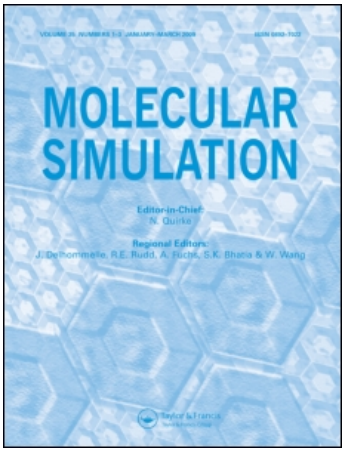

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COLLECTIVE CORRELATION FUNCTIONS IN SHEAR FLOW: A NON-EQUILIBRIUM MOLECULAR DYNAMICS AND GROUP THEORY STATISTICAL MECHANICS TREATMENT

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A combination of group theory and *NEMD* computer simulation confirms the existence of *new* asymmetric cross-current correlation functions excited in a monatomic fluid subjected to couette flow. The structure of these functions is explored and their implications for spectroscopic techniques such as depolarised light scattering and infra-red absorption are discussed.

KEY WORDS: Molecular dynamics, statistical mechanics, collective correlation functions, shear flow.

1 INTRODUCTION

Group theoretical statistical mechanics, *GTSM*, [1] and non-equilibrium molecular dynamics, *NEMD*, computer simulation [2] have recently revealed the existence of fundamentally new asymmetric cross-correlation functions *CCF*'s. produced by a shear rate, $\partial v_X/\partial Y$ applied to a fluid. These *new* time asymmetric cross correlation functions in the laboratory frame *XYZ* break the Onsager Casimir symmetry [3]. For example, for the velocity,

$$\langle v_X(0)v_Y(t)\rangle \neq \langle v_X(t)v_Y(0)\rangle. \tag{1}$$

where v_α is the α component of the centre of mass velocity, v of an atom diffusing in an ensemble. The theory was described that predicts those time-correlation functions existing in (symmetry breaking) simple planar shear flow, which are trivially zero in the absence of shear flow for symmetry reasons. The *new* cross correlation functions of this type are predicted by the third principle of group theoretical statistical mechanics, *GTSM*. Their observation using *SLLOD NEMD* [2] and subsequently by *PUT* in 2*D* and 3*D* [4] agreed with the predictions of the axioms of *GTSM*. In this work we pursue the implications of *GTSM* for **collective** correlation functions in couette shear flow, which have consequences for spectroscopy.

The D symmetry of shear in general is $D_g^{(0)} + D_g^{(1)} + D_g^{(2)}$, which is that of the tensor, vr^{-1}, *i.e.*, the general product of velocity, v, and inverse position, r^{-1}. The *D*

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symbols are irreducible representations of the rotation/reflection group $R_h^{(3)}$, and in shear flow can be thought of as representing $\nabla \cdot v$; $\nabla \times v$; and ∇v, resepectively the divergence, curl and dyadic of the velocity v. The divergence in pure shear is zero, the curl is antisymmetric in index reversal, and the dyadic, ∇v is symmetric. The light scattering spectrum reflects the weighted sum of $D_g^{(1)}$ and $D_g^{(2)}$ components, the curl and dyadic of the velocity, in our case the peculiar velocity. The curl of v, of $D_g^{(1)}$ symmetry, is usually regarded as the definition of vortex, and the dyadic ∇v is a symmetric deformation of $D_g^{(2)}$ symmetry. The induced correlation functions corresponding to the $D_g^{(1)}$ part of the shear stress are antisymmetric, representing vorticity, for example,

$$\langle v_X(0)v_Y(t) \exp (iq\cdot(r(0) - r(t))\rangle = - \langle v_Y(0)v_X(t) \exp (iq\cdot(r(0) - r(t))\rangle$$

and those corresponding to the $D_g^{(2)}$ part of the shear stress are symmetric, the minus sign in the above equation being replaced by a plus sign. The observed result is a **weighted** combination and is therefore asymmetric. Examples are given in this paper.

