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Velocity autocorrelation function for simple liquids and its application to liquid metals and alloys

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The single-particle Brownian motion in simple monatomic liquids has been described with the help of the equation of motion in terms of velocity autocorrelation function $\psi(t)$, where the particle is assumed to diffuse in a mean-time-dependent field. The equation of motion which is a second order differential equation in $\psi(t)$ has been solved in terms of nth order Bessel functions of the first and second kind. The solution is, in fact, the generalization of the solution given by Glass and Rice (GR) [Phys. Rev. **176**, 239 (1968)] for low density fluids. The generalized solution is an improvisation over the one by GR and the results demonstrate that, for high density liquids such as liquid metals where the GR solution fails to give a reasonable account of $\psi(t)$, the generalized solution could be very useful to calculate $\psi(t)$. The present approach has been applied to the liquid alkali metals and binary alloys. The results are found to be in close agreement with the molecular dynamics results.

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I. INTRODUCTION

The time-correlation functions are very useful in the theoretical and experimental study of dynamical and transport properties of liquids. For example, the self-diffusion processes in Lennard-Jones fluid [1], liquid lead [2], and liquid alkali metals [3,4], and the atomic dynamics in liquid metals [5–7] have been described in terms of the time-dependent correlation functions. The velocity autocorrelation function (VACF) is the simplest time-correlation function for the description of the dynamical correlation in the molecular motion in liquids. The exact determination of VACF is a complex dynamical problem involving the motion of many particles. In order to avoid this difficulty, many attempts have been made to approximate the time decay of VACF with the help of simple functional forms [1,8–10]. Alternatively, the memory function approach [11] has widely been adopted to approximate VACF where the so-called memory function is the kernel [say $K(t)$] of an integrodifferential equation describing the time development of the autocorrelation function [12,13]. Apart from this, various theories and models have been developed to give the description of VACF in simple liquids [1,14,15].

One way of theoretical derivation of VACF is the solution of the classical Langevin equation for the Brownian motion of small particles in a liquid. In a liquid, any given molecule is in continuous interaction with all its nearest neighbors. A molecule may be imagined to have an encounter with the nearest neighbor molecule during which strong repulsive forces act and then the molecule moves randomly in the rapidly fluctuating force field generated by the neighboring molecules. Therefore the motion of a molecule in a liquid is analogous to the motion of a massive Brownian particle. In such a description of the liquid, a friction constant (β) is related to the autocorrelation function of the force exerted by the surrounding on the molecule. As noted by Glass and Rice, Uhlenbeck and Ornstein [16] have described the Brownian motion of a harmonically bound particle and this simple model was further used by Rahman, Singwi, and Sjolander [14] to describe the atomic motion in liquids. However, in their work, care was not taken to make the VACF obey the boundary conditions at zero time.

The simple model used by Uhlenbeck and Ornstein [16] assumes that its first-order memory function (or retarded friction coefficient) has an exponential decay with single relaxation time, i.e., $K(t)=k\exp(-\beta t)$. Though this model accounts for the short-time features of the VACF, it tends to overestimate the deepness of the backscattering region (resulting due to the "cage" effect) as well as the subsequent oscillations at longer times, which subsequently leads to unreliable predictions for the diffusion coefficient and other transport properties as well. In practice, the static harmonic well (SHW) condition does not exist because of the fluctuations in the surrounding medium and the harmonic well is subject to quasirandom alterations as a function of time. In such a case, assuming the Brownian particle diffusing in a mean-time-dependent field, Glass and Rice [9] (referred to as GR now onwards) have modified the classical Langevin equation by adding another systematic force term representing the time-dependent force field. Subsequently, GR have derived an equation of motion in terms of VACF as

$$\frac{d^2\psi}{dt^2}+(\alpha+\beta)\frac{d\psi}{dt}+(\omega^2e^{-\alpha t}+\alpha\beta)\psi=0, \tag{1}$$

where α is the molecular relaxation time. It corresponds to the time (τ_0) for which an atom remains within the same local environment before diffusing away [17]. In other words, it is the time for the relaxation of the cage formed by surrounding neighbor atoms. Therefore molecular relaxation time α is taken to be equal to τ_0^{-1}.

The solution of Eq. (1) is the key subject of the present paper. The exact solution of this equation can be obtained if we know α and β *a priori*. Due to the difficulty in *a priori* calculation of α, a simplified solution of Eq. (1) is provided by GR assuming the molecular relaxation time to be equal to the friction constant, i.e., $\alpha=\beta$. While this assumption holds good for insulating fluid like Ar at 85 K, it is not true for high density liquids like liquid metals, e.g., for liquid Li, β is found to be three times as large as α. The principal difference between the insulating fluid (argon) and liquid metals is the presence of free electrons in liquid metals which is also responsible for the essential difference in their physical properties. Consequently, the GR formulation for the VACF has been found to be inadequate for the liquid metals. It is then imperative to look for a solution of Eq. (1) subject to the condition $\alpha\neq\beta$. Although it is difficult to calculate α and β exactly, one can estimate values from the work of Berne *et al.* [12]. Further, GR have employed a small-step diffusion assumption where the diffusion in a dense fluid is thought to proceed by a series of displacements each being small compared to the interatomic spacing. Here, we give a generalized solution of the second-order differential equation [Eq. (1)] when $\alpha\neq\beta$ and also doing away with the small-step diffusion assumption. We call it a generalized solution in the sense that the original GR formulation for $\alpha=\beta$ turns out to be a special case of our solution. The generalized solution is applied to the liquid alkali metals like Li, Na, and their binary alloys, viz., Li-Na, Li-Mg, and the results are compared with the molecular dynamics results. It has been found to give an excellent and physically more meaningful account of the VACF in these systems.

