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A new model for lattice systems

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A new model is derived for lattice systems (lattice gas and binary mixtures of monomers). This model is based on a generalization to three dimensions of the Ono–Kondo equations for the density profile near a flat surface. The internal energy is calculated and compared with previous models. Unlike many previous theories, this new model has the correct limiting behavior at infinite dilution, at high densities, when the interchange energy goes to zero and for the lattice gas. In addition, it displays the correct behavior for systems with very strong interactions (such as hydrogen bonds) in that it predicts that the energy saturates to a constant value at a low density. For one-component, monomer systems, the new theory also describes simulation data for square-well (off-lattice) molecules better than previous theories. © 1996 American Institute of Physics.
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INTRODUCTION

Lattice theories have been used extensively to model the properties of both pure fluids and multicomponent mixtures.¹ Most calculations of correlation functions for nonrandom configurations are based on statistical mechanical techniques.² This leads to equations that usually must be solved numerically. In this paper we present a new lattice theory based on a generalization of the Ono–Kondo (OK) equations to three dimensions. In one dimension, the OK equations describe the density profile near a surface and they have been used extensively to model adsorption phenomena.^{3–6} Recently,⁷ the one-dimensional OK equations were generalized and applied to the two-dimensional problem of adsorption on surfaces that have molecular-scale heterogeneities. Here we show how these concepts can be used to predict deviations from mean-field behavior (i.e., to take into account correlations between molecules) by considering the “adsorption” of molecules on a central molecule. This approach is different from the standard statistical mechanical techniques, in that these equations can be solved to give simple, analytical equations for the local composition and the energy of a fluid.

There have been a number of different models developed to describe the deviations from mean-field behavior in pure fluids and in mixtures.^{8–23} These models range from being phenomenological and essentially empirical to theoretical models that are nearly “exact” when compared to molecular simulations. An important point to note is that although these models are based on different physical concepts and different mathematical arguments, in some cases different approaches can provide similar results if they are carried to the same level of approximation. This is illustrated by the fact that chemical theory, quasichemical theory (bond or lattice concepts) and Ornstein–Zernike (OZ) integral equation calculations have been shown to give essentially identical analytical expressions for both the energy and equation of state for hydrogen-bonding systems.²⁴

A NEW LATTICE MODEL

Here we consider lattice theory for a binary mixture of spherical (monomer) molecules and define i, j , and k as the indices for the three dimensions of the lattice coordinates. Each site of the lattice is occupied by a molecule of type A or B . There are interactions between nearest neighbors with ϵ_{AA} , ϵ_{AB} , and ϵ_{BB} being the energies of intermolecular interactions. This approach can be used to analyze both bulk and adsorbed phases. For adsorption at a surface, Ono and Kondo³ derived equations for thermodynamic equilibrium to relate the density in each layer to the densities in the adjacent layers and to the density in the bulk. Their derivation uses the “mean-field” assumption,⁴ which is equivalent to the Bragg–Williams approximation,¹ however, it is applied in a way that gives correlations between molecules and a surface. The one-dimensional Ono–Kondo model has been used to calculate density gradients near surfaces.^{5–7} As shown below, it is possible to predict local densities in a solution by writing the three-dimensional analog to the Ono–Kondo equations. In this case, the boundary conditions describe interactions with a central molecule, rather than a surface. The central molecule plays the role of the adsorbent, and surrounding molecules are equivalent to the adsorbate.

The Ono–Kondo equations are based on relatively simple, local-density, mean-field assumptions. We assume a molecule of the first component, A , is on the site $(0,0,0)$. This is the central molecule and all other molecules are distributed around this central molecule with some densities (probabilities), which must be determined. These densities can be determined by assuming that there is an equilibrium distribution. Consider exchanging a molecule of type A at a site with coordinates i, j, k with a molecule of type B at a site infinitely distant from the site $(0,0,0)$:

$$A_{i,j,k} + B_{\infty} \rightarrow B_{i,j,k} + A_{\infty}. \quad (1)$$

If this exchange occurs at equilibrium, then

$$\Delta H - T \Delta S = 0, \quad (2)$$

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where ΔH and ΔS are the enthalpy and entropy changes, and T is the absolute temperature.