Consider the current correlation function for a monatomic fluid,

$$C_{XY} = \langle v_X(0)v_Y(t) \exp (iq\cdot(r(0)-r(t)))\rangle \tag{2}$$

Here q is the scattering vector and

$$r(t) - r(0) = \Delta r(t) = \int_0^t v(t)dt, \tag{3}$$

The shear-induced enhancement in mean square displacement is written as the integral over the asymmetric *CCF*,

$$\langle \Delta r^2(\tau)\rangle > = \int_0^\tau \int_0^\tau \langle v_X(t_1)v_Y(t_2)\rangle \, dt_1 dt_2 \tag{4}$$

$$= 2 \int_0^\tau (t - \tau)\langle v_X(0)v_Y(t)\rangle \, dt$$

The current *CCF* from Equation (2) is related to the self intermediate scattering function [5], by

$$F^s(q, t) = \langle \exp (iq\cdot(r(0) - r(t)))\rangle \tag{5}$$

which upon double differentiation provides,

$$\frac{d^2F_{XY}^s(q, \tau)}{d\tau^2} = - q^2 C_{XY}(\tau) \tag{6}$$

Equation (5) gives the result,

$$J_{XY}^s(q, \omega) = \frac{\omega^2}{q^2} S_{XY}^s(q, \omega) \tag{7}$$

where J is the temporal Fourier transform of C_{XY} and $S_{XY}^s(q, \omega)$ is the shear-induced component of the self-dynamic structure factor. Integrating Equation (6) gives,

$$\lim_{q\to 0} \frac{dF_{XY}^s(q, \tau)}{dt}_{\tau>\tau_l} = - q^2 \int_0^\infty \langle v_X(0)v_Y(t)\rangle dt \tag{8}$$

where τ_l is the correlation time. This shows that the dynamic structure factor under shear is a direct measure of the cross-correlation function of the type given in Equation (1). The function S_{XY}^s is in principle observable by *e.g.*, light-scattering. The scattering geometry is pictured in Figure 1. The initial polarisation vector has a

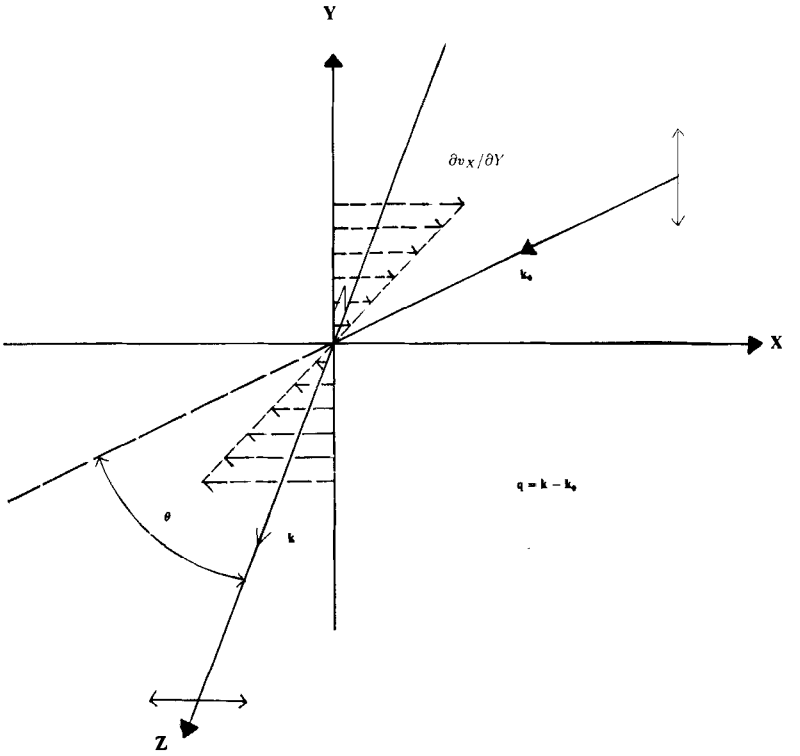

Figure 1 Scattering geometry for depolarised scattering from a fluid under shear. The geometry of the figure corresponds to $q = (0, 0, Z)$.

component along the X axis of the laboratory, XYZ frame. The scattered polarisation vector has a component along the y axis. It is well known that the Rytov, or shear wave, dip in depolarised light scattering [3] does not appear to be related to specific molecular structure, and has been attributed to 'local' strains set up by transverse shear waves. Similarly, it is proposed that a component of the depolarised spectrum due to Equation (8) exists for all atomic and molecular geometries in the steady state under an applied macroscopic shear strain rate. This component disappears at shear-free (isotropic) equilibrium.

