Multiple species of noninteracting molecules adsorbed on a Bethe lattice

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(Received 30 June 2008; published 15 October 2008)

A simple method, previously used to calculate the equilibrium concentration of dimers adsorbed on a Bethe lattice as a function of the dimer activity, is generalized to solve the problem of a Bethe lattice in contact with a reservoir containing a mixture of molecules. The molecules may have arbitrary sizes and shapes consistent with the geometry of the lattice and the molecules do not interact with one another except for the hard-core restriction that two molecules cannot touch the same site. We obtain a set of simultaneous nonlinear equations, one equation for each species of molecule, which determines the equilibrium concentration of each type of molecule as a function of the (arbitrary) activities of the various species. Surprisingly, regardless of the number of species, the equilibrium concentrations are given explicitly in terms of the solution of a single equation in one unknown which can be solved numerically, if need be. Some numerical examples show that increasing the activity of one species need not necessarily decrease the equilibrium concentration of all other species. We also calculate the adsorption isotherm of an "annealed" Bethe lattice consisting of two types of sites which differently influence the activity of an adsorbed molecule. We prove that if the reservoir contains a finite number of molecular species, regions of two different polymer densities cannot simultaneously exist on the lattice. The widely used Guggenheim theory of mixtures, which can also be construed as a theory of adsorption, assumes for simplicity that the molecules in the mixture are composed of elementary units, which occupy sites of a lattice of coordination number q. Guggenheim's analysis relies on approximate combinatorial formulas which become exact on a Bethe lattice of the same coordination number, as we show in an appendix. Our analysis involves no combinatorics and relies only on recognizing the statistical independence of certain quantities. Despite the nominal equivalence of the two approaches, the easily visualized properties of the Bethe lattice enable one to solve some apparently difficult problems by quite elementary methods.

DOI: 10.1103/PhysRevE.78.041116 PACS number(s): 05.50.+q, 02.10.Ox, 64.60.De

I. INTRODUCTION

Many calculations of the properties of a liquid mixture of several species of molecules, each of which may consist of multiple elementary units ("monomers"), are based on models in which it is assumed that the monomers can only live on the sites of some discrete lattice with the restriction that two monomers cannot occupy the same site [1]. If other interactions are ignored, the calculation of the grand partition function becomes strictly a combinatorial problem. Identical mathematics can describe a somewhat different physical situation, namely, a reservoir of molecules with specified chemical potentials, in contact with a lattice (usually a collection of sites on a surface) which can adsorb molecules. Such a model is relevant to problems in chemical engineering, metallurgy, and cell biology.

In this paper we study a particularly simple lattice, the Bethe lattice, in equilibrium with a reservoir containing (possibly) many different types of molecules of various sizes and shapes which can be adsorbed on the lattice and do not interact with each other on the lattice. Using quite simple reasoning based on the simple structure of the lattice, we make an exact calculation of the number of adsorbed molecules of each species, as a function of the activities of the various species. The calculation of this "adsorption isotherm" is our main goal and most important result. In a subsequent paper we shall discuss the adsorption of molecules which interact on the lattice, via interactions between atoms (belonging to different molecules) occupying adjacent lattice sites.

The equations most commonly used to describe a mixture of various molecules which live on the sites of a lattice are those given by Guggenheim [2–4]. His analysis is based on some approximate combinatorics and estimates of probabilities, which (for reasons which we discuss in Appendix C) become exact on the Bethe lattice. Guggenheim obtained an approximate formula for the number of distinct arrangements of N_1 molecules of type 1 (each molecule occupying n_1 sites), N_2 molecules of type 2 (each molecule occupying n_2 sites), etc., on a lattice in which each site has q nearest neighbors. The formula also involves a set of numbers [5] γ_i, which is the number of distinct arrangements of a molecule of type i on an empty lattice, when one monomer is pinned to a particular site, divided by the symmetry number of the pinned molecule.

Guggenheim's reasoning is applicable to molecules which are chains and branched chains, but specifically excludes molecules which include closed loops. Guggenheim appears to assume that all sites of the lattice are occupied, but his formula is equally valid if one defines a type 0 molecule as a vacancy. From Guggenheim's combinatorial formula one can derive formulas for the thermodynamic properties of the mixture as a function of $N_1, N_2, \ldots$ and the internal partition functions of the individual molecular species. In Ref. [2] Guggenheim ignores interactions (except hard-core restrictions) among the molecules, as we shall in the present work. He includes some interactions in another paper [4] which was published simultaneously with Ref. [2].

Somewhat earlier, Chang [6] applied the analog of Bethe's approximation, [7,8] which was derived for the study of binary alloys and the Ising model, to the problem of dimers on a planar lattice. Miller [9] extended Chang's method to trimers. Guggenheim's combinatorics yields

Chang's and Miller's results as special cases. Only considerably later was it recognized that the Bethe approximation is exact when the lattice is the central portion (far from the boundary) of a Cayley tree, which came to be known as the Bethe lattice (see footnote 12 of Ref. [10]). At least in the case of the dimer problem, the numerical relation between the dimer coverage and the dimer activity z on the Bethe lattice is very close to the corresponding relation on real lattices with the same coordination number [10–13]. Almost certainly, the agreement becomes worse when one considers larger and more complex molecules.

Locally, the Bethe lattice may not appear markedly different from other lattices with the same coordination number. On a larger scale, a striking difference (which makes exact solutions possible) is that there are no closed paths on the Bethe lattice. Thus, if one wishes to consider the sol-to-gel transition in polymers, in which the jello-like texture of the gel is due to the formation of a huge network of polymers cross linked to each other, a model in which the polymers are constrained to lie on a Bethe lattice would seem to prohibit much of the important connectivity.

Nagle [11] and Gaunt [12] have developed systematic approximations to the density of noninteracting dimers on various regular lattices, when the dimer activity z is specified. Van Craen and Bellemans [14] have studied the adsorption of trimers on regular lattices, using a generalization of Nagle's method. The leading term in Nagle's and Van Craen and Bellemans's series is the Bethe approximation, and the difficulty of calculating succeeding terms increases rapidly.

It is doubtful that with a reasonable amount of labor one can develop a useful series, more accurate than the Bethe approximation, to deal with the problem of a lattice which can simultaneously adsorb several or many species of molecules whose activities are specified and which do not interact (except for hard core restrictions) on the lattice. Assuming that the lattice is a Bethe lattice, we use quite simple reasoning to derive a set of coupled equations, one for each molecular species, relating the activities to the numbers of adsorbed molecules of each species. These equations are exact on the Bethe lattice, and the derivation does not utilize any combinatorics. Our set of coupled equations is easily soluble.

Graham *et al.* [15] have shown that the Bethe approximation [13] and Guggenheim's combinatorial approach yield identical equations when the reservoir contains only monomers and dimers ($\gamma_m=1$ and $\gamma_d=q/2$ for all lattices, where the subscripts m and d refer to monomers and dimers). In Appendix C we show that if the reservoir is a dilute solution with concentrations C_i of the various species and if we calculate the numbers of adsorbed molecules $\{N_i\}$ in terms of the $\{C_i\}$ and mass action constants empirically determined by experiments at very low concentrations, then all dependence on the γ_i disappears and Guggenheim's equations become identical with ours. Thus, if one accepts Guggenheim's method of counting and the consequences thereof, one is tacitly agreeing that it is reasonable to replace the lattice under study by a Bethe lattice of the same coordination number.

Ryu and Gujrati [16,17] have analyzed a lattice model of a mixture of polymers, in which all the constituent "monomers" of each polymer live on sites of a Bethe lattice. Their model includes nearest-neighbor interactions, and the resulting equations are exact, but increasingly difficult to solve as the number of species increases. Our equivalent set of equations are also difficult to solve when interactions are present (except for one important special case). However, our method of reasoning is quite different from that of Gujrati and coworkers, and, in our opinion, considerably simpler. The difference will be briefly discussed in Sec. II of this paper.

More specifically, as we see in Appendix C, Guggenheim's calculation of $W(N_1,N_2,\ldots)$ (the number of distinct configurations on the lattice with N_1 molecules of type 1, N_2 molecules of type 2, etc.) is based on an estimate of the probability $P_n(\{N_i\})$ that a given connected set of n sites are all vacant for arbitrary values of $\{N_i\}$. The estimate is exact only on the Bethe lattice, and it is difficult to make a better estimate for a general lattice.

Our equations, and Guggenheim's equivalent set, give the activities z_i of the various molecular species as explicit functions of $(N_1,N_2,\ldots)$, the numbers of each species on the lattice. If one is interested in calculating the thermodynamic properties of a mixture containing known amounts of the various constituents, this form of the equations is useful. However, this form is not so useful for obtaining properties as a function of the activities z_i. Accordingly, our goal, and a main result of this paper, is to give N_i as a function of the activities. We are not aware that explicit formulas for $N_i(z_1,z_2,\ldots)$ have been previously exhibited.

We use the term "polymer" to denote any molecule which occupies more than one site on the lattice, but do not claim to describe molecules with closed loops, since these cannot occur on the Bethe lattice. Our discussion assumes that we have a list of all the types of polymers in the reservoir, their activities, and their multiplicity factors γ. By adopting this assumption we avoid any discussion of the polymerization processes by which simple units coalesce to form more complicated objects [18,19].

In Sec. II of this paper we present our calculation of the polymer densities on the lattice when the polymer activities are specified. All densities are expressed in terms of the solution of a single equation, which is easily solved numerically for an arbitrary number of species. Section III discusses some applications of our results: (i) when all possible (on the Bethe lattice) polymers are present, and the activity of a polymer having n bonds is z^n; (ii) when only one species of polymer is present; and (iii) when the reservoir contains three types of polymers with specified activities, in which case we exhibit numerical results. Section IV discusses the adsorption of dimers on a Bethe lattice with two types (x and y) of adsorption sites, with different activities for a dimer adsorbed on two x sites, two y sites, or an x site and a y site. For the case of an annealed lattice an explicit solution is obtained in terms of the solution of the dimer problem on a lattice with only one type of adsorption site. In Sec. V we discuss the adsorption of arbitrary polymers on the annealed two-component Bethe lattice, with a particular assumption about the form of the dependence of the activity of an adsorbed polymer on the types of the underlying sites. Technical issues are treated in the Appendices. Appendix A shows

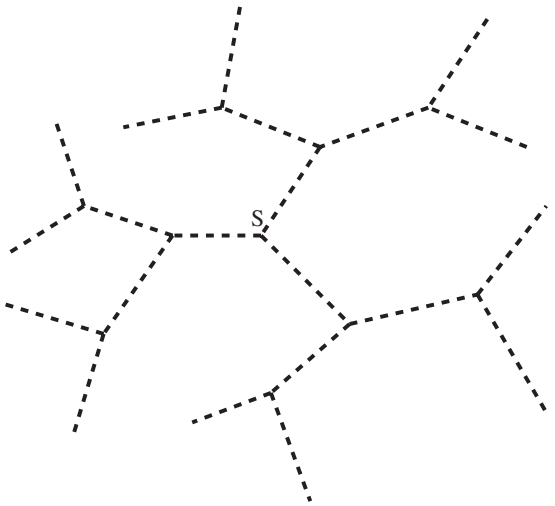

FIG. 1. Small section of a Bethe lattice with coordination number $q=3$. The seed site is labeled "S."

that there is no separation of phases on the one- or two-component lattice, provided that the number of polymer species in the reservoir is finite. Appendix B discusses flexible chain polymers on the one- and two-component Bethe lattices. In Appendix C we discuss the relation between our method and Guggenheim's combinatorial analysis.

II. METHOD OF CALCULATION

The Cayley tree is a structure constructed recursively as follows. From a central "seed" site one introduces connections (which we call [20] "edges") to a shell of q nearest neighboring sites. Then, recursively one adds $q-1$ edges to each site to obtain additional shells of sites. Thereby one obtains a structure in which all sites except boundary sites are connected to q nearest neighbors. Even in the limit of a large number of sites, the fraction of sites on the boundary of the Cayley tree remains of order unity. Consequently, the global properties of a Cayley tree are affected by the properties of boundary sites even in the limit of large system size. To overcome this undesirable property one usually considers the associated "Bethe lattice" in which only properties far from the boundary of the asymptotically large Cayley tree are considered. Figure 1 shows a section of a Bethe lattice with $q=3$.

The most important property of the Bethe lattice, which makes it tractable to analysis, is that it is a recursive structure which contains no closed loops of edges. If the lattice is in equilibrium with a reservoir containing dimers (a dimer is an object which covers the edge between two adjacent lattice sites), and if dimers on the lattice do not interact with each other, [1] it is possible to make an exact calculation of the relation between the dimer coverage and the dimer activity z (see Refs. [10–13] and references cited therein). As we have noted above, the Bethe lattice and the periodic lattices of the same coordination number exhibit almost the same numerical relation between the dimer coverage and the dimer activity z.

