Application of graph theory to the statistical thermodynamics of lattice polymers. I. Elements of theory and test for dimers

Olga D. Brazhnik and Karl F. Freed
The James Franck Institute, The University of Chicago,
Chicago, Illinois 60637

The lattice cluster theory (LCT) is extended to enable inclusion of longer range correlation contributions to the partition function of lattice model polymers in the athermal limit. A diagrammatic technique represents the expansion of the partition function in powers of the inverse lattice coordination number. Graph theory is applied to sort, classify, and evaluate the numerous diagrams appearing in higher orders. New general theorems are proven that provide for a significant reduction in the computational labor required to evaluate the contributions from higher order correlations. The new algorithm efficiently generates the correlation corrections to the Flory mean field approximation from as many as eight sterically interacting bonds. While the new results contain the essential ingredients for treating a system of flexible chains with arbitrary lengths and concentrations, the complexity of our new algorithm motivates us to apply the theory here to the simplest case of a system of lattice dimers as a means of first testing the theory by comparison to the dimer packing entropies from the work of Gaunt. This comparison demonstrates that the eight bond LCT is exact through order ϕ^5 for dimers in one through three-dimensions, where ϕ is the volume fraction of dimers. A subsequent work will use the contracted diagrams derived and tested here to treat the packing entropy for a system of flexible N-mers at a volume fraction of ϕ on hypercubic lattices.

I. INTRODUCTION

While polymer materials exhibit a variety of properties that are useful for industrial applications, the thermodynamic description of polymer systems encounters numerous difficult scientific questions. The goal of successfully manipulating the properties of polymeric materials requires the underpinnings of an adequate theory describing the linkage between the macroscopic properties of materials and the microscopic parameters of their constituents. Such a linkage is provided by statistical thermodynamics.

The statistical thermodynamics of polymer systems is further complicated beyond the theory of simple fluids due to the fact that polymer properties depend upon phenomena occurring on a vast array of length scales, from those associated with atomic and monomer dimensions to the sizes of individual chains. In order to simplify the impossible task of enumerating all possible states for the polymer system, lattice models are widely employed. These models replace continuous space by a lattice, and the monomers are restricted to lie at the sites of the lattice. Some sites may be left unoccupied in order to model the compressibility of realistic polymer systems.

Additional approximations emerge from attempts to solve the lattice model. The classical Flory-Huggins theory (FHT)[1,3–6] evaluates the packing entropy of lattice polymers as what is called the combinatorial entropy, and FHT also uses a random mixing assumption[7] for estimating the enthalpic terms. FHT explains the general incompatibility of polymer blends and appears to correlate the results of some experiments. However, the crude treatment of polymer connectivity and the gross overestimate for the number of contacts (compared to Monte Carlo simulations[8–10]) leads to the failure of the theory to produce reasonable quantitative predictions and to incorporate the important influences of chain architecture.

Numerous attempts have been undertaken to improve the FHT. The Guggenheim approach[11–13] includes some additional contributions from connectivity and end effects[14]. The quasi-chemical approximation[15] replaces the random mixing assumption by a temperature dependent phenomenological expression for the number of contacts. The BGY approach[16] evaluates this number of contacts from approximate pair correlation functions. The lattice cluster theory (LCT) of Freed and co-workers[17–21] develops a systematic algorithm for constructing the solution to the standard polymer lattice model, a solution which is free of any phenomenological assumptions. The formal LCT solution is written as a double expansion in the inverse coordination number z^{-1} and in the dimensionless nearest neighbor van der Waals energy ϵ. The theory also includes a dependence on the individual monomer architectures by permitting the monomer s to extend over several lattice sites and therefore more closely to resemble the actual monomer structures.

The LCT computations to date include contributions from local packing and interaction induced correlations involving contributions from up to four correlating bonds and/or interactions[20,21]. Comparisons with Monte Carlo simulations[10,22–24] indicate that the LCT provides an excellent description for the lattice model of the polymer-solvent system. The current lack of extensive computer simulations for compressible blends with structured monomers does not yet permit making similar tests for these systems. The available simulations indicate that the LCT is very accurate at higher temperatures but that errors of roughly $5-10\%$ in the internal energies of mixing become noticeable at lower temperatures of $T^* = kT/\epsilon = 3$, which is near the critical temperature. The comparison with recent simulations[9] further demonstrates that the influence of monomer structure is likewise adequately described at higher temperatures. Thus, the simulat ions indicate the need for higher order contributions at lower temperatures. In addition, consideration of the more complicated local correlations produced by more highly branched monomer structures suggests the need in these cases for checks concerning the relevance of higher order contributions.

The original derivation of the lattice cluster theory[17] uses field theoretical methods which are generally unfamiliar to polymer scientists. Later papers[18−21,25,26] contain an algebraic derivation of the LCT that produces significant computational simplifications in evaluating the thermodynamic properties of polymer systems. However, the calculation of higher orders presents an explosively growing task of accounting for all possible configurations of the correlating bonds. This combinatorial growth problem also applies to the alternative approach by Dill et al.[27] Therefore, there is need for new mathematical tools enabling the automatic computer generated classification and evaluation of all relevant configurations of the system. Techniques from graph theory are shown here to fulfill this need.

This paper describes the development of algorithms for evaluating higher order LCT contributions using some concepts from graph theory. The statistical thermodynamics is generalized to lattices of different dimensionality to enable the testing of our theory against exact results and because of extensive interest in this system[28]. Section II briefly describes required aspects of the current status of the lattice cluster theory for lattice model polymers and notes the shortcomings of the present theory that require the consideration of higher order contributions. Because the only derivation of the LCT diagram rules is presented in terms of the older, original field theoretic formulation and because these rules are used for proving essential theorems that yield significant simplifications, Section II sketches the requisite diagram rules. Section III discusses the application of graph theory to classify, distinguish, and evaluate the diagrams that represent these contributions. Section IV specializes our approach to the simplest system of lattice dimers where tests may be made of the new algorithms by comparing the LCT predictions with known results from other theories and from computer simulations. These comparisons provide a stringent check on the contracted diagrams that form the most essential and computationally difficult ingredients of the LCT for describing a system of N-mers on a lattice. The appendices present some technical details of the method.

II. LATTICE CLUSTER THEORY AND GENERAL SKETCH OF THE DIAGRAM METHOD

This section summarizes necessary background concerning the current status of the LCT, followed by a discussion in Sect. III of our new developments. The theory is described for a single component system of lattice polymer chains. The generalizations to several components and to chains with structured monomers is straightforward and will be presented elsewhere.

A. Analytic Representation of the Lattice Model

Lattice models replace the continuous space of real liquid systems by a lattice which restricts the allowed configurations for the polymer chains and which, therefore, significantly facilicates the enumeration of all possible states for the system. The topology of the lattice is fixed, in part, by the number of nearest neighbors z (called the coordination number). The position of lattice site i is denoted as $\mathbf{r}_i$, and the lattice vectors $\mathbf{a}_\beta$, $\beta = 1, ..., z$, designate the vectors from $\mathbf{r}_i$ to its z nearest neighbor lattice sites.

The partition function of the lattice polymers is formally written as the sum over all possible ways of placing p flexible linear polymer chains of length M on the lattice of N lattice sites[20,21],

$$W(p, M) = \frac{1}{p!2^p} \sum_{i_1^1 \neq \ldots \neq i_M^1 \neq i_1^2 \neq \ldots \neq i_M^2 \neq i_1^p \neq \ldots \neq i_M^p} \prod_{m=1}^{p} \left\{ \prod_{\alpha=1}^{M-1} \sum_{\beta_\alpha^m=1}^{z} \delta\left(i_\alpha^m, i_{\alpha+1}^m + \beta_\alpha^m\right) \right\}. \tag{2.1}$$

Here the shorthand notation $\delta(i, j + \beta) = \delta(\mathbf{r_i}, \mathbf{r_j} + \mathbf{a}_\beta)$ represents the bonding constraint that a pair of bonded monomers i and j lie at nearest neighbor sites. The superscripts in the argument of the Kronecker delta of Eq. (2.1) label the chain number, while the subscripts sequentially number the monomers along the chain. The summation over β_α^m appears because each bond may lie in any of the z different possible orientations. The factor of $(p!)^{-1}$ in Eq. (2.1) accounts for the indistinguishability of all chains, and the symmetry number is $1/2$ for each chain. The summation in Eq. (2.1) enforces the strict excluded volume constraint that prohibits any two monomers from occupying the same lattice site.

Equation (2.1) is an exact representation of the lattice model for the packing of linear polymers on a d-dimensional hypercubic lattice in the athermal limit. The Kronecker delta functions in Eq. (2.1) represent the condition prohibiting successively bonded monomers from occupying the same lattice sites, so the additional excluded-volume constraint $i_\alpha^m \neq i_{\alpha+1}^m$ is unnecessary for directly bonded monomers. However, the previous LCT treatments[17–21] insert this extra constraint both for notational symmetry and because it provides a useful check on the computations.

The partition function of Eq. (2.1) may be transformed into the form of a cluster expansion. After the introduction of lattice Fourier transforms[20,21], Eq. (2.1) becomes

$$W(p,M) = \frac{1}{p!2^p} \sum_{i_1^1 \neq \ldots \neq i_M^p} \prod_{m=1}^{p} \prod_{\alpha=1}^{M-1} \left[\frac{z}{N}\left(1 + X_{\alpha,m}\right)\right], \tag{2.2}$$

with each polymer bond α, m providing the correlation term

$$X_{\alpha,m} = \frac{1}{z} \sum_{\mathbf{q}_\alpha^m \neq 0}^{z} f(\mathbf{q}_\alpha^m) \exp\left[i\mathbf{q}_\alpha^m \cdot \left(\mathbf{r}_{i_\alpha}^m - \mathbf{r}_{i_{\alpha+1}}^m\right)\right], \tag{2.3}$$

where the single bond structure factor is

$$f(\mathbf{q}) = \sum_{\beta=1}^{z} \exp\left(-i\mathbf{q}\cdot\mathbf{a}_\beta\right). \tag{2.4}$$

As discussed below, the product form of (2.2) naturally generates a cluster expansion in much the same manner as in Mayer's cluster expansion for the statistical mechanics of nonideal gases[29].

The leading contribution to Eq. (2.2) arises from the factor of unity on the right hand side for each α and m, yielding the zeroth order mean-field approximation,

$$W^{MF}(p,M) = \frac{1}{p!2^p} \sum_{i_1^1 \neq \ldots \neq i_M^p} \prod_{m=1}^{p} \prod_{\alpha=1}^{M-1} \left(\frac{z}{N}\right). \tag{2.5}$$

The summand in Eq. (2.5) no longer depends on the monomer positions (the $\mathbf{r}_{i_\alpha}^m$), and thus Eq. (2.5) corresponds to Flory's approximation which effectively neglects all monomer correlations due to the contributions to Eq. (2.5) from the $f(\mathbf{q}_\alpha^m)$ terms in Eq. (2.3). Because of this absence of correlations, the summations in Eq. (2.5) are readily evaluated as

$$W^{MF}(p,M) = \frac{1}{p!2^p} \frac{N!}{(N-pN)!} \left(\frac{z}{N}\right)^{p(M-1)}. \tag{2.6}$$

Equation (2.6) recovers the classic Flory-Huggins combinatorial packing entropy for the p polymers (with immediate self-reversals permitted)[1,3]. The remaining terms from the cluster expansion in Eq. (2.2), therefore, produce the corrections to the Flory-Huggins approximation as arising from correlations, neglected entirely by Flory[1,3], between the placement of monomers and bonds on the lattice.

B. Cluster Expansion and Diagrammatic Representation for the Packing Entropy

The quantities $X_{\alpha,m}$ in Eq. (2.3) depend on the explicit positions of the two segments forming the αth bond on the mth polymer chain. Thus, the $X_{\alpha,m}$ represent the corrections arising from correlations introduced in monomer positions due to bonds between successive monomers. Expanding the product term in Eq. (2.2) leads to a cluster expansion of the form

$$1 + \sum_{\alpha,m} X_{\alpha,m} + \sum_{\alpha,m>\alpha',m'} X_{\alpha,m}X_{\alpha',m'} + \ldots, \tag{2.7}$$

where the designation $\alpha, m > \alpha^{'}, m^{'}$ indicates that the summation in Eq. (2.7) runs over all distinct pairs of bonds. The linear terms in (2.7) are called the one-bond contributions, the quadratic are the two-bond corrections, etc.

The contributions to the cluster expansion from Eq. (2.7) are conveniently represented in terms of diagrams in which each factor of $X_{\alpha,m}$ is depicted as a bond between a pair of neighboring lattice sites. Some examples of the LCT diagrams are presented in Fig. 1. Thus, the full partition function $W(p,M)$ is written symbolically as

$$W(p,M) = W^{MF}(p,M)\left(1 + \sum_{B} \gamma_D D_B\right), \tag{2.8}$$

where the $\{D_B\}$ represent the contributions from all possible diagrams with B bonds. The D_B in Eq. (2.8) designates the value of a particular diagram, and γ_D is a combinatorial factor describing the number of ways in which the B bonds depicted in the diagram may be selected from the whole system of p linear chains with polymerization index M.

The value of a diagram with B bonds and v vertices (monomers) is further factored into the product of two terms,

$$D_B = \alpha d_B, \tag{2.9}$$

where α depends only on the total number of lattice sites N and the number of vertices v in the diagram as

$$\alpha = [N(N-1)...(N-v+1)]^{-1}, \tag{2.10}$$

while the factor d_B (see below) is lattice dependent but architecture independent. For example, when $B = 1$, there is a single diagram, diagram a of Fig. 1 with $\gamma_{1(a)} = pM_1$, where M_1 is the total number of distinct bonds that may be chosen from a single chain, e.g.,

$$M_1 = (M-1)$$

for linear chains. Generalizations are straightforward for chains with structured monomers[18,21]. Diagram b of Fig. 1 has two sequential bonds, and its multiplicative factor is $\gamma_2 = pM_2$, where M_2 is the chain architecture dependent total number of distinct ways of selecting two sequential bonds on a single chain. Section III discusses the γ_D in more detail. Allowing the polymer to have other than a linear architecture leads to additional diagrams as illustrated in diagrams $e-g$ of Fig. 1. The incremental effort necessary for applying the theory to various different branched architectures merely involves the calculation of the appropriate $\{M_i\}$ for these structures and the evaluation of these extra branched diagrams[18,21].

