Group Theory Statistical Mechanics and Simulation Studies of Electrorheology

M. W. Evans*,† and **D. M. Heyes**

Department of Chemistry, Royal Holloway and Bedford New College, University of London, Egham, Surrey TW20 OEX, U.K. (Received: June 12, 1990)

Electrorheological, ER, fluids are colloidal dispersions that show an increase in yield stress and viscosity when subjected to an electric field. In this report, we investigate this phenomenon at a fundamental level by using group theory statistical mechanics, GTSM, and Brownian dynamics, BD, computer simulation. The effect can be produced by BD using a simple form for the field-induced colloidal particle interactions. In agreement with recent experimental observations, the simulations produce electric-field-induced "strings" of particles that span the electrodes. This field-induced aggregation of the particles is responsible for the major increase in the viscosity. The combination of shear and electric field produces a long-range microstructure that periodically develops and decays, as a result of the competing incompatible effects of electric field and shear rate. Using the symmetry principles of GTSM, we interpret at the molecular level dynamical consequences of applying an electric field to a sheared liquid. We predict and verify by BD the existence of *new* time correlation functions in the laboratory frame (X, Y, Z) induced by the shear flow. The simultaneous application of shearing and an electric field, through the use of rotating electrodes in the ER experiment has a pronounced effect on the autocorrelation functions and these new cross correlation functions. Several *new* ensemble averages appear in the frame (X, Y, Z). These predictions of GTSM are confirmed by these simulations. Suggestions are made for future applications of the ER effect.

1. Introduction

When certain particles of diameter ~ 1 μm are dispersed in an insulating liquid and subjected to an electric field of several kV mm^{-1}, a marked increase in the viscosity is observed. This is called the *electrorheological* (ER) *effect*. Following on from the pioneering work of Winslow,[1] who noted that moist silica gel particles of ~ 1 μm diameter, σ, suspended in kerosene at a volume concentration of $\sim 50\%$ had a strong ER effect, there have been a number of experimental,[2-4] and theoretical studies,[5] of this phenomenon. In this publication, our contribution to this field is to show that the essential features of the ER effect can be reproduced by atomistic computer simulation. We also specify the key statistical mechanics of the ER effect.

Major advances in two branches of physical chemistry, dielectric spectroscopy,[6] and studies of non-Newtonian rheology,[7] have been made in the last decade, helped by conventional[8] and nonequilibrium[7] molecular dynamics computer simulation. The range of dielectric spectroscopy has also been extended by the development of far infrared interpretative methods. The simple theories,[9,10] with which the experimental data were first interpreted,[11] have given way to a much more detailed and expansive understanding, using the principles of group theoretical statistical mechanics of GTSM.[12] This applies the principles of point group theory,[13-16] to thermodynamic ensemble averages at equilibrium, in the steady state out of equilibrium, and in the presence of applied external fields. GTSM describes the symmetry behavior of all ensemble averages in three simple axioms, or principles, which may be used to guide the experimentalist and computer simulator in dealing with the possibilities offered by the application of arbitrary field combinations to liquids, and related states of matter. In this paper, these principles are used to explore the ER effect. This enables us to define more closely, *new* ensemble averages and observables with new applications. In particular we are interested in time correlation functions, fluctuation-dissipation theorems and modified Green–Kubo relations,[17] caused by the simultaneous presence of shear and electric field.

The knowledge gathered in dielectric spectroscopy and non-Newtonian rheology over the past decade has helped us understand electrorheology. The electroshearing action is already known to affect the dielectric loss and dispersion, Kerr relaxation, power absorption spectra observable in low, radio, and microwave frequency spectroscopies and far infrared spectroscopy, respectively.[18]

On a much shorter (picosecond) time scale, the effects of electroshearing could also be studied in nonequilibrium molecular dynamics computer simulations, which give time correlation functions, both at equilibrium and in the transient region just after field application and removal. These simulated ensemble averages act as a bridge between the point group theory and the experimental observable. Some time cross correlation functions can be observed experimentally under certain conditions, for example the Weissenberg effect of non-Newtonian rheology is due to a time cross correlation function (ccf) between linear velocity components.[17] At field free equilibrium there is now known to be a set of time ccf's between the fundamental dynamical variables of translation, rotation, and normal mode vibration in a diffusing molecule, which the conventional theory of diffusion[19] assumes to vanish for all time in all frames of reference. Some members of this set have been characterized recently by the authors using nonequilibrium molecular dynamics computer simulation, producing results which are now known to be in complete agreement with the symmetry rules of group theoretical statistical mechanics. Computer simulation has also shown that the effect of external