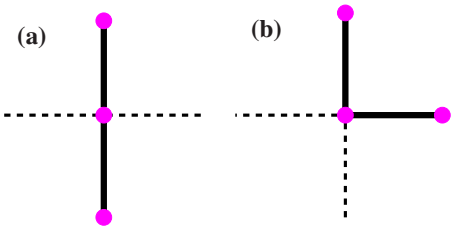

FIG. 2. (Color online) Panels (a) and (b) show two differently shaped polymers (represented by heavy solid lines) consisting of three monomers on a lattice of coordination number 4. If the energy is independent of the angle between adjacent bonds, then we treat the two polymers shown as different configurations of the *same* polymer. Otherwise, they are treated as different polymers.

The analysis of Gujrati and coworkers is based on writing recursion relations which allow one to work one's way in from the (remote) boundary of the lattice toward the central region. If the lattice consists of M generations (where $M \gg 1$ and the seed site is the zeroth generation), one can define partial partition functions on the sublattice $L_{(M-n)}$ between an edge in the $(M-n)$th generation and the boundary, subject to various information about what is occupying that edge. Recursion relations express the partial partition functions on the sublattice $L_{(M-n-1)}$ in terms of partial partition functions on $L_{(M-n)}$. Physical quantities (densities and probabilities) are ratios of partial partition functions and can be expected to approach definite limiting values when $n \gg 1$. By examining the fixed points of the recursion relations, Ryu and Gujrati calculate physical quantities, or equations relating physical quantities.

We entirely circumvent the above program, as well as Guggenheim's combinatorics, by invoking some simple considerations of statistical independence (induced by the very weak connectivity of the Bethe lattice, which becomes two disconnected lattices if any edge is removed) and homogeneity (equivalence of all sites in the central region).

Let us consider a lattice (not necessarily a Bethe lattice) in equilibrium with a reservoir containing various species of polymers. A polymer is a group of atoms ("monomers") connected by lines ("bonds"). When a polymer is adsorbed onto the lattice its bonds cover edges of the lattice and its atoms cover sites of the lattice. To model short-range repulsive atom-atom interactions of real polymers, we impose the rule that a site cannot be covered by more than one atom. We label the species of polymer by an index α and assume that polymers adsorbed on the lattice do not interact with each other [1]. The "activity" of the species α is $z_\alpha = e^{\beta\mu_\alpha} Z_\alpha$, where μ_α is the chemical potential of species α and Z_α is the partition function of the adsorbed polymer (including any internal degrees of freedom and interaction energy with the lattice). For simplicity (especially when counting the number of configurations of a given species of polymer), it is frequently convenient to assume that the activity of the polymer depends only on the topology of the polymer, and not on the angles between intrapolymer bonds [21]. Figure 2 shows some simple polymers on a lattice of coordination number 4.

The (unnormalized) probability of finding a particular configuration $\mathcal{C}$ of polymers on the lattice is

$$\prod_{\alpha} z_{\alpha}^{N_{\alpha}(\mathcal{C})}, \tag{1}$$

where $N_\alpha(\mathcal{C})$ is the number of α-polymers in the configuration $\mathcal{C}$. Usually one starts the discussion of the statistics of adsorption by considering the grand partition function, Q, defined as

$$Q(z_1,z_2,z_3\ldots) = \sum_{N_1=0}^{\infty}\sum_{N_2=0}^{\infty}\sum_{N_3=0}^{\infty}\ldots W(N_1,N_2,N_3,\ldots)z_1^{N_1}z_2^{N_2}z_3^{N_3}\ldots, \tag{2}$$

where $W(N_1,N_2,N_3,\ldots)$ is the number of configurations having N_1 polymers of type 1, N_2 polymers of type 2, etc. Then the average number (indicated by an overline) of adsorbed α-polymers (polymers of type α) is given by

$$\bar{N}_\alpha = z_\alpha \partial \ln Q/\partial z_\alpha. \tag{3}$$

A principal result of the present paper is that we can obtain the statistics of polymer adsorption on a Bethe lattice without having to perform a direct calculation of the grand partition function.

In Ref. [10] we discussed several statistical problems arising from consideration of dimers adsorbed on a Bethe lattice, and have also discussed a systematic procedure for calculating "loop corrections" to the dimer adsorption isotherm when the Bethe lattice is replaced by a periodic lattice (e.g. a square or triangular lattice) with the same coordination number. (Reference [10] also includes references to much of the previous work relating to dimers.) Section IIA of Ref. [10] presents what we believe to be the simplest derivation of the dimer adsorption isotherm (density of adsorbed dimers vs. z) on the Bethe lattice. It is to be noted that this derivation does not require calculation of the grand partition function. Moreover, as the present paper shows, the method is quite easily generalized to construct an exact solution (again, without calculating the grand partition function) when the Bethe lattice is in contact with a reservoir containing many species of polymers with arbitrary activities.

We consider a large finite lattice (not necessarily a Bethe lattice) which can adsorb various species of polymers (which do not interact with each other on the lattice) [1]. The probability $P(N_1,N_2,\ldots N_\alpha\ldots)$ of finding N_1 polymers of type 1, N_2 polymers of type 2, etc., on the lattice is proportional to the summand in Eq. (2), so that

$$P(N_1,N_2,\ldots N_\alpha\ldots) = Q(z_1,z_2,z_3\ldots)^{-1}W(N_1,N_2,N_3,\ldots)z_1^{N_1}z_2^{N_2}z_3^{N_3}\ldots. \tag{4}$$

If the lattice is large, the summand in Eq. (2) is a sharply peaked function of each N_α. If we vary N_α, holding the other N_i's constant, then the most probable value of N_α is proportional to the number of lattice sites N, and the half-width of the function $P(\ldots,N_\alpha,\ldots)$ is proportional to $\sqrt{N}$. Accordingly we need not distinguish between the most probable value of N_α and the average value $\bar{N}_\alpha$. Since P is stationary when we vary any N_α around its most probable value, we have

$$W(\overline{N_1},\overline{N_2}\ldots\overline{N_\alpha})z_1^{\bar{N}_1}z_2^{\bar{N}_2}\ldots z_\alpha^{\bar{N}_\alpha} = W(\bar{N}_1,\bar{N}_2\ldots\bar{N}_\alpha+1,\ldots)z_1^{\bar{N}_1}z_2^{\bar{N}_2}\ldots z_\alpha^{\bar{N}_\alpha+1}\ldots \tag{5}$$

and thus, for every α

$$\frac{W(\bar{N}_1,\bar{N}_2\ldots\bar{N}_\alpha+1,\ldots)}{W(\bar{N}_1,\bar{N}_2\ldots\bar{N}_\alpha,\ldots)} = \frac{1}{z_\alpha}. \tag{6}$$

Consider the set of configurations $\mathcal{C}(N_1,N_2,\ldots)$ which have N_1 polymers of type 1, N_2 of type 2, etc. We define an α-VACANCY to be a set of n_α empty sites on the lattice, where n_α is the number of monomers in the α-polymer (the polymer of type α) which are arranged in such a way that the set can accommodate an adsorbed α-polymer. We now consider the entire set of configurations $\mathcal{C}'$ which are obtained from the set of configurations $\mathcal{C}$ by placing an α-polymer on one of the $V_\alpha(\mathcal{C})$ α-vacancies in $\mathcal{C}$. By this construction we generate the complete set of configurations $\mathcal{C}'(N_1,N_2,..,N_\alpha+1,..)$. However, each configuration $\mathcal{C}'$ is generated $N_\alpha+1$ times, since any of the $N_\alpha+1$ type α polymers in $\mathcal{C}'$ could have been the one newly added. Thus we have

$$W(N_1,N_2\ldots N_\alpha+1,\ldots) = W(N_1,N_2\ldots N_\alpha,\ldots)\frac{V_\alpha(N_1,N_2\ldots N_\alpha,\ldots)}{N_\alpha+1}. \tag{7}$$

Strictly speaking, V_α does not have the same value for all configurations $\mathcal{C}(N_1,N_2,..,N_\alpha,..)$. But when $N_1,N_2,..,N_\alpha,..$ are large, the width of the distribution of V_α (consistent with this set of N's) is negligible compared to the average value $\bar{V}_\alpha$ and we may replace the N_α's by their average values $\bar{N}_\alpha$ to obtain

$$W(\bar{N}_1,\bar{N}_2\ldots\bar{N}_\alpha+1,\ldots) = W(\bar{N}_1,\bar{N}_2\ldots\bar{N}_\alpha,\ldots)\frac{\bar{V}_\alpha(\bar{N}_1,\bar{N}_2\ldots\bar{N}_\alpha,\ldots)}{\bar{N}_\alpha}. \tag{8}$$

Here we also replaced $N_\alpha+1$ by $\bar{N}_\alpha$ in the denominator of Eq. (8).

Combining Eqs. (6) and (8) we obtain, in equilibrium,

$$\bar{V}_\alpha/\bar{N}_\alpha = 1/z_\alpha \tag{9}$$

for every polymer species α. We note that Eqs. (6), (8), and (9) are valid for any large lattice. However, because of the simple recursive structure of the Bethe lattice we can calculate $\bar{V}_\alpha$ explicitly as a function of $\bar{N}_1,\bar{N}_2,\ldots\bar{N}_\alpha\ldots$, so that Eq. (9) becomes a set of simultaneous equations in $\bar{N}_1,\bar{N}_2,..,\bar{N}_\alpha,\ldots$. Fortunately, this system of equations is easily soluble.

In Eq. (9) $\bar{V}_\alpha$ and $\bar{N}_\alpha$ are, respectively, the average values of the total number of α-vacancies and α-polymers on the lattice. In the treelike structure whose central portion is the Bethe lattice, a finite fraction of the sites are at the boundary. Therefore one might worry about the correctness of replacing Eq. (9) by the local equation

$$\frac{\rho_{V_\alpha}}{\rho_\alpha} = \frac{1}{z_\alpha}, \tag{10}$$

where ρ_{V_α} is the density of α-vacancies (the number of α-vacancies per site) and ρ_α is the density of α-polymers in the central portion of the tree [22]. In equilibrium, the important set of configurations are the most probable ones. Let us consider two subregions of the lattice, $\mathcal{R}_1$ and $\mathcal{R}_2$, and suppose that

$$\frac{\rho_{V_\alpha}(\mathcal{R}_2)}{\rho_\alpha(\mathcal{R}_2)} > \frac{\rho_{V_\alpha}(\mathcal{R}_1)}{\rho_\alpha(\mathcal{R}_1)}. \tag{11}$$

Then the reasoning leading to Eq. (8) implies that we will obtain a more probable set of configurations by transferring an α-polymer from $\mathcal{R}_1$ to $\mathcal{R}_2$ [23]. Consequently we can infer that $\rho_{V_\alpha}/\rho_\alpha$ has the same value in all regions, and thus the global formula (9) implies the local formula (10).

Another, perhaps simpler, way to derive the local equation (10) is to focus our attention on a particular lattice site S. If $\mathcal{C}_1$ is a configuration in which S is occupied by a monomer of an α-polymer, removal of the α-polymer from $\mathcal{C}_1$ will create a configuration $\mathcal{C}_2$ in which S is part of an α-vacancy. If, in the configuration $\mathcal{C}_2$, the site S is part of n distinct α-vacancies, then there are n distinct configurations $\mathcal{C}_1$, in each of which S is occupied by a monomer of an α-polymer, which generate $\mathcal{C}_2$ when that α-polymer is removed. Since each of these configurations contains one more α-polymer than $\mathcal{C}_2$, it follows from Eq. (1) that $\rho_{V_\alpha}(S)/\rho_\alpha(S)=1/z_\alpha$ for every site S. Thus the local equation (10) is proved.

If the average number of α-polymers per site is ρ_α, then the probability f_α that a site is occupied by one of the monomers in an α-polymer is $f_\alpha=n_\alpha\rho_\alpha$, where n_α is the number of monomers in an α-polymer. Far from the boundary of the lattice, all sites are equivalent and thus f_α and ρ_α are not site dependent. The probability that a site is occupied is $f=\Sigma_\alpha f_\alpha$, and the probability that a site is vacant is $1-f$.

An *occupied* edge is defined as an edge which is covered by a bond of a polymer. A *vacant* edge is defined as an edge which has empty sites on both ends. A vacant edge is necessarily unoccupied, but an unoccupied edge is not necessarily vacant, since a monomer may sit on one or both of the sites at the ends of the edge. If boundary effects can be neglected, then the probability g_α that an edge is occupied by a bond of an α-polymer is

$$g_\alpha = (N_\alpha b_\alpha)/(Nq/2) = (2/q)\rho_\alpha b_\alpha, \tag{12}$$

where b_α is the number of bonds in an α-polymer. Since boundary effects on the Cayley tree are potentially relevant, we give a more careful derivation of the last equality of Eq. (12). We look at a particular site S far from the boundary and note that in equilibrium all nearby sites are equivalent. The average number of α-polymers touching S is f_α and the total number of bonds in those polymers is $f_\alpha b_\alpha$. Each bond touches two sites and each polymer touches n_α sites. Therefore the average number of α-bonds touching S is $2f_\alpha b_\alpha/n_\alpha=2\rho_\alpha b_\alpha$. The number of edges touching S is q, and thus the number of α-bonds per edge (which is equal to the probability that an α-bond lies on the edge, since an edge can accommodate at most one bond) is $2\rho_\alpha b_\alpha/q$. Thus Eq. (12) is proved.

