

Coordinate-space formulation of polymer lattice cluster theory

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Freed *et al.* have recently developed a lattice cluster theory of polymer solutions that involves series expansions in momentum space. Here we reformulate the lattice cluster theory in coordinate space. The present treatment has certain useful features. In particular, the terms in the reformulated theory can be obtained readily from existing exhaustive computer enumerations. Also, the Flory–Huggins theory can be shown to arise as the first term in a recentered coordinate-space expansion. Generalization to treat polymers in confined space is straightforward.

I. INTRODUCTION

The Flory–Huggins theory of polymer solutions¹ has been one of the most widely used theories in polymer chemistry. Its principal limitations are the two mean-field approximations used to compute the entropy and enthalpy. Until recently, no systematic improvement on the Flory–Huggins theory was available.

Recently Freed² and his colleagues^{2–18} have taken a major step forward and developed a series (cluster) expansion for the partition function for lattice polymer solutions. The zeroth-order term in the series corresponds to a mean-field approximation with the succeeding terms providing a systematic correction to the mean field.^{2,3} They have applied this theory to rods,⁴ semiflexible chains,⁵ chains with nearest-neighbor interaction energies,^{2,6} polymer blends,⁷ branched chains and more complex chain architectures,^{8–11} and cross linking in polymer networks.¹² Nemirovsky and Coutinho-Filho have applied the theory to count the number of conformations of a single self-avoiding walk as a function of density¹⁹ and have studied the packing properties of a collection of flexible polymers.²⁰ An off-lattice version of this cluster expansion has also been developed by Freed.¹³

A major contribution of the theory of Freed *et al.* is the insight it offers into the molecular origins of entropic contributions to the Flory–Huggins χ parameter.^{3,5,7,9,10,12,14} It shows the basis for the polymer concentration dependence of χ and it repairs the well-known problem of the shape of the phase diagram, which is not predicted accurately by the original Flory–Huggins theory.^{15,16}

The original derivation of Freed² is based on a field theory using a coupled-spin representation. It bears some similarity to the approach of de Gennes,²¹ which recognizes the mathematical equivalence of lattice polymers with excluded volume and the $n \rightarrow 0$ limit of a system of n -component lattice spins. An advantage of the Freed approach² is that the chain lengths of the polymers can be specified, whereas the chain length distribution is uncontrolled in the magnet analogy of de Gennes.

In light of the importance of the lattice cluster theory

of Freed and his colleagues, it is worthwhile to explore whether alternative formulations of the theory may have advantages. For example, Freed and his colleagues have found a simpler algebraic derivation not based on spin fields.^{16,17} More recently, analytic relations suggested by this lattice cluster expansion have been ingeniously combined with exact conformational enumerations to provide expansions, in inverse powers of the spatial dimensionality, for the partition function and end-to-end distance of a self-avoiding polymer with nearest-neighbor interactions.¹⁸

Here we develop an alternative formulation of the lattice cluster theory. Whereas the treatments of Freed *et al.* develop the theory using Fourier transforms and the diagrams for the expansion involve sums over \mathbf{q} vectors in momentum space, our approach is based on diagrammatic expansions in coordinate (real) space. Each of these approaches has its advantages; the final results of the two formulations are identical. It is noteworthy, however, that in certain applications of Feynman-type diagrammatics,²² a coordinate-space formulation²³ may offer insights that would have been more obscure in a momentum-space formulation.

The present reformulation of the lattice cluster theory has at least two useful features. First, it is quite flexible. For example, whereas the first term in the Freed expansion is not identical to the Flory–Huggins theory, in the present approach it is simple to center the expansion so that the first term is exactly the Flory–Huggins theory. Second, our coordinate-space formulation can draw readily on a large body of exact lattice enumeration results^{24–28} to compute the diagrams in the expansion. The coordinate-space treatment is particularly useful in dealing with nonperiodic lattice boundary conditions. This coupling of the analytical theory to computer simulation results should provide a simple way to obtain accurate expansions out to high order. It may be useful for testing the ansatz that is the basis for the current asymptotic expansions.¹⁸ The possibility of extending the present formulation to treat heteropolymers will also be discussed.

II. THE PARTITION FUNCTION

We follow the treatment of Dudowicz, Freed, and Madden¹⁶ and first review their notation.

Let \mathbf{a}_β ($\beta=1,2,\dots,z$; z is the lattice coordination number) designate the vectors from a given lattice site to z other nearest-neighbor lattice sites and let \mathbf{r}_i denote the position of the i th lattice site. The condition that the lattice sites i and j are nearest neighbors is

$$\mathbf{r}_i = \mathbf{r}_j + \mathbf{a}_\beta \quad (2.1)$$

for some $\beta=1,2,\dots,z$. Using the Kronecker δ ,

$$\delta(i,j) \equiv \begin{cases} 1, & \text{for } i=j \\ 0, & \text{for } i \neq j, \end{cases} \quad (2.2)$$

the constraint

$$\delta(i,j+\beta) \equiv \delta(\mathbf{r}_i, \mathbf{r}_j + \mathbf{a}_\beta) \quad (2.3)$$

ensures that lattice sites i and j are nearest neighbors.

Let i_α^m designate the lattice site occupied by the α th monomer of the m th chain. The partition function (i.e., total number of conformations) of n_p polymers each of length $N-1$ ($N-1$ bonds, N monomers) configured on a lattice with a total of N_l sites is

$$\Omega(n_p, N, N_l) = \sum_{\text{e.v.}} \prod_{m=1}^{n_p} \left[\prod_{\alpha=1}^{N-1} \sum_{\beta=1}^z \delta(i_\alpha^m, i_{\alpha+1}^m + \beta) \right], \quad (2.4)$$

where the summation over lattice sites

$$\sum_{\text{e.v.}} \equiv \sum_{\substack{i_1^1 \neq i_2^1 \neq \dots \neq i_N^1 \\ \neq i_1^2 \neq i_2^2 \neq \dots \neq i_N^2 \\ \dots \\ \neq i_1^{n_p} \neq i_2^{n_p} \neq \dots \neq i_N^{n_p}}} \quad (2.5)$$

is restricted to enforce the excluded volume (e.v.) constraint (such that no site may be occupied by more than one monomer). The product of the Kronecker δ 's in Eq. (2.4) then enforces the constraint that successively bonded monomers are nearest neighbors on the lattice. The n_p polymers and the two ends of each polymer are considered to be distinguishable in the partition function (2.4); if they are regarded as indistinguishable,¹⁶ Eq. (2.4) would be divided by $n_p! 2^{n_p}$. Equation (2.4) applies only to polymers with linear architecture, which is the focus of the present paper. However, the generalization to branched polymer architectures can easily be obtained by replacing the single Kronecker δ in Eq. (2.4) with multiple Kronecker δ 's.¹⁶

The definition

$$X_{\alpha,m} \equiv \frac{N_l}{z} \left[\sum_{\beta=1}^z \delta(i_\alpha^m, i_{\alpha+1}^m + \beta) \right] - 1 \quad (2.6)$$

allows the partition function (2.4) to be rewritten in the form

$$\Omega(n_p, N, N_l) = \sum_{\text{e.v.}} \prod_{m=1}^{n_p} \left[\prod_{\alpha=1}^{N-1} \left[\frac{z}{N_l} (1 + X_{\alpha,m}) \right] \right]. \quad (2.7)$$

It is clear from the last two equations that $X_{\alpha,m}/N_l$ is the *difference* between the exact value and a mean-field approximation of the insertion probability that monomer $\{\alpha+1, m\}$ is at position $i_{\alpha+1}^m$ given that monomer $\{\alpha, m\}$ is at position i_α^m . The exact probability is represented by a Kronecker δ which requires the two connected monomers to be spatial nearest neighbors. The mean-field approximation treats all monomers as if they were uncorrelated, hence the mean-field probability ($1/N_l$) is independent of the positions of the two monomers. Each single factor $X_{\alpha,m}$ represents the correction for inserting one bond. The correction for inserting B bonds will involve a product of B $X_{\alpha,m}$ factors. In the work of Freed and co-workers,²⁻²⁰ the correction factor $X_{\alpha,m}$ is Fourier transformed and represented as a summation over nonzero \mathbf{q} vectors in the first Brillouin zone (on the reciprocal lattice) in momentum space.²⁹ In our approach, we retain the coordinate-space form of Eq. (2.6).

