A Statistical Theory of Conformational Properties of Amphiphile Molecules at the Air-Water Interface

Young Shang Pak and Hyungsuk Pak[*]

*Department of Chemistry, College of Natural Sciences,
Seoul National University, Seoul 151-742. Received October 25, 1990.*

A lattice mean field theory is developed to investigate the conformational properties of monolayer amphiphiles at the air-water interface. By generalizing Dill and Cantor's method and by extending Whittington's recurrence equation, we derive the supermatrix recurrence equation which is applied to calculation of various segment density profiles and order parameter, *etc.* In deriving the equation, we incorporated the chain stiffness effect and the chain connectivity which are distinguished features of linear chain molecule. Our result shows that, as the surface coverage σ increases the chain ordering process with respect to vertical axis of the lattice system becomes dominant.

Introduction

Amphiphile molecules comprised of a hydrophilic head group and one or more flexible hydrocarbon tail segments associate in air-water interface by the constraint imposed by different solubility between head and tail group in water system. Nonpolar hydrocabon chain is thus in air phase, whereas polar head group is localized to the aqueous environment. Because of the flexibility nature of the tail chain, the amphiphile molecules can have many conformational states at the interface. Therefore we require the statistical mechanics to elucidate the general conformational properties, such as order parameter and mean segment density from interface, *etc.*

Flory and Dill,[1,2] with the concept of the chain flux in the cubic lattice, derived a set of constraint equations, which was extended by Dill and Cantor[3,4] who incorporated the effect of chain stiffness resulting from gauche and *trans* states of hydrocarbon chain. They assumed that a chain bond in the cubic lattice can have only two orientations; forward or lateral direction. This assumption implies that the possibility of downward direction of chain segment is forbidden. Nevertheless, their theory is very useful to elucidate the conformational properties of the interface in the region of high surface coverage. Recently Wang and Rice,[5] using the lattice adsorption theory of Scheutjens and Fleer,[6-8] have developed a statistical thermodynamic model of monolayer of flexible amphiphiles. However they did not consider the effect of chain stiffness and the detailed chain connectivity which are often neglected in the mean field approximation (Bragg-Williams approximation). Thus it is necessary that more refined lattice mean field theory be developed. In our paper, we assume that a chain bond in simple cubic lattice can have all the possible directions (forward, lateral, and downward directions) and that various chain conformations of the amphiphile molecule can be successively generated, step by step, subject to orientational dependent statistical weight assigned to the position of a chain segment to be generated with specific orientation. The orientational dependent statistical weights are derived by extending Whittington's recurrence equation[9]. Considering the chain connectivity in the nearest neighbor energy calculation and the chain stiffness effect in our mean field conformational statistics,

we obtain the supermatrix equations corresponding to segment density, direction dependent segment density, and order parameters which show conformational characteristics of the adsorbed amphiphiles.

Theory

Model. We consider 3-dimensional simple cubic lattice. The lattice is divided into m layers numbered $k=0, \cdots, m$ of sites parallel to the air-water interface labeled by $k=1$, each having L lattice sites, where m is maximum layer number chain segment can reach. Therefore maximum layer number m can be equal to the number of tail segment r. The length of lattice spacing is set to be a, and Z is lattice corrdination number in the lattice ($Z=6$ in case of cubic lattice). The amphiphile chains are comprised of a hydrophilic head group and r hydrophobic tail segments, occupying $r+1$ contiguous sites in the lattice. An aggregate of N amphiphiles is assumed to be distributed over the lattice sites such that a segment of the amphiphile can occupy only one lattice site. Following the Cantor and McIlroy's model system,[10] we assume that hydrophilic head group of the amphiphile is always anchored to the zeroth layer, which is taken to be aqueous side of interface, and that the zeroth bond composed of head group and first tail segment is perpendicular to the interfacial plane for all the given chains, so that head group of those amphiphiles serves to constrain the first tail segment to reside on the air-water interface. In order to reduce the number of energy parameters, we also assume that head group has no any thermodynamic effect on total energy system. In our paper, effect of surface shape is assumed to be negligible and discontinuous, so that the interface to be perfect ideal plane.

Chain Conformational Statistics. Tail chain being pendent from the first layer can have many geometrical rearrangements which characterize the conformational states of the amphiphiles. In order to describe the chain conformation with chain stiffness of amphiphiles incorporated, we need to consider possible orientations composed of at least 3 consecutive segments on which the conformational states of amphiphiles are assumed to depend. In generating chain conformations of amphiphile molecule, we adopt the method due to Levine *et al.*[9] They suppose that various conformations

of r segment chain can be generated by the product of successive r step statistical conformational weights, which are derived from Whittington's recurrence equation.[9] However their method could not explain direction-dependent properties of chain molecules. Therefore we need to extend their scheme further by employing the concept of direction of chain segment in the cubic system. 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[11-13] used to incorporate the chain stiffness of chain molecule, we now assume that straight and bent pairs correspond to *trans* and gauche states of real hydrocarbon chain, respectively, within the approximation of the lattice model. Although the first bond pair is of different chemical nature due to the presence of the hydrophilic head group, we define the bent energy ε_b with respect to straight pair as the same for all segment. Thus we can write the statistical bond weights of a bent and a straight pairs as $\exp(-\varepsilon_b/K_bT)$ and 1, respectively, where K_b is the Boltzmann constant and T is the absolute temperature. Let us imagine the process of adding the last amphiphile molecule, one segment at a time with specific direction, to the cubic lattice. Suppose that the first $n-1$ segments of the last amphiphile molecule have been introduced and that the nth segment (*i.e.*, tail segment) is being added to a given site r with specific directions in the cubic lattice. Then the $(n-1)$th segment has to be located at one of nearest neighbouring sites $r+a_j$, where a, represents one of the six nearest neighbouring vector($j=1, \cdots,$ 6) in the cubic lattice:

$$a_1 = (0, 0, a),\ a_2 = (a, 0, 0),\ a_3 = (0, a, 0)$$

$$a_4 = -a_3,\ a_5 = -a_2,\ a_6 = -a_1 \tag{1}$$

Let $P(r, n \mid r+a_i, n-1)$ be the n step statistical conformational weight that insertion of the nth segment occurs at a site r given that $(n-1)$th segment at $r+a_j$, and ΔE $(r, n \mid r+a_i, n-1; r+a_i+a_j, n-2)$ be the change in the nearest neighbor interaction energy of amphiphiles which results from placing the nth segment at r, given that the $(n-1)$th segment is at $r+a_i$ and the $(n-2)$th segment at $r+a_i+a_j$. By introducing statistical bond weights, $\exp(-\varepsilon_b/K_bT)$ and 1, the improved recurrence equations which can be applied to our monolayer amphiphiles are written as

