Crossover between short- and long-time behavior of stress fluctuations and viscoelasticity of liquids

Siegfried Hess,[1] Martin Kröger,[1,2] and Denis Evans[3]
[1]*Institut für Theoretische Physik, Technische Universität Berlin, Hardenbergstrasse 36, D-10623 Berlin, Germany*
[2]*Polymer Physics, Materials Science, ETH Zürich, CH-8092 Zürich, Switzerland*
[3]*Research School of Chemistry, The Australian National University, Canberra ACT 0200, Australia*
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An effective viscosity coefficient is introduced based on definite time averages of equilibrium stress fluctuations rather than stress correlations. Analysis of this quantity via molecular dynamics of a simple model liquid reveals a crossover between the expected short-time elastic and the long-time viscous behavior with increasing averaging time. The procedure allows us to extract the zero-rate shear viscosity when the averaging time becomes one order of magnitude larger than the relevant relaxation time. A relationship between this effective viscosity and the dynamic viscosities is established.

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I. INTRODUCTION

It has been demonstrated that the shear viscosity of a fluid can be inferred from ensemble averages of the mean square of time averages of the stress fluctuations [1,2]. In particular, the long-time behavior of the stress fluctuations was analyzed, where the time averages are taken over times large compared with a stress (Maxwell) relaxation time. Then a simple relation exists with the Green and Kubo [3] expression for linear transport coefficients. In this note we study the crossover between the behavior of stress fluctuations averaged over short times to that where the averaging times are long compared with relevant relaxation time. We present results from molecular dynamics (MD) computer simulations and compare them with analytical considerations for a model liquid where both limiting cases, viz., short and long averaging times, are accessible in the numerical calculations. An effective viscosity coefficient is introduced which depends on the averaging time. Analysis of this quantity reveals the transition from the short-time elastic to the long-time viscous behavior. The relation of the effective viscosity to the frequency dependent viscosity coefficient is discussed. Understanding the crossover behavior of the stress fluctuations is also important for the calculation of the viscous behavior of fluids with long relaxation times, where it may be difficult to reach the long-time limit. Expressions used here are similar to those applied in an analysis of the statistical dependence of data extracted from a dynamical interpretation of Monte Carlo simulations [4]. The present approach is also somewhat akin to the calculation of elastic constants from strain fluctuations [5], where their dependence on a spatial length rather than on the duration of a time–interval plays a crucial role. In Refs. [6–8] a ''hard'' interaction $1/r^n$—rather than the short range attractive ''SHRAT'' potential to be considered in the present work—with a large n had been used. The crossover from hard to soft spheres had been discussed, e.g., in Refs. [6,9], where it is argued that there are two relevant time scales: the Enskog mean free time, and the mean traversal time for a particle to cross the steep part of the potential.

II. STRESS FLUCTUATION FORMULA

Consider a system composed of N spherical particles with mass m and position vectors $\mathbf{r}^i$, $i=1,\ldots,N$ in a volume V. The number density is $n=N/V$. In the MD simulations, periodic boundary conditions and the ''minimum image convention'' are used in order to avoid boundary layer effects [10,11]. 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 $\sigma_{\mu\nu}$, which is the negative of the pressure tensor $p_{\mu\nu}$, which in turn is the sum of kinetic and potential contributions: $p_{\mu\nu}=p^{\rm kin}_{\mu\nu}+p^{\rm pot}_{\mu\nu}$, $p^{\rm kin}_{\mu\nu}=V^{-1}\Sigma_i mc^i_\mu c^i_\nu$, $p^{\rm pot}_{\mu\nu}=V^{-1}\frac{1}{2}\Sigma_{ij}r^{ij}_\mu F^{ij}_\nu$. 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.

In an equilibrium situation where one has $\mathbf{v}=0$, the shear stress, i.e., the off-diagonal 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 $t_{\rm av}$ [12]. More specifically, the definition of a time-interval average $\overline{\sigma}(t_{\rm av})=t_{\rm av}^{-1}\int_0^{t_{\rm av}}\sigma(t)dt$ is introduced. The time dependence of $\sigma(t)=-p_{12}(t)$ stems from the time dependence of the positions and momenta of the particles. It is understood that the integration limits 0 and $t_{\rm av}$ can be replaced by t_0 and $t_0+t_{\rm av}$ 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

$$\langle\overline{\sigma}(t_{\rm av})^2\rangle=t_{\rm av}^{-2}\int_0^{t_{\rm av}}dt_1\int_0^{t_{\rm av}}dt_2\langle\sigma(t_1)\sigma(t_2)\rangle. \qquad (1)$$

