Generating function methods for macromolecules at surfaces. I. One molecule at a plane surface

Cite as: J. Chem. Phys. **85**, 5299 (1986); https://doi.org/10.1063/1.451672
Submitted: 23 May 1986 . Accepted: 17 July 1986 . Published Online: 31 August 1998

B. E. Eichinger, David M. Jackson, and Brendan D. McKay

Generating function methods for macromolecules at surfaces. I. One molecule at a plane surface

B. E. Eichinger
Department of Chemistry BG-10, University of Washington, Seattle, Washington 98195

David M. Jackson
Department of Combinatorics and Optimization, University of Waterloo, Waterloo, Ontario N2L3G1, Canada

Brendan D. McKay
Computer Science Department, The Australian National University, GPO Box 4, Canberra, ACT 2601, Australia

(Received 23 May 1986; accepted 17 July 1986)

The problem of a macromolecule adsorbed on a single surface is treated by means of a generating function technique. The basic method has the virtues of simplicity and flexibility. The statistical weights that appear in the generating functions for tails, trains, and loops can be calculated with use of a variety of models. The essential physics of the adsorption process, and the occurrence of a critical point, are transparent in this treatment. Illustrative calculations are done for the simplest case, in which tails have unit weight, trains have binding energies proportional to their lengths, and loops are weighted by lattice walk statistics. Methods for treating more realistic models for chains, and for handling their interactions when there is multiple chain adsorption, are discussed.

INTRODUCTION

The problems of polymer adsorption on a surface and between two surfaces have attracted a great deal of attention.[1–14] The technical importance of both adhesion and colloid stabilization justifies the efforts devoted to them. There seems to be general agreement on the nature of the problems involved, but diverse opinions as to how best to formulate the statistical mechanical calculations. Two different, broadly characterized, techniques appear to have been most popular: (i) combinatorial enumeration and (ii) transfer matrix methods. The two methods must, when properly applied to the same model, give equivalent results. However, the ease of application of a theory is highly dependent upon the methods used in its formulation. Combinatorial methods tend to obscure the essentials of the problem in lengthy algebraic equations,[1–5] while matrix methods devolve into numerical evaluation at a very early state of their development.[8,10,11] It has occurred to us that generating function methods have a generality that is unexcelled, and that they permit one to explore successively higher approximations as experience dictates.

The last point is an important one that requires elaboration. It is a well established result that the loops that are present in a reasonably strongly bound homopolymer are fairly short. However, the models that are used for this calculation are all based on lattice walks. Real chains do not execute random walks on lattices; their statistics are better described in terms of the rotational isomeric state model.[15] How serious, then, is the error that might be introduced on using a lattice to calculate the weights for short chains, for which the law of large numbers does not rule the phenomena? Here is a situation where the weights might best be calculated by methods that are more or less independent of the surface *per se*, and which would serve as input to the generating functions.

It will be shown that by formulating the distribution of sequences of tails, trains, and loops in terms of generating functions that a very general formulation of the surface adsorption problem for a single chain may be realized. The expectation numbers for the lengths of these sequences are readily obtained as derivatives of the generating function. The general equations will then be applied to a specific example, chosen so that the weighting scheme is particularly simple, yet nonetheless applicable to the real situation of a macromolecule adsorbed on a liquid-gas interface. Finally, we will indicate how one might proceed to include the effects of mutual exclusion of configurations by means of a self-consistent treatment of site occupancy in the Flory–Huggins approximation.

GENERATING FUNCTION

Define the generating functions for tails, trains, and loops as

$$T(x) = \sum_{j>0} t_j x^j, \quad t_0 = 1,$$

$$C(x) = \sum_{j>1} c_j x^j, \tag{1}$$

$$R(x) = \sum_{j>1} r_j x^j.$$

The respective coefficients t_j, c_j, and r_j are statistical weights for a sequence of j backbone atoms of the appropriate class. If spring bead or lattice models are to be used, the units, j in number, will be chosen to be the beads or the occupied lattice points, rather than the springs or edges. In any event, the atoms, beads, or lattice points will be called vertices, and the bonds, edges. When either vertices or edges or both are discussed generically, they will be referred to as segments.

The weights in Eq. (1) can be calculated quite indepen-

 0021-9606/86/215299-07$02.10

dently of the basic formulas that will now be developed. Define the set $x = (x_1,x_2,x_3)$, and the generating function $F(x)$ for all configurations of tail, train, and loop sequences in molecules of all lengths. It is easily seen that

$$F(x) = T(x_1)\{C(x_2) + C(x_2)R(x_3)C(x_2) + C(x_2)R(x_3)C(x_2)R(x_3)C(x_2) + \cdots\}T(x_1) \tag{2}$$

generates all configurations for molecules that are bound to at least one site. The first term generates the sequences tail–train–tail, the second generates tail–train–loop–train–tail, and so on for the rest of the terms in the series. It will be noted that there might not be any nodes in the tail sequences, since the generating function $T(x)$ is defined with $t_0 = 1$.

