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## A Lattice Statistical Thermodynamic Study of Bilayer Amphiphile Molecules

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In order to elucidate conformational properties of bilayer semiflexible amphiphile molecules, we derive a expression of free energy separation with respect to bilayer width, and segment density profiles on the basis of cubic lattice model. Our result shows that at the moderate surface coverage region (*i.e.*,  $\sigma < 0.35$ ), bilayer system tends to have thermodynamically favorable bilayer width corresponding to free energy minimum condition resulting from the major contribution of attractive interaction between chain segments. However such a favorable bilayer width do not occur in the region of high surface coverage (*i.e.*,  $\sigma > 0.4$ ) where repulsive interaction between chain segments is considered to be dominant.

### Introduction

In aqueous environment, bilayer can be formed by amphiphile chain molecules due to their hydrophobic and hydrophilic natures. It plays an important role in biological sys-

tems such as membranes and vesicles. Because of the flexibility of hydrocarbon chain of the amphiphiles, the amphiphiles can have various conformational states, which result in fluidity of inner layer region. Recently, by making use of Self-Consistent Field theory based on Dolan and Edwards'

path integral formulation of polymer<sup>1</sup>, Muthukumar and Jyh-Shyong Ho<sup>2</sup> studied the conformational properties such as segment density profiles and free energy change of terminally attached polymer chains between parallel plates. However they did not consider the effect of chain stiffness of chain molecules. In order to incorporate chain stiffness effect, we make use of well known lattice model which is very convenient in treating short chain amphiphile molecules at high concentration. Recently, Wang and Rice<sup>3</sup>, using Scheutjens and Fleer approach,<sup>4-6</sup> have developed a theory of monolayer amphiphile chain molecules. Since they introduce the reasonable energy parameters which are suitable to describe the monolayer amphiphile chain molecules in liquid surface, we apply their model to our bilayer problem. Using our lattice theory, we attempt to account for favorable bilayer width and segment density profiles of bilayer amphiphile molecules having chain stiffness. With the concept of statistical weights in conformational statistics<sup>7</sup>, we can derive Fleer and Scheutjens type-nonlinear equations<sup>4</sup> of segment density profiles which make it possible to calculate free energy of amphiphile molecules. These nonlinear equations can be solved by numerical method.

### Theory

**Model.** We consider 3-dimensional simple cubic lattice consisting of  $D$  parallel layers numbered  $k=1\dots D$  of sites, where layers  $k=1$  and  $k=D$  represent two interfaces where the head groups of chain molecules are to be attached. Therefore we can regard  $D$  as the layer width of our model system. Each layer contains  $L$  lattice sites. We consider  $2N$  amphiphile molecules each consisting of  $r$  segments are distributed over the lattice such that a segment of the amphiphile occupies only one lattice site. To each interface, we assume that  $N$  hydrophilic head groups of the amphiphiles are always anchored respectively. Following Rice Model<sup>3</sup>, we take the interaction energy parameter as

- $\epsilon^{hh}$  : head-head nearest neighbor interaction energy
- $\epsilon^{ht}$  : head-tail nearest neighbor interaction energy
- $\epsilon^{tt}$  : tail-tail nearest neighbor interaction energy
- $\epsilon^{\epsilon}$  : tail-surface contact energy.

**Bond Pair Statistical Weight.** In order to incorporate chain stiffness effect in amphiphile chain molecules, we need to know exact bond pair forms composed of consecutive three segment of the chain molecule. Since a bond in the cubic lattice can occupy the two adjacent lattice sites by the way of three possible orientations; forward(F), lateral(L), and downward(D) directions, all the possible adjacent bond pairs have following 9 configurations:

$$\begin{bmatrix} (F, F) & (L, F) & (D, F) \\ (F, L) & (L, L) & (D, L) \\ (F, D) & (L, D) & (D, D) \end{bmatrix}$$

In the cubic lattice, there can be only two relative orientations of the adjacent bond pair, straight and bent at 90°. Following the conventional method<sup>8-10</sup> used to incorporate the chain stiffness of the linear chain molecule in the lattice system, we now assume that straight and bent pairs

correspond to *trans* and *gauche* states of real hydrocarbon chain respectively. Defining the bent energy with respect to straight pair as  $\epsilon_b$ , we can write the statistical weights of a bent and a straight pairs as  $\exp(-\epsilon_b/k_b T)$  and 1 respectively, where  $k_b$  is the Boltzmann constant and  $T$  is the absolute temperature. Let  $Z$  be lattice coordination number (in cubic lattice,  $Z=6$ ). In spirit of Dill and Cantor's Method,<sup>11,12</sup> incorporating the statistical weights of straight and bent pairs, we now determine the statistical bond pair weights assigned to the above 9 bond pairs as follows:

(1) (F, F): The bond is forward (from layer  $k-1$  to  $k$ ) and its preceding bond is also forward (from layer  $k-1$  to  $k-1$ ). This type of bond pair has only one straight pair. Therefore the bond pair weight  $DW(F, F)$  is 1.

(2) (L, F): The bond is forward (from layer  $k-1$  to  $k$ ) and its preceding bond is lateral (from layer  $k-1$  to  $k-1$ ). This type of bond pair has only one bent pair. Therefore the bond pair weight  $DW(L, F)$  is  $\exp(-\epsilon_b/k_b T)$ .

(3) (D, F): The bond is forward (from layer  $k-1$  to  $k$ ) and its preceding bond is downward (from layer  $k$  to  $k-1$ ). This type of bond pair is self-reversal. In order to exclude this unrealistic bond pair, we have to take the bond pair weight  $DW(D, F)$  to be zero.

(4) (F, L): The bond is lateral (from layer  $k$  to  $k$ ) and its preceding bond is forward (from layer  $k-1$  to  $k$ ). In this case, there are  $(Z-2)$  possible bent pairs, which give the bond pair weight  $DW(F, L)=(Z-2)\exp(-\epsilon_b/k_b T)$ .

(5) (L, L): The bond is lateral (from layer  $k$  to  $k$ ) and its preceding bond is also lateral (from layer  $k$  to  $k$ ). This type of bond pair can have  $(Z-4)$  bent pairs and 1 straight pair. Therefore the bond pair weight  $DW(L, L)$  is  $1+(Z-4)\exp(-\epsilon_b/k_b T)$ .

(6) (D, L): The bond is lateral (from layer  $k$  to  $k$ ) and its preceding bond is downward (from layer  $k+1$  to  $k$ ). This bond pair can have  $(Z-2)$  bent pairs. Therefore the bond pair weight  $DW(D, L)$  is  $(Z-2)\exp(-\epsilon_b/k_b T)$ .

(7) (F, D): The bond is downward (from layer  $k+1$  to  $k$ ) and its preceding bond is forward (from layer  $k$  to  $k+1$ ). This bond pair is self-reversal. In order to exclude the unrealistic bond pair, we take the bond pair weight  $DW(F, D)$  to be zero.

