

## Solution of lattice gas models in the generalized ensemble on the Bethe lattice

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We present the exact Bethe lattice solution for a lattice gas Potts model defined in the generalized ensemble which was previously studied in elucidating the anomalous thermodynamic properties of water. For this model the locus of density maxima (TMD), the locus of isothermal compressibility extrema, (TEC), the spinodal curve, and the percolation curve for four hydrogen bonded molecules are calculated using the Bethe lattice solution. The results confirm qualitative relationships between the TMD, the TEC, and the percolation curve obtained previously from a mean field calculation. [S1063-651X(99)17205-2]

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### I. INTRODUCTION

There is a long tradition in statistical mechanics of modeling physical systems and phenomena in terms of interacting discrete variables located on a suitably chosen lattice [1]. The classic example is the Ising model or the equivalent simple lattice gas, the study of which has been instrumental in our understanding of critical phenomena [2]. Relatively few such models are amenable to an exact solution [3], and hence a variety of approximations are used to study them. We study our model on the Bethe lattice, the interior of a Cayley tree, all of whose sites have the same coordination number and whose bonds permit no closed loops. The exact results obtained on it coincide with results obtained by the Bethe-Peierls [2] approximation on a regular lattice with the same coordination number [3]. As discussed by Gujrati [4], the solution of a model on the Bethe lattice is generally more reliable than conventional mean field approximations. Further, the availability of an exact solution method allows one to study aspects of the model not accessible to mean field approaches, such as geometric aspects *via* percolation.

In this paper, we consider a lattice gas Potts model studied previously to elucidate thermodynamic aspects of the unusual properties of water [5]. We calculate the equation of state of the model on the Bethe lattice. In order to allow volume fluctuations, as required by our model, we solve the model in the generalized ensemble, in which the state of the system is defined entirely by intensive variables [6], as opposed to the grand canonical ensemble in which lattice gas models are typically solved. The peculiarities of the generalized ensemble make the calculation of the thermodynamic properties of the model quite intricate; in particular, the relatively straightforward procedure for calculating the equation of state [2] in the Bethe-Peierls approximation proves inadequate. It is necessary to obtain a formal solution for the free energy in order to calculate the equation of state. In this paper we show how the calculation of the free energy of lattice models on the Bethe lattice, discussed by Peruggi, di Liberto, and Monroy [7] and Gujrati [4], may be extended to the generalized ensemble.

In Sec. II we describe the model we analyze. Section III

describes the solution procedure for the Bethe lattice. In Sec. IV we describe some results we obtain. Section V contains a summary and conclusions.

### II. MODEL

In this section, we describe the lattice gas Potts model we study. The model is defined to capture some basic aspects of the microscopic behavior of water [8,9], as described elsewhere [5]. We restrict ourselves here simply to those details necessary to define the model. Interested readers may refer to Ref. [5] for details relating to the physics of liquid water. We mention briefly here, however, that the model described below aims to capture the effect of strong hydrogen bonds (HB's) and the correlations between the formation of HB's and the local volume and entropy. These properties are dependent on the orientational states of the water molecules, which we model using the Potts variables defined at all occupied sites on the lattice.

Consider a simple cubic lattice (square lattice in two dimensions). At each site  $i$  we define occupancy variables  $n_i$  such that  $n_i=0$  if site  $i$  is unoccupied, and  $n_i=1$  if site  $i$  is occupied. For each occupied site  $i$ , and for each nearest neighbor site  $j$  on the lattice, we define a Potts variable  $\sigma_{i,j}$  [10].

Thus  $\sigma_{i,j}$  defines the orientation of molecule  $i$  with respect to molecule  $j$ . The full orientational state of molecule  $i$  is given by  $\sigma_{i,j_1}, \sigma_{i,j_2}, \dots, \sigma_{i,j_\gamma}$  where  $j_1, j_2, \dots, j_\gamma$  are the neighbors of  $i$ , and  $\gamma$  is the total number of neighbors (or coordination number). The variables  $\sigma_{i,j}$  so defined are independent of each other, i.e.,  $\sigma_{i,j_1}$  does not depend on  $\sigma_{i,j_2}$ , etc. In order to distinguish between the energies of strong HB's, we first define an interaction term  $-\epsilon n_i n_j$  between occupied neighbors, regardless of any requirement for HB formation. Thus we write the Hamiltonian as

$$\mathcal{H} = \mathcal{H}_{\text{NHB}} + \mathcal{H}_{\text{HB}} = -\epsilon \sum_{\langle ij \rangle} n_i n_j + \mathcal{H}_{\text{HB}}, \quad (1)$$

where  $\langle ij \rangle$  indicates the set of all nearest neighbor pairs. We define  $\sigma_{i,j} = \sigma_{j,i}$  to be the condition that  $i$  and  $j$  are properly

oriented for HB formation. If the  $\sigma_{i,j}$  have a range of possible values ( $=1,2,\dots,q$ ), the relative entropy (in terms of the available number  $q$  of microstates) for HB's is lower than the number of microstates for non-HB's (NHB's) by a factor  $\ln(q)$ . Defining the energy increment on HB formation to be  $-J$ , we write

$$\mathcal{H}_{\text{HB}} = -J \sum_{\langle ij \rangle} n_i n_j \delta_{\sigma_{i,j}, \sigma_{j,i}}. \quad (2)$$

