MOLECULAR DYNAMICS STUDY ON THE DYNAMICAL ASPECTS OF THE SHORT-RANGE ORDER IN A LIQUID METAL

MINORU TANAKA
Tohoku University, Department of Engineering Science, Faculty
of Engineering, Sendai 980, Japan

ABSTRACT

The collective dynamical aspects in the density-density correlation in classical monatomic liquids near the melting point, such as is reflected in the non-Markov characters of the velocity autocorrelation function of a constituent atom, are investigated through the molecular dynamics simulation of several space-time correlation functions defined with the group-velocity of local aggregation of atoms.

It is shown that the thermal motion of an atom is very coherent with those of neighbouring atoms corresponding to the first-peak of the pair distribution function. The oscillatory tail in the velocity autocorrelation function after its negative minimum is the result of back-and-forth relaxation of the initial momentum between the central and surrounding "cage" atoms. These coherent characteristics can be considered corresponding to the quasi-phonon peaks found in the dynamical structure factor measured by inelastic neutron scattering.

INTRODUCTION

The thermal motion of atoms in a classical liquid has been shown well-correlated over a wide-range of frequencies as well as of wave-numbers through the measurement of the dynamical structure factor $S(Q, \omega)$, i.e. the space-time Fourier transform of the van Hove correlation function $G(r,t)$ by the inelastic scattering of thermal neutrons. Many theoretical studies have been devoted to understand such dynamical aspects of the density-density correlation in liquid states from the microscopic point of view. The recent review article by Yoshida and Takeno [1] reports on the present stage of theoretical studies on this subject.

It should be emphasized that the computer experiments of the atomic properties of liquids, especially by the molecular dynamics method (MD) have added great achievements to the statistical mechanical theory of liquids. Among others, the lecture-notes edited by Ciccotti et al.[2] is useful to survey fruitful applications of the computer simulation methods to liquids.

Rahman [3] showed first by MD simulation that molten state of simple metals could be understood as classical monatomic liquid with a suitable pairwise additive interaction potential between screened metallic ions. We have reported a series of MD simulations of liquid rubidium in the wide-range of temperatures and densities[4,5] on the basis of the pseudopotential theory for the electron-ion interaction in the metallic state, and shown that collective aspects in the thermal motion of rubidium atoms are significant near the melting point. In MD simulation, any single atom can be used as a probe to investigate such collective characteristics of atomic motions in liquid rubidium.

In Fig. 1, we show the MD simulation of the velocity auto-

correlation function (VAF) of a rubidium atom near the melting point [5], with its memory function (MF).

The normalized VAF, ϕ (t) is defined by

$$\phi (t) = <V(t)V(0)>/<V^2>, \tag{1.1}$$

and its memory function, M(t) is defined through the generalized Langevin equation for VAF as

$$d\phi (t)/dt + \int_0^t M(t-t') \phi (t')dt' = 0. \tag{1.2}$$

According to the Kubo formula of VAF, the integral of ϕ (t) from t = 0 to infinity is equal to MD/kT, where D is the self-diffusion constant and M the mass of rubidium atom. In Fig. 1, it should be emphasized that VAF has an oscillating tail after the negative minimum, and is quite different from the simple exponential decay with the time constant τ = MD/kT, i.e. the dashed line denoted as Langevin. The memory function MF, M(t) is not the δ -function but has a complicated t-dependence such as a recovery of memory in the intermediate renge of time as well as a long tail. These complicated features of VAF and MF reflect certain collective interactions between the probe atom and its surroundings.

Yoshida and Takeno [1] have made a general discussion on the MF in the generalized Langevin equation by the continued fraction expansion method, i.e. in the framework of Mori formalism, but seems difficult to elucidate physical images of such collective thermal motions of atoms.

