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Conformation of Adsorbed Polymeric Chain. III

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Average properties of a copolymeric chain in which a segments of the kind A and b segments of the kind B occur alternatively are calculated for an infinite chain length. For the simplest case of $a=b=1$, *i.e.* an alternating copolymeric chain $(\text{-A-B-})_N$, the average number of adsorbed segments of A, $\bar{\nu}_A$, that of B, $\bar{\nu}_B$, and the mean square end-to-end distance $\overline{r^2}$ are computed numerically as functions of the adsorption energies ε_A and ε_B. The values of $\bar{\nu}_A$, $\bar{\nu}_B$, and $\overline{r^2}$ are proportional to N for larger values of η_A $(=\exp(\varepsilon_A/kT))$ than the critical value $(\eta_A)_c$ at fixed η_B, as found for the case of a homogeneous polymeric chain. It is seen that the behavior of the copolymeric chain near an interface is affected distinctively by the adsorption energies of the segments A and B, and the copolymeric chain is forced to adsorb even for a fairly low adsorption energy of the segment of one kind if the adsorption energy of the segment of the other kind is sufficiently large.

Statistical-mechanical theories of the adsorption of polymeric chains at interfaces have been presented by many investigators.[1-7] For the homogeneous polymeric chain which is a long sequence of segments of the same kind, it was shown that the conformation of the isolated polymeric chain near the interface changes discontinuously at a certain value of the adsorption energy which depends on a lattice model used. In the case of the polymeric chain consisting of $n+1$ segments on a simple cubic lattice we obtained results where the average number of adsorbed segments is given by

$$\begin{aligned} \bar{\nu} &= n\{1-\eta[2(\eta-1)]^{-1} + \eta[4(\eta-1)^2+(\eta-1)]^{-1/2}\}, && \eta>\eta_c \\ \bar{\nu} &= (5/2)(\pi n/6)^{1/2}, && \eta=\eta_c \\ \bar{\nu} &= 6/(6-5\eta), && \eta<\eta_c \end{aligned} \quad (1)$$

and the mean-square end-to-end distance by

$$\begin{aligned} \overline{r^2} &= 2l^2n(\eta-1)[4(\eta-1)^2+(\eta-1)]^{-1/2}, && \eta>\eta_c \\ \overline{r^2} &= (8/9)l^2n, && \eta=\eta_c \\ \overline{r^2} &= l^2n, && \eta<\eta_c \end{aligned} \quad (2)$$

where η is related to the energy gain per segment associated with the adsorption $-\varepsilon$, by the equation

$$\eta = \exp(\varepsilon/kT), \quad (3)$$

η_c equals 6/5, and l is the distance between neighboring segments.[6,7] It is interesting to estimate the effect

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of foreign segments introduced into the polymeric chain upon the above equations. This is useful to understand better the strange behavior of copolymers at interfaces.

We extended the theoretical treatment given in previous papers to a copolymeric chain consisting of segments of various kinds. For convenience, we consider a copolymeric chain in which the segments of kinds A and B, the same in size, occur in alternative succession of a segments of the kind A and b segments of B.

Theoretical

1. Probability of an Adsorbed Polymeric Chain. The behavior of polymer molecules near an interface is represented by a symmetrical random walker whose way is blocked by the interface when the self-excluded volume is neglected and the concentration is extremely dilute. We are concerned with a polymeric chain $(-A_a-B_b-)_N$ consisting of $(a+b)N$ segments lying in the positive z domain of a simple cubic lattice and adsorbing at the interface which is the xy plane through $z=0$. We also assume that the polymeric chain is always adsorbed by the end segments of the chain on the interface, because the dangling chain ends make a negligible contribution to the properties in an adsorbed state $(\eta>\eta_c)$.[4,7] A given conformation of the absorbed polymeric chain, of which one chain end is located at the origin and the other end at a point $(x,y,0)$, is characterized by a sequence of random walkers which touch the interface only at two ends and have probabilities $f_{k_j}(x_j,y_j)$. The probability of the adsorbed polymeric chain is then given by

$$p_{(a+b)N}(x,y,\eta_A,\eta_B) = \sum_m\sum_k\sum_{x,y} \eta_A\eta_B f_{k_m}(x_m,y_m) \prod_{j=1}^{m-1} \eta_j f_{k_j}(x_j,y_j), \tag{4}$$

where

$$\eta_A = \exp(\varepsilon_A/kT), \quad \eta_B = \exp(\varepsilon_B/kT), \tag{5}$$

and η_j takes η_A or η_B according to whether the j-th random walker terminates in the segments A or in B. A set of $\boldsymbol{k}$, $\boldsymbol{x}$, and $\boldsymbol{y}$ means a microscopic state satisfying the conditions

$$\sum_{j=1}^{m} k_j = (a+b)N - 1 \tag{6}$$

which come from the fact that the polymeric chain of $(a+b)N$ segments is replaced by the random walk of $(a+b)N-1$ steps,

$$\sum_{j=1}^{m} x_j = x, \quad \text{and} \quad \sum_{j=1}^{m} y_j = y, \tag{7}$$

