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Inverse Monte Carlo study on effective interaction potential of Ag–Rh alloy from pair correlation functions*

Zhang Jing-Xiang(张景祥)[a)b)†], Li Hui(李 辉)[a)], Song Xi-Gui(宋西贵)[a)], and Zhang Jie(张 洁)[a)]

[a)] *Key Lab of Liquid Structure and Heredity of Materials, Ministry of Education, School of Materials Science and Engineering, Shandong University, Jinan* 250061, *China*

[b)] *School of Information Science and Engineering, University of Jinan, Jinan* 250022, *China*

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This paper presents an inverse Monte Carlo method to reconstruct pair interaction potential from pair correlation function. This approach adopts an iterative algorithm on interaction potential to fit known pair correlation function by compelling deviations of canonical average to meet with Hamiltonian parameters on a basis of statistical mechanism. The effective interaction potential between particles in liquid Ag–Rh alloys has been calculated with the inverse Monte Carlo method. It demonstrates an effective and simple way to obtain the effective potential of complex melt systems.

Keywords: interatomic potential, Ag–Rh alloy, inverse Monte Carlo, x-ray diffraction
PACC: 1240Q

1. Introduction

The computational materials science plays an important role in the development of materials science for its bridging the gap between theory and real experiment. The goal of computational materials science is to help human beings to reach the state in that one is able to design a specific material with the intended microstructure and desired property from acquired knowledge and by relevant methods.[1−4] In order to conduct molecular dynamics (MD) simulation, one should define the rules governing the interaction of atoms in the concerned system so that the forces exerted on each atom can be calculated from the governed interaction. In classical and semi-classical simulations, these rules are often expressed in the form of potential functions, which describe how the potential energy of a system depends on the coordinates of atoms. It is well known that the interatomic potential plays an important role in MD simulation. To reproduce an experimental observation, the accuracy of a simulation depends mainly on the accuracy of the interatomic potential. Consequently, a great effort has been made to develop the relevant interatomic potentials. Up to now, several models have been proposed for transition metal systems with diversified physical and chemical characteristics.[5−7] The simplest one is the Lennard–Jones potential (also known as L–J potential or 12-6 potential),[8] which has extensively been applied in a wide range of research. Because the L–J potential is a sort of pair potential, i.e. two-body potential, which does not incorporate the many-body effect, there are some inherent drawbacks. For example, the pair potential of metals neither has environmental dependence nor accounts for the directional nature of the bonding. The L–J potential could therefore be the first choice for studies, where the focus is on fundamental issues, rather than on the properties of a specific material. In the 1980s, significant progress was made by developing many-body potential, especially for metals, based on the concept of local electron density.[9] The main physical feature of many-body potential is that the bonds become weaker when the local environment becomes more crowded. A variety of interatomic potentials have been developed and are currently being used in computational material science, such as the embedded atom method (EAM),[9] the modified embedded atom method,[10,11] Finnis–Sinclair potential,[12] and the second moment approximation of tight-binding (SMA-TB) potential.[13−15] Even if they share some similar analytical forms, these models differ vastly in the procedures to build the po-

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†Corresponding author. E-mail: zhangjxedu@163.com

tential functions, often resulting in rather different parameterizations for the same material. In many cases, researchers could guess the functions and fit the parameters to available and reliable experimental data. In practice, the parameters of potentials, especially of many-body potentials, are often determined by their fitting method. The initial values of potential parameters are given by experience and then physical properties, such as the cohesive energy, lattice constants, bulk modulus and elastic constants, are calculated from the constructing potential. The parameter values are adjusted again and again, according to discrepancies between the calculated and experimental properties, until the proper values are determined. It is usually a tiresome as well as a time-consuming task to obtain a realistic potential by such a fitting method. Researchers then often resort to simple parameterization. For example, Rosato *et al* [16] transformed four parameters to two in deriving SMA-TB potential for fcc transition metals. Johnson and Oh[17] used only the Voigt average shear modulus and bulk modulus, instead of six elastic constants, to determine the parameters of EAM potential for hcp metals. In spite of many advantages, there are two shortcomings for such fitting potentials. First, it cannot reproduce well the surface energies.[18] Second, transferabilities of these potentials are not very satisfactory. In spite of these problems, the fitting method is still widely used in practice, since it is somehow more feasible than other approaches.

