JOURNAL OF RESEARCH of the National Bureau of Standards — B. Mathematics and Mathematical Physics
Vol. 70B, No. 4, October–December 1966

A Random Walk Model of Chain Polymer Adsorption at a Surface

III. Mean Square End-to-End Distance

Robert J. Rubin

Institute for Basic Standards, National Bureau of Standards, Washington, D.C. 20234

(September 13, 1966)

A 6-choice simple cubic lattice model of adsorption of an isolated polymer chain at a solution surface is investigated. The mean square components $\langle x^2(N)\rangle$ and $\langle z^2(N)\rangle$ of the end-to-end distance are computed as a function of the adsorption energy per monomer unit in the limit of a very long polymer chain. In the calculation, one end of the polymer chain consisting of N monomer units is constrained to lie in the surface; and $\langle x^2(N)\rangle$ and $\langle z^2(N)\rangle$ are, respectively, the mean square displacement of the free end of the chain parallel to the solution surface in one of the lattice directions and normal to the solution surface. The limiting value of $\langle x^2(N)\rangle/N$ as $N\to\infty$ is a continuous function of θ, the dimensionless adsorption energy per monomer unit, and is equal to 1/3 for $\theta \leq \ln(6/5)$ and $(1/2)\ [1+(1/4)\ (e^\theta-1)^{-1}]^{-1/2}$ for $\theta \geq \ln(6/5)$. The limiting value of $\langle z^2(N)\rangle/N$ as $N\to\infty$ is a discontinuous function of θ and is equal to 2/3 for $\theta < \ln(6/5)$, 1/3 for $\theta = \ln(6/5)$, and 0 for $\theta > \ln(6/5)$. The relation of these results to earlier investigations and the generalization of these results to other cubic lattice models is discussed.

Key Words: Adsorption, chain polymer, critical energy, generating function, lattice model, partition function, random walk.

1. Introduction

In this paper we extend the investigation of a random walk lattice model of polymer chain adsorption at a solution surface [1, 2] [1] by computing the components of the mean square end-to-end distance in an adsorbed polymer chain. The random walk lattice model used is a generalization of the models introduced by Silberberg [3] and DiMarzio and McCrackin [4]. The physical properties of the model reflect the competition between (1) the energy gained by the polymer chain occupying as many surface sites as possible, and (2) the configurational entropy lost by the polymer chain remaining near the confining solution surface. In I and II the average fraction of monomer units which lie in the solution surface $\nu(\theta, N)$ was computed as a function of the reduced energy of adsorption per monomer unit $\theta = \epsilon/kT$. In the calculation one end of the polymer chain was constrained to lie in the surface, and the self-excluded volume of the polymer chain was neglected. In the limit in which the number of monomer units N is large, it was determined that there is a critical value of the reduced energy of adsorption per monomer unit θ_c such that for $\theta > \theta_c$, the molecule exists in an adsorbed state. For example, $\lim_{N\to\infty} \nu(\theta, N)$, the limiting average fraction of monomer units lying in the surface, is a positive constant independent of N indicating that a finite fraction of all monomer units lie in the solution surface. For $\theta < \theta_c$ this limiting fraction is zero.

The purpose of this paper is to calculate $\langle x^2(N)\rangle$, $\langle y^2(N)\rangle$, and $\langle z^2(N)\rangle$, the components of the mean square displacement of the free end of the polymer chain as a function of θ for $N \gg 1$ for the 6-choice simple cubic lattice model. It was shown in I that the mean distance of the free end of the chain from the solution surface $\langle z(N)\rangle$ has the following discontinuous form for the 6-choice

[1] Figures in brackets indicate the literature references at the end of this paper.

simple cubic lattice model

$$\lim_{N\to\infty} \langle z(N)\rangle/N^{1/2} = \begin{cases} (\pi/6)^{1/2}, & 0 \leqslant \theta < \ln(6/5) \\ (2/3\pi)^{1/2}, & \theta = \ln(6/5) \\ 0, & \theta > \ln(6/5). \end{cases}$$

It is shown in section 4 that there is a corresponding discontinuity in $\lim_{N\to\infty} \langle z^2(N)\rangle/N$ whereas for the other components, $\lim_{N\to\infty} \langle x^2(N)\rangle/N = \lim_{N\to\infty} \langle y^2(N)\rangle/N$ is a continuous function of θ. The recurrence equations for the probability distribution of the free end of the polymer chain are formulated in section 2 and are solved formally in section 3. Explicit expressions for the second moments are evaluated in the limit $N\to\infty$ in section 4. The results are summarized in section 5 and the qualitative behavior for the 2-choice and 4-choice simple cubic models is deduced.