$$P(r, n \mid r+a_i, n-1) =$$

$$+ \sum_{j=1}^{z} P(r+a_i, n-1 \mid r+a_i+a_j, n-2)$$

$$\{1-\phi(r \mid r+a_i, n-1; r+a_i+a_j, n-2)\} \times R_{j,\ z-i+1}\ K_{i,j}$$

$$\exp\{-\Delta E(r, n \mid r+a_i, n-1; r+a_i+a_j, n-2)/K_bT\};$$

$$n=2, \cdots, r \text{ and } i=1, \cdots, z \tag{2}$$

where $\phi(r \mid r+a_i, n-1; r+a_i+a_j, n-2)$ is the conditional probability that the site r is occupied by tail segment, given that the $(n-1)$th segment is at $r+a_i$ and the $(n-2)$th segment at $r+a_i+a_j$. Also $R_{j,\ z-i+1}$ and $K_{i,j}$ in Eq. (2) are given by

$$R_{j,\ z-i+1} = 1 - \delta_{j,\ z-i+1} \tag{3a}$$

$$K_{i,j} = 1 + (1-\delta_{i,j})[\exp(-\varepsilon_b/K_bT)-1] \tag{3b}$$

with $\delta_{i,j}=1$ if $i=j$ and $\delta_{i,j}=0$ otherwise. Here, Eqs. (3a) and (3b) are required to eliminate self-reversal step of three adjacent segment and to incorporate chain stiffness which depends on chain orientation respectively. Let ε_{tt} and ε_{ts} be the tail-tail and tail-surface nearest neighbour interaction energy parameters. We introduce $\phi(r+a_i+a_j' \mid r, n; r+a_i, n-1; r+a_i+a_j, n-2)$ as the conditional probability that some other polymer segment is located at $r+a_i+a$, when nth segment is already at $r+a_i$, the $(n-1)$th at $r+a_i$, and the $(n-1)$ th segment at $r+a_i+a_j$. Then the energy change can be written as

$$\Delta E(r, n \mid r+a_i, n-1; r+a_i+a_j, n-2) =$$

$$\varepsilon_{tt} \sum_{\substack{a_j' \\ + a_i \ne a_j}} \phi(r+a_i+a_j' \mid r, n; r+a_i, n-1; r+a_i+a_j, n-2)$$

$$+ \delta_{n,r} \times \varepsilon_{tt} \sum_{\substack{a_i' \\ + -a_i}} \phi(r+a_i' \mid r, n; r+a_i) + \delta_{h,o}\ \varepsilon_{ts} \tag{4}$$

where $\delta_{n,r}$ term the energy correction of last segment itself, and the subscript h of $d_{h,o}$ is a vertical component of vector $r+a_i$ of $(n-1)$th segment, which includes chain-surface interaction. Also $\sum_{\substack{a_j' \\ a_{tk}}}$ in Eq. (4) is the summation over nearest neighbour vectors a_i' ($i=1, \cdots, 6$) excluding a_k. It is convenient to employ approximate method in order to simplify Eqs. (2) and (4). At first, assuming that the probability is independent of occupation of $(n-2)$th segment, we can write conditional probability $\phi(r \mid r+a_i, n-1; r+a_i+a_j, n-2)$ as

$$\phi(r \mid r+a_i, n-1; r+a_i+a_j, n-2) = \phi(r \mid r+a_i, n-1) \tag{5}$$

Then Eq. (4) is approximately given by

$$\Delta E(r, n \mid r+a_i, n-1; r+a_i+a_j, n-2) =$$

$$\varepsilon_{tt} \sum_{\substack{a_j' \\ + a_i \ne a_j}} \phi(r+a_i+a_j' \mid r+a_i, n-1)$$

$$+ \delta_{n,r} \times \varepsilon_{tt} \sum_{\substack{a_i' \\ + -a_i}} \phi(r+a_i' \mid r+a_i, n-1) + \delta_{h,o}\ \varepsilon_{ts} \tag{6}$$

Eqs. (5) and (6) are very important to incorporate entropic and energetic effects in chain confromational statistics. From Eqs. (5) and (6), Eq. (2) is given by

$$P(r, n \mid r+a_i, n-1) =$$

$$+ \sum_{j=1}^{z} P(r+a_i, n-1 \mid r+a_{i+a}, n-2)[1-\phi(r \mid r+a_i, n-1)$$

$$R_{j,\ z-i-1}\ K_{i,j} \times \exp-\{\varepsilon_{tt} \sum_{\substack{a_j' \\ + -a_i \ne a_j}} \phi(r+a_j+a_j^\circ \mid r+a_i, n-1)$$

$$+ \delta_{n,r} \times \varepsilon_{tt} \sum_{\substack{a_i' \\ + -a_i}} \phi(r+a_{i'} \mid r+a_i, n-1) + \delta_{h,o}\ \varepsilon_{ts}\}/K_bT]$$

$$(n=2, \cdots, r, \text{ and } i=1, \cdots, Z) \tag{7}$$

Here we need to specify Eq. (7) in order to apply it to our model system. In the cubic lattice, there are only three directions (*i.e.*, forward, lateral, and downward directions) by which a segment can occupy the lattice. Averaging Eq. (7) over all lattice sites in a plane parallel to the interface according to the forward, lateral, and downward directions, we can easily see that $P(r, n \mid r+a, n-1)$ for $i=1, \cdots, Z$, in

Eq. (7) can be categorized as three distinct conformational weights denoted by layer notation k ($k=1, \cdots, r$); $P(k, n \mid k-1, n-1)$, $P(k, n \mid k-1, n-1)$, and $P(k, n \mid k-1, n-1)$ for forward (from layer $k-1$ to k), lateral (from layer k to k), and downward (from layer $k+1$ to k) steps of nth segment, respectively. Applied to our model system, $P(k, n \mid k-1, n-1)$, $P(k, n \mid k, n-1)$, and $P(k, n \mid k+1, n-1)$ for $2 \leq n \leq r$ and $1 \leq k \leq r$ can be written as

(i) for $n=2$;

$P(k, n \mid k-1, n-1)$

$\quad =P(k-1, n-1 \mid k-2, n-2) \times$

$\qquad \{1-\phi(k \mid k-1, n-1)\} \exp\{-\Delta E(k, n \mid k-1, n-1;$

$\qquad k-2, n-2)/K_b T)\}$, if $k=2$;

$\quad =0$, otherwise

$P(k, n \mid k, n-1)$

$\quad =P(k, n-1 \mid k-1, n-2) \times$

$\qquad \{1-\phi(k \mid k, n-1)\}(Z-2)\exp(-\varepsilon_h/K_b T) \times$

$\qquad \exp\{-\Delta E(k, n \mid k, n-1; k-1, n-2)/K_b T\}$, if $k=1$;

