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 CCFs 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 CCFs of atomic velocity and pressure tensor components are found to have a single time dependence 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 CCFs 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"). 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. 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-mechanical theory (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, making them sensitive probes of the physical consequences of nonequilibrium flow on the fluid. The shear flow, \( \dot{\gamma} = \frac{\partial \eta}{\partial \eta} \) (\( \dot{\gamma} \) 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 makes 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. 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 best by controversy. These problems are removed 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, of 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 build-up 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

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this method. Periodic boundaries in one of the three di-

mensions 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. Moreover, the nonequilibrium statistical mechanics have provided algo-
rithms that enable shear thinning to be simulated by 
molecular dynamics maintaining periodic boundary con-
ditions in all three directions. Therefore, the molecular 
dynamics cell is viewed as a subvolume in an infinite 
boundary-less, but still sheared, fluid. Of these, the 
SLLOD is not an acronym, the ori-
gin of which we refer the reader to Ref. 6.) These equa-
tions 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 
symmetric cross correlation functions (CCF's) in 
coarse flow at the shear-on steady state. 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 
\( \gamma = \partial u / \partial t \). They are exemplified by the velocity 
CCF's in an atomic ensemble, 

\[
\langle v_x(t) v_y(0) \rangle - \langle v_x(t) \rangle \langle v_y(0) \rangle ,
\]

where \( \langle \cdot \cdot \cdot \rangle \) denotes time average. This result was 
anticipated by the third principle of group-theoretical 
statistical mechanics (see Sec. II). Asymmetric cross 
correlations and transients in CCF's have been shown in this paper in not statistically stationary in the conventional definition, 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 microscopic or statistically stationary process is also 
microscopically reversible, implying that the time 
correlation functions and response functions must be ei-
ther 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 
response transients of this paper are therefore indicative of a 
dynamical process under shear which is irreversible 
at the microscopic scale, and which are not governed by 
simple Onsager-Casimir reciprocal relations. Both 
Newtonian and non-Newtonian responses are irreversi-
ble, leading to a much sought after method of investigat-
ing irreversibility. A further discussion of this point is 
given in Ref. 9.

Recent work \(^{1,5,9} \) has extended the NEMD simulation 
and symmetry analysis to combined shear and elonga-
tional flow, using new equations of motion which are capa-
bale of investigating simultaneously the effects of elonga-
tional and shear stress. The GTSM was tested with simu-
lation 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. The former produces symmetric diagno-
tal 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 symme-
try 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 en-
semble to the application and removal of both elongation-
al 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 Newtoni-
an 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 dielec-
tric rise and fall transients,\(^{11,14} \) stress-induced nonequi-
librium CCF's may be expected to show markedly different 
rise and fall transient time dependencies, providing in-
sight into non-Markovian and nonlinear statistical 
mechanics. In response to shear stress we have the addi-
tional 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 appli-
cation 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 fundamental\(^{13} \) of 
Newtonian rheology through the transient response of an 
ensemble to the imposition or removal of elongational-
 shear stress.

In Sec. II we derive 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 simple concepts, 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 equi-
librium 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 repre-
sentations of the point group, \( A_1, A_2 \) of all rotations 
and reflections, denoted by \( D_{12}^{1}, D_{12}^{1}, D_{12}^{1}, D_{12}^{1} \) or 
\( D_{2}, D_{2}^{1}, D_{2}^{1}, D_{2}^{1} \). The superscripts denote the order of
spherical harmonics, the subscripts positive (g) or negative (a) to parity inversion P. The D symmetry of a scalar is \(D^{(s)}_{0}\); of a pseudoscalar \(D^{(p)}_{0}\); of a polar vector \(D^{(l)}_{1}\); of an axial vector \(D^{(a)}_{1}\); and so on for higher-order tensor quantities. Higher-order D symmetries are generated through the Clebsch-Gordan theorem

\[
D^{(s)}(m) \otimes D^{(a)}(m) \otimes \cdots \otimes D^{(a)}(m-n)
\]