The disymmetric CCF's of the form,

$$\langle v_Y(t)r_X(0)\rangle \neq \langle v_X(t)r_Y(0)\rangle. \tag{9}$$

$$\langle r_Y(t)r_X(0)\rangle \neq \langle r_X(t)r_Y(0)\rangle. \tag{10}$$

exist in addition to those in Equation (1). The permanent molecular dipole moment, μ_0, is always expressible as the vector sum of the position vectors of the atoms in the XYZ frame. This then confirms the existence of the CCF's,

$$\langle \mu_{0Y}(t)\mu_{0X}(0)\rangle \neq \langle \mu_{0X}(t)\mu_{0Y}(0)\rangle. \tag{11}$$

and,

$$\langle \dot{\mu}_{0Y}(t)\dot{\mu}_{0X}(0)\rangle \neq \langle \dot{\mu}_{0X}(t)\dot{\mu}_{0Y}(0)\rangle. \tag{12}$$

The Fourier transform of Equation (11) is a disymmetric shear induced complex permittivity. The Fourier Transform of Equation (12) is the far infra red power absorption accompanied by a dispersion in the refractive index. Therefore the newly discovered shear induced *CCF*'s that have already been shown to be sensitive probes of the non-Newtonian state [6] are also proved here to influence a wide range of spectroscopic techniques, such as enhanced depolarised light scattering and infra-red absorption. Therefore, it is to be expected that the non-Newtonian state of the fluid is closely related to the magnitude of these spectroscopic effects.

Kim *et al.* [7] already demonstrated by *NEMD* that shear flow induces depolarised light scattering in simple monatomic fluids. In a subsequent paper they showed that there is a shear induced birefringence [8], which can be ascribed to the well-known [9, 10] steady state distortion of the fluid under shear. The shear induced molecular polarizability, $\langle \alpha_{XY} \rangle$, is given in the shear applied steady state,

$$\langle (\alpha_{XY} \rangle \propto \langle \mu_{0Y} \mu_{0X} \rangle, \tag{13}$$

Just as the dielectric polarisation can be expressed in a power series in the applied electric field, involving molecular polarisability ($\propto E$) and molecular hyperpolarisability ($\propto E^2$), so we can also define a shear induced polarisability and shear induced hyperpolarisability.

In the next section we outline simulations performed to verify the existence of these new *CCF*'s and explore their form.

2 SIMULATION DETAILS

The MD simulations followed particles of mass, m, interacting via the Lennard-Jones, *LJ*, potential,

$$\phi(r) = 4\varepsilon((\sigma/r)^{12} - (\sigma/r)^6), \tag{14}$$

The MD simulations were performed on a cubic unit cell of volume V containing $N(= 108)$ molecules. The interactions were truncated at $2.5\,\sigma$. We use LJ reduced unit throughout, *i.e.*, $k_B T/\varepsilon \rightarrow T$, and number density, $\rho = N\sigma^3/V$. Time is in $\sigma(m/\varepsilon)^{1/2}$, strain rate is in $(\varepsilon/m)^{1/2}/\sigma$, viscosity is in $(m\varepsilon)^{1/2}/\sigma^2$ and stress is in $\varepsilon\sigma^{-3}$. The temperature was fixed by velocity rescaling of the peculiar velocities [11]. The state point considered was a near triple point state, at $\rho = 0.8442$ and $T = 0.722$. The simulations were for 150,000 – 250,000 time steps of magnitude, 0.01.

Using the *PUT* algorithm [10] to promote shear flow in *MD*, we have produced some examples of the new current correlation function (2) for different q, for two strain rates, $\gamma = 1$ and $= 2$.

We calculated the shear viscosity, η, from,

$$\eta = -P_{XY}/\gamma, \tag{15}$$

where,

$$P_{XY} = \frac{1}{V}\left(\sum_{i=1}^{N} m_i \tilde{v}_{xi} \tilde{v}_{yi} - \sum_{i=1}^{N-1} \sum_{j>i}^{N} (r_{xij} r_{yij}/r_{ij}) \frac{d\phi(r_{ij})}{dr}\right) \tag{16}$$

where r_{xij} is the x component of r_{ij} and $V = (N/\rho)$, the volume of the MD cell. The peculiar velocity is $\tilde{v}$.