Multiplication of the $n_p(N-1)$ terms in the products in Eq. (2.7) over m and α yields

$$\Omega(n_p, N, N_l) = \left(\frac{z}{N_l} \right)^{n_p(N-1)} \{ T_0 + T_1 + T_2 + \dots + T_{n_p(N-1)} \}, \quad (2.8)$$

where the terms in the curly brackets are given by

$$T_B \equiv \sum_{\text{e.v.}} \left\{ \sum_{\alpha_1, m_1 > \alpha_2, m_2 > \dots > \alpha_B, m_B} X_{\alpha_1, m_1} X_{\alpha_2, m_2} \dots X_{\alpha_B, m_B} \right\}. \quad (2.9)$$

Here the shorthand notation $\alpha_1, m_1 > \alpha_2, m_2$ represents the condition that either (i) $\alpha_1 > \alpha_2$; or (ii) $m_1 > m_2$ for $\alpha_1 = \alpha_2$. The first summation in Eq. (2.9) is over possible *spatial* positions for all $n_p N$ monomers, whereas the second summation is over possibilities in choosing B bonds from the total of $n_p(N-1)$ bonds in the system. Because the product of $X_{\alpha,m}$'s in Eq. (2.9) is invariant under any permutation of the $\{\alpha, m\}$ sets, the equality

$$\sum_{\alpha_1, m_1 > \alpha_2, m_2 > \dots > \alpha_B, m_B} = \frac{1}{B!} \sum_{\alpha_1, m_1} \sum_{\alpha_2, m_2} \dots \sum_{\alpha_B, m_B} \quad (2.10)$$

holds for Eq. (2.9). The zeroth-order or zero-bond term in the series enclosed in curly brackets in Eq. (2.8) is

$$T_0 = \sum_{\text{e.v.}} 1. \quad (2.11)$$

For this $B=0$ term, because T_B does not involve any summation over $\{\alpha, m\}$, the excluded volume sum can be evaluated simply by restricting the limits on the multiple summations over i_α^m 's, viz.,

$$T_0 = \sum_{\text{e.v.}} 1 = \sum_{i_1^1=1}^{N_l} \sum_{i_2^1=1}^{N_l-1} \sum_{i_3^1=1}^{N_l-2} \dots \sum_{i_N^{n_p}=1}^{N_l-n_p N+1} 1 = \frac{N_l!}{(N_l - n_p N)!}. \quad (2.12)$$

Hence

$$\Omega(n_p, N, N_l) = \left(\frac{z}{N_l}\right)^{n_p(N-1)} \left[\frac{N_l!}{(N_l - n_p N)!} + \sum_{B=1}^{n_p(N-1)} T_B \right], \quad (2.13)$$

where the combinatorial term in Eq. (2.13) is the mean-field partition function [the original Flory-Huggins partition function¹ corresponds to this term with $z-1$ in place of z in the overall multiplicative factor $(z/N_l)^{n_p(N-1)}$], and the rest are $B > 0$ contributions that involve at least one $X_{\alpha,m}$ factor.

III. THE CLUSTER EXPANSION

We now consider the higher-order terms in Eq. (2.8); these are successive corrections to the mean-field approximation. The systematic evaluation of T_B 's may be conducted by first collecting the terms

$$X_{\alpha_1, m_1} X_{\alpha_2, m_2} \cdots X_{\alpha_B, m_B} = \prod_{r=1}^B X_{\alpha_r, m_r}, \quad (3.1)$$

in the summations in Eq. (2.9) over monomer labels $\{\alpha, m\}$'s into groups which are chosen such that every term of the form of Eq. (3.1) belonging to the same group sums to exactly the same final result when the last excluded-volume summation $\Sigma_{\text{e.v.}}$ over lattice sites is performed. We label these groups by Δ . That is, T_B in Eq. (2.9) can now be written as

$$T_B = \sum_{\text{e.v.}} \left[\sum_{\Delta} \left(\sum_{\{\alpha, m | \Delta\}} \prod_{r=1}^B X_{\alpha_r, m_r} \right) \right], \quad (3.2)$$

where Σ_{Δ} sums over different Δ groups, and $\Sigma_{\{\alpha, m | \Delta\}}$ sums only over products of B factors of $X_{\alpha, m}$'s that belong to a specific Δ group with the restriction $\alpha_1, m_1 > \alpha_2, m_2 > \cdots > \alpha_B, m_B$ of Eq. (2.9). The summations $\Sigma_{\text{e.v.}}$ and Σ_{Δ} can now be interchanged, hence

$$T_B = \sum_{\Delta} \left[\sum_{\text{e.v.}} \left(\sum_{\{\alpha, m | \Delta\}} \prod_{r=1}^B X_{\alpha_r, m_r} \right) \right]. \quad (3.3)$$

The main reason for factoring into Δ groups should now be clear. *By construction*, every product of B $X_{\alpha, m}$'s belonging to a specific Δ group contributes an equal amount when summed over by $\Sigma_{\text{e.v.}}$. Therefore the double summation $\Sigma_{\text{e.v.}} \Sigma_{\{\alpha, m | \Delta\}}$ in the above equation can be replaced by the product of the number $\gamma(B, \Delta)$ of distinct sets of B $\{\alpha, m\}$'s for the given Δ group and a single summation $\Sigma_{\text{e.v.}}$ over any one set of B $\{\alpha, m\}$'s belonging to the given Δ group. If elements of this set are denoted by $\{\tilde{\alpha}(\Delta), \tilde{m}(\Delta), r\}$ ($r = 1, 2, \dots, B$), then

$$T_B = \sum_{\Delta} T_{B(\Delta)}, \quad T_{B(\Delta)} \equiv \gamma(B, \Delta) \sum_{\text{e.v.}} \prod_{r=1}^B X_{\tilde{\alpha}(\Delta), \tilde{m}(\Delta), r}. \quad (3.4)$$

Here the tildes on $\tilde{\alpha}$ and \tilde{m} indicate the *specific* set of monomer labels chosen to represent a Δ group, whereas the α and m without tildes in Eqs. (3.2) and (3.3) are summation indices.

Each Δ group represents a different pattern of connectivity among the B bonds in the X 's. Each Δ group is

uniquely represented by a list (l_1, l_2, \dots, l_n) , where l_1 is the number of covalent bonds in a chain segment 1, l_2 is the number of covalent bonds in a different chain segment 2, etc. The sum of the lengths of segments $l_1 + l_2 + \cdots + l_n = B$ must add up to the number of bonds B in the Δ group. Chain segments are taken from within a given chain or among different chains. The shorthand notation $\gamma(B, \Delta)$ and $T_{B(\Delta)}$ in Eq. (3.4) will be replaced by $\gamma(l_1, l_2, \dots, l_n)$ and $T_{(l_1, l_2, \dots, l_n)}$ where necessary below to indicate the explicit connectivity pattern of the B bonds in a particular Δ group.

We now seek to establish a relation between the T_B 's and the numbers of conformations of chain segments. In view of our choice of the Δ groups, it is useful to define the following quantities:

$$S(0) \equiv \sum_{\text{e.v.}} 1, \quad (3.5a)$$

$$S(1) \equiv \sum_{\text{e.v.}} \left(\frac{N_l}{z}\right) \left[\sum_{\beta=1}^z \delta(i_{\tilde{\alpha}}^{\tilde{m}}, i_{\tilde{\alpha}+1}^{\tilde{m}} + \beta) \right], \quad (3.5b)$$

$$S(2) \equiv \sum_{\text{e.v.}} \left(\frac{N_l}{z}\right) \left[\sum_{\beta=1}^z \delta(i_{\tilde{\alpha}}^{\tilde{m}}, i_{\tilde{\alpha}+1}^{\tilde{m}} + \beta) \right] \left(\frac{N_l}{z}\right) \times \left[\sum_{\beta=1}^z \delta(i_{\tilde{\alpha}+1}^{\tilde{m}}, i_{\tilde{\alpha}+2}^{\tilde{m}} + \beta) \right], \quad (3.5c)$$

$$S(1,1) \equiv \sum_{\text{e.v.}} \left(\frac{N_l}{z}\right) \left[\sum_{\beta=1}^z \delta(i_{\tilde{\alpha}}^{\tilde{m}}, i_{\tilde{\alpha}+1}^{\tilde{m}} + \beta) \right] \left(\frac{N_l}{z}\right) \times \left[\sum_{\beta=1}^z \delta(i_{\tilde{\alpha}'}^{\tilde{m}'}, i_{\tilde{\alpha}'+1}^{\tilde{m}'} + \beta) \right], \quad (3.5d)$$

etc. [$S(0) = T_0$; see Eq. (2.11)]. The general S function is defined as

$$S(p, q, \dots, l) \equiv \left(\frac{N_l}{z}\right)^{(p+q+\cdots+l)} \sum_{\text{e.v.}} [(p \text{ consecutive } \delta\text{'s}) \times (q \text{ consecutive } \delta\text{'s}) \times \cdots \times (l \text{ consecutive } \delta\text{'s})], \quad (3.6)$$

where

$$(p \text{ consecutive } \delta\text{'s}) \equiv \prod_{s=0}^{p-1} \left[\sum_{\beta=1}^z \delta(i_{\tilde{\alpha}+s}^{\tilde{m}}, i_{\tilde{\alpha}+s+1}^{\tilde{m}} + \beta) \right]. \quad (3.7)$$

Because each δ in Eq. (3.7) represents a single polymeric bond, a factor of p consecutive δ 's represents a chain segment with p bonds. Owing to the fact that there are $N-1$ bonds along a chain, p, q, \dots, l in Eq. (3.6) satisfy the constraint that $0 \leq p, q, \dots, l \leq N-1$. Implicit in the definitions in Eqs. (3.6) and (3.7) are restrictions on the relationship between $\tilde{\alpha}$'s and \tilde{m} 's of different factors of consecutive δ 's. These restrictions are needed to ensure that chain segments represented by two different factors of consecutive δ 's are disconnected, such that no two factors, say of p and q consecutive δ 's, can be joined with each other to become a factor with a string of $p+q$ consecutive δ 's. For example, in the definition (3.5d) for $S(1,1)$, we require either

$\tilde{m} \neq \tilde{m}'$, or $\tilde{\alpha}' \neq \tilde{\alpha} \pm 1$ if $\tilde{m} = \tilde{m}'$. The meaning of the S -functions will become more apparent below.

