

# Structure Studies of Liquid Tin by Neutron Scattering Experiments and *Ab initio* Molecular-Dynamics Simulations

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**Abstract** The structure of liquid tin was studied at temperatures of 573, 773 and 1073 K by neutron scattering experiments. A shoulder was clearly observed in the high- $Q$  side of the first peak of the structure factor  $S(Q)$  at 573 K. Though with increasing temperature the existence of the shoulder becomes less clear due to the change of the overall shape of  $S(Q)$ , the structure related to this shoulder seems to remain even at 1073 K. Computer simulations for liquid tin were carried out using an *ab initio* molecular-dynamics method. The calculated results well reproduced  $S(Q)$  obtained by the neutron experiments. Moreover, we showed the existence of some fragments of the tetrahedral unit from an analysis of the angle distribution in the three-body distribution function of liquid tin.

## 1 Introduction

The accurate knowledge of liquid structure is essential in many fields of fundamental science. For example, the self-diffusion coefficient of liquids is one of the fundamental physical quantities and is closely related to the structure of liquids. However measurements of the diffusion coefficients are not easy because atoms are transported not only by the diffusion process but also by the convection. To reduce the contribution of the convection, the measurements of the self-diffusion coefficient  $D$  of liquid tin for a wide range of temperature have been carried out under microgravity environments[1, 2]. It is shown that the observed values of  $D$  are smaller than those measured on the ground. To clarify the mechanism of the self-diffusion and to construct a reliable model of the diffusion for a wide range of temperature, it is crucial not only to measure  $D$  accurately but also to understand the microscopic liquid structure.

For the study of liquid structures, it is important to perform neutron and X-ray scattering experiments supplemented by computer simulations. The latter computer simulations are important to extrapolate the former experimental structure analyses and extract information of the microscopic structure in detail. Up to date, the diffraction experiments for liquid tin have been performed in the limited temperature range[4, 3]. For simple metals, the interatomic potentials required for a classical computer simulation can be calculated from a view point of nearly free electron(NFE) theory. However, since the liquid tin is not a typical 'good' NFE metal, it is not always easy to calculate a reliable interatomic potential. Therefore, there are few molecular-dynamics studies of liquid tin.[5] On the other hand, recently, an *ab initio* molecular-dynamics

(AIMD) simulation is a very powerful tool for investigating various liquid metals. In this paper, we study the temperature dependence of the structure of liquid tin by using neutron scattering experiments and AIMD simulations.

## 2 Neutron Scattering Experiments

The sample was sealed in vacuo into a cylindrical quartz cell of 8.0 mm inner diameter, 8.6 mm outer diameter and 30 mm height. The sample was heated by an electrical furnace. The measurements were done at the temperatures of 573 K, 773 K and 1073 K. The neutron scattering measurements were carried out using the TAS-1 triple-axis spectrometer at the JRR-3M, JAERI, Japan. The incident wavelengths,  $\lambda$ , were 0.85, 0.95 and 2.44 Å, giving a range of scattering vector,  $Q = 4\pi \sin \theta / \lambda$ , of 0.2 to 12.1 Å<sup>-1</sup> where  $2\theta$  is the scattering angle. The data of scattering intensity were measured with the steps 0.05 and 0.1 Å<sup>-1</sup> for  $Q < 6.0$  Å<sup>-1</sup> and  $Q > 6.0$  Å<sup>-1</sup>, respectively. Counting times were typically 12 hours. Neutron scattering data were treated using standard procedure, which includes subtraction of cell intensities, absorption and multiple scattering corrections.

## 3 *Ab initio* MD Simulations

Our method of the AIMD calculation is based on the density functional theory with the local density approximation[6]. For the interaction between the valence electrons and the ion, we employ the norm-conserving pseudopotential by Troullier and Martins[7], which is derived from the calculation of the atomic electron configuration 5s<sup>2</sup> 5p<sup>2</sup> 5d<sup>0</sup>. The electronic wave functions are expanded in terms of a plane wave basis set with a cutoff energy of 11 Ryd. The  $\Gamma$  point is used to sample the Brillouin zone of the supercell. The Kohn-Sham energy functional is minimized by the preconditioned conjugate-gradient method[8, 9, 10]. Then the forces on the ions are calculated using the Hellmann-Feynman theorem. The MD simulations are carried out with 64 atoms in a cubic supercell from 773 to 1473 K. For the density of the system, the experimental data[11] are used. The mass and the number densities of the system are 6.82 ~ 6.36 g cm<sup>-3</sup> and 0.0346 ~ 0.0323 Å<sup>-3</sup>, respectively. The lengths of the side of the cubic supercells are 12.3 ~ 12.6 Å. The constant temperature simulations are performed using the Nosé-Hoover thermostat[12, 13] for 10000 steps with the time steps 150 ~ 200 a.u.(3.6 ~ 4.8 fs). The AIMD was performed using the supercomputer VPP500 at the Center for Promotion of Computational Science and Engineering(CCSE) of JAERI and the workstations at NASDA.

