

Statistical thermodynamics of lattice models

Jianhua Xing^{a)}

Department of Chemistry and Kenneth S. Pitzer Center for Theoretical Chemistry, University of California at Berkeley, and Chemical Science Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720-1460

(Received 5 July 2001; accepted 20 August 2001)

This work is a generalization of the work of Widom [J. Chem. Phys. **39**, 2808 (1963)] and of Henderson [Mol. Phys. **95**, 187 (1998)]. Based on geometric analysis and statistical thermodynamics arguments, a set of sum rules for two-component nearest-neighbor interaction models at thermodynamic equilibrium is derived. By choosing the density of one component ρ and the unlike-bond density ρ_{12} as two variables, it is shown that the energy is well-behaved; however, the entropy, $\bar{s}(\rho, \rho_{12})$, is independent of ρ within two-phase regions, but not outside. Temperature and chemical potentials determine the equilibrium ρ and ρ_{12} . The exact entropy function for 1-D systems can be calculated, and an exact free energy density function is formulated. The result shows that \bar{s} is always dependent on ρ except at $\rho_{12}=0$, which excludes the possibility of phase transitions at finite temperature. © 2001 American Institute of Physics. [DOI: 10.1063/1.1410115]

I. INTRODUCTION

Phase transitions have long been one of the central topics of physics. Among all the theoretical models studied, the Ising model¹ is undoubtedly one of the most important and widely studied. A major breakthrough was due to Onsager,² who solved the two-dimensional square lattice Ising model with zero external field. Subsequently Yang worked out the magnetic moment of this system at infinitesimal external field, and thus the coexistence curve.³ However, it still remains one of the greatest challenges in physics to solve the Ising model with dimension larger than 1, at nonzero external field, thus to reveal how first-order phase transitions occur.

In a seminal paper,⁴ Widom applied his potential distribution theory (PDT) to the lattice gas problem, which can be mapped to the Ising model exactly. With conventional methods, calculation of the partition function is required to solve the problem. Instead, based on geometric and statistical thermodynamics considerations, Widom obtained a set of sum rules to connect microscopic quantities, O_r , and thermodynamic quantities like internal energy. Here O_r is defined to be the equilibrium probability that an empty cell has exactly r filled neighbors. Then, with help of the Gibbs–Duhem equation, Widom transformed the one-dimensional lattice gas problem into a first-order differential equation. By solving this equation, he obtained the correct equation of state. For higher dimensions, however, more sum rules are needed.

Recently, Henderson re-examined Widom's approach to lattice gas problems.⁵ He introduced a notation \tilde{O}_r to denote the probability of finding exactly r occupied nearest-neighbors surrounding a filled cell. He discovered that \tilde{O}_r and O_r were not independent of each other. He proposed a set of relations to connect them, which will be called Henderson relations in the remaining part of the paper. Then he

could rederive Widom's sum rules in a slightly different way. Henderson also examined a test-site method to obtain approximate expressions for the pressure.

The present paper is a generalization of Widom's and Henderson's work, and provides a new way to look at phase transitions in nearest-neighbor interaction models. In Sec. II of this paper, Widom's formulation is generalized to models with arbitrary nearest-neighbor (nn) interactions, following essentially the route adopted by Henderson. Henderson's relations are also generalized and a simple proof is given. In Sec. III, some general features of two phase coexistence regions are explored. Then, specific analyses are taken for 1-D and higher-dimensional models. Especially an exact free energy function is constructed for the 1-D model, which is a major result of this work.

II. GENERALIZED WIDOM'S FORMULATION FOR NEAREST-NEIGHBOR INTERACTION MODELS

The system under consideration is defined on a lattice with coordination number z . Every cell on the lattice is occupied by either particle type 1 or type 2 (generalization to multi-component models is straightforward). Only nearest-neighbor pairs have interactions, and the Hamiltonian is given by

$$\mathcal{H} = \mu_1 N + \mu_2 (\mathcal{N} - N) + \sum_{\langle s_i, s_j \rangle} (-1)^{s_i + s_j + 1} e_{s_i, s_j}, \quad (2.1)$$

where s_i takes value 1 or 2; μ_1 and μ_2 refer to the chemical potentials of particle 1 and 2, respectively; \mathcal{N} is the total number of lattice cells, and N is the total number of type-1 particles; $-e_{11}$, e_{12} , and $-e_{22}$ correspond to the 1-1, 1-2, and 2-2 bond interactions (attractions between like particles are assumed), respectively; $\langle \cdot \rangle$ refers to nearest-neighbor pairs. Notice that the lattice gas model is obtained with the choice $e_{12} = e_{22} = \mu_2 = 0$ (the type 2 particles are empty

^{a)}Electronic mail: xing@neon.cchem.berkeley.edu

cells), and the Ising model is recover by setting $e_{12}=e_{22}=e_{11}$, $\mu_2=-\mu_1$ (which are really related to the external magnetic field h). The present version of the Ising model is slightly different from the usual definition since the current one is defined in the cells rather than on the lattice sites.