We now consider the first-order term in the expansion of Eq. (2.8). For $B=1$, only one factor of X is involved in the definition of T_1 [see Eq. (3.4)]. There is only one Δ group, therefore, the single set of representative monomer labels $\{\tilde{\alpha}, \tilde{m}\}$ may be taken to be $\{1,1\}$. For this case, the single γ factor is the number of ways of choosing one single bond from the n_p chains each having $N-1$ bonds, thus $\gamma(1) = n_p(N-1)$. Hence, it follows from Eq. (3.4) as well as the definitions of X and S 's in Eqs. (2.6), (3.5a), and (3.5b) that

$$T_1 = T_{(1)} = n_p(N-1) \sum_{\text{e.v.}} X_{1,1} = n_p(N-1) [S(1) - S(0)]. \quad (3.8)$$

As defined above after Eq. (3.4), the subscript (1) in $T_{(1)}$ is a label for the contributing Δ group. For this case, the Δ group contains only a single bond, $T_{(l_1, l_2, \dots, l_n)} = T_{(1)}$ because $l_1=1$ and $l_2=l_3=\dots=l_n=0$.

We next consider the second-order ($B=2$) term T_2 in Eq. (2.8). T_2 has two X 's, representing two bonds [see Eq. (2.9)]. In this case, there are two Δ groups, each of which corresponds to a particular arrangement of the two bonds—either the two bonds are (i) connected, i.e., $m_1 = m_2$ and $\alpha_1 = \alpha_2 \pm 1$, or (ii) disconnected, i.e., either $m_1 \neq m_2$ or $\alpha_1 \neq \alpha_2 \pm 1$, or both. Hence, according to Eq. (3.4),

$$T_2 = T_{(2)} + T_{(1,1)}, \quad (3.9)$$

where the subscripts (2) and (1,1) stand for the two cases of bond connectivity. For the case “(2)” with two connected bonds, there are altogether $n_p(N-2)$ such chain segments in the polymeric system. Because all these two-bond chain segments are equivalent with respect to the $\Sigma_{\text{e.v.}}$ summation, $\tilde{\alpha}_1=1$, $\tilde{\alpha}_2=2$, and $\tilde{m}_1=\tilde{m}_2=1$ may be used in Eq. (3.4) to evaluate $T_{(2)}$, therefore,

$$T_{(2)} = n_p(N-2) \sum_{\text{e.v.}} X_{1,1} X_{2,1}. \quad (3.10)$$

For the case “(1,1),” the two disconnected bonds may be located either in the same chain or in two different chains. However, this difference does not have any effect on the $\Sigma_{\text{e.v.}}$ summation. Therefore a single set of $\{\tilde{\alpha}, \tilde{m}\}$'s, e.g., $\tilde{\alpha}_1=\tilde{\alpha}_2=1$, $\tilde{m}_1=1$, and $\tilde{m}_2=2$ may be substituted into Eq. (3.4) to give

$$T_{(1,1)} = [n_p(N-2)(N-3)/2 + n_p(n_p-1)] \times (N-1)^2/2 \sum_{\text{e.v.}} X_{1,1} X_{1,2}, \quad (3.11)$$

where the first and second factors enclosed in square brackets are, respectively, the number of ways of putting two disconnected bonds (i) in the same chain and (ii) in two different chains. These factors are calculated as follows: (i) inserting two disconnected bonds to a single one of the n_p chains with $N-1$ bonds can either proceed by (a) inserting the first bond at one of the two chain ends, then the number of ways of inserting the second bond is $(N-3)$,

thus resulting in $2(N-3)$ different arrangements for this case; or (b) not inserting the first bond at the chain ends, then there are $(N-3)$ possible positions for the first bond and $(N-4)$ possible positions for the second bond, thus giving rise to $(N-3)(N-4)$ different arrangements. The sum of these two contributions is $(N-2)(N-3)$, which must then be divided by two because of the indistinguishability of the two bonds. This accounts for the first factor. (ii) If the two disconnected bonds are in different chains, the number of ways of choosing two among n_p chains is $n_p(n_p-1)/2$, and there are $N-1$ possible positions along the chain for each of the two bonds. This accounts for the second factor.

Substitution of the definitions of X [Eq. (2.6)] and S 's [Eq. (3.5)] into Eqs. (3.10) and (3.11) and a little algebra yields

$$T_{(2)} = n_p(N-2) [S(2) - 2S(1) + S(0)], \quad (3.12a)$$

$$T_{(1,1)} = [n_p(N-2)(N-3)/2 + n_p(n_p-1)(N-1)^2/2] \times [S(1,1) - 2S(1) + S(0)]. \quad (3.12b)$$

We have followed Freed and co-workers^{8,17} in writing each contribution to $T_{B(\Delta)}$ in Eq. (3.4) as a product of two factors. One is the combinatorial prefactor $\gamma(B, \Delta)$; it is dependent on the chain architecture (branching) and is equal to the number of ways the given set of l_1, l_2, \dots, l_n segments of a specific Δ group may be partitioned among the polymeric system. The other is the architecture-independent factor

$$\mathcal{D}(B, \Delta) \equiv \sum_{\text{e.v.}} \prod_{r=1}^B X_{\tilde{\alpha}(\Delta), \tilde{m}(\Delta), r}. \quad (3.13)$$

The reason for adopting the notation $\gamma(B, \Delta)$ and $\mathcal{D}(B, \Delta)$ instead of γ_D and D_B of Freed and co-workers^{8,17} is to underscore the dependence of these quantities on both the number of bonds B (Kronecker δ 's in X 's) and the pattern of connectivity Δ among these B bonds. When the connectivity pattern (l_1, l_2, \dots, l_n) among the B bonds is identical for $\mathcal{D}(B, \Delta)$ and D_B , our $\gamma(B, \Delta) = \gamma(l_1, l_2, \dots, l_n) = \text{Freed et al.'s } \gamma_D$, and our $\mathcal{D}(B, \Delta) = \mathcal{D}(l_1, l_2, \dots, l_n)$ is related to Freed et al.'s D_B by

$$\mathcal{D}(B, \Delta) = \mathcal{D}(l_1, l_2, \dots, l_n) |_{l_1+l_2+\dots+l_n=B} = [N! / (N_l - n_p N)!] D_B = T_0 D_B, \quad (3.14)$$

where the last equality follows from Eq. (2.12). An example of the factorization of T 's is provided by $T_{(2)}$ in Eq. (3.12a), where $\gamma(2) = n_p(N-2)$ and $\mathcal{D}(2) = S(2) - 2S(1) + S(0)$ in our notation.

It is straightforward to deduce from the expansions (2.8) and (2.9) that the γ 's satisfy the identity

$$\sum_{l_1+l_2+\dots+l_n=B} \gamma(l_1, l_2, \dots, l_n) = \binom{n_p(N-1)}{B}, \quad (3.15)$$

where

$$\binom{n}{r} \equiv \frac{n!}{r!(n-r)!}. \quad (3.16)$$

TABLE I. Architecture-independent factors $\mathcal{D}(l_1, l_2, \dots, l_n)$ as linear combinations of $S(p, q, \dots, l)$ for $B=l_1+l_2+\dots+l_n \leq 4$.

| Bond connectivity l_1, l_2, \dots, l_n | $\mathcal{D}(l_1, l_2, \dots, l_n)$ as a linear combination of $S(p, q, \dots, l)$'s |
|---|---|
| 1 | $S(1) - S(0)$ |
| 2 | $S(2) - 2S(1) + S(0)$ |
| 1,1 | $S(1,1) - 2S(1) + S(0)$ |
| 3 | $S(3) - 2S(2) - S(1,1) + 3S(1) - S(0)$ |
| 2,1 | $S(2,1) - 2S(1,1) - S(2) + 3S(1) - S(0)$ |
| 1,1,1 | $S(1,1,1) - 3S(1,1) + 3S(1) - S(0)$ |
| 4 | $S(4) - 2S(3) - 2S(2,1) + 3S(2) + 3S(1,1) - 4S(1) + S(0)$ |
| 3,1 | $S(3,1) - 2S(2,1) - S(1,1,1) - S(3) + 2S(2) + 4S(1,1) - 4S(1) + S(0)$ |
| 2,2 | $S(2,2) - 4S(2,1) + 2S(2) + 4S(1,1) - 4S(1) + S(0)$ |
| 2,1,1 | $S(2,1,1) - 2S(2,1) - 2S(1,1,1) + 5S(1,1) + S(2) - 4S(1) + S(0)$ |
| 1,1,1,1 | $S(1,1,1,1) - 4S(1,1,1) + 6S(1,1) - 4S(1) + S(0)$ |