C. Contracted Diagrams

The process of calculating the values associated with the cluster diagrams first involves the conversion of the restricted sums over monomer positions from Eq. (2.1) into a series of unrestricted sums. The simplest example is provided by the one-bond diagram a of Fig. 1 as

$$\sum_{i \neq j} h(i,j) = \sum_{i,j} h(i,j) - \sum_{i=j} h(i,j). \tag{2.11}$$

The condition $i = j$ in the right most summation corresponds to the merging of the ith and jth vertices in the original diagram. Therefore, this last term is represented diagrammatically by contracted diagrams in which the corresponding vertices of the original diagram are merged together[18]. Figure 2 displays examples of contracted diagrams. Appendix C presents the compete set of contributing contracted diagrams with two through eight bonds, a complete set that also applies for describing a system of N-mers, even those with structured monomers. Thus, this merging procedure converts each original diagram into a sum of contracted diagrams $\{R\}$ which then contain only unrestricted sums over lattice vectors as described below. The leading term with no contractions represents a zeroth order approximation to a diagram, an approximation in which excluded volume constraints are ignored for the bonds depicted in the diagram. The remaining contractions correct this leading term for the overcounting of configurations that violate the excluded volume constraints among the depicted bonds.

Each contracted diagram R contributes to the original diagram D_B with a coefficient f that depends on the number of ways of producing the given contracted diagram by merging vertices of the original diagram in all possible ways[20]. This contraction process is symbolically written as

$$d_B = \sum_{m} f_{B,m}^{(d)} R_{B,m}, \tag{2.12}$$

to indicate that given a parent diagram D_B containing B bonds and v' vertices we construct from D_B all possible contracted diagrams $R_{B,m}$ of B bonds and $v \leq v'$ vertices. The index m enumerates the distinct contractions with B bonds. The number of contracted diagrams generated from a given parent diagram grows exponentially with v. Since v increases with the number of bonds B, the number of contracted diagrams grows explosively with increasing order. Therefore, sophisticated methods are required for extracting and evaluating the nonzero contributions.

Contracted diagrams are lattice dependent and are evaluated as follows: Every bond carries a RmomentumS index $\mathbf{q}$ [see Eq. (2.3).] A factor of $[f(\mathbf{q})/\mathbf{z}]$ appears for each bond, a momentum conservation condition $N\delta(\sum \mathbf{q})$ applies at every vertex, and there is a sum over all momenta in the first Brillouin zone (with $\{\mathbf{q}\} = \mathbf{0}$ omitted). For example, diagram b of Fig. 2 produces the expression[18]

$$R_b = \sum_{\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3}{}' \left[\frac{f(\mathbf{q}_1)}{z}\right] \left[\frac{f(\mathbf{q}_2)}{z}\right] \left[\frac{f(\mathbf{q}_3)}{z}\right] \left(N\delta_{\mathbf{q}_1+\mathbf{q}_2+\mathbf{q}_3}\right)^2,$$

where the primed sum indicates that the sums involve $\mathbf{q}_1 \neq 0$, $\mathbf{q}_2 \neq 0$, and $\mathbf{q}_3 \neq 0$. The nonzero vectors $\{\mathbf{q}\}$ range through the first Brillouin zone, with $q_i = 2\pi n_i/a_i$, $n_i = 0, 1, 2, ..., N^{\frac{1}{3}} - 1$. Generalizing the algorithm described in Ref.[18], we express the value of the contraction $R_{B,m}$ with B lines and v vertices as

$$R_{B,m} = \frac{N^v}{z^B} \sum_{\mathbf{q}_1,\mathbf{q}_2,\ldots\mathbf{q}_l}{}' \left[\prod_{i=1}^{B} f(\mathbf{q_i})\right] \left[\prod_{i=1}^{v} \delta\left(\sum_{j=1}^{v_i} \mathbf{q_j}\right)\right]. \tag{2.13}$$

The sum $\sum_{j=1}^{v_i}$ runs over all bonds meeting at a common vertex v_i, where $\mathbf{q_j}$ is the momentum variable associated with the jth bond. The primed sum indicates that the sum involves only $\mathbf{q_j} \neq \mathbf{0}$ for all j.

The straightforward evaluation of these quantities (γ, R, f, and α) is possible for few bonds and has been accomplished for up to 4 bonds[20,21]. This procedure provides corrections to the zeroth order mean field entropy through orders z^{-2} and ϕ^4 for a system of flexible polymer chains with structured monomers. As noted above, the complexity of the computations increases exponentially with higher numbers of correlating bonds. The enumeration, classification, and evaluation of these diagrams requires new theoretical approaches which are described in the next section.

III. CALCULATION OF HIGHER ORDER CORRECTIONS. APPLICATION OF GRAPH THEORY.

The calculation of the higher order LCT corrections proceeds through the following steps:

1. Construct all parent diagrams D_B in Eq. (2.8).
2. Calculate the combinatorial factors γ_D, which describe the number of ways of extracting the bonds depicted in the parent diagram from all the bonds in the system.
3. Generate all possible contracted diagrams and choose all those that provide nonvanishing contributions in the thermodynamic limit.
4. Evaluate the values of the relevant contracted diagrams $\{R\}$ from Eq. (2.13).
5. Calculate the numerical factors $\{f\}$ in Eq. (2.12) for all relevant contractions obtained from each parent diagram.

Combining equations (2.7)- (2.13) then provides the LCT corrections to the partition function. Our goal is the developement of an efficient computer algorithm for automating this whole process.

The first two steps present relatively straightforward combinatorial problems. The third and the fourth steps are the most sophisticated ones. In order to facilitate the latter two steps, we develop graph theory methods, which are used widely in studying molecular structures[30] and the statistics and dynamics of polymers[31,32]. A major portion of this section is devoted to the complex task of the classification and evaluation of the contracted diagrams. The fifth step is accomplished using the algorithm of subsection D without modification, except for the special case of dimers where symmetry considerations provide significant simplifications and a full analytical treatment becomes possible. This analytical treatment is described below in Section IV in order to establish that the contracted diagrams are indeed correct before passing on to the more involved application of the theory to a system of N-mers with structured monomers where no such checks are currently available. We begin, however, with a general discussion for linear chains but note that the treatment of polymers with various branched and structured monomers requires only the generation of additional parent diagrams[18,21]. All other calculations are independent of the chain architecture.

A. Parent diagrams

The process of generating all possible parent diagrams for linear chains begins with representing all the partitions of the integer that equals the number of bonds B in the diagram. For example, all partitions of the integer 5 are

$$\begin{aligned}&\{\{5\}\}, \{\{4\}, \{1\}\},\\ &\{\{3\}, \{2\}\}, \{\{3\}, \{1\}, \{1\}\},\\ &\{\{2\}, \{2\}, \{1\}\}, \{\{2\}, \{1\}, \{1\}, \{1\}\},\\ &\{\{1\}, \{1\}, \{1\}, \{1\}, \{1\}\}.\end{aligned} \tag{3.1}$$

The first term in Eq. (3.1) designates a parent diagram with five sequential bonds, the second is a parent diagram with four sequential bonds on one chain and one bond on another, while the last term corresponds to five bonds selected from five different chains. Parts of these partitions can also represent bonds that belong to the same chain but that are non-sequential. A single chain diagram having, for example, non-sequential sets of $n_1, ..., n_r$ sequential bonds is represented as $\{\{n_1, ..., n_r\}\}$ in the above notation. When a chain is depicted in a diagram with more than one bond, there are parent diagrams with all these bonds occuring either sequential or nonsequential in all possible ways. Diagrams **b**, **c** and **d** of Fig. 1 illustrate all the two-bond parent diagrams, while Fig. 7 presents two examples for five bonds. The number of parent diagrams clearly grows rapidly with increasing numbers of bonds B (and with branching monomer structure). How ever, the combinatorial process for their enumeration is relatively straightforward by using a computer.

We now describe the construction of the general formula for the combinatorial factor γ_D as the product of three factors, $\gamma_D = \gamma_D^{(1)}\gamma_D^{(2)}\gamma_D^{(3)}$. The p_i separate chains depicted in a diagram contribute the chain counting multiplicative factor $\gamma_D^{(1)} = \prod_{i=0}^{i=p_i-1}(p-i)$. If a diagram contains j_i indistinguishable chain segments, there is an additional degeneracy multiplicative factor $\gamma_D^{(2)} = (j_i!)^{-1}$ for every such group. Thus, the diagram $\{\{2\}, \{2\}, \{1\}, \{1\}\}$ contains two indistinguishable two-bond and two indistinguishable one-bond portions. Hence, the two factors combine to yield $\gamma_D^{(1)}\gamma_D^{(2)} = \frac{p(p-1)(p-2)(p-3)}{(2!)^2}$. The remaining factor $\gamma_D^{(3)}$ depends on the lengths $\{l_i\}$ of the bond sequences in each of the chains depicted in the diagram. When all B_i bonds of a diagram occur sequentially on a linear chain, these bonds contribute the factor $\gamma_D^{(3)} = (M - B_i)$. If, on the other hand, a chain in the diagram has i non-sequential groups of bonds with sequential lengths B_{ij}, the linear chain contributes the monomer factor

$$\gamma_D^{(3)} = \prod_{j=0}^{i}\left(M - \sum_i B_{ij} - j\right).$$

For instance, the diagram $\{\{2, 3\}\}$ of Fig. 7 has $\gamma_D^{(3)} = (M-5)(M-6)$.

B. Representation of contractions with graph theory.

With an increasing number of bonds B in the diagram D_B, the geometrical characteristics of the possible contracted diagrams $R_{B,m}$ become more and more complicated. Since every contracted and parent diagram consists of lines (bonds) and vertices, these diagrams may, therefore, be considered as graphs. We now turn to graph theory to devise a consistent method for their enumeration, classification, and evaluation. The terms graphs and diagrams later are used interchangably.

1. Required elements from graph theory

We follow the terminology and definitions introduced in Ref.[33]. Figure 3 depicts the elements of the graphs and illustrates the terminology defined below.

A linear *graph* $G(N, C)$ is a set of elements N and a collection C of unordered pairs (a, b) of elements N. The elements N are represented by points, called *vertices*, and the pairs (a, b) of elements N are represented by lines, called *edges*. We denote the vertices by letters and the edges by numbers. The edge connecting the two vertices a_i and a_j is written as (a_i, a_j). An *edge sequence* is a sequence of these vertex pairs, where the same vertex occurs in a pair and in the next pair of the sequence, for example, the sequence $(a_1, a_2)(a_2, a_3)$... has a_2 in common for two successive edges. An edge appearing in the sequence more than once is called a *multiple edge*. (see Fig. 3).

A *path* is an edge sequence in which no edge is used more than once. The *length* of a path represents the number of distinct edges used in the formation of the sequence. Two vertices, connected by a path of unit length, are said to be *adjacent* vertices. A path that begins and ends at the same vertex is called a *cycle*. A *circuit* is a cycle containing each edge and each vertex only once. A circuit with an odd number of vertices is termed an $odd - circuit$ here. We also define a $self - loop$ as a circuit of unit length.

A graph G is *connected* if there exists at least one path between every pair of vertices in G. When a graph is not connected, it is designated as *disconnected*. A connected graph G is said to be $single - connected$ if the removal of an edge turns the graph into a disconnected graph. (see Fig. 3). If a disconnected graph is produced by removing an edge such that one component of the disconnected graph becomes a single vertex, this edge is called a *dangling end*. When more than two edges are connected at a vertex, this vertex is termed a *branched vertex*. If the removal of one vertex from a connected graph G transforms the graph into disconnected one, this vertex is defined as a $cut - point$.

One basic characteristic of a graph is the number of independent circuits n_c. A general relation for any graph proves that[33]

$$B - v = n_c - n_d, \tag{3.2}$$

where B, v, and n_d are the numbers of lines (bonds), vertices, and disconnected parts, respectively. For example, the graph depicted in Fig. 3 has $n_c(G_1) = n_c(G_2) = 2$ and $n_c(G_3) = 4$.

2. Representations of the graphs

Graph theory is useful for evaluating and classifying the contracted diagrams. Performing operations on the graphs with digital computers is facilitated by employing the matrix representations of the graphs. Several different matrix representations exist, but we mention three representations that are useful for our purposes.

The *incidence matrix* representation labels the edges as well as the vertices. The rows of the matrix represent the graph's vertices, while the columns represent graph edges. The matrix elements g_{ij} are defined as follows: $g_{ij} = 1$ if the edge j is incident on vertex i, and $g_{ji} = 0$ otherwise. An example of the incidence matrix representation for graph G_1 of Fig. 3 is given as

$$I(G_1) = \begin{array}{c|ccccc} & 1 & 2 & 3 & 4 & 5 \\ \hline a & 0 & 0 & 0 & 1 & 1 \\ b & 1 & 1 & 0 & 0 & 0 \\ c & 1 & 1 & 1 & 0 & 0 \\ d & 0 & 0 & 1 & 1 & 0 \end{array}$$

Another kind of matrix representation is provided by the *distance matrix*. The elements of this matrix d_{ij} are the distances between the i-th and j-th vertices. If a pair of vertices is not connected directly, we use an infinity symbol to define the distance between them. The distance matrix for the graph G_1 of Fig. 3 can be written in several different ways, for example, as

$$D(G_1) = \begin{array}{c|cccc|} & a & b & c & d \\ \hline a & 0 & 1 & \infty & 1 \\ b & 1 & 0 & 1 & \infty \\ c & \infty & 1 & 0 & 1 \\ d & 1 & \infty & 1 & 0 \end{array} = \begin{array}{c|ccc|} & a & b & c \\ \hline a & 0 & 1 & 2 \\ b & 1 & 0 & 1 \\ c & 2 & 1 & 0 \end{array},$$

depending on how many of the vertices are included into the matrix representation. Some calculations are more conveniently performed by treating several consecutive steps as a line of length equal to the number of steps. The two examples for $D(G_1)$ above employ different number of vertices. When the distance matrix contains fewer vertices, the bulkiness of the matrix operations is reduced. The distance matrix representation of a graph does not indicate whether the graph has multiple edges, but it provides important information about distances between vertices.

The third representation we use is a *list form* for the graph, i.e., an edge sequence. This form specifies the number of bonds and describes each bond separately. The list representation of the graph G_1 of Fig. 3 is

$$\{(a, b), (b, c), (b, c), (c, d), (a, d)\}.$$

Any of these graph representations may be transformed easily into another representation. Furthermore, neither of the representations uniquely defines the graph since a relabeling of the vertices and edges in the graph changes the matrices and lists representing the graph. Since the number of these permutations of matrix representations for a single graph grows rapidly with the number of vertices and edges, the treatment of many-bond graphs requires the unique characterization of the graphs. Thus, we face the problem of establishing an isomorphism between two equivalent matrix representations of the same graph.

