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Computation of the viscosity of a liquid from time averages of stress fluctuations

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The shear viscosity can be calculated from the standard deviation of an equilibrium ensemble of time averages of the shear stress computed along finite duration phase space trajectory segments. The mean square of the segment averages of the shear stress is proportional to the shear viscosity and inversely proportional to the duration of the trajectory segments and the number of particles. We test the fluctuation relation for the shear viscosity and show that it provides a simple but viable means of computing the zero strain rate shear viscosity. We decompose the shear viscosity computed using this fluctuation method, into its ‘‘kinetic’’ and ‘‘configurational’’ components. We also calculate the relevant relaxation times. We compare the computed results with standard nonequilibrium molecular dynamics simulations. Finally we compute the bulk viscosity using an analogous fluctuation method.

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I. INTRODUCTION

According to Green and Kubo [1], linear transport coefficients can be expressed as integrals over the appropriate time correlation functions. The time correlation functions have been computed in molecular dynamics (MD) simulations and transport coefficients were obtained by the Green-Kubo method for about the last 30 years [2–6]. Without explicitly calculating the time correlation function, the integral required for the transport coefficient can be computed from an analysis of time-segment averages of the relevant fluctuating quantity. Here we demonstrate that the shear viscosity of a fluid can be inferred from ensemble averages of the mean square of time averages of the stress fluctuations. For a particular state point of a Lennard-Jones type model fluid, the ‘‘kinetic’’ and ‘‘potential’’ (‘‘configurational’’) contributions, as well as the ‘‘total’’ shear viscosity are calculated. The numerical values agree, within statistical uncertainties, with the corresponding results, obtained in the small shear rate limit of nonequilibrium molecular dynamics (NEMD) simulations. We also present values for correlation or relaxation time coefficients, obtained by dividing the viscosities by the relevant (high frequency) elastic moduli, which are calculated in the simulation. We use the present method also to determine the bulk viscosity.

II. BASICS OF THE METHOD

A. Pressure and stress tensor

Consider a system composed of N spherical particles with mass m and position vectors $\mathbf{r}^i$, $i=1,\dots,N$ in a volume V. The number density is $n=N/V$. In the molecular dynamics simulations, periodic boundary conditions and the ‘‘minimum image convention’’ are used in order to avoid boundary layer effects [5,6].

In a streaming fluid, the stationary rheological properties such as the (non-Newtonian) viscosity and the normal pressure differences are obtained from long time averages of the Cartesian components of the stress tensor $\sigma_{\mu\nu}=-p_{\mu\nu}$ or of the pressure tensor $p_{\mu\nu}$ which is the sum of kinetic und potential contributions: $p_{\mu\nu}=p^{kin}_{\mu\nu}+p^{pot}_{\mu\nu}$,

$$p^{kin}_{\mu\nu}=V^{-1}\sum_i mc^i_\mu c^i_\nu, \quad p^{pot}_{\mu\nu}=V^{-1}\frac{1}{2}\sum_{ij} r^{ij}_\mu F^{ij}_\nu. \tag{1}$$

Here $\mathbf{c}^i$ is the peculiar velocity of particle i, i.e., its velocity relative to the flow velocity $\mathbf{v}(\mathbf{r}^i)$, $\mathbf{r}^{ij}=\mathbf{r}^i-\mathbf{r}^j$ is the relative position vector of particles i,j and $\mathbf{F}^{ij}$ is the force acting between them. The Greek subscripts μ,ν, which assume the values 1, 2, 3, stand for Cartesian components associated with the x,y,z directions.

B. Stress fluctuation formula for the viscosity

In an equilibrium situation where one has $\mathbf{v}=0$, the shear stress, i.e., the off-diagonol components of the stress tensor, e.g., $\sigma=-p_{12}$ and the normal stress differences, e.g., $p_{22}-p_{11}$ fluctuate about zero and their long time averages vanish. The mean square average of these fluctuating quantities depends on the averaging time t_{av} [7].

