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Velocity autocorrelation functions in model liquid metals

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Starting from interatomic potentials and static radial distribution functions, a self-consistent iteration scheme has been used to calculate velocity autocorrelation functions in liquid metals. The interatomic forces are treated directly. The calculation bypasses the details of the many-body dynamics and it is not necessary to introduce any additional parameters. Several simplifications may be used without introducing appreciable deviations. The results are in good agreement with computer experiments on liquid sodium at 383 °K, suggesting that the velocity autocorrelation function may be a simpler quantity than previously supposed.

I. INTRODUCTION

By combining the electron theories of metals and the distribution function theories of liquids, March, Paskin, and their co-workers[1-4] have obtained the static radial distribution functions $g(r)$ (also known as the pair correlation functions) and the interatomic potential $V(r)$ for liquid metals from x-ray and neutron diffraction data (r is the interatomic distance). In this paper, a procedure is developed for the calculations of velocity autocorrelation functions in liquid metals.

The time-correlation formalism, developed by Kubo, Zwanzig, Green, and others,[5-10] has been extensively used to describe atomic motions and transport properties. Because of the many-body interactions, explicit calculations of autocorrelation functions are difficult. It is often necessary to introduce additional parameters to describe the interactions between the atoms and the environment.[11-19] These parameters cannot easily be related to either $V(r)$ or $g(r)$.

We propose a self-consistent or iteration scheme such that a detailed knowledge about the many-body dynamics may not be necessary. The procedure has been applied to liquid sodium and our velocity autocorrelation functions may then be compared with the computer experimental results of Schiff,[20] and Paskin and Rahman[3,4] with satisfactory agreements. We will use $\Phi(t)=\langle\vec{v}(0)\cdot\vec{v}(t)\rangle$ for the velocity autocorrelation function and $\Psi(t)=\Phi(t)/\Phi(0)$ for the normalized (or reduced) velocity autocorrelation function with $\Psi(0)=1$, where v, t, and the angular brackets denote velocity, time, and a canonical ensemble average, respectively. Zwanzig, Gaskell, and others[7,8,17] have formulated the many-body problem into an integro-differential equation with memory function K:

$$\frac{d\Psi}{dt}+\int_0^t K(\tau)\Psi(t-\tau)\,d\tau=0. \qquad (1)$$

This equation may be regarded as a generalized Langevin equation,[21] the memory function being a generalized viscosity or frictional parameter.

We will focus our attention on one of the particles, defined as particle 0, and classify the particles in the fluid as follows: (a) particle 0; (b) its nearest neighbors numbered as i with $i=1,2,\ldots,n$, where n is the total number of nearest neighbors ($n\sim 12$); (c) all other particles forming a background. We will single out the interatomic forces $\vec{F}_{i0}$ exerted on particle 0 by its nearest neighbors and approximate all other interatomic forces by a memory function K. The motion of particle 0 may be described by Newton's equation

$$\frac{d\vec{v}_0}{dt}=\sum_i \vec{F}_{i0}=-\sum_i \vec{F}_{0i}\,. \qquad (2)$$

The units are chosen such that the mass m of the particle is unity ($m=1$). Since $V(r)$ is short ranged, and the forces from the outer-shell atoms tend to cancel each other, only the nearest-neighbor forces are expected to be important. We may also use a slightly modified form of (2):

$$\frac{d\vec{v}_0}{dt}=\sum_i \vec{f}_{i0}=-\sum_i \vec{f}_{0i}\,,\qquad \vec{f}_{i0}=\vec{F}_{i0}-(\vec{F}_{i0})_e\,, \qquad (3)$$

where $(\vec{F}_{i0})_e$ is the force $\vec{F}_{i0}$ at the equilibrium distance. Usually $(\vec{F}_{i0})_e$ is a weak repulsive force and $|(\vec{F}_{i0})_e|=|V'(a)|$, a being the nearest-neighbor distance derived from $g(r)$. We choose the initial velocity $\vec{v}_0(0)=\vec{u}$ at $t=0$. On solving (2) or (3), we may define the function ϕ and ψ for the zeroth particle:

