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Determination of the Friction Coefficient via the Force Autocorrelation Function. A Molecular Dynamics Investigation for a Dense Lennard-Jones Fluid

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For a large region of dense fluid states of a Lennard-Jones system, we have calculated the friction coefficient by the force autocorrelation function of a Brownian-type particle by molecular dynamics (MD). The time integral over the force autocorrelation function showed an interesting behavior and the expected plateau value when the mass of the Brownian particle was chosen to be about a factor of 100 larger than the mass of the fluid particle. Sufficient agreement was found for the friction coefficient calculated by this way and that obtained by MD calculations of the self-diffusion coefficient using the common relation between these coefficients. Furthermore, a modified friction coefficient was determined by integration of the force autocorrelation function up to the first maximum. This coefficient can successfully be used to derive a reasonable "soft part" of the friction coefficient necessary for the Rice–Allnatt approximation for the shear viscosity of simple liquids.

KEY WORDS: Transport coefficients; kinetic theory; Brownian dynamics; time-dependent properties of liquids and fluids; molecular dynamics; diffusion.

1. INTRODUCTION

In a previous work,(1) we compared the Rice–Allnatt theory with exact molecular dynamics results for the shear viscosity of dense fluids. The Rice–Allnatt equations require the "soft" part of the friction coefficient ζ_s for the evaluation of the shear viscosity constant. So we attempted to calculate ζ_s directly by MD using a Brownian-type particle. As these computations led partly to inconsistent results in comparison with those obtained by the self-

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diffusion coefficient, we undertook a systematic investigation to elucidate these differences between the values of the friction coefficient obtained by these two methods. To compute ζ via the motion of a Brownian-type particle we used the time integral over the force autocorrelation function (FACF), but integrated only over a certain period of time. This method can be derived from the properties of the Langevin equation. It will be described in detail in later sections. The time integral over the FACF was already discussed by Kirkwood and coworkers(2) and since that time has often been cited in later research.(3–5) We know, however, of no attempt to calculate this quantity by MD, with the exception of the work of Fisher *et al.*(6) These authors did compute the total FACF by MD, but considered a fluid particle itself and could not obtain sufficient information on ζ.

2. DEFINITION OF THE FRICTION COEFFICIENT BY THE LANGEVIN EQUATION

The motion of one Brownian particle in a liquid is describable by the ordinary Langevin equation. The Brownian particle is thereby idealized in the sense that it is large and massive enough to experience a resistive force corresponding to Stokes' law and that it is small enough to respond to fluctuations of the fluid molecules. We give the stochastic equation in terms of the total force $\mathbf{F}(t)$ acting on that particle:

$$\mathbf{F}(t) = \mathbf{X}(t) - (\zeta/M)\,\mathbf{p} \tag{1}$$

where ζ denotes the friction coefficient, M the mass of the Brownian particle, $\mathbf{p}$ the momentum, and $\mathbf{X}(t)$ the fluctuating force with statistical properties.

The $\mathbf{X}(t)$ is assumed to vanish in the mean, to be uncorrelated with the velocity, and to have an infinitely short correlation time (see, for instance, Ref. 7, p. 275).

By integrating Eq. (1), we can derive an expression of the following form for the total FACF (Ref. 3, pp. 258–260):

$$\begin{aligned}&\langle \mathbf{F}(t)\,\mathbf{F}(t+\tau)\rangle_{(1)}\\&\quad = 3\varphi(\tau) - 3kT(\zeta^2/M)\,e^{(\zeta/M)\tau} + (\zeta/M)^2\,e^{-(\zeta/M)(2t+\tau)}(p_0^2 - 3MkT)\end{aligned} \tag{2}$$

where the $\langle\cdots\rangle_{(1)}$ denotes the average over particles with initial momentum $\mathbf{p}_0$, $\varphi(\tau)$ denotes a sharply peaked function of time τ, proportional to ζ, compared to the time scale of the Brownian motion (Ref. 3, pp. 256–259; Ref. 8), k is the Boltzmann constant, and T is the equilibrium temperature.

In the limit of a particle of very large size and mass compared with the fluid particles, Eq. (2) gives the correct description of the FACF. However in a MD computation, this equation can only hold approximately, since the large size of the particle cannot be modeled by MD without changing appreciably the molecular interaction.

