Shear Induced Dipele 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 polarizability and polarisation and direct diastic cross correlations between orthogonal components of the permanent molecular dipole moment whose Fourier transform is a complex frequency dependent permittivity. The relaxation of the shear induced polarizability provides a direct method of investigating non-Raman phenomena such as shear thinning, thickening, and turbulence in dipolar media. The far infra red frequencies the direct shear induced cross correlation between orthogonal components of the molecular rotational velocity can be included and observed experimentally as a power absorption spectrum with crossed linear polarisers. Shear induced molecular cross-correlation also give rise to depolarised light scattering.

Introduction

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

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produced in an N atom ensemble under shear. The c.e.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.m.r. (6-9) to have the remarkable property

$$\langle \psi_1|\mu_s|\psi_2 \rangle \neq \langle \psi_1|\mu_s|\psi_0 \rangle$$

(2)

of being asymmetric in the indices X and Z of the strain state. This property (2) was exploited by g.t.s.m. by using a weighted sum of symmetric and antisymmetric components, respectively of \( \mu_{1s} \) and \( \mu_{2s} \) symmetry (1-5), representing shear induced viscosity and deformation. The symmetric and antisymmetric components are, respectively

$$\langle \psi_1|\mu_{1s}|\psi_0 \rangle = \langle \psi_1|\mu_{2s}|\psi_0 \rangle \quad (\bar{\Delta}^2)$$

(3)

and

$$\langle \psi_1|\mu_s|\psi_0 \rangle = -\langle \psi_1|\mu_s|\psi_0 \rangle \quad \left( \frac{\bar{\Delta}^3}{\bar{\Delta}^3} \right)$$

(4)

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

This paper introduces the concept of disymmetry shear induced c.e.f.'s to relaxation in dipolar molecular ensembles (15-20), and shows that shear induces polarization and complex permittivity, the relaxation of which is a shear induced permittivity spectrum. The latter can cover the frequency region of experimentally attainable stress rates (up to MHz) and may be used to investigate non-Newtonian effects experimentally. The high frequency regime of this shear induced frequency process, a far ir infra and power absorption (21-25) likewise has a shear induced component which is the Fourier transform of the shear induced disymmetric c.e.f. of the molecular rotational velocity

$$\langle \psi_1|\mu_s|\psi_0 \rangle \neq \langle \psi_1|\mu_s|\psi_0 \rangle$$

(5)

It is argued that this can be isolated and observed experimentally and directly with corona wire grid polarizers, 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

$$\Gamma(\gamma) = \bar{\Delta}^1 + \bar{\Delta}^2$$

(6)

a transverse, purely off-diagonal, symmetry with a vector part \( \bar{\Delta}^1 \) and a tensor part \( \bar{\Delta}^2 \). 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 disymmetric c.e.f.'s of type (2) at the atomic (for 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 assemblies, the disymmetric c.e.f.'s are exemplified by velocity c.e.f.'s of type (5), and also by related types (1) with the same symmetry, such as the mixed velocity-position c.e.f.'s (1)

\[ \langle v_{x}(v_{y}) \rangle > \langle v_{x}(v_{y}) \rangle > \langle v_{x}(v_{y}) \rangle \]  

(7)

and the position c.e.f.'s

\[ \langle v_{x}(v_{y}) \rangle > \langle v_{x}(v_{y}) \rangle > \langle v_{x}(v_{y}) \rangle \]  

(9)

In ensembles of dipole molecules, the per-cent molecular dipole moment, \( \mu_{0} \), is always expressible as the vector sum of the position vectors of the atoms of the molecules in frame (X, Y, Z). This implicitly implies the existence of the shear induced disymmetric c.e.f.'s of \( \mu_{0} \) and of its time derivative, the rotational velocity. A. We have the results

\[ \langle v_{x}(v_{y}) \rangle > \langle v_{x}(v_{y}) \rangle > \langle v_{x}(v_{y}) \rangle \]  

(9)

and

\[ \langle v_{x}(v_{y}) \rangle > \langle v_{x}(v_{y}) \rangle > \langle v_{x}(v_{y}) \rangle \]  

(10)

The Fourier transform of \( \phi \) is a disymmetric, shear induced complex permittivity. That is, if \( |\phi| = \phi \) is a disymmetric vector, the real part of the 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 dense probes of non-Newtonian phenomena.

**Shear Induced Molecular Polarizability and Polarization**

The terms "polarizability" and "polarization" are usually applied to the response of a dielectric to an applied electric field. However, the existence (1) of disymmetric c.e.f.'s of the molecular dipole moment implies that a shear induced molecular polarizability which is given in the shear applied steady state by

\[ \langle v_{x}(v_{y}) \rangle > \frac{\langle v_{x}(v_{y}) \rangle}{\mu_{0}} \]  

(11)

where \( \Delta \mu_{x} \) has the units of energy (s) and the polarizability has the units of C/m V. More conventionally, the polarizability is given in units of volume (the "volume definition") by dividing the r.h.s. of eqn. (11) by \( \mu_{0} \), where \( \mu_{0} \) is the permittivity of free space. The shear induced molecular polarizability then units of \( \mu_{0} \).