## 4 Results and Discussion

The structure factors  $S(Q)$ 's and the radial distribution functions  $g(r)$ 's obtained in the present study are shown in Figs.1 and 2, respectively. The lines and the circles show the results obtained from the AIMD simulation and from the neutron scattering, respectively. The calculated results are in excellent agreement with the experiments. In both the calculated and the experimental  $S(Q)$ , the shoulders are observed clearly on the high- $Q$  side of the first peak, around  $Q = 2.8$  Å<sup>-1</sup> at low temperatures. With increasing temperature, the first peak becomes lower and broader and the shoulder seems to disappear. The characteristic features in  $g(r)$  are the flatness and the large values in the region between the first and the second peaks compared with those of simple liquids. With increasing temperature, though the height of the first peak in  $g(r)$  becomes lower, the values of  $g(r)$  in this flat region are almost unchanged. Similarly, the values of  $S(Q)$  around the shoulder stay almost constant with varying temperature and the shape of the first peak of  $S(Q)$  is asymmetric even at the highest temperature of 1473 K.

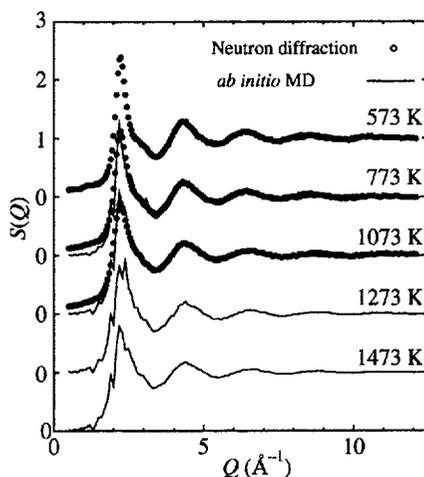


Figure 1. Structure factors of liquid tin at the temperatures from 573 to 1473 K.

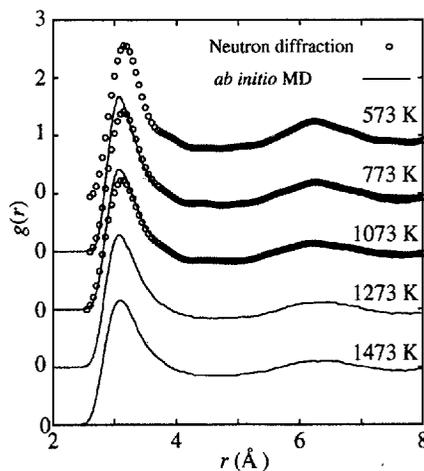


Figure 2. Radial distribution functions of liquid tin at the temperatures from 573 to 1473 K.

The present experimental data of  $S(Q)$  are similar to the previous data of liquid tin obtained by the neutron[3] and the X-ray[4] techniques. However, slight difference can be seen if we observe these data in detail. The present values of  $S(Q)$  for small- $Q$  range are larger than those of previous data. As for small- $Q$  range in the present experiment, there remain some interference effects which should be removed. In near future a small-angle scattering experiment is performed to obtain the correct scattered intensity in this  $Q$ -range. Anyway the contribution of this range is small on the determination of  $g(r)$  from  $S(Q)$ . The phase of the oscillation in the present results of  $S(Q)$  at 773 K and 1073 K is slightly different from the previous X-ray data in high- $Q$  range though good agreements were obtained for the data at 573 K and the height of shoulders at all temperatures. As for the shoulders, the present height is slightly lower than the data of the neutron scattering experiments[3].

To study the microscopic structure more in detail, a three-body angle distribution function  $g^{(3)}(\theta, r_c)$  is calculated from the atomic configuration obtained by the AIMD simulation and the results at 773 and 1473 K are shown in Fig.3. The three-body angle is formed by a pair of vectors drawn from a reference atom to any other two atoms within a cutoff radius  $r_c$  (see

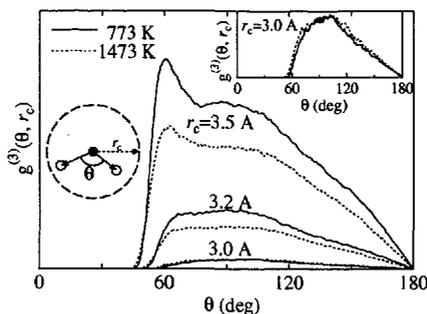


Figure 3. Bond angle distribution functions at 773 K and 1473 K, which are calculated from the atomic configurations obtained by the AIMD simulation.

the inset in Fig.3). When the cutoff radius  $r_c$  is 3.5 Å, which is longer than the average nearest neighbor distance,  $g^{(3)}(\theta, r_c)$  shows a clear peak centered at 60°. When an interatomic interaction is isotropic and the atoms are in closed-packed,  $g^{(3)}(\theta, r_c)$  should show the peak around 60°. Therefore this peak indicates a typical structure in a simple liquid. With decreasing the cutoff radius  $r_c$ , the peak at 60° disappears and  $g^{(3)}(\theta, r_c)$  shows only single broad peak distributed near 100° close to the tetrahedral bond angle of 109°. This peak suggests that there are complex local structures due to anisotropic interactions in liquid tin. With increasing temperature,  $g^{(3)}(\theta, r_c)$  becomes broad for  $r_c = 3.2$  and 3.5 Å, while that for  $r_c = 3.0$  Å is almost unchanged. This means that the short-range structure within 3 Å does not so much depend on the temperature in the temperature range of the present study.