Integration of Eq. (2) over τ shows that the first two terms on the right-hand side cancel (compare Ref. 3, pp. 256–259) and the third term yields

$$\int_0^\infty \langle \mathbf{F}(r)\,\mathbf{F}(t+\tau)\rangle_{(1)}\,d\tau = (\zeta/M)\,e^{-2(\zeta/M)t}(p_0^2 - 3MkT)$$

and proceeding to the average over initial momenta, we find

$$\int_0^\infty \langle \mathbf{F}(0)\,\mathbf{F}(\tau)\rangle\,d\tau = 0 \tag{3}$$

So in this limit, we lose the information about ζ. However, if $\varphi(\tau)$ is in fact a rapidly decaying time function relative to the time scale involved in the Brownian motion, Eq. (2) can be exploited for a determination of ζ. After averaging over the initial momenta, the equilibrium value of the FACF is given by the first two terms of the right-hand side of Eq. (2) if we have the following conditions:

(i) $\varphi(\tau) = 0 \quad \text{for} \quad \tau > \tau_1$

where τ_1 denotes the correlation time of the fluctuating force $\mathbf{X}(t)$, and

(ii) $\tau_1 \ll M/\zeta$

where M/ζ is the decay rate of exponentials appearing in Eq. (2).

In that case, the total FACF has large, positive values at short times and small, negative values for longer times. The integral of $\langle \mathbf{F}(0)\,\mathbf{F}(\tau)\rangle$ is given by (Ref. 3, pp. 256–259)

$$I(\tau_2) = 3\int_0^{\tau_2} \varphi(\tau)\,d\tau + 3\zeta kT(e^{-(\zeta/m)\tau_2} - 1) \tag{4}$$

where τ_2 denotes an arbitrary time, $0 \leqslant \tau \leqslant \tau_2$. The first term of the right-hand side of Eq. (4) reaches its maximum value very quickly, while the second term is still small. We have

$$I(\tau_2) = 3\zeta kT[1 - (\zeta/m)\tau_2 + \cdots] \approx 3\zeta kT$$

where we have used the relation

$$\int_0^{\tau_2} \varphi(\tau)\,d\tau \approx \int_0^\infty \varphi(\tau)\,d\tau$$

So the integral of the total force autocorrelation function reaches a "pseudoplateu," from which it falls back to zero in times of order (M/ζ). The friction coefficient should therefore be calculable by the integral of the total FACF for a certain period of time τ_2:

$$\zeta = \frac{1}{3kT} \int_0^{\tau_2} \langle \mathbf{F}(0)\, \mathbf{F}(\tau) \rangle \, d\tau; \qquad \tau_2 < \tau_1 \ll \frac{M}{\zeta} \tag{5}$$

3. FORCE AUTOCORRELATION FUNCTION FOR A FLUID PARTICLE

Before discussing the described method for determining ζ, we illustrate by simple equilibrium molecular dynamics calculations (MDC) that this method cannot be applied to a fluid particle itself. In that case the autocorrelation function of the projected force has to be used[9] (see discussion in Section 7).

Our MDC were performed for 256 particles in the $NVE\mathbf{p}$-ensemble, where N denotes the particle number, V the volume, E the total energy, and $\mathbf{p}$ the total momentum of the system. The particles were enclosed

Table I. Technical Details of the MD Calculations

A. MD	
Particle numbers	256; 500; 864
Equilibration time steps	500–1500
Production time steps	5000 for fluid particle correlation functions) 50,000–80,000 (for correlation functions of the Brownian-type particle)
Time step	1×10^{-14} sec($\hat{=} 0.032[m\sigma^2/(48\varepsilon)]^{1/2}$; m the atomic mass of argon)
Cutoff radius	2.5σ
Number of uncorrelated time origins for the correlation functions of the Brownian-type particle	2500–4500
B. Pair potential	
Lennard-Jones (12–6) with argon parameters	
ε/k (k the Boltzmann constant)	119.8 K
σ	3.405 Å
C. Reduced quantities	
$n^* = (N/V)\sigma^3$ (V the volume of the system)	
$T^* = Tk/\varepsilon$	

in a cubic box with periodic boundary conditions. The Störmer–Verlet integration algorithm was used and the pair potential was represented by the commonly employed Lennard-Jones (12–6) potential. Table I contains information about the details of the runs and the potential.

