Non-equilibrium molecular dynamics study on flow birefringence in simple fluids

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Abstract. Shear flow birefringence of simple fluids was studied by use of non-equilibrium molecular dynamics simulation, the results of which were comparable with the theoretical values calculated on the basis of the shear distortion of the radial pair distribution function for shear rates below $\dot{\varepsilon}_{xz} = 2.0$ (in Lennard-Jones reduced units).

1. Introduction

Simple liquids of spherical molecules under shear flow were shown to exhibit a flow birefringence due to an anisotropic distortion in the radial pair distribution function both theoretically (Eisenschitz 1949, Champion 1958) and experimentally (Champion 1960).

Many subsequent theoretical works on the flow birefringence, however, are based on the assumption that the fluids are composed of anisotropic molecules (Jerrad 1959). The theories of the form and the orientation birefringence for the fluids predict absolutely zero birefringence for fluids of atoms or spherical molecules where the atoms or molecules do not possess intrinsic optical anisotropy. Hence the fluids of theoretical as well as experimental interest with respect to the flow birefringence have been restricted to such systems as dilute solutions of colloidal particles or polymeric fluids (Stein 1964, Kestens 1975).

However, the well known empirical relation between the observed flow birefringence Δn and the shear rate $\dot{\varepsilon}$ widely accepted in engineering applications of the flow birefringence (Pindera and Krishnamurthy 1978) shows $\Delta n = K\tau\dot{\varepsilon}$, where K is the empirical Kundt constant and τ represents the Maxwell viscoelastic relaxation time. Even though this relationship immediately suggests, as first noticed by Eisenschitz (1949) and Champion (1958), that at low shear rates the flow birefringence may readily be observed only in extremely viscous fluids, it also indicates that the flow birefringence may not vanish even in monatomic fluids possessing neither the form nor orientation birefringence if the shear rate is so high as to make $\tau\dot{\varepsilon}$ appreciable. Approaching the critical point, fluids may exhibit extremely long structural relaxation times in the presence of shear flow and a strong shear may then be obtained at normal shear rates (Onuki and Kawasaki 1979a, b).

Unlike in solids where continuum mechanics works so well, the fluids cannot support elastic stress for long enough and we must investigate the details of molecular motions and structural relaxations to solve this problem of shear-induced birefringence in simple fluids. We should also take account of the molecular interactions which may be neglected in the usual cases of the form or orientation birefringence due to very low concentrations of dilute suspensions.

A very high shear rate or large amplitude shearing in simple liquids may also bring about non-linear shear strains (Heyes *et al* 1980, Hess and Hanley 1983, Schwarzl and Hess 1986) and possibly a phase transition anomaly in both dynamical and structural properties of the liquids (Erpenbeck 1984, Heyes 1986a, b, Kirkpatrick and Nieuwoudt 1986, Evans and Morriss 1986). Such dynamical changes may be best confirmed by depolarised scattering (Cohen and Leal 1978, Onuki and Kawasaki 1979b, Kim and Kim 1986, Schwarzl and Hess 1986) while structural changes may well be confirmed by flow birefringence.

We want to show here by the molecular dynamics computer calculation that at high shear rates simple liquids may also have a large flow birefringence.

2. Calculation of flow birefringence

If we take the streamline direction of the shear flow in the xz plane to be the x axis $\hat{e}_x$, the flow birefringence Δn is given by a CGS unit equation (Kirkwood 1967, Peterlin and Munk 1972)

$$\Delta n = \frac{4\pi}{3} \frac{(n_0^2+2)^2}{6n_0} \frac{N}{V} [(\bar{\alpha}_{xx} - \bar{\alpha}_{zz})^2 + 4\bar{\alpha}_{xz}^2]^{1/2} \tag{1}$$

where n_0 is the equilibrium refractive index of the fluid, N/V is the average number density of the atoms and $\bar{\alpha}_{xx}$, $\bar{\alpha}_{zz}$, $\bar{\alpha}_{xz}$ represent tensor components of the effective atomic polarisability.

