Statistics of a Polymer Molecule in the Presence of Asymmetric Obstacles

Edmund A. Di Marzio

National Institute of Standards and Technology, Gaithersburg, Maryland 20899

Received May 29, 1990; Revised Manuscript Received September 10, 1990

ABSTRACT: The number of configurations $W(N,z;r,\upsilon_r,\alpha_i;M,\beta_i,x_i)$ of a polymer in a field of fixed obstacles is obtained. The cubic lattice of N sites has a coordination number z and is of $d = z/2$ dimensions. The obstacles are modeled as rigid rods or rigid but bent polymers of length r and of volume fraction υ_r. A fraction α_i of the obstacle bonds are oriented in orientation i. The flexible polymer which we place into the field of rigid obstacles is of length M, has β_i of its bonds lying in orientation i, and has an end to-end-length given by x_i. The formula for W results in expectation values only a few percent different from the exact expressions for the known special cases. The β_i are not fixed numbers but rather occur with a probability given by W. With the maximum term method the dimensions of the polymer are calculated. The polymer is elongated in the direction of alignment of the obstacles. The volume of the polymer is found to increase with volume fraction of obstacles for isotropically ordered obstacles, but it decreases for high concentrations of obstacles if the obstacles are strongly aligned. The scaling law exponent ν describing molecular weight dependence of linear polymer dimension is 0.6 for each of the three dimensions but deviates from this value for large elongation. Seven possible applications of the formula are discussed.

I. Introduction

In a recent letter the statistics for a self-avoiding walk (SAW) polymer molecule in the presence of asymmetric obstacles was obtained.[1] A formula was derived that gave the number of configurations for a polymer immersed in a field of other polymers or of rigid rods of any degree of orientation, including unoriented or fully oriented, and in any concentration. In the limit of no obstacles the polymer statistics reduced to those of Flory for a polymer with self-excluded volume. The present paper is a more complete treatment of the problem.

In addition we have discovered that the Huggins version of the Flory–Huggins lattice model is much superior to the Flory version in treating the excluded-volume problem in the limit of no obstacles. In fact, as we will show in section II, the Huggins version gives results that numerically are almost identical with the Nemirovsky–Coutinho–Filho (NCF) field theoretic representation[2] taken to second order. For a square lattice the prediction for entropy per site is only several percent greater than the exact result of Duplantier and Saleur.[3] This is a worst case scenario because mean-field results approach exact results as the lattice coordination number increases. In section III we shall establish the statistics for stepping against nonspherical obstacles such as collections of rigid rods and/or stretched molecules. These statistics are a condensation of a previous work by me that gives the analogue of Huggins statistics for anisotropic distributions of polymer molecules.[4,5] They reduce to Huggins statistics for an isotropic orientation[4] and are known to be accurate for oriented systems.[6–8] In section IV we shall combine the statistics of II and III to evaluate the attrition factor of a nonintersecting polymer in a field of fixed but uniformly placed asymmetric obstacles. The nice feature of this synthesis is that the same physical insight is used to account both for self-interference and for interference with neighboring molecules over the whole range of concentration of obstacles. Section V gives the total number of configurations as the product of the number of configurations for an intersecting random walk times the attrition factor. Equation 5.8 or alternatively eq 5.6 is the main result of this paper. Section VI applies our new-found statistics to the problem of calculating the dimensions of a polymer. The main new feature that arises is that the polymer molecule is no longer spherical on average but rather is elongated in the direction of the rigid rods (if the obstacles are rigid rods) or in the direction of stretch (if the obstacles are stretched molecules). Finally in the discussion section, section VII, a statement of the applicability of the treatment to various polymer problems of interest is made. Also, it is suggested that path integral methods need to be generalized before they can properly describe orientation effects. Appendix A deals with the replica question and shows, I believe, that we are using the right kind of average. Appendix B compares the general formula with known limiting cases. Appendix C discusses the span of the polymer as a more proper measure of polymer size and suggests that the x_i of eq 5.10 can be interpreted as spans.

An important assumption of this work is that of a uniform placement of the fixed obstacles in space rather than a random placement. A real system may sometimes more nearly correspond to a random placement. For such a system we still expect an expansion of polymer size due to obstacles. However there is now an added effect. It is known that a statistical placement of obstacles results in holes or voids that the polymer prefers to be in because of a reduced entropy penalty. The polymer shrinks in size. Thus, the expansion effect that we have calculated here and the contraction effect calculated by Baumgartner and Muthukumar[9,10] (see also Edwards and Muthukumar[11]) oppose each other, and only a combined treatment of the problem can determine polymer size. A complete treatment of the problem involves the statistics developed here, the effects of a statistical placement of the obstacles as well as the fact that a polymer creates its own hole (see Discussion).

II. Excluded-Volume Problem Solved by Huggins Statistics

Let us build up a polymer one segment at a sime from one end and at every stage take proper account of the statistics. The first segment can go anywhere on the lattice. The second on any of z neighboring sites and subsequent segments have $z - 1$ possible sites since we do not allow

0024-9297/91/2224-1595$02.50/0

back stepping. This gives for the number of configuration W

$$W = z(z-1)^{M-2} \tag{2.1}$$

However this expression overcounts the number of configurations because the jth segment can interfere with one of the $j-1$ previously placed segments. The correct expression is

$$W = z(z-1)^{M-2}A \tag{2.2}$$

where the attrition factor A is the probability that M sequential sites chosen at random are distinct (have no overlaps). We write

$$A = \prod_{j=0}^{M-1} p_j \tag{2.3}$$

where p_j is the probability of stepping from the jth site to the $(j+1)$th site. More precisely, p_j is the probability that the $(j+1)$th site is empty given that the previous j sites (on which we placed j segments) were all empty. This expression is arrived at by induction. Obviously the probability that a specific set of j sites are empty is equal to the probability that $j-1$ of them are empty times the conditional probability that the jth site is empty given that the previous $j-1$ were empty. The solution to the excluded-volume problem that uses Flory statistics uses the volume fraction of emptiness for p_j:

$$p_j = 1 - j/N \tag{2.4}$$

The previous j segments are assumed to be spread at random throughout the hypercube consisting of $N = D^d$ sites in d-dimensional space. We obtain the Flory estimate

$$W_F = z(z-1)^{M-2}N!/[(N-M)!N^M] \tag{2.5}$$

A better estimate of p_j can be obtained by using the surface site fraction.[1] A step onto the $(j+1)$th lattice site from the neighboring jth site is successful if the $(j+1)$th site is empty (is a hole) and unsuccessful if the $(j+1)$th site is already occupied. A successful step is proportional to the number of neighbors to holes and an unsuccessful step is proportional to the number of neighbors to polymer. The number of neighbors to holes is $z(N-j)$ and the number of neighbors to the polymer (linear polymer of length j) is $(z-2)j+2$. Thus

$$p_j/(1-p_j) = z(N-j)/[(z-2)j+2] \tag{2.6}$$

Rearranging, we obtain the surface site fraction

$$p_j = z(N-j)/[z(N-j) + (z-2)j + 2]$$

$$1 - p_j = [(z-2)j+2]/[z(N-j) + (z-2)j + 2] \tag{2.7}$$

This yields

$$W_H = z(z-1)^{M-2}(z/2)^M \frac{N!(zN/2 - M + 1)!}{(N-M)!(zN/2+1)!} \simeq \frac{z(z-1)^{M-2}[(N-2M/z)!]^{z/2}}{(N-M)!(N!)^{z/2-1}} \tag{2.8}$$

which is considerably different from the version obtained by using Flory statistics, eq 2.5. The entropy is

$$S_H/kN = (\ln W_H)/N = v \ln (z-1) - (1-v)\ln(1-v) + (z/2 - v)\ln(1 - 2v/z), \quad v = M/N \tag{2.9}$$

In Figure 1 we have adapted a figure from the NCF paper[2] that displays the entropy in two dimensions for several approximations and then added the entropy from eq 2.9 as crosses. There are several observations. First, eq 2.9 gives results virtually identical with those derived by NCF to second order. These results in turn are only a few percent different from the exact results (for 2-D) of Duplantier and Saleur,[3] which are displayed by the solid line. Second, the difference between the mean field result and the exact result is expected to decrease with increasing coordination number and dimension. Thus we have displayed what is probably the worst case. Finally, there is more than just one mean field result. The Flory version, the Huggins version, and the leading term of the NCF expansion displayed in Figure 1 are three examples of mean field results. Many others can be created.

