilayer membrane in a homopolymer–rich matrix. In the next two sections, we calculate the long range part of the free energy of a vesicle in two and three dimensions starting with (7).

Before closing this section we make a remark about the free energy (7). Since the chain conformation is averaged out, the theory contains less information of each chain compared with other theories specific to polymeric systems. The characteristic feature of copolymers appears in the Coulomb type repulsive interaction due to the osmotic incompressibility. Thus although the theory may be less accurate for copolymers in the above sense, it does provide us with a fundamental and universal mechanism for modulated structures. In fact, the Coulomb type long range interaction predicts microphase separation in charged mixtures [24–26]. Actually competition of a long range repulsive interaction and a short range attractive interaction in

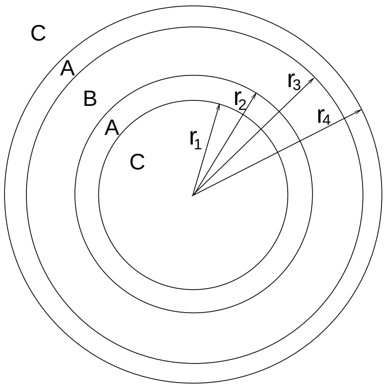

Fig. 2. A vesicle formed by a copolymer bilayer. The regions between r_1 and r_2 as well as r_3 and r_4 are A–rich domains whereas the middle region between r_2 and r_3 is the B–rich domain.

the Ginzburg–Landau free energy is the origin of modulated phases in various systems although the precise form of the long range interaction depends on the system considered [27]. It should also be mentioned that our theory can be easily extended to dynamics as has already been demonstrated [12,28].

3 Free energy of a cylindrical vesicle

In order to evaluate the rigidities κ and $\bar{\kappa}$ in the Helfrich Hamiltonian (1), one needs to calculate the long range part of the free energy (7) for cylindrical and spherical vesicles with a given radius. In this section, we carry out such a calculation for a cylindrical case. By a vesicle, we mean a closed membrane, the inside and the outside of which are in the homopolymer–rich phase.

Suppose that a bilayer takes a cylindrical form as shown in Figure 2 where $\phi'(r)$ is a function of the distance r from the center and is given by

$$\begin{aligned}\phi' &= A \qquad\qquad \text{for } r_1 < r < r_2 \text{ and } r_3 < r < r_4\\ &= -B \qquad\quad\; \text{for } r_2 < r < r_3.\end{aligned} \tag{13}$$

The neutrality condition $\bar{\phi}' = 0$ requires

$$A(r_2^2 - r_1^2) + A(r_4^2 - r_3^2) = B(r_3^2 - r_2^2). \tag{14}$$

The free energy (7) can be evaluated by using the analogy of the electro–static theory. In terms of a potential $V(r)$, equation (7) is written in two dimensions as

$$F_{2\mathrm{d}} = \pi\alpha \int_0^\infty \mathrm{d}r\; r\phi'(r)V(r) \tag{15}$$

where $V(r)$ is defined by

$$\frac{\mathrm{d}V(r)}{\mathrm{d}r} = -E(r). \tag{16}$$

The "electric" field E is readily obtained for the "charge" distribution as in Figure 2 by using the Gauss theorem

$$E(r) = \frac{\mathrm{A}}{2\mathrm{r}}(r^2 - r_1^2) \qquad \text{for } r_1 < r < r_2 \tag{17}$$

$$E(r) = \frac{1}{2r}\left\{-Br^2 + (A+B)r_2^2 - Ar_1^2\right\} \qquad \text{for } r_2 < r < r_3 \tag{18}$$

and

$$E(r) = \frac{\mathrm{A}}{2\mathrm{r}}(r^2 - r_4^2) \qquad \text{for } r_3 < r < r_4. \tag{19}$$

We have used the neutrality condition (14) in the derivation of (19).

Solving (16) by taking account of the continuity of $V(r)$ at $r = r_i$ ($i = 1, ..., 4$) and substituting $V(r)$ thus obtained into (15), we have after lengthy but straightforward calculations

$$\begin{aligned}F_{2\mathrm{d}} = \frac{\pi\alpha}{4}\Bigg\{ &\frac{A^2}{4}(r_1^4 - r_4^4) + \frac{A^2 - B^2}{4}(r_3^4 - r_2^4)\\ &+ A^2\left(r_1^4 \ln\frac{r_2}{r_1} + r_4^4 \ln\frac{r_4}{r_3}\right)\\ &+ [(A+B)r_2^2 - Ar_1^2][(A+B)r_3^2 - Ar_4^2]\ln\frac{r_3}{r_2}\Bigg\}.\end{aligned} \tag{20}$$

In this derivation we have again used (14).

Next we expand (20) in powers of the radius of a vesicle. For this purpose, we put

$$\begin{aligned}r_4 &= R + c\epsilon + a\\ r_3 &= R + \epsilon\\ r_2 &= R - \epsilon\\ r_1 &= R - c\epsilon - b\end{aligned} \tag{21}$$

where R is the distance from the center of the vesicle to the middle of the B layer and 2ϵ stands for the width of the B layer. The constant c is defined by

$$c = 1 + \frac{\mathrm{B}}{\mathrm{A}} = \frac{1}{1-f}\cdot \tag{22}$$

The unknown constants a and b, which vanish in the limit $R \to \infty$, are to be determined as a function of R and ϵ. The width w of the bilayer is given by

$$w = r_4 - r_1 = 2c\epsilon + a + b. \tag{23}$$

The smallness parameter of the system is w/R. The equilibrium value of the width w will be determined by minimization of the total free energy of a membrane.

