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The Friction Coefficient of a Lennard–Jones Fluid from the Random Force Autocorrelation Function Determined as a Memory Function by Molecular Dynamics Calculations

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A recent molecular dynamics (MD) study showed that the friction coefficient of a simple fluid is obtainable by the integral over the autocorrelation function (ACF) of the total force of a Brownian-type particle. The results indicated that mass ratios $50 \leqslant M/m \leqslant 200$ of the massive and the light particle suffice to yield accurate friction coefficients. Complementarily, we calculate the random force ACF of the light particle, which is the memory function force of the ACF of the velocity apart from a constant factor, for all the states of the Lennard–Jones system investigated previously. A detailed comparison is presented of the memory function, the total force ACF of the fluid particle, and the total force ACF of the massive particle. The MD results confirm quantitatively our theoretical predictions: (i) on a time scale corresponding to the dynamics of the massive particle the total force ACF of that particle approximates well the memory function, while there are slight differences between them on a short time scale, (ii) the total force ACF of the liquid particle deviates significantly from the memory function already after extremely short time and is thus completely useless for the determination of the friction coefficient, (iii) using the total force ACF of a heavy particle for the determination of the friction constant with mass ratios of $M/m = 50$ up to 200, the pseudo plateau value of the time integral is often not very noticeable, as the memory function is only approximated and the total force ACF of the massive particle has a negative part at medium times. In those cases the integration has to be extended to include the negative part.

KEY WORDS: Transport coefficients; Brownian dynamics; molecular dynamics; memory function.

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1. INTRODUCTION

In a previous report,[1] we showed that the total force autocorrelation function (FACF) of a massive particle immersed in a fluid of much lighter particles may successfully be used to determine the friction coefficient ζ of a model fluid by molecular dynamics (MD) calculations. Depending on the thermodynamic state, the mass of the heavy particle M has to be chosen to be factor of 50–150 times larger than that of the fluid particle m to generate friction coefficients in good agreement with values obtained by the integral over the velocity ACF of the light particle as usually exploited for the determination of this transport coefficient.

However, the pseudo plateau value of the integral of the total FACF of the massive particle appeared only when a suitable mass ratio M/m was chosen with some experience. Moderate increase of this ratio did not lead to more pronounced pseudoplateaus.

Though some of these features were explained by artificial effects introduced by the MD method, there remained open questions concerning the form of the total FACF of the massive particle depending on the mass ratio.

To clarify these points, we present here quantitative results for the total FACF of the light and the massive particle as well as the ACF of the random force, which is essentially represented by the memory function of the velocity ACF of the light particle. The Lennard-Jones fluid is considered as in the previous study and particlular interest is focused on the comparison of the total FACF of the massive particle with the memory function of the light particle. The latter functions may expected to be equal for sufficiently short times, as both functions give the same nearly mass independent friction coefficient ζ via the corresponding time integral when the ratio M/m is chosen large enough. In our previous analysis,[1] we showed that the total FACF of the heavy atom is given by the following expression:

$$\langle \mathbf{F}(0)\,\mathbf{F}(t)\rangle = 3\varphi(t) - 3(\zeta^2/M)k_B T e^{-(\zeta/M)t} \tag{1}$$

where $\varphi(t)$ is the random foce ACF defined according to the Langevin dynamics (see, for instance, refs. 2 and 5). k_B denotes the Boltzmann constant and T the temperature. The brackets $\langle\cdots\rangle$ indicate the thermal average. It was furthermore shown that integration of $\langle \mathbf{F}(0)\,\mathbf{F}(t)\rangle$ yields the friction coefficient when the integration is only performed for a certain time period $\tau_2 \ll M/\zeta$. In that case the second term of the right-hand side of Eq. (1) should make a negligible contribution, while the first term of the right-hand side of Eq. (1) gives ζ. We have

$$\zeta = \frac{1}{k_B T}\int_0^\infty \varphi(t)\,dt \approx \frac{1}{k_B T}\int_0^{\tau_2} \varphi(t)\,dt \approx \frac{1}{3k_B T}\int_0^{\tau_2} \langle \mathbf{F}(0)\,\mathbf{F}(t)\rangle\,dt \tag{2}$$

