Effective pair potentials of liquid tin and germanium: Inverse method

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Abstract The effective pair potentials of liquid germanium and tin are calculated from the experimental structure factors by an inverse method. The resultant effective pair potentials reproduce the experimetal self-diffusion coefficient with high accuracy.

1 Introduction

To investigate the structure of liquid metals using the molecular-dynamics (MD) simulation, we need first the information of the interaction between atoms. For the liquid alkali metals near the melting point, the pseudopotential perturbation theory, which is based on the nearly-free-electron (NFE) model, is used for calculating the effective pair potential. On the other hand, for the liquid silicon, germanium and tin, the NFE model may not be an appropriate approximation, since covalent bonds may remain even in the liquid states. However there is no reliable theoretical method for calculating the interatomic potentials for these liquid metals. In this case, the inverse method, in which the effective pair potential is derived from the experimental static structure factor, is one of the best methods to obtain the effective pair potential. In the present paper we apply the inverse method to the liquid germanium and liquid tin for obtaining the effective pair potentials. The purposes of this paper are as follows: (i) To derive the effective pair potential $\phi(r)$ of liquid tin and liquid germanium from experimental structural data near the melting points. (ii) To calculate the self-difusion coefficients of these liquid metals, the MD simulations are performed.

2 Predictor–corrector method for the inverse problem

We[1] showed that the predictor–corrector method originary proposed by Reatto *et al.*[2] is an accurate method for solving the inverse problem. This method is based on the integral equation theory and the computer simulation. In the integral equation theory, the effective pair potential $\phi(r)$ multiplied by $\beta = 1/k_{\mathrm{B}}T$ is given in the following,

$$\beta\phi(r) = g(r) - c(r) - \ln g(r) - 1 + B(r), \tag{1}$$

with the radial distribution function $g(r)$, the direct correlation function $c(r)$ and the bridge function $B(r)$. To calculate $\beta\phi(r)$ from the experimental structure factor $S_{\exp}(k)$ using equation (1) we need the experimental radial distribution function $g_{\exp}(r)$, the experimental direct correlation function $c_{\exp}(r)$ and the experimental bridge function $B_{\exp}(r)$. The pair distribution function $g_{\exp}(r)$ can be obtained from $S_{\exp}(k)$ by the Fourier transformation

$$g_{\exp}(r) = 1 + \frac{1}{2\pi^2 nr} \int_0^\infty (S_{\exp}(k) - 1)\, k \sin(kr) dk, \tag{2}$$

where n is the number density of ions. Using the Ornstein–Zernike relation,

$$g(r) - 1 - c(r) = n \int (g(|\boldsymbol{r} - \boldsymbol{r}'|) - 1)c(r')d\boldsymbol{r}' \tag{3}$$

together with equation (2), the $c_{\text{exp}}(r)$ can also be obtained from the $S_{\text{exp}}(k)$,

$$c_{\text{exp}}(r) = \frac{1}{2\pi^2 nr} \int_0^\infty \left(1 - \frac{1}{S_{\text{exp}}(k)}\right) k \sin(kr) dk. \tag{4}$$

The bridge function $B_{\text{exp}}(r)$, however, cannot be obtained directly from $S_{\text{exp}}(k)$. In the predictor–corrector method, we employ the bridge function of the hard sphere system $B_{\text{HS}}(r, \eta)$ as an initial estimate for $B_{\text{exp}}(r)$, where the packing fraction η is determined so as to minimise the free energy as is usually done in the modified hypernetted-chain(MHNC) approximation[3]. The condition [4] for the minimum free energy in the case of the inverse method is given by

$$\int (g_{\text{exp}}(r) - g_{\text{HS}}(r, \eta)) \frac{\partial B_{\text{HS}}(r, \eta)}{\partial \eta} dr = 0, \tag{5}$$

where $g_{\text{HS}}(r, \eta)$ is the radial distribution function for the hard sphere system with the packing fraction η. Thus the zeroth approximation for the effective pair potential is given by

$$\beta\phi_0(r) = g_{\text{exp}}(r) - 1 - c_{\text{exp}}(r) - \ln g_{\text{exp}}(r) + B_{\text{HS}}(r, \eta). \tag{6}$$

