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A lattice model for fluids with directional interactions

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Here we analyze a lattice model for fluids with directional interactions in the framework of the Ono–Kondo theory. The free energy of the system is represented as an explicit function of the temperature and bulk density. It is shown that the model predicts both order–disorder and vapor–liquid phase transitions. This theory predicts a tricritical point where the vapor–liquid and order–disorder phase transitions both disappear. Also, it predicts retrograde condensation where the boundary of phase stability becomes a multivalued function of concentration. In addition, predictions of the theory are compared with Monte Carlo simulation data. It is shown that the partition function cannot be factored to predict separately the contributions of, for example, dispersion and hydrogen bonding interactions. © 1999 American Institute of Physics. [S0021-9606(99)50829-5]

I. INTRODUCTION

Models with angle dependent interactions have been used to describe several different kinds of systems. Andersen¹ considered hydrogen bonding in dilute gases and in dense fluids using Mayer's cluster theory. Cummings and Blum² solved the Ornstein–Zernike equation for nonspherical molecules and analyzed associating systems with anisotropic surface adhesion. Wertheim³ expanded the Helmholtz free energy in a series of integrals of molecular distribution functions to develop a thermodynamic perturbation theory (TPT) capable of predicting both the effect of hydrogen bonding and the behavior of covalently-bonded polymers. These, and other approaches, have led to rigorous statistical mechanical theories for associating systems. However, all these approaches require simplifying assumptions (empirical potential functions for angle dependent interactions, pairwise additivity) and mathematical approximations (such as truncation of expansions when closed form analytical solutions are not possible). It has been shown by Economou and Donohue⁴ that after these simplifications, "rigorous" perturbation theory is mathematically identical to "empirical" chemical and quasicheical theories.

In contrast to these other approaches, lattice models allow one to include the essential physics but simplify the mathematics. This allows a rigorous calculation of the partition function for an ensemble of molecules on lattice sites⁵ and provides a convenient way to calculate thermodynamic properties of fluids. The classical Ising model considers a lattice with nearest neighbor interactions which do not depend on orientation.⁶ However, an exact solution has been found only for the one-dimensional problem.⁷ For the two-dimensional problem, the exact solution has been obtained only at the critical density.⁸ To date, no general solution to the Ising model has been found, and no three-dimensional problem yet has a solution that is both complete and exact.⁶

However, approximate methods, such as the molecular field approximation,⁹ minimizing free energy for finite-size phases,¹⁰ cluster expansions,^{11,12} low- and high-temperature expansions,⁶ cluster variation method,¹³ and its modifications,^{14–20} as well as molecular simulations²¹ have provided important insights.

In earlier publications,^{22,23} we proposed an approximate solution to the Ising problem based on a three-dimensional version of the Ono–Kondo equations.^{24,25} These equations take into account correlations between a central molecule and its neighbors, but there are no direct correlations with other molecules. In this regard, the Ono–Kondo approach relies on the mean-field approximation; however, it should be noted that the theory predicts corrections to mean-field behavior that are similar to the cluster variation method (CVM).^{13,23} It also should be noted that the Ono–Kondo mean-field assumptions^{24,25} are similar to those presented in Blume, Emery, and Griffiths (BEG) theory⁹ which is able to predict order–disorder phase transitions, end points, tricritical points, and effects of finite-size phases.¹⁰ However, there are problems which have not been discussed in detail in the framework of BEG, CVM, and Ono–Kondo methods. These include retrograde condensation effects² and the validity (or lack thereof) of the additivity assumption when there are both dispersion and directional terms. There also have not been explicit equations derived for the density distributions around a particular molecule, nor have there been, to our knowledge, comparisons with Monte Carlo simulations. These and other problems are discussed in this paper for the lattice model with directional interactions in the framework of the Ono–Kondo theory.

Lattice models with nearest-neighbor interactions are used to describe a wide variety of systems and phenomena.^{22–29} These include the lattice gas, binary liquid solutions, order–disorder transitions in alloys, ferromagnetism, and antiferromagnetism. It is well known that these models can be formulated using the lattice gas, magnetic, or binary system languages, but the resulting equations are

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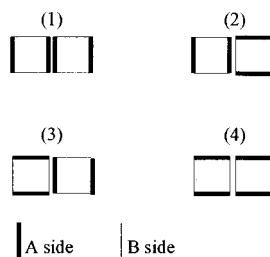


FIG. 1. Molecular configurations with directional interactions. There are energies $\epsilon_{AA}(1)$, $\epsilon_{AB}(2)$, $\epsilon_{BA}(3)$, and $\epsilon_{BB}(4)$. A special case is analogous to the lattice gas with $\epsilon_{AB} = \epsilon_{BA} = \epsilon_{BB} = 0$ and $\epsilon_{AA} \neq 0$.

equivalent.⁶ In this paper we use the terminology and notation of binary solutions.

II. DIRECTIONAL INTERACTIONS

Consider a lattice system with directional interactions between nearest neighbors as illustrated in Fig. 1.

Here, we analyze a two-dimensional system on a square lattice. However, generalization to three dimensions is straightforward in this framework. In Fig. 1, diagrams (1) and (4) illustrate AA and BB interactions. Diagrams (2) and (3) illustrate AB and BA interactions. We imply also that

$\epsilon_{AB} = \epsilon_{BA}$. One of these molecules in each pair will be considered the “central” molecule. To describe correlations between the central molecule and surrounding molecules, we consider the local density of this lattice gas near the central molecule.

For the system shown in Fig. 1, we consider a molecule sitting on the lattice site with coordinates i, j . There are two possible orientations for any molecule; parallel and perpendicular with respect to the central molecule. Assuming the A sides of the central molecule are oriented along the j -axis, we will consider probabilities, $x_{\parallel i, j}$ and $x_{\perp i, j}$, for orientations of neighbors with A sides along the j and along i axes, respectively. Also we assume that the central molecule is sitting on the site $(0, 0)$.

In the mean-field approximation, the energy of interaction, $\epsilon(i_1, j_1, i_2, j_2)$, between molecules on two neighboring sites, (i_1, j_1) and (i_2, j_2) , is

$$\epsilon(i_1, j_1, i_2, j_2) = x_{O_1 i_1 j_1} x_{O_2 i_2 j_2} \epsilon_{S_1 S_2}, \quad (1)$$

where O_1 and O_2 can be either \perp or \parallel (showing orientations), and S_1 and S_2 can be either A or B depending on interacting sides of molecules occupying sites (i_1, j_1) and (i_2, j_2) . Therefore, Hamiltonian function, H , can be written in the following form:

$$\begin{aligned} H = (1/2) \sum_{i=-i^*}^{i^*} \sum_{j=-j^*}^{j^*} & (x_{\perp i, j} x_{\perp i+1, j} \epsilon_{BB} + x_{\perp i, j} x_{\parallel i+1, j} \epsilon_{AB} + x_{\parallel i, j} x_{\perp i+1, j} \epsilon_{AB} + x_{\parallel i, j} x_{\parallel i+1, j} \epsilon_{AA} + x_{\perp i, j} x_{\perp i, j+1} \epsilon_{AA} \\ & + x_{\perp i, j} x_{\parallel i, j+1} \epsilon_{AB} + x_{\parallel i, j} x_{\perp i, j+1} \epsilon_{AB} + x_{\parallel i, j} x_{\parallel i, j+1} \epsilon_{BB} + x_{\perp i, j} x_{\perp i-1, j} \epsilon_{BB} + x_{\perp i, j} x_{\parallel i-1, j} \epsilon_{AB} + x_{\parallel i, j} x_{\perp i-1, j} \epsilon_{AB} + x_{\parallel i, j} x_{\parallel i-1, j} \epsilon_{AA} \\ & + x_{\perp i, j} x_{\perp i, j-1} \epsilon_{AA} + x_{\perp i, j} x_{\parallel i, j-1} \epsilon_{AB} + x_{\parallel i, j} x_{\perp i, j-1} \epsilon_{AB} + x_{\parallel i, j} x_{\parallel i, j-1} \epsilon_{BB}), \end{aligned} \quad (2)$$

where

$$x_{\parallel 0, 0} = 1, \quad (3)$$

and

$$x_{\perp 0, 0} = 0. \quad (4)$$

The values of i^* and j^* in Eq. (2) are limits for variation of i and j .