Equation (2) may be rearranged to

$$F(x) = T(x_1)^2C(x_2)[1 - C(x_2)R(x_3)]^{-1} \tag{3}$$

and when $x_1 = x_2 = x_3 = x$ this becomes

$$F(x) = F(x,x,x) = T(x)^2C(x)[1 - C(x)R(x)]^{-1}. \tag{4}$$

The general function, Eq. (3), will later be used to extract information on the sequence length distributions by differentiation. For the present, the statistical mechanical partition function for a canonical ensemble of single chains of n segments, each adsorbed on a surface, is the coefficient of x^n in Eq. (4). The operation of extracting this coefficient is denoted by $[x^n]F(x)$.[16] We choose not to use the grand ensemble, for which Eq. (4) is the partition function, so as to avoid the awkward interpretation of simultaneous adsorption and polymerization equilibria.

Equation (4) is essentially the same generating function as that formulated by Lifson[17] for the helix–coil equilibrium problem. In fact, any problem in statistical mechanics that can be represented by configurations of sequences of two symbols will have Eq. (4), or a minor variation thereof, as the generating function.

ASYMPTOTIC ANALYSIS

The generating functions T, C, and R must all have a radius of convergence > 0. This is certainly the case because each is a grand partition function for a single phase, with x being the activity. Let the radius of convergence of $F(x)$ in Eq. (4) be $\rho > 0$. What is needed to evaluate the coefficient of x^n is an asymptotic analysis of $F(x)$. This will be done with the aid of Darboux's Theorem,[18,19] the basic notion of which is that if $F(x) = \Sigma_j f_j x^j$ has a radius of convergence ρ, then $f_{j+1}/f_j \sim \rho^{-1}$ for large j. But note that, for large n, the segment chemical potential μ is given by

$$\mu = A_{n+1} - A_n = kT\ln(f_n/f_{n+1}) \quad \text{as } n\to\infty. \tag{5}$$

If the theory being developed is a statistical mechanical theory, which we presume it to be, then μ exists, as does $f_n/f_{n+1} \sim \lambda$ = thermodynamic activity. These comments suggest that λ is then related to ρ, and this we shall now prove with the first two theorems.

Theorem A

Let $F(x) = G(x)/[1 - H(x)]$, where

(1) $H(x) = \Sigma_j h_j x^j$, $h_1 = h_2 = \cdots = h_k = 0$, $h_{k+1} > 0$, and $h_j \geqslant 0$ for $j > k+1$.

(2) For $I = \{i - k - 1 | h_i \neq 0\}$, g.c.d.(I) = 1.

(3) The smallest positive root ρ of $H(x) = 1$ is less than the radius of convergence of the series $H(x)$.

(4) $G(x)$ has radius of convergence $> \rho$, and $G(\rho) \neq 0$.

Then $F(x)$ has a pole at $x = \rho$, and has no other singularities on the circle of convergence.

Proof

Rewrite $H(x)$ as $x^{k+1}(h_{k+1} + h_{k+2}x + \cdots) = x^{k+1}(b_0 + b_1x + \cdots)$. The power series $B(x) = b_0 + b_1x + \cdots$ has the property that the greatest common divisor of its exponents that actually appear is one. We want to prove that $|B(re^{i\theta})| = B(r)$ implies $\theta = 0$. Observe that

$$|B(re^{i\theta})| = |b_0 + b_1re^{i\theta} + b_2r^2e^{2i\theta} + \cdots + b_kr^ke^{ki\theta} + \cdots| \leqslant b_0 + b_1r + b_2r^2 + \cdots$$

with equality if and only if all the nonzero terms have the same argument. Since $b_0 > 0$, the latter can be true if $e^{ji\theta} = 1$, that is, $j\theta$ is a multiple of 2π for every j with $b_j > 0$. Thus θ is a rational multiple of 2π, say $\theta = 2(a/c)\pi$ for g.c.d.$(a,c) = 1$. For any j with $b_j \neq 0$, we thus have $ja = cs$ for some integer s. Since g.c.d.$(a,c) = 1$, it must be the case that c divides j. This contradicts condition (2) unless $c = 1$.

The singularity is a simple pole, since $H'(\rho) > 0$ by virtue of $H'(\rho)$ being a sum of positive terms.

The functions to be developed will depend upon parameters that appear in the statistical weights. Theorem A will apply to these functions for certain ranges of parameter values, and where it does not, because of failure of one or more of the conditions, the system is at a critical point. A trivial example of a generating function that does not satisfy condition (2) is $F(x) = F(v^2)$. Such a function might be constructed by counting objects in pairs, and could obviously be made to conform to condition (2) by simply redefining the elementary unit. The evaluation of the partition function and various averages for a chain of n nodes is contained in the next two theorems.

Theorem B

Let $F(z) = c(z)/d(z)$, where for some finite $\rho > 0$:

(1) $c(z)$ and $d(z)$ have a radius of convergence $> \rho$.

(2) ρ is the unique, simple zero of least modulus of $d(z)$.

