

The molecular dynamics simulations of complex liquids based on the modified hard sphere potential

Tadahiko Masaki¹, Hirokatsu Aoki² and Toshio Itami^{2,3}

1: Space Utilization Research Center, National Space Development Agency of Japan, 2-1-1, Sengen, Tsukuba, Ibaragi, 305-8505 Japan.

2: Space Utilization Research System, National Space Development Agency of Japan, 2-1-1, Sengen, Tsukuba, Ibaragi, 305-8505 Japan.

3: Graduate School of Science, Hokkaido Univ, N10W8, Kitaku, Sapporo, 060-0810 Japan.

1. Introduction

It is well known that some of liquid polyvalent metals show the characteristic liquid structure such as the shoulder in the high wave number side of the first peak of static structure factor, $S(Q)$ ¹. Up to date some specific models have been reported for the description of this kind of liquid structures. However, the origin of this “shoulder” has not yet been specified clearly. Recently, *ab initio* molecular dynamics simulations have been applied to such liquid metals^{2,3}. The liquid structures with “shoulder” are well reproduced by these *ab initio* molecular dynamics. Therefore, the quantum interaction between electrons and ions in liquid metals are the origin of such complicate structures.

Munejiri et al. evaluated the effective pair interatomic potential, $u(r)$, of liquid tin from the static structure factor due to the inverse method in our diffusion research project⁴. The obtained potential shows the specific feature that is characterized by the hard sphere like repulsive core with the “ledge” in $u(r)$. The same feature of pair potential can be seen in previous reports. For example, Hafner et al. evaluated similar types of pair interatomic potential of liquid germanium due to the NFE model with Ashcroft type pseudo potential. This interatomic potential well reproduces the shoulder of experimental $S(Q)$ ⁵.

The wiggling part of $u(r)$ such as the “ledge” may change the distribution of atoms from that of hard sphere like liquid. Therefore, the “ledge” can be regarded as one of origin of shoulder of $S(Q)$. In this report, the classical molecular dynamics simulation is performed due to the semi-hard sphere potential with the variation of intensity of the “ledge”, and the effect of “ledge” in $u(r)$ on the liquid structure, is investigated in detail.

2. Molecular dynamics simulations

2.1 Interatomic potential

In the case of liquid IVB elements, such as tin, germanium and silicon, ether inverse method or

NFE model deduces the similar type of effective pair potentials $u(r)$'s which possesses the repulsive core with a ledge in $u(r)$. For the mimic of this feature of $u(r)$, the following form of interatomic potential was assumed.

$$u(r) = \epsilon_0 (\sigma/r)^n + \epsilon_1(1-\text{Erf}(a(r - b\sigma)))/2$$

where σ is the core diameter of soft sphere, n is the hardness of soft sphere, ϵ_0 is the potential energy at $r = \sigma$ and can be taken to be equal to $k_B T$ (k_B : the Boltzman's constant, T : absolute temperature). The error function, $\text{Erf}(y)$, is superposed on soft sphere potential as the ledge in $u(r)$, where ϵ_1 is the amplitude of ledge, a is the parameter of slope and b is the parameter of the position of the ledge. The molecular dynamics simulations were performed with the use of this potential with the variation of ϵ_1 , a and b parametrically.

2.2 Simulation procedure

The molecular simulation of canonical ensemble was employed, in which the total number of atoms N , volume V and temperature T were held to be constant. The packing fraction, $y = N\pi\sigma^3/6V$, was fixed to be 0.4. The simple Verlet's algorithm was applied to integrate the Newtonian equation of motion. Total number of atoms was typically 256. For the convenience of numerical calculation, the σ , mass of atoms, m , and reduced temperature, $T_{\text{ref}} = k_B T / \epsilon_0$, were set to be unity. Concerning the stability of calculation, the step of non-dimensional time, Δt , was selected to be 0.0015. The non dimensional time is defined as $t = (m\sigma^2/n\epsilon_0)^{1/2}$. A periodic boundary condition was adopted on the three-dimensional boundary of a simple cubic cell. The fcc lattice of atomic configuration and gaussian distribution of velocity were assumed as the initial condition. The initial 3×10^4 steps were considered as the relaxation time of initial condition and 10^5 steps were continued for the evaluation of physical properties.