In Section 2 we derive another expression for ζ which is exactly of the form as the first part of Eq. (2), where, however, the integral extends over the memory function of the velocity ACF of the fluid particle. So the normalized integrand of the memory function and the third part of Eq. (2) should be equal for a certain time interval, at least on a time scale associated with the dynamics of the massive particle. We confirm this by our MD calculations, but we further more demonstrate that on the time scale of the dynamics of the fluid particle there appear small differences between these functions which are, however, in accordance with our predictions.

2. THE MEMORY FUNCTION OF THE VELOCITY ACF OF THE LIGHT PARTICLE (RANDOM FORCE ACF)

Treating a fluid particle itself rather than a Brownian particle dissolved in the fluid, the motion may be described by the generalized Langevin equation. This equation accounts for the "memory" of a particle colliding with the surrounding particles.[3] The generalized Langevin equation represents a special case of the memory function equation for a certain dynamic variable. We derive here an expression for the friction coefficient ζ, using the memory function formalism without detailed comment.[2–4]

Denoting the normalized velocity ACF by $\psi(t)$ and the memory function by $M(t)$, we have (ref. 2, p. 250)

$$\dot{\psi}(t) = -\int_0^t dt'\, M(t-t')\,\psi(t') \tag{3}$$

as the defining equation for the memory function, with

$$\psi(t) = \frac{\langle \mathbf{v}(0)\,\mathbf{v}(t)\rangle}{\langle \mathbf{v}(0)\,\mathbf{v}(0)\rangle}$$

where $\mathbf{v}$ denotes the particle velocity.

The Fourier–Laplace transform of Eq. (3) reads then

$$\tilde{\psi}(s) = 1/[s + \tilde{M}(s)]$$

where s denotes the Laplace variable and the tilde denotes the transformed function.

For $s = 0$ we find the expression

$$\tilde{\psi}(0) = 1/\tilde{M}(0) \tag{4}$$

Combining Eq. (4) with the Green–Kubo integral relation for the self-diffusion coefficient D in the Fourier–Laplace-transformed form,[3] we may write

$$D = \frac{1}{3} \frac{\langle \mathbf{v}^2 \rangle}{\tilde{M}(0)}$$

where we have left out the time argument of the particle velocity to indicate the time-independent value of the ACF. Transforming into the time regime and exploiting the Einstein relation $\zeta = k_B T/D$, we obtain

$$\zeta = m \int_0^\infty M(t)\, dt \tag{5}$$

Equation (5) is exactly of the form of the first part of Eq. (2), noting that $M(t)$ has been "normalized" by $\langle \mathbf{v}^2 \rangle$, and differs further only by a factor m^2 from a force ACF.

So the memory function of the velocity ACF is the stochastic FACF (apart from a mass factor), which is approximatively given by the total FACF of the massive particle, if we consider only a certain short time period τ_2.

Equation (5) has been used in this work to determine ζ, where $M(t)$ was obtained by MD, solving numerically the "Volterra equation" (3). We give details in the next section.

To emphasize here the difference between the total FACF of the fluid particle and the memory function of the VACF of the fluid particle, we present an additional equation linking these functions.[2] Denoting the total FACF of a fluid atom normalized by the time-independent value of the VACF by

$$\phi(t) = \frac{\langle \dot{\mathbf{v}}(0)\, \dot{\mathbf{v}}(t) \rangle}{\langle \mathbf{v}^2 \rangle}$$

the memory function equation for $\Phi(t)$ reads in Laplace-transformed formulation

$$\tilde{M}(s) = \frac{\tilde{\phi}(s)}{1 - s^{-1}\tilde{\phi}(s)} \tag{6}$$

where $\tilde{M}(s)$ is essentially the Fourier–Laplace transform of the memory function defined by Eq. (3). Converting Eq. (6) into the time regime, we find

$$M(t) = \phi(t) - \int_0^t dt'\, \dot{\psi}(t')\, M(t - t') \tag{7}$$

We see immediately that for $t=0$, $M(t)$ and $\phi(t)$ are identical, as it should be. Equation (7) shows furthermore that for short times the behavior of $M(t)$ and $\phi(t)$ cannot differ greatly, as the contribution from the integral remains small. We confirm this quantitatively by the results in later sections, but we also show that significant deviations between these functions occur already after very small times.