The combination of Eqs. (2.13), (3.4), (3.13), and (3.14) recovers the lattice cluster theory^{8,17}

$$\Omega(n_p, N, N_l) = \left(\frac{z}{N_l}\right)^{n_p(N-1)} \frac{N_l^l}{(N_l - n_p N)!} \times \left[1 + \sum_{B=1}^{n_p(N-1)} \sum_{\Delta} \gamma(B, \Delta) D_B \right], \quad (3.17)$$

where the summations in the square brackets can be written explicitly as

$$\frac{1}{T_0} \sum_{B=1}^{n_p(N-1)} \sum_{l_1+l_2+\dots+l_n=B} \gamma(l_1, l_2, \dots, l_n) \mathcal{D}(l_1, l_2, \dots, l_n). \quad (3.18)$$

Freed and co-workers have shown that the D_B 's [and therefore the $\mathcal{D}(l_1, l_2, \dots, l_n)$'s] can be represented conveniently by diagrams showing the connectivity among different bonds. In their work, the D_B 's are products of Fourier sums whose physical interpretation is not immediately obvious. The diagrammatic procedure for the evaluation of Freed *et al.*'s D_B 's is straightforward, but the algebra can be quite tedious for high order terms.

IV. ENUMERATING THE CONFORMATIONS AND EVALUATING THE DIAGRAMS

In this section, we evaluate the diagrams $\mathcal{D}(l_1, l_2, \dots, l_n)$ as linear combinations of the quantities $S(p, q, \dots, l)$, which in turn can be found as enumerations $C(p, q, \dots, l)$ of real-space lattice conformations. The first step of obtaining $\mathcal{D}(l_1, l_2, \dots, l_n)$ as linear combinations of $S(p, q, \dots, l)$ is straightforward. As illustrated by the calculation leading to Eq. (3.12), we substitute the definition of X [Eq. (2.6)] and of the S 's [Eqs. (3.5)–(3.7)] into Eq. (3.13). Table I shows the lowest order expression for $\mathcal{D}(l_1, l_2, \dots, l_n)$ counting up to four bonds ($B=l_1+l_2+\dots+l_n \leq 4$).

A. Diagrams $\mathcal{D}(l_1, l_2, \dots, l_n)$ as linear combinations of $S(p, q, \dots, l)$

Here we describe the general procedure for obtaining the linear combination of S 's for \mathcal{D} with any bond con-

nectivity pattern l_1, l_2, \dots, l_n . A basic quantity is the number of ways of arranging r disconnected chain segments with l_j bonds ($l_j > 0, j=1, 2, \dots, r$) along a continuous string of M monomers ($M-1$ bonds). This quantity is

$$\mathcal{P}(M-1 | l_1, l_2, \dots, l_r) \equiv \frac{r!}{\prod_{l=1}^{M-1} \nu(l)!} \binom{M - \sum_{j=1}^r l_j}{r}, \quad (4.1)$$

where $\nu(l)$ is the number of chain segments with length l (i.e., l bonds) among the r segment lengths l_1, l_2, \dots, l_r ; hence $\sum \nu(l) = r$. The first factor in Eq. (4.1) is the number of distinguishable linear orderings of the r chain segments. The second factor accounts for the number of ways of arranging a given ordering of these chain segments along the $M-1$ consecutive slots of possible bond positions ("bond slots"). At least $r-1$ empty bond slots are required to separate the r disconnected chain segments— \mathcal{P} is nonzero if and only if $M \geq r + \sum_{j=1}^r l_j$; otherwise $\mathcal{P} = 0$.

We expand $\mathcal{D}(l_1, l_2, \dots, l_n)$ defined in Eqs. (3.13) and (3.14). There are a total of $B = \sum_{i=1}^n l_i$ factors of X 's in the product of Eq. (3.14). We first identify groups of X 's whose Kronecker δ 's are consecutively connected. By definition of \mathcal{D} , there are n such groups and the number of X 's in these groups are l_1, l_2, \dots, l_n . Schematically,

$$\mathcal{D}(l_1, l_2, \dots, l_n) = \sum_{\substack{\text{e.v.} \\ l_1+l_2+\dots+l_n=B}} \underbrace{XX \cdots X}_B \text{ factors} = \sum_{\text{e.v.}} \underbrace{(XX \cdots X)}_{l_1 \text{ connected}} \underbrace{(XX \cdots X)}_{l_2 \text{ connected}} \cdots \underbrace{(XX \cdots X)}_{l_n \text{ connected}}, \quad (4.2)$$

where we have indicated the grouping of the X 's by their connectivities. Now consider each individual group of X 's. Each X factor consists of two parts—the Kronecker- δ part and the -1 part [see Eq. (2.6)]. Owing to the -1 part, the expansion of the product of any given l_i factors of X whose δ 's are connected gives rise to a weighted sum over terms which are products of multiple strings of consecutive δ 's. Obviously l_i is the maximum number of consecutive δ 's in any expansion term of l_i connected factors of X 's. The number of these expansion terms with any given number $r(i) \geq 0$ of strings with $l_{i,1}, l_{i,2}, \dots, l_{i,r(i)}$ consecutive δ 's is exactly equal to the number of ways of bond arrangement $\mathcal{P}(l_i | l_{i,1}, l_{i,2}, \dots, l_{i,r(i)})$ given by Eq. (4.1). Here each δ corresponds to a bond in a chain segment and each -1 corresponds to an empty bond slot. Hence the constraint $l_{i,1} + l_{i,2} + \dots + l_{i,r(i)} + r(i) \leq l_i + 1$ applies. Therefore the maximum value of $r(i)$ is $(l_i + 1)/2$ for l_i odd and $l_i/2$ for l_i even. The -1 part in X also results in a sign $(-1)^\sigma$. Thus the expansion is given by

$$\underbrace{(XX \cdots X)}_{l_i \text{ connected}} = \sum_{\{d(l_i)\}} (-1)^\sigma \mathcal{P}(l_i | l_{i,1}, l_{i,2}, \dots, l_{i,r(i)}) \times \prod_{j=1}^{r(i)} \left[\binom{N_l}{z}^{l_{i,j}} \sum_{\beta} \delta \sum_{\beta} \delta \cdots \sum_{\beta} \delta \right], \quad (4.3)$$

$\underbrace{\hspace{10em}}_{l_{i,j} \text{ consecutive } \delta\text{'s}}$

where

$$\sum_{\{d(l_i)\}} \equiv \sum_{l_{i,1}+l_{i,2}+\dots+l_{i,r(i)}+r(i) \leq l_i+1} \quad (4.4)$$

sums over all possible decompositions of l_i subject to the above constraint on $l_{i,1}, l_{i,2}, \dots, l_{i,r(i)}$, and $\sigma = \sigma(l_i | l_{i,1}, l_{i,2}, \dots, l_{i,r(i)}) \equiv l_i - \sum_{j=1}^{r(i)} l_{i,j}$.

This procedure is used to expand each of the n groups

$$\begin{aligned} \mathcal{D}(l_1, l_2, \dots, l_n) = & \sum_{\{d(l_1)\}} \sum_{\{d(l_2)\}} \dots \sum_{\{d(l_n)\}} \left[\prod_{i=1}^n (-1)^\sigma \mathcal{P}(l_i | l_{i,1}, l_{i,2}, \dots, l_{i,r(i)}) \right] \\ & \times S(l_{1,1}, l_{1,2}, \dots, l_{1,r(1)}, l_{2,1}, l_{2,2}, \dots, l_{2,r(2)}, \dots, l_{n,1}, l_{n,2}, \dots, l_{n,r(n)}). \end{aligned} \quad (4.5)$$

It is easy to verify that the $B \leq 4$ expansion of \mathcal{D} 's in Table I follows the general formula (4.5). For example, the coefficient of $S(0)$ in the expansion of any \mathcal{D} with B bonds is found to be $(-1)^B$ by setting $l_{i,j} = 0$ for all i, j in Eq. (4.5), which leads to $r(i) = 0$ and $\mathcal{P} = 1$. Similarly, the coefficient of $S(1)$ is determined by Eq. (4.5) to be $(-1)^{B-1} B$. Both of these relations are confirmed by the explicit calculations for $B \leq 4$ in Table I.