More specifically, the definition of a time-segment average

$$\overline{\sigma}(t_{av})=t_{av}^{-1}\int_0^{tav}\sigma(t)dt \tag{2}$$

is introduced. The time dependence of $\sigma(t)=-p_{12}(t)$ stems from the time dependence of the positions and momenta of the particles, cf. Eq. (1). It is understood that the integration limits 0 and t_{av} can be replaced by t_0 and t_0+t_{av} provided that these times are also within the time span for which the phase space trajectory is available. The mean square average is given by

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$$\langle \overline{\sigma}(t_{av})^2\rangle = t_{av}^{-2}\int_0^{t_{av}} dt \int_0^{t_{av}} dt' \langle \sigma(t)\sigma(t')\rangle$$

$$= 2t_{av}^{-1}\int_0^{t_{av}} dt \langle\sigma(t)\sigma(0)\rangle. \qquad (3)$$

The angular brackets $\langle \cdots \rangle$ indicate an ensemble averge, $\langle \overline{\sigma}(t_{av})\rangle = 0$ has been assumed. The second equality of Eq. (3) applies to a stationary situation where $\langle\sigma(t)\sigma(t')\rangle$ depends on the time difference $t-t'$ only. The factor 2 stems from replacing an integral from $-t_{av}$ to t_{av} by two times the integral from 0 to t_{av}, based upon the assumption that the equilibrium fluctuations cannot distinguish between ''past'' and ''future,'' i.e., $\langle\sigma(t)\sigma(0)\rangle = \langle\sigma(-t)\sigma(0)\rangle$. A charcteristic stress relaxation time τ is defined by $\int_0^\infty dt\langle\sigma(t)\sigma(0)\rangle = \tau\langle\sigma(0)\sigma(0)\rangle$. Provided that the averaging time t_{av} is large compared with the relaxation time τ, the mean square stress fluctuation is inversely proportional to the averaging time. Compared with the mean square fluctuation of the instantaneous quantity $\langle\sigma(0)^2\rangle$, the mean square fluctuation of the correponding time averaged quantity is reduced by the factor $2\tau t_{av}^{-1}$ [7].

In the same limit, $t_{av} \gg \tau$, the Green-Kubo formula for the shear viscosity $\eta = (N/nk_BT)\int_0^\infty dt\langle\sigma(t)\sigma(0)\rangle$ can be used to rewrite Eq. (3) as an expression applicable for the computation of the viscosity from the mean square of the fluctuations of the time averaged shear stress:

$$\eta = t_{av}(2nk_BT)^{-1}N\langle\overline{\sigma}(t_{av})^2\rangle. \qquad (4)$$

This is the key formula which is used here to compute viscosity coefficients. Recently, it has been derived from a more general fluctuation theorem [8].

As a side remark, it is mentioned that Eq. (4) can also be looked upon as an ''Einstein'' relation for the computation of the (total) viscosity, analogous to Einstein's prescription for the computation of the diffusion coefficient from the mean square displacement. To see this, notice that the total pressure tensor $p_{\mu\nu}$, for $\mathbf{v}=0$, is the time derivative of the tensor $V^{-1}q_{\mu\nu}$ with $q_{\mu\nu} = \Sigma_i m r^i_\mu c^i_\nu$. Thus one has $-t_{av}V\overline{\sigma}(t_{av}) = q_{12}(t_{av}) - q_{12}(0) = \Delta q_{12}(t_{av})$ and Eq. (4) is equivalent to $\eta = t_{av}^{-1}(2Vk_BT)^{-1}\langle\Delta q_{12}(t_{av})^2\rangle$. Problems associated with the application of Einstein-like expressions for the computation of transport coefficients are pointed out in Ref. [9]. The method presented here is intermediate between the conventional Green-Kubo and Einstein methods. Einstein relations do not exist for the partial viscosity coefficients, to be discussed next, which are of interest in connection with kinetic theory [10].