3 RESULTS AND DISCUSSION

Here we follow on from previous studies of the intermediate scattering function, $F(q, t)$ of *unsheared LJ* fluids [12, 13], we consider essentially the shear excited component of $F(q, t)$. The collective correlation functions are derived from Equation (2) using,

$$c_{qX} = \sum_{i=1}^{N} \tilde{v}_{xi} \cos (q_X r_{Xi} + q_Y r_{Yi}) \tag{17}$$

$$c_{qY} = \sum_{i=1}^{N} \tilde{v}_{Yi} \cos (q_X r_{Xi} + q_Y r_{Yi}) \tag{18}$$

$$s_{qX} = \sum_{i=1}^{N} \tilde{v}_{Xi} \sin (q_X r_{Xi} + q_Y r_{Yi}) \tag{19}$$

$$s_{qY} = \sum_{si=1}^{N} \tilde{v}_{Yi} \sin (q_X r_{Xi} + q_Y r_{Yi}) \tag{20}$$

Here the velocities are excess or 'peculiar' velocities, being the velocity deviation from the local spacial average. From Equations (17) to (20) we can construct a number of component collective correlation functions,

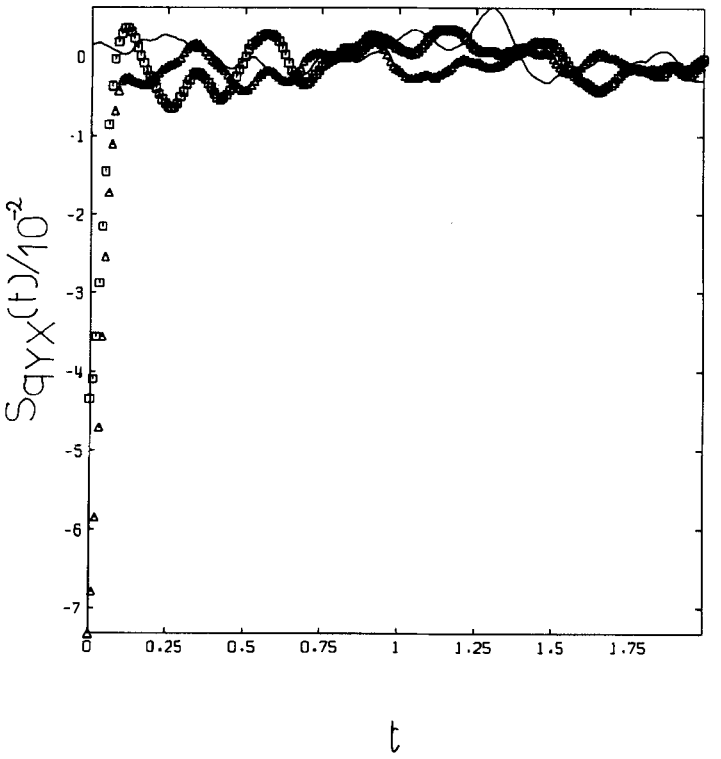

Figure 2 Some examples of the new shear induced current correlation functions. We give $S_{qYX}(t)$ and for $\gamma = 0, 1, 2$ and $q^* = (q^*_x, q^*_y, q^*_z) = (0, 0, 0)$. (a) $\gamma = 0$, solid line, (b) $\gamma = 1$, squares, (c) $\gamma = 2$, Δ.