Since the system is in the strong segregation limit, we may impose the condition for the layer positions r_i such that the area of the outer A layer in Figure 2 is the same as that of the inner A layer

$$r_4^2 - r_3^2 = r_2^2 - r_1^2. \tag{24}$$

It is readily found from (14, 24) that the unknown constant a satisfies

$$a^2 + 2a(R + c\epsilon) + (c^2 - 1)\epsilon^2 = 0, \tag{25}$$

the solution of which can be obtained perturbatively

$$\begin{aligned} a = &- \frac{c^2-1}{2R}\epsilon^2 + \frac{c(c^2-1)}{2R^2}\epsilon^3 - \frac{(c^2-1)(5c^2-1)}{8R^3}\epsilon^4 \\ &+ \frac{c(c^2-1)(7c^2-3)}{8R^4}\epsilon^5 + O(\epsilon^6). \end{aligned} \tag{26}$$

The other constant b is also given by (26) by replacing R by $-R$. Thus one obtains for a cylindrical vesicle

$$a + b = \frac{c(c^2-1)}{R^2}\epsilon^3 + \frac{c(c^2-1)(7c^2-3)}{4R^4}\epsilon^5 + O(\epsilon^7) \tag{27}$$

$$a - b = -\frac{c^2-1}{R}\epsilon^2 - \frac{(c^2-1)(5c^2-1)}{4R^3}\epsilon^4 + O(\epsilon^6). \tag{28}$$

By using the above results, the free energy (20) can be expanded in powers of ϵ/R. Some of the details are summarized in the Appendix. The final result up to $O(R^{-1})$ is given by

$$F_{2\mathrm{d}} = 2\pi R\alpha A^2 \left\{ \frac{c(c-1)^2}{3}\epsilon^3 + \frac{c}{15}(c-1)^2(2c^2+4c+1)\frac{\epsilon^5}{R^2} \right\}, \tag{29}$$

where the first term is a part of the interfacial energy of a flat membrane whereas the second term is a correction due to the curvature. Note that $F_{2\mathrm{d}}$ has been obtained from the long range part of the free energy (7).

4 Free energy of a spherical vesicle

The long range part of the free energy (7) can also be evaluated for a spherical vesicle in a way similar to that in Section 3. The spatial variation of the local volume fraction ϕ' is assumed to be the same as (13) where, however, r is the radial distance from the center of the sphere. The neutrality condition reads

$$A(r_2^3 - r_1^3) + A(r_4^3 - r_3^3) = B(r_3^3 - r_2^3). \tag{30}$$

The "electric" field E is given in this case by

$$E(r) = \frac{\mathrm{A}}{3}\left(r - \frac{r_1^3}{r^2}\right) \qquad \text{for } r_1 < r < r_2 \tag{31}$$

$$E(r) = \frac{\mathrm{A}}{3}\left(\frac{r_2^3 - r_1^3}{r^2}\right) - \frac{\mathrm{B}}{3}\left(r - \frac{r_2^3}{r^2}\right) \qquad \text{for } r_2 < r < r_3 \tag{32}$$

and

$$E(r) = \frac{\mathrm{A}}{3}\left(r - \frac{r_4^3}{r^2}\right) \qquad \text{for } r_3 < r < r_4. \tag{33}$$

In the last expression (33), the neutrality condition (30) has been used. Integrating (31) $\sim$ (33) to evaluate the potential $V(r)$ defined by (16) and using (30), one obtains the free energy of a spherical vesicle

$$\begin{aligned} F_{3\mathrm{d}} &= 2\pi\alpha \int_0^\infty \mathrm{d}r\, r^2 V(r)\phi'(r) \\ &= 2\pi\alpha \left\{ \frac{A^2}{5}(r_1^5 - r_4^5) + \frac{(A^2 - B^2)}{5}(r_3^5 - r_2^5) \right. \\ &\quad \left. + \frac{A(A+B)}{3}[r_2^2(r_2^3 - r_1^3) + r_3^2(r_4^3 - r_3^3)] \right\} \cdot \end{aligned} \tag{34}$$

As in Section 3, one may impose the requirement that the two A domains in a bilayer have the same volume

$$r_4^3 - r_3^3 = r_2^3 - r_1^3. \tag{35}$$

Now we expand (34) in powers of ϵ/R by putting r_i ($i = 1$, ..., 4) as (21). The correction a is given from (30, 35) by

$$\begin{aligned} a = &- \frac{c^2-1}{R}\epsilon^2 + \frac{5c(c^2-1)}{3R^2}\epsilon^3 - \frac{(10c^2-3)(c^2-1)}{3R^3}\epsilon^4 \\ &+ \frac{(c^2-1)(22c^3-13c)}{3R^4}\epsilon^5 + O\left(\frac{\epsilon^6}{R^5}\right) \cdot \end{aligned} \tag{36}$$

The other correction b is given by (36) after replacing R by $-R$. Thus one obtains up to the leading order

$$a + b = \frac{10c(c^2-1)}{3R^2}\epsilon^3 + \frac{2(c^2-1)(22c^3-13c)}{3R^4}\epsilon^5 \tag{37}$$

$$a - b = -\frac{2(c^2-1)}{R}\epsilon^2 - \frac{2(10c^2-3)(c^2-1)}{3R^3}\epsilon^4. \tag{38}$$

Substituting (21) into (34) and using (36) $\sim$ (38), one obtains after some manipulations (see Appendix.)

$$F_{3\mathrm{d}} = 4\pi R^2 \alpha A^2 \left\{ \frac{c(c-1)^2}{3}\epsilon^3 + \frac{c}{15}(c-1)^2(7c^2+14c+6)\frac{\epsilon^5}{R^2} \right\} \cdot \tag{39}$$

The first term in the curly brackets is the same as that in (29), which gives us a contribution to the interfacial tension of a flat bilayer membrane.

The vesicle free energies (29, 39) agree with those for $f = 1/2$ ($c = 2$) calculated previously [29]. We have verified the results (29, 39) by an independent calculation starting with (5) without diagonalization of the coefficient matrix $\alpha_{i,j}$.

5 Elasticity of a bilayer membrane

The results (29, 39) have been obtained by a particular choice of the radius R. Since the membrane width w is finite and the second and third terms in (1) are order of $(w/R)^2$, the moduli κ and $\bar{\kappa}$ in the Helfrich Hamiltonian (1) generally depend on the choice of the radius. In order to eliminate this ambiguity, we consider chain conformation constituting the bilayer. An alternative method will be presented in the next section.

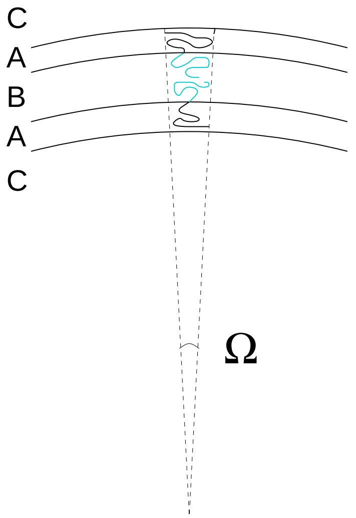

Fig. 3. Area occupied by a pair of copolymers in a bilayer membrane.

