Asymmetric Correlation Functions in a Sheared Ensemble, Consequences for Langevin Theory.

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Abstract

The observation by computer simulation of shear-induced asymmetric cross correlation functions is analyzed with linked Langevin equations in the linear, Markovian approximation. The difference between the analytical results and computer simulation is interpreted in terms of the fact that the simulated cross correlation functions are non-linear and non-Markovian, and also seem to be non-stationary, i.e., asymmetric to time displacement or index reversal. In this condition, the Onsager reciprocal relation, which pertain to equilibrium, reversible, linear, and stationary processes, no longer hold, and the simple Langevin equation is no longer able to describe the results of computer simulation.

Introduction

Recent computer simulations (1-5) have demonstrated the existence of new, asymmetric time cross correlation functions (c.c.f.'s) of the type

\[ \langle \tau_c (t_1) \rangle \neq \langle \tau_c (t_2) \rangle \]

in the steady state under a shear strain of type \( \gamma_0 \). The c.c.f. of type (1) cross correlates the orthogonal \( x \) and \( y \) components of linear atomic velocity in an N particle ensemble. This has been explained (1-3) as the grounds that a strain of this type produces a weighted combination of symmetric c.c.f.'s of type (2)

\[ \langle \tau_c (t_1) \rangle = \langle \tau_c (t_2) \rangle 
\]

and asymmetric c.c.f.'s of type (3)

\[ \langle \tau_c (t_1) \rangle 
eq \langle \tau_c (t_2) \rangle 
\]

Here the D symmetries are irreducible representations (4-8) of the rotation-reflection point group \( B_3 (3) \).

In this letter we make the first analytical attempt to understand the result (1) in terms of linked Langevin equations, developed from the Dula tensor equations of D. J. Evans and Moriya (9). These Langevin equations are written in the linear, Markovian, approximation for an ensemble of atoms under shear. To reproduce type (2), we use the friction coefficients which are symmetric in the indices X and Z of the laboratory frame (X, Y, Z), and for type (3) the friction coefficients are asymmetric. A comparison of these exact analytical results is then made with the symmetric c.c.f.'s of the computer simulation. The latter is a general non-linear and non-Markovian, non-asymmetric to time displacement and in the indices X and Z. The analytical treatment is on the other hand linear and Markovian, and produces results which are distinctly different, in the sense that the simulated c.c.f.'s are finite at \( t = 0 \), but the analytical counterparts vanish at \( t = 0 \).

Derivation and Solution of the Langevin Equations

The starting point of the derivation of the Langevin equations is eqn (3.48) of ref. (9).
\[ F_2 = m\ddot{x} + m\dddot{x} \]  
\[ F_1 = m\ddot{y} + m\dddot{y} \]  
\[ F_2 = m\ddot{y} + m\dddot{y} \]  
and the latter by the same equation but with a positive sign on the right-hand side of eqn (10). We assume that these equations can be written with
\[ \ddot{x} = \frac{\partial F_2}{\partial x} - \frac{\partial F_1}{\partial y} \]  
\[ \ddot{y} = \frac{\partial F_1}{\partial y} - \frac{\partial F_2}{\partial x} \]

The deterministic equations (5) are developed now into Langrana equations which are solved in the linear Markovian approximation for the approximate cross-correlation function of type (1), whose components are types (2) and (3). The Langrana equations corresponding to (5) are
\[ F_{\text{lin}} = m\ddot{x} + m\dddot{x} + \lambda m\ddot{x}\ddot{y} \]  
\[ F_{\text{lin}} = m\ddot{y} + m\dddot{y} + \lambda m\ddot{x}\ddot{y} \]

These equations have been written for \( \ddot{x} \) and type \( \ddot{y} \) variability. For \( \ddot{y} \) type deformation the minus sign on the right-hand side of eqn (10) is replaced by a plus sign. In eqn (6) the beta's are friction coefficients in the linear, Markovian approximation. It has been assumed that
\[ \beta_{\text{fric}} = \frac{\partial F_{\text{lin}}}{\partial x} = \frac{\partial F_{\text{lin}}}{\partial y} \]