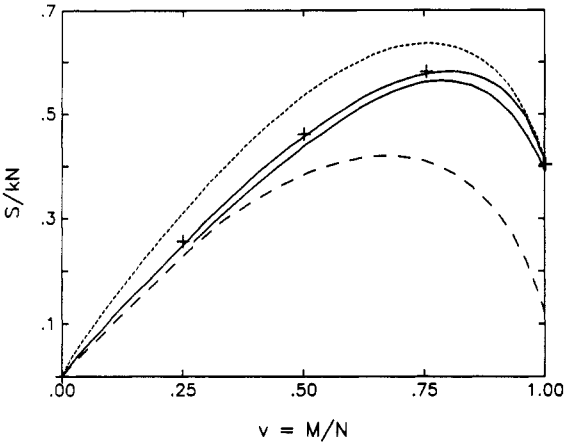

Figure 1. Entropy per lattice site for a polymer of length M on a two-dimensional square lattice of N sites vs volume fraction of the lattice occupied by polymer. Excluded volume is taken into account. Dash–dash, the venerable Flory formula, which though excellent at low concentrations fails at high concentrations. Dot–dot, the leading term of the Nemorovsky–Coutinho–Filho theory. Upper solid curve, the NCF theory to second order, which lies just above the exact results (solid curve) of Duplantier and Saleur. The crosses are from a simple adaptation of the Huggins method to this problem given by eq 2.9.

We called eq 2.5 the Flory version, because it gives results equivalent to those of Flory.[12] However, Flory used logs of probabilities (energy and entropy) rather than probabilities themselves. The use of probabilities allows a very simple treatment of the collapsed region in the SAW problem. The first use of probabilities as the prime variables appears to be in an appendix of a work by Simha.[13] We call eq 2.8 the Huggins version because of the use of the more accurate Huggins statistics.[14] Amazingly, the first use of Huggins statistics to solve the excluded-volume problem for an isolated polymer appears to be in the recent work by Di Marzio[1] and in this work.

III. Statistics for Stepping against Nonspherical Obstacles

If we are on a lattice site and wish to step into an adjacent lattice site, the step will be allowed if the site is empty and prohibited if the site is occupied. Since the site from which we step is a neighbor to the site into which we step, the important quantities are the number of neighbors to holes and the number of neighbors to obstacles. However, these numbers are now direction dependent. To see that this is so, imagine a cubic lattice partially filled with long rigid rods of length-to-width ratio r all aligned in one direction. The rods are the width of a lattice site, and each one occupies r rectilinear lattice sites. If we step along the direction of the rods, there is one possible interference site per rod. If we step perpendicular to the rod, there are r possible interference sites per rod. Our stepping

probabilities are therefore direction dependent. Let V_i be the probability of an unsuccessful step and $1 - V_i$ the probability of a successful step in the $+i$th direction. If the N_r rods all lie in the 3 orientation, then

$$(1 - V_3)/V_3 = N_0/N_r$$

$$(1 - V_2)/V_2 = N_0/rN_r$$

$$(1 - V_1)/V_1 = N_0/rN_r \tag{3.1}$$

where N_0 is the number of empty lattice sites (holes). The numerators represent the number of neighbors to holes in the $-i$ direction, and the denominators are the number of neighbors to rods in the $-i$ direction. Equations 3.1 give

$$V_3 = N_r/[N_0 + N_r]$$

$$V_2 = rN_r/[N_0 + rN_r]$$

$$V_1 = rN_r/[N_0 + rN_r] \tag{3.2}$$

Thus the probability of interference is equal to the mole fraction if we step parallel to the rods and to the volume fraction if we step perpendicular to the rods.

We can generalize this expression to an arbritrary distribution in orientation of the rigid rods if we realize that each rod contributes one interference site if it lies in the stepping direction and r interference sites if it lies perpendicular to the stepping direction. Thus

$$V_3 = [N_{r3} + rN_{r2} + rN_{r1}]/[N_0 + N_{r3} + rN_{r2} + rN_{r1}]$$

$$V_2 = [rN_{r3} + N_{r2} + rN_{r1}]/[N_0 + rN_{r3} + N_{r2} + rN_{r1}]$$

$$V_1 = [rN_{r3} + rN_{r2} + N_{r1}]/[N_0 + rN_{r3} + rN_{r2} + N_{r1}] \tag{3.3}$$

Where N_{ri} is the number of rods lying in orientation i. This expression is easily generalized to hypercubic lattices.

Equations 3.3 can be condensed to a very simple expression that leads to an added insight:

$$V_i = [r - \alpha_i(r-1)]N_r/[N_0 + (r - \alpha_i(r-1))N_r] \tag{3.4}$$

where α *is* the fraction of bonds that lie in orientation i. The reader should convince himself that eqs 3.4 and 3.3 give the same results for rigid rods.

The simple physics behind eq 3.4 is that the second of the two segments that form a bond cannot be an interference site provided the bond is in the same orientation as the step. Only the segment adjacent to the lattice site from which we are stepping can be an interference site for a step whose length is that of one bond. The second segment being two steps away is too far away to be stepped into. It is shielded by the first segment. Thus a rigid rod in orientation i displays only one interference site to a step in direction $+i$ since it has $(r-1)$ bonds in orientation i and the downstream segment of each bond is shielded by the previous segment and can never be an interference site. However, for molecules lying perpendicular to the step direction each segment is a possible interference site.

Equation 3.4 is also applicable to (obstacles consisting of) flexible but stretched polymer molecules! In stepping against a stretched molecule we have $r - \alpha_i(r-1)$ possible interference sites since each of the $\alpha_i(r-1)$ bonds lying in the step direction shields one segment. One easily proves that any reordering of the bonds within a chain that preserves the value of α_i also preserves the number of shielded sites. Also, one easily proves that eq 3.4 is valid for a system of polymers in which α_i (i.e., the set α_1, α_2, α_3) describes the average orientation of the system. Each polymer need not have identical values of α_i.

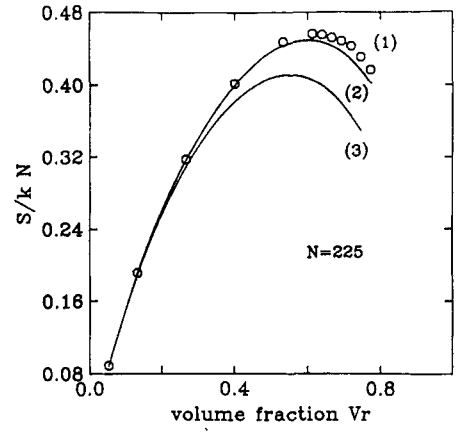

Figure 2. Entropy per lattice site for an isotropic distribution of rigid-rod trimers on a square lattice as a function of the volume fraction of the lattice occupied by trimers. Adapted from ref 7: (1) Monte Carlo results, which are presumed to be exact; (2) the Huggins version; (3) the Flory version.