II. MATHEMATICAL FORMULATION

We adopt the basic mathematical formulation given by GR as such, along with all underlying assumptions except two, for the description of the VACF in the present work. Our prime interest lies in the extension of the GR formulation for high density liquids, e.g., liquid metals. The normalized VACF is defined as

$$\psi(t)=\frac{\langle \boldsymbol{v}(0)\cdot\boldsymbol{v}(t)\rangle}{\langle v^2\rangle}, \tag{2}$$

where $\boldsymbol{v}(0)$ and $\boldsymbol{v}(t)$ are the velocities of a specified particle at time $t=0$ an $t=t$, respectively. $\langle\cdots\rangle$ represents a time average over the history of the particle, i.e., all the values of t. The VACF is subjected to the following boundary conditions:

$$\lim_{t\to 0}\psi(t)=1, \tag{3a}$$

$$\lim_{t\to 0}\frac{d\psi}{dt}=0, \tag{3b}$$

$$\lim_{t\to 0}\frac{d^2\psi}{dt^2}=-\omega_0^2=-\frac{\langle\nabla^2 V\rangle}{3m}, \tag{3c}$$

$$D=\frac{k_BT}{m}\int_0^\infty dt\ \psi(t). \tag{3d}$$

$\langle\nabla^2 V\rangle$ appearing in Eq. (3c) is the thermal average of the potential energy given by

$$\langle\nabla^2 V\rangle=4\pi\rho\int_0^\infty drr^2g(r)\left(\frac{\partial^2 V}{\partial r^2}+\frac{2}{r}\frac{\partial V}{\partial r}\right), \tag{4}$$

where $g(r)$ is the pair distribution function and ρ is the atomic number density. $(\partial V/\partial r)$ and $(\partial^2 V/\partial r^2)$ are the first and second order derivatives of the effective interatomic pair potential $V(r)$. The effective interatomic pair potentials in liquid metals can be derived using the pseudopotentials in second order perturbation theory. A brief description of the method used for the calculation of the interatomic pair potentials in the present work is given in the Appendix. Now, substituting

$$u=\left(\frac{2\omega}{\alpha}\right)e^{-(1/2)\alpha t} \tag{5}$$

in Eq. (1) the solution is found to be

$$\psi(t)=e^{-(1/2)(\alpha+\beta)t}\nu(u), \tag{6}$$

where $\nu(u)$ is a solution of Bessel's equation,

$$u^2\nu''+u\nu'+\nu[u^2-(\alpha-\beta)^2/\alpha^2]=0. \tag{7}$$

From the simple model of the particle dynamics considered by GR, *a priori* calculation of α is not possible. Therefore to simplify the solution, GR have assumed $\alpha=\beta$. The subsequent solution obtained is

$$\psi(t)=e^{-\beta t}[c_1J_0(u)+c_2Y_0(u)], \tag{8}$$

where J_0 and Y_0 are zero-order Bessel function of the first and second kinds, respectively. c_1 and c_2 are the constants of integration;

$$u=2\gamma e^{-(1/2)\beta t}, \tag{9}$$

where $\gamma=\omega/\beta$.

From the physical point of view, the insulating fluid Ar and the liquid metals are essentially different. The presence of conduction electrons distinguishes the liquid metals from the liquefied inert gases. The pair potential for a liquefied inert gas is well described by the Lennard-Jones potential which is composed of a harsh, short-range repulsion and a smoothly varying long-range attraction. On the other hand, the effective ion-ion interaction for liquid alkali metals shows a much softer repulsive core than that of rare gases and a deep attractive well followed by a long-range oscillatory tail, caused by the presence of conduction electrons. The softness or hardness of the repulsive core has been demonstrated to be strongly related to the oscillatory or nonoscillatory long-time tail of the VACF [18,19]. The VACF for liquid alkali metals exhibits a pronounced oscillatory behavior [18], in marked contrast to that of liquid argon [20,21]. The persistent oscillations in VACF of liquid alkali metals are due to the existence of the longitudinal modes of propagating collective excitations (well-defined oscillatory modes for the density fluctuations or acoustic-like modes) whereas such short wavelength longitudinal modes are completely overdamped in liquid argon, resulting into a smoothly varying nonoscillatory tail of VACF [22]. This is also corroborated by the findings that the interatomic collisions through hard cores do not favor the coherence of the atomic motions that is required for the propagation of the longitudinal modes associated with density fluctuations [23].

The above discussion implies that it is the soft core that makes the damping of very short wavelength longitudinal waves quite weak in liquid metals, and it is the hard Lennard-Jones-type core that makes the same damping very strong in liquid argon. Weak damping of the longitudinal waves in liquid metals indicates a large residence time for an atom in its nearest neighbor cage. In other words, an atom remains within the same local environment for a longer time before diffusing away. Therefore, "the time before diffusion" (denoted by τ_0) will be much longer for the liquid alkali metals. Further, in dense fluids, energy is mainly transferred by particle collision, in contrast to the low density situation where the motion of the particles themselves transfers the energy [17]. Consequently, at liquid alkali metal densities, the molecular relaxation time (α), which is equal to τ_0^{-1}, will be smaller than the friction coefficient (β) defined by kT/MD, i.e., $\beta > \alpha$. It is an indication that the motion of the atoms in monatomic liquid metals is very different from a simple diffusion.