Equations (2)–(4) give the configurational energy for the system where the site $(0, 0)$ is occupied by the central molecule. Note that the assumption given by Eq. (1) is equivalent to the molecular-field approximation of Blume, Emery, and Griffiths (BEG) [see Eq. (3.2) in Ref. 9]. The same as-

sumptions were in the theory developed earlier by Ono and Kondo.²⁴ However, the Ono–Kondo equations were considered only in one-dimensional form for application to density gradients near surfaces.²⁵

The entropy of the system (per one site) in the mean-field approximation can be written in the form

$$\begin{aligned} S = k_B \sum_{(i, j) \neq (0, 0)} \sum [x_{\perp i, j} \ln x_{\perp i, j} + x_{\parallel i, j} \ln x_{\parallel i, j} \\ + (1 - x_{\perp i, j} - x_{\parallel i, j}) \ln (1 - x_{\perp i, j} - x_{\parallel i, j})], \end{aligned} \quad (5)$$

where k_B is Boltzmann’s constant. From Eqs. (2) and (5), it follows that the free energy, A , is

$$\begin{aligned}
A = (1/2) \sum_{i=i^*}^{i^*} \sum_{j=-j^*}^{j^*} & (x_{\perp i,j} x_{\perp i+1,j} \epsilon_{BB} + x_{\perp i,j} x_{\parallel i+1,j} \epsilon_{AB} + x_{\parallel i,j} x_{\perp i+1,j} \epsilon_{AB} + x_{\parallel i,j} x_{\parallel i+1,j} \epsilon_{AA} + x_{\perp i,j} x_{\perp i,j+1} \epsilon_{AA} + x_{\perp i,j} x_{\parallel i,j+1} \epsilon_{AB} \\
& + x_{\parallel i,j} x_{\perp i,j+1} \epsilon_{AB} + x_{\parallel i,j} x_{\parallel i,j+1} \epsilon_{BB} + x_{\perp i,j} x_{\perp i-1,j} \epsilon_{BB} + x_{\perp i,j} x_{\parallel i-1,j} \epsilon_{AB} + x_{\parallel i,j} x_{\perp i-1,j} \epsilon_{AB} + x_{\parallel i,j} x_{\parallel i-1,j} \epsilon_{AA} \\
& + x_{\perp i,j} x_{\perp i,j-1} \epsilon_{AA} + x_{\perp i,j} x_{\parallel i,j-1} \epsilon_{AB} + x_{\parallel i,j} x_{\perp i,j-1} \epsilon_{AB} + x_{\parallel i,j} x_{\parallel i,j-1} \epsilon_{BB}) - k_B T \sum_{(i,j) \neq (0,0)} [x_{\perp i,j} \ln x_{\perp i,j} + x_{\parallel i,j} \ln x_{\parallel i,j} \\
& + (1 - x_{\perp i,j} - x_{\parallel i,j}) \ln(1 - x_{\perp i,j} - x_{\parallel i,j})], \quad (6)
\end{aligned}$$

where T is the absolute temperature.

Values of $x_{\parallel i,j}$ and $x_{\perp i,j}$ should be chosen so as to minimize A under the following constraint:

$$N \sum_{i=-i^*}^{i^*} \sum_{j=-j^*}^{j^*} (x_{\perp i,j} + x_{\parallel i,j}) = N_M, \quad (7)$$

where N is the total number of sites, and N_M is the total number of molecules in the system. This problem can be solved using the standard method of Lagrange's multipliers³⁰ by considering a function

$$\begin{aligned}
\Omega(x_{\parallel 0,1}; x_{\parallel 0,-1}; \dots; x_{\parallel i^*,j^*}; x_{\perp 0,1}; x_{\perp 0,-1}; \dots; x_{\perp i^*,j^*}) \\
= A(x_{\parallel 0,1}; x_{\parallel 0,-1}; \dots; x_{\parallel i^*,j^*}; x_{\perp 0,1}; x_{\perp 0,-1}; \dots; x_{\perp i^*,j^*}) \\
- \mu^* \left[\sum_{i=-i^*}^{i^*} \sum_{j=-j^*}^{j^*} (x_{\perp i,j} + x_{\parallel i,j}) - N_M/N \right], \quad (8)
\end{aligned}$$

which gives the following equations for the Lagrange's multiplier, μ^* ,

$$\partial \Omega / \partial x_{\perp i,j} = 0 \quad (9)$$

and

$$\partial \Omega / \partial x_{\parallel i,j} = 0. \quad (10)$$

Substituting Eq. (6) into Eq. (8) and then into Eqs. (9) and (10), we obtain for sites where (i,j) , $(i \pm 1,j)$, and $(i,j \pm 1)$ do not coincide with $(0,0)$,

$$\begin{aligned}
x_{\perp i+1,j} \epsilon_{BB} + x_{\perp i-1,j} \epsilon_{BB} + x_{\parallel i+1,j} \epsilon_{AB} + x_{\parallel i-1,j} \epsilon_{AB} + x_{\perp i,j+1} \epsilon_{AA} \\
+ x_{\perp i,j-1} \epsilon_{AA} + x_{\parallel i,j+1} \epsilon_{AB} + x_{\parallel i,j-1} \epsilon_{AB} + k_B T \ln[x_{\perp i,j} / \\
(1 - x_{\parallel i,j} - x_{\perp i,j})] = \mu^* \quad (11)
\end{aligned}$$

and

$$\begin{aligned}
x_{\parallel i+1,j} \epsilon_{AA} + x_{\parallel i-1,j} \epsilon_{AA} + x_{\perp i+1,j} \epsilon_{AB} + x_{\perp i-1,j} \epsilon_{AB} \\
+ x_{\parallel i,j+1} \epsilon_{BB} + x_{\parallel i,j-1} \epsilon_{BB} + x_{\perp i,j+1} \epsilon_{AB} + x_{\perp i,j-1} \epsilon_{AB} \\
+ k_B T \ln[x_{\parallel i,j} / (1 - x_{\parallel i,j} - x_{\perp i,j})] = \mu^*. \quad (12)
\end{aligned}$$

The value of μ^* can be obtained from the requirements that $x_{\perp i,j} \rightarrow x_{\infty}/2$ and $x_{\parallel i,j} \rightarrow x_{\infty}/2$ as the distance to the central molecule goes to infinity. This gives from Eq. (11),

$$x_{\infty}(\epsilon_{AA} + 2\epsilon_{AB} + \epsilon_{BB}) + k_B T \ln[(x_{\infty}/2)/(1 - x_{\infty})] = \mu^*. \quad (13)$$

Combining Eqs. (11) and (12) with Eq. (13) results in

$$\begin{aligned}
k_B T \ln\{x_{\perp i,j}(1 - x_{\infty}) / [(1 - x_{\parallel i,j} - x_{\perp i,j})(x_{\infty}/2)]\} + (x_{\perp i+1,j} - x_{\infty}/2) \epsilon_{AA} + (x_{\perp i-1,j} - x_{\infty}/2) \epsilon_{AA} + (x_{\parallel i+1,j} - x_{\infty}/2) \epsilon_{AB} \\
+ (x_{\parallel i-1,j} - x_{\infty}/2) \epsilon_{AB} + (x_{\perp i,j+1} - x_{\infty}/2) \epsilon_{BB} + (x_{\perp i,j-1} - x_{\infty}/2) \epsilon_{BB} + (x_{\parallel i,j+1} - x_{\infty}/2) \epsilon_{AB} + (x_{\parallel i,j-1} - x_{\infty}/2) \epsilon_{AB} = 0 \quad (14)
\end{aligned}$$

and

$$\begin{aligned}
k_B T \ln\{x_{\parallel i,j}(1 - x_{\infty}) / [(1 - x_{\parallel i,j} - x_{\perp i,j})(x_{\infty}/2)]\} + (x_{\parallel i+1,j} - x_{\infty}/2) \epsilon_{AA} + (x_{\parallel i-1,j} - x_{\infty}/2) \epsilon_{AA} + (x_{\perp i+1,j} - x_{\infty}/2) \epsilon_{AB} \\
+ (x_{\perp i-1,j} - x_{\infty}/2) \epsilon_{AB} + (x_{\parallel i,j+1} - x_{\infty}/2) \epsilon_{BB} + (x_{\parallel i,j-1} - x_{\infty}/2) \epsilon_{BB} + (x_{\perp i,j+1} - x_{\infty}/2) \epsilon_{AB} + (x_{\perp i,j-1} - x_{\infty}/2) \epsilon_{AB} = 0. \quad (15)
\end{aligned}$$