$\quad =0$, otherwise

$P(k, n \mid k+1, n-1)=0 \qquad\qquad (k=1, \cdots, r)$

$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad (8a)$

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

$P(k, n \mid k-1, n-1)$

$\quad =0$, if $k=1$;

$\quad =P(k-1, n-1 \mid k-2, n-2) \times$

$\qquad \{1-\phi(k \mid k-1, n-1)\} \exp\{-\Delta E(k, n \mid k-1, n-1;$

$\qquad k-2, n-2)/K_b T)\} +P(k-1, n-1 \mid k-1, n-2) \times$

$\qquad \{1-\phi(k \mid k-1, n-1)\} \exp(-\varepsilon_h/K_b T) \times$

$\qquad \exp\{-\Delta E(k, n \mid k-1, n-1; k-1, n-2)/K_b T\}$,

$\qquad$ otherwise

$P(k, n \mid k, n-1)$

$\quad =P(k, n-1 \mid k-1, n-2) \times$

$\qquad \{1-\phi(k \mid k, n-1)\}(Z-2)\exp(-\varepsilon_h/K_b T) \times$

$\qquad \exp\{-\Delta E(k, n \mid k, n-1; k-1, n-2)/K_b T\} +$

$\qquad P(k, n-1 \mid k, n-2) \times$

$\qquad \{1-\phi(k \mid k, n-1)\} \{1+(Z-4)\exp(-\varepsilon_h/K_b T)\} \times$

$\qquad \exp\{-\Delta E(k, n \mid k, n-1; k, n-2)/K_b T\} +$

$\qquad P(k, n-1 \mid k+1, n-2) \times$

$\qquad \{1-\phi(k \mid k, n-1)\}(Z-2)\exp(-\varepsilon_h/K_b T) \times$

$\qquad \exp\{-\Delta E(k, n \mid k, n-1; k+1, n-2)/K_b T\}$

$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad (k=1, \cdots, r)$

$P(k, n \mid k+1, n-1)$

$\quad =0$, if $k=r$;

$\quad =P(k+1, n-1 \mid k+1, n-2) \times$

$\qquad \{1-\phi(k \mid k+1, n-1)\} \exp(-\varepsilon_h/K_b T) \times$

$\qquad \exp\{-\Delta E(k, n \mid k+1, n-1; k+1, n-2)/K_b T\} +$

$\qquad P(k+1, n \mid k+2, n-1) \times$

$\qquad \{1-\phi(k \mid k+1, n-1)\} \exp(-\Delta E (k, n \mid k+1, n-1;$

$\qquad k+2, n-2)/K_b T\}$, otherwise $\qquad\qquad (8b)$

Eqs. (8a) and (8b) require an approximate method to progress our step further. Neglecting segment number dependency as an approximation, we can write the orientation-dependent probability terms $\phi(k \mid k-1, n-1)$, $\phi(k \mid k, n-1)$, and $\phi(k \mid k+1, n-1)$ in Eqs.(8a) and (8b) as

$$\phi(k \mid k-1, n-1)=\phi(k \mid k-1)$$

$$\phi(k \mid k, n-1)=\phi(k \mid k)$$

$$\phi(k \mid k+1, n-1)=\phi(k \mid k+1) \qquad (9)$$

where $\phi(k \mid k')$ is the probability that a site in layer k is occupied by some other tail segment, when it's adjacent site in layer $k'(k'=k-1, k$, and $k+1)$ is added by a tail segment. Since chain anisotropy was known as characteristic feature in determining conformational property of monolayer surfactant, we have to employ anisotropic mean field approximation[10,14,15] in our model system to calculate $\phi(k \mid k')$ for $k' =k-1, k$, and $k+1$. Let $\langle N_{F,k}\rangle$, $\langle N_{L,k}\rangle$, and $\langle N_{D,k}\rangle$ be the average orientation-dependent segment numbers of tail segments which enter a site in layer k by forward (from layer $k-1$ to k), lateral (from layer k to k), and downward (from layer $k+1$ to k) directions, respectively. Thus average segment number in layer k is given by

$$N_k=\langle N_{F,k}\rangle + \langle N_{L,k}\rangle + \langle N_{D,k}\rangle \qquad (10)$$

Let σ be the surface coverage of the head group such that $\sigma=N/L$. In spirit of Dimarzio's method,[14,15] $\phi(k \mid k-1)$, $\phi(k \mid k)$, and $\phi(k \mid k+1)$ are approximately given by

$$\phi(k \mid k-1)=(L-\langle N_{F,k}\rangle - \langle N_{L,k}\rangle - \langle N_{D,k}\rangle)/$$
$$(L-\langle N_{F,k}\rangle - \langle N_{D,k-1}\rangle)$$

$$\phi(k \mid k)=(L-\langle N_{F,k}\rangle - \langle N_{L,k}\rangle - \langle N_{D,k}\rangle)/(L-\langle N_{L,k}\rangle/2)$$

$$\phi(k \mid k+1)=(L-\langle N_{F,k}\rangle - \langle N_{L,k}\rangle - \langle N_{D,k}\rangle)/$$
$$(L-\langle N_{F,k+1}\rangle - \langle N_{D,k}\rangle) \qquad (11)$$

By introducing orientation-dependent segment densities $\langle f_k\rangle$, $\langle l_k\rangle$, and $\langle d_k\rangle$ defined as $\langle f_k\rangle = \langle N_{F,k}\rangle/L$, $\langle l_k\rangle = \langle N_{L,k}\rangle/L$, and $\langle d_k\rangle = \langle N_{D,k}\rangle$ respectively, we can rewrite Eq. (11) as

$$\phi(k \mid k-1)=(1-\langle f_k\rangle - \langle l_k\rangle - \langle d_k\rangle)/(1-\langle f_k\rangle - \langle d_{k-1}\rangle)$$

$$\phi(k \mid k)=(1-\langle f_k\rangle - \langle l_k\rangle - \langle d_k\rangle)/(1-\langle l_k\rangle/2)$$

$$\phi(k \mid k+1)=(1-\langle f_k\rangle - \langle l_k\rangle - \langle d_k\rangle)/(1-\langle f_{k+1}\rangle - \langle d_k\rangle) \qquad (12)$$

where the boundary condition requires

$$\phi(k \mid k-1)=0 \text{ in layer } k=1$$

$$\phi(k \mid k+1)=0 \text{ in layer } k=r \qquad (13)$$

By use of Eq. (12), the energetic contribution to statistical weights in Eqs. (8a) and (8b) can be approximately given

by

$$\Delta E(k, n \mid k-1, n-1; k-2, n-2)$$
$$= \varepsilon_{tt}[(Z-2)\phi(k-1 \mid k-1)+\delta_{n,r}\{\phi(k+1 \mid k)+$$
$$(Z-2)\phi(k \mid k)\}];$$

$$\Delta E(k, n \mid k-1, n-1; k-1, n-2)$$
$$= \varepsilon_{tt}[(Z-3)\phi(k-1 \mid k-1)+\phi(k-2 \mid k-1)+$$
$$\delta_{n,r}\{\phi(k+1 \mid k)+(Z-2)\phi(k \mid k)\}]+\delta_{k,2}\ \varepsilon_{ts};$$