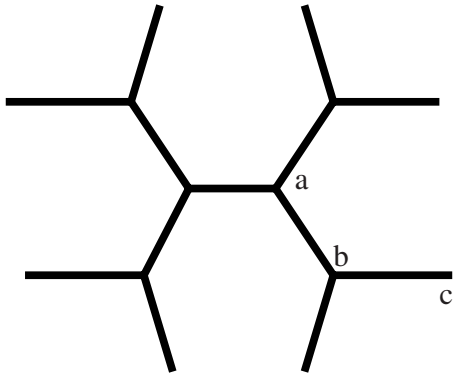

FIG. 3. Symmetry numbers for sites of a polymer. The symmetry numbers of sites a, b, and c are 2, 4, and 8, respectively, and the associated values of W are Q, $2Q$, and $4Q$, respectively, where $Q=q(q-1)^6(q-2)^6/2^6$. Thus γ for this polymer is $Q/2$.

The preceding is valid for any lattice. We now specialize to the Bethe lattice. Fortunately, for this case we can give an explicit formula for ρ_{V_α} in terms of $\rho_1,\rho_2,\ldots\rho_\alpha,\ldots$. Then Eq. (10) becomes a closed set of equations which determines $\rho_1,\rho_2,\ldots\rho_\alpha,\ldots$ as functions of $z_1,z_2,\ldots$. The development will involve "multiplicity factors" γ_α, which we now define. In words, γ_α is the number of α-vacancies per lattice site on the empty lattice. To calculate γ_α we proceed as follows. Each atom i in the α-polymer is characterized by a symmetry number $\xi_\alpha(i)$, which is the number of sites into which site i can be mapped via symmetry operations which leave the topology of the polymer invariant. Some examples of symmetry numbers are shown in Fig. 3. Now fix atom i of the polymer to cover the seed site and count the number of ways, $W_\alpha(i)$, that an α-polymer can be placed on the empty Bethe lattice with the seed site so fixed. Then $\gamma_\alpha=W_\alpha(i)/\xi_\alpha(i)$. (The quantity γ_α does not depend on i.) This algorithm is illustrated in Fig. 3 [24].

Now we can state the theorem which is the crux of our calculations.

Theorem. On a Bethe lattice

$$\rho_{V_\alpha} = \gamma_\alpha(1-f)^{n_\alpha}/(1-g)^{n_\alpha-1}, \tag{13}$$

where

$$f \equiv \sum_\alpha f_\alpha = \sum_\alpha n_\alpha\rho_\alpha, \tag{14}$$

and

$$g \equiv \sum_\alpha g_\alpha = (2/q)\sum_\alpha \rho_\alpha b_\alpha = (2/q)\sum_\alpha (n_\alpha-1)\rho_\alpha. \tag{15}$$

In writing Eq. (15) we have used Eq. (12), replacing b_α by $n_\alpha-1$.

For the case when the only polymers are dimers ($n_\alpha=2$) we have proved this theorem in Ref. [10] (Sec. IIA) and thus derived the explicit formula for the dimer density as a function of z. Now we give a general proof of the above theorem. First we write

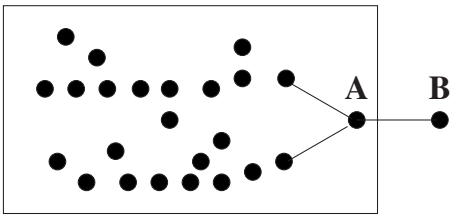

FIG. 4. The set Ω containing $n+1$ sites decomposed into a set Ω' (inside the rectangle) containing n sites, plus a site B (which is not in Ω') connected to only a single site (A) of Ω'.

$$\rho_{V_\alpha} = \gamma_\alpha P_\alpha, \tag{16}$$

where P_α is the probability that all n_α sites of the vacancy structure are actually vacant. The theorem will be proved if we can establish that for any connected set of n sites on the Bethe lattice, the probability that all the sites are vacant is

$$P_n = (1-f)^n/(1-g)^{n-1}. \tag{17}$$

We establish this relation by induction on n, the number of sites in the structure. Equation (17) is clearly true for $n=1$, since $1-f$ is the probability that a site is vacant. If Ω is a connected set of $n+1$ sites on a Bethe lattice, there are at least two sites which are at the end of a tail (i.e., the site is connected to the rest of the set by only one edge). Let B be such a site and let A be the site to which B is connected. In Fig. 4 the set Ω' (which includes site A) is the set of all sites in Ω, excluding B. With the notation that $P(\,)$ is the probability of the event in parentheses we can write

$$\begin{aligned} &P(\text{all sites in } \Omega \text{ are vacant}) \\ &\quad = P(\text{all sites in } \Omega' \text{ are vacant}) \\ &\qquad \times P(B \text{ is vacant} | \text{all sites in } \Omega' \text{ are vacant}), \end{aligned} \tag{18}$$

where we define $P(E_2|E_1)$ to be the conditional probability that E_2 occur given that E_1 is known to occur. In other words

$$P(E_2|E_1) \equiv P(E_2 \text{ and } E_1)/P(E_1). \tag{19}$$

The value of the first factor on the right side of Eq. (18) is given by the induction hypothesis, since Ω' contains n sites. On a Bethe lattice the only path from Ω' to B is through the edge AB. The edge AB divides the set of all the sites of the lattice into two disjoint sets S_1 (which contains A) and S_2 (which contains B). Define Ω_1 as S_1 plus all edges connecting sites in S_1 plus edge AB. Define Ω_2 as the set of all sites in S_2 and edges connecting sites in S_2. The only information about Ω_1 which is relevant to determining the set of possible configurations of Ω_2 is whether or not edge AB is *unoccupied*. In particular, the additional information that A is *vacant* (i.e., not only is edge AB unoccupied, but all the other edges touching A are unoccupied) does not affect the conditional probability that B is vacant. Consequently

$$\begin{aligned} &P(B \text{ is vacant} | \text{all sites in } \Omega' \text{ are vacant}) \\ &\quad = P(B \text{ is vacant} | \text{edge } AB \text{ is unoccupied}) \\ &\quad = P(B \text{ is vacant and edge } AB \text{ is unoccupied}) \\ &\qquad / P(\text{edge } AB \text{ is unoccupied}). \end{aligned} \tag{20}$$

But if B is vacant the edge AB *must* be unoccupied, and thus the numerator of the last member of Eq. (20) is just the probability that B is vacant. Therefore the second factor in Eq. (18) is $(1-f)/(1-g)$ (recall that g_α is the probability that AB is occupied by a bond of an α-polymer, and $g=\Sigma_\alpha g_\alpha$ is the probability that edge AB is occupied). Since the first factor in Eq. (18) is, by the induction hypothesis, $(1-f)^n/(1-g)^{n-1}$, it follows that

$$P(\text{all sites in } \Omega \text{ are vacant}) = (1-f)^{n+1}/(1-g)^n, \tag{21}$$

which proves that the probability that any connected set of n sites are all vacant is $(1-f)^n/(1-g)^{n-1}$. Thus Eq. (17) is proved and consequently we have established Eq. (13).

Equation (13) enables us to make a simple calculation of $\ln W(\rho_1,\rho_2,\ldots)$ and therefrom the entropy $S=k \ln W$. Equations (13) and (7) imply

$$(1/N)\partial \ln W(\rho_1,\rho_2,\ldots)/\partial\rho_\alpha = \ln[\gamma_\alpha(1-f)^{n_\alpha}/\rho_\alpha(1-g)^{(n_\alpha-1)}]. \tag{22}$$

If we introduce a parameter λ, which will vary from 0 to 1, then

$$\begin{aligned} &\ln W[(\lambda+d\lambda)\rho_1,(\lambda+d\lambda)\rho_2,\ldots] - \ln W(\lambda\rho_1,\lambda\rho_2,\ldots) \\ &\quad = d\lambda \sum_\alpha \rho_\alpha \partial \ln W/\partial\rho_\alpha, \end{aligned} \tag{23}$$

where the partial derivatives are evaluated at $(\lambda\rho_1,\lambda\rho_2,\ldots)$. Using Eqs. (14) and (15) and noting that $W(0,0,\ldots)=1$ we obtain after elementary integrations

$$\begin{aligned} (1/N)\ln W(\rho_1,\rho_2,\ldots) = &\sum_\alpha \rho_\alpha \ln(\gamma_\alpha/\rho_\alpha) - (1-f)\ln(1-f) \\ &+ (q/2)(1-g)\ln(1-g). \end{aligned} \tag{24}$$

This result was also obtained by Ryu and Gujrati and agrees with Guggenheim's expression for $\ln W$ [see Appendix C, Eq. (C1), and use Stirling's formula].

Since, by Eq. (10),

$$\rho_\alpha = z_\alpha \rho_{V_\alpha} = z_\alpha \gamma_\alpha \frac{(1-f)^{n_\alpha}}{(1-g)^{n_\alpha-1}} \tag{25}$$

and $f_\alpha = n_\alpha \rho_\alpha$, Eqs. (13)–(15) imply that

$$f = \sum_\alpha n_\alpha z_\alpha \gamma_\alpha (1-f)^{n_\alpha}/(1-g)^{n_\alpha-1} \tag{26}$$

and

$$g = (2/q)\sum_\alpha (n_\alpha - 1) z_\alpha \gamma_\alpha (1-f)^{n_\alpha}/(1-g)^{n_\alpha-1}. \tag{27}$$

If we define $u=1-f$ and $w=1-g$, then Eq. (26) becomes

$$1-u=w\sum_{\alpha} n_{\alpha}z_{\alpha}\gamma_{\alpha}(u/w)^{n_{\alpha}}, \tag{28}$$

and Eq. (27) becomes

$$1-w=(2/q)w\sum_{\alpha}(n_{\alpha}-1)z_{\alpha}\gamma_{\alpha}(u/w)^{n_{\alpha}}. \tag{29}$$

If u/w has been determined, this equation can be used to get w by

$$1/w=1+(2/q)\sum_{\alpha}(n_{\alpha}-1)z_{\alpha}\gamma_{\alpha}(u/w)^{n_{\alpha}}. \tag{30}$$

To determine u/w we combine Eqs. (28) and (29) to obtain

$$1=\frac{u}{w}+\left(1-\frac{2}{q}\right)\sum_{\alpha} n_{\alpha}z_{\alpha}\gamma_{\alpha}\left(\frac{u}{w}\right)^{n_{\alpha}}+\frac{2}{q}\sum_{\alpha} z_{\alpha}\gamma_{\alpha}\left(\frac{u}{w}\right)^{n_{\alpha}}. \tag{31}$$

Equation (31) can be solved numerically (or, in simple cases, algebraically) for u/w. Then Eq. (30) can be used to obtain w (and thence f and g). Equations (13) and (10) then yield $\rho_{V_{\alpha}}$ and ρ_{α}.

If the densities ρ_{α} are known, one can calculate pair correlations. Let $p_{\alpha\alpha'}$ be the probability that one end of an edge AB is occupied by a monomer of an α-polymer and the other end is occupied by a monomer of an α'-polymer (if $\alpha=\alpha'$, we define $p_{\alpha\alpha}$ as the probability that the two ends are occupied by monomers of different α-polymers). We write

$$\begin{aligned}P(A\text{ is }\alpha\text{ and }B\text{ is }\alpha')&=P(A\text{ is }\alpha\text{ and }AB\text{ is unoccupied})\\&\quad\times P(B\text{ is }\alpha'|AB\text{ is unoccupied and }A\text{ is }\alpha).\end{aligned} \tag{32}$$

On a Bethe lattice, the information that A is α does not affect the conditional probability [the second factor in Eq. (32)] and can be omitted. Since

$$P(A\text{ is }\alpha\text{ and }AB\text{ is unoccupied})+P(A\text{ is }\alpha\text{ and }AB\text{ is occupied})=P(A\text{ is }\alpha)=n_{\alpha}\rho_{\alpha} \tag{33}$$

and the second term on the left side of Eq. (33) is just the fraction of all edges which are occupied by bonds of α-polymers, i.e. $\rho_{\alpha}(n_{\alpha}-1)/(q/2)$, we find that

$$P(A\text{ is }\alpha\text{ and }AB\text{ is unoccupied})=\rho_{\alpha}[n_{\alpha}-(2/q)(n_{\alpha}-1)]. \tag{34}$$

Similarly, the second factor in Eq. (32) is $\rho_{\alpha'}[n_{\alpha'}-(2/q)(n_{\alpha'}-1)]/(1-g)$ and we obtain

$$\begin{aligned}p_{\alpha\alpha'}&=(2-\delta_{\alpha\alpha'})\rho_{\alpha}[n_{\alpha}-(2/q)(n_{\alpha}-1)]\\&\quad\times\rho_{\alpha'}[n_{\alpha'}-(2/q)(n_{\alpha'}-1)]/(1-g),\end{aligned} \tag{35}$$

where $\delta_{\alpha,\alpha'}$ is the Kronecker delta and the prefactor comes from the fact that the α' could have been on A and the α on B. If we let $\alpha=0$ denote vacancies (with $n_0=1$ and $\rho_0=f_0=1-f$), Eq. (35) is valid for $\alpha,\alpha'\geqslant 0$.