It should be noted that the results obtained for the correlation function (CF) of a fluid particle did not require more than 2 min CPU time(s) of a vector computer like the Cyber 205. This is in sharp contrast to the calculations described in later sections. Though the CF of the fluid particle was determined previously by Fisher and Watts$^{(6)}$, we have recalculated it to have the reference for our chosen thermodynamic state of $n^* = 0.85$ and $T^* = 1.0$.

In Fig. 1 we plot the FACF of a model fluid particle as a function of time together with the time integral over this CF. In agreement with the considerations of Section 2 and with earlier MD computations,$^{(6)}$ we find:

1. The FACF has large positive and negative parts at short times of about 0.2 psec. The area below the positive part of the FACF and the area above the negative part cancel each other and thus the integral over times larger than 0.2 psec vanishes.

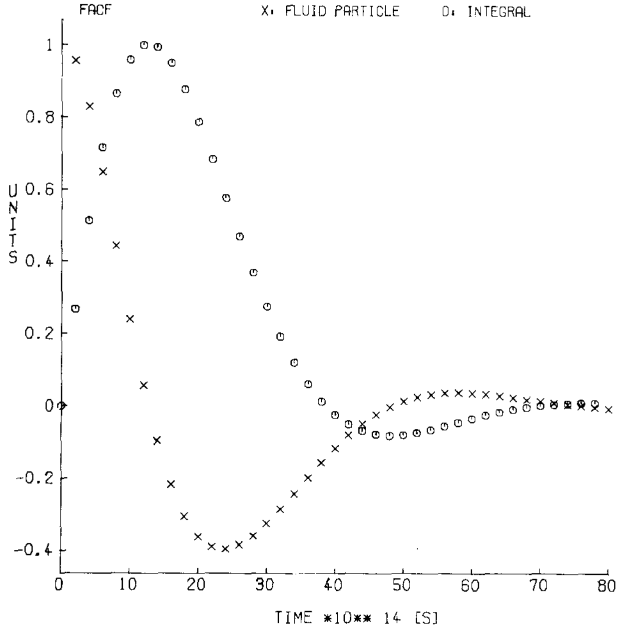

Fig. 1. (×) Force autocorrelation function and (○) the time integral over this function of a fluid particle. Both functions have been normalized: the FACF by its initial value, the integral by its maximal value. Thermodynamic state: $n^* = 0.85$, $T^* = 1.0$.

2. The integral over the FACF increases and decays rapidly, showing no plateau value.

3. The correlation time of the fluctuating force τ_1 might be of the order of the decay time of the FACF (decay for $1/e$), being ~ 0.15 psec.

Since we have chosen a fluid particle of mass m for the determination of the FACF, we are not able to find a time τ_2 such that

$$\tau_1 < \tau_2 \ll m/\zeta \tag{6}$$

is valid.

In the argon model studied, we have roughly a value of 0.5 psec for m/ζ and a value of 0.2 psec for τ_1. So the second relation of (6) is violated and the integral cannot show a plateau-type behavior. This is indeed the finding illustrated in Fig. 1. A determination of ζ by the total FACF of the fluid particle is thus impossible.

4. MOLECULAR DYNAMICS FOR A BROWNIAN PARTICLE OF THE MODEL FLUID

From the results of Section 3 we conclude that the mass of the Brownian particle must be of order ten times the mass of the fluid particle to generate an integral over the FACF that shows a plateau-type behavior. For $M/m = 20$, we have M/ζ of about 10 psec, while the correlation time of the fluctuating force remains at $\tau_1 \approx 0.15$ psec. So we can easily find a time s such that $0.15 < s \ll 10$ psec is valid. Enhancement of the mass of all the fluid particles will not help, since then τ_1 grows equivalently. The separation of the time scales of the Brownian and the fluid particles is of course substantial.