This approximation is called the predictor, and then $\phi_0(r)$ or $B_{\text{HS}}(r, \eta)$ are improved by the following iterative procedure, which is called the corrector: (i)The simulation is performed with $\phi_i(r)(= \phi_0(r)$ for the first run) and $g_i(r)$ is obtained, where i stands for ith step. (ii)$S_i(k)$ is obtained by Fourier transforming $g_i(r)$. (iii) $c_i(r)$ is obtained by using eq.(4), where the subscript exp is replaced by i. (iv) The revised bridge function $B_i(r)$ is given by

$$B_i(r) = \beta\phi_i(r) - g_i(r) + 1 + c_i(r) + \ln g_i(r). \tag{7}$$

An important point is that this bridge function $B_i(r)$ must be exact for the input effective pair potential $\phi_i(r)$, and if this condition is not satisfied, this iterative procedure would not converge. (v)The revised effective pair potential $\phi_{i+1}(r)$ is then given by

$$\beta\phi_{i+1}(r) = g_{\text{exp}}(r) - 1 - c_{\text{exp}}(r) - \ln g_{\text{exp}}(r) + B_i(r). \tag{8}$$

The iterative process (i)-(v) is repeated until the difference $|\phi_{i+1}(r) - \phi_i(r)|$ becomes smaller than the desired accuracy and an accurate estimate for $\phi(r)$ can finally be obtained.

To carry out this predictor–corrector method, we must take into account following points.

1. In general the experimental structure factor $S_{\text{exp}}(k)$ is available only in the limited k region. The radial distribution function obtained by Fourier transform of the original experimental data of $S_{\text{exp}}(k)$ is nonzero in the small r region, where the $g_{\text{exp}}(r)$ should be zero physically. Therefore in order to obtain $g_{\text{exp}}(r)$ accurately, we have to extrapolate $S_{\text{exp}}(k)$ both to larger and to smaller k region. For the smaller k region, we extrapolate the experimental data smoothly using spline functions to $S_{\text{exp}}(0)$ obtained from the isothermal compressibility. As for the larger k region, we perform the Fourier transform repeatedly between $S_{\text{exp}}(k)$ and $g_{\text{exp}}(r)$ until the unphysical structure of $g_{\text{exp}}(r)$ in the small r region is removed. In this way, we can get the 'experimental' structure factor for a whole k range. Since $g_{\text{exp}}(r)$ and $c_{\text{exp}}(r)$ are obtained from the same $S_{\text{exp}}(k)$, these $g_{\text{exp}}(r)$ and $c_{\text{exp}}(r)$ satisfy the Ornstein–Zernike relation.

2. As mentioned above, we must get the exact bridge function $B_i(r)$ in each step of the iterative procedure. To do so, we need first to obtain the data of $g_i(r)$ and $S_i(k)$ very accurately and then to get the $c_i(r)$ from thus obtained $S_i(k)$. The values of $S_i(k)$ in the region where

$S_i(k) < 1$ should be known very accurately to obtain the accurate values of $c_i(r)$, since as is seen from equation(4) $c_i(r)$ is the Fourier transform of $(1 - 1/S_i(k))/n$, which contains the term $1/S_i(k)$, so that the region where $S_i(k) \ll 1$ contributes substantially to the Fourier integral. Note that, near the triple point, $S_i(k)$ in the small k region are much smaller than unity. For this reason, we need the accurate data of $g_i(r)$ in the large r region, and therefore we must perform the simulation for a large system. Of course, at a low density near the critical point, the system size of the simulation must also be large, since the long range correlation is important.

3. Since $g_i(r)$ is obtained only for $r < L/2$, L being the side of the cubic cell used in the simulation, the data must be extrapolated to larger distances. We employ the Verlet extrapolation method[5], in which the Ornstein–Zernike relation is solved with the conditions that $g(r) = g_i(r)$ for $r < r_c$ and $c(r) = c_{PY}(r)$ for $r > r_c$, where $c_{PY}(r)$ is the direct correlation function in the Percus-Yevick(PY) approximation and r_c is the cutoff distance of $g_i(r)$.
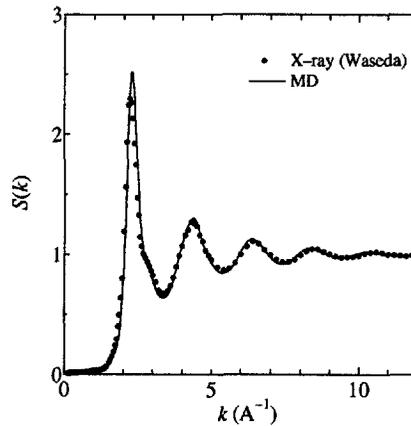
3 Results and discussion

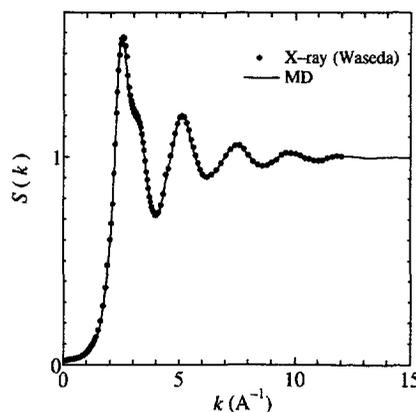

Figure 1. Structure factor of liquid Sn at 523 K

Figure 2. Structure factor of liquid Ge at 1253 K.

