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Transient ensemble averages in non-Newtonian flow: Symmetry and simulation

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Transient (nonequilibrium) cross correlation functions (CCF) are introduced for the characterization of non-Newtonian flow under conditions of shear startup or cessation. Arguments based on the principles of group-theoretical statistical mechanics imply that these are asymmetric for shearing and symmetric for elongational stress. These expectations are confirmed with nonequilibrium molecular dynamics. Nonequilibrium CCF's are evaluated in the rise transient regime, immediately following the application of shear stress, and in the fall transient regime immediately following its removal. The rise and fall transient CCF's of atomic velocity and pressure tensor components are found to have quite different time dependencies, in line with the rise and fall stress transients themselves. They also correlate well with the non-Newtonian characteristics of the fluid, in that, as the response to the stress becomes increasingly more non-Newtonian, the difference between the equilibrium and rise or fall transient CCF's develops an increasingly sharp peak at short time.

I. INTRODUCTION

At sufficiently low shear rates the viscosity of a fluid is independent of shear rate, this is called the Newtonian viscosity. At large shear rates the viscosity of a fluid decreases further below the Newtonian viscosity with increasing shear rate (called "shear thinning").[1] An objective of current research is to understand and specify the microscopic origins of these changes in terms of its associated statistical mechanics. Our contribution in recent papers has been to characterize these nonequilibrium fluids in terms of *new* time averages and time correlation functions introduced by the strain rate.[2,3] These changes in the fluid, introduced by the strain rate, have been predicted using group theory applied to statistical-mechanical ensemble averages (reviewed in Sec. II). Verification of the predictions of this group-theory statistical mechanics (GTSM) has swiftly followed using molecular-dynamics simulations. We have shown that a shear velocity field has a pronounced effect on the time correlation functions of a simple fluid,[2] making them sensitive probes of the physical consequences of nonequilibrium flow on the fluid. The shear flow, $\dot{\gamma}=\partial v_x/\partial y$ (v is the velocity), distorts the time correlation functions present at equilibrium so that the x, y, and z components are no longer equivalent. Most interestingly, however, there are certain time correlation functions that *only* have nonzero structure in the presence of shear flow, which make them particularly useful probes of the presence and magnitude of a differential flow velocity within a fluid.

It has been shown recently that the microscopic response of an atomic ensemble to shear is the appearance of asymmetric time correlation functions.[2] This is unknown in conventional non-Newtonian rheology, and was discovered by nonequilibrium computer simulation following indications provided by the third principle of group-theoretical statistical mechanics, which asserts that the complete symmetry of an external influence, in this case shear stress, must be imparted to thermodynamic ensemble averages, either in the field on steady state or in the transient condition immediately following the imposition of the external influence or, alternatively, its removal. In order to implement the third principle, a means must be found to measure the symmetry of (a) the influence itself, and (b) the thermodynamic averages. This is found through point-group theory, using the fact that the point group of an isotropic ensemble of atoms or molecules is the group of all rotations and reflections, with its irreducible representations. Without these symmetry considerations, conventional rheology, dependent as it is on continuum theory, is unable to say anything about the response of a structured ensemble to shear or elongational stress on the microscopic (molecular) scale. In this respect continuum hydrodynamics is still beset by controversies. These problems are removed by a combination of symmetry and simulation, which provides a variety of new and useful insights, some of which are presented for the first time in this paper. Group theory is an intrinsic and central part of this process.

In this report we describe the theory that predicts those time correlation functions, cf., existing in (symmetry-breaking) simple planar shear flow, which are trivially zero in the absence of shear flow for symmetry reasons. The specific application here is to apply group-theory statistical mechanics to nonlinear *dynamic* viscosity as probed by the buildup and decay of shear (and normal) stress on application and cessation of a shear strain rate to a fluid, respectively. This involves applying GTSM to nonlinear-response theory.

The earliest simulations of shear flow using molecular dynamics (MD) attempted to reproduce the experimental arrangement of boundary-driven flow. The contents of the MD cell were sheared by two boundaries translating in opposing directions on opposite faces of the cell (in three dimensions). See Ref. 4 for a recent application of this method. Periodic boundaries in one of the three dimensions was sacrificed to achieve this. As the viscosity is computed from a nonequilibrium steady state, we refer to this form of molecular dynamics as nonequilibrium molecular dynamics (NEMD). More recent advances in nonequilibrium statistical mechanics have provided algorithms that enable shear thinning to be simulated by molecular dynamics maintaining periodic boundary conditions in all three directions.[5,6] Therefore, the molecular dynamics cell is viewed as a subvolume in an infinite boundary-less, but still sheared, fluid. Of these, the SLLOD equations of motion were the first to be applied widely.[5] (The name SLLOD is not an acronym, the origin of which we refer the reader to Ref. 6.) These equations of motion maintain the desired velocity gradient on an atomic distance scale *throughout* the cell, and it is these equations of motion that we use here.