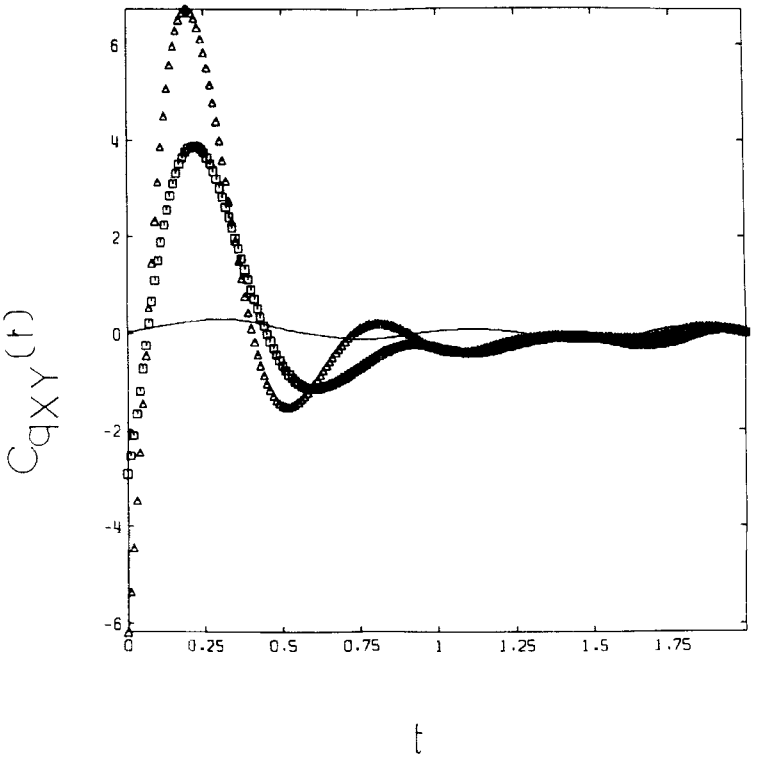

Figure 3 As for Figure 2 except that we give **a** $C_{qXY}(t)$, for $\gamma = 0, 1, 2$ and $q^* = (q^*_x, q^*_y, q^*_z) = (0, 1.25, 0)$; $\gamma = 0$, solid line; $\gamma = 1$, squares; $\gamma = 2$, Δ.

$$C_{qXY}(t) = \langle c_{qX}(0)c_{qY}(t)\rangle, \tag{21}$$

$$C_{qYX}(t) = \langle c_{qY}(0)c_{qX}(t)\rangle, \tag{22}$$

$$S_{qXY}(t) = \langle s_{qX}(0)s_{qY}(t)\rangle, \tag{23}$$

$$S_{qYX}(t) = \langle s_{qY}(0)s_{qX}(t)\rangle, \tag{24}$$

These functions are used in calculating the real and imaginary parts of the frequency transforms. In Figure 2 we give $S_{qYX}(t)$ and for $\gamma = 0, 1, 2$ and $q^* = (q^*_x, q^*_y, q^*_z) = (0, 0, 0)$. The $S_{qYX}(0)$ is negative at finite shear rates; a feature unforeseen in classical theories of dynamical motion in liquids. In Figure 3 we give a typical example of C_{qXY} and C_{qYX}, for $\gamma = 0, 1, 2$ and $q^* = (q^*_x, q^*_y, q^*_z) = (0, 1.25, 0)$. It shows that shear flow creates a nonzero time correlation function, which increases in magnitude with shear rate. (At $\gamma = 1, 2$ we find for $N = 108$ that $\eta = 2.06$ and 1.66, respectively.) A comparison between C_{qXY} and C_{qYX} in Figures 3(a) and (b) respectively, reveals that a time asymmetry appears in these collective functions as well as in the single particle cross correlation function, $\langle v_X v_Y\rangle$. As the only difference between the $C_{q\alpha\beta}$ *and* $S_{q\alpha\beta}$ is a translation of the position vectors they should be identical at all times and shear rates. We do find that S_{qXY} and S_{qYX} are statistically indistinguishable from C_{qXY} and c_{qYX}, which incidentally vindicates the boundary conditions used, that there

