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A Random Walk Model of Chain Polymer Adsorption at a Surface. II. Effect of Correlation Between Neighboring Steps

Robert J. Rubin

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A random walk lattice model of adsorption of an isolated polymer chain at a solution surface is investigated. The model is a modification of a simple cubic lattice in which there is a correlation between successive steps. The direction of each step is at right angles to the direction of the preceding step (all bond angles are 90°). One-dimensional characteristics of the monomer unit distribution are determined analytically in the limit of long polymer chains neglecting the self-excluded volume. The mean number of monomer units adsorbed in the surface layer $\nu(\theta, N)$ is determined assuming that one end of the polymer chain lies in the surface layer, where N is the mean number of monomer units in the chain and θ is the adsorption energy of each monomer unit in the surface layer measured in units of kT. In addition, the mean distance of the free end of the chain from the surface layer $z(\theta, N)$ is determined. The properties of this correlated step model are qualitatively similar to the properties which have been found in uncorrelated step models. In particular, there is a critical value of the adsorption energy θ_c such that for $\theta > \theta_c$, $\nu(\theta, N)$ is proportional to N. Numerical values of $N^{-1}\nu(\theta, N)$ and $z(\theta, N)$ are presented for $\theta > \theta_c = \ln(\sqrt{5}-1)$.

Key Words: Chain polymer, adsorption, random walk, lattice model, short range correlation, critical energy, partition function, generating function.

1. Introduction

We have recently studied a variety of random walk lattice models of polymer chain adsorption at a solution surface [1].[1] At the same time F. McCrackin [2] has completed a Monte Carlo investigation of still another lattice model of polymer chain adsorption at a solution surface in which he treats the effect of the self-excluded volume of the polymer chain. The lattice model treated by McCrackin is a simple cubic lattice in which the direction of each step must be at right angles to the direction of the preceding step. Thus there is a correlation between neighboring steps in his model. The purpose of this paper is twofold: (1) To generalize the methods developed in I in order to treat a lattice model with correlation between neighboring steps, and (2) to determine some of the moments of the monomer unit distribution which will serve as reference values for the excluded volume computations of McCrackin.

The averages which are calculated are $N^{-1}\nu(\theta, N)$, the average fraction of monomer units adsorbed in the solution surface, and $z(\theta, N)$, the mean distance of one end of the chain from the surface when the other end is in the surface. The parameter N is the number of monomer units in the chain, and θ is the energy of adsorption of a monomer unit measured in units of kT. The lattice model and recurrence equations for the associated generalized random walk are described in section 2. The recurrence equations are solved formally in section 3 by the method of generating functions; and formulas for $N^{-1}\nu(\theta, N)$ and $z(\theta, N)$ are obtained in terms of the generating function solution. It is shown in section 4 that there is a critical value of the adsorption energy $\theta_c = \ln(\sqrt{5}-1)$ such that for $\theta > \theta_c$ the molecule exists in an adsorbed state. In particular, for $\theta > \theta_c$ the fraction $N^{-1}\nu(\theta, N)$ is independent of N and greater than zero in the limit $N \to \infty$. The numerical results presented in section 4 for $N^{-1}\nu(\theta, N)$ and $z(\theta, N)$ cover only the adsorbed state of the chain molecule ($\theta > \theta_c$) and apply to the case in which the first two monomer units of one end of the chain lie in the solution surface. There are no qualitative differences between the lattice model investigated in this paper and the simpler lattice models studied in I.

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

2. Lattice Model and Recurrence Equations

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 subject to the restriction that the direction of each step must be at right angles to the direction of the preceding step. The physical presence of the surface is introduced by considering only random walks [3, 4] which never enter the lattice plane through $z=-1$. If a polymer chain is very far from the 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 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 in which the first two steps lie in the surface layer, the unnormalized or relative probability that at the Nth step the random walker is located at lattice point (m_x, m_y, m_z), where $m_z \geq 0$. There are actually three different relative probabilities $P_x(m_x, m_y, m_z; N+1)$, $P_y(m_x, m_y, m_z; N+1)$, and $P_z(m_x, m_y, m_z; N+1)$ associated with the three different directions from which the random walker arrives at (m_x, m_y, m_z). These three relative probabilities are related to the relative probabilities at the Nth step by the relations

$$P_x(m_x, m_y, m_z; N+1)=(1/4)(E_x^+ + E_x^-)[P_y(m_x, m_y, m_z; N)+P_z(m_x, m_y, m_z; N)],\ m_z \geq 1 \tag{1}$$

$$P_y(m_x, m_y, m_z; N+1)=(1/4)(E_y^+ + E_y^-)[P_x(m_x, m_y, m_z; N)+P_z(m_x, m_y, m_z; N)],\ m_z \geq 1 \tag{2}$$

$$P_z(m_x, m_y, m_z; N+1)=(1/4)(E_z^+ + E_z^-)[P_x(m_x, m_y, m_z; N)+P_y(m_x, m_y, m_z; N)],\ m_z \geq 1 \tag{3}$$