III. SPECIAL CASES

A. Reservoir contains all possible polymers, with $z_{\alpha}=z^{n_{\alpha}-1}$

In this section we show that the above formalism gives the exact result for the case when the reservoir contains every type of polymer which can fit onto a Bethe lattice and the activity of a polymer which has n_{α} monomers is

$$z_{\alpha}=z^{n_{\alpha}-1}. \tag{36}$$

For this case one can associate an activity z independently to each bond, in which case the probability that a given edge is occupied is $z/(1+z)$. Since each connected set of bonds on the lattice is a polymer, our analysis is applicable and should yield the results

$$1-g=\frac{1}{1+z} \tag{37}$$

and

$$1-f=\left(\frac{1}{1+z}\right)^{q}. \tag{38}$$

We now show that the above formalism reproduces these results. Note that for any F we may write

$$\sum_{\alpha}\gamma_{\alpha}F(n_{\alpha})=\sum_{n=2}^{\infty}F(n)W(n), \tag{39}$$

where $W(n)$ is the number (per site) of connected clusters of n sites that can be formed on a Bethe lattice. Thus we may write Eq. (31) as

$$\tau=1-\frac{\sigma-1}{\sigma+1}\tau\Phi'(z\tau)-\frac{2}{(\sigma+1)z}\Phi(z\tau), \tag{40}$$

where $\sigma=q-1$, $\tau\equiv u/w$, and

$$\Phi(x)=\sum_{n=2}^{\infty}W(n)x^{n}. \tag{41}$$

In Ref. [10] we used the exact expression for $W(n)$ given by Fisher and Essam [25] to evaluate $\Phi(x)$ as

$$\Phi(x)=-x+y_0-\frac{\sigma-1}{2}y_0^2, \tag{42}$$

where $y_0\equiv y_0(x)$ is the implicit solution of

$$y_0=x(1+y_0)^{\sigma} \tag{43}$$

which, for small x, is asymptotically equal to x. From these two equations one can also obtain the result that

$$\Phi'(x)=-1+(y_0/x)(1+y_0). \tag{44}$$

Then Eq. (40) yields

$$\tau=1-\frac{(\sigma-1)\tau}{\sigma+1}[-1+y_0(1+y_0)/(z\tau)]-\frac{2}{(\sigma+1)z}\left[y_0-\frac{\sigma-1}{2}y_0^2-z\tau\right], \tag{45}$$

where $y_0=y_0(z\tau)=z\tau[1+y_0(z\tau)]^{\sigma}$. Equation (45) yields

$$z = y_0(z\tau), \tag{46}$$

i.e. $z=z\tau(1+z)^{\sigma}$ and thus

$$\tau = (1+z)^{-\sigma}. \tag{47}$$

Then Eq. (29) is

$$\frac{1}{w} = 1 + \frac{2}{\sigma+1}\left[\tau\Phi'(z\tau) - \frac{1}{z}\Phi(z\tau)\right]. \tag{48}$$

Using Eqs. (42) and (44), we then find that

$$w = (1+z)^{-1} \tag{49}$$

and

$$u = w\tau = (1+z)^{-(\sigma+1)}, \tag{50}$$

in agreement with Eqs. (37) and (38), in accord with our expectations. We also find that the number of polymers per site with n bonds is $W(n+1)z^n/(1+z)^{(n+1)\sigma+1}$.

B. Reservoir contains only one type of polymer

If the reservoir contains only one type of polymer, which has n monomers, multiplicity γ, and activity z, then the previous mathematics can be somewhat simplified. Equations (10) and (13)–(15) yield

$$\rho = z\gamma\frac{[1-n\rho]^n}{[1-(2/q)(n-1)\rho]^{n-1}} \tag{51}$$

which determines ρ.

More generally, one can easily show that if the activity of one species (a polymer containing n monomers) approaches infinity, then the density ρ of that species approaches $1/n$ (i.e. every lattice site is occupied by a monomer belonging to a polymer of that species) and the fraction of edges which are covered is $g=(2/q)[1-(1/n)]$. If f is the fraction of sites occupied by the dominant species, and γ and z are respectively the multiplicity and activity of that species, then

$$1 - f \approx a(n,q)/(\gamma z)^{1/n}, \tag{52}$$

where

$$a(n,q) = \left[\frac{1}{n}\left(1 - \frac{2}{q} + \frac{2}{nq}\right)^{n-1}\right]^{1/n}. \tag{53}$$

If the reservoir contains several species of polymer (enumerated by the index α) all having the same number n of monomers, but with multiplicities γ_α and activities z_α, then Eqs. (10) and (13)–(15) imply

$$\rho_\alpha = z_\alpha\gamma_\alpha F(\rho), \tag{54}$$

$$F(\rho) = [1-n\rho]^n/[1-(2/q)(n-1)\rho]^{n-1}. \tag{55}$$

Since $\rho=\Sigma_\alpha\rho_\alpha$, we find that $\rho=(\Sigma_\alpha z_\alpha\gamma_\alpha)F(\rho)$ which determines ρ, and also find $\rho_\alpha/\rho=z_\alpha\gamma_\alpha/\Sigma_\alpha z_\alpha\gamma_\alpha$.

If the reservoir contains only dimers ($n=2$, $\gamma=q/2$, activity$=z$), Eq. (51) is quadratic in ρ and yields

$$\rho = \frac{q}{4}\left[\frac{2qz+1-\sqrt{1+4(q-1)z}}{1+q^2z}\right] \equiv B(z), \tag{56}$$

which was derived in Ref. [10], Sec. IIA.

C. Numerical examples

For specified values of the γ_α and z_α, a simple computer program yields the values of the f_α. We prefer to exhibit the f_α, which are all in the range [0,1], rather than $\rho_\alpha=f_\alpha/n_\alpha$. The presence of a large number of species presents no computational difficulties, but it is difficult to exhibit the results in a form which is enlightening to the reader.

We exhibit some results for the case where the reservoir contains three species: trimers ($n=3$), tetramers ($n=4$), and pentamers ($n=5$). In Fig. 5(a) we exhibit f_3, f_4, and f_5 as functions of $\gamma_5 z_5$, with $\gamma_3 z_3$, and $\gamma_4 z_4$ held constant. In Fig. 5(b) we vary $\gamma_4 z_4$, with $\gamma_3 z_3$ and $\gamma_5 z_5$ held constant. In Fig. 5(c) we vary $\gamma_3 z_3$, with $\gamma_4 z_4$ and $\gamma_5 z_5$ held constant.

We note that, in Fig. 5(a), f_5 is an increasing function of z_5, and f_3 and f_4 are decreasing functions of z_5. Similar remarks apply to Figs. 5(b) and 5(c). The fact that [in Fig. 5(a)] f_5 is an increasing function of z_5 follows from the form of the grand partition function, which implies that $z_\alpha\partial\overline{N_\alpha}/\partial z_\alpha=\overline{N_\alpha^2}-\overline{N_\alpha}^2>0$. It seems reasonable that, in the absence of any interactions except the hard-core restriction that at most one monomer can occupy a site, f_3 and f_4 should decrease as z_5 increases. We investigated a large number of numerical examples involving three species of molecules (A, B, and C) with a variety of sizes and activities and in each case found that, if z_B and z_C are held constant, f_B and f_C decrease as z_A increases.

Nevertheless, one could imagine the following scenario: (i) A and B are small molecules and C is a large molecule; (ii) the activities z_B and z_C are such that, in the absence of A's, most of the lattice sites are occupied by C's; (iii) as z_A increases from zero, an increasing number of type C vacancies are partially occupied by A's, decreasing the number of C's and making room for B's. Thus, for fixed z_B and z_C there might be a range of values of z_A within which f_B is an increasing function of z_A.

A very simple example suffices to show that there is no general prohibition against this scenario. Consider a lattice consisting of $\mathcal{N}$ clusters of sites, each cluster consisting of five sites arranged linearly (Fig. 6). The lattice is in equilibrium with a reservoir containing dimers, linear trimers, and linear tetramers with activities z_2, z_3, and z_4. An adsorbed molecule must lie entirely on a single cluster, and at most one monomer can occupy a lattice site. The grand partition function of the lattice is $\zeta^{\mathcal{N}}$, where

$$\zeta = 1 + 4z_2 + 3z_2^2 + 2z_2z_3 + 3z_3 + 2z_4. \tag{57}$$

The average numbers of tetramers and trimers on the lattice are $\overline{N_4}/\mathcal{N}=2z_4/\zeta$ and $\overline{N_3}/\mathcal{N}=z_3(2z_2+3)/\zeta$. We assume that $z_4 \gg z_3$ and $z_4 \gg 1$; thus, if $z_2=0$, almost all clusters are occupied by tetramers. If $z_2>0$, a dimer will displace a tetramer from some of the clusters and (depending on the location of the dimer) will create a vacancy which can be occupied by a trimer. Simple algebra yields $\partial\overline{N_3}/\partial z_2|_{z_2=0}>0$ if $z_4>2.5$, and $\partial\overline{N_3}/\partial z_2>0$ for $0\leq z_2\leq X$, where $X\approx(2z_4/3)^{1/2}$ when $z_4\gg 1$. When z_2 is sufficiently large (with z_3 and z_4 held constant), dimers dominate the lattice.

In Fig. 5, and in our other early calculations we assigned the value 6 to q, the number of nearest neighbors of a lattice

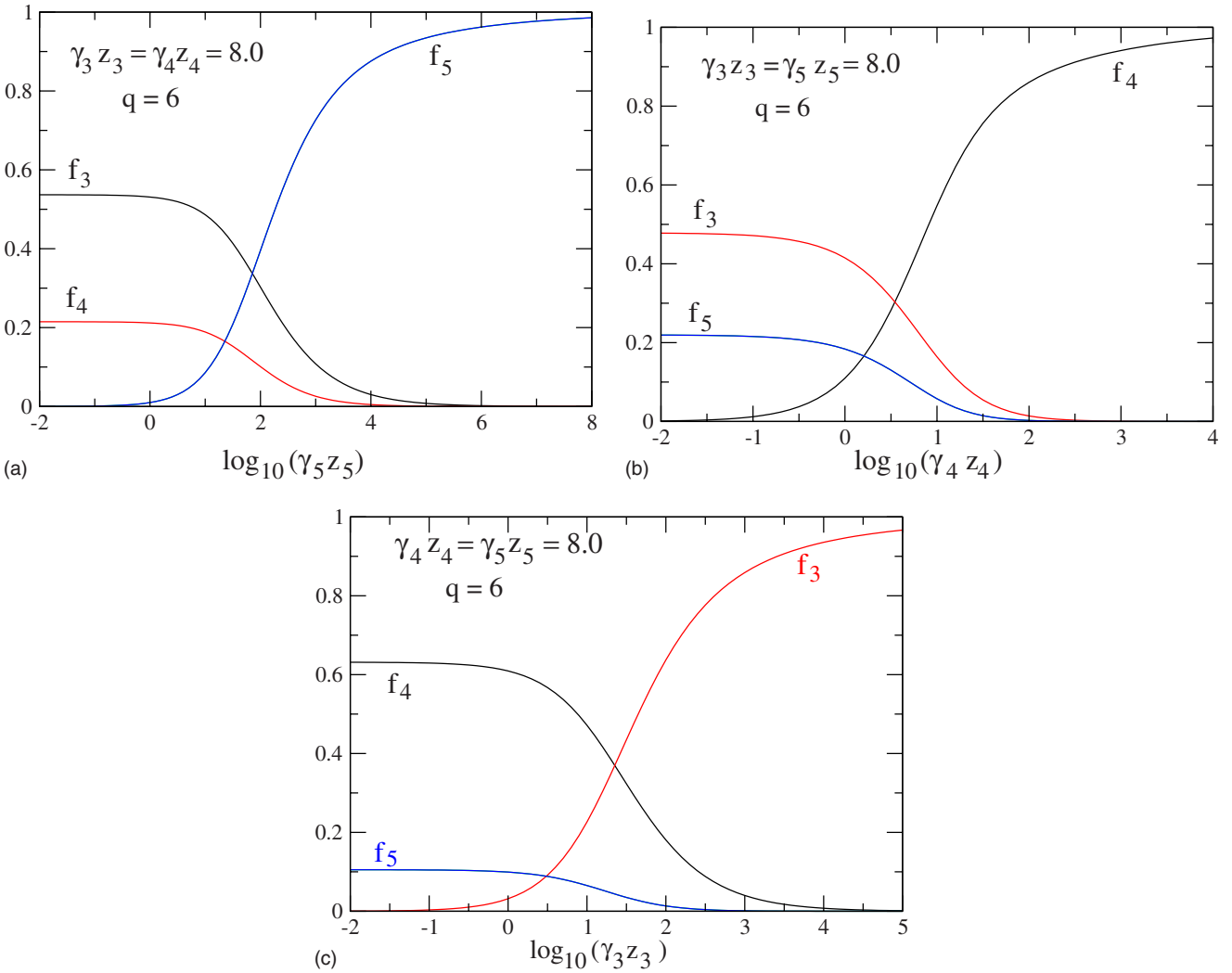

FIG. 5. (Color online) Fraction of sites occupied by trimers (f_3), tetramers (f_4), and pentamers (f_5) as (a) the pentamer activity, (b) the tetramer activity, and (c) the trimer activity is varied with the other activities held constant.

site, and found no cases in which $\partial f_B/\partial z_A > 0$. The previous example makes it clear that we should do some numerical calculations on the Bethe lattice with $q=2$ (linear chain), since a short molecule is most effective in blocking out a long molecule in one dimension. Figure 7 exhibits results for a linear chain in contact with a reservoir containing dimers, trimers, and 12-mers. There is clearly a region in which $\partial f_3/\partial z_2 > 0$. It is harder to find a clean example when $q=3$. Figure 8 exhibits results for a $q=3$ Bethe lattice in contact with a reservoir containing dimers, trimers, and 20-mers.