Recent NEMD simulations have revealed the existence of asymmetric cross correlation functions (CCF's) in couette flow at the shear-on steady state.[2] These violate the principle of microscopic reversibility and the Onsager-Casimir reciprocal principle because they are neither symmetric nor antisymmetric in the indices (X and Y) when caused by an applied strain rate $\dot{\gamma}=\partial v_X/\partial Y$.[7,8] They are exemplified by the velocity CCF's in an atomic ensemble,

$$\langle v_X(t)v_Y(0)\rangle \neq \langle v_Y(t)v_X(0)\rangle \ , \qquad (1)$$

where $\langle \cdots \rangle$ denotes a time average. This result was anticipated by the third principle of group-theoretical statistical mechanics (see Sec. II). Asymmetric cross correlations and transients as observed in this paper are not statistically stationary in the conventional definition,[2] because they are sums of antisymmetric and symmetric components. In the presence of shear stress, therefore, the principle of statistical stationarity does not apply to the time correlation functions and response functions which appear on the microscopic (single atom) level as the shear is applied. A statistically stationary process is also microscopically reversible, implying that the time correlation functions and response functions must be either symmetric or antisymmetric. If they are neither, then the process is irreversible on a microscopic level. Note that such a system no longer obeys the Onsager-Casimir reciprocal relations because these are based on either symmetry or antisymmetry. The asymmetric rise transients of this paper are therefore indicative of a dynamical process under shear which is irreversible on the microscopic scale, and which are not governed by simple Onsager-Casimir reciprocal relations. Both Newtonian and non-Newtonian responses are irreversible, leading to a much sought after method of investigating irreversibility. A further discussion of this point is given in Ref. 9.

Recent work[3,10] has extended the NEMD simulation and symmetry analysis to combined shear and elongational flow, using new equations of motion which are capable of investigating simultaneously the effects of elongational and shear stress. The GTSM was tested with simulation and found to be capable of anticipating, on the grounds of symmetry, the types of CCF expected from elongational and shear stress, applied independently or simultaneously.[3] The former produces symmetric diagonal time correlation functions in the stress applied steady state and the latter asymmetric off diagonal CCF's of type Eq. (1). Shear alone produces a depolarized light scattering;[10] a second-moment frequency spectrum which is the Fourier transform of asymmetric current CCF's akin to Eq. (1). Both findings were the result of a symmetry analysis based on GTSM.

These symmetry considerations are quite general, and apply equally well to transient and field-on steady states. We therefore expect transient (nonequilibrium) CCF's to follow the same pattern, and thus to provide immediate insight at a fundamental level to the response of an ensemble to the application and removal of both elongational and shear stress. In general, the asymmetric rise and fall nonequilibrium CCF's of various kinds will have different time dependencies, and the extent of this *difference* is an indicator of the departure from Newtonian rheology. For shear flow we have the additional feature that both rise and fall nonequilibrium CCF's are asymmetric in general (as indeed are the shear responses themselves). By analogy with what is known from dielectric rise and fall transients,[11-14] stress-induced nonequilibrium CCF's may be expected to show markedly different rise and fall transient time dependencies, providing insight into non-Markovian and nonlinear statistical mechanics. In response to shear stress we have the additional property of microscopic irreversibility and the violation of Onsager-Casimir symmetry shown by features analogous to Eq. (1).

In this work we introduce nonequilibrium asymmetric CCF's of various types which are produced either in the rise transient state immediately following upon the application of stress, or in the fall-transient regime after stress is instantaneously removed. The nonequilibrium rise and fall transient CCF's are computed for shear stress. In each case the rise and fall transient CCF's are correlated with indicators of the non-Newtonian (shear thinning) response of the ensemble. This provides an entirely new method of determining the fundamentals of non-Newtonian rheology through the transient response of an ensemble to the imposition or removal of elongational-shear stress.

In Sec. II we describe the group theory statistical mechanics and in Sec. III we explore its consequences for transient non-Newtonian flows.

