Prediction of Nonrandom Mixing in Lattice Model with Multi-references

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Abstract−A new lattice theory is proposed to describe nonrandom mixing behavior based on recently developed lattice model theory by Aranovich and Donohue. The present theory assumes multi-references in order to take into account interference effects on non-random mixing among pairs. The number of references was obtained from Monte Carlo simulations for monomer+hole mixtures. Monte Carlo simulation for hole [0]+monomer [1]+monomer [2] mixture shows that this theory is more accurate than Guggenheim's quasi-chemical theory or the Aranovich-Donohue model in a wide range of temperatures and densities. Especially, even under the stringent condition of zero interaction energy parameter $\varepsilon_{12}=0$, the present theory predicts well the extent of nonrandom mixing. For dimer fluid the non-randomness is calculated using the surface fraction. Here three references was used as in the case of monomer fluid with chain connectivity constraints. Comparison of the theory with Monte Carlo simulation results for dimer+hole system shows a good agreement.

Key words: Lattice Theory, Non-random Mixing, Aranovich and Donohue Lattice Model, Interference Effect, Dimer Fluid

INTRODUCTION

Recently Aranovich and Donohue (AD) developed a new approach to predict the thermodynamic properties of lattice gas by generalizing the ideas of Ono and Kondo [Ono and Kondo, 1960] to treat a lattice in three dimensions [Aranovich et al., 1996]. They extended the theory to multi-component mixtures of monomers [Aranovich and Donohue, 1997]. Their expressions for local compositions around each species were derived taking into account molecular interactions as well as molecular geometry and lattice structure. These expressions are simple and as accurate as Guggenheim's quasi-chemical theory (QC) [Guggenheim, 1952] in predicting nonrandom mixing energy. QC theory is widely used in nonrandom lattice fluid theory [Park et al., 1998; Shin et al., 1995, 1998, 2000; Kim et al., 1998; Kang et al., 1998; Yoo et al., 1997; Yoo and Lee, 1996, 2000]. However, both the theories underestimate the extent of non-random mixing at low temperatures. It is because these theories assume that different pairs do not interfere with one another.

In this work we propose a new approach which is able to predict an accurate non-randomness in a wide range of temperatures and densities. We consider interference among pairs through multi-references. Also, the non-randomness for dimer fluids is obtained by this approach with chain connectivity constraints.

NONRANDOM BEHAVIOR IN MONOMER MIXTURES

We consider a lattice containing ν different kinds of monomers. Interaction energy for an **i**–**j** pair are designated by $-\varepsilon_{ij}$. In this study, unlike the AD model, molecules of type **j** and **k** are considered as references, whereas in the AD model only molecule of type **j** is considered as reference. The reason that in this study multi-references

are employed is to take into account interferences among pairs. In real system, all other molecules around a given molecule act as references which influence the movement of the molecule. However, it is impossible to consider all the influences in calculation. For the square-well potential, the nearest neighbor molecules could be considered as references but the calculation is nearly impossible, since these references could interference each other. Therefore, we assume that these references are in positions of being independent of each other and being able to influence the given molecule through their neighbor molecules. This is an ad hoc procedure. This assumption fails at low enough temperatures, at which references interfere with each other.

Consider exchanging a molecule of type **i** which belongs to the first shell of a reference molecule of type **j** and also belongs to the second shell of another reference molecule of type **k** with a molecule of type *l* located at a site infinitely distant from both **j** and **k**.

If this exchange is assumed to occur at local equilibrium under constant temperature and volume, the Helmholtz energy does not change.

$$\Delta \mathbf{U} - \mathbf{T}\Delta \mathbf{S} = \mathbf{0} \tag{1}$$

where $\Delta \mathbf{U}$ and $\Delta \mathbf{S}$ are the energy and entropy changes, respectively, and $\mathbf{T}$ is the absolute temperature.