(8) (L, D): The bond is downward (from layer  $k+1$  to  $k$ ) and its preceding bond is lateral (from layer  $k+1$  to  $k+1$ ). This bond pair includes only one bent pair. Therefore the bond pair weight  $DW(L, D)$  is  $\exp(-\epsilon_b/k_b T)$ .

(9) (D, D): The bond is downward (from layer  $k+1$  to  $k$ ) and its preceding bond is also downward (from layer  $k+2$  to  $k+1$ ). This bond pair has only one straight bond pair. Therefore the bond pair weight  $DW(D, D)$  is 1.

Above nine bond pair weighting factors incorporating chain stiffness can be summarized as follows:

- 1) (F, F) :  $DW(F, F)=1$
- 2) (L, F) :  $DW(L, F)=\exp(-\epsilon_b/k_b T)$
- 3) (D, F) :  $DW(D, F)=0$  (i.e., eliminating back folding)
- 4) (F, L) :  $DW(F, L)=(Z-2)\exp(-\epsilon_b/k_b T)$
- 5) (L, L) :  $DW(L, L)=1+(Z-4)\exp(-\epsilon_b/k_b T)$
- 6) (D, L) :  $DW(D, L)=(Z-2)\exp(-\epsilon_b/k_b T)$
- 7) (F, D) :  $DW(F, D)=0$  (i.e., eliminating back folding)
- 8) (L, D) :  $DW(L, D)=\exp(-\epsilon_b/k_b T)$

$$9) (D, D) : DW(D, D) = 1.$$

**Conformational  $n$  Step Weight.** Since amphiphile chain molecule has chain flexibility nature, it can occupy the lattice with various conformational states. In order to treat numerous conformations of the chain molecules on the basis of chain statistics, we thus assume that the conformational states of the chain molecule with  $r$  segments can be generated by successive additions of consecutive  $r$  segments. At each addition step, we assign a conformational weight to the position to be generated with specific adjacent bond orientation. When describing the chain conformations by use of chain statistics, we have to include formally energetic and entropic contributions to the chain conformations. In order to incorporate those effects, we adopt and extend the method due to Levine *et al.*<sup>7</sup> Let  $\hat{P}(k, n)$  be the conformational weight that the first segment (for  $n = 1$ ) occupies as site in layer  $k$ , and then let  $\hat{P}(k, n; k', n - 1)$  be the conformational weight that the  $n$ th segment (for  $2 \leq n \leq k$ ), enters a site in layer  $k$  by forward ( $k' = k - 1$ ), lateral ( $k' = k$ ), or downward ( $k' = k + 1$ ) direction. Extending Whittington's recurrence equation<sup>7</sup> by introducing the bond pair weights from Eq. (1) to include chain stiffness, we can write  $\hat{P}(k, n; k', n - 1)$  as

(1) for  $n = 2$ :

$$\hat{P}(k, n; k - 1, n - 1) = \hat{P}(k - 1, n - 1) [1 - \phi(k | k - 1, n - 1)] \times \exp[-\Delta E(k, n | k - 1, n - 1) / k_b T]$$

$$\hat{P}(k, n; k, n - 1) = \hat{P}(k, n - 1) (Z - 2) [1 - \phi(k | k, n - 1)] \times \exp[-\Delta E(k, n | k, n - 1) / k_b T]$$

$$\hat{P}(k, n; k + 1, n - 1) = \hat{P}(k + 1, n - 1) [1 - \phi(k | k + 1, n - 1)] \times \exp[-\Delta E(k, n | k + 1, n - 1) / k_b T] \quad (2a)$$

where  $\phi(k | k', n - 1)$  is the conditional probability that the site in layer  $k$ , being one of the nearest neighbor sites of  $(n - 1)$ th segment, is occupied by tail or head segments given that the  $(n - 1)$ th segment is at a site in the  $k'$  ( $k' = k + 1, k, k - 1$ ).

(2) for  $3 \leq n \leq r$ :

$$\begin{aligned} \hat{P}(k, n; k - 1, n - 1) = & \hat{P}(k - 1, n - 1; k - 2, n - 2) DW(F, F) \\ & [1 - \phi(k | k - 1, n - 1; k - 2, n - 2)] \\ & \times \exp[-\Delta E(k, n | k - 1, n - 1; k - 2, n - 2) / k_b T] \\ & + \hat{P}(k - 1, n - 1; k - 1, n - 2) DW(L, F) \\ & [1 - \phi(k | k - 1, n - 1; k - 1, n - 2)] \\ & \times \exp[-\Delta E(k, n | k - 1, n - 1; k - 1, n - 2) / k_b T] \end{aligned}$$

$$\begin{aligned} \hat{P}(k, n; k, n - 1) = & \hat{P}(k, n - 1; k - 1, n - 2) DW(F, L) \\ & [1 - \phi(k | k, n - 1; k - 1, n - 2)] \\ & \times \exp[-\Delta E(k, n | k, n - 1; k - 1, n - 2) / k_b T] \\ & + \hat{P}(k, n - 1; k, n - 2) DW(L, L) \\ & [1 - \phi(k | k, n - 1; k, n - 2)] \end{aligned}$$

$$\begin{aligned} & \times \exp[-\Delta E(k, n | k, n - 1; k, n - 2) / k_b T] \\ & + \hat{P}(k, n - 1; k + 1, n - 2) DW(D, L) \\ & [1 - \phi(k | k, n - 1; k + 1, n - 2)] \\ & \times \exp[-\Delta E(k, n | k, n - 1; k + 1, n - 2) / k_b T] \\ \hat{P}(k, n; k + 1, n - 1) = & \hat{P}(k + 1, n - 1; k + 1, n - 2) DW(L, D) \\ & [1 - \phi(k | k + 1, n - 1; k + 1, n - 2)] \\ & \times \exp[-\Delta E(k, n | k + 1, n - 1; k + 1, n - 2) / k_b T] \\ & + \hat{P}(k + 1, n; k + 2, n - 1) DW(D, D) \\ & [1 - \phi(k | k + 1, n - 1; k + 2, n - 2)] \\ & \times \exp[-\Delta E(k, n | k + 1, n - 1; k + 2, n - 2) / k_b T] \quad (2b) \end{aligned}$$

where  $\phi(k | k', n - 1; k'', n - 2)$  is the conditional probability that the site in layer  $k$ , being one of the nearest neighbor sites of  $(n - 1)$ th segment, is occupied by head or tail segment, given that the  $(n - 2)$ th segment is at a site in layer  $k''$  ( $k'' = k - 2, k - 1, k, k + 1, k + 2$ ) and the  $(n - 1)$ th segment at a site in layer  $k'$  ( $k' = k - 1, k, k + 1$ ). Also  $\Delta E(k, n | k', n - 1)$  in Eq. (2a) and  $\Delta E(k, n | k', n - 1; k'', n - 2)$  in Eq. (2b) are defined as

(i)  $\Delta E(k, n | k', n - 1)$  for  $n = 2$ . The nearest neighbor segment-segment interaction energy of the  $(n - 1)$ th segment in layer  $k'$  which results from placing the  $n$ th segment at a site in layer  $k'$  given that the  $(n - 1)$ th segment is at a site in layer  $k'$ .