In light of this, we propose the solution of Eq. (1) when $\alpha \neq \beta$, with a particular reference to the liquid alkali metals. The agreement of our results with the molecular dynamics simulation proves our preposition to be well founded. It necessitates *a priori* knowledge of α and β. The approximate representation of memory function by Berne *et al.* [12] makes it possible to evaluate α in terms of $\langle \nabla^2 V \rangle$ [Eq. (4)], mass M, and friction coefficient β using the following equation:

$$\alpha\beta = \frac{\langle \nabla^2 V \rangle}{3M}. \tag{10}$$

β can be evaluated using the Einstein expression for the diffusion coefficient D,

$$D = \frac{k_B T}{M\beta}. \tag{11}$$

The values of α and β are important in the solution of the Bessel equation [Eq. (7)]. In the case of $\alpha = \beta$, Eq. (7) becomes a zeroth order Bessel equation. Though the numerical evaluation of α and β is approximate in nature, the brighter prospects of description of the VACF in liquid metals have led us to generalize the solution of Eq. (7) for any arbitrary order n, defined as

$$n = \frac{\beta}{\alpha} - 1. \tag{12}$$

The adequacy of this generalization can be tested *a posteriori*. Substituting Eq. (12) in Eqs. (5)–(7), we obtain

$$u = 2(n+1)\gamma e^{-\beta t/2(n+1)}, \tag{13}$$

$$\psi(t) = e^{-[\beta(n+2)/2(n+1)]t}\nu(u), \tag{14}$$

$$u^2\nu'' + u\nu' + \nu[u^2 - n^2] = 0. \tag{15}$$

Equation (15) is a nth order Bessel's equation. The general solution for the VACF can now be written as

$$\psi(t) = e^{-[\beta(n+2)/2(n+1)]t}[c_1 J_n(u) + c_2 Y_n(u)], \tag{16}$$

where $J_n(u)$ and $Y_n(u)$ are the integral order (n) Bessel function of the first and second kind, respectively.

Differentiating Eq. (16) and applying the boundary conditions (3a) and (3b), we obtain the expressions for c_1 [24] and c_2,

$$c_1 = -\frac{Y_n[2(n+1)\gamma] - \gamma Y_{n+1}[2(n+1)\gamma]}{J_n[2(n+1)\gamma]Y_{n+1}[2(n+1)\gamma] - J_{n+1}[2(n+1)\gamma]Y_n[2(n+1)\gamma]}, \tag{17}$$

$$c_2 = \frac{J_n[2(n+1)\gamma] - \gamma J_{n+1}[2(n+1)\gamma]}{J_n[2(n+1)\gamma]Y_{n+1}[2(n+1)\gamma] - J_{n+1}[2(n+1)\gamma]Y_n[2(n+1)\gamma]}. \tag{18}$$

The following general order recursion relations for the Bessel functions are used for simplification [25,26]:

$$J_n'(u) = nJ_n(u) - uJ_{n+1}(u), \tag{19}$$

$$J_n''(u) = \frac{J_{n+1}(u)}{u} - J_n(u) + \frac{u(u-1)J_n(u)}{u^2}. \tag{20}$$

Taking the second order derivative of Eq. (16) at $t=0$, and substituting the values of c_1 and c_2, we obtain

$$\omega^2\left[1 + \frac{1}{(n+1)\gamma^2}\right] = \frac{\langle \nabla^2 V \rangle}{3M}. \tag{21}$$

On applying the condition in Eq. (3d) we need the following integration formulas [25]:

$$\int_0^1 dx\, x^n J_{n-1}(ax) = J_n(a)/a, \tag{22}$$

$$\int_0^1 dx\, x^n Y_{n-1}(ax) = \frac{Y_n(a)}{a} + \frac{2^n\Gamma(n)}{a^{n+1}\pi}. \tag{23}$$

Substituting Eq. (16) in Eq. (3d) and utilizing the integral forms in Eqs. (22) and (23), we get

$$\frac{\beta}{\omega^2}\left[1 + \frac{c_2\Gamma(n+1)}{(n+1)^{n+1}\gamma^n\pi}\right] = \frac{mD}{k_BT}. \tag{24}$$

In the SHW model where only the friction coefficient term β is considered, Eq. (1) reduces to

$$\frac{d^2\psi}{dt^2} + \beta_0\frac{d\psi}{dt} + \omega_0^2 e^{-\alpha t}\psi = 0. \tag{25}$$

The terms β and ω are replaced by β_0 and ω_0, respectively. The solution of Eq. (25) subject to the boundary conditions in Eq. (3) turns out to be

$$\psi(t) = e^{-(1/2)^{\beta_0 t}}[\cos\xi t + (\beta_0/2\xi)\sin\xi t], \tag{26}$$

where

$$\xi^2 = \omega_0^2 - \frac{\beta_0^2}{4}, \tag{27}$$

$$\omega_0^2 = \frac{\langle\nabla^2 V\rangle}{3m}, \tag{28}$$

$$\beta_0 = \frac{mD}{k_BT}\omega_0^2. \tag{29}$$

Using the definitions of ω_0 and β_0 given by Eqs. (27) and (28), respectively, in Eq. (22) we obtain

$$\omega = \sqrt{n+1}\,\omega_0\gamma[1 + (n+1)\gamma]^{-1/2}, \tag{30}$$

$$\beta = \sqrt{n+1}\,\omega_0[1 + (n+1)\gamma]^{-1/2}, \tag{31}$$

where γ is determined by solving the following equation which is obtained by substituting Eqs. (30) and (31) in Eq. (25):

$$\left(1 + \frac{c_2\Gamma(n+1)}{(n+1)^{n+1}\gamma^n\pi}\right) = \sqrt{n+1}\,\frac{\beta_0}{\omega_0}\gamma^2[1 + (n+1)\gamma^2]^{-1/2}. \tag{32}$$