II. GROUP-THEORETICAL STATISTICAL MECHANICS

Group-theoretical statistical mechanics is made up of three principles, the third of which is of interest here.[15-19] This asserts that the complete symmetry of a strain rate is imparted to ensemble averages in the equilibrium and transient condition. It makes use of the D symmetries or irreducible representations of the point-group of molecular ensembles. For those of structurally achiral molecules, or atoms, they are irreducible representations of the point group, $R_h(3)$, of all rotations and reflections, denoted by $D_g^{(0)}, D_g^{(1)}, \ldots, D_g^{(n)}$ or $D_u^{(0)}, D_u^{(1)}, \ldots, D_u^{(n)}$. The superscripts denote the order of spherical harmonics, the subscripts positive (g) or negative (u) to parity inversion P. The D symmetry of a scalar is $D_g^{(0)}$; of a pseudoscalar $D_u^{(0)}$; of a polar vector $D_u^{(1)}$; of an axial vector $D_g^{(1)}$; and so on for higher-order tensor quantities. Higher-order D symmetries are generated through the Clebsch-Gordan theorem

$$D^{(n)}D^{(m)}=D^{(n+m)}+\cdots+D^{(n-m)}$$

and $g\times g=g$ and $g\times u=u$. A quantity such as strain rate, $vr^{(-1)}$, where v is velocity and r is position, is, in general, a complete (tensor) product of two vectors whose D symmetry is $D_g^{(0)}+D_g^{(1)}+D_g^{(2)}$, a sum of three parts by the Clebsch-Gordan theorem. This is an expression of the fact that the second rank tensor $A_{(ij)}$ is, in general, the sum $A_{(ij)}=A\delta_{(ij)}/3+C_k+S_{(ij)}$, where $A/3$ is the trace denoted by $D_g^{(0)}$. Here $\delta_{(ij)}$ is the Kronecker delta. $C_k=B_{(ij)}=(A_{(ij)}-A_{(ji)})/2$ is the antisymmetric component of the complete tensor, equivalent to a pseudovector through $C_k=\epsilon_{(ijk)}B_{(ij)}$, where $\epsilon_{(ijk)}$ is the Levi-Civita symbol. This part is denoted by $D_g^{(1)}$. The third part is the traceless symmetric component of the complete tensor denoted as $\frac{1}{2}(A_{(ij)}+A_{(ji)})-A\delta_{(ij)}/3$. Its D representation is $D_g^{(2)}$. The quantities A, C_k, and $S_{(ij)}$ form spherical tensors of rank 0, 1, and 2 transforming as the spherical harmonics Y_L^M, for $L=0,1,2$. As discussed fully elsewhere,[2,3] the D symmetry of stress σ is the sum,

$$\Gamma(\sigma)=D_g^{(0)}+D_g^{(1)}+D_g^{(2)}\ , \tag{2}$$

of scalar, vector, and tensor components, respectively. The third principle of GTSM implies that the same symmetry is imparted to ensemble averages, such as time CCF's, either in the steady state or in the transient condition between this and field-free equilibrium.

Elongational stress has the symmetry $D_g^{(0)}$ of diagonal components such as

$$\langle v_i(0)v_i(t)\rangle;\quad i=X,\ Y,\ \text{or}\ Z \tag{3}$$

(where $\langle\cdots\rangle$ means a time average) and produces no off-diagonal components. The strain rate tensor in planar couette flow of the type $\partial v_x/\partial y$ consists of a symmetric traceless or "pure strain rate" component and an antisymmetric component associated with vorticity. The latter causes a rotation of the primarily distorted fluid structure away from the $\pi/4$ and $3\pi/4$ directions. The GTSM reveals that there are two types of time cross correlation functions induced at the microscopic level by $\partial v_X/\partial Y$ flow. One is symmetric to time or index reversal [i.e., $(\mathbf{q},\mathbf{p})\rightarrow(\mathbf{q},-\mathbf{p})$] and represents the effect of the pure strain rate component. The other is antisymmetric to index reversal and represents the effect of vorticity. The sum of both influences is generally asymmetric to a time shift. Shear stress has the symmetry $D_g^{(1)}+D_g^{(2)}$, a combination of antisymmetric vorticity $D_g^{(1)}$,

$$\langle v_X(0)v_Y(t)\rangle=-\langle v_Y(0)v_X(t)\rangle\ , \tag{4}$$

and symmetric deformation $D_g^{(2)}$,

$$\langle v_X(0)v_Y(t)\rangle=\langle v_Y(0)v_X(t)\rangle\ . \tag{5}$$

A *weighted* combination of Eqs. (4) and (5) gives the observable result, Eq. (1).[3,10] Note that the response to shear stress is purely off-diagonal and asymmetric, and that to elongational stress is purely diagonal and symmetric. We concentrate on the shear flow case in this work.