Equations (14) and (15) are valid for any site (i,j) which is not neighboring to $(0,0)$. For the site $(1,0)$, Eqs. (14) and (15) have the following form:

$$\begin{aligned}
k_B T \ln\{x_{\perp 1,0}(1 - x_{\infty}) / [(1 - x_{\parallel 1,0} - x_{\perp 1,0})(x_{\infty}/2)]\} + (1 - x_{\infty}/2) \epsilon_{AA} - (x_{\infty}/2) \epsilon_{AB} + (x_{\perp 2,0} - x_{\infty}/2) \epsilon_{AA} + (x_{\parallel 2,0} - x_{\infty}/2) \epsilon_{AB} \\
+ (x_{\perp 1,1} - x_{\infty}/2) \epsilon_{BB} + (x_{\parallel 1,1} - x_{\infty}/2) \epsilon_{AB} + (x_{\perp 1,-1} - x_{\infty}/2) \epsilon_{BB} + (x_{\parallel 1,-1} - x_{\infty}/2) \epsilon_{AB} = 0 \quad (16)
\end{aligned}$$

and

$$\begin{aligned}
k_B T \ln\{x_{\parallel 1,0}(1 - x_{\infty}) / [(1 - x_{\parallel 1,0} - x_{\perp 1,0})(x_{\infty}/2)]\} + (1 - x_{\infty}/2) \epsilon_{AA} - (x_{\infty}/2) \epsilon_{AB} + (x_{\parallel 2,0} - x_{\infty}/2) \epsilon_{AA} + (x_{\perp 2,0} - x_{\infty}/2) \epsilon_{AB} \\
+ (x_{\parallel 1,1} - x_{\infty}/2) \epsilon_{BB} + (x_{\perp 1,1} - x_{\infty}/2) \epsilon_{AB} + (x_{\parallel 1,-1} - x_{\infty}/2) \epsilon_{BB} + (x_{\perp 1,-1} - x_{\infty}/2) \epsilon_{AB} = 0. \quad (17)
\end{aligned}$$

Equations for sites $(-1,0)$, $(0,1)$, and $(0,-1)$ are analogous to Eqs. (16) and (17).

III. APPROXIMATION THAT THE DENSITY IN THE SECOND SHELL IS EQUAL TO THE DENSITY IN THE BULK

In this approximation, $x_{\perp 2,0} = x_{\parallel 2,0} = x_{\perp 1,1} = x_{\parallel 1,1} = x_{\perp 1,-1} = x_{\parallel 1,-1} = x_{\infty}/2$. Therefore, Eq. (16) can be written in the following form:

$$\ln\{[x_{AA}(1-x_{\infty})]/[(1-x_{AA}-x_{AB})x_{\infty}z_A/z]\} + (\epsilon_{AA} - \epsilon_{AA}x_{\infty}z_A/z - \epsilon_{AB}x_{\infty}z_B/z)/k_B T = 0, \quad (18)$$

where x_{AA} is the probability of forming an AA bond (an A side of the molecule links to an A side of the central molecule), x_{AB} is the probability of forming an AB bond (a B side of the molecule links to an A side of the central molecule), and z_A and z_B are the numbers of AA and BB bonds possible for one molecule. Since we consider molecules with two types of “sides” (see Fig. 1), then $z_A + z_B$ is equal to the coordination number, z . For molecules like those illustrated in Fig. 1 on a two dimensional, square lattice, $z_A = z_B = 2$.

The equation describing probabilities for a B side of the molecule near an A side of the central molecule can be derived similarly. The result of this derivation is

$$\ln\{[x_{AB}(1-x_{\infty})]/[(1-x_{AA}-x_{AB})x_{\infty}z_B/z]\} + (\epsilon_{AB} - \epsilon_{AB}x_{\infty}z_A/z - \epsilon_{BB}x_{\infty}z_B/z)/k_B T = 0. \quad (19)$$

Equations (18) and (19) describe occupation of the site next to an A side of the central molecule. For the B side of the central molecule, there are analogous equations,

$$\ln\{[x_{BB}(1-x_{\infty})]/[(1-x_{BB}-x_{BA})x_{\infty}z_B/z]\} + (\epsilon_{BB} - \epsilon_{BB}x_{\infty}z_B/z - \epsilon_{BA}x_{\infty}z_A/z)/k_B T = 0 \quad (20)$$

and

$$\ln\{[x_{BA}(1-x_{\infty})]/[(1-x_{BB}-x_{BA})x_{\infty}z_A/z]\} + (\epsilon_{BA} - \epsilon_{BA}x_{\infty}z_B/z - \epsilon_{AA}x_{\infty}z_A/z)/k_B T = 0, \quad (21)$$

where x_{BB} is the probability of forming a BB bond (a B side of the molecule interacts with a B side of the central molecule), and x_{BA} is the probability of forming a BA bond (an A side of the molecule interacts with a B side of the central molecule).

A. Configurational energy

The configurational energy, U , for the system with directional interactions can be represented in the following form:

$$U = N[(\epsilon_{AA}x_{AA} + \epsilon_{AB}x_{AB})z_A + (\epsilon_{BA}x_{BA} + \epsilon_{BB}x_{BB})z_B]x_{\infty}/2. \quad (22)$$

Values of x_{AA} , x_{AB} , x_{BA} , and x_{BB} can be obtained from Eqs. (18)–(21) which gives

$$x_{AA} = z_A x_{\infty} / [z_A x_{\infty} + z(1-x_{\infty})\exp(\delta_{AA}) + z_B x_{\infty} \exp(\delta_{AA} - \delta_{AB})], \quad (23)$$

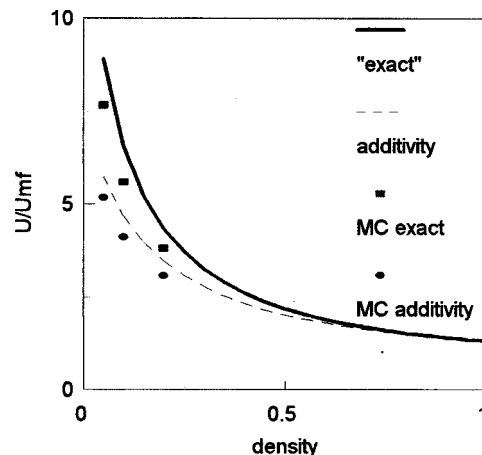


FIG. 2. Dependence of U/U_{∞} on density for the “exact” equation and for calculations based on additivity. Here $\epsilon'_{AA}/k_B T = -2.5$, $\epsilon'_{AB}/k_B T = \epsilon'_{BB}/k_B T = 0$, and $\epsilon''_{AA}/k_B T = \epsilon''_{AB}/k_B T = \epsilon''_{BB}/k_B T = -0.5$.

$$x_{AB} = z_B x_{\infty} / [z_B x_{\infty} + z(1-x_{\infty})\exp(\delta_{AB}) + z_A x_{\infty} \exp(\delta_{AB} - \delta_{AA})], \quad (24)$$

$$x_{BB} = z_B x_{\infty} / [z_B x_{\infty} + z(1-x_{\infty})\exp(\delta_{BB}) + z_A x_{\infty} \exp(\delta_{BB} - \delta_{BA})], \quad (25)$$

$$x_{BA} = z_A x_{\infty} / [z_A x_{\infty} + z(1-x_{\infty})\exp(\delta_{BA}) + z_B x_{\infty} \exp(\delta_{BA} - \delta_{BB})], \quad (26)$$

where

$$\delta_{AA} = (\epsilon_{AA} - \epsilon_{AA}x_{\infty}z_A/z - \epsilon_{AB}x_{\infty}z_B/z)/k_B T, \quad (27)$$

$$\delta_{AB} = (\epsilon_{AB} - \epsilon_{AB}x_{\infty}z_A/z - \epsilon_{BB}x_{\infty}z_B/z)/k_B T, \quad (28)$$

$$\delta_{BA} = (\epsilon_{BA} - \epsilon_{BA}x_{\infty}z_B/z - \epsilon_{AA}x_{\infty}z_A/z)/k_B T, \quad (29)$$

$$\delta_{BB} = (\epsilon_{BB} - \epsilon_{BB}x_{\infty}z_B/z - \epsilon_{BA}x_{\infty}z_A/z)/k_B T. \quad (30)$$

Equation (22) with Eqs. (23)–(30) determine the configurational energy for the system with interactions which depend on the orientation of molecules. It was mentioned earlier that we imply $\epsilon_{AB} = \epsilon_{BA}$. However, it follows from Eqs. (24), (26), (28), and (29) that this condition does not lead to $\delta_{AB} = \delta_{BA}$ or $x_{AB} = x_{BA}$.

