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Reply to "Comment on 'Brownian motion with time-dependent friction and single-particle dynamics in liquids'"

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In this reply, we respond to the comments by Lisý and Tóthová (LT) on our recent work [Phys. Rev. E **105**, 064107 (2022)], where we have extended the microscopic theory of molecular motion in atomic liquids that was originally proposed by Glass and Rice [Phys. Rev. **176**, 239 (1968)]. Contrary to our conclusion of nonavailability of a physically tractable analytical solution of the equation of motion involving dynamic friction, LT have attempted to obtain an analytical solution giving the velocity autocorrelation function in liquids. We show that the analytical solution of the equation of motion derived by LT is incomplete and not an appropriate solution for the description of atomic dynamics in liquids. It is demonstrated that the generalized statements made by LT regarding the equation of motion giving incorrect results are unjustified in the absence of substantial proofs. Also, until and unless proven otherwise, we do not find any reason for the reconsideration of the theory as suggested by LT.

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Glass and Rice (GR) [1] presented a theoretical formulation to compute the velocity autocorrelation function (VAF) in simple monatomic liquids assuming a Brownian particle in the liquid diffusing in mean-time-dependent harmonic force field. They derived a modified Langevin equation by adding another systematic force term representing the time-dependent force field. Subsequently, an equation of motion was derived in terms of VAF as [1]

$$\frac{d^2\psi}{dt^2} + (\alpha + \beta)\frac{d\psi}{dt} + \omega_0^2\, e^{-\alpha t}\,\psi = 0. \tag{1}$$

This equation involves two parameters α and β, where the former is associated with the local molecular relaxation and the latter with the friction coefficient. Apart from assuming β to be time independent, GR also considered it to be equal to α for low density simple liquids and obtained an analytical solution of Eq. (1) subject to the boundary conditions given by

$$\lim_{t\to 0}\psi(t) = 1, \tag{2a}$$

$$\lim_{t\to 0}\frac{d\psi}{dt} = 0, \tag{2b}$$

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

where ω_0 is the liquid-characteristic frequency associated with the harmonic potential well.

In our previous work [2,3], we have shown that while the assumption of $\alpha = \beta$ works reasonably well for the low density liquids like liquid argon, it is inadequate for high density liquids such as the liquid metals. We presented a generalized formulation for the solution of Eq. (1) to include the cases where $\alpha \neq \beta$ and demonstrated its application to the liquid metals and its alloys [2,3]. On further investigation on its applicability to less-simple metals like the transition metals in the liquid state, it became evident to us that the generalized formulation is not adequate for such liquids. Also, we noticed that even in the case of simple metals like the liquid alkali metals and their alloys [2,3], the results of VAF obtained using our generalized formulation deviate quite significantly from the molecular dynamics results in the backscattering region as well as the oscillatory region. This prompted us to look for the possible shortcomings in the original GR theory [1] and to address it for providing better quantitative results and hence a better description of the molecular motion in liquids. The subsequent investigations, modifications in the GR theory, and its application to a variety of liquids are reported in our recent publication [4] on which Lisý and Tóthová [5] (LT) have commented.

The major highlight of our work presented in Ref. [4] is the consideration of the time-dependent friction in the Brownian description of atomic motion in liquids and the derivation of the equation of motion,

$$\frac{d^2\psi}{dt^2} + (\alpha + \beta_0 e^{-\alpha t})\frac{d\psi}{dt} + \omega_0^2\, e^{-\alpha t}\,\psi = 0. \tag{3}$$

While we attempted to obtain analytical solution of Eq. (3), it was observed that the possible general solution invariably

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involves special mathematical functions which makes the determination of all the involved arbitrary constants subject to the boundary conditions in Eq. (2) physically intractable. In order to avoid inadvertent omission of any physically meaningful part of the general solution, we opted and proposed a numerical solution of Eq. (3) subject to the given boundary conditions in Eq. (2). We used the NDSolve, a built-in language function in Wolfram *Mathematica*, to obtain the numerical solution of Eq. (3).

We duly mentioned the nonavailability of a tangible analytical solution of Eq. (3) as a limitation of our work in the "Conclusion" section of Ref. [4]. Picking up the thread from this point, the comment authors (LT) focused on obtaining the analytical solution of Eq. (3). In the following, we discuss the derivation given by LT [5].