Two graphs G_1 and G_2 are said to be *equivalent* or *isomorphic* if there exists a one to one correspondence (called an isomorphism) between the vertex set of G_1 and the vertex set of G_2 such that the existence of an edge (or multiple edge) in G_1 implies the presence of a corresponding edge (or multiple edge respectively) in G_2 and conversely[33]. The same isomorphism problem, of deciding whether or not two given graphs are isomorphic, arises frequently in many graph theoretic contexts[34]. Appendix A explains our solution to this isomorphism problem for the graphs representing the contracted diagrams. This solution involves the construction of an invariant that uniquely specifies the graph and that is represented on a digital computer as a single integer number (a computer word).

C. Classification of contracted diagrams

Among the vast variety (roughly exponential in v) of contracted diagrams that can be created from parent diagrams with B bonds and v vertices, there are broad classes of contracted diagrams that do not contribute to the partition function in the thermodynamic limit. These unimportant terms arise from the contracted diagrams containing dangling ends, self-loops, odd cycles (for hypercubic lattices), or singly-connected lines. The proof of this general result is given in Appendix B, and the results for diagrams with singly-connected lines are new. Several examples of non-contributing contractions are depicted in Fig. 4.

The incidence matrix representation is particularly useful for extracting, sorting, and studying the relevant contractions, i.e., those without self-loops, dangling ends, or odd cycles. The presence of self-loops is evidenced by the existence of incidence matrices elements with $g_{ij} \geq 2$. The incidence matrix for diagrams with dangling ends has rows containing only a single non-zero element.

The location of odd circuits requires the use of more sophisticated graph theory methods. All incidence matrices describing contracted diagrams have two non-zero (i.e., equal to 1) elements in each row because each bond always connects two vertices. The incidence matrices of the contributing graphs G are special cases of the class H of matrices having all its matrix elements either 0, 1 or -1. (The elements of the contributing G are 0 and 1 only). A matrix $B = (b_{ij})$ is said to be *unimodular* if the determinant of any square submatrix of B equals $0, 1$, or -1. A useful theorem for this kind of matrix is the following[33]:

Theorem 1. Let $B \in H$ be a matrix such that every column contains at most two non-zero elements. If the rows of B can be divided into two disjoint sets $R1$ and $R2$, such that one non-zero element of each pair of non-zero elements is in $R1$ and the other one is in $R2$, then B is unimodular.
Unimodular matrices have a property that provides us with a method of excluding irrelevant contractions containing odd cycles.

Corollary. If $I(G)$ is the incidence matrix of a linear graph G, then $I(G)$ is unimodular if and only if G has no circuits of odd length.
The presence of multiple edges has no influence on this corollary. Multiple edges may or may not occur in G. A graphical illustration of this property is depicted on Fig. 5.

The contracted diagrams are formed sequentially from a parent diagram B by successively contracting a pair of vertices, generating an operation with a tree-like structure. If one of these successive contractions of a pair of vertices can transform the contracted diagram into a new contracted diagram having only two vertices and no self-loops (like diagram b of Fig. 2), this contracted diagram does not have any odd cycles. Theorem 1 provides us with a method of determining whether the matrix under consideration is unimodular and, thus, whether it contains odd cycles. Triangular and other lattices permit the occurrence of odd cycles, and in generalizing the LCT to these other lattices, the unimodular property is useful for separating graphs with odd cycles as a portion of the isomorphism problem.

1. Values of contracted diagrams

The values associated with the contracted diagrams are calculated from Eq. (2.13). The first step in evaluating the contracted diagrams involves replacement of the restricted summations over the $\mathbf{q_i}$ by a sums of contributions with unrestricted summations, as illustrated by

$$\sum_{\mathbf{q_1},\mathbf{q_2}}{}' F(\mathbf{q_1},\mathbf{q_2}) = \sum_{\mathbf{q_1},\mathbf{q_2}} F(\mathbf{q_1},\mathbf{q_2}) - \sum_{\mathbf{q_1}} F(\mathbf{q_1},0) - \sum_{\mathbf{q_2}} F(0,\mathbf{q_2}) + F(0,0). \tag{3.3}$$

This transformation converts Eq. (2.13) into the form

$$R_{B,m} = \frac{N^v}{z^B} \sum_{\mathbf{q_1},\mathbf{q_2},\ldots \mathbf{q_B}}{}' \left[\prod_{i=1}^{B} f(\mathbf{q_i})\right] \left[\prod_{i=1}^{v} \delta\left(\sum_{j=1}^{v_i} \mathbf{q_j}\right)\right]$$

$$= \frac{N^v}{z^B} \left\{ \sum_{\mathbf{q_1},\mathbf{q_2},\ldots \mathbf{q_B}} U - z\left[\sum_{i=1}^{B} \left(\sum_{\mathbf{q_i}=\mathbf{0}}{}' U\right)\right] + z^2 \left[\sum_{i=1}^{B-1} \sum_{j=i+1}^{B} \sum_{\mathbf{q_i}=\mathbf{q_j}=\mathbf{0}}{}' U\right] - z^3 [] \ldots \right\}, \tag{3.4}$$

where U is given by

$$U = \left[\prod_{i=1}^{B} f(\mathbf{q_i})\right] \left[\prod_{i=1}^{v} \delta\left(\sum_{j=1}^{v_i} \mathbf{q_j}\right)\right].$$

Equation (3.4) uses the definition of the nearest-neighbor structure factor in (2.4) to provide a factor z for every $f(\mathbf{q_i} = \mathbf{0})$ that appears by virtue of the $\mathbf{q_i} = \mathbf{0}$ terms from the analog of Eq. (3.3). Figure 6 illustrates the modification of a contracted diagram upon setting some $\mathbf{q_i} = \mathbf{0}$. The modified contraction is called a derivative diagram.

Theorem 2. The value of a contracted diagram consisting of B bonds and v vertices can be written in the form

$$R_{B,m} = \frac{N^{v+n_c}}{z^B} \left(r_{unrestr} + O(\frac{1}{N}) \right), \tag{3.5}$$

where $r_{unrestr}$ is a pure geometrical quantity which describes the number of ways for placing geometrical structure, corresponding to the contracted diagram, on the given lattice. The calculation of $r_{unrestr}$ is described in Appendix D.

Corollary. Derivative diagrams with $B \leq 8$ do not contribute to the entropy in the thermodynamic limit. The corollary may apply for larger B, but a general proof has not been found.

The proof of this theorem and the corollary are given in Appendix C. The only term from Eq. (3.4) that contributes in the thermodynamic limit for $B \leq 8$ is the first term on the right hand side with an unrestricted sum over all momentum variables. Thus, all further computations concerning contracted diagrams take them as having unrestricted $\mathbf{q}$-sums.

D. Programming algorithms

Since the number of permutations and operations grows exponentially with the number of bonds and vertices, a computer eventually becomes necessary to perform the labor. The computer code consists of two portions: an analytical part (using Mathematica) and a numerical part, written in the computer language C. The analytical portion includes specifying and evaluating all parent diagrams, calculating the values of contractions, and constructing the expression for entropy of the system. The numerical part consists of routines for creating and sorting all relevant contractions and for calculating the numerical factors $f^{(d)}_{B,m}$ of Eq. (2.12).

The generation of all parent diagrams and the computation of the combinatorial factors γ_D are straightforward combinatorial processes that are easily performed with Mathematica. The program begins with all partitions of the integer equal to the number of bonds under consideration as illustrated in Eq. (3.1) for five bonds. Then, the program assigns the partitioned integers to the number of consecutive bonds on the interacting chains. For every partition, the program also generates all possible distinct combinations of non-sequential and disconnected segments. The generation and classification of the contracted diagrams is the most sophisticated step of the algorithm. This step employs the above described matrix representations of graphs to create a complete set of relevant contractions from one parent diagram.

All relevant contractions with B bonds can be found from a parent diagram consisting only of B dimers. However, the B-dimer diagram has $v = 2B$ vertices, making it the most time consuming case of B-bond diagrams. (Based on experience with computer enumeration and on approximate combinatorial arguments, the number of contracted diagrams grows exponentially with increasing v.) For example, we generate all eight-bond contracted diagrams using a parent diagram having a mixture of dimers and trimers, such that this case provides all relevant contractions with minimal computer time because of the minimum number of vertices involved. We find that the diagram $\{\{2\},\{2\},\{2\},\{1\},\{1\}\}$ yields all contracted diagrams that can be formed from eight bonds. This parent diagram generates $\approx 10^6$ contracted diagrams, but not all of these must be enumerated. The contraction process is a tree-like operation that is depicted in Fig. 8 and is performed as follows: Starting with the parent diagram, the program sequentially creates all possible single contractions of the parent diagram, then all possible double contractions, which either produce the merging of three vertices or two pairs of contracted vertices, etc. For example, consider the parent diagram $\{\{3\},\{2\}\}$ of Fig. 7 whose list representation is $\{(1,2),(2,3),(3,4),(5,6),(6,7)\}$. The program lists the different vertices as $\{1,2,3,4,5,6,7\}$ and then finds all possible contractions among these vertices, namely,

$$\begin{array}{c} \{1,1,2,3,4,5,6\},\ \{1,2,1,3,4,5,6\},... \\ \{1,2,2,3,4,5,6\},\ \{1,2,3,2,4,5,6\},... \\ .....\{1,2,1,2,3,4,3\}\, etc. \\ until\ \{1,1,1,1,1,2,2\}, \end{array} \tag{3.6}$$

where repeated numbers in braces imply the contraction of the corresponding vertices of the parent diagram and the vertices have been renumbered. The first four terms in Eq. (3.6) contain a single contraction, the fifth has two contractions, while the last contains five contractions. The number of differently numbered vertices in any contraction can never be less than two (otherwise the contraction is full of self-loops).

A special algorithm avoids repetitions. For $n_c \geq n_d$, the program tests the contracted diagrams for the presence of self-loops and odd-cycles. If either one of them occurs, this branch of the contraction process (i.e., the generation of higher order contracted diagrams from this one) is interrupted, because once either a self-loop or an odd-cycle appears in a contracted diagram, they never disappear in the process of further sequential contraction. This interruption reduces the number of contractions to be tested by $\approx 50\%$. The remaining contracted diagrams without dangling ends are retained as possibly relevant. Then, the invariant GI of the contracted diagram $I(G)$ is calculated in the manner explained in Appendix A. The invariant GI is compared with the other invariants already obtained from the given parent diagram. If the GI matches a previous one, the program retains the sum of their numerical factors as $f^{(d)}_{B,m}$ of Eq. (2.12). If the GI is new, it is added to the list of the GI for the relevant contractions. Due to its bulkiness, the test and elimination of the singly-connected contracted diagr ams runs after all contractions are created. All relevant contracted diagrams are also sorted and classified by the numbers of vertices and of disconnected parts.

All the testing procedures, described above, are performed only for one parent diagram for each B to produce the complete list of all relevant contracted diagrams that is presented in Appendix C. These contracted diagrams will be used in a future work to treat the packing entropy for polymer systems. (The latter work will include applications to polymers with structured monomers, while Section IV specializes the LCT to a system of dimers on a lattice as a means for testing the correctness of these contracted diagrams before applying the theory to N-mers where similar tests are currently not available.) The contraction process for all other parent diagrams then only requires comparing the invariants GI of the contracted diagrams produced with the GI from the complete list of contributing contracted diagrams. Despite the fact that this procedure is the fastest among all the other tests, the most time consuming part of the program is associated with calculating the numerical factors $f^{(d)}_{B,m}$ for every contributing contraction $R_{B,m}$ that emerges from each different parent diagram. Although, the numerical factors $f^{(d)}_{B,m}$ Eq. (2.12) are calculated in the contraction process, the same contracted diagram may occur with different (permutationally e quivalent) realizations which therefore have the same GI. For example, the two trimer parent diagram may create the "infinity shaped" contracted diagram in several different ways (two of which are displayed in Fig. 9). Each realization appears with different numerical factors $f^{(d)}_{B,m}$. All these numerical factors from different realizations of the same contracted diagram are added together to produce the full contribution $f^{(d)}_{B,m}$ from every contracted diagram produced by a parent diagram. When B is greater than 5, the calculation of numerical factors $f^{(d)}_{B,m}$ can be performed analytically only for dimers.

After evaluating the contributions from all parent diagrams, the program constructs the partition function Z and calculates the entropy per site S as

$$\begin{aligned} S &= \tfrac{\log(Z)}{N} \\ &= \tfrac{\log(Z_{MF})}{N} + \tfrac{\log(1+\sum_B \gamma_B D_B)}{N} \\ &= S_{MF} + \tfrac{clustered\ diagrams}{N} \\ &= S_{MF} + N^{-1}\left[\textstyle\sum_B \gamma_B D_B - \frac{1}{2}\left(\sum_B \gamma_B D_B\right)^2 + \frac{1}{3}\left(\sum_B \gamma_B D_B\right)^3 + ...\right]. \end{aligned} \tag{3.7}$$

The cluster diagrams are grouped by their topology[18] into cumulant clusters diagrams as represented in Fig. 10.

IV. SPECIALIZATION TO SYSTEM OF DIMERS

The fundamental difference between the LCT and the classical lattice model description of a simple fluid is the fact that the LCT explicitly includes contributions arising from the connectivity of monomers in polymer chains. The simplest and at the same time physically interesting example with connectivity is provided by the system of dimers

(one bond connecting two monomers). The statistics of dimers has drawn attention for decades in a wide variety of contexts, including the lattice gas, the Ising problem, absorption phenomena, etc. Comprehensive reviews of these works are given in Refs.[28,35]. Despite the fact that the description of dimer statistics has been of interest for so long, the exact solution for the entropy is known only for two special cases: one-dimensional (1d) systems at all ϕ and two-dimension (2d) dimers at full coverage. However, the enumeration method of Gaunt[2] provides more than adequate information for assessing the correctness of our contracted diagrams for a system of dimers before using these same diagrams to treat polymer chains, the real object of our new methods.

For a fixed total number of bonds, our general algorithm becomes the most time consuming for dimers, because the computational difficulty scales with the number of vertices. However, important simplifications emerge from the symmetry of dimers (see Appendix E), making dimers, in fact, the easiest case to treat. The availability of Gaunt's theory for dimers also makes this system the ideal test case for the new algorithms.

