

Mapping of Short-Range Interatomic Potentials onto Lattice-Gas Models: Potential Renormalization Theory

Kaoru Ohno

Department of Physics, Graduate School of Engineering, Yokohama National University,
79-5 Tokiwadai, Hodogaya-ku, Yokohama 240-8501, Japan
Fax: 81-45-338-3020, e-mail: ohno@ynu.ac.jp

In order to build a bridge between molecular dynamics simulations of atomistic (off-lattice) models and Monte Carlo simulations of lattice-gas models, or to map the realistic interatomic potentials elaborated for molecular dynamics simulations onto lattice-gas models used by Monte Carlo simulations, a tractable two-step renormalization scheme is presented within the framework of the potential renormalization theory. Its applications to the solidification of semiconductors, the order-disorder transition of alloys, and the statistics of semi-flexible polymer solutions are discussed briefly.

Key words: partition function, free energy, coarse grain, phase transition, phase diagram

1. INTRODUCTION

Lattice-gas models and their Monte Carlo simulations (or cellular automata) have been used as an efficient numerical approach to study various thermodynamic properties, conformations and phase transitions of wide variety of materials including vapors, liquids, solutions, solids, alloys and mixtures. However, this approach has a strong limitation in the description of disordered or liquid-like phases. That is, even for crystals or alloys, displacement of atoms from regular lattice points may become important at high temperatures. As a result, for example, lattice-gas models generally overestimate order-disorder phase transition temperatures, if one uses bare interatomic potentials, which are elaborated for molecular dynamics simulations, directly as interaction parameters in lattice-gas models. This is because the internal entropy on a length scale shorter than the lattice constant is not taken into account in those treatments.

On the other hand, the time scale of atomic diffusion in solids is generally so long that one cannot treat order-disorder phase transitions by means of molecular dynamics simulations. This is a fundamental difficulty. How would it be possible to map (or "renormalize") bare interatomic potentials so as to fit to lattice-gas models?

The author has proposed potential renormalization theory [1] which may offer a solution of this problem. The point of this theory is to expect that lattice-gas models with "renormalized potentials" must have the same thermodynamic properties as the original off-lattice models with bare potentials. Explicitly, it is assumed that an original off-lattice system and a renormalized lattice system have the same partition function at a given temperature. Then, a two-step renormalization scheme using A, B sublattices dividing whole space was proposed and formulated in a closed and tractable way [1], and so far applied to a few problems including the solidification of Si [2] and the order-disorder transition of $\text{Cu}_x\text{Au}_{1-x}$ [3].

The rest of this paper is organized as follows. In Section 2, the two-step renormalization scheme is explained in detail. In this scheme, short-range interatomic potentials can be mapped appropriately onto the generalized lattice-gas models, in which the particle number at each lattice point may exceed unity. The assumption of short-range potentials is not so unrealistic, because many preexisting interatomic potentials, which have been used in molecular dynamics, are sufficiently short-ranged. In Section 3, it is demonstrated briefly that the present scheme is in principle applicable to the solidification of semi-conductors like C(diamond), Si, Ge and GaP, the order-disorder transition of A_xB_{1-x} alloys like Cu-Au, Cu-Zn, Cu-Pd and Cu-Pt systems, and the statistics of semi-flexible polymer solutions.

2. THEORY

2.1 Basic Idea

The basic idea of potential renormalization in a classical N -particle system is to determine a new potential function so as not to change the partition function, when we discretize the configurational space in a course of the coarse graining procedure. Let the original partition function be expressed in terms of the bare potential $U(x_1, \dots, x_N)$ as

$$Z = (2\pi m / \beta \hbar^2)^{3N/2} \int dx_1 \dots \int dx_N \exp[-\beta U(x_1, \dots, x_N)] / N!, \quad (1)$$

where we put $\beta = 1/k_B T$. Then we assume that this partition function (1) is reproduced by its discretized version,

$$Z = (2\pi m / \beta \hbar^2)^{3N/2} \sum_{i_1, \dots, i_N} \exp[-\beta W(i_1, \dots, i_N)] / N!. \quad (2)$$

In (2), i_k ($k = 1, \dots, N$) runs over all M lattice points, and $W(i_1, \dots, i_N)$ denotes the desired renormalized potential yet to be determined.

