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Circular birefringence and dichroism due to shear stress: optical measurement of non-Newtonian viscosity

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The semi-classical molecular theory is given of circular birefringence, dichroism and laser ellipticity due to shear stress, the angle of rotation being given in terms of the shear strain rate and non-Newtonian shear viscosity through a perturbation of the imaginary part of the dynamic frequency dependent molecular polarisability. The non-Newtonian shear viscosity can be measured spectroscopically in terms of the angle of rotation at a given frequency (for example a visible laser line) for a given strain rate and sample dimension.

1. Introduction

It is important to have available methods for the experimental measurement of non-Newtonian viscosities in condensed matter, and this paper provides a theory of circular birefringence and dichroism due to shear stress, showing a theoretical relation between angle of rotation, for example, and non-Newtonian viscosity for a given measuring frequency, strain rate, and sample dimension.

A fluid is non-Newtonian if there is no longer a simple linear relation between stress and strain tensors [1] and it is being realised that non-Newtonian behaviour is prevalent, for example in sedimentation, levelling, lubrication, gel stability, viscoelasticity, thixotropy, and dilatency. Non-equilibrium computer simulation [2–5] has also revealed that simple atomic ensembles exhibit a variety of non-Newtonian behaviour, characterised by novel asymmetric cross correlation functions at the fundamental molecular or atomic level. In general terms, applied shear stress results in several distinct regimes of non-Newtonian response. The material can show steady state shear thinning and thickening as the applied shear stress increases, and ultimately develop viscoelasticity. A similar range of behaviour is observed in amorphous solids and glasses, composites polymers, and bio-materials.

In this paper, a semi-classical molecular theory of shear induced circular birefringence and dichroism is developed in terms of the shear strain rate and non-Newtonian viscosity, using a Voigt Born perturbation by the applied shear stress of the imaginary part of the dynamic molecular polarisability $\alpha''_{\alpha\beta}$. The latter is an asymmetric second rank polar tensor (mathematically equivalent to a first rank axial vector) which is negative to motion reversal T and positive to parity inversion P. It is activated in the laboratory frame by the T negative shear stress, analogously with the activation of $\alpha''_{\alpha\beta}$ by the T negative magnetic flux density ($\boldsymbol{B}$) of the Faraday effect (circular birefringence and dichroism due to $\boldsymbol{B}$ [6]). An equation is derived for the optical measurement of non-Newtonian shear viscosity, which can be applied to materials using the rotation of the plane of polarisation of a visible probe laser for a given strain rate and sample dimension.

2. Symmetry

The shear stress tensor is related to the shear strain rate tensor $\dot{\gamma}_{\alpha\beta}$ through the non-Newtonian

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$$S_{\alpha\beta}=\eta(\dot{\gamma}_{\alpha\beta})\dot{\gamma}_{\alpha\beta}\,, \tag{1}$$

where $\eta(\dot{\gamma}_{\alpha\beta})$ is the scalar viscosity. The shear strain rate tensor is the second rank antisymmetric

$$\dot{\gamma}_{\alpha\beta}=\frac{\partial v_\alpha}{\partial r_\beta}-\frac{\partial v_\beta}{\partial r_\alpha} \tag{2}$$

where $\boldsymbol{v}$ is velocity in the laboratory frame (X, Y, Z). This is a T negative, P positive second rank polar tensor, equivalent to the first rank axial vector $\dot{\gamma}_\alpha$ through the Levi–Civita symbol $\epsilon_{\alpha\beta\gamma}$

$$\dot{\gamma}_\alpha=\epsilon_{\alpha\beta\gamma}\dot{\gamma}_{\beta\gamma}\,. \tag{3}$$

The shear stress tensor can also be written as an axial vector

$$S_\alpha=\epsilon_{\alpha\beta\gamma}S_{\beta\gamma}\,, \tag{4}$$

so that the non-Newtonian relation between stress and strain becomes

$$S_\alpha=\eta(\dot{\gamma}_\alpha)\dot{\gamma}_\alpha\,. \tag{5}$$

In this form, both the stress and the strain are T negative, P positive axial vectors with the same P and T symmetries as magnetic flux density $\boldsymbol{B}$. This is an important symmetry analogy leading to the expectation of circular birefringence and dichroism due to shear stress through the Voigt Born perturbation

$$\alpha''_{\alpha\beta}(S_Z)=\alpha''_{\alpha\beta}+\alpha''_{\alpha\beta Z}S_Z+\cdots\,, \tag{6}$$

of the relevant [6] imaginary part of the dynamic molecular or atomic polarisability by the P_Z pressure component of the applied shear stress. Note that the pressure component P_Z is the well known

$$P_Z=-S_Z\,, \tag{7}$$

[2–5] Weissenberg pressure due to shear stress, which can be strong enough to fracture roller bearings, for example.