One may define the type 1 particle density as $\rho=N/\mathcal{N}$, and the entropy per site, \tilde{s} . Two quantities related to the thermodynamic energy U are defined as

$$\tilde{u}=-U/\mathcal{N}, \tag{2.2}$$

$$u=-U/N-\tilde{u}/\rho. \tag{2.3}$$

In addition, units are chosen so that $e_{11}=1$, and the Boltzmann constant $k_B=1$. Then the free energy per site, \tilde{F} ,⁶ is given by

$$\tilde{F}=-\tilde{u}-T\tilde{s}-\mu_1\rho-\mu_2(1-\rho). \tag{2.4}$$

Pure geometric considerations give

$$\sum_r O_r=1, \tag{2.5}$$

$$\sum_r \tilde{O}_r=1, \tag{2.6}$$

$$\sum_r rO_r=z\rho_\omega, \tag{2.7}$$

$$\sum_r r\tilde{O}_r=z\tilde{\rho}_\omega, \tag{2.8}$$

$$1-\tilde{\rho}_\omega=f\rho_\omega, \tag{2.9}$$

$$1=\rho_{11}+\rho_{12}+\rho_{22}, \tag{2.10}$$

$$2\rho=2\rho_{11}+\rho_{12}, \tag{2.11}$$

$$\rho_{11}=\rho\left(\sum_r r\tilde{O}_r\right)/z, \tag{2.12}$$

$$\rho_{12}=2(1-\rho)\left(\sum_r rO_r\right)/z, \tag{2.13}$$

$$\rho_{22}=(1-\rho)\left(z-\sum_r rO_r\right)/z, \tag{2.14}$$

where

$$f=\frac{1-\rho}{\rho}. \tag{2.15}$$

And $\{\rho_{ij}\}$ are related to the total number of $i-j$ type bond v_{ij} by

$$\rho_{ij}=2v_{ij}/(z\mathcal{N}). \tag{2.16}$$

$\tilde{\rho}_\omega$ and ρ_ω refer to the conditional probability of finding a type 1 particle next to a type 1 particle and a type 2 particle, respectively. In addition, one has the following relation:

$$\rho_{11}-\rho_{12}e_{12}+\rho_{22}e_{22}=2\rho u/z=2\tilde{u}/z. \tag{2.17}$$

On the other hand, one may focus on a block of sites (which may have arbitrary shape), and treat the surroundings

as the environment. In this case, the grand canonical ensemble is appropriate. If P_a is the probability of finding a particular configuration a , one has

$$P_a=\gamma_a e^{\beta[\mu_1 n_a+\mu_2(1-n_a)]} e^{-\beta U_a^I} e^{-\beta U_a^S}/\Xi, \tag{2.18}$$

where $\beta=1/T$, n_a is the number of type 1 particles in configuration a , Ξ is the usual grand canonical partition function of the system, and γ is the symmetry number of the configuration. For example, on a two-dimensional rectangular lattice, a cluster which includes a central particle 1, plus one particle 1 and three particle 2 neighbors, has $\gamma=4$ if the location of the outer particle 1 is not distinguished. U^S and U^I are the cluster self-interaction and the interaction between the cluster and the surrounding, respectively. (If one applies a mean-field approximation to U^I , the so-called Bethe's approximation and higher-order approximations can be obtained.⁷) With nearest-neighbor interactions, U^I is only dependent on the boundary configuration of the cluster. Therefore, for two different clusters a and b with the same boundary configuration, the cluster-surrounding interactions are the same, and one has

$$\frac{P_a}{P_b}=\frac{\gamma_a}{\gamma_b} e^{\beta\mu_1(n_a-n_b)+\beta\mu_2[(1-n_a)-(1-n_b)]} e^{-\beta(U_a^S-U_b^S)}. \tag{2.19}$$