and the sums are taken over all possible values. On introducing generating functions

$$\sum_{x,y} p_{(a+b)N}(x,y,\eta_A,\eta_B)\exp(ix\theta+iy\phi) = P_{(a+b)N}(\theta,\phi,\eta_A,\eta_B)$$

$$\sum_{N=1}^{\infty} P_{(a+b)N}(\theta,\phi,\eta_A,\eta_B)w^{(a+b)N-1} = P(\theta,\phi,\eta_A,\eta_B;w) \tag{8}$$

and

$$\sum_{x,y} f_{(a+b)n+k}(x,y)\exp(ix\theta+iy\phi) = F_{(a+b)n+k}(\theta,\phi)$$

$$\sum_{n=0}^{\infty} F_{(a+b)n+k}(\theta,\phi)w^{(a+b)n+k} = F_k(\theta,\phi;w), \tag{9}$$

Eq. (4) becomes

$$P(\theta,\phi,\eta_A,\eta_B;w) = \eta_A\boldsymbol{a}\left(\sum_{m=1}^{\infty}\mathbf{M}^m\right)\boldsymbol{\beta}^+ = \eta_A\boldsymbol{a}\mathbf{M}(\mathbf{I}-\mathbf{M})^{-1}\boldsymbol{\beta}^+, \tag{10}$$

where

$$\mathbf{M} = \begin{pmatrix} \eta_A F_{a+b} & \eta_A F_1 & \cdots \eta_A F_{a-1} & \eta_B F_a & \cdots \eta_B F_{a+b-1} \\ \eta_A F_{a+b-1} & \eta_A F_{a+b} & \cdots \eta_A F_{a-2} & \eta_B F_{a-1} & \cdots \eta_B F_{a+b-2} \\ \cdots & \cdots & \cdots & \cdots & \cdots \\ \eta_A F_1 & \eta_A F_2 & \cdots \eta_A F_a & \eta_B F_{a+1} & \cdots \eta_B F_{a+b} \end{pmatrix}, \tag{11}$$

$$\boldsymbol{a} = (1\ 0\ \cdots\ 0), \text{ and } \boldsymbol{\beta} = (0\ \cdots\ 0\ 1).$$

Substituting Eq. (A9) in the Appendix into the above equation, we obtain

$$P(\theta,\phi,\eta_A,\eta_B;w) = \eta_A\Delta_1(1)/D(1), \tag{12}$$

where

$$D(1) = (-1)^{a+b}\begin{vmatrix} \eta_A F_{a+b}-1 & \eta_A F_1 & \cdots \eta_B F_{a+b-1} \\ \eta_A F_{a+b-1} & \eta_A F_{a+b}-1 & \cdots \eta_B F_{a+b-2} \\ \cdots & \cdots & \cdots \\ \eta_A F_1 & \eta_A F_2 & \cdots \eta_B F_{a+b}-1 \end{vmatrix} \tag{13}$$

and

$$\Delta_1(1) = \begin{vmatrix} \eta_A F_1 & \eta_A F_2 \cdots \eta_B F_{a+b-1} \\ \eta_A F_{a+b}-1 & \eta_A F_1 \cdots \eta_B F_{a+b-2} \\ \cdots & \cdots \\ \eta_A F_3 & \eta_A F_4 \cdots \eta_B F_1 \end{vmatrix} \tag{14}$$

It is now necessary to know $F_k(\theta,\phi;w)$ as a function of θ, ϕ, and w in order to have an explicit expression of $P(\theta,\phi,\eta_A,\eta_B;w)$.

2. Evaluation of $F_k(\theta,\phi;w)$. There exist relations between the probabilities $f_{(a+b)n+k}(x,y)$ and corresponding probabilities $u_{(a+b)n+k}(x,y)$ of an unrestricted random walk:

$$\begin{aligned} u_{(a+b)n+k}(x,y) &= \sum_{x',y'} f_1(x',y')u_{(a+b)n+k-1}(x-x',y-y') \\ &+ 2\sum_j\sum_{x',y'} f_{(a+b)j+1}(x',y')u_{(a+b)(n-j)+k-1}(x-x',y-y') \\ &+ \cdots\cdots \\ &+ 2\sum_j\sum_{x',y'} f_{(a+b)(j+1)}(x',y')u_{(a+b)(n-j-1)+k}(x-x',y-y'), \\ &k = 1, 2, \cdots, a+b. \end{aligned} \tag{15}$$