2. Recurrence Equations for the Probability Distribution of the Free End of the Polymer Chain

We consider a simple-cubic lattice model of the solution-surface system in which the solution surface corresponds to the x-y lattice plane through the point $z=0$. Successive lattice planes through $z=1, 2, \ldots$ represent the solution phase of the system. Polymer chain configurations in the solution correspond to paths generated in a random walk on the lattice between nearest-neighbor sites. The physical presence of the surface is introduced by considering only random walks in the lattice planes through $z=0, 1, 2, \ldots$ which never enter the lattice plane through $z=-1$. In the absence of a solution surface, all random walk configurations of a given length are equally likely. However, we are primarily interested in the influence of an adsorbing solution surface on the average conformation of a polymer chain. In our lattice model, all random walk paths of N steps with n steps lying in the surface layer $z=0$ have the same *a priori* probability. Relative to a random walk configuration of N steps with $n-1$ steps lying in the surface, the *a priori* probability of a walk with n steps in the surface layer is greater by the factor e^{θ} where $\theta=\epsilon/kT$ and ϵ is the adsorption energy of a monomer unit.

For convenience, we use a random walk terminology. Consider the problem of computing, for a random walk originating in the surface layer, the unnormalized or relative probability $P(x, y, z; N+1)$ that at the $N+1$th step the random walker is located at lattice point (x, y, z), where $z \geqslant 0$. The relative probability $P(x, y, z; N+1)$ is related to the relative probabilities at the Nth step by the relations

$$P(x, y, z; N+1) = \frac{1}{6}\{E_x^+ + E_x^- + E_y^+ + E_y^- + E_z^+ + E_z^-\}P(x, y, z; N), \qquad z \geqslant 1 \tag{1}$$

and

$$P(x, y, 0; N+1) = \frac{1}{6}e^{\theta}\{E_x^+ + E_x^- + E_y^+ + E_y^- + E_z^+\}P(x, y, 0; N) \tag{2}$$

where $E_x^{\pm}$ are operators defined by the relation

$$E_x^{\pm}P(x, y, z; N) = P(x\pm 1, y, z; N). \tag{3}$$

The operators $E_y^{\pm}$ and $E_z^{\pm}$ have similar definitions. Equation (1) describes the relation between the relative probability of being at lattice site x, y, z with $z \geqslant 1$ at the $N+1$th step and the relative probabilities of being at neighboring sites at the Nth step. The factor e^{θ} in eq (2) accounts for the fact that relative to those configurations where $z \geqslant 1$ at the $N+1$th step, the relative probabilities for those configurations where $z=0$ at the $N+1$th step are greater by the factor e^{θ}. The absence of E_z^- in eq (2) is related to the fact that the random walker enters the $z=0$ layer only from one direction. Equations (1) and (2) will be solved in section 3 for the initial condition

$$P(x, y, z; 0)=\begin{cases} e^{\theta}, \ x=0, \ y=0, \ z=0 \\ \\ 0, \text{ for all other lattice points.} \end{cases} \tag{4}$$

From the solution, the mean square end-to-end distance after N steps can be computed from the expression

$$R_N^2=\langle x^2(N)\rangle+\langle y^2(N)\rangle+\langle z^2(N)\rangle=\sum_{x=-\infty}^{\infty}\sum_{y=-\infty}^{\infty}\sum_{z=0}^{\infty}(x^2+y^2+z^2)P(x, y, z; N)/Q(\theta, N) \tag{5}$$

where

$$Q(\theta, N)=\sum_{x=-\infty}^{\infty}\sum_{y=-\infty}^{\infty}\sum_{z=0}^{\infty}P(x, y, z; N). \tag{6}$$

3. Solution of Recurrence Equations

The recurrence eqs (1) and (2) can be solved for the starting condition eq (4) by introducing a generating function as in I and II. It is convenient first to rewrite eq (2) as

$$[1-(1-e^{\theta})]P(x, y, 0; N+1)=(1/6)[E_x^+ + E_x^- + E_y^+ + E_y^- + E_z^+]P(x, y, 0; N). \tag{7}$$

Multiply eqs (1) and (7) for $P(x, y, z; N+1)$ by $(2\pi)^{-3/2}\exp\{ix\xi+iy\eta+iz\zeta\}$ and sum over all integer values of x and y and all $z \geqslant 0$. The result is

$$-(1-e^{-\theta})(2\pi)^{-1/2}p(\xi, \eta; 0; N+1)+G(\xi, \eta, \zeta; N+1)$$

$$=\frac{1}{3}[\cos\xi+\cos\eta+\cos\zeta]G(\xi, \eta, \zeta; N)-\frac{1}{6}e^{-i\zeta}(2\pi)^{-1/2}p(\xi, \eta; 0; N) \tag{8}$$

where

$$G(\xi, \eta, \zeta; N)=(2\pi)^{-3/2}\sum_{x=-\infty}^{\infty}\sum_{y=-\infty}^{\infty}\sum_{z=0}^{\infty}P(x, y, z; N)\exp(ix\xi+iy\eta+iz\zeta) \tag{9}$$

and

$$p(\xi, \eta; z; N)=(2\pi)^{-1}\sum_{x=-\infty}^{\infty}\sum_{y=-\infty}^{\infty}P(x, y, z; N)\exp(ix\xi+iy\eta). \tag{10}$$