Consequently, we have performed MD for 255 fluid particles and one Brownian particle, the latter differing only in mass from the others. However, calculations of this type are substantially more extensive than those reported in the previous section. The correlation function must be evaluated from the trajectory of the massive particle alone. Therefore, the averaging level can only be enhanced by extending this trajectory in time. We indeed used runs of 50,000–80,000 integration steps to ensure 2500–4000 uncorrelated time origins for an accurate evaluation of the CF (see Table I).(10)

For two different temperatures at the same density of $n^* = 0.85$, we have plotted the FACF of the Brownian particle for mass ratios of $M/m = 60$ and 100 in Fig. 2 and 3. The plots confirm roughly what we expected from the discussion in Section 2. A positive part of the FACF appears for the time interval between 0 and 1.5 psec, while for larger time

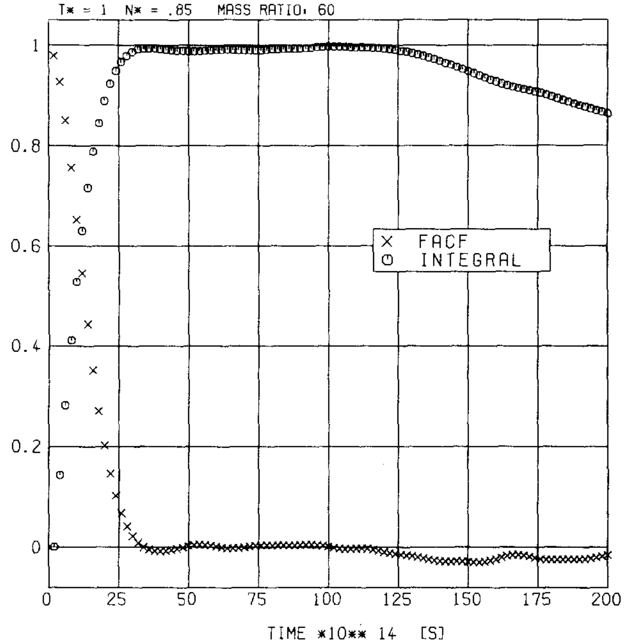

Fig. 2. As in Fig. 1, but for a Brownian-type particle.

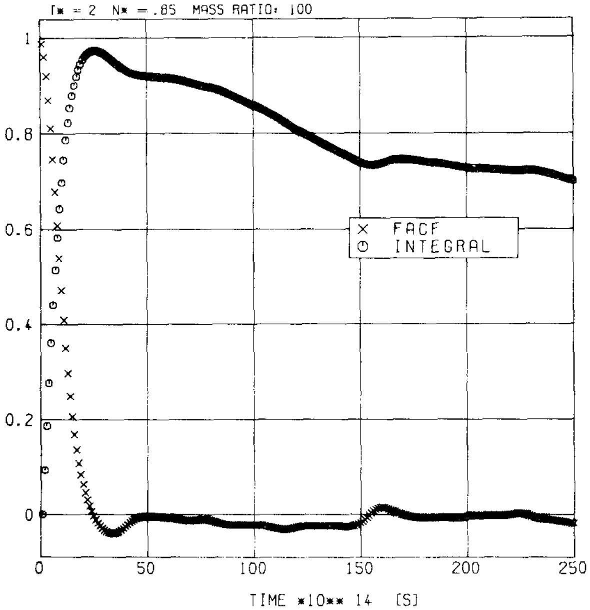

Fig. 3. As in Fig. 2, but for $T^* = 2$.

the function becomes negative, but with a very small amplitude. The integrals over the FACF, which are also displayed in these figures, show a maximum near 0.25 psec and a pseudoplateau near .75 and 2.0 psec. For later time, the integral decays markedly, as is only seen in Fig. 2.

In Fig. 4, we compare the velocity autocorrelation function (VACF) of the Brownian and the fluid particles for $T^* = 1$. The large separation of the two times scales is evident, being characteristic of Brownian motion. We see additionally that the VACF of the massive particles is to a good approximation exponential (Ref. 3, pp. 437–443).

We have checked the mass dependence of the plateau value of the integral. Results are compared in Figs. 5 and 6, where for three different mass ratios the integral value is plotted as a function of time. Apparently for $T^* = 1$ the mass ratio of 16 and for $T^* = 2$ that of 20 do not suffice to produce a plateau. On the other hand, for mass ratios larger than 40 and larger than 100 in the case of $T^* = 2$ the plateau value is accessible by MD calculations and seems to be independent of the mass ratio, at least within the statistical error of the computation.