(ii)  $\Delta E(k, n | k', n - 1; k'', n - 2)$  for  $3 \leq n \leq r$ . The nearest neighbor segment-segment interaction energy of the  $(n - 1)$ th segment in layer  $k'$  which results from placing the  $n$ th segment at a site in layer  $k$ , given that the  $(n - 2)$ th segment is at a site in layer  $k''$  and the  $(n - 1)$ th segment at a site in layer  $k'$ .

Eqs. (2a) and (2b), with chain stiffness incorporated, can be regarded as the extended version of Whittington's recurrence equation which obeys Self-Consistent diffusion equations.<sup>13-14</sup> Also, it is possible that we can approximately derive diffusion equations from Eqs. (2a) and (2b) by using the same approximation as Levine *et al.*'s. Therefore Eqs. (2a) and (2b), in spite of their lattice description, could have some correspondence to diffusion equation approach of polymer system.<sup>13</sup> However this topic is not our concern here.

Let  $\phi(k)_t$  be the probability that a site in layer  $k$  is occupied by the tail segment and  $\sigma$  be the surface coverage of the head group (*i.e.*,  $\sigma = N/L$  where  $N$  is total number of amphiphiles adsorbed at one interface). The boundary condition at the two interfaces requires

$$\begin{aligned} \phi(k)_t = 0 & \text{ at } k < 1 \\ \phi(k)_t = 0 & \text{ at } k > D \end{aligned} \quad (3)$$

Considering chain connection up to two bond order and using the simple mean field approximation,<sup>15</sup> we can write the energy terms in Eqs. (2a) and (2b) as follows:

$$\begin{aligned} \text{(i) for } n = 2: \\ \Delta E(1, 2 | 1, 1) = & \phi(1)_t \cdot \epsilon^{ht} + (Z - 3) [\phi(1)_t \cdot \epsilon^{ht} + \sigma \cdot \epsilon^{hh}] \\ \Delta E(2, 2 | 1, 1) = & (Z - 2) [\phi(1)_t \cdot \epsilon^{ht} + \sigma \cdot \epsilon^{hh}] \\ \Delta E(D, 2 | D, 1) = & \phi(D - 1)_t \cdot \epsilon^{th} + (Z - 3) [\phi(D)_t \cdot \epsilon^{ht} + \sigma \cdot \epsilon^{hh}] \end{aligned}$$

$$\Delta E(D-1, 2 | D, 1) = (Z-2) [\phi(D)_t \cdot \epsilon^{ht} + \sigma \cdot \epsilon^{ht}] \quad (4a)$$

(ii) for  $3 \leq n \leq r$ :

$$\begin{aligned} \Delta E(k, n | k-1; k-2, n-2) &= (Z-2) \phi(k-1)_t \cdot \epsilon^{ht} \\ &+ \delta_{n,r} \{ [\phi(k+1)_t + (Z-2) \phi(k)_t] \epsilon^{ht} + \delta_{k,D-1} \cdot \sigma \cdot \epsilon^{ht} \\ &+ \delta_{k,D} [(Z-2) \sigma \cdot \epsilon^{ht} + \epsilon^{to}] \} \quad (3 \leq k \leq D-1) \end{aligned}$$

$$\begin{aligned} \Delta E(k, n | k-1, n-1; k-1, n-2) &= \\ &[(Z-3) \phi(k-1)_t + \phi(k-2)_t] \epsilon^{ht} \\ &+ \delta_{k,z} [(Z-3) \sigma \cdot \epsilon^{ht} + \epsilon^{to}] + \delta_{k,3} \cdot \sigma \cdot \epsilon^{ht} \\ &+ \delta_{n,r} \{ [\phi(k+1)_t + (Z-2) \phi(k)_t] \epsilon^{ht} \\ &+ \delta_{k,D} \cdot \sigma \cdot \epsilon^{ht} + \delta_{k,D} [(Z-2) \sigma \cdot \epsilon^{ht} + \epsilon^{to}] \} \quad (2 \leq k \leq D) \end{aligned}$$

$\Delta E(k, n | k-1, n-1; k, n-2)$ : forbidden (self-reversal case)

$$\begin{aligned} \Delta E(k, n | k, n-1; k-1, n-2) &= \\ &[\phi(k+1)_t + (Z-3) \phi(k)_t] \epsilon^{ht} \\ &+ \delta_{k,D-1} \cdot \sigma \cdot \epsilon^{ht} + \delta_{k,D} [(Z-3) \sigma \cdot \epsilon^{ht} + \epsilon^{to}] \\ &+ \delta_{n,r} \{ [\phi(k+1)_t + (Z-3) \phi(k)_t + \phi(k-1)_t] \epsilon^{ht} \\ &+ \delta_{k,z} \cdot \sigma \cdot \epsilon^{ht} + \delta_{k,D-1} \cdot \sigma \cdot \epsilon^{ht} + \delta_{k,D} [(Z-3) \sigma \cdot \epsilon^{ht} + \epsilon^{to}] \} \\ &\quad (2 \leq k \leq D) \end{aligned}$$

$$\begin{aligned} \Delta E(k, n | k, n-1; k, n-2) &= \\ &[\phi(k+1)_t + (Z-4) \phi(k)_t + \phi(k-1)_t] \epsilon^{ht} \\ &+ \delta_{k,1} [(Z-4) \sigma \cdot \epsilon^{ht} + \epsilon^{to}] + \delta_{k,z} \cdot \sigma \cdot \epsilon^{ht} \\ &+ \delta_{k,D-1} \cdot \sigma \cdot \epsilon^{ht} + \delta_{k,z} [(Z-4) \sigma \cdot \epsilon^{ht} + \epsilon^{to}] \\ &+ \delta_{n,r} \{ [\phi(k+1)_t + (Z-3) \phi(k)_t + \phi(k-1)_t] \epsilon^{ht} \\ &+ \delta_{k,1} [(Z-3) \sigma \cdot \epsilon^{ht} + \epsilon^{to}] + \delta_{k,z} \cdot \sigma \cdot \epsilon^{ht} \\ &+ \delta_{k,D-1} \cdot \sigma \cdot \epsilon^{ht} + \delta_{k,D} [(Z-3) \sigma \cdot \epsilon^{ht} + \epsilon^{to}] \} \\ &\quad (1 \leq k \leq D) \end{aligned}$$

$$\begin{aligned} \Delta E(k, n | k, n-1; k+1, n-2) &= \\ &[(Z-3) \phi(k)_t + \phi(k-1)_t] \epsilon^{ht} \\ &+ \delta_{k,1} [(Z-3) \sigma \cdot \epsilon^{ht} + \epsilon^{to}] + \delta_{k,z} \cdot \sigma \cdot \epsilon^{ht} \\ &+ \delta_{n,r} \{ [\phi(k+1)_t + (Z-3) \phi(k)_t + \phi(k-1)_t] \epsilon^{ht} \\ &+ \delta_{k,1} [(Z-3) \sigma \cdot \epsilon^{ht} + \epsilon^{to}] + \epsilon^{to} + \delta_{k,z} \cdot \sigma \cdot \epsilon^{ht} \\ &+ \delta_{k,D-1} \cdot \sigma \cdot \epsilon^{ht} \} \quad (1 \leq k \leq D-1) \end{aligned}$$