Next multiply eq (8) by w^{N+1} and sum over all values of N to obtain

$$\Gamma(\xi, \eta, \zeta; w)-G(\xi, \eta, \zeta; 0)-(1-e^{-\theta})(2\pi)^{-1/2}[\rho(\xi, \eta; 0; w)-p(\xi, \eta; 0; 0)]$$

$$=\frac{1}{3}w[\cos\xi+\cos\eta+\cos\zeta]\Gamma(\xi, \eta, \zeta; w)-\frac{w}{6}e^{-i\zeta}(2\pi)^{-1/2}\rho(\xi, \eta; 0; w) \tag{11}$$

where

$$\Gamma(\xi, \eta, \zeta; w)=\sum_{N=0}^{\infty}w^N G(\xi, \eta, \zeta; N) \tag{12}$$

and

$$\rho(\xi, \eta; z; w)=\sum_{N=0}^{\infty}w^N p(\xi, \eta; z; N). \tag{13}$$

In eq (11) the quantities $G(\xi, \eta, \zeta; 0)$ and $p(\xi, \eta; 0; 0)$ are simply

$$G(\xi, \eta, \zeta; 0)=(2\pi)^{-3/2}e^{\theta} \tag{14}$$

and

$$p(\xi, \eta; 0; 0)=(2\pi)^{-1}e^{\theta}. \tag{15}$$

Substituting eq (14) and (15) in eq (11) and solving for $\Gamma(\xi, \eta, \zeta; w)$, one obtains

$$\Gamma(\xi, \eta, \zeta; w)=\frac{(2\pi)^{-3/2}+(2\pi)^{-1/2}\left[1-e^{-\theta}-\frac{1}{6}we^{-i\zeta}\right]\rho(\xi, \eta; 0; w)}{1-\frac{1}{3}w[\cos\xi+\cos\eta+\cos\zeta]}. \tag{16}$$

Equation (16) is an implicit equation for $\rho(\xi, \eta; 0; w)$ because according to the definitions of $\Gamma(\xi, \eta, \zeta; w)$, $G(\xi, \eta, \zeta; N)$, $\rho(\xi, \eta; z; w)$, and $p(\xi, \eta; z; N)$ in eqs (9), (10), (12), and (13)

$$\begin{aligned}\Gamma(\xi, \eta, \zeta; w)&=(2\pi)^{-3/2}\sum_{x=-\infty}^{\infty}\sum_{y=-\infty}^{\infty}\sum_{z=0}^{\infty}\sum_{N=0}^{\infty}P(x, y, z; N)w^{N}\exp(ix\xi+iy\eta+iz\zeta)\\&=(2\pi)^{-1/2}\sum_{z=0}^{\infty}e^{iz\zeta}\rho(\xi, \eta; z; w).\end{aligned} \tag{17}$$

The following relation for determining $\rho(\xi, \eta; 0; w)$ can be obtained by multiplying eq (16) by $(2\pi)^{-1/2}$ and integrating with respect to ζ from $-\pi$ to π

$$\rho(\xi, \eta; 0; w)=(2\pi)^{-1}I_0(\xi, \eta; w)+\left[(1-e^{-\theta})I_0(\xi, \eta; w)-\frac{1}{6}wI_{-1}(\xi, \eta; w)\right]\rho(\xi, \eta; 0; w) \tag{18}$$

where

$$\begin{aligned}I_k(\xi, \eta; w)&=(2\pi)^{-1}\int_{-\pi}^{\pi}\frac{e^{ik\zeta}d\zeta}{1-w(\cos\xi+\cos\eta+\cos\zeta)/3}\\&=\left[1-w(\cos\xi+\cos\eta)/3\right]^{-1}\left[1-\left(\frac{w/3}{1-w(\cos\xi+\cos\eta)/3}\right)^{2}\right]^{-1/2}\\&\quad\times\left\{\frac{1-\left[1-\left(\frac{w/3}{1-w(\cos\xi+\cos\eta)/3}\right)^{2}\right]^{1/2}}{\frac{w/3}{1-w(\cos\xi+\cos\eta)/3}}\right\}^{|k|}.\end{aligned} \tag{19}$$

