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Application of transient correlation functions to shear flow far from equilibrium

Gary P. Morriss and Denis J. Evans
Research School of Chemistry, Australian National University, Canberra ACT 2601 Australia

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Morriss and Evans recently developed a generalization of the Green-Kubo relations which is valid for nonequilibrium steady states far from equilibrium. This formalism relates the nonequilibrium response to transient time correlation functions which *connect* the nonequilibrium steady state to the equilibrium state. In the linear regime, the transient time correlation functions reduce to simple equilibrium Green-Kubo relations. The transient time correlation function method thus provides a long-sought-after fundamental relation between nonequilibrium molecular dynamics algorithms and the Green-Kubo formalism which is only valid close to equilibrium. In this paper we demonstrate the use of the transient time correlation function formalism for isothermal planar Couette flow. The results show that the nonlinear steady-state response can be calculated by integrating the appropriate transient response time correlation function. In particular, the nonlinear shear stress and pressure calculated in this way agree with the values calculated directly.

I. INTRODUCTION

The Green-Kubo relations[1] are fundamental to our understanding of linear transport processes close to equilibrium. For linear transport they play a role analogous to that played by the partition function in equilibrium statistical mechanics. Like the partition function, Green-Kubo relations are highly nontrivial to evaluate. They do however provide an exact starting point for approximate theoretical treatments. They can also be evaluated directly in equilibrium molecular dynamics simulations. More recently they have been used to develop efficient nonequilibrium molecular dynamics algorithms for the calculation of linear transport coefficients.[2] A major limitation for nonequilibrium statistical mechanics has been the lack of a corresponding theoretical basis for nonlinear transport processes far from equilibrium. This has not been for the lack of trying. However, essentially all previous attempts have either resulted in incorrect expressions for nonlinear transport, or have led to expressions which although formally exact, are nonetheless very difficult to analyze and interpret.

In 1979 Dufty and Lindenfeld[3] developed a readily interpretable expression for the nonlinear response which took the form of an integral of a time correlation function. Unlike the Green-Kubo expressions, this correlation function involved correlating the fluctuations of microscopic quantities in the initial equilibrium (or local equilibrium) state with the corresponding values of these quantities during the establishment of the nonequilibrium state (the transient response). This transient correlation function can be constructed from an ensemble of trajectories, which at the initial time are equilibrium states, but are then propagated forward in time with a field-dependent propagator. Unfortunately the Dufty-Lindenfeld transient correlation functions can easily be seen to diverge. This is because in the absence of a thermostat, there can be no steady state. The thermodynamic properties of the system continue to change in time.

Recently Evans, Morriss, and Holian have made major improvements in our understanding of the thermostatted behavior of nonequilibrium systems. These developments have their origins in the formulation by Hoover and Evans[4,5] of the so-called Gaussian thermostat. This thermostat is implemented by a change in the equations of motion of N-particle systems so that the heat produced irreversibly in nonequilibrium systems is continuously and instantaneously removed. Although the original formulation of the thermostat was *ad hoc*, its validity as a means of studying nonequilibrium steady states has since been established. Evans and Morriss[6] derived the equilibrium N-particle distribution function for an isolated system evolving under Gaussian isokinetic equations of motion. They proved that in the thermodynamic limit, equilibrium time correlation functions computed under Gaussian dynamics, are the same as the corresponding correlation functions computed under Newton's equations of motion.[7] Later it was verified that if one computes the linear response of Gaussian thermostatted systems to an external field, one does indeed find that the susceptibility is governed by an equilibrium time correlation function of Green-Kubo form but with time propagation generated by the field-free Gaussian isokinetic propagator.[8] This, combined with the earlier result showing the equivalence of Gaussian and Newtonian equilibrium time correlation functions, shows that to linear order in the external field the adiabatic and thermostatted responses are identical.[8,9] A corresponding series of results[9,10] have been derived for the Nose-Hoover thermostat.[11]

In this paper we give a simplified derivation of the transient correlation function expressions for the thermostatted nonlinear response of N-particle systems to planar Couette flow. We also show how the transient time correlation formalism is related to the isothermal generalization,[8] of Kawasaki's expression[12] for the nonlinear response. We test the validity of the transient correlation theory by using nonequilibrium molecular dynamics (NEMD) simulations of planar Couette flow, far from equilibrium.

