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Conformation of Adsorbed Polymeric Chain. IV

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In order to develop further the theoretical treatment of a polymeric chain adsorbed at an interface, a random walk model, in which each step has the same probability except that no step can retrace the preceding one on a simple cubic lattice, has been used. The average number of adsorbed segments $\bar{\nu}$, the average number of trains $\bar{m}$, and the mean square end-to-end distance $\overline{r^2}$ are calculated as functions of the adsorption energy of segment ε and the number of segments n when n is infinitely large. The average numbers of segments in a train and a loop, $\bar{k}'$ and $\bar{k}$, are also calculated. Through the increment in the value of critical adsorption energy ε_c, prohibition of immediate reversal for the random walk fairly influences the average properties of adsorbed polymeric chain. The decrease in $\bar{m}$ and the increase in $\bar{k}'$ with ε/kT at its large values are remarkable in comparison with those of the symmetric random walk, which may be accounted for by the diminution of the chance of making loops. It is shown that $\overline{r^2}$ is equivalent to the mean square two-dimensional end-to-end distance of a restricted random walk without immediate reversals on a simple cubic lattice at ε_c/kT and approaches that on a simple square lattice in the limit $\varepsilon/kT\rightarrow\infty$.

In the previous papers[1-3] the adsorption of polymeric chains at an interface was analyzed by making use of the symmetric random walk in which the probability of the next step at any stage is not influenced by that of the preceding one. McCrackin[4] and Bluestone and Cronan[5] have estimated numerically average

1) K. Motomura and R. Matuura, *Mem. Fac. Sci., Kyushu Univ.*, **C6**, 97 (1968).
2) K. Motomura and R. Matuura, *J. Chem. Phys.*, **50**, 1281 (1969); *ibid.*, **51**, 4681 (1969).
3) K. Motomura, K. Sekita, and R. Matuura, This Bulletin, **44**, 1243 (1971).
4) F. L. McCrackin, *J. Chem. Phys.*, **47**, 1980 (1970).
5) S. Bluestone and C. L. Cronan, *J. Phys. Chem.*, **70**, 306 (1966).

properties of the adsorbed polymeric chain having a relatively small number of segments by performing a Monte Carlo calculation to treat the effect of the self-exclusion. Rubin[6] has derived the expressions for the average number of adsorbed segments per polymeric chain and the mean distance of the end of a polymeric chain from the interface by means of a random walk model, when the number of segments of the polymeric chain is much larger than unity. In his model the direction of each step is assumed to be at right angles to the direction of the preceding step. A better knowledge about the behavior of a polymer molecule at an interface in an extreme dilution may be obtained by taking a correlation between steps of a random walker into consideration.

In this paper we wish to consider a restricted random walk in which each step has the same probability except that any step is forbidden to retrace its previous one on the simple cubic lattice and to know how the correlation between neighboring steps affects the conformation of the adsorbed polymeric chain.

Theoretical

1. Probability of an Adsorbed Polymeric Chain. As we are concerned only with the behavior of a polymeric chain in an adsorbed state, we assume that both the end segments of the polymeric chain are adsorbed on an interface; the adsorbed polymeric chain consists of an alternate sequence of trains and loops. Denoting the probabilities of loop and train by $f_{kj}(x_j, y_j)$ and $g_{k'j}(x'_j, y'_j)$, the probability of the adsorbed polymeric chain composed of $n+1$ segments is given by

$$p_n(x,y,t,\eta) = \sum_m \sum_{\mathbf{k}} \sum_{\mathbf{x},\mathbf{y}} \prod_{j=1}^{m} [t\eta^{k'_j+1} g_{k'_j}(x'_j,y'_j)] \prod_{j=1}^{m-1} f_{k_j}(x_j,y_j) \tag{1}$$

where

$$\eta = \exp(\varepsilon/kT). \tag{2}$$

Here $-\varepsilon$ is the energy gain per segment associated with the adsorption and t is the parameter to evaluate the number of trains. A set of $\mathbf{k}$, $\mathbf{x}$, and $\mathbf{y}$ means a microscopic state satisfying

$$n = \sum_j k_j + \sum_j k'_j, \quad x = \sum_j x_j + \sum_j x'_j,$$
$$\text{and} \quad y = \sum_j y_j + \sum_j y'_j$$