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

$$\Delta E(k, n \mid k, n-1; k-1, n-2)$$
$$= \varepsilon_{tt}[\phi(k+1 \mid k)+(Z-3)\phi(k \mid k)]+\delta_{n,r}[\varepsilon_{tt}\{\phi(k+1 \mid k)$$
$$+(Z-3)\phi(k \mid k)+\phi(k-1 \mid k)\}+\delta_{k,1}\ \varepsilon_{ts}];$$

$$\Delta E(k, n \mid k, n-1; k, n-2)$$
$$= \varepsilon_{tt}[\phi(k+1 \mid k)+(Z-4)\phi(k \mid k)+\phi(k-1 \mid k)]+$$
$$\delta_{k,1}\ \varepsilon_{ts}+\ \delta_{n,r}[\varepsilon_{tt}\{\phi(k+1 \mid k)+(Z-3)\phi(k \mid k)+$$
$$\phi(k-1 \mid k)\}+\delta_{k,1}\ \varepsilon_{ts}];$$

$$\Delta E(k, n \mid k, n-1; k+1, n-2)$$
$$= \varepsilon_{tt}\{(Z-3)\phi(k \mid k)+\phi(k-1 \mid k)+\delta_{k,1}\ \varepsilon_{ts}\}+$$
$$\delta_{n,r}[\varepsilon_{tt}\{\phi(k+1 \mid k)+(Z-3)\phi(k \mid k)+$$
$$\phi(k-1 \mid k)\}+\delta_{k,1}\ \varepsilon_{ts}];$$

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

$$\Delta E(k, n \mid k+1, n-1; k+1, n-2)$$
$$= \varepsilon_{tt}\{\phi(k+2 \mid k+1)+(Z-3)\phi(k+1 \mid k+1)\}+$$
$$\delta_{n,r}[\varepsilon_{tt}\{(Z-2)\phi(k \mid k)+\phi(k-1 \mid k)\}+\delta_{k,1}\ \varepsilon_{ts}];$$

$$\Delta E(k, n \mid k+1, n-1; k+2, n-2)$$
$$= \varepsilon_{tt}(Z-2)\phi(k+1 \mid k+1)+\ \delta_{n,r}[\varepsilon_{tt}\{(Z-2)\phi(k \mid k)+$$
$$\phi(k-1 \mid k)\}+\delta_{k,1}\ \varepsilon_{ts}] \tag{14}$$

Eq. (8a) is required to generate the first tail bond for $n=2$ which consists of pure tail segment. Let $P(1, 1 \mid 0, 0)$ in Eq. (8a) be simply defined as the probability that the first tail segment which is connected to the head group in the zeroth layer can occupy a site in layer $k=1$. Thus $P(1, 1 \mid 0, 0)$ in Eq. (8a) can be approximately given by

$$P(1, 1 \mid 0, 0)=1-[f^t]-[l^t]-[d^t] \tag{15}$$

By use of Eqs. (9), (12), and (15), Eqs. (8a) and (8b) are

(i) for $n=2$;

$$P(k, n \mid k-1, n-1)$$
$$= (1-\langle f_{k-1}\rangle-\langle l_{k-1}\rangle-\langle d_{k-1}\rangle)\times$$
$$\{1-\phi(k \mid k-1)\}\exp[-\Delta E(k, n \mid k-1, n-1; k-2,$$
$$n-2)/K_bT\}, \text{ if } k=2;$$

$=0$, otherwise

$$P(k, n \mid k, n-1)$$
$$= (1-\langle f_k\rangle-\langle l_k\rangle-\langle d_k\rangle)\times$$
$$\{1-\phi(k \mid k)\}(Z-2)\exp(-\varepsilon_b/K_bT)\times$$
$$\exp\{-\Delta E(k, n \mid k, n-1; k-1, n-2)/K_bT\}, \text{ if } k=1;$$

$=0$, otherwise

$$P(k, n \mid k+1, n-1)=0 \qquad (k=1, \cdots, r) \tag{16a}$$

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

$$P(k, n \mid k-1, n-1)$$
$$= 0, \text{ if } k=1;$$
$$= P(k-1, n-1 \mid k-2, n-2)\times W_{FF, k}+$$
$$P(k-1, n-1 \mid k-1, n-2)\times W_{FL, k}, \text{ otherwise}$$

$$P(k, n \mid k-1, n-1)$$
$$= P(k, n-1 \mid k-1, n-2)\times W_{FL, k}+P(k, n-1 \mid k, n-2)$$
$$\times W_{LL, k}+P(k, n-1 \mid k+1, n-2)\times W_{DL, k}$$
$$(k=1, \cdots, r)$$

$$P(k, n \mid k+1, n-1)$$
$$= 0, \text{ if } k=r;$$
$$= P(k+1, n-1 \mid k+1, n-2)\times W_{LD, k}+P(k+1, n \mid k+2,$$
$$n-1)\times W_{DD, k}\ , \text{ otherwise} \tag{16b}$$

with

$$W_{FF, k}=\{1-\phi(k \mid k-1)\}\exp\{-\Delta E(k, n \mid k-1, n-1; k-2,$$
$$n-2)/K_bT\}$$

$$W_{LF, k}=\{1-\phi(k \mid k-1)\}\exp(-\varepsilon_b/K_bT)$$
$$\exp\{-\Delta E(k, n \mid k-1, n-1; k-1, n-2)/K_bT\}$$

$$W_{FL, k}=\{1-\phi(k \mid k)\}(Z-2)\exp(-\varepsilon_b/K_bT)$$
$$\exp\{-\Delta E(k, n \mid k, n-1; k-1, n-2)/K_bT\}$$

$$W_{LL, k}=\{1-\phi(k \mid k)\}\{1+(Z-4)\exp(-\varepsilon_b/K_bT)$$
$$\exp\{-\Delta E(k, n \mid k, n-1; k, n-2)/K_bT\}$$

$$W_{DL, k}=\{1-\phi(k \mid k)\}(Z-2)\exp(-\varepsilon_b/K_bT)$$
$$\exp\{-\Delta E(k, n \mid k, n-1; k+1, n-2)/K_bT\}$$

$$W_{LD, k}=\{1-\phi(k \mid k+1)\}\exp(-\varepsilon_b/K_bT)$$
$$\exp\{-\Delta E(k, n \mid k+1, n-1; k+1, n-2)/K_bT\}$$

$$W_{DD, k}=\{1-\phi(k \mid k+1)\}\exp\{-\Delta E(k, n \mid k+1, n-1; k+2,$$
$$n-2)/K_bT\} \tag{17}$$

where the energy terms in Eq. (17) is given by Eq. (14). Then Eqs. (16a), (16b), and (17) determining statistical conformational weights in chain generation steps, can be easily implemented by introducing generating matrix G and column vector $P(n)$:

174 *Bull. Korean Chem. Soc., Vol. 12, No. 2, 1991*

Young Shang Pak and Hyungsuk Pak

$$G = \begin{bmatrix} L_1 & D_1 & 0 & 0 & 0 & & \\ F_2 & L_1 & D_2 & 0 & 0 & \cdots\cdots\cdots & 0 \\ 0 & F_3 & L_3 & D_3 & 0 & & \\ \vdots & & & & & 0 & \\ & & & & & & \\ 0 & & & & & & \\ \vdots & & & & & F_{r-1} & L_{r-1} & D_{r-1} \\ 0 & \cdots\cdots\cdots & & 0 & & 0 & F_r & L_r \end{bmatrix}$$

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

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

$P(n) = \text{col}[P(n, 1), P(n, 2), \cdots, P(n, r-1), P(n, r)];$

$P(n, k) = B_{n,k;F} + B_{n,k;L} + B_{n,k;D};$

$B_{n,k;F} = [P(k, n \mid k-1, n-1), 0, 0]$

$B_{n,k;L} = [0, P(k, n \mid k, n-1), 0]$

$B_{n,k;D} = [0, 0, P(k, n \mid k+1, n-1)]$ (18)

Therefore from Eq. (18), Eqs. (16a) and (16b) is

$$P(n) = G \cdot P(n-1) = G^2 \cdot P(n-2) = \cdots = G^{n-2} \cdot P(2)$$

$(3 \leq n \leq r)$ (19)

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 layer($k=1$). From Eq. (16a), $P(2)$ is given by

$P(2) = \text{col}[P(2,1), P(2,2), o, \cdots, o];$

$P(2, 1) = B_{2,1;L}, \quad P(2, 2) = B_{2,2;F}, \quad o = (0, 0, 0)$ (20)

Thus the sum over all elements of $P(r)$ in Eq. (19) can be identified as the chain partition function, which is given by

$$Q = U \cdot G^{r-2} \cdot P(2)$$ (21)

where U is $1 \times r$ row vector each element u of which is a 1×3 vector; $u = (1, 1, 1)$.

Let $P(n, k; r)_F$, $P(n, k; r)_L$ and $P(n, k; r)_D$ be the conformational weights of r segments chain whose nth segment enters a site in layer k by forward(from layer $k-1$ to k), lateral (from layer k to k), and downward(from layer $k+1$ to k) directions, respectively. Then $P(n, k; r)_F$, $P(n, k; r)_L$, and $P(n, k; r)_D$ can be defined as

(i) for $n=1$;

$P(n, k; r)_F = \delta_{k,1} \, U \cdot G^{r-2} \cdot P(2) = \delta_{k,1} \, Q$

$P(n, k; r)_L = P(n, k; r)_D = 0$ $(k=1, \cdots, r)$

     (22a)

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

$P(n, k; r)_F = U \cdot G^{r-n} \cdot [P(n)]_{k,F}$

$P(n, k; r)_L = U \cdot G^{r-n} \cdot [P(n)]_{k,L}$

$P(n, k; r)_D = U \cdot G^{r-n} \cdot [P(n)]_{k,D}$ $(k=1, \cdots, r)$

     (22b)

where $[P(n)]_{k,F}$, $[P(n)]_{k,F}$ and $[P(n)]_{k,D}$ are given by

$[P(n)]_{k,F} = \text{col}[o, \cdots, o, b_{n,k;F}, o, \cdots, o]$

$[P(n)]_{k,L} = \text{col}[o, \cdots, o, b_{n,k;L}, o, \cdots, o]$

$[P(n)]_{k,D} = \text{col}[o, \cdots, o, b_{n,k;D}, o, \cdots, o]$

(elements $b_{n,k;F}$, $b_{n,k;L}$, and $b_{n,k;D}$ in kth positions)

     (23)

From Eqs. (22a), (22b), and (23), extending Scheutjens and Fleer's method,[6] we can define the orientational dependent segment density of each layer k; $\langle f_k \rangle$, $\langle l_k \rangle$, $\langle d_k \rangle$ in Eq. (12) that chain segment enters a site in layer k by forward, lateral, and downward directions, respectively, as follows:

$$\langle f_k \rangle = \frac{\sigma}{Q} \sum_{n=1}^{r} P(n, k; r)_F = \frac{\sigma}{Q} \sum_{n=1}^{r} U \cdot G^{r-n} \cdot [P(n)]_{k,F}$$

$$\langle l_k \rangle = \frac{\sigma}{Q} \sum_{n=1}^{r} P(n, k; r)_L = \frac{\sigma}{Q} \sum_{n=1}^{r} U \cdot G^{r-n} \cdot [P(n)]_{k,L}$$

$$\langle d_k \rangle = \frac{\sigma}{Q} \sum_{n=1}^{r} P(n, k; r)_D = \frac{\sigma}{Q} \sum_{n=1}^{r} U \cdot G^{r-n} \cdot [P(n)]_{k,D}$$

     (24)

which give Scheutjens and Fleer's segment density[6] in layer k;

$$\phi_k = \frac{\sigma}{Q} \sum_{n=1}^{r} U \cdot G^{r-n} \cdot \{[P(n)]_{k,F} + [P(n)]_{k,L} + [P(n)]_{k,D}\}$$

$$= \langle f_k \rangle + \langle l_k \rangle + \langle d_k \rangle$$ (25)

Also from Eqs. (22a), (22b), and (23), the probability that a chain terminates in layer k is

$$T_k = \frac{1}{Q} \sum_{H=F,L,D} P(r,k;r)_H = \frac{\sum_{H=F,L,D} P(r, k; r)_H}{U \cdot G^{r-2} \cdot P(2)}$$ (26)