The most convenient way is to define the free energy per area Σ occupied by a pair of copolymer molecules as shown in Figure 3. For this purpose, we rewrite the free energy as

$$F'_{\rm mem} = \Sigma\left(\sigma_0\epsilon^3 + \frac{\sigma_2\epsilon^5}{R^2}\right) + (\Sigma_4+\Sigma_1)\sigma_{\rm AC} + (\Sigma_3+\Sigma_2)\sigma_{\rm AB} \tag{40}$$

where we have from (29, 39)

$$\sigma_0 = \frac{\alpha A^2}{3}c(c-1)^2. \tag{41}$$

Note that $F'_{\rm mem}$ is a free energy per chain in a membrane and is different from $F_{\rm mem}$ in (1) defined per area. The correction σ_2 is given in two dimensions by

$$\sigma_2 = \alpha A^2\frac{c}{15}(c-1)^2(2c^2+4c+1) \tag{42}$$

and in three dimensions by

$$\sigma_2 = \alpha A^2\frac{c}{15}(c-1)^2(7c^2+14c+6). \tag{43}$$

In (40) we have added the contribution from the interfacial energies σ_{ij} for an interface between i and j domains. These come from the short range part $F_{\rm S}$ of the free energy. The area Σ and Σ_i ($i = 1 \sim 4$) are related to the solid angle Ω per chain as

$$\Omega = \frac{\Sigma_4}{r_4^{d-1}} = \frac{\Sigma_3}{r_3^{d-1}} = \frac{\Sigma}{R^{d-1}} = \frac{\Sigma_2}{r_2^{d-1}} = \frac{\Sigma_1}{r_1^{d-1}} \tag{44}$$

where $d = 2$ for a cylinder and $d = 3$ for a sphere. The solid angle is, in turn, written in terms of $N_{\rm B}$ as

$$\Omega = \frac{2dN_{\rm B}}{r_3^d - r_2^d}\,\cdot \tag{45}$$

A similar relation holds also in terms of $N_{\rm A}$. Note that the volume occupied by a monomer has been put to be unity.

By using the above relations (44, 45), the membrane free energy in two dimensions can be written as

$$F'_{\rm mem} = N_{\rm B}\left\{\sigma_0\epsilon^2 + \frac{\sigma_2\epsilon^4}{R^2} + \frac{2}{\epsilon}(\sigma_{\rm AC}+\sigma_{\rm AB}) - \frac{\sigma_{\rm AC}}{R^2}(c^2-1)\epsilon\right\}\cdot \tag{46}$$

The unknown parameter ϵ, which is related with the width w as $w = 2c\epsilon$ for a flat membrane is determined by minimization of $F'_{\rm mem}$ with respect to ϵ so that one obtains

$$\epsilon^* = \left(\frac{\sigma_{\rm T}}{\sigma_0}\right)^{1/3} \tag{47}$$

with $\sigma_{\rm T} = \sigma_{\rm AC}+\sigma_{\rm AB}$. Note that the $O(R^{-2})$ corrections in (46) do not influence the equilibrium value. Substituting this into (46) yields

$$F'_{\rm mem} = \frac{N_{\rm B}}{\epsilon^*}\left\{\sigma_{\rm eff} + \left(\frac{2c^2+4c+1}{60c^2} - \frac{\sigma_{\rm AC}}{12\sigma_{\rm T}}\frac{c^2-1}{c^2}\right)\frac{\sigma_{\rm eff}\,w^{*2}}{R^2}\right\} \tag{48}$$

where

$$\sigma_{\rm eff} = 6c\epsilon^*\sigma_{\rm T}/w^* = 3\sigma_{\rm T}. \tag{49}$$

Note that the higher order difference of order of $1/R^2$ between w and $2c\epsilon$ does not contribute to (48). We have factored out $(N_{\rm B}/\epsilon^*)$ which is the area occupied by a copolymer chain in the flat bilayer. Note that the Kuhn statistical length has been put to be unity. Therefore the part in the curly brackets is the membrane free energy per area.

The membrane free energy in three dimensions can be obtained similarly. From (40) one obtains

$$F'_{\rm mem} = N_{\rm B}\left\{\sigma_0\epsilon^2 - \frac{\sigma_0\epsilon^4}{3R^2} + \frac{\sigma_2\epsilon^4}{R^2} + \frac{2}{\epsilon}\sigma_{\rm T} + 2\sigma_{\rm AC}\left(\frac{2\epsilon}{3R^2} - \frac{(c^2-1)\epsilon}{R^2}\right) + \frac{4\sigma_{\rm AB}\epsilon}{3R^2}\right\}\cdot \tag{50}$$

Minimization with respect to ϵ gives us the same equilibrium value as (47) and the free energy is given by

$$F'_{\rm mem} = \frac{N_{\rm B}}{\epsilon^*}\left\{\sigma_{\rm eff} + \left(\frac{7c^2+14c+11}{60c^2} - \frac{\sigma_{\rm AC}}{6\sigma_{\rm T}}\frac{c^2-1}{c^2}\right)\frac{\sigma_{\rm eff}w^{*2}}{R^2}\right\}\cdot \tag{51}$$

Comparing the terms in the curly brackets of (48, 51) with (1) by putting $R_1 = R$ and $R_2 = \infty$ in two dimensions and $R_1 = R_2 = R$ in three dimensions, we finally obtain the elastic rigidities as

$$\kappa = \left\{\frac{f^2-6f+7}{30} - \frac{\sigma_{\rm AC}}{6\sigma_{\rm T}}f(2-f)\right\}\sigma_{\rm eff}w^{*2} \tag{52}$$

$$\bar{\kappa} = \left\{\frac{7f^2-12f+4}{60} + \frac{\sigma_{\rm AC}}{6\sigma_{\rm T}}f(2-f)\right\}\sigma_{\rm eff}w^{*2} \tag{53}$$

where we have used $1-f = 1/c$. These are the main results in the present paper.