C. Kinetic and potential contributions

As stated above, the stress is the sum of kinetic and potential contributions. In molecular dynamics simulations, the contributions $\overline{\sigma^{kin}}(t_{av})$ and $\overline{\sigma^{pot}}(t_{av})$ can be extracted seperately. The viscosity coefficients $\eta^{(kk)}, \eta^{(kp)} = \eta^{(pk)}$, and $\eta^{(pp)}$ can be calculated in analogy to Eq. (4) with $\overline{\sigma}(t_{av})^2$ replaced by $[\overline{\sigma^{kin}}(t_{av})]^2$, $\overline{\sigma^{kin}}(t_{av})\overline{\sigma^{pot}}(t_{av})$, and $[\overline{\sigma^{pot}}(t_{av})]^2$, respectively. It is understood that the quantities multiplied in the cross term pertain to the same time segment of a phase space trajectory. The viscosities η^{kin} and η^{pot} which can be computed in NEMD simulations by dividing the kinetic and the potential parts of the shear stress by the imposed shear rate are, in the small shear rate limit, linked with the partial viscosity coefficients $\eta^{(kk)}$, etc., obtained via the fluctuation formula, by

$$\eta^{kin} = \eta^{(kk)} + \eta^{(kp)}, \quad \eta^{pot} = \eta^{(pp)} + \eta^{(kp)}. \qquad (5)$$

The total viscosity is also given by

$$\eta = \eta^{kin} + \eta^{pot} = \eta^{(kk)} + 2\,\eta^{(kp)} + \eta^{(pp)}. \qquad (6)$$

Notice that $\eta, \eta^{(kk)}$, and $\eta^{(pp)}$ are positive, as inferred from the stress fluctuation expressions for these quantities. The coefficient $\eta^{(kp)}$, on the other hand, can have either sign. Its magnitude, however, is bounded according to $(\eta^{(kp)})^2 < \eta^{(kk)}\eta^{(pp)}$, since positive entropy production requires the total shear viscosity η to be positive. The kinetic contribution to the viscosity dominates in dilute gases [11]. In dense fluids (liquids) the potential contribution is more important.

D. Shear modulus, relaxation times

In the fluid phase, the mean square average of the instantaneous potential part of the shear stress is related to the high frequency shear modulus G by $\langle(\sigma^{pot}(0))^2\rangle = N^{-1}nk_BTG$. Incidentally, this expression can be derived from standard thermodynamic fluctuation theory for a linear elastic medium with a shear modulus G. When applied to a fluid, where the low frequency elastic modulus vanishes, one has to use the high frequency shear modulus, instead. This quantity, sometimes referred to as ''Maxwell shear modulus,'' can also be computed by the Born-Green expression which is the average of a two-particle quantity, viz.

$$G = \frac{1}{15V}\left\langle \sum_{i<j} [r^{-2}(r^4\phi')']^{ij} \right\rangle. \qquad (7)$$

The prime denotes the derivative with respect to r. The low frequency shear modulus is the difference between the Born-Green and the fluctuation expressions given above. Both have equal magnitude for a system in the fluid (but not in the solid) state [12].

Division of the viscosity $\eta^{(pp)}$ by the shear modulus G yields the ''Maxwell'' relaxation time $\tau^{(pp)}$. In connection with the kinetic part, nk_BT plays the role of G, for the cross term it is $(nk_BTG)^{1/2}$, thus

$$\eta^{(kk)} = nk_BT\tau^{(kk)}, \quad \eta^{(kp)} = (nk_BTG)^{1/2}\tau^{(kp)}, \quad \eta^{(pp)} = G\tau^{(pp)}. \qquad (8)$$

Next, the formulas given are tested for a simple model fluid. First, its verified that the mean square of the time averaged contributions to the shear stress are inversely proportional to the averaging time. Then the various viscosity and relaxation time coeffiencts are calculated.

