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Transient-time-correlation functions and the rheology of fluids

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In this paper we use the recently developed transient-time-correlation function formalism (TTCF) to study the transient rheology of classical fluids. We compare this approach to the calculation of fluid transport properties using the Green-Kubo method (valid only in the linear-response regime), with direct nonequilibrium molecular dynamics (NEMD) simulations, and with the NEMD subtraction technique. The various approaches are compared for a system undergoing isothermal, planar Couette flow. Although less efficient than direct NEMD at large strain rates, the TTCF results agree with direct NEMD to high accuracy. At low strain rates where direct NEMD is not applicable, the TTCF approach is clearly more efficient than the subtraction method.

I. INTRODUCTION

We have recently developed a formally exact description of nonequilibrium steady states.[1] Unlike earlier attempts,[2] our theory includes an explicit treatment of thermostatting terms so that true steady states may be achieved. The theory gives an exact representation of the nonlinear response of classical many-body systems to the dissipative perturbation induced by an external field. Our theory relates the nonlinear *thermostatted* response to expressions which are both calculable and verifiable. A number of nonlinear response theories that have been proposed over the years lead to exact but mathematically intractable results. The path towards tractability was first shown by Kawasaki.[3] Somewhat later Dufty and Lindenfeld[4] and, independently, Cohen[5] developed alternative but formally equivalent forms for the nonlinear *adiabatic* response. We use the term adiabatic to denote the fact that these theories contained no thermostatting mechanism[6] and thus were incapable of treating extremely interesting questions concerning the nature of that state *parallel* to equilibrium, the nonequilibrium steady state.

The nonequilibrium steady state is characterized by the fact that although work is performed on the system preventing its relaxation to equilibrium, heat is extracted from it at precisely the rate required to balance the entropy production induced by the external forces. The macroscopic properties of the system become independent of time, and by definition, the *steady* state is stable with respect to small fluctuations in the state-defining variables. (Of course not all thermostatted nonequilibrium states are steady states.) In spite of these parallels with true equilibrium states, many questions remain concerning the nature of nonequilibrium steady states outside the linear regime where local thermodynamic equilibrium is valid. For example, a theory predicting the stability of steady states from a microscopic variational principle—a statistical mechanical version of the second law of thermodynamics—is not known.

Two tractable representations of the adiabatic nonlinear response have been proposed: the so-called Kawasaki representation and the transient-time-correlation function (TTCF) approach. We have recently shown how these representations may be generalized to include thermostatting terms. We have also shown how a variety of other representations can be given. Of these various representations the TTCF representation is the one which is most amenable to direct application in computer simulations and is of direct relevance to rheology as it corresponds exactly to a stress-growth experiment.[7] The Kawasaki representation and a third representation proposed by the present authors are far more difficult to evaluate numerically.[8]

The Kawasaki representation is, however, the one which thus far has proved to be the most revealing in its use as a nonequilibrium partition function. It leads to steady-state fluctuation expressions for the derived properties, the specific heats,[9] the thermal expansion coefficients, and the compressibilities.[10] These expressions show how the derived properties are related to steady-state fluctuations and steady-state time-correlation functions. The corresponding expressions derived from the TTCF representation are less useful because they relate the derived properties to equilibrium fluctuations and to the more difficult to evaluate, transient-time-correlation functions. A transient-time-correlation function is defined as the time-dependent correlation of fluctuations in a phase variable evaluated at equilibrium (i.e., when the external perturbation is applied, usually taken as $t=0$), and fluctuations in another phase variable evaluated at intermediate times during which the nonequilibrium steady state is established, hence the term transient-time-correlation function.

In this paper we compare the predictions of the thermostatted TTCF formalism with a number of other ways of calculating the nonlinear nonequilibrium response. The other approaches compared include direct computer simulation,[11] nonequilibrium molecular dynamics (NEMD), a refinement of direct simulation known variously as the subtraction technique,[12] or differential NEMD, and the linear, Green-Kubo[13] response formulas.

