Shear Induced Dipole Relaxation, Far Infra red Absorption, and Depolarised Light Scattering.

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Abstract

Recent non-equilibrium molecular dynamics computer simulations have revealed the existence of new shear induced cross-correlation functions between orthogonal components of atomic linear velocity in an N particle ensemble. In a dipolar molecular ensemble these imply the existence of shear induced polarisability and polarisation and direct dissymetric cross correlation between orthogonal components of the permanent molecular dipole moment whose Fourier transform is a complex frequency dependent permittivity. The relaxation of the shear induced permittivity provides a direct method of investigating non-Newtonian phenomena such as shear thinning, thickening, and turbulence in dipolar media. At far infra red frequencies the direct shear induced cross correlation between orthogonal components of the molecular rotational velocity can be isolated and observed experimentally as a power absorption spectrum with crossed wire grid polarisers. Shear induced molecular cross-correlation also gives rise to depolarised light scattering.

Introduction

Non-equilibrium molecular dynamics (n.e.m.d.) computer simulation has recently revealed the existence [1] of fundamentally new dissymetric cross correlation functions (c.c.f.'s) induced in the laboratory frame (X, Y, Z) by the strain rate

$$\dot{\gamma} = \frac{\partial v_X}{\partial Z} \tag{1}$$

produced in an N atom ensemble under shear. The c.c.f.'s were anticipated to exist by the symmetry arguments of group theoretical statistical mechanics (g.t.s.m.), recently developed {2-5} through the application of point group theory to statistical mechanics, and were observed by n.c.m.d. {6-14} to have the remarkable property

$$< v_X(t)v_Z(0) > \neq < v_Z(t)v_X(0) > \tag{2}$$

of being dissymmetric in the indices X and Z of the strain rate. This property (2) was explained by g.t.s.m. by using a weighted sum of symmetric and antisymmetric components, respectively of $D_x^{(1)}$ and $D_x^{(2)}$ symmetry {1-5}, representing shear induced vorticity and deformation. The symmetric and antisymmetric components are, respectively

$$< v_X(t)v_Z(0) > = < v_Z(t)v_X(0) > ; \quad (D_g^{(2)}) \tag{3}$$

and

$$< v_X(t)v_Z(0) > = - < v_Z(t)v_X(0) > ; \quad (D_g^{(1)}) \tag{4}$$

where v is the linear velocity of an atom diffusing at shear applied equilibrium. These c.c.f.'s are unknown in customary rheology but are characteristic and unique signatures of the non- Newtonian nature of the sheared liquid at the fundamental (atomic) level.

This paper introduces the concept of dissymmetric shear induced c.c.f.'s to relaxation in dipolar molecular ensembles {15-20}, and shows that shear induces polarisation and complex permittivity, the relaxation of which is a shear induced permittivity spectrum. The latter can cover the frequency regions of experimentally obtainable strain rates (up to MHz) and may be used to investigate non- Newtonian effects experimentally. The high frequency adjunct of this shear induced frequency process, a far infra red power absorption {21-25} likewise has a sheared induced component which is the Fourier transform of the shear induced dissymmetric c.c.f. of the molecular rotational velocity

$$< \dot{\mu}_Z(t)\dot{\mu}_X(0) > \neq < \dot{\mu}_X(t)\dot{\mu}_Z(0) > \tag{5}$$

It is argued that this can be isolated and observed experimentally and directly with crossed wire grid polarisers, providing another direct probe of non-Newtonian rheology.

Symmetry and Theory

Using the language of irreducible D representations {1-5} the symmetry of strain rate of type (1) is

$$\Gamma(\dot{\gamma}) = D_g^{(1)} + D_g^{(2)} \tag{6}$$

a traceless, purely off-diagonal, symmetry with a vector part $D_x^{(1)}$ and a tensor part $D_x^{(2)}$. The third principle of g.t.s.m. {2-5} imparts this symmetry to ensemble averages at the shear-applied steady state, giving rise {1} to dissymmetric c.c.f.'s of type (2) at the atomic (or molecular) level. Conventional rheology does not postulate the existence of atoms and molecules, and in consequence is unable to explain this fundamental result.