Finally we quantify the change in local density as a result of HB formation, also in terms of the orientational variables  $\sigma_{i,j}$ . The total volume  $V$  of the system is first written as the sum of specific volumes  $V_i$  of sites  $i$ . The specific volumes  $V_i$  are in turn expressed in terms of contributions  $b_{i,j}$  that depend on the interaction state between sites  $i$  and  $j$ . Thus

$$V = \sum_i V_i \equiv \sum_{\langle i,j \rangle} b_{i,j}. \quad (3)$$

When  $i$  has a HB interaction with  $j$ , the local volume  $b_{i,j}$  increases, leading to a larger specific volume  $V_i$ . We define two possible values for  $b_{i,j}$ : (i)  $b_{i,j} = b$  for NHB states, and when  $n_i$  or  $n_j = 0$ ; and (ii)  $b_{i,j} = b + \delta b$  for HB states. Thus

$$\begin{aligned} V &= \sum_{\langle i,j \rangle} b_{i,j} = \sum_{\langle i,j \rangle} (b + \delta b n_i n_j \delta_{\sigma_{i,j}, \sigma_{j,i}}) \\ &= N v_o + \delta b \sum_{\langle i,j \rangle} n_i n_j \delta_{\sigma_{i,j}, \sigma_{j,i}}, \end{aligned} \quad (4)$$

where  $N$  is the number of lattice sites, and  $v_o \equiv \gamma b/2$  is the volume associated with a site when no hydrogen bonds are present. Thus we can write the system Hamiltonian  $\mathcal{H}$  and an ‘‘enthalpy’’ function  $W$  as

$$\mathcal{H} = -\epsilon \sum_{\langle ij \rangle} n_i n_j - J \sum_{\langle ij \rangle} n_i n_j \delta_{\sigma_{i,j}, \sigma_{j,i}} \quad (5)$$

$$W = \mathcal{H} + PV$$

$$\begin{aligned} &= -\epsilon \sum_{\langle ij \rangle} n_i n_j + PN v_o \\ &\quad - (J - P \delta b) \sum_{\langle ij \rangle} n_i n_j \delta_{\sigma_{i,j}, \sigma_{j,i}} \end{aligned} \quad (6)$$

In order to evaluate the partition function for this model, we must sum the appropriate Boltzmann weight over all values of  $n_i$  and  $\sigma_{i,j}$ . In doing so, however, the number of molecules as well as the volume of the system are variables. Thus the appropriate Boltzmann weight is  $e^{-\beta(\mathcal{H} + PV - \mu N)}$ , where  $\beta = 1/T$  is the inverse temperature in the units of the Boltzmann constant, and the independent variables of this ensemble are  $(P, \mu, T)$ , all intensive. The thermodynamic potential  $\Delta(P, \mu, T)$ , obtained by successive Legendre transforms with respect to  $N$ ,  $V$ , and  $S$ , can be seen to be identically zero [ $\Delta(P, \mu, T) = U - TS + PV - \mu N = 0$ ]. This provides an implicit relation between the variables  $P$ ,  $\mu$ , and  $T$ . In Ref. [5], the equation of state was calculated using the conventional mean field approximation [11]. In addition, es-

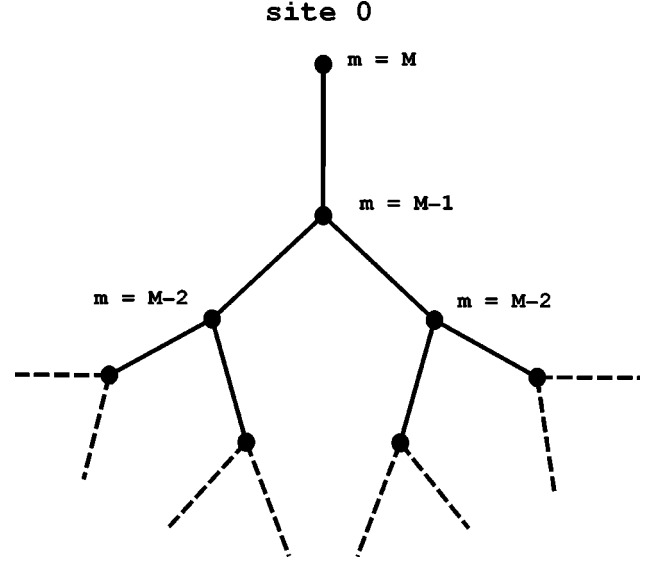


FIG. 1. The generation of the Cayley tree. Starting from the site labeled *root site*, one adds  $\gamma$  ( $= 3$  in this illustration) first neighbors, to each of which  $\gamma - 1$  neighbor sites are connected in the next iteration. One of the  $\gamma$  resulting branches of the tree are shown here. The sites are labeled with their distance from the surface of the tree. Thus, for a tree constructed by adding  $M$  generations of sites ( $M$  steps in the iterative procedure), the origin or root site is labeled by  $M$ , the first generation sites are labeled by  $M - 1$ , etc.

timates were obtained for the hydrogen bond probability and of the percolation threshold for sites with four (with coordination number  $\gamma = 4$ ) hydrogen bonds. In what follows, we evaluate both thermodynamic and percolation quantities exactly for the Bethe lattice. In Sec. V, we compare the results obtained from the present calculations to previous simple mean field (Bragg-Williams) results.

### III. SOLUTION

In this section we describe the exact solution of the model defined in Sec. II in the interior of the Cayley tree (Bethe lattice). The Bethe-Peierls approximation, which improves on the conventional mean field approximation by taking into account the local correlation between sites, consists of writing the occupation probability of a given site (‘‘central site’’) in terms of the occupancies of its neighbor sites. The influence of the rest of the system is introduced through an effective chemical potential that acts on the neighbor sites. The equation of state (EOS) of the system is found using the translational invariance of the system, i.e., by demanding the occupation number of the neighbor sites to be the same as that of the central site.