In the dipole-induced-dipole (DID) approximation the induced-dipole moment of an atom i in the N-atomic system under the external field E_0 is given by (Alder *et al* 1975)

$$P_i = \alpha_0 E_0 + \alpha_0 \sum_{j \neq i}^{N} [T_{ij}] P_j \tag{2}$$

where α_0 is the free atomic polarisability, $[T_{ij}] = (3\hat{e}_{ij}\hat{e}_{ij} - [I])/r_{ij}^3$, $\hat{e}_{ij} = r_{ij}/r_{ij}$ and r_{ij} is the distance between the ith and jth atoms. We take an average to obtain $\bar{\alpha}_{xx}$ as

$$\bar{P}_{ix} = \frac{1}{N} \sum_{i=1}^{N} P_{ix} = \bar{\alpha}_{xx} E_{0x}. \tag{3}$$

Up to order of α_0^2 we thus obtain from equations (2) and (3)

$$\bar{\alpha}_{xx} = \frac{1}{N} \left(N\alpha_0 [I]_{xx} + \alpha_0^2 \sum_{i=1}^{N} \sum_{j \neq i}^{N} [T_{ij}]_{xx} \right). \tag{4}$$

Similarly, we can obtain

$$\bar{\alpha}_{zz} = \frac{1}{N}\left(N\alpha_0[I]_{zz} + \alpha_0^2 \sum_{i=1}^{N}\sum_{j\neq i}^{N}[T_{ij}]_{zz}\right) \tag{5}$$

$$\bar{\alpha}_{xz} = \frac{1}{N}\left(\alpha_0^2 \sum_{i=1}^{N}\sum_{j\neq i}^{N}[T_{ij}]_{xz}\right). \tag{6}$$

From equations (1), (4), (5) and (6) we obtain

$$\Delta n = \frac{2\pi}{n_0}\left(\frac{n_0^2+2}{3}\right)^2 \frac{N}{V}\left[\left(\frac{1}{N}\alpha_0^2\sum_{i=1}^{N}\sum_{j\neq i}^{N}\frac{3(x_{ij}^2-z_{ij}^2)}{r_{ij}^5}\right)^2 + 4\left(\frac{1}{N}\alpha_0^2\sum_{i=1}^{N}\sum_{j\neq i}^{N}\frac{3x_{ij}z_{ij}}{r_{ij}^5}\right)^2\right]^{1/2}. \tag{7}$$

We performed the non-equilibrium molecular dynamics calculations to obtain Δn for the $N = 108$ Lennard-Jones system at $\rho = 0.8442$ and $T = 0.772$, simulating the argon-like fluid near the triple point under shear flow. We have also calculated for the same system the shear stress given by

$$\sigma_{xz} = -\frac{1}{V}\left(\sum_{i=1}^{N}mv_{ix}v_{iz} - \frac{1}{2}\sum_{i=1}^{N}\sum_{j\neq i}^{N}\frac{x_{ij}z_{ij}}{r_{ij}}\frac{\partial\phi}{\partial r_{ij}}\right) \tag{8}$$

where ϕ is the Lennard-Jones interaction potential.

To compare our results of the molecular dynamics calculation with the empirical relation $\Delta n = K\tau\dot{\varepsilon}$ we have also calculated the shear rigidity modulus G_∞ from (Zwanzig and Mountain 1965)

$$G_\infty = \rho k_B T + \frac{2\pi}{15}\rho^2\int_0^\infty dr\, g_0(r)\frac{d}{dr}\{r^4\, d\phi/dr\} \tag{9}$$

where the radial distribution function $g_0(r)$ was calculated as a part of the molecular dynamics. We have equilibrated the system for $4100\Delta t$ ($\Delta t = 0.005$) before applying the shear flow. A subtraction technique (Heyes *et al* 1980) was used for each segmental run of $400\Delta t$ to extract the shear field effect from the equilibrium noise background, and the steady state values of observables were determined by averaging over six segments. Typical runs for Δn at various shear rates are shown in figures 1 and 2. In
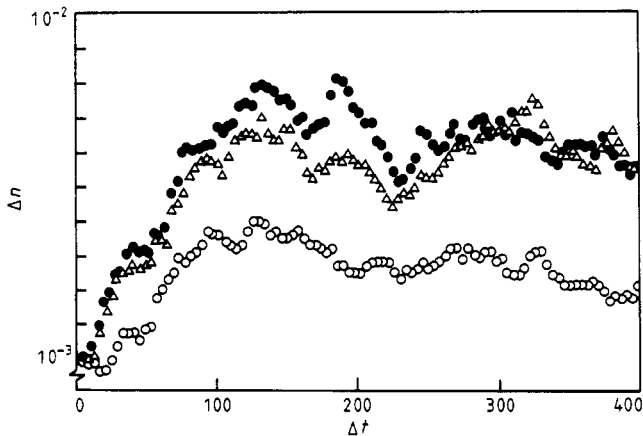