Equations (12)–(18), (21), (24), and (30)–(32) give the generalized set of equations in the GR formulation for the VACF. It should be noted that for $n=0$, the whole set of equations reduces to the GR results. GR solves Eq. (32) in small-step diffusion approximation where $\omega_0=\beta_0=mD/k_BT$. The diffusion coefficient is an important parameter and should be known from experiments. However, we continue to use the value evaluated using Eqs. (28) and (29). Thus our generalized formulation differs from the one proposed by GR in two ways: (i) it assumes that the two parameters α and β are not equal. Hence it is expected to give more realistic results for the high density liquids like liquid metals, and (ii) it does not take into account the small-step diffusion approximation.

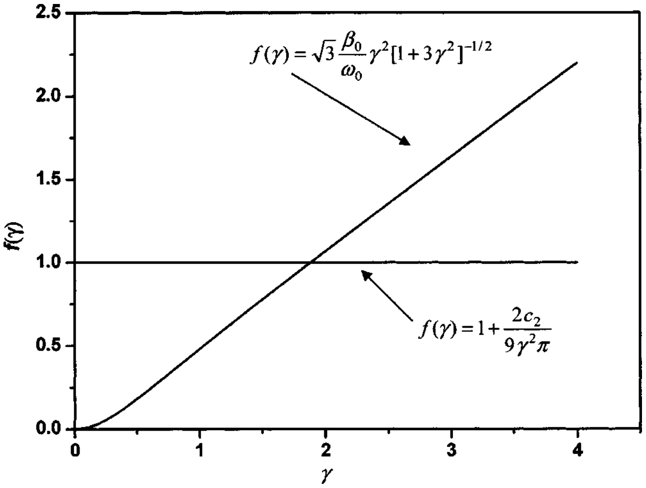

FIG. 1. Two sides of Eq. (32) plotted as a function of γ for the case of $\beta_0 \neq \omega_0$.

The generalized solution has been tested for obtaining VACF's in liquid Li, Na, and $Li_{0.61}Na_{0.39}$, $Li_{0.70}Mg_{0.30}$ alloys.

III. RESULTS

A. Velocity autocorrelation function for liquid Li at 470 K

The experimental value of the diffusion coefficient D of liquid Li at 470 K is 6.3×10^{-5} cm^2 sec^{-1} [27]. Then, Eq. (12) gives β to be equal to 8.94×10^{13} sec^{-1}. The effective pair potential and its first and second order derivatives liquid lithium are calculated following the method described in the Appendix . The thermal average of the potential energy, $\langle\nabla^2 V\rangle$ can be evaluated in terms of the first and second order derivatives of the pair potential and the pair distribution function [28] [Eq. (4)]. It turns out to be 8.49×10^5 erg cm^{-2} for liquid Li at 470 K. α has been calculated using Eq. (11) and is equal to 2.74×10^{13} sec^{-1}. The order of Bessel's equation (8) is found to be 2, i.e., $n=2$. The value of n is, in fact, rounded off to get an integral order.

To determine γ, the two sides of Eq. (32) have been plotted as a function of γ (Fig. 1). Noting that there is one root, we find $\gamma=1.8858$, $c_1=2.4896$, $c_2=3.6097$. Similarly, the necessary parameters to calculate the velocity autocorrelation function for other systems under investigation are obtained and are summarized in Table I.

The velocity autocorrelation for liquid Li at 470 K is shown in Fig. 2. As we have already mentioned in the earlier discussion, the SHW model overestimates the characteristic features of the VACF in liquids, i.e., the "backscattering" region and the long time oscillations. The GR formulation, on the contrary, underestimates the depth of the backscattering region and the long time oscillations are almost absent. Compared to these results, the present approach gives a good description of the VACF in closer agreement with the molecular dynamics results [29].

B. Velocity autocorrelation function for liquid Na at 378 K

Figure 3 shows the VACF for liquid sodium at 378 K. the parameters used to calculate VACF are given in Table I. The

TABLE I. Parameters used to calculate velocity autocorrelation function.

			$Li_{0.61}Na_{0.39}$		$Li_{0.70}Mg_{0.30}$	
	Li	Na	Li-Li	Na-Na	Li-Li	Mg-Mg
T(K)	470	378	590	590	875	875
$M(10^{-23}$ g)	1.152	3.8163	1.152	3.8163	1.152	4.0346
$\rho(10^{24}$ cm$^{-3})$	0.0444	0.0242	0.043	0.0229	0.042	0.0383
D (10^{-5} cm^2 sec^{-1})	6.3	4.2	8.0	8.2	9.4	9.1
$\langle\nabla^2 V\rangle$ (10^5 erg cm^{-2})	0.8486	0.3521	0.8985	0.3871	1.429	0.8378
$\alpha(10^{13}$ sec$^{-1})$	2.75	0.946	2.94	1.3	3.71	1.86
$\beta(10^{13}$ sec$^{-1})$	8.94	3.25	8.83	2.6	11.14	3.72
$\beta_0(10^{14}$ sec$^{-1})$	0.2748	0.0945	0.2943	0.13	0.3714	0.2116
$\omega_0(10^{14}$ sec$^{-1})$	0.4945	0.1754	0.5099	0.1839	0.6431	0.2631
γ	1.8858	1.937	1.818	1.508	1.8169	1.4251
c_1	2.4890	1.2815	3.6680	−3.2518	3.6822	−3.2172
c_2	3.6097	4.2458	2.2775	−0.6612	2.2524	0.4805

VACF corresponding to Bessel's equation of order $n=2$ is a better approximation to the molecular dynamics (MD) results [30]. It can be seen that the MD result shows a smaller backscattering region and oscillations at smaller times. The difference should be due to the difference in the value of the diffusion coefficient which is available experimentally for 373 K. It has been already noted that the diffusion coefficient in an important parameter in the formulation used for the calculation of VACF. So, an accurate experimental value of D at 378 K is expected to give better results.