Asymmetric CCF's are measures of non-Newtonian rheology. Asymmetry and non-Newtonian are *not* interchangeable concepts. Of course, the asymmetry is always there, but increases as the non-Newtonian response increases. Even a Newtonian shear stress is asymmetric at the microscopic level.

III. COMPUTATION OF NONEQUILIBRIUM CCF's

A nonequilibrium CCF is defined, in general, as the running time average $\langle A(0)B(t)\rangle$, where $A(0)$ is sampled in the equilibrium condition,[20] and $B(t)$ out of equilibrium. Special numerical techniques are needed[21-23] for the proper evaluation of a nonequilibrium CCF. For rise transient nonequilibrium CCF's, $A(0)$ is taken at field-free equilibrium and $B(t)$ in the transient condition between equilibrium and the attainment of the field-on steady state. Conversely, for fall transients, $A(0)$ is taken at the field-on steady state and $B(t)$ in the transient condition between this and the reattainment of field-free thermodynamic equilibrium.

In this paper $A(0)$ and $B(t)$ represent velocity, position, and appropriate components,[2] of the pressure tensor, both for elongational and shear stress. The rise and fall transient responses are correlated with independent indicators of the non-Newtonian rheology of the ensemble as measured by the shear viscosity. The full time dependencies of representative rise and fall transient nonequilibrium CCF's are given as figure illustrations. In this section we describe methods for incorporating planar shear flow in the classical equations of motion of molecular dynamics.

The MD simulations followed particles of mass m interacting via the Lennard-Jones (LJ) potential

$$\phi(r)=4\epsilon[(\sigma/r)^{12}-(\sigma/r)^{6}]\ . \tag{6}$$

The basic technique is the same as used elsewhere.[1] The MD simulations were performed on a cubic unit cell of volume V containing $N=256$ LJ molecules. The interactions were truncated at 2.5σ. We use LJ reduced units throughout, i.e., $k_BT/\epsilon\rightarrow T$, and number density $\rho=N\sigma^3/V$. Time is in $\sigma(m/\epsilon)^{1/2}$, strain rate is in $(\epsilon/m)^{1/2}/\sigma$, viscosity is in $(m\epsilon)^{1/2}/\sigma^2$, and stress is in $\epsilon\sigma^{-3}$. The time step was 0.015. The state point considered was a near triplet-point state at $\rho=0.8442$ and $T=0.722$.

We used the SLLOD algorithm in most of the calculations.[5] The peculiar or thermal velocity is denoted by $\bar{v}$. For molecular position $\mathbf{R}$,

$$\dot{R}_X = v_X = \tilde{v}_X + \dot{\gamma} R_Y \ , \tag{7}$$

$$\dot{R}_Y = v_Y = \tilde{v}_Y \ , \tag{8}$$

$$\dot{R}_Z = v_Z = \tilde{v}_Z \ , \tag{9}$$

$$\frac{d\tilde{v}_X}{dt} = F_X/m - \dot{\gamma}\tilde{v}_Y \ , \tag{10}$$

$$\frac{d\tilde{v}_Y}{dt} = F_Y/m \ , \tag{11}$$

$$\frac{d\tilde{v}_Z}{dt} = F_Z/m \ , \tag{12}$$

where the α component of the force on a particle is F_α, the velocity is v_α, and the peculiar velocity is $\tilde{v}_\alpha$ (i.e., that component of the velocity in excess of the streaming flow velocity). We maintain constant kinetic energy ("temperature") within the Verlet algorithm using a profile assumed thermostat by *velocity* rescaling applied to $\tilde{v}_\alpha$.

We calculated the shear viscosity η from

$$\eta = -P_{XY}/\dot{\gamma} \ , \tag{13}$$

where

$$P_{XY} = \frac{1}{V}\left[\sum_{i=1}^{N} m_i \tilde{v}_{xi}\tilde{v}_{yi} - \sum_{i=1}^{N-1}\sum_{j>i}^{N} \frac{r_{xij} r_{yij}}{r_{ij}} \frac{d\phi(r_{ij})}{dr}\right] , \tag{14}$$

and where r_{xij} is the x component of $\mathbf{r}_{ij}$ and $V = (N/\rho)$ the volume of the MD cell. In the sheared case $\dot{\gamma} = 1.0$ produces $\eta = 2.1$ (about 30% shear thinning) and $\dot{\gamma} = 3.0$ produces $\eta = 0.6$[1] These two shear rates therefore span a significant region of the shear thinning curve.