3. Results and discussion

The radial distribution function was evaluated with the variation of interatomic potential. Fig. 1 shows the typical interatomic potentials, $u(r)$, and the radial distribution function, $g(r)$, obtained from the present molecular

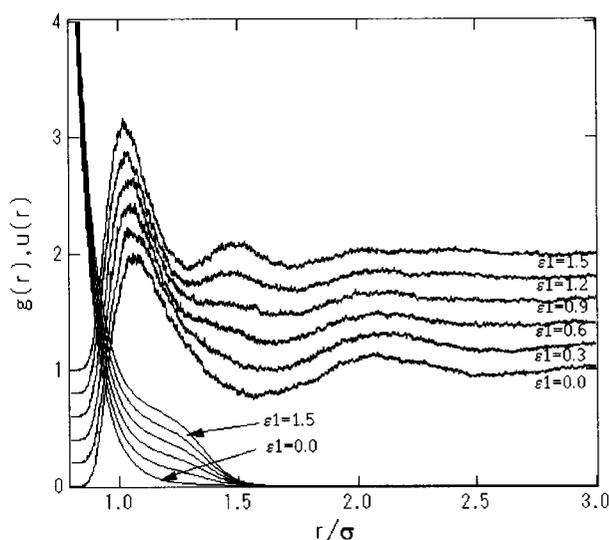


Fig.1 Interatomic potential and radial distribution function

dynamics simulation. Adopted parameters were $n=12$, $\epsilon_0=1.0$, $a=7.0$ and $b=1.35$ and ϵ_1 was systematically changed between 0.0 and 1.5. It is obvious that the positions of second peak of $g(r)$ were gradually sifted to smaller r region with the increase of the intensity of the ledge in $u(r)$. This aspect of $g(r)$ derived from the shape of $u(r)$ because the atoms whose kinetic energies are higher than ϵ_1 can only overcome the ledge and contact each other at $r=\sigma$. Other atoms with lower kinetic energies are reflected at the position of ledge. The static structure factor, $S(Q)$, was evaluated from $g(r)$ due to the Fourier transformation, as shown in Fig. 2. The shoulder in high Q side of the first peak of $S(Q)$ was clearly observed in the case of $\epsilon_1=1.5$. With the decrease of the intensity of the ledge, the shoulder was reduced. From these results, the ledge of repulsive core of $u(r)$ is one of the origin of the shoulder in $S(Q)$.

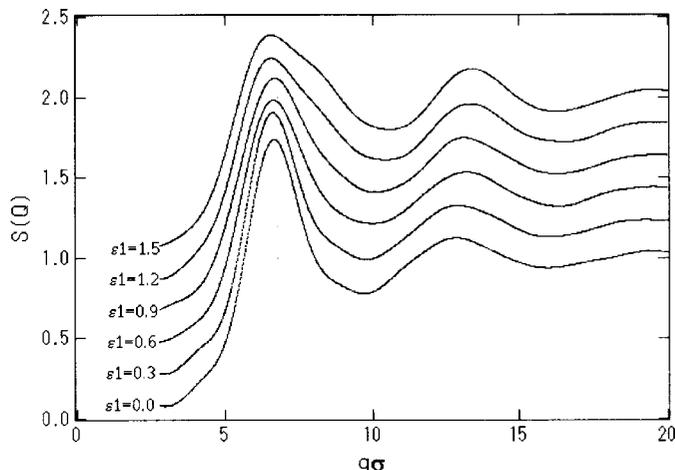


Fig.2 Static structure factors

The angular distribution of atomic coordination shows a much interesting feature. The angular distribution around atom i was evaluated for the angle between the vectors $\mathbf{r}_{ij} = \mathbf{r}_j - \mathbf{r}_i$ and $\mathbf{r}_{ik} = \mathbf{r}_k - \mathbf{r}_i$ (\mathbf{r}_i , \mathbf{r}_j and \mathbf{r}_k denote the position vector of atom i , j and k respectively). In this case, atom j and atom k are placed within a sphere whose center is situated at the position of atom i and whose radius is R_c . Fig. 3 shows the angular distribution for $R_c=1.06$, which corresponds to the distance of first peak of $g(r)$. In this figure, the simulation results of $\epsilon_1=1.5$ were compared with those of soft sphere with $\epsilon_1=0.0$.