3. SOLUTION OF THE VOLTERRA EQUATION

We saw that the determination of the friction coefficient reduces to the integral over the memory function of the VACF of a fluid particle (hereafter referred to as the memory function). Unfortunately, the memory function $M(t)$ is not directly accessible by MD calculations and one is left with the numerical solution of Eq. (3) or Eq. (7). These equations have the form of the Volterra differential equation for which quickly converging solution schemes exist.[6] We have indeed used Eq. (7) for the determination of $M(t)$ by computing $\phi(t)$ directly as the FACF and $\dot{\psi}(t')$ as the time derivative of the VACF. Knowing these functions with sufficient accuracy, one can also obtain the memory function accurately.

In the present case, the ACFs of the velocity and the total force of the fluid particle may be calculated very accurately due to their one-particle property. So we estimate the statistical error for the normalized ACFs to be smaller than 0.02 and that of the normalized memory function to be smaller than 0.03. Details of the algorithm adopted for the evaluation of $M(t)$ can be found in the Appendix.

4. THE MD CALCULATIONS

Our MD calculations for the Lennard-Jones fluid were performed in the same manner as described in ref. 1. However, the MD results for the Brownian-type particle were carried over from our previous work, and no additional computations were done. Thus, the present computations include only production runs of 5000 time steps, as sufficient for the accurate determination of the total FACF and the VACF. In most cases, we studied 256-particle systems, but considered also 108-particle systems for pilot investigations. The accuracy of the friction cofficient obtained by the velocity ACF or the memory function of the fluid particle via the integral amounts to 3–6%, depending on the state point considered.

To check the influence of the integration time step of the MD computation on the evaluation of the FACF and the subsequent determination of the memory function, we performed calculations with time increments of

Table I. MD Calculations

I. Potential: Lennard-Jones (12-6), cutoff radius 2.5σ

$$\varepsilon k_B^{-1} = 119.8 \text{ K}, \qquad \sigma = 3.40 \text{ Å}$$

II. Runs

Particle number	108–256
Number of time steps for production	5000
Integration time step	10^{-14} sec $\triangleq 0.0056(m\sigma^2/\varepsilon)^{1/2}$
Mass of the fluid particle	39.95 a.u.

III. Computation times

0.6 sec (108) per 100 steps (Cyber 205)
1.9 sec (256) per 100 steps (Cyber 205)

[2 sec evaluation of the memory function (Cyber 855)]

0.5×10^{-14} and 10^{-14} sec. These computations indicated insignificant differences between the resulting functions. Table I summarizes some technical details of the present calculations.

5. RESULTS FOR THE MEMORY FUNCTION, THE TOTAL FACF OF THE FLUID PARTICLE, AND THE FACF OF A BROWNIAN-TYPE PARTICLE

5.1. Liquid State

5.1.1. Short-Time Behavior. For a liquid state, state3 (see Table II), we show the short-time behavior of the normalized ACFs of the total force of the light and the heavy particle and the memory function in Figs. 1 and 2. Figure 2 indicates that the total FACF of the massive particle and the memory function behave very similarly, while the total FACF of the fluid particle decays more quickly than the former and has a pronounced negative part. On a larger time scale corresponding to M/ζ the differences between the memory function and the total FACF of the massive particle would scarcely be noticeable, as expected from our introductory remarks. The plots in Figs. 1 and 2 are interesting from two points of view. First, considering Eq. (7), we may expect the total FACF of the fluid particle to decay more strongly than the memory function only for longer times, when the integral term subtracts significantly from the first term. We see, however, that there are remarkable differences between the two curves already after 10^{-13} sec. So the total FACF of the light particle