III. MOLECULAR DYNAMICS

A. The potential

For the test calculations, the short range attractive potential, referred to as the ''SHRAT'' potential,

$$\phi^{SHRAT}(r)=(512/27)\Phi_0(1-r/r_0)(3-2r/r_0)^3, \quad r\leqslant 1.5r_0, \tag{9}$$

and $\phi^{SHRAT}(r)=0$ for $r>1.5r_0$, is used. The quantities Φ_0 and r_0 set the characteristic energy and length scales. The intersection with the horizontal axis and the depth of the potential minimum, occurring at $r=1.125r_0$, are analogous to that of the Lennard-Jones (LJ) potential. In units of Φ_0/r_0, the force at $r=r_0$ is $512/27\approx 19$. The corresponding value for the LJ potential is 24. Here, the cutoff is rather short ranged and smooth, such that not only the potential but also its first and second derivatives vanish at the cutoff distance. Notice that this potential is finite at $r=0$, viz. $\phi^{SHRAT}(0)=512\Phi_0$. For temperatures less than $10\Phi_0/k_B$, this is of no practical concern since the Boltzmann factor $\exp(-\Phi_0/k_BT)$ governing the fraction of particles which can reach this distance is smaller than 6×10^{-23}. In numerical calculations and in the graphs displayed here, all physical quantities are expressed in the standard LJ units of, e.g., lengths and energies are given in units of r_0 and Φ_0. Following common practice the dimensionless variables are denoted by the same symbols as the corresponding physical quantities when no danger of confusion exists. In dimensionless notation, the SHRAT potentials reads $\phi^{SHRAT}(r)=(512/27)(1-r)(3-2r)^3$, $r\leqslant 3/2$, whereas $\phi^{SHRAT}(r)=0$ for $r>3/2$. Similarly, the number density $n=N/V$, where N and V are the number of particles and the volume of the system, and the temperature T are expressed in units of $n_{ref}=r_0^{-3}$ and $T_{ref}=\Phi_0/k_B$, respectively. The unit for the pressure is $p_{ref}=\Phi_0 r_0^{-3}$. The reference value for the time is $t_{ref}=r_0/v_{ref}$ where $v_{ref}=(\Phi_0/m)^{1/2}$ is a reference velocity. The reference viscosity is $\eta_{ref}=p_{ref}t_{ref}$.

Thermophysical properties of this model system in its gaseous, liquid, and solid state have recently been calculated [13]. Here results are presented for a state point with the number density $n=0.75n_{ref}$ and the temperature $T=T_{ref}$ which corresponds to a compressed fluid, somewhat above the critical temperature (which is at $0.8T_{ref}$), with a density of more than twice the critical density (about $0.32n_{ref}$) but well below that one where a fcc crystalline solid exists, under a considerably higher pressure, at the same temperature.

B. Simulation details

In the simulations, the equations of motion of $N=4\times 8^3=2048$ particles were integrated with the velocity Verlet algorithm with the time step $\delta t/t_{ref}=0.004$. A cubic simulation box with volume V and periodic boundary conditions were used. Initially, the particles were placed on fcc lattice sites and they had random velocities with a mean square corresponding to the desired temperature $T/T_{ref}=1.0$. For this temperature, kept constant by rescaling the magnitude of the particle velocities which corresponds to the Gaussian constraint of constant kinetic energy, and the constant number density $n/n_{ref}=0.75$, the crystal melts and a fluid state is approached quickly. The system was well equilibrated by running it for 100 LJ time units t_{ref} (corresponding to 25 000 time steps).

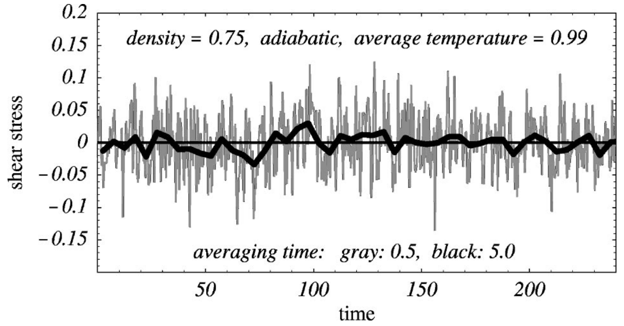

FIG. 1. The fluctuating shear stress (in units of p_{ref}) as function of the time (in units of t_{ref}), pre-averaged over intervals of length $0.5t_{ref}$ (gray curve) and $5.0t_{ref}$ (black curve).