In most computer simulations, effective site–site pair potential has been applied, which is parameterized to reproduce some set of experimental data. The interaction potentials obtained from quantum mechanical calculations are more reliable than the empirically parameterized simple pair potentials. However, such *ab initio* potentials are more time-expensive to use because of their complicated functional form. An effective approach for potential calculation from a set of canonical averages would be of great importance to molecular simulations.[19] McGreevy and Pusztai[20] used reverse Monte Carlo method to obtain atomic configurations from experimental structure factor data. In this procedure, no input potentials are needed and simulations could be performed by iteratively approaching the satisfaction of referenced structure factors.

The pair correlation functions (PCFs) are of important shape spectrum parameters to illustrate the microstructures of liquid and glassy materials. The microstructures of materials are governed by their interaction potential. Thus, there are close correlation between the pair correlation function and the interaction potential. The Pair correlation functions are usually obtained by means of molecular dynamics simulation based on the accurate interaction potential. Then, the question is raised: how could the pair correlation function be used to calculate the effective potential in an inverse way? The main purpose of this paper is to present an approach to reconstruct the effective interaction potential from the pair correlation functions.

2. Theoretical methods and modeling process

The reconstruction of the effective interaction potentials, $V_{\text{eff}}(r)$, from the pair correlation function was performed using an inverse Monte Carlo (IMC) technique,[19] previously applied to melts of small ions.[21,22] For the present system, the procedure involves Monte Carlo (MC) simulations of a system containing atoms only with iterative correction of the trial potential in order to reproduce PCFs of the full system using exact statistical-mechanical relations. Consider the following Hamiltonian with pair interactions:

$$H = \sum_{i,j} V(r_{ij}), \tag{1}$$

where $V(r)$ is pair potential and r_{ij} is the distance between particles i and j. Let us use a grid approximation to the potential, approximating a continuous function $V(r)$ by its values on a grid

$$\bar{V} = V(r_\alpha) = V_\alpha, \tag{2}$$

where

$$\begin{aligned} &(r_\alpha - 1)/(2M) < r < r_\alpha + 1/(2M), \\ &r_\alpha = \alpha r_{\text{cut}}/M \quad \alpha = 1, 2, \ldots, M. \end{aligned} \tag{3}$$

Then the Hamiltonian (1) can be written as

$$H = \sum_\alpha V_\alpha S_\alpha, \tag{4}$$

where S_α is the number of pairs between the particles with the distances found inside α-slice. Evidently, S_α is an estimator of the PCF: $\langle S_\alpha \rangle = 4\pi r^2 \rho(r) N^2/(2V)$. The average values of S_α are some function of the potential V_α, and we can write the expansion as

$$\Delta \langle S_\alpha \rangle = \sum_\gamma \frac{\partial \langle S_\alpha \rangle}{\partial V_\gamma} \Delta V_\gamma + o(\Delta V^2), \qquad (5)$$

where the derivatives $\partial \langle S_\alpha \rangle / \partial V_\gamma$ are expressed by using exact statistical mechanics relationship

$$\frac{\partial \langle S_\alpha \rangle}{\partial V_\varepsilon} = -\left(\langle S_\alpha S_\gamma \rangle - \langle S_\alpha \rangle \langle S_\gamma \rangle \right) / (kT). \qquad (6)$$

The equations (1)–(6) allow us to obtain the interaction potential V_α from the PCFs. Let V_α^T be a trial potential such as $V_\alpha^T = -KT \ln \rho(r_\alpha)$. By performing the standard MC simulations, we can estimate the averages $\langle S_\alpha \rangle$ and their deviations from the reference values S_α^* which is defined from the given PCFs: $\Delta \langle S_\alpha \rangle^{(0)} = \langle S_\alpha \rangle^{(0)} - S_\alpha^*$, thus, the corrections of the potential $\Delta V_\alpha^{\mathrm{T}}$ are obtained. Then the procedure is repeated with the new potential $V_\alpha^1 = V_\alpha^{\mathrm{T}} + \Delta V_\alpha^{\mathrm{T}}$, until a convergence is reached. The whole procedure resembles a solution of multi-dimensional non-linear equation using the Newton–Raphson's methods.[23]

