

# Effective pair potential and self-diffusion coefficient of liquid tin

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**Abstract** The effective pair interatomic potential of liquid tin was derived by an inverse method from the experimental structure factors obtained by the neutron and the small-angle X-ray scattering experiments at the temperatures from 573 to 1873 K. The resultant interatomic potentials were applied to the molecular-dynamics simulations and the self-diffusion coefficients were calculated. The results of the self-diffusion coefficient were in good agreement with the experimental data which were measured with no convection under low gravity.

## 1 Introduction

To understand the microscopic mechanism of diffusion properties in liquid metals, an interatomic interaction and a liquid structure are important physical quantities. For the liquid alkali metals near the melting point, the pseudopotential perturbation theory, which is based on the nearly-free-electron (NFE) model, can be used successfully for deriving the effective pair potential. On the other hand, for 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 problem, in which the effective pair potential is derived from the experimental static structure factor, is one of the best methods to calculate the effective pair potential.

Munejiri *et al.* [1] reported that the effective pair potential of liquid rubidium from this method can reproduce the dynamic structures including the self-diffusion coefficient. However, it is not obvious whether the effective *pair* potential can be always used to study the dynamic structures, especially when many-body forces are important.

In this study, the effective pair potential of liquid tin was calculated by the inverse problem and the self-diffusion coefficient was evaluated from the molecular-dynamics (MD) simulation. The calculated self-diffusion coefficient was compared with the experimental data measured under low gravity conditions.

## 2 Methods

### 2.1 Diffraction experiments

The structure factor  $S(Q)$  of liquid tin was measured by a neutron and a small-angle X-ray scattering experiments. The data of  $S(Q)$  in a low wave-number region are important to evaluate the effective pair potential because  $1/S(Q)$  is dominant for the calculation of the direct correlation function and finally the effective pair potential (see equations (4) and (8)). Therefore, the data of  $S(Q)$  in the low  $Q$  region ( $0.4 < Q < 2.0 \text{ \AA}^{-1}$ ) were measured carefully by a small-angle X-ray scattering experiment at the temperatures of 573, 773 and 1073 K. The X-ray source, the goniometer and the proportional counter were installed in the glove box which was filled with high purity argon gas in order to prevent the oxidation of liquid tin at high temperature. The liquid tin was held between thin graphite crystal plates whose gap was 0.1 mm wide. The angular dependence of the scattering intensity was measured by the symmetrical transmission method. The temperature of the sample was elevated by the resistance heater.

The structure factors for  $1.5 < Q < 10.4 \text{ \AA}^{-1}$  were measured by the neutron scattering at the six temperatures of 573, 773, 1073, 1473, 1673 and 1873 K. The experiment was performed with the use of Triple Axis Spectrometer (TAS-1) installed at JRR3M in Japan Atomic Energy Research Institute. A fused silica ampoule was used for the experiments at the temperatures of 573, 773 and 1073 K. In addition to this, a glassy carbon ampoule was developed for the higher temperatures of 1473, 1673 and 1873 K. The sample was placed in a high temperature radiation furnace with a Nb foil heating element. The counting time at each temperature was typically 8–12 hours. The raw data observed by the neutron and the X-ray scattering experiments were treated by a standard procedure, which includes a subtraction of cell intensities and a correction for absorption.

### 2.2 Predictor-corrector method for the inverse problem

In this paper the predictor-corrector method [2] was used 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  $\beta = 1/k_B T$  is given in the following equation,

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

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  $S_{\text{exp}}(Q)$  using equation (1) we need the experimental radial distribution function  $g_{\text{exp}}(r)$ , the experimental direct correlation function  $c_{\text{exp}}(r)$  and the experimental bridge function  $B_{\text{exp}}(r)$ . The pair distribution function  $g_{\text{exp}}(r)$  can be obtained from  $S_{\text{exp}}(Q)$  by the Fourier transformation

$$g_{\text{exp}}(r) = 1 + \frac{1}{2\pi^2 nr} \int_0^\infty (S_{\text{exp}}(Q) - 1) Q \sin(Qr) dQ, \quad (2)$$