Table II. Comparison of the Friction Coefficient[a] Computed via the Integral of the VACF and the Memory Function of the Light Particle and as Integral over the Total FACF of the Massive Particle

State	T^* ($\triangleq k_B T/\varepsilon$)	n^* [$\triangleq (N/V)\sigma^3$]	From VACF	From Memory function	From FACF
1	0.70	0.85	7.5	7.5	7.4
2	0.87	0.85	6.5	6.9	6.8
3	0.98	0.85	6.4	6.0	6.4
4	1.50	0.85	5.8	5.6	6.2
5	1.97	0.85	5.6	5.4	5.5
6	0.87	0.80	4.9	5.0	5.2
7	0.98	0.80	4.9	4.9	5.1
8	1.50	0.80	4.6	4.8	4.3
9	1.97	0.80	4.7	4.8	4.6
10	0.98	0.75	3.75	3.85	3.95
11	1.50	0.75	3.70	3.70	3.65
12	1.97	0.75	3.70	3.75	3.90

[a] In Units of 10^{-13} kg sec^{-1} [divide by 0.3089×10^{-13} to convert into reduced units of $(m\varepsilon/\sigma^2)^{1/2}$]. The statistical error for the values in each column amounts to 3–6% (see Section 4). Mass ratios of $50 \leqslant M/m \leqslant 200$ were used for the MD.

cannot be used as a good short-time approximation for the memory function. Second, Eq. (1) predicts a weaker decline of the total FACF of the massive particle compared with the memory function for longer times, when the exponential term subtracts less from the first term. Figure 2 corroborates this nicely for times between 0.1 and 0.2 psec.

Figure 1 illustrates, on the other hand, that all three correlation functions are equal for very short times, $\leqslant 0.03$ psec. Note that our plots present these functions normalized by their initial values.

In Fig. 3 we compare the total FACF of the Brownian-type particle of different mass ratios with the memory function. The figure gives no indication of a significant mass ratio dependence of the FACF of the heavy atom. Thus, we may conclude that our calculations approximate well the asymptotic limit $M/m \to \infty$, at least for the short time range of the dynamics. This is consistent with our previous findings.

5.1.2. Behavior at Longer Times. For longer times the memory function is compared with the total ACF of the massive particle for two mass ratios in Fig. 4. We see from this figure that for the chosen liquid state the memory function shows a very small positive branch up to ~ 1.5 psec. Neither of the total FACFs of the Brownian-type particle

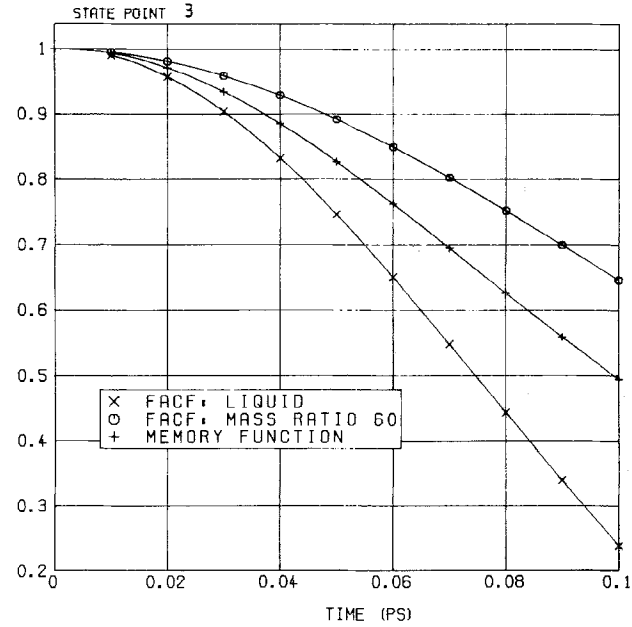

Fig. 1. Short-time behavior of the total force autocorrelation function of the liquid particle and the massive particle (characterized by the mass ratio M/m) compared with the short-time behavior of the memory function of the velocity autocorrelation function of the liquid particle. All functions are normalized by their initial values. The time scale can be converted to reduced units of $(m\sigma^2/\varepsilon)^{1/2}$ by deviding by 21.65×10^{-13} (see Table I).

