Application of mode coupling theory to group IVB liquids

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Abstract

The atomic dynamics of liquid Ge, Sn and Na are studied based on the mode coupling theory. The memory functions for the velocity autocorrelation functions (VAF) are obtained for liquid Ge, Sn and Na numerically from the VAF obtained by the molecular-dynamics simulations and are divided into the binary-collision term and the mode-coupling term. For the liquid Na the memory functions are also calculated theoretically by the mode-coupling theory and compared with that obtained numerically. The characteristic features of the memory functions for the liquid Ge and Sn near the triple point are qualitatively different from those for the typical liquids and are similar to those of the memory function of the liquid Na at high temperatures, which cannot be described by the mode-coupling theory.

§ 1. Introduction

Though the self-diffusion coefficient D is an experimentally measurable physical quantity which describes the atomic diffusion in liquids, it does not give rise to the direct information about the atomic motion in liquids. This is because D is defined by the average quantity as follows([1]-[3]):

$$D = \lim_{t\to\infty} \frac{<r^2(t)>}{6t} \tag{1.1}$$

$$= \frac{k_B T}{m} \int_0^\infty dt\, \phi(t) \tag{1.2}$$

where $<r^2(t)>$ is the root-mean-square displacement of atoms, $\phi(t)=<v(0)\cdot v(t)>/<v^2(0)>$ is the normalized velocity-autocorrelation function (VAF) and the brackets $<>$ mean the ensemble average. Therefore it is necessary to investigate the time dependence of $\phi(t)$ to get the detailed information about the atomic dynamics during the diffusion process. The $\phi(t)$ is easily obtained by the molecular-dynamics (MD) simulation, though it is difficult to obtain $\phi(t)$ experimentally.

As a typical example for the $\phi(t)$ of liquid metals, we show the $\phi(t)$ of the liquid Na near the triple point (T=380 K) in Fig.1 (for details, see § 4). With increasing time, the $\phi(t)$ decreases rapidly, takes a negative minimum value and approaches zero with a damped

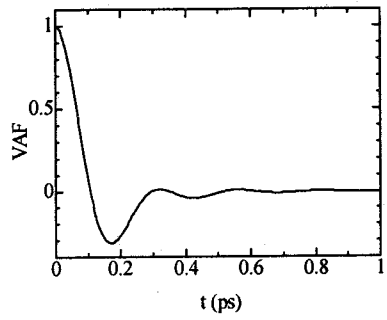

Fig.1 The velocity-autocorrelation function (VAF) $\phi(t)$ of the liquid Na

oscillation. The negative value of $\phi(t)$ comes from the large change of the velocity of an atom due to the scattering with the surrounding atoms, which is called *'the cage effect'* or *'the back-scattering effect'*. In general, the behaviour of $\phi(t)$ gives the information about the interatomic potential in the short-time region, the atomic dynamics in the intermediate region and the collective motion in liquids in the long-time region.

The purposes of this study are (i)to obtain the memory functions for the liquid Ge, Sn and Na numerically from the velocity-autocorrelation functions obtained by the molecular-dynamics simulations, (ii)to analyze the memory functions based on the mode-coupling theory and (iii)to obtain the detailed information about the atomic diffusion in these liquids.

§ 2. Method of Calculation

To investigate the detailed behaviour of the $\phi(t)$, it is convenient to introduce the memory function $K(t)$ defined by the following equation ([1]-[3]):

$$\frac{d\phi(t)}{dt} = -\int_0^t dt' K(t-t')\phi(t'). \tag{2.1}$$

We obtained the $K(t)$ by solving eq.(2.1) numerically([4],[5]) using the ϕ (t) obtained by the MD simulations.

In the mode-coupling theory[3], the $K(t)$ is written as a sum of two terms as follows;

$$K(t) = K_B(t) + K_{MC}(t) \tag{2.2}$$

where the $K_B(t)$ is the short-time term, the so-called binary-collision term, which describes the uncorrelated binary collision due to the short-range force and the $K_{MC}(t)$ is the long-time term called as the mode-coupling term, which describes the collective dynamics of atoms. As a typical example for the $K(t)$, $K_B(t)$ and $K_{MC}(t)$, we show those of the liquid Na near the triple point(see § 4) in Fig.2. The $K(t)$ is well divided into the $K_B(t)$ and $K_{MC}(t)$ in the sense that they contribute to the $K(t)$ separately in the different time range.