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

$$P_n(\theta,\phi,t,\eta) = \sum_{x,y} p_n(x,y,t,\eta) \exp(ix\theta + iy\phi)$$
$$P(\theta,\phi,t,\eta;w) = \sum_{n=1}^{\infty} P_n(\theta,\phi,t,\eta) w^n \tag{3}$$

and the corresponding ones for $f_k(x, y)$ and $g_k(x, y)$, we obtain

$$P(\theta,\phi,t,\eta;w) = t\eta G(\theta,\phi;\eta w)/[1-t\eta G(\theta,\phi;\eta w)F(\theta,\phi;w)]. \tag{4}$$

It is now necessary to calculate $F(\theta, \phi; w)$ and $G(\theta, \phi; \eta w)$. Let us define the probability of the restricted random walk which arrives at a point $(x, y, 0)$ from the origin after n steps are $q_n(x, y)$ and that in which the direction of the final step is $-z$ as $q_n^{-z}(x, y)$. There exists a relation between $q_n(x, y)$, $q_n^{-z}(x, y)$, and $f_n(x, y)$:

$$q_n^{-z}(x,y) = \sum_{x',y'} \sum_{l=3}^{n} [q_{n-l}(x-x', y-y') - q_{n-l}^{-z}(x-x', y-y')] f_l(x', y'). \tag{5}$$

Introducing the generating functions analogous to Eq. (3), the above equation becomes

$$F(\theta,\phi;w) = [Q(\theta,\phi;w) - 1/6]/[Q(\theta,\phi;w) - Q^{-z}(\theta,\phi;w)] - 1. \tag{6}$$

With the help of the generating function of the random walk with no immediate reversals on the simple cubic lattice derived by Domb and Fisher[7]

$$Q(\theta,\phi,\psi;w) = [15-(\cos\theta+\cos\phi+\cos\psi)w]/[15-6(\cos\theta+\cos\phi+\cos\psi)w + 3w^2], \tag{7}$$

$Q(\theta, \phi; w)$ is given by the expression

$$Q(\theta,\phi;w) = (1/2\pi)\int_{-\pi}^{\pi} Q(\theta,\phi,\psi;w)d\psi = (1/6)\{(25-w^2)[(5-2cw+w^2)^2 - 4w^2]^{-1/2} + 1\}, \tag{8}$$

where

$$c = \cos\theta + \cos\phi. \tag{9}$$

By a similar procedure, it follows that

$$Q(\theta,\phi;w) - Q^{-z}(\theta,\phi;w) = (5/12)\{5+2cw-w^2+[(5-2cw+w^2)^2-4w^2]^{1/2}\}[(5-2cw+w^2)^2-4w^2]^{-1/2}. \tag{10}$$

Substituting Eqs. (8) and (10) into Eq. (6), we obtain

$$F(\theta,\phi;w) = (1/5)\{25-10cw+3w^2-5[(5-2cw+w^2)^2 - 4w^2]^{1/2}\}/\{5+2cw-w^2+[(5-2cw+w^2)^2 - 4w^2]^{1/2}\}. \tag{11}$$

On the other hand, $g_n(x, y)$ is the probability of a two-dimensional random walk in which the probability of each step is equal to 1/5 except that no step retraces the previous one on a simple square lattice and is correlated with the probability of the corresponding symmetric random walk $u_n(x, y)$:

$$u_{n+2}(x,y) = (1/9)u_n(x,y) + (1/12)\sum_{l=1}^{n} \sum_{x',y'} (5/6)^l g_l(x',y') \times u_{n-l}(x-x', y-y') + (5/6)^{n+2} g_{n+2}(x,y). \tag{12}$$

By applying the generating function

$$U(\theta,\phi;w) = \sum_{n=0}^{\infty} (6/5)^n U_n(\theta,\phi) w^n = \sum_{n=0}^{\infty} (6/5)^n w^n [\sum_{x,y} u_n(x,y) \exp(ix\theta+iy\phi)] = 5/(5-2cw) \tag{13}$$

and the generating function of $g_n(x, y)$ to Eq. (12), we can obtain an explicit expression for $G(\theta,\phi;w)$:

$$G(\theta,\phi;w) = 2(5c-2w)w/(25-10cw+3w^2). \tag{14}$$

Substituting Eqs. (11) and (14) into Eq. (4) and rearranging the resulting equation, we obtain the general solution for the adsorbed polymeric chain

6) R. J. Rubin, *J. Res. Nat. Bur. Stand.*, **B69**, 301 (1965).