Defining generating functions

$$\sum_{x,y} u_{(a+b)n+k}(x,y)\exp(ix\theta+iy\phi) = U_{(a+b)n+k}(\theta,\phi)$$

$$\sum_{n=0}^{\infty} U_{(a+b)n+k}(\theta,\phi)w^{(a+b)n+k} = U_k(\theta,\phi;w)^{8)} \tag{16}$$

analogous to Eq. (9), Eq. (15) becomes

$$\begin{aligned} U_k(\theta,\phi;w) &= [2F_1(\theta,\phi;w) - wF_1(\theta,\phi)]U_{k-1}(\theta,\phi;w) \\ &+ 2F_2(\theta,\phi;w)U_{k-2}(\theta,\phi;w) + \cdots \\ &+ 2F_{a+b}(\theta,\phi;w)U_k(\theta,\phi;w), \\ &k = 1, 2, \cdots, a+b-1 \end{aligned}$$

$$\begin{aligned} U_{a+b}(\theta,\phi;w) - U_0(\theta,\phi) &= [2F_1(\theta,\phi;w) \\ &- wF_1(\theta,\phi)]U_{a+b-1}(\theta,\phi;w) \\ &+ 2F_2(\theta,\phi;w)U_{a+b-2}(\theta,\phi;w) + \cdots \\ &+ 2F_{a+b}(\theta,\phi;w)U_{a+b}(\theta,\phi;w). \end{aligned} \tag{17}$$

Rearranging the above equations after introducing

8) For $k=a+b$ the equation is slightly modified by adding $U_0(\theta,\phi)$ to the left-hand side.

$$U_0(\theta,\phi) = 1 \text{ and } F_1(\theta,\phi) = c/3 \tag{18}$$

where

$$c = \cos\theta + \cos\phi, \tag{19}$$

we obtain

$$\begin{aligned} &U_{k-1}(\theta,\phi;w)F_1(\theta,\phi;w) + U_{k-2}(\theta,\phi;w)F_2(\theta,\phi;w) + \cdots \\ &\quad + U_k(\theta,\phi;w)F_{a+b}(\theta,\phi;w) = (1/2)[U_k(\theta,\phi;w) \\ &\quad + (cw/3)U_{k-1}(\theta,\phi;w)], \quad k = 1, 2, \cdots, a+b-1 \\ &U_{a+b-1}(\theta,\phi;w)F_1(\theta,\phi;w) + U_{a+b-2}(\theta,\phi;w)F_2(\theta,\phi;w) + \cdots \\ &\quad + U_{a+b}(\theta,\phi;w)F_{a+b}(\theta,\phi;w) = (1/2)[U_{a+b}(\theta,\phi;w) \\ &\quad + (cw/3)U_{a+b-1}(\theta,\phi;w) - 1]. \end{aligned} \tag{20}$$

These equations allow us to evaluate $F_k(\theta, \phi, w)$. We have

$$\begin{aligned} &F_1(\theta,\phi;w) = cw/6 + D_1/D \\ &F_k(\theta,\phi;w) = D_k/D, \quad k = 2, 3, \cdots, a+b-1 \\ &F_{a+b}(\theta,\phi;w) = 1/2 + D_{a+b}/D, \end{aligned} \tag{21}$$

where

$$D = \begin{vmatrix} U_{a+b} & U_{a+b-1} \cdots U_1 \\ U_1 & U_{a+b} \cdots U_2 \\ \cdots\cdots & \cdots\cdots \\ U_{a+b-1} & U_{a+b-2} \cdots U_{a+b} \end{vmatrix} \tag{22}$$

and D_k is the determinant obtained on replacing the respective elements in the k-th column of D by

$$0, 0, \cdots, 0, -1/2.$$

$U_j(\theta, \phi; w)$ in the determinants are given by

$$\begin{aligned} U_j(\theta,\phi;w) &= \frac{1}{2\pi}\int_{-\pi}^{\pi} \mathrm{d}\phi \left[\frac{w}{3}(c+\cos\phi)\right]^j \Big/ \\ &\qquad \left\{1-\left[\frac{w}{3}(c+\cos\phi)\right]^{a+b}\right\} \\ &= [3/(a+b)]\sum_{l=0}^{a+b-1}\{1/\omega^{(a+b-j)l}[(3-cw/\omega^l)^2 \\ &\qquad - (w/\omega^l)^2]^{1/2}\}, \quad j = 1, 2, \cdots, a+b, \end{aligned} \tag{23}$$

where

$$\omega = \exp[2\pi i/(a+b)]. \tag{24}$$

3. Expressions for Average Properties. We may write $P(\theta, \phi, \eta_A, \eta_B; w)$, which we will denote by $P(c, \eta_A, \eta_B; w)$ hereafter, as an explicit function of c, η_A, η_B, and w. It is now possible to calculate the average properties of the adsorbed polymeric chain. Taking into account Eqs. (4) and (8), the mean square end-to-end distance is given by

$$\overline{r^2} = l^2[c\{\partial P_{(a+b)N}(c,\eta_A,\eta_B)/\partial c\}/P_{(a+b)N}(c,\eta_A,\eta_B)]_{c=2}, \tag{25}$$

where $P_{(a+b)N}(c, \eta_A, \eta_B)$ is used instead of $P_{(a+b)N}(\theta, \phi, \eta_A, \eta_B)$. On the other hand, the average number of adsorbed segments of the kind A per polymeric chain is computed by

$$\bar{\nu}_A = \eta_A\{\partial P_{(a+b)N}(2,\eta_A,\eta_B)/\partial\eta_A\}/P_{(a+b)N}(2,\eta_A,\eta_B) \tag{26}$$

and that of B by

$$\bar{\nu}_B = \eta_B\{\partial P_{(a+b)N}(2,\eta_A,\eta_B)/\partial\eta_B\}/P_{(a+b)N}(2,\eta_A,\eta_B). \tag{27}$$