The purpose of the present work is to investigate the characteristics of collective motions of atoms through MD simulation of several space-time correlation functions of the group velocities of local aggregation of atoms, and to elucidate the origin of the negative minimum and the oscillating tail of VAF in Fig.1.
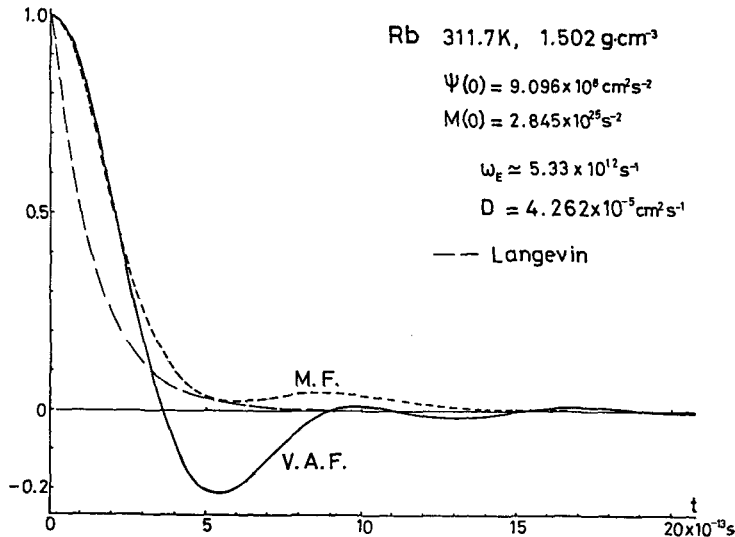

Fig. 1. VAF ϕ (t) of liquid rubidium near the melting point. ω_E is the Einstein frequency, $\sqrt{M(0)}$.

GROUP-VELOCITY CORRELATION FUNCTIONS

The velocity autocorrelation function in Fig. 1 shows the thermal relaxation of the momentum of a single atom, say No.1, with the following initial conditions,

$$t = 0, \quad V_1 = V(0), \quad \sum_j' V_j = - V(0). \qquad (2.1)$$

and the non-Markov characteristics of time dependence suggest that the initial momentum of the central atom is shared for t>0 by surrounding atoms in well correlated way. We can define several space-time correlation functions for the local velocity-field to investigate the collective relaxation mechanism as is shown in Fig. 1.

First we define the group velocity of atoms surrounding the central atom No.1 within the distance r as

$$U(r;t) = \sum V_j \Theta (r - |R_j(t) - R_1(t)|), \qquad (2.2)$$

where $\Theta (x)$ is the Heaviside step-function , and the number of atoms within the distance r including the central one is denoted as

$$N(r;t) = \sum \Theta (r - |R_j(t) - R_1(t)|). \qquad (2.3)$$

The velocity of the center of mass of the group of atoms and the total velocity of of atoms in the shell between distance r_1 and r_2 are thus given as follows;

$$V_G(r;t) = U(r;t)/N(r;t), \qquad (2.4)$$

$$U^e(r_1,r_2;t) = U(r_2;t) - U(r_1;t). \qquad (2.5)$$

With these definitions of the group velocity of local aggregation of atoms, we define the following three types of space-time correlation functions denoted simply as the total GVCF, the inclusive GVCF and the exclusive GVCF as follows;

total GVCF: $\qquad \Psi^{(t)}(r;t) = <V_G(r;0)V_G(r;t)>, \qquad (2.6)$

inclusive GVCF: $\Psi^{(i)}(r;t) = <V(0)U(r;t)> = <U(r;0)V(t)>, \qquad (2.7)$

and

exclusive GVCF: $\Psi^{(e)}(r_1,r_2;t) = <V(0)U^e(r_1,r_2;t)>$

$$= <U^e(r_1,r_2;0)V(t)>. \qquad (2.8)$$

The physical meaning of these correlation functions is clear and we expect to deepen our understanding about the collective aspects of thermal motion of atoms in classical liquid. In the next section we show the results of MD simulation of these correlation functions in liquid rubidium. In MD simulation the average over thermal equilibrium states denoted by < > in the above definitions is calculated by sampling of the initial time t = 0 from the steady MD records as well as by taking all atoms of the MD system as the central atom at that instant.

MOLECULAR DYNAMICS SIMULATION OF THE GROUP VELOCITY CORRELATION FUNCTIONS

The liquid state of rubidium (Rb)(T_m = 311K) at 311.7K and 1.502gcm^{-3} is simulated by the system of 864 neutral pseudo-atoms with the mass of rubidium atom and the effective pair potential using the microcanonical MD method.

Details of the simulation and the effective pair potential can be found in [4]. The MD calculation of the pair distribution function g(r) of liquid Rb at this temperature is shown in Fig. 2, and is found in good agreement with the experimental data.