The IMC modeling is a variation of the standard Metropolis MC method. The aim is to produce a structural model which is consistent with one or more sets of experimental data within their errors and subject to a set of constraints.[24] Firstly, 1000 atoms are placed in a cell with periodic boundary conditions. Normally cubic cells are used but other geometries may be chosen. The atomic number density should be the same as the experimental value. The positions of the atoms may be chosen randomly, they may have a known crystal structure or they may be taken from a different simulation or model. The combination of atom coordinates and cell dimensions is known as a configuration. Secondly, the partial radial distribution functions are obtained from the configuration based on the equation:

$$g_{\alpha\beta}^{\mathrm{o}}(r) = \frac{N_{\alpha\beta}(r)}{4\pi r^2 \mathrm{d}r \rho c_\alpha}. \qquad (7)$$

Here, ρ is the atomic number density, c_α is the concentration of atoms type α and $N_{\alpha\beta}(r)$ is the number of atoms type β at a distance between r and $r + \mathrm{d}r$ from a central atom of type α, averaged over all atoms as centers. Superscript "o" means 'old' and its significance will become clear in the following steps. So, the Fourier transform can be used to obtain the partial structure factor $S(Q)$

$$S_{\alpha\beta}^{\mathrm{O}}(Q) = \rho \int_0^\infty 4\pi r^2 (g_{\alpha\beta}^{\mathrm{o}} - 1) \frac{\sin Qr}{Qr} \mathrm{d}r, \qquad (8)$$

and the total structure factor can be calculated based on the following equation

$$S_{\mathrm{tot}}^{\mathrm{O}} = \sum c_\alpha c_\beta b_\alpha b_\beta (S_{\alpha\beta}^{\mathrm{O}}(Q) - 1). \qquad (9)$$

Thirdly, the difference between the measured total structure factors $S_{\mathrm{tot}}^{\mathrm{E}}$, and that determined from the configuration, $S_{\mathrm{tot}}^{\mathrm{O}}$ can be calculated from

$$\chi_{\mathrm{O}}^2 = \sum_{i=1}^m (S_{\mathrm{tot}}^{\mathrm{O}}(Q_i) - S_{\mathrm{tot}}^{\mathrm{E}}(Q_i))^2 / \sigma^2(Q_i). \qquad (10)$$

Fourthly, move one atom at random; in practice there is a maximum move distance. If any two atoms approach closer than a predefined (cut-off) distance, then the move is rejected, a new atom is chosen and a new move is made. Calculate the new partial pair correlation function, $g_{\alpha\beta}(r)$, the new partial structure factors, $S_{\alpha\beta}^N(Q)$, the new total structure factor $S^N(Q)$, and the difference

$$\chi_N^2 = \sum_{i=1}^m (S^N(Q_i) - S_{\mathrm{tot}}^{\mathrm{E}}(Q_i))^2 / \sigma^2(Q_i).$$

If $\chi_N^2 < \chi_{\mathrm{O}}^2$, then the move is accepted, i.e. the 'new' configuration becomes the 'old' configuration. If $\chi_N^2 > \chi_{\mathrm{O}}^2$ it is accepted with probability $\exp(-(\chi_N^2 - \chi_{\mathrm{O}}^2)/2)$. Otherwise it is rejected. As the number of accepted atom moves increases, χ^2 will initially decrease until it reaches an equilibrium value, about which it will then oscillate. Here we have chosen to fit the PCFs determined from the experimental data.

The inverse simulations, aiming at obtaining the effective potentials, are carried out in the NVT ensemble, using the same box size and the same number of particles as in the original MD simulations. Possible size effects on the PCFs should therefore to a large degree cancel out in the direct MD and the inverse Monte Carlo simulations. To control this, we have carried out several calculations of the PCFs and the effective potentials at the same atomic concentration but different system sizes.