We now consider the transient response of simple liquids to shear flow suddenly applied at time $t = 0$, averaged over typically 100 distinct starting phase points. They were performed with an assumed profile thermostat using the technique devised by Morriss and Evans.[22]

In transient flows the nonequilibrium cross correlation functions $\langle v_X(s) v_Y(0)\rangle$ and $\langle v_Y(s) v_X(0)\rangle$ appear in response to shear. Here the time argument 0 is taken from an equilibrium ensemble and s from the transient flow state. The observed transients are weighted sums of the vorticity and deformational transients. Rise transients and fall transient CCF's of velocity can be defined in the nonequilibrium condition. The former occur immediately after a field is applied at the equilibrium point $t = 0$. The nonequilibrium CCF is built up with one variable in the equilibrium condition and the other in the rise transient condition at $t = s$, for example, $\langle v_X(0) v_Y(s)\rangle$. Fall transient CCF's are defined with v_Y having reached the field-on steady state. After reaching the steady state the field is switched off at $t = 0$ and the nonequilibrium CCF constructed by correlating v_Y at this instant with v_X in the fall transient condition at $t = s$. The CCF is therefore $\langle v_Y(0) v_X(s)\rangle$. We see that one CCF is generated from the other by a time shift, or index reversal. The velocity rise and fall transients are asymmetric and become approximately symmetric only when the external field goes to zero. In the finite-field case, however, the rise and fall transient velocity CCF's cannot have the same time dependence. The velocity transient CCF's are molecular probes of the non-Newtonian nature of the sheared ensemble. Therefore, we have gone part way to bringing together rheology, dielectrics, and the dynamical Kerr effect within a common theoretical framework.

In Fig. 1 we show the *difference* in the transient CCF's $\langle v_X(0) v_Y(t)\rangle$ in rise and fall conditions. The shear rate is $\dot{\gamma} = 1$ and the SLLOD algorithm was applied for typically 100 transients, starting from prepared equilibrium starting states. For the rise event CCF is

$$\langle v_X(0) v_Y(t)\rangle_{\dot{\gamma}} - \langle v_X(0) v_Y(t)\rangle_{\dot{\gamma}=0} \ ,$$

where at time $t = 0$ the two ensembles depart due to the different strain rate histories. The "background" steady state is the unsheared fluid. For the fall situation the CCF is

$$\langle v_X(0) v_Y(t)\rangle_{\dot{\gamma}=0} - \langle v_X(0) v_Y(t)\rangle_{\dot{\gamma}} \ .$$

In this case we have the reverse situation of a steady-state sheared fluid and an instantaneously "applied" unsheared state. The two difference CCF's in Fig. 1 are clearly asymmetric. We observe that in the rise transient the time function has a sharp peak at $t = 0.15$, whereas the corresponding fall transient has a dip at the same position. The corresponding "difference" mean-square displacements (M.S.D.) in the x ("streaming") direction are shown in Fig. 2.[23] (The position increments due to the peculiar momenta are only used in calculating these.) Figure 2 shows that the presence of shear causes enhanced self-diffusion in the transient state compared to the unsheared state. The corresponding y and z m.s.d. curves are all positively increasing, indicating that any sudden change of shear rate (application or cessation) to a fluid causes at least a temporary enhancement of self-diffusion in the y and z directions.

Rise transients and fall transients of shear-induced velocity provide information analogous to that in orienta-

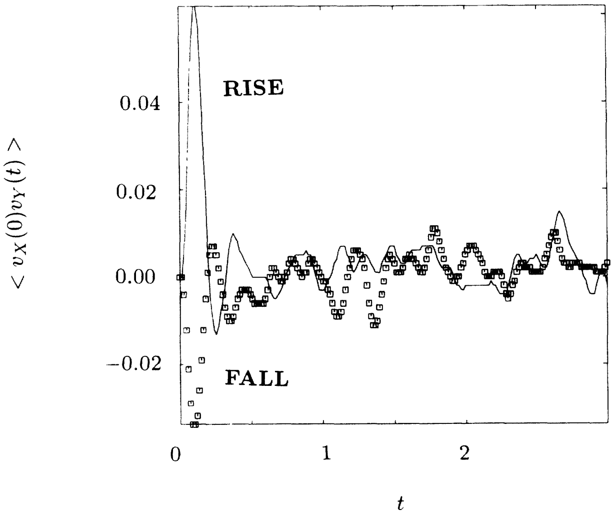

FIG. 1. The difference CCF's in rise and fall transients ($\dot{\gamma} = 1$). The solid line is for the rise CCF $\langle v_X(0) v_Y(t)\rangle_{\dot{\gamma}} - \langle v_X(0) v_Y(t)\rangle_{\dot{\gamma}=0}$. The squares are for the fall CCF $\langle v_X(0) v_Y(t)\rangle_{\gamma=0} - \langle v_X(0) v_Y(t)\rangle_{\dot{\gamma}}$.