II. TRANSIENT CORRELATION FUNCTIONS FOR PLANAR COUETTE FLOW

It is well known[13,14] that the equations of motion for an N-body system undergoing planar Couette flow can be written as,

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

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 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 $\mathbf{p}_i$.[12,13] These equations (1), are known as the Sllod equations of motion for shear flow.[13]

Isothermal response theory[8] shows that the adiabatic rate of change of the internal energy $H_0 = \Sigma(\mathbf{p}_i^2/2m + \Phi)$, 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 $AI\Gamma$ (Refs. 8 and 9) is satisfied. $AI\Gamma$ is satisfied by all the commonly used NEMD algorithms including the Sllod equations of motion for Couette flow. If $AI\Gamma$ 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:

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

Consider a canonical ensemble (or isothermal ensemble[8,9]) of systems suddenly subject to a constant shearing deformation at $t = 0$. The N-particle distribution function at some later time t is $f(\Gamma, t)$, where Γ denotes the $6N$-dimensional position of the system in phase space $\Gamma = (\mathbf{q}, \mathbf{p}) = (\mathbf{x}, \mathbf{y}, \mathbf{z}, \mathbf{p}_x, \mathbf{p}_y, \mathbf{p}_z)$. (Each of the components $\mathbf{x}, \mathbf{y}, \mathbf{z}, \mathbf{p}_x, \mathbf{p}_y, \mathbf{p}_z$ is itself an N-dimensional vector.) The average value of a phase variable $B(\Gamma)$ at time t is,

$$\langle B(t) \rangle = \int d\Gamma\, B(\Gamma) f(t) = \int d\Gamma\, f(0) B(\Gamma; t) \ , \tag{4}$$

where the second equality is a consequence of the equivalence of the Schrödinger and Heisenberg representations.[15] For *time-independent* external fields, differentiating the Heisenberg form with respect to time we obtain

$$\frac{d\langle B(t) \rangle}{dt} = \int d\Gamma\, f(0) \dot{\Gamma} \cdot \frac{\partial B(t)}{\partial \Gamma} \ . \tag{5}$$

In deriving Eq. (5) we have used the result that $dB(t)/dt = iL \exp(iLt) B = \exp(iLt) iLB$. This is only true if the external field is time independent since in that circumstance the Liouvillean iL, contains no explicit time dependence, and hence commutes with its associated propagator. Integrating (5) by parts we see that,

$$\frac{d\langle B(t) \rangle}{dt} = -\int d\Gamma\, B(t) \frac{\partial}{\partial \Gamma} \cdot \dot{\Gamma} f(0) \ . \tag{6}$$

The boundary term vanishes because the distribution function $f(0)$, approaches zero as the magnitudes of the momenta become infinite, and $f(0)$ can be taken to be periodic with respect to the coordinates. We are explicitly using the simulation periodic boundary conditions in the derivation.

Integrating (6) with respect to time we see that the nonlinear nonequilibrium response can be written as,

$$\langle B(t) \rangle = \langle B(0) \rangle - \int_0^t ds \int d\Gamma\, B(s) \frac{\partial}{\partial \Gamma} \cdot \dot{\Gamma} f(0) \ . \tag{7}$$

The dynamics implicit in $B(s)$ is of course driven by the full field-dependent, thermostatted equations of motion. For a system subject to the thermostatted shearing deformation, $\dot{\Gamma}$ is given by Eqs. (1) and (2). If $f(0)$ is the Gaussian isokinetic or the canonical distribution function[8,6] it is straightforward to show that $(\partial/\partial\Gamma) \cdot [\dot{\Gamma} f(0)]$ is $\beta V P_{xy} f(0)$. Thus $\langle B(t) \rangle$ becomes,

$$\langle B(t) \rangle = \langle B(0) \rangle - \beta \gamma V \int_0^t ds \langle B(s) P_{xy}(0) \rangle \ . \tag{8}$$

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 $\langle B(t) \rangle \langle P_{xy}(0) \rangle$, which is zero because $\langle P_{xy}(0) \rangle = 0$. For systems that exhibit mixing, Eq. (8) can therefore be rewritten as,

$$\langle B(t) \rangle = \langle B(0) \rangle - \beta \gamma V \int_0^t ds \langle \Delta B(s) P_{xy}(0) \rangle \ , \tag{9}$$

where,

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

The adiabatic systems treated by Dufty and Lindenfeld[3] cannot exhibit mixing because in the absence of a thermostat $d\langle B(t) \rangle/dt$ does not go to zero at large times. Thus the integral of the associated transient correlation function cannot converge. Other systems which are not expected to exhibit mixing are turbulent systems or systems which execute quasiperiodic oscillations.