In our case direct NEMD simply involves simulating a classical fluid undergoing thermostatted planar Couette

flow.[14] The periodic boundary conditions that are employed are known as Lees-Edwards[15] boundary conditions. They replace the usual orthogonal periodic boundary conditions with time-varying nonorthogonal periodic boundaries that isochorically shear all the periodic images of primitive-cell particles at a prescribed strain rate.

Very close to equilibrium direct NEMD becomes very inefficient because the signal-to-noise ratio goes to zero. The systematic nonequilibrium response becomes comparable or even smaller than the equilibrium fluctuations in the phase variables of interest. Ciccotti *et al.*[12] developed a noise reduction modification of direct NEMD which enables the computation of the systematic nonequilibrium response at small but necessarily nonzero fields. This subtraction method simply involves averaging the difference of phase variables computed with and without the perturbing external field. The two trajectories begin from *exactly* the same point in phase space. For short times the two phase-space trajectories are highly correlated, meaning that the noise apparent in the nonequilibrium trajectory is very similar to that seen in the equilibrium trajectory. At larger times the two trajectories become uncorrelated, and the noise in the difference of the two trajectories returns. Unfortunately the time at which the correlation disappears and the noise returns is not usually long enough to enable a clear-cut characterization of the steady-state averages. Very recently we have used the TTCF formalism to calculate the purely nonlinear shear viscosity, extending the accessible range of field strengths to 7 orders of magnitude.[16]

The Green-Kubo (GK) calculation of the nonequilibrium response proceeds completely differently. Linear-response theory predicts that the nonequilibrium average of a phase variable is related to the time integral of an *equilibrium* time-correlation function. The linear response can therefore be calculated by using an equilibrium simulation to calculate the appropriate time-correlation function. Although much better behaved than the subtraction technique, the GK method also becomes difficult at long times. The relative fluctuations in the correlation function become large at long times. This is more important than it might otherwise be, because of the presence of long-time tail phenomena, at least for the Navier-Stokes transport processes. The GK correlation functions do not decay to zero in an exponential fashion but rather in a slow power-law way. This decay is so slow that in two dimensions, for instance, the integrals of the GK correlation functions actually diverge. In three dimensions the decay is fast enough to ensure convergence but slow enough to make the calculation difficult. The final limitation of the GK formulas is, of course, that they are only valid for the linear response. They tell us nothing about the variation of the transport coefficients with the magnitude of the perturbing field.

The transient-time-correlation function approach is the natural nonlinear generalization of the GK formulas. In the zero-field limit the TTCF's reduce to GK correlation functions. (It is also true that the Kawasaki representation reduces to GK in this limit.) In contrast to the subtraction technique the TTCF approach can be applied at zero field where it is identical to GK. As we shall see, the TTCF method is superior to the subtraction technique at small fields. At large fields TTCF becomes less efficient than direct NEMD.

Apart from the application of TTCF at zero field, both the TTCF and subtraction approaches are hampered by the fact that they both analyze the transient response. In both cases the steady-state response is calculated by monitoring the behavior of systems during the establishment of the steady state. This is inconvenient and is inherently less efficient than direct steady-state simulations.

II. TRANSIENT-CORRELATION FUNCTIONS FOR PLANAR COUETTE FLOW

The equations of motion for an N-body system undergoing planar Couette flow can be written as

$$\begin{aligned}\dot{\mathbf{q}}_i &= \frac{\mathbf{p}_i}{m} + \mathbf{n}_x \gamma y_i \ , \\ \dot{\mathbf{p}}_i &= \mathbf{F}_i - \mathbf{n}_x \gamma p_{yi} - \alpha \mathbf{p}_i \ ,\end{aligned} \tag{1}$$

where $\mathbf{n}_x$ is the unit vector in the x direction, γ is the strain rate, and $\mathbf{p}_i$ is the momentum of particle i measured in a coordinate frame moving at the local streaming velocity γy_i. The term $\alpha \mathbf{p}_i$ is the Gaussian thermostat. When α is chosen to be