Solving eq (18) for $\rho(\xi, \eta; 0; w)$ and substituting the result in eq (16), we obtain an explicit solution of the recurrence eqs (1) and (2) for the initial condition (4)

$$\Gamma(\xi, \eta, \zeta; w)=\frac{(2\pi)^{-3/2}}{1-w(\cos \xi+\cos \eta+\cos \zeta)/3}\left\{\frac{1+(w/6)\,[I_1(\xi, \eta; w)-e^{-i\zeta}I_0(\xi, \eta; w)]}{1+(w/6)I_1(\xi, \eta; w)-(1-e^{-\theta})I_0(\xi, \eta; w)}\right\}. \tag{20}$$

The mean square end-to-end distance (5) can be expressed in terms of the generating function $\Gamma(\xi, \eta, \zeta; w)$. First note that the normalizing sum $Q(\theta, N)$, defined in eq (6), is proportional to the coefficient of w^N in the expansion of $\Gamma(0, 0, 0; w)$ [see eq (17)]

$$\Gamma(0, 0, 0; w)=(2\pi)^{-3/2}\sum_{N=0}^{\infty} w^N \sum_{x=-\infty}^{\infty}\sum_{y=-\infty}^{\infty}\sum_{z=0}^{\infty} P(x, y, z; N)=(2\pi)^{-3/2}\sum_{N=0} w^N Q(\theta, N) \tag{21}$$

Using Cauchy's formula and eq (20), we obtain the following explicit expression for $Q(\theta, N)$

$$Q(\theta, N)=\frac{(2\pi)^{3/2}}{2\pi i}\int_{C_0}\Gamma(0, 0, 0; w)\frac{dw}{w^{N+1}}=\frac{1}{2\pi i}\int_{C_0}\frac{1+[(1-w/3)/(1-w)]^{1/2}}{[(1-w)(1-w/3)]^{1/2}-1-(2w/3)+2e^{-\theta}}\frac{dw}{w^{N+1}}, \tag{22}$$

where C_0 is a counterclockwise contour of integration around $w=0$. It also follows from eq (17) and the symmetry in the x and y coordinates that the numerator in eq (5) is proportional to the coefficient of w^N in

$$-\left[2\frac{\partial^2}{\partial \xi^2}+\frac{\partial^2}{\partial \zeta^2}\right]\Gamma(\xi, 0, \zeta; w)\bigg|_{\xi=0,\,\zeta=0}=(2\pi)^{-3/2}\sum_{N=0}^{\infty} w^N \sum_{x=-\infty}^{\infty}\sum_{y=-\infty}^{\infty}\sum_{z=0}^{\infty}(x^2+y^2+z^2)\,P(x, y, z; N). \tag{23}$$

The explicit expression for the numerator in eq (5) is

$$2\mathscr{I}_x(N)+\mathscr{I}_z(N)=\frac{-(2\pi)^{3/2}}{2\pi i}\int_{C_0}\left[2\frac{\partial^2}{\partial \xi^2}+\frac{\partial^2}{\partial \zeta^2}\right]\Gamma(\xi, 0, \zeta; w)\bigg|_{\xi=0,\zeta=0}\frac{dw}{w^{N+1}}, \tag{24}$$

or

$$\mathscr{I}_x(N)=\frac{1}{2\pi i}\int_{C_0}\left\{\frac{(w/3)^2}{(1-w/3)^{1/2}(1-w)^{3/2}}\frac{1}{D(\theta, w)}+\frac{w/3}{1-w}\frac{1}{D^2(\theta, w)}\right.$$

$$\left.\times\left[1+\left(\frac{1-w}{1-w/3}\right)^{1/2}\right][1-(2w/3)+(1-w/3)^{1/2}(1-w)^{1/2}]\right\}\frac{dw}{w^{N+1}} \tag{25}$$

and

$$\mathscr{I}_z(N)=\frac{1}{2\pi i}\int_{C_0}\frac{1/3}{D(\theta, w)}\left(\frac{(1-w/3)^{1/2}}{(1-w)^{3/2}}\right)\frac{dw}{w^N} \tag{26}$$

where

$$D(\theta, w) = [(1-w)(1-w/3)]^{1/2} - 1 - (2w/3) + 2e^{-\theta}. \tag{27}$$

In eq (24) $\mathscr{I}_x(N)$ and $\mathscr{I}_z(N)$ are, respectively, the unnormalized mean square x and z components of the position of the free end of the chain. The explicit expressions (25) and (26) for $\mathscr{I}_x(N)$ and $\mathscr{I}_z(N)$ are evaluated in the limit $N \to \infty$ in the next section.