On the change of variable by substituting $x = (\beta_0/\alpha)\, e^{-\alpha t}$, Eq. (3) turns out to be

$$\frac{d^2\psi}{dx^2} - x\frac{d\psi}{dt} + \left(\frac{\omega_0^2}{\alpha\beta_0}\right)\psi = 0. \tag{4}$$

Considering this to be a special case of the confluent hypergeometric equation (Kummer's equation), a general solution of Eq. (3) has been obtained in terms of two linearly independent solutions as

$$\psi(x) = c_1 x\, {}_1F_1\left(1 - \frac{\omega_0^2}{\alpha\beta_0}; 2; x\right) + c_2 G_{1,2}^{2,0}\left(-x\left|\begin{matrix}1 - \frac{\omega_0^2}{\alpha\beta_0}\\ 0, 1\end{matrix}\right.\right), \tag{5}$$

where ${}_1F_1\left(1-\frac{\omega_0^2}{\alpha\beta_0}; 2; x\right)$ is a hypergeometric function and $G_{1,2}^{2,0}\left(-x\left|\begin{matrix}1-\frac{\omega_0^2}{\alpha\beta_0}\\ 0, 1\end{matrix}\right.\right)$ is the Meijer G function.

The knowledge of the coefficients c_1 and c_2 is necessary to obtain a complete solution $\psi(x)$. To this end, LT use the condition that the VAF should decay to zero at an infinite time, i.e., $\psi(x) \to 0$ for $x \to 0$, which basically corresponds to $\psi(t) \to 0$ for $t \to \infty$. As the function $G_{1,2}^{2,0}\left(-x\left|\begin{matrix}1-\frac{\omega_0^2}{\alpha\beta_0}\\ 0, 1\end{matrix}\right.\right)$ in Eq. (5) does not converge to zero for $x \to 0$ while ${}_1F_1\left(1-\frac{\omega_0^2}{\alpha\beta_0}; 2; x\right)$ converges to zero, it has been argued that the condition of $\psi(x) \to 0$ for $x \to 0$ will be satisfied only if c_2 is taken to be equal to zero.

Elimination of c_2 from Eq. (5) leads to an easy determination of c_1 using the boundary condition $\psi\left(x = \frac{\beta_0}{\alpha}\right) = 1$ and, subsequently, an analytical expression for the VAF which will decay to zero at $t \to \infty$ for both the cases $\alpha < 0$ and $\alpha > 0$. The expression for VAF obtained by LT is [5]

$$\psi(x) = x\frac{\alpha}{\beta_0}\frac{{}_1F_1\left(1 - \frac{\omega_0^2}{\alpha\beta_0}; 2; x\right)}{{}_1F_1\left(1 - \frac{\omega_0^2}{\alpha\beta_0}; 2; \frac{\beta_0}{\alpha}\right)}. \tag{6}$$

The VAF results obtained using Eq. (6) for two cases of LJ fluids are compared with those obtained by numerical solution of Eq. (3) given in Ref. [4]. On the basis of the difference observed between these results and stressing the need of the fulfillment of the condition $\psi(t) \to 0$ for $t \to \infty$, LT draw the following main conclusions regarding our theoretical treatment and results in Ref. [4]:

(1) The parameters α, β_0, and ω_0 given in Ref. [4] are unreliable.

(2) The equation of motion [Eq. (3)] for a Brownian particle in liquids obtained in Ref. [4] assuming the time dependence of its friction coefficient gives incorrect results if solved under the condition $\frac{d\psi}{dt} = 0$ at $t = 0$.

(3) The interesting theory [1] with possible important consequences for the physics of fluids and the Brownian motion should be reconsidered.

For the first point, we acknowledge that in our paper [4] there are typographical mistakes in reporting the values of β_0 and ω_0 in Table I for the LJ system at $\rho = 0.2$. The correct values of β_0 and ω_0 are $5.5\times10^{12}\,\mathrm{s}^{-1}$ and $36.9\times10^{12}\,\mathrm{s}^{-1}$ respectively. All the other values reported in Tables I–III are correct. We have already given a detailed discussion on the derivation of the values of α, β_0, and ω_0, its physical significance, and reliability in Ref. [4]. The fact that the results obtained using the numerical solution of Eq. (3) are in close agreement with the classical molecular dynamics (MD) results for a variety of liquids with a wide range of density is a testimony to the reliability of the parameters. In the following discussion, we show that the other two remarks about the theoretical treatment and the results reported in our paper [4] are unjustified because the derivation of the analytical solution, Eq. (6), is flawed from the viewpoint of physics involved in Eq. (3) that represents the equation of motion of a Brownian particle in a liquid.