In order to carry out the calculation of Eqs. (25), (26), and (27), it is necessary to know $P_{(a+b)N}(c, \eta_A, \eta_B)$ and its derivatives with respect to c, η_A, and η_B. These functions are found by applying Cauchy's residue theorem to Eq. (8). We obtain

$$\begin{aligned} P_{(a+b)N}(c,\eta_A,\eta_B) &= (1/2\pi i)\oint_{C_0}(1/w^{(a+b)N}) \\ &\quad \times P(c,\eta_A,\eta_B;w)\mathrm{d}w, \end{aligned} \tag{28}$$

$$\begin{aligned} [\partial P_{(a+b)N}(c,\eta_A,\eta_B)/\partial c]_{c=2} &= (1/2\pi i)\oint_{C_0}(1/w^{(a+b)N}) \\ &\quad \times [\partial P(c,\eta_A,\eta_B;w)/\partial c]_{c=2}\mathrm{d}w, \end{aligned} \tag{29}$$

$$\begin{aligned} \partial P_{(a+b)N}(2,\eta_A,\eta_B)/\partial\eta_A &= (1/2\pi i)\oint_{C_0}(1/w^{(a+b)N}) \\ &\quad \times \{\partial P(2,\eta_A,\eta_B;w)/\partial\eta_A\}\mathrm{d}w, \end{aligned} \tag{30}$$

and

$$\begin{aligned} \partial P_{(a+b)N}(2,\eta_A,\eta_B)/\partial\eta_B &= (1/2\pi i)\oint_{C_0}(1/w^{(a+b)N}) \\ &\quad \times \{\partial P(2,\eta_A,\eta_B:w)/\partial\eta_B\}\mathrm{d}w, \end{aligned} \tag{31}$$

where the contour C_0 includes only the pole at $w=0$.

4. Average Properties of (–A–B–)$_N$. Taking up the simplest case $a=b=1$, *i.e.* an alternating copolymeric chain (–A–B–)$_N$, we will consider the effect of different adsorption energies of segments A and B on the conformation. Let us first derive the generating functions of unrestricted random walk $U_1(c;w)$ and $U_2(c;w)$ which are necessary for knowing $F_1(c;w)$ and $F_2(c;w)$. This is done by introducing $a=b=1$ and $\omega=-1$ resulting from Eq. (24) into Eq. (23); we have

$$\begin{aligned} U_1(c;w) &= (3/2)\{[(3-cw)^2-w^2]^{-1/2} - [(3+cw)^2-w^2]^{-1/2}\} \\ U_2(c;w) &= (3/2)\{[(3-cw)^2-w^2]^{-1/2} + [(3+cw)^2-w^2]^{-1/2}\}. \end{aligned} \tag{32}$$

Substituting these equations and Eq. (22) into Eq (21), we get

$$\begin{aligned} F_1(c;w) &= cw/6 - (1/12)\{[(3-cw)^2-w^2]^{1/2} \\ &\quad - [(3+cw)^2-w^2]^{1/2}\} \\ F_2(c:w) &= 1/2 - (1/12)\{[(3-cw)^2-w^2]^{1/2} \\ &\quad + [(3+cw)^2-w^2]^{1/2}\}. \end{aligned} \tag{33}$$

The generating function of the probability of adsorbed polymeric chain is connected with $F_1(c;w)$ and $F_2(c;w)$ with the aid of Eqs. (12), (13), and (14), and is expressed as the explicit function of c, η_A, η_B, and w:

$$P(c,\eta_A,\eta_B;w) = \eta_A\eta_B F_1(c;w)/D(c,\eta_A,\eta_B,w), \tag{34}$$

where

$$\begin{aligned} D(c,\eta_A,\eta_B,w) &= 1 - (\eta_A+\eta_B)F_2(c;w) \\ &\quad + \eta_A\eta_B[F_2(c:w)^2 - F_1(c;w)^2] \\ &= \frac{(\eta_A+\eta_B)^2}{4\eta_A\eta_B}\left\{\left(1-\frac{1}{6}\frac{2\eta_A\eta_B}{\eta_A+\eta_B}(3+cw\right.\right. \\ &\quad \left. - [(3-cw)^2-w^2]^{1/2})\right)\left[1-\frac{1}{6}\frac{2\eta_A\eta_B}{\eta_A+\eta_B}\right. \\ &\quad \left. \times(3-cw-[(3+cw)^2-cw^2]^{1/2})\right) \\ &\quad \left. - \left(\frac{\eta_A-\eta_B}{\eta_A+\eta_B}\right)^2\right\}. \end{aligned} \tag{35}$$