$$\alpha = \frac{\sum_i (\mathbf{F}_i \cdot \mathbf{p}_i - \gamma p_{xi} p_{yi})}{\sum_i \mathbf{p}_i^2} \ , \tag{2}$$

the peculiar kinetic energy is a constant of the motion. If we take the peculiar kinetic energy per degree of freedom as a measure of the temperature, then the Gaussian thermostat maintains the system at a constant temperature. The transformation in (1) of the boundary condition which drives planar Couette flow into the form of an external mechanical perturbation is achieved by writing the equations of motion in terms of the peculiar momenta $\mathbf{p}_i$. These equations are known as the SLLOD equations of motion for shear flow.[14]

Isothermal response theory[1] shows that the adiabatic rate of change of the internal energy $H_0 = \sum_i (\mathbf{p}_i^2/2m + \Phi)$, plays an essential role in determining the thermostatted response. The adiabatic derivative of the internal energy dH_0/dt is usually written as $-JF_e$, where J is the dissipative flux and F_e is the external field. Strictly speaking this is only true when the adiabatic incompressibility of phase space (AIΓ)[1] is satisfied. AIΓ is satisfied by all the commonly used NEMD algorithms including the SLLOD equations of motion for Couette flow. If AIΓ is not satisfied, the form of the response equations is modified somewhat. For planar Couette flow J is easily seen to be the shear stress P_{xy} times the system volume V

$$\begin{aligned}(\dot{H}_0)^{\text{ad}} = -JF_e &= -\gamma \sum_i \left[\frac{p_{xi} p_{yi}}{m} + y_i F_{xi} \right] \\ &= -\gamma P_{xy} V \ .\end{aligned} \tag{3}$$

If a canonical ensemble (or isothermal ensemble[17]) of sys-

tems is suddenly subject to a constant shearing deformation at $t=0$. If we use the notation $B(t_\gamma)$ to denote the field-dependent, thermostatted value of an arbitrary phase variable at time t, then the time-dependent average $\langle B(t_\gamma)\rangle$ can be shown to be

$$\langle B(t_\gamma)\rangle = \langle B(0)\rangle - \beta\gamma V\int_0^t ds\langle B(s_\gamma)P_{xy}(0)\rangle \ . \quad (4)$$

This expression relates the nonequilibrium value of a phase variable B at time t, to the integral of a transient-time-correlation function [the correlation between P_{xy} in the equilibrium starting state, $P_{xy}(0)$, and B at time s after the field is turned on]. The time-zero value of the transient correlation function is an equilibrium property of the system. For example, if $B=P_{xy}$, then the time-zero value is $\langle P_{xy}^2(0)\rangle$. Under some, but by no means all circumstances, the values of $B(s)$ and $P_{xy}(0)$ will become uncorrelated at large times. If this is the case, the system is said to exhibit mixing. The transient-correlation function will then approach $\langle B(t_\gamma)\rangle\langle P_{xy}(0)\rangle$, which is zero because $\langle P_{xy}(0)\rangle=0$. For systems that exhibit mixing, Eq. (4) can, therefore, be rewritten as

$$\langle B(t_\gamma)\rangle = \langle B(0)\rangle - \beta\gamma V\int_0^t ds\langle \Delta B(s_\gamma)P_{xy}(0)\rangle \ , \quad (5)$$

where

$$\Delta B(s)=B(s)-\langle B(s)\rangle \ .$$

Although the adiabatic systems treated by Dufty and Lindenfeld[4] do not lead to stationary states, there is some evidence that mixing occurs.[18] In the absence of a thermostat $d\langle B(t_\gamma)\rangle/dt$ does not go to zero at large times, and its value is related to the functional dependence of B upon the temperature. Turbulent or quasiperiodic systems, however, are not expected to exhibit mixing.