The results of reference (1) show that as \( s = 0 \), the "equilibrium value"

\[ \langle v_{x}(v_{y}) \rangle > \frac{\langle v_{x}(v_{y}) \rangle}{\mu_{0}} \]  

(12)

so that the shear equilibrium value of the polarizability, given by eqn. (11), is not disymmetric in \( X \) and \( Z \). The equilibrium value of the energy in the denominator of eqn. (1) is then the energy of formation of the numerator, the \( s = 0 \) value of the cross-correlation function of the permanent molecular dipole moment in the shear-on set state.
The existence of the shear induced molecular polarizability indicates that the sample is polarized by shear. This is formally analogous to the polarization created by an electric field, which is the basis of dielectric spectroscopy, but is due to the field of forces exerted by shear, the "shearing field." We refer to this as the shear-induced polarization. In the same way that dielectric polarization may be expressed as a power series in the applied electric field, these induced polarization is a power series in the applied shear field. The coefficients of the series in electric field induced polarization are: the molecular polarizability (multiplied by the electric field), the molecular hyperpolarizability (multiplied by the electric field squared) and so on. Those in shear-induced polarization are: the shear-induced molecular polarizability, shear induced molecular hyperpolarizability, and so on.

The shear-induced polarization may be expressed through a total molecular dipole moment with components $X$ and $Y$. There are terms of the sheared components of the permanent molecular dipole moment and the shear-induced by shear. This is again formally analogous to the total dipole moment produced by electric polarization, which is a sum of the permanent dipole, that induced by the product of polarizability and the electric field, and so on. For shear on equihbrium the total molecular dipole components are:

$$X_{\text{ind}} = \mu_x + \mu_y + \mu_z + \ldots$$

$$Y_{\text{ind}} = \mu_x + \mu_y + \mu_z + \ldots$$

We now express the shear induced dipole components, $X_{\text{ind}}$ and $Y_{\text{ind}}$ in terms of integrals over a symmetric c.e. of type (9). This is accomplished using a theorem developed recently by Marcuse and Frens (26).

Adaptation of the Morin / Evans Theorem (26)

The Morin / Evans Theorem is a generalization of the Green - Kubo theorem (28) 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:

$$\langle B(t) \rangle = \langle B(0) \rangle - \frac{\mathcal{D}_X}{kT} \int_0^t \langle B(t') \rangle dt'$$

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

$$\frac{dB(t)}{dt} = -\mathcal{D}_X$$

where $\mathcal{D}_X$ is the hamiltonian. Eqs. (14) describes the non-equilibrium transient state of $B$ at time $t$ to the initial value in a transient time correlation function, denoted by $\langle \ldots \rangle$, the non-equilibrium ensemble average.
Taking the first induced term in eqn (16), we have, by definition,

\[ \mu_{\text{ind}} > = \mu_0 \text{Re} \left\{ \log \left( \frac{2 \pi \eta \omega}{\mu_0} \right) \right\} > = \mu_{\text{ind}} \]

(16)

where \( \mu_{\text{ind}} \) is the sheared field. The structure of the Morris-F一家 turned allows this to be written as

\[ < \mu_{\text{ind}} > = \frac{\text{Const}}{\lambda^2} \int - \mu_0 \text{Re} \left\{ \log \left( \frac{2 \pi \eta \omega}{\mu_0} \right) \right\} \, \text{d}k \]

(17)

with a similar expression for \( < \mu_{\text{ind}} > \).

In eqs (17) we have taken the \( t \to \infty \) limit of the Morris-F一家 turned which implies that the non-equilibrium average \( < \mu > \) becomes the steady state average \( < \mu > \), 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 eqs (17) can be expressed in the form

\[ \text{Const} \, \frac{\text{Mx}}{\eta \omega} \]

(18)

where the 'constant' is the shear induced polarization constant.

Shure's induced Dipole Relaxation, Far Infrared Power Absorption, and Depolarized Light Scattering

These are three of the many areas of observation affected by the phenomenon implied by eqn (1), and specifically by the existence of asymmetric c.e.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 occurs over several frequency decades, is expressed in spectral terms through the Fourier transformation of the shear induced dipole c.e.f. In the shear-on steady state it causes polarization, which is the result of statistical correlation between orthogonal X and Z component of the permanent molecular dipole moment. The polarization may be isotropically detected by a special arrangement of detectors, one in the X plane and the other in the Z plane, one detector being perpendicular to the other and both being perpendicular to the plane of shear. XZ in the 12 to 18 kHz frequency region, the relaxation of the shear induced polarization may be detected with a Wayne Kerr bridge, and with other types of bridge technique and frequency separation up to the kHz range. Direct measurements with orthogonal electrodes of shear induced polarization seem never to have been made, but would include the cross-correlation between the X and Z components of the permanent molecular dipole moment.

Analogously, the high frequency adjust of the shear induced dipole relaxation process is a far infrared power absorption and accompanying radiation index dispersion. The power absorption spectrum in the far infrared can be isolated in principle by the use of orthogonal wave guides. One polarization is oriented in the Z axis between the two ports of a far infrared interferometer and the sheared sample, and the other in the
In contrast to the above absorption process, light scattering involves an induced dipole moment, equivalent to $\mu(t)$. Conventionally, this is attributed to the molecular polarizability $\beta$. In the shear applied steady state, the shear induced molecular polarizability can cause depolarized light scattering related to the Fourier transform of

$$<e^{2i(2\pi s \cdot r)} \exp[i(\omega t - \mathbf{q} \cdot \mathbf{r})]>_t$$

(19)

where $r$ is the centre of mass position vector of the molecule and $q$ is the scattering vector [19]. This depolarized light scattering spectrum is disymmetric (1) in the indices $X$ and $Z$ of the strain rate. Light polarized 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-Brownian and photon correlation spectroscopy reflectively). In this case it is mixed with the weak component of depolarized light scattering (19) caused by the permanent molecular polarizability anisotropy which is always present in a dipolar molecule.

Conclusions

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

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