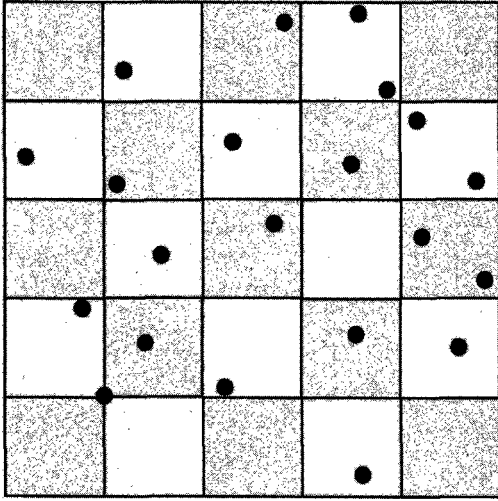


Fig. 1. The A, B sublattice division of whole space.

Let the lattice be composed of two sublattices, A and B and can be discretize the configurational space into cells, which are polyhedrons centered at sublattice points. The cell centered at a sublattice point R_k is defined as a Wigner-Seitz cell surrounded by planes, each of which is perpendicular to a line connecting the point R_k and its adjacent B sublattice point, and intersects the mid point of this line. We call the cell centered at an A or B sublattice point an A-cell or a B-cell. Here we assume that two different A-cells do not have any common (surface) plane nor do two different B-cells. If there is inevitably a common plane, the common area should be sufficiently small. Such a sublattice division is possible, for example, in a simple cubic (SC) lattice.

The bare potential $U(x_1, \dots, x_N)$ in (2) is assumed to be short-ranged and three-body,

$$U(x_1, \dots, x_N) = \sum_{j \neq i} \sum_{j' \neq i} [u_2(x_i, x_j) + \sum_{j'' \neq j, j'} u_3(x_i, x_j, x_{j''})]. \quad (3)$$

Here, u_2 and u_3 denote two-body and three-body parts, respectively. (The generalization to the case of an n -body potential is straightforward.) The cutoff length of the potential is assumed to be shorter than the lattice constants. There is no restriction on the total number of particles N nor on the total number of lattice points M (i.e., the total number of cells). It is possible to assume either $N \leq M$ or $N > M$. In the case $N > M$, the present way of discretizing the space introduces a generalized lattice-gas model, in which more than one particle can occupy the same lattice point [1]. On the other hand, in the case $N \leq M$, one may retrieve usual lattice-gas models, in which each cell contains at most one particle inside. In what follows, I will explain the two-step renormalization scheme, which presents a tractable way of determining the interaction parameters in lattice-gas models.

2.2 The First Step

Let us consider one A-cell, labeled k and centered at R_k , and its neighboring h_B B-cells, labeled $l, l+1, \dots, l+h_B-1$ (here, h_B is the number of neighboring B-cells). The number of particles in the k th A-cell is designated

by n_k , and the number of particles in the $(l+i)$ th B-cell ($i = 0, 1, \dots, h_B-1$) is designated by m_{l+i} . The particle positions inside the $(l+i)$ th B-cell are designated by $x_{l+i,j}$ ($j = 1, \dots, m_{l+i}$).

It is possible to evaluate the trace (the integral) of the configurational exponential with respect to the particle positions inside the k th A-cell as

$$Z_k = \int_{\text{kth A-cell}} dx_{k,1} \dots dx_{k,n_k} \exp[-\beta \sum_{j=1}^{n_k} \{ (\sum_{j'=j+1}^{n_k} u_2(x_{k,j}, x_{k,j'}) + \sum_{j'=j+1}^{n_k} u_3(x_{k,j}, x_{k,j'}, x_{k,j''})) + \sum_{i=0}^{h_B-1} \sum_{j'=0}^{m_{l+i}} (u_2(x_{k,j}, x_{l+i,j'}) + \sum_{j''=j+1}^{n_k} u_3(x_{k,j}, x_{l+i,j'}, x_{l+i,j''})) + \sum_{i=0}^{h_B-1} \sum_{j'=0}^{m_{l+i}} u_3(x_{k,j}, x_{l+i,j'}, x_{l+i,j''}) + \Phi_{AB} \} + \Phi_{AA} \}], \quad (4)$$

where Φ_{AB} and Φ_{AA} denote "the edge interactions" [1] between particles inside different A-cells. They are given, respectively, by a summation with respect to the A-cells adjacent to the $(l+i)$ th B-cell,

$$\Phi_{AB} = \sum_{i'}^{A-B} \sum_{j'=1}^{n_{i'}} u_3(x_{k,j}, x_{l+i,j'}, x_{i',j''}), \quad (5)$$

and a summation with respect to the A-cells in the vicinity of the k th A-cell,

$$\Phi_{AA} = \sum_{i'}^{A-A} \sum_{j'=1}^{n_{i'}} [u_2(x_{k,j}, x_{i',j'}) + \sum_{j''=j}^{n_k} u_3(x_{k,j}, x_{k,j'}, x_{i',j''}) + \sum_{j''=j'}^{n_{i'}} u_3(x_{k,j}, x_{i',j'}, x_{i',j''})]. \quad (6)$$