Then the thermostat was turned off and the adiabatic (isoenergetic) simulation was run for $960t_{ref}$, with the quantities of interest computed and recorded in 1920 time intervals of length $0.5t_{ref}$. Within each time intervall, data were actually extracted at every 25th of the 125 time steps. Averaged over the full runtime, the values for the potential energy per particle, the pressure and the (Born-Green) shear modulus are $e^{pot}/\Phi_0=-2.77\pm 0.01$, $p/p_{ref}=1.63\pm 0.04$, and $G/p_{ref}=15.3\pm 0.1$. The average temperature, both computed by the ''kinetic'' and the ''configurational'' expressions [14], is $T/T_{ref}=0.99\pm 0.01$.

C. Fluctuating shear stress

The fluctuating shear stress, preaveraged over $t_{av}=0.5t_{ref}$, as recorded over the first 240 time units, is displayed in Fig. 1 (gray curve). For comparison, the same quantity, but now preaveraged over tenfold longer time in-

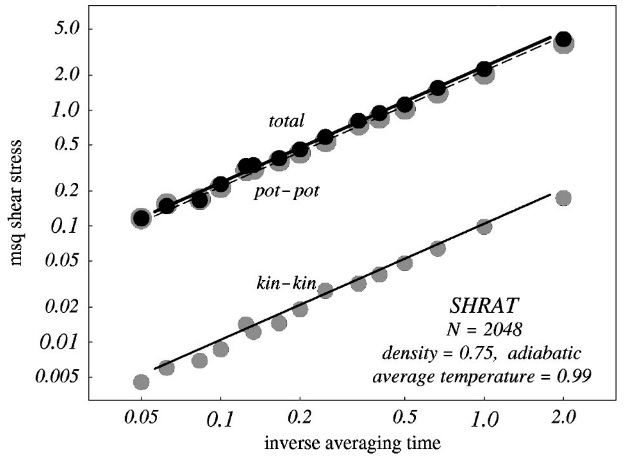

FIG. 2. The ensemble average of the square of the fluctuating shear stress (in units of p_{ref}) as function of the inverse averaging time (in units of t_{ref}). The black, large and small gray dots mark the results for the total shear stress, its potential, and its kinetic parts, respectively.

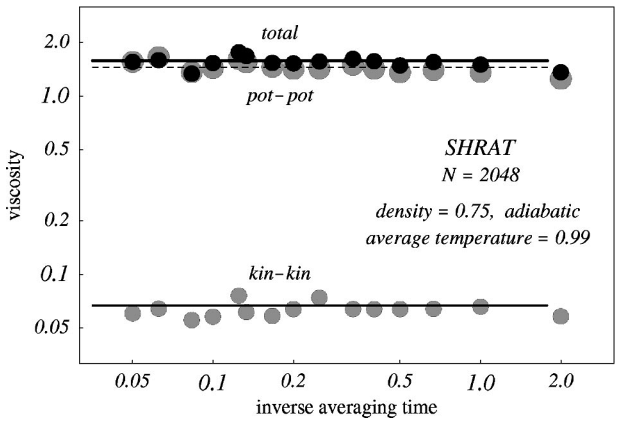

FIG. 3. The shear viscosity (in units of $\eta_{ref}=p_{ref}t_{ref}$) as function of the inverse averaging time (in units of t_{ref}). The black, large, and small gray dots mark the results for the total viscosity, its potential and its kinetic contributions, respectively.

tervals is shown by the thick black curve. Clearly, and as expected, the amplitude of the fluctuations are reduced when t_{av} is larger.