4. Evaluation of R_N^2 for $N \gg 1$

We now consider the problem of obtaining asymptotic formulas in the limit $N \gg 1$ for the x and z components of R_N^2 in eq (5). The explicit expressions which must be evaluated are

$$\langle x^2(N) \rangle = \mathscr{I}_x(N)/Q(\theta, N)$$

and

$$\langle z^2(N) \rangle = \mathscr{I}_z(N)/Q(\theta, N)$$

where $\mathscr{I}_x(N)$, $\mathscr{I}_z(N)$, and $Q(\theta, N)$ are given in eqs (25), (26), and (22). The details of the evaluation of these contour integrals in the limit $N \gg 1$ are straightforward but lengthy and depend as in I upon whether $\theta > \theta_c$, $\theta = \theta_c$, or $\theta < \theta_c$ where $\theta_c = \ln(6/5)$. All three integrands have branch points at $w=1$ and $w=3$. As in I, we introduce a cut in the w-plane between these branch points as shown in figure 1. In addition to the branch points, when $\infty > \theta > \theta_c$, there is a zero of $D(\theta, w)$ on the real axis between $w=0$ and $w=1$. Details are given in I where it is shown that the expression for this zero is

$$w_+ = 6\{-2(1-e^{-\theta}) + [4(1-e^{-\theta})^2 + e^{-\theta}(1-e^{-\theta})]^{1/2}\}. \tag{28}$$

It is also shown that w_+ approaches 0 as $\theta \to \infty$ and it approaches 1 as $\theta \to \theta_c = \ln(6/5)$. Thus when $\theta = \theta_c$, the pole of the integrands at w_+ coincides with the branch point at $w=1$. In the remainder of this section we obtain asymptotic formulas for the contour integrals (25), (26), and (22) in the limit $N \gg 1$ for the three cases $\theta > \theta_c$, $\theta = \theta_c$, and $\theta < \theta_c$.

$\theta > \theta_c$. For $\theta > \theta_c$ the contour integrals $\mathscr{I}_x(N)$, $\mathscr{I}_z(N)$, and $Q(\theta, N)$ all satisfy the relation

$$\frac{1}{2\pi i}\int_{C_0} R(w)dw = -\frac{1}{2\pi i}\int_{C_1} R(w)dw + \frac{1}{2\pi i}\int_{C_2} R(w)dw \tag{29}$$

where the integral on the left-hand side of eq (29) stands for $\mathscr{I}_x(N)$, $\mathscr{I}_z(N)$, or $Q(\theta, N)$ and the contours are shown in figure 1. In the limit $N \gg 1$, the second integral on the right-hand side of eq (29) is negligible compared to the first integral. Therefore, the asymptotic values of $\mathscr{I}_x(N)$, $\mathscr{I}_z(N)$, and $Q(\theta, N)$ are given by the residues of the appropriate integrand at w_+. The values are

$$Q(\theta, N) \cong -w_+^{-(N+1)}\{1 + [(1-w_+/3)/(1-w_+)]^{1/2}\}/D'(\theta, w_+) \tag{30}$$

$$\mathscr{I}_z(N) \cong -\frac{1}{3}w_+^{-N}(1-w_+/3)^{1/2}/(1-w_+)^{3/2}D'(\theta, w_+) \tag{31}$$

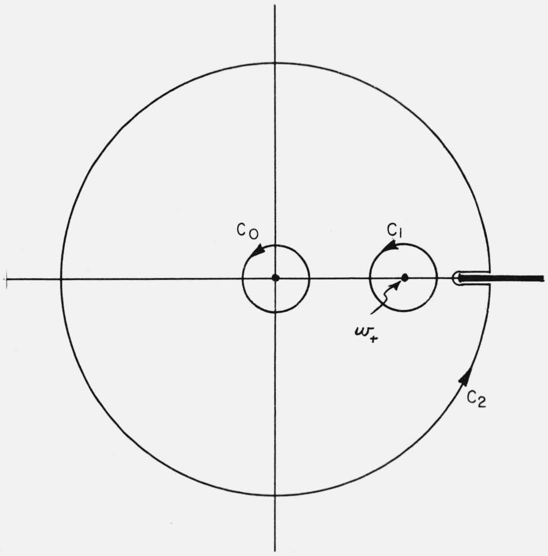

FIGURE 1. *Integration contours* C_0, C_1, *and* C_2 *in the complex w-plane.*
The contour C_2 is indented around the left end of the cut terminating at $w=1$.

and

$$\mathscr{I}_x(N) \cong \frac{N}{w_+^{N+2}} \frac{w_+/3}{1-w_+} \left[1+\left(\frac{1-w_+}{1-w_+/3}\right)^{1/2}\right]$$

$$\times \left[1-(2w_+/3)+(1-w_+/3)^{1/2}(1-w_+)^{1/2}\right]\left[D'(\theta, w_+)\right]^{-2} \qquad (32)$$

where $D'(\theta, w_+)$ denotes $(d/dw)D(\theta, w)|_{w=w_+}$ and where terms proportional to N^0 in eq (32) have been neglected. Equation (30) is a special case of eq (37) in I. Combining eqs (30) and (31), we obtain for the mean square z-component of $\langle R_N^2\rangle$

$$\langle z^2(N)\rangle \cong \frac{w_+}{3}\frac{(1-w_+/3)^{1/2}}{(1-w_+)^{3/2}} \Big/ \left[1+\left(\frac{1-w_+/3}{1-w_+}\right)^{1/2}\right] \cong \frac{w_+}{2}\left(\frac{1-w_+/3}{1-w_+}\right)^{1/2}\left[\left(\frac{1-w_+/3}{1-w_+}\right)^{1/2}-1\right]. \qquad (33)$$