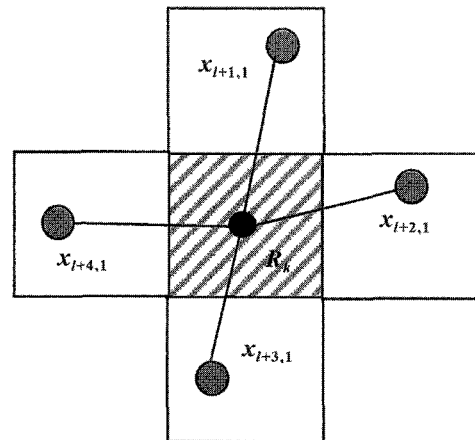


Fig. 2. After evaluating the trace of the k th A cell, the result depends on the particle positions in the neighboring B cells.

If the edge interactions are zero or negligibly small, Z_k (Eq.(4)) depends only on the positions of particles in the neighboring B-cells. Such a situation would occur when the interaction is sufficiently short-ranged and at most one particle exists in a cell, because the probability that three particles come in the vicinity of each other is small. If this is the case, one may evaluate independently the trace of the k th A-cell and write the result as

$$Z_k = \Omega_A \exp[-\beta(\epsilon_k^A + w_k(\{x_{l+i,j}\}; R_k))], \quad (7)$$

where Ω_A denotes the volume of an A-cell; ϵ_k^A is the renormalized on-site energy at the k th A-cell depending only on the occupation numbers $n_k, m_p, m_{l+1}, \dots, m_{k+h_B}$, and w_k is the renormalized potential, depending on all the particle positions in the neighboring B-cells ($l, \dots, l+h_B-1$) and also on R_k .

Thus, one may evaluate the trace of the k th A-cell independently for a given set of particle positions $x_{l+i,j}$ for $j=1, \dots, m_{l+i}$ in the h_B neighboring B-cells ($l+i=1, \dots, l+h_B-1$), and for a given number of particles in the k th A-cell, n_k . In this way, one may evaluate the trace of the A sublattice, independently, for a given set of particle numbers n_k in the A-cells and a given set of particle positions $x_{i,j}$ ($j=1, \dots, m_i$) in the B-cells.

To proceed further, let me introduce a parametrization of the renormalized potential, which can be regarded as a decoupling approximation, and assume that w_k is a sum of terms, each depending only on the particle positions in one neighboring B-cell, say the $(l+i)$ th B-cell, as

$$w_k = \sum_{i=0}^{h_B-1} w_{k,l+i}(x_{l+i,1}, \dots, x_{l+i,m_{l+i}}; R_k). \quad (8)$$

Then the first step of the potential renormalization is to find the parametrized potential $w_{k,l+i}$ as a function of n_k, R_k and the m_{l+i} particle positions $x_{l+i,1}, \dots, x_{l+i,m_{l+i}}$.

2.3 The Second Step

The second step is to evaluate the trace of the B sublattice. The potential acting on the particles inside the l th B-cell is given by

$$\sum_{j=1}^{m_l} \{ \sum_{j'=j+1}^{m_l} u_2(x_{l,j}, x_{l,j'}) + \sum_{j'=j+1}^{m_l} u_3(x_{l,j}, x_{l,j'}, x_{l,j''}) \} + \Phi_{BB} + \sum_{i=1}^{h_A-1} w_{k+l,i}(x_{l,1}, \dots, x_{l,m_l}). \quad (9)$$

In the third term, the summation with respect to i runs over all h_A A-cells ($k, \dots, k+h_A-1$) which are neighbors of the l th B-cell (h_A stands for the number of the neighboring A-cells); one of them is, of course, the k th A-cell. In the second term, Φ_{BB} denotes the interaction affecting different B-cells and given by a summation with respect to B-cells in the vicinity of the l th B-cell (the "edge interaction"):

$$\Phi_{BB} = \sum_{j=1}^{m_l} \sum_{j'=1}^{m_l} u_2(x_{l,j}, x_{l,j'}) + \sum_{j=1}^{m_l} \sum_{j'=1}^{m_l} u_3(x_{l,j}, x_{l,j'}, x_{l,j''}) + \sum_{j=1}^{m_l} u_3(x_{k,j}, x_{l,j'}, x_{l,j''}). \quad (10)$$