These examples show that, even in the absence of attractive interactions and in the presence of hard-core repulsions, an increase in the activity of one species of molecule may also increase the number of another species adsorbed on the lattice. These examples also illustrate the calculational usefulness and simplicity of our exact solution.

FIG. 6. A portion of a lattice consisting of linear clusters of five sites. An adsorbed molecule must lie entirely on a single cluster.

IV. DIMERS ON AN ANNEALED TWO-COMPONENT LATTICE

We now consider a lattice which has two types of sites, x sites and y sites. Dimers can be adsorbed on a pair of adjacent sites with activities z_{xx}, z_{yy}, or z_{xy} depending on the types of the two sites [26]. The numbers of sites of type x and y, N_x and N_y, respectively, are specified, but it is assumed that the time scale of adsorption measurements is long enough to permit the lattice to anneal (i.e., the sites can permute until the thermodynamically most favorable configuration is attained). In this case the grand partition function (GPF) of the two-component lattice is readily expressed in terms of the GPF of the one-component lattice, and the adsorption isotherms of the two systems are simply related.

It is mathematically convenient to draw the sites from a "site reservoir," with activities ξ_x and ξ_y whose values are so chosen that the average numbers of x and y sites assume the

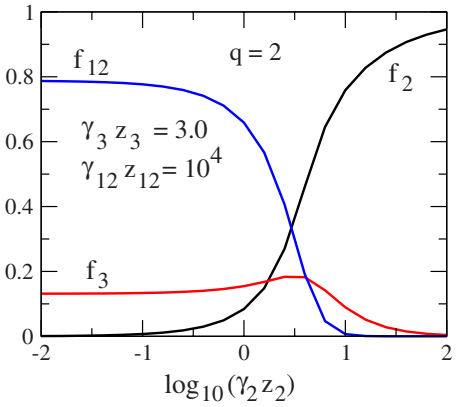

FIG. 7. (Color online) Fraction of sites occupied by dimers, trimers, and 12-mers as the dimer activity is varied with the other activities held constant. Note that near $\log_{10}(\gamma_2 z_2)=0.5$ there is a region in which an increase in the dimer activity increases the trimer coverage.

specified values N_x and N_y, respectively. Since, as usual, this ensemble yields negligible fractional fluctuations in the numbers of x and y sites when N (the number of lattice sites) is large, it is equivalent to an ensemble in which the numbers of x and y sites are exactly fixed. It may already be obvious that the only relevant parameter is ξ_x/ξ_y.

We assume that the geometry of the lattice is already specified. Let G' denote a "labeled graph" on the lattice, in which dimers cover some pairs of adjacent sites and every site is labeled as an x site or a y site. The grand partition function is

$$\tilde{Q} = \sum_{G'} z_{xx}^{N_D^{xx}(G')} z_{xy}^{N_D^{xy}(G')} z_{yy}^{N_D^{yy}(G')} \xi_x^{N_x(G')} \xi_y^{N-N_x(G')}, \tag{58}$$

where $N_D^{st}(G')$ is the number of dimers in G' which cover an s and a t site, where s and t assume the values x and y, and $N_x(G')$ is the number of x sites in G'. The probability of occurrence of the configuration G' is the summand of Eq. (58) divided by $\tilde{Q}$. Defining $\xi \equiv \xi_x/\xi_y$, we have that $\tilde{Q} = \xi_y^N Q(\xi, z_{xx}, z_{xy}, z_{yy})$, where

$$Q = \sum_{G'} z_{xx}^{N_D^{xx}(G')} z_{xy}^{N_D^{xy}(G')} z_{yy}^{N_D^{yy}(G')} \xi^{N_x(G')}. \tag{59}$$

The average number of x sites is

$$\bar{N}_x = \xi_x \partial \ln \tilde{Q}/\partial \xi_x = \xi \partial \ln Q/\partial \xi \tag{60}$$

and the average numbers of dimers covering specified types of sites are

$$\bar{N}_D^{xx} = z_{xx} \partial \ln Q/\partial z_{xx}, \tag{61}$$

$$\bar{N}_D^{xy} = z_{xy} \partial \ln Q/\partial z_{xy}, \tag{62}$$

$$\bar{N}_D^{yy} = z_{yy} \partial \ln Q/\partial z_{yy}. \tag{63}$$

The grand partition function of a one-component (only one type of adsorption site) lattice in contact with a reservoir of dimers, whose activity is z, is

$$Q_0(z) = \sum_G z^{N_D(G)}, \tag{64}$$

where G is an unlabeled graph with dimers on the lattice (the sum also includes a term 1 from the graph in which there are no dimers on the lattice). When we label the sites as x or y, each unlabeled graph G becomes the parent of 2^N labeled graphs G'.

Let us consider a particular graph G. The term in $Q_0(z)$ associated with G contains a factor z for each dimer and a factor 1 for each empty site. Suppose we now associate a factor $\xi^2 z_{xx} + \xi z_{xy} + \xi z_{yx} + z_{yy}$, (where $z_{xy} = z_{yx}$) with each dimer in G and a factor $\xi + 1$ with each empty site in G. Then the product

$$(\xi^2 z_{xx} + \xi z_{xy} + \xi z_{yx} + z_{yy})^{N_D(G)} (\xi + 1)^{N-2N_D(G)} \tag{65}$$

is equal to the sum of the contributions to Q [Eq. (59)] from all the graphs G' whose parent is G. If this is not obvious,

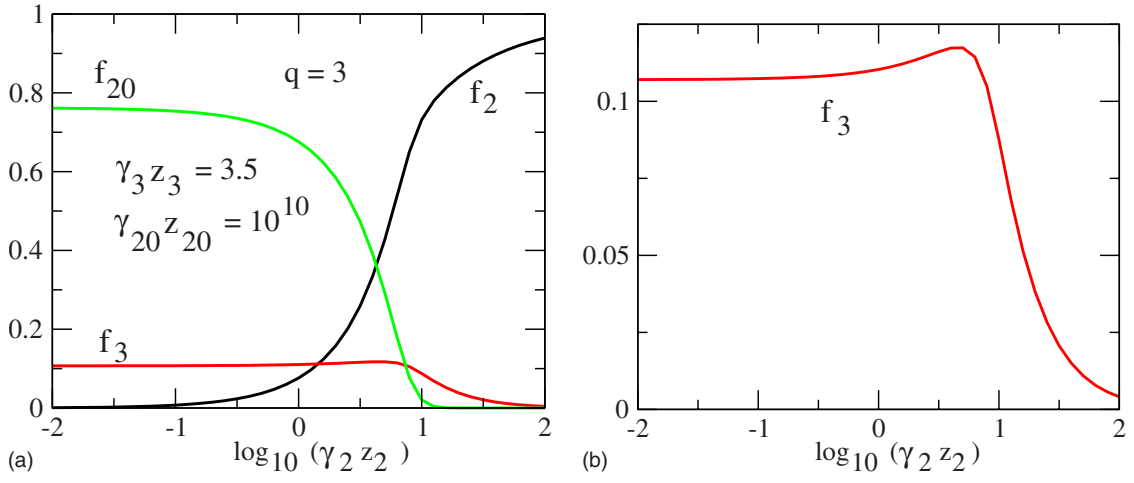

FIG. 8. (Color online) Left: Fraction of sites occupied by dimers, trimers, and 20-mers as the dimer activity is varied with the other activities held constant. Right: Detail of f_3, showing that there is a region in which an increase in the dimer activity increases the trimer coverage. Note that it is harder for dimers to block large polymers on a $q=3$ lattice than on a $q=2$ (linear) lattice.

define $A=(\xi^2 z_{xx}+\xi z_{xy}+\xi z_{yx}+z_{yy})$ and $B=(\xi+1)$ and write the expression (65) as $AA\ldots A\ BB\ldots B$, where each factor of A is associated with a particular dimer in G (the terms in A correspond to the dimer sitting on two x sites, an x site and a y site, or two y sites) and each factor in B is associated with a particular empty site (which may be type x or type y). Then, if we make a complete expansion of the product $AA\ldots A\ BB\ldots B$ there will be $4^{N_D(G)}2^{N-2N_D(G)}=2^N$ terms, each equal to the contribution to Eq. (59) from one of the graphs G' whose parent is G.

Thus we obtain

$$Q=(\xi+1)^N Q_0(s), \tag{66}$$

where

$$s=\frac{\xi^2 z_{xx}+2\xi z_{xy}+z_{yy}}{(\xi+1)^2}. \tag{67}$$

The preceding formulas are valid for dimers on any lattice and include edge effects.

The average number of dimers on the lattice is

$$\bar{N}_D=s[d\ln Q_0(s)/ds]. \tag{68}$$

If we define $F_x\equiv N_x/N$, then Eq. (60) becomes

$$F_x=\frac{\xi}{1+\xi}\left[1+\frac{2\bar{N}_D(s)}{N}\frac{\xi(z_{xx}-z_{xy})+z_{xy}-z_{yy}}{\xi^2 z_{xx}+2\xi z_{xy}+z_{yy}}\right]. \tag{69}$$

Thus, for the two-component Bethe lattice with a specified fraction of x sites, ξ is determined by the equation

$$F_x=\frac{\xi}{1+\xi}\left[1+2B(s)\frac{\xi(z_{xx}-z_{xy})+z_{xy}-z_{yy}}{\xi^2 z_{xx}+2\xi z_{xy}+z_{yy}}\right], \tag{70}$$

where $B(s)$ is given by Eq. (56). For given values of F_x, q, z_{xx}, z_{xy}, and z_{yy}, the computer easily solves Eq. (70) for ξ. Then, defining ρ^{xx} as the number of dimers per site which cover a pair of x sites, and with similar definitions of ρ^{xy} and ρ^{yy} we obtain from Eqs. (61)–(63)

$$\rho^{xx}=B(s)\xi^2 z_{xx}/(\xi^2 z_{xx}+2\xi z_{xy}+z_{yy}), \tag{71}$$

$$\rho^{xy}=B(s)2\xi z_{xy}/(\xi^2 z_{xx}+2\xi z_{xy}+z_{yy}), \tag{72}$$

$$\rho^{yy}=B(s)z_{yy}/(\xi^2 z_{xx}+2\xi z_{xy}+z_{yy}). \tag{73}$$

From Eq. (68) [and consistent with the sum of Eqs. (71)–(73)] we identify $B(s)$ with ρ, the number of dimers per site.

For arbitrary z_{xx}, z_{xy} and z_{yy}, if $F_x=1$, then Eqs. (69) and (67) yield $\xi=\infty$ and $s=z_{xx}$, and we recover the results of the one-component lattice.

If $z_{xx}=z_{xy}=z_{yy}$, Eq. (67) yields $s=z_{xx}$ and we obtain $\rho=B(z_{xx})$, as expected. In this case we also expect that the presence of dimers does not induce any correlations between x sites and y sites on the lattice; i.e., the probabilities that a pair of nearest neighbors are both x, both y, or an x and a y are F_x^2, $(1-F_x)^2$, and $2F_x(1-F_x)$, respectively. We note that in this case Eq. (70) yields $\xi/(1+\xi)=F_x$ and Eqs. (71)–(73) yield

$$\rho^{xx}=\rho F_x^2,\quad \rho^{xy}=2\rho F_x(1-F_x),\quad \rho^{yy}=\rho(1-F_x)^2, \tag{74}$$

which is consistent with the absence of correlations between sites on the lattice [27].

If $z_{xy}=z_{yy}=0$, then $s=z_{xx}[\xi/(1+\xi)]^2$ and Eq. (70) becomes

$$F_x=\frac{\xi}{1+\xi}\left[1+\frac{2}{\xi}B(z_{xx}\xi^2/(1+\xi)^2)\right]. \tag{75}$$

It is interesting to examine Eq. (75) when $z_{xx}\gg 1$ and $F_x<1$. First, we suppose that ξ remains finite as $z_{xx}\to\infty$. Under that assumption, if s, which is the argument of B, becomes very large, then $B(s)\to 1/2$ and Eq. (75) becomes $F_x=1$, which is not true. We therefore conclude that ξ must be proportional to $z_{xx}^{-1/2}$ and $s=z_{xx}\xi^2$. Thus, when $z_{xx}\gg 1$, we find that $F_x=2B(s)$. Since $\rho=B(s)$ we obtain $\rho=F_x/2$. This result is exactly what we would have expected. The x sites pair off with each other, and a dimer sits on each pair [28].