Then, for some $\theta_1 > \rho$,

$$[z^n]F(z) = -c(\rho)/d'(\rho)\rho^{n+1} + O(\theta_1^{-n}). \tag{6}$$

Proof

Let $H(z) = c(\rho)/(z - \rho)d'(\rho)$. (The denominator is approximated by the first term of the Taylor's series expansion about the zero of least modulus.) Then $H(z)$ has the same least-modulus singularity as does $F(z)$, and $F(z) - H(z)$ has radius of convergence $> \theta_1 > \rho$ for some θ_1. Thus,

$$[z^n][F(z)-H(z)] = O(\theta_1^{-n}).$$

But

$$[z^n]F(z) = [z^n]H(z) + [z^n][F(z)-H(z)]$$
$$= -c(\rho)/d'(\rho)\rho^{n+1} + O(\theta_1^{-n}),$$

as can be seen by expanding $(z-\rho)^{-1} = -1/\rho(1-z/\rho)$.

Theorem 4 of Ref. 18 is a variation of this theorem applied to a pole of arbitrary weight; it will be our Theorem D. If the singularity is not a simple pole, then the physical system is at a critical point. Theorem B gives the free energy everywhere except at these isolated critical points.

To evaluate certain expectation values we require the following variation of the last theorem.

Theorem C

Let

$$F(x,y) = \sum_{j,k>0} f_{j,k}x^j y^k$$
$$= c(x,y)/d(x,y),$$

where $f_{j,k} \geqslant 0$ for $j,k \geqslant 0$, and c, d are power series. For $n \geqslant 0$, define

$$\langle k \rangle_n = \sum_{k>0} k f_{n,k} \Big/ \sum_{k>0} f_{n,k},$$

if the sums converge and the denominator is nonzero. For the function $F(x,y)$, denote $\partial F(x,y)/\partial x$ by $F_x(x,y)$, etc. Suppose

(C1) $F(z,1)$ and $F_y(x,1)$ have a common finite radius of convergence $\rho > 0$.

(C2) $d(x,1)$ has a unique least-modulus zero at $x = \rho$.

(C3) $c(x,1)$, $d(x,1)$, and $m(x) = c_y(x,1)d(x,1) - c(x,1)d_y(x,1)$ have radius of convergence $\geqslant \rho$.

(C4) $d_x(\rho,1) \neq 0$.

Then, for sufficiently large n, $\langle k \rangle_n$ exists and

$$\langle k \rangle_n = C_1 n + C_2 + O(\theta^n), \tag{7}$$

where

$$C_1 = \frac{d_y(\rho,1)}{\rho d_x(\rho,1)},$$

$$C_2 = C_1 + \frac{d_{xx}(\rho,1)d_y(\rho,1)}{d_x(\rho,1)^2} + \frac{c_y(\rho,1)}{c(\rho,1)} - \frac{d_{yx}(\rho,1)}{d_x(\rho,1)} - \frac{d_y(\rho,1)c_x(\rho,1)}{c(\rho,1)d_x(\rho,1)}, \quad 0<\theta<1.$$

Proof

By (C1) and (C2), the point $x = \rho$ is the unique least-modulus singularity of $F(x,1)$. By (C3) and (C4), $x = \rho$ must be a simple zero of $d(x,1)$ and a simple pole of $F(x,1)$, and $c(\rho,1) \neq 0$.

Define $f_n = \Sigma_{k>0} f_{n,k} = [x^n]F(x,1)$ and $f_n\langle k \rangle_n = \Sigma_{k>0} k f_{n,k} = [x^n]F_y(x,1)$. These exist by (C3). Following Darboux's method described in Theorem B, we estimate f_n and $\langle k \rangle_n$ by finding simpler functions with the same first singularity:

$$f_n = [x^n]\frac{c(x,1)}{d(x,1)}$$
$$= [x^n]\frac{c(\rho,1)}{(x-\rho)d_x(\rho,1)} + O(\theta_1^{-n}) \quad \text{for some } \theta_1 > \rho$$
$$= -\frac{c(\rho,1)}{\rho^{n+1}d_x(\rho,1)} + O(\theta_1^{-n}).$$

To estimate $\langle k \rangle_n$, define $m(x) = d(x,1)c_y(x,1) - d_y(x,1)c(x,1)$. Then

$$f_n\langle k \rangle_n = [x^n]\frac{m(x)}{d(x,1)^2}$$
$$= [x^n]\left(\frac{m(\rho)}{d_x(\rho,1)^2}(x-\rho)^{-2} + \left[\frac{m_x(\rho)}{d_x(\rho,1)^2} - \frac{m(\rho)d_{xx}(\rho,1)}{d_x(\rho,1)^3}\right](x-\rho)^{-1}\right)$$
$$+ O(\theta_2^{-n}), \quad \text{for some } \theta_2 > \rho$$
$$= \frac{(n+1)m(\rho)}{d_x(\rho,1)^2}\rho^{-n-2} - \left(\frac{m_x(\rho)}{d_x(\rho,1)^2} - \frac{m(\rho)d_{xx}(\rho,1)}{d_x(\rho,1)^3}\right)\rho^{-n-1} + O(\theta_2^{-n}).$$

The theorem now follows.