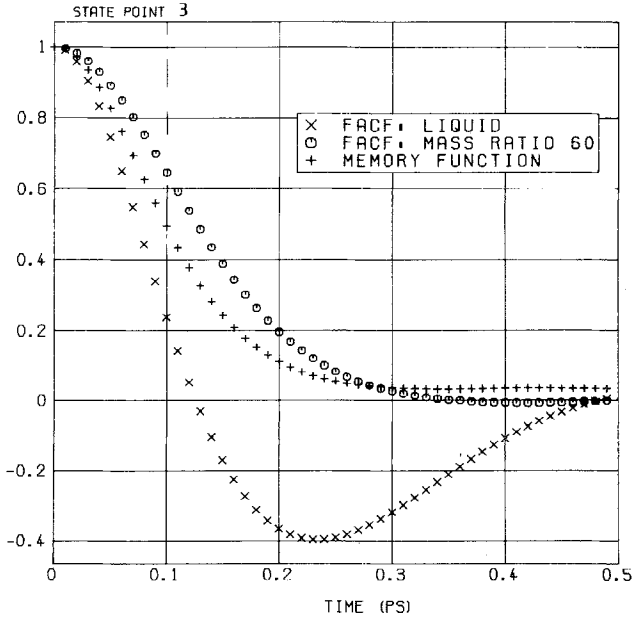

Fig. 2. As in Fig. 1, but up to longer times.

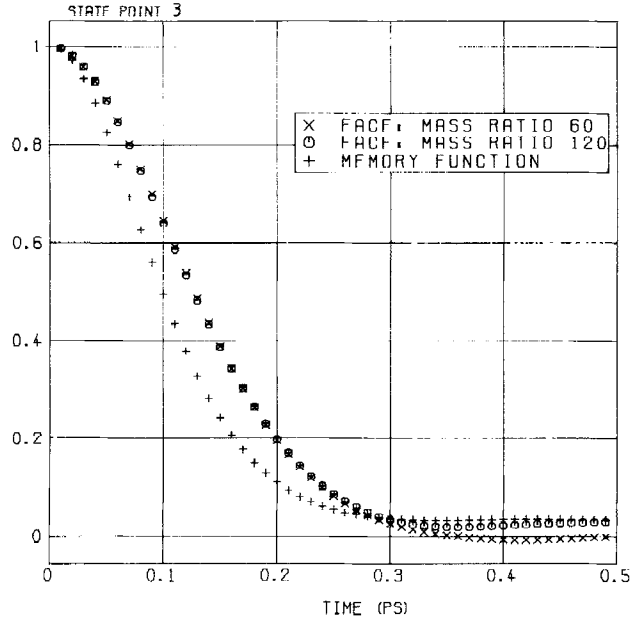

Fig. 3. Total force autocorrelation function of the massive particle for different mass ratios compared with the memory function.