Equations (22)–(30) for the configurational energy, U , are not a linear function of the energies of interactions, ϵ_{AA} , ϵ_{AB} , and ϵ_{BB} . Consider a molecule that has both nondirectional (dispersion) interactions and directional (polar or hydrogen bonding) interactions. In this case, we can factor each intermolecular energy into a dispersion (') term and a directional (") term. The internal energy of this system, U , which is a function of the four energies, $\epsilon_{AA} (= \epsilon'_{AA} + \epsilon''_{AA})$, $\epsilon_{AB} (= \epsilon'_{AB} + \epsilon''_{AB})$, $\epsilon_{BA} (= \epsilon'_{BA} + \epsilon''_{BA})$, and $\epsilon_{BB} (= \epsilon'_{BB} + \epsilon''_{BB})$, is different from the internal energy one would obtain if one assumed the partition function is factorable, i.e., $U(\epsilon'_{AA} + \epsilon'_{AB} + \epsilon'_{BA} + \epsilon'_{BB}, \epsilon''_{AA} + \epsilon''_{AB} + \epsilon''_{BA} + \epsilon''_{BB}) \neq U(\epsilon'_{AA}, \epsilon'_{AB}, \epsilon'_{BA}, \epsilon'_{BB}) + U(\epsilon''_{AA}, \epsilon''_{AB}, \epsilon''_{BA}, \epsilon''_{BB})$. This point is illustrated in Fig. 2 where “exact” configurational energy is $U(\epsilon'_{AA} + \epsilon''_{AA}, \epsilon'_{AB} + \epsilon''_{AB}, \epsilon'_{BA} + \epsilon''_{BA}, \epsilon'_{BB} + \epsilon''_{BB})$ calculated from Eq. (22) and the sum is $U(\epsilon'_{AA}, \epsilon'_{AB}, \epsilon'_{BA}, \epsilon'_{BB}) + U(\epsilon''_{AA}, \epsilon''_{AB}, \epsilon''_{BA}, \epsilon''_{BB})$. In Fig. 2, $\epsilon'_{AA}/k_B T =$

-2.5 , $\epsilon'_{AB}/k_B T = \epsilon'_{BB}/k_B T = 0$, and $\epsilon''_{AA}/k_B T = \epsilon''_{AB}/k_B T = \epsilon''_{BB}/k_B T = -0.5$. As seen from Fig. 2, the additivity assumption is reasonable for high densities (>0.5) but it does not hold for small densities (<0.25).

B. Case of $\epsilon_{AB} = \epsilon_{BA} = \epsilon_{BB} = 0$

We have considered a system with interactions that depend on molecular orientations. The simplest special case of this system is when $\epsilon_{AB} = \epsilon_{BA} = \epsilon_{BB} = 0$ but $\epsilon_{AA} = \epsilon \neq 0$. For this case Eq. (18)–(21) have the following simple form:

$$\ln\{[x_{AA}(1-x_\infty)]/[(1-x_{AA}-x_{AB})x_\infty z_A/z]\} + (1-x_\infty z_A/z)\epsilon/k_B T = 0, \quad (31)$$

$$\ln\{[x_{AB}(1-x_\infty)]/[(1-x_{AA}-x_{AB})x_\infty z_B/z]\} = 0, \quad (32)$$

$$\ln\{[x_{BB}(1-x_\infty)]/[(1-x_{BB}-x_{BA})x_\infty z_B/z]\} = 0, \quad (33)$$

and

$$\ln\{[x_{BA}(1-x_\infty)]/[(1-x_{BB}-x_{BA})x_\infty z_A/z]\} - \epsilon x_\infty z_A/z k_B T = 0. \quad (34)$$

For this case, from Eq. (22) it follows that

$$U/U_{mf} = (z/z_A)/\{x_\infty + (z/z_A - x_\infty) \times \exp[(1-x_\infty z_A/z)\epsilon/k_B T]\}, \quad (35)$$

where U_{mf} is the mean-field configurational energy,

$$U_{mf} = \lim_{T \rightarrow \infty} U. \quad (36)$$

C. Free energy

Having equations for the configurational energy, U , and the entropy, S , one can calculate the free energy, A ,

$$A/T = \int_0^{1/T} U d(1/T) - S|_{T \rightarrow \infty}, \quad (37)$$

or

$$(A - A_{\text{pure}})/T = \int_0^{1/T} (U - U_{\text{pure}}) d(1/T) - (S - S_{\text{pure}})|_{T \rightarrow \infty}, \quad (38)$$

where A_{pure} , U_{pure} , and S_{pure} are thermodynamic functions for the pure component.

Substituting U from Eq. (35) into Eq. (38) and integrating leads to the following:

$$\begin{aligned} \frac{A - A_{\text{pure}}}{k_B T} = & \frac{x_\infty z_A}{2(1 - z_A/z)} \ln \left[1 - \frac{z_A}{z} + \frac{z_A}{z} \right. \\ & \times \exp \left[-\frac{\epsilon}{k_B T} \left(1 - \frac{z_A}{z} \right) \right] \Bigg] \\ & - \frac{x_\infty z_A}{2(1 - x_\infty z_A/z)} \ln \left[1 - \frac{x_\infty z_A}{z} + \frac{x_\infty z_A}{z} \right. \\ & \times \exp \left[-\frac{\epsilon}{k_B T} \left(1 - \frac{z_A}{z} \right) \right] \Bigg] - \frac{(S - S_{\text{pure}})|_{T \rightarrow \infty}}{k_B}, \end{aligned} \quad (39)$$

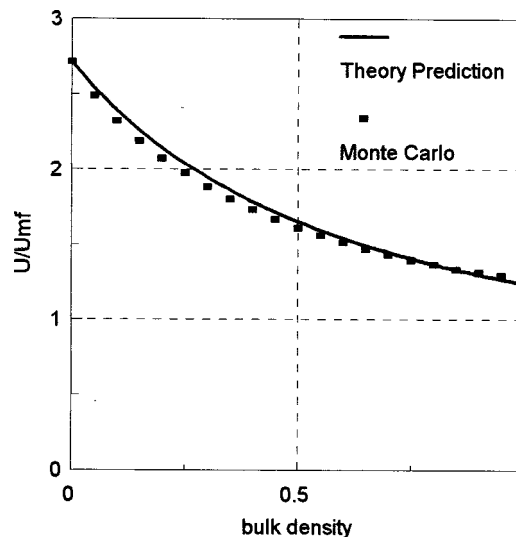


FIG. 3. Dependence of U/U_{mf} on the bulk density predicted by Eq. (35) at $\epsilon_{AA}/k_B T = -1$.

where

$$(S - S_{\text{pure}})|_{T \rightarrow \infty} = -k_B [x_\infty \ln x_\infty + (1 - x_\infty) \ln(1 - x_\infty)]. \quad (40)$$

D. Comparison with Monte Carlo simulations

Monte Carlo simulations were performed in the framework of the canonical ensemble for molecules with directional interactions as illustrated in Fig. 1, i.e., a two-dimensional, square lattice with $z_A = z_B = 2$. Moves were either rotations, exchange of a molecule with another molecule having a different orientation, or an exchange of a molecule with a hole. Moves were accepted or rejected according to the Metropolis algorithm. After an equilibration phase of one to four million moves, energies were averaged over between one million and forty million moves, depending on conditions. The criterion for equilibration was that there was no further change of the density distribution.