V. ARBITRARY POLYMERS ON AN ANNEALED TWO COMPONENT BETHE LATTICE

We now consider an annealed two-component lattice in contact with a reservoir which contains arbitrary polymers whose types are enumerated by an index α and whose shapes are consistent with the geometry of the lattice. The activity z_α of an adsorbed polymer of type α will, in general depend on the types of sites (x or y) which the polymer covers. With a reasonable assumption about the form of this dependence, we can express the grand partition function (GPF) of the two-component lattice in terms of the GPF of a one-component lattice in contact with a similar reservoir.

Let $z_{0\alpha}$ be the activity of an α polymer (containing n_α monomers) adsorbed on n_α sites, all of type x. We assume that the nature of the underlying sites does not affect the internal degrees of freedom of the polymer, but that there is an interaction energy (ϵ_x or ϵ_y) between each monomer and the underlying site. Then the activity of an α polymer adsorbed on m sites of type x and $(n_\alpha-m)$ sites of type y is $z_{0\alpha}\eta^{n_\alpha-m}$, where $\eta=\exp[-\beta(\epsilon_y-\epsilon_x)]$. We have assumed that all monomers of an α polymer are of the same type, and will further assume that the same type of monomer is present in all polymers (otherwise η depends on α and the subsequent analysis becomes excessively complicated).

As in Sec. IV, we associate a factor ξ with each x site, and the value of ξ will eventually be chosen so as to yield the desired number of x sites. A labeled graph G' is one in which all sites are labeled x or y and polymers of various types occupy some of the sites. Each unlabeled graph G on the one-component lattice is the parent of 2^N labeled graphs G'.

The term in the GPF contributed by a particular graph G' is a product of factors associated with each polymer in G' and factors associated with each empty site in G'. The factor associated with a polymer of type α sitting on m x sites and $(n_\alpha-m)$ y sites is $\xi^m z_{0\alpha}\eta^{n_\alpha-m}$. The factor associated with an empty site is ξ or 1, depending on whether the site is type x or y. Thus, the total contribution to the GPF from the 2^N labeled graphs G' which are the descendents of the unlabeled

graph G, which contains $N_1(G)$ polymers of type 1, $N_2(G)$ polymers of type 2, etc., is

$$[z_{01}(\xi+\eta)^{n_1}]^{N_1(G)}[z_{02}(\xi+\eta)^{n_2}]^{N_2(G)} \cdots [\xi+1]^{N-n_1N_1(G)-n_2N_2(G)-\cdots} \tag{76}$$

and the GPF of the two-component annealed lattice is

$$Q_2=(\xi+1)^N Q_1(\tilde{z}_1,\tilde{z}_2,\ldots), \tag{77}$$

where

$$\tilde{z}_\alpha = z_{0\alpha}\left(\frac{\xi+\eta}{\xi+1}\right)^{n_\alpha} \tag{78}$$

and Q_1 is the GPF of the one-component lattice, defined (without the subscript "1") by Eq. (2).

The average number of x sites is $\bar{N}_x=\xi\partial \ln Q/\partial\xi$, and thus we have

$$F_x=\frac{N_x}{N}=\frac{\xi}{1+\xi}+\frac{\xi}{N}\sum_\alpha \tilde{z}_\alpha\frac{\partial \ln Q_1}{\partial \tilde{z}_\alpha}\left(\frac{1}{\tilde{z}_\alpha}\frac{\partial \tilde{z}_\alpha}{\partial \xi}\right)$$

$$=\frac{\xi}{1+\xi}+\frac{\xi(1-\eta)}{(1+\xi)(\xi+\eta)}\sum_\alpha n_\alpha\rho_\alpha(\tilde{z}_1,\tilde{z}_2,\ldots), \tag{79}$$

where $\rho_\alpha(\tilde{z}_1,\tilde{z},\ldots)$ is the number of α polymers per site on the one-component lattice when the activities of the species are $\tilde{z}_1,\tilde{z}_2,\ldots$. The preceding discussion is valid for every lattice, but now we specialize to the Bethe lattice. We use the notation of Sec. II, with z_α replaced by $\tilde{z}_\alpha$. Thus, $f\equiv f(\tilde{z}_1,\tilde{z}_2,..)$ and $g\equiv g(\tilde{z}_1,\tilde{z}_2,..)$, $u\equiv 1-f$, and $w\equiv 1-g$. We define

$$y\equiv\frac{u}{w}\frac{\xi+\eta}{\xi+1}, \tag{80}$$

$$F(y)\equiv\sum_\alpha n_\alpha z_{0\alpha}\gamma_\alpha y^{n_\alpha}, \tag{81}$$

$$G(y)\equiv\sum_\alpha z_{0\alpha}\gamma_\alpha y^{n_\alpha}, \tag{82}$$

and

$$H(y)\equiv 1+\frac{2}{q}[F(y)-G(y)]. \tag{83}$$

Then Eq. (30) becomes

$$w=1/H(y) \tag{84}$$

and Eq. (31) becomes

$$\frac{\xi+1}{\xi+\eta}y+F(y)=H(y). \tag{85}$$

Instead of using ξ as a basic unknown, it is convenient to introduce $\lambda\equiv(\xi+1)/(\xi+\eta)$. Then $\xi/(\xi+1)=(\eta-1/\lambda)/(\eta-1)$ and $(1-\eta)/(\xi+\eta)=\lambda-1$. Then Eq. (85) becomes

$$\lambda=\frac{1}{y}[H(y)-F(y)] \tag{86}$$

and Eq. (79) becomes

$$F_x=\frac{\eta-1/\lambda}{\eta-1}\left[1+(\lambda-1)\frac{F}{H}\right]. \tag{87}$$

For a given value of F_x, a computer easily solves Eq. (87) for y, since the functions $\lambda(y)$, $F(y)$, and $H(y)$ are known. The average number (per site) of polymers of type α is

$$\rho_\alpha=\tilde{z}_\alpha\gamma_\alpha u^{n_\alpha}/w^{n_\alpha-1}=z_{0\alpha}\gamma_\alpha y^{n_\alpha}/H(y). \tag{88}$$

From the definition of λ we find that $\xi=(1-\eta\lambda)/(\lambda-1)$. The probability distribution for the number of x sites under a single α polymer is the binomial distribution

$$P(\text{the number of } x \text{ sites}=m)=\binom{n_\alpha}{m}\left(\frac{\xi}{\xi+\eta}\right)^m\left(\frac{\eta}{\xi+\eta}\right)^{n_\alpha-m} \tag{89}$$

and the average number of x sites under a single α polymer is $n_\alpha\xi/(\xi+\eta)$.

VI. SUMMARY

We have studied a Bethe lattice in contact with a reservoir containing an arbitrary number of molecular species, of various sizes and shapes, which can be adsorbed on the lattice. The molecules do not interact [1]. Assuming that the activities of the various species are specified, we make an exact calculation of the number of adsorbed molecules of each species. The calculations are simple and essentially instantaneous on a desktop computer. One slightly surprising result is that, if more than two species are present, an increase in the activity of one species can in some cases increase the number of adsorbed molecules of another species.

We also considered adsorption of molecules on a two-component Bethe lattice which contains two types of sites (x and y) whose numbers are specified and which anneal into the thermodynamically most favorable configuration. The exact solution of the adsorption problem on this lattice is expressed in terms of the exact solution on the one-component lattice for two cases: (i) when the reservoir contains only dimers, with arbitrary values of the activities z_{xx}, z_{yy}, and z_{xy}; (ii) when the reservoir contains arbitrary (perhaps many) species of molecules, with a reasonable assumption about the form of the dependence of the activity of an adsorbed molecule on the types of the underlying sites.

ACKNOWLEDGMENT

One of the authors (M.C.) wishes to acknowledge his indebtedness to the late Mark Kac, who introduced him to the meaning and usefulness of the concepts of statistical independence and conditional probability.

APPENDIX A: ABSENCE OF COEXISTENCE OF TWO PHASES

We show here that, if the reservoir contains only a finite number of species of polymers, then for any values of the activities z_α the one-component lattice does not separate into regions with different densities of polymers or different densities of any species of polymer. Furthermore, we shall show

that the two-component lattice does not separate into regions with different fractions of x sites, or different densities of any polymer species [29].

We first discuss the one-component lattice. The grand partition function $Q_1(z_1,z_2\ldots)$ is given by Eq. (2) (the subscript "1" indicates that there is only one type of site on the lattice). If the reservoir contains only one type of polymer with activity z, the work of Lee and Yang [30] shows that two different densities can coexist if and only if the limit, as $N\to\infty$, of $(1/N)d\ln Q_1(z)/dz$ exhibits a finite jump (discontinuity) at some value z_0. The magnitude of the jump, multiplied by z_0, is the difference in the densities of the coexisting phases. The analysis is readily extended to a system in contact with a reservoir containing many species with activities $z_1,z_2,\ldots$. Since the density of species α is $\rho_\alpha = N^{-1}z_\alpha\partial\ln Q_1/\partial z_\alpha$, different densities can coexist only if one or more of the ρ_α is not a continuous function of $(z_1,z_2,\ldots)$.

From Eqs. (10) and (13) we have

$$\rho_\alpha = z_\alpha\gamma_\alpha w(u/w)^{n_\alpha}, \tag{A1}$$

(where $u=1-f$ and $w=1-g$). We shall show that u and w are continuous functions of $(z_1,z_2,\ldots)$.

Since we have assumed that only a finite number of species of polymers are in the reservoir, the right side of Eq. (31) is a finite series. All terms are non-negative and are increasing functions of u/w. Equation (31) has a unique positive root $(u/w)_0$. Since the right side of (31) is a continuous function of u/w, it is clear that $(u/w)_0$ is a continuous (and decreasing) function of every z_α. From Eq. (30) we see that w is a continuous function of every z_α, and thus u is also a continuous function of every z_α. Finally, from Eq. (A1) we see that ρ_α is a continuous function of $(z_1,z_2,\ldots)$ and therefore there is no region of coexistence of different densities of polymers (or different densities of some species).

Thus, even without exhibiting $Q_1(z_1,z_2,\ldots)$ we have proved that if the number of species of polymer is finite, the limit as $N\to\infty$ of $(1/N)d\ln Q_1/dz_\alpha$ is a continuous function of $(z_1,z_2,\ldots)$.

The argument is readily extended to the two-component lattice, whose grand partition function, Q_2, is given by Eqs. (77) and (78). The density of polymers of type α is

$$\rho_\alpha = \lim_{N\to\infty}\frac{\tilde{z}_\alpha}{N}\frac{\partial}{\partial\tilde{z}_\alpha}\ln Q_2(\xi,\tilde{z}_1,\tilde{z}_2,\ldots) \tag{A2}$$

$$= \lim_{N\to\infty}\frac{\tilde{z}_\alpha}{N}\frac{\partial}{\partial\tilde{z}_\alpha}\ln Q_1(\tilde{z}_1,\tilde{z}_2,\ldots). \tag{A3}$$

The right side of Eq. (A3) is a continuous function of $(\tilde{z}_1,\tilde{z}_2,\ldots)$ and since $\xi>0$, Eq. (78) shows that $\tilde{z}_\alpha$ is a continuous function of ξ and $z_{0\alpha}$. Furthermore, Eq. (79) shows that F_x is a continuous function of $(\xi,\tilde{z}_1,\tilde{z}_2,\ldots)$. Thus, the densities of all polymer species and the fraction F_x of x sites are continuous functions of $(\xi,z_{01},z_{02},\ldots)$ and there is no possibility of the coexistence of two phases with different F_x and/or different ρ_α [31].

APPENDIX B: LINEAR POLYMERS ON THE BETHE LATTICE

We consider a one-component (only one type of site) Bethe lattice (coordination number $q=\sigma+1$) in equilibrium with a reservoir containing only linear polymers which are simply chains of n bonds, with $n=1,2,3,\ldots$. Each bond connects two monomers and the activity of a polymer with n bonds (and $n+1$ monomers) is taken to be z^n. It is not necessary to impose an upper limit on n.

The multiplicity γ associated with a chain of n bonds is $(1/2)(\sigma+1)\sigma^{n-1}$. [If we fix one end to the seed site, then the first bond can point in $\sigma+1$ directions and each succeeding bond can point in σ directions. But since the two ends of the chain are equivalent we have the factor of $(1/2)$.] Thus, Eq. (31) (with $n_\alpha=n+1$) becomes

$$1 = \frac{u}{w} + (u/w)\frac{\sigma+1}{2\sigma}\sum_{n=1}^{\infty}(\sigma z u/w)^n + (u/w)\frac{\sigma-1}{2\sigma}\sum_{n=1}^{\infty}n(\sigma z u/w)^n. \tag{B1}$$

Equivalently, if we set $r\equiv\sigma z u/w$, this equation (which fixes r as a function of z) is

$$\sigma z = r\left[1+\frac{\sigma+1}{2\sigma}\frac{r}{1-r}+\frac{\sigma-1}{2\sigma}\frac{r}{(1-r)^2}\right]. \tag{B2}$$

Similarly, we obtain w by writing Eq. (30) as

$$\frac{1}{w} = 1+\frac{1}{\sigma^2 z}\frac{r^2}{(1-r)^2}. \tag{B3}$$

For the special case of a one-dimensional lattice ($\sigma=1$) we have the solution that

$$r = \frac{z}{1+z} \tag{B4}$$

so that

$$g = 1-w = 1-\frac{1}{1+z} = \frac{z}{1+z} \tag{B5}$$

and

$$u = 1-f = \frac{1}{(1+z)^2}. \tag{B6}$$

Since the only possible polymers on a one-dimensional lattice are chains, our calculation in Sec. III A covers this case and Eqs. (B5) and (B6) indeed agree with the results of Sec. III A when $\sigma=1$.