7) C. Domb and M. D. Fisher, *Proc. Cambridge Phil. Soc.*, **54**, 48 (1958).

$$P(\theta, \phi, t, \eta; w) = N(c, t, \eta, w)/D(c, t, \eta, w) \quad (15)$$

where

$$N(c, t, \eta, w) = 10t\eta^2 w(5c-2\eta w)\{5+2cw-w^2 + [(5-2cw+w^2)^2-4w^2]^{1/2}\} \quad (16)$$

and

$$D(c, t, \eta, w) = 5(25-10c\eta w+3\eta^2 w^2)\{5+2cw-w^2 + [(5-2cw+w^2)^2-4w^2]^{1/2}\} - 2t\eta^2 w(5c-2\eta w) \times\{25-10cw+3w^2-5[(5-2cw+w^2)^2-4w^2]^{1/2}\}. \quad (17)$$

2. Evaluation of Average Properties. It is now possible to evaluate average properties of the adsorbed polymeric chain based on the model in which the random walk has no immediate reversals. The average number of adsorbed segments per polymeric chain $\bar{\nu}$ can be obtained by noting Eqs. (1) and (3):

$$\bar{\nu} = \eta[dP_n(2, 1, \eta)/d\eta]/P_n(2, 1, \eta) \quad (18)$$

where $P_n(c, t, \eta)$ is used instead of $P_n(\theta, \phi, t, \eta)$. In a similar manner we have for the average number of trains per polymeric chain the following equation:

$$\bar{m} = [\partial P_n(2, t, \eta)/\partial t]_{t=1}/P_n(2, 1, \eta). \quad (19)$$

It also follows that

$$\overline{r^2} = a^2[c\partial P_n(c, 1, \eta)/\partial c]_{c=2}/P_n(2, 1, \eta), \quad (20)$$

where $\overline{r^2}$ is the mean square end-to-end distance and a is the distance between neighboring segments.

Explicit expressions for $P_n(c, t, \eta)$ and its derivatives are immediately derived from Eq. (15). According to Cauchy's residue theorem, $P_n(2, 1, \eta)$ is found to be

$$P_n(2, 1, \eta) = (1/2\pi i)\oint_{C_0}(1/w^{n+1})P(2, 1, \eta; w)dw = (1/2\pi i)\oint_{C_0}(1/w^{n+1})[N(2, 1, \eta, w)/D(2, 1, \eta, w)]dw, \quad (21)$$

where C_0 includes only the pole at $w=0$. Denoting the smallest root of

$$0 = D(2, 1, \eta, w) = (5-\eta w)[5(5-3\eta w)\{5+4w-w^2+[(5-4w+w^2)^2 -4w^2]^{1/2}\}-4\eta^2 w\{25-20w+3w^2-5[(5-4w+w^2)^2 -4w^2]^{1/2}\}] \quad (22)$$

by w_1, which coincides with the branch-point $w=1$ at the value $\eta=5/4$ which corresponds to the critical value of the adsorption energy, the integral of Eq. (21) may be approximated by the residue at $w=w_1$ when n is infinitely large. Thus we obtain

$$P_n(2, 1, \eta) = -\frac{1}{w_1^{n+1}}\frac{N(2, 1, \eta, w_1)}{\partial D(2, 1, \eta, w_1)/\partial w} \quad (23)$$

where

$$\partial D(2, 1, \eta, w_1)/\partial w = -(5-\eta w_1)[(5-4w_1+w_1^2)^2-4w_1^2]^{-1/2} \times\{[25(4\eta^2+3\eta-4)-10(16\eta^2-12\eta-5)w_1+9\eta(4\eta-5)w_1^2] \times[(5-4w_1+w_1^2)^2-4w_1^2]^{1/2}-5\eta(4\eta-3)[(5-4w_1+w_1^2)^2 -4w_1^2]+10[5+\eta(4\eta-3)w_1](10-11w_1+6w_1^2-w_1^3)\}. \quad (24)$$

The derivative of $P_n(2, 1, \eta)$ with respect to η in the numerator of Eq. (18) is evaluated similarly. If terms which are not proportional to n are dropped, we have

$$\frac{dP_n(2, 1, \eta)}{d\eta} = \frac{1}{2\pi i}\oint_{C_0}\frac{1}{w^{n+1}}\frac{\partial P(2, 1, \eta; w)}{\partial \eta}dw = -\frac{n}{w_1^{n+2}}\frac{N(2, 1, \eta, w_1)dD(2, 1, \eta, w_1)/d\eta}{[\partial D(2, 1, \eta, w_1)/\partial w]^2} \quad (25)$$

where

$$dD(2, 1, \eta, w_1)/d\eta = -(5-\eta w_1)w_1\{25(8\eta+3)-20(8\eta-3)w_1 + 3(8\eta-5)w_1^2-5(8\eta-3)[(5-4w_1+w_1^2)^2-4w_1^2]^{1/2}\}. \quad (26)$$