There is no contention about the general solution of Eq. (3) given by Eq. (6) in terms of the special functions, namely the hypergeometric function and the Meijer G function. In fact, as mentioned earlier, we were also aware of the analytical solution of Eq. (3) in terms of special functions in the case of $\alpha \neq 0$. However, a complete and correct solution warrants rigorous determination of the arbitrary constants c_1 and c_2 appearing in the general solution subject to the boundary conditions in Eq. (2). For this, it is essential that any special function that is a part of the general solution should be a regular and continuous function in the given range of time. For example, in the GR formulation [1] and our generalized GR formulation [2,3] with time-independent friction coefficient, the equation of motion could be reduced in the form of a Bessel differential equation and its general solution consists of the Bessel functions of the first and the second kind which are regular and continuous functions in the time range of interest. For this case, a systematic method, employing the boundary conditions [Eq. (2)], has been prescribed by GR [1] for the determination of c_1 and c_2.

Thus, if Eq. (6) is to present a complete solution encompassing the correct physical scenario of the atomic dynamics of the liquid, it is imperative to determine c_1 and c_2 subject to the boundary conditions that, in the present case, turn out to be

$$\lim_{x\to\beta_0/\alpha} \psi(x) = 1, \tag{7a}$$

$$\lim_{x\to\beta_0/\alpha} \frac{d\psi}{dx} = 0, \tag{7b}$$

$$\lim_{x\to\beta_0/\alpha} \frac{d^2\psi}{dx^2} = -\omega_0^2/\beta_0^2. \tag{7c}$$

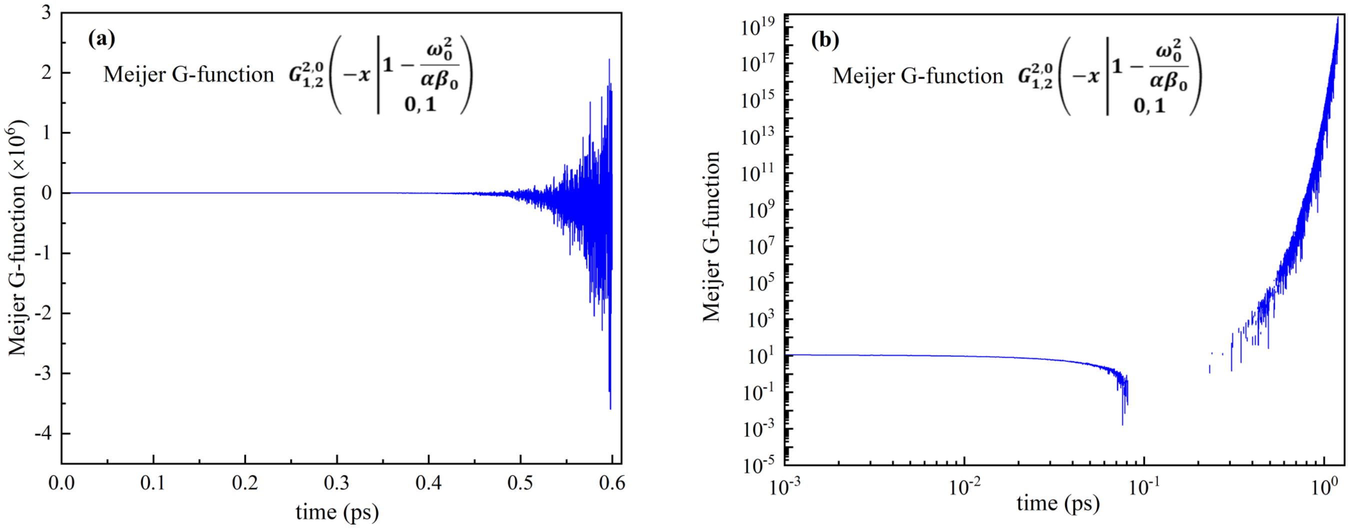

FIG. 1. Meijer G function as a function of time on (a) linear scale and (b) log scale. The irregularity and discontinuity of the function becomes evident when plotted on the log scale.