$\Delta E(k, n | k+1, n-1; k, n-2)$ : forbidden (self-reversal case)

$$\begin{aligned} \Delta E(k, n | k+1, n-1; k+1, n-2) &= \\ &[\phi(k+2)_t + (Z-3) \cdot \phi(k+1)_t] \epsilon^{ht} \\ &+ \delta_{k,D-2} \cdot \sigma \cdot \epsilon^{ht} + \delta_{k,D-1} [(Z-3) \cdot \sigma \cdot \epsilon^{ht} + \epsilon^{to}] \\ &+ \delta_{n,r} \{ [(Z-2) \phi(k)_t + \phi(k-1)_t] \epsilon^{ht} \\ &+ \delta_{k,1} [(Z-2) \sigma \cdot \epsilon^{ht} + \epsilon^{to}] + \delta_{k,z} \cdot \sigma \cdot \epsilon^{ht} \} \\ &\quad (1 \leq k \leq D-1) \end{aligned}$$

$$\Delta E(k, n | k+1, n-1; k+2, n-2) = (Z-2) \phi(k+1)_t \cdot \epsilon^{ht}$$

$$\begin{aligned} &+ \delta_{n,r} \{ [(Z-2) \phi(k)_t + \phi(k-1)_t] \epsilon^{ht} + \delta_{k,1} [(Z-2) \sigma \cdot \epsilon^{ht} \\ &+ \epsilon^{to}] + \delta_{k,z} \cdot \sigma \cdot \epsilon^{ht} \} \quad (1 \leq k \leq D-2) \end{aligned} \quad (4b)$$

where  $\delta_{ij}$  is Kronecker delta, and these energy terms are some what different from monolayer case due to the presence of another interface. The terms including  $\delta_{n,r}$  correspond to the correction energy of the  $r$ th segment (end segment). We must realize that above 9 energy terms are contributed by the only nearest neighbor interaction energy of the chain molecules. The bent energy is automatically included in the statistical bond pair weights  $\{DW\}$  corresponding to each orientation of 9 bond pairs. In order to simplify Eqs. (2a) and (2b), we assume independent approximation in each layer.<sup>16</sup> Therefore all the conditional probability terms  $\phi(k, \dots)$  in Eqs. (2a) and (2b) can be approximated by

$$\phi(k | \dots) \approx \phi(k) = \phi(k)_t + \sigma(\delta_{k,1} + \delta_{k,D}) \quad (5)$$

where last term comes from the density of head groups which are anchored to layers  $k=1$  and  $k=D$ . In fact, Eqs. (4a), (4b), and (5) neglect the chain bond correlation which was already known as very important in explaining anisotropic nature of monolayer amphiphile molecules.<sup>17</sup> We are now studying this anisotropic effect by employing more sophisticated approximation. From Eq. (5), Eqs. (2a) and (2b) can be rewritten as

(1) for  $n=2$ ;

Defining  $\hat{P}(k', n-1)$  as  $1-\phi(k')$ , we have

- (i).  $\hat{P}(k, n; k', n-1)$   
 $= \hat{P}(k', n-1)(Z-2)[1-\phi(k)] \times \exp[-\Delta E(k, n | k', n-1)/k_b T] = [1-\phi(k')](Z-2)[1-\phi(k)] \times \exp[-\Delta E(k, n | k', n-1)/k_b T]$ ; for  $k=1$  and  $k'=1$ , or  $k=D$  and  $k'=D$
- (ii).  $\hat{P}(k, n; k', n-1)$   
 $= \hat{P}(k', n-1)[1-\phi(k)] \times \exp[-\Delta E(k, n | k', n-1)/k_b T] = [1-\phi(k')][1-\phi(k)] \times \exp[-\Delta E(k, n | k', n-1)/k_b T]$ ; for  $k=2$  and  $k'=1$ , or  $k=D-1$  and  $k'=D$
- (iii).  $\hat{P}(k, n; k', n-1) = 0$ ; otherwise.

(2a')

(2) for  $3 \leq n \leq r$ ;

$$\begin{aligned} \hat{P}(k, n; k-1, n-1) &= \hat{P}(k-1, n-1; k-2, n-2) W_{FF,k} \\ &+ \hat{P}(k-1, n-1; k-1, n-2) W_{LF,k} \\ \hat{P}(k, n; k, n-1) &= \hat{P}(k, n-1; k-1, n-2) W_{FL,k} \\ &+ \hat{P}(k, n-1; k, n-2) W_{LL,k} + \hat{P}(k, n-1; k+1, n-2) W_{DL,k} \\ \hat{P}(k, n; k+1, n-1) &= \hat{P}(k+1, n-1; k+1, n-2) W_{LD,k} \\ &+ \hat{P}(k+1, n-1; k+2, n-2) W_{DD,k} \end{aligned}$$

where

$$\begin{aligned} W_{FF,k} &= [1-\phi(k)] DW(F, F) \\ &\times \exp[-\Delta E(k, n | k-1, n-1; k-2, n-2)/k_b T] \end{aligned}$$

$$W_{LF,k} = [1 - \phi(k)] DW(L, F) \\ \times \exp[-\Delta E(k, n | k-1, n-1; k-1, n-2) / k_b T]$$

$$W_{FL,k} = [1 - \phi(k)] DW(F, L) \\ \times \exp[-\Delta E(k, n | k, n-1; k-1, n-2) / k_b T]$$

$$W_{LL,k} = [1 - \phi(k)] DW(L, L) \\ \times \exp[-\Delta E(k, n | k, n-1; k, n-2) / k_b T]$$

$$W_{DL,k} = [1 - \phi(k)] DW(D, L) \\ \times \exp[-\Delta E(k, n | k, n | k, n-1; k+1, n-2) / k_b T]$$

$$W_{LD,k} = [1 - \phi(k)] DW(L, D) \\ \times \exp[-\Delta E(k, n | k+1, n-1; k+1, n-2) / k_b T]$$

$$W_{DD,k} = [1 - \phi(k)] DW(D, D) \\ \times \exp[-\Delta E(k, n | k+1, n-1; k+2, n-2) / k_b T] \\ (2b')$$

In Eq. (2b'), each element of the set  $\{W_{ab,k} | a, b = F, L, D\}$  represents one-step conformational weight of a chain segment to be generated with (b) direction in layer  $k$  when its previous adjacent segment already occupied a site with (a) direction, where (a) and (b) denote one of the three directions (*i.e.*, forward (F), lateral (L), and downward (D) directions).