B. The relationship between $S(p, q, \dots, l)$ and $C(p, q, \dots, l)$

Next, the key step is to relate the $S(p, q, \dots, l)$ quantities to the total number of conformations $C(p, q, \dots, l)$ for a polymeric system configured on the same lattice with the same total number of N_l sites as the original system. Instead of the $n_p(N-1)$ -bond chains of the original system, the system represented by $C(p, q, \dots, l)$ contains a p -bond chain, a q -bond chain, etc. For example, because $\tilde{\alpha} = 1$ and $\tilde{m} = 1$ may be substituted into the definition of $S(2)$ in Eq. (3.5c) without loss of generality, we have

$$\begin{aligned} S(2) = & \left(\frac{N_l}{z} \right)^2 \sum_{\text{e.v.}} \sum_{\beta_1=1}^z \sum_{\beta_2=1}^z \delta(i_1^1, i_2^1 + \beta_1) \delta(i_2^1, i_3^1 + \beta_2) \\ = & \left(\frac{N_l}{z} \right)^2 \sum_{\substack{i_4^1 \neq i_5^1 \neq \dots \neq i_N^1 \\ \neq i_1^2 \neq i_2^2 \neq \dots \neq i_N^2 \\ \dots \\ \neq i_1^p \neq i_2^p \neq \dots \neq i_N^p}} \left[\sum_{i_1^1 \neq i_2^1 \neq i_3^1} \sum_{\beta_1=1}^z \sum_{\beta_2=1}^z \delta(i_1^1, i_2^1 \right. \\ & \left. + \beta_1) \delta(i_2^1, i_3^1 + \beta_2) \right] = \left(\frac{N_l}{z} \right)^2 \frac{(N_l - 3)!}{(N_l - n_p N)!} C(2), \end{aligned} \quad (4.6)$$

where the indices β in the two sums in Eq. (3.5c) are renamed β_1 and β_2 . In the second line of Eq. (4.6), the sum $\sum_{\text{e.v.}}$ [Eq. (2.5)] over lattice positions of the $n_p(N-1)$ monomers is separated into two terms. (i) The term inside the square brackets ($\sum_{i_1^1 \neq i_2^1 \neq i_3^1}$) sums over the *correlated monomers* represented by the Kronecker δ 's in this case, it corresponds to a trimer (two-bond chain). (ii) The sum

of X 's in Eq. (4.2). Then the only operation remaining in the calculation of \mathcal{D} is the excluded-volume summation $\sum_{\text{e.v.}}$ over monomer positions. Equation (4.3) implies that terms in this final summation are proportional to concatenations of factors of $(N_l/z) \sum_{\beta} \delta$ from all n groups of X 's. Now we substitute S 's [defined in Eq. (3.6)] for all these concatenations to yield the expansion of \mathcal{D} as a linear combination of S factors,

preceding the square brackets is over all the other *uncorrelated monomers*. The quantity $C(2)$, which arises from the term in the brackets, is simply the count of all the trimer conformations on the lattice, in the absence of the other monomers. The sum preceding the brackets, which is over the positions of the $n_p N - 3$ uncorrelated monomers, leads to the combinatoric factor $(N_l - 3)! / (N_l - n_p N)!$ in the third line. The generalization of this relation between S and C is

$$\begin{aligned} S(p, q, \dots, l) = & \left(\frac{N_l}{z} \right)^{(p+q+\dots+l)} \\ & \times \frac{[N_l - (p+1) - (q+1) - \dots - (l+1)]!}{(N_l - n_p N)!} \\ & \times C(p, q, \dots, l). \end{aligned} \quad (4.7)$$

In Eq. (4.7), one factor of (N_l/z) occurs for each bond [see Eq. (3.5)]; the third factor accounts for correlating monomers—it is the total number of conformations for a collection of polymers with a p -bond [($p+1$)-monomer] chain, a q -bond [($q+1$)-monomer] chain, etc., as defined above; and the second factor gives the number of ways of placing the remaining $n_p N - (p+1) - (q+1) - \dots - (l+1)$ uncorrelated (unconnected) monomers. Therefore, $S(p, q, \dots, l)$ is the product of $(N_l/z)^{(p+q+\dots+l)}$ and the total number of configurations of $n_p N$ monomers having a connectivity pattern just specified.

Equation (4.7) provides a recipe for evaluating the S factors in the expansion (4.5). This requires expressions for the partition functions (the number of configurations) for short single and multiple chains on the relevant lattice. Since the partition function for multiple chains is equal to the product of the partition functions for individual chains minus the number of configurations forbidden by excluded volume, every multiple-chain partition function can be expressed as a function of single-network partition functions [a single chain is a special case of single networks (see Figs. 1 and 2)]. Hence all lattice-dependent features of the expansion (4.5) are supplied by the single-network partition

| Topology | C(p) | Partition function on hypercubic lattices |
|----------|------|---|
| | C(1) | $N_l z$ |
| | C(2) | $N_l z(z-1)$ |
| | | 0 |
| | | $N_l z(z-1)(z-2)$ |
| | C(3) | $N_l z(z-1)^2$ |
| | | $N_l z(z-2)$ |
| | C(4) | $N_l z[(z-1)^3 - (z-2)]$ |
| | | $N_l z(z-1)^2(z-2)$ |
| | | $N_l z(z-1)(z-2)(z-3)$ |
| | | 0 |

| Topology | C(p,q,...,k) | Multiple-chain partition function |
|----------|--------------|--|
| | C(1,1) | $[C(1)]^2 - 2C(2) - 2C(1)$ |
| | C(2,1) | $C(2)C(1) - 4C(2) - 4C(3) - 2 \left(\begin{smallmatrix} \text{---} \\ \text{---} \end{smallmatrix} \right) - 2 \left(\begin{smallmatrix} \text{---} \\ \text{---} \end{smallmatrix} \right)$ |
| | C(1,1,1) | $C(1,1)C(1) - 8C(2,1) - 4C(1,1) - 8C(3)$ |
| | C(3,1) | $C(3)C(1) - 6C(3) - 4C(4) - 2 \left(\begin{smallmatrix} \text{---} \\ \text{---} \end{smallmatrix} \right)$ |
| | C(2,2) | $[C(2)]^2 - 2C(2) - 4C(3) - 4C(4) - 4 \left(\begin{smallmatrix} \text{---} \\ \text{---} \end{smallmatrix} \right) - 4 \left(\begin{smallmatrix} \text{---} \\ \text{---} \end{smallmatrix} \right) - 4 \left(\begin{smallmatrix} \text{---} \\ \text{---} \end{smallmatrix} \right) - 8 \left(\begin{smallmatrix} \text{---} \\ \text{---} \end{smallmatrix} \right) - 8 \left(\begin{smallmatrix} \text{---} \\ \text{---} \end{smallmatrix} \right)$ |
| | | $[C(1) - 6] \left(\begin{smallmatrix} \text{---} \\ \text{---} \end{smallmatrix} \right) - 6 \left(\begin{smallmatrix} \text{---} \\ \text{---} \end{smallmatrix} \right) - 6 \left(\begin{smallmatrix} \text{---} \\ \text{---} \end{smallmatrix} \right)$ |
| | | $[C(1) - 6] \left(\begin{smallmatrix} \text{---} \\ \text{---} \end{smallmatrix} \right) - 6 \left(\begin{smallmatrix} \text{---} \\ \text{---} \end{smallmatrix} \right)$ |
| | C(2,1,1) | $C(2,1)C(1) - 4C(3,1) - 4C(2,2) - 6C(2,1) - 8C(4) - 4 \left(\begin{smallmatrix} \text{---} \\ \text{---} \end{smallmatrix} \right) - 2 \left(\begin{smallmatrix} \text{---} \\ \text{---} \end{smallmatrix} \right) - 2 \left(\begin{smallmatrix} \text{---} \\ \text{---} \end{smallmatrix} \right) - 2 \left(\begin{smallmatrix} \text{---} \\ \text{---} \end{smallmatrix} \right)$ |
| | C(1,1,1,1) | $C(1,1,1)C(1) - 12C(2,1,1) - 24C(3,1) - 6C(1,1,1)$ |

FIG. 1. Single-network partition functions with at most four bonds. The diagrammatic representations of the partition functions show the topologies of the networks. The relevant C(p) are listed for the single linear chains [see Eq. (4.7)]. The value of the partition functions for networks configured on d-dimensional hypercubic lattices are given, where z=2d is the lattice coordination number. The multiplicative factor N_l (the total number of lattice sites) in the partition functions accounts for the translational degrees of freedom on lattices with periodic boundary conditions.

functions. Figure 1 lists all possible topologies for single networks with at most four bonds (B ≤ 4) and the values of their partition functions on hypercubic lattices (with periodic boundary conditions) in terms of the lattice coordination number z. Figure 2 gives general lattice-independent expressions for some multiple-chain partition functions as functions of single-network partition functions.