Thus, it is seen that if $\theta > \ln(6/5)$, then $w_+ < 1$; and the limiting value of $\langle z^2(N)\rangle/N$ is

$$\lim_{N\to\infty} \langle z^2(N)\rangle/N = 0. \qquad (34)$$

Combining eqs (30) and (32), we obtain for the mean square x-component of $\langle R_N^2\rangle$

$$\langle x^2(N)\rangle \cong -\frac{N}{3}\left[1+\frac{1-(2w_+/3)}{(1-w_+)^{1/2}(1-w_+/3)^{1/2}}\right]\left[D'(\theta, w_+)\right]^{-1} \cong \frac{N}{2}\left[1+\frac{1}{4}\frac{e^{-\theta}}{1-e^{-\theta}}\right]^{-1/2}. \qquad (35)$$

In obtaining eq (35) we used the relation

$$D'(\theta,\, w_+) = \frac{1}{3}\left[\frac{-2+w_+}{(1-w_+)^{1/2}\ (1-w_+/3)^{1/2}} - 2\right] = -\frac{1}{3}\left[\frac{4(1-e^{-\theta})+w_+/3}{1+(2w_+/3)-2e^{-\theta}}\right] \tag{36}$$

and eq (28) for w_+. The limiting value of $\langle x^2(N)\rangle/N$ is

$$\lim_{N\to\infty}\ \langle x^2(N)\rangle/N = \frac{1}{2}\left[1+\frac{1}{4}\,\frac{e^{-\theta}}{1-e^{-\theta}}\right]^{-1/2}. \tag{37}$$

$\theta = \theta_c$. For $\theta=\theta_c=\ln(6/5)$ the factor $[D(\theta,\, w)]^{-1}$ appearing in the integrands of $Q(\theta,\, N)$, $\mathscr{I}_x(N)$, and $\mathscr{I}_z(N)$ can be written as

$$[D(\theta_c,\, w)]^{-1} = \frac{9}{5+w}\left[\left(\frac{1-w/3}{1-w}\right)^{1/2} - \frac{2}{3}\right]. \tag{38}$$

When $[D(\theta_c,\, w)]^{-1}$ is replaced by eq (38), the expressions for $Q(\theta,\, N)$, $\mathscr{I}_z(N)$, and $\mathscr{I}_x(N)$ become

$$Q(\theta,\, N) = \frac{1}{2\pi i}\int_{C_0}\frac{9}{5+w}\left[\frac{1-w/3}{1-w}+\frac{1}{3}\left(\frac{1-w/3}{1-w}\right)^{1/2} - \frac{2}{3}\right]\frac{dw}{w^{N+1}}. \tag{39}$$

$$\mathscr{I}_z(N) = \frac{1}{2\pi i}\int_{C_0}\frac{3}{5+w}\left[\frac{1-w/3}{(1-w)^2} - \frac{2}{3}\,\frac{(1-w/3)^{1/2}}{(1-w)^{3/2}}\right]\frac{dw}{w^{N}} \tag{40}$$

and

$$\mathscr{I}_x(N) = \frac{1}{2\pi i}\int_{C_0}\left\{\frac{w^2}{5+w}\left[\frac{1}{(1-w)^2} - \frac{2/3}{(1-w/3)^{1/2}(1-w)^{3/2}}\right]\right.$$

$$+\frac{27w}{(5+w)^2}\left[\frac{1-w/3}{(1-w)^2} - \frac{4}{3}\,\frac{(1-w/3)^{1/2}}{(1-w)^{3/2}} + \frac{4/9}{1-w}\right]$$

$$\times\left[1+\left(\frac{1-w}{1-w/3}\right)^{1/2}\right]\left[1-(2w/3)+(1-w/3)^{1/2}(1-w)^{1/2}\right]\frac{dw}{w^{N+1}}. \tag{41}$$

The three contour integrals now satisfy the relation

$$\frac{1}{2\pi i}\int_{C_0} R(w)\,dw = \frac{1}{2\pi i}\int_{C_2} R(w)\,dw. \tag{42}$$