It is trivial to see that in the linear regime the transient-correlation-function expression for the system response reduces to the usual Green-Kubo expression

$$\langle B(t_\gamma)\rangle = \langle B(0)\rangle - \beta\gamma V\int_0^t ds\langle \Delta B(s)P_{xy}(0)\rangle \ . \quad (6)$$

The Green-Kubo expression for the linear response is identical in form to the corresponding transient-correlation relation except that the time evolution in the second term on the right-hand side is governed by the field-free thermostatted propagator in the linear case and by the thermostatted field-dependent propagator in the nonlinear regime. The Green-Kubo correlation function is an equilibrium correlation function. We know that in the thermodynamic limit there is no difference between the thermostatted equilibrium time-correlation function and the corresponding Newtonian or adiabatic correlation function.[19]

The coincidence at small fields of the Green-Kubo and transient-correlation formulas means that unlike direct NEMD, the transient-correlation method can be used at small fields. This is *impossible* for direct NEMD because in the small-field limit the signal-to-noise ratio goes to zero. The signal-to-noise ratio for the transient-correlation function becomes equal to that for the equilibrium Green-Kubo method—a small, but nonzero number. Thus at small fields the efficiency of the transient-correlation method is comparable to that of Green-Kubo. The transient-correlation-function method forms a bridge between the Green-Kubo method which can only be used at equilibrium, and direct NEMD which is the most efficient strong-field method.

It is also easy to see that at short times there is no difference between the linear and nonlinear stress response. It takes time for the nonlinearities to develop. The way to see this is to expand the transient-time-correlation function in a power series in γt (assuming such an expansion exists). The first term in this series for the response of the shear stress is just $\beta V\langle P_{xy}^2\rangle$, the infinite frequency shear modulus, G_∞. Since this is an equilibrium property its value is unaffected by the strain rate and is the same in both the linear and nonlinear cases. If we look at the response of a quantity like the pressure whose linear response is zero, the leading term in the short-time expansion is nonlinear in the strain rate and in time. The linear response, of course, is the first to appear.

III. NUMERICAL RESULTS

Computer simulations were carried out for two different systems. The first was a system of 72 soft disks $[\phi=4\epsilon(\sigma/r)^{12}]$ in two dimensions at a reduced density of $\rho^*=\rho\sigma^2=0.6928$, a reduced temperature $T^*=kT/\epsilon=1$ for a range of the strain rates, $\gamma^*=\gamma(m/\epsilon)^{1/2}\sigma=\partial u_x/\partial y(m/\epsilon)^{1/2}\sigma$. This state point has been studied previously[20] although not at this system size. A fourth-order Runge-Kutta method with a timestep of $0.005t^*$ $[t^*=t(\sigma(m/\epsilon)^{1/2})^{-1}]$ was used to integrate the equations of motion. The potential was truncated at $r^*=1.5$.

The second system was studied more extensively. It consisted of 256 Lennard-Jones particles with the potential truncated at the Lennard-Jones potential minimum $r_c=r_c^*\sigma=2^{1/6}\sigma$. The system was three dimensional and the density was set to $\rho^*=\rho\sigma^3=0.8442$, while the temperature was $T^*=kT/\epsilon=0.722$. A second-order Runge-Kutta integrator with a reduced timestep of $0.0025t^*$ was used. The Runge-Kutta method was used rather than the more common Gear or leapfrog algorithms because unlike the latter, the Runge-Kutta method is self-starting. Since we are interested in the transient response we need to be able to calculate the system trajectories from a specified initial phase. The Gear and leapfrog algorithms only achieve accuracy after an initial startup period and are, therefore, unsuitable for calculating transient responses.

In each simulation the direct average of the shear stress, pressure, normal stress difference, and thermostat multiplier α were calculated along with their associated transient-correlation functions using typically 60 000 nonequilibrium starting states. For the three-dimensional system each nonequilibrium trajectory was run for a reduced time of 1.5 (i.e., 600 timesteps). Each 60 000 starting-state simulation consisted of a total of 54 million timesteps made up of $2\times15\,000\times600$ timesteps at equilibrium and $4\times15\,000\times600$ perturbed nonequilibrium timesteps. The reader is referred to Ref. 1 for details of the symmetry mappings employed in the simulations.