Theorem D

Suppose that the function $F(x) = \Sigma_j f_j x^j$ has only one singularity of least modulus at ρ, and that near ρ, $F(x)$ can be written as an analytic function plus a finite sum of terms of the form $(1-x/\rho)^{-w}g(x)$, where $g(x)$ is analytic near ρ and $g(\rho) \neq 0$. The real part of w is the *weight* of the singularity, and $w \neq 0, -1, -2, \cdots$. Then the dominant term in f_n is contributed by the singularity of highest weight $w = \mathrm{Re}(w)$, and

$$f_n = \frac{g(\rho)n^{w-1}}{\Gamma(w)\rho^n}[1 + O(\theta^n)], \quad \theta < 1.$$

The proof is obtained by expansion of the singular term in a binomial series, and then using Stirling's approximation to evaluate the factorial functions.

We now have the necessary tools to evaluate the free energy, given the generating functions. Theorem A tells us that there will only be one singularity to contend with, Theorems B and C give simple methods to evaluate the equations, and Theorem D enables us to handle critical point.

EXPECTATION VALUES

To evaluate various averages pertaining to the configurations of the adsorbed chains it is convenient to define several auxiliary functions. Let

$$F^t(x,y) = T(xy)^2C(x)/[1-C(x)R(x)],$$
$$F^r(x,y) = T(x)^2C(x)/[1-C(x)R(xy)],$$
$$F^b(x,y) = T(x)^2C(xy)/[1-C(xy)R(x)],$$
$$F^1(x,y) = T(x)^2C(x)/[1-C(x)yR(x)]. \tag{8}$$

It is easily seen that the terms of $[x^n]F^t(x,y)$, for example,

are weighted by factors of y^k, where k is the number of vertices in the tail sequences. Similarly, all vertices in loops are counted in F^r, the bonded vertices are counted with F^b, and the number of loop sequences is contained in F^1. Let $F^c(x,y)$ be any one of these functions that counts objects in class c. The averages that are sought are all of the form

$$\langle k_c \rangle_n = \frac{[x^n]F_y^c(x,1)}{[x^n]F^c(x,1)}$$

which may be evaluated by application of Theorem C, or by Theorem D at a critical point.

EXAMPLE: WALKS ON LATTICES

To illustrate the use of the equations, especially those for the asymptotic analysis, the generating function for paths will be developed.[20] All paths considered are nearest-neighbor walks on the integer half-space $\{(x,y,z)|z\geqslant 0\}$. The walks are normalized by considering only those which touch the plane $P=\{(x,y,z)|z=0\}$ and for which the first point on P is (0,0,0).

For any class X of such walks and any weighing function wt, the *generating function* (gf) is

$$\text{gf} = \sum_{w\in X} \text{wt}(w)x^{|w|},$$

where $|w|$ is the number of vertices in w. Clearly, one might just as well count edges in the paths; the choice is arbitrary.

First consider the gf $R(\sigma,x)$ for all walks that start at (0,0,0) and end on P, with the weighting factor σ for each vertex on P, and one for all other vertices. We determine $R(\sigma,x)$ by dividing the possibilities as shown in Fig. 1. The walk may consist of a single vertex, with gf $=\sigma x$. If the walk has more than one vertex, the first step might be horizontal. The vertex at the origin has a weight σ, and the first step can be in any of four directions. The remainder of the walk has gf $=R(\sigma,x)$, so that these configurations are generated by $4\sigma R(\sigma,x)$, as indicated in the figure. If the first step is vertical, there must be at least one other vertical step in the walk, since $R(\sigma,x)$ counts walks that end on P. The sequence between the first step and the next vertical step that returns to P is generated by $R(1,x)$. The remainder of the walk, beyond the first step that returns to P, is generated by $R(\sigma,x)$. Walks in this class are thus generated by $\sigma xR(1,x)R(\sigma,x)$, so that the recurrence relation for $R(\sigma,x)$ is

$$R(\sigma,x) = \sigma x + 4\sigma xR(\sigma,x) + \sigma xR(1,x)R(\sigma,x) \quad (9)$$

or

$$R(\sigma,x) = \frac{\sigma x}{1-4\sigma x-\sigma xR(1,x)}. \quad (10)$$

For the case $\sigma = 1$, it follows from Eq. (9) that

$$xR(1,x)^2 + (4x-1)R(1,x) - x = 0$$

or

$$R(1,x) = \frac{1-4x-\sqrt{(1-2x)(1-6x)}}{2x}. \quad (11)$$

The next walks to be considered are those that start at (0,0,0) and end anywhere in $\{(x,y,z)|z\geqslant 0\}$. The weights will be as above. The possibilities are displayed in Fig. 2, and these lead to a recurrence relation for the gf $V(\sigma,x)$ of the simple form

$$V(\sigma,x) = \sigma x + 4\sigma xV(\sigma,x) + \sigma xR(1,x)V(\sigma,x) + \sigma xV(1,x)$$

or

$$V(\sigma,x) = \frac{\sigma x[1+V(1,x)]}{1-4\sigma x-\sigma xR(1,x)}. \quad (12)$$

Again, when $\sigma = 1$ it is seen that

$$V(1,x) = \frac{x}{1-5x-xR(1,x)} \quad (13)$$

so that

$$V(\sigma,x) = \frac{[1-4x-xR(1,x)]}{[1-5x-xR(1,x)]}\frac{\sigma x}{[1-4\sigma x-\sigma xR(1,x)]}. \quad (14)$$

From Eq. (13) it follows that walks that begin at (0,0,0) and never return to P are generated by $1+V(1,x)$ if the vertex at (0,0,0) has unit weight.