A remark is now in order. We have considered only the interfacial energies and the long range part F_L of the free energy for a vesicle in (46, 50). However, the local part of the free energy (4) generally produces another contribution proportional to the volume of a vesicle. Here we will show that this bulk energy does not enter into the above results. First of all, the first term of (4) can be ignored in the bulk contribution since ϕ_i is equal either to 0 or 1 in the strong segregation limit. Thus we may consider only the second term of (4). Putting $\phi_\mathrm{A} = 1$ in the A–domains and $\phi_\mathrm{B} = 1$ in the B–domain, the local part (4) gives rise to the free energy of a vesicle per area occupied by a molecule as

$$F_\mathrm{bulk} = \frac{\Omega}{d}[u_\mathrm{AA}(r_4^d - r_1^d) - (u_\mathrm{AA} - u_\mathrm{BB})(r_3^d - r_2^d)] \quad (54)$$

where $d = 2$ for a cylindrical vesicle and $d = 3$ for a spherical vesicle. Using the relations (45) and the neutrality conditions (14, 30), one obtains

$$F_\mathrm{bulk} = 2N_\mathrm{B}[cu_\mathrm{AA} - u_\mathrm{AA} + u_\mathrm{BB}]. \quad (55)$$

As is expected, (55) is independent of the radius R so that it does not contribute to the elastic moduli in the Helfrich free energy.

Now we discuss the properties of the elastic rigidities κ and $\bar{\kappa}$. First we consider the case $\sigma_\mathrm{AC} = 0$ in (52, 53). Equation (52) shows that the bending rigidity κ is always positive. On the other hand, the curvature rigidity $\bar{\kappa}$ changes its sign by changing the block ratio f. That is, when $f > f_\mathrm{c} = (6 - 2\sqrt{2})/7 = 0.453$, $\bar{\kappa}$ is negative, whereas if $f < f_\mathrm{c}$, it turns out to be positive.

Since $w^* \sim N^{2/3}$ and $\sigma_\mathrm{eff} \sim N^0$, the rigidities have an $N^{4/3}$–dependence. This is not altered when $\sigma_\mathrm{AC} \neq 0$. Note also that both w^* and σ_eff are independent of f provided that σ_AC and σ_AB are f–independent.

The results (52, 53) with $\sigma_\mathrm{AC} = 0$ should be compared with those obtained by Ajdari and Leibler [16]:

$$\kappa_\mathrm{AL} = \frac{8}{3^{5/3}} f(1-f) N^{4/3} \Gamma^{5/3} \quad (56)$$

$$\bar{\kappa}_\mathrm{AL} = \frac{2}{3^{5/3}} \left\{3(1-f)^2 - 1\right\} N^{4/3} \Gamma^{5/3} \quad (57)$$

where Γ is an interfacial tension. Note that f in reference [16] has been replaced by $1 - f$ in the above expressions since the relative molecular weight of B block incompatible with the homopolymer is defined as f in reference [16].

First of all, $\bar{\kappa}_\mathrm{AL}$ in (57) changes the sign at $f = 1 - 1/\sqrt{3} = 0.423$. This is qualitatively consistent with (53). The moduli (56, 57) exhibit $N^{4/3}$ dependence supposing that Γ is N-independent, which is also consistent with our result. However, the f–dependence of κ is quite different although both theories give us positive bending rigidity for finite values of f. In the present result (52), the bending modulus is asymmetric with respect to $f = 1/2$ while (56) is invariant under the replacement of f by $1 - f$. Because no detailed explanation is given in reference [16] about the interaction between the two monolayers, the origin of this discrepancy is unclear for us. In our opinion, there must be the asymmetry of the system since A block is always outside the layer whereas B block is inside the layer.

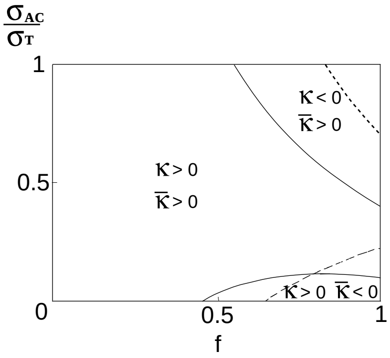

Fig. 4. The sign of κ and $\bar{\kappa}$ on the $\sigma_\mathrm{AC}/\sigma_\mathrm{T}$–$f$ plane. The dotted line is a line where $2\kappa + \bar{\kappa} = 0$. Below the broken line a bilayer is unstable in comparison with micelles.

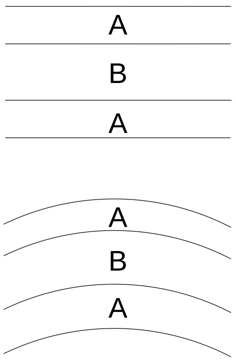

Fig. 5. Change of domain width upon bending.

When σ_AC is finite, the stability of a bilayer membrane is substantially altered. The sign of the rigidities is shown on the σ_AC–f plane in Figure 4. As can be seen from (52, 53), the interfacial energy between A block and C homopolymer tends to decrease κ and to increase $\bar{\kappa}$. For instance, when $\sigma_\mathrm{AC}/\sigma_\mathrm{T} = 1/2$, κ becomes negative for $f > 0.89$ and $\bar{\kappa}$ is positive in the entire interval $0 < f < 1$.

When κ is negative, a flat membrane is unstable for undulation. To stabilize the short wavelength deformation, one has to introduce higher order gradient terms in the Helfrich free energy. The region where $2\kappa + \bar{\kappa}$ is negative appears only at the upper–right corner in Figure 4 as is indicated by the dotted line.

The reason why the bending rigidity κ becomes small by increasing σ_AC is as follows. If the membrane bends as shown in Figure 5, the width of the outer A domain decreases whereas that of the innner A domain increases due to mass conservation. Therefore the average radius of curvature of the two AC interfaces becomes smaller than R. This makes the free energy lower and amount of the reduction is proportional to σ_AC. Consequently the membrane becomes softer as σ_AC is increased.

The curvature rigidity $\bar{\kappa}$ increases by increasing σ_AC. The two AC interfaces tend to contract when σ_AC is large, which causes a conflict between these two interfaces. To accommodate it, the membrane tends to deform with a negative curvature.

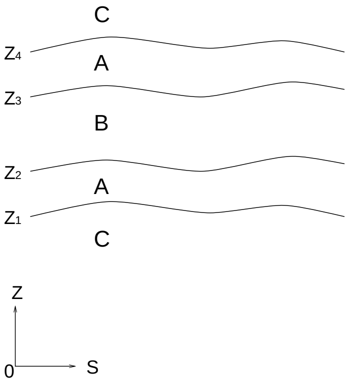

Fig. 6. Weakly deformed membrane.

A similar situation occurs when one decreases f for $\sigma_{\rm AC} = 0$. For smaller values of f, B block occupies larger volume compared with A block so that the membrane tends to take a concave deformation. As a result, the curvature modulus becomes positive for small values of f [16].