**Derivation of Conformational Properties.** Eqs. (2a') and (2b') are basic equations which are required to generate the various conformations of chain molecule in the inhomogeneous system. Since these equations are too complicated to treat, we employ the concept of matrix formalism which has been used by many authors.<sup>4-7</sup> However it is necessary to extend the matrix formalism in order to adopt our method. Therefore, by careful inspection, we introduce  $3D \times 3D$  generating matrix  $G$  and  $3D \times 1$  column vector  $P(n)$  which are similar to the matrix of Markov theory.<sup>16</sup> Detailed notations for  $G$  and  $P(n)$  satisfying Eqs. (2a') and (2b') are given by

$$G = \begin{bmatrix} L_1 & D_1 & 0 & 0 & 0 & \dots & \dots & 0 \\ L_2 & L_2 & D_2 & 0 & 0 & & & \vdots \\ 0 & F_3 & L_3 & D_3 & 0 & & & \vdots \\ \vdots & \vdots & & & \vdots & & 0 & \vdots \\ \vdots & 0 & & & \vdots & & & \vdots \\ \vdots & \vdots & & & F_{D-2} & L_{D-2} & D_{D-2} & 0 \\ \vdots & \vdots & & & 0 & F_{D-1} & L_{D-1} & D_{D-1} \\ 0 & \dots & & & 0 & 0 & F_D & L_D \end{bmatrix}$$

$$F_k = \begin{bmatrix} W_{FF,k} & W_{LF,k} & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \quad L_k = \begin{bmatrix} 0 & 0 & 0 \\ W_{FL,k} & W_{LL,k} & W_{DL,k} \\ 0 & 0 & 0 \end{bmatrix}$$

$$D_k = \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & W_{LD,k} & W_{DD,k} \end{bmatrix} \quad 0 = \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

$$P(n) = \begin{bmatrix} P(n, 1) \\ P(n, 2) \\ \vdots \\ P(n, k) \\ \vdots \\ P(n, D-1) \\ P(n, D) \end{bmatrix} \quad P(n, k) = \begin{bmatrix} \hat{P}(k, n; k-1, n-1) \\ \hat{P}(k, n; k, n-1) \\ \hat{P}(k, n; k+1, n-1) \end{bmatrix} \\ (6)$$

where the boundary condition at the two interfaces require

$$\hat{P}(1, n; 0, n-1) = \hat{P}(D, n; D+1, n-1) = 0. \quad (7)$$

Therefore, from Eq. (6), we can rewrite Eqs. (2a') and (2b') as matrix notation:

$$P(n) = G \cdot P(n-1) = G^2 \cdot P(n-2) = \dots = G^{n-1} \cdot P(2) \\ ; \text{ for } 3 \leq n \leq r. \quad (8)$$

where  $P(2)$  represents the bond initiation column vector corresponding to all the possible orientations of the first bond whose one end ( $n=1$ ) is localized to the first of last interface ( $k=1$  or  $D$ ). From Eq. (2a'),  $P(2)$  is given by

$$P(2) = \begin{bmatrix} P(2, 1) \\ P(2, 2) \\ 0 \\ \vdots \\ 0 \\ \vdots \\ 0 \\ P(2, D-1) \\ P(2, D) \end{bmatrix} \quad (9)$$

where each element of  $P(2)$  is

$$P(2, 1) = \begin{bmatrix} 0 \\ \hat{P}(1, 2; 1, 1) \\ 0 \end{bmatrix} \quad P(2, 2) = \begin{bmatrix} \hat{P}(2, 2; 1, 1) \\ 0 \\ 0 \end{bmatrix} \\ P(2, D-1) = \begin{bmatrix} 0 \\ 0 \\ \hat{P}(D-1, 2; D, 1) \end{bmatrix} \quad P(2, D) = \begin{bmatrix} 0 \\ \hat{P}(D, 2; D, 1) \\ 0 \end{bmatrix} \\ (10)$$

We can think that the bond initiation column vector  $P(2)$  is composed of two vectors  $P_1(2)$  and  $P_D(2)$  which are the bond initiation vectors of the chain molecule whose first segment is anchored to the first ( $k=1$ ) and the second ( $k=D$ ) interfaces

$$P_1(2) = \begin{bmatrix} P(2, 1) \\ P(2, 2) \\ 0 \\ 0 \\ \vdots \\ 0 \\ \vdots \\ 0 \end{bmatrix} \quad P_D(2) = \begin{bmatrix} 0 \\ \vdots \\ 0 \\ \vdots \\ 0 \\ P(2, D-1) \\ P(2, D) \end{bmatrix} \quad (11)$$

respectively. Thus  $P_1(2)$  and  $P_2(2)$  can be written as  $P_1(2) + P_2(2) = P(2)$ . The free energy expressions<sup>7</sup> of the chain molecule attached to each interface at layer width  $D$  (case of no solvent) are given as

(i) The free energy of the chain molecule at the first interface;

$$F_1(D)/k_b T = -\ln[U^T \cdot G^{r-1} \cdot P_1(2)] \quad (12a)$$

(ii) The free energy of the molecule at the second interface;

$$F_2(D)/k_b T = -\ln[U^T \cdot G^{r-1} \cdot P_2(2)], \quad (12b)$$

where the vector  $U$  is  $3D \times 1$  column vector whose elements are all 1, and superscript  $T$  means transpose of the vector. Because of the symmetry of the bilayer system, Eq. (12a) is equal to Eq. (12b). Therefore

$$F_1(D)/k_b T = F_2(D)/k_b T. \quad (13)$$

This symmetry property comes from our assumption that equal number of molecules is anchored to each interface. The free energy of separation,<sup>7</sup>  $\Delta F(D)$  relative to when the interfaces are separated by  $2r$  which represents minimum layer width where the two regions of tail segments in bilayer no longer overlap each other in the cubic lattice, is

$$\Delta F(D)/k_b T = [F_1(D)/k_b T + F_2(D)/k_b T - F_1(2r)/k_b T - F_2(2r)/k_b T]. \quad (14)$$

Using the symmetry property of free energy in Eq. (13), we can reduce Eq. (14) to

$$\Delta F(D)/k_b T = 2\sigma[F_1(D)/k_b T - F_1(2r)/k_b T] = 2\sigma[F_2(D)/k_b T - F_2(2r)/k_b T]. \quad (14')$$

Although we use the free energy separation of short chain molecule in the lattice, Eqs. (14) and (14') correspond to Muthukumar's free energy expression which was derived on the basis of Self-Consistent field method.<sup>12</sup>