On introducing Eq. (34) into Eq. (28), the generating function $P_{2N}(2, \eta_A, \eta_B)$ is given by

$$P_{2N}(2,\eta_A,\eta_B) = \frac{1}{2\pi i}\oint_{C_0}\frac{1}{w^{2N}}\frac{\eta_A\eta_B F_1(2;w)}{D(2,\eta_A,\eta_B,w)}\mathrm{d}w. \tag{36}$$

It is seen from Eq. (35) that the equation $D(2, \eta_A, \eta_B, w)=0$ has two roots w_1 and w_2 which are related to each other by

$$w_1 = -w_2 \tag{37}$$

and coincide with branch-points $w=1$ and -1 respectively for a set of η_A and η_B satisfying

$$36 - 6(3-6^{1/2})(\eta_A+\eta_B) - 5(24^{1/2}-1)\eta_A\eta_B = 0. \tag{38}$$

We are interested in the behavior of the adsorbed polymeric chain only when the values of η_A and η_B are larger than the critical values given by Eq. (38), because the polymeric chain is in reality in the adsorbed state for the values of η_A and η_B. If the values of η_A and η_B are larger than the critical values and N is infinitely large, the principal contribution to the integral of Eq. (36) comes from residues of w_1 and w_2.[5,6] Thus we have

$$P_{2N}(2, \eta_A, \eta_B) = -\frac{1}{w_1^{2N}}\frac{\eta_A\eta_B F_1(2;w_1)}{\partial D(2, \eta_A, \eta_B, w_2)/\partial w} - \frac{1}{w_2^{2N}}\frac{\eta_A\eta_B F_1(2;w_2)}{\partial D(2, \eta_A, \eta_B, w_2)/\partial w}, \tag{39}$$

where $\partial D(2, \eta_A, \eta_B, w_1)/\partial w$ and $\partial D(2, \eta_A, \eta_B, w_2)/\partial w$ denote the values of $\partial D(2, \eta_A, \eta_B, w)/\partial w$ at $w=w_1$ and w_2, respectively. Combining

$$\partial D(2, \eta_A, \eta_B, w)/\partial w = -(\eta_A+\eta_B)\partial F_2(2;w)/\partial w + 2\eta_A\eta_B[F_2(2;w)\partial F_2(2;w)/\partial w - F_1(2;w)\partial F_1(2;w)/\partial w] \tag{40}$$

where

$$\partial F_1(2;w)/\partial w = 1/3 + (1/4)\{(2-w)[(3-2w)^2-w^2]^{-1/2} + (2+w)[(3+2w)^2-w^2]^{1/2}\}$$
$$\partial F_2(2;w)/\partial w = (1/4)\{(2-w)[(3-2w)^2-w^2]^{-1/2} - (2+w)[(3+2w)^2-w^2]^{-1/2}\} \tag{41}$$

with Eq. (37), we obtain

$$\partial D(2, \eta_A, \eta_B, w_1)/\partial w = -\partial D(2, \eta_A, \eta_B, w_2)/\partial w. \tag{42}$$

From this and

$$F_1(2;w_1) = -F_1(2;w_2), \tag{43}$$

Eq. (39) is reduced to

$$P_{2N}(2, \eta_A, \eta_B) = -\frac{2}{w_1^{2N}}\frac{\eta_A\eta_B F_1(2;w_1)}{\partial D(2, \eta_A, \eta_B, w_1)/\partial w} \tag{44}$$

On the other hand, the substitution of the derivative of $P(c, \eta_A, \eta_B; w)$ with respect to c into Eq. (29) gives

$$\left(\frac{\partial P_{2N}(c, \eta_A, \eta_B)}{\partial c}\right)_{c=2} = \frac{1}{2\pi i}\oint_{C_1}\frac{dw}{w^{2N}}\left(\frac{\eta_A\eta_B\partial F_1(2;w)/\partial c}{D(2, \eta_A, \eta_B, w)} - \frac{\eta_A\eta_B F_1(2;w)\partial D(2, \eta_A, \eta_B, w)/\partial c}{D(2, \eta_A, \eta_B, w)^2}\right), \tag{45}$$

where

$$\partial D(2, \eta_A, \eta_B, w)/\partial c = -(\eta_A+\eta_B)\partial F_2(2;w)/\partial c + 2\eta_A\eta_B[F_2(2;w)\partial F_2(2;w)/\partial c - F_1(2;w)\partial F_1(2;w)/\partial c] \tag{46}$$

in which

$$\partial F_1(2;w)/\partial c = w/6 + (w/12)\{(3-2w)[(3-2w)^2-w^2]^{-1/2} + (3+2w)[(3+2w)^2-w^2]^{-1/2}\}$$
$$\partial F_2(2;w)/\partial c = (w/12)\{(3-2w)[(3-2w)^2-w^2]^{-1/2} - (3+2w)[(3+2w)^2-w^2]^{-1/2}\}. \tag{47}$$

Carrying out integration in a similar way and retaining the predominant term in the limit $N\gg 1$, Eq. (45) becomes

$$\left[\frac{\partial P_{2N}(c, \eta_A, \eta_B)}{\partial c}\right]_{c=2} = -\frac{2N}{w_1^{2N+1}}\frac{\eta_A\eta_B F_1(2;w_1)\partial D(2, \eta_A, \eta_B, w_1)/\partial c}{[\partial D(2, \eta_A, \eta_B, w_1)/\partial w]^2}. \tag{48}$$