The cluster considered by Henderson⁵ is a star type cluster composed of a center and its neighbor cells. If a refers to a star cluster with the center cell occupied by a type 1 particle, and b a star cluster with a type 2 particle in its center, one has

$$\frac{P_a}{P_b}=\zeta x^r, \tag{2.20}$$

where

$$\zeta=e^{\beta(\mu_1-\mu_2)} e^{-z\beta(e_{12}+e_{22})}, \tag{2.21}$$

$$x=e^{\beta(1+2e_{12}+e_{22})}. \tag{2.22}$$

Since the cluster is in equilibrium with the whole lattice, one can easily show that

$$\frac{\rho\tilde{O}_r}{(1-\rho)O_r}=\frac{P_a}{P_b}=\zeta x^r, \tag{2.23}$$

where $\tilde{O}_r(O_r)$ denotes the probability of finding exactly r type 1 particles surrounding a cell occupied by a type 1(2) particle, following Henderson's notation. For lattice gas systems, the above set of relations reduce to those obtained by Henderson. It should be pointed out that the above relations hold even for nonuniform systems, but ρ , \tilde{O}_r , and O_r should then refer to local quantities.

By rearranging the above equations to eliminate ρ_ω , $\tilde{\rho}_\omega$, $\{\rho_{ij}\}$, and \tilde{O}_r , we obtain the final results:

$$\sum_r O_r=1, \tag{2.24}$$

$$\sum_r x^r O_r=\frac{1}{f\zeta}, \tag{2.25}$$

$$\sum_r r O_r = \frac{z(1+fe_{22})-2u}{f(1+2e_{12}+e_{22})}, \quad (2.26)$$

$$\sum_r rx^r O_r = \frac{z[2e_{12}+(1-f)e_{22}]+2u}{f\xi(1+2e_{12}+e_{22})}. \quad (2.27)$$

It should be pointed out that the reduced energy u (or \bar{u}) is a function only of the geometric quantities ρ and ρ_{12} . From Eqs. (2.10), (2.11), (2.17), one can easily see that only two of the quantities $\{\rho_{ij}\}$, ρ , and u (or \bar{u}) are independent, except in one of the following two situations: $e_{22}=0$, and $e_{12}=-1/2$; or $1+e_{22}+2e_{12}=0$. Therefore, specifying any two of them will fix the remaining ones. This is a crucial observation for the following discussion.

One may define analogous quantities of $\{O_r\}$ and $\{\bar{O}_r\}$ for larger clusters, e.g., a cluster composed of two adjacent sites and their nearest-neighbors. Following a procedure similar to what discussed in this section, one may obtain sum rules for these quantities.

III. GENERAL FEATURES OF PHASE TRANSITIONS

According to the second law of thermodynamics, for a reversible process with fixed temperature T , chemical potential μ , and volume (or the total number of lattice sites \mathcal{N}), the following relation holds:

$$dU = T dS + \Delta\mu dN, \quad (3.1)$$

where U , S , and N are the internal energy, entropy, and the number of particle one, respectively, and $\Delta\mu = \mu_1 - \mu_2$ is the chemical potential difference of the two components. The usual pressure-volume term has been dropped for lattice models.⁷ By dividing \mathcal{N} on both sides, one obtains the following relation involving only intensive quantities:

$$-d\bar{u} = T d\bar{s} + \Delta\mu d\rho. \quad (3.2)$$

One can easily show that the above relation is equivalent to minimize the following free energy function at fixed T , and $\Delta\mu$,

$$\mathcal{F}(\bar{u}, \rho) = -\bar{u} - T\bar{s}(\bar{u}, \rho) - \Delta\mu\rho. \quad (3.3)$$

Due to geometric constraint, for a given density ρ, ρ_{12} can only take values within $[0, 2\rho]$ if $\rho \leq \frac{1}{2}$, and within $[0, 2(1-\rho)]$ if $\rho > \frac{1}{2}$. From Eqs. (2.10), (2.11), (2.17), one obtains

$$\bar{u} = \frac{z}{2} \left[(1-e_{22})\rho - \frac{1}{2}(1+2e_{12}+e_{22})\rho_{12} + e_{22} \right]. \quad (3.4)$$

Then \mathcal{F} can be viewed as a function of ρ and ρ_{12} .

First, let's examine the symmetric case where $e_{22}=e_{11}=1$. The above equation shows that on the $(\rho-\rho_{12})$ plane, the isoenergetic lines are straight lines with zero slope. Furthermore, when ρ varies inside the two-phase region, the percentages of the two phases vary, but the total energy is unchanged. Therefore, the portion of an isoenergetic line within the two-phase region must be part of an isotherm for certain temperature. This implies the entropy per site \bar{s} is independent of ρ within the two-phase region. This final con-