A Flory–Huggins lattice calculation using eq 3.4 has been used to obtain the entropy for systems of ordered rigid rods[4,5] and stretched molecules.[15,16] It is perhaps not generally appreciated by the polymer community how accurate these statistics are. Figure 2 displays the entropy per site for a system of trimers on a 2-dimensional lattice. There are equal numbers of molecules in the two orientations. The circles are Monte Carlo calculations from ref 7 and can be taken to be exact within the accuracy of the plot. The curve using the above statistics, which for isotropic orientation is equivalent to Huggins statistics, is accurate to within several percent. The lowermost curve uses Flory statistics and is not nearly as accurate. The statistics are even more accurate for partially ordered systems, becoming exact in the limit of complete orientation (in the thermodynamic limit). The statistics give results equivalent to the Freed–Bawendi expansion up to third order.[8]

One can use the idea of shielded segments to evaluate entropies for disks as well as rods and for molecules thicker than one lattice site. Herzfeld, using similar ideas, has calculated the entropy of a system of molecules represented by orthogonal parallelepipeds of arbritrary dimensions.[17]

Finally, we make the observation that eq 3.4 is valid for arbritrary dimension. As a check we can recover the surface site fraction from 3.4 for an isotropic system in $d = z/2$ dimensions by substituting $\alpha_i = 2/z$ and obtaining

$$V_i = [(z-2)r + 2]N_r/[zN_0 + ((z-2)r + 2)N_r] \tag{3.5}$$

We shall use this expression in the next section.

IV. Evaluation of the Orientation-Dependent Attrition Factor

The expression for the attrition factor A is still the same function of p_j for it (eq 2.3) is nothing more than a formula for the probability of a compound event, but p_j itself is now different. When we place the jth segment, we can have interferences from either the previously placed segments of the same molecule or we can have interferences from segments of the other molecules (obstacles). This is a tricky situation, so we shall proceed slowly. The simplest case to solve as if the V_i are all equal. The polymer is forced to reside in a volume of N sites. As we go to place

the $(j+1)$th segment, the total number of segments in the volume is $j + v_r N$, where v_r is the volume fraction of obstacles ($v_0 = 1 - v_r$). The number of empty lattice sites is $N - j - v_r N = v_0 N - j$. The surface site fraction is then

$$p_j = z(v_0 N - j)/[z(v_0 N - j) + (z-2)j + 2 + ((z-2)r + 2)v_r N/r] \quad (4.1)$$

The numerator is the number of neighbors to holes, and the denominator is the sum of the number of neighbors to holes, the number of neighbors to polymer, and the number of neighbors to obstacles. W is easily calculated and is

$$W = z(z-1)^{M-2}(z/2)^M \times \frac{(v_0 N)!((z/2)N[1 - v_r 2(r-1)/zr] - M + 1)!}{(v_0 N - M)!((z/2)N[1 - v_r 2(r-1)/zr] + 1)!} \quad (4.2)$$

For the case of no obstacles this reduces to eq 2.8.

Let us now solve the problem when the obstacles are ordered and when the polymer is ordered. As before α_i represents the fraction of bonds of obstacle molecules that lie in orientation i. We define β_i to be the fraction of bonds in the polymer that lie in orientation i. p_j is now orientation dependent, so we indicate it as $p_j(i)$. $p_j(i)$ is a random variable. It equals $p_j(i)$ with probability β_i because at stage j we lay down the jth bond in orientation i with probability β_i. If we step from site j to site $j+1$ in the ith direction, then we need to know the number of neighbors to holes in the $-i$th direction which is $N - j - v_r N = v_0 N - j$, and we need to know the number of neighbors to polymer in the $-i$th direction, which is $[r - \alpha_i(r-1)]v_r N/r + [j - \beta_i(j-1)]$. The first bracketed term is the number of neighbors to obstacles, and the second bracketed term is the number of neighbors to the j-mer. The probability of a successful step is then

$$p_j(i) = [v_0 N - j]/[v_0 N - j + (r - \alpha_i(r-1))v_r N/r + (j - \beta_i(j-1))] \quad (4.3)$$

Obviously the probability of stepping is independent of whether we step in the plus or minus direction, $p_j(-i) = p_j(+i) = p_j(i)$. Also, $\sum \beta_i = 1$, and the probability of a successful step plus the probability of an unsuccessful step equals 1. These are two probabilities involved here. The first is the probability of attempting a step in the ith direction, i.e., β_i, the second is the probability of success when this step is attempted, i.e., $p_j(i)$.

The attrition factor for the molecule is

$$A(z,N;\alpha_i,v_r,r;\beta_i,M) = \prod_{j=0}^{M-1}[\prod_{i=1}^{z/2}[p_j(i)]^{\beta_i}] \quad (4.4)$$

where the walk is on a $z/2$-dimensional hypercube of N lattice sites. A fraction v_r ($v_r = 1 - v_0$) of the sites are occupied by obstacles consisting of oriented polymers of molecular weight r. The number of bonds lying in orientation i is α_i. The polymer we are building has β_i of its M bonds lying in orientation i. Equation 4.4 expresses A as a product over j of geometric means. One might be tempted to use instead of eq 4.4 the quantity

$$A = \prod[\sum \beta_i p(i)] \quad (4.5)$$

which is a product over j of arithmetic means. In appendix A we argue for the validity of eq 4.4. The attrition factor A can be easily evaluated. For each i we can represent the product over j as a product of factorials. The numerator of eq 4.3 leads to $(v_0 N)!/(v_0 N - M)!$. The denominator can be represented as the ratio of two factorials by first factoring out a β_i. We obtain

$$A = \frac{(v_0 N)!}{(v_0 N - M)!} \times \prod_{i=1}^{Z/2}\left\{\frac{\beta_i^{-\beta_i M}\left[\left(\frac{v_0 N + (r - \alpha_i(r-1))v_r N/r}{\beta_1} - M + 1\right)!\right]^{\beta_i}}{\left[\left(\frac{v_0 N + (r - \alpha_i(r-1))v_r N/r}{\beta_i} + 1\right)!\right]^{\beta_i}}\right\} \quad (4.6)$$

The contribution to the entropy arising from eq 4.6 requires a little more labor. One can show that

$$\frac{\ln(A)}{v_0 N} = -\left(1 - \frac{M}{v_0 N}\right)\ln\left(1 - \frac{M}{v_0 N}\right) - \sum_{i=1}^{Z/2}\left(1 + \frac{v_r(r - \alpha_i(r-1))}{v_0 r}\right)\ln\left(1 + \frac{v_r(r - \alpha_i(r-1))}{v_0 r}\right) + \sum_{i=1}^{Z/2}\left(1 + \frac{v_r(r - \alpha_i(r-1))}{v_0 r} - \frac{\beta_i M}{v_0 N}\right) \times \ln\left(1 + \frac{v_r(r - \alpha_i(r-1))}{v_0 r} - \frac{\beta_i M}{v_0 N}\right) \quad (4.7)$$

In Appendix B, eq 4.6 is compared to known special cases. It represents them accurately and we presume that eq 4.6 or equivalently eq 4.7 is accurate for intermediate cases as well.

One might be tempted to evaluate the configurational entropy by adding the expression $\ln(z(z-1)^{M-2})$ to $\ln(A)$. But this is incorrect because the number of steps in the plus direction is unequal to the number in the minus direction when the polymer is being elongated. This means that we must replace the factor $z(z-1)^{M-2}$. This problem is addressed in the next section. As we have pointed out, the attrition factor is independent of whether the steps are in the plus or minus directions; it depends only on the number in each *orientation*.