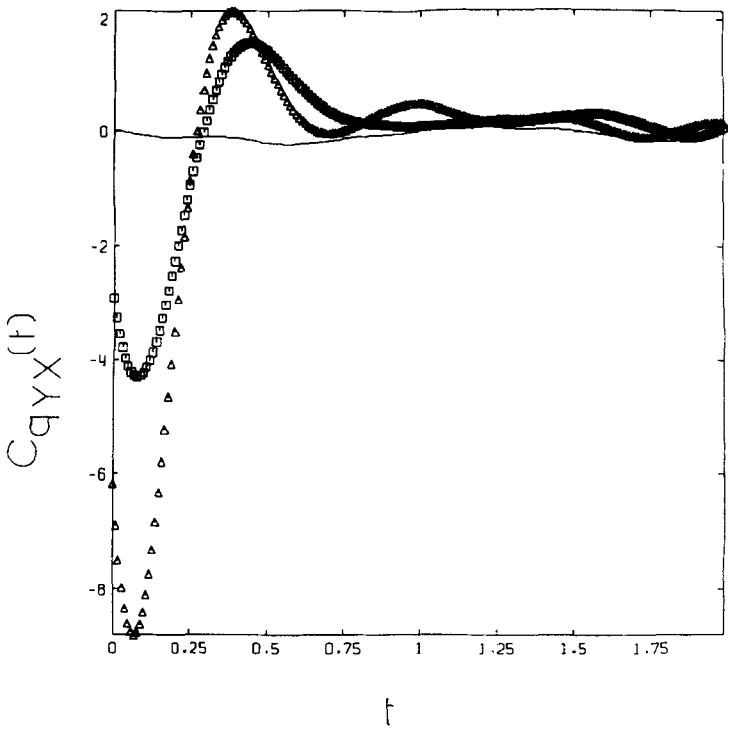

Figure 3 As for Figure 2 except that we give **b** $C_{qYX}(t)$ for $\gamma = 0, 1, 2$ and $q^* = (q^*_x, q^*_y, q^*_z) = (0, 1.25, 0)$; $\gamma = 0$, solid line; $\gamma = 1$, squares; $\gamma = 2$, Δ.

are no velocity discontinuities across the *MD* cell boundaries. The periodic boundary need to be ruled out in this work, because this is a frequent cause of controversy in the literature on collective *CCF*'s in light and neutron scattering.

In Figure 4, we consider S_{qYX}, for $\gamma = 0, 1, 2$ and $q^* = (q^*_x, q^*_y, q^*_z) = (1.25, 0, 0)$. This function is quite different in appearance from Figure 3, despite having the same q. These collective cross correlation functions are therefore sensitive to q. In Figure 5, we consider C_{qYX}, for $\gamma = 0, 1, 2$ and $q; = (q^*_x, q^*_y, q^*_z) = (1.25, 1.25, 0)$. These functions are similar to those in Figure 3.

We note that in some cases (*e.g.*, in Figures (4) and (5)), the collective *CCF*'s are non-zero even in the absence of shear for finite t. This is more evident at high q. This extra correlation we believe is statistical in origin, coming from the definition in equations (17) and (18) and finite sampling of a c_{qX} and c_{qY}. These figures (consistently) show the remnants of such correlation at $\gamma = 0$ in the very small amplitude oscillations of the solid line.

We clarify the fact that the shear induced cross correlation functions of Kim*et al.* [7, 8] are the well-known collision induced functions first discovered by McTague and Birnbaum in the late 1960's, corresponding to induced absorption in the far infra red. The present *CCF*'s have a quite different origin, and depend on no collision induced process. They are related, rather, to the Rytov family of phenomena, and in this paper are shown clearly to be exclusively due to shear and its various non-Newtonian response phenomena.