In Fig. 1 we present the results obtained for the reduced shear stress $P_{xy}^* = P_{xy}(\sigma^2/\epsilon)$, in two dimensions. The imposed reduced strain rate is unity. The values of the shear stress calculated from the transient-correlation-function expression agree within error bars with those calculated directly. The errors associated with the direct average are less than the size of the plotting symbols whereas the error in the integral of the transient-correlation function is approximately $\pm 2.5\%$ at the longest times. Although the agreement between the direct simulation results and the TTCF prediction is very good, it must be remembered that the total response for the shear stress is the sum of a large linear effect which could be correctly predicted by the Green-Kubo formula and a smaller ($\sim 25\%$) nonlinear effect. Thus the statistical agreement regarding the TTCF prediction of the intrinsically nonlinear component of the total response is, therefore, approximately 10%.

The shear-induced increase in pressure with increasing strain rate (shear dilatancy) is an intrinsically nonlinear effect and is not observed in Newtonian fluids. The Green-Kubo formulas predict that there is no coupling of the pressure and the shear stress because the equilibrium correlation function $\langle \Delta p(t) P_{xy}(0) \rangle$ is exactly zero at all times. In Fig. 2 we present the direct and transient-correlation-function values of the difference between the pressure $p^* = p(\sigma^2/\epsilon)$ and its equilibrium value ($\Delta p^* = p^* - p_0^*$). The agreement between the direct average and the value obtained from the transient-correlation-function expression at $\gamma^* = 1.0$ is impressive. It is important to note that the agreement between theory and simulation shown in Fig. 2 is a test of the predictions of the theory for an *entirely* nonlinear effect. It is a more convincing check on the validity of the TTCF formalism than are the results for the shear stress because there is no underlying linear effect.

The results for the x-y element of the pressure tensor in the three-dimensional system are given in Fig. 3. Again the agreement between the TTCF prediction and the direct simulation is excellent. We also show the long-time steady-state stress computed by conventional

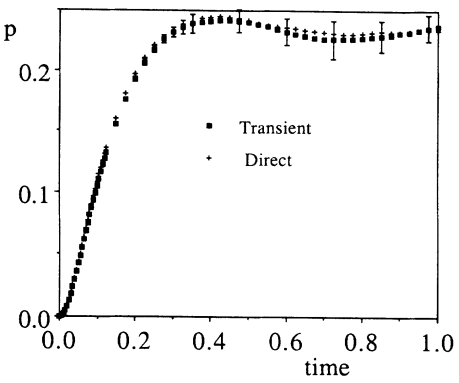

FIG. 2. The direct and transient-time-correlation-function results for the pressure in two-dimensions at $\rho^* = 0.6928$, $T^* = 1$, and $\gamma^* = 1.0$.

NEMD. It is clear that our time limit for the integration of the transient-time-correlation functions is sufficient to obtain convergence of the integrals (i.e., to ensure relaxation to the nonequilibrium steady state) for the shear rates considered here. We also show the Green-Kubo prediction for the stress. A comparison of the linear and nonlinear responses shows that the intrinsically nonlinear response is only generated at comparatively late times. The response is essentially linear until the stress overshoot time ($t^* \sim 0.3$). The figure also shows that the total nonlinear response converges far more rapidly than does the linear GK response. The linear GK response has obviously not relaxed to its steady-state limiting value at a t^* value of 1.5. This is presumably because of long-time-tail effects which predict that the linear response relaxes very slowly as $t^{-1/2}$, at long times.