The value of ΔS can be represented in the form

$$\Delta S = k_B \ln W_1 - k_B \ln W_2, \quad (3)$$

where W_1 is the number of configurations where the site with coordinates i, j, k is occupied by a molecule of type A and the infinitely distant site is occupied by a molecule of type B , and W_2 is the number of configurations where the infinitely distant site is occupied by a molecule of type A and the site with coordinates i, j, k is occupied by a molecule of type B . Here k_B is the Boltzmann constant.

If the overall number of configurations for the system is W_0 , then in the mean-field approximation,

$$W_1 / W_0 = x_{i,j,k} (1 - x_\infty) \quad (4)$$

and

$$W_2 / W_0 = (1 - x_{i,j,k}) x_\infty, \quad (5)$$

where $x_{i,j,k}$ is the probability that the site with coordinates i, j, k is occupied by a molecule of type A , and x_∞ is the bulk mole fraction of A molecules.

Substituting Eqs. (4) and (5) into Eq. (3), we have

$$\Delta S = k_B \ln \{ [x_{i,j,k} (1 - x_\infty)] / [(1 - x_{i,j,k}) x_\infty] \}. \quad (6)$$

Calculating the change in enthalpy requires specification of the lattice type and coordination number. Here, for simplicity, we assume a cubic lattice with a coordination number of six. The change in enthalpy can be calculated in the Bragg–Williams approximation¹ by considering the number of neighboring sites that are occupied near the central molecule compared to the bulk. Then

$$\Delta H = (x_{i+1,j,k} + x_{i-1,j,k} + x_{i,j+1,k} + x_{i,j-1,k} + x_{i,j,k+1} + x_{i,j,k-1} - 6x_\infty) \Delta, \quad (7)$$

where Δ is the interchange energy defined as

$$\Delta = 2\epsilon_{AB} - \epsilon_{AA} - \epsilon_{BB}. \quad (8)$$

From Eq. (2) and Eqs. (6) and (7) it follows that

$$\begin{aligned} & \ln \{ [x_{i,j,k} (1 - x_\infty)] / [(1 - x_{i,j,k}) x_\infty] \} - (x_{i+1,j,k} + x_{i-1,j,k} + x_{i,j+1,k} + x_{i,j-1,k} + x_{i,j,k+1} + x_{i,j,k-1} - 6x_\infty) \Delta / k_B T \\ & = 0. \end{aligned} \quad (9)$$

Equation (9) is applicable to all sites with $i^2 + j^2 + k^2 > 1$. For site (1,0,0) we have a boundary condition:

$$\begin{aligned} & \ln \{ [x_{1,0,0} (1 - x_\infty)] / [(1 - x_{1,0,0}) x_\infty] \} \\ & = (1 + x_{2,0,0} + x_{1,1,0} + x_{1,0,1} + x_{1,-1,0} + x_{1,0,-1} - 6x_\infty) \Delta / k_B T. \end{aligned} \quad (10)$$

Sites (1,1,0), (1,0,1), (1,-1,0), (1,0,-1), and (2,0,0) are the neighbors around site (1,0,0). The unity on the right-hand side of Eq. (10) is due to the fact that we have assumed there is a molecule of type A on the site at (0,0,0).

Other boundary conditions are

$$x_{0,1,0} = x_{0,0,1} = x_{-1,0,0} = x_{0,-1,0} = x_{0,0,-1} = x_{1,0,0}. \quad (11)$$

Equations (9), (10), and (11) differ from the standard Ono–Kondo equations^{3,4} in that they are three dimensional. They relate the local density in each site (i, j, k) to the densities in adjacent sites and in the bulk.