If there is no edge interaction, the second trace can be evaluated easily by integrating the configurational exponential with respect to all the particle positions belonging to the l th B-cell and by equating the result to

$$\int_{l\text{th B-cell}} dx_{l,1}, \dots, dx_{l,m_l} \exp \left[-\beta \sum_{j=1}^{m_l} \{ \sum_{j'=j+1}^{m_l} u_2(x_{l,j}, x_{l,j'}) + \sum_{j'=j+1}^{m_l} u_3(x_{l,j}, x_{l,j'}, x_{l,j''}) \} + \Phi_{BB} + \sum_{i=0}^{h_A-1} w_{k+l,i}(x_{l,1}, \dots, x_{l,m_l}) \} \right] = \Omega_B \exp[-\beta \epsilon_l^B]. \quad (11)$$

Here, Ω_B denotes the volume of a B-cell, and ϵ_l^B the on-site energy of the l th B-cell, which depends on the occupation numbers of the h_A A-cells (n_k, \dots, n_{k+h_A-1}) and

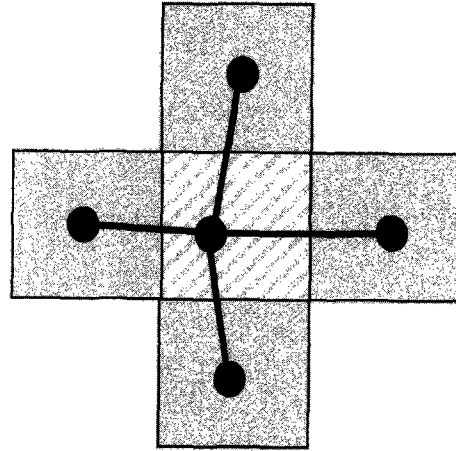


Fig. 3. As a result of the parametrization (8), the trace of the l th B cell can be evaluated independently in the second step.

of their neighboring B-cells (m_p, \dots, m_{l+h_B-1}).

Thus one may obtain the renormalized potential W in (2) in a slightly different form as

$$Z = (2\pi m / \beta h^2)^{3N/2} \sum_{n_1, \dots, n_{M_A}} \sum_{m_1, \dots, m_{M_B}} \exp[-\beta (\sum_{k=1}^{M_A} \epsilon_k^A + \sum_{l=1}^{M_B} \epsilon_l^B)] / M, \quad (12)$$

where the summations with respect to the occupation numbers n_k and m_l are restricted summations so as to guarantee the sum rule

$$\sum_{k=1}^{M_A} n_k + \sum_{l=1}^{M_B} m_l = N. \quad (13)$$

In this way, one can derive the renormalized potential, which is not an n.n. pair interaction but inevitably a many-body interaction.

If the edge interactions Φ_{AB} , Φ_{AA} and Φ_{BB} in (5), (6) and (10) are not negligible, the two-step renormalization scheme explained here is no longer valid. It would be possible to take the edge interactions into account by treating them perturbatively or by carrying out a four-step (or multistep) renormalization in place of the two-step renormalization. To carry out the latter, one has to decompose the A-sublattice further into two or more sublattices.

3. POSSIBILITY OF APPLICATIONS

The two-step renormalization scheme explained in the previous section is useful in the simulation of the liquid-solid phase transition of semiconductors which have the diamond-like crystalline structure. For this purpose, the BCC lattice gas model can be used. A regular diamond structure can be realized by a 50% filling of the BCC lattice positions. Then one may assume that each lattice point has at most one particle inside. For a realistic interatomic potential, one may use, for example, Tersoff's short-range three-body potential. For this system, the most important configuration is such that one atom is surrounded by four atoms at the tetrahedral

sites. The renormalized potential on the BCC lattice-gas can be calculated for various configurations. Then, one may perform, for example, Monte Carlo simulations on the basis of the resulting renormalized BCC lattice-gas model at various temperatures to investigate the liquid-solid phase transition and other thermodynamic properties. In the case of silicon, Sahara et al. [2] calculated the liquid-solid phase coexistence curve and compare the result with that of the molecular-dynamics study performed by Cook and Clancy [13], who used the same Tersoff potential. The transition temperatures are close to each other, although they are much higher than the experimental value.