and

$$P_x(m_x, m_y, 0; N+1)=e^{\theta}(1/4)(E_x^+ + E_x^-)[P_y(m_x, m_y, 0; N)+P_z(m_x, m_y, 0; N)] \tag{4}$$

$$P_y(m_x, m_y, 0; N+1)=e^{\theta}(1/4)(E_y^+ + E_y^-)[P_x(m_x, m_y, 0; N)+P_z(m_x, m_y, 0; N)] \tag{5}$$

$$P_z(m_x, m_y, 0; N+1)=e^{\theta}(1/4)E_z^+[P_x(m_x, m_y, 0; N)+P_y(m_x, m_y, 0; N)] \tag{6}$$

where $E_x^{\pm}$ is an operator which is defined by the relation

$$E_x^{\pm}P_j(m_x, m_y, m_z; N)=P_j(m_x \pm 1, m_y, m_z; N). \tag{7}$$

The operators $E_y^{\pm}$ and $E_z^{\pm}$ have similar definitions. Equations (1) to (3) describe the relations between the relative probabilities at the $N+1$th and the Nth steps outside the surface layer. The factor e^{θ} in eqs (4) to (6) accounts for the fact that relative to those configurations where $m_z \geq 1$ at the $N+1$th step, the relative probabilities for those configurations where $m_z=0$ at the $N+1$th step are greater by the factor e^{θ}. The absence of E_z^- in eq (6) is related to the fact that the random walker enters the $z=0$ layer from only one direction.

We are interested in deriving from the solution of eqs (1) to (6) the values of $z(\theta, N)$ the mean distance from the surface at the Nth step and $\nu(\theta, N)$ the mean number of steps in the surface

layer. The definitions of these quantities are

$$\nu(\theta, N) = \left(\frac{d}{d\theta} Q(\theta, N)\right) / Q(\theta, N) = \frac{d}{d\theta} \ln Q(\theta, N) \tag{8}$$

and

$$z(\theta, N) = \sum_{m_x=-\infty}^{\infty} \sum_{m_y=-\infty}^{\infty} \sum_{m_z=0}^{\infty} \sum_{j=1}^{3} m_z P_j(m_x, m_y, m_z; N) / Q(\theta, N) \tag{9}$$

where

$$Q(\theta, N) = \sum_{m_x=-\infty}^{\infty} \sum_{m_y=-\infty}^{\infty} \sum_{m_z=0}^{\infty} \sum_{j=1}^{3} P_j(m_x, m_y, m_z; N) \tag{10}$$

plays the role of a partition function. The subscript $j=1, 2, 3$ denotes respectively, x, y, and z. It was noted in I and it follows from the structure of the recurrence equations that if one starts a random walk with the first two steps in the surface layer and generates in succession the relative probabilities $P_x(m_x, m_y, m_z; r)$, $P_y(m_x, m_y, m_z; r)$, and $P_z(m_x, m_y, m_z; r)$, these probabilities are linear combinations of exponentials $e^{n\theta}$ where $2 \leq n \leq r+2$. Differentiation of $Q(\theta, N)$ with respect to θ has the effect of generating the sum required for computing the average number n of steps in the surface layer.

It should be noted that the probabilities $P_j(m_x, m_y, m_z; N)$ contain more information than is required to calculate the z component of the mean displacement after N steps and the mean number of steps in the surface layer. In fact, we will not solve eqs (1) to (6). Instead we will proceed as in I and for each value of m_z we will sum the appropriate equations in (1) to (6) over all values of m_x and m_y. The result is

$$p_x(m_z; N+1) = (1/2)[p_y(m_z; N) + p_z(m_z; N)], \; m_z \geq 1 \tag{11}$$

$$p_y(m_z; N+1) = (1/2)[p_x(m_z; N) + p_z(m_z; N)], \; m_z \geq 1 \tag{12}$$

$$p_z(m_z; N+1) = (1/4)(E_z^+ + E_z^-)[p_x(m_z; N) + p_y(m_z; N)], \; m_z \geq 1 \tag{13}$$

and

$$[1 - (1 - e^{-\theta})]\, p_x(0; N+1) = (1/2)[p_y(0; N) + p_z(0; N)] \tag{14}$$

$$[1 - (1 - e^{-\theta})] p_y(0; N+1) = (1/2)[p_x(0; N) + p_z(0; N)] \tag{15}$$

$$[1 - (1 - e^{-\theta})] p_z(0; N+1) = (1/4) E_z^+ [p_x(0; N) + p_y(0; N)] \tag{16}$$

where

$$p_j(m_z; N) = \sum_{m_x=-\infty}^{\infty} \sum_{m_y=-\infty}^{\infty} P(m_x, m_y, m_z; N). \tag{17}$$