3. Results and discussion

The IMC algorithm is easily modified for simultaneous fitting to different sets of data as long as the function of specific data, e.g. $S(Q)$ or $g(r)$, can be calculated in terms of configurations. The PCFs obtained by atomistic molecular dynamics simulations or experimental methods were used as input to the inverse Monte Carlo procedure to compute the effective potentials. The aim of this procedure is to obtain interaction potentials which, within the fitting model in the melts, yield the same structural properties (PCFs)

as all-atomic molecular dynamics simulations in the explicit solvent. Figure 1 shows the results of the partial pair correlation function of Ag–Rh alloy at different temperatures. These curves display the short-range order in the liquid alloys, it means that the probability of finding an atom in the nearest neighborhood of a specified atom. Among these three kinds of partial pair correlation function, the value of the Rh–Rh partial pair correlation function is the largest which means that the short range order in Ag–Rh glasses is dominated by the strong Rh–Rh bond. The obvious behavior of the PCFs is the splitting of the second peak which is the characteristic feature of amorphous formation. The splitting of the second peak in the PCF for rapidly quenched metals was studied by Li's research group.[25,26] From the results we know that the shapes of pair correlation functions at 250 K and 2050 K are rather alike, suggesting a structural similarity between the glass and the liquid. The Ag–Ag pair correlation function has a first contact maximum at r around 2.754 Å (1 Å=0.1 nm), and a second maximum at $r = 5.16$ Å. The PCFs of Ag–Rh and Rh–Rh have their first maxima at distances of 2.772 Å and 2.695 Å respectively.

