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Generating function methods for macromolecules at surfaces. II. One molecule between two planes

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The configuration statistics for a macromolecule that is sandwiched between and either repelled or adsorbed by a pair of plane parallel surfaces are developed by means of a generating function technique. The theory is based on our previous work [J. Chem. Phys. **85**, 5299 (1986)] on the problem of a single plane; it has the advantages of simplicity and flexibility. The generating functions that are constructed are used to evaluate expectation values for the lengths of loops, bridges, and tails as well as the number of bound segments. The canonical partition function for a molecule of n lattice steps is extracted from the generating function by use of numerical integration.

INTRODUCTION

The first paper in this series¹ (hereafter referred to as I) dealt with the formulation of a generating function to describe the configurations of a macromolecule of any length that is adsorbed to a single surface. The statistical weights were chosen such that a segment in solution has a weight of unity, whereas a bound segment is given the weight $\exp(-\epsilon/kT)$, where ϵ is the binding free energy relative to the free segment in solution. Here we use the same weighting scheme, and thus are restricted to deal with an infinitely dilute system.

Several previous theories of the adsorption of macromolecules between planes have made extensive use of the matrix method introduced in the seminal work by Rubin² and DiMarzio and Rubin.³ Levine, Thomlinson, and Robinson⁴ studied the multiple chain adsorption problem with use of the transfer matrix method, and showed how this treatment is related to the diffusion equation theory of Edwards.^{5,6} More recently, the research group in Wageningen, The Netherlands, has applied this method to an exceptionally wide range of problems. Among the publications of this group, that of Scheutjens and Fleer⁷ on the adsorption and depletion stabilization of colloids is most closely related to content of the present paper. Furthermore, the generating functions that were introduced by DiMarzio and Rubin³ for the two surface problem are structured much like ours.

There are also close similarities between our method and that so clearly developed by Wiegel and Perelson.⁸ What we have to offer that is new is: (i) simple techniques for constructing recurrence relations for the generating functions that are easy to learn and modify, (ii) theorems that greatly facilitate calculations, especially for long chains, and (iii) methods that are not strictly dependent on a lattice. Although the treatment in I was discussed in terms of a lat-

tice, an indication there of how the statistical weights for successive steps of the walks can be otherwise chosen showed how the method is adaptable to more realistic descriptions of chain configuration statistics. Here too the presentation is in terms of a simple cubic lattice so as to keep the equations as simple as they might be; some of the techniques are based on the work of Goulden and Jackson.⁹

GENERATING FUNCTIONS

The generating functions for walks that are constrained to lie on and between the planes $P_0 = \{x, y, 0\}$ and $P_m = \{x, y, m\}$ are defined much like those in paper I. We now must also consider bridges, and leave open the possibility that the two surfaces have different binding energies. Let subscript α ($\alpha = 0, m$) denote either surface. The generating function for trains (C_α) depends upon the surface, but those for tails (T), loops (R), and bridges (B) do not. All these functions are series of the generic form

$$G(x) = \sum_{n>0} g_n x^n. \quad (1)$$

As in the previous paper, x will mark vertices, so that n in Eq. (1) is the number of vertices in the walk. To develop the recurrence relations for these functions it is convenient to define three auxiliary functions $H^{(m)}(x)$, $V^{(m)}(x)$, and $J^{(m)}(x)$, which will be defined in terms of the types of walks for which they are the generating functions. The superscript will enable us to keep track of the maximum altitude that the walks may attain.

The key to the combinatorics is that the length of a walk formed by concatenating two walks is the sum of the lengths of the latter walks. This is preserved in the product of generating functions. Further reference to this point will not be made.

$H^{(m)}(x)$

Let $H^{(m)}(x)$ denote the generating function for walks that begin at the origin and end on P_0 , and which never touch P_m . The maximum altitude of the walks is thus $m - 1$. There are three distinct possibilities for such walks: (i) they consist of a single vertex, or (ii) they take a first step on the surface, or (iii) the first step is off the surface. These possibilities are depicted in Fig. 1, where the contribution of each to the recurrence relation is also given. (For the present, the walk is taken to lie on the lattice lines of a simple cubic lattice, and the weights are all unity. We will later generalize the weights.) Since $H^{(m)}(x)$ generates all walks of the type specified, and since there are only these three distinct possibilities for the walks, the recurrence relation for $H^{(m)}(x)$ is

$$H^{(m)}(x) = x + 4xH^{(m)}(x) + xH^{(m-1)}(x)H^{(m)}(x) \quad (2)$$

or

$$H^{(m)}(x) = x/[1 - 4x - xH^{(m-1)}(x)] \quad (3)$$

with $H^{(0)}(x) = 0$. Recurrence relations such as Eq. (3) occur in several contexts—notably in the expansion of tridiagonal matrices. Experience with those problems leads one to seek a solution in trigonometric terms. It is found that the solution of the recurrence relation is

$$H^{(m)}(x) = \frac{\sinh(m\phi)}{\sinh[(m+1)\phi]},$$

with $\cosh(\phi) = \frac{1-4x}{2x}$. (4)

This solution, with ϕ real, covers the range $0 < x \leq 1/6$. Unlike the single plane case, there are also solutions for

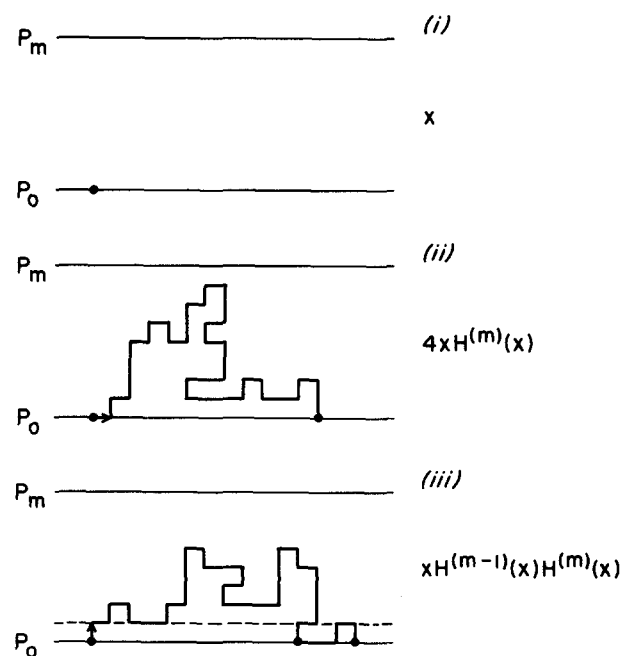


FIG. 1. Various configurations that contribute to the generating function for walks that begin at the origin and terminate on P_0 , and which do not touch P_m . The walks consist of (i) a single vertex, or (ii) the first step is on the surface, or (iii) the first step is off the surface. The generating function for $H^{(m)}(x)$ is the sum of the three contributions.

$1/6 < x < 1/2$, and for these ϕ is a pure imaginary. Alternatively, the hyperbolic functions are replaced throughout by the trigonometric for $1/6 < x < 1/2$.