It is well known that  $S(Q)$ 's of liquid silicon and germanium also have the shoulder on the high- $Q$  side of the first peak[4] and at the same time their  $g^{(3)}(\theta, r_c)$ 's show the peak around 100°[14, 15, 16, 9]. On the other hand, for liquid lead, which is also the group IV element, there is no shoulder in  $S(Q)$ [4] and no single peak around 100° in its  $g^{(3)}(\theta, r_c)$ [17]. These facts imply that the shoulder in  $S(Q)$  is related to the short-range structure making the peak around 100° in  $g^{(3)}(\theta, r_c)$ . From the results of  $g(r)$ ,  $S(Q)$  and  $g^{(3)}(\theta, r_c)$  in the present study, it is considered that the shoulder in  $S(Q)$  of liquid tin does not disappear but is merely covered by the broadened first peak at high temperatures.

The coordination number,  $n$ , is usually calculated by the integration of  $g(r)$ . For the liquid tin, however, since the position of the first minimum is not clear and the first peak is asymmetric, the definition of the coordination number is difficult. Therefore the distribution of the coordination number with the cutoff length  $r_c$  is investigated and the results at 773 K and 1473 K are shown in Fig. 4. Though, from the structure in the solid state with  $n = 4$  and from the bond angle distribution function for  $r_c = 3.0$  Å, the existence of the tetrahedral structure is implied, few four-fold structures are found in  $d(n)$  within  $r_c = 3.0$  Å. When  $r_c$  is fixed, the average coordination number decreases with increasing temperature for  $r_c \geq 3.2$  Å. For  $r_c = 3.0$  Å, however,  $d(n)$  is almost unchanged with changing temperature. This means that the short-range structure does not so much depend on the temperature.

From these results of  $g^{(3)}(\theta, r_c)$  and  $d(n)$ , we concluded that there are no complete tetrahedral structures but their fragments persist in liquid at high temperature of 1473 K.

In Fig. 5, a snapshot of liquid tin at 773 K is shown. The contour shows the density distribution of the valence electrons for the corresponding ionic configuration.

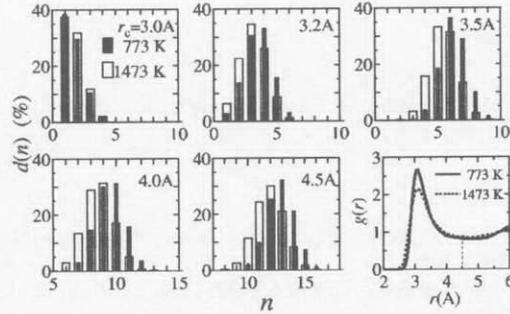


Figure 4. Distributions of the coordination number  $d(n)$  of liquid tin at 773 K and 1473 K, which are calculated from the atomic configurations obtained by the AIMD simulation. The radial distribution functions at 773 K and 1473 K are also shown.

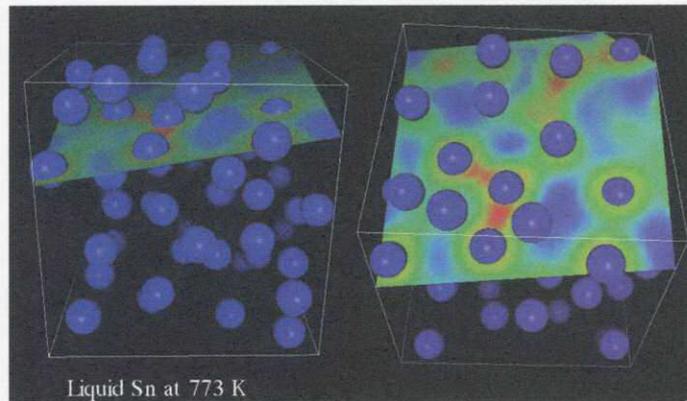


Figure 5. Snapshot of liquid tin at 773 K.

## 5 Summary

In this study, the neutron scattering experiments and the AIMD simulations were performed for liquid tin. From the neutron scattering experiments, a shoulder on the high- $Q$  side of the first peak of  $S(Q)$  can be clearly seen at 573 K and 773 K. Even at 1073 K, such a shoulder may be present though it becomes unclear in the change of overall pattern of  $S(Q)$ . From the simulations, a broad peak around  $100^\circ$  in the three body distribution function is observed up to 1473 K. The coordination number with cutoff radius of  $3.0 \text{ \AA}$  does not change with the increase of temperature from 773 K to 1473 K though it decreases with the increase of temperature in the case of larger cutoff radius. These features indicate that the fragments of covalent bond unit may persist even at high temperatures in the liquid tin and we are now investigating this issue by analyzing electronic structures obtained from the AIMD simulation. In the next stage it is important to perform the neutron scattering experiments at higher temperatures up to 1773 K. In addition, inelastic neutron scattering experiments are desired for the analysis of atomic dynamics in relation to the role of covalent bond units.

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