V. Statistics for a Self-Excluded-Volume Polymer in a Field of Nonspherical Molecules

In the absence of excluded volume, the number of configurations W_0 for a chain of $M+1$ monomers is easily calculated as a problem in combinatorics. If the only constraint is that $\beta_i M$ bonds lie in *orientation* i, we have

$$W_0 = M!/\prod(\beta_i M)! \quad (5.1)$$

Suppose we were to further constrain the system so that $\beta_{i+}M$ of the bonds lie in *direction* $+i$ and $\beta_{i-}M$ of the bonds lie in *direction* $-i$. The number of configurations would then be given by

$$W_0 = M!/\prod(\beta_{i+}M)!\prod(\beta_{i-}M)! \quad (5.2)$$

One way to have direction as well as orientation is to fix the end-to-end length with components x_i. Then since $\beta_{i+} + \beta_{i-} = \beta_i$ and $x_i = \beta_{i+}M - \beta_{i-}M$ imply that

$$\beta_{i+}M = (\beta_i M + x_i)/2 \qquad \beta_{i-}M = (\beta_i M - x_i)/2 \quad (5.3)$$

we obtain

$$W_0 = M!/\prod((\beta_i M + x_i)/2)!\prod((\beta_i M - x_i)/2)! \quad (5.4)$$

This exact result can be changed into the less exact but

more easily recognized and perhaps more convenient form by use of Stirling's approximation:

$$W_0 = 2^M \frac{M! \exp(-\sum x_i^2/2\beta_i M)}{\prod(\beta_i M)! \prod(\sqrt{2\pi\beta_i M})} \quad (5.5)$$

The total number of configurations consistent with a given specification β_i and α_i is given by the product of A and W_0:

$$W = W_0 A \quad (5.6)$$

with W_0 given by eq 5.5 and A given by eq 4.6. The entropy is a function of $5 + 3d$ different variables (equals 14 in three dimensions):

$$S = k \ln (W) = S(N,z;r,v_r,\alpha_i;M,\beta_i,x_i) \quad (5.7)$$

The two variables characterizing the lattice are N, the number of lattice sites comprising the box in which the polymer is confined, and z, the coordination number of the lattice, which for cubic lattices is equal to twice the dimension d. In this paper we have avoided the complications that arise when $d \neq z/2$. They can be dealt with later by the methods used in a previous publication.[4] The $2 + d$ variables that characterize the obstacles that can be either rigid rods or flexible polymer are r, the length of the rod or polymer, v_r, the volume fraction of rods or polymer, and α_i, the fraction of bonds lying in orientation i. The $1 + 2d$ variables that characterize the nonintersecting random walk are the number of steps M, the fraction of bonds β_i lying in orientation i, and the components of the end-to-end vector, x_i. Our final result is

$$S/k = M \ln 2 - {}^1/_2 \ln (2\pi M) - \sum[\beta_i M \ln \beta_i + x_i^2/2\beta_i M + {}^1/_2 \ln \beta_i] + v_0 N[-(1-D)\ln(1-D) - \sum(1+E_i)\ln(1+E_i) + \sum(1+E_i-\beta_i D)\times \ln(1+E_i-\beta_i D)] \quad (5.8)$$

where

$$D = M/v_0 N \qquad E_i = (1-\alpha_i(r-1)/r)v_r/v_0 \quad (5.9)$$

$$\sum \alpha_i = 1 \qquad \sum \beta_i = 1 \quad (5.10)$$

$$1 + E_i = \frac{v_0}{v_0} + \frac{[1-\alpha_i(r-1)/r]v_r}{v_0} = \frac{1 - v_r\alpha_i(r-1)/r}{v_0} \quad (5.11)$$

Equation 5.8 for the entropy is the main result of this paper.

In section VI we shall determine the size of the polymer by a maximization of the entropy. This requires that we now express the dimensions of the molecule in terms of the parameters of the theory that describe the molecule. They are β_i, M, and x_i. Conventional wisdom has been to imagine the polymer confined within a bag whose radius is the end-to-end length of the polymer so that the volume of the polymer was $4\pi r^3/3$. This gave good results previously.[18] The use of radius of gyration or span or Hollingsworth radius as a measure of polymer size gave equivalent results.[19] In section II the polymer was confined to a (hyper)cube whose volume is equal to N. Because we expect the polymer to be elongated by oriented obstacles, we imagine that the cube becomes a rectangular parallelepiped. We therefore have

$$N = \prod a_i \quad (5.12)$$

where a_i are the polymer sizes in each direction.

If the distribution function of the obstacles has cylindrical symmetry, then the parallelepiped will have a square cross section. But of course we do not expect a polymer to have square corners, so that an ellipsoid of revolution would be more realistic. The relevant mensuration formulas are in our real world of three dimensions:

$$N = a^2 b \quad \text{for parallelipiped of square cross-section} \quad (5.13a)$$

$$N = \pi a^2 b/6 \quad \text{for ellipsoid of revolution} \quad (5.13b)$$

where in each case $a = a_1$ is the width and $b = a_3$ the length. The polymer is imagined during the calculation to have constant density within the volume and zero density without. Assuming otherwise makes the problem too difficult. Once a and b are obtained, they can be used as measures of the smooth density distribution functions that characterize real polymers. In the remainder of this paper we shall assume cylindrical distribution functions for the obstacles and formulas 5.13 for the shape of the imbedded molecule. We now assume that $a_i = x_i$, where x_i are the coordinates of the end-to-end length in our equations. The assumption that end-to-end length is the proper measure of polymer size is not obvious when we consider that a ring polymer has a size even though it does not have an end-to-end length. In Appendix C we discuss the use of the span as a alternate measure of polymer size,[20] and in the course of this discussion provide added justification for the use of eq 5.5. as a probability distribution function for polymer size for the case of an intersecting random walk.

VI. Determination of Molecular Size by Maximization of the Entropy

The polymer chain is specified by the fraction of bonds in each of the three orientations in space, β_1, β_2, β_3, and by the three coordinates of its end-to-end length x_1, x_2, x_3. W, properly normalized, gives the probability distribution for these variables, and the moments are given by

$$\langle x_1^m x_2^n x_3^o \beta_1^p \beta_2^q \beta_3^r \rangle = \frac{\int x_1^m x_2^n x_3^o \beta_1^p \beta_2^q \beta_3^r W \, dx_1 \, dx_2 \, dx_3 \, d\beta_1 \, d\beta_2 \, d\beta_3}{\int W \, dx_1 \, dx_2 \, dx_3 \, d\beta_1 \, d\beta_2 \, d\beta_3} \quad (6.1)$$

Instead of eqs 6.1 we shall use the maximum term method to estimate the expected values of the x's and the β's. We shall work only with the entropy so that the phenomena that depends only on the entropy will be starkly displayed. According to the method of undetermined multipliers the values of the x's and the β's that maximize S are obtained by equating to zero the derivatives of $S + \lambda(1 - \sum\beta_i)$ with respect to these variables. Recognizing that the volume of the polymer is given by eq 5.12 and that $\partial N/\partial x_i = N/x_i$ and that $\partial D/\partial x_i = -D/x_i$, we obtain

$$-\ln \beta_i - 2 + x_i^2/2\beta_i^2 M^2 - 1/2\beta_i M - \ln(1 + E_i - \beta_i M/v_0 N) = k\lambda/M \quad (6.2)$$

$$x_i^2/\beta_i M = v_0 N[-\ln(1 - M/v_0 N) + \sum_{j=1}^{3}(1+E_j)\ln(1 - \beta_j M/v_0 N[1+E_j])] \quad (6.3)$$

These six equations plus the equation of constraint on β_i determine the x's and β's.

The first observation we make is that the right-hand side of eq 6.3 is independent of i, so that

$$x_1^2/\beta_1 M = x_2^2/\beta_2 M = x_3^2/\beta_3 M \tag{6.4}$$

This does not mean however that x_i varies as the square root of $\beta_i M$ because the right-hand side is a function of M and N.

