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

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Recently, Lad, Patel, and Pratap [Phys. Rev. E **105**, 064107 (2022)] revisited a microscopic theory of molecular motion in liquids, proposed by Glass and Rice [Phys. Rev. **176**, 239 (1968)]. They argued that the friction coefficient for a Brownian particle in a liquid should exponentially depend on time and derived an equation of motion for the particle's velocity autocorrelation function (VAF). The equation was solved numerically and fitted to the results of molecular dynamics simulations on different liquids. We show that this solution, obtained under the condition of zero derivative of the VAF at time $t = 0$, is physically incorrect at long times. This is evidenced by our exact analytical solution for the VAF, not found by Lad *et al.*, and numerically, by using the same method as in the commented work.

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In Ref. [1], the authors revisit the theory by Glass and Rice (G&R) [2] of the molecular motion in classical monoatomic liquids. G&R introduced a formalism that was utilized to calculate the velocity autocorrelation function (VAF) of a particle in a liquid. They assumed that the fluctuations arising from the motion of the molecules in the long-range soft part of the intermolecular field are sufficiently rapid to result in an irregular Brownian motion. In addition, G&R represented the effects of the strong short-ranged repulsive core collisions by a time-dependent average force field. The resulting equation of motion corresponds to the classical Langevin equation with the frictional force proportional to the instantaneous velocity $\vec{v}(t)$ of the particle with a constant friction coefficient β and an additional systematic force. The obtained equation is transformed into the equation for the normalized VAF, $\psi(t) = \langle\vec{v}(0)\vec{v}(t)\rangle/\langle v^2(0)\rangle$,

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

where ω_0 is a liquid-characteristic frequency associated with the harmonic potential well and α is a molecular relaxation rate. The VAF is subjected to the conditions $\lim_{t\to 0}\psi(t) = 1$, $\lim_{t\to 0} d\psi(t)/dt = 0$, and $\lim_{t\to 0} d^2\psi(t)/dt^2 = -\omega_0^2$. Equation (1) is then solved in [2] assuming $\alpha = \beta$. In Ref. [1], it is shown that Eq. (1) yields $\lim_{t\to 0} d^2\psi(t)/dt^2 = -(\omega_0^2 + \alpha\beta)$ and thus does not satisfy the last of the above limits. It is proposed to resolve this inconsistency (for $\beta \neq 0$ at $t = 0$ and nonzero α) by considering the time-dependent friction coefficient β. With this assumption and employing the conditions at $t \to 0$, the authors derive, instead of (1), the equation [Eq. (21) in Ref. [1]]

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

where β_0 is the initial value of the time-dependent friction $\beta(t) = \beta_0 e^{-\alpha t}$. Equation (2) is the main feature of the work [1]. Next, the authors use α, β_0, and ω_0 as fitting parameters, solve Eq. (21) numerically, and determine these quantities from the best agreement with the molecular-dynamics results for the VAF for various systems at different densities and temperatures. According to Ref. [1], the equation of motion (2) gives an excellent account in a broad range of liquid densities. A better description of the VAF in low-density fluids was demonstrated for $\alpha > 0$, whereas $\alpha < 0$ is inevitable to obtain consistent results for high-density liquids. However, an elaborate quantitative analysis and physical interpretation, especially for the case $\alpha < 0$, is constrained due to the nonavailability of a tangible analytical solution of Eq. (2) [1]. It was concluded that "This is the primary issue that yet remains to be addressed to acquire an in-depth understanding of the time dependence of the dynamical friction and its implications on the dynamical correlations at short times in liquids."

Here we show that Eq. (2) can be solved exactly in terms of the well-known and widely studied special functions. The solution can be obtained in the following way. After changing the variable t to $x = (\beta_0/\alpha)\exp(-\alpha t)$, Eq. (2) becomes

$$x\frac{d^2\psi}{dx^2} - x\frac{d\psi}{dx} + \frac{\omega_0^2}{\alpha\beta_0}\psi = 0. \qquad (3)$$

This is a special case of Kummer's equation or the confluent hypergeometric equation; see, e.g., [3] (Chap. 13) or [4] (Chap. VI)

$$x\frac{d^2\psi}{dx^2} + (\gamma - x)\frac{d\psi}{dx} - a\psi = 0, \qquad (4)$$

where $a = -\omega_0^2/\alpha\beta_0$. Two linearly independent solutions to this equation are confluent hypergeometric function $\Phi(a,\gamma;x) = {}_1F_1(a;\gamma;x)$ and $x^{1-\gamma}\,{}_1F_1(a-\gamma+1, 2-\gamma; x)$ [5] (Chaps. 8, 9, 9.2). In the case $\gamma = 0$ the series representing the former solution diverges and one can choose