 $V^{(m)}(x)$

Next consider all walks that begin at the origin and never touch P_m , regardless of where they stop and how many times they touch P_0 . The generating function for walks of this class will be $V^{(m)}(x)$; their maximum altitude is $m - 1$. The walks either end on P_0 or they do not. Those that end on P_0 have the generating function $H^{(m)}(x)$, and those that do not are generated by $H^{(m)}(x)V^{(m-1)}(x)$, as shown in Fig. 2. For the latter, the portion of the walk between $(0,0,0)$ and the last point on P_0 is generated by $H^{(m)}(x)$, and the remainder is contained in $V^{(m-1)}(x)$. The recurrence relation for $V^{(m)}(x)$ is thus

$$V^{(m)}(x) = H^{(m)}(x) + H^{(m)}(x)V^{(m-1)}(x), \quad (5)$$

the solution of which is

$$V^{(m)}(x) = \frac{\sum_{k=1}^m \sinh(k\phi)}{\sinh[(m+1)\phi]} = \frac{\sinh(m\phi/2)}{2 \sinh(\phi/2) \cosh[(m+1)\phi/2]}. \quad (6)$$

 $J^{(m)}(x)$

Walks that are generated by $J^{(m)}(x)$ start at the origin and end on P_m , and touch P_0 and P_m any number of times; their maximum altitude is m . They all have a last vertex on P_0 ; the portion of the walk between $(0,0,0)$ and the last vertex on P_0 is generated by $H^{(m+1)}(x)$. The altitude of this portion of the walk must be m , since $J^{(m)}(x)$ is defined to contact P_m any number of times. The walk then leaves P_0 for the last time, and the remainder of it is generated by $J^{(m-1)}(x)$, as shown in Fig. 3. The recurrence relation for $J^{(m)}(x)$ is

$$J^{(m)}(x) = H^{(m+1)}(x)J^{(m-1)}(x),$$

$$J^{(0)}(x) = H^{(1)}(x), \quad J^{(-1)}(x) = 1 \quad (7)$$

which is solved by

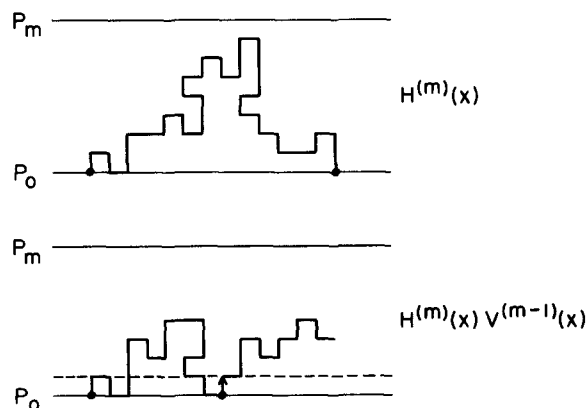


FIG. 2. Walks that begin at the origin and end anywhere below the upper plane P_m and which do not touch P_m consist of (i) walks that end on P_0 , and (ii) those that do not. The walks in the latter category have a last vertex on P_0 , and the remainder of the walk beyond the last step off P_0 is generated by $V^{(m-1)}(x)$.

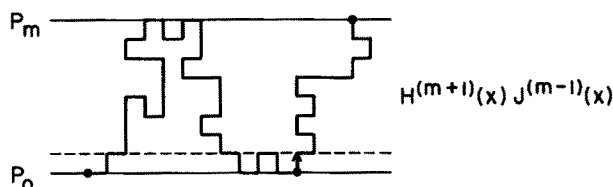


FIG. 3. Walks that begin at the origin and end on P_m , and which touch P_m any number of times have a last vertex on P_0 . The portion of the walk between the origin and the last vertex on P_0 is generated by $H^{(m+1)}(x)$. The walk then steps off P_0 for the last time, and the remainder is generated by $J^{(m-1)}(x)$.

$$J^{(m)}(x) = \frac{\sinh(\phi)}{\sinh[(m+2)\phi]} \quad (8)$$

These functions will be used to construct the generating function for all walks that meander between and on the two surfaces. To construct these walks it is convenient, but not essential, to use an elementary transfer matrix method.

A walk begins and ends with a tail sequence (possibly empty). We will read the configuration from left to right. The initial tail is followed by a sequence generated by $H_\alpha^{(m)}(x)$, followed by a bridge or by a terminal tail. The subscript α signifies that the walk contacts the surface labeled α , on which the binding free energy is ϵ_α . If there is a bridge, the next sequence must be in $H_\beta^{(m)}(x)$, $\beta \neq \alpha$. Then again there is another bridge or the terminal tail, and so on. It is easy to see that

$$F = (TH_0, TH_m) \sum_{k \geq 0} \begin{pmatrix} 0 & BH_m \\ BH_0 & 0 \end{pmatrix}^k \begin{pmatrix} T \\ T \end{pmatrix} \quad (9)$$

generates all configurations. The superscripts and arguments have been temporarily suppressed for clarity. The sum is seen to be

$$\begin{aligned} & \sum_{k \geq 0} \begin{pmatrix} 0 & BH_m \\ BH_0 & 0 \end{pmatrix}^k \\ &= \begin{pmatrix} 1 & -BH_m \\ -BH_0 & 1 \end{pmatrix}^{-1} \\ &= (1 - B^2 H_0 H_m)^{-1} \begin{pmatrix} 1 & BH_m \\ BH_0 & 1 \end{pmatrix} \end{aligned}$$

so that the generating function is

$$F = T^2(H_0 + H_m + 2BH_0 H_m)/(1 - B^2 H_0 H_m). \quad (10)$$

If the statistical weights at the two surfaces are the same, $H = H_0 = H_m$, and Eq. (9) simplifies to

$$F = 2T^2 H/(1 - BH). \quad (11)$$

To complete the evaluation of $F = F^{(m)}(x)$ we need to relate $T^{(m)}(x)$ and $B^{(m)}(x)$ to the generating functions $V^{(m)}(x)$ and $J^{(m)}(x)$ defined above.

A tail sequence is either empty or the first step is off the surface. The former is generated by $x^0 = 1$, and the latter by $V^{(m-1)}(x)$. We thus have

$$\begin{aligned} T^{(m)}(x) &= 1 + V^{(m-1)}(x) \\ &= \frac{\sinh[(m+1)\phi/2]}{2 \sinh(\phi/2) \cosh(m\phi/2)}. \end{aligned} \quad (12a)$$

Alternatively, with use of Eq. (5), this may be written as

$$T^{(m)}(x) = 1 + H^{(m-1)}(x)T^{(m-1)}(x). \quad (12b)$$

The generating function for bridges is obtained from the following observation: A bridge leaves P_α with a vertical step, it then meanders anywhere between and on two planes that are separated by $m-2$ spacings, and it takes a final, vertical step to arrive at P_β . The portion of the walk between the planes separated by $m-2$ spacings is generated by $J^{(m-2)}(x)$. It follows that

$$B^{(m)}(x) = J^{(m-2)}(x) = \frac{\sinh(\phi)}{\sinh(m\phi)} \quad (13)$$

generates bridges containing at least m steps.