However, the mass ratio must not be enhanced too much, since then the dynamics of the Brownian particle is violated, since it is not able to follow the erratic motion of the fluid particles on a discrete time scale. We

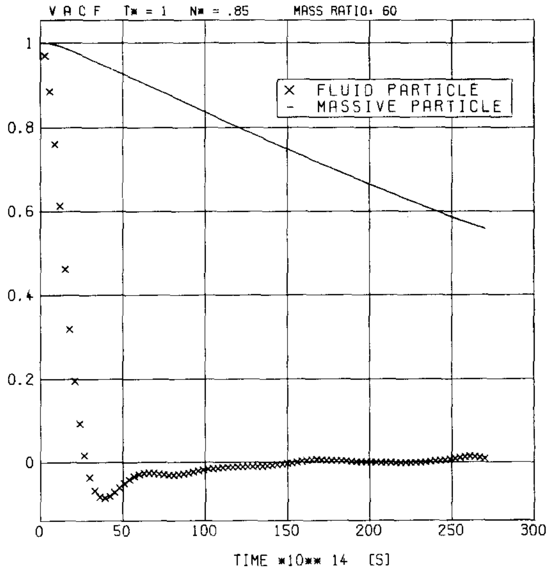

Fig. 4. Velocity autocorrelation function of a fluid particle (× × ×) and the Brownian particle. Both functions are normalized by their initial values. Mass ratio: 60. State: $n^* = 0.85$, $T^* = 1.0$.

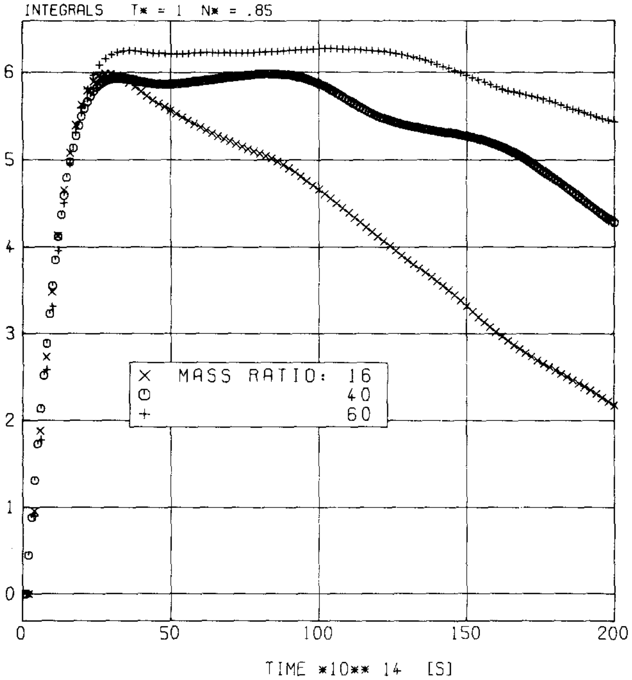

Fig. 5. Integral value of the FACF of the massive particle for mass ratios 16, 40, and 60 normalized to give the friction coefficient in 10^{-13} kg sec^{-1}.

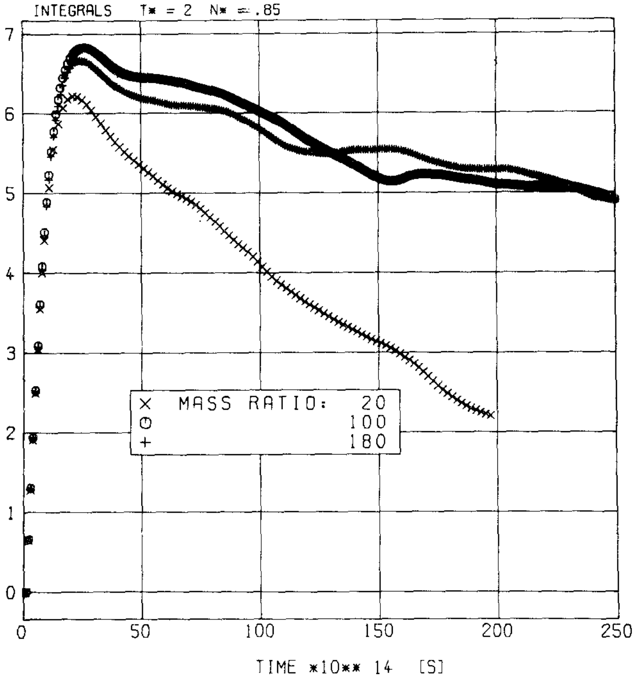

Fig. 6. As in Fig. 5, but for $T^* = 2$ and mass ratios of 20, 100, and 180.