LOCAL COMPOSITION

The local composition in the first coordination shell is determined by the value of $x_{1,0,0}$. From Eq. (10) it follows that

$$x_{1,0,0} = x_\infty / [x_\infty + (1 - x_\infty) \exp(-\lambda \Delta / k_B T)], \quad (12)$$

where

$$\lambda = 1 + x_{2,0,0} + x_{1,1,0} + x_{1,0,1} + x_{1,-1,0} + x_{1,0,-1} - 6x_\infty. \quad (13)$$

Equations (9) and (10) can be solved numerically to give the density profile away from each molecule. Here, we are interested in developing an expression for the local density, i.e., the density (or composition) in the first shell around a central molecule. If we are not near a critical point, the correlation length is small and we can assume that the density in the second and subsequent shells is the same as in the bulk, i.e.

$$x_{2,0,0} = x_{1,1,0} = x_{1,0,1} = x_{1,-1,0} = x_{1,0,-1} = x_\infty. \quad (14)$$

Then

$$\lambda = 1 - x_\infty. \quad (15)$$

Substituting Eq. (15) into Eq. (12), we have

$$x_{1,0,0} = x_\infty / \{ x_\infty + (1 - x_\infty) \exp[-(1 - x_\infty) \Delta / k_B T] \}. \quad (16)$$

From Eq. (11), the right side of Eq. (16) represents the composition in the first coordination sphere. In the approximation of independent pairs, the internal energy of the lattice, U , is given by the equation²²

$$\begin{aligned} U &= (Nz/2) [\epsilon_{AA} x_\infty + \epsilon_{BB} (1 - x_\infty)] + (N_{AB} z/2) \\ & \times (2\epsilon_{AB} - \epsilon_{AA} - \epsilon_{BB}), \end{aligned} \quad (17)$$

where

$$N_{AB} = (N/2) [x_\infty (1 - x_{1,0,0}) + (1 - x_\infty) (1 - y_{1,0,0})]. \quad (18)$$

Here z is the coordination number (which is 6 for the simple cubic lattice), N is the total number of molecules, N_{AB} is the number of AB bonds, and $y_{1,0,0}$ is $x_{1,0,0}$ at the composition $(1 - x_\infty)$

$$y_{1,0,0} = (1 - x_\infty) / [(1 - x_\infty) + x_\infty \exp(-x_\infty \Delta / k_B T)]. \quad (19)$$

For $\Delta = 0$, Eq. (17) gives $U_0 = (Nz/2) [\epsilon_{AA} x_\infty + \epsilon_{BB} (1 - x_\infty)]$, which is the sum of the internal energies for the pure components. This is an exact result.^{22,23} It should be noted that many other models for nonrandom behavior (BGY,²¹ NRSF,²⁰ NRTL,¹³ Wilson,¹⁵ UNIQUAC¹⁹) do not give the correct limit as $\Delta \rightarrow 0$.

ONE-COMPONENT SYSTEM

Lattice theory can be used to describe one-component systems by having one of the species represent a vacancy. For a one-component system of species A we have $\epsilon_{AB} = \epsilon_{BB} = 0$ and Eq. (16) can be simplified to

$$x_{1,0,0} = x_{\infty} / \{x_{\infty} + (1 - x_{\infty}) \exp[(1 - x_{\infty}) \epsilon / k_B T]\}, \quad (20)$$

where $\epsilon = \epsilon_{AA}$. Also, for a one-component lattice we have instead of Eq. (17)

$$U = (Nz/2) \epsilon x_{\infty} - (N_{AB} z/2) \epsilon. \quad (21)$$

Substituting Eq. (18) into Eq. (21), we obtain

$$U = (Nz \epsilon / 2) \{x_{\infty} - [x_{\infty} (1 - x_{1,0,0}) + (1 - x_{\infty}) (1 - y_{1,0,0})] / 2\}. \quad (22)$$

COMPARISON WITH OTHER MODELS

Lattice models have been used to interpret the behavior of a wide variety of molecular behavior. Here we present a comparison of the new model with predictions of other lattice models, with Monte Carlo simulations, and with an accurate equation for off-lattice square-well molecules.