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The experimental structure factor $S_{exp}(k)$ of liquid tin at 523 K [6] and that of liquid germanium at 1253 K [6] are shown in figures 1 and 2, respectively. The effective pair potentials derived from these structure factors by the inverse method are shown in figures 3 and 4, respectiveply. Unlike effective pair potentials of simple liquids, a small hump exists in the core repulsive region of $\phi(r)$ for both tin and germanium. Though the existence of a hump is expected from the pseudopotential perturebation theory, this characteristic feature is confirmed by the inverse method. Note that, since the shape of $\phi(r)$ is very sensitive to the experimental structure factor, we do not discuss the details of $\phi(r)$.
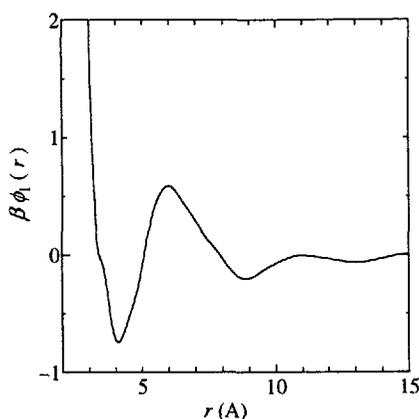

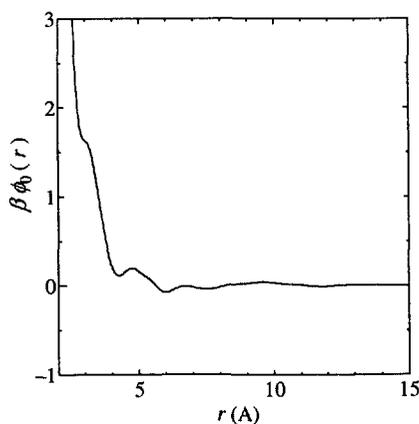Figure 3. Effective pair potential of liquid Sn at 523 K.

Figure 4. Effective pair potential of liquid Ge at 1253 K.

It is obvious from the character of the inverse method that $\phi(r)$ derived from this method can reproduce the experimental static structure factor accurately. In figures 1 and 2, we show the structure factors calculated by the MD simulation using the effective pair potentials in figures 3 and 4. On the other hand, though it is not evident that such an effective pair potential can also reproduce the dynamic structure of liquid metals, Munejiri et al. [7] have shown that the effective pair potential of liquid rubidium derived from the experimental structure factor can reproduce the experimental dynamic structure factors.

The MD simulations are performed for liquid tin at 523 K and for liquid germanium at 1253 K. We use 4096 atoms in the cubic MD cells with periodic boundary conditions. The number

densities and L are 0.0352 Å^{-3} and 48.8 Å for the liquid tin and 0.0461 Å^{-3} and 44.6 Å for the liquid germanium. The temperature is controled by Nosé thermostat[8]. The cut-off distances of the pair potentials are 17.5 Å and 14.0 Å for liquid tin and for liquid germanium, respectively. To obtain the self-diffusion coefficient D, the maen square displacements of atoms and the velocity autocorrelation function are calculated. The calculated value of D for liquid tin and liquid germanium are compared with experiments and other calculations in table 1. Our results are in good agreement with the experimental data.

4 Summary

The effective pair potentials $\phi(r)$ of liquid tin and liquid germanium are derived from the experimental structure factors. we have shown that $\phi(r)$ reproduce the self-diffusion coefficients for liquid tin and even for liquid germanium. In spite of these good results of the self-diffusion coefficient, we cannot judge whether many-body correlation functions and dynamic structures in the real liquid system are also reproduced or the self-diffusion coefficients happen to be good results. To investigate the validity of the effective pair potential, we have to compare the dynamic structures or many-body correlation functions obtained with the effective pair potentials with those obtained by first-principles MD simulations or neutron inelastic scattering experiments.

Table 1. The self-diffusion coefficient D of liquid tin and liquid germanium.

	Sn	D (10^{-5} cm^2 s^{-1}) Ge
Present	2.5 (523 K)	12 (1253 K)
Experiment(μg)	2.5 (526 K) [9]	7.8 (1243 K) [11]
Experiment($1g$)	2.2 (543 K)[10]	7.8–12.1 (1253 K) [12]
MD (*ab initio*)		12 (1250 K) [13], 10 (1230 K) [14]
MD (Empirical potential)		4.4 (1250 K) [15]

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