We introduce one further transformation in eqs (11) to (16)

$$p(m; N) = p_z(m_z; N) \tag{18}$$

and

$$q(m; N) = (1/2)[p_x(m_z; N) + p_y(m_z; N)]. \tag{19}$$

In terms of these relative probabilities for being in the lattice plane which is m units from the solution surface at the Nth step, we can rewrite eqs (11) to (16) as

$$q(m;\ N+1)=(1/2)[q(m;\ N)+p(m;\ N)],\ m\geq 1 \tag{20}$$

$$p(m;\ N+1)=(1/2)[q(m+1;N)+q(m-1;\ N)],\ m\geq 1 \tag{21}$$

$$[1-(1-e^{-\theta})]q(0;\ N+1)=(1/2)[q(0;\ N)+p(0;\ N)] \tag{22}$$

$$[1-(1-e^{-\theta})]p(0;\ N+1)=(1/2)q(1;\ N). \tag{23}$$

Equations (20) and (22) are obtained by combining (11), (12) and (14), (15), respectively.

The sums in eqs (8) to (10) for $\nu(\theta, N)$ and $z(\theta, N)$, which involve the $P_j(m_x, m_y, m_z; N)$'s, can be replaced by simpler sums involving $p(m; N)$ and $q(m; N)$

$$z(\theta, N)=\sum_{m=0}^{\infty} m[2q(m;\ N)+p(m;\ N)]/Q(\theta, N) \tag{24}$$

and

$$Q(\theta, N)=\sum_{m=0}^{\infty}[2q(m;\ N)+p(m;\ N)]. \tag{25}$$

The starting condition for the random walk, namely, that the first two steps are in the surface layer, corresponds to the statement

$$p(m,\ 0)=0,\ m\geq 0 \tag{26}$$

and

$$q(0,\ 0)=e^{2\theta},\ q(m,\ 0)=0,\ m\geq 1. \tag{27}$$

3. Solution of Recurrence Equations

The recurrence equations (20) to (23) can be solved by introducing generating functions. The procedure used is similar to that used in I. Multiply the equation for $q(m, N+1)$ by $(2\pi)^{-1/2}e^{im\phi}$ and sum over all values of $m\geq 0$. The result is

$$-(1-e^{-\theta})(2\pi)^{1/2}q(0;\ N+1)+\mathcal{Q}(\phi, N+1)=\tfrac{1}{2}\{\mathcal{P}(\phi, N)+\mathcal{Q}(\phi, N)\}, \tag{28}$$

where

$$\mathcal{Q}(\phi, N)=(2\pi)^{-1/2}\sum_{m=0}^{\infty} e^{im\phi}q(m;\ N) \tag{29}$$

and

$$\mathcal{P}(\phi, N)=(2\pi)^{-1/2}\sum_{m=0}^{\infty} e^{im\phi}p(m;\ N). \tag{30}$$

The corresponding equation obtained by combining the equations for the $p(m;\ N+1)$'s is

$$-(1-e^{-\theta})(2\pi)^{-1/2}p(0;\ N+1)+\mathscr{P}(\phi,\ N+1)=\cos\phi\ \mathscr{Q}(\phi,\ N)-\tfrac{1}{2}\ (2\pi)^{-1/2}e^{-i\phi}q(0;\ N). \tag{31}$$

Next multiply eqs (30) and (31) by y^{N+1}, and sum each over all values of N to obtain the pair

$$-(1-e^{-\theta})(2\pi)^{-1/2}[k_0(y)-q(0;\ 0)]+\Lambda(\phi,\ y)-\mathscr{Q}(0,\ 0)=\tfrac{1}{2}y[\Gamma(\phi,\ y)+\Lambda(\phi,\ y)] \tag{32}$$

and

$$-(1-e^{-\theta})(2\pi)^{-1/2}[h_0(y)-p(0;\ 0)]+\Gamma(\phi,\ y)-\mathscr{P}(0,\ 0)=y\cos\phi\ \Lambda(\phi,\ y)-\tfrac{1}{2}\ y(2\pi)^{-1/2}e^{-i\phi}k_0(y) \tag{33}$$

where

$$\Lambda(\phi,\ y)=\sum_{N=0}^{\infty}\ y^N\mathscr{Q}(\phi,\ N), \tag{34}$$

$$\Gamma(\phi,\ y)=\sum_{N=0}^{\infty}\ y^N\mathscr{P}(\phi,\ N), \tag{35}$$

$$h_m(y)=\sum_{N=0}^{\infty}\ y^Np(m;\ N), \tag{36}$$

and

$$k_m(y)=\sum_{N=0}^{\infty}\ y^Nq(m;\ N). \tag{37}$$

The definitions (29), (30), (36), and (37), when combined with the starting conditions (26) and (27), are substituted in (32) and (33). The result is

$$-\tfrac{1}{2}\ y\Gamma(\phi,\ y)+(1-\tfrac{1}{2}\ y)\Lambda(\phi,\ y)=(2\pi)^{-1/2}[(1-e^{-\theta})k_0(y)+e^{\theta}] \tag{38}$$

and

$$\Gamma(\phi,\ y)-y\cos\phi\Lambda(\phi,\ y)=(2\pi)^{-1/2}[(1-e^{-\theta})h_0(y)-\tfrac{1}{2}ye^{-i\phi}k_0(y)]. \tag{39}$$