The same procedure gives the expressions for $[\partial P_n(2, t, \eta)/\partial t]_{t=1}$ and $[\partial P_n(c, 1, \eta)/\partial c]_{c=2}$ in the limit $n \gg 1$. The results are

$$\left\{\frac{\partial P_n(2, t, \eta)}{\partial t}\right\}_{t=1} = -\frac{n}{w_1^{n+2}}\frac{N(2, 1, \eta, w_1)\partial D(2, 1, \eta, w_1)/\partial t}{[\partial D(2, 1, \eta, w_1)/\partial w]^2} \quad (27)$$

and

$$\left\{\frac{\partial P_n(c, 1, \eta)}{\partial c}\right\}_{c=2} = -\frac{n}{w_1^{n+2}}\frac{N(2, 1, \eta, w_1)\partial D(2, 1, \eta, w_1)/\partial c}{[\partial D(2, 1, \eta, w_1)/\partial w]^2} \quad (28)$$

where

$$\partial D(2, 1, \eta, w_1)/\partial t = -4\eta^2 w_1(5-\eta w_1)\{25-20w_1+3w_1^2 - 5[(5-4w_1+w_1^2)^2-4w_1^2]^{1/2}\} \quad (29)$$

and

$$\partial D(2, 1, \eta, w_1)/\partial c = -10w_1[(5-4w_1+w_1^2)^2-4w_1^2]^{-1/2} \times\{[25(\eta^2+\eta-1)-40\eta(\eta-1)w_1+\eta(4\eta^2-5)w_1^2] \times[(5-4w_1+w_1^2)^2-4w_1^2]^{1/2}-5\eta(\eta-1)[(5-4w_1+w_1^2)^2 -4w_1^2]+[25+20\eta(\eta-1)w_1-\eta^2(4\eta-3)w_1^2] \times(5-4w_1+w_1^2)\}. \quad (30)$$

We can now calculate the average properties of the polymeric chain adsorbed on an interface in the limit $n \gg 1$. Combining Eqs. (23) and (25) with Eq. (18), the expression for the average number of adsorbed segments per polymeric chain is obtained:

$$\bar{\nu} = n\frac{\eta}{w_1}\frac{dD(2, 1, \eta, w_1)/d\eta}{\partial D(2, 1, \eta, w_1)/\partial w}. \quad (31)$$

For the average number of trains per polymeric chain and the mean square end-to-end distance, we obtain

$$\bar{m} = n\frac{1}{w_1}\frac{\partial D(2, 1, \eta, w_1)/\partial t}{\partial D(2, 1, \eta, w_1)/\partial w} \quad (32)$$

and

$$\overline{r^2} = a^2 n\frac{2}{w_1}\frac{\partial D(2, 1, \eta, w_1)/\partial c}{\partial D(2, 1, \eta, w_1)/\partial w}. \quad (33)$$

The derivatives on the right-hand side of the above formulas are already given explicitly in Eqs. (24), (26), (29), and (30).

Discussion

The average properties of the adsorbed polymeric chain based on the model in which no step of a random walk can retrace the previous one on the simple cubic lattice have been evaluated as functions of the adsorption energy and the chain length for infinite chain length. Computing w_1 satisfying Eq. (22) and substituting this value into Eq. (31) with Eqs. (24) and (26), we obtain

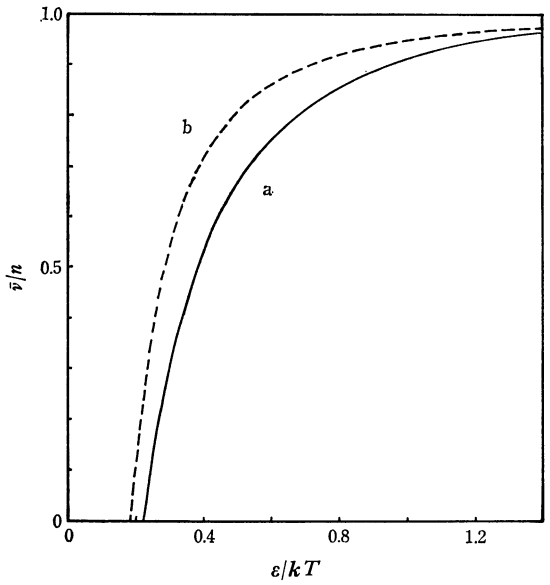

Fig. 1. The ratio of $\bar{\nu}$ to n is plotted against ε/kT in the limit $n \gg 1$: (a) restricted random walk without immediate reversal, (b) symmetric random walk.[1]