To illustrate our scheme for computing S's as a linear

FIG. 2. Topologies of multiple-chain (and multiple-network) partition functions are shown by their diagrammatic representations on the left. The column on the right gives the lattice-independent relationships between multiple-chain and multiple-network partition functions (with at most a total of four bonds) in terms of previously defined partition functions in Figs. 1 and 2. Recursive substitutions give explicit expressions of the multiple-chain partition functions C(p,q,...,l) in terms of the single-network partition functions in Fig. 1.

combination of numbers of short-chain configurations, we evaluate S(3) explicitly by first using Table I for the expansion of S(3) in terms of S's, then Eq. (4.7) for the expressions of S's in terms of C's [the explicit expression for S(0) = T_0 is given in Eq. (2.12)], and last Figs. 1 and 2 for the explicit values of C's. We find

$$\begin{aligned}
 \mathcal{D}(3) &= S(3) - 2S(2) - S(1,1) + 3S(1) - S(0) \\
 &= \left(\frac{N_l}{z}\right)^3 \frac{(N_l-4)!}{(N_l-n_p N)!} C(3) - 2 \left(\frac{N_l}{z}\right)^2 \frac{(N_l-3)!}{(N_l-n_p N)!} C(2) - \left(\frac{N_l}{z}\right)^2 \frac{(N_l-4)!}{(N_l-n_p N)!} C(1,1) + 3 \left(\frac{N_l}{z}\right) \\
 &\quad \times \frac{(N_l-2)!}{(N_l-n_p N)!} C(1) - \frac{N_l!}{(N_l-n_p N)!} \\
 &= \frac{N_l}{(N_l-n_p N)!} \left[z(z-1)^2 \left(\frac{N_l}{z}\right)^3 (N_l-4)! - 2z(z-1) \left(\frac{N_l}{z}\right)^2 (N_l-3)! \right. \\
 &\quad \left. - [N_l z^2 - 4z(z-1) - 2z] \left(\frac{N_l}{z}\right)^2 (N_l-4)! + 3z \left(\frac{N_l}{z}\right) (N_l-2)! - (N_l-1)! \right] \\
 &= \frac{N_l(N_l-4)!}{(N_l-n_p N)!} \left(\frac{N_l^3}{z^2} - \frac{8N_l^2}{z} + N_l^2 + 7N_l + 6 \right). \tag{4.8}
 \end{aligned}$$

The same result is obtained by momentum-space diagrammatic rules in Eq. (3.16d) of Ref. 3.

C. Calculation of the combinatorial prefactors

$\gamma(l_1, l_2, \dots, l_n)$

We now turn to the $\gamma(l_1, l_2, \dots, l_n)$ term in Eq. (3.18). This combinatorial prefactor is defined as the number of ways of extracting the set of chain segments with l_1, l_2, \dots, l_n bonds from the system of n_p $(N-1)$ -bond chains. Some short-chain γ prefactors for a variety of chain architectures are tabulated in Ref. 8. Here we briefly discuss a general procedure for evaluating these prefactors for linear chains.

Consider the location of the n chain segments with l_1, l_2, \dots, l_n correlating bonds. Let $A(a)$ denote a specific way of dividing the n segments into a groups. The number of chain segments in these groups are $u(1), u(2), \dots, u(a)$, therefore $\sum_{j=1}^a u(j) = n$. The segment lengths l_1, l_2, \dots, l_n are now renamed $l_1^{(1)}, l_2^{(1)}, \dots, l_{u(1)}^{(1)}, l_1^{(2)}, l_2^{(2)}, \dots, l_{u(2)}^{(2)}, \dots, l_1^{(a)}, l_2^{(a)}, \dots, l_{u(a)}^{(a)}$. If the condition

$$\sum_{i=1}^{u(j)} (l_i^{(j)} + 1) \leq N \tag{4.9}$$

is satisfied for $j=1, 2, \dots, a$, each of these a groups of chain segments can fit into an $(N-1)$ -bond chain [see Eq. (4.1)].

The number of ways of choosing a chains among n_p for the location of the chain segments is

$$\binom{n_p}{a}, \tag{4.10}$$

while the number of ways of arranging the chain segments with $l_1^{(j)}, l_2^{(j)}, \dots, l_{u(j)}^{(j)}$ bonds along individual polymer chains with $N-1$ bonds is provided by the function \mathcal{P} in Eq. (4.1). Thus we arrive at the general formula for evaluating the γ prefactors

$$\begin{aligned} \gamma(l_1, l_2, \dots, l_n) &= \sum_{a=1}^n \binom{n_p}{a} \\ &\times \sum_{A(a)} \prod_{j=1}^a \mathcal{P}(N-1 | l_1^{(j)}, l_2^{(j)}, \dots, l_{u(j)}^{(j)}), \end{aligned} \tag{4.11}$$

where the summation $\sum_{A(a)}$ is over all possible assignments of the n chain segments to a groups.

D. The relationship between the two formulations

In the work of Freed and co-workers, the contribution of a diagram $\gamma_D D_B$ corresponds to a specific list of chain segments with l_1, l_2, \dots, l_n correlated bonds *as well as* a specific assignment A of these chain segments to different chains (e.g., see Refs. 8 and 17). In contrast, our $\gamma(l_1, l_2, \dots, l_n) \mathcal{D}(l_1, l_2, \dots, l_n)$ contains *all* contributions with l_1, l_2, \dots, l_n correlated bonds regardless of the locations of these bonds among the different chains. However, because the value of \mathcal{D} depends solely on l_1, l_2, \dots, l_n [see Eq. (4.5)], the proportionality relation (3.14) holds for any diagram D_B of Freed *et al.* if its B bonds are partitioned into segments of l_1, l_2, \dots, l_n . Aside from the constant T_0 in Eq. (3.14), the only difference between the two definitions of diagrams is in the γ prefactors. In general, one γ of ours corresponds to the sum of several γ_D 's of Freed *et al.* because a summation over $A(a)$ is included in our evaluation of γ [Eq. (4.11)].

Freed and co-workers also consider the quantity^{8,17}

$$d_B \equiv \frac{N!}{(N_I - \mu)!} D_B, \tag{4.12}$$

where μ is the number of monomers involved in the bonds of the given diagram D_B . Equation (3.14) implies that d_B is equivalent to

$$d(l_1, l_2, \dots, l_n) \equiv \frac{N!}{(N_I - n - \sum_{i=1}^n l_i)!} \frac{\mathcal{D}(l_1, l_2, \dots, l_n)}{T_0} \tag{4.13}$$

in our formulation. Using Eqs. (2.12), (4.5), and (4.7), it is straightforward to obtain the explicit form

$$\begin{aligned} d(l_1, l_2, \dots, l_n) &= \sum_{\{d(l_1)\}} \sum_{\{d(l_2)\}} \dots \sum_{\{d(l_n)\}} \left[\prod_{i=1}^n (-1)^{\sigma} \mathcal{P}(l_i | l_{i,1}, l_{i,2}, \dots, l_{i,r(i)}) \right] \left(\frac{N_I}{z} \right)^{\sigma'} \frac{[N_I - \sum_{i=1}^n \sum_{j=1}^{r(i)} (l_{i,j} + 1)]!}{[N_I - \sum_{i=1}^n (l_i + 1)]!} \\ &\times C(l_{1,1}, l_{1,2}, \dots, l_{1,r(1)}, l_{2,1}, l_{2,2}, \dots, l_{2,r(2)}, \dots, l_{n,1}, l_{n,2}, \dots, l_{n,r(n)}) \end{aligned} \tag{4.14}$$

for this quantity, where the number of bonds σ' in the C 's is a function of the summation variables $l_{i,j}$'s,

$$\begin{aligned} \sigma' &= \sigma'(l_{1,1}, l_{1,2}, \dots, l_{1,r(1)}, l_{2,1}, l_{2,2}, \dots, l_{2,r(2)}, \dots, l_{n,1}, l_{n,2}, \dots, l_{n,r(n)}) \\ &\equiv \sum_{i=1}^n \sum_{j=1}^{r(i)} l_{i,j}. \end{aligned} \tag{4.15}$$

Table II summarizes the correspondence between the notation used in the present paper and that of Freed *et al.*

V. INTERMONOMER INTERACTIONS

The sections above describe a treatment of the chain conformational entropy. We now consider the incorporation of nearest neighbor interaction energies. Again we

TABLE II. A comparison of notation; $B=l_1+l_2+\dots+l_n$.