A Cayley tree, illustrated in Fig. 1, is constructed by starting from a central site  $o$  and adding  $\gamma$  sites (in the following called first generation), all connected to the site  $o$ . To each site belonging to the first generation,  $\gamma - 1$  sites (second generation) are then added. The iteration of such procedure generates a graph which contains no closed loops. Although in a Cayley tree the number of surface sites (the last generation) grow exponentially, if the number of generations is sufficiently large, the local properties of the interior sites in the graph are not surface dependent [3]. Sites which are not af-

fectured by surface effects constitute the Bethe lattice [12].

The Bethe-Peierls approximation for any lattice gas model furnishes a relation between the density and the external fields, i.e., gives the EOS for the model. In the case of a model defined in the generalized ensemble, such a relation is not sufficient to reconstruct the EOS, since one needs in addition to specify the relation between the intensive parameters  $P$ ,  $\mu$ , and  $T$ . Such a relation is implicit in the fact that for the generalized ensemble, the free energy  $\Delta$  is identically zero. Hence the full solution of the EOS requires also a formal evaluation of the free energy.

Before discussing the calculation of the EOS and the free energy for the model defined in Sec II, we introduce some definitions: The number of generations in the Cayley tree is represented by  $M$ , which is then also the distance between the surface sites and the central site  $o$ . We represent a Cayley tree with  $M$  generations as  $\mathcal{T}_M$ . The number of generations between a selected site and the surface is labeled  $m$ ; hence, for the central site  $o$ ,  $m=M$ . Each site  $i$  is associated to an occupation variable  $n_i$  and (when  $n_i=1$ )  $\gamma$  Potts variable  $\sigma_{i,j}$ , with  $1 \leq \sigma_{i,j} \leq \gamma$ . The set of  $(\gamma-1)$  nearest neighbors of a site  $i$  in the next generation are represented by  $\tau_i$ . As we typically discuss a single site at a given generation in the calculations below, we refer to such a site simply by its distance from the surface when no confusion is caused (as, e.g., the  $m$  site), even though, in the generation at distance  $m$  away from the surface, there are  $(\gamma-1)^{M-m}$  sites. We define  $Z_m^k(n_m, \{\sigma\}_m^k)$  as the partial partition function sum over sites on one of the branches  $\mathcal{B}_m^k$  rooted in one of the sites at distance  $m$  from the surface, keeping fixed its occupation number  $n_m$  and the orientation variables  $\sigma_{m,j_m}^k$ , where  $j_m$  can be any of the nearest neighbor sites of  $m$ . When  $n_m=0$ , the orientations  $\sigma_{m,j_m}^k$  are not defined, and hence we write  $Z_m(0)$  in this case. When no confusion is caused, we suppress the branch index  $k$ . Finally, we define  $\mathcal{Z}_M$  to be the partition function for a Cayley tree with  $M$  generations. Note that  $\mathcal{Z}_M$  can be obtained from  $Z_M^k(n_M, \{\sigma\}_M)$  by ‘‘hooking’’ the  $\gamma$  branches  $k$  at the site  $M$  and summing over its occupation number  $n_M$  and orientation variables  $\sigma_{M,M-1}$ .

### A. Recursive relations for the partition function on a Cayley tree

Because in a Cayley tree the number of the boundary sites is not negligible compared to the inner ones, the free energy of the system depends on the surface. Techniques to calculate the free energy for the inner sites of the Cayley tree were presented by Peruggi, di Liberto, and Monroy [7] and Gujrati [4] for models defined in the canonical or grand-canonical ensemble. In Sec. III B we extend it to the case of the generalized ensemble, and we solve the model presented in Sec. II. The technique of Gujrati [4] builds on the standard recursive methods for the calculation of the partition function on the Cayley tree [3], which we review in this section to facilitate the reading of the present paper for the case of standard Ising model with coupling  $K'$  (with  $K=\beta K'$ ) in the presence of a magnetic field  $h'$  (with  $h=\beta h'$ ). We then calculate the recursive relation for the partition function and the EOS for our model.

In the Ising model on of the  $M$  generations Cayley tree, the total partition function  $\mathcal{Z}_M$  is

$$\mathcal{Z}_M = \sum_{\{S\}} e^K \sum_{ij} S_i S_j + h \sum_i S_i \equiv \sum_{\{S\}} P(S), \quad (7)$$

where  $\sum_{\{S\}}$  is the sum over all the possible spin configurations, and  $\sum_{ij}$  is the sum over all sites  $i$  and its nearest neighbors in the next generation of the tree,  $j$ .

As the Cayley tree is the union of  $\gamma$  identical branches all joined in the root site, we can factorize  $P(S)$ ,

$$P(S) = e^{hS_M} \prod_{k=1}^{\gamma} Q_M(\{S\}_{M-1}^k | S_M), \quad (8)$$

where  $S_M$  is the spin on the root site, the product is on all the  $\gamma$  sub-branches  $k$  emanating from the root site, and

$$Q_M(\{S\}_{M-1}^k | S_M) = e^K \sum_{S_i} S_i S_j + K S_{M-1} S_M + h \sum_{S_i} S_i, \quad (9)$$

where  $\sum_{\mathcal{B}_M^{k*}}$  is the sum over all sites on branch  $\mathcal{B}_M^k$  excluding the site at the origin of the tree. The notation  $Q_M(\{S\}_{M-1}^k | S_M)$  indicates that  $Q_M$  depends on spins of generation  $M-1$  and higher on the  $k^{\text{th}}$  branch. With  $W(S_M) = e^{hS_M}$ , we can rewrite the partition function as

$$\begin{aligned} \mathcal{Z}_M &= \sum_{S_M} e^{hS_M} \prod_{k=1}^{\gamma} \sum_{\{S\}}^{\mathcal{B}_M^{k*}} Q_M(S_{M-1}^k | S_M) \\ &\equiv \sum_{S_M} W(S_M) \prod_{\gamma} Z_M(S_M). \end{aligned} \quad (10)$$