Next solve eqs (38) and (39) for $\Gamma(\phi,\ y)$ and $\Lambda(\phi,\ y)$ and obtain

$$\Gamma(\phi,\ y)=\frac{(2\pi)^{-1/2}}{1-\frac{1}{2}\ y-\frac{1}{2}\ y^2\cos\phi}\{[(1-e^{-\theta})h_0(y)-\tfrac{1}{2}\ ye^{-i\phi}k_0(y)](1-\tfrac{1}{2}\ y)+[(1-e^{-\theta})k_0(y)+e^{\theta}]y\cos\phi\} \tag{40}$$

$$\Lambda(\phi,\ y)=\frac{(2\pi)^{-1/2}}{1-\frac{1}{2}\ y-\frac{1}{2}\ y^2\cos\phi}\{(1-e^{-\theta})k_0(y)+e^{\theta}+\tfrac{1}{2}\ y[(1-e^{-\theta})h_0(y)-\tfrac{1}{2}\ ye^{-i\phi}k_0(y)]\}. \tag{41}$$

Equations (40) and (41) constitute a pair of implicit equations for the functions $h_0(y)$ and $k_0(y)$ because according to the definitions of $\Gamma(\phi,\ y)$, $\Lambda(\phi,\ y)$, $h_m(y)$, and $k_m(y)$ in (34) to (37) and $\mathscr{P}(\phi,\ N)$ and $\mathscr{Q}(\phi,\ N)$ in (29) and (30)

$$\Gamma(\phi,\ y)=(2\pi)^{-1/2}\sum_{m=0}^{\infty}\ e^{im\phi}h_m(y) \tag{42}$$

and

$$\Lambda(\phi, y)=(2\pi)^{-1/2}\sum_{m=0}^{\infty}e^{im\phi}k_m(y). \tag{43}$$

A pair of equations for determining $h_0(y)$ and $k_0(y)$ can be obtained by multiplying eqs (40) and (41) by $(2\pi)^{-1/2}$ and integrating with respect to ϕ from $-\pi$ to π

$$h_0(y)=[(1-e^{-\theta})I_0(y)h_0(y)-\tfrac{1}{2}yI_1(y)k_0(y)](1-\tfrac{1}{2}y)+y[(1-e^{-\theta})k_0(y)+e^{\theta}]I_1(y) \tag{44}$$

and

$$k_0(y)=[(1-e^{-\theta})k_0(y)+e^{\theta}]I_0(y)+\frac{1}{2}y(1-e^{-\theta})h_0(y)I_0(y)-\frac{1}{4}y^2k_0(y)I_1(y) \tag{45}$$

where

$$I_m(y)=\frac{1}{2\pi}\int_{-\pi}^{\pi}\frac{e^{im\phi}d\phi}{1-\frac{1}{2}y-\frac{1}{2}y^2\cos\phi}=\left[(1-y)\left(1+\frac{1}{4}y^2+\frac{1}{4}y^3\right)\right]^{-1/2}$$

$$\times\left\{\frac{1-\frac{1}{2}y-\left[(1-y)\left(1+\frac{1}{4}y^2+\frac{1}{4}y^3\right)\right]^{1/2}}{\frac{1}{2}y}\right\}^{|m|} \tag{46}$$

Solving (44) and (45) for $h_0(y)$ and $k_0(y)$, we obtain

$$h_0(y)=\left\{ye^{\theta}I_1(y)\left[1-(1-e^{-\theta})I_0(y)+\frac{1}{4}y^2I_1(y)\right]-ye^{\theta}I_0(y)I_1(y)\left[\frac{1}{2}\left(1-\frac{1}{2}y\right)-(1-e^{-\theta})\right]\right\}/\mathscr{D}(\theta, y) \tag{47}$$

and

$$k_0(y)=\{e^{\theta}I_0(y)[1-(1-\tfrac{1}{2}y)(1-e^{-\theta})I_0(y)]+\tfrac{1}{2}y^2I_0(y)I_1(y)(e^{\theta}-1)\}/\mathscr{D}(\theta, y) \tag{48}$$

where

$$\mathscr{D}(\theta, y)=1+(1-e^{-\theta})\left(\frac{1}{2}y-2\right)I_0(y)+\frac{1}{4}y^2I_1(y)+(1-e^{-\theta})^2I_0(y)[I_0(y)\left(1-\frac{1}{2}y\right)-\frac{1}{2}y^2I_1(y)]. \tag{49}$$

Equations (47) to (49) can be simplified with the aid of eq (46) to give

$$h_0(y)=\tfrac{1}{2}ye^{\theta}I_1(y)/\mathscr{D}(\theta, y) \tag{50}$$

and

$$k_0(y)=I_0(y)/\mathscr{D}(\theta, y) \tag{51}$$

where

$$\mathscr{D}(\theta, y)=\left[(1-y)\left(1+\frac{1}{4}y^2+\frac{1}{4}y^3\right)\right]^{-1/2}\left\{\frac{1}{2}\left[(1-y)\left(1+\frac{1}{4}y^2+\frac{1}{4}y^3\right)\right]^{1/2}-\frac{1}{2}+\frac{1}{4}y-\frac{1}{2}ye^{-\theta}+e^{-2\theta}\right\}. \tag{52}$$