When f is larger than $f_{\rm c}$ and $\sigma_{\rm AC}$ is small, $\bar{\kappa}$ is negative, which is favorable for a vesicle formation. However, as will be shown in Section 7, a bilayer membrane is unstable compared with micelles in the parameter region below the broken line in Figure 4. Hence formation of a vesicle is very limited in the $\sigma_{\rm AC}$–f plane.

6 Deformation of a flat membrane

In Section 5, we have derived the bending and curvature moduli κ and $\bar{\kappa}$ in the Helfrich free energy. In order to obtain these expressions independent of the choice of the radius R, we have employed the picture of polymer chain conformation. However, the starting model free energy (2) is not represented in terms of the chain conformation. In fact, (2) is not restricted to copolymer systems but is applicable to other mesophases. Therefore one needs to develop a theory to derive the Helfrich free energy for a bilayer without using the chain picture.

In this section we will show an alternative method to evaluate κ and $\bar{\kappa}$. Let us consider a slightly deformed membrane as shown in Figure 6. The deformation of each interface is represented by

$$\begin{aligned} z_1 &= -c\epsilon + h^{(1)}(x,y) \\ z_2 &= -\epsilon + h^{(2)}(x,y) \\ z_3 &= \epsilon + h^{(3)}(x,y) \\ z_4 &= c\epsilon + h^{(4)}(x,y). \end{aligned} \tag{58}$$

One needs to express the long range part of the free energy (7) in terms of $h^{(i)}$ (i =1,...4). By introducing the Fourier transform

$$\phi'_{\mathbf{q}} = \int \phi'(\mathbf{r}) {\rm e}^{i\mathbf{q}\cdot\mathbf{r}} {\rm d}\mathbf{r} \tag{59}$$

one obtains

$$F_{\rm L} = \frac{\alpha}{2} \int \frac{{\rm d}\mathbf{q}}{(2\pi)^3} \frac{1}{q^2} \phi'_{\mathbf{q}} \phi'_{-\mathbf{q}}. \tag{60}$$

Since $\phi' = A$ and $\phi' = -B$ in A-rich and B-rich domains, respectively, the Fourier component can be written as

$$\begin{aligned} \phi'_{\mathbf{q}} = \int {\rm d}\mathbf{s}\, {\rm e}^{i\mathbf{p}\cdot\mathbf{s}} \frac{1}{iq_z} \, &[A({\rm e}^{iq_z z_2} - {\rm e}^{iq_z z_1}) \\ &- B({\rm e}^{iq_z z_3} - {\rm e}^{iq_z z_2}) + A({\rm e}^{iq_z z_4} - {\rm e}^{iq_z z_3})] \end{aligned} \tag{61}$$

where $\mathbf{s}$ and $\mathbf{p}$ are two–dimensional vectors within a layer defined such that $\mathbf{q} = (\mathbf{p}, q_z)$ and $\mathbf{r} = (\mathbf{s}, z)$.

Substituting (58) into (60) with (61) and expanding it in powers of $h^{(i)}$, one obtains up to the bilinear order

$$F_{\rm L} = \frac{\alpha}{2} \sum_{i,j} \int \frac{{\rm d}\mathbf{p}}{(2\pi)^2} [D_{ij}(\mathbf{p}) + 2C_i] h^{(i)}_{\mathbf{p}} h^{(j)}_{-\mathbf{p}} \tag{62}$$

where the zeroth order term has been omitted. The Fourier component $h^{(i)}_{\mathbf{p}}$ is defined in a way similar to (59) in a two-dimensional space. After carrying out the integral over q_z, the coefficients are given by

$$\begin{aligned} &D_{11} = D_{44} = \frac{A^2}{2p},\ D_{22} = D_{33} = \frac{A^2c^2}{2p}, \\ &D_{12} = D_{34} = D_{21} = D_{43} = -\frac{A^2c}{2p} {\rm e}^{-\epsilon(c-1)p}, \\ &D_{13} = D_{24} = D_{31} = D_{42} = \frac{A^2c}{2p} {\rm e}^{-\epsilon(c+1)p}, \\ &D_{14} = D_{41} = -\frac{A^2}{2p} {\rm e}^{-2\epsilon cp},\ D_{23} = D_{32} = -\frac{A^2c^2}{2p} {\rm e}^{-2\epsilon p} \end{aligned} \tag{63}$$

and

$$\begin{aligned} &C_1 = C_4 = 0, \\ &C_2 = C_3 = -\frac{AB}{2} c\epsilon = -\frac{A^2}{2} c(c-1)\epsilon. \end{aligned} \tag{64}$$

In the derivation of (64), we have used the formula

$$\int_0^\infty {\rm d}x \frac{1}{x^2} \sin ax \sin bx = \frac{\pi}{2} a \tag{65}$$

for $0 < a < b$. By taking account of the interfacial energies, the total free energy of a deformed membrane is given by

$$\begin{aligned} F_{\rm m} = \sigma_{\rm AC} &\int {\rm d}\mathbf{r} [(1 + (\nabla h^{(1)})^2)^{1/2} + (1 + (\nabla h^{(4)})^2)^{1/2}] \\ &+ \sigma_{\rm AB} \int {\rm d}\mathbf{r} [(1 + (\nabla h^{(2)})^2)^{1/2} + (1 + (\nabla h^{(3)})^2)^{1/2}] + F_{\rm L}. \end{aligned} \tag{66}$$

Now we have to compare (66) with the Helfrich free energy (1) to identify the elastic moduli. The Helfrich free energy for an infinitesimally thin membrane ignores any internal structure. On the other hand, (66) contains four degrees of freedom. Therefore one has to make a reduction to express it in terms only of one independent variable. First of all, we may put $h^{(1)} = h^{(4)}$ and $h^{(2)} = h^{(3)} \equiv h$ by symmetry. It is easily found that the simplest choice $h^{(1)} = h^{(4)} = h$ does not give us the results equivalent with (52, 53). This implies that $h^{(1)}$ and $h^{(4)}$ must have a correction term:

$$h^{(1)} = h^{(4)} = h + g. \tag{67}$$

In order to determine the correction g, we note from (58) that

$$z_4 + z_1 = 2h + 2g. \tag{68}$$

This should be compared with

$$r_4 + r_1 - 2R = -\frac{c^2 - 1}{R}\epsilon^2 + O\left(\frac{1}{R^2}\right) \tag{69}$$

which is obtained from (21, 28) for a cylindrical vesicle. Since $\nabla^2 h = -1/R$ for $h(x) = \sqrt{R^2 - x^2} \approx R - x^2/(2R)$, (68) is consistent with (69) if and only if one chooses

$$g = \frac{c^2 - 1}{2}\epsilon^2 \nabla^2 h. \tag{70}$$

It is easily verified that one can arrive at the same conclusion as (70) for a spherical vesicle by using (38) and putting $h(x, y) = R - (x^2 + y^2)/(2R)$.