A. Results

We consider a system of lattice dimers in the athermal limit where non-bonded interactions are negligibly small. The entropy is then defined from the partition function Z as $S = -ln(Z)$ (in units of Boltzmann's constant). Hence, all considerations are represented in terms of the entropy. The LCT produces the entropy per lattice site of athermal dimers in the form,

$$S_{LCT} = \frac{lnZ}{N} = (1-\phi)ln(1-\phi) - \frac{\phi}{2}ln\frac{\phi}{z} - \frac{\phi}{2} + \Delta S, \tag{4.1}$$

where ΔS designates the LCT correction to the zeroth order MF entropy. This correction incorporates contributions from all possible topologically distinct diagrams. The LCT yields ΔS as a double series in the dimer volume fraction ϕ and in the inverse z^{-1} lattice coordination number. As succesively more interacting dimers are included in the computation, the LCT corrections $\Delta S(n)$ to the zeroth order mean field entropy are called the n-dimer approximations and are obtained as

$$\begin{aligned}
\Delta S(1) =& \; 0, \\
\Delta S(2) =& \; \tfrac{\phi^2}{4z}, \\
\Delta S(3) =& \; \tfrac{\phi^2}{4z} + \tfrac{\phi^3}{3z^2}, \\
\Delta S(4) =& \; \tfrac{\phi^2}{4z} + \tfrac{\phi^3}{12z^2} + \tfrac{\phi^4}{8z^2}, \\
\Delta S(5) =& \; \tfrac{\phi^2}{4z} + \tfrac{\phi^3}{12z^2} + \phi^4(\tfrac{1}{8z^2} + \tfrac{-5}{8z^3}) + \phi^5(\tfrac{1}{z^3} + \tfrac{-3}{5z^4}), \\
\Delta S(6) =& \; \tfrac{\phi^2}{4z} + \tfrac{\phi^3}{12z^2} + \phi^4(\tfrac{1}{8z^2} + \tfrac{-5}{24z^3}) + \phi^5(\tfrac{1}{2z^3} + \tfrac{-31}{10z^4}) + \phi^6(\tfrac{1}{3z^3} + \tfrac{15}{4z^4} + \tfrac{-16}{3z^5}), \\
\Delta S(7) =& \; \tfrac{\phi^2}{4z} + \tfrac{\phi^3}{12z^2} + \phi^4(\tfrac{1}{8z^2} + \tfrac{-5}{24z^3}) + \phi^5(\tfrac{1}{2z^3} - \tfrac{1}{10z^4}) + \phi^6(-\tfrac{5}{3z^3} - \tfrac{69}{4z^4} - \tfrac{16}{3z^5}) \\
& + \phi^7(-\tfrac{1}{z^4} + \tfrac{12}{z^5} - \tfrac{116}{7z^6}), \\
\Delta S(8) =& \; \tfrac{\phi^2}{4z} + \tfrac{\phi^3}{12z^2} + \phi^4(\tfrac{1}{8z^2} - \tfrac{5}{24z^3}) + \phi^5(\tfrac{1}{2z^3} - \tfrac{39}{40z^4}) + \phi^6(\tfrac{1}{3z^3} - \tfrac{1}{2z^4} + \tfrac{83}{12z^5}) \\
& + \phi^7(-\tfrac{13}{4z^4} - \tfrac{22}{z^5} + \tfrac{537}{28z^6}) + \phi^8(\tfrac{27}{16z^4} + \tfrac{299}{8z^5} + \tfrac{4053}{16z^6} - \tfrac{4989}{16z^7}).
\end{aligned} \tag{4.2}$$

The introduction of more dimers in the computations leads to the appearance of higher order terms in ϕ and z^{-1}. A term by term comparison demonstrates the convergence of the lower order contributions in ϕ and z^{-1} as n increases. For example, the $\frac{\phi^2}{4z}$ contribution appears for the two-dimer approximation and remains unchanged in higher approximations. The $\frac{\phi^3}{z^2}$ term appears first for three bonds, and its coefficient becomes converged in the four-bond approximation, remaining unchanged for $n \geq 4$. It appears that the coefficient of the ϕ^{n+1} order term is converged for the $2n$-dimer approximation.

B. Comparison with earlier theories

This subsection compares the LCT computations for dimers with the exact results for specific cases as well as with the most accurate dimer theory of Gaunt[2] and with the widely used approximate theory of DiMarzio[36]. First, in accordance with the results of Nagle[37], Eqs. (4.1) and (4.2) imply that the limit of infinite dimensional lattices ($z \to \infty$) renders negligible the correction to the zeroth order Flory mean field entropy, and this simple Flory approximation becomes exact.

1. One-dimensional system

The exact entropy per lattice site for p rods of length M on a one-dimensional lattice is easily evaluated as

$$Z_p(z=2) = \frac{[N-(M-1)p]!}{p!(N-Mp)!}. \tag{4.3}$$

Equation (4.3) simply counts the number of ways to place p linear molecules and $N_0 = N - Mp$ holes on a linear lattice (using periodic boundary condition). Taking the thermodynamic limit of $N \to \infty$ in (4.3) produces the entropy density for dimers ($M = 2$) on an infinitely long linear lattice as

$$S^{1d}_{exact} = \frac{lnZ}{n} = (1-\phi)ln(1-\phi) - \frac{\phi}{2}ln\frac{\phi}{2} - (1-\frac{\phi}{2})ln(1-\frac{\phi}{2}). \tag{4.4}$$

The LCT expression for ΔS contains a series in both ϕ and z^{-1}. The first two terms on the right hand sides of Eqs. (4.1) for $z = 2$ and of (4.4) are identical. In order to compare the remainders, we expand the third term ΔS_{exact} from Eq. (4.4) as a series in the volume fraction,

$$\Delta S^{1d}_{exact} = \frac{\phi^2}{8} + \frac{\phi^3}{48} + \frac{\phi^4}{192} + \frac{\phi^5}{640} + \frac{\phi^6}{1920} + \frac{\phi^7}{5376} + \frac{\phi^8}{14336} + ... \tag{4.5}$$

Setting $d = 1$ or $z = 2$ transforms the LCT corrections $\Delta S^{1d}_{LCT}(n)$ into a series in ϕ for the ($n \leq 8$)-dimer approximations,

$$\begin{aligned}
\Delta S^{1d}_{LCT}(2) &= \tfrac{\phi^2}{8}, \\
\Delta S^{1d}_{LCT}(3) &= \tfrac{\phi^2}{8} + \tfrac{\phi^3}{12}, \\
\Delta S^{1d}_{LCT}(4) &= \tfrac{\phi^2}{8} + \tfrac{\phi^3}{48} + \tfrac{5\phi^4}{64}, \\
\Delta S^{1d}_{LCT}(5) &= \tfrac{\phi^2}{8} + \tfrac{\phi^3}{48} - \tfrac{3\phi^4}{64} + \tfrac{7\phi^5}{80}, \\
\Delta S^{1d}_{LCT}(6) &= \tfrac{\phi^2}{8} + \tfrac{\phi^3}{48} + \tfrac{\phi^4}{192} - \tfrac{21\phi^5}{160} + \tfrac{7\phi^6}{64}, \\
\Delta S^{1d}_{LCT}(7) &= \tfrac{\phi^2}{8} + \tfrac{\phi^3}{48} + \tfrac{\phi^4}{192} - \tfrac{9\phi^5}{160} - \tfrac{93\phi^6}{64} + \tfrac{3\phi^7}{56}, \\
\Delta S^{1d}_{LCT}(8) &= \tfrac{\phi^2}{8} + \tfrac{\phi^3}{48} + \tfrac{\phi^4}{192} + \tfrac{\phi^5}{640} + \tfrac{29\phi^6}{128} + \tfrac{1059\phi^7}{1792} + \tfrac{5751\phi^8}{2048}.
\end{aligned} \tag{4.6}$$

The coefficient of ϕ^2 is already correctly converged for $n = 2$. A ϕ^3 contribution first appears for the three-dimer approximation and becomes correctly converged for $n = 4$. Continuing the comparison in this way indicates that the $2n$-dimer approximation of the LCT precisely yields the exact solution through $(n+1)$th order in ϕ. Comparing Eq. (4.5) term by term against Eqs. (4.6) verifies that the $z = 2$, eight-bond approximation is indeed correct through order ϕ^5. The relative difference between the exact entropy and the S_{LCT} through order ϕ^5 is shown in Fig. 11. Even for volume fractions close to full coverage, this difference is generally below 1%. Since the LCT is valid for an arbitrary d-dimensional hypercubic lattice, Eqs. (4.1) must also be correct through order ϕ^5 for hypercubic lattices in any dimension.

At complete coverage of dimers on an infinite planar square lattice, Fisher and others[38–41] have found the entropy density to be

$$S_{exact}(\phi = 1, z = 4) = 0.291561.$$

Expanding Eqs. (4.1) and (4.2) for an arbitrary hypercubic lattice and setting $d = 2$ ($z = 4$) yield for dimers at full coverage,

$$S_{LCT}(\phi = 1) = \frac{ln(z)}{2} - \frac{1}{2} + \frac{1}{4z} + \frac{5}{24z^2} + \frac{5}{8z^3} - \frac{243}{80z^4} + O(z^{-5}). \tag{4.7}$$

The coefficient of the contribution in z^{-n} begins to appear for the $(n+1)$-dimer approximation and becomes converged for the $(2n)$-dimer approximation. Thus, the eight-bond approximation correctly produces all terms through order z^{-4}. When considering general ϕ and d, it becomes necessary to decide whether to truncate $\Delta S_{LCT}(n)$ by interpreting it as a series in ϕ or in z. Figure 12 displays the convergence of the LCT entropy S_{LCT} to the exact solution for 2d dimers at full coverage. The order ϕ^n corrections through ϕ^5 regularly and smoothly bring S_{LCT} towards the exact solution, while the successive corrections in z^{-1} behave irregulary. Thus, at present, it appears more reasonable to consider the entropy expansion as a series in ϕ. The evaluation of the S_{LCT} in the order ϕ^5 approximation yields,

$$S^{2d}_{LCT}(\phi = 1) = 0.2694167,$$

which departs by 7.6% from the exact solution and which represents a significant improvement over the Flory mean field theory (a 33.4% error) and a modest improvement over the DiMarzio theory (a 10.3% error). Figure 13 depicts the dependence of the full coverage dimer entropy on the lattice coordination number z.

Differences between the DiMarzio model entropy in S_{DM} and the LCT begin in order $\frac{\phi^4}{z^2}$,

$$\begin{aligned} S_{LCT} - S_{DM} &= \phi^4(\tfrac{1}{8z^2} - \tfrac{1}{4z^3}) + \phi^5(\tfrac{1}{2z^3} - \tfrac{1}{z^4}) + \phi^6(\tfrac{1}{3z^3} - \tfrac{1}{2z^4} + \tfrac{207}{30z^5}) - \phi^7(...) \\ &= \tfrac{\phi^4}{4z^2}(\tfrac{1}{2} - \tfrac{1}{z}) + \tfrac{\phi^5}{z^3}(\tfrac{1}{2} - \tfrac{1}{z}) + ... \\ &= \tfrac{\phi^4}{8z^2} - \tfrac{1}{z^3}(\tfrac{\phi^4}{4} - \tfrac{\phi^5}{2} - \tfrac{\phi^6}{3}) - \tfrac{1}{z^4}(\phi^5 + \tfrac{\phi^6}{2}) \end{aligned} \tag{4.8}$$

Figure 14 presents a surface plot of the relative percentage difference $100(S_{LCT} - S_{DM})/S_{DM}$ between the LCT (through fifth order in ϕ) and the DiMarzio approximation for various dimensionalities and volume fractions. The best agreement between these two theories lies in the range of lower dimensionalities and lower volume fractions. The perfect fit of these two theories in one-dimension ($z = 2$) then deteriorates sharply for the unphysical dimensionality $d \approx 1.2$. This large difference is obviously connected with the approximation of DiMarzio theory. For dimensionalities $d > 1$ and for high volume fractions, the approximate DiMarzio theory starts to miss some configurations, while the LCT computes them explicitly.

One of the most valuable tests of our approach is provided by comparison with the most accurate dimer theory by Gaunt[2]. Gaunt's approach utilizes methods developed in studies of the Ising model. Gaunt computes the series representation of the grand partition function for dimers on various lattices, retaining 16 coefficients for square lattices and 12 for simple cubic ones. After transforming his series to expansions in the dimer volume fraction ϕ, we obtain

$$\begin{aligned} S_{Gaunt}(square) = {} & 2\phi[1 - ln(\phi)] - 7\phi^2 - \tfrac{31\phi^3}{3} - \tfrac{121\phi^4}{6} - \tfrac{471\phi^5}{10} - \tfrac{1867\phi^6}{15} \\ & - \tfrac{7435\phi^7}{21} - \tfrac{4211\phi^8}{4} - \tfrac{116383\phi^9}{36} - \tfrac{459517\phi^{10}}{45} - \tfrac{1821051\phi^{11}}{55} \\ & - \tfrac{7255915\phi^{12}}{66} - \tfrac{9687973\phi^{13}}{26} - \tfrac{16697149\phi^{14}}{13} - \tfrac{157001097\phi^{15}}{35} \\ S_{Gaunt}(cubic) = {} & \tfrac{\phi}{2}[1 - ln(\tfrac{\phi}{6})] - \tfrac{11\phi^2}{24} - \tfrac{71\phi^3}{432} - \tfrac{419\phi^4}{5184} - \tfrac{31\phi^5}{640} \\ & - \tfrac{15031\phi^6}{466560} - \tfrac{89951\phi^7}{3919104} - \tfrac{539963\phi^8}{31352832} - \tfrac{3244127\phi^9}{241864704} \end{aligned} \tag{4.9}$$

Comparing equations (4.9) with the corresponding LCT expressions (4.1) and (4.2) for $z = 4$ and $z = 6$ shows that all the corresponding terms through ϕ^5 are identical. It is important to mention that Gaunt's series does not yield the correct limit for $\phi \to 1$, where it deviates by 18% from the exact solution in two-dimensions. Gaunt analyzes the $\phi \to 1$ limit, where he demonstrates the Flory-Hugging-like limiting form of $\gamma(1-\phi)ln(1-\phi)$ with γ different from unity. Our use of the Flory-Huggins model as the zeroth order approximation, therefore, enables the LCT to cover the whole range of ϕ, whereas a simple density expansion in ϕ [as in (4.9)] becomes difficient as ϕ approaches unity. Figure 15 displays the relative difference $\frac{S_{LCT}-S_{Gaunt}}{S_{Gaunt}}$ for $z=4$ and $z=6$. The relative difference between the LCT and Gaunt theory entropies is less than 1% for $\phi < 0.8$. A comparison with theoretical and Monte-Carlo simulations by Lin and Lai[42] for two dimensional dimers yields the data for Fig. 16. The difference is less than 1% for $\phi < 0.9$.