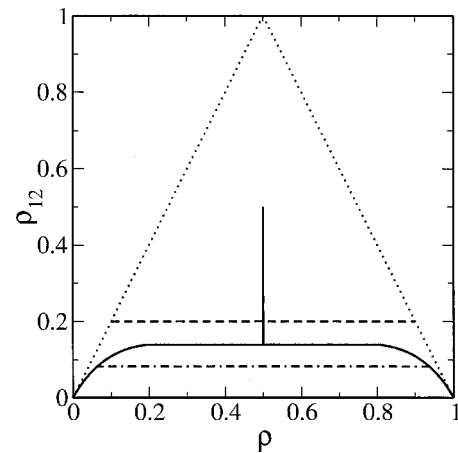


FIG. 1. Thermodynamic quantities on the $\rho-\rho_{12}$ plane. Under the dotted lines is the physical region. The dashed line is a typical isoenergetic line; the dash-dotted line, an isoentropic line inside the two-phase coexistence region; the solid line, the coexistence curve of a 2-D rectangular Ising model calculated from Onsager's result.

clusion also holds for asymmetric cases within the same region on the $\rho-\rho_{12}$ plane, since \bar{s} is independent of the interaction parameters.

The principles of thermodynamics then dictate that the equilibrium free energy of the system \bar{F} is obtained by minimizing \mathcal{F} ,

$$\frac{\partial \mathcal{F}}{\partial \rho_{12}} = \frac{z}{4}(1+2e_{12}+e_{22}) - T \frac{\partial \bar{s}}{\partial \rho_{12}} = 0, \quad (3.5)$$

$$\frac{\partial \mathcal{F}}{\partial \rho} = -\frac{z}{2}[1-e_{22}] - T \frac{\partial \bar{s}}{\partial \rho} + (\mu_1 - \mu_2) = 0. \quad (3.6)$$

Figure 1 shows the physically accessible region on the $\rho-\rho_{12}$ plane. A typical isoenergetic line is given. The coexistence curve of a 2-D rectangular Ising model calculated from Onsager's result is also shown. Within the coexistence region, \bar{s} is independent of ρ , as shown in the figure.

What happens at the boundary of the two-phase region? \bar{s} might no longer be independent of ρ in the one-phase region. This implies that the underlying reason for phase transitions and critical phenomena in nn models is purely *geometric*: $\bar{s}(\rho, \rho_{12})$ has different behaviors in two regions on the $\rho-\rho_{12}$ plane, which has nothing to do with thermodynamic quantities like the temperature T , not even the interaction parameters. A direct consequence is that all of the nn models defined on the same lattice should have the same coexistence curve on the $\rho-\rho_{12}$ plane.

To illustrate that \bar{s} becomes dependent on ρ outside the two-phase region, a formula is derived in the Appendix to calculate \bar{s} at the limit of small ρ and small ρ_{12} . Some results are shown in Fig. 2. Because only three types of clusters are included, the resulting free energy function has a double-well shape, as is typical for any mean-field type free energy function. It can be seen that \bar{s} reaches its maximum faster when the coordination number z increases. When all types of clusters are correctly included, \bar{s} is expected to reach its maximum at $\rho=1/2$ (for the 1-D case) or reaches a constant plateau (for higher dimensions).