We now restrict ourselves to the case of $\alpha_1 = \alpha_2$. Substituting from eq 6.4 into eq 6.2, we find that $\beta_1 = \beta_2$. Equation 6.4 then yields $x_1 = x_2$. These values represent an orthogonal parallelepiped, or with the mensuration formula 5.13b these values represent (to within small multiplicative factors) a cylindrically symmetric molecule. We now have four equations to determine x_1, x_3, β_1, and β_3:

$$-\ln(\beta_1) + x_1^2/2\beta_1^2M^2 - 1/2\beta_1 M - \ln(1 + E_1 - \beta_1 M/v_0 N) = -\ln(\beta_3) + x_3^2/2\beta_3^2M^2 - 1/2\beta_3 M - \ln(1 + E_3 - \beta_3 M/v_0 N) \tag{6.5}$$

$$\beta_3 = 1 - 2\beta_1 \tag{6.6}$$

$$x_1^2/\beta_1 M = x_3^2/\beta_3 M = v_0 N[-\ln(1 - M/v_0 N) + \sum_{j=1}^{3}(1 + E_j)\ln(1 - \beta_j M/v_0 N[1 + E_j])] \tag{6.7}$$

These equations are presumably valid over the whole range of variables. For large molecular weight, M, and provided the polymer is not elongated so much that its length is proportional to molecular weight, we have

$$\ln(\beta_1) + \ln(1 + E_1) = \ln(\beta_3) + \ln(1 + E_3) \tag{6.8}$$

Which in conjunction with 6.6 yields

$$\beta_1 = \frac{1 - v_r\alpha_3(1 - 1/r)}{(3 - 2v_r\alpha_3(1 - 1/r) - v_r\alpha_1(1 - 1/r))} \tag{6.9}$$

$$\beta_3 = \frac{1 - v_r\alpha_1(1 - 1/r)}{(3 - 2v_r\alpha_3(1 - 1/r) - v_r\alpha_1(1 - 1/r))} \tag{6.10}$$

The β's of these equations have the properties that we would expect on intuitive grounds. First, for $\alpha_1 = \alpha_2 = \alpha_3 = {}^1/_3$ we would expect the β's to be equal to ${}^1/_3$ and they are. Second, for $r = 1$, which is a symmetric placement of obstacles, we would expect the b's to be again equal to ${}^1/_3$ and they are. Third, suppose that v_r is close to 1 and α_3 is 1. This describes densely packed parallel rods. Then we would expect that the only voids that exist would be runs of empty lattice sites lying along the rods. The flexible polymers that we placed on the lattice would be strung along these voids. Thus we would expect β_3 to be close to 1 and β_1 close to zero. Equations 6.9 and 6.10 actually give

$$\beta_3 = r/(r + 2), \quad \beta_1 = 1/(r + 2) \tag{6.11}$$

These values are obviously correct for $r = 1$ and for r very large. They are also consistent with the original idea that stepping perpendicular to a rod gives r interference sites, and stepping parallel to a rod gives one interference site. Thus even though eq 6.8 is an approximation, it seems to retain much of the physics over the whole manifold of parameter variations.

To obtain the dimensions of the polymer, we expand the logarithms on the right-hand side of eq 6.7 to second order. The first-order terms cancel, giving

$$x_1^2/\beta_1 M = x_3^2/\beta_3 M = (M^2/2v_0 N)(1 - \sum[\beta_i^2/(1 + E_i)]) = (M^2/2v_0 N)(K) \tag{6.12}$$

$$K = 1 - \sum[\beta_i^2/(1 + E_i)] = 1 - \sum[v_0\beta_i^2/(1 - v_r\alpha_i(1 - 1/r))] \tag{6.13}$$

The quantities of interest are easily obtained from eq 6.12. They are the ratio of width squared to length squared of the ellipsoid:

$$x_1^2/x_3^2 = \beta_1/\beta_3 = (1 - v_r\alpha_3(1 - 1/r))/(1 - v_r\alpha_1(1 - 1/r)) \tag{6.14}$$

The volume

$$\text{Vol} = N = x_1^2 x_3 = M^{1.8}(\beta_1)^{0.4}(\beta_3)^{0.2}(K/2v_0)^{0.6} \tag{6.15}$$

and the two coordinates themselves

$$x_1 = M^{0.6}\beta_1^{0.3}\beta_3^{-0.1}(K/2v_0)^{0.2} \tag{6.16}$$

$$x_3 = M^{0.6}\beta_3^{0.4}\beta_1^{-0.2}(K/2v_0)^{0.2} \tag{6.17}$$

The first thing to notice is that each of the dimensions varies as the 0.6 power of molecular weight. This will be true as long as v_0 is not small. When v_0 is small, the representation of the logarithms by their first two terms fails and x_3 can be expected to approach linearity with respect to molecular weight.

The second thing to notice is that the asymmetry ratio of the ellipsoid is determined by the number of bonds in each of the two orientations. From eq 6.7 we see that this is true for any degree of elongation.

For an isotropic distribution of orientation for the obstacle molecules, $\alpha_i = {}^1/_3$, which gives $\beta_i = {}^1/_3$. Using eq 6.13 we obtain from eq 6.15 the volume of the polymer:

$$\text{Vol}/M^{1.8} = ([1/(1 - v_r) - 1/(3 - v_r(1 - 1/r))]/6)^{0.6}, \quad \text{isotropic obstacles} \tag{6.18}$$

The other extreme is for the obstacles to be infinitely long rigid rods ($\alpha_3 = 1$, $r = \infty$). We obtain $\beta_3 = 1/(3 - 2v_r)$, $\beta_1 = \beta_2 = (1 - v_r)/(3 - 2v_r)$, which results in

$$\text{Vol}/M^{1.8} = (1 - v_r)^{0.4}(3 - v_r^2)^{0.6}/(3 - 2v_r)^{1.8}, \quad \text{parallel rods} \tag{6.19}$$

We have plotted these functions in Figure 3. The uppermost curve is for isotropic obstacles when $r = 1$. The curve nearest to it is for isotropic obstacles for $r = \infty$. All other r give curves that fall between these two extremes. The bottommost curve is for infinitely long rigid rod obstacles that are perfectly aligned.

VII. Discussion of Results

We have obtained an expression for the number of configurations of a polymer molecule that suffers interference with a field of uniformally placed *fixed* obstacles. The polymer is modeled as a nonintersecting random walk (SAW) of M steps on a cubic lattice in three dimensions or more generally as a nonintersecting random walk on a hypercubic lattice in d dimensions. The obstacles are modeled as polymer molecules consisting of r segments; each segment occupies one lattice site. A fraction α_i of the $r - 1$ bonds connecting the r segments lie in orientation i, and the volume fraction of polymer is v_r. Thus the polymer obstacles can be aligned rigid rods, partially aligned or unaligned rigid rods, or stretched or unstretched

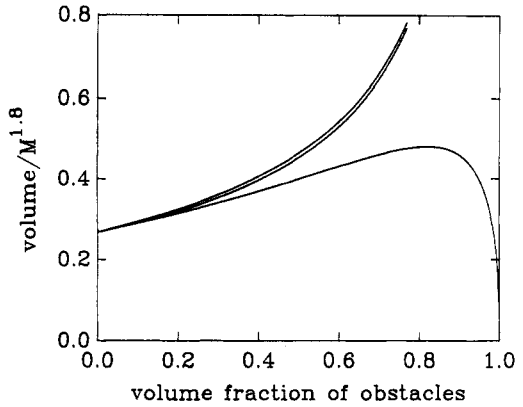

Figure 3. Uppermost curve gives the volume (in units of molecular weight to the 1.8 power) when the obstacles are uniformly placed one site occupiers. The curve immediately below it is for an isotropic distribution of long rigid rods. All the isotropic distributions fall between these two curves. The bottommost curve is for a polymer immersed in a field of perfectly aligned long rigid rods.

flexible polymers. The effect of the obstacles is to align the polymer in the alignment direction of the obstacles. The polymer is characterized by its number of segments, $M+1$, the fraction β_i of the M bonds, lying in orientation i, and by its spans, x_i, in the three mutually perpendicular directions. The formula for the number of configurations is given by eq 5.6, and that for the entropy is given by eq 5.8.

The theory is a mean field theory. There can be many mean field theories. Figure 1 displays three different mean field theories for the nonintersecting random walk with no obstacles: the Flory mean field theory,[12] the NCF mean field theory[2], which is the leading term of their expansion, and the mean field theory derived in this paper. These mean field approaches differ widely in their accuracy, the best being that of this paper. It superimposes nicely onto the NCF field theory expansion to second order, which differs by a few percent from the exact result in two dimensions. In higher dimensions the predictions are expected to be even more accurate. A favorable aspect of this theory is that the ansatz used to account for the interference is the same no matter what the concentration is for the obstacles. The interference with obstacles is treated the same as the interference with previous segments of the chain. The formula for entropy is expected to be as accurate over the whole range of obstacle concentration as it is for the self-excluded volume problem with no obstacles.