V. CONCLUSIONS

We introduce graph theory methods to extend the capability of the lattice cluster theory (LCT), originally formulated using field theory by Bawendi and Freed[17] and subsequently reformulated into a more convenient algebraic form[19–21]. The central feature of this new approach lies in developing a connection between the diagramatic LCT methods and fast and effective computer algorithms for evaluating the higher order LCT corrections. The number of parent diagrams grows rapidly with increasing numbers of bonds B in the diagrams, but greater difficulties are present in evaluating individual diagrams. This difficulty emerges because the evaluation involves a contraction process that generates a roughly exponentially in v number of contracted diagrams from a parent diagram with v vertices. The greatest computational difficulty is then encountered in the enumeration, extraction, and evaluation of the small subset of contributing contracted diagrams.

This complicated, computer intensive process is facilitated by treating the diagrams as graphs. The matrix representations of the graphs provide convenient mathematical tools for manipulating the parent and contracted diagrams. The graph theory methods enable developing a combinatorial computer algorithm for contracting LCT parent diagrams and for representing the contracted diagrams as unique mathematical objects. General new theorems are proven concerning the properties of contracted diagram and their contributions. A consistent method is developed for evaluating the contracted diagrams. An important simplification is provided by our proof that only the leading order in N (the number of lattice sites) contribution from contracted diagrams survives in the thermodynamic limit for diagrams with up to eight bonds. This leading term, in turn, requires only unrestricted summations. The values of contracted diagrams are shown to equal a pure geometrical quantity $r_{unrestr}$ which depends only on lattice properties. These latter two features decrease significantly the computational effort required in implementing the LCT. Additional simplifications emerge from our new proof that singly-connected contracted diagrams likewise do not contribute.

We develop the LCT machinery through contributions from eight-bonds since this approximation suffices for studying stiff 3d-branched molecules that provide models of liquid crystalline systems. The theory is explicitly applied to lattice model dimers because comparisons are possible in this case with exact known results. This comparison generates a stringent test of the contracted diagrams before their application to longer polymers. The symmetry of the dimer system also enables the analytical performance of certain otherwise tedious computations, thereby providing some additional checks on our computer algorithm for longer chains. The comparison of the LCT approximation with known exact results for dimers validates our new algorithms. The comparison with Gaunt's theory demonstrates the important feature of the LCT in using expansions about the non-ideal Flory-Huggins theory and suggests that improved accuracy might emerge for ϕ near unity when an better zeroth order reference approximation is used.

The new methods are in the process of being applied for studying the properties of polymers with various molecular architectures, i.e., with structured monomers. It is likewise possible to extend the new lattice cluster theory methods to include the van der Waals interactions and thereby provide a more realistic lattice model description of polymer blends, liquid crystalline systems, block-copolymers, and other interesting systems. The present study provides several essential ingredients for these developments.

ACKNOWLEDGEMENTS

This research is supported, in part, by a NRC Grant (CAST program) and by NSF Grant No. DMR 9223804. We are grateful to Ken Foreman for fruitful discussions and to Jacek Dudowicz for helpful comments on the manuscript.

APPENDIX A: SOLUTION OF ISOMORPHISM PROBLEM

The problem of determining whether two given graphs G_1 and G_2 are isomorphic can be formulated in terms of their incidence matrices as follows: Let I_1 and I_2 be the incidence matrices of G_1 and G_2, which have V_1 and V_2

vertices and E_1 and E_2 edges, respectively. Then the graph $G_1 = (V_1, E_1)$ is isomorphic to $G_2 = (V_2, E_2)$ if there exists a permutation of the rows and columns of I_1 which transforms I_1 into I_2. (This permutation is equivalent to a relabelling of the vertices and edges of G_1 to make the latter correspond to the labels on the vertices and edges in G_2). In principle, the construction of all possible permutations of the labels enables discovering whether or not G_1 and G_2 are isomorphic. However, the generation of all permutations is obviously impractical for arbitrarily large graphs.

A more effective approach to the isomorphism problem is based on the construction of a graph invariant (GI). We have used the following method for constructing GI: Define a symmetric matrix M_G with nondiagonal elements $M_G(i,j)$ equal to the number of edges connecting the two vertices a_i and a_j in the graph, and let the diagonal elements $M_G(i,i)$ equal the number of edges incident into vertex a_i. A unique characteristic GI of the matrix and, hence, of the graph is defined by

$$GI = \sum_{n=1}^{J} k^{n-1} \left[M_G^n(i,i)\right]^2 = \sum_{n=1}^{J} k^{n-1} T_{M_G}(n), \tag{A1}$$

where $T_{M_G}(n)$ is shorthand notation, and k is some number used to assign different weights to various powers of M_G. We choose $k = 16$ because this choice puts the individual terms of the sum GI in different places of one long number (a computer word) that provides a unique specification of the graph in a computer code.

It is well known from linear algebra that invariants of a matrix M may be constructed from the traces of $M, M^2, \ldots$. However, the trace of M_G equals twice the number of bonds. Thus, this trace contains useless information, because we only compare contractions with the same number of bonds. Therefore, we use a sum of squared diagonal matrix elements for different powers of M_G. In practice, the invariant is constructed as the string of integer numbers in the order

$$\left| \begin{array}{c} number\ of \\ disconnected \\ parts \end{array} \right| \begin{array}{c} number \\ of \\ vertices \end{array} \left| \; T_{M_G}(J) \;\right| \ldots \left|\; T_{M_G}(3) \;\right| \; T_{M_G}(2) \;\left|\; T_{M_G}(1) \;\right|$$

The eight-bond diagrams require $J = 3$, six-bond diagrams require $J = 2$, while $J = 1$ suffices for the four-bond case.

APPENDIX B: IRRELEVANT CONTRACTED DIAGRAMS

Contracted diagrams containing odd-circuits are irrelevant due to the restriction of our study to hypercubic lattice. Hence, cycles in contributing contractions may contain only an even number of bonds (or vertices). Previous work has shown[24] that contracted diagrams with dangling ends vanish due to the application of the condition $\sum_i exp(i\mathbf{q_i}\cdot\mathbf{r_i}) = \mathbf{0}$ (since $\mathbf{q_i} \neq \mathbf{0}$) at the dangling end vertex i. The position of the dangling end vertex may be chosen as the first summation over $\mathbf{r_i}$, so this summation is unrestricted. In addition, we have used the fact that the $\mathbf{q_i}$ are restricted by Eq. (2.13) to be nonzero.

A dangling end is a special case of a singly-connected line. The treatment of diagrams with singly-connected lines is illustrated by the example in Fig. 4. More general cases may have the (b, c) edge be a longer line with no loops, and the diagram may have several singly connected portions, such as the cycles with edges 1 and 2 and with edges 3 and 4 in Fig.4. Every singly-connected portion of the diagram must contain at least one closed cyclic structure and be connected to the rest of the diagram by a cut-point. The full diagram therefore has at least two cut-points joining these singly-connected portions. However, it suffices to explain the vanishing of singly-connected diagrams for the simple example with only one pair of singly connected portions as shown in Fig. 4.

Application of the momentum conservation condition at a cut-point requires the momentum vector $\mathbf{q}$ for the singly-connected edge to equal to the sum of several other vectors, as illustrated in a diagram with two singly-connected parts(see caption to Fig. 4). Thus, the sum of the momentum vectors for the closed cycle structure equals the single momentum vector from the connecting edge sequence. This process always leads to conditions analogous to those presented in the figure caption for the simplest case in Fig. 4. Hence, all singly-connected contracted diagrams vanish identically.

A self-loop is a special case of an odd-circuit, but because the self-loops do not contribute for all lattices, we consider them separately. The existence of a bond between two consecutive monomers along the polymer chain is described by the bonding delta function $\delta(i, i+1+\beta)$ in Eq. (2.1). The condition imposed by this bonding delta function excludes the occurrence of self-loops which would imply $\mathbf{r_i} = \mathbf{r_{i+1}} + \mathbf{a}_\beta$ and which violates the constraint represented by the bonding delta function. Equation (2.1) and previous LCT treatments include the extra excluded volume condition between bonded monomers, e.g., $\mathbf{r_i} \neq \mathbf{r_{i+1}}$, $\mathbf{r_i} \neq \mathbf{r_{i-1}}$, in the restricted sums in order to mantain symmetry and to provide a useful check on the algebra, namely on the vanishing identically of all contributions to the entropy from contracted diagrams with self-loops. If instead these extra excluded volume constraints between bonded monomers are omitted, the sums appear in the form

$$\sum_{r_i \neq r_1, \ldots, r_{i-2}, r_{i+2}, \ldots, r_N} \tag{B1}$$

and the contraction process can never produce self-loops.

APPENDIX C: EXACT VALUES OF CONTRACTED DIAGRAMS

Here we present the proof of Theorem 2 and the derivation of an expression for evaluating the contracted diagrams.

Consider an arbitrary graph (a contracted diagram) with n_c independent cycles. Let L be the length of a line connecting two vertices at which branching occurs. Hence, L is the number of bond vectors along this line. The momentum conservation condition in Eq. (2.13) ensures that all the $\mathbf{q_i}$ momentum vectors belonging to the same line L must equal each other. Thus, by setting any one of these $\mathbf{q_i}$ equal to zero in the process of converting restricted sums over the $\mathbf{q_i}$ to unrestricted sums, all the $\mathbf{q_i}$ belonging to L likewise vanish. Every null $\mathbf{q}$-vector contributes a factor of $f(\mathbf{q} = \mathbf{0}) = \mathbf{z}$. The transition from restricted to unrestricted summation is written generally as

$$R' = [\sum_{\mathbf{q_1}, \ldots, \mathbf{q_n}}{}' F(\mathbf{q_1}, ..., \mathbf{q_n})] = \sum_{\mathbf{q_1}, \ldots, \mathbf{q_n}} \prod_{\mathbf{i}} [\mathbf{1} - \delta(\mathbf{q_i})] F(\mathbf{q_1}, ..., \mathbf{q_n}), \tag{C1}$$

and produces a change of a sign for every additional $\mathbf{q_i}$ set to zero. For example, consider the contribution from Eq. (C1) when a single $\mathbf{q_i}$ becomes zero. This process yields the factor of $-z$ in the front of the $\sum'$ (where the prime still applies to the other $\mathbf{q_i}$, that do not belong to the line L), and it destroys one independent cycle in the graph as explained below. For example, setting $\mathbf{q_i} = \mathbf{0}$ in the graph of Fig. 6(a) produces the graph depicted in Fig. 6(b). This graph has n_c less by one than the n_c in the original graph.

The elimination of the line of length L may occur because the $\delta(\mathbf{q_i})$ in Eq. (C1) may set to zero any of the $1, 2, ..., L$ $\mathbf{q_i}$-vectors for this line in all possible ways, i.e., as introduced by products of the form $\delta(\mathbf{q_i})\delta(\mathbf{q_j}), \ldots$. Because all contracted diagrams with this line removed have identical values, it necessary first to compute the number of these terms and then to determine the overall signs arising from the minus signs in Eq. (C1). This calculation is conveniently performed before applying the momentum conservation conditions. The number of possible ways in which a line of length L may be removed by application of one or more $\delta(\mathbf{q_i})$ from Eq. (C1) is readily enumerated as follows:
There are L ways to choose one of the L $\mathbf{q}$-vectors,
$L(L-1)/2!$ ways to choose 2 of the L $\mathbf{q}$-vectors to vanish,
$L(L-1)(L-2)/3!$ ways to choose 3 vectors to be equal to zero, and so on up to
$L(L-1)....(L-(L-1))/L! = 1$ ways to choose all L vectors as having vanishing $\mathbf{q_i}$. Since the momentum conservation conditions then ensure that setting any of the L $\mathbf{q}$-vectors equal to zero makes all other vectors belonging to this line vanish, all the above contributions are identical apart from signs and from the above enumerated combinatorial factors. The signs of the contributions follow from (C1) as being negative when there is an odd number of $\mathbf{q}$-vectors set to zero by an odd number of $\delta(\mathbf{q_i})$ factors from Eq. (C1). The sign is positive for an even number of $\delta(\mathbf{q_i})$ factors. Thus, the sum of all these contributions yields the overall sign-combinatorial factor of

$$1 - L + \frac{L(L-1)}{2!} - \frac{L(L-1)(L-2)}{3!} + ... - 1 = (1-1)^L - 1 = -1. \tag{C2}$$

Hence, eliminating any one line of the length L contributes the factor $(-1)z^L$. A factor of z^L arises because the line contributes L factors of $f(\mathbf{q_j} = \mathbf{0})$ to the summand of Eq. (2.13).

Recalling the lattice identity

$$\sum_{\mathbf{q}} \exp(i\mathbf{q} \cdot \mathbf{r_j}) = \mathbf{N}\delta_{\mathbf{r_j},\mathbf{0}}. \tag{C3}$$

makes it clear that the summation over every independent $\mathbf{q}$- vector, i.e. every cycle, provides a contribution of order N. Thus, eliminating a cycle by setting one of the $\mathbf{q}$-vectors from the cycle equal to zero, removes one power of N from the value of diagram. The general expression for an arbitrary contracted diagram is then reduced to the form

$$R'(L_1, L_2, ...L_k) = \begin{array}{l} R_{unrestricted} - \frac{1}{N}\sum_{i=1}^{k} z^{L_i} R(without\ L_i) \\ +\frac{1}{N^2}\sum_{i=1}^{k-1}\sum_{j=i+1}^{k} z^{L_i+L_j} R(without\ L_i, L_j) - \frac{1}{N^3}\sum ..., \end{array} \tag{C4}$$

where $R_{unrestricted}$ indicates the middle term in Eq. (C1) with no restrictions on the $\mathbf{q}$-summations, and $R(without\ L_i, L_j...)$ indicates unrestricted $\mathbf{q}$-sums with the lines $L_i, L_j...$ removed from the summand $F(\mathbf{q_1}, ..., \mathbf{q_n})$ in Eq. (C1). After substituting the definition of $f(\mathbf{q_i})$ from Eq. (2.4) into Eq. (C4), the evaluation of the unrestricted $\mathbf{q}$-sums yields a product of Kronecker delta functions involving the lattice vectors $\mathbf{a}_{\beta_i}$. Applying the above procedure to Eq. (3.4) produces the final result in the form

$$R_{B,m} \approx \frac{N^{v+n_c}}{z^B}\left(r_{unrestr} + O(\frac{1}{N})\right)$$

Thus, theorem 2 is proven. Figure 19 presents a complete list of contributing contracted diagrams for $B \leq 8$.