The angular brackets $\langle\cdots\rangle$ indicate an ensemble average, $\langle\overline{\sigma}(t_{\rm av})\rangle=0$ has been assumed. In a stationary situation $\langle\sigma(t_1)\sigma(t_2)\rangle$ depends on the time difference $t=t_1-t_2$ only. Upon the assumption that the equilibrium fluctuations cannot distinguish between ''past'' and ''future,'' i.e., $\langle\sigma(t)\sigma(0)\rangle=\langle\sigma(-t)\sigma(0)\rangle$, the integral over t, ranging from $-t_{\rm av}$ to $t_{\rm av}$ is replaced by two times the integral from 0 to $t_{\rm av}$. Furthermore, one has to take into account that the time variable $t_m=(t_1+t_2)/2$, for fixed $t>0$, lies between $t/2$ and $t_{\rm av}-t/2$.

Performing the integration over the time variable t_m yields a factor $t_{\rm av}-t$. Thus Eq. (1) reduces to [10–12]

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

A characteristic 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 $t_{\rm av}$ is large compared with the relaxation time, the term $t/t_{\rm av}$ can be neglected in the expression $(1-t/t_{\rm av})\langle\sigma(t)\sigma(0)\rangle$ occurring in Eq. (2). Then 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 corresponding time averaged quantity is reduced by the factor $2\tau t_{\rm av}^{-1}$. In the same limit, $t_{\rm av}\gg\tau$, 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. (2) as an expression applicable for the computation of the viscosity from the mean square of the fluctuations of the time averaged shear stress. The corresponding formula has also been derived from a more general fluctuation theorem Ref. [13]. It was used in [2] to compute viscosity coefficients of a fluid. Here we analyze the dependence of the mean square of the stress fluctuations on the averaging time $t_{\rm av}$, in particular the crossover from $t_{\rm av}<\tau$ to $t_{\rm av}\gg\tau$. We define an effective viscosity

$$\eta[t_{\rm av}]=t_{\rm av}(2nk_BT)^{-1}N\langle\overline{\sigma}(t_{\rm av})^2\rangle, \qquad (3)$$

with Eq. (2). Note that $\eta[t_{\rm av}]$ reduces to η in the limit $t_{\rm av}\gg\tau$. For simplicity, we present only results for the total stress rather than for its kinetic and potential contributions separately. A remark on the short-time limit corresponding to $t_{\rm av}\ll\tau$ is in order. In this case, $\sigma(t)$ can be replaced by $\sigma(0)$ in Eq. (2). Without the factor $1-t/t_{\rm av}$, the right hand side of this equation would yield a result too large by a factor 2. The crucial factor 1/2 follows from the time integral of $(1-t/t_{\rm av})/t_{\rm av}$.

III. SHEAR MODULUS, TIME CORRELATION FUNCTION

In the fluid phase, the mean square average of the instantaneous shear stress is related to the high frequency shear modulus G by $\langle\sigma(0)^2\rangle=N^{-1}nk_BT(nk_BT+G)$. The quantity G, 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., $G=(15V)^{-1}\langle\Sigma_{i<j}[r^{-2}(r^4\phi')']^{ij}\rangle$. The prime denotes the derivative with respect to r. Born-Green and the fluctuation expressions are equal for a system in the fluid (but not in the solid) state [14]. The shear stress time correlation function $C(t)$, with $C(0)=1$, is defined by $\langle\sigma(t)\sigma(0)\rangle=\langle\sigma(0)^2\rangle C(t)$. Then Eq. (2) is equivalent to

$$\langle\overline{\sigma}(t_{\rm av})^2\rangle/\langle\sigma(0)^2\rangle=2t_{\rm av}^{-1}\int_0^{t_{\rm av}}(1-t/t_{\rm av})C(t)dt. \qquad (4)$$

For an exponentially decaying correlation function $C(t)=e^{-t/\tau}$ with the relaxation time τ, one finds $R=\langle\overline{\sigma}(t_{\rm av})^2\rangle/\langle\sigma(0)^2\rangle=2\tau/t_{\rm av}[1-(\tau/t_{\rm av})(1-e^{-t_{\rm av}/\tau})]$. Limiting cases for $t_{\rm av}\gg\tau$ and $t_{\rm av}\ll\tau$ are $2\tau/t_{\rm av}$ and 1, respectively.