Substitute the expressions for $h_0(y)$ and $k_0(y)$ obtained in (50) and (51) into eqs (40) and (41) for $\Gamma(\phi, y)$ and $\Lambda(\phi, y)$, and then form the quantity $\Gamma(\phi, y)+2\Lambda(\phi, y)$

$$\Gamma(\phi, y)+2\Lambda(\phi, y)=\frac{(2\pi)^{-1/2}(1+\frac{1}{2}y)}{[1-\frac{1}{2}y-\frac{1}{2}y^2\cos\phi]^{1/2}}\left\{\frac{\frac{1}{2}y(e^{\theta}-1)I_1(y)+I_0(y)\left[-\frac{1}{2}ye^{-i\phi}+2(1-e^{-\theta})\frac{2+y\cos\phi}{2+y}\right]}{\mathscr{D}(\theta, y)}\right.$$
$$\left.+2e^{\theta}\frac{2+y\cos\phi}{2+y}\right\}. \tag{53}$$

Equation (53) constitutes an explicit solution of the recurrence equations (20) to (23) which can be used to compute the sums appearing in eqs (24), (25), and (8). In particular, from the definitions of $\Gamma(\phi, y)$ and $\Lambda(\phi, y)$ we have

$$\Gamma(\phi, y)+2\Lambda(\phi, y)=(2\pi)^{-1/2}\sum_{N=0}^{\infty}y^N\sum_{m=0}^{\infty}e^{im\phi}[p(m; N)+2q(m; n)]. \tag{54}$$

If we set $\phi=0$ and select the coefficient of y^N in eq (54) using Cauchy's formula, we obtain an explicit expression for $Q(\theta, N)$

$$Q(\theta, N)=\frac{1}{2\pi i}\oint_{C_0}\frac{dy}{y^{N+1}}(2\pi)^{1/2}[\Gamma(0, y)+2\Lambda(0, y)] \tag{55}$$

where C_0 is a closed contour in the complex y-plane which encloses only the pole of the integrand at $y=0$. Substituting eq (53) in (55) and using eqs (46) and (52), one obtains the explicit formula

$$Q(\theta, N)=\frac{1}{2\pi i}\oint_{C_0}\frac{dy}{y^{N+1}}\frac{1}{1-y}\left\{\frac{\frac{1}{2}y(e^{\theta}-1)I_1(y)+I_0(y)[2(1-e^{-\theta})-\frac{1}{2}y]}{\mathscr{D}(\theta, y)}+2e^{\theta}\right\} \tag{56}$$

or

$$Q(\theta, N)=2e^{\theta}+\frac{1}{2\pi i}\oint_{C_0}\frac{dy}{y^{N+1}}\frac{2}{1-y}$$
$$\times\left\{\frac{(e^{\theta}-1)\left[1-\frac{1}{2}y-\sqrt{(1-y)\left(1+\frac{1}{4}y^2+\frac{1}{4}y^3\right)}\right]y^{-1}+2(1-e^{-\theta})-\frac{1}{2}y}{\sqrt{(1-y)\left(1+\frac{1}{4}y^2+\frac{1}{4}y^3\right)}-1+\frac{1}{2}y-ye^{-\theta}+2e^{-2\theta}}\right\}. \tag{57}$$

The sum $\sum_{m=0}^{\infty}m[p(m; N)+2q(m; N)]$ appearing in eq (24) can be extracted from eq (54)

$$\sum_{m=0}^{\infty}m[p(m; N)+2q(m; N)]=\frac{1}{2\pi i}\oint_{C_0}\frac{dy}{y^{N+1}}\frac{(2\pi)^{1/2}}{i}\frac{d}{d\phi}[\Gamma(\phi, y)+2\Lambda(\phi, y)]\Big|_{\phi=0}. \tag{58}$$

The explicit formula obtained from eq (58) after inserting (53) is

$$\sum_{m=0}^{\infty}m[p(m; N)+2q(m; N)]=\frac{1}{2\pi i}\oint_{C_0}\frac{dy}{y^N}\frac{\frac{1}{2}I_0(y)}{(1-y)\mathscr{D}(\theta, y)} \tag{59}$$

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or

$$\sum_{m=0}^{\infty} m[p(m;\, N)+2q(m;\, N)]=\frac{1}{2\pi i}\oint_{C_0}\frac{dy}{y^N}\frac{1}{1-y}$$

$$\times\left\{\sqrt{(1-y)\left(1+\frac{1}{4}y^2+\frac{1}{4}y^3\right)}-1+\tfrac{1}{2}y-ye^{-\theta}+2e^{-2\theta}\right\}^{-1}. \qquad (60)$$

4. Calculation of $\nu(\theta, N)$ and $z(\theta, N)$ for $N\gg 1$

In this section we evaluate the contour integrals in eqs (57) and (60) for $N \gg 1$ and so obtain expressions for $\nu(\theta, N)$ from eq (8) and $z(\theta, N)$ from eq (24). The procedure which we use to evaluate the contour integrals is similar to that used in I.