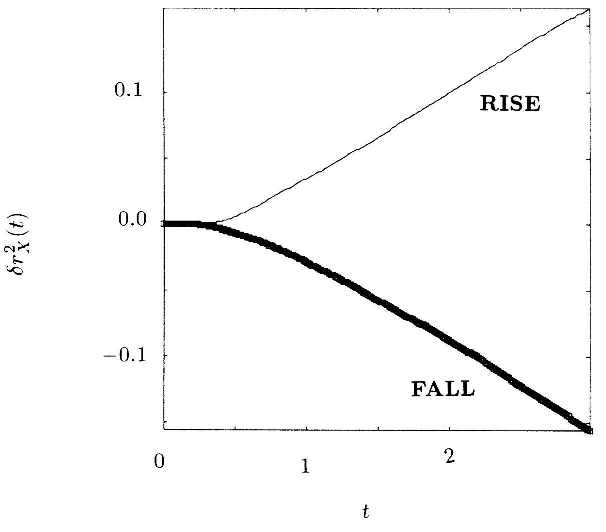

FIG. 2. As for Fig. 1 except that the corresponding difference mean-square displacements in the x direction are given.

tional transients induced by an electric field. The latter depend on field strength when the response is nonlinear. The rise transients in electric field show field-induced oscillations, recently confirmed by computer simulation,[24,25] and the fall transients are accelerated with respect to the equivalent equilibrium correlation function. The latter is an exclusive indicator of nonlinear response, and is also expected to occur in the contexts of shear and elongational flow. Oscillations in the rise transient are indicative of non-Markovian nonlinear statistical mechanics.

In Fig. 3, we compare the difference in the rise transients, $\langle v_X(0)v_Y(t)\rangle$, for two states at $\dot{\gamma}=1$ and $\dot{\gamma}=3$. Both curves show peaks at $t\sim 0.15$. Figure 3 clearly shows that the magnitude of the rise transient increases with shear rate, following the extent of the distortion of the fluid structure and resulting in viscosity reduction.

In Fig. 4 we show the *difference* in the transient CCF's, $\langle v_Y(0)v_X(t)\rangle$, in the rise condition. The shear rates are $\dot{\gamma}=1$ and $\dot{\gamma}=3$. For the rise event the CCF is

$$\langle v_Y(0)v_X(t)\rangle_{\dot{\gamma}}-\langle v_Y(0)v_X(t)\rangle_{\dot{\gamma}=0}\ .$$

The "background" steady state is the unsheared fluid. For the fall situation the CCF is

$$\langle v_Y(0)v_X(t)\rangle_{\dot{\gamma}=0}-\langle v_Y(0)v_X(t)\rangle_{\dot{\gamma}}\ .$$

Note that the shape of the difference rise transients for $\langle v_X(0)v_Y(t)\rangle$ (Fig. 3) and $\langle v_Y(0)v_X(t)\rangle$ (Fig. 4) are quite different as predicted by GTSM. The former is characterized by an initial peak, whereas the latter has a minimum before a following maximum. The rise and fall transients are again approximately antisymmetric. In all of these CCF's we attribute the oscillations beyond $t\simeq 0.5$ as statistical noise.

In Fig. 5 we investigate the fall difference CCF's formed out of $\langle P_{XY}(0)P_{XY}(t)\rangle$. In Fig. 6 we show the rise and fall difference CCF's formed out of $\langle P_{XX}(0)P_{XY}(t)\rangle$. The collective CCF's clearly show a sensitivity to shear rate and are distinct in rise or fall situations.