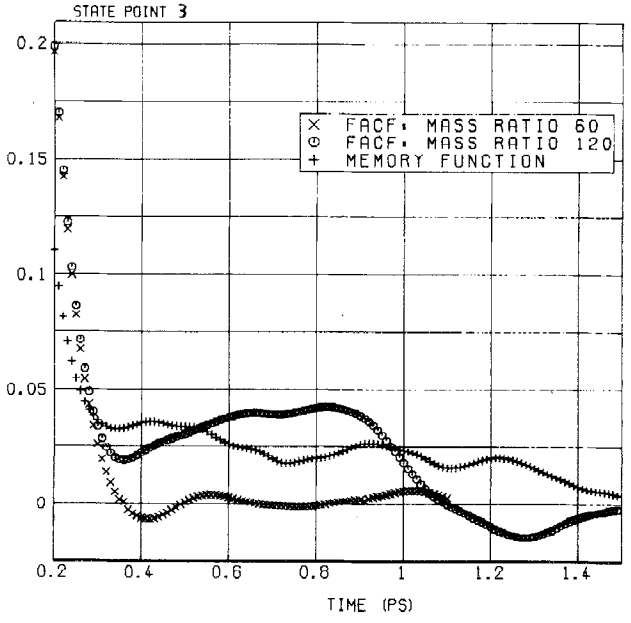

Fig. 4. As in Fig. 3, but for the long-time behavior.

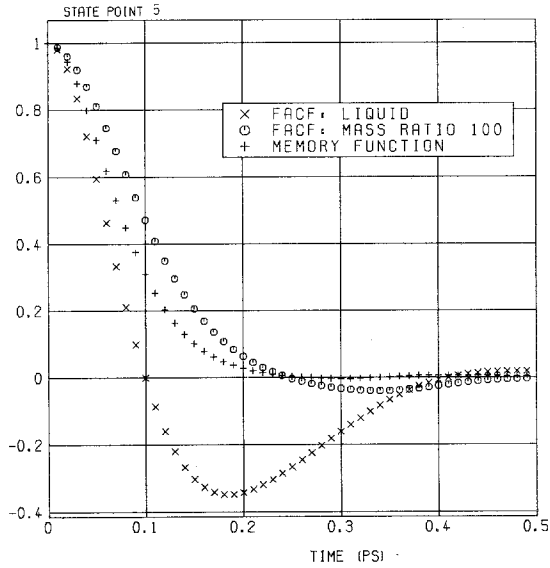

Fig. 5. As in Fig. 2, but for a fluid state and another mass ratio for the massive particle.

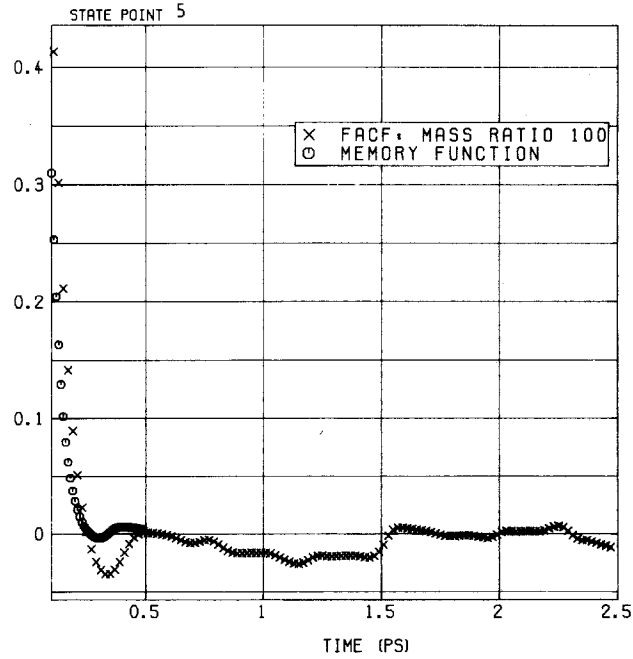

Fig. 6. Total force autocorrelation function of the massive particle compared with memory function for longer times.

reproduces this behavior. The function corresponding to the higher mass ratio approximates this part of the memory function on average. So we may conclude that the "long-time" form of the total FACF of the Brownian-type particle is slightly affected by the mass ratio M/m, giving on average a better approximation of the memory function for larger M/m. We see, however, from the figure that we are discussing very small effects which are scarcely larger than the statistical errors involved in the computations.