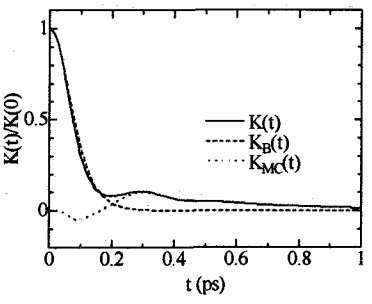

Fig.2 The memory functions $K(t)$, $K_B(t)$ and $K_{MC}(t)$ for the VAF ϕ (t) of the liquid Na at 380K.

Using the Laplace transform of eq.(2.1), $\tilde{\phi}(s) = (s+\tilde{K}(s))^{-1}$, the diffusion coefficient D can be expressed by the $K(t)$, $K_B(t)$ and $K_{MC}(t)$ as

$$D = \frac{k_B T}{m}\tilde{\phi}(0) \tag{2.3}$$

$$= \frac{k_B T}{m}\left(\int_0^\infty dt\, K(t)\right)^{-1} \tag{2.4}$$

$$= \frac{k_B T}{m}\left(\int_0^\infty dt\, K_B(t) + \int_0^\infty dt\, K_{MC}(t)\right)^{-1}, \tag{2.5}$$

where $\tilde{\phi}(s)$ and $\tilde{K}(s)$ are the Laplace transforms of ϕ (t) and $K(t)$, respectively. If we define the D_B, for the case when only binary collisions are taken into account, by

$$D_B = \frac{k_B T}{m} \left(\int_0^\infty dt\, K_B(t) \right)^{-1} \tag{2.6}$$

the D can be written by

$$D = D_B \left(1 + \int_0^\infty dt\, K_{MC}(t) / \int_0^\infty dt\, K_B(t) \right)^{-1} \tag{2.7}$$

$$= D_B / \zeta , \tag{2.8}$$

where the ζ corresponds to 'the back-scattering factor'.

We employ the following approximate expression for the $K_B(t)$ as [3]

$$K_B(t) = K(0)\, \mathrm{sech}^2 (t / \tau_B). \tag{2.9}$$

Then, with the integration formula

$$\int_0^\infty \mathrm{sech}^2 (x)\, dx = 1 \tag{2.10}$$

we have

$$D_B = k_B T / mK(0)\, \tau_B , \tag{2.11}$$

where 'the binary-collision time' τ_B is given by (see, *e.g.* p112 of [3])

$$\tau_B = [\, |\ddot{K}(0)| / 2K(0)]^{-1/2}. \tag{2.12}$$

§ 3. Results for liquid Ge and liquid Sn

3.1 Liquid Ge

The effective pair potential $\phi(r)$ for the liquid Ge is obtained based on the pseudopotential perturbation theory with the Ashcroft pseudopotential (the core radius: r_c=0.98 a.u.) and is shown in Fig.3. It should be noted that the $\phi(r)$ for the liquid Ge is repulsive at the average nearest-neighbour distance, r 2.7 Å. For the liquid Ge, we have carried out the MD simulations using this pair potential for the system of 4096 atoms at T=1253K and 2000K for 50,000 - 100,000 steps with Δt

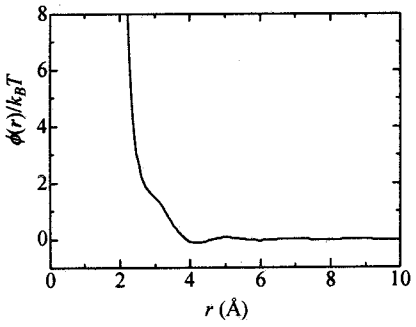

Fig.3 The effective pair potential $\phi(r)$ for the liquid Ge at 1253K obtained

= 2.4 fs and obtained the $\phi(t)$ and the D.