Factorizing  $Q_M(\{S\}_{M-1}^k | S_M)$  as

$$\begin{aligned} Q_M(\{S\}_{M-1}^k | S_M) \\ = e^{KS_M S_{M-1} + hS_{M-1}} \prod_{k=1}^{\gamma-1} Q_{M-1}(\{S\}_{M-2}^k | S_{M-1}), \end{aligned} \quad (11)$$

we obtain

$$Z_M(S_M) = \sum_{S_{M-1}} W(S_M, S_{M-1}) \prod_{k=1}^{\gamma-1} Z_{M-1}(S_{M-1}^k), \quad (12)$$

and the final recursive equation

$$Z_m(S_m) = \sum_{S_{m-1}} W(S_m, S_{m-1}) \prod_{k=1}^{\gamma-1} Z_{m-1}(S_{m-1}^k), \quad (13)$$

which connects partial partition function sums for successive subtrees indexed by different  $m$  values.

Now we obtain the recursive relation for the model presented in Sec. II by a simple extension of the above procedure. In this case the Boltzmann weight  $W(n_m, \sigma_{m,m-1}, n_{m-1}, \sigma_{m-1,m})$  associated with the interaction between the site  $m$  and one of the sites in the set  $\tau_m$  (the  $\gamma-1$  next generation nearest neighbors) depends on both the occupation number and the Potts orientational variables; thus  $W(n_m, \sigma_{m,m-1}, n_{m-1}, \sigma_{m-1,m})$  contains the Boltzmann weights corresponding to the interaction between the site  $m$  and site  $m-1$  and the interaction with the external fields  $P$

( $e^{-\beta P b}$ ) and  $\mu$  ( $e^{\beta \mu}$ ). Using the notation already introduced in Sec. II, we write the recurrence relation

$$Z_m(n_m, \{\sigma\}_m) = \sum_{n_{m-1}, \{\sigma\}_{m-1}} W(n_m, \sigma_{m,m-1}, n_{m-1}, \sigma_{m-1,m}) \prod_{k=1}^{\gamma-1} Z_{m-1}^k(n_{m-1}, \{\sigma\}_{m-1}), \quad (14)$$

where the sum is over all the possible states of  $n_{m-1}$ , and orientation variables associated with the  $m-1$  site,  $\sigma_{m-1, j_{m-1}}$ . The total partition function for the tree is

$$Z_M = \sum_{n_M, \{\sigma\}_M} W(n_M) \prod_{k=1}^{\gamma} Z_M^k(n_M, \{\sigma\}_M), \quad (15)$$

where  $W(n_M)$  is now the Boltzmann weight due to the interaction between the root site and the external field  $\mu$ .

We can explicitly rewrite the recurrence equations:

$$Z_m(1, \{\sigma\}_m) = [e^{\beta \mu} e^{\beta \epsilon} e^{-\beta P b} \{e^{\beta(J-P\delta b)} + (q-1)\}] q^{\gamma-1} [Z_{m-1}(1, \{\sigma\}_{m-1})]^{\gamma-1} + e^{-\beta P b} [Z_{m-1}(0)]^{\gamma-1}, \quad (16)$$

or, by defining  $X = e^{\beta \epsilon'}$ ,  $e^{\beta \epsilon'} = e^{\beta \epsilon} [1 + 1/q(e^{\beta(J-P\delta b)} - 1)]$ , and  $Y = q^\gamma e^{\beta \mu}$ ,

$$Z_m(1, \{\sigma\}_m) = XY e^{-\beta P b} [Z_{m-1}(1, \{\sigma\}_{m-1})]^{\gamma-1} + e^{-\beta P b} [Z_{m-1}(0)]^{\gamma-1} \quad (17)$$

and

$$Z_m(0) = Y e^{-\beta P b} [Z_{m-1}(1, \{\sigma\}_{m-1})]^{\gamma-1} + e^{-\beta P b} [Z_{m-1}(0)]^{\gamma-1}, \quad (18)$$

In deriving Eq. (16), we have included the fact that when the sites in generation  $m$  and  $m-1$  are occupied, there is a contribution to the partition function which includes (i) the occupation of site  $m-1$  ( $e^{\beta \mu}$ ); (ii) a contribution from the Potts variables  $\sigma_{m-1, m-2}$  ( $q^{\gamma-1}$ ) [13]; (iii) a contribution to the volume from  $b_{m, m-1}$  ( $e^{-\beta P b}$ , and  $e^{-\beta P \delta b}$  in the hydrogen bond term below); (iv) a contribution due to the possibility to form a hydrogen bond ( $e^{\beta J} e^{-\beta P \delta b}$ ); and (v) a contribution due to  $q-1$  orientational states where no hydrogen bond is formed.

In the case when the site in generation  $m$  is occupied while the site in iteration  $m-1$  is empty, only the volume effect (ii) is considered. Equation (18) is derived in a similar way.

