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

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Abstract

The observation by computer simulation of shear-induced asymmetric cross correlation functions is analysed 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 relations, 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

$$< v_X(t)v_Z(0) > \neq < v_Z(t)v_X(0) > \quad (1)$$

in the steady state under a shear strain of type $\frac{\partial v_X}{\partial Z}$. The c.c.f. of type (1) cross correlates the orthogonal v_X and v_Z components of linear atomic velocity in an N particle ensemble. This has been explained {1-5} on the grounds that a strain rate of this type produces a weighted combination of symmetric c.c.f.'s of type $D_g^{(2)}$

$$< v_X(t)v_Z(0) > = < v_Z(t)v_X(0) > \quad (2)$$

and antisymmetric c.c.f.'s of type $D_g^{(1)}$

$$< v_X(t)v_Z(0) > = - < v_Z(t)v_X(0) > \quad (3)$$

Here the D symmetries are irreducible representations {6-8} of the rotation-reflection point group $R_h(3)$.

In this letter we make the first analytical attempt to understand the result (1) in terms of linked Langevin equations, developed from the Dolls tensor equations of D. J. Evans and Morriss {9}. These Langevin equations are written in the linear, Markovian, approximation for an ensemble of atoms under shear. To reproduce type (2), use is made of cross 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 asymmetric c.c.f.'s of the computer simulation. The latter is in general non-linear and non-Markovian, and 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)

$$m\dot{v} = \mathbf{F} - \nabla \mathbf{u} \cdot m v \tag{4}$$

where $\mathbf{F}$ is the force and $\mathbf{v}$ is the velocity of a particle externally subjected to shear. The latter is represented by the tensor $\nabla \mathbf{u}$ with nine components in general. It is assumed that the shear causes a strain rate response in the N particle ensemble consisting of $D_g^{(1)}$ type vorticity, and $D_g^{(2)}$ type deformation {1-5}. The former is represented from eqn (4) as

$$F_X = m\dot{v}_X + m\frac{\partial u_X}{\partial Z} v_Z \tag{5a}$$

$$F_Z = m\dot{v}_Z - m\frac{\partial u_Z}{\partial X} v_X \tag{5b}$$

and the latter by the same equations but with a positive sign on the right hand side of eqn (5b). We assume that these equations can be written with

$$\dot{\gamma}_{XZ} = \frac{\partial u_X}{\partial Z} \; ; \; \dot{\gamma}_{ZX} = \frac{\partial u_Z}{\partial X}$$

The deterministic equations (5) are developed now into Langevin equations which are solved in the linear Markovian approximation for the asymmetric cross correlation function of type (1), whose components are types (2) and (3). The Langevin equations corresponding to (5) are

$$F_{X\ stochastic} = m\dot{v}_X + m\beta v_X + m\beta_{XZ} v_Z \tag{6a}$$

$$F_{Z\ stochastic} = m\dot{v}_Z + m\beta v_Z - m\beta_{ZX} v_X \tag{6b}$$

These equations have been written for $D_g^{(1)}$ type vorticity. For $D_g^{(2)}$ type deformation the minus sign on the r.h.s. of eqn. (6b) is replaced by a plus sign. In eqns (6) the beta's are friction coefficients in the linear, Markovian approximation. It has been assumed that

$$\beta_{XZ} = \frac{\partial u_X}{\partial Z} \; ; \; \beta_{ZX} = \frac{\partial u_Z}{\partial X} \tag{7}$$

i.e. that the components of the strain rate response can be identified with cross-friction coefficients in the linear, Markovian approximation. More generally, the friction coefficients are non-Markovian memory functions {10}, and the Langevin equation is non-linear {11}. However, in the linear, Markovian approximation (6) the Langevin equations may be solved for the cross correlation functions of interest

$$< v_X(t) v_Z(0) > = \frac{< v_X(0) v_X(0) >}{(c - b^2)^{1/2}} \beta_{XZ} e^{-bt} \sin\{(c - b^2)^{1/2} t\} \; ; \; c > b^2 \tag{8a}$$

$$< v_X(t) v_Z(0) > = \frac{< v_X(0) v_X(0) >}{(b^2 - c)^{1/2}} \beta_{XZ} e^{-bt} \sinh\{(b^2 - c)^{1/2} t\} \; ; \; b^2 > c \tag{8b}$$