Substituting $h^{(2)} = h^{(3)} = h$ and (67) with (70) into (66) yields up to the fourth order of the gradient expansion

$$F_{\mathrm{m}} = \int \frac{\mathrm{d}\mathbf{p}}{(2\pi)^2}\Big[\frac{\alpha A^2 \epsilon^5}{15} c(c-1)^2(2c^2 + 4c + 1) - \sigma_{\mathrm{AC}}\epsilon^2(c^2 - 1)\Big] p^4 h_{\mathbf{p}} h_{-\mathbf{p}} \tag{71}$$

where the p^2 term vanishes identically due to the equilibrium condition for the domain width. Since $p^4 h_{\mathbf{p}} h_{-\mathbf{p}}$ corresponds to $1/R^2$ and $3\sigma_{\mathrm{T}} w^{*2} = 12c^2\epsilon^5\sigma_0$, the factor in the bracket in (71) precisely agrees with (48) for a cylindrical vesicle and hence with the bending modulus κ as in (52). Once the rigidity κ is identified, the other modulus $\bar{\kappa}$ can be extracted from the free energy for a spherical vesicle (39) as has already been demonstrated from (51) to (53).

It is remarked that the direct comparison of (71) with (51) is not correct to identify $2\kappa + \bar{\kappa}$. Note that (71) is for an open membrane while (51) is for a closed membrane and hence these structures have a different Euler number.

It is mentioned here that one can examine the linear stability of a membrane for a peristaltic deformation putting $h^{(1)} = h^{(2)} = -h^{(3)} = -h^{(4)}$. The bilayer membrane is found to be linearly stable against this mode. However, this fact does not guarantee the stability of membrane compared with other morphology such as micelles. We will address this question in Section 7.

To summarize, in order to derive the Helfrich free energy for a bilayer membrane, one has to evaluate the free energy for three different configurations, *i.e.*, cylindrical and spherical forms and a membrane deformed around a flat configuration. By taking into account the correction for the interface position due to the finite radius of curvature as (68, 69), one can determine the elastic rigidities. It should be noted that the term with σ_{AC} in (71) cannot be obtained only from the free energy for a cylindrical geometry.

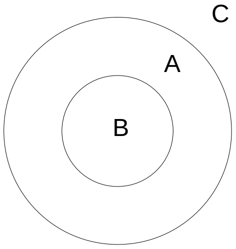

Fig. 7. Micelle with the core of B–blocks and the corona of A–blocks.

We emphasize that the theory shown here is free from the molecular picture employed in the previous study [16] and provides us with a general procedure to derive the elastic moduli for bilayer membrane starting with a field theoretic model like (2).

7 Formation of micelles

In the previous three sections, we have studied the elastic property of a bilayer membrane. However, one cannot exclude other configurations of block copolymers in a homopolymer matrix. For instance, it is possible that spherical micelles with a core of B blocks surrounded by A blocks are formed when the block ratio f is large as shown in Figure 7.

In this section, we examine the relative stability of a flat membrane, a worm–like (cylindrical) micelle and a spherical micelle. Assuming that the volume fraction of the block copolymers is sufficiently small, we do not consider any interactions between these aggregates. An inverse micelle such that the core is occupied by A blocks and the corona is formed by B blocks is not considered since we have assumed a strong repulsive interaction between B blocks and C homopolymers.

The equilibrium free energy of a flat membrane per area of a pair of molecules is given from (48) or (51) with $R \to \infty$ by

$$F_{\mathrm{m}} = \frac{3N_{\mathrm{B}}\sigma_{\mathrm{T}}}{\epsilon^*}\,. \tag{72}$$

Suppose that the membrane has a linear dimension L. Since the number of the pair of molecules is given by $M_{\mathrm{p}} = L^2/\Sigma$, the total free energy can be written as

$$F_{\mathrm{m}}^{\mathrm{T}} = F_{\mathrm{m}} M_{\mathrm{p}} = 3\sigma_{\mathrm{T}} L^2. \tag{73}$$

Next consider the equilibrium free energy for a spherical micelle. In this case, we may apply the result in Section 4. In the strong segregation limit, the profile ϕ' is approximated by $\phi' = -B$ for $0 < r < r_1$, $\phi' = A$ for $r_1 < r < r_2$ and $\phi' = 0$ for $r > r_2$. Hence by using equation (34), one obtains the long range interaction for an isolated micelle

$$F_{\mathrm{L}} = 4\pi\alpha A^2 r_1^5 \frac{c(2c - 3c^{2/3} + 1)}{30} \tag{74}$$

where the neutrality condition $r_2^3 = cr_1^3$ has been used. The free energy of a micelle per molecule can be written as

$$F_{\rm s} = \Sigma_1 r_1^3 g_{\rm s}(c) + \Sigma_2\sigma_{\rm AC} + \Sigma_1\sigma_{\rm AB} \tag{75}$$

where $g_{\rm s}(c)$ is defined by

$$g_{\rm s}(c) = \alpha c A^2\left\{\frac{2c - 3c^{2/3}+1}{30}\right\}\cdot \tag{76}$$

In this case, we have $\Sigma_1 = 3N_{\rm B}/r_1$ and $\Sigma_2 = 3cN_{\rm B}/r_2$. Minimization of $F_{\rm s}$ with respect to r_2 leads to the equilibrium free energy

$$F_{\rm s} = \frac{3N_{\rm B}}{r_1^*}\left(\frac{3}{2}\right)(c^{2/3}\sigma_{\rm AC}+\sigma_{\rm AB}) \tag{77}$$

with the equilibrium radius

$$r_2^{*3} = \frac{c^{5/3}\sigma_{\rm AC}+c\sigma_{\rm AB}}{2g_{\rm s}(c)}\cdot \tag{78}$$

Since the number of molecules in a micelle is given by $n = 4\pi r_1^2/\Sigma_1 = 4\pi r_1^3/(3N_{\rm B})$ and the number of micelles must be equal to $2M_{\rm p}/n$, one obtains the total free energy of spherical micelles

$$F_{\rm s}^{\rm T} = 3\sigma_{\rm T} L^2\chi_{\rm s} \tag{79}$$

where

$$\chi_{\rm s} = \left(\frac{3w^*}{2c^{2/3}r_2^*}\right)\frac{c^{2/3}\sigma_{\rm AC}+\sigma_{\rm AB}}{\sigma_{\rm T}} \tag{80}$$

with w^* the equilibrium width of a bilayer membrane. This factor appears in (80) because we have compared the free energies by fixing the total number of copolymer molecules.