In order to derive the equation of segment density, let  $W(n, k; r)$  be  $r$  step conformational weight of  $r$  segments amphiphile whose  $n$ th segment occupies a site in layer  $k$  ( $k=1, \dots, D$ ). Using Eqs. (6)–(11) and applying Scheutjens and Fleer's method to our bilayer problem, we can write  $W(n, k; r)$  as follows:

$$(1) W(n, k; r) = \delta_{n,1} [U^T \cdot G^{r-1} \cdot P_1(2)] \quad (15a)$$

$$+ \delta_{n,D} [U^T \cdot G^{r-1} \cdot P_2(2)] \text{ for } n=1;$$

$$(2) W(n, k; r) = U^T \cdot G^{r-n} \cdot [G^{n-1} \cdot P(2)]_k \quad (15b)$$

$$= U^T \cdot G^{r-n} \cdot [P(n)]_k \text{ for } 2 \leq n \leq r.$$

where  $[P(n)]_k$  is

$$[P(n)]_k = \begin{bmatrix} 0 \\ \vdots \\ 0 \\ 0 \\ \vdots \\ 0 \end{bmatrix} \quad \left. \vphantom{\begin{bmatrix} 0 \\ \vdots \\ 0 \\ 0 \\ \vdots \\ 0 \end{bmatrix}} \right\} \text{The } k \text{th vector element defined in Eq. (6)} \quad (16)$$

Following the method due to Scheutjens and Fleer<sup>4</sup>, we assume that segment density of head and tail group in layer  $k$ ,  $\phi(k)$ , is proportional to the summation of  $W(n, k; r)$  over all the  $r$  chain segments. By some algebra, we obtain

$$\phi(k) = 2\sigma \sum_{n=1}^r W(n, k; r) / U^T \cdot G^{r-1} \cdot P(2); \quad (17)$$

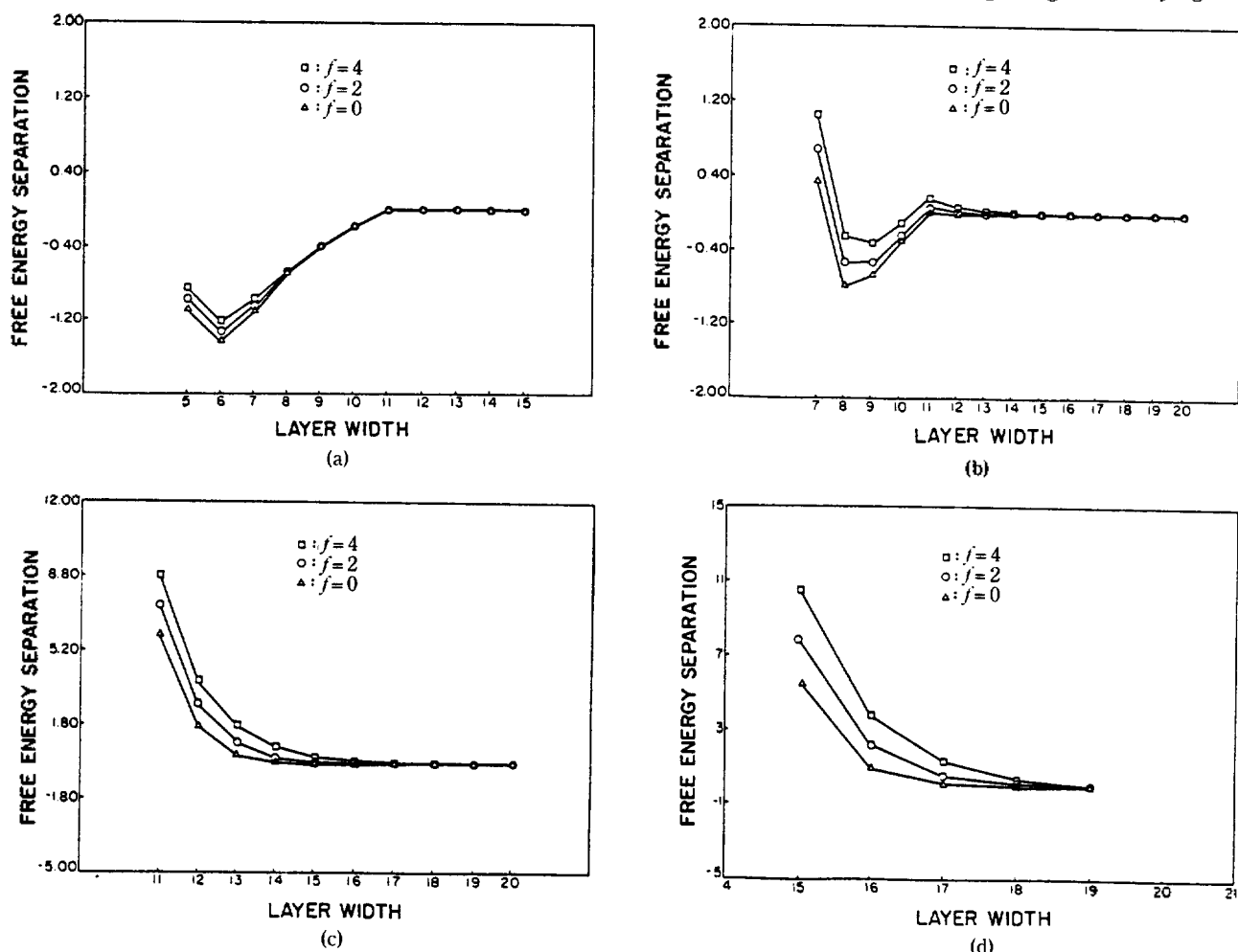
for  $k=1, \dots, D$ .

where the factor 2 results from the existence of two interfaces. Eq. (17) is the  $D$  simultaneous nonlinear equations having  $D$  variables  $\{\phi(k); k=1, \dots, D\}$  which can be solved by numerical scheme.

**Computational Method.** Eq. (17) is the  $D$  simultaneous nonlinear equations with  $D$  unknown variables  $\{\phi(k), k=1, \dots, D\}$ . These equations can be solved by numerical method. We make use of the iteration method based on Min-Pack algorithm<sup>18</sup> which is very efficient in nonlinear equations. As the first computational step, we assign a plausible set of  $\{\phi(k)\}$  by initial guess. Because the value of  $\phi(k)$  is confined to the region  $0 \leq \phi(k) \leq 1$ , we convert variable  $\phi(k)$  into  $X_k = \ln[\phi(k)/(1-\phi(k))]$ . Taking  $\{X_k\}$  to be the iteration variables of our numerical procedure and substituting these initial variables into Eq. (17) and using the powerful algorithm which is designed to improve the speed of convergence, we obtain new set of variables, which subsequently enters following iteration cycle. This iteration cycle is repeated until reasonable precision is achieved (in our paper, error limit  $10^{-6}$ ). In our paper, for the convenience's sake, we adopt Rice's energy parameters<sup>3</sup> which are  $\epsilon^{hh} = -150$  K,  $\epsilon^{ht} = \epsilon^{th} = \epsilon^{tt} = -100$  K in unit of absolute temperature. We choose  $r=10$  and  $T=300$  K. Also we define the stiffness parameter as  $f = -\epsilon_{ij}/kT$ .<sup>19</sup> Using IBM 3090 computer, we obtain the mean density profiles  $\{\phi(k)\}$  of amphiphile chain with various stiffness parameters ( $f=0, 2, 4$ ) and surface coverages ( $0.2 \leq \sigma \leq 0.7$ ).