3. Semi-classical expressions for circular birefringence and dichroism due to shear stress

The standard semi-classical theory of circular birefringence and dichroism [6] due to $\boldsymbol{B}$ (the Faraday effect) can now be adapted straightforwardly using eq. (6). Recall that the semi-classical theory of the Faraday effect leads to the circular birefringence

$$\Delta\theta \doteq \tfrac{1}{2}\omega c\mu_0 lN(\alpha''_{XY}(f)+\alpha''_{XYZ}(f)B_Z+\cdots) \tag{8}$$

and laser ellipticity

$$\eta \doteq \tfrac{1}{2}\omega c\mu_0 lN(\alpha''_{XY}(g)+\alpha''_{XYZ}(g)B_Z+\cdots) \tag{9}$$

and similar expressions will be derived using the shear stress vector component S_Z in place of B_Z, the applied Z axis static magnetic flux density of the well known Faraday effect. In eqs. (8) and (9) ω is the angular frequency in rad s^{-1} of the plane polarised probe laser, c the velocity of light in m s^{-1}; μ_0 the permeability in vacuo in S.I. units; l the sample length in metres; N the number of molecules per m^3 and the other quantities are the B_Z activated (i.e. non-vanishing) imaginary part of the dynamic polarisability, defined by Buckingham and Stephens [6] and by Barron [7].

Note that the imaginary part of the molecular polarisability $\alpha''_{\alpha\beta}$ is negative to motion reversal (T), and positive to parity inversion (P), and is a rank two polar tensor mathematically equivalent to a rank one axial vector α''_α. Because of its negative symmetry with respect to T, it vanishes [6,7] at field free equilibrium in the absence of a T negative external influence. In the Faraday effect, this is static magnetic flux density, in the effect introduced in this paper, it is the vector S_Z of eq. (2). Because of the activation of $\alpha''_{\alpha\beta}$ by B_Z in the Faraday effect, the latter is observable in general [7] in diamagnetic and paramagnetic ensembles. Similarly, the activation of the tensor $\alpha''_{\alpha\beta}$ by S_α of eq. (4) implies that circular birefringence due to shear stress S_α will be observable in diamagnetic and paramagnetic media.

Resonance occurs if the probe laser is tuned to a natural transition frequency ω_{ij}, i.e. the molecular property tensors are greatly increased in magnitude.

Using the Voigt Born perturbation (6), the following expression is obtained for the angle of rotation of a plane polarised probe laser traversing a sample under the shear stress S_Z:

$$\langle\Delta\theta\rangle=-\tfrac{1}{12}\omega\mu_0 clNS_Z\epsilon_{\alpha\beta\gamma}\times[(V_\alpha/kT)\alpha''_{\beta\gamma}(f)+\alpha''_{\alpha\beta\gamma}(f)]\,. \tag{10}$$

Here V_α is a vector defined by the Hamiltonian

$$\Delta H=-S_\alpha V_\alpha+\cdots\,, \tag{11}$$

with the units m^3, arising from the standard definition [1,2] of the interaction energy associated with the antisymmetric part of the shear stress

$$\Delta H = -S_{\alpha\beta} V_{\alpha\beta} + \cdots ,$$

$$\Delta H \equiv -S_\alpha V_\alpha + \cdots . \qquad (12)$$

The energy (12) is formally analogous to the magnetic dipole flux density product in the theory of the Faraday effect. Similarly there is circular dichroism due to shear stress, which is expressed in the following equation in terms of the difference in the power absorption coefficient as measured with right and left circularly polarised laser or broad band probe radiation traversing the shear stressed sample

$$\left(\frac{S_3}{S_0}\right)_Z = \left(\frac{I_R - I_L}{I_R + I_L}\right)_Z = \tanh[\omega\mu_0 c l N \langle \alpha''_{XY}(S_Z)\rangle] . \qquad (13)$$

Finally, the ellipticity developed in a probe laser due to shear stress is

$$\langle \eta \rangle = -\tfrac{1}{12}\omega\mu_0 c l N S_Z \epsilon_{\alpha\beta\gamma} \times [(V_\alpha/kT)\alpha''_{\beta\gamma}(g) + \alpha''_{\alpha\beta\gamma}(g)] . \qquad (14)$$