If the binding energy ϵ is nonzero, the recurrence relation for $H^{(m)}(\sigma, x)$ is (see I)

$$\begin{aligned} H^{(m)}(\sigma, x) &= \sigma x [1 + 4H^{(m)}(\sigma, x) \\ &\quad + H^{(m)}(\sigma, x)H^{(m-1)}(x)] \end{aligned} \quad (14a)$$

or

$$H^{(m)}(\sigma, x) = \frac{\sigma x}{1 - 4\sigma x - \sigma x H^{(m-1)}(x)}, \quad (14b)$$

where $H^{(m)}(x) = H^{(m)}(1, x)$ and $\sigma = \exp(-\epsilon/kT)$. The solution of this equation is

$$H^{(m)}(\sigma, x) = \frac{\sigma \sinh(m\phi)}{\sinh[(m+1)\phi] - (\sigma - 1)\{4 \sinh(m\phi) + \sinh[(m-1)\phi]\}}. \quad (15)$$

An alternative version of Eq. (14b) follows from the constructions in I. Let $C(x)$ be the generating function for walks, i.e., sequences of trains, on the plane, and further let $R^{(m)}(x)$ be the generating function for loops. It follows from the discussion in I that

$$H^{(m)}(\sigma, x) = C(x)[1 + R^{(m)}(x)C(x) + R^{(m)}(x)C(x)R^{(m)}(x)C(x) + \dots] = C(x)/[1 - C(x)R^{(m)}(x)]. \quad (16)$$

It is clear that Eqs. (14b) and (16) can be combined to give

$$C(x) = \frac{\sigma x}{1 - 4\sigma x} \quad (17)$$

and

$$R^{(m)}(x) = H^{(m-1)}(x) = \frac{\sinh[(m-1)\phi]}{\sinh(m\phi)}. \quad (18)$$

The superscript (m) is not required for $C(x)$, since the generating function for trains on one or another of the planes P_0 and P_m does not depend upon the presence of the other plane.

If the binding free energies on the two planes are not identical, one will be required to define two generating functions for trains, $C_0(x)$ and $C_m(x)$, depending respectively on σ_0 and σ_m . However, the equations are sufficiently lengthy at this point to discourage one from pursuing the general case of unequal binding. We therefore concentrate on the equal binding case, Eq. (11), for which a single σ suffices. The generating function for all walks is readily shown to be

$$F^{(m)}(x) = \frac{\sigma \operatorname{sh}(m\phi) \{ \operatorname{ch}[(m+1)\phi] - 1 \}}{[\operatorname{ch}(\phi) - 1][\operatorname{ch}(m\phi) + 1] \{ \operatorname{sh}[(m+1)\phi] - \sigma \operatorname{sh}(\phi) - (\sigma - 1) \{ 4 \operatorname{sh}(m\phi) + \operatorname{sh}[(m-1)\phi] \} \}}, \quad (19)$$

where, to save typescript, $\operatorname{sh}(\cdot) = \sinh(\cdot)$ and $\operatorname{ch}(\cdot) = \cosh(\cdot)$.

EXPECTATION VALUES

Several probe functions are required to determine the expected number of sequences of various types, or the number of vertices in them. To define these, return to Eq. (11) and substitute Eq. (16) for $H = H^{(m)}(\sigma, x)$ appearing therein to obtain

$$F^{(m)}(x) = \frac{2[T^{(m)}(x)]^2 C(x)}{1 - C(x)[B^{(m)}(x) + R^{(m)}(x)]}. \quad (20)$$

Suppose now that one wants to determine the expected number of vertices in bridges. The function

$$F^b(x, y) = \frac{2[T^{(m)}(x)]^2 C(x)}{1 - C(x)[B^{(m)}(xy) + R^{(m)}(x)]} \quad (21)$$

contains terms of the form $y^k x^n$, where $k, 0 \leq k < n$, is the number of vertices in bridges in a subset of the configurations of a chain of n vertices. Differentiation with respect to y , according to

$$F_y^b(x, 1) = \left. \frac{\partial F^b(x, y)}{\partial y} \right|_{y=1}, \quad (22)$$

yields a series with a factor of $k > 0$ in each term that contains at least one bridge sequence. The expected number of vertices in bridges is then given by

$$\langle n_b \rangle = \frac{[x^n] F_y^b(x, 1)}{[x^n] F(x)}, \quad (23)$$

where $[x^n]$ denotes the operator that extracts the coefficient of x^n in the series that it acts upon. [We will henceforth suppress the superscript (m).] The denominator of Eq. (23) is just the canonical partition function for a chain of n vertices. These techniques have been described in detail in I.

Define $C = C(x)$, $T = T^{(m)}(x)$, etc., and $D = 1 - C(B + R)$, so that Eq. (20) becomes

$$F = 2T^2 C / D.$$

The result of applying the operation in Eq. (22) to Eq. (21) may be written as

$$F^b(x, 1) = 2xT^2 C^2 B' / D,$$

where

$$B' = dB^{(m+1)}(x) / dx.$$

Proceeding in a similar vein, one may formulate the several functions shown in Table I to facilitate the computation of expectation values.

Other details of the paths may be uncovered by "unwinding" the generating function. To investigate configura-

tions that contain no, one, two, etc. bridges, the generating function, Eq. (20), should be written in the form

$$\begin{aligned} F &= \frac{2T^2 C}{(1 - CR)[1 - CB/(1 - CR)]} \\ &= \frac{2T^2 C}{(1 - CR)} + \frac{2T^2 C(CB)}{(1 - CR)^2} + \dots \\ &= \frac{2T^2 C}{(1 - CR)} + \frac{2T^2 C^2 B}{(1 - CR)[1 - C(B + R)]}. \end{aligned} \quad (24)$$

The sequential terms in the series form have 0, 1, 2, etc., bridges. In the second form, Eq. (24), the first term enumerates all configurations with no bridges, while the second counts all the configurations that contain at least one bridge.

Various methods may be used to extract coefficients from the functions in Table I, as required for the application of Eq. (23). For large n , the asymptotic formulas provided by Darboux's Theorem (see I) give good estimates of the coefficients. For small n , the coefficients can be computed directly by finding the Taylor's series expansions for the functions, most conveniently with use of a computer algebra program. The coefficients can also be obtained by numerically evaluating the integral

$$[x^n] G(x) = \frac{1}{2\pi i} \int_C \frac{G(z)}{z^{n+1}} dz, \quad (25a)$$

where the contour C encloses the origin, but does not enclose a pole of $G(z)$.

TABLE I. Functions for the computation of expectation values.

Quantity to be calculated	Required function ^a
Partition function	$T^2 C / D$
Length of each tail	$xTT' C / D$
At least one bridge	$T^2 C^2 B / D(1 - CR)$
Length of one bridge	$xT^2 C^2 B' / D(1 - CR)$
Total length of bridges	$xT^2 C^2 B' / D^2$
Number of bridges	$T^2 C^2 B / D^2$
At least one loop	$T^2 C^2 R / D(1 - CB)$
Length of one loop	$xT^2 C^2 R' / D(1 - CB)$
Total length of loops	$xT^2 C^2 R' / D^2$
Number of loops	$T^2 C^2 R / D^2$
Length of one train	$xT^2 C' / D$
Total length of trains	$xT^2 C' / D^2$
Number of trains	$T^2 C' / D^2$

^a See the text for the definitions of symbols; $D = 1 - C(B + R)$. Note that the factor of 2 in the generating function will cancel from all ratios.