The derivation of our fundamental Eq. (8), is simpler than that given in Ref. 8. In that paper equation (8) was derived from the Kawasaki form of the nonequilibrium distribution function. The derivation depended upon a lemma which gives an exact relationship between distribution function propagators and their adjoints, phase variable propagators. It is also interesting to note that the present derivation is given in the Heisenberg picture rather than the customary Schrödinger picture.[15]

We can use recursive substitution to derive the Kawasaki form for the nonlinear response from our transient time correlation formula, Eq. (8). The fact that we can derive the transient and Kawasaki forms of response theory from each other shows the fundamental equivalence of both representations. The first step in the derivation of the Kawasaki representation is to rewrite the transient correlation relation using iL to denote the phase variable Liouvillean, and $-i\mathscr{L}$ to denote its non-Hermitean adjoint, the distribution function Liouvillean. Thus $dB/dt \equiv iLB$ and $\partial f/\partial t \equiv -i\mathscr{L}f$. Using this notation Eq. (8) can be written as,

$$\begin{aligned}\langle B(t)\rangle &= \int d\Gamma\, Bf(0) \\ &\quad -\beta\gamma V\int_0^t ds\int d\Gamma\, f(0)e^{iLs}Be^{-iLs}J \qquad (10)\\ &= \int d\Gamma\, Bf(0) \\ &\quad -\beta\gamma V\int_0^t ds\int d\Gamma[e^{-i\mathscr{L}s}f(0)]Be^{-iLs}J\ . \qquad (11)\end{aligned}$$

Equation (11) can be written more simply as,

$$\begin{aligned}\langle B(t)\rangle &= \int d\Gamma\, Bf(0) \\ &\quad -\beta\gamma V\int_0^t ds\int d\Gamma\, B(0)J(-s)f(s)\ . \qquad (12)\end{aligned}$$

We can now successively substitute the transient correlation function expression for the nonequilibrium distribution function namely,

$$f(t)=f(0)-\beta\gamma V\int_0^t ds\, J(-s)f(s) \qquad (13)$$

into the right-hand side of (12). This gives,

$$\begin{aligned}\langle B(t)\rangle &= \int d\Gamma\, Bf(0)-\beta\gamma V\int_0^t ds_1\int d\Gamma\, B(0)J(-s_1)f(0)\\ &\quad +(\beta\gamma V)^2\int_0^t ds_1\int_0^{s_1} ds_2\int d\Gamma\, B(0)J(-s_1)J(-s_2)f(0)+\cdots \qquad (14)\\ &= \int d\Gamma\, B(0)\exp\left[-\beta\gamma V\int_0^t ds\, J(-s)\right]f(0)\ .\end{aligned}$$

This is precisely the isothermal Kawasaki form of the nonlinear response.[8,12] Comparing the transient time correlation expression for the nonlinear response with the Kawasaki representation, we see that the difference simply amounts to a time shift. In the transient time correlation form it is the dissipative flux J, which is evaluated at time zero, whereas in the Kawasaki form the response variable B, is evaluated at time zero. For equilibrium or steady-state time correlation functions the stationarity of averages means that such time shifts are essentially trivial. For transient response correlation functions there is of course no such invariance principle, consequently the time translation transformation is accordingly more complex.

The evaluation of the time-dependent response using the Kawasaki form directly, Eq. (14), is numerically unstable. The inevitable errors associated with the inaccuracy of the trajectory, as well as those associated with the finite grid size in the calculation of the integral itself, combine and are magnified by the exponential. This exponential is then multiplied by the phase variable $B(0)$, before the ensemble average is performed. In contrast the calculation of the response using the transient correlation expression, Eq. (9), is, as we shall see, far more stable.

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. 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 of (8) 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[7,9] that in the thermodynamic limit there is no difference between the thermostatted equilibrium time correlation function and the corresponding Newtonian or adiabatic correlation function.