The free energy for a worm–like micelle with length L can be evaluated in a similar manner. The final result is given by

$$F_{\rm c}^{\rm T} = 3\sigma_{\rm T} L^2\chi_{\rm c} \tag{81}$$

where

$$\chi_{\rm c} = \left(\frac{w^*}{c^{1/2}r_2^*}\right)\frac{c^{1/2}\sigma_{\rm AC}+\sigma_{\rm AB}}{\sigma_{\rm T}}\cdot \tag{82}$$

The equilibrium radius r_2^* is given for a cylindrical micelle by

$$r_2^{*3} = \frac{c^2\sigma_{\rm AC}+c^{3/2}\sigma_{\rm AB}}{2g_{\rm c}(c)} \tag{83}$$

with

$$g_{\rm c}(c) = \frac{\alpha c A^2}{16}[1-c+c\ln c]. \tag{84}$$

Comparing (73, 79, 81) we note that a bilayer membrane has the lowest free energy for $f \to 0$ ($c \to 1$) and hence it is energetically most favorable in this limit. The behavior for large values of f depends crucially on $\sigma_{\rm AC}$. When $\sigma_{\rm AC}$ is identically zero, a spherical micelle is found to be most stable for $f \to 1$ ($c \to \infty$). Figures 8 and 9 compare the free energies as a function of f for $\sigma_{\rm AC}/\sigma_{\rm T} = 0$ and $\sigma_{\rm AC}/\sigma_{\rm T} = 0.048$ respectively. When $\sigma_{\rm AC}$ exceeds some critical value given below, neither spherical nor cylindrical micelles is stable even for $f \to 1$. This can be understood as follows; note that the number of molecules in a micelle decreases with increasing f so that the number of micelles increases. As a result, the total interface area between A blocks and C homopolymers becomes larger than that of a flat membrane. In fact, (79, 81) indicate that when $\sigma_{\rm AC}/\sigma_{\rm T} > 0.23$ ($\sigma_{\rm AC}/\sigma_{\rm AB} > 0.29$) a bilayer membrane is the most stable configuration for the entire block ratio $0 < f < 1$.

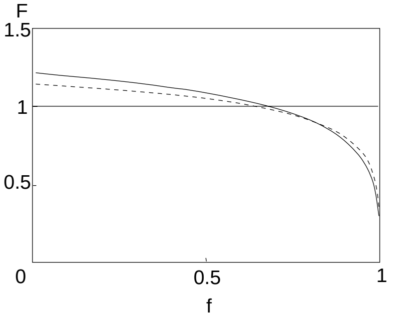

Fig. 8. Comparison of free energies for a flat bilayer (flat straight line), a cylindrical micelle (dotted line) and a spherical micelle (full line) for $\sigma_{\rm AC}/\sigma_{\rm T} = 0$.

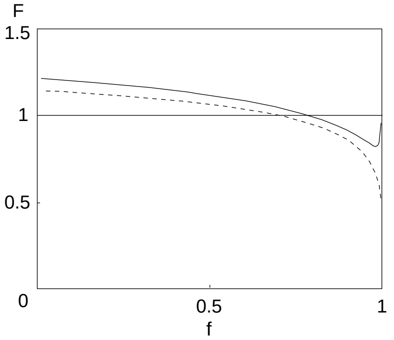

Fig. 9. Comparison of free energies for a flat bilayer (flat straight line), a cylindrical micelle (dotted line) and a spherical micelle (full line) for $\sigma_{\rm AC}/\sigma_{\rm T} = 0.048$.

Finally we make a remark that a similar comparison with the free energy of a vesicle is not possible in the present theory since one has no way to determine the equilibrium radius because of the absence of the spontaneous curvature.

8 Discussion

We have derived the Helfrich free energy for a bilayer membrane starting from the field theoretic model for copolymer–homopolymer mixtures. The bending and Gaussian curvature moduli κ and $\bar{\kappa}$ have been obtained with and without the molecular picture.

In the case that a membrane does not have any internal structures, the neutral surface defined at the midpoint of the membrane, where there is neither stretching nor contraction upon bending can be used to investigate the bending elasticity [30]. However since bilayer membrane studied in this paper consists of A–B–A domains, the neutral surface is not determined by a simple geometrical argument. The radius R introduced in (21) is actually the distance from the center of cylinder to the midplane of the B domain. This is different from $R+(a-b)/2$ with $a-b$ given by (28), which is the location of the midpoint of the A–B–A layers. The analysis in Section 5 indicates that this difference gives rises to the σ_{AC} term in the bending rigidity. What we have shown here is that the membrane energy can be obtained without specifying the location of the neutral surface even when the interfacial energy between C homopolymers and A blocks is finite.

The results for the elastic moduli indicate that the interfacial energy σ_{AC} between the A blocks and C homopolymers plays an important role for the morphology of membrane. In the region that σ_{AC} is small and f is around 0.5, κ is positive and $\bar{\kappa}$ is negative. This is a necessary condition for a vesicle formation. On the other hand, in the region where the absolute value of κ is small and $\bar{\kappa}$ is positive a sponge phase is expected to be a favorable state.

These results may be modified slightly by taking account of shape fluctuations since they renormalize the elastic rigidities. However, what we have aimed in this paper is to derive the Helfrich free energy. The main problem was to find the principle how to make the reduction of the degrees of freedom arising from the internal structure. Once the rigidities are obtained as a function of the relevant parameters such as f and σ_{AC}, renormalization can be carried out by the standard method [31–34].

When κ is negative, the Helfrich free energy is not well-behaved. The higher order gradient terms are necessary. One of the generalization is the following Euclidean invariant form

$$F_{\mathrm{mem}} = \sigma + 2\kappa H^2 + \bar{\kappa} K + \beta(\nabla H)^2 \tag{85}$$

provided that β is positive. The gradient ∇ in (85) is defined on a two-dimensional surface. In terms of h introduced in Section 6, we have $(\nabla H)^2 = (\nabla^3 h)^2$ up to the bilinear order. Thus this is a simplest but nontrivial term to stabilize the short length deformation. The constant β can, in principle, be evaluated by generalizing the method given in Section 6. However since the actual calculation is fairly involved, we do not enter into this problem here.