We may obtain expressions for $\partial P_{2N}(2, \eta_A, \eta_B)/\partial \eta_A$ and $\partial P_{2N}(2, \eta_A, \eta_B)/\partial\eta_B$ by using a method similar to that used to derive the above equation:

$$\frac{\partial P_{2N}(2, \eta_A, \eta_B)}{\partial \eta_A} = -\frac{2N}{w_1^{2N+1}}\frac{\eta_A\eta_B F_1(2;w_1)\partial D(2, \eta_A, \eta_B, w_1)/\partial\eta_A}{[\partial D(2, \eta_A, \eta_B, w_1)/\partial w]^2}$$
$$\frac{\partial P_{2N}(2, \eta_A, \eta_B)}{\partial \eta_B} = -\frac{2N}{w_1^{2N+1}}\frac{\eta_A\eta_B F_1(2;w_1)\partial D(2, \eta_A, \eta_B, w_1)/\partial\eta_B}{[\partial D(2, \eta_A, \eta_B, w_1)/\partial w]^2} \tag{49}$$

where

$$\partial D(2, \eta_A, \eta_B, w)/\partial\eta_A = -F_2(2;w) + \eta_B[F_2(2;w)^2-F_1(2;w)^2]$$
$$\partial D(2, \eta_A, \eta_B, w)/\partial\eta_B = -F_2(2;w) + \eta_A[F_2(2;w)^2-F_1(2;w)^2]. \tag{50}$$

The final equations for the average properties are derived by substituting Eqs. (44), (48), and (49) into Eqs. (25), (26), and (27):

$$\overline{r^2} = 2Nl^2\frac{2}{w_1}\frac{\partial D(2, \eta_A, \eta_B, w_1)/\partial c}{\partial D(2, \eta_A, \eta_B, w_1)/\partial w}, \tag{51}$$

$$\bar{\nu}_A = 2N\frac{\eta_A}{w_1}\frac{\partial D(2, \eta_A, \eta_B, w_1)/\partial\eta_A}{\partial D(2, \eta_A, \eta_B, w_1)/\partial w}, \tag{52}$$

and

$$\bar{\nu}_B = 2N\frac{\eta_B}{w_1}\frac{\partial D(2, \eta_A, \eta_B, w_1)/\partial\eta_B}{\partial D(2, \eta_A, \eta_B, w_1)/\partial w}. \tag{53}$$

We can now calculate the average values $\overline{r^2}$, $\bar{\nu}_A$, and $\bar{\nu}_B$ of the polymeric chain (–A–B–)$_N$ at the interface as functions of η_A and η_B and compare them with previous results.

Discussion

Let us first consider how the average number of adsorbed segments of kind A in the alternating copolymeric chain (–A–B–)$_N$ varies with η_A in the limit $N\gg 1$ when η_B has a given value. This is determined by numerical calculation of Eq. (52) which is made by evaluating one root w_1 of the equation $D(2, \eta_A, \eta_B, w)=0$ at a given set of η_A and η_B and then substituting the root into Eq. (52) with Eqs. (40) and (50). The variation of $\bar{\nu}_A$ with η_A at few fixed values of η_B is illustrated in Fig. 1, where the ratio $\bar{\nu}_A/2N$ is plotted against ε_A measured in the unit kT. It is seen that the average number of adsorbed segments is proportional to the total number of segments of the copolymeric chain for values of η_A larger than the critical value $(\eta_A)_c$ derived from Eq. (38) at given η_B, as found for the case of a homogeneous polymeric chain consisting of identical segments. The critical value $(\eta_A)_c$ increases remarkably with the decrease in η_B. The increase of $\bar{\nu}_A$ with η_A is slower than the corresponding one of the homogeneous polymeric chain calculated by Eq. (1).

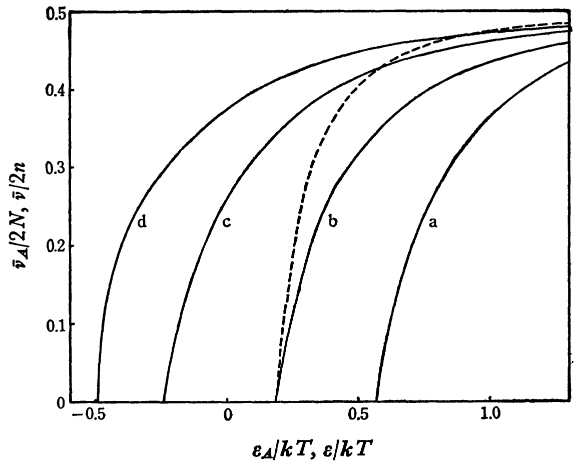

Fig. 1. The ratio $\bar{\nu}_A/2N$ of the copolymeric chain $(\text{-A-B-})_N$ is plotted against ε_A/kT in the limit $N \gg 1$: (a) $\varepsilon_B/kT = -0.223$, (b) 0.182, (c) 0.588, (d) 0.916. The dotted line corresponds to the homogeneous polymeric chain calculated by Eq. (1).