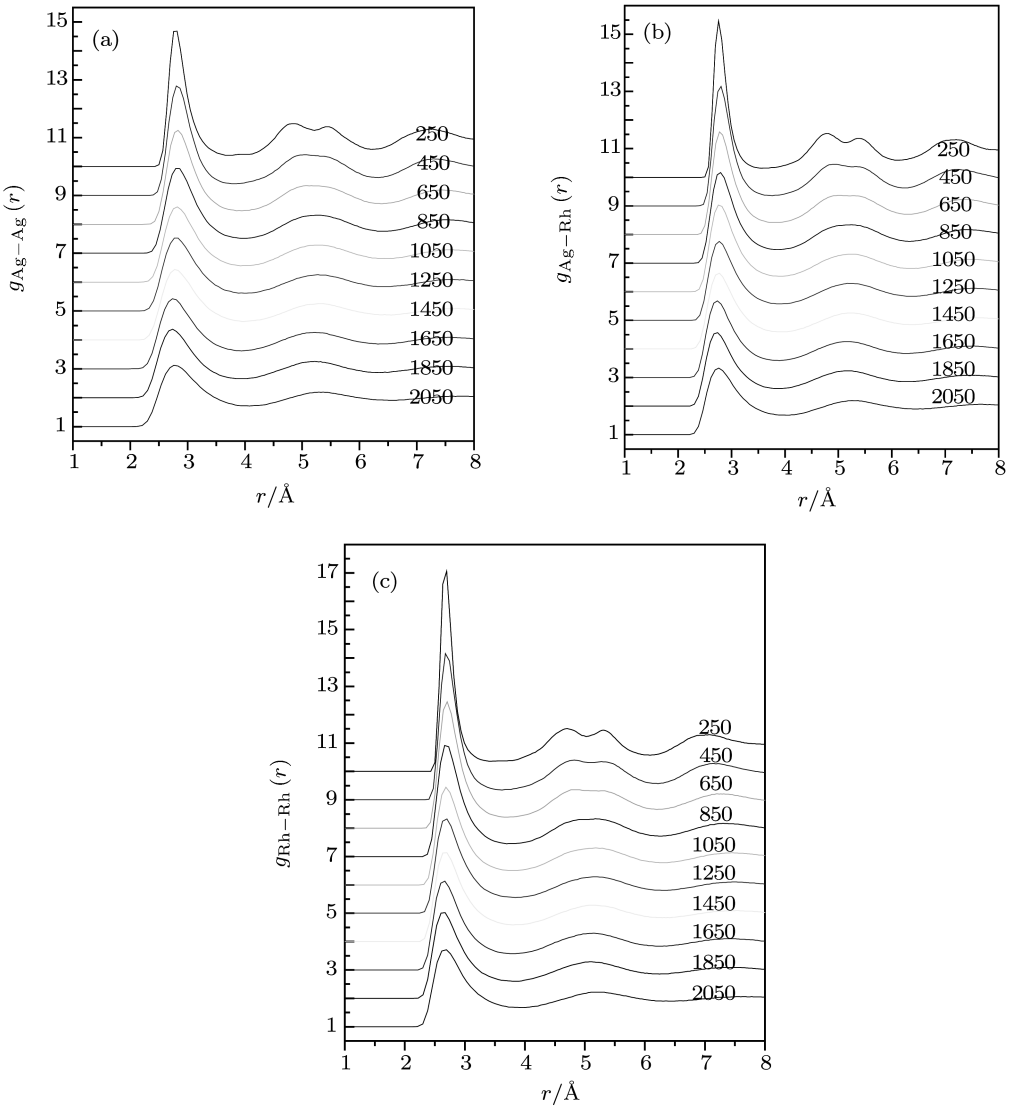


Fig.1. Partial pair correlation function for Ag–Rh alloy at different temperatures: (a) Ag–Ag partial pair correlation functions; (b) Ag–Rh partial pair correlation functions; and (c) Rh–Rh partial pair correlation functions. There are splitting peaks in partial pair correlation function at 250 K, which manifests the glassy character.

The PCFs and the corresponding effective potentials for Ag–Rh alloy are shown in Fig.2. It is clear to see that the differences in the effective potentials are more pronounced than the differences of PCFs. In all

the cases the effective potential makes 1–2 times oscillations, thereby reflecting the atomic nature of the melts, and then finally approaches the primitive model potential. The negligible size dependence and the behavior of effective potentials approaching the Coulomb potential at larger distances make it possible to calculate effective potentials. It may seem at first sight that the effective potential is only a shifted potential. At the cutoff distance, the difference of three potentials is quite little. At a smaller distance (when r is less than equilibrium distance), this difference increases. From the fact that the Rh–Rh potential decays faster than others and the absolute value of the attraction potential is somewhat lower than others, we can conclude that the attraction part of the Rh–Rh bonding is larger than that of the Ag–Ag and Ag–Rh. The calculation of effective interaction may initially require relatively long computer simulation runs for the full system to obtain the corresponding pair correlation function, but, once calculated, the effective potentials can be used for simulations of liquid systems on a larger scale.