## Result and Discussion

Figures 1(a)–(d) represent free energy separation curve vs. layer width at various surface coverage ( $\sigma=0.2, 0.3, 0.5$ , and  $0.7$ ). At the moderate surface coverage ( $\sigma=0.2$  and  $0.3$ ), free energy curves tend to have minimum value. These results show that the bilayer system can have favorable layer width corresponding to the state having favorable free energy separation. However at the high coverage ( $\sigma=0.5$  and  $0.7$ ), as shown by Figures 1(c) and (d), the system does not have such a favorable layer width. Although we do not calculate the free energy separation throughout all the range (*i.e.*,  $0 \leq \sigma \leq 1$ ), we do not exclude the possibility that critical  $\sigma_c$ , where the minimum region of free energy separation disappears, will exist. In our free energy data, although the value of  $\sigma_c$  may depend on lattice type, it is assumed to be in the region of  $0.35 < \sigma_c < 0.4$ . At  $\sigma < 0.35$ , since there are relatively little segment density, the two interfacial regions of chain molecules can approach each other to have thermodynamically favorable bilayer width. Therefore we can realize that at that coverage region, major contribution to the chain conformation of amphiphiles results from attraction energy (*i.e.*, energetic effect) between chain segments. As shown by Figures 1(a) and (b), the pattern of free energy



**Figure 1.** Free energy separation  $F(D)/k_b T$  as a function of layer width  $D$  at  $T=300$  K and  $r=10$ , with the variation of chain stiffness parameter  $f$  ( $f=0, 2, 4$ ); (a)  $\sigma=0.2$ , (b)  $\sigma=0.3$ , (c)  $\sigma=0.5$ , and (d)  $\sigma=0.7$ .

minimum range at  $\sigma=0.2$  is broader than that of at  $\sigma=0.3$ . These results show that in the region of  $\sigma < 0.35$ , the degree of stability for the bilayer formation depends on the degree of chain attractive interaction which is affected by the variation of surface coverage. Therefore at  $\sigma < 0.35$ , even if favorable bilayer formation is possible, the stability problem for the bilayer formation has to be considered when  $\sigma$  becomes more dilute. At  $\sigma > 0.4$ , however, above favorable bilayer width do not exist. These results represent that at that region, bilayer system must increase its width to minimize increased repulsive interaction (*i.e.*, packing effect) caused by high segment density of inner layer region.

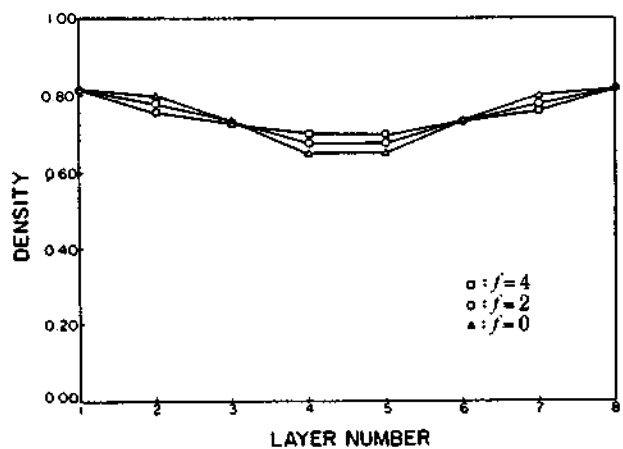
Also Figures 1(a)–(d) show that at  $\sigma=0.2, 0.3, 0.5$ , and  $0.7$  flexible chain has lower free energy than semiflexible chain, which implies that high degree of stiffness of tail chain in the bilayer system makes the chain conformation somewhat unstable. However, as the layer width increases, the contribution of chain stiffness to free energy separation becomes much smaller, so that at relatively high layer width, chain stiffness effect can be negligible. Thus we can realize that effect of chain stiffness occur mainly in the region of small layer width where two regions of tail chains overlap each other to a large extent. At  $\sigma < 0.35$ , where favorable layer width occurs, we can also see that the range of favorable

layer width is little affected by chain stiffness.

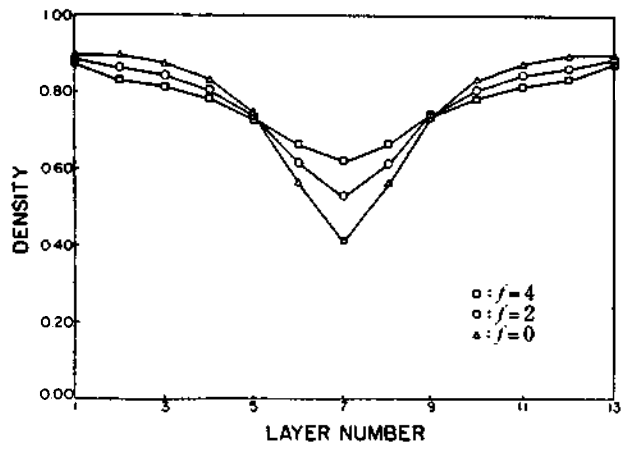
Figures 2 and 3 show segment density profiles with to layer number. These patterns are similar to Muthukumar's result<sup>2</sup>. However we can see that segment density of semiflexible chain is higher than that of flexible chain in the inner layer region of bilayer system whereas the former is smaller than the latter in the region close to two interfaces. Therefore segment density profiles of semiflexible chain in bilayer can be characterized by smoother patterns than those of flexible chain.