$$\phi(u,t)=\vec{u}\cdot\vec{v}_0(t),\quad \psi(u,t)=\phi(u,t)/u^2. \qquad (4)$$

The functions ϕ and ψ may be regarded as the velocity correlation function and normalized velocity correlation function for particles with a specified initial velocity u. It is then necessary to average over the Boltzmann distribution to obtain $\Phi(t)$

and $\Psi(t)$:

$$\Phi(t)=\frac{\int_0^\infty \phi(u,t)e^{-u^2/U^2}u^2\,du}{\int_0^\infty e^{-u^2/U^2}u^2\,du}$$
$$=\frac{\int_0^\infty \psi(u,t)e^{-u^2/U^2}u^4\,du}{\int_0^\infty e^{-u^2/U^2}u^2\,du}\,, \tag{5}$$
$$\Psi(t)=\frac{\Phi(t)}{\Phi(0)}=\frac{\int_0^\infty \psi(u,t)P(u)\,du}{\int_0^\infty P(u)\,du}\,,$$

where $U=(2kT)^{1/2}$ is the most probable velocity of the Boltzmann velocity distribution, $P(u)=u^4e^{-u^2/U^2}$ represents a probability distribution, and k and T are the Boltzmann constant and temperature. The maximum value of $P(u)$ occurs at $u=\sqrt{2}\,U$. The median value is $1.47U$ for $P(u)$.

Similarly, for particle i, we have

$$\frac{d\vec{v}_i}{dt}=\sum_\alpha \vec{f}_{\alpha i}=\vec{f}_{0i}+\sum_{\alpha\neq 0}\vec{f}_{\alpha i}, \tag{6}$$

where the nearest neighbors of particle i are denoted by α, one of them being particle 0. We will now replace $\sum_{\alpha\neq 0}\vec{f}_{\alpha i}$ by the sum of a generalized friction term and a fluctuating force $\vec{A}(t)$; thus (6) may be written as follows:

$$\frac{d\vec{v}_i}{dt}=\vec{f}_{0i}-\int_0^t K(\tau)\vec{v}_i(t-\tau)\,d\tau+\vec{A}(t). \tag{7}$$

In (1) and (7), the memory functions involve n and $n-1$ nearest neighbors; since $n\sim 12$, the difference is expected to be negligible. We also have assumed that K is independent of initial velocities. For liquid sodium, we did find that $\psi(u,t)$ was only slightly dependent on u (see Fig. 4). The statistical properties of the fluctuating force $\vec{A}(t)$ have been reviewed by Chandrasekhar[21] and others.

II. SELF-CONSISTENT PROCEDURE

A self-consistent or iteration procedure may now be developed. For an arbitrary initial choice of $\Psi^{(0)}$, then $K^{(0)}$ may be evaluated from (1). With $\vec{v}_0=\vec{u}$ and other initial conditions, (2) and (7) may be solved simultaneously to give $\psi(u,t)$ (numerical time integration will be performed, proceeding from time t to $t+\Delta t$). On canonical averaging over various values of u, $\Psi^{(1)}(t)$ is obtained from (5). The iteration may then be repeated to obtain $\Psi^{(2)}$, $\Psi^{(3)},\ldots,$ until self-consistency is reached.

Our first iteration starts with an arbitrarily chosen $\Psi^{(0)}(t)$. It is well known[1-4] that the static radial distribution function $g(r)$ has a very sharp maximum at the nearest-neighbor distance a. The initial configuration would be very close to a spherical nearest-neighbor shell of radius a surrounding the zeroth particle. Approximating this configuration by either the face-centered cubic or hexagonal close-packed structure,[22] we have 12 nearest neighbors, $i=1$ at $\theta=0$, $i=2$ at $\theta=\pi$, $i=3,4$ at $\theta=\pi/2$, $i=5,\ldots,8$ at $\theta=\pi/3$, and $i=9,\ldots,12$ at $\theta=2\pi/3$, where θ is the colatitude angle in the spherical coordinate system. Because of the sharp maximum of $g(r)$, we will neglect the correlations between $g(r)$ and u.