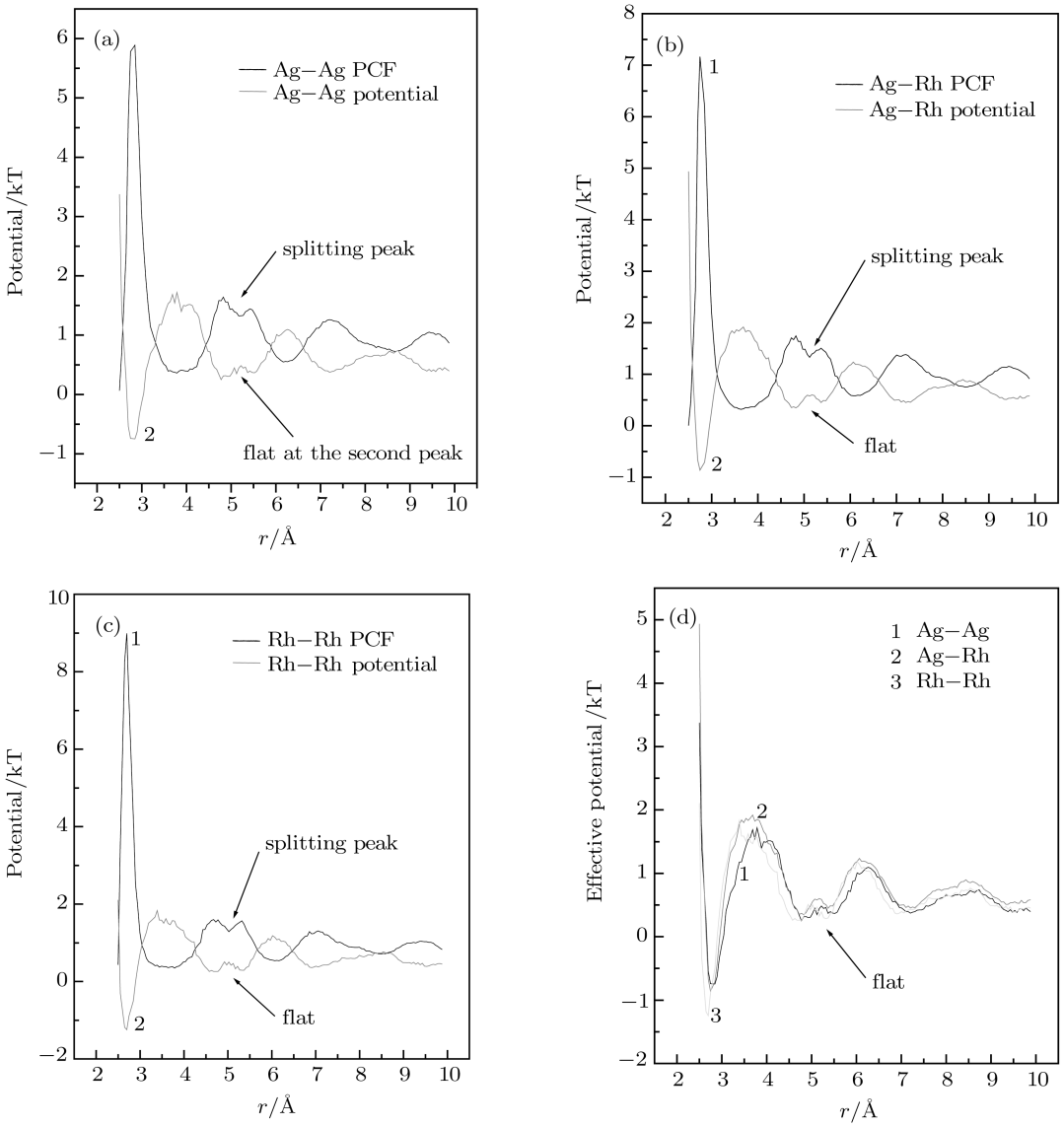


Fig.2. The comparison of the PCF and the effective interaction potentials obtained by IMC methods at a temperature of 250 K: (a) Ag–Ag partial pair correlation functions and effective interaction potential; (b) Ag–Rh partial pair correlation functions and effective interaction potential; (c) Rh–Rh partial pair correlation functions and effective interaction potential; and (d) the comparison of three partial pair potential. The splitting peak of the PCF has strong correlation with the flat in the effective interaction potential curves at the distance where the second peak is splitting.

The comparison between the PCF and the effective potential illustrates that there is close correlation between the splitting peak of PCFs and the flat of the potential curves. From three partial interaction potentials

we can see that at the distance $r = 5.34$ Å where the splitting peak of PCFs exists, a flat in the potential curve is observed. This result provides that the changes of the potential have great effect on the glass formation.

The results on effective potentials at different temperatures are presented in Fig.3. At high temperature the absolute values of the effective potentials are slightly lower than that at low temperatures. This may be interpreted as a lowering of dielectric constant at high temperature. The dependence of the effective potential on temperature is rather significant. This makes it impossible to apply the effective potentials, obtained at one temperature, to study the liquid metals at other temperatures. Figure 3 shows that the attraction increases as temperature decreases. It means that the liquid tends to be condensed at low temperatures.