It is probable that the adsorption of the segment A in the copolymeric chain is obstructed by the existence of the segment B having a low adsorption energy when $\eta_B > 6/5$ ($\varepsilon_B/kT < 0.182$). On the other hand, when $\eta_B > 6/5$, adsorption is preferred at the initial stage, becomes equal to that of the homogeneous polymeric chain at $\eta_A = \eta_B$, and then accepts a negative contribution at larger η_A.

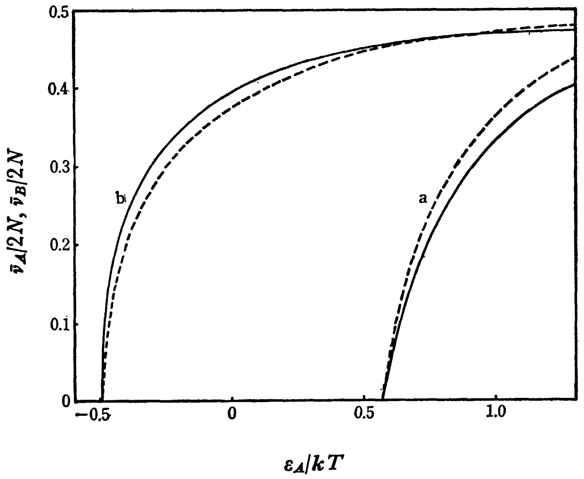

Fig. 2. Comparison of $\bar{\nu}_B/2N$ *versus* ε_A/kT (solid line) and $\bar{\nu}_A/2N$ *versus* ε_A/kT (dotted line) at (a) $\varepsilon_B/kT = -0.223$ and (b) 0.916.

It is also interesting to see the variation of the average number of adsorbed segments of kind B with η_A when η_B is given. The plot of $\bar{\nu}_B/2N$ against ε_A/kT is shown in Fig. 2 where the curves are calculated by Eq. (53) by a similar procedure. Adsorption of segment B occurs and increases gradually with η_A even when η_B has a value lower than 6/5 at which the homogeneous polymeric chain consisting of B segments does not exist in the adsorbed state. For $\eta_B > 6/5$, the value of $\bar{\nu}_B$ increases fairly steeply with η_A.

From the above results, we can know the effect of the adsorption energy of the segments on the total average number of adsorbed segments of the alternating copolymeric chain. In Fig. 3, the sum of $\bar{\nu}_A/2N$ and $\bar{\nu}_B/2N$ given in Figs. 1 and 2 *versus* ε_A/kT curves at fixed values of η_B are illustrated together with the curve of a homogeneous polymeric chain calculated by Eq. (1). It is noticeable that the behavior of the copolymeric chain near an interface is affected distinctly by the adsorption energies of segments A and B, and the copolymeric chain is forced to adsorb even for a fairly low adsorption energy of the segment of one kind if the adsorption energy of the segment of the other kind is sufficiently large.

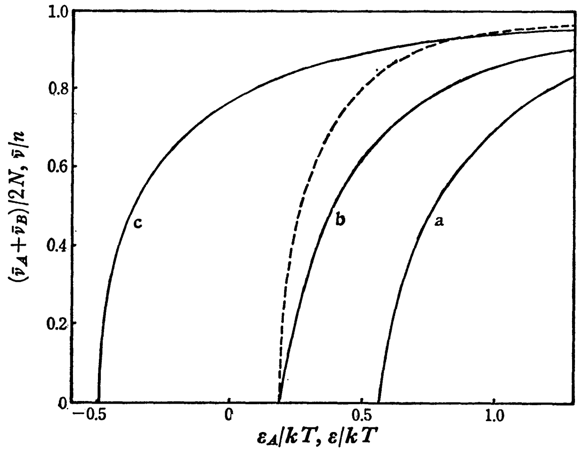

Fig. 3. The sum $(\bar{\nu}_A+\bar{\nu}_B)/2N$ is plotted against ε_A/kT: (a) $\varepsilon_B/kT = -0.223$, (b) 0.182, (c) 0.916. $\bar{\nu}/n$ of Eq. (1) is shown by the dotted line.

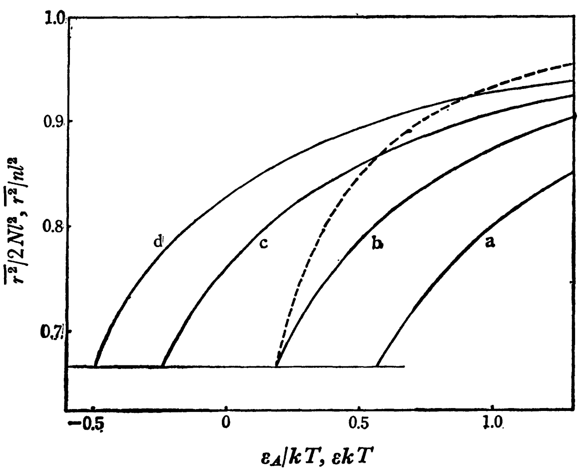

Fig. 4. The ratio $\overline{r^2}/2Nl^2$ of the copolymeric chain is plotted against ε_A/kT: (a) $\varepsilon_B/kT = -0.223$, (b) 0.182, (c) 0.588, (d) 0.916. The dotted line indicates $\overline{r^2}/nl^2$ given by Eq. (2).