Using Eq. (24), we define normalized bond stepping probability[16,17] that the bond is forward(from layer k to $k+1$), lateral (from layer k to k), or downward(from layer k to $k-1$) as
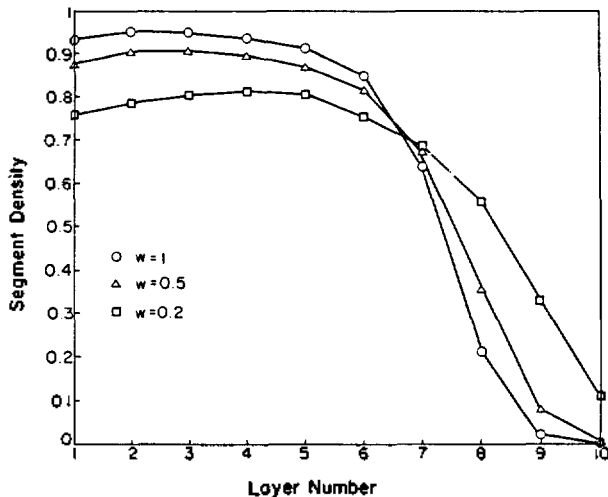
$$\langle F_k \rangle = \frac{\langle f_{k+1} \rangle}{\langle f_{k+1} \rangle + \langle l_k \rangle + \langle d_{k-1} \rangle}$$ (forward step)

$$\langle L_k \rangle = \frac{\langle l_k \rangle}{\langle f_{k+1} \rangle + \langle l_k \rangle + \langle d_{k-1} \rangle}$$ (lateral step)

$$\langle D_k \rangle = \frac{\langle d_{k-1} \rangle}{\langle f_{k+1} \rangle + \langle l_k \rangle + \langle d_{k-1} \rangle}$$ (downward step)

     (27)

respectively, where $\langle F_k \rangle + \langle L_k \rangle + \langle D_k \rangle = 1$ (28)

Let θ be the angle formed between a bond and the direction normal to the interface. In the cubic lattice, θ can have only two values, 0 and $\pi/2$. The order parameter,[3,17] which is the bond orientational characteristic in layer k, is given

Figure 1. Mean segment density distribution $\{\phi_k\}$ as a function of layer number($k=1, \cdots, 10$) for $T=298.25$ K, $\sigma=0.64$, and $r=10$, with the variation of chain stiffness parameter $w(w=1, 0.5,$ and $0.2)$

by

$$S_k = 1/2 \cdot (3 \cdot <\cos^2\theta>_k - 1) \qquad (k=1, \cdots, r-1)$$
$$\tag{29}$$

Substituting Eq. (27) into Eq. (29) and using Eq. (28), we obtain the order parameter in layer k;

$$S_k = 1/2\{3 \cdot (<F_k>\cos^2 0 + <L_k>\cos^2\pi/2 + <D_k>\cos^2 0) - 1\}$$

$$= 1/2(2 - 3<L_k>) \tag{30}$$

By the same method as in Eq. (30), another order parameter, S^*_n, also giving the bond orientational characteristic of nth segment, can be defined as

$$S^*_n = 1/2(2 - 3p_{n,L}) \tag{31}$$

where $p_{n,L}$ is

$$p_{n,L} = \frac{1}{Q} \sum_{k=1}^{r} P(n, k;r)_L = \frac{\sum\limits_{k=1}^{r} P(n, k;r)_L}{U \cdot G^{-2} \cdot P(2)} \tag{32}$$

Computational Method

Eq. (24) is the $3r$ simultaneous nonlinear equations with $3r$ unknown variables $\{<f_k>, <l_k>, <d_k>; k=1, \cdots, r\}$. These equations can be solved by numerical method. In our paper, we make use of the iteration method based on MinPack algorithm[18]. As the first computational step, we assign a plausible set of $\{<f_k>, <l_k>, <d_k>; k=1, \cdots, r\}$ as a initial step for calculation. Substituting initial variables into Eq. (24) 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 is 10^{-6}). We take ε_{tt} to be -100 K in unit of absolute temperature, which was used by Wang and Rice[5], and ε_{ts} to be zero in order to obtain the property resulting from only tail-tail interaction in our model system.
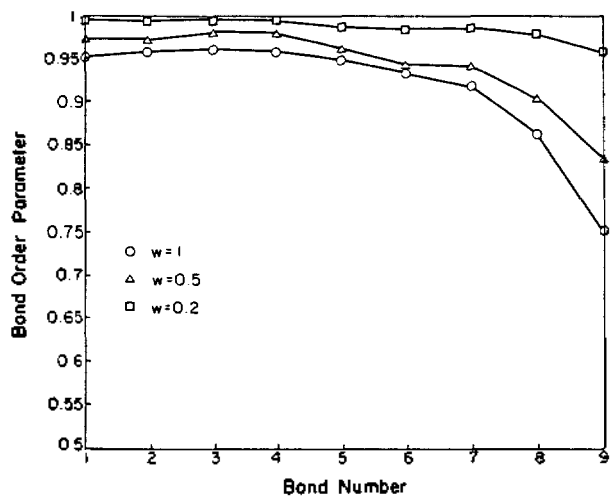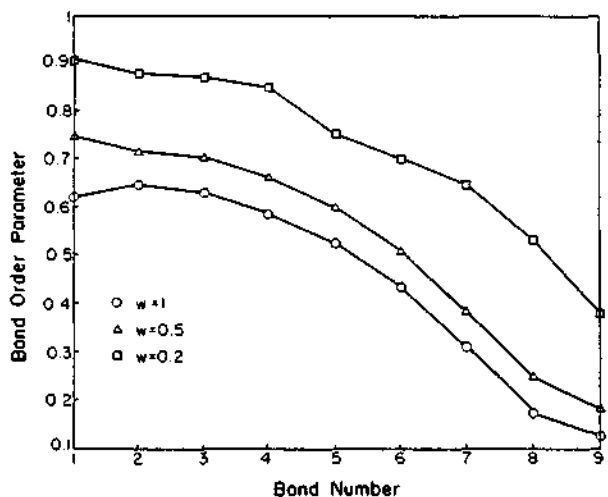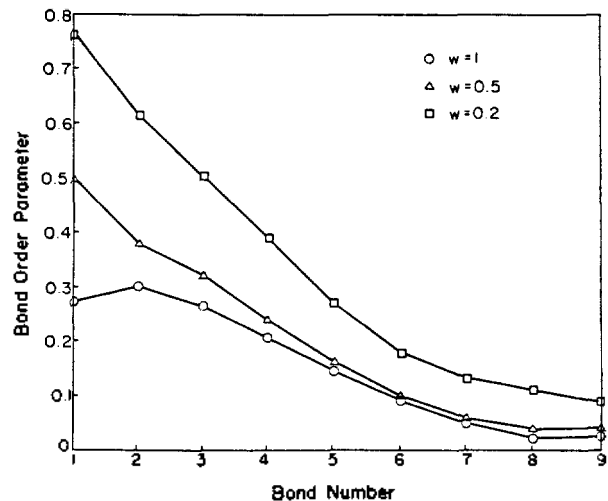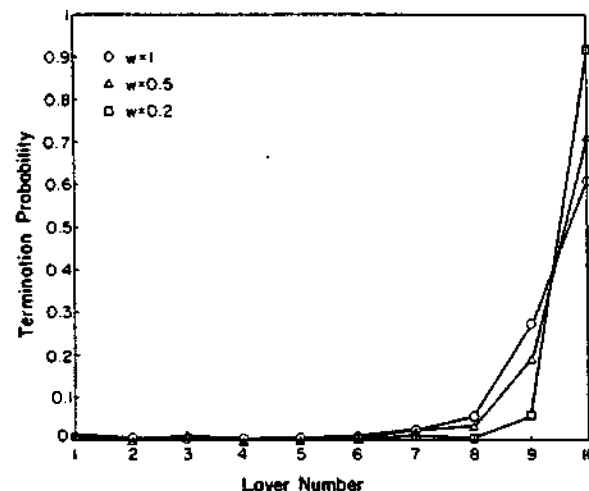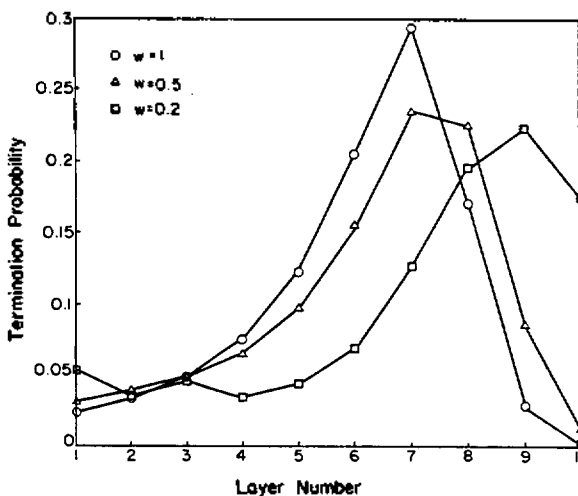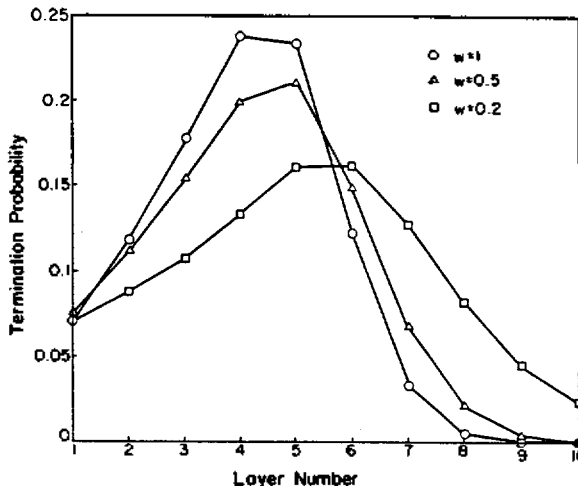