For small deviations from the equilibrium configurations, the harmonic (small vibration) approximation may be used. Since many vibrational modes are excited at liquid temperatures and these vibrational modes have random phases, there is no velocity cross correlation between neighboring molecules:

$$\frac{\langle\vec{v}_0(0)\cdot\vec{v}_i(0)\rangle}{\langle\vec{v}_0(0)\cdot\vec{v}_0(0)\rangle}=0. \tag{8}$$

Hence we may use the initial condition $\langle\vec{v}_i(0)\rangle=0$.

We will now consider the case of u along the $+z$ direction (other cases will be discussed later). It is well known that the interatomic force $V'(r)$ is strongly repulsive ("hard core") for small distances and is relatively weak at large distances. We expect $\vec{F}_{10}$ to be the dominating term in (2); hence we may approximate $\vec{F}_{i0}$ for $i=2,\ldots,12$ without introducing appreciable errors. From (4), it is only necessary to consider the z component of the forces for the calculations of ψ and Ψ.

Let us now consider particle 2. The canonical average of (7) may be written as

$$\frac{d\langle\vec{v}_2\rangle}{dt}=\vec{f}_{02}-\int_0^t K(\tau)\langle\vec{v}_2(t-\tau)\rangle\,d\tau. \tag{9}$$

The solution of (9) will give us the average velocity $\langle\vec{v}_2\rangle$ and the average position $\langle z_2\rangle$. It is also necessary to consider the diffusion effects. For an arbitrary initial choice of $\Psi^{(0)}(t)$, the diffusion coefficient D is given by[6,9]

$$D=kT\int_0^\infty \Psi^{(0)}(t)\,dt. \tag{10}$$

Let $p_2(z_2,t)$ be the probability (not normalized) of finding particle 2 at position z_2 at time t. With a weak force $\vec{f}_{02}$, then we get free-particle diffusion about the average position z_2,

$$p_2(z_2,t)=e^{-(z_2-\langle z_2\rangle)^2/4Dt}. \tag{11}$$

From the probability $p_2(z_2,t)$, the force F_{02} is given by

$$F_{02}(t)=\frac{\int p_2(z_2,t)V'(z_0-z_2)\,dz_2}{\int p_2(z_2,t)\,dz_2}. \tag{12}$$

Along the directions perpendicular to the 02 interatomic vector, the diffusion effects should not influence $\vec{F}_{02}$ significantly, and hence they have been neglected. Similar equations may be written for $\vec{F}_{0i}$ for $i=3,\ldots,12$.

To obtain the position of particle 1, it is necessary to solve (7), with an initial value $\vec{v}_1(0)$ (and then average over the Boltzmann distribution later). However, it is difficult to solve (7) in general.[23] We will solve (7) by numerical integration from time t to $t+\Delta t$. Following the notations of Chandrasekhar,[21] the effect of the fluctuating force $\vec{A}(t)$ over the time interval $(t, t+\Delta t)$ is given by its integral $\vec{B}(\Delta t)$:

$$\vec{B}(\Delta t)=\int_t^{t+\Delta t}\vec{A}(\xi)\,d\xi. \tag{13}$$

The probability of occurrence of different values for $B(\Delta t)$ is then governed by the unnormalized distribution function w:

$$w=e^{-DB^2/4k^2T^2\Delta t}. \tag{14}$$

The integral $B(\Delta t)$ represents the velocity change over the time interval $(t, t+\Delta t)$ due to the fluctuating force. Although the initial position and velocity of particle 1 are fixed, they will spread out later because of the fluctuating forces.

The procedure may be summarized as follows: We start with an initial configuration of particle 0 surrounded by its nearest neighbors, $i=1$ at $\theta=0$, $i=2$ at $\theta=\pi$, etc., $r=a$. An arbitrary $\Psi^{(0)}(t)$ was chosen, and $K^{(0)}(t)$ and D may be calculated from (1) and (10). Using diffusion for $i=2,\ldots,12$ as given by (11), we solve (2) and (7) simultaneously with the initial velocities $\vec{v}_0(0)=\vec{u}$ along the z axis and $\vec{v}_i(0)$ for particles 0 and 1, respectively; after averaging over the Boltzmann distribution of v_1, the new velocity autocorrelation function $\Psi^{(1)}(t)$ is obtained from (4) and (5). The procedure is then repeated to obtain $\Psi^{(2)}(t)$, $\Psi^{(3)}(t)$, etc., until self-consistency is reached.