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. The first term in this series for the response of the shear stress is just $V\langle P_{xy}^2\rangle/kT$, the infinite frequency shear modulus, G_∞. Since this is an equilibrium property its value is unaffected by the strain rate and is thus 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. PHASE-SPACE MAPPINGS

In this paper we use nonequilibrium molecular dynamics of shear flow in simple fluids to illustrate the transient correlation function formalism. The initial ensemble of starting states was generated from a single field-free Gaussian isokinetic trajectory. At equally spaced intervals along this single field-free trajectory, shearing simulations were started and followed for approximately 200 time steps. The response calculated from the integral of the transient correlation functions was compared with the direct response computed by averaging $\langle B(t)\rangle$. In practice the calculation proceeded by performing an equilibrium isokinetic molecular dynamics simulation for N_e time steps followed by a nonequilibrium run of N_n time steps. Each of these cycles gives one initial phase Γ, for the transient correlation function. The number N_n should be greater than the characteristic time required for the system to relax to a steady state. N_e is chosen to ensure that the initial phases are sufficiently uncorrelated. Here we used $N_e=N_n=200$. This process can be made more efficient if we use the equilibrium starting state generated by N_e time steps, to provide more than one initial phase for the nonequilibrium trajectories.

We note that given an initial starting phase $\Gamma_1=(\mathbf{x},\mathbf{y},\mathbf{p}_x,\mathbf{p}_y)$ then new starting phases, which occur within the equilibrium distribution with the same probability as the Γ_1, can be obtained using the following mappings:

$$\Gamma_2=(-\mathbf{x},-\mathbf{y},\mathbf{p}_x,\mathbf{p}_y)\ ,$$

$$\Gamma_3=(-\mathbf{x},\mathbf{y},-\mathbf{p}_x,\mathbf{p}_y)\ ,$$

$$\Gamma_4=(-\mathbf{x},\mathbf{y},\mathbf{p}_x,-\mathbf{p}_y)\ .$$

These three new configurations, along with the original one, give four different starting states and four different shearing trajectories from the single equilibrium run of N_e time steps. Each of the mappings consists of a pair of reflections in a coordinate or momentum axis. The mapping which produces Γ_2 for example, is obtained by reflecting in both the **x** and **y** axes. The resulting particle configurations are then imaged by the usual periodic boundary conditions. The overall effect of this mapping is to rotate the simulation cell through 180°. In total there are 2^4 states that can be obtained using the reflections of a two-dimensional phase space; however, only 2^3 of these states will result in *at most* a sign change in the shear stress. Only 2^2 of the remaining mappings lead to different shearing trajectories. The shearing trajectories obtained from Γ_i and $-\Gamma_i$ are identical. The probability of each of these states occurring within the equilibrium distribution of states, is identical because the Hamiltonian H_0, is invariant under these reflections and inversions of Γ.

There is a second, more important, advantage of this procedure. If we examine the transient response formula (8), we see that at long time the correlation function becomes $\sim\langle B(\infty)\rangle\langle P_{xy}(0)\rangle$. The steady-state average of B is usually nonzero. This is not the case for equilibrium time correlation functions. To minimize the statistical uncertainties in calculating the transient correlation integral, it is convenient to evaluate $\langle P_{xy}(0)\rangle$ in a constrained ensemble in which $\sum_i P_{xy}(\Gamma_i)$ is identically zero. The phase mapping procedure described above achieves this. If the shear stress computed from the original starting phase is $P_{xy}(\Gamma_1)$, then the shear stress of Γ_2 is also equal to $P_{xy}(\Gamma_1)$, but the shear stresses of both Γ_3 and Γ_4 are equal to $-P_{xy}(\Gamma_1)$. This means that the sum of the shear stresses of these four starting phases is *exactly* zero. The statistical difficulties at long time, associated with a small nonzero value the average of $P_{xy}(0)$, are eliminated. These mappings can be trivially generalized to three dimensions, and as the **z** coordinate does not appear in P_{xy} we obtain the same four starting phases and precisely the same advantage is gained.