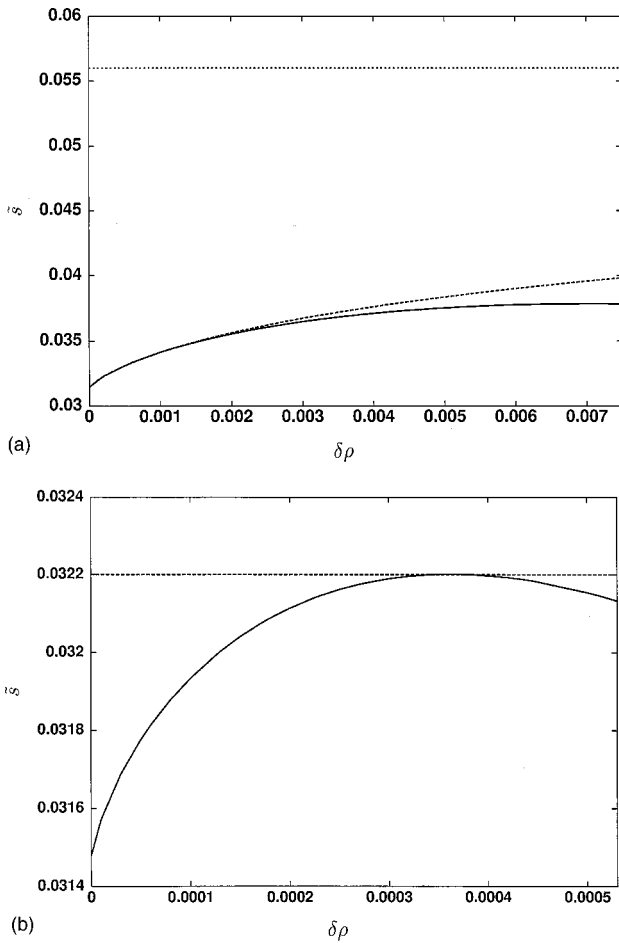


FIG. 2. Entropy \bar{s} calculated by Eq. (A3) with different coordination numbers 2(a), 4(b). The value of ρ_{12} is taken as 0.01, and the x axis is $\delta\rho = \rho - \rho_{12}/2$. On a, the long-dashed line is the result calculated with the exact formula Eq. (4.3), and the short-dashed line refers to the exact value of \bar{s} at $\rho = 1/2$. On b, the long-dashed line refers to the exact value of \bar{s} at $\rho = 1/2$ from Onsager's result.

The effect of temperature T on the system is to locate the equilibrium state. At $T=0$ and $\Delta\mu=0$, the system chooses $\rho_{12}=0$. When T increases, the system moves up on the $\rho - \rho_{12}$ plane. At infinite T limit, the system reaches $\rho = \rho_{12} = 1/2$, where \bar{s} reaches its maximum. On the $\rho - \rho_{12}$ plane, the region above $\rho_{12} = 1/2$ corresponds to the case that the interactions between like particles are repulsive (the anti-ferromagnet case for an Ising model). In this region, the density ρ is not a good variable to describe phase transitions.

An infinitesimal external field can shift the system from the two-phase region to one of the coexistence boundary, due to the term $\Delta\mu\rho$.

IV. FREE ENERGY FUNCTION OF A 1-D ISING MODEL

For simplicity we will focus on the Ising-type model in the following discussion (that is, $e_{12}=e_{22}=1$), although it can be generalized to general 1-D nn models.

The main step of the calculation is to determine the configuration degeneracy g with a fixed number of type 1 particles, N , and energy $U = -\mathcal{N}\bar{u}$. The problem is equivalent to finding g with fixed N and $\{v_{ij}\}$, the number of each type of bonds. For 1-D systems, the degeneracy can be worked out

in the following way. One can easily show that v_{12} is even. First, $v_{12}/2$ type 1 particles are placed at every other site starting from site 1, and $v_{12}/2$ type 2 particles are placed at every other site starting from site 2. Next, the remaining type 1 particles are inserted one by one between two nn sites with at least one existing type 1 particle, and the remaining type 2 particles are inserted one by one between two nn sites with at least one existing type 2 particle. This procedure is equivalent to assigning v_{11} indistinguishable bosons to $v_{12}/2$ degenerate states, and v_{22} other indistinguishable bosons to another $v_{12}/2$ degenerate states. Therefore, g is given by

$$g = 2 \frac{(v_{11} + v_{12}/2)! (v_{22} + v_{12}/2)!}{v_{11}!(v_{12}/2)! v_{22}!(v_{12}/2)!} \tag{4.1}$$

The factor 2 comes from the fact that one can redo the above procedures except switching the particle types.

By applying Stirling's formula in the thermodynamic limit and using Eqs. (2.10), (2.11), and (2.17), one obtains

$$\begin{aligned} \frac{2}{z}\bar{s} &= \frac{\ln g}{z\mathcal{N}/2} = (\rho_{11} + \rho_{12}/2)\ln(\rho_{11} + \rho_{12}/2) \\ &\quad + (\rho_{22} + \rho_{12}/2)\ln(\rho_{22} + \rho_{12}/2) - \rho_{11}\ln\rho_{11} \\ &\quad - \rho_{12}\ln(\rho_{12}/2) - \rho_{22}\ln\rho_{22} \\ &= \frac{z\rho}{2}\ln\frac{z\rho}{2} + \frac{z(1-\rho)}{2}\ln\frac{z(1-\rho)}{2} - \frac{z-2\rho u}{4} \\ &\quad \times \ln\frac{z-2\rho u}{8} + \frac{2\rho(u-2z)+3z}{8} \\ &\quad \times \ln\frac{2\rho(u-2z)+3z}{8} + \frac{2\rho(u+2z)-z}{8} \\ &\quad \times \ln\frac{2\rho(u+2z)-z}{8}, \end{aligned} \tag{4.2}$$

where $z=2$. A contour plot of \bar{s} is shown in Fig. 3. No portion of the plot shows that \bar{s} is independent of ρ except at $\rho_{12}=0$, which excludes the possibility of phase transitions in 1-D nn interaction systems at finite temperature.