The entropy term is given by

$$\Delta \mathbf{S} = \mathbf{S_2} - \mathbf{S_1} = \mathbf{k} \ln\left(\frac{\mathbf{x}_i^{\bullet} \mathbf{x}_l^{j,k}}{\mathbf{x}_i^{j,k} \mathbf{x}_l^{\bullet}}\right) \tag{2}$$

where $\mathbf{S_1}$ is the entropy before the exchange, $\mathbf{S_2}$ is the entropy after the exchange, $\mathbf{x}_i^{j,k}$ is the probability of finding a molecule of type **i** in the first shell of the reference molecule of type **j** and also in the second shell of the reference molecule of type **k**, and $\mathbf{x}_i^{\bullet}$ is the probability of finding a molecule of type **i** in the bulk.

Here we consider a simple cubic lattice (coordination number $\mathbf{z}=\mathbf{6}$). We further assume that the compositions in the second and the higher shells of reference molecules do not differ from those in

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the bulk.

Local energies around molecules **i** and *l* before and after the exchange are then written as follows:

$$\mathbf{U_1} = \left\{ (\mathbf{z}-\alpha)\sum_m \mathbf{x}_m^{\infty}\boldsymbol{\varepsilon}_{im} + \boldsymbol{\varepsilon}_{ij} + (\alpha-1)\sum_m \mathbf{x}_m^{k,j}\boldsymbol{\varepsilon}_{im} \right\} + \mathbf{z}\sum_m \mathbf{x}_m^{\infty}\boldsymbol{\varepsilon}_{lm} \tag{3}$$

$$\mathbf{U_2} = \left\{ (\mathbf{z}-\alpha)\sum_m \mathbf{x}_m^{\infty}\boldsymbol{\varepsilon}_{lm} + \boldsymbol{\varepsilon}_{ij} + (\alpha-1)\sum_m \mathbf{x}_m^{k,j}\boldsymbol{\varepsilon}_{lm} \right\} + \mathbf{z}\sum_m \mathbf{x}_m^{\infty}\boldsymbol{\varepsilon}_{im} \tag{4}$$

$$\Delta\mathbf{U} = (\boldsymbol{\varepsilon}_{ij}-\boldsymbol{\varepsilon}_{ij}) - \sum_m \mathbf{x}_m^{\infty}(\boldsymbol{\varepsilon}_{lm}-\boldsymbol{\varepsilon}_{im}) + (\alpha-1)\sum_m (\mathbf{x}_m^{k,j}-\mathbf{x}_m^{\infty})(\boldsymbol{\varepsilon}_{lm}-\boldsymbol{\varepsilon}_{im}) \tag{5}$$

where the summation runs over all species (ν), and α is the number of references. The first two terms of Eq. (5) are energy changes when interference is neglected and in the case of a single reference ($\alpha=1$), the above expression reduces to the AD model.

From Eqs. (1), (2) and (5) it follows that

$$\frac{\mathbf{x}_l^{j,k}}{\mathbf{x}_i^{j,k}} = \frac{\mathbf{x}_l^{\infty}}{\mathbf{x}_i^{\infty}}\exp\left[\frac{\Delta\mathbf{U}}{\mathbf{kT}}\right] \tag{6}$$

Applying the following conservation law to Eq. (6),

$$\sum_l^{\nu}\mathbf{x}_l^{j,k} = 1 \tag{7}$$

we obtain expressions for local composition as

$$\mathbf{x}_i^{j,k} = \frac{\mathbf{x}_i^{\infty}}{\sum_l \mathbf{x}_l^{\infty}\exp[\Delta\mathbf{U}/\mathbf{kT}]} \tag{8}$$