IV. MD SIMULATION RESULTS

For the test calculations, and reasons discussed in Ref. [15], the SHRAT potential $\phi^{\rm SHRAT}(r)=(512/27)\Phi_0(1-r/r_0)(3-2r/r_0)^3$, $r\leqslant 1.5r_0$, and $\phi^{\rm SHRAT}(r)=0$ for $r>1.5r_0$, is used. The quantities Φ_0 and r_0 set the characteristic energy and length scales. 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. 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 $\phi^{\rm SHRAT}(r)=(512/27)(1-r)(3-2r)^3$, $r\leqslant 3/2$, whereas $\phi^{\rm SHRAT}(r)=0$ 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 $n_{\rm ref}=r_0^{-3}$ and $T_{\rm ref}=\Phi_0/k_B$, respectively. The unit for the pressure is $p_{\rm ref}=\Phi_0 r_0^{-3}$. The units for the pressure, time, velocity, and viscosity are $p_{\rm ref}=\cdots$, $t_{\rm ref}=\cdots$, $v_{\rm ref}=\cdots$, and $\eta_{\rm ref}=\cdots$, respectively. Thermophysical properties of this model system in its gaseous, liquid, and solid state have recently been calculated [15]. Here results are presented for a state point with the number density $n=0.75n_{\rm ref}$, and the temperature $T=T_{\rm ref}$ which corresponds to a compressed fluid, somewhat above the critical temperature (which is at $0.8T_{\rm ref}$), with a density of more than twice the critical density (about $0.32n_{\rm ref}$) but well below that one where a fcc crystalline solid exists, under a considerably higher pressure, at the same temperature.

In the simulations, the equations of motion of $N=4\times 8^3$ particles were integrated with the velocity Verlet algorithm with the time-step $\delta t/t_{\rm ref}=0.004$. Initially, the particles were placed on fcc lattice sites and they had random velocities with a mean square corresponding to the desired temperature $T/T_{\rm ref}=1.0$. 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 $n/n_{\rm ref}=0.75$, the crystal melts and a fluid state is approached quickly. The system was well equilibrated by running it for 100 LJ time units $t_{\rm ref}$. Then the thermostat was turned off and the adiabatic (isoenergetic) simulation was run for another 40 LJ time units $t_{\rm ref}$. Afterwards, the integration time step was reduced to $\delta t/t_{\rm ref}=0.002$ and the quantities of interest were computed and recorded in 4800 10 time-step intervals with duration $0.02t_{\rm ref}$. Averaged over the full runtime, the values for the potential energy per particle, the pressure and the (Born-Green) shear modulus are $e^{\rm pot}/\Phi_0=-2.77\pm 0.01$, $p/p_{\rm ref}=1.63\pm 0.04$, and $G/p_{\rm ref}=15.3\pm 0.1$. The average temperature, both computed by the "kinetic" and the "configurational" expressions [16], is $T/T_{\rm ref}=0.99\pm 0.01$. In order to