In atomic ensembles, the dissymmetric c.c.f.'s are exemplified by velocity c.c.f.'s of type (2), and also by related types {1} with the same symmetry, such as the mixed velocity-position c.c.f.'s {1}

$$< v_Z(t)r_X(0) > \neq < v_X(t)r_Z(0) > \tag{7}$$

and the position position c.c.f.'s

$$< r_Z(t)r_X(0) > \neq < r_X(t)r_Z(0) > \tag{8}$$

In ensembles of dipolar molecules, the permanent molecular dipole moment, μ_0 is always expressible as the vector sum of the position vectors of the atoms of the molecule in frame (X, Y, Z). This immediately implies the existence of the shear induced dissymmetric c.c.f.'s of μ_0, and of its time derivative, the rotational velocity, $\dot{\mu}_0$. We have the results

$$< \mu_{0Z}(t)\mu_{0X}(0) > \neq < \mu_{0X}(t)\mu_{0Z}(0) > \tag{9}$$

and

$$< \dot{\mu}_{0Z}(t)\dot{\mu}_{0X}(0) > \neq < \dot{\mu}_{0X}(t)\dot{\mu}_{0Z}(0) > \tag{10}$$

The Fourier transform of (9) is a dissymmetric, shear induced complex permittivity. That of (10) is a dissymmetric far infra red power absorption accompanied by a dispersion in the refractive index. Thus, the results of reference (1) immediately give new types of observable, shear induced spectra, which are direct probes of non-Newtonian phenomena.

Shear Induced Molecular Polarisability and Polarisation

The terms "polarisability" and "polarisation" are usually applied to the response of a dielectric to an applied electric field. However, the existence {1} of dissymmetric c.c.f.'s of the molecular dipole moment implies that of a shear induced molecular *polarisability* which is given in the shear applied steady state by

$$< \alpha_{XZ} > = \frac{< \mu_{0Z}\mu_{0X} >}{\Delta E_{shear}} \tag{11}$$

where ΔE_{shear} has the units of energy (J), and the polarisability has the units of $C^2m^2J^{-1}$. More conventionally, the polarisability is given in units of volume (the "volume definition") by dividing the r.h.s. of eqn. (11) by $4\pi\varepsilon_0$, where ε_0 is the permittivity of free space. The shear induced molecular polarisability then has units of m^3.

The results of reference (1) show that at $t = 0$, (the "equilibrium value")

$$< v_Z(0)v_X(0) > = < v_X(0)v_Z(0) > \tag{12}$$

so that the shear-on equilibrium value of the polarisability, given by eqn. (11), is not dissymmetric in X and Z. The equilibrium value of the energy in the denominator of eqn. (11) is then the energy of formation of the numerator, the $t = 0$ value of the cross-correlation function of the permanent molecular dipole moment in the shear-on steady state.

The existence of the shear induced molecular polarisability implies that the sample is **polarised by shear**. This is formally analogous to the polarisation caused by an electric field, which is the basis of dielectric spectroscopy, but is due to the field of force caused by shear, the "shearing field". We refer to this as shear induced polarisation. In the same way that dielectric polarisation may be expressed as a power series in the applied electric field, shear induced polarisation is a power series in the applied shearing field. The coefficients of the series in electric field induced polarisation are: the molecular polarisability (multiplied by the electric field); the molecular hyperpolarisability (multiplied by the electric field squared) and so on. Those in shear-induced polarisation are the shear-induced molecular polarisability; shear induced molecular hyperpolarisability, and so on.

The shear induced polarisation may be expressed through a total molecular dipole moment with components X and Z. These are sums of the equivalents for the permanent molecular dipole moment and those induced by shear. (This is again formally analogous to the total dipole moment produced by electric polarisation, which is a sum of the permanent dipole, that induced by the product of polarisability and the electric field, and so on.) At shear-on equilibrium the total molecular dipole components are

$$\mu_{X,\,total} = \mu_{0X} + \mu_{1X} + \mu_{2X} + \dots \tag{13a}$$

and

$$\mu_{Z,\,total} = \mu_{0Z} + \mu_{1Z} + \mu_{2Z} + \dots \tag{13b}$$

We now express the shear induced dipole components μ_{1Z} and so on in terms of integrals over dissymmetric c.c.f.'s of type (9). This is accomplished using a theorem developed recently by Morriss and Evans {26}.

Adaptation of the Morriss / Evans Theorem {26}

The Morriss / Evans Theorem is a generalisation of the Green · Kubo relations {26} and a fusion of linear and non-linear response theory, providing a new framework for fluctuation-dissipation theorems in general. It can be expressed as

$$< B(t) > = < B(0) > - \frac{F_e}{kT}\int_0^t << B(s).J(0) >> ds \tag{14}$$

where B (t) is a phase variable and J and F_e are the dissipative flux and external force field respectively, defined by

$$\frac{dH_0}{dt} = - JF_e \tag{15}$$

where H_0 is the hamiltonian. Eqn. (14) relates the non-equilibrium transient value of B at time t to the integral over a transient time correlation function, denoted by $<< >>$, the non-equilibrium ensemble average {26}.

Taking the first induced term in eqns (13), we have, by definition

$$< \mu_{1X} > = \frac{F_{shear}}{\Delta E_{shear}} < \mu_{0X}(0)\mu_{0Z}(0) > = < \mu_{1Z} > \tag{16}$$

where F_{shear} is the shearing field. The structure of the Morriss/Evans Theorem allows this to be written as

$$< \mu_{1Z} > = -\frac{F_{shear}}{\Delta E_{shear}} \int_0^\infty \ll \mu_{0X}(t)\mu_{0Z}(0) \gg \, dt \tag{17}$$

with a similar expression for $< \mu_{1X}(t) >$.