| The present notation | Notation of Freed <i>et al.</i> |
|---|-------------------------------------|
| $\mathcal{D}(l_1, l_2, \dots, l_n)/T_0$ | D_B |
| $\gamma(l_1, l_2, \dots, l_n)$ | $\sum_{a=1}^n \sum_{A(a)} \gamma_D$ |
| $N! \mathcal{D}(l_1, l_2, \dots, l_n) / [(N! - n - \sum_{i=1}^n l_i)! T_0]$ | d_B |

start with the formulation of Freed *et al.*^{16,17} For a polymer-solvent or a polymer-void system, the total interaction energy is given by

$$E = \epsilon \sum_{\alpha, m > \alpha', m'} \sum_{\beta=1}^z \delta(i_{\alpha}^m, i_{\alpha'}^{m'} + \beta), \quad (5.1)$$

where ϵ is the interaction energy per monomer-monomer contact and all possible monomer pairs $\alpha, m > \alpha', m'$ are summed to give the total energy. For any given configuration specified by the set of positions i_{α}^m for all monomers labeled by $\alpha=1, 2, \dots, N$ and $m=1, 2, \dots, n_p$, the Boltzmann factor is

$$\begin{aligned} & \exp\left(-\frac{E}{kT}\right) \\ &= \exp\left[-\frac{\epsilon}{kT} \sum_{\alpha, m > \alpha', m'} \sum_{\beta=1}^z \delta(i_{\alpha}^m, i_{\alpha'}^{m'} + \beta)\right] \\ &= \prod_{\alpha, m > \alpha', m'} \exp\left[-\frac{\epsilon}{kT} \sum_{\beta=1}^z \delta(i_{\alpha}^m, i_{\alpha'}^{m'} + \beta)\right] \\ &= \prod_{\alpha, m > \alpha', m'} \left[1 + \sum_{\beta=1}^z \delta(i_{\alpha}^m, i_{\alpha'}^{m'} + \beta) \left[\exp\left(-\frac{\epsilon}{kT}\right) - 1\right]\right], \end{aligned} \quad (5.2)$$

where k is the Boltzmann constant and T is absolute temperature. The third line follows because for any given set of monomer positions, the summation over δ 's in the second line of Eq. (5.2) can be either 1 or 0. This Boltzmann

factor is combined with the (athermal) partition function (2.4) for the conformational entropy to yield the full partition function with monomer-monomer interaction energies

$$\begin{aligned} & \Omega(n_p, N, N_l; \epsilon) \\ &= \sum_{\text{e.v.}} \left\{ \prod_{m=1}^{n_p} \prod_{\alpha=1}^{N-1} \sum_{\beta=1}^z \delta(i_{\alpha}^m, i_{\alpha+1}^m + \beta) \right\} \\ & \times \left[\prod_{\alpha, m > \alpha', m'} \left[1 + f \sum_{\beta=1}^z \delta(i_{\alpha}^m, i_{\alpha'}^{m'} + \beta) \right] \right], \end{aligned} \quad (5.3)$$

where

$$f = f(\epsilon) \equiv \exp\left(-\frac{\epsilon}{kT}\right) - 1 \quad (5.4)$$

is the Mayer function. All possible monomer positions that do not violate excluded volume constraints are summed over by $\sum_{\text{e.v.}}$ in Eq. (5.3). For any given set of monomer positions, terms in the first pair of curly brackets in Eq. (5.3) are either 1 or 0, depending on whether the set of monomer positions satisfies or violates the polymer connectivity constraints. If the set of monomer positions is viable, its weight is given by the ϵ -dependent Boltzmann factor in the second pair of curly brackets.

In their systematic analysis of the energy part of Eq. (5.3), Freed and co-workers proceed as with the entropy expansion and replace the Kronecker δ 's with Fourier sums in momentum space.^{9,16,17} We now explore the energy expansion in coordinate space.

We first combine the full energy expansion series in the second pair of curly brackets of Eq. (5.3) with only the single *leading* term of the entropy series in the first pair of curly brackets [see Eqs. (2.8) and (2.11)]. Freed and co-workers call this formulation of the theory the "extended mean field" approximation,^{6,9} for which the partition function is expanded as a standard Mayer³⁰ cluster series

$$\begin{aligned} & \left(\frac{z}{N_l}\right)^{n_p(N-1)} \sum_{\text{e.v.}} \prod_{\alpha, m > \alpha', m'} \left[1 + f \sum_{\beta=1}^z \delta(i_{\alpha}^m, i_{\alpha'}^{m'} + \beta) \right] \\ &= \left(\frac{z}{N_l}\right)^{n_p(N-1)} \sum_{\text{e.v.}} \left[1 + f \sum_{\alpha, m > \alpha', m'} \sum_{\beta=1}^z \delta(i_{\alpha}^m, i_{\alpha'}^{m'} + \beta) \right. \\ & \quad \left. + f^2 \underbrace{\sum_{\alpha_1, m_1 > \alpha'_1, m'_1} \sum_{\alpha_2, m_2 > \alpha'_2, m'_2} \sum_{\beta_1=1}^z \sum_{\beta_2=1}^z \delta(i_{\alpha_1}^{m_1}, i_{\alpha'_1}^{m'_1} + \beta_1) \delta(i_{\alpha_2}^{m_2}, i_{\alpha'_2}^{m'_2} + \beta_2)}_{\alpha_1, m_1 > \alpha_2, m_2} + O(f^3) \right] \\ &= \left(\frac{z}{N_l}\right)^{n_p(N-1)} \left[\frac{N_l}{(N_l - n_p N)!} + f \frac{(N_l - 2)}{(N_l - n_p N)!} \binom{n_p N}{2} C(1) + O(f^2) \right], \end{aligned} \quad (5.5)$$

where $C(1)$ is given in Fig. 1. Comparison with the entropy expansion in Sec. IV shows that the products of δ 's (nearest-neighbor constraints) in Eq. (5.5) correspond to partition functions for single and multiple networks on the given lattice, with low-order corrections represented by small networks. Different networks correspond to different topologies, i.e., different connectivities among the δ 's.

Contributions to the extended mean field partition function (5.5) from any given topology of δ 's are given by the value of the corresponding "diagram" \mathcal{D} and an appropriate combinatoric prefactor γ . A factor of f^k is associated with a diagram with k energetic interactions. Since each interaction contributes a factor of δ instead of a δ and an additional constant term in X [Eq. (2.6)], only a single C is required for any given \mathcal{D} of the extended mean field partition function (5.5), in contrast to the linear combinations of C 's required for the entropic \mathcal{D} 's [Eqs. (4.5) and (4.7)]. Thus the evaluation of the energy corrections proceeds more simply than for the entropy corrections in this respect. Using a similar analysis as in Sec. IV, it is easy to see that the diagram for any given collection of networks (including the special case of a single network) involving k energetic interactions among μ monomers is given by

$$\mathcal{D} = f^k \frac{(N_l - \mu)!}{(N_l - n_p N)!} C, \quad (5.6)$$

where C is the number of ways of configuring the given set of networks on the lattice, and the combinatoric factor $(N_l - \mu)! / (N_l - n_p N)!$ is the number of ways of positioning the monomers which are not involved in the networks. The γ prefactor for a diagram contributing to Eq. (5.5) corresponds to the number of ways of extracting the number of monomers involved in that diagram from the entire system of $n_p N$, hence

$$\gamma = \binom{n_p N}{\mu} \quad (5.7)$$

for any diagram with μ monomers.

We now consider the simultaneous expansion of both the entropy and energy series in Eq. (5.3). The procedure is straightforward, but tedious because of the presence of mixed entropy-energy terms. The nearest-neighbor constraints now include both the δ 's for the correlating bonds and the δ 's for energy interactions. Each correlating bond from the entropy expansion contributes a factor of X [Eq. (2.6)], while each interaction from the energy expansion contributes a factor of $f \sum_{\beta=1}^z \delta(i_{\alpha}^m, i_{\alpha'}^{m'} + \beta)$. These products of X 's and energy δ 's may be expanded in a manner similar to that given in Table I. Again, aside from an overall constant, expansion terms contributing to the general partition function (5.3) are decomposed into products of γ and \mathcal{D} . For any given topology of correlating bonds and nearest-neighbor interactions, the γ prefactor gives the number of ways of extracting the given topology from the system of $n_p N$ -monomer chains. As in the entropy expansion [Eqs. (4.5) and (4.7)], the diagram \mathcal{D} of a given

topology can be expressed as a linear combination of C 's which are now numbers of ways of configuring subsets of the given topology on the lattice.

As an illustration of this general procedure, we calculate the contribution $\gamma \mathcal{D}$ to the partition function (5.3) from the nearest-neighbor topology that has one monomer connected to another by a correlating bond and also one of the correlating monomers interacting with a third unconnected monomer (Fig. 2, b_2 of Ref. 9). The combinatoric γ prefactor

$$\gamma = 2n_p(N-1)(n_p N - 2) \quad (5.8)$$

for this contribution is the product of two factors— $n_p(N-1)$ is the number of ways of extracting one correlating bond from the polymeric system with $n_p N$ -monomer chains, while $n_p N - 2$ is the total number of monomers not participating in the correlating bond and therefore available to interact energetically with either one of the two monomers of the bonded pair (hence the overall factor of 2). As in the entropy expansion, the contribution of the diagram \mathcal{D} for this topology is evaluated by choosing any one assignment of $\{\alpha, m\}$'s consistent with the diagram's topology. Therefore, using Eqs. (3.6) and (4.7), and Fig. 1,

$$\begin{aligned} \mathcal{D} &= \sum_{\text{c.v.}} \left\{ \left[\frac{N_l}{z} \sum_{\beta_1=1}^z \delta(i_1^1, i_2^1 + \beta_1) \right] - 1 \right\} \\ &\quad \times \left\{ f \sum_{\beta_2=1}^z \delta(i_2^1, i_1^2 + \beta_2) \right\} \\ &= f \left(\frac{z}{N_l} \right) [S(2) - S(1)] = \frac{f N_l (2z - N_l) (N_l - 3)!}{(N_l - n_p N)!} \end{aligned} \quad (5.9)$$

is computed for this diagram.