the average number of adsorbed segments per polymeric chain. This is graphically shown in Fig. 1 where the ratio of $\bar{\nu}$ to n is plotted against the adsorption energy ε measured in unit kT. For comparison the ratio $\bar{\nu}/n$ for the symmetric random walk model discussed in Part I is also given in Fig. 1. We see that the prohibition of immediate reversals for the random walk fairly influences the amount of segments adsorbed on the interface. The resulting enhancement of critical adsorption energy and diminution of the average number of adsorbed segments can be explained by the difference between decreases in statistical weights of the two-dimensional and three-dimensional random walks, due to the restriction for the step to retrace the preceding step.

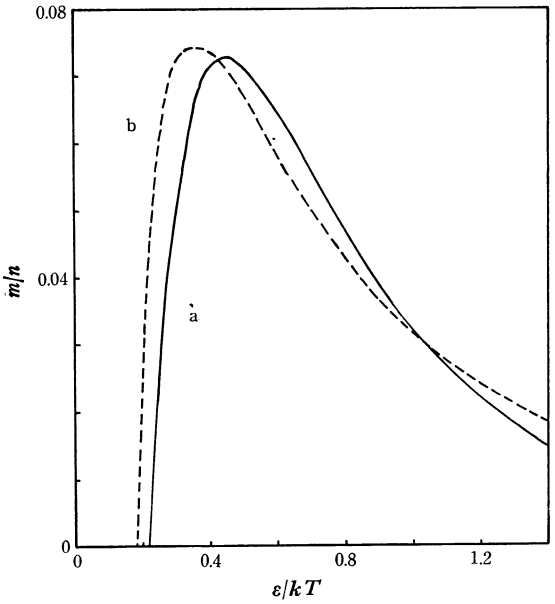

Fig. 2. The ratio $\bar{m}/n$ is plotted against ε/kT: (a) restricted random walk without immediate reversal, (b) symmetric random walk.[2]

The average number of trains per polymeric chain $\bar{m}$ is calculated in the same way. The plot of ratio $\bar{m}/n$ against ε/kT is illustrated in Fig. 2 with the corresponding one of the symmetric random walk. Shapes of the curves, $\bar{m}/n$ *versus* ε/kT, seem to be alike as a whole, while the decrease of the value of $\bar{m}/n$ of the restricted random walk without immediate reversals at large values of η is rather steep. The smaller average number of trains (the smaller average number of loops) for large values of η may be accounted for by the diminution of the chance of making loops. The smallest number of segments in the loop for the restricted random walk without immediate reversals is $\bar{k}=2$ instead of $\bar{k}=1$ for the symmetric random walk, where $\bar{k}$ is the average number of segments in the loop and is given by

$$\bar{k} = (n-\bar{\nu})/(\bar{m}-1). \tag{34}$$

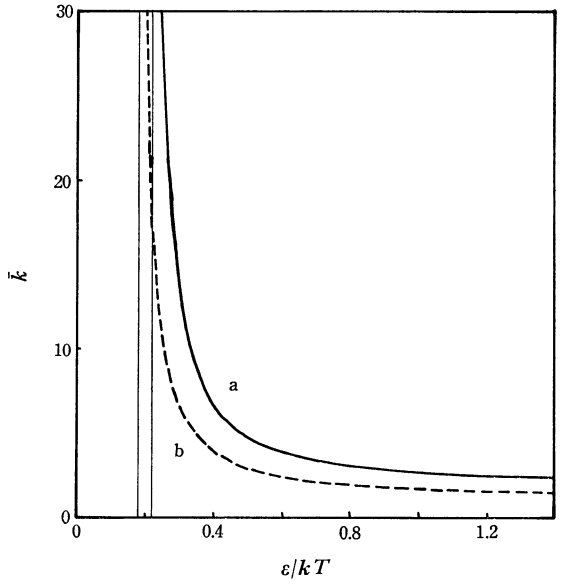

Fig. 3. $\bar{k}$ is plotted against ε/kT: (a) restricted random walk without immediate reversal (b) symmetric random walk.[2]