It is readily verified that in each case the dominant contribution to the integrals (40) to (42) around the contour C_2 comes from the most singular terms in $(1-w)$. In (40) to (42) these singularities are simple poles. Evaluating the residues at these poles and retaining terms proportional to the highest power of N only, one obtains

$$Q(\theta_c, N) \cong 1, \tag{43}$$

$$\mathscr{I}_z(N) \cong N/3, \tag{44}$$

and

$$\mathscr{I}_x(N) \cong N/3. \tag{45}$$

The limiting values of $\langle z^2(N)\rangle/N$ and $\langle x^2(N)\rangle/N$ are

$$\lim_{N\to\infty} \langle z^2(N)\rangle/N = \frac{1}{3} \tag{46}$$

and

$$\lim_{N\to\infty} \langle x^2(N)\rangle/N = \frac{1}{3}. \tag{47}$$

$\theta < \theta_c$. For $\theta < \theta_c$, the contour integrals (22), (26), and (25) satisfy the relation (42). The dominant contribution to the contour integrals for $Q(\theta, N)$, $\mathscr{I}_z(N)$, and $\mathscr{I}_x(N)$ around C_2 comes from the most singular terms in $(1-w)$ in the immediate vicinity of $w=1$. The expressions for these dominant contributions are

$$Q(\theta, N) \cong \frac{1}{2\pi i}\int_Q^R \left(\frac{1-w/3}{1-w}\right)^{1/2} \frac{1}{D(\theta, w)} \frac{dw}{w^{N+1}}, \tag{48}$$

$$\mathscr{I}_z(N) \cong \frac{1}{2\pi i}\int_Q^R \frac{(1-w/3)^{1/2}}{(1-w)^{3/2}} \frac{1/3}{D(\theta, w)} \frac{dw}{w^N}, \tag{49}$$

and

$$\mathscr{I}_x(N) \cong \frac{1}{2\pi i}\int_Q^R \frac{1/9}{(1-w/3)^{1/2}(1-w)^{3/2}} \left(\frac{1}{D(\theta, w)}\right) \frac{dw}{w^{N+1}} \tag{50}$$

where the points Q and R are shown in figure 1. It is possible to avoid the explicit evaluation of the contour integrals in (48) to (50) because we are interested only in obtaining asymptotic formulas for $\mathscr{I}_x(N)/Q(\theta, N)$ and $\mathscr{I}_z(N)/Q(\theta, N)$. To demonstrate this fact, integrate by parts in (50) to reduce the order of the singularity in $(1-w)$. The result for $\mathscr{I}_x(N)$ is

$$\mathscr{I}_x(N) \cong \frac{1}{2\pi i}\int_Q^R \frac{2N/9}{(1-w)^{1/2}} \frac{1}{(1-w/3)^{1/2}D(\theta, w)} \frac{dw}{w^N} \tag{51}$$

where we have neglected contributions of lower order in N. We also remark that the singularities in $1-w$ in (49) and (50) are identical, as are the singularities in $(1-w)$ in (48) and (51). Consequently, the asymptotic formula for $\mathscr{I}_z(N)$ can be deduced from that of $\mathscr{I}_x(N)$ by multiplying $\mathscr{I}_x(N)$ by the factor

$$\lim_{w\to 1} 3(1-w/3) = 2;$$

and the asymptotic formula for $\mathscr{I}_x(N)$ can be deduced from $Q(\theta, N)$ by multiplying $Q(\theta, N)$ by the factor

$$\lim_{w\to 1} \frac{2N}{9}\frac{1}{1-w/3}=\frac{N}{3}.$$

Thus we have the relations

$$\mathscr{I}_z(N)=2\mathscr{I}_x(N)$$

and

$$\mathscr{I}_x(N)=NQ(\theta, N)/3 \tag{52}$$

for $N \gg 1$. The limiting values of $\langle x^2(N)\rangle/N$ and $\langle z^2(N)\rangle/N$ are then

$$\lim_{N\to\infty} \langle x^2(N)\rangle/N=1/3 \tag{53}$$

and

$$\lim_{N\to\infty} \langle z^2(N)\rangle/N=2/3. \tag{54}$$

5. Summary and Remarks

The limiting mean square components of the end-to-end displacement parallel to the solution surface are equal and have the value

$$\lim_{N\to\infty} \langle x^2(N)\rangle/N=\lim_{N\to\infty} \langle y^2(N)\rangle/N$$
$$=\begin{cases} \frac{1}{3}, & 0\leq \theta < \ln (6/5) \\ \frac{1}{3}, & \theta=\ln (6/5) \\ \frac{1}{2}\left[1+\frac{1}{4}(e^{\theta}-1)^{-1}\right]^{-1/2}, & \theta > \ln (6/5). \end{cases} \tag{55}$$