By defining

$$B_m = [Y e^{-\beta P b} Z_{m-1}^{\gamma-1}(1, \{\sigma\}_{m-1}) + e^{-\beta P b} Z_{m-1}^{\gamma-1}(0)] = Z_m(0) \quad (19)$$

and

$$B_m t_m = [XY e^{-\beta P b} Z_{m-1}^{\gamma-1}(1, \{\sigma\}_{m-1}) + e^{-\beta P b} Z_{m-1}^{\gamma-1}(0)] = Z_m(1, \{\sigma\}_m). \quad (20)$$

the recurrence equations (16) and (18) become

$$B_m = e^{-\beta P b} (Y t_{m-1}^{\gamma-1} + 1) B_{m-1}^{\gamma-1}, \quad (21)$$

$$t_m = \frac{XY t_{m-1}^{\gamma-1} + 1}{Y t_{m-1}^{\gamma-1} + 1}. \quad (22)$$

In the limit of  $M$  going to infinity, Eq. (22) becomes an implicit relation for the unknown variable  $t$ ,

$$t = \frac{XY t^{\gamma-1} + 1}{Y t^{\gamma-1} + 1}. \quad (23)$$

In order to obtain a solution for  $t$ , as input we need a consistent set of values  $P$ ,  $\mu$ , and  $T$  implicitly present in the equation above. As described earlier, such a relation is obtained from a formal evaluation of the free energy  $\Delta$ . Before turning to the calculation of  $\Delta$ , we indicate here how various important quantities may be calculated once the value of  $t$  is known.

It is easily seen that the average occupation number for the root site is given by:

$$\langle n_M \rangle = \frac{q^\gamma e^{-\beta \mu} Z_M^\gamma(1, \{\sigma\}_M)}{q^\gamma e^{-\beta \mu} Z_M^\gamma(1, \{\sigma\}_M) + Z_M^\gamma(0)},$$

that, in the limit of  $M$  goes to infinity, and using Eqs. (19) and (20), becomes

$$\langle n_M \rangle = \langle n \rangle = \frac{Y t^\gamma}{Y t^\gamma + 1}. \quad (24)$$

To write down the equation for the average number of bonds in the system, we have to consider the contribution 1 to the total partition function by the configurations with at least one bond between the root site and one of its nearest neighbors. The total partition function  $Z_M$  may be written, using Eqs. (17) and (18) as

$$Z_M = q^\gamma e^{-\beta\mu} Z_M^\gamma(1, \{\sigma\}_M) + Z_M^\gamma(0) = Y Z_M^{\gamma-1}(1, \{\sigma\}_M) [X Y e^{-\beta P b} Z_{M-1}^{\gamma-1}(1, \{\sigma\}_{M-1}) + e^{-\beta P b} Z_{M-1}^{\gamma-1}(0)] + Z_M^{\gamma-1}(0) \times [Y e^{-\beta P b} Z_{M-1}^{\gamma-1}(1, \{\sigma\}_{M-1}) + e^{-\beta P b} Z_{M-1}^{\gamma-1}(0)]. \quad (25)$$

The number of configurations with one bond between two particles is

$$e^{\beta\mu} q^\gamma Z_M^{\gamma-1}(1, \{\sigma\}_M) e^{\beta\epsilon} e^{\beta J} e^{-\beta P \delta b} q^{\gamma-1} e^{\beta\mu} Z_{M-1}^{\gamma-1}(1, \{\sigma\}_{M-1}) = \frac{e^{\beta\epsilon} e^{\beta J} e^{-\beta P \delta b} e^{-\beta P b}}{q} Y^2 Z_M^{\gamma-1}(1, \{\sigma\}_M) Z_M^{\gamma-1}(1, \{\sigma\}_{M-1}). \quad (26)$$

Finally we can write

$$\langle n_b \rangle = \frac{e^{\beta\epsilon} e^{\beta J} e^{-\beta P \delta b} e^{-\beta P b}}{q} \frac{Y^2 Z_M^{\gamma-1}(1, \{\sigma\}_M) Z_M^{\gamma-1}(1, \{\sigma\}_{M-1})}{Z_M}, \quad (27)$$

which, in the limit of  $M \rightarrow \infty$  and using Eqs. (19) and (20), becomes

$$\langle n_b \rangle = \frac{e^{\beta\epsilon} e^{\beta J} e^{-\beta P \delta b}}{q} \frac{(Y t^{\gamma-1})^2}{Y t^{\gamma-1} (X Y t^{\gamma-1} + 1) + (Y t^{\gamma-1} + 1)}. \quad (28)$$

Finally, the volume per molecule is given by the volume of the system [given by definition (4)] divided by the number of molecules in the system, i.e.,

$$v = \frac{\langle v_{\text{site}} \rangle}{\langle n \rangle} = \frac{v_o + \frac{\delta b}{2} \gamma \langle n_b \rangle}{\langle n \rangle} = v_o + v_o \frac{Y t^{\gamma-1} + 1}{Y t^{\gamma-1} (Y t^{\gamma-1} e^{\beta\epsilon'} + 1)} + \frac{\delta b}{2} \gamma \frac{e^{\beta\epsilon} e^{\beta J} e^{-\beta P \delta b}}{q} \frac{Y t^{\gamma-1}}{(X Y t^{\gamma-1} + 1)}. \quad (29)$$

## B. Calculation of the free energy in the generalized ensemble

We now calculate the free energy for Bethe lattice sites by implementing the method proposed by Gujrati [4]. The Cayley tree  $\mathcal{T}_M$  is the union of  $\gamma$  branches  $\mathcal{B}_M$  connected together at the root site. Similarly, we define  $(\gamma-1)$  trees  $\mathcal{T}_{M-1}^i$ ,  $i = 1, \dots, \gamma-1$ , each of which we obtain as the union of  $\gamma$  branches  $\mathcal{B}_{M-1}$  connected together at the  $\gamma-1$  sites labeled  $M-1$ . Comparing the tree  $\mathcal{T}_M$  with the set  $\mathcal{T}_{M-1}^i$ ,  $i = 1, \dots, \gamma-1$ , it can easily be verified that  $\mathcal{T}_M$  has the same number of surface sites [=  $\gamma(\gamma-1)^{M-1}$ ] as the  $\gamma-1$  trees  $\mathcal{T}_{M-1}^i$  [=  $(\gamma-1) \times \gamma(\gamma-1)^{M-2}$ ]. On the other hand, the number of sites on  $\mathcal{T}_M$  (=  $1 + [\gamma/(\gamma-2)]\{(\gamma-1)^M - 1\}$ ) is greater than the total number of the  $\gamma-1$  copies