Figure 2. Bond order parameter S_n^* as a function of chain bond position $n(n=1, \cdots, 9)$ for $T=298.15$ K and $r=10$, with the variation of chain stiffness parameter $w(w=1, 0.5,$ and $0.2)$; (a) $\sigma=0.35$, (b) $\sigma=0.64$, and (c) $\sigma=0.95$.
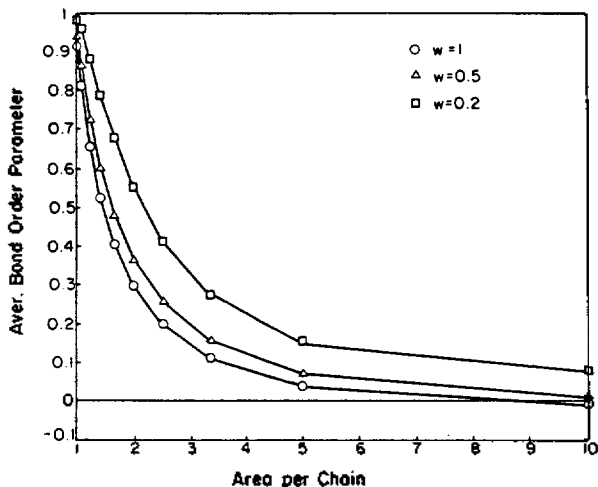
Also we choose $r=10$ and $T=298.15$ K. Using IBM 3090 computer, we obtain $\{<f_k>, <l_k>, <d_k>; k=1, \cdots, r\}$ with the various bent energy parameters $w=1, 0.5$ and 0.2 at $0.1 \leq \sigma \leq 0.95$, where $w=\exp(-\varepsilon_b/k_bT)$. By the set of solution of Eq.
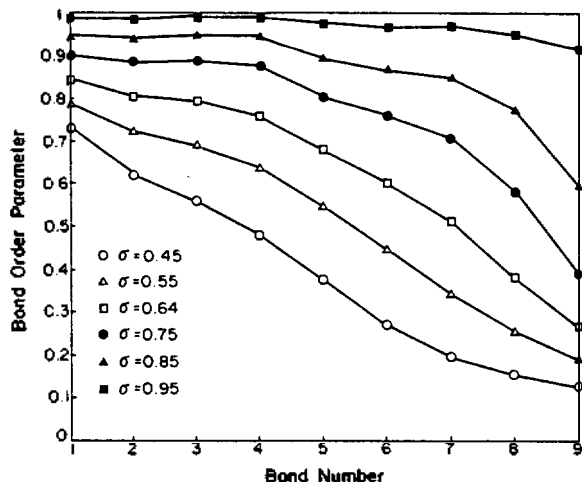
Figure 3. Bond order parameter S_n^* as a function of chain bond position $(n = 1, \cdots, 9)$ for $T = 298.15$ K and $r = 10$, and $w = 0.3$, with the variation of σ: $\sigma = 0.45$, 0.55, 0.64, 0.75, 0.85, and 0.95.

Figure 4. Average order parameter $\langle S \rangle$ as a function of σ^{-1}, for $T = 298.15$ K and $r = 10$, with the variation of chain stiffness parameter $w(w = 1, 0.5, \text{ and } 0.2)$.

(24), we can calculate the conformational proerties such as Eqs. (25), (26), and (31).