Except for the case $\Delta\mu=0$ ($\zeta = x^{-1}$), one can solve for u from Eqs. (2.24)–(2.27):

$$u = \frac{4\rho[x(z-2)-z] + z - zx + \zeta x[8 - 8\rho + z(x-1)]}{2\rho(x-1)(\zeta x - 1)} \tag{4.4}$$

In Eq. (3.3), ρ cannot vary freely, but is constrained by the requirement that $\{O_r\}$ must be in the range of $[0, 1]$. The thermodynamic equilibrium state is located by minimizing the above function with respect to ρ at fixed x and ζ . Numerical tests verified that the resultant equilibrium ρ , u , and F agree with those obtained through the partition function.⁸ The possible range that ρ can vary decreases as $|\Delta\mu|$ decreases. For $\Delta\mu=0$ and finite temperature, Eqs. (2.24)–(2.27) have no solution except for $\rho=1/2$, in which case an infinite number of solutions exist. Therefore, the equilibrium thermodynamic quantities can only be obtained by minimizing the free energy functional with respect to u . This shrink-

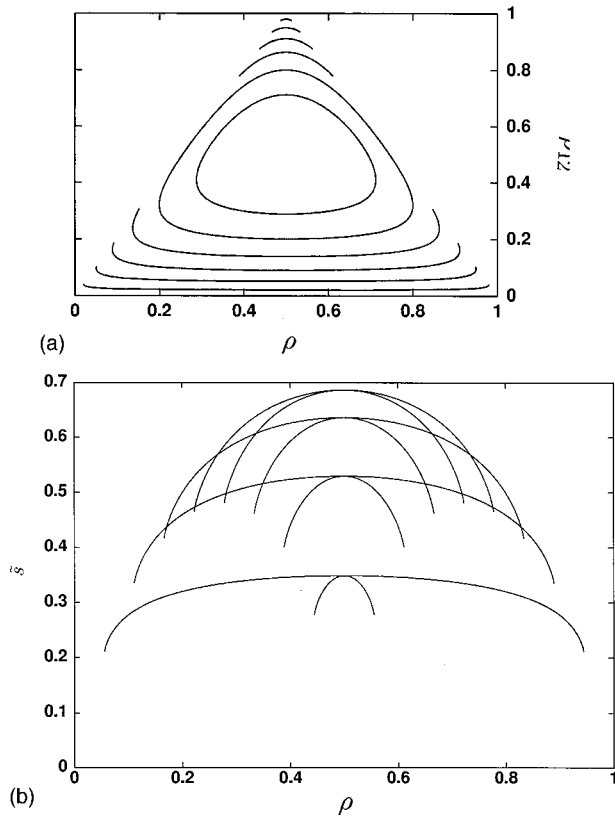


FIG. 3. (a) Contour plot of \bar{s} as a function of ρ and ρ_{12} for 1-D systems. The contour lines are equally spaced with 0.1 units from 0.1 to 0.6. (b) \bar{s} as a function of ρ with fixed ρ_{12} valued from 0.0 to 1.0 with interval 0.1. The possible range of ρ decreases with increasing ρ_{12} . Notice that values of \bar{s} at $\rho_{12}=0.0$ and $\rho_{12}=1.0$ are zero.

ing of the range of ρ again excludes the possibility of phase transitions. Some typical results are shown in Fig. 4.

For higher dimensions, it is expected that the contour plot of \bar{s} is similar to the 1-D case, and also has a maximum

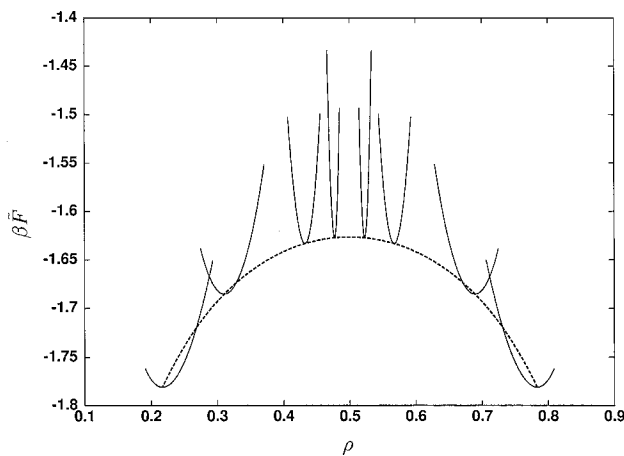


FIG. 4. Equilibrium free energy $\beta\bar{F}$ of a 1-D Ising model as a function of ρ with $\Delta\mu$ varied from -0.5 to 0.5 (dashed line). The temperature T is fixed at 2.0 . The results calculated from Eq. (3.3) agree with those calculated from the partition function. The solid lines are the free energy functions $\beta\bar{F}$ defined in Eq. (3.3) with $\Delta\mu$ takes the value (from left to right) $-0.5, -0.3, -0.1, -0.05, 0.05, 0.1, 0.3, 0.5$, respectively. Notice that the possible varying range of ρ decreases when $\Delta\mu$ approaches zero.