The $\phi(t)$ for the liquid Ge at 1253K shown in Fig.4 decreases monotonically and does not become negative, which is a qualitatively different behaviour from that of the $\phi(t)$ for the typical liquid metals as is shown in Fig.1. This means that the cage effect is very weak for the liquid Ge. Since the VAF of the liquid Ge changes a little from 1253K to 2000K, the temperature dependence of the $K(t)$ is also very small and therefore we do not show the results for 2000K. The $K(t)$, $K_B(t)$ and $K_{MC}(t)$ at 1253K are shown in Fig.5. The behaviour of the $K(t)$ for the liquid Ge is also qualitatively different from that of typical liquid metals shown in Fig.2; i.e. the $K(t)$ decreases with increasing time, becomes negative and then approaches zero. The $K_{MC}(t)$ is always negative for the liquid Ge.

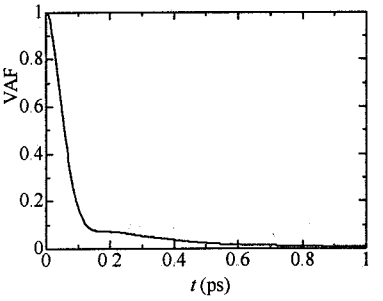

Fig.4 The VAF ϕ (t) for the liquid Ge at 1253K.

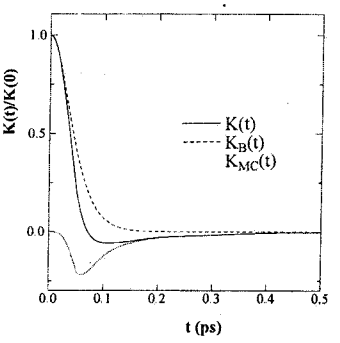

Fig.5 The memory functions $K(t)$, $K_B(t)$ and $K_{MC}(t)$ of the liquid Ge at 1253K.

The relevant quantities to the diffusion coefficient of the liquid Ge are shown in TableI, in which the n(Å^{-3}) is the number density and T_m the melting temperature.

Table I Various physical quantities of the liquid Ge (T_m =1209 K)

T (K)	1253	2000
D_B (x10^{-5}cm^2/s)	7.33	13.2
τ_B (ps)	0.0496	0.0426
ζ	0.535	0.542
D (x10^{-5}cm^2/s)	13.7	24.4
n (Å^{-3})	0.0466	0.0438

3.2 Liquid Sn

The effective pair potential for the liquid Sn is obtained from the observed structure factor by the inverse method [6] and is shown in Fig.6. We have carried out the MD simulation for the system of 4096 Sn atoms at 523, 1073 and 1473K for 50,000 steps with Δt = 3.0 fs and obtained the $\phi(t)$ and the D. From the temperature dependence of the $\phi(t)$ shown in Fig.7, the weak cage effect at 523K becomes much weaker with increasing temperature.

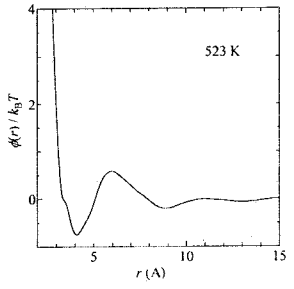

Fig.6 The effective pair potential $\phi(r)$ for the liquid Sn at 523K derived by the inverse method.

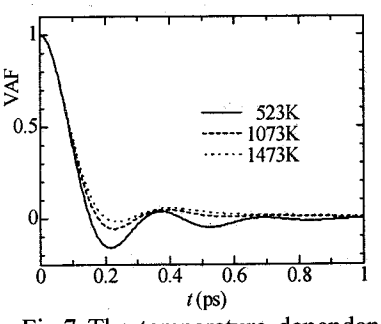

Fig.7 The temperature dependence of the VAF ϕ (t) for the liquid Sn.

The $K(t)$, $K_B(t)$ and $K_{MC}(t)$ of the liquid Sn for these temperatures are shown in Fig.8. Though the $K(t)$ at 523K decreases with increasing time, takes a negative value, and approaches zero with damped oscillation, the $K(t)$'s at 1073K and 1473K approach zero without oscillation. Furthermore the $K_{MC}(t)$ is almost negative as shown in Fig. 9.