VI. APPLICATIONS

The present coordinate-space formulation is in some respects more amenable to generalization than the momentum-space formulation of the lattice cluster expansion of Freed *et al.* A simple example is the ease with which immediate self-reversals may be removed from the partition function to obtain the conventional Flory-Huggins approximation as the zeroth order term. This can be achieved simply by substituting $z-1$ for z in the definition of X in Eq. (2.6)³¹

$$X_{\alpha, m} \rightarrow \frac{N_l}{(z-1)} \left[\sum_{\beta=1}^z \delta(i_{\alpha}^m, i_{\alpha+1}^m + \beta) \right] - 1. \quad (6.1)$$

In comparison, the leading $q=0$ conformational entropy term that arises naturally from the momentum-space formulation of Freed *et al.* differs from the conventional Flory-Huggins approximation by a factor of $[(z-1)/z]^{n_p(N-1)}$, though it is possible to obtain the conventional Flory-Huggins mean field as the leading expansion term in the momentum-space formulation if immediate re-

versals of the chains are eliminated by formulating the theory as a special case of semiflexible chains.⁵

The lowest-order term in the energy expansion of nearest-neighbor interactions in the formulation of Freed *et al.*^{2,6,7,9,16} corresponds to the case with zero interaction. The extended mean field approximation,^{6,9} which retains only the mean field entropy contribution, but retains all parts of the energy contribution, gives extra higher-order terms in addition to the conventional Flory–Huggins contact energy. To recover the random-mixing contact energy in Flory–Huggins theories,¹ the $q=0$ and $q\neq 0$ contributions of energy diagrams have to be separated.^{9,16} By contrast, it is relatively straightforward to obtain the conventional Flory–Huggins random-mixing interaction energy as the zeroth approximation in the coordinate-space formulation. To this end, Eq. (5.2) is rewritten as

$$\exp\left(-\frac{E}{kT}\right) = \prod_{\alpha, m} \prod_{\alpha', m'} \left[\exp\left(-\frac{z\epsilon}{kTN_l}\right) (1 + Y_{\alpha, \alpha'}^{m, m'}) \right], \quad (6.2)$$

where

$$Y_{\alpha, \alpha'}^{m, m'} \equiv \exp\left(\frac{z\epsilon}{kTN_l}\right) - 1 + f(\epsilon) \exp\left(\frac{z\epsilon}{kTN_l}\right) \times \sum_{\beta=1}^z \delta(i_{\alpha}^m, i_{\alpha'}^{m'} + \beta). \quad (6.3)$$

Thus the zeroth-order term in Eq. (6.3) is the product of $\exp[-z\epsilon/(kTN_l)]$ over all monomer labels $\alpha, m > \alpha', m'$. The zeroth-order interaction energy is therefore given by the Flory–Huggins random-mixing result

$$\frac{z\epsilon}{N_l} \binom{n_p N}{2}. \quad (6.4)$$

As for the X factor defined in Eq. (2.6), the Y factor in Eq. (6.3) is a sum of a constant and a Kronecker- δ term. Hence the energy expansion of Eq. (6.2) has the same structure as the entropic expansion with X 's, with products of Y 's giving rise to linear combinations of C 's.

It is more straightforward to deal with nonperiodic lattice boundary conditions in the coordinate-space formulation than in the momentum-space formulation with Fourier transforms. Nonperiodic lattice boundary conditions are needed in the study of polymeric systems with geometric constraints. For instance, hard boundary conditions are useful in treating polymers in confined space. Here the general relation (4.7) between the S 's and the C 's allows for the calculation of diagrams in the cluster expansion with any set of boundary conditions by simply evaluating the C 's with the same set of boundary conditions. As an illustration, Fig. 3 gives a few small-network partition functions (C 's) on an L^3 -site three-dimensional cubic lattice with hard boundary conditions ($N_l = L^3$). To obtain the hard-boundary expression for $\mathcal{D}(3)$, e.g., it is only necessary to replace in Eq. (4.8) the C 's computed using periodic boundary conditions (from Fig. 1) by the C 's in Fig. 3.

| Topology | Partition function |
|----------|--|
| | $6L^2(L-1)$ |
| | $6L^2(L-2) + 24L(L-1)^2$ |
| | 0 |
| | $72L(L-1)(L-2) + 48(L-1)^3$ |
| | $72L(L-1)(L-2) + 48(L-1)^3 + 24L(L-1)^2 + 6L^2(L-3)$ |
| | $24L(L-1)^2$ |
| | $120L(L-1)(L-2) + 72L(L-2)^2 + 288(L-1)^2(L-2) + 144(L-1)^3 + 6L^2(L-4) + 96L(L-1)(L-3)$ |
| | $72L(L-2)^2 + 96L(L-1)(L-2) + 288(L-1)^2(L-2) + 96(L-1)^3 + 48L(L-1)(L-3)$ |
| | $72L(L-2)^2 + 288(L-1)^2(L-2)$ |
| | 0 |

FIG. 3. Single-network partition functions (with at most four bonds) on a three-dimensional simple cubic lattice ($z=6$) with hard boundary conditions. The dimension of the lattice is equal to $L \times L \times L$, hence $N_l = L^3$.

The formalism of Freed *et al.* and its present formulation in coordinate space provides a means to approximate the partition function for a polymer solution of arbitrary complexity by using partition function C 's for the relevant short chains and small networks that contribute to the expansion. Conformational properties of short single chains have been studied extensively by exact computer enumerations.^{24–28} These computer results provide many of the terms required for evaluation of higher-order corrections in the series, and conversely, as shown by Nemirovsky *et al.*,¹⁸ the lattice cluster expansion provides a recipe for extrapolation from short chain results to the properties of longer chains. The present coordinate-space formulation of the lattice cluster theory may help assess the issue of convergence and to elucidate the general validity of the suggested analytic properties of the cluster series (see, e.g., Ref. 18).

The present treatment is generalizable to heteropolymers such as proteins. More diagrams will be needed for heteropolymers because diagrams will arise from the many different segments of monomer sequences (subsequences) that have to be taken into account for a given heteropolymer sequence in addition to those contributing to the homopolymer case. For instance, if there are $h > 0$ types of monomers in each of the N -monomer chains and N_1, N_2, \dots, N_h (> 0) are the numbers of monomers belonging to these different monomer types ($\sum_{i=1}^h N_i = N$), the $\gamma \mathcal{D}$ expression for a diagram involving k nearest-neighbor energetic interactions among μ monomers would be modified from Eqs. (5.6) and (5.7) for homopolymers to

$$\gamma_{\mathcal{D}} = \left\{ \sum_{\mu_1 + \mu_2 + \dots + \mu_h = \mu} \left[\prod_{i=1}^h \binom{n_p N_i}{\mu_i} \right] \right. \\ \left. \times \sum_{\mathbf{c}(\mu_1, \mu_2, \dots, \mu_h)} f[\mathbf{c}(\mu_1, \mu_2, \dots, \mu_h)] \right\} \frac{(N_l - \mu)!}{(N_l - n_p N)!} C \quad (6.5)$$

for heteropolymers. Here μ_i is the number of monomers of type i among the μ monomers in the diagram, $\mathbf{c}(\mu_1, \mu_2, \dots, \mu_h)$'s are the $\mu! / (\prod_{i=1}^h \mu_i!)$ different arrangements of the $\mu = \mu_1 + \mu_2 + \dots + \mu_h$ monomers among the μ positions prescribed by the given diagram (topology) C . Owing to the heterogeneity of the interactions, the Boltzmann weight f now depends on the specific types of monomers involving in the k nearest-neighbor contacts in the diagram, and is therefore a function of the monomer position \mathbf{c} . All possible Boltzmann weights that arise from all possible monomer positions \mathbf{c} are included. The quantity in curly brackets in Eq. (6.5) may be viewed as a heteropolymeric decomposition of the γf^k factor for homopolymers. While this step greatly reduces analytic tractability, it should require only a slight increase in bookkeeping if these terms are to be determined by computer enumerations. A similar procedure for dealing with sequence heterogeneity applies to mixed energy-entropy diagrams such as those in Eqs. (5.8) and (5.9). In particular, the combinatorial prefactor γ should be modified to account for the different number of ways of choosing a specific set of subsequences from the system of n_p heteropolymeric sequences.

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