In Fig. 4 we show the corresponding results for shear dilatancy in three dimensions. Again the TTCF predictions are in statistical agreement with the results from direct simulation. We also show the steady-state pressure shift obtained using conventional NEMD. Again it is apparent that $t^* = 1.5$ is sufficient to obtain convergence of

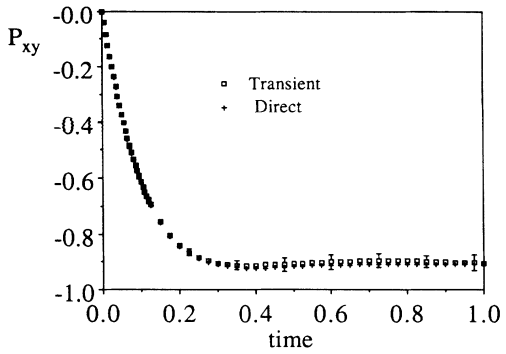

FIG. 1. The direct and transient-time-correlation-function results for the shear stress in two dimensions at $\rho^* = 0.6928$, $T^* = 1$, and $\gamma^* = 1.0$. A typical error bar for the direct is less than the size of the symbols, while for the transient-time-correlation function it is typically 2.5% at $t^* = 1$.

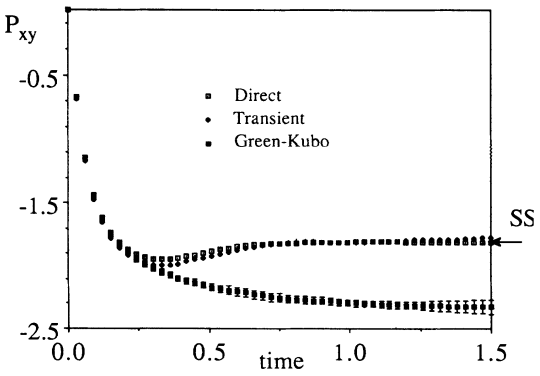

FIG. 3. The direct and transient-time-correlation-function results for the shear stress in three dimensions at $\rho^* = 0.8442$, $T^* = 0.722$, and $\gamma^* = 1.0$. The linear-response contribution to the shear stress is given by the integral of the Green-Kubo equilibrium time-correlation function with error estimates shown.

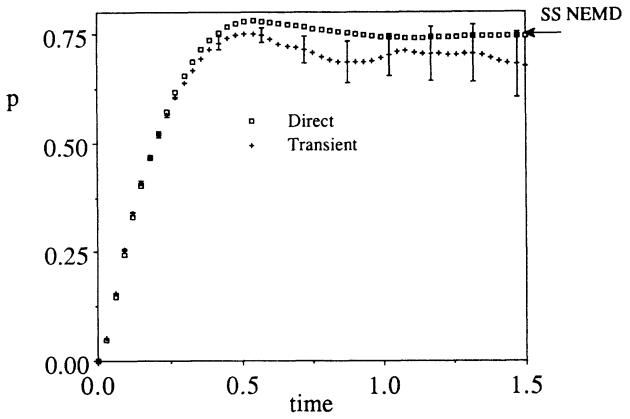

FIG. 4. The direct and transient-time-correlation-function results for the pressure in three dimensions at $\rho^*=0.8442$, $T^*=0.722$, and $\gamma^*=1.0$.

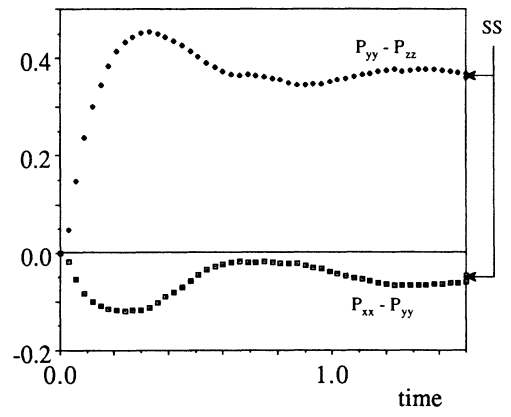

FIG. 5. The transient-time-correlation-function results for the normal stress differences P_{xx}-P_{yy} and P_{yy}-P_{zz} in three dimensions at $\rho^*=0.8442$, $T^*=0.722$, and $\gamma^*=1.0$. The arrowed points on the right-hand side are the steady-state NEMD results.

the TTCF integral. Although it is not easy to see in the figure, the initial slope of the pressure response is zero. This contrasts with the initial slope of the shear stress response which is G_∞. This is in agreement with the predictions of the transient-time-correlation formalism made in Sec. II. Figures 1 and 3 clearly show that at short time the stress is controlled by linear-response mechanisms. It takes time for the nonlinearities to develop, but paradoxically perhaps, convergence to the steady-state asymptotic values is ultimately much faster in the nonlinear, large-field regime.