Location of singularities. It is first necessary to locate the singularities of the integrands in (57) and (60). In addition to the poles at $y=0$ and $y=1$, there are branch point singularities associated with zeros of the square root function $\sqrt{(1-y)\left(1+\frac{1}{4}y^2+\frac{1}{4}y^3\right)}$, namely, singularities at $y=1$ and at the roots of the cubic equation

$$1+\frac{1}{4}y^2+\frac{1}{4}y^3=0. \qquad (61)$$

It is shown in the appendix that these three roots, y_a, y_b, and y_c, lie outside the unit circle in the complex y-plane. In view of the occurrence of these branch point singularities, we introduce cuts in the complex y-plane as shown in figure 1 in order to define the integrands in eqs (57) and (60) uniquely. The cuts start at the branch points and extend radially outward. The square root function is taken as real and positive on the real axis between $y=0$ and 1. With this definition of the square root function, there may be an additional singularity of the integrands in (57) and (60)

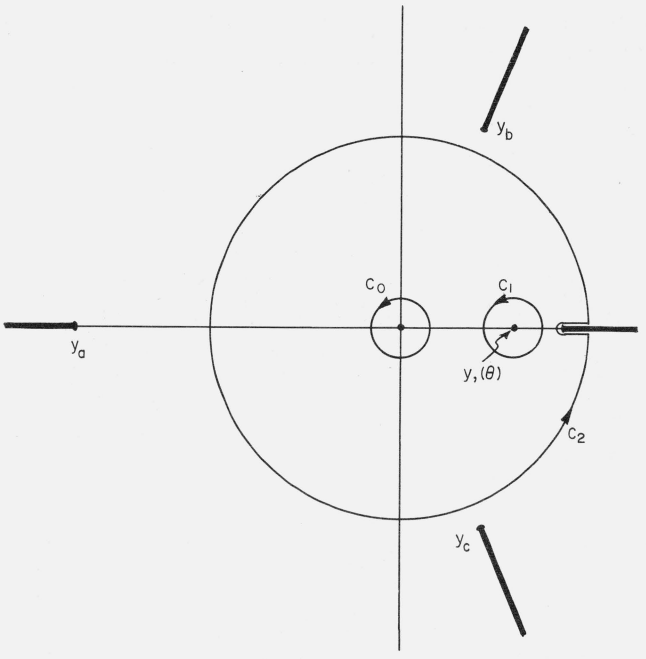

FIGURE 1. *Singularities of integrands, cuts, and contours of integration in the complex y-plane.*

arising from a zero of the denominator

$$g(\theta, y)=\sqrt{(1-y)\left(1+\frac{1}{4}y^2+\frac{1}{4}y^3\right)}-1+\frac{1}{2}y+2e^{-2\theta}-ye^{-\theta}. \tag{62}$$

A numerical investigation of $g(\theta, y)$ for different values of θ shows that there is never more than one root of $g(\theta, y)$ inside the unit circle. When there is a root of $g(\theta, y)$ inside the unit circle, it is real, and it lies between $y=0$ and 1. In order to determine the condition on θ for which there is a real root $y_1(\theta) \leq 1$ of $g(\theta, y)$, consider the plots of the two functions $F(y)=\sqrt{(1-y)\left(1+\frac{1}{4}y^2+\frac{1}{4}y^3\right)}$ and $L(\theta, y)=1-2e^{-2\theta}-(\frac{1}{2}-e^{-\theta})y$ shown in figure 2. The occurrence of the root $y_1(\theta)$ corresponds to an intersection of $F(y)$ and $L(\theta, y)$. For $\theta=\ln 2$, the line $L(\theta, y)$ becomes $L(\ln 2, y)=\frac{1}{2}$. For $\theta > \ln 2$, the slope of $L(\theta, y)$ is negative; and as θ increases the intersection of $L(\theta, y)$ and $F(y)$ moves up toward the point (0, 1), i.e., toward smaller values of $y_1(\theta)$ than $y_1(\ln 2)$. For $\theta < \ln 2$, the slope of $L(\theta, y)$ is positive; and as θ decreases the intersection of $L(\theta, y)$ and $F(\theta, y)$ moves down toward the point (1, 0). The critical value of θ, for which the intersection of $L(\theta, y)$ and $F(y)$ occurs at (1, 0) can be determined by solving the equation $g(\theta, 1)=0$, i.e.,

$$-1+\tfrac{1}{2}+2e^{-2\theta}-e^{-\theta}=0. \tag{63}$$

The value of θ at which $y_1(\theta)=1$ is

$$\theta_c=\ln(\sqrt{5}-1). \tag{64}$$

There are no other singularities of the integrands in (57) and (60).