A convenient initial choice for $\Psi^{(0)}(t)$ is the Gaussian form

$$\Psi^{(0)}(t)=e^{-st^2/2}, \tag{15}$$

where s is an arbitrary constant. This choice satisfies the general conditions for $\Psi(t)$:

$$\Psi(0)=1,\quad \dot{\Psi}(0)=0,\quad \Psi(\infty)=0.$$

In this procedure, we have assumed that $\psi(\vec{u},t)$ is independent of the direction and magnitude of $\vec{u}$. Furthermore, our computational task would be greatly eased by several plausible simplifications: (a) The interatomic forces from particle 3 to 12 cancel each other and have very little effect on the velocity autocorrelation function of particle 0, since these particles are far away from the z axis. (b) The fluctuating force $\vec{A}(t)$ for particle 1 averages out and does not change the velocity autocorrelation function of particle 0; thus (7) may be replaced by

$$\frac{d\vec{v}_1}{dt}=\vec{f}_{01}-\int_0^t K(\tau)\vec{v}_1(t-\tau)\,d\tau. \tag{16}$$

(c) The effects of the Boltzmann distribution of $\vec{v}_1(0)$ also average out to zero as far as the velocity autocorrelation function of particle 0 is concerned. That is, as an initial condition, we may use

$$v_1(0)=0 \quad\text{at}\quad t=0. \tag{17}$$

However, it is difficult to prove our assumptions and our simplifications. Hence the procedure will be applied to liquid metals and the effects of our assumptions and simplifications may be assessed directly. Our results may also be compared with computer experiments.

II. RESULTS

The procedure will now be applied to liquid sodium at 383°K. We use $\sigma=3.24$ Å as the unit of length, the mass of the sodium atom $m=3.82\times10^{-23}$ g as the unit of mass, and 10^{-13} sec as the unit of time. Then we have $kT=0.0132$, $U=0.162$, and $\sqrt{2}U=0.23$. In these units, the interatomic potential $V(r)$ for $0<r<1.5$ is

$$V(r)=0.0204[(Ar^{-3}+Br^{-5})\cos 2kr + (Cr^{-4}+Dr^{-6})\sin 2kr+E\,e^{F-Gr/r_0}], \tag{18}$$

where $A=-0.42$, $B=-0.56$, $C=-2.96$, $D=1.46$, $E=15.11$, $F=5.07$, $G=10.79$, $r_0=1.15$, $2k=5.987$. This potential is identical to $V_3(r)$ of Schiff[20] and is also very similar to the LRO-1 potential of Paskin and Rahman,[3,4] which was chosen to fit the x-ray diffraction data. Both the interatomic potential $V(r)$ and the interatomic force $V'(r)$ are shown in Fig. 1. In accordance with March, Paskin, Rahman, Schiff, and others,[1-4,20] we have omitted the three-body forces, since very little is known about the electron correlation effects. The nearest-neighbor distance[1-4] is $a=1.145$.

Preliminary iterations are shown in Fig. 2, $\Psi^{(0)}$, $\Psi^{(1)}$, and $\Psi^{(2)}$ being the dashed lines, solid lines, and circles, respectively. Two different Gaussian functions given by (15) and with $s=1.9$ and 0.04 are used for $\Psi^{(0)}$. Although the initial choices of $\Psi^{(0)}$ are vastly different for the two values of s, the first iteration results are quite similar, and further iterations do not change Ψ appreciably. It may be concluded that the convergence is satisfactory for our iteration procedure.