$$\begin{aligned} \mathcal{T}_{M-1}^i &= (\gamma-1) \times \{1 + [\gamma/(\gamma-2)]\{(\gamma-1)^{M-1} - 1\}\} \\ &= 1 + [\gamma/(\gamma-2)]\{(\gamma-1)^M - 1\} - 2 \end{aligned}$$

by 2. Similarly,  $\mathcal{T}_M$  has  $\gamma$  more bonds than the  $\gamma-1$  copies  $\mathcal{T}_{M-1}^i$ .

Thus, the ratio of the partition function  $\mathcal{Z}_M$  for  $\mathcal{T}_M$  and the sum of partition functions for the  $\gamma-1$  copies  $\mathcal{T}_{M-1}^i$  (=  $\sum_{i=1}^{\gamma-1} \mathcal{Z}_{M-1}^i$ ), in the limit  $M \rightarrow \infty$ , yields the free energy for two sites (or equivalently,  $\gamma$  bonds) on the Bethe lattice. The Bethe lattice, or bulk, free energy per bond  $\Delta_b$  is thus

$$\Delta_b = \lim_{M \rightarrow \infty} \frac{-k_B T}{\gamma} \left[ \ln \mathcal{Z}_M - \sum_{i=1}^{\gamma-1} \ln \mathcal{Z}_{M-1}^i \right]. \quad (30)$$

$$\mathcal{Z}_M = Y [Z_M(1, \sigma_{M, M-1})]^\gamma + [Z_M(0)]^\gamma = B_M^\gamma (Y t_M^\gamma + 1), \quad (31)$$

$$\mathcal{Z}_{M-1} = B_{M-1}^\gamma (Y t_{M-1}^\gamma + 1), \quad (32)$$

where  $Y$  is as defined earlier, and

$$B_M^\gamma = [e^{-\beta P b} (Y t_{M-1}^{\gamma-1} + 1) B_{M-1}^{\gamma-1}]^\gamma. \quad (33)$$

The final expression for the free energy, in the limit  $M \rightarrow \infty$ , is thus

$$\begin{aligned} \Delta_b &= \frac{1}{\gamma} \ln \left[ \frac{B_M^\gamma}{(B_{M-1}^\gamma)^{\gamma-1}} \frac{(Y t^\gamma + 1)}{(Y t^{\gamma-1} + 1)^{\gamma-1}} \right] \\ &= \frac{1}{\gamma} \ln \left[ e^{-\beta P b \gamma} \frac{(Y t^{\gamma-1} + 1)^\gamma}{(Y t^\gamma + 1)^{\gamma-2}} \right], \end{aligned} \quad (34)$$

which follows from using the relation between  $B_M$  and  $B_{M-1}$  from the previous step, and noting that as  $M \rightarrow \infty$ ,  $t_M = t_{M-1} = t$ , given by Eq. (23). Now, using the fact that the free energy  $\Delta$  in the generalized ensemble is identically zero, we obtain the implicit relation between  $P$ ,  $\mu$ , and  $T$ :

$$e^{\beta P b} = \frac{(Y t^{\gamma-1} + 1)}{(Y t^\gamma + 1)^{(\gamma-2/\gamma)}}. \quad (35)$$

Thus Eqs. (35) and (23) constitute a system of two equations for the four unknown  $t$ ,  $P$ ,  $\mu$ , and  $T$  which, once resolved, allow the evaluation of the EOS (with  $P$  and  $T$  as independent thermodynamic variables) for the model defined

in the generalized ensemble [14]. At the same time, from the  $t$  values it is possible to calculate the average number of hydrogen bonds [Eq. (28)], in addition to the system volume [Eq. (29)] and other thermodynamic quantities of interest.

Before concluding this section, we write the exact solution for our model in one dimension, which can be obtained from the results above simply by choosing  $\gamma=2$ , since the Bethe lattice for  $\gamma=2$  is identical to the one-dimensional regular lattice. With  $\gamma=2$ , Eq. (35) becomes

$$Yt^{\gamma-1} = e^{\beta P b} - 1, \quad (36)$$

$$v = b + b \frac{e^{\beta P b}}{(e^{\beta P b} - 1)[(e^{\beta P b} - 1)e^{\beta \epsilon'} + 1]} + \delta b \frac{e^{\beta \epsilon} e^{\beta J} e^{-\beta P \delta b}}{q} \frac{(e^{\beta P b} - 1)}{[(e^{\beta P b} - 1)e^{\beta \epsilon'} + 1]}, \quad (37)$$

which coincide with the previously derived one-dimensional result [5].

### C. Percolation quantities

The solution of lattice models on the Bethe lattice is particularly useful if we require thermodynamic information together with the evaluation of connectivity properties [15]. In the case of water, it has been suggested that the hydrogen bond connectivity [16], and in particular the connectivity of the four-bonded molecules, plays a significant role in the liquid dynamics [17,18] and thermodynamic behavior. Because the model we consider does not introduce any correlation between adjacent bonds [as seen from the Hamiltonian in Eq. (5)], the percolation problem is of the correlated site-random bond type [19,20]. Starting from an occupied site at the origin of the tree, the probability to have a hydrogen bond between two sites can be written as the conditional probability to find both sites occupied  $P(1|1)$  times the probability  $p_b$  that a hydrogen bond exists between them. From well known results for the Cayley tree [21], an infinite spanning cluster of hydrogen bonds appears when the probability to have a hydrogen bond becomes equal to  $(\gamma - 1)^{-1}$ .