METHODS OF EVALUATION

The calculation of the coefficients $[x^n]G(x)$ from the closed-form expressions given in Eqs. (4), (12a), (13), (18), and (19) is not an easy task. Instead, we have chosen to work exclusively with the generating functions. The lower order coefficients have been evaluated exactly with the use of the developmental computer algebra program SCRATCHPAD II.¹⁰ More extensive results have been obtained from numerical calculations based on Eq. (25a) by the method to be described.

Let $r < \rho$ be the radius of a circle centered on the origin of the complex plane, where ρ is the radius of convergence of $G(z)$. Let $z = r \exp(i\theta)$, so that Eq. (25a) becomes

$$g_n = [x^n]G(x) = \frac{1}{2\pi r^n} \int_0^{2\pi} e^{-in\theta} G(re^{i\theta}) d\theta. \quad (25b)$$

This is an integral with periodic boundary conditions, and the trapezoidal rule gives rapid convergence. Define

$$I_m = \frac{1}{r^n 2^m} \sum_{i=0}^{2^m-1} \exp(-2\pi i n t / 2^m) \times G[r \exp(2\pi i t / 2^m)]. \quad (26)$$

Then it can be shown that $I_1, I_2, \dots \rightarrow g_n$.

Suppose now that $G(z)$ has a pole of order α at ρ . In the vicinity of the pole the integrand in Eq. (25a) is approximated by $\Gamma(\rho)(z-\rho)^{-\alpha} z^{-(n+1)}$, where $\Gamma(\rho)$ is the analytic part of $G(z)$. This function has a minimum at

$$r = \frac{(n+1)}{(n+1+\alpha)} \rho,$$

which would be the point to use in an asymptotic analysis. This, however, is not the best choice of r for numerical evaluation using Eq. (26). We have found that somewhat different values of r give better numerical convergence.

To analyze the numerical integration in more detail, let

$$G(z) = \sum_{j=0}^{\infty} g_j r^j \exp(ij\theta)$$

and

$$I(n, M, r) = \frac{1}{r^n M} \sum_{i=0}^{M-1} \sum_{j=0}^{\infty} g_j r^j \exp[2\pi i(j-n)t/M],$$

where 2^m in Eq. (26) has been replaced by M . The sum on t vanishes unless $(j-n) \bmod M = 0$, which gives the simple result

$$I(n, M, r) = \sum_{k=0}^{\infty} g_{n+kM} r^{kM}.$$

$$\langle n_b \rangle = \frac{9216\sigma^6 + 36480\sigma^5 + 85640\sigma^4 + 149361\sigma^3 + 200898\sigma^2 + 183778\sigma}{131072\sigma^9 + 131072\sigma^8 + 186880\sigma^7 + 260480\sigma^6 + 354346\sigma^5 + 469361\sigma^4 + 604121\sigma^3 + 754100\sigma^2 + 910740\sigma + 1060592} \quad (27)$$

while the expected number of bridges, $\langle n_b \rangle$ for the same values of m and n is given by

$$\langle n_b \rangle = (3072\sigma^6 + 9600\sigma^5 + 18776\sigma^4 + 28197\sigma^3 + 33378\sigma^2 + 27276\sigma) / \text{Denom}, \quad (28)$$

TABLE II. Summary of recurrence relations.

Generating functions	
$C(x) = \sigma x / (1 - 4\sigma x)$	
Initial values:	$R^{(1)}(x) = 0; B^{(1)}(x) = 1; T^{(1)}(x) = 1$
	$R^{(m)}(x) = x / [1 - 4x - xR^{(m-1)}(x)], m > 1$
	$B^{(m)}(x) = B^{(m-1)}(x)R^{(m)}(x), m > 1$
	$T^{(m)}(x) = 1 + R^{(m)}(x)T^{(m-1)}(x), m > 1$
Derivative functions	
Definition: $dG = x dG / dx$	
Initial values:	$dR^{(1)}(x) = 0; dB^{(1)}(x) = 0; dT^{(1)}(x) = 0$
	$dR^{(m)}(x) = R^{(m)}(x)\{1 + R^{(m)}(x)[4 + R^{(m-1)}(x) + dR^{(m-1)}(x)]\}, m > 1$
	$dB^{(m)}(x) = dB^{(m-1)}(x)R^{(m)}(x) + B^{(m-1)}(x)dR^{(m)}(x), m > 1$
	$dT^{(m)}(x) = dT^{(m-1)}(x)R^{(m)}(x) + T^{(m-1)}(x)dR^{(m)}(x), m > 1$

Now, it would appear that to optimize the numerical calculation, one wants to make r as small as possible, so as to force all but the first term in Eq. (26) to be very small, while also making M as large as possible. On the other hand, M should not be too large, or the computation times become excessively long. It was found that rounding errors make the computation unstable for very small r , and that M had to be at least as large as n to get a good approximation to the integral. After some trial and error, it was found that $r = (1 - 10/n)\rho$ is suitable for $n \geq 50$, while for $n < 50$ the value $r = 0.8\rho$ was used. These choices for r , and M in the range from $5n$ to $10n$, gave convergence in most cases to more than 10 decimal digits using 16-digit arithmetic.

The Fortran program generated the functions for various values of m and z with use of the recurrence relations summarized in Table II. A table of exponentials, as required for Eq. (26), was precomputed. After performing the numerical integrations, the averages were calculated as the ratios demanded by Eq. (23) for a large number of values of n , m , and σ .

RESULTS AND DISCUSSION

To illustrate the utility of algebra programs for calculations of the type that are required here, we cite just two results. The expected number of vertices in bridges $\langle n_b \rangle$, for a chain of $n = 10$ vertices confined between planes separated by $m = 4$ edges is found to be

where "Denom" is the same denominator as in Eq. (27). (The polynomial Denom is actually a factor of $1/4\sigma$ times the partition function for a chain of 10 vertices confined by planes separated by 4 step lengths. Cancellation of a factor of 4σ was achieved by SCRATCHPAD II.) From Eqs. (27) and (28) the average number of vertices per bridge, defined as

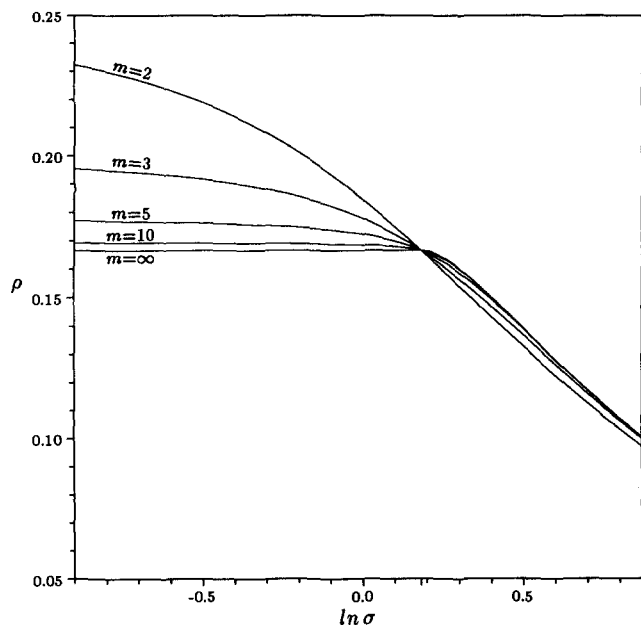


FIG. 4. The location of the singularity $x = \rho$ of the generating function, Eq. (19), as a function of $\ln \sigma = -\epsilon/kT$, where ϵ is the binding free energy to the surface. The figure depicts the variation in the location of the pole for a variety of different spacings m between the planes.