As we assumed that reference molecules **j** and **k** are independent of each other, the local composition or the probability of finding two molecules in the vicinity of each other, $\mathbf{x}_i^j$ can be obtained as follows:

$$\mathbf{x}_i^j = \sum_k \mathbf{x}_k^{\infty}\mathbf{x}_i^{j,k} \tag{9}$$

We define nonrandomness factor by

$$\Gamma_{ij} = \Gamma_{ji} = \frac{\mathbf{x}_j^{\infty}\mathbf{x}_i^j + \mathbf{x}_i^{\infty}\mathbf{x}_j^i}{2\mathbf{x}_i^{\infty}\mathbf{x}_j^{\infty}} \tag{10}$$

The non-randomness factor, Γ_{11} can be calculated using Eqs. (8), (9), and (10), and it gives the correct low density limit. In the case of a completely random mixture, Γ_{ij} is equal to unity. Finally, internal energy **U** can be written in the form as

$$\frac{\mathbf{U}}{\mathbf{N}_s} = \frac{\mathbf{z}}{2}\sum_{i,j}\mathbf{x}_i^{\infty}\mathbf{x}_j^{\infty}\mathbf{\Gamma}_{ij}\boldsymbol{\varepsilon}_{ij} \tag{11}$$

where $\mathbf{N}_s$ is the total number of lattice sites.

NON-RANDOM BEHAVIOR IN DIMER MIXTURES

For a dimer in simple cubic lattice structure, the number of external contact points is ten and eight of them have interference with segments attracted by bonded segments. A bonded segment can be regarded as a reference. As a result, these sites of dimers have one more reference than that of monomer. In other words, dimer has two kinds of sites. One kind has three references and the other kind has four references. Here we regard dimer as two components because of the two kinds of sites.

Local energies around molecules **i** and *l* before and after the exchange are then written as follows:

$$\mathbf{U_1} = (\mathbf{z}-\alpha-\delta_{jB})\sum_m \boldsymbol{\theta}_m^{\infty}\boldsymbol{\varepsilon}_{im} + \boldsymbol{\varepsilon}_{ij} + (\alpha-1)\sum_m \boldsymbol{\theta}_m^{k,j}\boldsymbol{\varepsilon}_{im}$$
$$+ \delta_{jB}\sum_m \boldsymbol{\theta}_m^{i,j}\boldsymbol{\varepsilon}_{im} + \mathbf{z}\sum_m \boldsymbol{\theta}_m^{\infty}\boldsymbol{\varepsilon}_{im} \tag{12}$$

$$\mathbf{U_2} = (\mathbf{z}-\alpha-\delta_{jB})\sum_m \boldsymbol{\theta}_m^{\infty}\boldsymbol{\varepsilon}_{lm} + \boldsymbol{\varepsilon}_{ij} + (\alpha-1)\sum_m \boldsymbol{\theta}_m^{k,j}\boldsymbol{\varepsilon}_{lm}$$
$$+ \delta_{jB}\sum_m \boldsymbol{\theta}_m^{i,j}\boldsymbol{\varepsilon}_{lm} + \mathbf{z}\sum_m \boldsymbol{\theta}_m^{\infty}\boldsymbol{\varepsilon}_{im} \tag{13}$$

$$\Delta\mathbf{U} = (\boldsymbol{\varepsilon}_{ij}-\boldsymbol{\varepsilon}_{ij}) - \sum_m \boldsymbol{\theta}_m^{\infty}(\boldsymbol{\varepsilon}_{lm}-\boldsymbol{\varepsilon}_{im}) + (\alpha-1)\sum_m (\boldsymbol{\theta}_m^{k,j}-\boldsymbol{\theta}_m^{\infty})(\boldsymbol{\varepsilon}_{lm}-\boldsymbol{\varepsilon}_{im})$$
$$+ \delta_{jB}\sum_m (\boldsymbol{\theta}_m^{i,j}-\boldsymbol{\theta}_m^{\infty})(\boldsymbol{\varepsilon}_{lm}-\boldsymbol{\varepsilon}_{im}) \tag{14}$$

where δ_{iB} is the Kronecker delta and $\delta_{iB}=1$ if the site of type **j** is in dimer and has interference with segments attracted by bonded segments.