In our model the probability  $P(11)$  of finding two molecules in two nearest neighbor sites (using calculations analogous to Sec. II) is given by

$$P(11) = \frac{X(Yt^{\gamma-1})^2}{Yt^{\gamma-1}(XYt^{\gamma-1} + 1) + (Yt^{\gamma-1} + 1)}. \quad (38)$$

Using the law of conditional probability [ $P(A|A) = P(AA)/P(A)$ ], obtaining the occupation probability of an arbitrarily chosen site [ $P(A)$ ] from Eqs. (24), we have

$$P(1|1) = \frac{Yt^{\gamma-1}X}{XYt^{\gamma-1} + 1}. \quad (39)$$

The probability to have a bond between two occupied sites is

$$p_b = \frac{e^{\beta J} e^{-\beta P \delta b}}{(q-1) + e^{\beta J} e^{-\beta P \delta b}}. \quad (40)$$

The percolation curve is then given by:

$$P(1|1)p_b = \frac{e^{\beta J} e^{-\beta P \delta b}}{(q-1) + e^{\beta J} e^{-\beta P \delta b}} \frac{XYt^{\gamma-1}}{XYt^{\gamma-1} + 1} = \frac{1}{\gamma-1}. \quad (41)$$

The expression above, in the limit of  $p_b=1$ , becomes the expression for a correlated site percolation problem on the lattice and, with the substitution [22]  $z=Yt^{\gamma-1}$ , coincides with the result previously derived by Murata [23] in the mean field approximation. The percolation properties of the four-bonded molecules [16] can also be derived within the framework of the present model. Let us consider a tree with coordination number  $\gamma=4$ . If a chosen site  $i$  belongs to a given cluster of four-bonded molecules, the probability that a neighbor site  $j$  also belongs to the same cluster is equal to the probability for this site to have three more occupied neighbors which are hydrogen bonded to it, since the initial site  $i$  is already known to be occupied and hydrogen bonded with  $j$  (indeed the site  $i$  must have four bonds to belong to the cluster). The percolation curve for four-bonded molecules on a lattice with  $\gamma=4$  is then given by

$$[p_b P(1|1)]^3 = \frac{1}{3}, \quad (42)$$

or

$$\frac{e^{\beta J} e^{-\beta P \delta b}}{(q-1) + e^{\beta J} e^{-\beta P \delta b}} \frac{Yt^{\gamma-1}X}{XYt^{\gamma-1} + 1} = \left(\frac{1}{3}\right)^{1/3}. \quad (43)$$

Note that this result is applicable to the percolation of occupied ‘‘four-bonded’’ sites.

## IV. RESULTS

In this section we compare the predictions of the model presented in Sec. II solved exactly on the Bethe lattice with the previously derived mean-field (Bragg-Williams) results. We evaluated the EOS for the same parameters chosen in Ref. [5], i.e.,  $\gamma=4$ ,  $\delta b/b=0.953$ ,  $J/\epsilon=0.25$ , and  $q=100$ . We have evaluated the locus of density maxima (TMD), i.e., the curve along which, by following an isobaric path, the density has a maximum, the locus of the isothermal compressibility extrema (TEC), the spinodal curve (where the compressibility diverges), and the percolation curve for the four-bonded molecules. Note that the spinodal line, as well as *metastable* extensions of the liquid phase (also gas), arise in mean field and related solutions of phase behavior. Both can exist at negative pressures. While equilibrium states (and solutions) can only occur at positive pressures (see, e.g., Ref. [24]), negative pressure states (and metastable states in general) are routinely observed on experimental (and longer) time scales for real materials. The TMD and TEC lines arise in liquids which show density anomalies, i.e., liquids which show a nonmonotonic dependence of the density on the temperature at a constant pressure. The model we study was indeed originally developed to clarify the relation between the temperature dependence of density and isothermal compressibility. We refer the reader interested in the thermodynamics of liquids with a TMD to Refs. [8,9]. In this paper,