To understand the meaning of $r_{unrestr}$ we rewrite the term with unrestricted summation from Eq. (3.4) in the form

$$\sum_{q_1,...,q_n} F(q_1, ..., q_n) = \sum_{\beta}\prod_{j}\delta(\mathbf{a}^{\mathbf{j}}_{\beta_1} \pm \mathbf{a}^{\mathbf{j}}_{\beta_2} \pm ... \pm \mathbf{a}^{\mathbf{j}}_{\beta_n}). \tag{C5}$$

where the last equality follows from substituting Eq. (2.4) for the single bond structure factors and from using Eq. (C3) to perform the $\mathbf{q}$-summations. The $\pm$ signs in Eq. (C5) appear because the application of momentum conservation conditions interrelates groups of the $\mathbf{q}$-vectors. The product in Eq. (C5) contains $j \leq n$ factors. Consider the contribution from a single Kronecker delta term in Eq. (C5). The sequence $\mathbf{a}^{\mathbf{j}}_{\beta_1}, ..., \mathbf{a}^{\mathbf{j}}_{\beta_n}$ represents a random walk of n steps, and the condition imposed by the Kronecker delta requires the vanishing of the end-to-end vector. The sum over all $\{\beta\}$ in Eq. (C5) gives the total number of n-step random walks between the two end sites of the walk. Appendix D describes the calculation of the numbers of walks.

The proof of the corollary requires analyzing the N-dependence of various diagram contributing to the entropy. The dominant portion of the combinatorial factor from Eq. (2.10) for a parent diagram with l bonds is of order N^{-l}. A contracted diagram consisting of n_d disconnected parts has the leading term of order N^{n_d}. According to Eq. (3.5), the factor in front of a contracted diagram is of order N^{v+n_c}. The graph theory relation of Eq. (3.2) enables substituting $n_c + v$ for $l + n_d$. After multiplying the value of the contracted diagram R by its combinatorial coefficient γ_D, the contribution to the entropy from a contracted diagram with n_d disconnected parts is of order $N^{l+n_d-l} = N^{n_d}$. This result implies that contributions to the partition function from individual disconnected contracted diagrams can be hyper-extensive in N, with orders higher than unity. The two trimer diagram in Fig. 9 is of order N^2 as is the square of t he single trimer diagram. However, in the expansion of the partition function [see Eq. (3.7)] to produce the entropy, a cancellation of all higher than unity orders of N occurs through the formation of cumulant clusters[18]. The cumulant cluster diagrams are formed by grouping together diagrams according to their similar topologies, as illustrated in Fig. 10 for a three-dimer and a two trimer system. The terms in parentheses arise from the square or cube terms on the right hand side of Eq. (3.7). We find that all hyper-extensive contributions through $l = 8$ cancel between the combinatorial coefficients from the different parts of the cumulant. For instance, the intra-trimer contractions of the two-trimer primary term on the left ihand side of Fig. 9 yield the identical contracted diagrams as the term with the square of the single trimer diagrams. Denoting the overall combinatorial factors of these two terms as $\gamma_{primary}$ and γ_{square}, r espectively, we find that the difference $\gamma_{primary} - \gamma_{square}$ removes all hyper-extensive contributions through $l = 8$. Because this cancellation leaves only terms of order N, all derivative diagrams with $l \leq 8$ vanish in the thermodynamic limit as having lower orders in N than unity. Therefore, in considering the thermodynamic limit only, the lengthy calculation of derivative diagrams is unnecessary, and only the terms in $R_{v,l}$ with the highest power of N are required. We conjecture that this result may be generally valid, but a proof has not yet been found.

APPENDIX D: z-DEPENDENCE OF CONTRACTIONS

Every contracted diagram may be described by any of its numerous permutationally equivalent different realizations. This value of a contracted diagram has a geometrical meaning as shown in Eq. (C5) and depends only on the number of nearest neighbors to a lattice site, that is, on the coordination number z. A hypercubic lattice has $z = 2d$. Therefore, every contracted diagram yields a function $P_R(z)$, which is shown below to be a polynomial in z. (The label R is used here to identify a contracted diagram).

Consider a polymer chain on a cubic lattice. Every vertex of a contracted diagram is represented by a site of the lattice. Any two neighboring sites have their coordinates differing by a single lattice vector (a unit minimal distance) along one of the d-directions and have the same coordinates in the other $(d-1)$-directions. Define the *minimal distance* as the minimal number of steps along the lattice sites for passing from one specified lattice site to another. The terminology *walk* describes the sequence of steps made from one site to another. The walks of interest here represent the sequence of steps $\mathbf{a}^{\mathbf{j}}_{\beta_{\mathbf{i}}}$ [see Eq. (C5)], while the minimal distance equals the distance between the two ends of the walk, the external termini of $\mathbf{a}^{\mathbf{j}}_{\beta_{\mathbf{1}}}$ and $\mathbf{a}^{\mathbf{j}}_{\beta_{\mathbf{n}}}$. If the minimal distance exceeds unity, there are more than z realizations for the walk. Figure 17 presents the set of reachable sites for one and two step walks on a square lattice. The random walk starting in the middle (denoted by the square in Fig. 17) ends on the circled sites for possible one-step walks or on the sites with crosses for two step walks (including those walks returning to the center). Sites reachable by one-step walks are unreachable for two-step walks and vise versa.

The walk between two lattice sites with coordinates of $\mathbf{r_1} = (x_1\mathbf{a_1}, x_2\mathbf{a_2}, ..., x_d\mathbf{a_d})$ and $\mathbf{r_2} = (y_1\mathbf{a_1}, y_2\mathbf{a_2}, ..., y_d\mathbf{a_d})$ on an arbitrary d-dimensional lattice can be characterized by the *relative parity* of the walk. If the quantity $\sum_{i=1}^{d}(x_i - y_i)$ is an even number, the relative parity of the walk between $\mathbf{r_1}$ and $\mathbf{r_2}$ is defined as zero; otherwise it equals unity. When the relative parity vanishes, the pair of sites is termed as having an even minimal distance; otherwise, an odd one. All sites, reachable in a given walk of a fixed length have the same parity. All sites with an even minimal distance from the origin can be reached in walks with an even number of steps, etc., for the odd case.

In order to calculate the dependence of a contracted diagram on the lattice dimensionality d (or z), we must enumerate all different possible realizations of a given contracted diagram on the lattice. Obviously, if a walk between two sites and the minimal distance between two sites have unequal parities, the walk can not have these lattice sites as end-points. For instance, an odd-step walk can not return to itUs origin.

1. Generating Functions for Numbers of Walks

The main components of all relevant contracted diagrams are cycles of various lengths. These cycles may be represented as closed random walks of various lengths. Equation (C5) represents the value of contracted diagrams in terms of the number of ways to realize a set of closed random walks on the lattice. Since the graphs representing these walks and the contracted diagrams have at least two branch points, the counting is simplified by separately performing the enumerations for each leg between branch points in the contracted diagram. The legs may have end points that are displaced from each other along one or more directions. The analysis below begins with closed random walks and then proceeds to open ones.

Consider first a simple $(2L)$-step cycle in one dimension. A one-dimensional random walk has the steps proceed in only two directions. Denote a left step as a^- and a right step as a^+. A one-dimensional closed $(2L)$-step random walk must contain as many a^+ as there are a^-. Different realizations of the walk differ only in the succession of the a^+ and a^-. For example, when $L = 2$, they could be

$$a^+a^+a^-a^-,$$
$$a^+a^-a^+a^-,$$
$$a^-a^+a^-a^+, \text{ etc.}$$

Thus, the number of different realizations is determined by the number of combinations, which equals

$$N^{(1)}_{2L} = \frac{(2L)!}{(L!)^2}. \tag{D1}$$

It is convenient to collect the number from (D1) for all different L in a generating function with a formal parameter t,

$$Q_1(t) = \sum_{L=0}^{\infty} \frac{t^{2L}}{(2L)!} N^{(1)}_{2L} = \sum_{L=0}^{\infty} \frac{t^{2L}}{(L!)^2}. \tag{D2}$$

The closed d-dimensional walk contains possible positive and negative steps in d different directions. Thus, if m_i denotes the number of a^+ in direction i, the number of realizations for the walk is given by

$$N^{(d)}_{2L} = \frac{(2L)!}{(m_1!)^2(m_2!)^2...(m_d!)^2}\Big|_{\sum_0^\infty m_i = L}. \tag{D3}$$

The inconvenience of having the restricted sum as a constraint in Eq. (D3) is avoided by again using generating functions as

$$Q_d(t) = \sum_{L=0}^{\infty} \frac{t^{2L}}{(2L)!} N_{2L}^{(d)} = \sum_{L=0}^{\infty} \frac{t^{2(\sum m_i)}}{\prod_i (m_i!)^2} = \sum_m \left[\frac{t^{2m}}{(m!)^2}\right]^d = \left[Q_1(t)\right]^d . \tag{D4}$$

Thus, the polynomial giving the generating function for the number of closed random walks on d-dimensional cubic lattice appears as the d-th power of the polynomial for a one-dimensional lattice.

The coefficient of t^{2L} from Eq. (D4), when multiplied by $(2L)!$, provides the desired number distinct closed random walks of L-steps. In order to express this number as a function of the coordination number z, we rewrite $Q_1(t)$ as

$$\begin{aligned} Q_1(t) &= 1 + s(t), \\ s(t) &= \textstyle\sum_{m=1}^{\infty} \frac{t^{2m}}{(m!)^2}. \end{aligned} \tag{D5}$$

Then, Eq. (D4) with $d = 2z$ yields

$$\begin{aligned} Q(t) &= (1+s)^{\frac{z}{2}}, \\ &= 1 + \tfrac{z}{2}s + \tfrac{z(z-2)}{8}s^2 + \tfrac{z(z-2)(z-4)}{3!8}s^3 + ... \end{aligned} \tag{D6}$$

The expression (D6) provides an algorithm for calculating the polynomials $P(2L, \{0\})$ giving the number of closed cycle $2L$-step random walks. For example, in evaluating $P(2L, \{0\})$ for closed $2L$-step cycles containing up to six steps we must retain terms through 6th order in t,

$$s = t^2 + \frac{t^4}{4} + \frac{t^6}{36}, \tag{D7}$$

producing $Q(t)$ in the form

$$\begin{aligned} Q(z,t) &= 1 + \left(t^2 + \tfrac{t^4}{4} + \tfrac{t^6}{36}\right)\tfrac{z}{2} + \left(t^4 + 2\tfrac{t^6}{4}\right)\tfrac{z(z-2)}{8} + t\tfrac{z(z-2)(z-4)}{6\cdot 8} \\ &= 1 + \tfrac{t^2}{2}z + \tfrac{t^4}{4!}\left[3z + 3z(z-2)\right] + \tfrac{t^6}{6!}\left[10z + 45z(z-2) + 15z(z-2)(z-4)\right] + ... \end{aligned} \tag{D8}$$

Extracting the coefficients of $\frac{t^2}{2!}$, $\frac{t^4}{4!}$, and $\frac{t^6}{6!}$ provides the numbers of realizations of 2,4, and 6-step cycles on d-dimensional hypercubic lattice as

$$\begin{cases} P(2, \{0\}) = z, \\ P(4, \{0\}) = 3z(z-1), \\ P(6, \{0\}) = 5z(3z^2 - 9z + 2), \end{cases}$$

respectively. In the same way we calculate

$$P(8, \{0\}) = 35z\left(3z^3 - 18z^2 - 10z - 33\right),$$

and so on, where the $\{0\}$ designates the minimal distance between the two end sites of the walk.

2. Contracted Diagrams with Two Branched Vertices and k Lines of Equal Parity

The next important step in evaluating the contracted diagrams involves treating diagrams with two branched vertices that are connected by $k > 2$ lines. These k lines have the same parity, have the lengths L_k, and produce $k-1$ cycles. The case of $k = 2$ corresponds to a closed walk described above. Diagrams **b** and **f** of Fig. 2 and diagram **a** of Fig. 6 have $k = 3$, while the bottom diagram in Fig. 5 has $k = 7$. The minimal distance between vertices b and c in Fig. 3 is unity. The minimal distance is calculated in the general case by using the distant calculation method, which is described on pages 215-217 of Ref.[33]. (See also[33,34,43].)

For eight-bond diagrams, the minimal distance between the vertices in contracted diagrams can not exceed two [in units of lattice constants] if the number of cycles is greater than unity. Figure 18 illustrates the fact that nine bonds is the smallest number for producing $k > 2$ and a minimal distance equal to three. Consider now an eight-bond contracted diagram with $k \geq 3$ and the longest minimal distance of two. The two ends of the walk can be separated by two steps in any one of z different directions, by one step along two distinct directions (there are $\frac{z(z-2)}{2}$ pairs of directions), or the two ends can coincide. We designate these three cases by $\{2\}$, $\{1,1\}$ and $\{0\}$ respectively, and the polynomial for the eight bond contracted diagram is written as the sum of these three types of contributions,

$$P_2 = \prod_{i=1}^{k} P(L_i, \{0\}) + z \prod_{i=1}^{k} P(L_i, \{2\}) + \frac{z(z-2)}{2} \prod_{i=1}^{k} P(L_i, \{1,1\}), \tag{D9}$$

where $P(L, \{2\})$ is a polynomial for an L-step random walk with end-points separated by two lattice constants in a given direction, and the factor of z arises from the z possible directions. Likewise, $P(L, \{1,1\})$ is the polynomial for an L-step random walk with the two end point displaced from each other by one step in two different directions. The product in Eq. (D9) runs over all the k-legs of the contracted diagram.

If the minimal distance between the end vertices equals unity, the end vertices are separated from each other by only one step in any one of the z directions. Hence, the polynomial contains an overall factor of z which is extracted as

$$P_1 = z \prod_{i=1}^{k} P(L_i, \{1\}),$$

where the next computational problem, therefore, lies in calculating the polynomials for L-step walks with various relative locations of the two ends.