The conventional foundation of detailed balancing and microscopic reversibility rests on time-reversal symmetry in achiral ensembles.[26] However, in the presence of shear stress, which is of $D_g^{(1)}+D_g^{(2)}$ symmetry, and which is neither symmetric nor antisymmetric to time reversal, it is doubtful whether detailed balancing and microscopic reversibility can still be obeyed. In this case there is no microscopic time-reversal symmetry even in correlation functions in the steady state, and the concept is even less

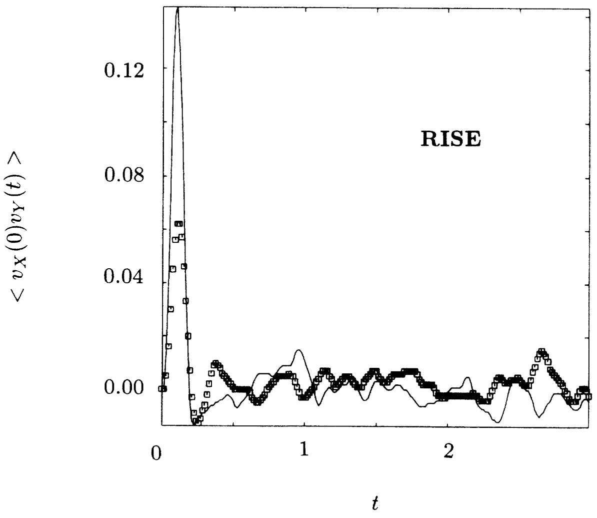

FIG. 3. The difference CCF's in rise transients. The solid line is for the rise CCF $\langle v_X(0)v_Y(t)\rangle_{\dot{\gamma}}-\langle v_X(0)v_Y(t)\rangle_{\dot{\gamma}=0}$, for ($\dot{\gamma}=3$). The squares are for the same rise CCF using $\dot{\gamma}=1$.

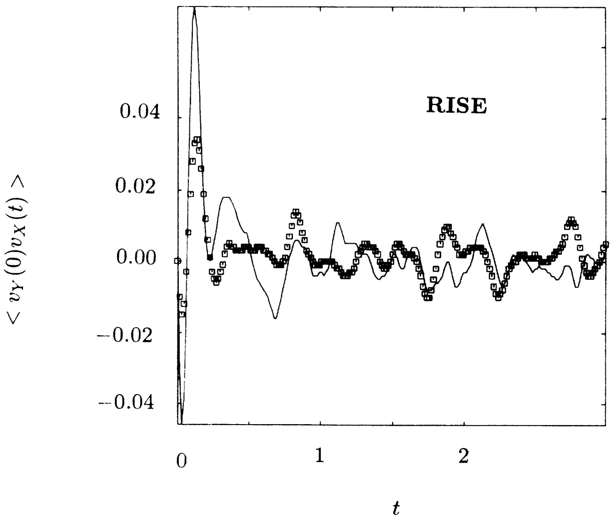

FIG. 4. The difference CCF's in rise transients. The solid line is for the rise CCF $\langle v_Y(0)v_X(t)\rangle_{\dot{\gamma}}-\langle v_Y(0)v_X(t)\rangle_{\dot{\gamma}=0}$, for $\dot{\gamma}=3$. The squares are for the same rise CCF but at $\dot{\gamma}=1$.

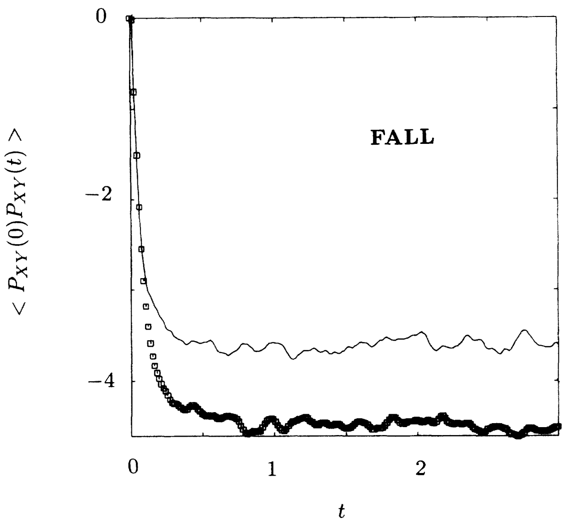

FIG. 5. The difference CCF's in the fall transients $\langle P_{XY}(0)P_{XY}(t)\rangle_{\dot{\gamma}=0}-\langle P_{XY}(0)P_{XY}(t)\rangle_{\dot{\gamma}}$. The solid line is for $\dot{\gamma}=3$ and the squares are for the same rise CCF but at $\dot{\gamma}=1$.

valid in the transient regime considered in this paper. It is important to note that the present system conserves reversality because the complete time-reversed experiment is clearly possible, but in the time-reversed experiment the correlation and transient functions would also be asymmetric, neither symmetric nor antisymmetric to index reversal. This type of asymmetry reinforces the general conclusion that it is the unitarity of matrices, rather than microscopic reversibility, that is necessary for the validity of Boltzmann's *H* theorem, one of the foundations of statistical mechanics. Thus irreversibility is used here in the sense that the time correlation functions and transients of $D_g^{(1)}+D_g^{(2)}$ symmetry, imparted by shear stress, are asymmetric in index reversal.