### Conclusion

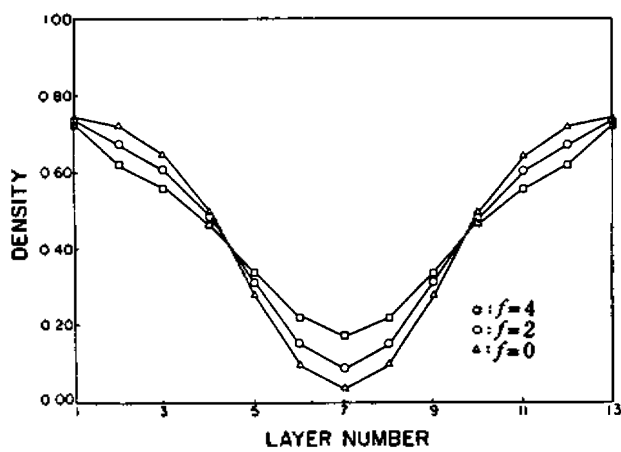
We derive free energy expression and segment density profiles of bilayer amphiphile molecules having various chain stiffness by use of lattice model. Our result shows that within moderate surface coverage region, bilayer system for the case of no other constraints except two interfaces, can have favorable layer width corresponding to free energy minimum conditions which is mainly caused by attractive interaction between chain segments, whereas at high surface coverage region, bilayer can not have such a favorable layer width due to increased segment density of inner layer region which makes repulsive interaction between chain segments domi-



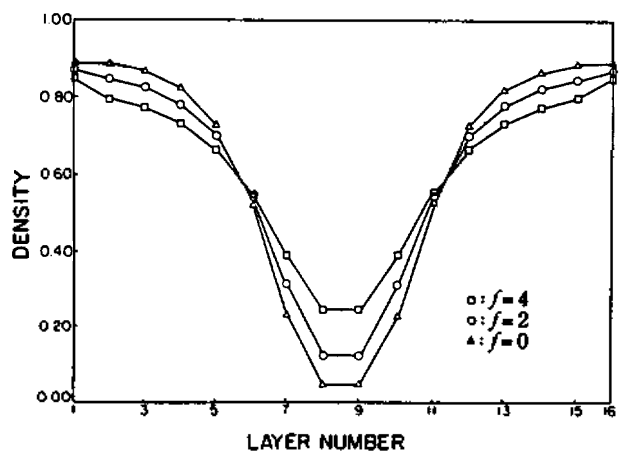
(a)



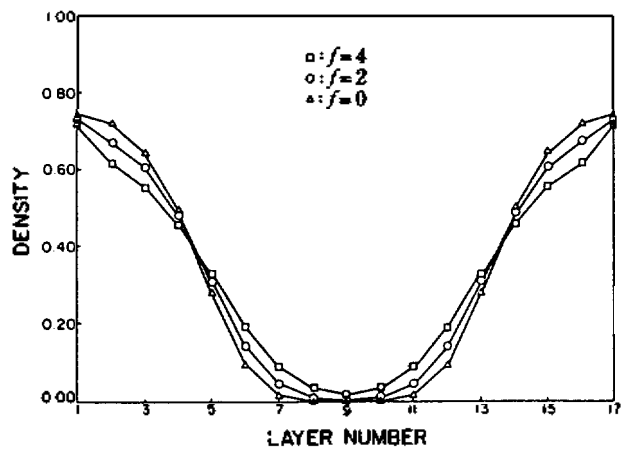
(a)



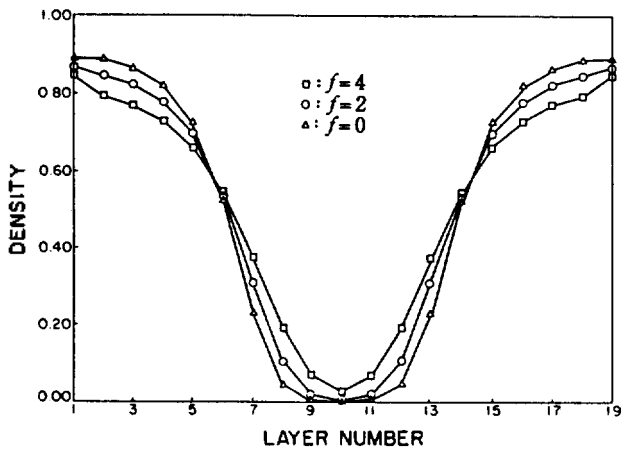
(b)



(b)



(c)



(c)

**Figure 2.** Mean Segment density distribution  $\{\phi(k)\}$  as a function of layer number,  $k$ , at  $T=300$  K,  $\sigma=0.3$ , and  $r=10$ , with the variation of chain stiffness parameter  $f$  ( $f=0, 2, 4$ ); (a)  $D=8$ , (b)  $D=13$ , and (c)  $D=17$ .

**Figure 3.** Mean Segment density distribution  $\{\phi(k)\}$  as a function of layers number,  $k$ , at  $T=300$  K,  $\sigma=0.5$ , and  $r=10$  with the variation of chain stiffness parameter  $f$  ( $f=0, 2, 4$ ); (a)  $D=13$ , (b)  $D=16$ , and (c)  $D=19$ .

nant. In deriving Eqs. (14) and (17), we use the conventional simple approximations (see Eqs. (4a), (4b), (5)) which disregard detailed chain bond correlation. Therefore it may mistreat entropic and enthalpic contributions to conformational properties, but our result has the same trend as Muthukumar's self-consistent theory which is described by

polymer diffusion equation<sup>2</sup>. Now, we are studying effect of bond correlation which is regarded as very important in anisotropic inhomogeneous system as Cantor and Maclory<sup>17</sup> already showed in their paper on the monolayer amphiphile molecules. They show that chain bond correlation which incorporates the anisotropy partly has severe effect on the



monolayer surfactant. Therefore, in order to consider the effect of the anisotropy, we must use more refined approximation by which both energetic and entropic contributions to free energy are well described. In the future, by introducing the chain anisotropy in our approximation, we will study more general behavior of terminally anchored chain molecules.

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## A Calculation for the Viscosity of Liquid Metals

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A phenomenological theory of viscosity which has been proposed by authors is applied to liquid metals for which the calculation is a severe test for liquid theories. The thermodynamic properties used in the calculations can be obtained by using the Roulette liquid theory. The calculated values of the viscosities for liquid metals are in good agreements with the observed values.

### Introduction

The viscosities of liquid metals play an important role in liquid metal processing operation. Interests in the viscosity of liquid metals today stem from practical consideration, such as their use as atomic reactor coolants and from philosophical consideration, such as the fact that their structural simplicity makes them good media to test the current theories of the liquid state.

For liquid metals low pressures at melting, small differences in volume between liquid and solid, and rather large temperature ranges of the liquid state can lead to large differences between observed and calculated values for thermodynamic properties. Viscosity data<sup>1</sup> indicate that the hole size in metal melts is small relative to the size of metal atom

but is comparable to the volume of metal ion differently from other liquids. Therefore the calculation for liquid metals is a severe test for liquid theories.

Among the current theories used in the calculation of the viscosity of liquid metals, the model theories of Andrade<sup>2</sup> and Eyring<sup>3</sup> have been often used. Their equations for the viscosity of liquid metals have proved to be useful for the calculation of the viscosity, but they have adjustable parameters and exponential form which is not physically meaningful.

A phenomenological theory<sup>4</sup> of viscosity which was proposed by authors had been successfully applied to normal liquid, water<sup>5</sup> and helium<sup>6</sup> which exhibits abnormal behavior compared to other ordinary liquids. This theory also can be used in the form of the reduced equation<sup>7</sup> because it does not