Now we treat the case when $\sigma>1$. Since the right side of Eq. (B2) is an increasing function of r and approaches infinity as $r\to1$, this equation has a unique solution for r in the range $0<r<1$. Now we obtain explicit results when z is very large. In this case, we expect $f\to1$ and $g\to2/(\sigma+1)$, since every site should be covered by a very long chain which thereby (neglecting end effects) covers two of the $\sigma+1$ edges which touch that site. If z is large, r is close to 1 and the last term on the right in Eq. (B2) is dominant and one finds that

$$r = 1 - \frac{1}{\sigma}\sqrt{\frac{\sigma-1}{2z}} + \mathcal{O}(1/z). \tag{B7}$$

If one uses Eq. (B3) as it stands, one needs the coefficient of $1/z$ in Eq. (B7) in order to calculate w through order in $1/\sqrt{z}$. Accordingly we use Eq. (B2) to rewrite the last term of Eq. (B3) and obtain

$$\frac{1}{w} = 1 + \frac{2\sigma}{\sigma^2(\sigma-1)z}\left[\sigma z - \frac{\sigma+1}{2\sigma}\frac{r^2}{1-r} - r\right]. \tag{B8}$$

We then find

$$\frac{1}{w} = 1 + \frac{2}{\sigma-1} - \frac{(\sigma+1)\sigma}{\sigma^2 z(\sigma-1)\sqrt{(\sigma-1)/(2z)}} + \mathcal{O}(1/z)$$
$$= \frac{\sigma+1}{\sigma-1}\left[1 - \frac{1}{\sigma z}\sqrt{\frac{2z}{\sigma-1}}\right] + \mathcal{O}(1/z), \tag{B9}$$

so that

$$g = 1 - w = \frac{2}{\sigma+1} - \frac{2}{\sigma(\sigma+1)}\sqrt{\frac{\sigma-1}{2z}} + \mathcal{O}(1/z). \tag{B10}$$

We also find

$$u = 1 - f = \frac{\sigma-1}{\sigma(\sigma+1)z} + \mathcal{O}(1/z^{3/2}). \tag{B11}$$

The average length of the polymer chains is

$$\bar{n} \equiv \sum_n n\rho_n \Big/ \sum_n \rho_n = 1/(1-r). \tag{B12}$$

Thus for large z and $\sigma > 1$ we have

$$\bar{n} \approx \sigma z^{1/2}\sqrt{2/(\sigma-1)}. \tag{B13}$$

In these results the appearance of factors of $(\sigma-1)$ indicates that the asymptotic behavior at large z for $\sigma=1$ differs from that for $\sigma>1$. For $\sigma=1$, $\bar{n}=1+z$ for all z.

The right side of Eq. (B2) is a continuous function of r, and the r which satisfies this equation is a continuous function of z. Therefore u/w is a continuous function of z. Equation (30) implies that w is a continuous function of z. It follows from Eq. (B3) that the densities of all polymer species are continuous functions of z, and therefore there is no region of coexistence of different phases.

If the polymers are adsorbed on a two-component annealed lattice, and if the dependence of the activity of the adsorbed polymers on the types (x or y) of the underlying sites has the form assumed in Sec. V, there is still no coexistence of different phases. The proof relies on Eqs. (77) and (78). We enumerate the species by the index n, the number of bonds in the polymer. Thus $z_{0n}=z^n$ and

$$\tilde{z}_n = z^n\left(\frac{\xi+\eta}{\xi+1}\right)^{n+1}. \tag{B14}$$

If the exponent in the second factor of Eq. (B14) were n instead of $n+1$, the GPF of the two-component system would be $(1+\xi)^N$ times the GPF of the one-component system evaluated at a renormalized value of z. Since this is not the case, the argument is slightly more tedious.

Equation (85) yields

$$\sigma z = \frac{\xi+1}{\xi+\eta}R + \frac{R}{\sigma}\left[\frac{\sigma+1}{2}\frac{R}{1-R} + \frac{\sigma-1}{2}\frac{R}{(1-R)^2}\right], \tag{B15}$$

where $R=\sigma z[(\xi+\eta)/(\xi+1)][u/w]$. Thus we see that R is a continuous function of ξ and z, and u/w is a continuous function of ξ and z. Equation (84) becomes

$$\frac{1}{w} = 1 + \frac{1}{\sigma^2 z}\left(\frac{R}{1-R}\right)^2 \tag{B16}$$

which is identical in form with Eq. (B3) [32].

Therefore, u and w are continuous functions of ξ and z and [from Eq. (88)] the densities of all species are continuous functions of ξ and z. Finally, Eq. (79) becomes

$$F_x = \frac{\xi}{1+\xi}\left[1 + \frac{1-\eta}{\xi+\eta}\frac{\sigma+1}{2\sigma^2}\frac{w}{z}\left(\frac{R^2}{(1-R)^2} + \frac{R^2}{1-R}\right)\right]. \tag{B17}$$

The right side of Eq. (B17) is a continuous function of ξ and z. Therefore, there is no coexistence of phases with different densities of x sites and/or different densities of any polymer species.

APPENDIX C: RELATION OF PRESENT METHOD TO GUGGENHEIM'S COMBINATORIAL METHOD

Guggenheim's method is equivalent to finding the largest term in the grand partition function [Eq. (2)], using his approximate form for $W(N_1,N_2,\ldots)$ [4]. He uses logarithmic differentiation with respect to N_i, and we (equivalently) set the ratio of adjacent terms (differing in the value of only one of the N_i) equal to unity. If the activities $\{z_i\}$ are specified, this procedure determines the $\{N_i\}$. If the $\{N_i\}$ are specified, this procedure determines the $\{z_i\}$.

As we have noted in the introduction, Guggenheim assumes that all lattice sites are occupied. His analysis applies equally well to a lattice with vacancies if we define the species $i=0$ as a vacancy (with activity 1) which occupies one site ($n_0=1$, $z_0=1$). Thus $W=W(N_0,N_1,N_2,\ldots)$ and $\Sigma_{i\geqslant 0}n_iN_i=N$, where N is the number of sites on the lattice. In the following, Σ means $\Sigma_{i\geqslant 0}$ and Σ' means $\Sigma_{i\geqslant 1}$. Guggenheim's (approximate) combinatorial formula, which assumes that the adsorbed molecules have no closed loops, is

$$\ln W(N_0,N_1,\ldots) = \frac{1}{2}q\ln\left[\left(\sum_i Q_iN_i\right)!\right] - \sum_i \ln(N_i!)$$
$$-\left(\frac{q}{2}-1\right)\ln(N!) + \sum_i N_i \ln\gamma_i, \tag{C1}$$

where

$$Q_i = \left(1 - \frac{2}{q}\right)n_i + \frac{2}{q}. \tag{C2}$$

If $(N_1,N_2,\ldots)$ are the N_i which are associated with a set of activities $(z_1,z_2,\ldots)$, the bars in Eq. (9) are redundant, we can write

$$V_\alpha/N_\alpha = 1/z_\alpha, \quad \text{for } \alpha \geqslant 1 \tag{C3}$$

and can use Eq. (7) to evaluate V_α/N_α [we ignore the difference between N_α and $N_\alpha+1$ in the denominator when $N \gg 1$ and recall that Eqs. (1)–(12) are valid on any lattice]. If we increase the number of type α molecules by 1 we must decrease the number of vacancies by n_α. Thus Eq. (C3) becomes

$$\ln W(N_0 - n_\alpha, N_1, N_2, \ldots N_\alpha + 1, \ldots) - \ln W(N_0, N_1, N_2, \ldots N_\alpha, \ldots) = -\ln z_\alpha. \tag{C4}$$

Using Eq. (C1) we evaluate the left side of Eq. (C4) as

$$\frac{q}{2}\ln\left(\frac{\{[1-2/q]N + [2/q][(\Sigma N_i) + 1 - n_\alpha]\}!}{[(1-2/q)N + (2/q)(\Sigma N_i)]!}\right) - \ln\left(\frac{(N_0 - n_\alpha)!}{N_0!}\right) - \ln(N_\alpha + 1) + \ln\gamma_\alpha. \tag{C5}$$

Using $N=N_0+\Sigma' n_i N_i$, we find that

$$(1-2/q)N + (2/q)\sum N_i = N_0 + \sum{}' N_i[(1-2/q)n_i + (2/q)] = N - (2/q)\sum{}'(n_i - 1)N_i. \tag{C6}$$

Since all the terms in Eq. (C6) are proportional to N and $(1-n_\alpha)$ is of order unity, the argument of the first logarithm in Eq. (C5) is

$$\left[N - \frac{2}{q}\sum{}'(n_i - 1)N_i\right]^{-(2/q)(n_\alpha - 1)}. \tag{C7}$$

Similarly, the argument of the second logarithm in Eq. (C5) is

$$\left[N - \sum{}' n_i N_i\right]^{-n_\alpha}. \tag{C8}$$

Thus Eq. (C4) becomes

$$\gamma_\alpha \frac{[N - \sum{}' n_i N_i]^{n_\alpha}}{[N - (2/q)\sum{}'(n_i - 1)N_i]^{n_\alpha - 1}} \frac{1}{N_\alpha} = \frac{1}{z_\alpha}. \tag{C9}$$

Dividing the numerator and denominator of Eq. (C9) by N^{n_α} we find that

$$\rho_\alpha = z_\alpha \gamma_\alpha \frac{(1-f)^{n_\alpha}}{(1-g)^{n_\alpha - 1}}, \tag{C10}$$

where $\rho_\alpha = N_\alpha/N$ and $f=\Sigma' n_i \rho_i$ is the probability that a site is occupied and $g=(2/q)\Sigma'(n_i-1)\rho_i$ is the probability that an edge is occupied by a bond (provided that the molecules are chains or branched chains, with no closed loops).

Equation (C10) is identical to Eq. (25) and leads immediately to Eqs. (28)–(31). Furthermore, as we showed in Sec. II, the preceding argument can be inverted. Equations (7) and (13) can be used to generate Guggenheim's formula, Eq. (C1), for $W(N_0,N_1,N_2,\ldots)$.

We define ρ_α^G as the density of (noninteracting) type α molecules adsorbed on a lattice, calculated from Guggenheim's combinatorics. Similarly, ρ_α^B is the density on the Bethe lattice. For a given coordination number q and given activities z_i, the only difference between ρ_α^G and ρ_α^B is due to the difference in the lattice-dependent multiplicity factors γ_α. In particular, Guggenheim's approximations and our exact solution on the Bethe lattice yield the same formula [Eq. (17)] for $P_n(\{N_i\})$, the probability that a connected set of n sites are all vacant when $(N_1,N_2,\ldots)$ are all specified.

Depending on the structure of the molecule α and the structure of the lattice, the multiplicity γ_α may or may not differ significantly from γ_α^B, the multiplicity on a Bethe lattice of the same coordination number. For example, $\gamma=q/2$ for a dimer on any lattice. For a spider with n legs, each leg being a single bond, $\gamma=q!/[(q-n)!n!]$ on any lattice. For a flexible linear chain of n bonds on a planar square lattice $(q=4)$, $\gamma=\gamma_B$ for $n<4$ and, for $n=4$, $\gamma/\gamma^B=25/27$. If the chain is on a planar triangular lattice $(q=6)$, then $\gamma=\gamma^B$ for $n<3$ and $\gamma/\gamma^B=23/25$ for $n=3$.

In order to make contact with experiments, let us assume that the reservoir is a dilute solution in which the concentrations $\mathcal{C}_\alpha$ (number of type α molecules per unit volume) of the various molecular species are sufficiently low to justify neglecting interactions between molecules of the same or different species. Then the grand partition function of the solution is the product of the grand partition functions Q_α^{res} of the various species, where

$$Q_\alpha^{\text{res}} = \sum_{n=0}^{\infty} \frac{1}{n!} e^{n\beta\mu_\alpha}[V\zeta_\alpha(T)]^n = \exp[Ve^{\beta\mu_\alpha}\zeta_\alpha(T)]. \tag{C11}$$

In Eq. (C11), $V\zeta_\alpha(T)$ is the partition function of one type α molecule. The factor V (the volume of the reservoir) arises from the overall translational degree of freedom. If interactions with the solvent are important, then $\zeta_\alpha(T)$ should include these interactions averaged over all configurations of the solvent atoms appropriately weighted with Boltzmann factors. Fortunately, as we shall see, this calculation can be circumvented by introducing an empirically determined factor.