Fig. 2. PDF g(r) of liq. Rb

The radii r, r_1 and r_2 in eqs.(2.6) to (2.8) are continuous variables by definition, but can be referred to the positions of maxima and minima of g(r) in Fig. 2, which are listed in Table I. For r < 4.0Å, U(r,t) reduces to V_1(t).
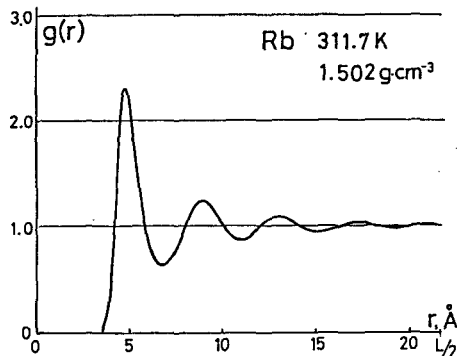
Table I. Positions of maxima and mimima of g(r) in Å.

	1st	2nd	3rd	4th
maximum	4.8	8.9	13.0	17.1
minimum	6.7	10.9	15.0	19.2

Total GVCF

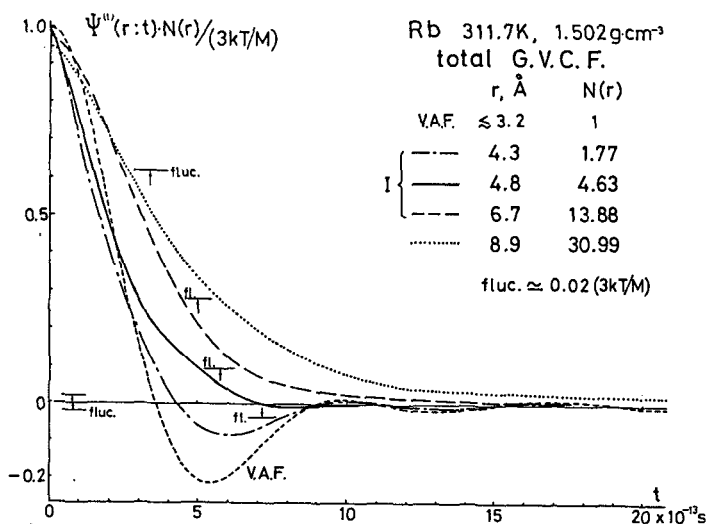In Fig. 3, MD simulation of the total GVCF, eq.(2.6) is shown for r = 4.3, 4.8, 6.7 and 8.9Å with VAF for comparison.

Fig. 3. Simulation of the total GVCF for the values of r inside the first minimum of g(r) in Fig. 2.

As r increases in Fig. 3, the structure of the total GVCF
becomes simpler without the negative minimum of VAF. We consider
that the memory of the initial velocity of the center of mass of
even a small local aggregation of atoms disappears quickly with-
out translational movement as a whole. In Fig. 3 and in the
following, N(r) denotes the average number of atoms inside the
sphere of radius r including the central one, i.e. <N(r,t)>.
     Relative statistical errors denoted as short horizontal bars
(fluc. or fl.) in Fig. 3 become significant in the calculation of
the total GVCF for r > 8.9 Å , which also suggests the smallness
of the magnitude of the velocity of translational movement as a
whole.

Inclusive GVCF

     The MD calculation of the inclusive GVCF eq.(2.7) is shown
in Fig. 4 for four values of r which correspond to positions of
the first maximum and the successive three minima of g(r).   The
inclusive GVCF shows how long the initial momentum of the cen-
tral atom to be shared and held by neighbouring atoms within r.
In Fig. 4, we can see how the initial momentum of the central
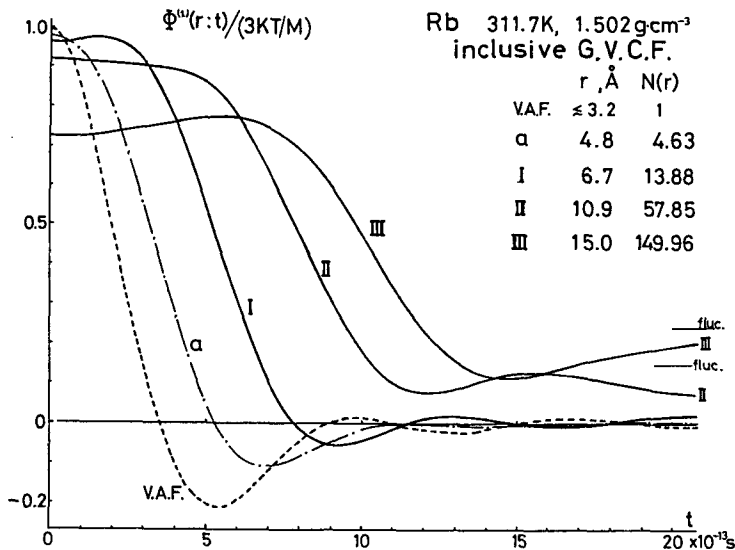atom is distributed among surrounding atoms in liquid state.