The effects of our simplifications are examined in Fig. 3. We have calculated $\psi(0.24,t)$ [at the median velocity of $P(u)$] for $\vec{u}$ along the z axis with all three simplifications, and the results are shown as the solid lines. In Fig. 3(a) the effects of particles 3 to 12 are included, with the results given as open triangles. In Fig. 3(b) the effects of the fluctuating forces $\vec{A}(t)$ are included, with the results given as closed triangles. In both cases,

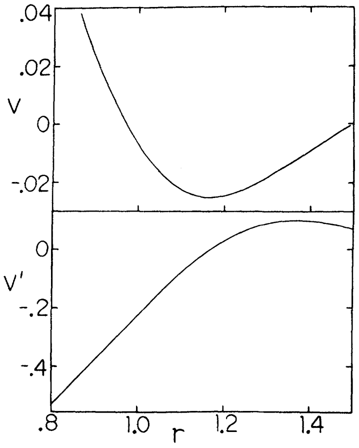

FIG. 1. Interatomic potential $V(r)$ (in units of 4.01×10^{-12} ergs $= 2.50$ eV) and interatomic force $V'(r)$ (in units of 1.24×10^{-4} dyn) vs distance r (in units of 3.24×10^{-8} cm) between sodium atoms. The force is repulsive for $V' < 0$ and attractive for $V' > 0$.

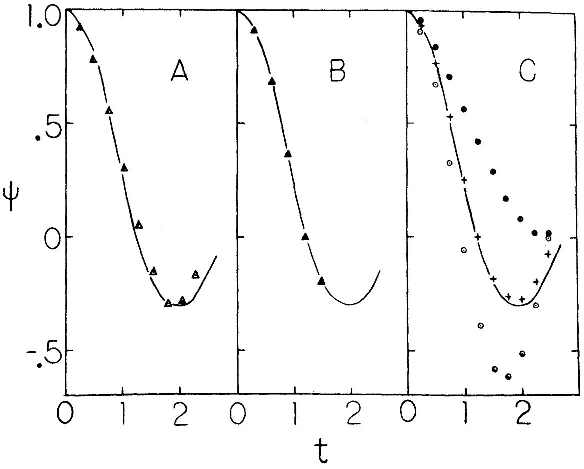

FIG. 3. Effects of the simplifications on $\Psi(0.24, t)$ with $\vec{u}$ along the z axis. Solid lines, all three simplifications; open triangles, effects of particles 3 to 12 included; closed triangles, effects of $\vec{A}(t)$ of particle 1 included; open and closed circles, $v_1 = 0.12$ along $-z$ and $+z$ directions, respectively; crosses, $\psi(t)$ on averaging over the Boltzmann distribution of v_1. The time t is shown in units of 10^{-13} sec.

the effects are slight. In Fig. 3(c) we have included the velocities v_1 parallel to the interatomic z axis. (The effects of the perpendicular components are expected to be small.) The results for $v_1 = \pm 0.12$ are shown. On averaging over the Boltzmann distribution $e^{-v_1^2/U^2}$ of the z component of the velocity with $U = 0.16$, the results shown as crosses are not very different from our $v_1 = 0$ results, shown as the solid line.

In Fig. 4 we have examined our assumption that $\psi(\vec{u}, t)$ is independent of the magnitude and direction of $\vec{u}$. In Fig. 4(a) we have given $\psi(u, t)$ for several values of u, their directions being along the z axis. These results are only slightly different from each other. The canonically averaged $\Psi(t)$ is closely approximated by $\psi(0.24, t)$, where $u = 0.24$ is the median value of the distribution function $P(u)$. In Fig. 4(b) we have given $\psi(0.24, t)$ for two different directions of u, along the z axis ("head-on" collision) and at $\pi/6$ or 30° away from z axis ("triangular" collision). In the latter case we have considered four nearest neighbors at distance a and along the directions $(0, 0)$, $(\pi/3, 0)$, $(\pi, 0)$, and $(2\pi/3, \pi)$ and the initial velocity vector