Figure 1. Time dependence of flow birefringence at various shear rates: $\bigcirc$, $\dot{\varepsilon} = 0.1$; $\triangle$, $\dot{\varepsilon} = 1.0$; $\bullet$, $\dot{\varepsilon} = 1.5$.
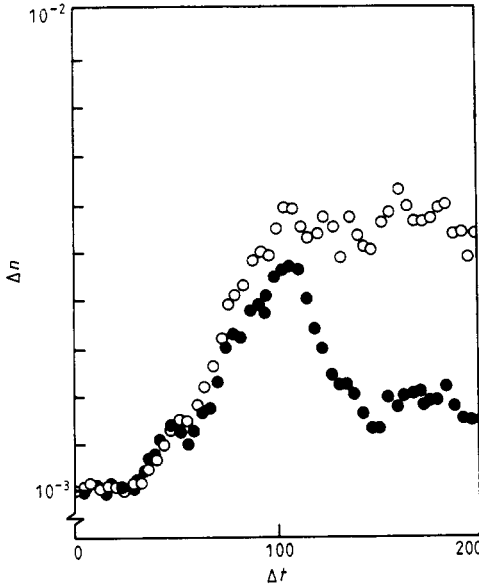
Figure 2. Time dependence of flow birefringence: ○, $\dot{\varepsilon} = 2.0$; ●, $\dot{\varepsilon} = 5.0$.

Table 1. Dependence of flow birefringence (Δn), Maxwell relaxation time (τ) and Kundt constant (K) on shear rate ($\dot{\varepsilon}_{xz}$). The shear rate and Maxwell relaxation time are in Lennard-Jones reduced units (see, e.g., Heyes *et al* (1983) for the Lennard-Jones units of various quantities).

$\dot{\varepsilon}_{xz}$	Δn	τ	K
0.1	0.28×10^{-2}	0.47	0.06
0.5	0.54×10^{-2}	0.27	0.04
1.0	0.72×10^{-2}	0.18	0.04
1.5	0.72×10^{-2}	0.12	0.04
2.0	0.56×10^{-2}	0.07	0.04

table 1 we have shown the shear rate dependence of various quantities as obtained in the present work. We have used $\sigma_{xz}(t \to \infty) = G_\infty \dot{\varepsilon}_{xz}\tau$, with $G_\infty = 22.5$ as calculated in this work, to obtain the Kundt constant K from $K = \Delta n/(\dot{\varepsilon}_{xz}\tau)$.

3. Discussions and conclusion

The sum in equation (7) can be transformed into the integral forms using the radial distribution function $g(r)$ as follows:

$$\delta_1 = \sum_{i=1}^{N} \sum_{j \neq i}^{N} \frac{3(x_{ij}^2 - z_{ij}^2)}{r_{ij}^5} = \frac{N}{2} \int_v \frac{3(x^2 - z^2)}{r^5} g(r) \, \mathrm{d}^3 r \tag{10}$$

$$\delta_2 = \sum_{i=1}^{N} \sum_{j \neq i}^{N} \frac{3x_{ij}z_{ij}}{r_{ij}^5} = \frac{N}{2} \int_v \frac{3xz}{r^5} g(r) \, \mathrm{d}^3 r. \tag{11}$$