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the other independent solution $e^{x/2}W_{a,-1/2}(-x)$ [4] (Chap. VI, 6.9). Whittaker's function W can be expressed through the more general Meijer G function, $G^{2,0}_{1,2}(-x|^{1+\omega_0^2/\alpha\beta_0}_{0,\ 1}) = e^{x/2}W_{-\omega_0^2/\alpha\beta_0,-1/2}(-x)$ [4] (Chap. V, 5.6). The general solution to Eq. (3) thus can be written as

$$\psi(x) = c_1 x_1 F_1\left(1-\omega_0^2/\alpha\beta_0; 2; x\right) + c_2 G^{2,0}_{1,2}\left(-x\middle|\begin{matrix}1+\omega_0^2/\alpha\beta_0\\ 0,\ 1\end{matrix}\right). \tag{5}$$

The same form of the solution of Eq. (3) is obtained by the Wolfram *Mathematica* differential equation solver DSolve [6]. The coefficients c_1 and c_2 can be determined from the used in Ref. [1] initial conditions $\psi(t=0)=1$ and $d\psi/dt = 0$ at $t=0$ which, for $\psi(x)$, are

$$\psi\left(x=\frac{\beta_0}{\alpha}\right)=1, \qquad \left.\frac{d\psi(x)}{dx}\right|_{x=\beta_0/\alpha}=0. \tag{6}$$

However, the VAF must satisfy the physical condition $\psi(t)\to 0$ at $t\to\infty$ corresponding to the loss of correlation with the initial value $\psi(0)$ with the increase of time, which is inconsistent with the solution obeying the conditions (6). So, for $\alpha>0$ one has at $t\to\infty$ $(x\to 0)$ $\lim_{x\to 0}x_1F_1(1-\omega_0^2/\alpha\beta_0;2;x)=0$ but $\lim_{x\to 0}G^{2,0}_{1,2}(-x|^{1+\omega_0^2/\alpha\beta_0}_{0,\ 1}) = 1/\Gamma(1+\omega_0^2/\alpha\beta_0)$, where $\Gamma(z)$ is the Gamma function [6]. The solution (5) thus can be physically correct only when $c_2=0$. For $\alpha<0$ at $t\to\infty$ $(x\to-\infty)$, $\psi(x)$ from Eq. (5) converges to 0. To have the solution applicable for both $\alpha>0$ and $\alpha<0$, we put $c_2=0$ and use the necessary condition $\psi(x=\beta_0/\alpha)=1$ that follows from the definition of the normalized VAF. The Meijer G function can be excluded from the solution (5) also because at $\alpha>0$ it is a complex function and at $\alpha<0$ because of an irregular behavior making it unusable to describe the systems of interest (see the note on numerical calculations below). Then the solution for $\psi(x)$ has the form

$$\psi(x) = x\frac{\alpha}{\beta_0}\frac{{}_1F_1\left(1-\omega_0^2/\alpha\beta_0;2;x\right)}{{}_1F_1\left(1-\omega_0^2/\alpha\beta_0;2;\beta_0/\alpha\right)}. \tag{7}$$

The behavior of $\psi(x)$ does not agree with the results obtained in Ref. [1]. This is illustrated by the plots of this function in Figs. 1 and 2 using the parameters that are given in Ref. [1] as obtained from the fit of the numerical solution of Eq. (2) to the molecular dynamics simulation for Lennard-Jones fluids at two different densities. At the same time, numerical solutions of Eq. (2) subjected to the conditions $\psi(t)=1$ and $d\psi(t)/dt=0$ at $t=0$ are shown. These solutions are obtained in the same way as in Ref. [1], i.e., by using NDSolve [6]. It is seen that the analytical solution (7) significantly differs from the numerical solutions of Eq. (2). The calculations are presented in Fig. 1 (for $\alpha>0$) and Fig. 2 ($\alpha<0$) for the same time range as in [1], up to 3 ps and 1.5 ps, respectively. The slope of $\psi(t)$ is much slower than in Ref. [1] and it converges to a nonzero constant for $\alpha>0$ ($\approx$0.95 in this case). The value of $\psi(t)$ at $t=3$ ps is slightly larger than 0.95, while in [1] it is about 0.25. The calculations in [1] thus should be corrected. However, the most important merit of this figure is the demonstration that the numerical solution does not satisfy the condition $\psi(t)\to 0$ at $t\to\infty$. The numerical