We now have the pieces needed for the gfs for tail, train, and loop sequences. Tails leave the surface never to return; they are generated by

$$T(x) = 1 + V(1,x) = \frac{1-4x-xR(1,x)}{1-5x-xR(1,x)}. \quad (15)$$

The intervening sequences of trains and loops are generated by

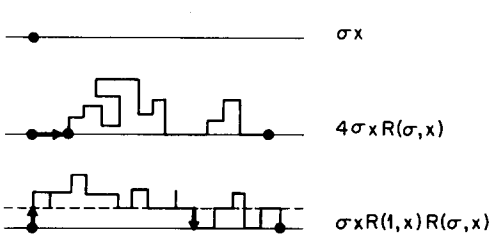

FIG. 1. Terms in the generating function for paths that begin at the origin and end anywhere on the surface. The weight for a vertex on the surface is σ, x is the counting variable, and $R(\sigma,x)$ is the generating function. On the first line, the path consists of a single vertex; on the second, the path takes its first step in any of four directions on the surface, and is then followed by a path in the same class; on the third, the path takes its first step in the vertical direction, it then becomes a path in the class $R(1,x)$ at a lattice layer once removed from the surface, and then it returns to the surface to continue as $R(\sigma,x)$.

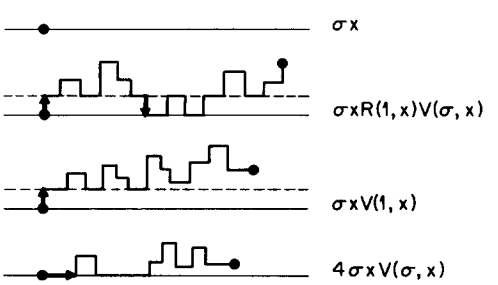

FIG. 2. Same as Fig. 1, but for paths that begin at the origin and end anywhere on or above the surface. The generating function for paths of this class is $V(\sigma,x)$. Otherwise, the terms are constructed much as they are in Fig. 1.

$$R(\sigma,x)=\frac{\sigma x}{1-4\sigma x-\sigma xR(1,x)}=\frac{C(x)}{1-C(x)R(x)}$$

from which it follows that

$$C(x)=\frac{\sigma x}{1-4\sigma x} \tag{16}$$

and

$$R(x)=R(1,x)=\frac{1-4x-\sqrt{(1-2x)(1-6x)}}{2x}. \tag{11}$$

The equation for $C(x)$ is obviously true, and that for $R(x)$ will be seen to be correct on referring to Fig. 1, where the sequence between the vertical steps is stated to have the gf $R(1,x)$. We thus have, for this simple model,

$$F(x)=\left(\frac{1-4x-xR(x)}{1-5x-xR(x)}\right)^2\frac{\sigma x}{[1-4\sigma x-\sigma xR(x)]}. \tag{17}$$

It is of interest to note that the asymptotic behavior of the coefficients of $R(x)$ is

$$r_n\sim(3/2\pi)^{1/2}6^n n^{-3/2} \tag{18}$$

as determined with use of Theorem D. This coincides with the weights for Gaussian random walks[14] to within constant terms that depend upon the details of the models.

EXAMPLE: EVALUATION

The partition function and expectation values will now be evaluated from the foregoing equations for walks on lattices. The free energy will be obtained from Eq. (17) by application of Theorem B, and expectation values for the number of vertices in tails, trains, and loops, and the number of loops, are obtained from Eqs. (8), (11), (15), and (16) by application of Theorem C. There is a critical point in this problem, and it is handled separately with Theorem D.

We begin by simplifying the equation for $T(x)$. Upon substituting Eq. (11) into Eq. (15), it is easy to show that

$$[T(x)]^2=\frac{1-4x+\sqrt{(1-2x)(1-6x)}}{2(1-6x)}, \tag{19}$$

so that Eq. (17) becomes

$$F(x)=\frac{x[1-4x+\sqrt{(1-2x)(1-6x)}]}{(1-6x)[2\sigma^{-1}-1-4x+\sqrt{(1-2x)(1-6x)}]}. \tag{20}$$

Location of pole

When $\sigma=1$, terms in the numerator and denomination of Eq. (20) cancel, and we are left with

$$F(x)=x/(1-6x),\quad \sigma=1. \tag{21}$$

It is easy to see that $[x^n]F(x)=6^{n-1}$ in this case.

It is also instructive to apply Theorem B to Eq. (21). We have $c(x)=x, d(x)=1-6x, \rho=1/6$, and $d'(\rho)=-6$, so that

$$[x^n]F(x)=-\frac{1/6}{(1/6)^{n+1}(-6)}=6^{n-1}. \tag{22}$$

This equation is readily interpreted: There are six choices for each step of the walk, with one vertex fixed at the origin. Clearly Eq. (22) is the partition function for polymer chain that is modeled by a walk on a cubic lattice. Since there is an entropic disadvantage in being attached to the surface, and no energetic advantages, the chain shuns the surface, and in fact acts as if the surface were not present.