The fact that we have a good estimate for the entropy does not mean that our expression is an accurate function of the 14 variables $N,z;r,\upsilon_r,\alpha_i;M,\beta_i,x_i$. It is possible for a mean field theory to be exact in its prediction of certain expectation values and of thermodynamic entropy but not others. What a mean field theory cannot do is predict all of the fluctuations correctly. In fact mean field theories are notorious in not being able to give critical point scaling laws correctly because of the large fluctuations that occur near critical points. In the context of our problem this means that not all of the moments of eqs 6.1 are given correctly. According to the interpretation of entropy given originally by Einstein,[21] the probability of occurrence of a given macroscopic specification $\{\alpha_i\}$ is given by $\exp(S(\{\alpha_i\})/k)$. From the definition of the partition function we see that this relation is valid even when the α_i are microscopic variables.[22] Our mean field approach does indeed estimate the fluctuations since we calculate entropy as a function of β_i and x_i but probably not to the same accuracy as for integrals or expectation values of these quantities. The approximation resides in our estimation of the interferences that are treated in an average way. A molecule that is instantaneously in a swollen state will not have the same self-interferences as one that is instantaneously in a condensed state. Yet, our estimate of the interference is dependent on the average volume of the molecule and not on any other measures of its size. It is noted that the mean field calculations predict the scaling law ($\nu = 0.6$) very accurately. However, we would expect the method to fail near critical points. Perhaps the coherent anomaly method (CAM) of Suzuki[23] can be adapted to our problem.

We have treated a polymer in a field of fixed obstacles, but a real system should show a different behavior. First, the obstacles will be distributed somewhat randomly about the average concentration, especially at low density. Second, the polymer creates its own hole.

The first effect has been modeled as a random placement of fixed obstacles. There is much literature on this subject,[9-11,24-33] and it is presently an intense area of study. The problem in its simplest form is isomorphic to the problem of electron localization.[24] A random placement of obstacles results in high-density regions and in low-density or void regions. The polymer prefers to reside in the low-density regions. This is because there is more attrition in the high-density region; therefore the chain entropy is less in such regions; therefore there is an entropy force pushing the polymer to the void regions. It has been shown both by computer modeling[9,10] and by analytic treatment[11] that the polymer tends to collapse into the voids. This effect is opposite to the swelling effect, described in this paper, that occurs when the obstacles are placed uniformly. Obviously these two effects need to be treated together to determine whether the net effect is a swelling or a contraction. (We are here speaking only of entropy effects. If there is an energetic interaction between the polymer and the obstacles, the effect can be for the chain to seek voids or to seek concentrations of obstacles, depending on whether the energies are repulsive or attractive.) There is presently no combined treatment in the literature. Yamazaki et al.[34,35] have discussed spin systems with an isotropic distribution of structured defects randomly placed in space. The results should be transcribable to polymer systems, but anisotropic distributions were not considered.

The fact that a polymer creates its own hole can probably be overlooked when the chain is in an expanded state or in a Θ condition, for then the effect is small, but for the collapsed state or for certain bulky molecules such as star molecules we must consider the problem. The first observation is that we no longer have a quenched system. The polymer distorts the field of obstacles in such a way that the effect must be dealt with in a self-consistent manner.

One can ask whether path integral methods are adequate to treat the effects associated with orientation. There are three factors that prevent immediate application. First, the generalized Edwards Hamiltonian[11,25]

$$H = (3/2l)\int \left(\frac{dr}{ds}\right)^2 ds + \sum \int [r(s) - R_i]\, ds + \omega \int\int \delta(r(s) - r'(s)) \quad (7.1)$$

should be augmented by terms that contain dr/ds such as $A\, dr/ds$, $B(dr/ds)^2$. In general the energy can be constructed as a sum of an infinite number of invariants contracted from the relevant vector and tensor variables

of the system.[36] We feel that the first-order term $A\,dr/ds$ is a relevant contribution that expresses the orienting effect of an anisotropic field.[37] The $B(dr/ds)^2$ term serves to rescale the Wiener measure (this should make us worry[38]). Other low-order terms may be important. Second, we do not see how, in the context of the path integral formulation, to account for the shielding effect which is so important in our treatment. Perhaps what one needs is a random placement not of points but of clusters of points. One wonders if it would not be better to develop a path integral method where the basic variables are bonds that are added to form paths rather than points that are added to form paths. Third, the creation of a hole by the polymer cannot be treated except in a mean field way unless a generalized version of the path formalism that treats the obstacles on the same footing as the polymer is used. Although difficult, path integral methods should be used in an attempt to derive improvements to the statistics developed here.

A listing of the problems that can be treated with the results of this work is given along with a statement of added complexities that would need to be considered:

(1) Full treatment of the shape of a polymer in a field of oriented rods. We need to add energy that will allow for collapse in order to see if a collapsed molecule is more or less sensitive to the orienting effects of the external field (we believe it is less sensitive). The evaluation of this energy requires special treatment, first because it can be orientation dependent and second because we expect other than simple van der Waals forces in rigid rod systems. An interesting new feature will be that ν will deviate from its value of 0.6 when orientation is high. This fact is already evident from our equations. The collapsed molecules will find it easier to be located in the interstitial voids, and of course phase separation will be strongly dependent on the state of polymer collapse. If we allow the rigid rods to be mobile, then the nematic to isotropic liquid crystal transition will couple to the collapse transition possibly making the collapse transition first order rather than second order.[39]

(2) Star molecules. Star molecules will force us to face the question of distortion of the field of obstacles by the imbedded polymer. In fact star molecules are a good model system for studying this effect. Otherwise the treatment is a straightforward application of this paper to previous results.[19]

(3) Ring molecules. Here the question of span vs end-to-end length as a measure of polymer size becomes the predominant question. We need to know the number of configurations W_0 for the self-intersecting ring as a function of the fraction of bonds β_i in the ith orientation and of the spans x_i. We are not aware of treatments of spans of stretched molecules. Our identification of spans with the x_i made in Appendix C is crude and needs improvement.

(4) Free polymer dissolved in block copolymer. Here the added difficulty is the presence of the two containing surfaces. A prescription has been given previously[19] for treating the excluded-volume problem in the presence of a surface, and it is easily adapted to this problem. One simply uses the number of configurations of the intersecting random walk polymer in the presence of the surface(s) but with no obstacle molecules and then multiplies this quantity which is the new W_0 by the attrition factor A.

(5) Free polymer dissolved in a stretched rubber. A polymer attached at one end only should behave similarly. These polymers will be elongated by the stretched cross-linked molecules even though they are not part of the cross-linked network.[40]

(6) Self-consistent treatment of a stretched molecule in the presence of similarly stretched molecules: (a) application to rubber elasticity; (b) dimensions of diblock copolymers; (c) polymers attached to a flat surface. A self-consistent treatment requires that the obstacles have the same properties as the polymer being placed in the field of obstacles. This means that the obstacle molecules must be viewed as pliable and therefore be allowed to suffer deformations and displacements; they can no longer be viewed as fixed obstacles. There will be a concentration fluctuation in the obstacle molecules. Also, the molecule being placed creates its own hole. These effects should reduce overlap.

There are two attrition effects occurring simultaneously. One is the attrition due to the obstacles, which is the subject of this paper. The other is the hemming-in that results from the cocconlike web formed by the cross-linking among those molecules that surround the polymer molecule. Each of these problems has been treated separately in the context of rubber elasticity,[15,16,41,42] but a combined treatment is not yet available.

(7) What are the dimensions of the polymer molecules in bulk polymer? The answer that Flory gave (which was that the dimensions are the same as a polymer in a theta solvent) has been verified by experiment, but it was the result of intuition rather than a calculation. Can we use the results of this work to derive the Flory intuition? The conventional Flory–Huggins model treats the molecules asymmetrically because the first molecule placed on the lattice sees no interference with other molecules, while subsequent molecules see an increasing amount of interference. We can avoid this problem by building up the molecules simultaneously, one segment at a time. All that is required is that we keep tabs on the polymer size as we build it.