Figure 3 shows predictions from Eq. (35) for U/U_{mf} as a function of the bulk density at $\epsilon_{AA}/k_B T = \epsilon/k_B T = -1$. As seen in Fig. 3, U does not reach U_{mf} at $x_\infty = 1$. This is because directional interactions result in ordering even at $x_\infty = 1$. Figure 3 shows that predictions of Eq. (35) are in good agreement with Monte Carlo simulation data over the entire range of the bulk densities.

Figures 4–6 show predictions of Eq. (22) with Eq. (23)–(30) for $\epsilon_{AA}/k_B T = -0.5$ and different values of $\epsilon_{AB}/k_B T$ and $\epsilon_{BB}/k_B T$. Figures 4–6 also show close agreement between the theoretical predictions and Monte Carlo simulations.

IV. SPECIAL CASE OF $z_A = 2$, $\epsilon_{AB} = \epsilon_{BB} = 0$

For $z_A = 2$ and only AA interactions (i.e., $\epsilon_{AB} = \epsilon_{BB} = 0$), there is a special case where clusters of molecules can grow only in one dimension even though the lattice is two- or three-dimensional. In this case, the model inherits features of both three-dimensional and one-dimensional structures. Here we demonstrate how this is possible.

Figure 7 shows the excess free energy

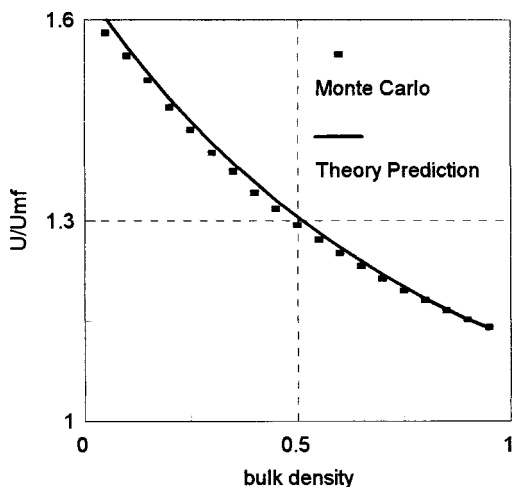


FIG. 4. Dependence of U/U_{mf} on the bulk density predicted by Eq. (22) for $\epsilon_{AA}/k_B T = -0.5$, and $\epsilon_{AB}/k_B T = \epsilon_{BB}/k_B T = 0$.

$$a = (A - A_{pure})/k_B T \quad (41)$$

predicted by Eq. (39) and its first, $\partial a / \partial x_\infty$, second, $\partial^2 a / \partial x_\infty^2$, and third, $\partial^3 a / \partial x_\infty^3$ derivatives at constant temperature, as functions of the density for $z=4$, $z_A=2$, and $\epsilon/k_B T = -1.5$. As illustrated in Fig. 7, there are no instability boundaries of first-order phase transitions because the second derivative is never zero. Numerical analysis of Eq. (39) indicates that $\partial^2 a / \partial x_\infty^2$ never crosses the density axis if $z_A=2$. Figure 8 shows that, even for very large $\epsilon/k_B T$, we have $\partial^2 a / \partial x_\infty^2 > 0$ for $z_A=2$.

For $z_A > 2$, $\partial^2 a / \partial x_\infty^2$ can become zero. However, even a slight increase of z_A over 2 leads to dramatic changes. Figure 9 illustrates this point for $z_A=2.1$ [while the coordination number should be an integer, Eq. (39) can be analyzed for any z_A]. As seen from Fig. 9, a small change of z_A over 2 leads to the appearance of a phase transition with $\partial^2 a / \partial x_\infty^2 = 0$. This analysis shows that the model can have “vapor-liquid” phase transition only for $z_A > 2$. In other words, for

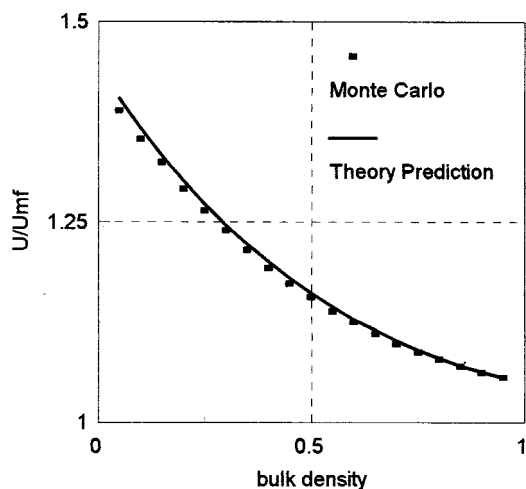


FIG. 5. Dependence of U/U_{mf} on the bulk density predicted by Eq. (22) for $\epsilon_{AA}/k_B T = -0.5$, and $\epsilon_{AB}/k_B T = \epsilon_{BB}/k_B T = -0.1$.

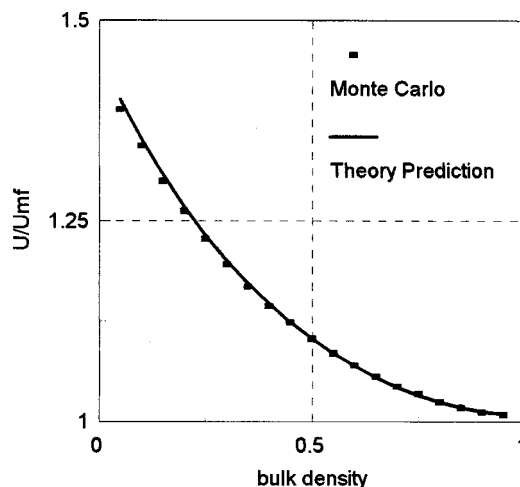


FIG. 6. Dependence of U/U_{mf} on the bulk density predicted by Eq. (22) for $\epsilon_{AA}/k_B T = -0.5$, and $\epsilon_{AB}/k_B T = \epsilon_{BB}/k_B T = -0.3$.

$z_A=2$, the model has the characteristic of a one-dimensional system in that a first-order phase transition cannot occur.

V. LONG RANGE ORDERING AND PHASE DIAGRAMS

Here we consider long range ordering. Equation (39) is derived from Eq. (35) which is based on the assumption that the central molecule influences only the composition in its first shell. This means that the correlation length is equal to the distance between molecules. To analyze long range ordering, we consider two-dimensional equations of equilibrium which do not constrain the correlation length.

A. Asymptotic equations

For lattice gas with $\epsilon_{AB} = \epsilon_{BB} = 0$ and $\epsilon_{AA} = \epsilon$, Eq. (14) can be written in the following form:

$$k_B T \ln \{ x_{\perp i,j} (1 - x_\infty) / [(1 - x_{\parallel i,j} - x_{\perp i,j})(0.5x_\infty)] \} + \epsilon(x_{\perp i,j-1} + x_{\perp i,j+1} - x_\infty) = 0. \quad (42)$$

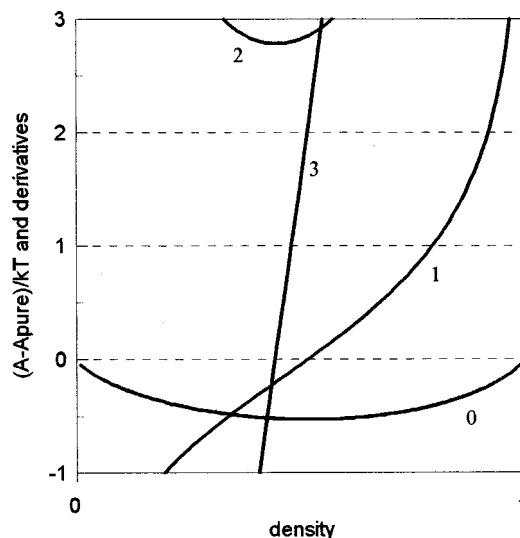


FIG. 7. Density dependence of free energy (0) and its first (1), second (2), and third (3) derivatives with respect to density at $z=4$, $z_A=2$, and $\epsilon_{AA}/k_B T = -1.5$.