3. Calculation of Numbers of Walks

Suppose a walk has its end-point coordinates differing in two directions, with an m step difference in the first direction and an n step separation in the second one. Along each of the two directions there are both positive steps a^+ and negative steps a^-. If the length of the walk is L, the number of ways of realizing this walk is

$$N(L, \{m,n\}) = \sum \frac{L!}{(K_1+m)!K_1!(K_2+n)!K_2!(K_3!)^2 ... (K_d!)^2} \Big|_{(\sum_{i=1}^{d} K_i) = L}.$$

Here the number of steps in the positive ith direction is $K_i + m_i$, while K_i is the number of negative steps in the ith direction. To eliminate the restricted sum, we introduce a generating polynomial in t as

$$\begin{aligned} Q(t, \{m,n\}) &= \textstyle\sum_{L=0}^{\infty} \frac{t^L}{L!} N(L, \{m,n\}) \\ &= t^{m+n} \textstyle\sum_{L=0}^{\infty} \frac{t^{2\sum K_i}}{(K_1+m)!K_1!(K_2+n)!K_2!(K_3!)^2 ...} \\ &= t^{m+n} \left[\textstyle\sum_{K_1=0}^{\infty} \sum_{K_2=0}^{\infty} \frac{t^{2(K_1+K_2)}}{(K_1+m)!K_1!(K_2+n)!K_2!} \right] Q_0^{d-2}(t). \end{aligned}$$

Thus, to calculate the generating polynomial for a walk with end point coordinate differences in r directions, we can calculate the generating polynomial in an r-dimensional space and then multiply the result by the generating polynomial for closed cycles in $(d-r)$-dimensions. As before, the coefficient of t^{2L}, multiplied by $(2L)!$, provides the polynomial in z, that gives the value of the contracted diagram. The number of bonds in a diagram, i.e., the lengths of the random walks, restricts the possible powers of t. Table 1 presents the values of all polynomials necessary for evaluating diagrams with up to eight bonds (eight-step walks).

There are two corollaries for evaluating contracted diagrams.

1. The z-polynomial $P(z)$ for a disconnected diagram or a diagram with a cut-point is equal to the product of values of all its constituent parts.

2. Multiple edges do not change the z-polynomial for contracted diagram.

APPENDIX E: SYMMETRY OF DIMERS. CALCULATING THE NUMBER OF CONTRACTIONS

The numerical factors $\{f^d_{R,m}\}$ of Eq. (2.13) for each contracted diagram may be calculated more easily for a system of dimers. The number of equivalent permutations D of the site labels for k dimers is

$$D = 2^k k!. \tag{E1}$$

The factor of 2^k emerges by permuting the vertex labels within each pair of dimers, while $k!$ comes from permutating the dimers among themselves. Each contraction can be formed in D different ways, unless the contracted diagram contains an additional degeneracy (or symmetry) with g equivalent cases. Thus, this process yields $M = \frac{D}{g}$ distinct contracted diagrams. For example, consider the two-vertex diagrams **a** and **b** of Fig. 2 with one bond in each line. Diagram (a) has two equivalent lines, giving $g = 2(2!)$, while diagram (b) has three equivalent lines and $g = 2(3!)$. The factor of 2 arises from symmetry (reflection about the middle) of the contracted diagram, and the factorial term is due to the equivalent permutations among the multiple lines. If the contracted diagram consists of several disconnected parts, g equals the product of the g_i's for each part.

The degeneracy parameter g for connected contracted diagrams is defined as the product of the symmetry parameter of the contracted diagram (for example, an even n-gon has $2n$ symmetries), and the number of permutations among multiple equivalent lines. The g for disconnected contracted diagrams equals the product of g_i for each disconnected piece, multiplied by the number of permutations among similar pieces. A detailed discussion of this problem can be found for instance in Ref.[44]. Tables II and III present the degeneracy parameters g and the values $R_{B,m}$ for all contributing contracted diagrams with $B \leq 8$ bonds using the numbering scheme from Fig. 19.

FIG. 1. Examples of contributing diagrams that represent corrections to the zeroth order mean field approximation. The diagrams consist of vertices connected by bonds. The segments joined by wiggly lines, as in diagram c, belong to the same chain but lie nonsequentially along the chain. Diagram a is the only one-bond diagram. There are three different two-bond diagrams, $b - d$. Diagrams $e - g$ are examples of six-bond diagrams for chains with various architectures.

FIG. 2. Examples of contributing contracted diagrams.

FIG. 3. The graph (i.e., diagram) G_3 is a disconnected graph consisting of two connected graphs G_1 and G_2. Adjacent vertices, such as (a, b), and (c, d) and others are connected by edges. A path from vertex a to vertex c can be written as a sequence of adjacent vertices, e.g., $(a, d), (d, c)$ or $(a, b), (b, c)$. A cycle is an edge sequence that returns to the starting vertex, e.g., $(h, g), (g, f), (f, e), (e, g), (g, h)$. A circuit is a cycle with no edge repeated, e.g., $(e, f), (f, g), (g, e)$. The circuit (e, e) is called a self-loop. The cycle $(b, c), (c, b)$ is a multiple edge. The graph G_2 is single connected. The edge (g, h) is singly-connected since removing this edge decomposes G_2 into two disconnected portions. The edge (i, j) is called a dangling end. The vertex g is termed a cut-point.

FIG. 4. Examples of noncontributing contracted diagrams. Diagram **a** has a self-loop, **b** has a dangling end, and **c** has an odd cycle. Applying momentum conservation conditions at every vertex of the singly-connected diagram **d** produces the set of conditions $\mathbf{q_2} - \mathbf{q_1} = \mathbf{0}, \mathbf{q_1} - \mathbf{q_2} - \mathbf{q_3} = \mathbf{0}, \mathbf{q_4} - \mathbf{q_5} + \mathbf{q_3} = \mathbf{0}$, and $\mathbf{q_5} - \mathbf{q_4} = \mathbf{0}$, which may be rearranged to $\mathbf{q_3} = \mathbf{0}, \mathbf{q_1} - \mathbf{q_2} = \mathbf{0}$, and $\mathbf{q_5} - \mathbf{q_4} = \mathbf{0}$.

FIG. 5. There exist a consecutive contraction process that transforms the top diagram of a into the two-vertex bottom diagram. In contrast, there is no such process for odd-cycled diagram of b.

FIG. 6. Use of the momentum conservation conditions in Eq. (2.13) leads to the presence of only two summation variables $\mathbf{q_i}$ and $\mathbf{q_j}$ for the contracted diagram a. Setting $\mathbf{q_i} = \mathbf{0}$ transforms the contracted diagram a into the derivative diagram b.

FIG. 7. Two parent diagrams corresponding to $\{\{3, 2\}\}$ and $\{\{3\}, \{2\}\}$. The notation $\{\{3\}, \{2\}\}$ designates that the consecutive three and two-bond segments belong to different chains. The notation $\{\{3, 2\}\}$ indicates that groups of three and two sequential bonds occur nonsequentially on the same chain.

FIG. 8. Starting with the parent diagram, the program first finds sequentially all different possible contractions with two of the vertices contracted. These once-contracted diagrams have the number of vertices reduced by unity from the parent diagram. Every subsequent contraction diminishes the number of vertices in the contracted diagram by unity in all possible ways. Thus, the second step of the program creates all possible twice-contracted diagrams, which may have either three vertices contracted into one or two pairs of contracted vertices. The program proceeds in this manner until further contractions become irrelevant because of the presence of self-loops.

FIG. 9. Examples of two different realizations of the "infinity shaped" contracted diagram that emerges with different numerical factors from the contraction of the two-trimer parent diagram. The vertices of the contracted diagrams are labelled by the vertices of the original diagram. The contraction process A contracts vertices a and d, b and e, and c and f, while process B merges the four vertices a, c, d, and f into one. The contraction process A produces the factor $f_A = (-1)^3 3! = -6$, while process B produces $f_B = (-1)^3 1! = -1$. The contribution $f^{(d)}_{B,m}$ from every contracted diagram is the sum of all the numerical factors obtained from its various permutationally equivalent realizations in contracting a parent diagram.

FIG. 10. Two examples of cumulant cluster diagrams.

FIG. 11. The percentage relative difference $100(S_{exact} - S_{LCT})/S_{exact}$ between the exact one-dimensional per site entropy and S_{LCT} through fifth order in ϕ.

FIG. 12. The convergence of the LCT per site entropy S_{LCT} to the exact solution for 2d dimers at full coverage as series in z (stars) and in ϕ (dots). The solid line gives the extrapolation of the series in ϕ by use of an exponential function. $S_{LCT} = Aexp(B\phi)$.

FIG. 13. The dependence of the dimer per site entropy at full coverage on a the lattice coordination number z.

FIG. 14. Surface of relative percentage difference $100\frac{S_{LCT}-S_{DM}}{S_{DM}}$ between the LCT and DiMarzio theory per site entropies for dimers at different ϕ and z.

FIG. 15. The percentage relative difference $100\frac{S_{LCT}-S_{DM}}{S_{DM}}$ between the DiMarzio theory and LCT per site entropy for $z = 4$.

FIG. 16. Comparison of the LCT predictions with Monte-Carlo simulations by Lin and Lai for two dimensional dimers. The graph presents the percentage relative difference $100\frac{S_{LCT}-S_{LL}}{S_{LL}}$.

FIG. 17. Walks, and minimal distances on a square lattice. If the first vertex is located in the middle, then walks of length two can go from the middle to sites marked by crosses (including returning to the center). The crosses form a square with a side of length three and a set of nine reachable sites. Circles denote the sites reachable by one-step walks. The dotted line presents a six-step walk between sites with a minimal distance of 2 units. The walks and minimal distances between a pair of sites always have the same parity.

FIG. 18. a). A minimal distance is defined as equal to $min(\{L_i\})$, where $\{L_i\}$ are the lengths of all possible paths between these vertices. b). A contracted diagram with a minimal distance of three requires nine edges (bonds) to produce a diagram with $n_c \geq 2$ and two branched vertices. The nine-bond diagram is beyond our consideration of eight bonds.

FIG. 19. All contributing contracted diagram with two through eight bonds. The values for $R_{B,m}$ are given in Tables II and III.

[1] P. J. Flory, J. Chem. Phys. **9**, 660 (1941).
[2] D. S. Gaunt, Phys. Rev. **179**, 174 (1969).
[3] P. J. Flory, J. Chem. Phys. **10**, 51 (1942).
[4] M. L. Huggins, J. Chem. Phys. **9**, 440 (1941).
[5] M. L. Huggins, J. Chem. Phys. **46**, 151 (1942).
[6] M. L. Huggins, Ann. N. Y. Acad. Sci. **41**, 1 (1942).
[7] P. J. Flory, *Principles of Polymer Chemistry* (Cornell University, Ithaca, 1953).
[8] R. Dickman and C. K. Hall, J. Chem. Phys. **85**, 3023 (1986).
[9] A. Falsafi and W. G. Madden, Macromolecules **27**, 3094 (1994).
[10] A. Sariban and K. Binder, Macromolecules **21**, 711 (1988).
[11] A. R. Miller, Proc. Cambridge Philos. Soc. **39**, 54 (1943).
[12] E. A. Guggenheim, Proc. R. Soc. London, Ser.A **183**, 203, 213 (1944).
[13] E. A. Guggenheim, *Mixtures* (Oxford University, Oxford, 1952).
[14] K. W. Foreman and K. F. Freed, J. Chem. Phys. **102** (1995).
[15] H. Tompa, *Polymer Solutions* (Butterworths, London, 1956).
[16] J. E. G. Lipson and P. K. Brazhnik, J. Chem. Phys. **98**, 8178 (1993).
[17] M. G. Bawendi and K. F. Freed, J. Chem. Phys. **85**, 3007 (1986).
[18] A. M. Nemirovsky, M. G. Bawendi, and K. F. Freed, J. Chem. Phys. **87**, 7272 (1987).
[19] K. F. Freed and M. G. Bawendi, J. Chem. Phys. **93**, 2194 (1989).
[20] J. Dudowicz, K. F. Freed, and W. G. Madden, Macromolecules **23**, 4803 (1990).
[21] J. Dudowicz and K. F. Freed, Macromolecules **24**, 5076 (1991).
[22] A. Sariban and K. Binder, J. Chem. Phys. **86**, 5859 (1987).
[23] W. Madden, A. I. Pesci, and K. F. Freed, Macromolecules **23**, 1181 (1990).
[24] M. G. Bawendi, K. F. Freed, and U. Mohanty, J. Chem. Phys. **84**, 7036 (1986).
[25] S. E. Huston, A. M. Nemirovsky, and K. F. Freed, J. Chem. Phys. **99**, 2149 (1993).
[26] A. M. Nemirovsky, S. E. Huston, R. G. Graham, and K. F. Freed, J. Chem. Phys. **101**, 510 (1994).
[27] D. Baker, H. S. Chan, and K. A. Dill, J. Chem. Phys. **98**, 9951 (1993).
[28] R. J. Baxter, *Exactly Solved Models in Statistical Mechanics* (Academic Press, New York, 1982).
[29] J. E. Mayer and M. G. Mayer, *Mixtures* (Winley, New York, 1940).
[30] K. Balasubramanian, Chem. Phys. Lett. **232**, 415 (1995).
[31] K. Nitta, J. Chem. Phys. **101**, 4222 (1994).
[32] E. I. Kornilov and V. B. Priezzhev, Teor. i Mat. Fiz. **98**, 90 (1994).
[33] C. Marshall, *Applied Graph Theory* (Wiley-Interscience, New York, 1971).
[34] L. Foulds, *Graph Theory Applications* (Springer-Verlag, New York, 1992).
[35] R. Fowler and G. Rushbrooke, Trans. Faraday Soc. **33**, 1272 (1937).
[36] E. A. DiMarzio, J. Chem. Phys. **35**, 658 (1961).
[37] J. F. Nagle, Proc. R. Soc. London Ser. A **337**, 569 (1974).
[38] M. E. Fisher, Phys. Rev **124**, 1664 (1961).
[39] P. W. Kasteleyn, Physica **27**, 1209 (1961).
[40] E. H. Lieb, J. Math. Phys **8**, 2339 (1967).
[41] A. E. Ferdinand, J. Math. Phys **8**, 2332 (1967).
[42] G. J. Lin and P. Y. Lai, Physica A **211**, 465 (1994).
[43] F. Harary and E. M. Palmer, *Graphical Enumeration* (Academic Press, New York and London, 1973).
[44] A. Fucker, *Applied Combinatorics* (John Wiley & Sons, INC, New York, 1995).