Result and Discussion

Figure 1 depicts the mean segment density profile $\{\phi_k: k = 1, \cdots, r\}$ of the amphiphiles. At small distance from the interface, the density profile of the totally flexible chain$(w = 1)$ is higher than that of semiflexible chain$(w = 0.5, 0.2)$. At large distance from the interface, however, ϕ_k of flexible chain is smaller than that of semiflexible chain. This reversal trend of layer density with respect to chain stiffness implies that the stiffer the chain is, the higher the mean thickness is. The reversal trend always occurs in our calculated region $0.1 \leq \sigma \leq 0.95$. The segment density $\{\phi_k\}$, being highest at the interfacial region, decreases continuously with increasing distance from it. However it is abruptly decreased at the layer region far from the interface which has to be occupied by somewhat latter part of chain segments. However as σ is

Figure 5. Termination probability T_k as a function of layer number $k(k = 1, \cdots, 10)$ for $T = 298.15$ K and $r = 10$, with the variation of chain stiffness parameter $w(w = 1, 0.5, \text{ and } 0.2)$: (a) $\sigma = 0.35$, (b) $\sigma = 0.64$, and (c) $\sigma = 0.95$.

increases, degree of the decrement pattern is small and smooth, thus amphiphile system having nearly uniform density throughout all layer number at $\sigma \leq 0.95$.

Figure 2 shows bond order parameters as a function of

layer number at $w=1$, 0.5 and 0.2 with the variation of $\sigma(\sigma = 0.35, 0.64,$ and 0.95). They show gradual ordering pattern with respect to vertical axis when σ increases. As the chain stiffness(w) increases, the order parameter of each bond also increases, which implies that stiff chain has more vertical bond orientation than flexible chain does. In Figure 3, the general ordering pattern of chains with respect to increasing σ is represented for $w=0.3$. Figure 4 shows average order parameter versus area per chain(*i.e.*, σ^{-1}), which gives similar trend to Dill and Cantor's. As Dill and Cantor did, the general pattern of average bond order parameter$\langle S \rangle$ can be fitted to a form of exponential function. Although we generalize Dill and Cantor's method by incorporating energetic contribution and allowing downward direction of chain bond in concept of statistical weight, the general patterns of order parameter are the same as their result except slight difference. From Figures 2 and 3, we can see that end chain has less ordered state than other part of segments, so that it can have relatively large degree of freedom for rearranging itself in the hydrophobic tail region. In fact, with increasing σ, the end chain experiences the largest change of ordering process in all segments along the chain(see Figure 3). Also Figures 2 and 3 show that the first bond along the chain is in most highly ordered state, which makes it possible for the hydrophobic tail region to have well-ordered interfacial structure by compact packing of the segments.

Figure 5 represents that termination probability of end chain being in layer k, from which we can see the change of global chain conformation. At relatively small σ, chain conformation can be characterized by tilted states to a large extent from the vertical direction. As σ increases, chain molecule from its tilted states tends to have the conformation of less tilted states in order to avoid increased repulsive chain interaction. At extremely high $\cdot$ where the chain system is assumed to exist in form of crystalline state, most end chains are found in top layer region, which represents highly ordered conformational states(Figure 5(c)). Also, from Figure 5, it can be seen that with increasing σ, the layer position where the termination probability is maximum tends to shift to the top layer region as a result of ordering process of chain molecule. The chain stiffness also makes contribution to ordering process such that stiff chain has more ordered conformational states than flexible chain does.

Although we do not include in this paper, our calculation shows that downward direction density $\langle d_k \rangle$ in comparison with forward$\langle f_k \rangle$ or lateral segment density $\langle l_k \rangle$ has relatively small contribution to the conformation of the chain molecules in the region of our calculated surface coverage(0.1 $\leq\sigma\leq$0.95). This result corroborates roughly the validity of Flory and Dill's assumption[1,2] which disregards the possibility of downward direction of the chain bond, and energetic contribution to chain statistics. With increasing σ, the contribution to segment density comes mainly from the forward direction density, which represents the amphiphiles are largely aligned to vertical ordering axis, giving the chain system highly anisotropic conformational states with high ordering pattern. This anisotropic nature at high surface coverage characterizes the structure of the monolayer amphiphiles at the interface.

In this paper, we developed a lattice mean field theory of the monolayer adsorption of amphiphile molecule at the air-water interface. By taking account of detailed chain bond pair characteristics, and incorporating entropic and energetic contribution to the statistical weight systematically, we can derive supermatrix equation(Eq. (21)) which makes conformational features of the adsorbed amphiphile easily elucidated. Our method also avoids the unrealistic self-reversal effect of chain segment. Therefore our method can be regarded as a generalized version of Dill and Cantor's treatment[3,4] of amphiphile molecules. Although our lattice statistics is only valid in the region of high surface coverage(0.1$\leq\sigma\leq$0.9), it is useful to elucidate the detailed structure of chain molecule which is in confined geometry at high σ. Recently, we calculated conformational properties of bilayer system[19] by employing simple approximation which neglects the chain orientation effect in packing the chain molecules. So we need to incorporate anisotropic mean field approximation[14,15] by using Eq. (11) in that bilayer problem, which can be easily studied by our method.

References

1. K. A. Dill and P. J. Flory, *Proc. Natl. Acad. Sci. U.S.A.* **77**, 3115 (1980).
2. K. A. Dill and P. J. Flory, *Proc. Natl. Acad. Sci. U.S.A.* **78**, 676 (1981).
3. K. A. Dill and R. S. Cantor, *Macromolecules*, **17**, 380 (1984).
4. K. A. Dill and R. S. Cantor, *Macromolecules*, **17**, 384 (1984).
5. Z. Wang and S. A. Rice, *J. Chem. Phys.* **88**, 1290 (1988).
6. J. M. H. M. Scheutjens and G. J. Fleer, *J. Phys. Chem.*, **83**, 1619 (1979).
7. J. M. H. M. Scheutjens and G. J. Fleer, *J. Phys. Chem.*, **84**, 178 (1980).
8. J. M. H. M. Scheutjens and G. J. Fleer, *Macromolecules*, **18**, 1882 (1985).
9. S. Levine, M. M. Thomlinson, and K. Robinson, *Discuss. Faraday Soc.*, **65**, 202 (1978).
10. R. S. Cantor and P. M. McIlroy, *J. Chem. Phys.*, **91**, 416 (1989).
11. P. J. Flory, *Proc. Roy. Soc.(London)* A234, 60 (1956).
12. J. F. Nagle, P. D. Gujrati, and M. Goldstein, *J. Phys. Chem.*, **88**, 4599 (1984).
13. M. G. Bawendi and K. F. Freed, *J. Chem. Phys.*, **86**, 3720 (1987).
14. E. A. DiMarzio, *J. Chem. Phys.*, **35**, 658 (1961).
15. E. A. DiMarzio, *J. Chem. Phys.*, **36**, 1563 (1962).
16. D. N. Theodorou, *Macromolecules*, **21**, 1391 (1988).
17. D. N. Theodorou, *Macromolecules*, **21**, 1400 (1988).
18. MinPack-1 algorithm, National technical information service U.S. department of commerce (1980).
19. Y. S. Pak and H. S. Pak, *Bull. Korean Chem. Soc.*(to be published)