Appendix A: Do We Use Arithmetic or Geometric Averages?

The use of the expression 4.4 rather than 4.5 was justified on the following grounds. Let us suppose that $p_j(i)$ varies slowly with j. Then, for a set of l steps

$$\prod p_j(i) = [p_j(1)]^{\beta_1 l}[p_j(2)]^{\beta_2 l}[p_j(3)]^{\beta_3 l} \qquad \text{(A.1)}$$

since in this interval we would have chosen β_i steps in orientation i, each one of which contributes a factor $p_j(i)$. We wish to show that eq A.1 is a geometric mean of the attrition factor A. If we have a one-step process that results in a number $p(i)$ with probability β_i, then the arithmetic (AM) and geometric means (GM) of the $p(i)$ are defined by

$$\text{AM} = \sum \beta_i p(i) \qquad \text{(A.2)}$$

$$\text{GM} = \prod [[p(i)]^{\beta_i}] \qquad \text{(A.3)}$$

Equation A.1 is the product of l geometric means:

$$[p_j(1)]^{\beta_1 l}[p_j(2)]^{\beta_2 l}[p_j(3)]^{\beta_3 l} = (\prod [p_i^{\beta_i}])^l \qquad \text{(A.4)}$$

We now show that this quantity is equal to the geometric mean associated with the l-step process that defines the attrition factor A. For clarity of presentation we work in the context of only two orientations and three steps. Generalization to $z/2$ orientations and l steps is immediate.

We have

$$\mathrm{GM} = [p^3(1)]^{\beta_1^3}[p^2(1)\,p(2)]^{\beta_1^2\beta_2}[p(1)\,p(2)\,p(1)]^{\beta_1^2\beta_2} \times [p(2)\,p^2(1)]^{\beta_1^2\beta_2}[p(1)\,p^2(2)]^{\beta_1\beta_2^2}[p(2)\,p(1)\,p(2)]^{\beta_1\beta_2^2} \times [p^2(2)\,p(1)]^{\beta_1\beta_2^2}[p^3(2)]^{\beta_2^3} = [p^3(1)]^{\beta_1^3}[p^2(1)\,p(2)]^{3\beta_1^2\beta_2} \times [p(1)\,p^2(2)]^{3\beta_1\beta_2^2}[p^3(2)]^{\beta_2^3} = [p(1)]^{3\beta_1}[p(2)]^{3\beta_2} \quad \text{(A.5)}$$

Thus, the geometric mean of the three-step probabilities is equal to the geometric mean of the one step probabilities taken to the third power. Because

$$l\beta_1^{\,l} + l(l-1)\beta_1^{\,l-1}\beta_2 + l[(l-1)(l-2)/2]\beta_1^{\,l-2}\beta_2^{\,2} + \ldots = l\beta_1 \quad \text{(A.6)}$$

we obtain in general

$$\mathrm{GM} = [p(1)]^{\beta_1 l}[p(2)]^{\beta_1 l} = [[p(1)]^{\beta_1}[p(2)]^{\beta_2}]^l \quad \text{(A.7)}$$

Thus *the geometric mean of the l-step probabilities is equal to the geometric mean of the one-step probabilities taken to the lth power.*

By expanding the trinomial series eq 4.5, we see that *the arithmetic mean of the l-step probabilities is equal to the arithmetic mean of the one-step probabilities taken to the lth power.*

Generalization of these statements to an arbitrary number of orientations is immediate.

These expressions remind us of the problem that replica theory is meant to solve. For macroscopic systems we want to average free energies, not partition functions. Thus for macroscopic systems eq 4.5, which averages partition functions, is considered inappropriate. Equation 4.4 averages logs of partition functions and is therefore considered to be the proper expression. However, the partition function itself is an arithmetic average. Thus as the size our system increases we go from the need to use an arithmetic average for very small systems to a need to use a geometric average for very large systems. Unfortunately a polymer molecule is somewhere in the middle. What do we do?

Let us consider an example. Consider two parallel plates connected covalently by a large number of polymer molecules, each of which bridges the gap between the plates. To calculate the force between the plates, we need to know W_T, the total number of configurations for each value of the plate separation D:

$$W_T = \prod W(D,M) \quad \text{(A.8)}$$

The total partition function is a product of the individual polymer molecule partition functions. If M is interpreted as molecular weight and if the number of polymer molecules of molecular weight M is $\rho(M)$, then we have

$$\ln (W_T) = \sum \rho(M) \ln (W(D,M)) \quad \text{(A.9)}$$

Thus this problem requires the arithmetic mean of the logarithms, which is the same as the geometric mean of the molecule partition functions. Thus, at least sometimes, the geometric mean is the proper one. In using the equations developed in the text, one must first check to see what kind of average is needed.

These problems do not arise for isotropic systems because when $p(i) = p(k)$, the arithmetic and geometric means are equal. But for systems with large anisotropy they can be different.

Appendix B: Comparison of the General Formula with Special Cases

For the isotropic case $\alpha_i = 2/z$ and $\beta_i = 2/z$: A simple calculation shows that eq 4.6 reduces to eq 4.2, which is the formula for an isotropic distribution of both obstacle bonds and of polymer bonds. Equation 4.2 in turn reduces to eq 2.8 when there are no obstacles.

The next special case is a rigid rod (polymer) placed parallel to other rigid rods (obstacles). The attrition factor A_1 is given by use of mole fractions:

$$A_1 = [v_0/(v_0 + v_r/r)]^M \quad \text{(B.1)}$$

This result is obviously exact when $r = \infty$ since then there is no possibility of interference with the ends as we step parallel to the rigid-rod obstacles. Also, we have pointed out previously that this result is thermodynamically exact (i.e., to order N in entropy) for finite r. More precisely, the use of A_1 in the Flory–Huggins counting procedure to calculate the entropy gives the exact result.

Equation 4.6 yields for this case ($\alpha_1 = 1$, $\beta_1 = 1$)

$$A = v_0N(v_0N-1)\ldots(v_0N-k)\ldots(v_0N-(M-1))/(v_0N + v_rN/r)\ldots(v_0N + v_rN/r - k)\ldots(v_0N + v_rN/r - (M-1)) \quad \text{(B.2)}$$

These attrition factors are not very different if we choose N to be on the order of M^3, which gives the smallest lattice that can accommodate the polymer. For $v_0 = 1$ they are identical and correct.

The last special case that we consider is when a rigid rod (polymer) is placed perpendicular to other rigid rods (obstacles). Here we obtain

$$A_2 = [v_0]^M \quad \text{(B.3)}$$

Formula 4.6 gives ($\alpha_1 = 1$, $\alpha_i = 0$ for $i \neq 1$; $\beta_2 = 1$, $\beta_i = 0$ for $i \neq 2$)

$$A = \frac{v_0N(v_0N-1)\ldots(v_0N-k)\ldots(v_0N-(M-1))}{N(N-1)\ldots(N-k)\ldots(n-(M-1))} \quad \text{(B.4)}$$

Again, for $v_0 = 1$ the attrition factors both reduce to the correct results. The difference between eqs B.3 and B.4 is again determined by M/v_0N and is small when this quantity is small.

Finally, we should observe that the mixed case of self-excluded volume and obstacle-excluded volume uses the same level of approximation and the same ansatz that we used for each case separately. There is then no reason for the mixed case to be any less accurate than the accuracy displayed in Figures 1 and 2.