and \(g \times g = u, g \times u = u\). A quantity such as strain rate, \(\varepsilon_{ij}^{(2)}\), where \(v\) is velocity and \(r\) is position, is, in general, a complete (tensor) product of two vectors whose D symmetry is \(D^{(2)}_{0} + D^{(2)}_{1} + D^{(2)}_{2}\), 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 \(A_{ij} = A_{ij}^{(0)} + A_{ij}^{(1)} + A_{ij}^{(2)}\), where \(A^{(2)}\) is the trace denoted by \(D^{(2)}_{0}\). Here \(\delta_{ij}\) is the Kronecker delta. \(C_{ij} = B_{ij}^{(2)} = (A_{ij} - A_{ij}/2)\) is the antisymmetric component of the complete tensor, equivalent to a pseudovector through \(C_{ij} = e_{ijkl}B_{kl}\), where \(e_{ijkl}\) is the Levi-Civita symbol. This part is denoted by \(D^{(2)}_{1}\). The third part is the traceless symmetric component of the complete tensor denoted as \(A_{ij}^{(1)} = A_{ij}^{(2)} - \delta_{ij}A^{(2)}/2\). Its representation is \(D^{(2)}_{2}\). The quantities \(A, B, C, \text{and } S_{ijkl}\) form spherical tensors of rank 0, 1, and 2, and transforming as the spherical harmonics \(Y_{L}^{M}\), for \(L = 0, 1, 2, \ldots\) as discussed fully elsewhere.\(^{5,6}\) The D symmetry of stress \(\sigma\) is the sum

\[
\Gamma(\sigma) = D^{(0)}_{0} + D^{(1)}_{1} + D^{(2)}_{2}
\]

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 \(D^{(2)}_{2}\) of diagonal components such as

\[
\langle \varepsilon_{ij}(0)\sigma_{ij}(t) \rangle, \quad i = X, Y, \text{ or } Z
\]

(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 \(\partial \omega_{ij}/\partial y\) consists of a symmetric traceless or "pure strain rate" component and an antisymmetric component associated with vorticity. The latter causes a rotation of the normally distorted fluid structure away from the \(x/4\) and \(3x/4\) directions. The GTSM reveals that there are two types of time cross correlation functions induced at the microscopic level by \(\partial \omega_{ij}/\partial y\) flow. One is symmetric to time or index reversal [i.e., \((q,p) \leftrightarrow (q,-p)\)] 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 \(D^{(2)}_{1} + D^{(2)}_{2}\), a combination of antisymmetric vorticity \(D^{(2)}_{2}\),

\[
\langle \varepsilon_{xy}(0)\sigma_{xy}(t) \rangle = -\langle \varepsilon_{yx}(0)\sigma_{yx}(t) \rangle.
\]

(4)

and symmetric deformation \(D^{(2)}_{1}\),

\[
\langle \varepsilon_{xy}(0)\sigma_{yx}(t) \rangle = \langle \varepsilon_{yx}(0)\sigma_{xy}(t) \rangle.
\]

(5)

A weighted combination of Eqs. (4) and (5) gives the observable result, Eq. (1).\(^{10}\) Note that the response to shear stress is purely off-diagonal and asymmetric, and that to elongational stress is purely diagonal and symmetrical. 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

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

(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 \(2.5\sigma\). We used LJ reduced units throughout, i.e., \(k_{B}T/e = T\) and number density \(\rho = N/V\). Time is in \(\sigma/\sqrt{m}\), strain rate is in \(\sqrt{m/\sigma}\), viscosity is in \(\eta \sigma^{2}/m\), and stress is in \(\sigma\). The time step was 0.005. 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.\(^{2}\) The peculiar or thermal velocity is denoted by \(\theta\). For molecular position \(\mathbf{r}\),
\[ R_x = \gamma_x R_x + \gamma \frac{d}{dt} R_y, \]
\[ R_y = \gamma_y R_y, \]
\[ 0 = \gamma_y R_x, \]
\[ \frac{dx}{dt} = F_x/m - \gamma \frac{d}{dt} R_y, \]
\[ \frac{dy}{dt} = F_y/m, \]
\[ \frac{dz}{dt} = F_z/m, \]

where the \( \alpha \) component of the force on a particle is \( F_\alpha \), the velocity is \( u_\alpha \), and the peculiar velocity is \( v_\alpha \) (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 \( u_\alpha \).

We calculated the shear viscosity \( \eta \) from
\[ \eta = \frac{F_{xy}}{\gamma_y}, \]

where
\[ F_{xy} = \sum_{i=1}^{N} \sum_{j=1}^{N} m_i \mu_{ij} \frac{\partial}{\partial r_{ij}} \delta(r_{ij}), \]
and where \( r_{ij} \) is the \( x \) component of \( r_{ij} \) and \( \mu_{ij} = (m_i m_j) / (m_i + m_j) \) the volume of the MD cell. In the sheared case \( \gamma = 1 \) (about 30% shear thinning) and \( \gamma = 3 \) produces \( \eta = 0.6 \). 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 generally 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 Morris and Evans. In transient flows the nonequilibrium cross correlation functions \( \langle \gamma_x(t) \gamma_y(t) \rangle \) and \( \langle \gamma_x(t) \gamma_z(t) \rangle \) appear in response to shear. Here the time argument \( 0 \) is taken from an equilibrium ensemble and \( t \) 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 occurs 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 as \( t = 0 \), for example, \( \langle \gamma_x(t) \gamma_y(0) \rangle \).