Following the procedure of the case of monomer, we obtain expressions for local surface fractions as

$$\boldsymbol{\theta}_i^{j,k} = \frac{\boldsymbol{\theta}_i^{\infty}}{\sum_l \boldsymbol{\theta}_l^{\infty}\exp[\Delta\mathbf{U}/\mathbf{kT}]} \tag{15}$$

As we assumed that references **j** and **k** are independent with each other, local surface fractions between two sites, $\boldsymbol{\theta}_i^j$ can be obtained as follows:

$$\boldsymbol{\theta}_i^j = (1-\delta_{jB})\sum_k \boldsymbol{\theta}_k^{\infty}\boldsymbol{\theta}_i^{j,k} + \delta_{jB}\boldsymbol{\theta}_i^{i,j} \tag{16}$$

where the Kronecker delta arises from chain connectivity constraints.

COMPARISON WITH SIMULATION

A lattice gas is a binary mixture of holes [0] and molecules [1]. ε_{00} and ε_{10} or ε_{01} are set to zero. The number of references, α is tested with 2, 3, and 4. Comparison of the present theory with Monte Carlo simulation of hole-monomer mixture shows that $\alpha=3$ is appropri-
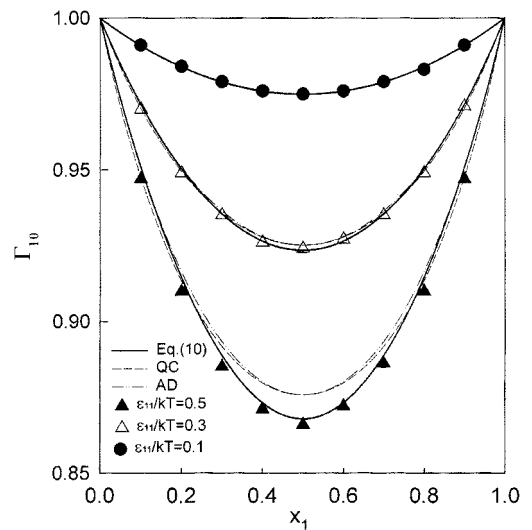

Fig. 1. Non-randomness factor in a lattice gas at $\varepsilon_{11}/\mathbf{kT}=0.1, 0.3, 0.5$.

ate to simple cubic structure. The predictions of the present theory with $\alpha=4$ deviate from Monte Carlo simulation data at low temperatures because of interferences of the references. Therefore, in this study α is set to 3. For body-centered cubic structure or face-centered cubic structure, α would be above 3, since its larger coordination number accommodates the more references without interferences each other.
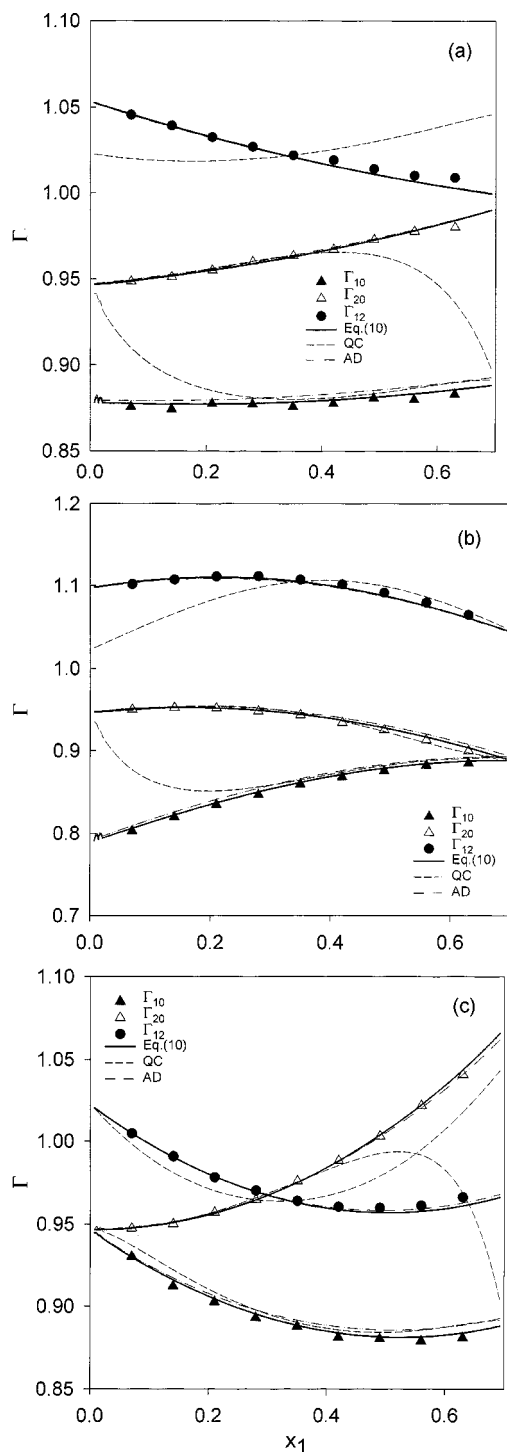
For a lattice gas, Guggenheim's quasi-chemical theory (QC) is nearly identical with the AD model. The present model is superior to QC theory and AD model at a low temperature (Fig. 1). It is because the present theory considers interferences between pairs through multi-references.