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

$$g(r) - 1 - c(r) = n \int (g(|r - r'|) - 1) c(r') dr' \quad (3)$$

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

$$c_{\text{exp}}(r) = \frac{1}{2\pi^2nr} \int_0^\infty \left( 1 - \frac{1}{S_{\text{exp}}(Q)} \right) Q \sin(Qr) dQ. \quad (4)$$

The bridge function  $B_{\text{exp}}(r)$ , however, cannot be obtained directly from  $S_{\text{exp}}(Q)$ . 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  $\eta$  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

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

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

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

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  $i$ th step. (ii)  $S_i(Q)$  is obtained by Fourier transforming  $g_i(r)$ . (iii)  $c_i(r)$  is obtained by using equation (4), where the subscript *exp* is replaced by *i*. (iv) The revised bridge function  $B_i(r)$  is given by

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

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

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

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.

### 3 Results and Discussions

The results of the experimental structure factor are shown in figure 1. The open and solid circles show the results observed by the small-angle x-ray and the neutron scattering experiments, respectively. The effective pair interatomic potentials were calculated by the inverse method at 573, 773 and 1073 K. The convergence of the iterative procedure was quite well. The obtained pair interatomic potentials are shown in figure 2. As can be seen in figure 2, the repulsive part of the potential is dominant, which can be divided into two parts; one is the hard part around 3 Å and the other is gradually decreasing repulsive part (soft part) from 3 to 10 Å. In addition, it can be said that some hump can be seen around the position of the crossover between the *hard part* and the *soft part*. Silbert and Young [5] proposed a ledge type interatomic potential for liquid metals whose structure

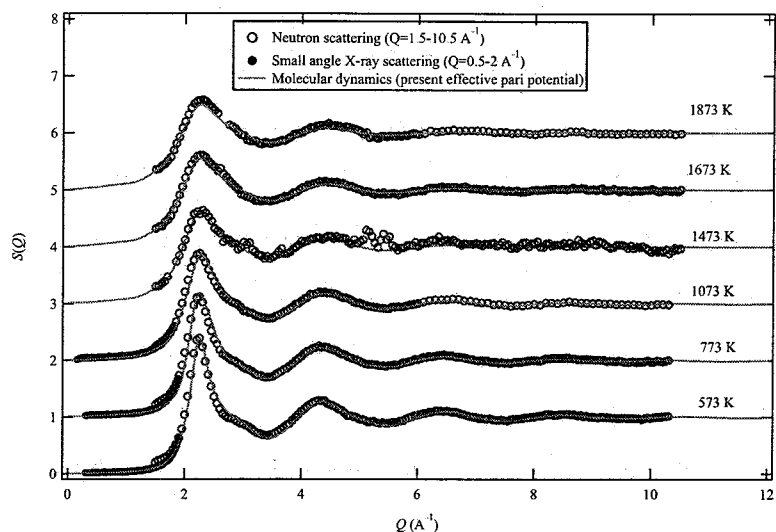


Figure 1. Structure factors of liquid tin from 573 K to 1873 K. The solid lines show the results obtained by the MD simulations. The open and solid circles show the results observed by the small-angle x-ray and the neutron scattering experiments, respectively.

factor has a shoulder. A similar ledge type interatomic potential was also shown by the pseudopotential theory. Since the numerical values of interatomic potential derived from the inverse method is sensitive to a small error of  $S(Q)$  especially in the low  $Q$  region, it is difficult to discuss the detailed shape of the effective pair potential. Nevertheless the hump of the repulsive part of interatomic potentials may be an essential feature.

The effective pair potential at 1073 K is also applied to the liquid tin at higher temperatures of 1473, 1673 and 1873 K. We used 4096 atoms in the cubic MD cells with periodic boundary conditions. The number densities were employed from the experimental values of  $0.0353 \sim 0.0312 \text{ \AA}^{-3}$ . The temperature is controlled by the Nosé thermostat. The MD simulation with the obtained effective pair potential reproduces the experimental structure factor  $S(Q)$  at each temperature as shown in figure 1.