Fig. 4. Simulation og the inclusive GVCF. The four values of r
        correspond to the first maximum and the successive three
        minima of g(r) in Fig.1.

Exclusive GVCF

     Collective aspects in the distribution of the initial momen-
tum of an arbitrary central atom among neighbours for t > 0 shown
in Fig. 4 can be elucidated by analysis of the exclusive GVCF
eq.(2.8). In Fig. 5, we show the correlation between the central
atom and atoms in each of three "shells" corresponding to the
first, the second and the third peaks of g(r), and the average

number of atoms in each shell is denoted as $\Delta N(r) = N(r_2) - N(r_1)$.

As is seen clearly in Fig.5, the initial momentum of the central atom is distributed at first to the innermost shell and then to the outer ones in turn. It should be noted here that the negative minimum of VAF corresponds to "excitation" of the group velocity of the first shell atoms, and also that the oscillating tail of VAF is a result of the back-and-forth exchange of momentum between the central and the first shell atoms.
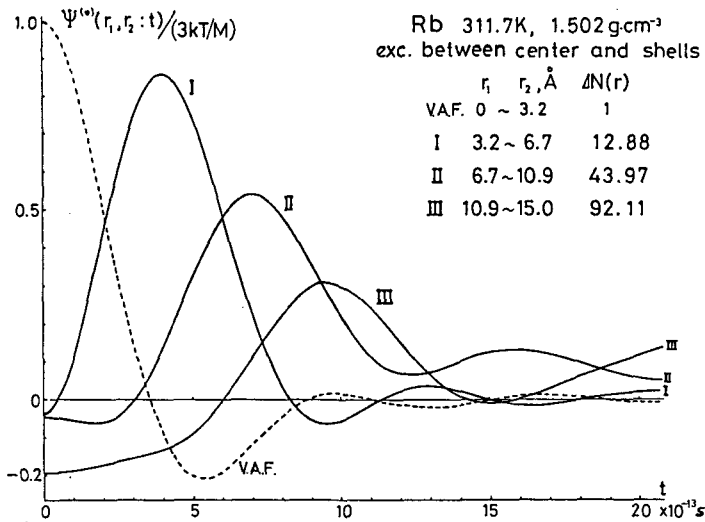

Fig. 5. Simulation of the exclusive GVCF. Three curves I , II , III correspond to correlations with the first, the second and the third shell atoms, respectively.
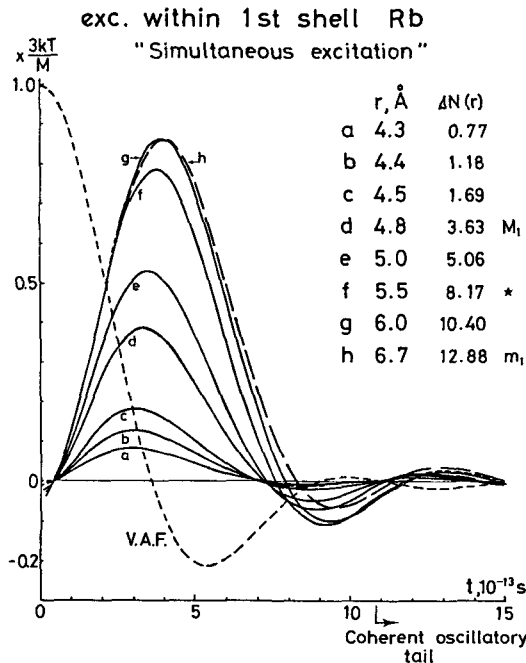

Fig. 6. Simulation of the exclusive GVCF inside the first shell.