The average number of type α molecules in the reservoir is

$$\mathcal{N}_\alpha = \beta^{-1}\partial \ln Q_\alpha^{\text{res}}/\partial\mu_\alpha = V\zeta_\alpha(T)e^{\beta\mu_\alpha} \tag{C12}$$

and thus

$$\mathcal{C}_\alpha = \mathcal{N}_\alpha/V = \zeta_\alpha(T)e^{\beta\mu_\alpha}. \tag{C13}$$

Recalling that $z_\alpha = e^{\beta\mu_\alpha}Z_\alpha(T)$, where Z_α is the partition function of an adsorbed α molecule, we find that

$$z_\alpha = \mathcal{C}_\alpha Z_\alpha(T)/\zeta_\alpha(T). \tag{C14}$$

We can combine Eqs. (10) and (C14) to obtain a law of mass action, in which the rate of adsorption (which involves a type α-molecule in solution impinging on a type α vacancy and is proportional to $\mathcal{C}_\alpha\rho_{V_\alpha}$) is equated to the rate of desorption (which is proportional to ρ_α if interactions between molecules on the lattice and solute molecules are negligible),

$$\frac{\rho_\alpha}{\mathcal{C}_\alpha \rho_{V_\alpha}} = \frac{Z_\alpha(T)}{\zeta_\alpha(T)}. \tag{C15}$$

Finally, Eq. (C10) can be written as

$$\rho_\alpha = K_\alpha(T)\mathcal{C}_\alpha(1-f)^{n_\alpha}/(1-g)^{n_\alpha - 1}, \tag{C16}$$

where

$$K_\alpha(T) = \gamma_\alpha Z_\alpha(T)/\zeta_\alpha(T) \tag{C17}$$

and

$$\gamma_\alpha z_\alpha = K_\alpha(T)\mathcal{C}_\alpha. \tag{C18}$$

If one can perform an adsorption experiment in which only type α molecules are present in the solution, then as $\mathcal{C}_\alpha \to 0$, Eq. (C16) becomes

$$\rho_\alpha = K_\alpha(T)\mathcal{C}_\alpha. \tag{C19}$$

Thus, if we introduce the measured slope $K_\alpha(T)$ into our equations and replace $\gamma_\alpha z_\alpha$ by $K_\alpha(T)\mathcal{C}_\alpha$ in Eqs. (28)–(31), then Eqs. (25) and (C10) are identical. The coordination number q still appears in Eqs. (28)–(31) which determine f and g; but γ_α, Z_α, and ζ_α are all contained in the empirically determined $K_\alpha(T)$.

Accordingly, we consider it accurate to state that the exact equations for adsorption of noninteracting molecules on a Bethe lattice yield an adsorption isotherm identical with that calculated from Guggenheim theory on a lattice of the same coordination number, provided we introduce the empirically determined parameters $K_\alpha(T)$ into the equations.

Since Guggenheim [2] frequently does not distinguish between formulas which are exact and formulas which are only approximately true, some effort is required to identify assertions which are true only on the Bethe lattice. His formula for $W(N_0, N_1, N_2, \ldots)$ is derived by extending his analysis of a lattice on which every site is occupied by a monomer (which we will take to mean a vacancy) or by an element of an r-mer (in this discussion the word "monomer" excludes the elements of an r-mer). Clearly, the probability that a particular site is occupied by a monomer is $N_1/(N_1 + rN_r)$. However, his expression for the probability that a chosen pair of adjacent sites are both occupied by monomers is exact only on the Bethe lattice.

Considering a particular r-mer occupying a group of r sites, Guggenheim [33] defines Qq (our notation) as "the number of pairs of neighboring sites of which one is a member of the group occupied by the given r-mer and the other is not." He states that if the r-mer is a simple chain or a branched chain without closed rings

$$Qq = (q-2)r + 2 \tag{C20}$$

and that, as a consequence of the "completely random" arrangement of the molecules "if a site is occupied by a monomer, then the chances that a given neighboring site is occupied by another monomer or by an r-mer are as N_1 to QN_r." If we label the two sites as a and b and let $M(a)$, $M(b)$, and $R(b)$ denote respectively the events "site a is occupied by a monomer," "site b is occupied by a monomer," and "site b is occupied by an r-mer," then the previous assertion (using the language of conditional probabilities) is

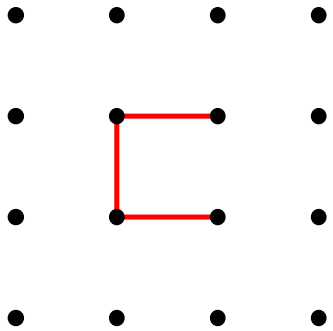

FIG. 9. (Color online) Tetramer which violates Eq. (C20).

$$\frac{P[M(b)|M(a)]}{P[R(b)|M(a)]} = \frac{N_1}{QN_r}. \tag{C21}$$

Equation (C20) is true on the Bethe lattice, but not on periodic lattices of two or higher dimensions. For example, the definition of Qq yields $Qq = 8$ for the tetramer of Fig. 9 on a planar square lattice, whereas Eq. (C20) yields $Qq = 10$. However, one can go back to the definition of Qq and insert the correct value for any particular r-mer. Equation (C21) presents a more serious problem. Recalling that on the Bethe lattice

$$\begin{aligned} P(M(b)|M(a)) &= (1-f)/(1-g) \\ &= [1 - rN_r/N]/[1 - (r-1)N_r/(Nq/2)], \end{aligned} \tag{C22}$$

where $N = N_1 + rN_r$, and noting that

$$P[R(b)|M(a)] = 1 - P[M(b)|M(a)], \tag{C23}$$

we find that Eq. (C21) [using Eq. (C20) for Q] is true on the Bethe lattice. However, Guggenheim evidently has another way of thinking about Eq. (C21), which leads him to write the equation directly without the algebra involved in our calculation. The most direct argument we can construct which leads to Eq. (C21) is the following.

Let E be the set of all unoccupied edges (i.e., edges which are not covered by a bond of an r-mer) which terminate on two monomers or on a monomer and an r-mer, or on elements of two different r-mers. The set E does not include unoccupied edges both of whose ends are elements of the same r-mer. We look at both ends of each edge ab in the set E and count the number of ends (qN_1) touching a monomer and the number of ends (QqN_r) touching an r-mer. We use the symbol $\in$ to denote membership in a set, and find

$$P[M(b)|ab \in E]/P[R(b)|ab \in E] = N_1/(QN_r). \tag{C24}$$

As we have discussed earlier, if the only path from a to b is through the edge ab (i.e., if there are no closed paths on the lattice, in which case E is the set of all unoccupied edges), then $P[M(b)|ab \in E] = P[M(b)|M(a)]$ and $P[R(b)|ab \in E] = P[R(b)|M(a)]$ and Eq. (C24) implies Eq. (C21). The "completely random" arrangement of the mol-

ecules is not sufficient to justify Eq. (C21), which may be a reasonable approximation but is exact only on a Bethe lattice. The essential step in deriving Eq. (C1) is the extension of Eq. (C21) to calculate the probability that a group of r contiguous sites are vacant. Foreman and Freed [34] have discussed a number of possible ways to "improve" the Guggenheim theory (which they call the "Huggins-Guggenheim-Miller theory"), including a more accurate calculation of the "surface fraction" Qq, and find that simple "improvements" generally diminish the accuracy of the theory, when compared with the results of Monte Carlo simulations.

[1] Throughout this paper when we refer to polymers which are "noninteracting," it is to be understood that they obey the "hard-core" restriction that two monomers cannot occupy the same site.

[2] E. A. Guggenheim, Proc. R. Soc. London, Ser. A **183**, 203 (1944).

[3] The reader of Ref. [2] may find it difficult to distinguish between statements (estimates of probabilities) which are exactly true and statements which are "reasonable" but not exactly true.

[4] E. A. Guggenheim, Proc. R. Soc. London, Ser. A **183**, 213 (1944).

[5] In Guggenheim's notation our q, n_i, and γ_i are his z, r_i, and ρ_i, respectively.

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[10] A. B. Harris and M. Cohen, J. Chem. Phys. **125**, 184107 (2006). We are indebted to Professor B. Widom for informing us that the result of Sec. V, regarding the limiting density of dimers randomly deposited on a one-dimensional lattice, was previously obtained by B. Widom, J. Chem. Phys. **58**, 4043 (1973) and by P. Flory, J. Am. Chem. Soc. **61**, 1518 (1939).

[11] J. F. Nagle, Phys. Rev. **152**, 190 (1966).

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[17] J.-H. Ryu and P. D. Gujrati, Korea Polymer J. **7**, 259 (1999).

[18] T. C. Lubensky and J. Isaacson, J. Phys. (France) **42**, 175 (1981).

[19] P. G. de Gennes, *Scaling Concepts in Polymer Physics* (Cornell University Press, Ithaca, 1979).

[20] What we call "edges" are usually referred to as "bonds." In this paper "bonds" refers to the connections between monomer units of a polymer. It is useful to distinguish "edges" which are bonds of the lattice and "bonds" which are bonds of the polymer.

[21] This assumption is inessential. If the activity does depend on the angles between intrapolymer bonds, then we simply classify the different shapes as being different polymers.

[22] One might also wonder whether the local densities are well defined. One operational definition is the following: (a) consider a large number of identical Bethe lattices, all in contact with the same reservoir; (b) examine the same site S on all the lattices and measure the fraction f_α of lattices on which S is occupied by a monomer which is part of an α-polymer; then $\rho_\alpha(S)=f_\alpha/n_\alpha$, where n_α is the number of monomers in an α-polymer. (c) A site may be a part of more than one α-vacancy. If we define a random variable $X_\alpha(S)$, which is equal to the number of α-vacancies of which S is a part, then $\rho_{V_\alpha}(S)=\bar{X}_\alpha(S)/n_\alpha$, where the overbar denotes an average over the ensemble of lattices.

[23] Reference [10], Sec. IIA, presents this argument somewhat more explicitly. We define $\rho_\alpha(R)$ to be the average value of ρ_α over all sites S in R, etc. It is also assumed that R_1 and R_2 are large compared with the size of an α-polymer and small compared with the size of the lattice.

[24] An equivalent algorithm, easier to state but more tedious to execute, is the following: Count the number, W_α, of all the distinct α-polymers which can be placed on the empty lattice, with the restriction that the polymer touches the seed site (i.e., the seed site is covered by some monomer, not necessarily the same monomer in every case). Then $\gamma_\alpha=W_\alpha/n_\alpha$.

[25] M. E. Fisher and J. W. Essam, J. Math. Phys. **2**, 609 (1961).

[26] We are indebted to Dr. Joel Cohen for explaining the biological relevance of this model. In a more realistic calculation [J. A. Cohen and M. Cohen (unpublished)] it is necessary to take account of the fact that the adsorbed dimers, as well as the lattice, carry electric charge which acts back on the reservoir (an ionic solution).

[27] In general, we expect dimer binding to induce correlations between the types of adjacent sites on the lattice. With the aid of some sum rules one can calculate the probabilities that a pair of adjacent sites are both x, both y, or an x and a y, but we omit the calculation here.

[28] The lattice does not separate into two phases with different densities of x sites unless adsorbed dimers interact with each other (Ref. [10] gives an exact solution of interacting dimers on a one-component Bethe lattice; if the attractive interaction is strong enough, two phases can coexist at a certain value of the activity). The present model includes no interactions except for the hard-core restriction. Equations (68), (67), and (56) show that, within the Bethe approximation, the density of dimers is an analytic function of s on the positive real axis and, since s is an analytic function of the activities on the positive real axis, there is no phase separation. The work of O. J. Heilmann and E. H. Lieb, Commun. Math. Phys. **25**, 190 (1972), extends this result to realistic planar lattices.

[29] The discussion is limited to the Bethe lattice. Appendix B extends these conclusions to a particular system in which the reservoir contains an infinite number of polymer species (lin-

ear chains), with a reasonable assumption about the activities of the species. We cannot give a completely general discussion of the case when there are an infinite number of polymer species.

[30] C. N. Yang and T. D. Lee, Phys. Rev. **87**, 404 (1952).

[31] There is a unique positive ξ for each F_x in the range (0,1). This follows from the fact that (for any lattice) the summand in the GPF depends on ξ only through the factor ξ^{N_x}. Thus, if $Q_2(\xi,\ldots)$ is the GPF of a two-component system, we have $\bar{N}_x=\xi\partial \ln Q_2/\partial\xi$ and $\xi\partial\bar{N}_x/\partial\xi=\overline{N_x^2}-(\bar{N}_x)^2>0$. Thus, F_x is an increasing function of ξ and there is a unique ξ for each F_x.

[32] However, for a given value of z, $r\neq R$ unless $\xi=\infty$ (as for a one-component lattice having all sites of type x) or $\eta=1$ (when $\epsilon_x=\epsilon_y$ so that there is no difference between the two types of sites).

[33] E. A. Guggenheim, *Mixtures* (Oxford University Press, Oxford, 1952), pp. 193–194.

[34] K. W. Foreman and K. F. Freed, J. Chem. Phys. **102**, 4663 (1995).