Appendix C: Use of the Span as a Measure of Polymer Size

Suppose we place the two ends of the random-walk polymer on the z axis, which is the direction of elongation. We have from eq 5.5

$$W_0 = \frac{2^M M!\exp(-z^2/2\beta_3 M)}{[(\beta_1 M)!]^2(\beta_3 M)!} \quad \text{(C.1)}$$

Then the width of the polymer is no longer measured by the value of x, which is now equal to zero but is rather given by the span in the x direction. The spans are defined to be the dimensions of the smallest box with sides parallel to the coordinate axis which completely contain the polymer.[43] Spans have been discussed recently by Rubin and Weiss.[20] It makes sense to use spans because even if a molecule has no components of end-to-end length in the transverse dimensions, as would be the case if the two end points of the molecule were constrained to the z axis, it would still have a span on the order of $(\beta_1 M)^{1/2}$ units. The

three spans taken together characterize the shape of the molecule: the x span, which equals the y span, and the z span. For rings also the spans are more usefull measures of polymer size than end-to-end length.

Consider the span in the z direction. The average value of the span for the case of free ends is $0.921(\beta_3 M)^{1/2}$, while the root-mean-square end-to-end length is $(\beta_3 M)^{1/2}$. Both of these values are virtually the same. Another point of similarity is that the probability distribution for end-to-end length contains z only as a function of z^2/M, whereas the probability distribution for the span R contains R only as a function of R^2/M. The kth moment of each distribution therefore varies as $M^{k/2}$. This suggests that the use of the probability distribution for spans would give the same kind of molecular weight dependence *and prefactor* as the use of the Gaussian probability distribution for end-to-end length. Unfortunately, for a constrained chain with a fixed value of z the span seems not to have been calculated, so it is difficult to proceed further. Still it seems reasonable to expect that the use of the Gaussian form will give the same kind of results as the use of the span probability distribution function were we to have it.

Now consider the span in the x direction. What we need and do not have is the span probability distribution. If we had it, then the maximum term method that we used with the Gaussian probability distributions could be used to solve our problem. We now argue as in the above paragraph that use of the Gaussian distribution in place of the span distribution gives the same results as use of the span distribution. Thus, we have justified, at least partially, the use of the Gaussian forms in eq 5.5 as measures of polymer size.

Acknowledgment. I thank Mark P. Taylor for several helpful suggestions.

References and Notes

(1) Di Marzio, E. A. *Phys. Rev. Lett.* **1990**, *64*, 2791.
(2) Nemirovsky, A. M.; Coutinho-Filho, M. D. *J. Stat. Phys.* **1989**, *53*, 1139.
(3) Duplantier, B.; Saleur, H. *Nucl. Phys. B* **1987**, *290*, 291.
(4) Di Marzio, E. A. *J. Chem. Phys.* **1961**, *35*, 658.
(5) Di Marzio, E. A. *J. Chem. Phys.* **1977**, *66*, 1160.
(6) McCrackin, F. L. *J. Chem. Phys.* **1978**, *69*, 5419.
(7) van der Schoot, P. Towards a Theory for the Orientation Dependent Packing Entropy of Inhomogeneous Polymer Systems U.S. Dept. of Commerce, 1986, NBSIR 86-3466.
(8) Bawendi, M. G.; Freed, K. F. *J. Chem. Phys.* **1986**, *85*, 3007; **1987**, *86*, 3720; **1988**, *88*, 2741.
(9) Baumgartner, A.; Muthukumar, M. *J. Chem. Phys.* **1987**, *87*, 3082.
(10) Muthukumar, M.; Baumgartner, A. *Macromolecules* **1989**, *22*, 1937.
(11) Edwards, S.; Muthukumar, M. *J. Chem. Phys.* **1988**, *89*, 2435.
(12) Flory, P. J. *J. Chem. Phys.* **1949**, *17*, 303. Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953.
(13) Simha, R. *J. Res. NBS* **1951**, *47*, 298.
(14) Treatments of the Huggins and Flory versions of the statistics of polymer chains are found in: Miller, A. R. *Theory of Solutions of High Polymers* Oxford University Press: New York, 1948. Guggenheim, E. A. *Mixtures*; Oxford University Press: London, 1952.
(15) Di Marzio, E. A. *J. Chem. Phys.* **1962**, *36*, 1563.
(16) Tanaka, T.; Allen, G. *Macromolecules* **1977**, *10*, 426.
(17) Herzfeld, J. *J. Chem. Phys.* **1982**, *76*, 4185.
(18) Di Marzio, E. A. *Macromolecules* **1984**, *17*, 969.
(19) Di Marzio, E. A.; Guttman, C. M. *J. Phys. Chem.* **1989**, *21*, 7004.
(20) Recent treatments of polymer spans have been given by: Rubin, R. J.; Weiss, G. H. *J. Chem. Phys.* **1983**, *78*, 2039.
(21) Einstein, A. *Ann. Phys.* **1910**, *33*, 1275. See also: Callen, H. B. *Thermodynamics*; Wiley: New York, 1960.
(22) If there are no energies, then the partition function is $Q = \sum \exp(S(\{\alpha_i\})/k)$, where $\alpha_i = f(j)$ and j are the state variables, $\exp(S(\{\alpha_i\}/n)$ is the sum of the terms in $Q = \sum Z_j$ for which $\alpha_i = f(j)$.
(23) Suzuki, M. *Phys. Lett.* **1986**, *A116*, 375; *J. Phys. Soc. Jpn.* **1986**, *55*, 4205. Suzuki, M.; Katori, M.; Hu, X. *J. Phys. Soc. Jpn.* **1987**, *56*, 3092. See also: Tanaka, F.; Doi, M.; Ohta, T. *Space-Time Organization in Macromolecular Fluids*; Springer Series in Chemical Physics; Springer-Verlag: New York, 1989, Vol. 51.
(24) Douglas, J. F. *Macromolecules* **1988**, *21*, 3515.
(25) Thirumalai, D. *Phys. Rev. A* **1988**, *37*, 269.
(26) Aharony, A.; Harris, A. B. *J. Stat. Phys.* **1989**, *54*, 1091.
(27) Lee, S. B.; Nakanishi, H. *Phys. Rev. Lett.* **1988**, *61*, 2022.
(28) Harris, A. B. *Z. Phys.* **1983**, *B49*, 347.
(29) Kremer, K. *Z. Phys.* **1981**, *B45*, 149.
(30) Honeycutt, J. D.; Thirumalai, D.; Klimov, D. K. *J. Phys. A, Math. Gen.* **1988**, *22*, L169.
(31) Honeycutt, J. D.; Thirumalai, D. *J. Chem. Phys.* **1989**, *90*, 4542.
(32) Honeycutt, J. D.; Thirumalai, D. *Influence of Optimal Cavity Shapes on the Size of Polymer Molecules in Random Media*; private communication.
(33) Machta, J.; Kirkpatrick, T. R. *Self-Avoiding Walks and Minifolds in Random Environments*; private communication.
(34) Yamazaki, Y.; Moyuru, O.; Holz, A.; Fukuda, Y. *Phys. Rev. B* **1986**, *33*, 3474.
(35) Yamazaki, Y.; Fukuda, Y.; Holz, A.; Ochiai, M. *Physica* **1986**, *136A*, 303.
(36) All invariants can be constructed by contracting the relevant vector and tensor variables describing the system along with the generalized Kronecker δ and permutation symbol. For a masterful application to liquid crystals see: Frank, F. C. *Discuss. Faraday. Soc.* **1958**, *25*, 19.
(37) A treatment with this term in the context of quantum mechanics is given by: Schulman, L. S. *Techniques and Applications of Path Integration*; Wiley: New York, 1981. A is then the electromagnetic vector potential.
(38) If $\sum_{j=0}^{N-1} \epsilon((X_{j+1} - X_j)/\epsilon)^2$ becomes the Wiener measure, then $\sum_{j=0}^{N-1} \epsilon((X_{j-1} - X_j)/\epsilon)^4$ becomes infinite, so that higher terms in the series present difficulties.
(39) Rice, O. K. *J. Chem. Phys.* **1954**, *22*, 1535.
(40) Gaylord, R. J.; Lohse, D. *J. Polym. Eng. Sci.* **1978**, *18*, 359.
(41) Di Marizio, E. A. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1968**, *9*, 256.
(42) Gaylord, R.; Douglas, J. F. *Polym. Bull.* **1987**, *18*, 347.