Thus $\lim_{N\to\infty} \langle x^2(N)\rangle/N$ is a continuous function of the reduced adsorption energy per monomer unit which increases monotonically from 1/3 to 1/2 in the θ-interval $[\ln (6/5), \infty)$. The limiting mean square component of the end-to-end displacement normal to the solution surface is

$$\lim_{N\to\infty} \langle z^2(N)\rangle/N=\begin{cases} \frac{2}{3}, & 0\leq \theta < \ln (6/5) \\ \frac{1}{3}, & \theta=\ln (6/5) \\ 0, & \theta > \ln (6/5). \end{cases} \tag{56}$$

It is seen in (55) and (56) that at $\theta=\theta_c$ the limiting mean square components of the end-to-end distance are equal to 1/3, the value which would be obtained in the absence of the solution surface. This behavior at the critical energy was deduced by DiMarzio and McCrackin [4]. DiMarzio [5] has obtained our result in the special case $\theta=0$, but for a general lattice model. In this case ($\theta=0$), the mean square normal component is twice the mean square lateral components which are in turn equal to the value obtained in the absence of the solution surface. It is seen in (55) and (56) that as $\theta\to\infty$ and the molecule becomes confined to the solution surface, the mean square

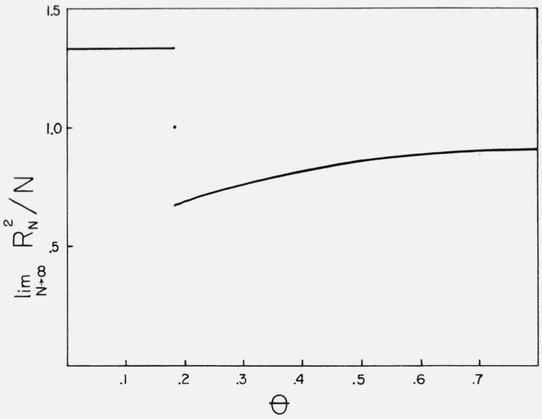

FIGURE 2. *Limiting form of the mean square end-to-end distance per step versus the adsorption energy θ.*

TABLE 1

Values of mean square components of the end-to-end displacement in the 6-choice, 4-choice, and 2-choice simple cubic lattice models

	$\langle x^2(N)\rangle/N$	$\langle z^2(N)\rangle/N$
$0\leq\theta<\theta_c$	1/3	2/3
$\theta=\theta_c$	1/3	1/3
$\theta=\infty$	1/2	0

lateral components approach the value which would be obtained for a random walk on a 4-choice planar square lattice. Combining the limiting forms for the mean square components of the end-to-end distance, we obtain finally for the mean square end-to-end distance per step

$$\lim_{N\to\infty} R_N^2/N=\begin{cases}\frac{4}{3}, & 0\leq\theta<\ln(6/5)\\ 1, & \theta=\ln(6/5)\\ \left[1+\frac{1}{4}(e^{\theta}-1)^{-1}\right]^{-1/2}, & \theta>\ln(6/5).\end{cases} \tag{57}$$

This function is plotted versus θ in figure 2.

We now consider the question of determining qualitatively the components of the mean square displacement in the 4-choice and the 2-choice simple cubic lattice models. These models have been studied [1, 2] and the critical energies $\theta_c=\ln(5^{1/2}-1)$ and $(1/3)\ln 2$, respectively, have been obtained. We expect that analogous to the result in the 6-choice simple cubic lattice model, the mean square components of the end-to-end distance in the adsorption energy range $0<\theta<\theta_c$ are equal to the values obtained at $\theta=0$ by DiMarzio [5]. We also expect that at $\theta=\theta_c$, the mean square components of the end-to-end distance are equal to their free space values. As $\theta\to\infty$, the mean square components parallel to the surface approach the values for the corresponding planar lattice. In table 1 we list the limiting values of the mean square components of the end-to-end distance which are obtained on the basis of the foregoing arguments and note that values listed are the same in the 2-, 4-, and 6-choice simple cubic lattice models. Only the critical energies and the rates of approach to the $\theta=\infty$ values are different. The results for the 4-choice simple cubic lattice model are useful as reference values in McCrackin's Monte Carlo calculations of R_N^2 taking into account the self-excluded volume of the polymer chain [6].

6. References

[1] R. J. Rubin, J. Chem. Phys. **43,** 2392 (1965), referred to as I.
[2] R. J. Rubin, J. Res. NBS **69B,** 301 (1965), referred to as II.
[3] A. Silberberg, J. Phys. Chem. **66,** 1872 (1962).
[4] E. A. DiMarzio and F. L. McCrackin, J. Chem. Phys. **43,** 539 (1965).
[5] E. A. DiMarzio, J. Chem. Phys. **42,** 2101 (1965).
[6] F. L. McCrackin, Bull. Am. Phys. Soc. **10,** 380 (1965), manuscript submitted to J. Chem. Phys.

(Paper 70B4–185)