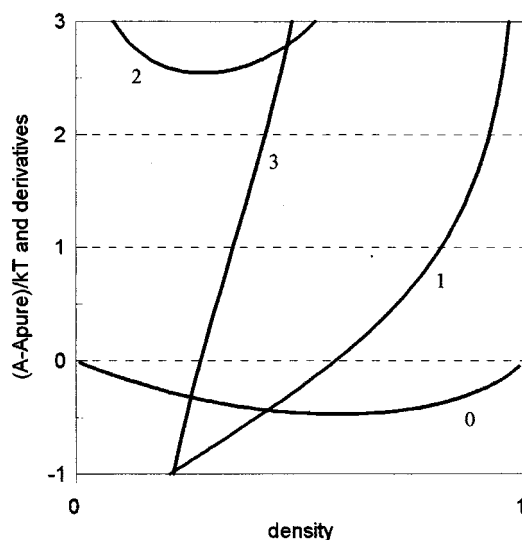


FIG. 8. Density dependence of free energy (0) and its first (1), second (2), and third (3) derivatives with respect to density at $z=4$, $z_A=2$, and $\epsilon_{AA}/k_B T = -100$.

For molecules oriented in the other direction, the result is

$$k_B T \ln \{x_{\parallel i,j}(1-x_\infty)/[(1-x_{\parallel i,j}-x_{\perp i,j})(0.5x_\infty)]\} + \epsilon(x_{\parallel i-1,j} + x_{\parallel i+1,j} - x_\infty) = 0. \quad (43)$$

Linearization of Eq. (42) and (43) with respect to $\delta_{i,j}$ $= x_{\perp i,j} - x_\infty/2$ and $\gamma_{i,j} = x_{\parallel i,j} - x_\infty/2$ gives

$$\delta_{i,j}(2-x_\infty)/[x_\infty(1-x_\infty)] + \gamma_{i,j}/(1-x_\infty) + (\delta_{i,j-1} + \delta_{i,j+1})\epsilon/k_B T = 0 \quad (44)$$

and

$$\gamma_{i,j}(2-x_\infty)/[x_\infty(1-x_\infty)] + \delta_{i,j}(1-x_\infty) + (\gamma_{i-1,j} + \gamma_{i+1,j})\epsilon/k_B T = 0. \quad (45)$$

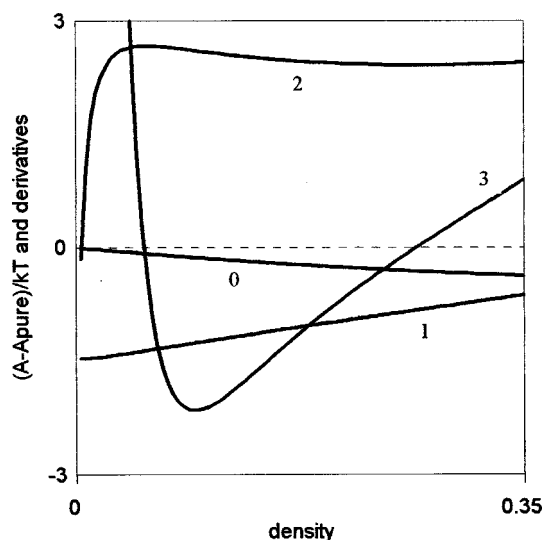


FIG. 9. Density dependence of free energy (0) and its first (1), second (2), and third (3) derivatives with respect to density at $z=4$, $z_A=2.1$, and $\epsilon_{AA}/k_B T = -8$.

Substitution of $\gamma_{i,j}$ from Eq. (44) into Eq. (45) results in the following finite difference equation with respect to $\delta_{i,j}$:

$$(\delta_{i-1,j} + \delta_{i+1,j} + \delta_{i,j-1} + \delta_{i,j+1})(2-x_\infty)/x_\infty + (\delta_{i-1,j-1} + \delta_{i+1,j-1} + \delta_{i-1,j+1} + \delta_{i+1,j+1})(\epsilon/k_B T) \times (1-x_\infty) + \delta_{i,j} 4(k_B T/\epsilon)/x_\infty^2 = 0. \quad (46)$$

For positive i and j , the solution of Eq. (46) can be represented in the form

$$\delta_{i,j} = \text{Const } \alpha^i \beta^j. \quad (47)$$

Substituting this result into Eq. (46) gives the characteristic equation for α and β ,

$$(\alpha + 1/\alpha + \beta + 1/\beta)(2-x_\infty)/x_\infty + [1/(\alpha\beta) + \alpha\beta + \alpha/\beta + \beta/\alpha](\epsilon/k_B T)(1-x_\infty) + 4(k_B T/\epsilon)/x_\infty^2 = 0. \quad (48)$$

Note that for a three-dimensional system we would have $\delta_{i,j,k} = A \alpha^i \beta^j \gamma^k$ in Eq. (47) and a more cumbersome, but similar, expression in Eq. (48).

From Eq. (47), the boundaries for phase stability are at

$$|\alpha| = 1 \quad (49)$$

and

$$|\beta| = 1. \quad (50)$$

For $|\alpha| \geq 1$ or for $|\beta| \geq 1$, $\delta_{i,j}$ does not vanish as i or j goes to ∞ .

Since $x_{\perp i,j}$ decreases monotonically as i and/or j go up, we consider only positive α and β in Eq. (49) and (50). Substitution of $\alpha=1$ and $\beta=1$ in Eq. (48) results in the following:

$$(2-x_\infty)/x_\infty + (\epsilon/k_B T)(1-x_\infty) + (k_B T/\epsilon)/x_\infty^2 = 0. \quad (51)$$

Equation (51) determines the boundaries of phase stability. For $x_\infty \neq 0$ and $k_B T/\epsilon \neq 0$, this equation can be rewritten in the following form:

$$(k_B T/\epsilon + x_\infty)[k_B T/\epsilon + x_\infty(1-x_\infty)] = 0. \quad (52)$$

B. Order parameters and relation to Landau's theory

In Landau's theory, the free energy is represented by the expansion³¹

$$A = A_0 + (A_1/2)\eta_0^2 + (A_2/4)\eta_0^4 + \dots, \quad (53)$$

where A_k are coefficients of expansion, and η_0 is the order parameter. For the binary system, the phase diagram for an order-disorder phase transition is determined by the following equation:

$$A_1(x_\infty, T) = 0. \quad (54)$$

In the variables of our theory, there are two order parameters,

$$\eta_1 = (x_{\perp i,j} - x_\infty)/(1-x_\infty) \quad (55)$$

and

$$\eta_2 = (x_{\parallel i,j} - x_\infty)/(1-x_\infty). \quad (56)$$

Equilibrium values of η_1 and η_2 are determined by the following equations:

$$\partial A / \partial \eta_1 = 0 \quad (57)$$

and

$$\partial A / \partial \eta_2 = 0. \quad (58)$$

From Eqs. (6), (53), (55), and (56) we obtain

$$\begin{aligned} (A_{11}\eta_1 + A_{12}\eta_1^3 + \dots)/(1-x_\infty) \\ = k_B T \ln \{ x_{\parallel i,j}(1-x_\infty)/[(1-x_{\parallel i,j}-x_{\perp i,j})(0.5x_\infty)] \} \\ + \epsilon(x_{\parallel i-1,j} + x_{\parallel i+1,j} - x_\infty) \end{aligned} \quad (59)$$

and

$$\begin{aligned} (A_{21}\eta_2 + A_{22}\eta_2^3 + \dots)/(1-x_\infty) \\ = k_B T \ln \{ x_{\perp i,j}(1-x_\infty)/[(1-x_{\parallel i,j}-x_{\perp i,j})(0.5x_\infty)] \} \\ + \epsilon(x_{\perp i,j-1} + x_{\perp i,j+1} - x_\infty). \end{aligned} \quad (60)$$

As seen from Eqs. (59), (60), and (55), (56), A_{11} and A_{21} are the coefficients for the linear terms in expansions of the right-hand sides of Eqs. (59) and (60).