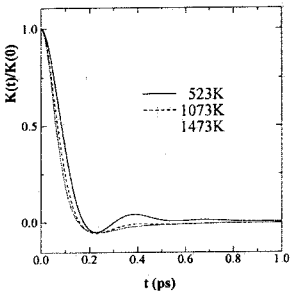

Fig.8 The temperature dependence of the memory function $K(t)$ for the liquid Sn.

The relevant quantities to the diffusion coefficient of the liquid Sn are shown in TableII.

Table II Various physical quantities of the liquid Sn (T_m = 505 K)

T (K)	523	1073	1473
D_B (x10^{-5}cm^2/s)	2.34	5.75	8.50
τ_B (ps)	0.0969	0.0793	0.0723
ζ	0.932	0.708	0.667
D (x10^{-5}cm^2/s)	2.51	8.12	12.7
n (Å^{-3})	0.0354	0.0335	0.0323

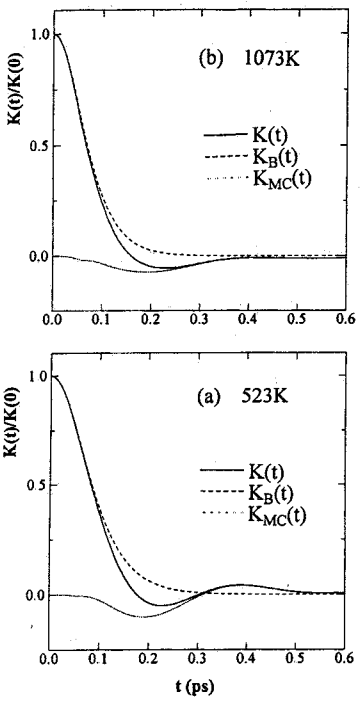

Fig.9 The temperature dependence of the memory functions $K(t)$, $K_B(t)$ and $K_{MC}(t)$ for the liquid Sn at (a) 523K and (b) 1073K.

3.3 Discussion

From the results shown above we can conclude that the dynamical behaviour of the liquid Ge and the liquid Sn is different from that of typical liquid metals. The anomalous behaviour of memory functions $K(t)$ for these liquids results in the negative value for $K_{MC}(t)$. Therefore the back-scattering factor $\zeta < 1$ for these liquids as shown in Table I and Table II, which is in contrast with $\zeta > 1$ for typical liquids such as the liquid alkali metals and the liquid Ar near triple points, in which the pair potential has its deep minimum around the nearest-neighbour distance as will be shown in § 4. For the latter cases, it is known that the behaviour of the memory functions can be well explained by the mode-coupling theory [3].

As was pointed out by Gudowski *et al.* [9], for the liquid Pb, which belongs to the same group IV as the liquid Ge and Sn, the pair potential has not a minimum value near the nearest-neighbour distance and the behaviour of the memory function for the VAF cannot be described by the mode-coupling theory, though the $K_{MC}(t)$ is positive for the liquid Pb in contrast with the liquid Ge and Sn. They also pointed out that the $K_B(t)$ and the $K_{MC}(t)$ are not well separated and the intermediate time range is important for the

liquid Pb.

Since, for the liquid Ge and Sn, the $K_{MC}(t) = K(t) - K_B(t)$ is negative, the division of $K(t)$ into $K_B(t)$ and $K_{MC}(t)$ is not appropriate physically for these systems.

§ 4. Mode-coupling analysis for the liquid Na

In the previous section we have shown that the VAF and its memory function for the liquid Ge and Sn have different behaviour from those of typical liquids. To clarify the reason for the anomalous behaviour we have carried out the mode-coupling analysis for the liquid Na, which is considered as the simple liquid metal.

4.1 MD simulations for the liquid Na

The pair potentials are calculated based on the pseudopotential perturbation theory using the HHWY pseudopotential [7] and shown in Fig.10. Using these pair potentials, the MD simulations are carried out for the system of 4096 atoms at 380K, near the triple point, and at the higher temperature of 900K and the $\phi(t)$'s are obtained as shown in Fig.11 .