4. Order of magnitude estimate of the angle of rotation

Considering the component

$$\langle \Delta\theta \rangle = -\tfrac{1}{12}\omega\mu_0 c l N S_Z \epsilon_{\alpha\beta\gamma}(V_\alpha/kT)\alpha''_{\beta\gamma}(f) \qquad (15)$$

of eq. (10), an order of magnitude for the angle of rotation can be made assuming a laser frequency of about 10^{15} rad s^{-1}; in the red part of the visible. Using the number of molecules per metre cubed for N and an order of magnitude of 10^{-38} J^{-1} C^2 m^2 for $\alpha''_{\beta\gamma}(f)$ in a transparent part of the absorption spectrum of the molecule [8,9], we obtain

$$\Delta\theta \doteqdot -10^3 \eta(\dot\gamma_Z)\dot\gamma_Z(V_Z/kT) \text{ rad m}^1 , \qquad (16)$$

where V_Z is in units of m^3. The angle of rotation is therefore proportional to the product of the shear strain rate and the shear viscosity $\eta(\dot\gamma_Z)$. For a known strain rate and sample volume, it is possible to obtain the shear viscosity from the simple optical measurement represented by the rotation of the plane of polarisation of the probe laser. This method appears to have great potential application in the systematic laboratory characterisation of, for example, viscoelasticity.

It is clear therefore that the angle of rotation for a given strain rate increases with viscosity. By tuning the plane polarised probe to a transition frequency, the order of magnitude of 10^{-38} J^{-1} C^2 m^2 used for $\alpha''_{\alpha\beta}(f)$ increases by resonance, and the probe radiation is absorbed by the sample. The order of magnitude of $\alpha''_{\alpha\beta}$ can be estimated from experimental data [8] or from ab initio computation [9]. Laboratory shear strain rates are usually of the order 1.0 s^{-1}, but can be increased by up to six orders of magnitude. The energy ratio

$$\frac{S_Z V_Z}{kT} = -\frac{\eta(\dot\gamma_Z)\dot\gamma_Z V_Z}{kT} \qquad (17)$$

is of the order unity for a viscosity of about 10^6 N s m^{-2} for a strain rate of 1.0 s^{-1} and a value for V_Z of 1.0 m^3, since NkT at 300 K is 2.4×10^6 J for 6×10^{26} molecules per m^3, so that

Table 1
Estimated angles of rotation for materials under shear stress [10], from eq. (16).

Material	Shear viscosity ($N s m^{-2}$)	Strain rate (s^{-1})	Angle, $\lvert\Delta\theta\rvert$ (rad m^{-1})
Corn Syrup	11.0	0.18–71.1	0.0001–0.38
0.644% carboxy methylcellulose/water	20.6	2.15–34.1	0.02–0.34
7.48% water/corn syrup	18.0	1.08–17.0	0.01–0.15
0.036% separam and 4.32% water in sweetol	3.0	0.86–88.0	0.0015–0.15

$kT/V = 2.4 \times 10^6 \text{ J m}^{-3}$.

The factor determining the angle of rotation under these conditions is therefore the product of the shear viscosity and the shear strain rate. Some examples [10] are tabulated, together with the theoretically estimated angle of rotation in radians per metre of sample.

It is seen from table 1 that at 300 K, the angle of rotation from one component of eq. (15) appears to be easily measurable at experimentally measurable strain rates and known examples of non-Newtonian shear viscosity. Contemporary spectropolarimeters are capable of milliradian accuracy or better, producing what appears to be a vast range of potential application for optical rheometry with modified rheogoniometer plates with windows for the probe laser. circular dichroism due to shear is clearly frequency dependent, and is a potential source of information on the molecular nature of non-Newtonian rheology.

5. Discussion

We have demonstrated that there is a relation between shear stress and circular birefringence. Its observation needs a modified rotating plate rheogoniometer [2,4,7], in which shear stress is applied to the fluid by an arrangement of two co-axial cylinders, the inner one rotating with respect to the fixed outer cylindrical wall about the observation axis Z in which plane polarised radiation is directed through windows situated at either end of the co-axial cylinders. Another possibility is to adapt a standard rotating plate rheogoniometer by replacing its metal plates with rigid polymeric material transparent to the measuring radiation. Similarly, other shear stress rheogoniometer designs [2] can be adapted by replacing the metal parts by transparent rigid polymer such as perspex to allow through a beam of plane polarised electromagnetic probe radiation.

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