$\langle n_b \rangle / \langle n_B \rangle$, is readily calculated. Other averages were similarly calculated on an IBM 4381 mainframe computer with a code that ran in about 7 min of CPU time.

Extensive results for a wide range of values of σ , m , and n were obtained by numerical integrations described above. Figure 4 shows the location, ρ , of the zero of least modulus of the denominator $D = 1 - C(B + R)$ of the generating function, Eq. (20), for a variety of values of m . The critical point for $m = \infty$ (equivalent to a single chain at a single surface) is at $\sigma = 6/5$.^{1,3} All other curves pass through this point where $\rho = 1/6$, as is most clearly seen from Eq. (19). Expansion of Eq. (19) around $\phi = 0$ shows that, for $\sigma = 6/5$, the generating function varies as ϕ^{-2} . Thus $\phi = 0$, i.e., $x = 1/6$, is a pole of $F^{(m)}(x)$, independent of m .

The real zero of $D = 1 - C(B + R)$ was found to machine precision by bisection. The interval $[10^{-5}, \rho^{(\infty)} - 10^{-7}]$ was inspected for $\sigma > 6/5$, where $\rho^{(\infty)}$ is the location of the zero for $m = \infty$. As shown in I, this value is $\rho^{(\infty)} = [(4 - 3/\sigma)(1 - 1/\sigma)]^{1/2} - 2(1 - 1/\sigma)$. On the other hand, for $\sigma < 6/5$, the zero of the denominator of Eq. (19) is the solution of

$$2 \sin(m\phi)(2 + \cos\phi) = \sigma \{ \sin\phi + 4 \sin(m\phi) + \sin[(m-1)\phi] \}.$$

If σ is very small, $\phi \approx \pi/m$ is an approximate solution. Equation (4), with $\cosh(\phi)$ replaced by $\cos(\phi)$, then gives $x = \rho_{\text{est}} \approx 1/[4 + 2 \cos(\pi/m)]$. Using this estimate, the real zero of D was found in the interval $[1/6, \rho_{\text{est}} - 10^{-5}]$.

The numerical quadratures were performed as described in the previous section, with convergence to a relative precision of 10^{-8} for a range of values of σ , m , and n to be described.

At the level of approximation that we are working at, the various types of sequences do not interact with one an-

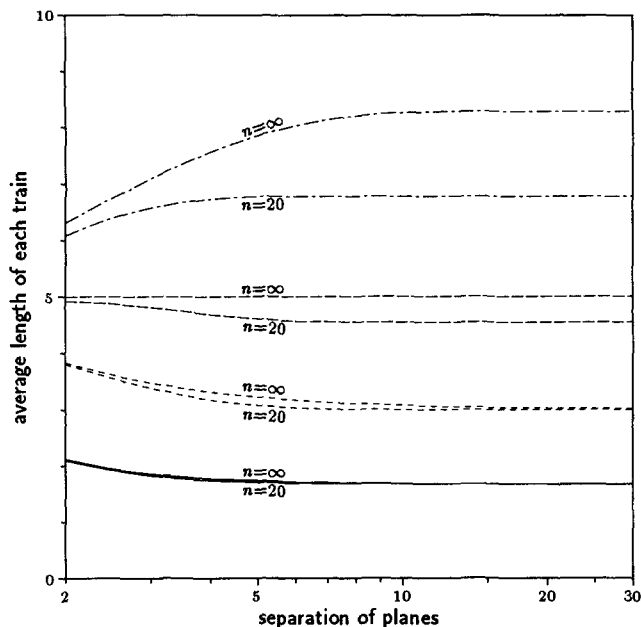


FIG. 5. The average length of each train for $\sigma = 0.6$, —; $\sigma = 1.0$, ---; $\sigma = 1.2$, - - -; and $\sigma = 1.4$, - · - ·; plotted as a function of the separation between the planes for chain lengths of $n = 20$ and $n = \infty$.

other. That is, the average lengths of the first train sequence, say, is the same as the average length of any train sequence. As prescribed in Table I, the average length of a train in a chain of n vertices is given by

$$\frac{[x^n] x T^2 C' / D}{[x^n] T^2 C / D} \quad (29)$$

Results for this quantity are shown in Fig. 5. It is somewhat surprising that even for a repulsive potential, i.e., $\sigma < 1$, there are sequences of trains containing approximately three or fewer vertices, regardless of the value of n . Using the asymptotic techniques in I, it is easy to show that the average length

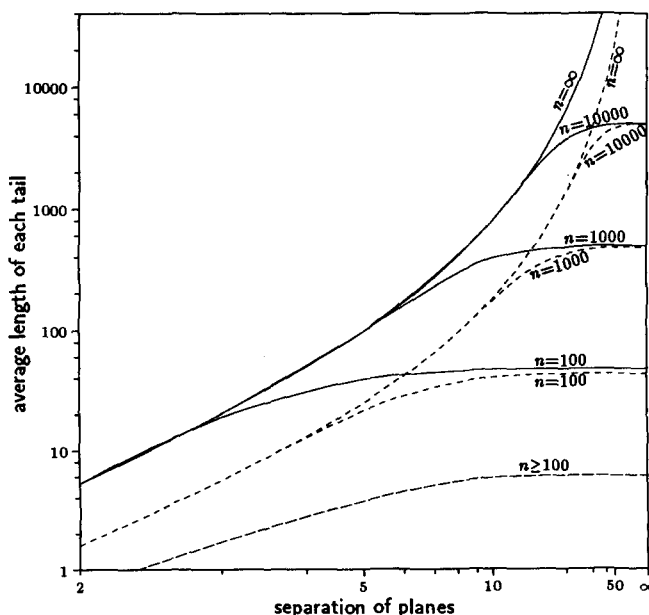


FIG. 6. The average length of the tail segments for $\sigma = 0.6$, —; $\sigma = 1.0$, ---; $\sigma = 1.4$, - - -.