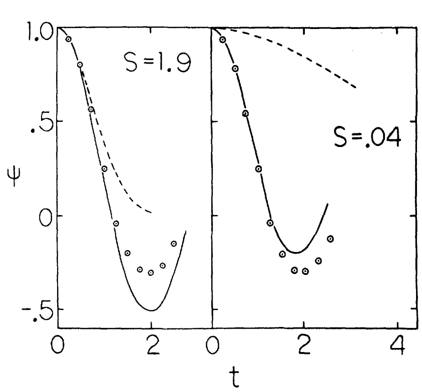

FIG. 2. Preliminary iteration results with $\Psi^{(0)}$, $\Psi^{(1)}$, and $\Psi^{(2)}$ shown as dashed lines, solid lines, and circles. Gaussian function $e^{-st^2/2}$ is used for $\Psi^{(0)}$. The time t is shown in units of 10^{-13} sec.

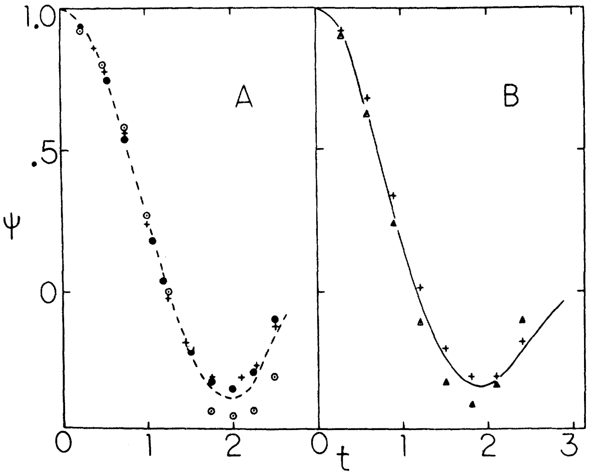

FIG. 4. $\psi(u, t)$ vs t. (a) For u along the z axis; the open circles, crosses, and closed circles are for $u = 0.16$, 0.24, and 0.32, respectively. The dashed line is the canonical averaged Ψ from (5). (b) Solid line, Schiff's computer experiment; crosses and triangles, $\psi(0.24, t)$ for $\vec{u}$ along the z axis and at $\pi/6$ off the z axis. The time t is shown in units of 10^{-13} sec.

$\vec{u}$ along the direction ($\pi/6,0$), in the spherical coordinate system. Again these two results are not very different.

In Fig. 4(b) the solid curve is the velocity autocorrelation function of Schiff[20] by computer experiments from the potential (18). (Very similar computer results have been given by Paskin and Rahman[3,4] for a slightly different potential.) The average of our two sets of $\psi(0.24, t)$, with $\vec{u}$ along the z axis and $\pi/6$ away from the z axis (head-on and triangular collisions), is very close to Schiff's computer results.

It is somewhat surprising that good agreement with computer experiments has been obtained [see Fig. 4(b)] despite the numerous approximations and simplifications. The liquid structure is apparently solidlike for short times of the order of 10^{-13} sec. Also, the velocity autocorrelation function $\Psi(t)$ is primarily (but not completely) determined by one "hard" collision between one particle pair (01 in our notation). Only approximate considerations of the other particles are necessary since their effects are weak. Whereas $\Psi(t)$ is derived from the motions of particle 0, we have approximated the motions of particles $1, 2, \ldots$; hopefully, these approximations would influence $\Psi(t)$ only indirectly. Apparently, many fluctuation terms cancel or average to zero. Often, these self-cancellations are of great importance, and have been used, for example, by Cohen and Heine,[24] to justify the applications of energy-band theories to solids. We also note that $\Psi^{(j)}(t)$ is not very sensitive toward the choice of $K^{(j-1)}(t)$ of the neighboring particles from the previous iteration; hence the iterations converge quickly. It is therefore possible to bypass the details of the many-body dynamics.

Our calculations suggest that the velocity autocorrelation function may be a simpler quantity than was previously supposed. Similar conclusions have also been obtained by us[25] for liquid argon with the Lennard-Jones potential, our correlation function being in good agreement with Rahman's computer experiments.[26] It would be interesting to know why the calculations may be made so simply or why the fluctuation terms nearly average to zero. However, these may be very difficult questions.

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