The Meijer G function in Eq. (3) is a complex function for $\alpha > 0$. For $\alpha < 0$, it is an irregular function showing oscillations with large increasing amplitudes as shown in Fig. 1. If we see the time dependence of the Meijer G function on linear scale, it shows negligibly small fluctuations about zero for the initial period of ~0.5 ps and then it exhibits oscillations with rapidly increasing amplitudes [Fig. 1(a)]. However, to get a better perspective of the behavior of the Meijer G function in the time range of interest, we plot it on a log scale in Fig. 1(b). It clearly demonstrates the irregular and discontinuous time dependence of the function. Therefore, it is evident that it is not possible to determine both the constants c_1 and c_2 by using the boundary conditions in Eq. (7). As a result, the LT stress on determination of these coefficients is based on the condition that the VAF should decay to zero at an infinite time, i.e., $\psi(x) \to 0$ for $x \to 0$ which basically corresponds to $\psi(t) \to 0$ for $t \to \infty$. As $\lim_{x\to 0} {}_1F_1\left(1-\frac{\omega_0^2}{\alpha\beta_0}; 2; x\right) = 0$ and the Meijer G function converges to a nonzero finite value given by $\lim_{x\to 0} G^{2,0}_{1,2}\left(-x\middle|\begin{matrix}1-\frac{\omega_0^2}{\alpha\beta_0}\\ 0,\ 1\end{matrix}\right) = \frac{1}{\Gamma(1+\frac{\omega_0^2}{\alpha\beta_0})}$, it is suggested that Eq. (5) would be physically meaningful [i.e., $\psi(x) \to 0$] only if c_2 is considered to be zero. This argument implies that the hypergeometric function and the Meijer G function in Eq. (5) must converge to zero simultaneously for $x \to 0$. It rules out the possibility of finding a combination of the values of c_1 and c_2 (like the case of GR formulation [1]) such that $\psi(x) = 0$ for nonzero values of the special functions. As the Meijer G function is complex for $\alpha > 0$ and an irregular function for $\alpha < 0$, it is excluded from the analytical solution. In such a scenario, Eq. (6) presents a partial solution of Eq. (3) and it does not include all the possible dynamical information

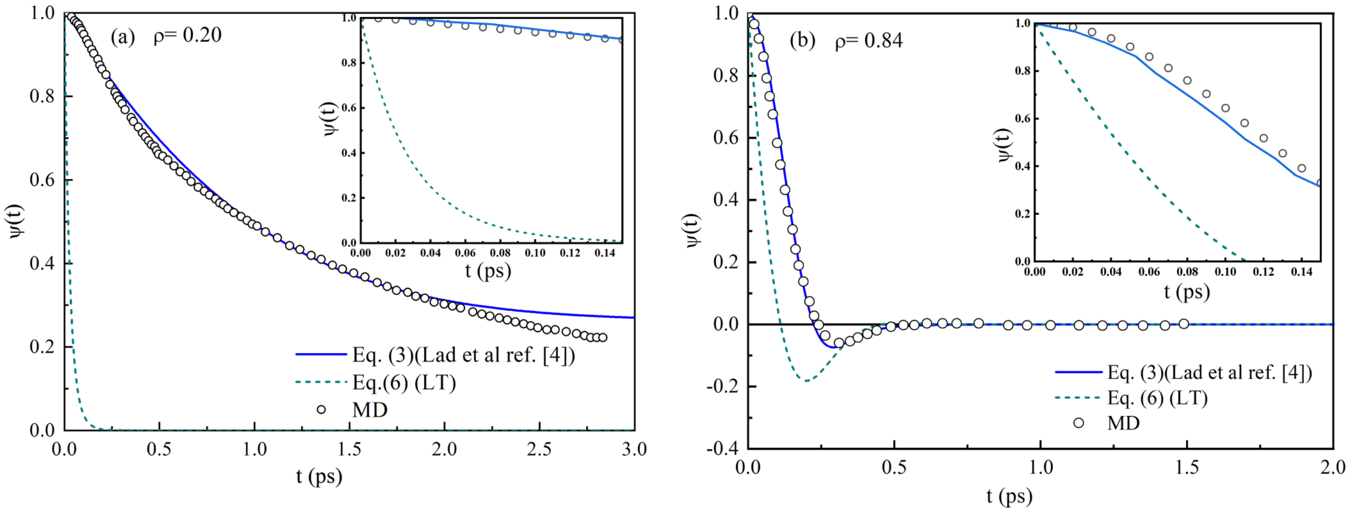

FIG. 2. VAF for LJ system at $T = 1.5$ with density, (a) $\rho = 0.2$ where the correct values of β_0 and ω_0 are 5.5×10^{12} s^{-1} and 36.9×10^{12} s^{-1} respectively. The value of $\alpha = 2.03\times10^{12}$ is correct. (b) $\rho = 0.84$ where all the necessary parameters reported in Ref. [4] are correct. The insets in the figure indicate that the first order derivative of VAF are nonzero at $t = 0$.

