分子動力学シミュレーションによる高温高圧下における液体金属の構造の研究

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Molecular-dynamics study on the structure of expanded liquid metals at high temperatures and high pressures

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1. Introduction

The structures of expanded liquid metals such as liquid alkali metals and liquid mercury have been extensively studied over past decades. The most interesting feature of these metals is that when they are expanded from the triple point up to near the critical point, where both temperature and pressure are high, there occurs a metal-nonmetal(M-NM) transition, in other words the interionic interaction, which determines the ionic structure, changes continuously with density variation.

Owing to recent progress of experimental techniques at high temperature and high pressure, the static structure factor $S_{\rm exp}(k)$ of liquid rubidium, caesium and mercury have been measured. As for dynamic properties, the dynamic structure factor $S(k,\omega)$ of expanded liquid rubidium and the velocity of sound of expanded liquid mercury for a wide range of density have been measured. From these experiments, various characteristic features of the density dependence of the structure of expanded liquid metals are known. In particular, as for the velocity of sound of liquid mercury the following interesting feature is known: With decreasing density from near the triple point along the liquid-vapour coexistence curve, the velocity of sound of liquid mercury decreases linearly until near the M-NM transition region, whereas its decreasing rate becomes slower over that region until near the critical region.

On the theoretical side, however, there have been few studies of expanded liquid metal because there is no reliable method to derive the effective pair potential of liquid metals except for the state near the triple point, where the effective pair potential $\phi_{\rm ps}(r)$ calculated by the pseudopotential perturbation theory based on the nearly-free-electron model can be used. In fact it is known that near the critical point, both integral equation theory and simulation using $\phi_{\rm ps}(r)$ can reproduce neither static nor dynamic structures especially in a small k-region. Under these circumstances the relation between the density dependence of the structure of expanded

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liquid metals and that of the effective pair potential has not been well understood so far.

In this situation, one of the most effective approaches to derive the effective pair potential $\phi(r)$ is the inverse method, in which $\phi(r)$ is derived from the experimental structure factor $S_{\mathrm{exp}}(k)$. To obtain a reliable effective pair potential for expanded liquid metals by the inverse method, we have investigated the accuracy of the predictor-corrector (P-C) method for the inverse problem, which consists of the integral equation theory and the computer simulation, and improved it in some points.

In this thesis, first, we derive $\phi(r)$ of expanded liquid metals by the inverse method and next we investigate the dynamic properties of expanded liquid metals by the molecular-dynamics (MD) simulation using $\phi(r)$ thus obtained. The purposes of this thesis are as follows:

1. To investigate the density dependence of the effective pair potentials $\phi(r)$ of expanded liquid rubidium, caesium and mercury by deriving them from the experimental static structure factors $S_{\mathrm{exp}}(k)$ using the P-C method for the inverse problem.
2. To clarify whether $\phi(r)$ thus derived can reproduce the experimental dynamic properties or not, by investigating the dynamic structures of expanded liquid rubidium with the MD simulation using $\phi(r)$.
3. To clarify the relation between the density dependence of the velocity of sound and that of $\phi(r)$ of liquid mercury, by investigating the velocity of sound of liquid mercury using the large-scale parallelized MD simulation.

2. Effective pair potential by inverse method

In chapter 2, the P-C method is explained at first.In the integral equation theory, $\phi(r)$ multiplied by the inverse temperature $\beta=1/k_{\mathrm{B}}T$ is written as

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

where $g(r)$, $c(r)$ and $B(r)$ are the radial distribution function, the direct correlation function and the bridge function, respectively. Though $g(r)$ and $c(r)$ can be obtained from $S_{\mathrm{exp}}(k)$, $B(r)$ cannot be obtained directly from $S_{\mathrm{exp}}(k)$. Therefore $B(r)$ is calculated by the iterative procedure using the computer simulation.

Next we have derived $\phi(r)$ of expanded liquid rubidium, caesium and mercury using the P-C method from the triple point to near the critical point along the liquid-vapour coexistence curve and investigated their density dependence in detail. We have found that the effective pair potential $\phi(r)$ of liquid rubidium and caesium have a similar density dependence: With decreasing density, (i) the repulsive $\phi(r)$ shifts toward a shorter distance and becomes softer, (ii) the oscillatory behaviour of $\phi(r)$ disappears and (iii) the attractive part of $\phi(r)$ becomes weaker and longer-ranged. As for expanded liquid mercury, we have derived $\phi(r)$ for three states: (I)1273K, 10.98g/cm^3(metallic state), (II)1673K, 9.25g/cm^3(near M-NM transition region) and (III)1803K, 6.8g/cm^3(near the critical point, nonmetallic state). Following interesting feature is shown. The repulsive part of $\phi(r)$ shifts to a shorter distances when the state changes from (I) to (II), while that shifts to a longer distances when the state changes from (II) to (III). This feature is important to understand the density dependence of the velocity of sound of the liquid mercury discussed in chapter 4.