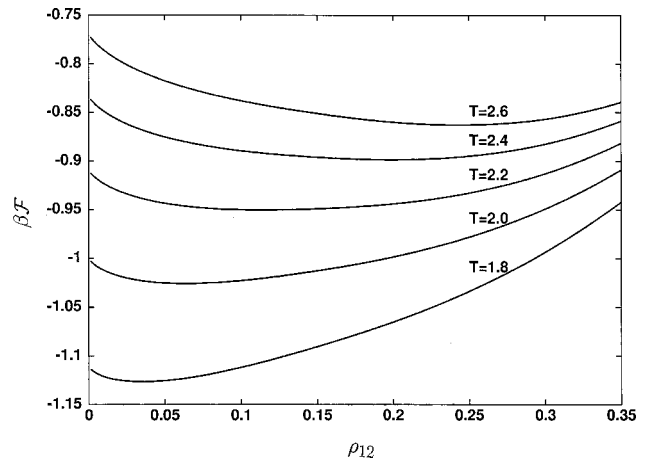


FIG. 5. The free energy function $\beta\mathcal{F}$ defined in Eq. (3.3) for a 2-D rectangular Ising model as a function of ρ_{12} . The entropy function \bar{s} is calculated from Eq. (5.1). ρ is fixed at 0.5 , and $\Delta\mu=0$. The minima of $\beta\mathcal{F}$ are the equilibrium free energy βF at different temperature T , respectively. Within the two-phase region, $\beta\mathcal{F}$ is independent of ρ .

at $\rho=\rho_{12}=1/2$. The only difference from the 1-D case is that there exists a value of $\rho_{12}<1/2$. Below this ρ_{12} value, there are regions where \bar{s} is independent of ρ .

V. HIGHER DIMENSIONAL SYSTEMS

In the above discussion, a central step is to calculate the degeneracy $g(N, \mathcal{N}, \nu_{12})$, or the entropy density $\bar{s}(\rho, \rho_{12})$. For systems in higher dimensions, it is very difficult to calculate \bar{s} . However, since \bar{s} is just a geometry factor, once one nn interaction model is solved, solutions for other nn models defined on the same type of lattice can be obtained from the existing solution by minimizing the free energy density function Eq. (3.3).

To demonstrate that the minimum of Eq. (3.3) does give the correct thermodynamic equilibrium state, a square lattice Ising model is studied within the two-phase region, while $\Delta\mu=0$, the entropy function $\bar{s}_{\rho, \rho_{12}}$ is given by

$$\bar{s}(\rho, \rho_{12}) = \frac{1}{T^*(\rho, \rho_{12})} [-\tilde{F}^*(\rho, \rho_{12}) - \rho u^*(\rho, \rho_{12})], \quad (5.1)$$

where \tilde{F}^* , u^* , and T^* are the equilibrium quantities of the Ising model obtained from Onsager's solution at certain values of ρ and ρ_{12} .² It is found that Eq. (3.3) does have its minimum at $T=T^*$, as it should be. Some results are shown in Fig. 5.

VI. CONCLUDING REMARKS

For first-order phase transitions, some of the first derivatives of the free energy have discontinuities when phase transition happens. In usual studies, thermodynamic quantities are expressed as functions of the temperature T and the chemical potential μ . The origin of the nonanalytic behaviors is not obvious. However, by choosing ρ and ρ_{12} as the two independent variables, it becomes easier to analyze the behavior of each thermodynamic function in the whole phase space. Within the physically accessible region in the $\rho-\rho_{12}$ plane, the energy is a well-behaved function, but the partial

derivate of the entropy relative to ρ remains zero inside the two-phase coexistence region. The latter behavior of the entropy is responsible for the first-order phase transition in the nearest-neighbor interaction models with $d \geq 2$ dimensions. It remains to be seen if the current approach offer any new understandings of critical phenomena.

Widom's relations and Henderson's relations for lattice gas systems are generalized in the present work to general nearest-neighbor interaction models. These relations may find applications in computer simulations as well as in theoretical studies. For example, Henderson's relations may be helpful for checking whether simulations have achieved equilibrium.