IV. NUMERICAL RESULTS

To test the validity of the transient correlation function formalism we carried out a series of molecular dynamics simulations of shear flow in two and three dimensions. We used a second-order Runge-Kutta method to integrate the equations of motion with a time step of $0.005t^*$ in two dimensions, and $0.004t^*$ in three dimensions $[t^*=t(\sigma(m/\epsilon)^{1/2})^{-1}]$. The Runge-Kutta method was used rather than the more common Gear or leap-frog 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 leap-frog algorithms only achieve accuracy after an

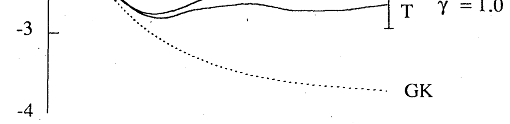

FIG. 1. The direct (D) and transient time correlation function (T) results for the shear stress in two dimensions at $\gamma^*=0.1$, 0.5, and 1.0. A typical error bar is included on the $\gamma^*=1$ transient time correlation function result at $t^*=1$. For comparison we include (GK) the Green-Kubo equilibrium estimate for the response $-\beta\gamma V\int_0^t ds\langle P_{xy}(s)P_{xy}(0)\rangle$ evaluated at $\gamma^*=0.5$ and 1.0.

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 thermostatic multiplier α, were calculated along with their associated transient correlation functions using typically 2000—3000 starting states. In Fig. 1 we present the results obtained for the shear stress $P_{xy}^* = P_{xy}(\sigma^2/\epsilon)$ in two dimensions. The two-dimensional simulations used a system of 896 soft disks $[\phi = 4\epsilon(\sigma/r)^{12}]$, at a density of $\rho^* = \rho\sigma^2 = 0.9238$, a temperature, $T^* = kT/\epsilon = 1$, and a range of values of the strain rate, $\gamma^* = \gamma(m/\epsilon)^{1/2}\sigma$. The potential was truncated at $r^* = (r/\sigma) = 1.5$. 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 width of the lines on the graph, whereas the error in the integral of the transient correlation function is approximately 15%.

The curves labeled GK give the linear response, as calculated from the Green-Kubo relations. The GK curves thus give the response of a hypothetical Newtonian fluid whose thermophysical properties exactly match the thermodynamic and *linear* transport properties of this soft disk fluid. The reduced zero shear rate shear viscosity, $\eta^* = \eta\sigma^2(m\epsilon)^{-1/2}$, at this state point is 3.8. When the time integration is truncated at $t^* = 1$, the Green-Kubo estimate is 3.7 ± 0.2. The statistical uncertainties of Green-Kubo and transient correlation calculations of equivalent length are similar. Both are substantially less accurate, at these strain rates, than direct NEMD calculations. At a reduced strain rate of one we see that the steady-state shear stress is reduced to approximately two thirds of the value it would have if the fluid was completely Newtonian. This is reflected in both the direct NEMD results and in the response predicted by the transient time correlation functions. They are in good statistical agreement. It is also clear that this fluid exhibits stress overshoot, a well-known property of non-Newtonian fluids. Stress overshoot is apparent both in the direct NEMD results and in the transient time correlation function predictions for γ^* of 0.5 and 1.

At the lower shear rate, $\gamma^* = 0.1$, the response is closer to the linear prediction given by the Green-Kubo relations and there is no evidence of stress overshoot. Indeed the linear response is indistinguishable from the transient correlation function result. The presence of stress overshoot indicates that for $\gamma \geq \sim 0.1$, the transient time correlation function, the derivative of the response, is negative at long times. This has never been observed in the *equilibrium* stress autocorrelation function.

The shear-induced increase of pressure with increasing strain rate is known as shear dilatancy. It is an intrinsically nonlinear effect and is not observed in Newtonian fluids nor is it predicted by the linear Green-Kubo theory. 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 Green-Kubo predictions are of course zero because the equilibrium correlation function, $\langle \Delta p(t) P_{xy}(0) \rangle$ is exactly zero at all times. The agreement between the direct average, and the value obtained from the transient correlation function expression at $\gamma^* = 0.5$ and 1.0 is impressive. At $\gamma^* = 0.1$, we are in the turnover regime[16] where shear dilatancy has all but vanished. 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 transient correlation formalism than are the results for the shear stress because there is no underlying linear effect.

The three-dimensional simulation was performed for the Lennard-Jones fluid $(\phi = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6])$, at its triple point $(\rho^* = 0.8442,\ T^* = 0.722)$. The simulations employed 108 atoms and a potential cutoff at $r = 2.5\sigma$. The results are presented in Fig. 3. The agreement between the direct average and the transient correlation function expression is again very good for both the shear stress and the pressure.