In order to analyze the dependence of the mean square fluctuations of the various contributions to the shear stress, the available data are further averaged in blocks of length 2,3,4,5,6,8,10,12,15,16,20,24,32,40 (divisors of 1920) corresponding to time segments with

$$t_{av}/t_{ref}=1.0,1.5,2.0,\ldots,16.0,20.0.$$

The ensemble average needed to evaluate the mean square fluctuation of the shear stress is provided by an average over the various blocks. Notice that we have 960 of them of length $t_{av}/t_{ref}=1.0$ but only 48 of length $t_{av}/t_{ref}=20.0$.

In Fig. 2, the (logarithm of the) ensemble averages of the mean square of the time average of the shear stress fluctuations, multiplied by the number of particles $N=2048$, are displayed as functions of the (logarithm of the) inverse averaging time t_{av}. The black dots stand for the total shear stress, the large and small gray dots for the potential and the kinetic contributions, respectively. The cross term ''kin-pot'' was also computed. It is positive and still smaller than the ''kin-kin'' part. For clarity of the presentation, it is not shown in the graph. The straight lines (with slope -1) indicate that the mean square fluctuations, for $t_{av}/t_{ref}\geqslant 1.0$ indeed decrease inversely proportional to the averaging time t_{av}, cf. Eq. (3). This proves that the relevant relaxation times are definitely shorter than t_{ref}. Hence the expression (4) can be applied to the computation of the viscosity coefficients.

TABLE II. The relaxation time coefficients, in units of t_{ref}.

τ	$\tau^{(kk)}$	$\tau^{(kp)}$	$\tau^{(pp)}$
0.098 ± 0.006	0.093 ± 0.013	0.009 ± 0.003	0.095 ± 0.005

D. Viscosity coefficients

Shear viscosity coefficients, computed from the mean square fluctuations according to Eq. (4) are displayed in Fig. 3 as functions of the inverse averaging time t_{av} (double logarithmic plot). The black dots mark the total viscosity η, the large and small gray dots stand for $\eta^{(pp)}$ and $\eta^{(kk)}$. The cross term $\eta^{(kp)}$ has also been computed, but is not shown in the graph for the sake of clarity.

The values for the various viscosity coefficients are given in Table I. The averages and deviations have been determined from the relevant time averages with t_{av}/t_{ref} ranging from 1.0 to 20.0. Also listed are, where available, the corresponding values inferred from an NEMD simulation [13]. There the fluid showed an approximate newtonian behavior, i.e., the viscosities were practically independent of the shear rate for shear rates less than $1/t_{ref}$. Data were accumulated and used for determination of the viscosities for shear rates between $10^{-2}t_{ref}^{-1}$ and $1.0t_{ref}^{-1}$. The viscosities obtained by both methods agree well, within the computational uncertainties. Notice that the coefficients which are missing in the NEMD row cannot, in principle, be computed by that method.

Ensemble averages of time averages of the shear stress could also be evaluated for shorter averaging times, comparable to the relaxation time τ. A comparison of the resulting deviations of the points from the straight lines in Fig. 3, with a NEMD calculation of the frequency dependence of the viscosity [16], for frequencies comparable to τ^{-1}, is of interest. This, however, is outside the scope of the present study.

E. Relaxation time coefficients

The viscosity relaxation time τ, obtained by dividing the shear viscosity η by nk_BT+G, as well as the other relaxation time coefficients defined above, are listed in Table II. Except for the cross correlation time $\tau^{(kp)}$, which is smaller than the others by about one order of magnitude, the relaxation time coefficients have rather similar values, of about $0.1t_{ref}$.

The relaxation time $\tau^{(pp)}$ is of particular interest for the kinetic theory, termed ''Stokes-Maxwell'' approach, used to study the shear-induced distortions of the structure of a fluid as revealed in the pair-correlation function or the static structure factor [15].

TABLE I. The viscosity coefficients, in units of η_{ref}, obtained by the present method based on the analysis of stress fluctuations (labeled ''flct''), and by NEMD simulations.