Fig. 2, (a) shows non-randomness when $\varepsilon_{12} = \sqrt{\varepsilon_{11}\varepsilon_{22}}$. As one composition is closer to zero, Γ_{10} and Γ_{20} from QC theory get to deviate from simulation results. Though the present model and the AD model show the similar values of Γ_{10} and Γ_{12}, the present model is slightly better than the AD model in Γ_{10}. It is because the present model is more accurate than the AD model at a low temperature. Fig. 2, (b) shows the case of $\varepsilon_{12}=\varepsilon_{11}$. This is the case that 1-2 interaction is strong. It is interesting that in this case, QC theory is more accurate than in the former case. Fig. 2, (c) shows the case of $\varepsilon_{12}=\varepsilon_{22}$. This is the case that 1-2 interaction is weak. Also in this case, QC theory is more accurate than that in the case (a).

Fig. 3. shows non-randomness when $\varepsilon_{12}=0$. It is the case that the two components do not interact with each other. As hole density increases, the accuracy of QC theory deteriorates. Though the present model and the AD model show the similar values of Γ_{10} and Γ_{20}, the present model is better than the AD model in Γ_{12}.

Fig. 4. shows non-randomness of dimer fluid. $\mathbf{r}$ is the chain length. $\mathbf{N_0}$ and $\mathbf{N_1}$ are the number of holes [0] and the number of

Fig. 2. Non-randomness factors in a ternary mixture at $\varepsilon_{11}/kT = 0.5$, $\varepsilon_{22}/kT=0.25$, $x_0=0.3$.
(a) $\varepsilon_{12} = \sqrt{\varepsilon_{11}\varepsilon_{22}}$, (b) $\varepsilon_{12}=\varepsilon_{11}$, (c) $\varepsilon_{12}=\varepsilon_{22}$
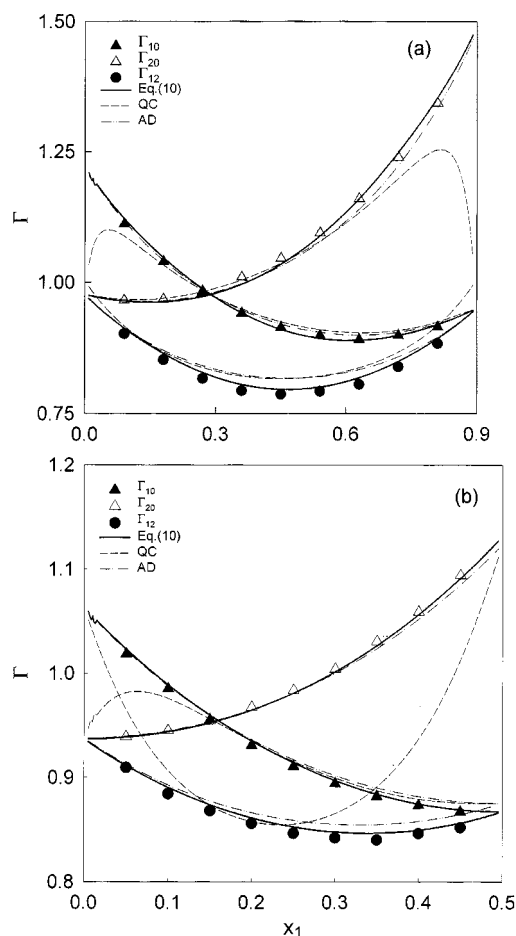