Equation (54) can be written for order-disorder phase transitions for two phases with different orientations

$$A_{11}(x_\infty, T) = 0 \quad (61)$$

and

$$A_{21}(x_\infty, T) = 0. \quad (62)$$

After algebraic manipulations, from Eq. (59) we have

$$\begin{aligned} A_{11}\delta_{i,j}/[(1-x_\infty)] \\ = (\delta_{i-1,j} + \delta_{i+1,j} + \delta_{i,j-1} + \delta_{i,j+1})(2-x_\infty)/x_\infty \\ + (\delta_{i-1,j-1} + \delta_{i+1,j-1} + \delta_{i-1,j+1} + \delta_{i+1,j+1})(\epsilon/k_B T) \\ \times (1-x_\infty) + \delta_{i,j}4(k_B T/\epsilon)/x_\infty^2. \end{aligned} \quad (63)$$

Substitution of $\delta_{i,j}$ from Eq. (47) into Eq. (63) gives

$$\begin{aligned} A_{11}/[(1-x_\infty)] = (\alpha + 1/\alpha + \beta + 1/\beta)(2-x_\infty)/x_\infty \\ + [1/(\alpha\beta) + \alpha\beta + \alpha/\beta + \beta/\alpha] \\ \times (\epsilon/k_B T)(1-x_\infty) + 4(k_B T/\epsilon)/x_\infty^2. \end{aligned} \quad (64)$$

It follows from Eq. (64) that Eq. (61) is equivalent to Eq. (48) if $x_\infty \neq 1$.

Thus Eq. (62) gives the boundaries for ordered and disordered phases. This equation is equivalent to the following two equations:

$$k_B T/\epsilon + x_\infty = 0 \quad (65)$$

and

$$k_B T/\epsilon + x_\infty(1-x_\infty) = 0. \quad (66)$$

Figure 10 illustrates the phase diagram that results from Eqs. (65) and (66). Equation (65) specifies a boundary between ordered and nonordered phases. Equation (66) gives a vapor/liquidlike phase transition. In Fig. 10, the region between lines 1 and 2 has ordered domains. In each domain,

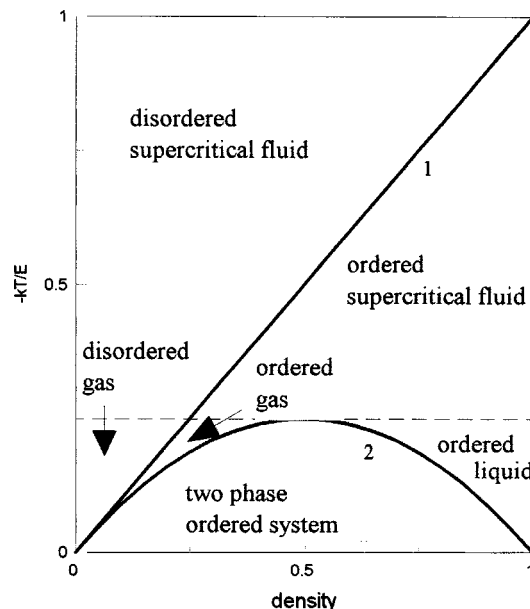


FIG. 10. Phase diagram for the system with directional interactions. Line 1 indicates beginning of ordering, and line 2 shows condensation.

molecules are ordered, but the domains are disordered with respect to each other. Below line 2, the whole fluid can be represented as one domain where chains of ordered molecules are alternated with chains of voids. The chains of molecules interrupted with some voids constitute one phase (“liquid”), and chains of voids with some molecules form another phase (“vapor”). However, the “liquid” phase is not really liquid because the chains are not correlated to each other; they coexist independently. Therefore, line 2 is not a two-dimensional condensation—it is a condensation of one-dimensional chains in a two-dimensional space. This contrasts with a true one-dimensional system when there cannot be a phase transition.

In these calculations, there are errors arising from the mean-field assumptions. However, qualitatively, Eqs. (65) and (66) give a reasonable description of the phase behavior for systems with directional interactions. We have shown that decreasing temperature leads first to an order-disorder phase transition and then to condensation of one-dimensional chains in a two-dimensional space. The critical point for the order-disorder phase transition is at $x_\infty = 1$. Mean-field critical temperature given by Eq. (65) is $T_c = -\epsilon/k_B$. So, one would expect that actual (non-mean-field) critical temperature to be 1.76 times less. This assumption is based on relation between mean-field and exact critical temperatures for the classical two-dimensional Ising model⁶ without directional interactions.

Figure 11 presents Monte Carlo simulation data for the dependence of the configurational energy on $-\epsilon/k_B T$. As shown by Fig. 11, this dependence is linear for small and for high energies of interaction. However, between these two linear sections, there is an inflection point at energies in the range of $-\epsilon/k_B T$ between 1.7 and 2.2. In this range, the behavior is nonlinear and there is a second-order phase transition.³² For the system shown in Fig. 1, this is a transition from an ordered phase to a disordered phase.

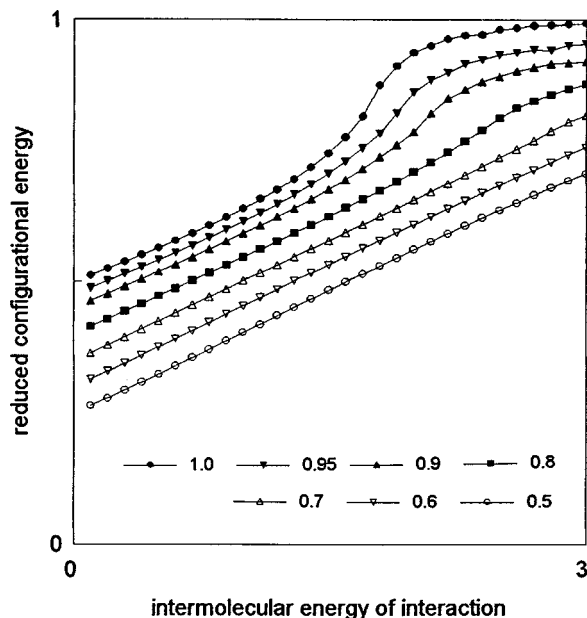


FIG. 11. Dependence of reduced configurational energy, $U/N\epsilon$, on $\epsilon/k_B T$ for different bulk densities.

C. Tricritical points

Here, we consider the case where ϵ_{AA} , ϵ_{BB} , and ϵ_{AB} are not zero. Linearization of Eqs. (14) and (15) with respect to asymptotically small parameters, $\delta_{i,j} = x_{\perp i,j} - x_{\infty}/2$ and $\gamma_{i,j} = x_{\parallel i,j} - x_{\infty}/2$, gives

$$k_B T [2\delta_{i,j}/x_{\infty} + (\delta_{i,j} + \gamma_{i,j})/(1-x_{\infty})] + (\delta_{i+1,j} + \delta_{i-1,j})\epsilon_{AA} + (\gamma_{i+1,j} + \gamma_{i-1,j})\epsilon_{AB} + (\delta_{i,j+1} + \delta_{i,j-1})\epsilon_{BB} + (\gamma_{i,j+1} + \gamma_{i,j-1})\epsilon_{AB} = 0 \quad (67)$$

and

$$k_B T [2\gamma_{i,j}/x_{\infty} + (\delta_{i,j} + \gamma_{i,j})/(1-x_{\infty})] + (\gamma_{i+1,j} + \gamma_{i-1,j})\epsilon_{AA} + (\delta_{i+1,j} + \delta_{i-1,j})\epsilon_{AB} + (\gamma_{i,j+1} + \gamma_{i,j-1})\epsilon_{BB} + (\delta_{i,j+1} + \delta_{i,j-1})\epsilon_{AB} = 0. \quad (68)$$

The summation of Eqs. (67) and (68) leads to the following equation:

$$2k_B T \theta_{i,j} / [x_{\infty}(1-x_{\infty})] + (\theta_{i+1,j} + \theta_{i-1,j})(\epsilon_{AA} + \epsilon_{AB}) + (\theta_{i,j+1} + \theta_{i,j-1})(\epsilon_{BB} + \epsilon_{AB}) = 0, \quad (69)$$

where

$$\theta_{i,j} = \delta_{i,j} + \gamma_{i,j}. \quad (70)$$

For positive i and j , the solution of Eq. (69) can be represented in the form

$$\theta_{i,j} = \text{Const } \alpha_{\theta}^i \beta_{\theta}^j. \quad (71)$$

Substituting this into Eq. (69) gives the characteristic equation for α_{θ} and β_{θ} ,

$$2k_B T / [x_{\infty}(1-x_{\infty})] + (\alpha_{\theta} + 1/\alpha_{\theta})(\epsilon_{AA} + \epsilon_{AB}) + (\beta_{\theta} + 1/\beta_{\theta})(\epsilon_{BB} + \epsilon_{AB}) = 0. \quad (72)$$