3. Dynamic structures of expanded liquid rubidium

In chapter 3, to investigate the applicability of $\phi(r)$ derived from $S_{\mathrm{exp}}(k)$ for expanded liquid rubidium to the dynamical properties, we calculate the van Hove correlation function, the intermediate scattering function, the dynamic structure factor, the velocity autocorrelation function and the self-diffusion coefficient from the triple point to near the critical point, *i.e.* at the temperature 350K, 1700K and 1900K, using the constant temperature MD simulation. The MD simulation is carried out for a system of 512 atoms in a cubic cell. The equations of motion are solved via the velocity Verlet algorithm with a time step of 4.8fs. The quantities of interest are obtained by averaging over 100,000 time steps. Next the MD simulation for a larger system of 8,000 atoms is carried out to investigate the dynamical properties in a smaller k-region at 1900K, where there has been neither experimental nor theoretical study. The following features are shown:(i) Near the triple point, we need to employ the very accurate static structure factor as the input data for solving the inverse problem to reproduce the dynamic structure in a small k-region using $\phi(r)$, since the dynamical properties in such a k-region are very sensitive to the effective pair potential. (ii) At low density near the critical point, $\phi(r)$ derived from $S_{\mathrm{exp}}(k)$ can reproduce the dynamic structure very well within the pair additive approximation, while $\phi_{\mathrm{ps}}(r)$ can reproduce neither static nor dynamic structures. (iii) There exists the propagating density fluctuation mode for $k \sim 0.1\mathrm{A}^{-1}$ at 1900K.

4. Velocity of sound of expanded fluid mercury obtained by the large-scale molecular-dynamics simulation

In chapter 4, to explain the relation between the density dependence of the velocity of sound and that of $\phi(r)$ of expanded liquid mercury, we have calculated the velocities of sound of liquid mercury at three states (I), (II) and (III) using the large-scale MD simulation with $\phi(r)$ obtained from $S_{\mathrm{exp}}(k)$. In the MD simulation the velocity of sound is obtained from the gradient of the dispersion curve of $S(k, \omega)$ in a small k-region. To obtain the velocity of sound near the critical point, where large-scale density fluctuation is important, we have to carry out the large-scale simulation with the long runs. Therefore we have parallelized the program of the MD simulation with the atom decomposition algorithm and carried out this MD simulation over 200,000 steps with a time step of 4.8fs for a large system of 64,000 atoms using the parallel computer. We have shown that the results of the velocities of sound thus obtained are in very good agreement with the experiments and $\phi(r)$ obtained from the static structure factors can reproduce the characteristic features of the density dependence of them. We have clarified that the repulsive part of $\phi(r)$ plays an essentially important role for the change in the density dependence of the velocity of sound of liquid mercury at the M-NM transition. We have also shown that the density dependence of the self-diffusion coefficient of liquid mercury changes at the M-NM transition.

5. Conclusions

In this thesis, we have shown the following things:

1. The P-C method for solving the inverse method is very useful to derive the effective pair potential of expanded liquid metals from the experimental structure factors.

2. The effective pair potential thus obtained can be used for the MD simulation to investigate the dynamic properties of expanded liquid metals.
3. The large-scale MD simulation using the parallel computer is powerful for studying the long-wavelength fluctuation in liquid metals near the critical point.

Publications

Some parts of this thesis have been published and the rest of it will be published as follows:

"An accurate method of deriving effective pair potential from structural data of liquid alkali metals" S. Munejiri, F. Shimojo, K. Hoshino and M. Watabe *J. Phys. Soc. Jpn.* 64 (1995) 344.

"Effective pair potential of expanded liquid rubidium obtained by the inverse method" S. Munejiri, F. Shimojo, K. Hoshino and M. Watabe *J. Non-Cryst. Solids* 205-207 (1996) 278.

"The effective pair potential of expanded liquid caesium obtained by the inverse method" S. Munejiri, F. Shimojo, K. Hoshino and M. Watabe *J. Phys.:Condens. Matter* 9 (1997) 3303.

"The density dependnece of the volocity of sound in expanded liquid mercury studied means of a large-scale molecular-dynamics simulation" S. Munejiri, F. Shimojo and K. Hoshino *J. Phys.:Condens. Matter* 10 (1998) 4963.

"Dynamic structure of expanded liquid rubidium by the molecular-dynamics simulation" S. Munejiri, F. Shimojo and K. Hoshino To be submitted to *J. Phys. Soc. Jpn.*