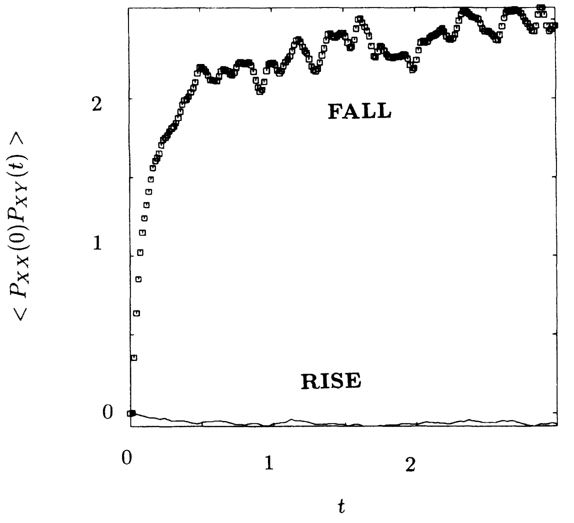

FIG. 6. The difference CCF's in the rise and fall transients $\langle P_{XX}(0)P_{XY}(t)\rangle_{\dot{\gamma}}-\langle P_{XX}(0)P_{XY}(t)\rangle_{\dot{\gamma}=0}$ and $\langle P_{XX}(0)P_{XY}(t)\rangle_{\dot{\gamma}=0}-\langle P_{XX}(0)P_{XY}(t)\rangle_{\dot{\gamma}}$, respectively. The solid line is for the rise CCF at $\dot{\gamma}=1$ and the squares are for the fall CCF at the same shear rate.

The methods developed in this paper have potential application for a wide range of useful materials, including glasses, rheids, alloys, and composites under shear and elongational stress. A glass, for example, can be simulated using the well-developed techniques of *slam quenching*, and reacts to imposed shear stress according to the rate at which the stress is applied. Glass can flow, bend, or shatter under this stress. Quickly applied it is shattered by shear stress; if the latter is applied slowly glass can be flexed; and glass can also flow. These processes are all characterized by the asymmetries of our indicator transient CCF's, which are spectral measures of the various ways in which glassy material flows, flexes, and shatters. If a glass is shattered in a computer simulation, transient CCF's are the *only* available measures of response to the quickly applied shear stress, because the material obviously never reaches equilibrium.

The study of ensembles of atoms, as in this paper, can be extended straightforwardly to simple metal mixtures (alloys, for example), stressed to the critical degradation point and beyond, using transient CCF's to study the degradation process on the picosecond time scale. An understanding of the microdynamics of metal failure would be useful in the design of new materials (alloys, composites, and polymers) with greater tolerance to shear and elongational stress. Finally, simple graphitic and diamond models for material failure in carbon-based composites can be constructed straightforwardly from the present code for Lennard-Jones atom ensembles. The methods developed here are equally valid for molecular and liquid crystalline ensembles, where we have the added dimensions of rotation and orientation, with considerably enhanced scope for cross correlation between rotational, translational, and orientational variables.

IV. CONCLUSIONS

The group-theoretical statistical mechanics theory has predicted the existence of new time correlation functions which only exist *during* the buildup or decay of shear flow in a fluid. They have a damped oscillatory appearance and are sensitive indicators of the transient state. It is concluded that on the fundamental, single-atom level, the imposition of elongational stress produces symmetric rise transients and time correlation functions in the steady state. Removal of the elongational stress produces symmetric fall transients. Shear stress results in rise and fall transients and steady-state correlation functions which are asymmetric, consisting of a linear combination of symmetric and antisymmetric components in each case. Accordingly, the microscopic description of shear stress is irreversible and statistically nonstationary. The simple type of Onsager-Casimir reciprocal relation is no longer a valid description of the microscopic statistical response of an atomic ensemble under shear stress. There is also a relation between the asymmetry of the response and correlation functions and the degree to which the ensemble departs from Newton's linear relation between stress and strain. The shear stress always produces asymmetric response and correlation functions even in the Newtonian limit. Furthermore, the correlation functions produced by shear stress cannot be described as a simple Langevin equation[9] and are, in consequence, both non-Markovian and nonlinear in the sense that linearity in the friction coefficient or memory function of the Langevin equation fails completely to describe them.

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