C. Velocity autocorrelation functions in $Li_{0.61}Na_{0.39}$ at 590 K

The study of this alloy is of interest because of its strong phase separation tendency. The VACF for Li-Li in $Li_{0.61}Na_{0.39}$ has been obtained using the solution of second order $(n=2)$ Bessel's equation [Eq. (8)]. It approximates the MD results of Canales *et al.* [31] very closely as shown in Fig. 4. The value of the self-diffusion coefficient D for Li-Li in the given alloy is reported to be 11.8×10^{-5} cm^{-2} sec^{-1} and no equivalent experimental data are available. The small-step diffusion theory [32] and the linear trajectory theory [33] lead to unreasonable values for the diffusion coefficient. So, in the case of nonavailability of an experimental value of D at a given temperature, we had to resort to a sort of fitting procedure to obtain the reliable value of D. By deciding the order $n=2$ in advance, we can determine the ratio (β/α) using Eq. (13) and subsequently we can make use of Eqs. (11) and (12) to determine D. This procedure has been adopted to calculate D in binary alloys at a given temperature. It raises some doubts about uncertainty in the determination of n. However, if we look at the results presented

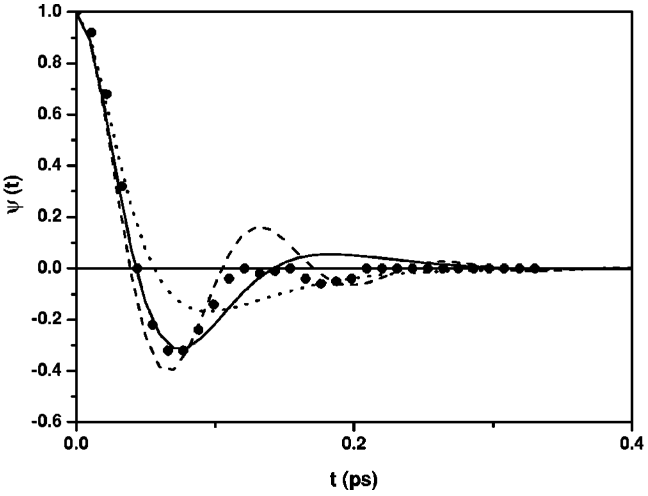

FIG. 2. Velocity autocorrelation function for liquid Li at 470 K: the dashed line represents the SHW model; the square-dotted line the GR formulation; the solid line the present results [Eq. (16) for $n=(\beta/\alpha)-1=2$]; and the round-dotted line the MD results (Ref. [29]).

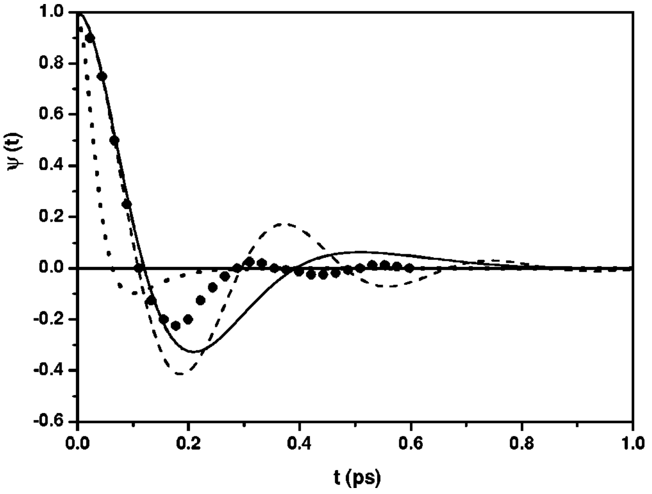

FIG. 3. Velocity autocorrelation function for liquid Na at 378 K: the dashed line represents the SHW model; the square-dotted line the GR formulation; the solid line the Present results [Eq. (16) for $n=(\beta/\alpha)-1=2$]; and the round-dotted line the MD results (Ref. [30]).

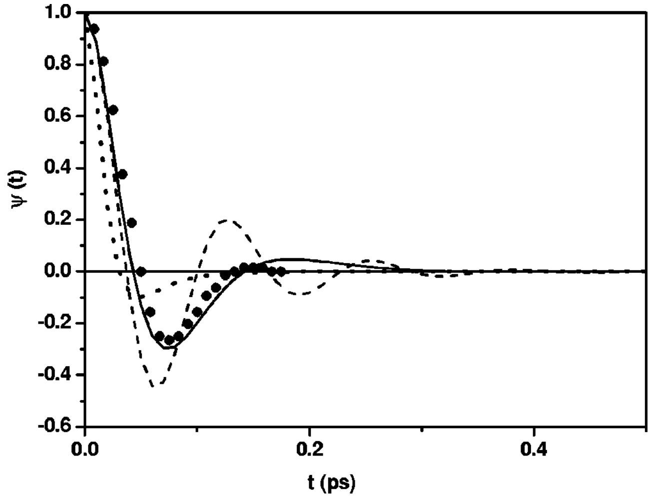

FIG. 4. Velocity autocorrelation function for liquid Li-Li in $Li_{0.61}Na_{0.39}$ at 590 K: the dashed line represents the SHW model; the square-dotted line the GR formulation; the solid line the Present results [Eq. (16) for $n=(\beta/\alpha)-1=2$]; and the round-dotted line the MD results (Ref. [31]).