Fig. 3. Non-randomness factors in a ternary mixture at $\varepsilon_{11}/kT = 0.5$, $\varepsilon_{22}/kT=0.25$, $\varepsilon_{12}/kT=0$.
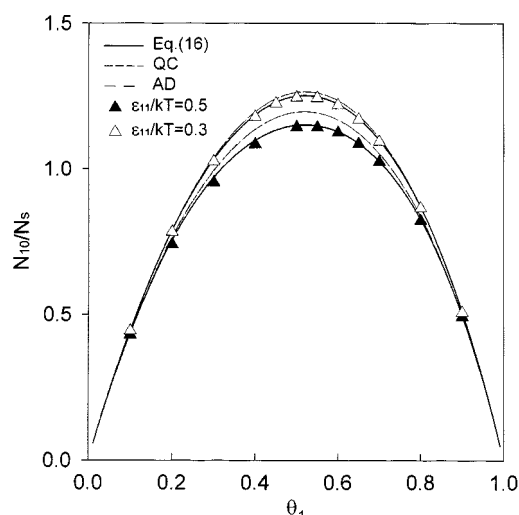(a) $x_0=0.1$, (b) $x_0=0.5$

Fig. 4. Non-randomness factor in dimer fluids at $\varepsilon_{11}/kT=0.3, 0.5$.

dimers [1], respectively. These non-randomnesses from the three theories were calculated by using the surface fractions. Though these theories show similar values at a high temperature, only the present model is accurate at a low temperature.

CONCLUSIONS

We propose a new approach which can accurately predict the extent of non-random mixing in a lattice fluid model. This approach is a modification of recent lattice model theory of Aranovich and Donohue, which employs multi-references. It has the effect of considering interferences among molecules and leads to an accurate prediction of non-randomness even at low temperatures. Dimer fluid has one more reference than that of monomer fluid. It is because a neighboring segment exists. In addition, chain connectivity constraint is considered. Non-randomness predicted by the present model is more accurate than those from quasi-chemical theory or the Aranovich-Donohue model.

ACKNOWLEDGMENT

NOMENCLATURE

N_i : the number of species
N_s : the number of total lattice sites
r   : chain length
S   : the energy and entropy changes
T   : temperature
U   : configurational energy
$x_i^{j,k}$: the probability of finding a molecule of type **i** in the first shell of the reference molecule of type **j** and also in the second shell of the reference molecule of type **k**
x_i^∞ : the probability of finding a molecule of type **i** in the bulk
z   : coordination number

Greek Letters
α : the number of references
δ_{jB} : Kronecker delta
       $\delta_{jB}=1$, if the molecule of type **j** is dimer and the site has a neighboring bonded segment
       $\delta_{jB}=0$, otherwise
ε_{ij} : interaction energy for **i−j** pair
Γ_{ij} : non-randomness factor of **i−j**
ν : the number of all species
θ : surface fraction

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