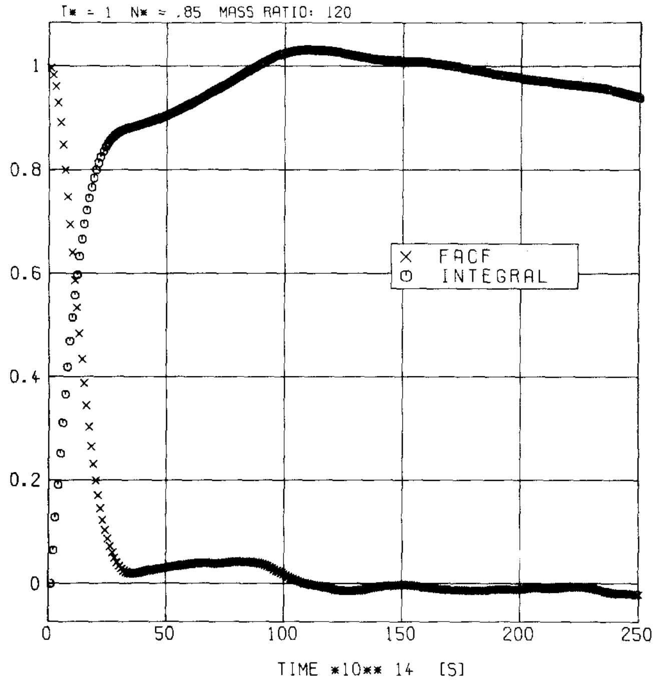

Fig. 7. As in Fig. 2, but for the mass ratio 120.

illustrate this by plots of the FACF and the integral for $T^* = 1$ and $M/m = 120$ in Fig. 7. Here the FACF shows a perturbed behavior around 0.25 psec, and consequently the integral has no plateau value.

5. COMPARISON OF THE FRICTION COEFFICIENT CALCULATED BY THE FACF AND BY THE SELF-DIFFUSION COEFFICIENT

We have calculated ζ using the pseudoplateau value of the integral over the FACF for 3–5 temperatures and reduced densities of 0.70–0.85. Simultaneously we have determined the self-diffusion coefficient D via the VACF of the fluid particle, which we have integrated over a time of 2.4 psec (compare Fig. 4). Using the relation

$$\zeta = kT/D \tag{7}$$

we obtained a second number for ζ, which has a statistical error of 5%. Errors due to temperature differences do not occur, since we used the same runs for the determination of both numbers.

The results for the friction coefficient obtained by these two methods are summarized in Table II. Agreement between both sets of numbers is evident, although deviations of 10% exist. However, these discrepancies lie within the mutual error bars for these quantities. The value given in parentheses represents the result from a computation with a larger particle number. It agrees well with the other data, indicating that a systematic failure is not present. One additional remark sould be in order. All the states considered are liquid or fluid states, which correspond to pressures between 0 and 3000 bar.

6. EVALUATION OF A "SOFT PART" OF ζ USABLE FOR THE RICE–ALLNATT THEORY OF THE SHEAR VISCOSITY OF SIMPLE FLUIDS

To exploit the Rice–Allnatt theory(3,4) for the determination of the shear viscosity η of a fluid, a "soft" and a "hard" part of the friction coefficient ζ_s and ζ_h have to be known. Such a splitting of ζ is not uncritical and a bit arbitrary.(11) We have, however, attempted to determine a reasonable separation of the friction coefficient into these parts by introducing a modified total friction coefficient ζ_m that coincides with ζ for the liquid range, but varies with temperature similar to the "hard" part of ζ. This "hard" part ζ_h is usually evaluated by the formula of Enskog(3,12) (see Appendix). It can also be computed by MD using the FACF of a fluid particle and integrating up to the zero crossing of that function.