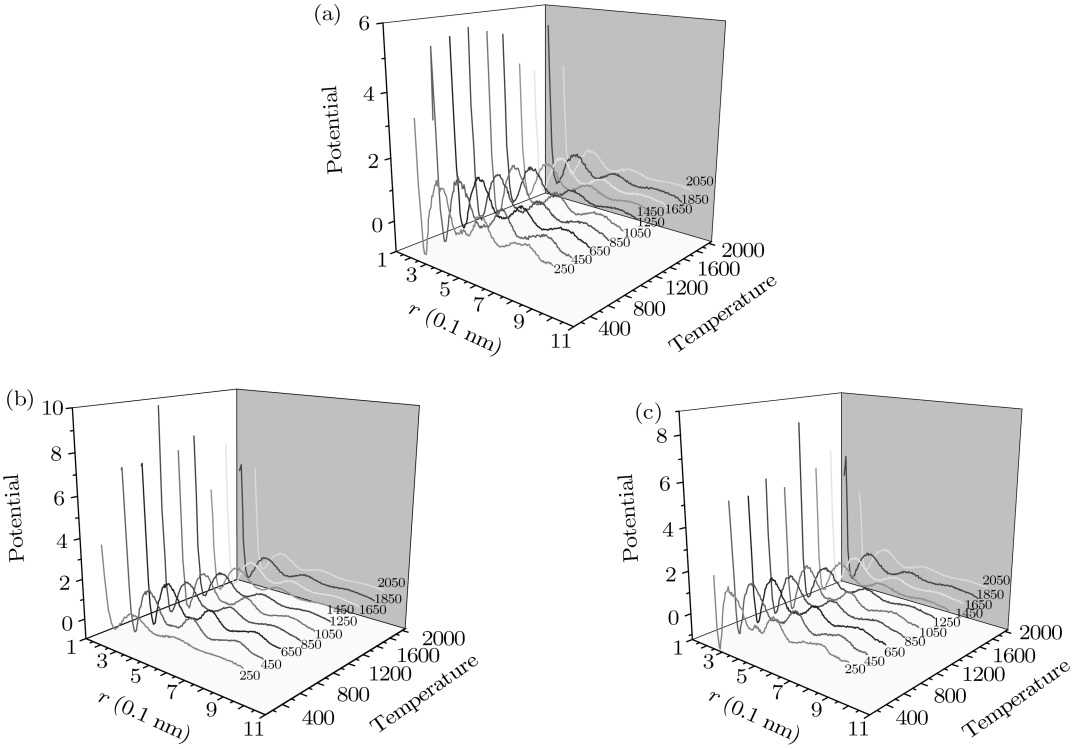


Fig.3. Temperature dependence of the effective interaction potential: (a) Ag–Ag effective interaction potential; (b) Ag–Rh effective interaction potential; and (c) Rh–Rh effective interaction potential.

All experimental data or calculated data usually contain errors, which are commonly underestimated. This means that, even if a constraint is 'known' to be correct, it might not be consistent with a particular data set. Similarly different data sets might not be consistent with each other. In such cases an IMC model cannot be expected to fit all the data and constraints, but more frequently it is the fault of data or constraints. For example, relatively rigid covalent bonds give rise to high-Q oscillations in x-ray diffraction (XRD) pattern. However, inelastic scattering effects can broaden and de-phase these oscillations in a way that we do not yet know how to correct them. This can result either in a coordination number from data that differ from the 'correct' values, or an effective broadening of the allowed bond lengths compared to those obtained from e.g. spectroscopy. If the IMC model is constrained to the 'correct' coordination or a narrow bond-length distribution, then it will not fit the data as well. It must be left to the judgment of the user whether the constraints or data are given for greater weighting. Although in some cases the small changes in PCFs may correspond to large changes in the interaction potentials, these effective potentials can be used in MC or MD simulations on a large scale without explicit consideration of solvent atoms. Since the effective potentials are constructed from the pair correlation functions, they are intended to reproduce the structural properties. As to thermo-dynamical properties, possible concentration dependences of the effective potentials should be taken into account. Although

the dependence is not significant in most cases, the concentration dependence should be studied.