so far and a few more in the next section, it can be observed that the value of $n=2$ works better. Nevertheless, in the case of binary alloys $n=2$ works for the lighter atoms whereas $n=1$ is suitable for the heavier atoms. Further, the procedure is more justified when we see that the so-obtained D while used in our generalized solution gives much better results in agreement with the MD results (Fig. 4).

For Na-Na the original GR formulation for $n=0$ and $\alpha=\beta$ seems to provide better results compared to the generalized solution [Eq. (16)] for $n=1$ (Fig. 5). However, it should be noted that for the shorter times it shows very rapid decay and does not agree with the MD results.

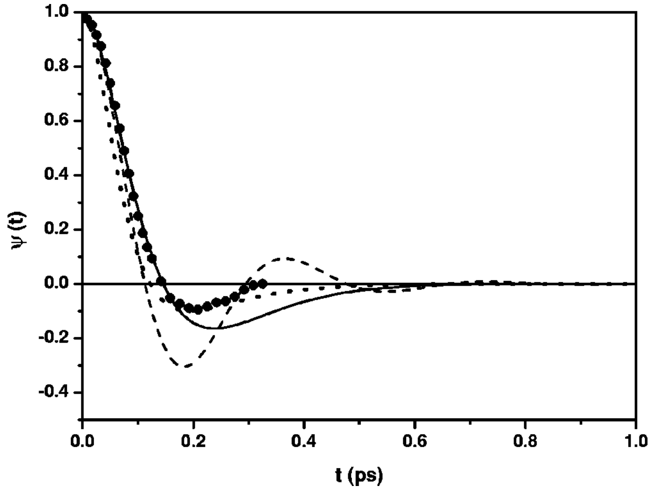

FIG. 5. Velocity autocorrelation function for liquid Na-Na in $Na_{0.61}Na_{0.39}$ at 590 K: the dashed line represents the SHW model; the square-dotted line the GR formulation; the solid line the Present results [Eq. (16) for $n=(\beta/\alpha)-1=1$]; and the round-dotted line the MD results (Ref. [31]).

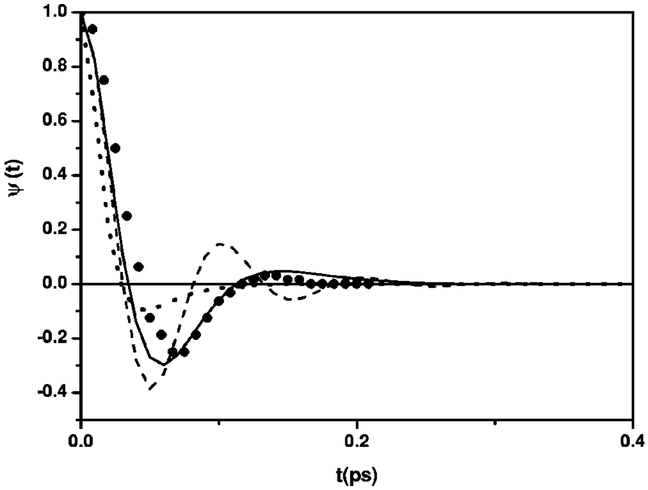

FIG. 6. Velocity autocorrelation function for liquid Li-Li in $Li_{0.70}Mg_{0.30}$ at 875 K: the dashed line represents the SHW model; the square-dotted line the GR formulation; the solid line the Present results [Eq. (16) for $n=(\beta/\alpha)-1=2$]; and the round-dotted line the MD results (Ref. [31]).

D. Velocity autocorrelation functions in $Li_{0.70}Mg_{0.30}$ at 875 K

In Li-Mg the difference in electronegativity between Li and Mg atoms is larger and it is thought to be a borderline case for the treatment of simple liquid metallic alloys by standard methods. It exhibits a weak heterocoordination tendency [34]. The VACF for Li-Li and Mg-Mg in $Li_{0.70}Mg_{0.30}$ alloy at 875 K are shown in Figs. 6 and 7, respectively. The necessary parameters are given in Table I. It can be seen that the generalized solution with $n=2$ gives results in excellent agreement with the MD results [31]. The VACF for Mg-Mg are shown in Fig. 7.