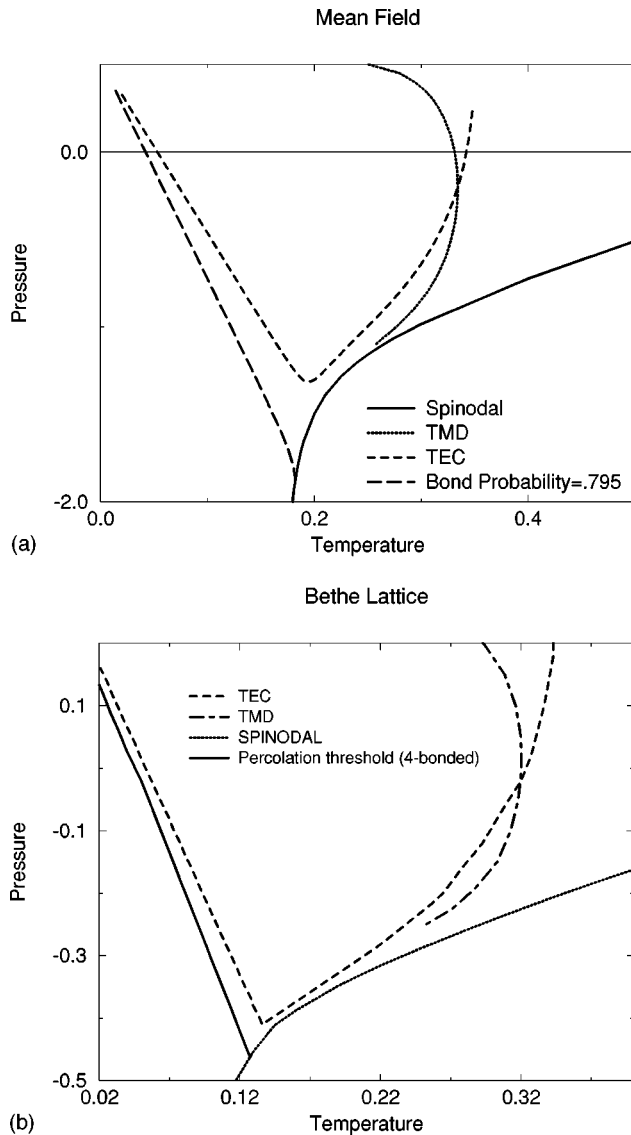


FIG. 2. Comparison between the phase diagram obtained in the Bragg-Williams mean field approximation [5] (top graph) and in the Bethe-Peierls approximation (bottom graph). Both of these diagrams show the TMD line, spinodal line, and TEC line. The TEC line meets the TMD line at the retracting point. Note that below  $T$ , at which the  $K_T$  extrema locus displays a minimum, the extrema are maxima, while above they are minima. Also shown is the  $p_b = 0.795$  locus in the top graph and the percolation curve for four-bonded molecules in the bottom graph. Temperature is expressed in units of  $\epsilon/k_B$ , and pressure in units of  $\epsilon/v_o$ .

which is focused on the possibility of solving models defined in the generalized ensemble on the Bethe lattice, we limit ourselves to the comparison of the EOS, which is presented in Fig. 2.

Apart from an upward shift of  $T$  and  $P$ , the shape of the phase diagram does not change on going from the Bragg-Williams approximation to the Bethe lattice solution. We confirm that the TMD line changes slope in the  $(P, T)$  plane and that it does not meet the spinodal line, which does not retrace (i.e., whose pressure values do not display an extremum as a function of temperature), in accordance with thermodynamic analyses which show that the intersection of the TMD and the spinodal would require such retracing for ther-

modynamic consistency [25,26]. The TMD meet the TEC with an infinite slope, as it must for thermodynamic consistency [5]. The TEC has a minimum which separates the temperature range of compressibility maxima (left side) and minima (right side).

We also calculate the percolation curve for four-bonded molecules. This evaluation constitutes a consistent determination of such a line within the framework of a well defined microscopic model of water. Unlike previous attempts, we take into account the correlation between the positions of the molecules (site occupation in our model). We find that the percolation curve is almost coincident with the TEC line. We note that the “percolation model” of the anomalous properties of water, while predicting a percolation transition, does not predict any thermodynamic anomalies at the percolation line, and, further, predicts a compressibility extremum that is not coincident with the percolation threshold [16].

## V. CONCLUSIONS

In this paper we have described a procedure to solve exactly lattice gas models defined in the generalized ensemble on the Bethe lattice. We have applied this method to a recently proposed model which includes a coupling between bond energy and local volume and which requires the use of the generalized ensemble. The apparent disadvantage of working in an overdefined ensemble, i.e., in an ensemble where the corresponding free energy is identically zero, is utilized as a consistency condition to obtain a relation between intensive variables  $P$ ,  $\mu$ , and  $T$ . In order to do so, we have extended to the generalized ensemble the method of Gujrati [4] for the calculation of the free energy on the Bethe lattice. By specializing the calculation of  $\Delta$  to the model described in Sec. II, we have calculated the equation of state, and compared with the previously published mean field (Bragg-Williams) results [5].

The improvement over the basic mean field approximation achieved with the solution on the Bethe lattice is particularly important because it allows a simultaneous determination of thermodynamic and percolation properties. In the case of liquid water, percolation properties have been discussed at length [16,18,17], but they have never been calculated consistently from a well defined microscopic model. The results presented here suggest that, in our model, a direct relation does not exist between the location of the percolation threshold for four-bonded molecules and the line of compressibility extrema. We also note that the present model does not include any correlation between hydrogen bonds, which has been thought to be relevant for the understanding of the behavior of supercooled water. An extension of the present model to include hydrogen bond correlations and an exact solution on the Bethe Lattice is feasible, and will be pursued in the future with the approach described in this paper.

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The generalized ensemble arises as the appropriate ensemble to describe a physical system when the system is in thermal (exchange of heat), mechanical (change of volume), and material (exchange of particles) equilibrium with its surroundings. A simple example of such a system is a crystal immersed in a solution of the same material. More practical and real world examples may be found, such as the typical setup for osmotic stress experiments [27] that have been used extensively to probe forces organizing biomolecular systems.
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- [10] Note that no orientational states are associated with an unoccupied site. Thus the orientational degeneracy of an unoccupied site is equal to 1.
- [11] The exact solution of the model was also obtained in one dimension in Ref. [5], which reduces to the correct result for a simple lattice gas in the appropriate limit of fixed volume per site and orientational state.
- [12] Restricting attention to nearest neighbor interactions, the equivalence of an exact solution for the Bethe lattice and the Bethe-Peierls approximation can easily be seen by noting that the absence of loops in the Cayley tree makes it possible to represent exactly the influence of the ‘rest of the system’ by an effective chemical potential.
- [13] Note in this context that the  $\{\sigma\}_{m-1}$  in the  $Z_{m-1}$ ’s above indicates that the  $Z_{m-1}$  are evaluated for an arbitrary fixed value of the  $\{\sigma\}_{m-1}$ ; the degeneracies are accounted for explicitly as described in points (ii), (iv), and (v) of Sec. III A.
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