A direct comparison of our model with other theories is not very informative because the mean-field term provides the dominant contribution to all the equations. However, the effects of the mean-field term can be eliminated either by dividing the energy by the mean-field value or by subtracting the mean-field value from the energy. Below we present both types of comparison. Taking the ratio of the energy to the mean-field (random mixing) energy gives

$$U/U_{mf} = \{x_{\infty} - [x_{\infty} (1 - x_{1,0,0}) + (1 - x_{\infty}) \times (1 - y_{1,0,0})] / 2\} / x_{\infty}^2, \quad (23)$$

where $U_{mf} = \epsilon x_{\infty}^2 Nz / 2$ is the energy of the system in the mean-field approximation. Here we compare Eq. (23) with $x_{1,0,0}$ and $y_{1,0,0}$ given by Eqs. (16) and (19) to other lattice theories, to quasichemical theory, and to perturbation theory.

For a one-component, monomer system, the Born–Green–Yvon²¹ and Non-Random Surface Fraction²⁰ models give the following equations, respectively:²³

$$U/U_{mf} = 1 / [x_{\infty} + (1 - x_{\infty}) \exp(\epsilon / k_B T)] \quad (24)$$

and

$$U/U_{mf} = 1 / \{x_{\infty}^2 + [2x_{\infty}(1 - x_{\infty}) + (1 - x_{\infty})^2] \exp(\epsilon / k_B T)\}. \quad (25)$$

A similar result can be obtained from Guggenheim's quasichemical theory

$$U/U_{mf} = [1 - 2(1 - x_{\infty}) / (\beta + 1)] / x_{\infty}, \quad (26)$$

where

$$\beta = \{1 - 4x_{\infty}(1 - x_{\infty})[1 - \exp(-\epsilon / k_B T)]\}^{1/2}. \quad (27)$$

Finally, we would like to compare our model with the behavior of off-lattice, square-well molecules. Bokis and

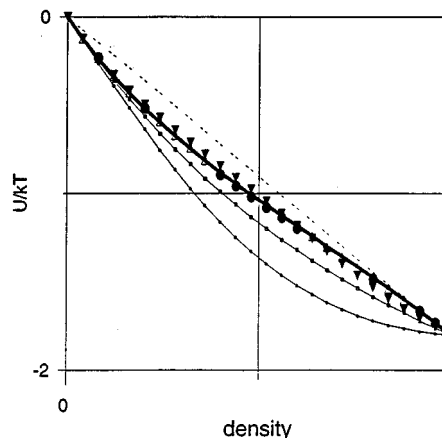


FIG. 1. Dependence of U/kT on density for $\epsilon/kT = -0.6$. In this figure lines for Freed's theory and Eq. (22) cannot be distinguished. Guggenheim theory also is very close to Eq. (22). —, Eq. (22); ---, Freed; —■—, NRSF; —○—, BGY; ▼, square well; △, Guggenheim; ●, Monte Carlo; ---, Bragg–Williams.

Donohue²⁵ have shown that internal energy for square-well fluid can be calculated very accurately by an equation of the form

$$U/U_{mf} = \exp(P \epsilon / k_B T), \quad (28)$$

where P is a polynomial in density

$$P = 1 - 5.41651 \eta + 8.41582 \eta^2 + 6.67298 \eta^3 - 19.39 \eta^4 + 2.04454 \eta^5 - 9.92956 \eta^6 + 11.946 \eta^7. \quad (29)$$

This equation represents the molecular dynamics simulation data of Alder *et al.*²⁶ more accurately than any other theory, including Alder's original 24 term expansion. Here η is the volume fraction of square-well molecules. For a cubic lattice model,

$$\eta = (\pi/6) x_{\infty}. \quad (30)$$

Figure 1 shows the dependence of the reduced internal energy, $U/k_B T$, on the density predicted by Eq. (22). Also shown are predictions of the theories discussed above. As shown in Fig. 1, Eq. (22) gives the best agreement with the Monte Carlo simulation data for a monomeric lattice gas and with the BD fit of the molecular dynamics simulation data for molecules with square-well interactions. The internal energy shown in Fig. 1 is approximately a linear function of density because the energy is dominated by the mean-field term. However, as noted above, the differences between these theories can be seen more clearly if we either divide by the mean-field term or subtract the mean-field term.