Finally we evaluate the end-to-end distance of the copolymeric chain $(\text{-A-B-})_N$ in the limit $N \gg 1$. The value of $\overline{r^2}$ calculated from Eq. (51) by a similar procedure is given as a function of ε_A/kT at the constant value of ε_B/kT in Fig. 4. The effect of adsorption energies on the end-to-end distance is remarkably large in comparison to those on the average number of adsorbed segments. This seems in part due to the fact that the symmetric random walk model which allows any step to retrace the previous one on a simple cubic lattice shortens specifically the end-to-end distance of the alternating copolymeric chain at the small value of η_B.

Average properties of copolymeric chains of other kinds will be discussed elsewhere.

Appendix

The square matrix of order $a+b$, **M**, of Eq. (11) is related to a diagonal matrix by

$$\mathbf{M} = \mathbf{T}\Lambda\mathbf{T}^{-1}, \tag{A1}$$

where

$$\Lambda = \begin{pmatrix} \lambda_1 & 0 \cdots 0 \\ 0 & \lambda_2 \cdots 0 \\ \cdots & \cdots \\ 0 & 0 \cdots \lambda_{a+b} \end{pmatrix}, \tag{A2}$$

λ_i being the eigenvalues of **M**. The eigenvectors of **M** can be obtained by solving simultaneous equations:

$$\begin{aligned} &(\eta_A F_{a+b}-\lambda_j)t_{1,j} + \eta_A F_1 t_{2,j} + \cdots + \eta_B F_{a+b-1} t_{a+b,j} = 0 \\ &\eta_A F_{a+b-1} t_{1,j} + (\eta_A F_{a+b}-\lambda_j)t_{2,j} + \cdots + \eta_B F_{a+b-2} t_{a+b,j} = 0 \\ &\cdots\cdots \\ &\eta_A F_1 t_{1,j} + \eta_A F_2 t_{2,j} + \cdots + (\eta_B F_{a+b}-\lambda_j)t_{a+b,j} = 0, \\ &\qquad j = 1, 2, \cdots, a+b. \end{aligned} \tag{A3}$$

For notational simplicity it may be taken that

$$t_{1,j} = 1, \quad j = 1, 2, \cdots, a+b. \tag{A4}$$

The other vector elements are obtained from the $a+b-1$ equations out of Eq. (A3); we have

$$t_{i,j} = \Delta_i(\lambda_j)/\Delta_1(\lambda_j), \quad i = 2, 3, \cdots, a+b. \quad \text{and} \quad j = 1, 2, \cdots, a+b, \tag{A5}$$

where

$$\Delta_1(\lambda_j) = \begin{vmatrix} \eta_A F_1 & \eta_A F_2 \cdots \eta_B F_{a+b-1} \\ \eta_A F_{a+b} - \lambda_j & \eta_A F_1 \cdots \eta_B F_{a+b-2} \\ \cdots & \cdots \\ \eta_A F_3 & \eta_A F_4 \cdots \eta_B F_1 \end{vmatrix} \tag{A6}$$

and $\Delta_i\ (\lambda_j)$ is the determinant obtained on replacing the respective elements in the $(i-1)$-th column of $\Delta_1(\lambda_j)$ by

$$-(\eta_A F_{a+b}-\lambda_j),\ -\eta_A F_{a+b-1},\ \cdots,\ -\eta_A F_2.$$

The transformation matrix **T** consists of the eigenvectors obtained above:

$$\mathbf{T} = (t_{i,j}) \tag{A7}$$

$$\mathbf{T}^{-1} = (t_{i,j}{}^{-1}) \tag{A8}$$

where

$$t_{i,j}{}^{-1} = \text{cofactor}\ (t_{j,i})/|\mathbf{T}|.$$

By use of Eq. (A1) with Eqs. (A2), (A7), and (A8), it follows that

$$\begin{aligned} \boldsymbol{\alpha}\mathbf{M}(\mathbf{I}-\mathbf{M})^{-1}\boldsymbol{\beta}^+ &= \boldsymbol{\alpha}\mathbf{T}\Lambda(\mathbf{I}-\Lambda)^{-1}\mathbf{T}^{-1}\boldsymbol{\beta}^+ \\ &= \sum_{j=1}^{a+b} t_{1,j}\lambda_j(1-\lambda_j)^{-1}t_{j,a+b}{}^{-1} \\ &= \Delta_1(1)/D(1), \end{aligned} \tag{A9}$$

where

$$D(1) = (-1)^{a+b}|\mathbf{M}-\mathbf{I}| \tag{A10}$$

and $\Delta_1(1)$ is Eq. (A6) where λ_j is equated to unity.