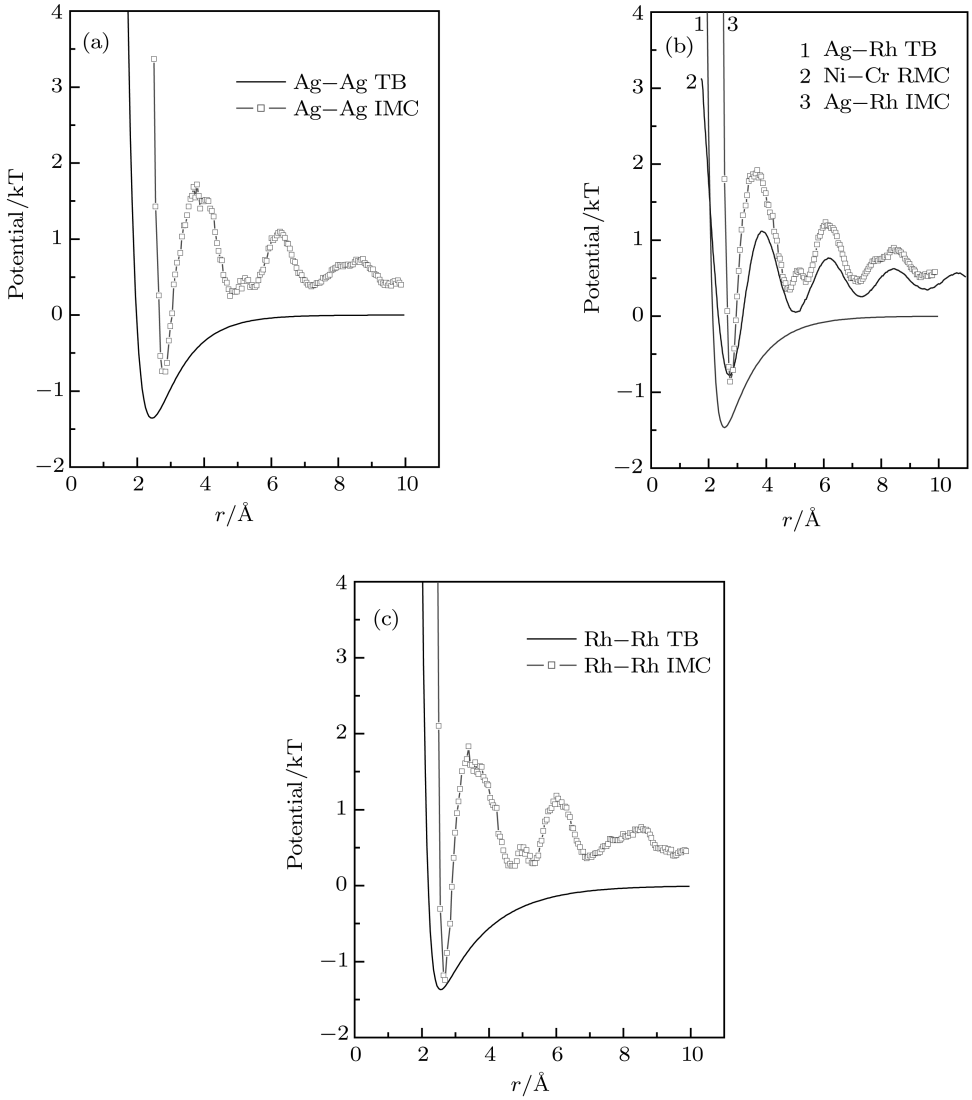


Fig.4. Comparison of our calculated effective pair potential with the other researcher's result and tight binding potentials: (a) Ag–Ag pair potential and tight binding potential; (b) Ag–Rh pair potential, Ni–Cr pair potential and tight binding potential; (c) Rh–Rh pair potential and tight binding potential.

In this paper, the evaluation of the precision of the calculated effective pair potential has been done by comparing with calculated results from other researchers and empirical tight binding (TB) potentials. For comparison, the results of the inverse Monte Carlo calculations obtained in Ni–Cr alloy studied by Schweika and Haubold[27] are displayed in Fig.4. Despite many approximations to the inverse calculations, our calculation accords with Haubold's research results very well. Similar IMC study of the Ni–Si potential done by Osaka *et al* [28] is also in agreement with ours in shape. A discrepancy is observed between the IMC and the TB potential for large distances where the inverse Monte Carlo method shows, as expected, that the interactions are oscillatory in contrast to the TB–SMA theoretical results.[13] The disagreement between the IMC and TB potentials comes from the difference of two kinds of potential models. The tight binding potential is an empirical many-body potential, in which the particle–particle interaction is described as an effective band term plus a short range repulsive pair potential. The main advantage of the tight binding–SMA is the ability to better describe the interaction of the transition metals, the drawback of

the TB is not suited for the noble metals.

4. Conclusion

In this paper, the effective pair interaction potentials of Ag–Rh alloy at different temperatures have been obtained from XRD data by use of the IMC method. The reliability of the IMC has been judged by comparing our results with that of Ni–Cr alloy. Our simulated effective pair potential is in good agreement with Haubold's result, but does not accord with the TB–SMA potential. The IMC methods give us an effective way to study potentials of various liquid systems.

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