The relative stability of a bilayer membrane compared with micelles has been investigated. It has been shown that the interfacial energy σ_{AC} plays again a crucial role for the morphologies. When σ_{AC} is small, micelles are more stable for large values of the block ratio f while when σ_{AC} is sufficiently large, a bilayer membrane is the dominant morphology for all the values of f. Since these conclusions have been obtained by omitting the translational entropy of a micelle, the stability limit may be changed slightly by taking account of the entropy effect. However, we believe that the property mentioned above is qualitatively unaltered. It should also be pointed out that we have assumed only the stripe domain of A– and B–blocks in a membrane. When the block ratio f is large, one cannot exclude, for instance, the possibility of formation of cylindrical or spherical domains of B-blocks arrayed periodically in a membrane as indicated in Figure 10. However we do not go into the detail of such an internal domain morphology in this paper.

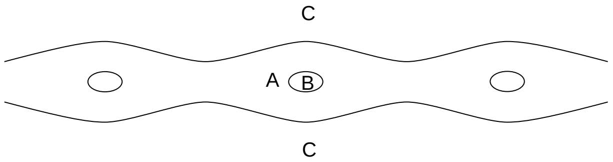

Fig. 10. Membrane where the B–blocks constitute spherical disconnected domains.

In Sections 4 and 5, we have assumed that the number of the copolymer chains in a bilayer is unchanged upon bending. This is justified when the deformation of a membrane is sufficiently weak. Wang [17] has shown that change of the copolymer number is important when the block ratio is close to unity where the A–domain is thicker than the B–domain. As shown in Figure 4, however, a bilayer membrane is unstable compared to a micelle when σ_{AC} is small. Nevertheless, the number change cannot be ignored when the radius of a vesicle is small or σ_{AC} is large. It is remarked that the number change can be incorporated into the present theory by removing the conditions (24, 35) and minimizing the free energy with respect to each domain width.

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Appendix

Here we describe some details of manipulations used in the derivations of (29, 39).

First let us consider the case of a cylindrical vesicle in Section 3. By using (21, 27, 28), one obtains

$$r_3^4 - r_2^4 = 8R^3\epsilon + 8R\epsilon^3 \tag{A.1}$$

and

$$r_4^4 - r_1^4 = c(8R^3\epsilon + 8R\epsilon^3). \tag{A.2}$$

Note that the terms of order of $1/R$ exactly cancel out each other and do not exist in (A.2).

In order to calculate the last term in (20), we use the relation

$$cr_2^2 - r_1^2 = cr_3^2 - r_4^2 = \frac{\mathrm{B}}{2\mathrm{A}}(r_3^2 + r_2^2) \qquad \text{(A.3)}$$

which is readily proved from (14, 24). Therefore one obtains up to $O(1/R)$

$$\begin{aligned}(cr_2^2 - r_1^2)(cr_3^2 - r_4^2)\ln\frac{r_3}{r_2} &= \frac{B^2}{4A^2}(r_3^2 + r_2^2)^2 \ln\frac{r_3}{r_2}\\ &= \frac{B^2}{A^2}\left(2R^3\epsilon + \frac{14}{3}R\epsilon^3 + \frac{56}{15}\frac{\epsilon^5}{R}\right).\end{aligned} \qquad \text{(A.4)}$$

Evaluation of the third term in (20) is mostly involved. Substituting (21) into it, one obtains after tedious but elementary calculations

$$\begin{aligned}r_4^4 \ln\frac{r_4}{r_3} + r_1^4 \ln\frac{r_2}{r_1} = {} & R^3[2\epsilon(c-1) + a + b]\\ & + R^2\left[\frac{7}{2}(a^2 - b^2) + \epsilon(a-b)(7c-4)\right]\\ & + R\left[\epsilon(13c-6)(a^2+b^2)\right.\\ & + \epsilon^2(a+b)(13c^2 - 12c + 2)\\ & \left. + \epsilon^3\left(\frac{26}{3}c^3 - 12c^2 + 4c - \frac{2}{3}\right)\right]\\ & + \epsilon^3(a-b)\left(\frac{25}{3}c^3 - 12c^2 + 6c - \frac{4}{3}\right)\\ & + \frac{2\epsilon^5}{R}\left(\frac{c^5}{5} - c^4 + 2c^3 - 2c^2 + c - \frac{1}{5}\right).\end{aligned} \qquad \text{(A.5)}$$

Using (27, 28) in (A.5) and putting (A.1, A.2, A.4, A.5) together, one finally obtains the free energy for a cylindrial vesicle (29).

Next we describe the derivation of (39). Substituting (21) into the second term of (34), one obtains

$$\frac{1}{5}\left(1 - \frac{B^2}{A^2}\right)(r_3^5 - r_2^5) = c(2-c)(2R^4\epsilon + 4R^2\epsilon^3 + \frac{2}{5}\epsilon^5). \qquad \text{(A.6)}$$

From (30, 35) one notes the relation

$$r_4^3 - r_3^3 = r_2^3 - r_1^3 = \frac{c-1}{2}(r_3^3 - r_2^3) \qquad \text{(A.7)}$$

so that

$$r_2^2(r_2^3 - r_1^3) + r_3^2(r_4^3 - r_3^3) = \frac{2}{3}c(c-1)(3R^4\epsilon + 4R^2\epsilon^3 + \epsilon^5). \qquad \text{(A.8)}$$

Similarly the first term of (34) can be written as

$$\begin{aligned}\frac{1}{5}(r_1^5 - r_4^5) = {} & -R^4(2c\epsilon + a + b) + 2R^3[2c\epsilon(b-a) + (b^2 - a^2)]\\ & - 2R^2[2c^3\epsilon^3 + 3c^2\epsilon^2(a+b) + 3c\epsilon(a^2+b^2)]\\ & + 4Rc^3\epsilon^3(b-a) - \frac{2}{5}c^5\epsilon^5.\end{aligned} \qquad \text{(A.9)}$$

Substituting (37, 38) into (A.9), one obtains, from (A.6, A.8, A.9), the free energy (39) for a spherical vesicle.

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