Under the uniform and homogeneous shear flow in the xz plane the distortion of the radial distribution function can be written in a form (Pryde 1966, Heyes *et al* 1980), neglecting the smaller non-Newtonian terms (Hess and Hanley 1982),

$$g(\boldsymbol{r}) = g_0(r)(1 + f(\theta, \phi))$$

$$= g_0(r) + (g_0'(r)xz/r)\Delta\varepsilon_{xz} + \tfrac{1}{2}[(g_0(r)z^2/r)$$

$$- (g_0'(r)/r^3)x^2z^2 + (g_0''(r)/r^2)x^2z^2](\Delta\varepsilon_{xz})^2 + \dots$$

$$= g_0(r) + \Delta\varepsilon_{xz}g_0'(r)r\sin\theta\cos\theta\cos\phi + \tfrac{1}{2}(\Delta\varepsilon_{xz})^2$$

$$\times (g_0'(r)r - g_0'(r)r\sin^2\theta\cos^2\phi + g_0''(r)r^2\sin^2\theta\cos^2\phi)\cos^2\theta + \dots \quad (12)$$

where (r, θ, ϕ) are spherical coordinates and $\Delta\varepsilon_{xz}$ is a recoverable shear strain. We can obtain from equations (7), (10), (11) and (12) in the first-order approximation with respect to $\Delta\varepsilon_{xz}$

$$\Delta n = \left[\frac{8}{5}\frac{\pi^2}{n_0}\left(\frac{n_0^2 + 2}{3}\right)^2\frac{N}{V}\alpha_0^2\left|\int g'(r)\,\mathrm{d}r\right|\right]\Delta\varepsilon_{xz}. \quad (13)$$

Molecular dynamics study (Heyes *et al* 1980) proved the validity of $\Delta\varepsilon_{xz} = \sigma_{xz}/G_\infty = \dot{\varepsilon}_{xz}\tau$ for a wide range of shear rates, from which we can rewrite (13) as $\Delta n = K\dot{\varepsilon}_{xz}\tau$, where K is given by

$$K = \frac{8\pi^2}{5n_0}\left(\frac{n_0^2 + 2}{3}\right)^2\frac{N}{V}\alpha_0^2\left(\int g'(r)\,\mathrm{d}r\right). \quad (14)$$

In general we have $\int_V g'(r)\,\mathrm{d}r = N/V$. Hence we find

$$K = \frac{8\pi^2}{5n_0}\left(\frac{n_0^2 + 2}{3}\right)^2\left(\frac{N}{V}\right)^2\alpha_0^2. \quad (15)$$

If we substitute $n_0 = 1$, $\rho = 0.8442$ and $\alpha_0 = 0.0416$ (Alder *et al* 1975), we obtain $K \simeq 0.02$. This value of the first-order theory is less than our computer simulation value of $K = 0.04$ at below $\dot{\varepsilon}_{xz} = 2.0$ as can be seen from table 1. We may ascribe this discrepancy to the shortcomings in both our expansions of the distorted radial distribution function and our computer simulations. Our theory neglected any higher-order contribution of order higher than α_0^2 to the effective polarisability and also higher-order terms of order higher than $\Delta\varepsilon_{xz}$ in the shear-induced distortion of the radial distribution function. Meanwhile the molecular dynamics simulation cannot avoid the finite-size effects and some artefact anisotropy is introduced by the periodic boundary conditions (Mandell 1976, Pratt and Haan 1981) and we need much higher shear rates than experimentally available to see the shearing effects. It thus seems that our first-order theory may underestimate the K value while the molecular dynamics calculation overestimates it as compared with the experimental reality.

However, our molecular dynamics values of flow birefringence at very high shear rates of the order of 5×10^{11} s^{-1} (for argon) shown in table 1 agree with the experimental value of flow birefringence $\Delta n = 7.1 \times 10^{-8}$ for spherical simple molecules measured at the shear rate of 5×10^4 s^{-1} ($\simeq 0.64 \times 10^{-6}$ in Lennard-Jones reduced units for CCl$_4$) (Champion 1960).

At extremely high shear rates when the kinetic terms become more important our algorithm for the shear stress calculation should be modified to the SLLOD type algorithm (Evans and Morriss 1984, Heyes 1986a) and the shear rigidity modulus G_{xz} is no longer constant but drops sharply (Heyes 1986a, b). Our $\dot{\varepsilon}_{xz} = 5.0$ result of figure 2

should not, therefore, be taken too seriously. However, it shows qualitatively that an extremely high shear rate gives the overshoot response before the steady state is reached. This may be an indication that the extremely high stress built up in the simple Lennard-Jones liquid may relax through a phase transition, which may correspond to the string phase formation as observed in the molecular dynamics study (Heyes 1986a, b) in conformity with the cigar-type growth of correlation in the fluids under strong shear (Onuki and Kawasaki 1979).

Acknowledgments

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