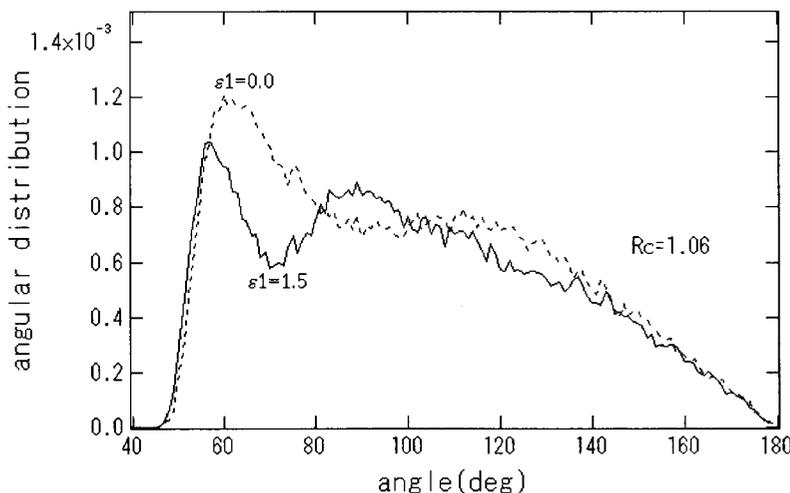


Fig.3 Angular distribution of atoms (cut of radius $R_c=1.06$)

The angular distribution for $u(r)$ with ledge clearly increased around 90 degrees. On the other hand, the case of $\epsilon_1=0.0$ only shows the peak around 60 degrees, which is the indication of close-packed structure. The same feature of angular distribution was observed between $R_c=1.015$ and 1.08. The ledge in $u(r)$ induces the short range order of liquid

not only on the radial distribution function but on angular distribution function.

Finally, the effect of the ledge on the diffusion coefficient is discussed. The self diffusion coefficient, D_0 , can be simply obtained from the mean square displacement of atoms. In this case, D_0 was evaluated from the numerical curve fitting in

the linear region (between 0.5 and 1.0 as non-dimensional time) of mean square displacement. The relation between the intensity of ledge in $u(r)$ and D_0 is shown in Fig.4. The D_0 slightly increased with the increase of the ledge in $u(r)$. The increase of ledge in $u(r)$ may be roughly regarded as the increase of diameter of atoms. As easily considered, D_0 should be small in the system of large spheres. However the results of this simulation show the opposite tendency. The result of present simulation shows that the wiggle of $u(r)$ also affects the transport properties. In this study, the temperature was controlled by the velocity control method and the temperature of system was adopted to be constant through present all simulations. As the next step, the temperature dependence of D_0 will be researched.

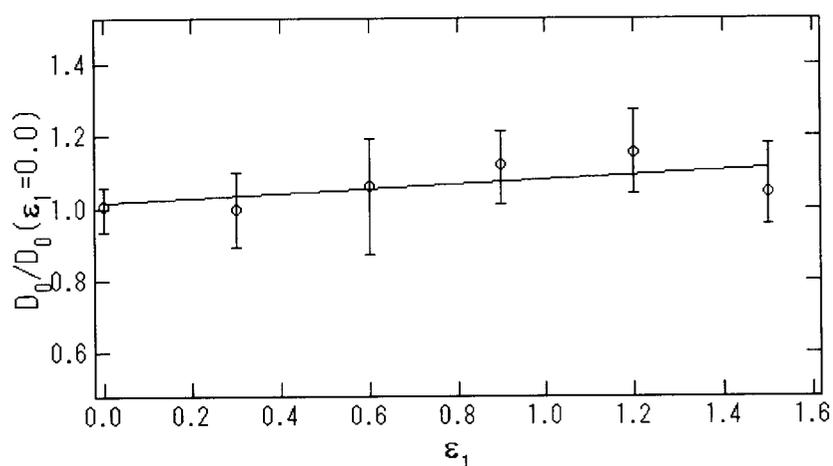


Fig.4 Diffusion coefficient (non-dimensional unit) as a function of the intensity of ledge.

Error bars were estimated from the maximum and minimum value of D_0 obtained.

References

- 1) Y. Waseda, "The Structure of Non-Crystalline Materials, Liquid and Amorphous Solid" (McGraw-Hill, New York, 1980).
- 2) R. Car and M. Parrinello, Phys. Rev. Lett **55**, 2471(1985).
- 3) R. V. Kalukani, W. G. Aulbur and D. Stroud, Phys. Rev. B **55**, 6896(1997).
- 4) S. Munejiri et al., "Modeling and Precise Experiments of Diffusion Phenomena in Melts under Microgravity, Annual Report 2000", NASDA-TMR-010019E, pp-73(2002).
- 5) J. Hafner and V. Heine, J. Phys. F: Metal Phys. **13**,2475(1984).