TABLE I. z-polynomials $P(L_i, \{\text{distance between ends}\})$ for calculations in Appendix D.

distance between ends	$P(L_i, \{\})$	distance between ends	$P(L_i, \{\})$
$L_i = 1$		$\{4,1\}$	$21(-13+5z)$
$\{1\}$	1	$\{3,3,1\}$	140
$L_i = 2$		$\{3,2,2\}$	210
$\{2\}$	1	$\{3,2,1,1\}$	420
$\{1,1\}$	2	$\{3,2\}$	$35(-17+6z)$
$\{0\}$	z	$\{3,1,1,1,1\}$	840
$L_i = 3$		$\{3,1,1\}$	$210(-7+2z)$
$\{3\}$	1	$\{3\}$	$21(21-20z+5z^2)$
$\{2,1\}$	3	$\{2,2,2,1\}$	630
$\{1,1,1\}$	6	$\{2,2,1,1,1\}$	1260
$\{1\}$	$3(-1+z)$	$\{2,2,1\}$	$210(-11+3z)$
$L_i = 4$		$\{2,1,1,1,1,1\}$	2520

$\{4\}$	1
$\{3,1\}$	4
$\{2,2\}$	6
$\{2,1,1\}$	12
$\{2\}$	$2(-4+3z)$
$\{1,1,1,1\}$	24
$\{1,1\}$	$12(-2+z)$
$\{0\}$	$3(-1+z)z$
$L_i = 5$	
$\{5\}$	1
$\{4,1\}$	5
$\{3,2\}$	10
$\{3,1,1\}$	20
$\{3\}$	$5(-3+2z)$
$4\{2,2,1\}$	30
$\{2,1,1,1\}$	60
$\{2,1\}$	$10(-7+3z)$
$\{1,1,1,1,1\}$	120
$\{1,1,1\}$	$60(-3+z)$
$\{1\}$	$5(8-9z+3z^2)$
$L_i = 6$	
$\{6\}$	1
$\{5,1\}$	6
$\{4,2\}$	15
$\{4,1,1\}$	30
$\{4\}$	$3(-8+5z)$
$\{3,3\}$	20
$\{3,2,1\}$	60
$\{3,1,1,1\}$	120
$\{3,1\}$	$30(-5+2z)$
$\{2,2,2\}$	90
$\{2,2,1,1\}$	180
$\{2,2\}$	$30(-8+3z)$
$\{2,1,1,1,1\}$	360
$\{2,1,1\}$	$60(-10+3z)$
$\{2\}$	$15(11-11z+3z^2)$
$\{1,1,1,1,1,1\}$	720
$\{1,1,1,1\}$	$360(-4+z)$
$\{1,1\}$	$30(22-15z+3z^2)$
$\{0\}$	$5z(8-9z+3z^2)$
$L_i = 7$	
$\{7\}$	1
$\{6,1\}$	7
$\{5,2\}$	21
$\{5,1,1\}$	42
$\{5\}$	$7(-5+3z)$
$\{4,3\}$	35
$\{4,2,1\}$	105
$\{4,1,1,1\}$	210
$\{2,1,1,1\}$	$420(-13+3z)$
$\{2,1\}$	$105(27-17z+3z^2)$
$\{1,1,1,1,1,1,1\}$	5040
$\{1,1,1,1,1\}$	$2520(-5+z)$
$\{1,1,1\}$	$630(14-7z+z^2)$
$\{1\}$	$35(-33+41z-18z^2+3z^3)$
$L_i = 8$	
$\{8\}$	1
$\{7,1\}$	8
$\{6,2\}$	28
$\{6,1,1\}$	56
$\{6\}$	$4(-12+7z)$
$\{5,3\}$	56
$\{5,2,1\}$	168
$\{5,1,1,1\}$	336
$\{5,1\}$	$56(-8+3z)$
$\{4,4\}$	70
$\{4,3,1\}$	280
$\{4,2,2\}$	420
$\{4,2,1,1\}$	840
$\{4,2\}$	$28(-44+15z)$
$\{4,1,1,1,1\}$	1680
$\{4,1,1\}$	$168(-18+5z)$
$\{4\}$	$14(68-63z+15z^2)$
$\{3,3,2\}$	560
$\{3,3,1,1\}$	1120
$\{3,3\}$	$560(-3+z)$
$\{3,2,2,1\}$	1680
$\{3,2,1,1,1\}$	3360
$\{3,2,1\}$	$280(-23+6z)$
$\{3,1,1,1,1,1\}$	6720
$\{3,1,1,1\}$	$1680(-9+2z)$
$\{3,1\}$	$56(148-90z+15z^2)$
$\{2,2,2,2\}$	2520
$\{2,2,2,1,1\}$	5040
$\{2,2,2\}$	$2520(-4+z)$
$\{2,2,1,1,1,1\}$	10080
$\{2,2,1,1\}$	$1680(-14+3z)$
$\{2,2\}$	$140(98-57z+9z^2)$
$\{2,1,1,1,1,1,1\}$	20160
$\{2,1,1,1,1\}$	$3360(-16+3z)$
$\{2,1,1\}$	$840(49-23z+3z^2)$
$\{2\}$	$28(-228+265z-105z^2+15z^3)$
$\{1,1,1,1,1,1,1,1\}$	40320
$\{1,1,1,1,1,1\}$	$20160(-6+z)$
$\{1,1,1,1\}$	$1680(68-27z+3z^2)$
$\{1,1\}$	$280(-3+z)(38-18z+3z^2)$
$\{0\}$	$35z(-33+41z-18z^2+3z^3)$

TABLE II. Contracted diagrams containing up to 7 bonds: degeneracy parameters g and the values $R_{B,m}$. D_i is the permutation number in Eq. (E1).

contracted diagram	degeneracy parameter g	value $R_{B,m}$	contracted diagram	degeneracy parameter g	value $R_{B,m}$
2 bonds	$D_2 = 2^2 2! = 8$		6,14	$2 \cdot 2$	$3N^7(z-1)/z^4$
2,1	$2(2!)$	N^3/z	6,15	12	$5N^7(3z^2-9z+8)/z^5$
3 bonds	$D_3 = 2^3 3! = 48$		6,16	$(3!)(2!)^3$	N^7/z^3
3,1	$2(3!)$	N^4/z^2	7 bonds	$D_7 = 2^7(7!)$	
4 bonds	$D_4 = 2^4 \cdot 4! = 384$		7,1	$2(7!)$	N^8/z^6
4,1	$2(4!)$	N^5/z^3	7,2	$2 \cdot 2 \cdot 2(5!)$	N^9/z^5
4,2	$(2 \cdot 2!)^2 2!$	N^6/z^2	7,3	$2(5!)$	N^8/z^6
4,3	$(2!)^2 2$	N^5/z^2	7,4	$2(4!)2(3!)$	N^9/z^5
4,4	$2 \cdot 4$	$N^5 \cdot 3(z-1)/z^3$	7,5	$(4!)(3!)$	N^8/z^5
5 bonds	$D_5 = 2^5 5! = 3840$		7,6	$2^2 4^2 (3!)$	N^{10}/z^z
5,1	$2 \cdot 5!$	N^6/z^4	7,7	$2 \cdot 4(3!)$	N^9/z^4
5,2	$2(3!)2(2!)$	N^7/z^3	7,8	$2^4(3!)$	N^9/z^4
5,3	$2(3!)$	N^6/z^3	7,9	$2^3(3!)$	N^8/z^4
5,4	$2 \cdot 2$	$N^6 \cdot 3(z-1)/z^4$	7,10	$2^2(3!)$	N^8/z^4
6 bonds	$D_6 = 2^6(6!) = 46080$		7,11	$2^3(3!)$	N^8/z^4
6,1	$2(6!)$	N^7/z^5	7,12	$2(4!)$	$3N^8(z-1)/z^6$
6,2	$2(4!)2(2!)$	N^8/z^4	7,13	$2(3!)$	$3N^8(z-1)/z^6$
6,3	$(4!)(2!)$	N^7/z^4	7,14	$2^2(3!)$	$3N^8(z-1)/z^6$
6,4	$(2 \cdot 3!)^2 \cdot 2!$	N^8/z^4	7,15	2^4	$3N^8(z-1)/z^6$
6,5	$2(3!)^2$	N^7/z^4	7,16	$8(3!\ 2)$	$3N^9(z-1)/z^5$
6,6	$(2 \cdot 2!)^3(3!)$	N^9/z^3	7,17	$2(3!)$	$3N^8(z-1)/z^5$
6,7	$2(2!)^2 \cdot 2(2!)$	N^8/z^3	7,18	2^4	$3N^9(z-1)/z^5$
6,8	$2(2!)^3$	N^7/z^3	7,19	2^2	$3N^8(z-1)/z^5$
6,9	$2(3!)$	$3N^7(z-1)/z^5$	7,20	2^2	$3N^8(z-1)/z^5$
6,10	$4(2!)^2$	$3N^7(z-1)/z^5$	7,21	2^2	$3N^8(3z^2-9z+8)/z^6$
6,11	$2(2!)^2$	$3N^7(z-1)/z^5$	7,22	2^2	$3N^8(z-1)/z^6$
6,12	$2(3!)$	$N^7(z^2+4z-7)/z^5$	7,23	2^2	$3N^8(z^2+4z-7)/z^6$
6,13	$(8)(2 \cdot 2!)$	$3N^8(z-1)/z^4$			

TABLE III. Contracted diagrams containing 8 bonds: degeneracy parameters g and the values $R_{B,m}$. The combinatorial parameter for 8 dimers is $D_8 = 2^8(8!)$.

contracted diagram	degeneracy parameter g	value $R_{B,m}$	contracted diagram	degeneracy parameter g	value $R_{B,m}$
8,1	$2(8!)$	N^9/z^6	8,40	$2(3!)4$	$3N^{10}(z-1)/z^6$
8,2	$2^3(6!)$	N^{10}/z^6	8,41	$2(3!)$	$3N^9(z-1)/z^6$
8,3	$2(6!)$	N^9/z^6	8,42	$2(3!)$	$3N^9(z-1)/z^6$
8,4	$2(5!)2(3!)$	N^{10}/z^6	8,43	$2^2 4^2$	$3N^{10}(z-1)/z^6$
8,5	$(5!)(3!)$	N^9/z^6	8,44	2^3	$3N^9(z-1)/z^6$
8,6	$2(2(4!))^2$	N^{10}/z^6	8,45	$2^2 4$	$3N^{10}(z-1)/z^6$
8,7	$2(4!)^2$	N^9/z^6	8,46	2^4	$3N^9(z-1)/z^6$
8,8	$2\cdot 4^2 2(4!)$	N^{11}/z^6	8,47	2^2	$3N^9(z-1)/z^6$
8,9	$4(4!2!)$	N^{10}/z^5	8,48	2^4	$3N^9(z-1)/z^6$
8,10	$2^4(4!)$	N^{10}/z^5	8,49	2^4	$N^9(z^2+4z-7)/z^7$
8,11	$(2!)^2(4!)$	N^9/z^5	8,50	2^3	$N^9(z^2+4z-7)/z^7$
8,12	$2^3(4!)$	N^9/z^5	8,51	2^3	$N^9(z^2+4z-7)/z^7$
8,13	$2(2!)^2(4!)$	N^9/z^5	8,52	$2(3!)$	$N^9(z^2+4z-7)/z^7$
8,14	$2\cdot 4(2(3!))^2$	N^{11}/z^5	8,53	$2\cdot 4^2 8$	$3N^{11}(z-1)/z^5$
8,15	$2\cdot 4(3!)^2$	N^{10}/z^5	8,54	$8(2^3)$	$3N^{10}(z-1)/z^5$
8,16	$2(3!)(2!)(3!)$	N^{10}/z^5	8,55	$2^2 4$	$3N^{10}(z-1)/z^5$
8,17	$(2!)(3!)^2$	JN^9/z^5	8,56	2^3	$3N^9(z-1)/z^5$
8,18	$2(2!)(3!)^2$	N^9/z^5	8,57	2^4	$3N^9(z-1)/z^5$
8,19	$2(2!)(3!)^2$	N^9/z^5	8,58	2^3	$3N^9(z-1)/z^5$
8,20	$2(5!)$	$3N^9(z-1)/z^7$	8,59	2^4	$3N^9(z-1)/z^5$
8,21	$2^2(4!)$	$3N^9(z-1)/z^7$	8,60	$2(4!)$	$N^9(z^3+8z-15)/z^7$
8,22	$2(4!)$	$3N^9(z-1)/z^7$	8,61	2^3	$5N^9(3z^2-9z+8)/z^7$
8,23	$2^2(3!)^2$	$3N^9(z-1)/z^7$	8,62	2^3	$5N^9(3z^2-9z+8)/z^7$
8,24	$2^2(3!)$	$3N^9(z-1)/z^7$	8,63	2^4	$5N^9(3z^2-9z+8)/z^7$
8,25	$2^3(3!)$	$3N^9(z-1)/z^7$	8,64	2^3	$9N^9(z-1)^2/z^7$
8,26	$2^4 8$	$3N^9(z-1)/z^7$	8,65	2	$9N^9(z-1)^2/z^7$
8,27	$4^4(4!)$	N^{12}/z^4	8,66	2^2	$9N^9(z-1)^2/z^7$
8,28	$2^4 4^2$	N^{11}/z^4	8,67	$2(3!)$	$5N^9(3z^2-9z+8)/z^7$
8,29	$2(2(2)^2)^2$	N^{10}/z^4	8,68	4	$N^9(5z^2-2z-8)/z^7$
8,30	$2^4 4$	N^{10}/z^4	8,69	$2(8^2)$	$9N^{10}(z-1)^2/z^6$
8,31	$2^4 2$	N^9/z^4	8,70	2^3	$9N^{10}(z-1)^2/z^6$
8,32	$2^4 2$	N^9/z^4	8,71	16	$35N^9(3z^3-18z^2+41z-33)/z^7$
8,33	$2^4(4!)$	N^9/z^4	8,72	$(2!)^2$	$5N^9(3z^2-9z+8)/z^7$
8,34	$2^3(3!)4$	N^{10}/z^4	8,73	$2(2!)$	$N^9(3z^3+21z^2-90z+88)/z^7$
8,35	$8(2(4!))$	$3N^{10}(z-1)/z^6$	8,74	2^3	$N^9(z^2+4z-7)$
8,36	$2(4!)$	$3N^9(z-1)/z^6$	8,75	$(2!)(3!)$	$N^9(z^2+4z-7)$
8,37	$(2^2)2(3!)$	$3N^{10}(z-1)/z^6$	8,76	$(2!)(3!)^2$	$3N^9(z-1)/z^6$
8,38	$2(3!)$	$3N^9(z-1)/z^6$	8,77	$2(2!)12$	$N^{10}(3z^2-9z+8)/z^7$
8,39	$2(3!)$	$3N^9(z-1)/z^6$	8,78	$2(2!)2(3!)$	$N^{10}(z^2+4z-7)$