For $\sigma\neq 1$, the application of Theorem B requires that one find the zero of least modulus of the denominator of Eq. (20), i.e., the solution of

$$d(\rho)=(1-6\rho)[2\sigma^{-1}-1-4\rho+\sqrt{(1-2\rho)(1-6\rho)}]=0 \tag{23}$$

is required. Either $\rho=1/6$ or

$$2\sigma^{-1}-1-4\rho+\sqrt{(1-2\rho)(1-6\rho)}=0. \tag{24}$$

Since ρ is the zero of least modulus, solution of Eq. (24) requires $\rho\leqslant 1/6$ and $4\rho+1-2\sigma^{-1}\geqslant 0$, or $1/6\geqslant\rho\geqslant 1/2\sigma-1/4$, which implies $\sigma\geqslant 6/5$. Thus, when $\sigma=6/5$, there is a nonsimple zero. In fact, for this case,

$$d(\rho)=(2/3)(1-6\rho)^{3/2}[\sqrt{1-6\rho}+(3/2)\sqrt{1-2\rho}],$$
$$\sigma=6/5. \tag{25}$$

Further examination of this critical point is deferred to a later section.

The following results are thus established: For $\sigma<6/5$ the zero of least modulus is $\rho=1/6$ and is simple; for $\sigma=6/5$ the zero of least modulus is still $\rho=1/6$, but the weight of the pole of $F(x)$ is 3/2; and for $\sigma>6/5$ the zero of least modulus is

$$\rho=\sqrt{(4-3/\sigma)(1-1/s)}-2(1-1/\sigma) \tag{26}$$

by solution of Eq. (24), and again the zero is simple.

Expectation values

The following equations are obtained from Eqs. (8) with use of Eqs. (11), (16), and (19):

$$F^t(x,y)=\frac{x[1-4xy+\sqrt{(1-2xy)(1-6xy)}]}{(1-6xy)[2\sigma^{-1}-1-4x+\sqrt{(1-2x)(1-6x)}]}, \tag{27}$$

$$F^r(x,y)=\frac{xy[1-4x+\sqrt{(1-2x)(1-6x)}]}{(1-6x)[2\sigma^{-1}y-1-4xy+\sqrt{(1-2xy)(1-6xy)}]}, \tag{28}$$

$$F^b(x,y)=\frac{xy[1-4x+\sqrt{(1-2x)(1-6x)}]}{(1-6x)[2\sigma^{-1}-y-4xy+y\sqrt{(1-2x)(1-6x)}]}, \tag{29}$$

$$F^t(x,y)=\frac{x[1-4x+\sqrt{(1-2x)(1-6x)}]}{(1-6x)[2\sigma^{-1}-y-8x+4xy+y\sqrt{(1-2x)(1-6x)}]}. \tag{30}$$

The analysis of these equations will be illustrated with a thorough discussion of Eq. (27), which is typical of the set. There are three cases to consider: $\sigma<6/5$, $\sigma=6/5$, and $\sigma>6/5$. The first and third are covered by Theorem C, and the second by Theorem D.

(i) $\sigma<6/5$. As required by Theorem C, the factor

$$d(x,y)=1-6xy \tag{31}$$

in the denominator of Eq. (27) locates the zero of least modulus. The balance of Eq. (27), i.e.,

$$c(x,y)=\frac{x[1-4xy+\sqrt{(1-2xy)(1-6xy)}]}{2\sigma^{-1}-1-4x+\sqrt{(1-2x)(1-6x)}}, \tag{32}$$

satisfies the conditions of Theorem C. It follows that $d_y(\rho,1)=-1$, $d_x(\rho,1)=-6$, $\rho=1/6$, so that $C_1=1$. Thus, all of the segments are in tail sequences when $\sigma<6/5$.

(ii) $\sigma=6/5$. At the critical point, Eq. (27) may be expressed as

$$F^t(x,y)=\frac{x[1-4xy+\sqrt{(1-2xy)(1-6xy)}][3\sqrt{1-2x}-2\sqrt{1-6x}]}{(1-6xy)\sqrt{1-6x}(2x+5/3)}. \tag{33}$$

The dominant contribution to $[x^n]F^t(x,1)$ is contained in

$$(1-6x)^{-3/2}\frac{3x(1-4x)\sqrt{1-2x}}{2x+5/3}.$$

The other terms in Eq. (33) are of lower weight. The derivative $F^t_y(x,y)$ consists of several terms, the dominant one being

$$(1-6x)^{-5/2}\frac{18x^2(1-4x)\sqrt{1-2x}}{2x+5/3}$$

as may be shown by differentiation of Eq. (33). Application of Theorem D yields

$$\frac{[x^n]F^t_y(x,1)}{[x^n]F^t(x,1)}=\frac{\Gamma(3/2)}{\Gamma(5/2)}n=2n/3. \tag{34}$$

Thus, at the critical point, two-thirds of the segments are in tail sequences.