Although it is not easy to see in the figures, the initial

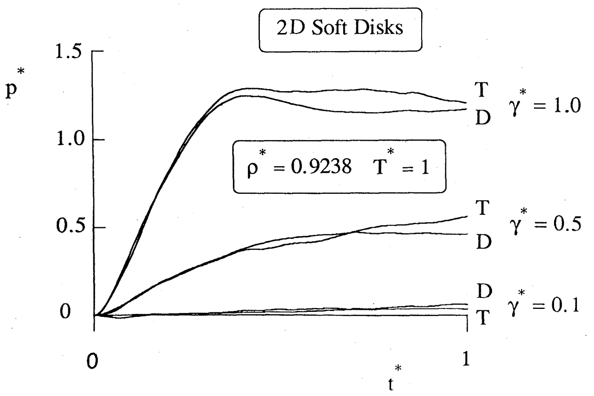

FIG. 2. The direct (D) and transient time correlation function (T) results for the pressure in two dimensions at $\gamma^* = 0.1$, 0.5, and 1.0.

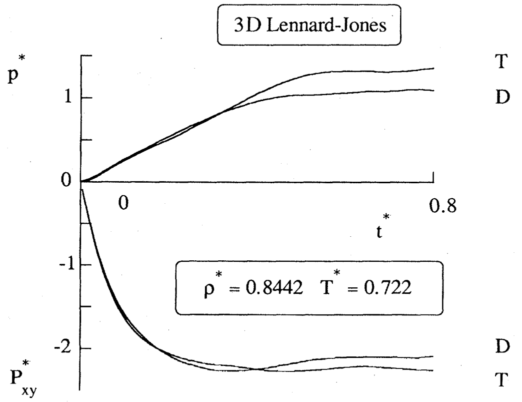

FIG. 3. The direct (D) and transient time correlation function (T) results for the shear stress and pressure in three dimensions at $\gamma^* = 1.0$. Note the positive y axis is the reduced pressure while the negative y axis is the reduced shear stress.

slope of the pressure response curves 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.

Comparing the statistical uncertainties of the transient correlation and direct NEMD results shows that, at the fields studied in these calculations, direct NEMD is about 2 orders of magnitude more efficient than the transient correlation function approach. On the other hand, the transient correlation method has a computational efficiency which is similar to that of the equilibrium Green-Kubo method. It appears that the efficiency of the transient correlation function method *decreases* slightly with *increasing* field strength, although further calculations are required to confirm this observation. This is to be contrasted with direct NEMD whose efficiency increases with increasing field. However, direct NEMD has zero efficiency at zero field.

V. CONCLUSION

We have outlined and tested a new formalism for analyzing the nonlinear response of many-body systems. In the past, many people have conjectured that nonlinear transport coefficients, or at least their derivatives with respect to the perturbing field, might be related to steady-state time correlation functions in much the same way that linear transport coefficients are related to equilibrium fluctuations. The present formalism does not satisfy this implicit wish. Instead we have shown that the nonlinear response is related in a very simple way to correlations between the initial equilibrium state and the transient which establishes the steady state. The simulation studies support the correctness of the resulting expressions.

In contrast with many previous approaches, the transient time correlation formalism does not require the use of *ad hoc* convergence factors as in Zubarev's method,[17] nor does it require the use of difficult to interpret or analyze projection operators.[18] It is also the first of any of these methods to be tested directly, either by comparison with experiment or with simulation data.

At high fields, $\gamma^* \sim 1$, the transient correlation function method is clearly not as efficient as the direct NEMD. At low fields, however, this situation will be reversed. This is because at low fields the transient time correlation functions reduce to Green-Kubo correlation functions. Although these functions are difficult to calculate with high accuracy, they *can* be calculated. On the other hand, direct NEMD calculations cannot be performed at zero field. There is therefore a critical-field value below which the transient correlation function approach is more efficient and above which direct NEMD will be more efficient. The transient time correlation approach should therefore prove useful in attempts to settle the controversy,[19] over the form of the low-field, asymptotic nonlinear response. Previously the only method which was applicable to very low (but *nonzero*) applied fields was the differential trajectory method.[20] The Kawasaki representation for the response does not appear to be directly useful in computer simulations.

The most important aspect of the transient time correlation formalism is likely to be theoretical rather than computational, however. It is possible that the transient time correlation form of the nonequilibrium N-particle distribution function can be used to form a nonequilibrium partition function. Indeed, some preliminary results are already available. Evans[21] has recently used the transient time correlation function expression for the internal energy of the steady state to derive a theoretical expression for the specific heat of a nonequilibrium steady state. Preliminary simulation results[22] support the validity of the specific-heat expressions so derived.

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