Comparing the statistical uncertainties of the transient correlation and direct NEMD results shows that at reduced strain rates of unity conventional NEMD is clearly the most efficient means of establishing the steady-state response. For example, under precisely the same conditions after 54 million timesteps, the TTCF expression for P_{xy} is accurate to $\pm 0.05\%$, but the directly averaged transient response is accurate to $\pm 0.001\%$. Because time is not wasted in establishing the steady state from each of 60 000 time origins, conventional steady-state NEMD needs only 120 000 timesteps to obtain an uncertainty of $\pm 0.0017\%$. If we assume that errors are inversely proportional to the run length then the relative uncertainties for a 54-million timestep run would be $\pm 0.05\%$, $\pm 0.001\%$, and $0.000\,08\%$, respectively. Steady-state NEMD is about 600 times more accurate than TTCF for the same number of timesteps. On the other hand, the transient-correlation method has a computational efficiency which is similar to that of the equilibrium Green-Kubo method. The main difference being that for GK calculations time origins can be taken more frequently than for TTCF's. For TTCF's time origins cannot be taken more frequently than the time interval over which the TTCF's are calculated. The advantage of the TTCF formalism is that it models the rheological problem of stress growth,[7] not simply steady shear flow, and we can observe the associated effects such as stress overshoot and the time development of normal stress differences.

Figure 5 shows the transient responses for the normal stress differences, P_{yy}-P_{zz} and P_{xx}-P_{yy}, for the three-dimensional system at a reduced strain rate of unity. The normal stress differences are clearly more subtle than either the shear stress or the hydrostatic pressure. Whereas the latter two functions seem to exhibit a simple overshoot before relaxing to their final steady-state values, the normal stress differences show two maxima before achieving their steady-state values (indicated SS in the figure). As before it is apparent that $t^*=1$ is sufficient time for an essentially complete relaxation to the steady state.

Figure 6 shows the shear stress for the three-dimensional system at the comparatively small field $\gamma^*=10^{-3}$. At this field strength conventional steady-state NEMD is swamped by noise. However, the subtraction technique can be used to substantially improve the statistics. Figure 6 compares the results obtained using the subtraction method with results obtained using the TTCF approach. It is important to note that both the subtraction and TTCF techniques are based on an analysis of the transient response of systems. The results compared in Fig. 6 were computed for *exactly* the same

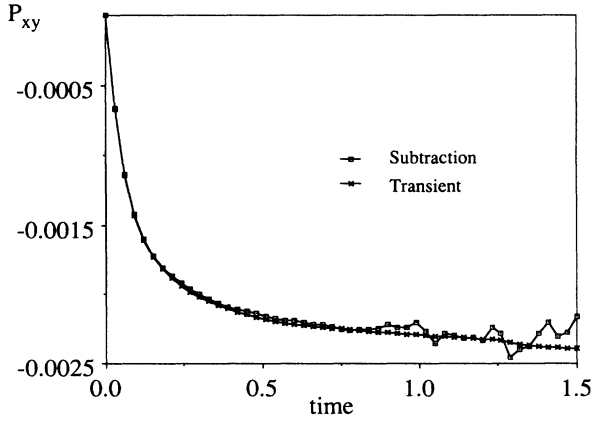

FIG. 6. The subtraction and transient-time-correlation-function results for the shear stress in three dimensions at $\rho^*=0.8442$, $T^*=0.722$, and $\gamma^*=10^{-3}$.

system using *exactly* the same number of simulation timesteps. The only difference between the two sets of results is how the data were analyzed. It is well known that at longer times the subtraction method fails because the equilibrium and nonequilibrium trajectories become decorrelated thus destroying the noise-reduction mechanism. This is clearly evident in Fig. 6 where at longer times, during which we expect the slow nonlinearities to complete the relaxation to the steady state, the subtraction technique becomes very noisy. We believe the superiority of the TTCF formalism for small shear rates is due to the judicious use of the symmetry-related starting states. This removes the small fluctuations in $\langle P_{xy}(0)\rangle$ which magnify the tail of $\langle B(t)P_{xy}(0)\rangle$ and would otherwise make the resultant nonequilibrium shear stress fluctuate. The starting states ensure that the only nonzero contribution to the transient-time-correlation function comes from correlations between $B(t)$ and $P_{xy}(0)$.