In eqn. (17) we have taken the $t \to \infty$ limit of the Morriss / Evans integral which implies that the non- equilibrium average $\ll\,\gg$ becomes the shear-on steady state average $<\,>$, because the external field is applied for an infinite time, allowing the system to reach a steady state.

We note finally that the factor before the integral in eqn. (17) can be expressed in the form

$$\frac{F_{shear}}{\Delta E_{shear}} = \frac{Constant}{\mu_{0X}} \frac{\partial v_X}{\partial Z} \tag{18}$$

where the "constant" is the shear induced polarisation constant.

Shear Induced Dipole Relaxation, Far Infra-red Power Absorption, and Depolarised Light Scattering

These are three of the many areas of observation affected by the phenomenon implied by reference (1), and specifically by the existence of dissymmetric c.c.f.'s of the permanent molecular dipole moment and its time derivative in frame (X, Y, Z).

Shear induced dipole relaxation, a relatively low frequency process which can cover several frequency decades, is expressed in spectral terms through the Fourier transformation of the shear induced dipole c.c.f. In the shear-on steady state it causes polarisation, which is the result of statistical correlation between orthogonal X and Z components of the permanent molecular dipole moment. The polarisation may be isolated and detected experimentally by a special arrangement of electrodes, one in the XY plane and the other in the ZY plane, one electrode being perpendicular to the other and both being perpendicular to the plane of shear, XZ. In the Hz to kHz frequency region, the relaxation of the shear induced polarisation may be detected with a Wayne Kerr bridge, and with other types of bridge technique and sweep frequency apparatus up to the MHz range. Direct measurements with orthogonal electrodes of shear induced polarisation seem never to have been made, but would isolate the cross-correlation between the X and Z components of the permanent molecular dipole moment.

Analogously, the high frequency adjunct of the shear induced dipole relaxation process is a far infra-red power absorption and accompanying refractive index dispersion. The power absorption spectrum in the far infra red can be isolated in principle by the use of orthogonal wire grid polarisers. One polariser is oriented in the Z axis between the exit port of a far infra red interferometer and the sheared sample, and the other in the

X axis bewtcen the sample and the detector. The orthogonal polarisers block out all radiation if the cross correlation between the X and Z components of the molecular rotational velocity is absent. If not, radiation is detected which is the Fourier transform of the c.c.f., isolated from all other effects.

Careful choice of sample and conditions, with accessible laboratory strain rates, leads to this far infra red spectrum, which is a direct measurement of the non-Newtonian molecular rotational velocity c.c.f. The fundamental reason for this is that the far infra-red power absorption is always the high frequency adjunct of a dipole relaxation process which occurs at much lower frequencies, and the high and low frequency parts of the overall dynamical process are never independent. This has been demonstrated experimentally by Evans and Reid {27-30} using supercooled liquids and glasses, work which isolated the far infra red gamma process as the high frequency, ever present, adjunct of much lower frequency alpha and beta processes in supercooled liquids and glasses. The gamma process may be separated from the other two by a dozen frequency decades, but is always observable. Similarly, the accessible laboratory strain rate may be only a few kHz at most, but the molecular response extends from Hz to THz frequencies in general. This is simply due to the fact that a molecular diffusion process evolves temporally from the picosecond scale onwards.

In contrast to the above absorption processes, light scattering involves an induced dipole moment, equivalent to our μ_1. Conventionally, this is attributed to the molecular polarisability. However, in the shear applied steady state, the shear induced molecular polarisability can also cause depolarised light scattering related to the Fourier transform of

$$< \alpha_{XZ}(t)\alpha_{XZ}(0) \exp((r(t) - r(0)) \cdot q) > \tag{19}$$

where r is the centre of mass position vector of the molecule and q is the scattering vector {19}. This depolarised light scattering spectrum is dissymmetric {1} in the indices X and Z of the strain rate. Light polarised in the X axis is scattered in the Z axis due to the applied strain rate, and this effect can be measured with conventional light scattering apparatus at high or low frequencies (Rayleigh Brioullin and photon correlation spectroscopy respectively). In this case it is mixed with the weak component of depolarised light scattering {19} caused by the permanent molecular polarisability anisotropy which is always present in a dipolar molecule.

Conclusions

Three new experimental techniques have been suggested, based on the observation by n.e.m.d. {1} of a fundamentally new type of dissymmetric c.c.f. in response to shear. The techniques aim to isolate experimentally the relevant c.c.f. in each case through the observation of its spectrum, or Fourier transform. These methods directly investigate the non-Newtonain response to shear of a dipolar medium, molecular liquid, liquid crystal, colloidal aggregate and so forth.

Acknowledgement

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