5.2. Fluid State

For a fluid state, state point 5 (see Table II), we display the total FACF of the light and the heavy particle and the memory function in Fig. 5. As for the liquid state, the memory function decays more quickly than the total FACF of the massive particle and more slowly than the total FACF, as far as the short-time behavior is concerned. For larger times both the memory function and the total FACF of the light particle disappear, as we have ensured by several computations of these functions up to longer times. The total FACF of the massive particle shows a slight negative branch up to 1.5 psec, which is presented together with the memory function in Fig. 6. For clarity, the plot of the memory function is suppressed for $t \geqslant 0.5$ psec. Since for this fluid state a further increase of the mass ratio by a factor 2 does not alter the form of the total FACF of the massive particle, we have omitted here also the plot for a higher mass ratio (compare Fig. 6 of ref. 1). Compared with the liquid state, the memory function here dies off very rapidly, in agreement with the findings for the VACF, which is known to have a long-time behavior only for the liquid state.[3]

So we have confirmed our result already obtained for the liquid state that the short-time behavior of the total FACF of the massive particle deviates slightly from that of the memory function and does not depend on the mass ratio. In contrast to the liquid state, for the fluid state there is no influence of the mass ratio on the long-time behavior of the total FACF.

6. THE DETERMINATION OF THE FRICTION COEFFICIENT VIA THE MEMORY FUNCTION, THE VACF OF THE LIGHT PARTICLE, AND THE TOTAL FACF OF THE MASSIVE PARTICLE

For the 12 thermodynamic states previously investigated in ref. 1, we compare the friction coefficient obtained by integrating the memory

function and the VACF of the light particle as well as the total FACF of the massive particle in Table II. Our experience showed that an integration period of about 2.5 psec is satisfactory to obtain accurate values for all the considered states. The usual way of determining the friction coefficient or the self-diffusion coefficient is integration of the VACF or evaluation of the slope of the mean square displacement of a fluid particle. The latter method has previously been used by other authors[9–11] to compute the self-diffusion coefficient of LJ argon for several states. We have compared in detail with the data provided by Erpenbeck[11] and found very good agreement, including the particle number dependence of the results.

The ζ values in Table II calculated in these three different ways also agree well within the indicated statistical errors. The friction coefficient evaluated by integration of the total FACF of the massive particle was computed by MD runs of mass ratios $50 \leqslant M/m \leqslant 200$ and the integration was restricted to a range $1 \leqslant t \leqslant 2.5$ psec.[1] We see from the plots in Figs. 3 and 4 that the total FACF of the massive particle approximates the memory function rather well, but exceeds the latter slightly at short times, which would lead to an overestimate of ζ if the integration were truncated after short time. For larger times, the total FACF of the massive particle has a negative part which lowers the integral value subsequently when the integration is extended. Because of this behavior of the FACF, the pseudo plateau of the integral is not well detectable. For sufficient long times $> \tau_2$ the integral value must in any case decrease with time, as we have shown in ref. 1! So, using mass ratios of $50 \leqslant M/m \leqslant 200$ for the MD computations, there remains some uncertainty in the determination of ζ via the total FACF of the Brownian-type particle.

7. DISCUSSION AND CONCLUSIONS

We have shown that the memory function of the VACF of a light particle of a LJ fluid containing additionally one massive particle can be well approximated by the total FACF of a massive particle on a time scale corresponding to M/ζ when M is chosen to be 50–200 times larger than the mass of the light particle. Differences between these functions appear, however, on a short time scale corresponding to the light particle dynamics, where the total FACF of the massive particle lies above the memory function for the initial time interval of about 0.25 psec and below it for the subsequent time interval of 0.25–1 psec. To determine accurately the friction coefficient by the total FACF of the massive particle, the integration has to be performed over a time interval which includes the second negative part of the FACF but excludes the long-time behavior of this function, which is always negative, as we saw in ref. 1.

Investigation of larger mass ratios of $M/m > 1000$ requires a modified MD integration algorithm to provide the accurate dynamics for such a model system. Even then, a much smaller integration time step is necessary, which would unreasonably enlarge the computation times to yield the correlation functions. For these very large mass ratios, we expect the memory function of the VACF of the light particle to be represented by the total FACF of the heavy particle to a very good approximation, even on a time scale comparable with the dynamics of the light atoms. On the other hand, mass ratios of 50–200 can be used to determine the friction coefficient from the total FACF of the heavy particle with reasonable accuracy when the integration is extended up to sufficiently long time of 1–2 psec.