Figure 2 shows predictions of Eq. (23) with $x_{1,0,0}$ and $y_{1,0,0}$ given by Eqs. (16), (19), and of the BGY, NRSF, Guggenheim, BD square-well fluid, and Monte Carlo simulation data for $\epsilon/k_B T = -0.6$. The ratio U/U_{mf} is approximately unity at high densities but increases as the density decreases. In the limit of zero density, this ratio goes to the Boltzmann factor. All of the theories discussed here have the correct limits for U/U_{mf} at high and low densities but they differ in the rate that they decay from the Boltzmann factor

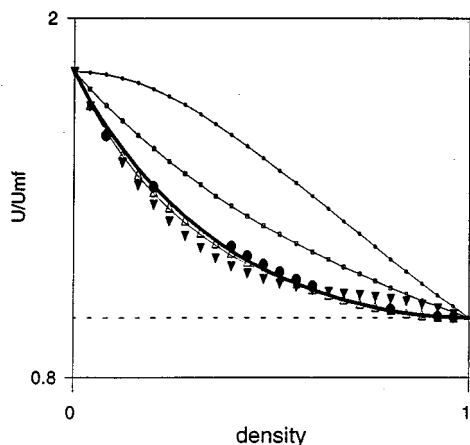


FIG. 2. Dependence of U/U_{mf} on density for $\epsilon/kT = -0.6$. —, Eq. (23); —, Freed; —■—, NRSF; —○—, BGY; ▼, square well; △, Guggenheim; ●, Monte Carlo; ---, Bragg-Williams.

to mean-field behavior. As seen from Fig. 2, Eq. (23), Freed, and Guggenheim predictions are in close agreement with Monte Carlo simulation data. It is of interest to note the similarity in the behavior of the lattice calculations (theory and simulations) with off-lattice calculations for square-well

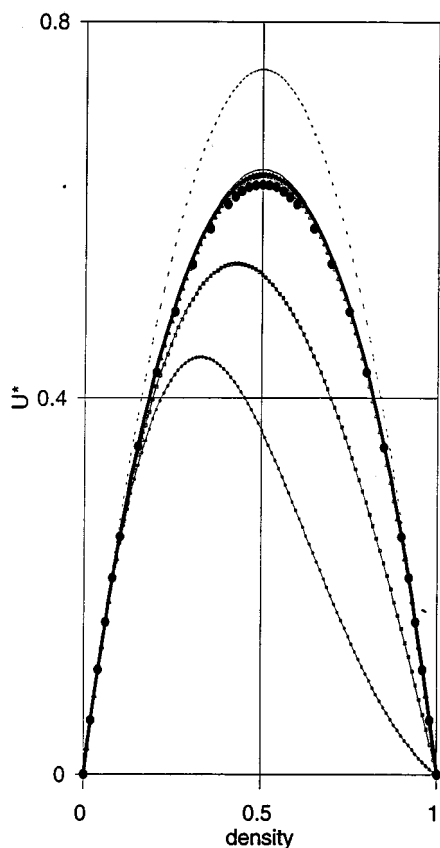


FIG. 3. Dependence of U^* on density for different theories. Guggenheim's theory and Eq. (22) are in close agreement everywhere. Freed's theory agrees with Eq. (22), except near the critical point. —, Eq. (22); —, Freed; —■—, NRSF; —○—, BGY; △, Guggenheim; ●, Monte Carlo; ---, Bragg-Williams.