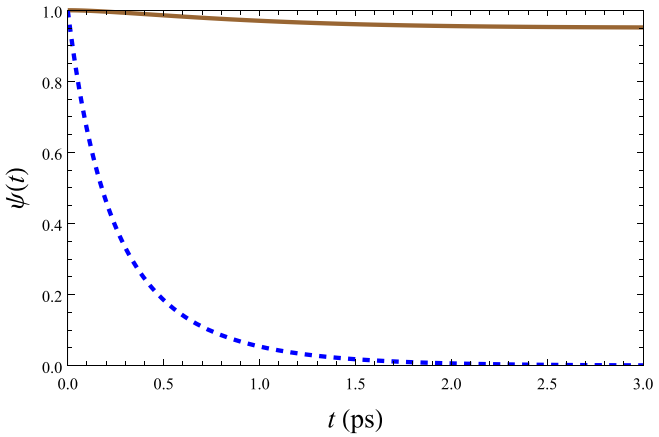

FIG. 1. VAF for Lennard-Jones system calculated numerically from Eq. (2) (full line) subjected to conditions $\psi(0)=1$, $(d\psi/dt)_{t=0}=0$, and from the analytical solution (7) with the condition $\psi(0)=1$ and $\psi(t\to\infty)\to 0$ (dashed line). The parameters are from Ref. [1]: $\alpha = 2.03\times10^{12}\,\mathrm{s}^{-1}$, $\beta_0 = 3.69\times10^{12}\,\mathrm{s}^{-1}$, and $\omega_0 = 0.55\times10^{12}\,\mathrm{s}^{-1}$.

solution for the VAF [with the condition $d\psi(t)/dt=0$ at $t=0$] shown in Fig. 2 also differs from that presented in Ref. [1] where the minimum of the VAF curve is reached at a larger time and its absolute value is slightly smaller. In this case the limit of $\psi(t)$ at $t\to\infty$ is correct. Note that at $\alpha<0$ the Meijer G function changes from approximately 11 at $t=0$ to -1.6×10^{29} at $t=1.5$ ps. It is a rapidly oscillating function with an increasing amplitude that approaches the value $\sim10^{386}$ at t around 3.4 ps, then it abrupts to $\sim3\times10^2$ and slowly goes to 0 as $t\to\infty$ [6]. Such irregular behavior and giant oscillations support the exclusion of this function from the general solution (5).

Figures 1 and 2 evidence that the calculations presented in Ref. [1] possess unreliable parameters α, β_0, and ω_0. We conclude that the equation for the VAF of a Brownian particle in liquids obtained in Ref. [1] assuming the time dependence of its friction coefficient gives incorrect results if solved under the condition $d\psi(t)/dt=0$ at $t=0$. This suggests that the otherwise interesting theory [1] with possible important

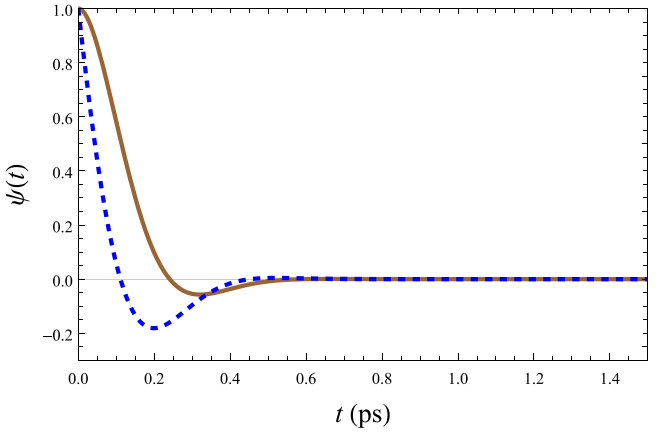

FIG. 2. The same as in Fig. 1 for parameters [1] $\alpha = -1.17\times10^{12}\,\mathrm{s}^{-1}$, $\beta_0 = 14.79\times10^{12}\,\mathrm{s}^{-1}$, and $\omega_0 = 11.71\times10^{12}\,\mathrm{s}^{-1}$.

consequences for the physics of fluids and the Brownian motion should be reconsidered.

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