IV. DISCUSSION

The GR formulation for the insulating fluid argon assumes the two relaxation times α and β to be equal. How-

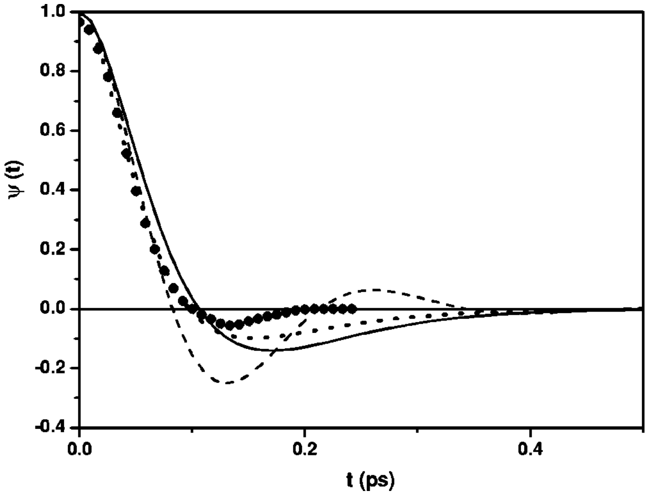

FIG. 7. Velocity autocorrelation function for liquid Mg-Mg in $Li_{0.70}Mg_{0.30}$ at 875 K: the dashed line represents the SHW model; the square-dotted line the GR formulation; the solid line the Present results [Eq. (16) for $n=(\beta/\alpha)-1=1$]; and the round-dotted line the MD results (Ref. [31]).

ever, from Eq. (10), it can be observed that $\alpha\beta$ is proportional to $\langle\nabla^2 V\rangle$ which increases with the increase in the number density. β also increases with the increase in the density. Further, since the liquid's self-diffusion coefficient is proportional to the time integral of the velocity autocorrelation function [Eq. (3d)]; the long-time oscillations in VACF produce a substantial decrease in the diffusion coefficient and it would ultimately increase the value of β [Eq. (11)]. Therefore at higher densities β tends to be greater than α, i.e., $\beta > \alpha$. It suggests that the motion of the atoms is very different from simple diffusion. In liquids, the microscopic motion is demonstrated to consist of diffusive motion of temporal extent τ_D interspersed by vibratory motions of period τ_ν with $\tau_D \gg \tau_\nu$ [35]. The vibratory and diffusive components are not independent and the low-frequency vibratory modes merge into diffusive contributions. In the present work, we find $\beta = 3\alpha$ and it seems reasonably universal among the four liquid metals studied. This result is in line with the earlier observations of the universal behavior of VACF and self-diffusion coefficient in liquid alkali metals [4]. The liquid alkali metals are often thought to present scalable properties [36]. The ratio (β/α) gives an indication of the proportion of the total degrees of freedom of the liquid which are associated with diffusive rather than vibratory motion [17]. It should be noted that the self-diffusion in a liquid represents only a part of the thermal motion of the atoms, and hence absorbs only a fraction of the total number of degrees of freedom of the system [37].

The negative backscattering region and subsequent long-range oscillations are the essential features of VACF in high density liquids. The backscattering region is due the reversal of the velocity of an atom on collision with the wall of the cage formed by the nearest neighbors. The cage is, of course, not stationary and is subject to quasirandom fluctuations. It gives a push to the backscattered atom in its original direction of motion resulting in the appearance of long-time oscillations in the VACF. The oscillations in the VACF persist up to the time when the cage relaxes due to cooperative rearrangement of atoms. In liquid metals, the presence of conduction electrons gives rise to an attractive force. Dean and Kushick [38] have studied the role of the attractive force in cage effects in simple liquids and have pointed out that the principal role of the attractive force is to enhance the cohesiveness of the cages. The increased cohesiveness of the cage increases the time (τ_0) that an atom spends before diffusing away and since $\alpha = \tau_0^{-1}$, α becomes smaller compared to β in liquid metals. Due to strong cohesion, when an atom collides with a neighbor, the momentum transfer is with a significant part of the nearest neighbor shell and the atom rebounds from the greater mass [39]. Hence the decay of the VACF in liquid metals is highly damped as observed from the present results and the MD results. The qualitative behavior of VACF in the present work is in agreement with the study reported by Endo and Endo [40] indicating the coordination number to be 10 which is indeed the case for liquid metals [41].

It can be observed from Table I that the values of diffusion coefficients (D) calculated using Eq. (12) for Li-Li, Na-Na, and Mg-Mg in the case of Li-Na and Li-Mg liquid alloys display completely different behavior. In the $\mathrm{Li}_{0.61}\mathrm{Na}_{0.39}$ alloy, $D_{\text{Li-Li}}$ is smaller than $D_{\text{Na-Na}}$; whereas in the case of $\mathrm{Li}_{0.70}\mathrm{Mg}_{0.30}$, $D_{\text{Li-Li}}$ is greater than $D_{\text{Mg-Mg}}$. This observation is also in agreement with earlier studies on these alloys [31,34]. This can be understood by noting that the self-diffusion coefficient is proportional to the time integral of the velocity autocorrelation function [Eq. (3d)]. The backscattering region and subsequent long-time oscillations play an important role in the determination of D. In $\mathrm{Li}_{0.61}\mathrm{Na}_{0.39}$, where homocoordination is preferred, the cohesiveness of the cage surrounding a Li atom will be greater and the backscattering region will be deeper in Li-Li as compared to Na-Na (Figs. 4 and 5). The deeper backscattering region in the absence of significant long-time oscillations produces a substantial relative reduction in $\mathrm{D}_{\text{Li-Li}}$ as compared to $D_{\text{Na-Na}}$. Further, the smaller value of $D_{\text{Li-Li}}$ compared with $D_{\text{Na-Na}}$ may be associated with the deeper minimum of the Li-Li potential [31]. On the other hand, $\mathrm{Li}_{0.70}\mathrm{Mg}_{0.30}$ exhibits weak heterocoordination tendency. Due to this Mg is preferred in the nearest neighbor of Li over Li itself. However, the concentration of Mg is less as compared to Li in this alloy. Under this circumstance, the backscattering effects in the alloy are strongly reduced for Li with respect to Mg in Li-Mg system in contrast to the Li-Na alloy. It may also be noted that the depth of potential in Mg is more than that of Li.