Figure 7 shows the corresponding results for shear dilatancy. Here the subtraction technique is essentially useless. Even the TTCF method becomes somewhat noisy at long times. The TTCF results clearly show the existence of a measureable, intrinsically nonlinear effect even at this small-strain rate.

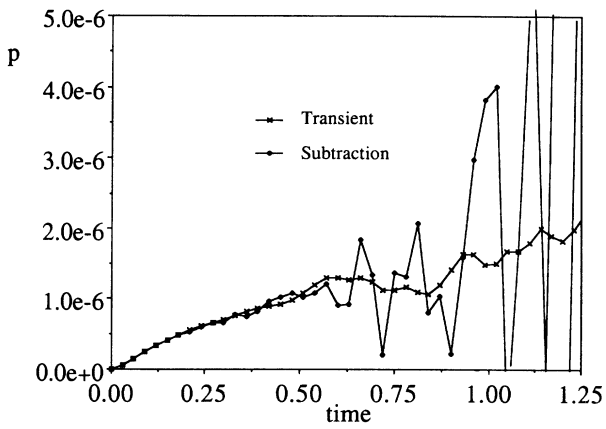

FIG. 7. The subtraction and transient-time-correlation-function results for the pressure in three dimensions at $\rho^*=0.8442$, $T^*=0.722$, and $\gamma^*=10^{-3}$.

IV. CONCLUSION

Over the years a number of numerical comparisons have been made between the Green-Kubo expressions and the results of NEMD simulations. In this paper we have taken this comparison one step further. We have compared NEMD simulation results with our thermostatted, nonlinear generalization of the Green-Kubo formulas. We have presented convincing numerical evidence for the usefulness and correctness of the transient-time-correlation function formalism. This theory is the natural thermostatted, nonlinear generalization of the Green-Kubo relations. Our simulation data unambiguously shows that at very small external fields, the TTCF formalism provides the most efficient presently known means of calculating transport properties. That is for the same number (and length) of nonequilibrium trajectories the TTCF formalism is superior to the subtraction technique. For strong fields, of order unity in reduced units, conventional NEMD is the most efficient known technique.

The recent study by Ryckaert *et al.*[13] of the Lennard-Jones fluid at a dense liquid-state point found no evidence for a nonanalytic variation of the viscosity with strain rate. This result is not surprising as it has long been realized that the coefficient of the $\gamma^{1/2}$ dependence increases dramatically as the glass transition is approached, and for the state point they consider the coefficient is very small. Indeed the strongest evidence for the square-root dependence is from the Lennard-Jones triple-point data. Some recent mode-coupling theory[21] work gives more support to the connection between the glass transition and square-root behavior of viscosity (in this case the frequency dependence of η). We believe the numerical results presented here are the most accurate produced to date. Each state point consists of 60 000 nonequilibrium trajectories covering a time range of $0 \le t \le 1.5$ (by contrast in Ref. 13 the longest simulation consisted of only 1400 nonequilibrium trajectories and a time range of $0 \le t \le 0.8$.

Although we have concentrated in this paper on using the TTCF formalism for direct numerical computations, it is apparent that perhaps the most important application of the theory of nonequilibrium steady states will turn out to be the derivation of steady-state fluctuation formulas and sum rules, a nonequilibrium generalization of the equilibrium fluctuation relations. As at equilibrium these relations should prove useful in characterizing the thermodynamic stability of systems near nonequilibrium phase transitions.

ACKNOWLEDGMENT

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