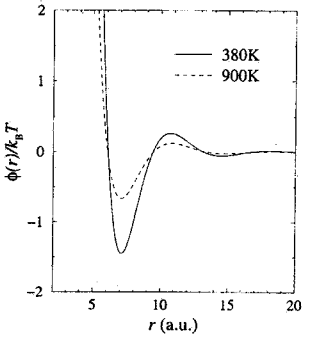

Fig.10 The effective pair potential $\phi(r)$ of the liquid Na at 380K and 900K obtained by the pseudopotential perturbation theory.

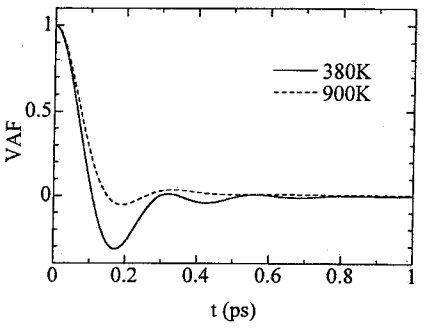

Fig.11 The VAF $\phi(t)$ of the liquid Na at 380K and 900K.

4.2 Memory functions

Using the $\phi(t)$'s obtained by the MD simulations, the $K(t)$'s are obtained by solving eq.(2.1) numerically and shown in Fig.12. The $K(t)$, $K_B(t)$ and $K_{MC}(t)$ are also shown in Fig.13. From these figures it is seen that both $\phi(t)$ and $K(t)$ for the liquid Na at 380K show a behaviour for typical liquids; i.e. the $\phi(t)$ decreases rapidly with increasing time, becomes negative and then approaches zero with a damped oscillation, which is a typical cage effect, and as for the memory function, the $K(t)$ is positive and composed of the rapidly decreasing short-time term $K_B(t)$ and the slowly-decreasing long-time term $K_{MC}(t)$.

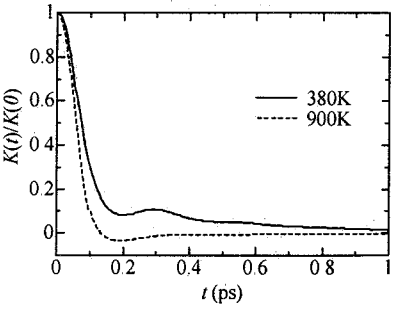

Fig.12 The memory function K(t) of the liquid Na at 380K and 900K.

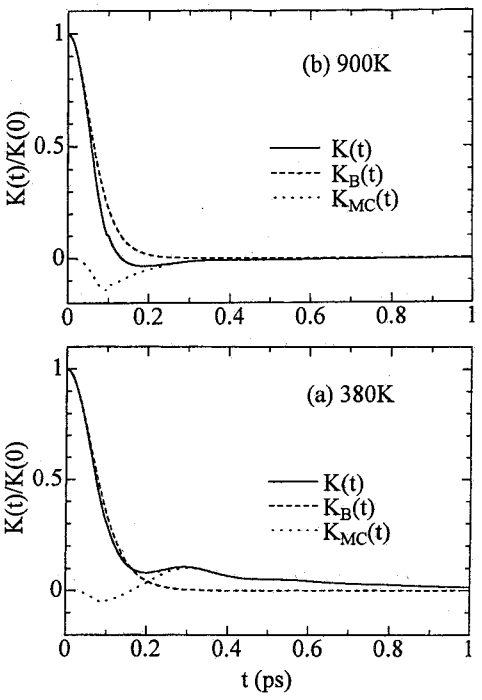

Fig.13 The memory functions $K(t)$, $K_B(t)$ and $K_{MC}(t)$ of the liquid Na at (a) 380K and (b) 900K.