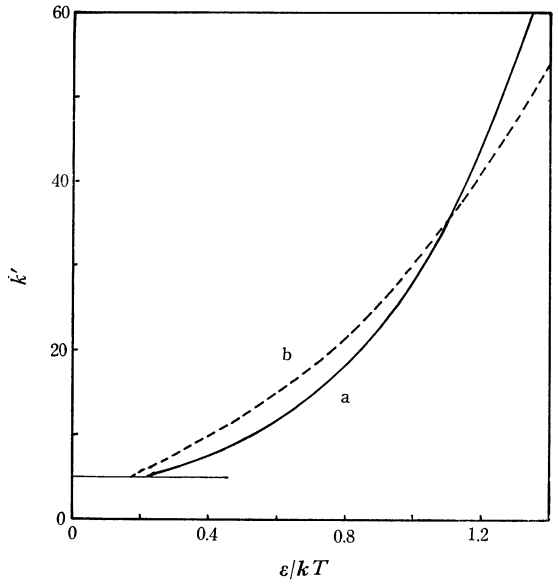

Fig. 4. $\bar{k}'$ is plotted against ε/kT: (a) restricted random walk without immediate reversal, (b) symmetric random walk.[2]

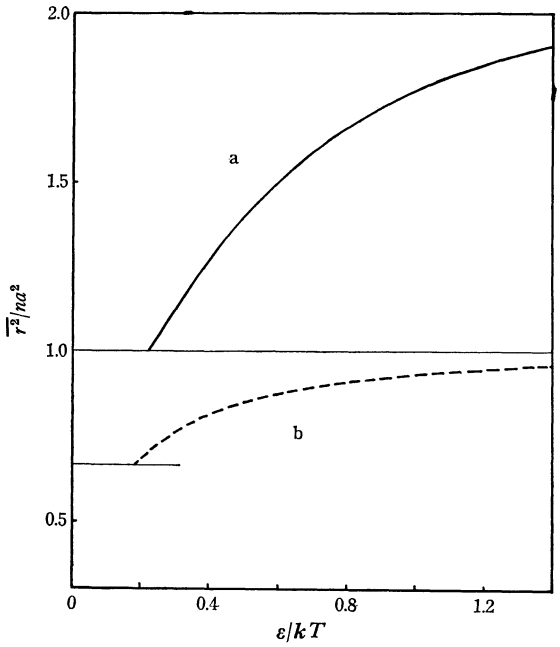

Fig. 5. The ratio $\overline{r^2}/na^2$ is plotted against ε/kT: (a) restricted random walk without immediate reversal, (b) symmetric random walk.[1]

The value of $\bar{k}$ computed is plotted against ε/kT in Fig. 3. We might expect that the average number of segments in the train $\bar{k}'$ increases rapidly with the adsorption energy. The value of $\bar{k}'$ is easily evaluated by the relation

$$\bar{k}' = \bar{\nu}/\bar{m}, \tag{35}$$

which is depicted against ε/kT in Fig. 4. Increase of $\bar{k}'$ *versus* ε/kT curve is remarkable compared with that obtained previously.[2]

Finally the mean square end-to-end distance in the limit $n \gg 1$ is calculated from Eq. (33) with Eqs. (24) and (30) by a similar procedure. The result is illustrated in Fig. 5 where the ratio $\overline{r^2}/na^2$ is plotted against ε/kT. It is clear that the polymeric chain of the restricted random walk without immediate reversals has a fairly extended conformation in comparison with that of the symmetric random walk in spite of the small value of the average number of adsorbed segments per polymeric chain. The value of $\overline{r^2}$ is na^2 at the critical adsorption energy and approaches $2na^2$ for infinite adsorption energy. According to Domb and Fisher,[7] the mean square end-to-end distance of the restricted random walk with no immediate reversals on lattices in the limit $n \gg 1$ is given by

$$(\overline{r^2})_{\mathrm{DF}} = na^2(1+\delta)/(1-\delta) \tag{36}$$

where

$$\delta = 1/(q-1), \tag{37}$$

q being the coordination number of lattice used. Equation (36) results in $(\overline{r^2})_{\mathrm{DF}} = (3/2)na^2$ for the random walk on a simple cubic lattice and $(\overline{r^2})_{\mathrm{DF}} = 2na^2$ on a simple square lattice. It is easily recognized that the mean square end-to-end distance of the adsorbed polymeric chain is equivalent to that of the restricted random walk without immediate reversals, of which both ends are located on xy plane through $z=0$ in the simple cubic lattice, at the critical adsorption energy and approaches that of the two-dimensional one on the simple square lattice for infinite adsorption energy.