	η	$\eta^{(kk)}$	$\eta^{(kp)}$	$\eta^{(pp)}$	η^{kin}	η^{pot}
flct	1.58 ± 0.08	0.07 ± 0.01	0.03 ± 0.01	1.45 ± 0.08	0.10 ± 0.02	1.48 ± 0.09
NEMD	1.61 ± 0.08				0.12 ± 0.01	1.50 ± 0.07

F. Bulk viscosity

The bulk viscosity η_V has been treated by the same method. Here the deviations of the scalar pressure p (one-third of the trace of the pressure tensor) from its average, viz. $\overline{\delta p}(t_{av}) = \overline{p}(t_{av}) - \langle \overline{p}(t_{av}) \rangle$, with $\overline{p}(t_{av}) = t_{av}^{-1} \int_0^{tav} p(t)dt$, is used in the viscosity expression analogous to Eq. (4), instead of the shear stress. The (preliminary) results are $\eta_V = 1.6 \pm 0.1$, for the total bulk viscosity and $\eta_V^{kk} = 0.012 \pm 0.001$, $\eta_V^{kp} = -0.05 \pm 0.05$, $\eta_V^{pp} = 1.7 \pm 0.1$ for the partial coefficients. The small value found for the ''kk'' part may not be surprising in view of the fact that this coefficient is exactly zero for a dilute gas of particles without internal degrees of freedom. The cross term is also small, but negative. The total bulk viscosity happens to be nearly equal to the shear viscosity. The relaxation time $\tau_V^{(pp)}$, seems to be somewhat larger (by a factor of ≈ 1.5) than the shear relaxation time $\tau^{(pp)}$. These results, however, should be considered as preliminary and a comparison with corresponding NEMD results is needed. For the Lennard-Jones liquid close to the triple point, the bulk viscosity has been computed previously [17] and found to be smaller than the shear viscosity by a factor of about 0.5. The experimentally determined ratio between the bulk and the shear viscosity of liquid argon varies from about 0.6, in the vicinity of the triple point, to over 2, at smaller densities and higher temperatures [18]. So the ratio of about 1 for the viscosities found at the state point studied here is quite plausible. Furthermore, it deserves mentioning that the occurrence of a negative ''cross'' contribution η_V^{kp} to the bulk viscosity has been predicted [17] for soft spheres. The ratios between the various contributions found here, however, differ from the soft spheres values $\eta_V^{kk} : 2\eta_V^{kp} : \eta_V^{pp} = (1/4)\nu^2 : -\nu : 1$ for an interaction potential proportional to $r^{-\nu}$ [17].

IV. CONCLUDING REMARKS

In this paper, it has been demonstrated that the expression (4) involving an ensemble average of the square of time-segment averages of the fluctuating shear stress can be used efficiently to compute the shear viscosity and associated relaxation time coefficients of a fluid. Preliminary results were also given for the bulk viscosity. Generalizations to other transport coefficients, in particular to heat conductivity, as well as to complex fluids, e.g., liquid crystals [18–21] and polymeric liquids [22], as well as to fluids in restricted geometries [23,24], is desirable and feasible. In anisotropic fluids, where preferential directions exist, be it by a spontaneous ordering as in liquid crystals or imposed by external fields or by a wall, the fluctuations of the various Cartesian components of the shear stress will reflect the broken spatial symmetry of the fluid. Then a larger set of coefficients is needed to characterize the anisotropy of the viscosity [21].

A remark on computational demands is in order. Here data were analyzed from a similation run over about 10^4 relaxation times τ. A run time of $10^3\tau$ is the minimal value needed for the determination of a transport coefficient. This means the computation becomes more demanding for systems (complex fluids, e.g., composed of reptating polymers) with relaxtion times which are several orders of magnitude larger than that one encountered here. On the other hand, the ensemble average can also be obtained from shorter (say $10^2\tau$) parallel runs starting from statistically independent initial states. A computation of the viscosity of systems with a relaxation time up to $10^3 t_{ref}$, which requires a total of a few hundred million MD time steps, seems to be feasible by the present method.

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