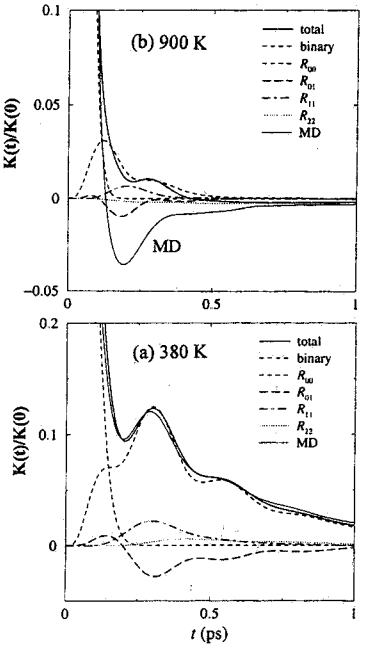

Fig.14 The memory functions of liquid Na at (a) 380K and (b) 900K calculated by the mode-coupling theory ('total') are compared with those ('MD') obtained numerically from the VAF obtained by the MD simulations.

On the other hand, at 900K, the $\phi(t)$ is always positive and decreases monotonically with increasing time and the $K(t)$ decreases rapidly, becomes negative and approaches zero. These behaviour of the $\phi(t)$ and $K(t)$ for the liquid Na at 900K is very similar to those obtained for the liquid Ge and Sn near the triple point.

The relevant quantities to the diffusion coefficient of the liquid Na are shown in Table III.

Table III Various physical quantities of the liquid Na (T_m = 371 K)

T (K)	380	900
D_B (x10^{-5}cm^2/s)	5.37	18.5
τ_B (ps)	0.089	0.073
ζ	1.39	0.712
D (x10^{-5}cm^2/s)	3.87	26.0
n (Å^{-3})	0.0242	0.0210

4.3 Memory functions calculated by the mode-coupling theory

In the mode-coupling theory formulated by Sj gren and Sj lander [8] and Gudowski *et al.* [9] the memory function can be calculated theoretically based on the pair potential and the structure factor obtained by the simulation. In Fig.14 we compare the memory

functions of liquid Na at 380K and 900K obtained theoretically (shown by 'total') with those obtained numerically (shown by 'MD') from the VAF obtained by the MD simulation. In the figure we also show the contributions due to four mode-coupling terms ([9],[10]), *i.e.* R_{00}; the density-density coupling term, R_{01} and R_{11}; the density-longitudinal current coupling terms, and R_{22}; the density-transverse current coupling term. At 380K the R_{00} contributes mainly to the $K(t)$ and the theoretical $K(t)$ agrees well with the numerically obtained $K(t)$, while the agreement between them is very poor at 900K. It is difficult to describe the negative $K(t)$ by the mode-coupling theory. These results mean that the mode-coupling theory is valid for the liquid Na at 380K (see [10]) but is not valid at 900K.

Since the bahaviour of the $\phi(t)$ and the $K(t)$ for the liquid Na at 900K is similar to those for the liquid Ge and Sn near the triple point, we conclude that the mode-coupling theory cannot describe the atomic dynamics of liquid Ge and Sn.

§ 5. Summary

The VAF and the memory functions of the liquid Ge and Sn show a quite different behaviour from the typical liquids even near the triple point. Though the liquid Na behaves as a typical liquid near the triple point, it shows qualitatively different behaviour at higher temperature, which is rather similar to those of the liquid Ge and Sn near the triple point.

Why the atomic dynamics of the liquid Ge and Sn near the triple point are similar to that of the liquid Na at higher temperature? The common feature for these systems is that the average coordination number is smaller, 6-8, than the typical liquids, 10-12. The smaller coordination number corresponds to a more free space around each atom, i.e. the *'incomplete'* cage is formed, and therefore the cage effect is weak. For these reasons the VAF has not a negative value and, as a result, the $K(t)$ has a negative value in the intermediate time range, which is difficult to describe by the mode-coupling theory.

We conclude that the atomic dynamics of the liquid Ge and Sn as well as the liquid Na at high temperature cannot be described by the present mode-coupling theory, in which the memory function is divided into the binary-collision term and the mode-coupling term. When the pair potential has not a minimum but a repulsive part near the nearest-neighbour distance, as is the case for the liquid Ge (Fig.3) and for the liquid Sn (Fig.6), the binary-collision term is difficult to treat and the coordination number tends to be smaller than the typical liquid.

Acknowledgements

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