Deformation of the contour of integration. Having determined the positions and types of singularities of the integrands in the integral representations of $Q(\theta, N)$ and $\sum_{m=0}^{\infty} m[p(m; N)+2q(m; N)]$, we will now evaluate these integrals in the limit in which N is large and $\theta > \theta_c$. As in I, the details of the calculation are different, depending upon whether $\theta > \theta_c$, $\theta < \theta_c$, or $\theta=\theta_c$.

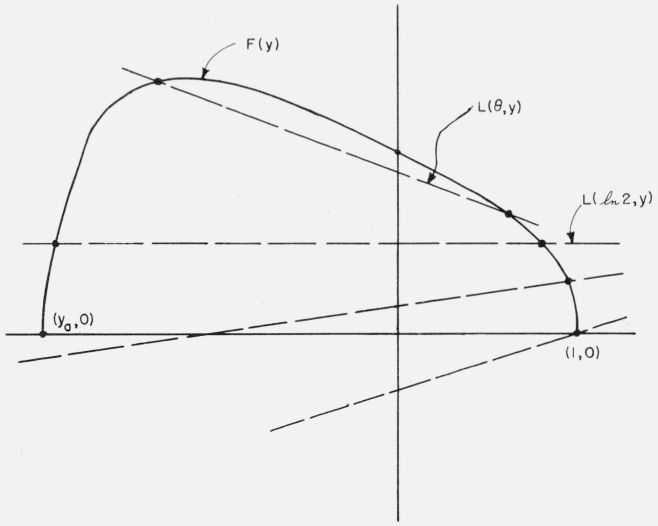

FIGURE 2. *Plots of* $F(y)=\left[(1-y)\left(1+\frac{1}{4}y^2+\frac{1}{4}y^3\right)\right]^{1/2}$ *and* $L(\theta, y)=1-2e^{-2\theta}-\left(\frac{1}{2}-e^{-\theta}\right)y$ *versus* y *for real* y, $0 \leq y \leq 1$.

The results in each case are qualitatively the same as in I. Therefore, we will limit our discussion to the case $\theta > \theta_c$.

Consider the integral

$$\mathcal{I} = \frac{1}{2\pi i} \oint \frac{f(y)}{g(\theta, y)} \frac{dy}{y^{N+1}} \tag{65}$$

around the three contours C_0, C_1, and C_2 shown in figure 1. Denote these integrals by $\mathcal{I}_0$, $\mathcal{I}_1$, and $\mathcal{I}_2$, respectively. Suppose that the integrand $f(y)/g(\theta, y)y^{N+1}$ is the integrand in eq (57) or (60) so that $\mathcal{I}_0 = Q(\theta, N)$ or $\mathcal{I}_0 = \sum_{m=0}^{\infty} m[p(m; N) + 2q(m; N)]$, respectively. The contour C_1 encloses $y_1(\theta)$, and the contour C_2 consists of a circular part whose radius is $1+\delta$, and an indented part around the branch point at $y=1$. With these definitions, the integrals satisfy the relation

$$\mathcal{I}_0 = \mathcal{I}_2 - \mathcal{I}_1 \tag{66}$$

We first evaluate $\mathcal{I}_1$ and indicate why $\mathcal{I}_2$ is negligible compared to $\mathcal{I}_1$ for $N >> 1$. The value of $\mathcal{I}_1$ is simply the residue [5] at $y_1 = y_1(\theta)$

$$\mathcal{I}_1 = f(y_1)/g'(\theta, y_1)y_1^{N+1} \tag{67}$$

where $g'(\theta, y_1)$ denotes $\frac{d}{dy} g(\theta, y)|_{y=y_1}$. Thus $\mathcal{I}_1$ is proportional to the $(N+1)^{st}$ power of a number which is larger than one. As in I, it can be verified in the case of the contour integral $\mathcal{I}_2$ that the contribution from the circular part of the contour is proportional to $(1+\delta)^{-N}$, and that the contribution from the remaining part of the contour is small compared to $\left(\frac{1}{y_1}\right)^{N+1}$. Therefore, in the limit $N \gg 1$, we can neglect $\mathcal{I}_2$ compared to $\mathcal{I}_1$ and write eq (66) as

$$\mathcal{I}_0 \doteq -\mathcal{I}_1 \tag{68}$$

This approximation is excellent for large finite values of N provided that θ is not too close to θ_c, i.e., provided that y_1 is not too close to the branch point $y=1$. Having established the relations (67) and (68) for both integrals (57) and (60), we can now calculate the values of $\nu(\theta, N)$ and $z(\theta, N)$. First we have from eq (8)

$$\nu(\theta, N) = \frac{\partial}{\partial \theta} \ln Q(\theta, N) \doteq -N \frac{\partial y_1}{\partial \theta} \Big/ y_1. \tag{69}$$