i.e., that the components of the mean rate response can be identified with cross-friction coefficients in the linear, Markovian approximation. More generally, the friction coefficients are non-Markovian memory functions (19), and the Langrana equation is non-linear (11). Quo vadis, in the linear, Markovian approximation (2), the Langrana equation may be solved for the cross-friction coefficients of interest
\[ \langle \phi(t) \phi(t+\theta) \rangle = \frac{\langle \phi(t) \phi(t+\theta) \rangle }{\langle \phi(t) \phi(t+\theta) \rangle} = \beta_{\text{fric}} \delta(t) \delta(t+\theta) \]  
\[ \langle \phi(t) \phi(t+\theta) \rangle = \frac{\langle \phi(t) \phi(t+\theta) \rangle }{\langle \phi(t) \phi(t+\theta) \rangle} = \beta_{\text{fric}} \delta(t) \delta(t+\theta) \]

where
\[ \delta = 0 \]  
\[ \epsilon = s^2 - \beta_{\text{fric}} \]
with a similar expression for $<\nu_f(\theta_f) >$ with $\nu_f$ replaced by $\nu_k$. For shear induced vorticity

$$\nu_{kx} = - \nu_{xx}$$

(5a)

and for shear induced deformation

$$\nu_{kx} = \nu_{xx}$$

(5b)

The final asymmetric cross correlation function of type (5) is assumed to be a weighted sum of both types

$$<\nu_f(\theta_f) > = A <\nu_f(\theta_f) >_{\text{vorticity}} + B <\nu_f(\theta_f) >_{\text{approximation}}$$

(5a)

and

$$<\nu_f(\theta_f) > = A <\nu_f(\theta_f) >_{\text{approximation}} + B <\nu_f(\theta_f) >_{\text{vorticity}}$$

(5b)

where $A$ and $B$ are weighting constants. If $A << B$ for example, the cross correlation functions from eqn (10) will be slightly asymmetric, i.e. nearly of type (5), and nearly of type (5) for $A >> B$. There will be intermediate cases of varying asymmetry. However, despite being able to explain qualitatively the major feature of the simulation, i.e. that the cross correlation functions are asymmetric, eqns (10) are not able to show why the simulated $c.e.F.'s$ (1-5) remain finite at $t = 0$. Equations (10) produce $c.e.F.'s$ which vanish at $t = 0$.

The simple linear, Markovian approach thus fails qualitatively at short times.

Discussion

The failure of the Langvin equations (6) to describe the results from computer simulation is an important indication of the fact that non-Newtonian sheared $N$ particle ensembles have several features which are fundamentally different from their equilibrium counterparts:

1) The sheared ensemble supports cross correlation functions of type (1) which are asymmetric in time displacement and in the indices $X, Z$ of the shear plane. These $c.e.F.'s$ have the property (1-5)

$$<\nu_f(\theta_f) > \neq 0$$

(11)

which is not reproduced by the linear Markovian approximation represented in equ (6). This is unlikely to be remedied by developing the friction coefficients into memory functions, thus making the system non-Markovian, and we are led to conclude

2) That the system is non-linear. In one sense it is non-linear because the stress and the strain rate are not linearly related, as in Newtonian's law of shear stress. In this sense the system is non-linear because it is non-Newtonian. If we are to attempt an approach to the slow $c.e.F.'s$ (1) with Langvin equations, we are led to the conclusion from (1) that the friction coefficients are no longer simple linear multiples of velocity, as in equ (6), because this approach fails qualitatively at $t = 0$ both for Markovian and non-Markovian approximations to the rigorous equ (5). More generally, the Langvin equation can be non-linear, containing friction
coefficients that multiply powers of velocity on the right-hand side. In general the equation would contain a sum of terms, with interesting analytical applications (12).

3) The new cross-correlation functions of type (1) are observed by numerical simulation to be asymmetric in time displacement (eqn 3). They are not therefore stationary (12) in the conventional sense, because they are neither symmetric in time displacement (eqn 3), nor antisymmetric (eqn 3).

6) This leads directly to the conclusion that in the presence of shear, the N particle ensemble no longer obeys the Ogston reciprocal relations (1, 4), which are true for N particle ensembles at thermodynamic equilibrium, where the system is referred.

The overall conclusion is that an N particle ensemble in the steady state under shear which is non-Newtonian produces asymmetric time cross-correlation functions which indicate a physical process which is non-linear, irreversible, non-Markovian and asymmetric in time displacement, being in this sense non-stationary. In consequence a simple linear Markovian description fails qualitatively (1-7). This leads to an entirely new appreciation of non-Newtonian N particle dynamics.

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