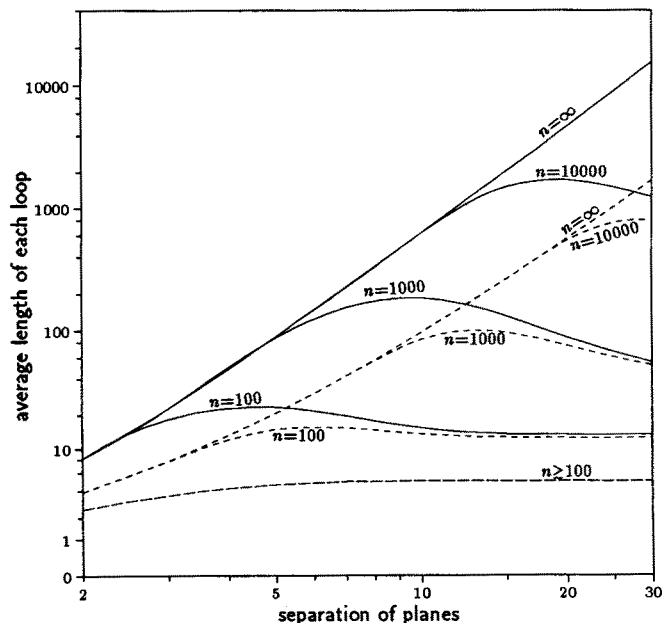


FIG. 7. The average length of loop sequences for $\sigma = 0.6$, —; $\sigma = 1.0$, ---; $\sigma = 1.4$, -.-.

of one train sequence is 3 for $\sigma = 1$, $m \rightarrow \infty$, and $n \rightarrow \infty$. From Fig. 5, it is seen that this limit is essentially reached for $m = 7$ and $n = 20$. As we shall see, there are some properties, such as this one, for which the asymptotic results are quite good for small n . On the other hand, other properties are very sensitive to n .

Tail sequences are highly dependent on n , and in fact on m and σ as well. The average length of each tail is shown in Fig. 6 for a few values of σ and n , as a function of m . It will be noted that the asymptotic, $n \rightarrow \infty$, result will be a good approximation for small n if the binding energy is large, regardless of the distance separating the planes. But, for neutral to repulsive surface interactions, there are significant departures

between the $n \rightarrow \infty$ and finite n results as the spacing becomes large. It is further seen that tail sequences are negligibly short for strong binding, but that they comprise a substantial fraction of the chain if the interaction is repulsive.

We next consider loops, as shown in Fig. 7. As observed in I, the loops are quite short if the binding is strong; the asymptotic result is a good approximation for all $n \geq 100$. For larger binding energy the systematic departures from the $n \rightarrow \infty$ result follow the same qualitative trends as was seen in Fig. 6 for tail sequences. There is an interesting comparison to be made between tails, loops, and bridges (Fig. 8) for small spacings and large n . First of all, these sequences are quite large compared to m . For example, for $\sigma = 0.6$ and $m = 5$, the average length of tail, loop, and bridge sequences are all about 100. That is, a walk that leaves a repulsive surface meanders about between the two planes for quite a large number of steps, and then terminates, returns to the plane from where it started, or lands on the other plane, all more or less indiscriminately.

The maxima for finite n that are seen in Fig. 7 for neutral to repulsive interactions result primarily from the growing length of bridge sequences. By the comments above, a walk that leaves the surface, which it wants to do to avoid an unfavorable interaction, is quite long for even small separations. Loops and bridges are of nearly equal average length for small spacing, but as the planes move apart the bridges *must* become longer, on the average. This increase in bridge length with increasing m robs the loops of some of their segments, and diminishes their length as the planes are pulled apart.

The probability that there is at least one bridge is very strongly dependent on the binding energy, as Fig. 9 shows. First of all, if the chain is much longer than the spacing between planes there will certainly be a bridge, unless the energy is extremely repulsive. Shorter chains, on the other

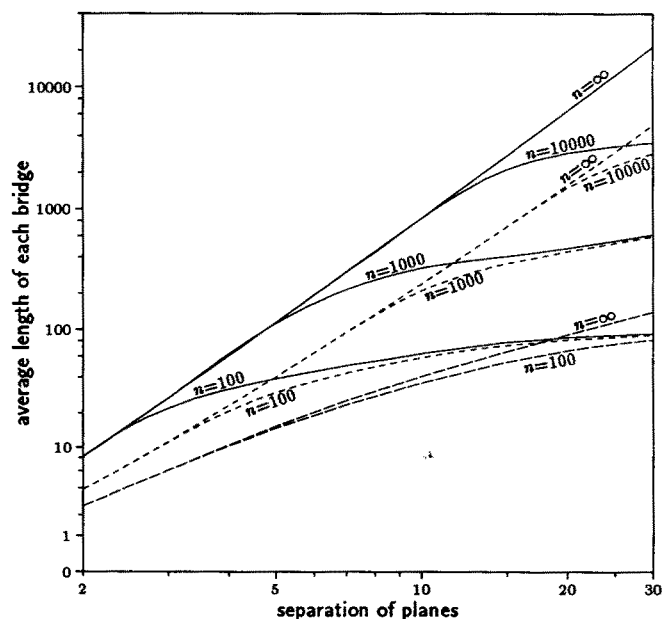


FIG. 8. The average length of bridge sequences for $\sigma = 0.6$, —; $\sigma = 1.0$, ---; $\sigma = 1.4$, -.-.

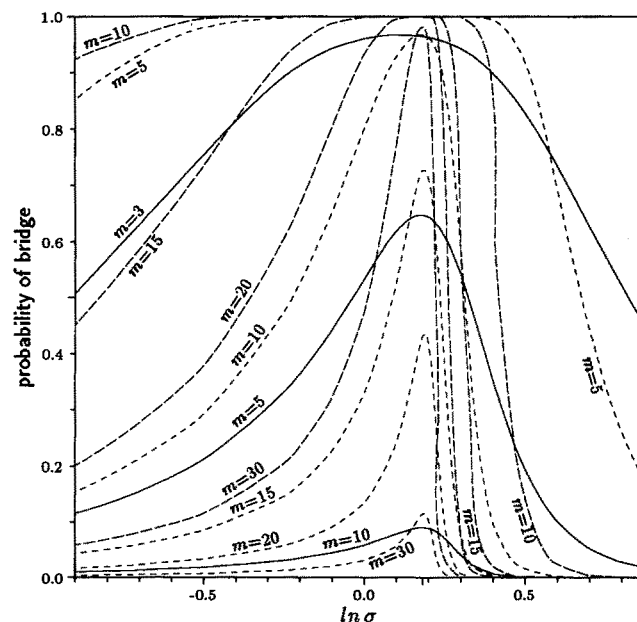


FIG. 9. The probability of occurrence of at least one bridge for chains of length $n = 100$, —; $n = 1000$, ---; $n = 10000$, -.-; the critical point at $\sigma = 6/5$ is indicated by the extra tick at $\ln \sigma \approx 0.18$.