Let us elucidate the "exitation" of the first shell atoms by the impact of the initial momentum of the central one, i.e. the curve denoted as I in Fig. 5. In Fig. 6, we show the exclusive GVCF inside the first shell taking the values of r_2 from 4.3 to 6.7 Å with fixing r_1 = 3.2 Å. It can be seen here that the transfer of the momentum from the central atom to the first shell atoms is very coherent inside the first shell, in other words, that the first shell atoms are well-correlated with each other in the momentum space. We can say that an arbitrary atom in liquid rubidium near the melting point is always in a "cage" of surrounding neighbours corresponding to the first peak of g(r). Such a cage model for the local structure of atoms in a classical liquid has been proposed first for understanding the structure in the X-ray diffraction pattern, i.e. the structure of g(r) as is shown in Fig. 1. The present MD simulation proves first time that the cage model is useful to understand the non-Markov relaxation mechanism in the thermal motion of atoms in a liquid state near the melting point.

The collective aspects in the coupling between the central and the first shell atoms can be seen clearly in the coherent oscillatory long tail of the exclusive GVCF of the first shell atoms as is shown in Fig. 7, which is the continuation of each curve a to h in Fig. 6 to t > 0.6ps. The coherence in the motion of atoms in the first shell can be seen clearly as if the vibration of the "cage". It should be noted here that the oscillations of the exclusive GVCF are in antiphase to those of VAF suggesting the back-and-forth exchange of momentum inside the "cage". The back-flow of the momentum to the central atom are seen also from the second shell neighbours as is shown in Fig. 5. The recovery of the memory function, a small hump of M(t) in Fig. 1, can be understood as the result of such correlated back-flow of momentum to the central atom.
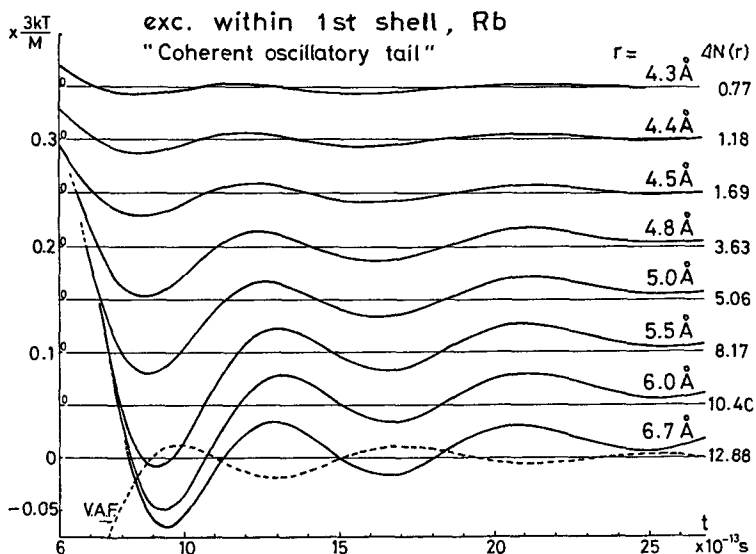

Fig. 7. Oscillatory tails of the exclusive GVCF inside the first shell. Each curve is continuation for t > 0.6ps of the corresponding one in Fig. 6 to show the coherent and antiphase oscillations between the central and the "cage" atoms.

CONCLUDING REMARKS

Relaxation mechanism in the thermal motion of atoms in a liquid metal is examined with the molecular dynamics simulation of three types of the space-time correlation function on the group velocity of local aggregation of atoms. Correlated motions of atoms are found in the spatial scale of about 20 to 30 Å over about 2ps, which reflect in the non-Markov decay of the velocity autocorrelation function of an atom. Such coherent motions can be considered corresponding to the quasi-phonon peaks at large wave-numbers found in the inelastic scattering spectra of thermal neutrons by liquid metals. We have analyzed the frequency spectra of these GVCF, and details will be reported elsewhere.

We have made similar MD simulations for liquid argon near its melting point, and found that the coherence in the thermal motion of argon atoms is much weaker than in liquid rubidium. The difference can be interpreted with the characteristics of effective pair potential between rubidium atoms compared to the ordinary Lennard-Jones potential of argon.

ACKNOWLEDGEMENTS

REFERENCES

[1] F. Yoshida and S. Takeno, PHYSICS REPORTS,**173** (1989) 301.
[2] SIMULATION OF LIQUIDS AND SOLIDS, edited by G. Ciccotti, D. Frenkel and I.R. McDonald (North-Holland, Amsterdam, 1987).
[3] A. Paskin and A. Rahman, Phys. Rev. Letters,**16** (1966) 300.
[4] M. Tanaka, J. Phys. F:Metal Phys.,**10** (1980) 2581.
[5] M. Tanaka, Prog. Theor. Phys. Supplment **69** (1980) 439.