V. CONCLUDING REMARKS

The aim of this paper is to extend the GR formulation for the single-particle Brownian motion in simple liquids to high density liquids like liquid metals. A generalized solution [Eq. (16)] to the equation of motion [Eq. (1)] in terms of VACF has been provided removing the two assumptions used by GR. The application of the generalized solution [Eq. (16)] to the liquid alkali metals (Li, Na) and binary liquid alloys (Li-Na, Li-Mg) has been found to give promising results which consequently suggests that the solution of Eq. (16) for $n = 2$ could be used to obtain VACF in pure liquid alkali metals. The ratio β/α of the two relaxation times is found to be reasonably universal for the liquids studied. In context to the universal properties exhibited by the liquid metals, it would be interesting to explore the physical property associated with the ratio. It should be noted that the diffusion coefficient D is an important parameter in the calculation of VACF. However, there is a practical difficulty in determination of the diffusion coefficient D at a temperature of interest and availability of experimental data is not always possible. In such a case, our generalized solution provides flexibility, though at the risk of increasing ambiguity, in the calculation of VACF. In the future work, we intend to eliminate the parameter D by employing the small-step diffusion approximation in our generalized solution. Also, the description of atomic motion in terms of VACF is not complete in itself. It can further be understood in terms of the frequency spectrum of VACF. The mean square displacement, the dynamical structure factor and quasiphonon dispersion curves can also be derived in terms of VACF. Thus the full potentiality of the new generalized solution for VACF remains yet to be explored and leaves broad room for future work.

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APPENDIX: EFFECTIVE PAIR POTENTIALS IN LIQUID METALS

The effective pair potential between the ions in the liquid metal can be written as

$$V(r) = \frac{(Ze)^2}{r} + \frac{2(Ze)^2}{\pi} \int dq \frac{\sin(qr)}{qr} F_N(q). \tag{A1}$$

The first term on the right-hand side of Eq. (A1) represents the Coulombic ion-ion interaction which is repulsive in nature whereas the second term gives an attractive force arising due to the presence of conduction electrons. $F_N(q)$ is the wave-number-energy characteristic and is given by [42]

$$F_N(q) = \frac{\Omega^2 q^4}{16\pi^2 z^2 e^4}\left(\frac{1}{\varepsilon(q)} - 1\right)\left(\frac{1}{1 - G(q)}\right) W_b^2(q), \tag{A2}$$

where $W_b(q)$ is the form factor and the Fourier transform of the empty-core potential is defined as [43]

$$W(r) = \begin{cases} 0; & r < r_c \\ -\dfrac{Ze^2}{r}; & r \geqslant r_c \end{cases} \tag{A3}$$

and the Fourier transform is

$$W(q) = -\frac{4\pi Ze^2}{q^2\Omega}\cos(qr_c), \tag{A4}$$

where the core radius r_c is a parameter at one's disposal.

The ions in the metal are screened by conduction electrons. The dielectric screening function $\varepsilon(q)$ plays an important role in the pseudopotential theory. The dielectric screening function proposed by Ichimaru and Utsumi [44] based on the linear response theory is given by

$$\varepsilon(q) = 1 - \frac{(4\pi e^2/q^2)\chi(q)}{1 + (4\pi e^2/q^2)\chi(q)\mathrm{G}(q)}, \tag{A5}$$

where $G(q)$, known as the local-field exchange correlation function, arises due to the effects of exchange and correlation among the conduction electrons. The form of $G(q)$ significantly affects the potential and its choice is important for pseudopotential calculations. A variety of expressions for $G(q)$ are available in the literature [44–48]. The one given by Sham [46] is

$$G(q) = \frac{q^2}{2(q^2 + \xi k_F^2)} \tag{A6}$$

with

$$\xi = \frac{2}{1 + (0.153/\pi k_F)}. \tag{A7}$$

$\xi=1$ corresponds to the original Hubbard expression for $G(q)$ [38]. Hafner and Schumuck [49] have taken

$$\xi = \frac{2}{1 + \dfrac{0.153}{\pi k_F}}. \tag{A8}$$

k_F is the Fermi wave number defined as

$$k_F = (3\pi^2 zn)^{1/3}. \tag{A9}$$

$\chi(q)$, which appears in Eq. (A5), takes into account the coulomb interaction between the electrons and is expressed as

$$\chi(q) = -\frac{mk_F}{\pi^2 h^2}\left[\frac{1}{2} + \frac{4k_F^2 - q^2}{8k_F q}\ln\left|\frac{2k_F + q}{2k_F - q}\right|\right]. \tag{A10}$$

In the case of binary alloys of liquid metals A_xB_{1-x} can be considered as a liquid mixture of two types of atomic species of component metals A and B in proportions x and $(1-x)$, respectively. Three types of ion-ion interactions viz. A-A, B-B, and A-B need to be considered in this case. The effective potential can be a concentration weighed average of the three partial pair potentials V_{AA}, V_{BB}, and V_{AB}. It is given by

$$V(r) = C_A^2 V_{AA} + 2C_A C_B V_{AA} V_{BB} + C_B^2 V_{BB}, \tag{A11}$$

where

$$C_A = \frac{x\Omega_A}{x\Omega_A + (1-x)\Omega_B}, \tag{A12}$$

$$C_B = \frac{(1-x)\Omega_B}{x\Omega_A + (1-x)\Omega_B}. \tag{A13}$$

Ω_A and Ω_B are the molar volumes.

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