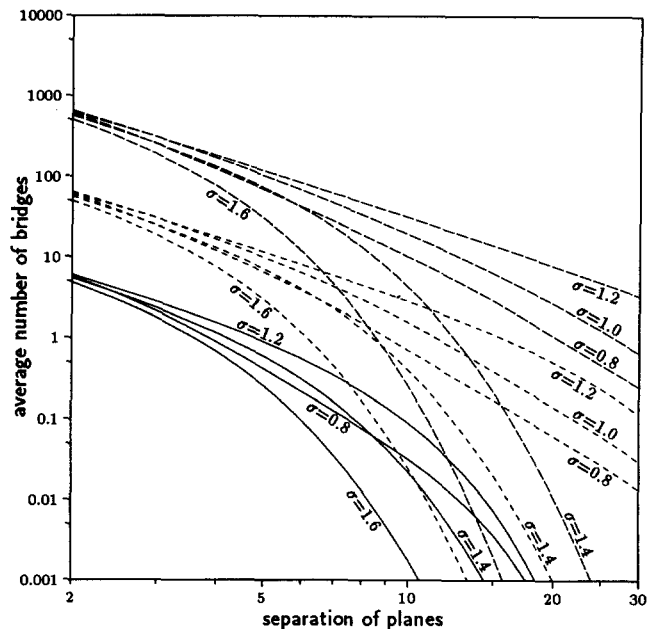


FIG. 10. The average number of bridges for chains of length $n = 100$, —; $n = 1000$, ---; $n = 10000$, - -.

hand, will be pinned to one surface all the more as the binding energy becomes more attractive. Thus, for highly repulsive energies ($\ln \sigma \ll 0$) the chain will be forced to avoid contacts with the surface, and will be a pure tail sequence. For highly attractive energies ($\ln \sigma \gg 0$) the chain will remain on, or very close to, one or the other surface. The probability that a bridge will form is therefore maximal at an intermediate value of σ . This occurs at the critical point $\sigma_c = 6/5$ (shown by the extra tick on the abscissa of Fig. 9) for $n \rightarrow \infty$. For finite n , somewhat smaller values of σ maximize this probability.

The average number of bridges is shown in Fig. 10 for three different chain lengths and for a variety of values of σ . It is instructive to inspect Figs. 9 and 10 to assess the importance of bridging as it might influence the steric stabilization of colloids. Focusing attention on the curves for $n = 1000$, which might represent a typical chain length for steric stabilization applications, one finds that at $\sigma = 6/5$ and $m = 30$ approximately one chain in ten would have a bridge. Now, if the distance between the planes is halved, the probability that there is one bridge increases to ~ 0.7 , and the average number of bridges is about one. If steric stabilization is to be effective, the chains must be tightly bound if the suspension is dense or they will form bridges and induce coagulation.

Before addressing other presentations of the results, a comment about the interplay between entropy and energy in the repulsive regime for small separation of the planes is in order. First of all, if $\sigma < 6/5$ and $m = \infty$, essentially the entire chain avoids the surface; it is just a tail sequence. Now, as the planes approach one another, the chain can either avoid an unfavorable interaction with the planes altogether, in which case it is confined to a domain of breadth $m - 2$, or it can gain some entropy, at the expense of an unfavorable energy, by increasing its span to m and making contact with the surfaces. The dominant configurations are of the latter type.

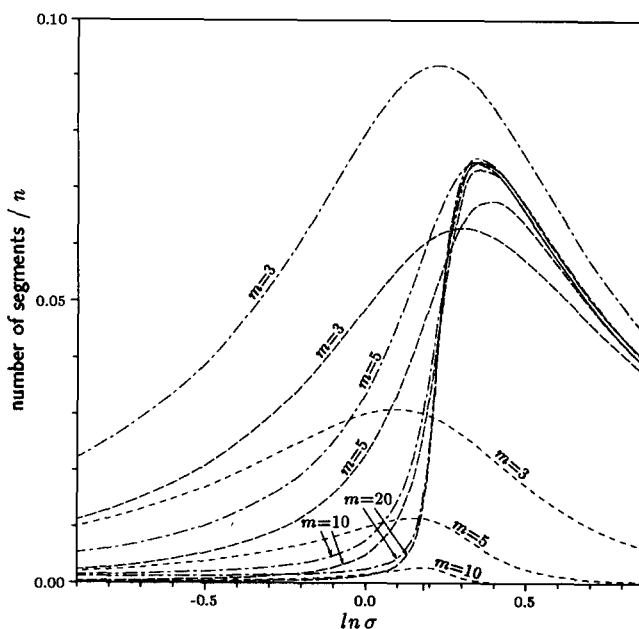


FIG. 11. The average number of sequences of various types for chains of length 1000. Shown are trains, - - -; bridges, ---; and loops, - -; for various values of the spacing m between planes. The critical point at $\sigma = 6/5$ is indicated by the extra tick at $\ln \sigma \approx 0.18$.

The train sequences are not very long on the average (see Fig. 5), and the energy penalty is therefore not too great.

The last several figures will enable us to make comparisons between the various types of sequences. Figure 11 shows the average number of sequences, or segments, relative to the chain length ($n = 1000$ in this case). On inspecting the curves for, say $m = 5$, one finds that there are more trains than loops, and far more loops than bridges. As σ increases the number of bridges falls to zero, and the number of loop segments is constrained to be one less than the number of train segments. The sharp increase in the number of segments of any kind near $\sigma = 6/5$ reflects the fact that at the critical point the units of the chain are drawn equally to the surface and to the gap. The entropy is maximized by having many short segments of the three kinds.

The final rendition of the extensive results of the numerical integrations is the proportion of vertices that are found in the various sequences. The first of these, Fig. 14, shows the proportion of tails, bridges, loops, and trains in chains of 1000 vertices for various values of σ as a function of the separation between the planes. It is seen that if the binding is strong ($\sigma = 1.6$), approximately 80% of the vertices are in trains, and those that are not in trains are almost certainly in loops, as bridges and tails are insignificant. For $\sigma = 1.2$, on the contrary, trains are dominant only for small separations; for $m = 10$ approximately 15% of the vertices are in trains, 50% are in loops, 25% are in bridges, and 10% are in trains. On comparison with Fig. 10, one sees that for these values of σ and m the expected number of bridges is about six, which can also be gleaned from Fig. 11. The bridges are thus 4–5 times larger than m ; the bridge chains meander about a great deal. It will also be seen from Fig. 12

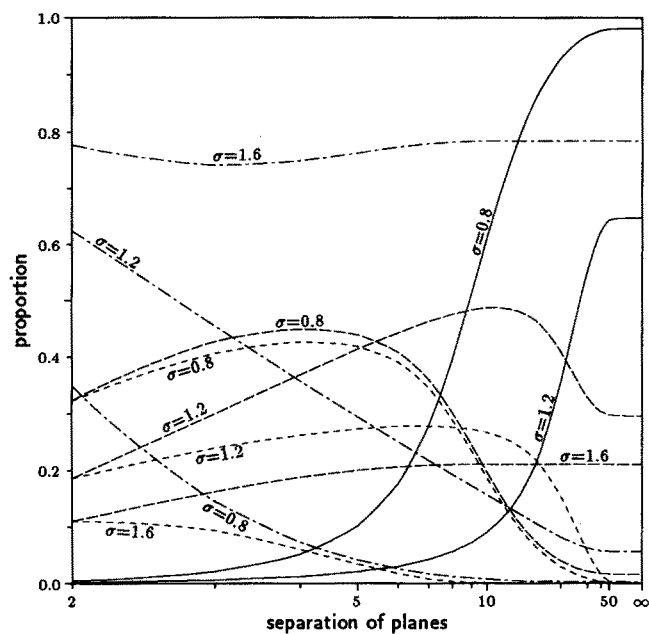


FIG. 12. The proportion of vertices of the chain that reside in the sequences: tails, —; bridges, ---; loops, - - -; trains, - · - ·; for chains of 1000 vertices.

that tail sequences are very important for this value of n when the interaction energy is at or below the critical point when the spacing is large.