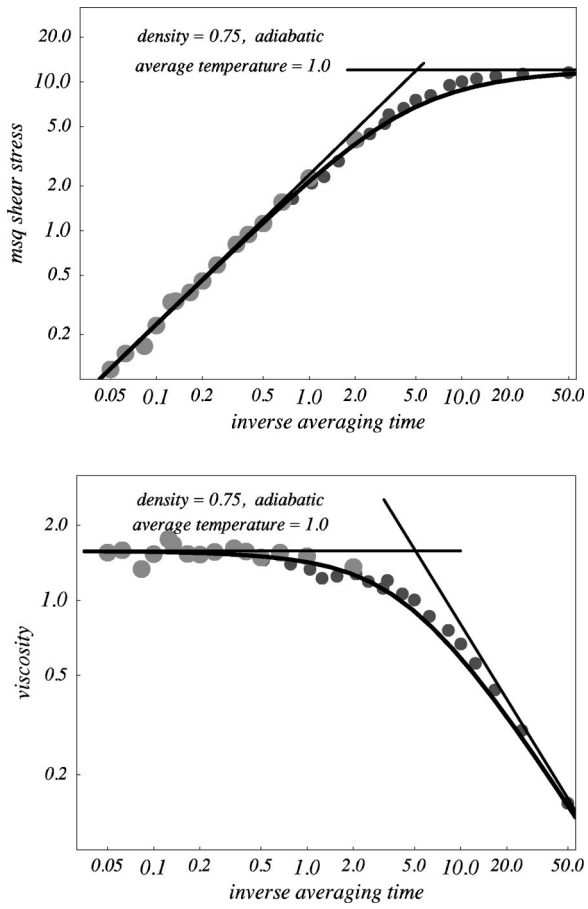

FIG. 1. (a) The ensemble average of the square of the fluctuating shear stress (in units of p_{ref}), multiplied by the number of particles, and (b) the (effective) viscosity (in units of $p_{\mathrm{ref}}t_{\mathrm{ref}}$), both as function of the inverse averaging time (in units of t_{ref}). The black dots mark the new data for shorter values of the averaging times. The gray dots mark the results previously presented in Ref. [2]. The straight lines indicate the limiting values for averaging times very short-elastic behavior, horizontal line in a), slope -1 in (b)—and very long—viscous behavior, slope 1 in (a), horizontal line in (b)—compared with the stress relaxation time, respectively. The curve describing the intermediate viscoelasticity follows from an exponentially decaying time correlation function.

analyze the dependence of the mean square fluctuations of the various contributions to the shear stress, the available data are further averaged in blocks (divisors of 4800). This means, time intervals of length $t_{\mathrm{av}}/t_{\mathrm{ref}}=0.02,0,04,0.06,\ldots,1.28,1.92$ are considered. 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 4800 of them of length $t_{\mathrm{av}}/t_{\mathrm{ref}}=0.02$ but only 50 of length $t_{\mathrm{av}}/t_{\mathrm{ref}}=1.92$.

V. FLUCTUATING SHEAR STRESS

In Fig. 1(a), 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 $N=2048$, is displayed as function of the (logarithm of the) inverse averaging time t_{av}. The approach of the points to the straight line with slope 1 (left side of the diagram) shows that the mean square fluctuations, for $t_{\mathrm{av}}/t_{\mathrm{ref}}\geqslant 1.0$, indeed decrease inversely proportional to the averaging time t_{av}. This proves that the relevant relaxation time is definitely shorter than t_{ref}, see also Ref. [6] for a discussion of this point for the case of fluids with an $1/r^n$ interaction (large n). A quantitative analysis yields $\tau/t_{\mathrm{ref}}=0.1$ [2]. From the position of this asymptotic line one determines a value for the shear viscosity, found to be 1.58, in reduced units. The horizontal line indicates the short-time behavior (see Sec. III), involving the shear modulus G which was computed independently with the help of the Born-Green expression. The thick curve is calculated from Eq. (4) with the exponentially decaying stress correlation function $C(t)=e^{-t/\tau}$. This curve gives a reasonably good approximation for the description of the crossover behavior. The relaxation time is the ratio between the viscosity and the shear modulus nk_BT+G, quantities which determine the asymptotic behavior for $t_{\mathrm{av}}\gg\tau$ and $t_{\mathrm{av}}\ll\tau$. Thus the curve shown which describes the intermediate behavior does not involve any additional fit parameter.

VI. EFFECTIVE VISCOSITY

The effective viscosity $\eta[t_{\mathrm{av}}]$ is defined by relation (3) for arbitrary values of t_{av}. It is displayed in Fig. 1(b) as function of the inverse averaging time t_{av} (double logarithmic plot). The black dots mark the data computed here for small values of t_{av}, the larger gray dots stand for the results presented previously for larger values of the averaging time. The horizontal line indicates the shear viscosity, viz., $\eta/\eta_{\mathrm{ref}}=1.58$, with $\eta_{\mathrm{ref}}=p_{\mathrm{ref}}t_{\mathrm{ref}}$. It agrees very well with the value $\eta/\eta_{\mathrm{ref}}=1.61\pm 0.08$ obtained for the shear viscosity by nonequilibrium MD simulations in the limit of small shear rates [15]. The line on the right hand side of Fig. 1(b), with slope -1, stems from the expression $(nk_BT+G)t_{\mathrm{av}}$ which is valid in the limit $t_{\mathrm{av}}\ll\tau$. As in Fig. 1(a) the thick curve linking both asymptotic regimes is based on Eq. (4) with an exponentially decaying time correlation function. As stressed before, the relaxation time needed to describe the crossover from the elastic to the viscous behavior is already determined by the viscosity and the shear modulus occurring in the asymptotic regimes.