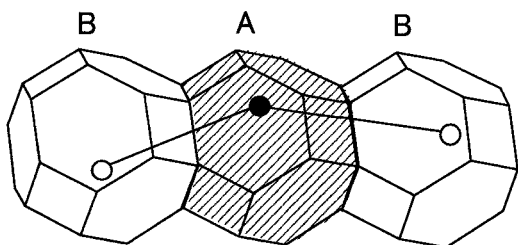


Fig. 4. The A, B cells in the sublattice division of the BCC lattice.

As a second example, one can treat the order-disorder phase transition of binary alloys like Cu_3Au with an FCC lattice-gas model. For this purpose, for example, one can adopt the Finnis-Sinclair embedded-atom potential. A preliminary result on the order-disorder phase transition temperature of the Cu-Au system was already reported elsewhere [3]. The emphasize should be made, however, on the fact that the present approach is in principle applicable to any binary alloys exhibiting a order-disorder phase transition.

As a last example, I will discuss here the possibility of treating the solution of semi-flexible polymer chains. In this case, one can consider many atoms connecting linearly inside each cell (see Fig. 4). Let me assume that each cell contains single chain and does not contains two separate chains. Then, at the first step of the renormalization, the trace inside the k th A-cell can be evaluated with the fixed positions of two atoms, which are located inside the neighboring B-cells and connected directly to the outermost atoms in the k th A cell. The resulting local partition function (7) then becomes only the function of the two atomic positions in one or two neighboring B-cells. Then after the parametrization, the result will depend also on the number of atoms inside the k th A-cell. Next, at the second step of the renormalization, the trace inside the l th B-cell is evaluated to give the final potential as a function of the number of atoms at each cell as well as the bonding orientations. The resulting lattice-gas model for the semi-flexible polymer solution has the interaction parameters depending on the discrete bond angles and on the additional internal degrees of freedom which is related to the number of atoms inside each cell.

4. SUMMARY

In this paper, I have explained in detail the potential

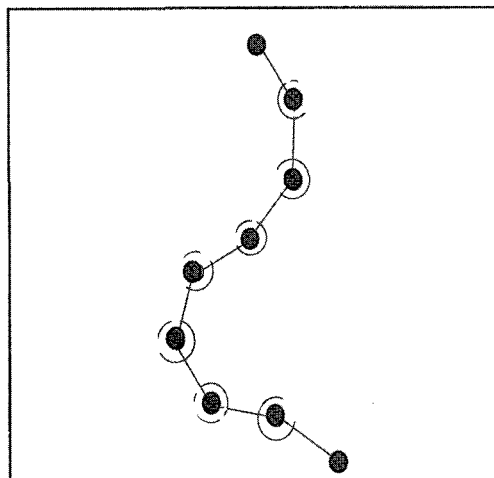


Fig. 5. The semi-flexible polymer chain inside a cell.

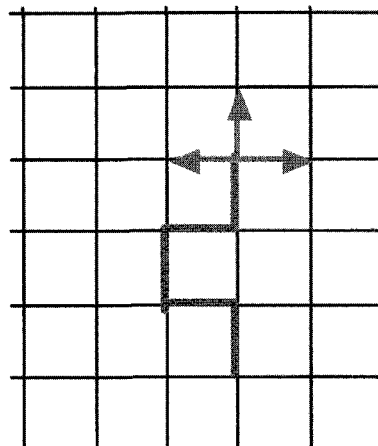


Fig. 6. The resulting lattice-gas model of the semi-flexible polymer chain

renormalization theory and its two-step renormalization scheme. The present scheme is applicable not only to the liquid-solid phase transition of semiconductors like C(diamond), Si, Ge and GaP, and the order-disorder phase transition of A_xB_{1-x} alloys like Cu-Au, Cu-Zn, Cu-Pd and Cu-Pt systems, but also to the statistics of semi-flexible polymer solutions.

REFERENCES

- [1] K. Ohno, Sci. Rep. Res. Inst. Tohoku Univ. A **43**, 17 (1997); see also, K. Ohno, K. Esfarjani and Y. Kawazoe, "Computational Materials Science: From Ab Initio to Monte Carlo Methods" Section 4.4 (Springer Verlag, Berlin, Heidelberg, 1998).
- [2] R. Sahara, H. Mizuseki, S. Uda, K. Ohno and Y. Kawazoe, J. Chem. Phys. **110**, 9608 (1999).
- [3] H. Ichikawa, R. Sahara, H. Mizuseki, K. Ohno and Y. Kawazoe, Mater. Trans., JIM **40**, 911 (1999).
- [4] S. J. Cook and P. Clancy, Phys. Rev. B **47**, 7686 (1993).