Asymptotic results were obtained from calculated values of ρ (Fig. 4) with use of Darboux's Theorem, as explained in I. Tails are never important, for $n \rightarrow \infty$, as is shown in Fig. 13. Instead, loops replace tails. This stands to reason: the proportion of bound vertices is practically the same for $n = 1000$ and $n = \infty$, and therefore the proportion of free segments is about the same. There are only two tails regardless of the value of n , and as $n \rightarrow \infty$ the proportion of vertices in tails must fall to zero. As the chain length grows, an in-

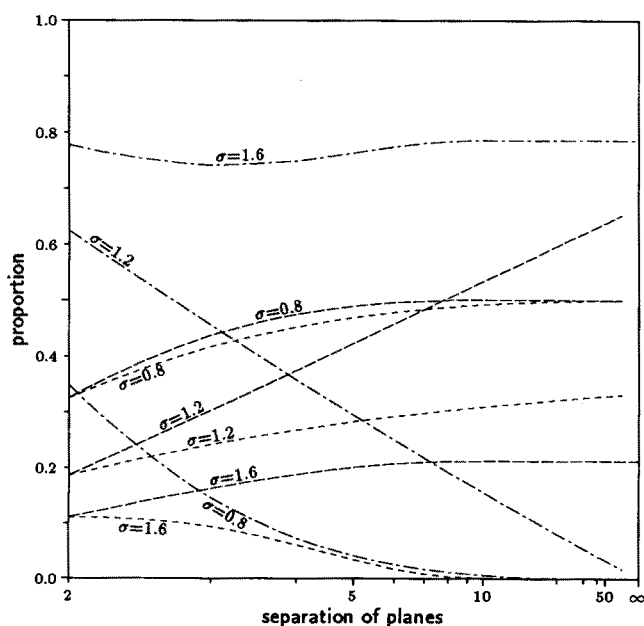


FIG. 13. Same as Fig. 12, but for $n = \infty$. Tails, since there are only two of them, contribute nothing in the long chain limit.

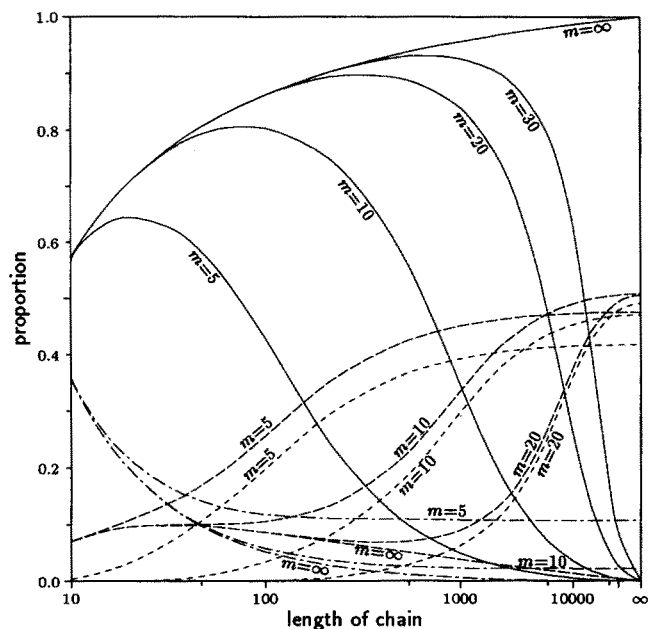


FIG. 14. The population of vertices for $\sigma = 1.0$ for a variety of values of the plane separation as a function of chain length. Shown are the proportion of vertices in: tails, —; bridges, ---; loops, - - -; and trains, - · - ·.

creasing proportion of the vertices are found in loops and bridges for larger separations. Apart from these facts, the general features of the populations for $n = 1000$ and $n = \infty$ are much the same.

The last two figures, 14 and 15, display the chain length dependence of the populations for neutral surfaces ($\sigma = 1.0$, Fig. 14) and for attractive surfaces ($\sigma = 1.6$, Fig. 15). The vastly different behavior of the chain in these regimes is evident. For $\sigma = 1.0$ and n finite, most of the nodes of the chain are in tail sequences, regardless of the value of m for $m \geq 5$. On the other hand, for $\sigma = 1.6$ most of the nodes are in trains, with the remaining approximately 20% residing in

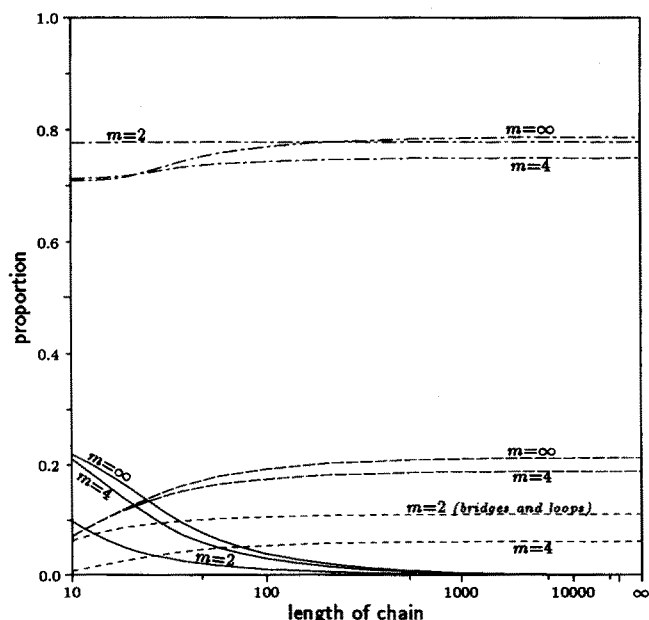


FIG. 15. Same as Fig. 14, but for $\sigma = 1.6$.

loops for $n \geq 100$ and $m \geq 4$. These two figures are most suggestive of the nature of the phases above and below the critical point at $\sigma = 1.2$. As might be surmized, the populations at $\sigma = 1.2$ (not shown) are intermediate between those for $\sigma = 1.0$ and 1.6 .

CONCLUSION

The generating function techniques that were explained and developed in our previous work¹ have been applied to enumerate the configurations of single chains that are sandwiched between two planes. The critical point at $\sigma = 6/5$ separates a phase in which the chain predominantly avoids the surfaces ($\sigma < 6/5$) from one in which it is predominantly at the surfaces. For a given binding energy and small separation of the planes there is a plethora of bridges; as the spacing between the planes increases, bridges become less prevalent while the number of loops increases. Bridges can be expected to form if the separation between the planes is less than about $1/2$ of the root-mean-square end-to-end distance of the polymer chain that is represented by the lattice walks that have been considered here.

ACKNOWLEDGMENT

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