Fall transient CCF's are defined with \( t = 0 \) 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 \( \gamma_x \) at this instant with \( \gamma_x \) in the fall transient condition at \( t = 0 \). The CCF is therefore \( \langle \gamma_x(t) \gamma_y(t) \rangle \). We see that one CCF is generated from the other by a time shift, or index reversal. The velocity rise and fall transients are asymptotic 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 KCL effect within a common theoretical framework.

In Fig. 1 we show the difference in the transient CCF's \( \langle \gamma_x(0) \gamma_y(t) \rangle \) in rise and fall conditions. The shear rate is \( \gamma = 1 \) and the SLLOD algorithm was applied for typically 100 transients, starting from prepared equilibrium starting states. For the rise event CCF is
\[ \langle \gamma_x(0) \gamma_y(t) \rangle \gamma \longrightarrow -\langle \gamma_x(0) \gamma_y(t) \rangle \gamma, \]
where at time \( t = 0 \) the two ensembles depart to the different strain rate histories. The "background" steady state is the unsheared fluid. For the fall situation the CCF is
\[ \langle \gamma_x(0) \gamma_y(t) \rangle \gamma \longrightarrow -\langle \gamma_x(0) \gamma_y(t) \rangle \gamma, \]

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. The (positive) moments and the peculiar momenta are only used in calculating these. The CCF's show a plateau at small times but rapidly decrease as \( t \) increases, with a slow fall after the peak.

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 (\( \gamma = 1 \)). The solid line is for the rise CCF \( \langle \gamma_x(0) \gamma_y(t) \rangle \gamma \longrightarrow -\langle \gamma_x(0) \gamma_y(t) \rangle \gamma \). The squares are for the fall CCF \( \langle \gamma_x(0) \gamma_y(t) \rangle \gamma \longrightarrow -\langle \gamma_x(0) \gamma_y(t) \rangle \gamma \).](image-url)
transient 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,\textsuperscript{26,27} 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, \( \langle y(t) \rangle_{(0,y)} - \langle y(t) \rangle_{(0,0)} \), for two states at \( y=1 \) and \( y=3 \). 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. 6 we show the difference in the transient CCFs, \( \langle y(t) \rangle_{(0,y)} - \langle y(t) \rangle_{(0,0)} \). In the rise condition. The shear rates are \( \gamma=1 \) and \( \gamma=3 \). For the rise event the CCF is

\[ \langle y(t) \rangle_{(0,y)} - \langle y(t) \rangle_{(0,0)} \]

The “background” steady state is the unheaped fluid.

For the fall situation the CCF is

\[ \langle y(t) \rangle_{(0,y)} - \langle y(t) \rangle_{(0,0)} \]

Note that the shape of the difference rise transients for \( \langle y(t) \rangle_{(0,y)} - \langle y(t) \rangle_{(0,0)} \) (Fig. 3) and \( \langle y(t) \rangle_{(0,y)} - \langle y(t) \rangle_{(0,0)} \) (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 CCFs we attribute the oscillations beyond \( t\approx 0.5 \) as statistical noise.

In Fig. 5 we investigate the fall difference CCF's formed out of \( \langle y(t) \rangle_{(0,y)} - \langle y(t) \rangle_{(0,0)} \). In Fig. 6 we show the rise and fall difference CCF's formed out of \( \langle y(t) \rangle_{(0,y)} - \langle y(t) \rangle_{(0,0)} \). The collective CCFs 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.\textsuperscript{24} However, in the presence of shear stress, which is of \( D^{11} \times D^{12} \) 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

\[ \langle y(t) \rangle_{(0,y)} - \langle y(t) \rangle_{(0,0)} \]

\[ \langle y(t) \rangle_{(0,y)} - \langle y(t) \rangle_{(0,0)} \]
valid in the transient regime considered in this paper. It is important to note that the present system conserves reversibility 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 3rd theorem, one of the foundations of statistical mechanics. Thus irreversibility is used here in the sense that the time correlation functions and transients of $D^{(1)}(t)$ and $D^{(2)}(t)$, imparted by shear stress, are asymmetric in index reversal.

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 simm quenching, and react 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 moves, 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 graphic and diagram 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 produced 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 symmetric, 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 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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