The self-diffusion coefficient was evaluated from the MD simulation from the mean square displacement and velocity autocorrelation function. The calculated results are shown in figure 3 together with the experimental data which were measured under normal gravity (1g) [6, 7] and low gravity [8, 9]. The low gravity circumstances have been known to be ideal for the measurements of diffusion coefficient of melts because of the absence of convection. As a result, an agreement between low gravity data is rather excellent. On the other hand, diffusion data on the ground differ each other considerably depending on data sources probably due to the convection, though data of Bruson and Gerl [7] is rather close to the low gravity data. The obtained self-diffusion coefficients from the present MD simulations are extremely in good agreement with the self-diffusion data under low

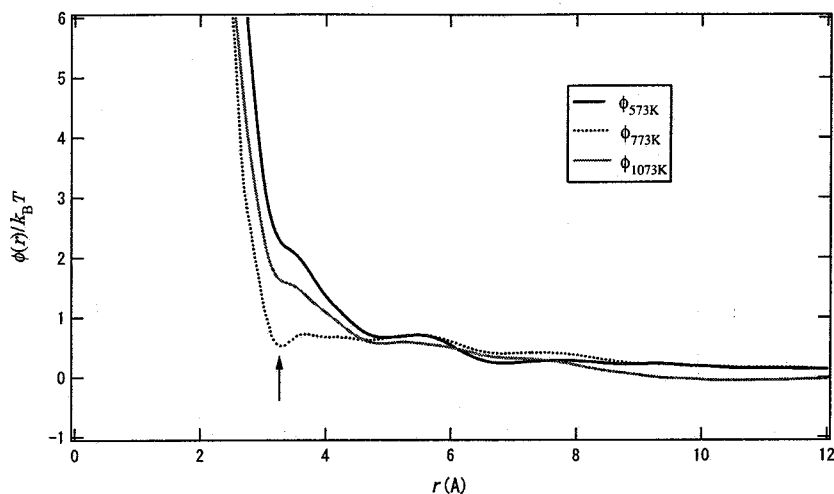


Figure 2. The effective pair potential of liquid tin derived from the experimental structure factors from the inverse method. The arrow indicates the averaged nearest neighbor distance of atoms.

gravity in the wide range of temperature.

It is well known that the diffusion coefficient of liquid metals can be predicted as a zeroth approximation by the simple hard sphere model [10]. The validity of this model is derived from the fact that the gross feature of liquids can be determined by the packing of atoms. In fact, good results were obtained by the hard sphere model for the self-diffusion coefficient of liquid tin particularly in the low temperature range [11]. In principle, the hard sphere diameters should be determined theoretically. However, it is not always easy to determine the hard sphere diameter from the standard thermodynamic theory of liquids [12]. In this respect, the present scheme for the evaluation of the self-diffusion coefficient has advantages because of the absence of any parameters.

#### 4 Conclusion

The effective pair interatomic potentials of liquid tin were evaluated by the inverse problem scheme. By using this effective pair potential, the self-diffusion coefficient was calculated from MD simulation. Obtained self-diffusion coefficients are in good agreement with the experimental values observed in space in the wide range of the temperature. The excellent agreement between the present results and the microgravity diffusion data suggests that the inverse method and the MD simulation are powerful tools for the prediction of the self-diffusion coefficient in liquid.

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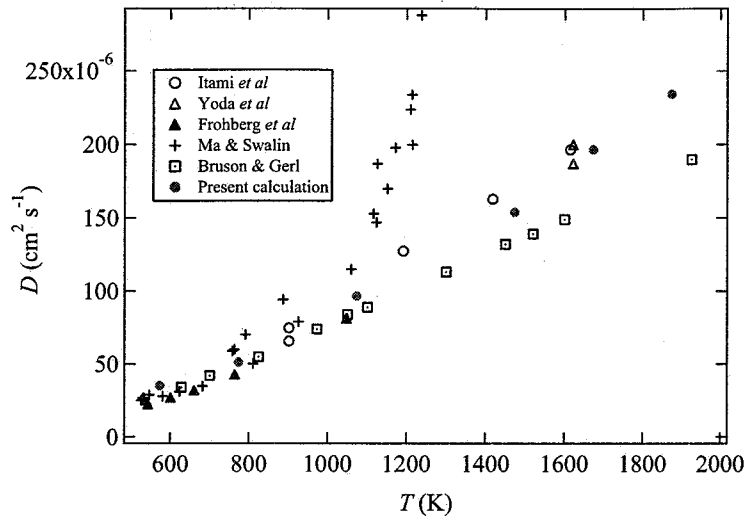


Figure 3. Self-diffusion coefficient of liquid tin for a wide range of the temperature.

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