where

$$b = 4\beta \; ; \; c = \beta^2 - \beta_{XZ}\beta_{ZX}$$

with a similar expression for $< v_Z(t)v_X(0) >$ with β_{XZ} replaced by β_{ZX}. For shear induced vorticity

$$\beta_{XZ} = -\beta_{ZX} \tag{9a}$$

and for shear induced deformation

$$\beta_{XZ} = \beta_{ZX} \tag{9b}$$

The final asymmetric cross correlation function of type (1) is asumed to be a weighted sum of both types

$$< v_X(t)v_Z(0) > = A < v_X(t)v_Z(0) >_{vorticity} + B < v_X(t)v_Z(0) >_{deformation} \tag{10a}$$

and

$$< v_Z(t)v_X(0) > = -A < v_Z(t)v_X(0) >_{vorticity} + B < v_Z(t)v_X(0) >_{deformation} \tag{10b}$$

where A and B are weighting constants. If A < < B for example, the cross correlation functions from eqns (10) will be slightly asymmetric, i.e. nearly of type (2), and nearly of type (3) 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.c.f.'s {1-5} remain finite at t = 0. Eqns. (10) produce c.c.f.'s which vanish at t = 0.

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

Discussion

The failure of the Langevin 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.c.f's have the property {1-5}

$$< v_X(0)v_Z(0) > \neq 0 \tag{11}$$

which is not reproduced by the linear Markovian approximation represented in eqns (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 consider

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 Newton's law of sheared fluids. In this sense the system is non-linear because it is non-Newtonian. If we are to attempt an approach to the new c.c.f.'s (1) with Langevin equations, we are led to the conclusion from (1) that the friction coefficients are no longer simple linear multiples of velocity, as in eqn (6), because this approach fails qualitatively at t→0 both for Markovian and non-Markovian approximations to the rigorous eqn (5). More generally, the Langevin 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 such terms, with interesting analytical implications {12}.

3) The new cross correlation functions of type (1) are observed by numerical simulation to be asymmetric in time displacement (eqn (1)). They are not therefore stationary {13} in the conventional sense, because they are neither symmetric in time displacement (eqn (2)), nor antisymmetric (eqn (3)).

4) This leads directly to the conclusion that in the presence of shear, the N particle ensemble no longer obeys the Onsager reciprocal relations {13,14}, which are laws applicable to N particle ensembles at thermodynamic equilibrium, where the system is reversible.

5) The c.c.f.'s (1) are therefore indicative of a dynamical process under shear which is irreversible, in the sense that they are not governed by Onsager's reciprocal relation.

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 statistical 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 as $t \rightarrow 0$. This leads to an entirely new appreciation of non-Newtonian N particle dynamics.

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1. M. W. Evans and D. M. Heyes, Mol. Phys., 65 (1989) 1441.
2. M. W. Evans and D. M. Heyes, Phys. Rev. B, in press (1989).
3. M. W. Evans and D. M. Heyes, Phys. Rev. Lett., in press (1989).
4. M. W. Evans, Phys. Lett. A, 134 (1989) 409.
5. M. W. Evans, Chem. Phys. 127 (1988) 413.
6. R. L. Flurry, Jr., Symmetry groups, theory and applications (Prentice-Hall, Englewood Cliffs, 1980).
7. J. A. Salthouse and M. J. Ware, Point group character tables (Cambridge Univ. Press, Cambridge, 1972).
8. D. S. Urch, Orbitals and symmetry (Penguin, Harmondsworth, 1970). Polarisation", (Elsevier, Amsterdam, 1973, 1979), vols. 1 and 2.
9. D. J. Evans and G. P. Morriss, Computer Phys. Rep., 1 (1984) 297.
10. M. W. Evans, G. C. Lie, and E. Clementi, J. Chem. Phys., 88 (1988) 5157.
11. M. W. Evans, G. J. Evans, W. T. Coffey and P. Grigolini, Molecular dynamics and the theory of broad band spectroscopy (Wiley Interscience, New York, 1982).

12. M. W. Evans, P. Grigolini, G. Pastori-Parravicini, I. Prigogine, and S. A. Rice (eds.) Advances in chemical physics (Wiley Interscience, New York, 1985) vol. 62.

13. P. Resibois and M. de Leener, Classical kinetic theory of fluids, (Wiley Interscience, New York, 1977).

14. L. D. Landau and E. M. Lifshitz, Statistical physics, (Pergamon, Oxford, 1978), vol. 1, par. 120.