VII. COMPARISON WITH THE COMPLEX VISCOSITY

Qualitatively, the curve for the effective viscosity as function of the inverse averaging time t_{av}^{-1} looks somewhat similar to that for the complex viscosity as function of the frequency, used for periodically varying shear rates. The interrelation between these two types of viscosities can be inferred from Eq. (4) involving the stress time correlation function $C(t)$. To be more specific, we note that one has $\eta(\omega)=(nk_BT+G)\int_0^\infty e^{-i\omega t}C(t)dt=\eta'-i\eta''$, where η' and η'' stand for the real and imaginary parts of the complex viscosity. The back transformation reads $(nk_BT+G)\,C(t)=(2\pi)^{-1}\int_0^\infty e^{i\omega t}\eta(\omega)d\omega$. Insertion of this relation into Eq. (4), the use of Eq. (3) for the definition of the effective vis-

cosity $\eta[t_{\mathrm{av}}]$ and subsequent integration over the time leads to

$$\eta[t_{\mathrm{av}}]=\int_0^\infty h(x)\,\eta'\left(\frac{x}{t_{\mathrm{av}}}\right)dx+\int_0^\infty g(x)x\,\eta''\left(\frac{x}{t_{\mathrm{av}}}\right)dx, \quad (5)$$

where the functions h and g are defined by $h(x)=2x^{-2}\pi^{-1}[1-\cos(x)]$, and $g(x)=2x^{-2}\pi^{-1}[1-\sin(x)/x]$. Integration of these functions over the dimensionless variable x from zero to infinity yields 1 and 1/2, respectively. Due to the interrelation $G(\omega)=i\omega\eta(\omega)$ between the complex shear modulus $G(\omega)=G'+iG''$ and the complex viscosity, the term $x\eta''(x/t_{\mathrm{av}})$ in Eq. (5) is equivalent to $t_{\mathrm{av}}G'(x/t_{\mathrm{av}})$. Results for very large values of the averaging time are found again when one takes into account that η'' vanishes for small frequencies. Similarly, for short averaging times, the results given above are recovered when one observes that η' vanishes and that G' approaches the value (nk_BT+G) for large frequencies. It is desirable to approximate relation (5) involving integrals by an expression involving the complex viscosity or the complex shear modulus at representative frequencies proportional to $1/t_{\mathrm{av}}$. For the case of an exponentially decaying time correlation function $\eta[t_{\mathrm{av}}]\approx\eta'(2\pi/t_{\mathrm{av}})+(1/2)t_{\mathrm{av}}G'(\pi/t_{\mathrm{av}})$ is an excellent approximation. This relation should also provide a reasonable approximation for more general cases.

VIII. CONCLUDING REMARKS

In this article, the dependence of the stress fluctuations on the averaging time was analyzed. In the limiting cases where this time is short and long in comparison with the relevant relaxation time, the mean square fluctuations are related to the (high frequency) shear modulus and to the (Newtonian) viscosity, respectively. In these limits, excellent quantitative agreement is found with theoretical expressions involving the shear modulus and the viscosity determined independently. Numerical results for the crossover between the elastic and viscous behavior were presented. An effective viscosity coefficient depending on the averaging time was introduced and displayed graphically. In fact, it is closely related to the real parts of the complex viscosity and of the complex shear modulus. The crossover behavior is described satisfactorily well by a theoretical expression based on an exponentially decaying time correlation function. Here and in the previous study [2] data were analyzed from a simulation run over about 10^4 relaxation times τ. A run time of about $10^3\tau$ is needed for the determination of a transport coefficient. When the functional form of the time correlation function is known and the crossover behavior is analyzed only up to $t_{\mathrm{av}}\approx 10\tau$, run times of about $10^3\tau$ may be sufficient. The computation is more demanding for complex fluids with relaxation times which are several orders of magnitude larger than that one of the simple liquid considered here. On the other hand, the required ensemble average can also be obtained from shorter (say 10τ) parallel runs starting from statistically independent initial states. Generalizations of the present method to a study not only the viscosity but other transport coefficients, such as the bulk viscosity and the heat conductivity [7], as well as an extension to complex fluids, e.g., liquid crystals, ferro-fluids [17,18] and polymeric liquids [19], and to fluids in restricted geometries [20,21], is desirable and feasible.

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