Table II. Comparison of Values for the Friction Coefficient Obtained by the FACF of a Massive Particle ($M/m = 60$–180) (Method A) and the Self-Diffusion Coefficient of the LJ Fluid via the VACF (Method B)[a]

	$n^* = 0.85$		$n^* = 0.80$		$n^* = 0.75$	
T^*	*A*	*B*	*A*	*B*	*A*	*B*
0.70	7.4[b]	7.5	—	—	—	—
0.87	6.8	6.5	5.2	4.9	—	—
0.98	6.4 (6.1)[c]	6.4	5.1	4.9	3.95	3.75
1.50	6.2	5.8	4.3	4.6	3.65	3.70
1.97	5.5	5.6	4.6	4.7	3.90	3.70

[a] The statistical uncertainty for the value of the friction coefficient is 8% for method A and 5% for method B.

[b] In Units of 10^{-13} kg sec^{-1} [divide by 2.1404×10^{-13} to convert into reduced units of $(48m\varepsilon/\sigma^2)^{1/2}$].

[c] From computations with 864 particles.

Commonly the "soft" part of ζ is obtained by subtraction of ζ_h from ζ, with ζ computed by numerical methods or taken from experiment. Using this difference, one finds an unreasonably steep decay of ζ_s with temperature when ζ is obtained from MD by any of the computations described in Section 5. To avoid this strong decrease of ζ_s with temperature, which causes disagreement between predictions of η by the Rice–Allnatt theory and MD results, we introduced a modified total friction constant ζ_m determined by the integral of the FACF of a massive particle up to the first maximum value. This can be done by MD calculations with a high accuracy of 3–5%. The reasons for this are: (i) the maximum of the FACF is always well determinable for mass ratios of 15–60 for the Brownian particle; (ii) the mass dependence of the integral value at this maximum is nearly a linear function of m/M; (iii) extrapolation of the integral value to $m/M=0$ is easily done with a few computations for different mass ratios. An example is presented in Fig. 8, where for three temperatures and at a density of 0.85, the integral value, i.e., the friction coefficient ζ_m, is plotted against the inverse mass ratio. Table III contains the extrapolated values for $m/M=0$ together with ζ_h computed from the Enskog formula (see Appendix). The difference between ζ_m and ζ_h yields a "soft" part of the friction coefficient ζ_s that is approximately independent of temperature in the range investigated here. With this ζ_s, the Rice–Allnatt equations predict

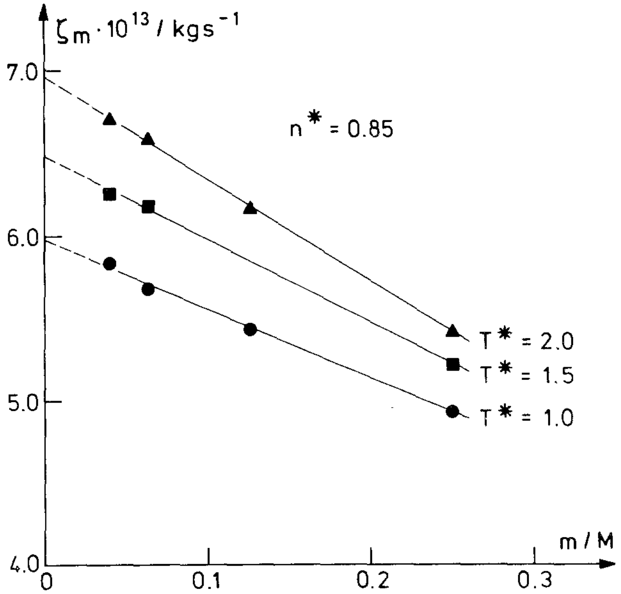

Fig. 8. Modified friction coefficient ζ_m determined by the FACF as a function of the inverse mass ratio m/M for various thermodynamic states.