(iii) $\sigma>6/5$. The zero of least modulus is now determined by the second term in the denominator of Eq. (27). Since this term is independent of y, $d_y(\rho,1)=0$, and the proportion of segments in tail sequences is negligible for large n. In this instance, C_2 in Theorem C is easily computed, as the only term that contributes is $c_y(\rho,1)/c(\rho,1)$. Since

$$c(x,y)=\frac{x[1-4xy+\sqrt{(1-2xy)(1-6xy)}]}{(1-6xy)},$$

one finds

$$C_2=4+\rho\left(\frac{6}{1-6\rho}+\frac{2}{1-1/\sigma}\right)$$

which shows that the tails are only a few segments in length.

The other three equations, (28)–(30), are treated similarly. The following results are obtained:

$$\rho=\sqrt{(4-3/\sigma)(1-1/\sigma)}-2(1-1/\sigma), \tag{35}$$

$$\theta_b=\frac{4\sigma\rho+\sigma-2}{4\sigma\rho\sqrt{(4\sigma-3)(\sigma-1)}}, \tag{36}$$

$$\langle l\rangle_n/n=(1-4\sigma\rho)\theta_b, \tag{37}$$

$$\langle n_l\rangle=\frac{1-\theta_b}{(1-4\sigma\rho)\theta_b}. \tag{38}$$

Here θ_b is the fraction of bound vertices, $\langle l_n\rangle$ is the average number of loops in a chain of n vertices, and $\langle n_l\rangle$ is the ratio of the average number of unbounded vertices to the average number of loops, which is essentially the expected length of a loop. Figure 3 depicts these results for various values of $\ln\sigma=-\epsilon/kT$, where ϵ is the (negative) binding energy and kT has its usual meaning.

DISCUSSION

The critical point at $\sigma=6/5$ deserves attention to determine the nature of the transition that occurs there. The chemical potential μ of a chain segment is given by $\mu=kT\ln\rho$ with use of Theorem B and the rules of statistical thermodynamics. The first temperature derivative of μ is

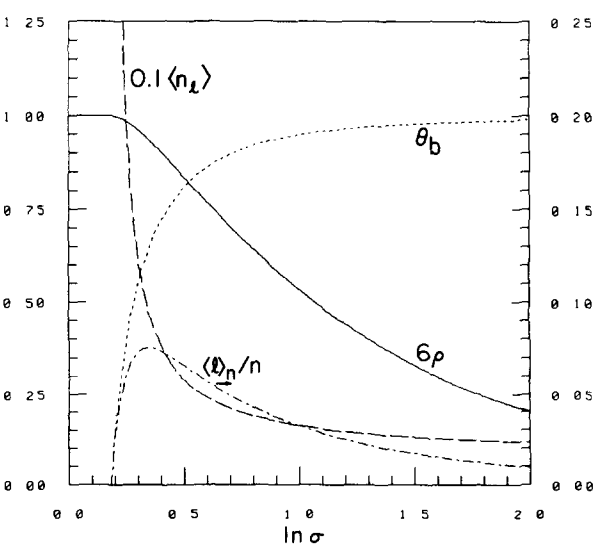

FIG. 3. Results of numerical calculations based on Eqs. (35)–(38). The symbols are defined by those equations and the sequel. Curves for $\langle n_l\rangle$, θ_b, and ρ are to be read from the scale on the left, and that for $\langle l\rangle_n/n$ from the scale on the right. The critical point is at $\sigma=6/5$, $\ln(6/5)=0.18$, and the transition from unbound to bound states that occurs there is of second order.

$$\frac{\partial \mu}{\partial T} = -\frac{d\rho}{d\sigma}\frac{k\sigma}{\rho}\ln\sigma$$

$$= \begin{cases} 0, & \sigma \leqslant 6/5 \\ \dfrac{k\ln\sigma}{\rho}\left[\dfrac{-7+6/\sigma}{2\sqrt{(4\sigma-3)(\sigma-1)}}\right]+2/\sigma, & \sigma > 6/5 \end{cases}$$

which is continuous at the critical point. The second derivative is discontinuous:

$$\lim_{\sigma\to 6/5_-}\frac{\partial^2\mu}{\partial T^2} = 0,$$

$$\lim_{\sigma\to 6/5_+}\frac{\partial^2\mu}{\partial T^2} = -150[k\ln(6/5)]^2,$$

and the transition is thus of second order.

It is important to observe that the loops that are formed in a fairly strongly bound polymer are quite short. For example, Fig. 3 shows that at $-\epsilon/kT = 0.5$, the average loop contains about three vertices. The model leading to this result is based on the lattice, but the generating function, Eq. (4), may be formulated independently of a lattice. It is imperative that more accurate representations of the statistical weights be developed, by means of the rotational isomeric state model, for example, before attaching too much significance to the precise values calculated for this aspect of the adsorbed molecule.