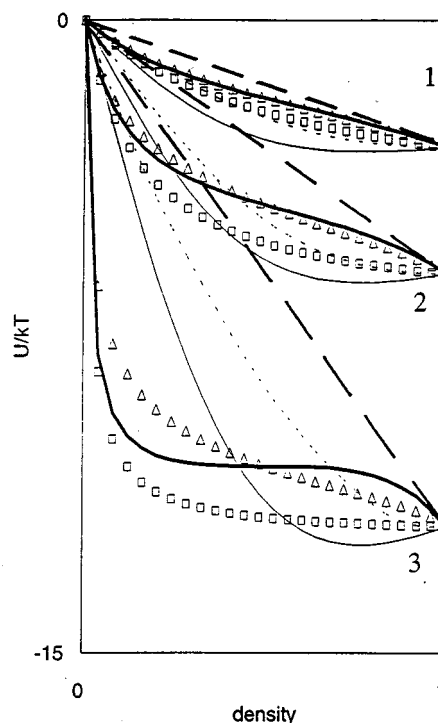


FIG. 4. Saturation phenomenon in dependence of U/kT on density at large ϵ/kT : -1(1), -2(2), -4(3). —, Eq. (22); □, BGY; △, Guggenheim; —, NRSF; ---, Freed; ---, Bragg-Williams.

molecules, as predicted by the theory of Bokis and Donohue.²⁵ Therefore, Eq. (23) would be quite accurate for off-lattice systems if an off-lattice mean-field term is used.

Figure 3 illustrates the dependence of $U^* = (U - U_0)/\epsilon$ on the density obtained from Eq. (22) and from different theories. Here U_0 is the internal energy of the pure component. As seen from Fig. 3, Eq. (22) gives a value of U^* that is very close to Guggenheim, Freed, and Monte Carlo simulation data. There is a large difference between the NRSF and BGY models and the simulation results. Both of these theories show excellent agreement with Freed's theory for mixtures of small molecules with polymers.²⁰ However, both fail to give the correct behavior as Δ goes to zero. The results shown in Fig. 3 demonstrate that they both show significant deviations for the lattice gas also.

A final point about this new model concerns its behavior for highly attractive systems such as molecules that hydrogen bond. For weak van der Waals interactions, the energy is approximately a linear function of density and composition. However, for very strong interactions, such as hydrogen bonding, the energy quickly "saturates" and reaches a constant value. This is illustrated in Fig. 4. For $\epsilon/k_B T = -1$, the energy varies linearly with density. For $\epsilon/k_B T = -2$, the region where U varies linearly with density is small. For $\epsilon/k_B T = -4$ there is a wide range of density where the internal energy is constant. Shown are calculations from Eq. (22) and other theories. Again, the difference between Eq. (22) and Guggenheim theory is small. BGY theory gives qualitatively correct behavior for these high-energy systems also.

CONCLUSIONS

The three-dimensional form of the one-dimensional Ono–Kondo equations provides a new method to predict local compositions for lattice systems. Simple, analytic equations have been obtained by assuming that the composition in the second coordination sphere is equal to that in the bulk. For binary systems this results in a new equation (16) that can be used to calculate the internal energy from Eq. (17). Unlike many previous theories for nonrandom systems, this approach gives the correct limit as $\Delta \rightarrow 0$. This new model also displays the correct behavior for systems with very strong interactions (such as hydrogen bonds), in that it predicts that the energy saturates to a constant value at a low density. Finally, for one-component systems, a simple equation is obtained that agrees with lattice-gas Monte Carlo simulation data and molecular dynamics simulation data for square-well molecules better than previous theories.

Though derived using different approaches, there is close agreement between Eq. (12), Freed's theory, and Guggenheim's theory. There also is fairly close agreement between these two lattice models and the theory for off-lattice square-well molecules. This is reminiscent of the similarities between chemical theory, quasichemical theory, and results from the Ornstein–Zernike equation observed previously for hydrogen bonding systems.²⁴ However, it should be noted that there is a fundamental difference between Eq. (12) and Guggenheim's theory in the way they depend on the coordination number and lattice structure.

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