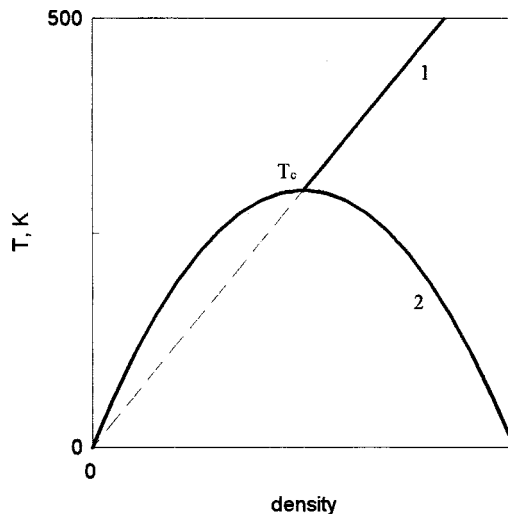


FIG. 12. Phase diagram for the system with directional interactions for $\epsilon_{AA}/k_B = -100$ K, $\epsilon_{BB}/k_B = -200$ K, and $\epsilon_{AB}/k_B = -450$ K. Line 1 indicates beginning of ordering, and line 2 shows condensation. The intersection of these lines is at the tricritical point, T_c .

Since $\theta_{i,j}$ decreases monotonically as i and/or j go up, we consider only positive α_{θ} and β_{θ} . Substitution of $\alpha_{\theta} = 1$ and $\beta_{\theta} = 1$ (boundaries of conversion) in Eq. (71) results in the following:

$$k_B T / [x_{\infty}(1-x_{\infty})] + (\epsilon_{AA} + \epsilon_{BB} + 2\epsilon_{AB}) = 0. \quad (73)$$

Note that, for $\epsilon_{BB} = \epsilon_{AB} = 0$, Eq. (73) coincides with Eq. (66).

From Eqs. (70) and (71), it follows that

$$\delta_{i,j} = \text{Const } \alpha_{\theta}^i \beta_{\theta}^j - \gamma_{i,j}. \quad (74)$$

Substitution of Eq. (74) into Eq. (68) gives

$$k_B T [2\gamma_{i,j}/x_{\infty} + \text{Const } \alpha_{\theta}^i \beta_{\theta}^j / (1-x_{\infty})] + (\gamma_{i+1,j} + \gamma_{i-1,j})\epsilon_{AA} + (\text{Const } \alpha_{\theta}^{i+1} \beta_{\theta}^j - \gamma_{i+1,j} + \text{Const } \alpha_{\theta}^{i-1} \beta_{\theta}^j - \gamma_{i-1,j})\epsilon_{AB} + (\gamma_{i,j+1} + \gamma_{i,j-1})\epsilon_{BB} + (\text{Const } \alpha_{\theta}^i \beta_{\theta}^{j+1} - \gamma_{i,j+1} + \text{Const } \alpha_{\theta}^i \beta_{\theta}^{j-1} - \gamma_{i,j-1})\epsilon_{AB} = 0. \quad (75)$$

Equation (75) is a linear, nonhomogeneous, finite-difference equation of second order. Its general solution can be written as sum of the particular solution for the nonhomogeneous equation and the general solution for the homogeneous equation. This homogeneous equation is

$$2k_B T \gamma_{i,j} / x_{\infty} + (\gamma_{i+1,j} + \gamma_{i-1,j})\epsilon_{AA} - (\gamma_{i+1,j} + \gamma_{i-1,j})\epsilon_{AB} + (\gamma_{i,j+1} + \gamma_{i,j-1})\epsilon_{BB} - (\gamma_{i,j+1} + \gamma_{i,j-1})\epsilon_{AB} = 0. \quad (76)$$

For positive i and j , the solution of Eq. (76) can be represented in the form

$$\gamma_{i,j} = \text{Const } \alpha_{\gamma}^i \beta_{\gamma}^j. \quad (77)$$

Substitution of this expression into Eq. (76) results in the following characteristic equation:

$$2k_B T / x_{\infty} + (\alpha_{\gamma} + 1/\alpha_{\gamma})(\epsilon_{AA} - \epsilon_{AB}) + (\beta_{\gamma} + 1/\beta_{\gamma})(\epsilon_{BB} - \epsilon_{AB}) = 0. \quad (78)$$

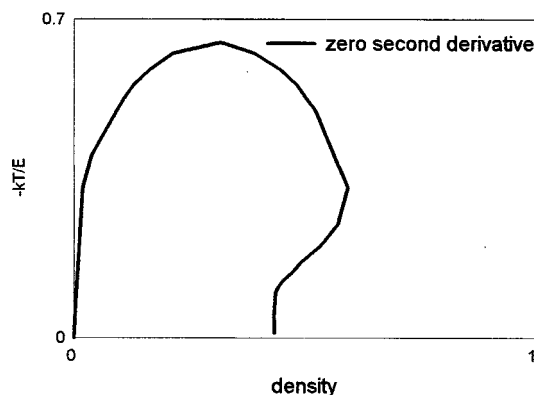


FIG. 13. Boundary of the phase stability for $z_A=6$ and $z=12$. Here $\epsilon_{AA}=\epsilon$, and $\epsilon_{AB}=\epsilon_{BB}=0$.

Substitution of $\alpha_\gamma=1$ and $\beta_\gamma=1$ (boundaries of conversion) into Eq. (78) gives

$$k_B T/x_\infty + (\epsilon_{AA} + \epsilon_{BB} - 2\epsilon_{AB}) = 0. \quad (79)$$

Equations (73) and (79) describe the phase diagram for the system with directional interactions. Equation (73) characterizes the “vapor–liquid” boundary of stability, and Eq. (79) gives the boundary of stability for “order–disorder” phase transition.

It is interesting to note that a tricritical point can occur as line (79) crosses line (73) at the critical point. This happens when

$$\epsilon_{AA} + \epsilon_{BB} = (2/3)\epsilon_{AB}. \quad (80)$$

Figure 12 shows the phase diagram for a system with a tricritical point for $\epsilon_{AA}/k_B = -100$ K, $\epsilon_{BB}/k_B = -200$ K, and $\epsilon_{AB}/k_B = -450$ K. Note that the slope of line 1, in Fig. 12, is $\Delta = (2\epsilon_{AB} - \epsilon_{AA} - \epsilon_{BB})/k_B$. If $\Delta=0$, the “order–disorder” phase transition is not possible.

D. Retrograde condensation

The discussions above have been for a two-dimensional lattice. While there is much to be investigated about this model, it is not possible to consider all aspects of this theory in one paper. However, to show the nontrivial behavior of this model, we consider the boundary of the phase stability for the three-dimensional case with $z_A=6$ and $z=12$ (three-dimensional hexagonal lattice). This boundary is the dependence of the temperature on the bulk density where $\partial^2 A / \partial x_\infty^2 = 0$. Figure 13 shows this boundary predicted by Eq. (39). As seen from Fig. 13, the phase diagram indicates an effect referred to as retrograde condensation.²

VI. CONCLUSION

Two-dimensional Ono–Kondo equations have been derived for the lattice model with directional interactions. These equations lead to explicit expressions for the configurational energy as a function of the temperature and bulk density that are in agreement with Monte Carlo simulation

data. It has been shown that the commonly-made assumption that the partition function can be factored into dispersion and directional (polar and hydrogen bonding) interactions is not valid at low densities. Analysis of the phase diagram for the system has been performed by considering two-dimensional equations of equilibrium and by linearization of the equations with respect to excess density. It is shown that this procedure is consistent with the classical theory of order–disorder phase transitions.

It has been shown that the Ono–Kondo model is able to predict tricritical points and retrograde condensation.

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