To illustrate how the configurational freedom of the chain might influence the binding, assume that the total (normalized) configuration space available to a segment in d-dimensional space is ω_d. In Eq. (9), the factor 4 in the second term of the right-hand side is replaced by ω_2, and the coefficient of the last term becomes $[(\omega_3-\omega_2)2]^2$. The last follows if it is assumed that $\omega_3-\omega_2$ represents the number of steps that leave a surface to enter 3-space, and one-half of these leave the surface in either the upward or the downward direction. The radical in Eq. (11) then becomes

$$\sqrt{(1-2x)(1-6x)} \to \sqrt{(1-\omega_3 x)[1-(2\omega_2-\omega_3)x]}.$$

The critical point is now located at $\sigma_c = 2\omega_3/(\omega_3+\omega_2)$; for $\sigma < \sigma_c$, $\rho = 1/\omega_3$ and the chemical potential of a segment is $-kT\ln\omega_3$. The critical point depends upon the chain stiffness through ω_3 and the influence of the surface on the chain configurations through ω_2. It is reasonable to assume that the stiffer the chain, the closer is ω_3 to ω_2, and the closer is the critical point to $\sigma = 1$, i.e., zero binding energy. This discussion is not pursued further, since it is only intended to illustrate the versatility of the technique, rather than being definitive on the binding of one type of molecule vs another. A more careful consideration of the configuration statistics of chains would take us far afield of the present purpose.

CONCLUSIONS

The generating functions that have been developed, and the theorems that are used to evaluate the partition functions and averages, have been shown to be easily manipulated and interpreted. One advantage of the technique, at least at this stage of its development, is that it is algebraic to the end, requiring no more than elementary computations for reduction to numerical form. As we consider more intricate problems this will doubtless change, but the salient features of the adsorption problem are now clear.

Polymer chains have much entropy to lose by binding to a surface, and will do so only if the attractive energy is sufficient to overcome this disadvantage. It is interesting to observe that the chain acts as if the surface were not present if the binding energy is too small. Except for a very small range of energies very near to the critical energy, the bound chain is adsorbed very strongly, as evidenced by the shortness of the loops that exist, and the fact that there is a relatively large number of loops. For example, it will be seen on inspection of Fig. (3) that at $\ln\sigma \simeq 0.3$, where the number of loops is maximal, about 1 in 14 segments initiates a loop sequence that is about five vertices long. Approximately 60% of the segments are bound at this energy. This is a consequence of the apparent fact that the entropy of the bound chain is greater when it contains many short sequences than it is when it contains only a few long sequences.

In future papers of this series we will address in succession the problems of adsorption between two parallel planes and multiple chain adsorption. The generating functions for these problems are more intricate, but the method remains powerful.

ACKNOWLEDGMENTS

This work was supported in part by a Department of Energy Grant (DE-FG06-84ER45123) to B.E.E. The authors wish to thank Professor C. Godsil for the hospitality afforded them at the Combinatorics Workshop at Simon Fraser University in July, 1985; this work was conceived at that meeting. Support for the Workshop was provided by Simon Fraser University and the Natural Sciences and Engineering Research Council of Canada. We are also indebted to Professor B. Richmond, Department of Combinatorics and Optimization, University of Waterloo, for supplying the proof of Theorem A. Numerical computations and computer graphics were done by L. Y. Shy.

[1] H. L. Frisch, R. Simha, and F. R. Eirich, J. Chem. Phys. **21**, 365 (1953).
[2] H. L. Frisch and R. Simha, J. Chem. Phys. **27**, 702 (1957).
[3] A. Silberberg, J. Phys. Chem. **66**, 1872 (1962).
[4] A. Silberberg, J. Phys. Chem. **66**, 1884 (1962).
[5] C. A. J. Hoeve, E. A. DiMarzio, and P. Peyser, J. Chem. Phys. **42**, 2558 (1965).
[6] C. A. J. Hoeve, J. Chem. Phys. **44**, 1505 (1966).
[7] R. J. Roe, J. Chem. Phys. **44**, 4264 (1966).
[8] E. A. DiMarzio and R. J. Rubin, J. Chem. Phys. **55**, 4318 (1971).
[9] R. J. Roe, J. Chem. Phys. **60**, 4192 (1974).
[10] J. M. H. M. Scheutjens and G. J. Fleer, J. Phys. Chem. **83**, 1619 (1979).
[11] J. M. H. M. Scheutjens and G. J. Fleer, J. Phys. Chem. **84**, 178 (1980).
[12] H. A. Van der Schee and J. Lyklema, J. Phys. Chem. **88**, 6661 (1984).
[13] J. Papenhuijzen, H. A. Van der Schee, and G. J. Fleer, J. Colloid Interface Sci. **104**, 540 (1985).
[14] G. J. Fleer and J. Lyklema, in *Adsorption from Solution at the Solid/Liquid Interface*, edited by G. D. Parfitt and C. H. Rochester (Academic, London, 1983).
[15] P. J. Flory, *Statistical Mechanics of Chain Molecules* (Interscience, New York, 1969).
[16] I. P. Goulden and D. M. Jackson, *Combinatorial Enumeration* (Wiley–Interscience, New York, 1983).
[17] S. Lifson, J. Chem. Phys. **40**, 3705 (1964).
[18] R. Courant and D. Hilbert, *Methods of Mathematical Physics, Vol. I* (Interscience, New York, 1953), pp. 532–535.
[19] E. A. Bender, Soc. Ind. Appl. Math. Rev. **16**, 485 (1974).
[20] See Ref. 16, Chap. 5.