We should like to consider a molecular model potential for the Brownian particle to account more realistically for the large size of such a particle.

APPENDIX

Let $y(t)$ be the normalized autocorrelation function of a dynamic variable $A(t)$

$$y(t) = \frac{\langle A(0)\, A(t)\rangle}{\langle A(0)^2\rangle} \tag{A1}$$

where the $\langle \cdot \rangle$ denote the ensemble average; then $y(t)$ is given by the generalized Langevin equation[7]

$$\dot{y}(t) = i\Omega y(t) - \int_0^{s=t} M(s)\, y(t-s)\, ds \tag{A2}$$

with

$$i\Omega = \dot{y}(0) = 0$$

$M(t)$, the memory function, is the autocorrelation function of the stochastic force $f(t)$ (see Section 2):

$$M(t) = \frac{\langle f(0)\, f(t)\rangle}{\langle A(0)^2\rangle} \tag{A3}$$

with $M(0) = -\ddot{y}(0)$, where

$$\ddot{y}(0) = \frac{\langle \dot{A}(0)\, \dot{A}(0)\rangle}{\langle A(0)^2\rangle} \tag{A4}$$

For $A(t)$ the velocity of a particle $\mathbf{v}_i$ and denoting the total force on that particle by $\mathbf{F}_i = m\dot{\mathbf{v}}_i$, we have

$$M(0) = \frac{\langle \mathbf{F}_i(0)^2 \rangle}{2mk_B T}$$

Taking the time derivative of Eq. (A2), we obtain a Volterra-type integral equation for $M(t)$:

$$M(t) = -\ddot{y}(t) - \int_0^s M(s)\, \dot{y}(t-s)\, ds \tag{A5}$$

For Eq. (A5) we may write out a discretized form:

$$M(t_i) = -\ddot{y}(t_i) - \sum_{j=0}^{i-1} w_j M(t_j)\, \dot{y}(t_i - t_j) \tag{A6}$$

where w_j denotes a certain weighting factor depending on the numerical integration procedure. We used a combination of the ordinary Simpson rule and the so called "3/8"-quadrature formula. $\dot{y}(t)$ was evaluated by a cubic spline with the boundary conditions $\dot{y}(t=0) = \dot{y}(t=t_{\max}) = 0$. In order to achieve quick converge, we exploited the MD total FACF of the light particle as the second derivative of $y(t)$.

Day[8] suggested a method of accurate evaluation of the starting values for Eq. (A6) based on replacing the integral in (A5) by various quadrature formulas. He obtained a system of three linear equations for $M(t_1)$, $M(t_2)$, and $M(t_3)$. In our case these equations have the following form:

$$\ddot{y}(t_1) + \tfrac{9}{24}\Delta t \dot{y}(t_1)\, M(t_0) = -M(t_1) - \tfrac{5}{24}\Delta t \dot{y}(t_1)\, M(t_2) - \tfrac{1}{24}\Delta t \dot{y}(t_2)\, M(t_3)$$

$$\ddot{y}(t_2) + \tfrac{1}{3}\Delta t \dot{y}(t_2)\, M(t_0) = -\tfrac{4}{3}\Delta t \dot{y}(t_1)\, M(t_1) - M(t_2)$$

$$\ddot{y}(t_3) + \tfrac{3}{8}\Delta t \dot{y}(t_3)\, M(t_0) = -\tfrac{9}{8}\Delta t \dot{y}(t_2)\, M(t_1) - \tfrac{9}{8}\Delta t \dot{y}(t_1)\, M(t_2) - M(t_3)$$

where Δt is the time increment and t_0, t_1, t_2, and t_3 are the first four time steps of $y(t)$.

We used the Gauss–Seidel algorithm with Pivot search and reiteration to solve this set of equations.

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