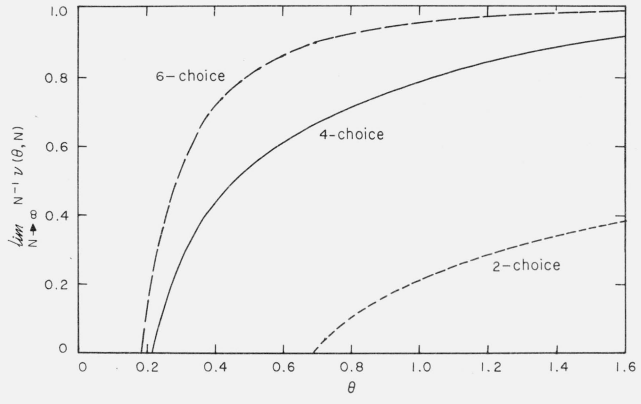

FIGURE 3. *Average fraction of adsorbed monomer units* $N^{-1}\nu(\theta, N)$ *versus adsorption energy* θ *(solid curve) for* $\theta > \theta_c$.
For comparison, the corresponding curves for the 6-choice simple cubic lattice (dashed curve) and the 2-choice simple cubic (dotted curve) are included, from reference I.

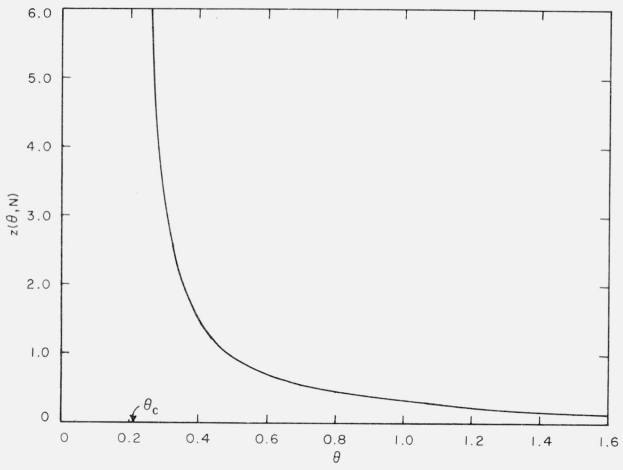

FIGURE 4. *Mean distance of end of polymer chain from surface* $z(\theta, N)$ *versus adsorption energy* θ *for* $\theta > \theta_c$.

In eq (69), we have dropped terms which are not proportional to N. It is seen that the result obtained here for the case of the 4-choice s.c. lattice when $\theta > \theta_c$ is similar to the result obtained in I, namely, on the average a finite fraction of all steps are adsorbed in the surface for $N \gg 1$. In the case of eq (24) we have

$$z(\theta, N) \doteq \frac{1}{2} y_1 \left\{ (e^{\theta} - 1) \left[1 - \frac{1}{2} y_1 - \sqrt{(1 - y_1)\left(1 + \frac{1}{4} y_1^2 + \frac{1}{4} y_1^3 \right)} \right] y_1^{-1} + 2(1 - e^{-\theta}) - \frac{1}{2} y_1 \right\}^{-1}, \tag{70}$$

a result which is independent of N for $N \gg 1$.

The values of $N^{-1}\nu(\theta, N)$ and $z(\theta, N)$ in eqs (69) and (70) have been determined numerically by F. McCrackin; and the results are presented graphically in figures 3 and 4 for $\theta > \theta_c$. Values of $N^{-1}\nu(\theta, N)$ obtained in I for the 6-choice simple cubic lattice and the 2-choice simple cubic lattice are also included in figure 3 for comparison. Although results have only been presented for adsorption energies greater than θ_c, examination of the behavior of the integrands in (57) and (60) for $\theta < \theta_c$ and $\theta = \theta_c$ in the neighborhood of $y = 1$ shows that the results for the 4-choice simple cubic lattice are qualitatively similar to the results for the lattices studied in I over the entire range of values of θ.

I thank F. McCrackin for calculating the numerical values of $N^{-1}\nu(\theta, N)$ and $z(\theta, N)$.

5. Appendix

The roots of the cubic equation

$$\frac{1}{4} y^3 + \frac{1}{4} y^2 + 1 = 0 \tag{A1}$$

are the reciprocals of the roots of the equation

$$z^3 + \frac{1}{4} z + \frac{1}{4} = 0.$$

Therefore the roots of (A1) are

$$y_a = -2\{[(1+1/27)^{1/2}+1]^{1/3}-[(1+1/27)^{1/2}-1]^{1/3}\}^{-1}$$

$$\cong -1.968$$

$$y_b = 4\{[(1+1/27)^{1/2}+1]^{1/3}-[(1+1/27)^{1/2}-1]^{1/3}-i\sqrt{3}([(1+1/27)^{1/2}+1]^{1/3}+[(1+1/27)^{1/2}-1]^{1/3})\}^{-1}$$

$$\cong 0.497+1.308i$$

$$y_c \cong 0.497-1.308i$$

Thus all three roots, y_a, y_b, and y_c, lie outside the unit circle.

6. References

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