Table III. Modified Friction Coefficient ζ_m Determined by MD Compared with the "Hard" Part of the Friction Coefficient Calculated by the Enskog Equation

T^*	ζ_m 10^{-13} kg sec^{-1}	ζ_m 10^{-13} kg sec^{-1}
0.75	5.9	3.32
0.90	6.1	3.46
1.0	6.0	3.51
1.5	6.5	3.75
2.0	6.9	3.94

[a] $n^* = 0.85$. Statistical error for ζ_m is 5%.

fairly well the density and temperature dependence of the shear viscosity in the fluid and liquid region of the LJ system compared with direct MD results.(1)

For illustration of the temperature dependence of ζ_s and ζ_h, we show these quantities as a function of the reduced temperature in Fig. 9.

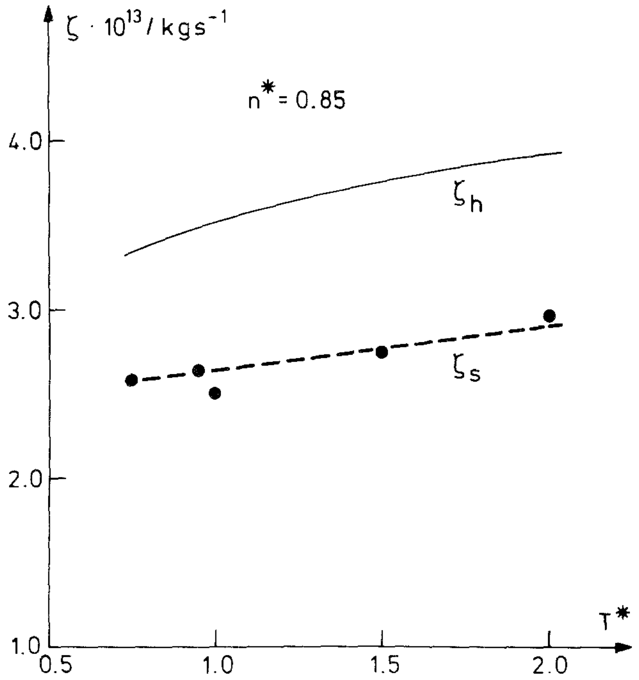

Fig. 9. "Soft" and "hard" parts of the friction coefficient determined by MD and calculated by the Enskog equation.

7. DISCUSSION AND CONCLUSIONS

We have shown that the friction coefficients obtained by integration of the FACF of a Brownian-type particle and calculated by the self-diffusion coefficient of the fluid agree well when mass ratios of 60–180 are used. For all the states investigated, we found a first maximum of the integral over the FACF near 0.25 psec and a pseudoplateau value after about 1 psec for mass ratios of 20–60. This first maximum of the integral value was exploited to determine a second modified friction coefficient, which agrees with the genuine ζ in the liquid range of the model system, but has a different temperature dependence. While the latter decreases with temperature, the former grows slightly. The modified friction coefficient involves a larger, "hard" contribution, which governs its temperature dependence at high-temperature states. This is nicely confirmed by Fig. 3, which displays that the maximum of the integral value is about 20% higher than the pseudoplateau value due to the fact that the negative part of the FACF (also shown in the figure) does not contribute to the maximum. Such a behavior of ζ_m is better suited for the Rice–Allnatt theory, which seems to require a very weak temperature dependence of the "soft" part of the coefficient, as we have shown by comparison with "exact" machine data.(1,11)

The computations of ζ via the force autocorrelation function will be continued using a fluid particle itself. However, in that case, we have to consider the generalized Langevin equation, of which the generalized dissipation coefficient is given by(9)

$$\tilde{\gamma}(s) = \frac{\tilde{\phi}(s)}{1 - s^{-1}\tilde{\phi}(s)}$$

$\tilde{\phi}(s)$ is the Laplace-transformed autocorrelation function of the generalized force.

APPENDIX

The "hard" part of the friction coefficient ζ_h can be calculated by the Enskog relation(3,12)

$$\zeta_h = \tfrac{8}{3}\zeta d^2 g(d)(\pi m k T)^{1/2}$$

where $g(d)$ denotes the hardsphere pair correlation function at the hard sphere parameter d of the equivalent hard sphere potential, ρ denotes the number density, m the particle mass, k the Boltzmann constant, and T the temperature of the system. Using the criterion of Weeks *et al.*(13,14) for d, one can easily evaluate the ζ_h value with the perturbation approximation for $g(r)$. We have applied the Baxter formalism for $g(r)$ with the Percus–Yevick closure.(15,16)

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