ACKNOWLEDGMENTS

The author wishes to thank Professor B. Widom, Professor J. R. Henderson, and Professor W. H. Miller for reading the manuscript and providing many helpful comments and Professor D. Chandler for calling Ref. 5 to attention. The author gratefully acknowledges financial support for this work from the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

APPENDIX

Here we will show that \bar{s} is dependent on ρ at small ρ and small ρ_{12} limit.

When $\rho = \rho_{12}/2$, contributions to \bar{s} are those configurations that all the type 1 particles have only type 2 neighbors—type 1 particles only form monomers. When ρ increases, type 1 particles have to form clusters in order to keep ρ_{12} fixed. At the limit $\rho_{12} \rightarrow 0$, we may just consider monomer, dimer, and trimer clusters formed by type 1 particles, and denote their numbers as ν_1, ν_2 , and ν_3 , respectively. Also we define three cluster densities to be $\rho_i = \nu_i/\mathcal{N}$. ρ_2 and ρ_3 can be expressed by ρ_1 due to the following relations:

$$\rho_1 + 2\rho_2 + 3\rho_3 = \rho, \tag{A1}$$

$$z\rho_1 + (2z-2)\rho_2 + (3z-4)\rho_3 = z\rho_{12}/2. \tag{A2}$$

Then the number of allowed configurations is approximately the product of the following terms:

- (1) the number of selecting $(\nu_1 + \nu_2 + \nu_3)$ sites from \mathcal{N} lattice sites;
- (2) the number of selecting $(\nu_2 + \nu_3)$ sites from $z(\nu_1 + \nu_2 + \nu_3)$ sites;
- (3) the number of selecting ν_3 sites from $(2z-2)\nu_3$ lattice sites;
- (4) a factor to compensate overcounting.

Putting these terms together, we obtain

$$\begin{aligned} \bar{s}(\rho, \rho_{12}) &= \frac{1}{\mathcal{N}} \ln \left\{ \sum_{\nu_1, \nu_2, \nu_3} C_{\mathcal{N}}^{(\nu_1 + \nu_2 + \nu_3)} C_{z(\nu_1 + \nu_2 + \nu_3)}^{(\nu_2 + \nu_3)} C_{(2z-2)(\nu_2 + \nu_3)}^{\nu_3} (2!)^{(-\nu_2)} (3!)^{(-\nu_3)} \right\} \\ &= -(\rho_1^* + \rho_2^* + \rho_3^*) \ln(\rho_1^* + \rho_2^* + \rho_3^*) - (1 - \rho_1^* - \rho_2^* - \rho_3^*) \ln(1 - \rho_1^* - \rho_2^* - \rho_3^*) + z(\rho_1^* + \rho_2^* + \rho_3^*) \ln[z(\rho_1^* + \rho_2^* + \rho_3^*)] \\ &\quad - (\rho_2^* + \rho_3^*) \ln[\rho_2^* + \rho_3^*] - [z(\rho_1^* + \rho_2^* + \rho_3^*) - \rho_2^* - \rho_3^*] \ln[z(\rho_1^* + \rho_2^* + \rho_3^*) - \rho_2^* - \rho_3^*] \\ &\quad + (2z-2)(\rho_2^* + \rho_3^*) \ln[(2z-2)(\rho_2^* + \rho_3^*)] - \rho_3^* \ln \rho_3^* - [(2z-2)(\rho_2^* + \rho_3^*) - \rho_3^*] \ln[(2z-2)(\rho_2^* + \rho_3^*) - \rho_3^*] \\ &\quad - \rho_2^* \ln 2 - \rho_3^* \ln 6. \end{aligned} \tag{A3}$$

In the second step, we have used the maximum term approximation, and $\{\rho_1^*, \rho_2^*, \rho_3^*\}$ are located by the requirement

$$\left. \frac{d\bar{s}}{d\rho_1} \right|_{\{\rho_1^*, \rho_2^*, \rho_3^*\}} = 0. \tag{A4}$$

¹E. Ising, *Z. Phys.* **31**, 253 (1925).

²L. Onsager, *Phys. Rev.* **65**, 117 (1944).

³C. N. Yang, *Phys. Rev.* **85**, 808 (1952).

⁴B. Widom, *J. Chem. Phys.* **39**, 2808 (1963).

⁵J. R. Henderson, *Mol. Phys.* **95**, 187 (1998).

⁶For chemical systems, it is the grand potential; for magnetic systems (μ is related to the external magnetic field), it is the Gibbs free energy.

⁷T. L. Hill, in *Statistical Mechanics* (Dover, New York, 1987).

⁸D. Chandler, in *Introduction to Modern Statistical Mechanics* (Oxford University Press, New York, 1987).