in the equation of motion. It is for this reason that the VAFs obtained using Eq. (6) for LJ fluids (Fig. 2) decay rapidly compared to the MD results and those obtained from the numerical solution of Eq. (3).

Another problem that points to the inappropriateness of the analytical solution in Eq. (6) is that it does not satisfy the necessary boundary conditions in Eqs. (7b) and (7c). The insets in Fig. 2 clearly indicate that the first order derivatives of the VAFs are nonzero at $t = 0$, which is contrary to the boundary condition in (7b). To demonstrate that Eq. (6) does not obey the boundary conditions in Eqs. (7a) and (7b), we derive the following expressions for the first and second order derivates of VAF in Eq. (6) using the formulas for the derivatives of ${}_1F_1(\mu;\nu;x)$ [6]:

$$\frac{\partial\psi(x)}{\partial x} = \frac{\alpha}{\gamma\beta_0}\left[{}_1F_1(a;2;x) + \frac{ax}{2}\,{}_1F_1(a+1;3;x)\right], \tag{8}$$

$$\frac{\partial^2\psi(x)}{\partial x^2} = \frac{\alpha a}{\gamma\beta_0}\left[{}_1F_1(a+1;3;x) + \frac{(a+1)}{6}\,{}_1F_1(a+2;4;x)\right], \tag{9}$$

where $\gamma = {}_1F_1(a;2;\frac{\beta_0}{\alpha})$ and $a = 1-\frac{\omega_0^2}{\alpha\beta_0}$.

In the case of LJ fluid at $\rho = 0.2$, using $\omega_0 = 5.5\times 10^{12}\ \mathrm{s}^{-1}$, $\beta_0 = 36.9\times10^{12}\ \mathrm{s}^{-1}$, and $\alpha = 2.03\times10^{12}\ \mathrm{s}^{-1}$, it is found that $\frac{\partial\psi(x)}{\partial x}\Big|_{x=\beta_0/\alpha} = 0.97$ and $\frac{\partial^2\psi(x)}{\partial x^2}\Big|_{x=\beta_0/\alpha} = 0.14$ which clearly violates the boundary conditions (7b) and (7c). Similar results can be found for the LJ fluid at $\rho = 0.84$.

We are surprised that LT have ignored the above aspects. Moreover, they have overlooked the checking of validity of the VAFs obtained using Eq. (6) by comparing it with the MD results. It is understandable that the starkly different VAF obtained by numerical solution of Eq. (3) for the case of LJ fluid with $\rho = 0.2$ (due to an unintended typographical error in the values of the parameters in Ref. [4]) might have led LT to believe that there is either a problem with the parameters or Eq. (3) itself. However, they did not see that the VAF given by Eq. (3) for LJ fluid with $\rho = 0.84$ is still in excellent agreement with the MD results whereas those obtained using Eq. (6) show large deviations from MD results (Fig. 2).

We would like to emphasize that, in our paper [4], we have reported a total of 21 results of VAFs obtained using Eq. (3) for a variety of liquids along with the necessary parameters. Except for the nonreproducibility of the VAF from Eq. (3) for just one LJ system using reported values of the parameters in [4], the LT do not present any other substantial results that show any lacunae in the theory and the results presented by us in Ref. [4]. Therefore, the generalized statements made by the Comment authors regarding our work [4], like “the parameters α, β_0, and ω_0 are unreliable,” “Eq. (3) giving incorrect results,” and “the need of reconsideration of the theory,” are not warranted.

To summarize, it is sufficiently clear that the analytical solution [Eq. (6)] derived by LT is not complete and it does not satisfy all the necessary boundary conditions. So, it is not an appropriate analytical solution of Eq. (3) for the description of atomic dynamics in liquids. Also, until and unless proven otherwise, we do not find any problem in the equation of motion, Eq. (3), that is derived by us in Ref. [4].

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