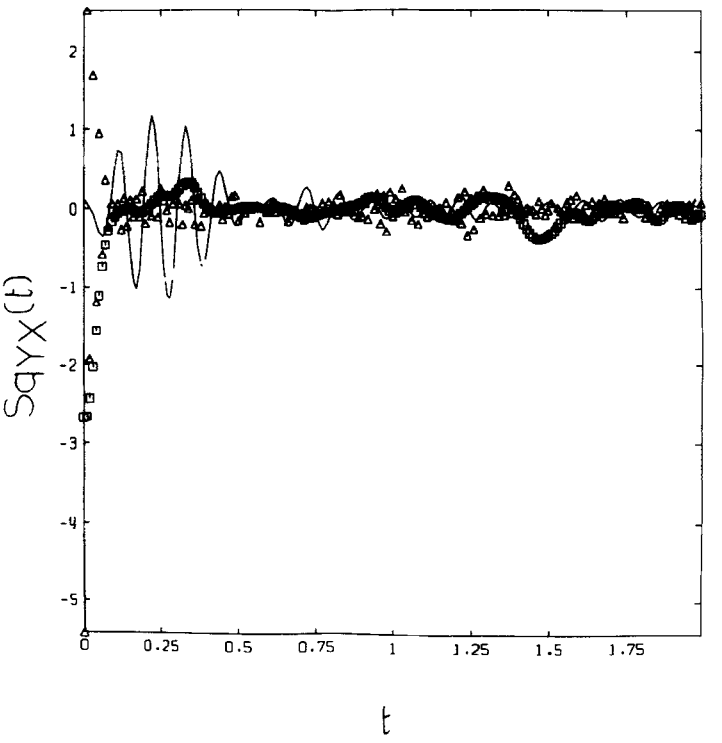

Figure 4 $S_{qYX}(t)$ for $\gamma = 0, 1, 2$ and $q^* = (q_x^*, q_y^* q_z^*) = (1.25, 0, 0)$; $\gamma = 0$, solid line; $\gamma = 1$, squares; $\gamma = 2$, Δ.

The new light scattering spectrum predicted by computer simulation in this paper has several potential applications. We first note that the spectrum is dissymmetric in interchange of the indices X and Y of shear, a property which can be exploited experimentally by reversing the direction of the shear. The experimental arrangement for observing depolarised light scattering from a sheared fluid consists of a couette made up of two co-axial cylinders, the inner cylinder creates the shear while the outer is a static glass wall, transparent to the incoming laser frequency. The overall scattering geometry is as illustrated in Figure 1. The rate of shear achievable in the laboratory is usually no greater than a megahertz, and to create a non-Newtonian response at this shear rate requires a colloidal dispersion or liquid crystal rather than a simple molecular fluid. The time decay of the new cross *CCF*'s is roughly compatible with the inverse rate of shear, so that photon correlation techniques rather than high frequency Rayleigh/Brioullin scattering are necessary if the shear rate is in the MHz, equivalent to time scales in the microsecond range. Depolarised scattering is usually observed from laser radiation, but cyclotron or neutron radiation could be used in principle. Inelastic collisions of neutrons with the particles of a sheared fluid deal directly with exchange of momentum, which is the dynamical variable basically responsible for the depolarised, shear induced spectrum. Cyclotron radiation is now available over a very wide range of frequencies with which to probe the non-Newtonian nature of a sheared fluid.

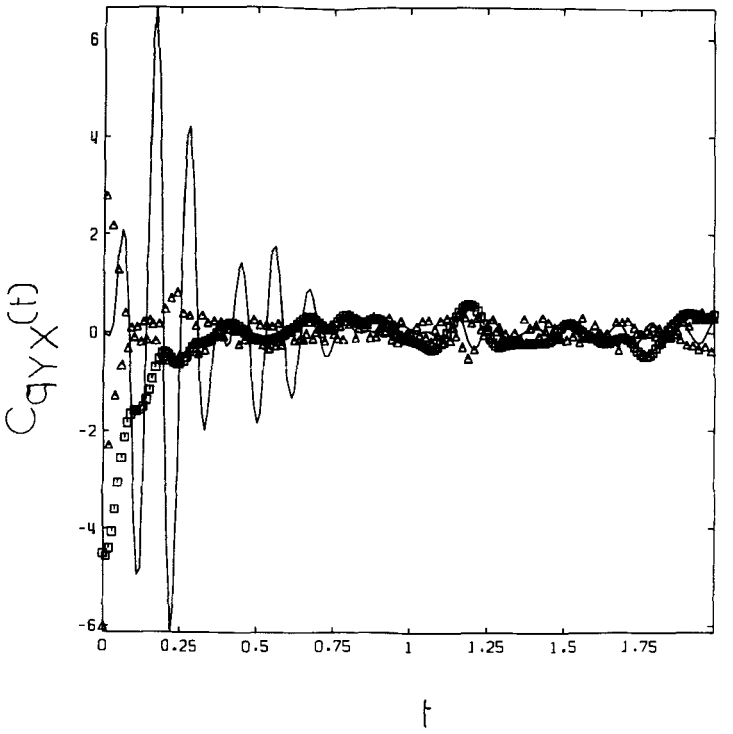

Figure 5 $C_{qYX}(t)$ for $\gamma = 0, 1, 2$ and $q^* = (q^*_x, q^*_y, q^*_z) = (1.25, 1.25, 0)$; $\gamma = 0$, solid line; $\gamma = 1$, squares, $\gamma = 2$, Δ.

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