(1) Winslow, W. M. *J. Appl. Phys.* **1949**, *20*, 1137.
(2) Sprecher, A. F.; Carlson, J. D.; Conrad, H. *Mater. Sci. Eng.* **1987**, *95*, 187.
(3) Block, H.; Kelly, J. P. *J. Phys. D: Appl. Phys.* **1988**, *21*, 1661.
(4) Klass, D. L.; Martinek, T. W. *J. Appl. Phys.* **1967**, *38*, 67, 75.
(5) Adriani, P. M.; Gast, A. P. *Phys. Fluids* **1988**, *31*, 2757.
(6) Evans, M. W.; Evans, G. J.; Coffey, W. T.; Grigolini, P. *Molecular Dynamics*; Wiley/Interscience: New York, 1982.
(7) Heyes, D. M. *Comput. Phys. Rep.* **1988**, *8*, 71.
(8) Evans, M. W. *Phys. Rev. Lett.* **1985**, *55*, 1551; **1990**, *63*, 2909.
(9) Debye, P. *Polar Molecules*; Chem. Cat. Co.: New York, 1929.
(10) Hill, N. E.; Vaughan, W. E.; Price, A. H.; Davies, M. *Dielectric Properties and Molecular Behaviour*; van Nostrand Reinhold: London, 1969.
(11) Davies, M. (Senior Reporter). *Dielectric and Related Molecular Processes*; Chemical Society: London, 1972-1977; Vols. 1-3.
(12) Evans, M. W. *Chem. Phys.* **1988**, *127*, 413.
(13) Salthouse, J. A.; Ware, M. J. *Point Group Character Tables*; Cambridge Univ. Press: Cambridge, UK 1972.
(14) Flurry, R. L., Jr. *Symmetry Groups, Theory and Applications*; Prentice Hall: Englewood Cliffs, NJ 1980.
(15) Cotton, F. A. *Chemical Applications of Group Theory*; Wiley/Interscience: New York, 1963.
(16) Urch, D. M. *Orbitals and Symmetry*; Penguin: Harmondsworth, UK, 1971.
(17) Evans, M. W.; Heyes, D. M. *Mol. Phys.* **1989**, *66*, 1057.
(18) Block, H.; Goodwin, K. M. W.; Gregson, E. M.; Walker, S. M. *Nature (London)* **1978**, *275*, 632.
(19) Grigolini, P. In *Memory Function Approaches to Stochastic Problems in Condensed Matter*; Evans, M. W., Grigolini, P., Pastori, G., Prigogine, I., Rice, S. A., Eds.; Advances in Chemical Physics, Vol. 63; Wiley/Interscience: New York, 1985.
(20) Evans, M. W. *Phys. Lett. A* **1984**, *102*, 248.
(21) Evans, M. W. *Phys. Rev. A* **1985**, *31*, 3947.
(22) Evans, M. W. *Physica* **1985**, *131B,C*, 273.

†Also at Dept. of Physics, Univ. of Lancaster, LA1 47B, U.K., and Dept. 48B/428, IBM, Neighborhood Road, Kingston, NY 12401. Present address: Theory Center, Cornell University, Ithaca, NY 14853. 1990-1991: Institute of Physical Chemistry, University of Zurich, Winterhurerstrasse 190, CH 8057, Zurich, Switzerland.

fields is to make the set of nonvanishing ccf's much larger; i.e., the fields induce the existence of ensemble averages which are normally nonexistent at field-free equilibrium. The early simulations, using simple static electric fields,[23,24] showed a definite symmetry relation between the field and the induced ccf, a quantity that conventional theory had considered not to exist. Recently, comparable computer simulations of atomic liquids subjected to non-Newtonian strain rates have also shown the same relation[17] between the applied field (in this case a shear) and the induced ccf's (between angularly resolved linear velocity components). These symmetry relations between the applied field and the induced ensemble averages are now embodied in the third principle of GTSM. This principle is used here to explore the consequences of a simultaneously applied shear and electric field, both static and alternating (i.e., time independent and time dependent, respectively).

In the next section, the three principles of GTSM are stated after a discussion of general symmetry principles. They are then applied to an electrosheared molecular ensemble, both for a static and alternating applied electric field, by constructing the D representation in frame (X, Y, Z) or the laboratory frame of the combination of the electric and shearing fields. In the simulation details (section 3), we describe the Brownian dynamics (BD) model applied to electroshearing in the ER effect. The BD technique is applied to the ER effect.

2. GTSM Theory

The principles of group theoretical statistical mechanics are derived from a consideration of the rotation reflection group $R_h^{(3)}$ of three-dimensional isotropic space, such as that occupied by a molecular or atomic liquid. The irreducible representations of this point group are described by the well-known D representations, $D_g^{(0)}, ..., D_g^{(n)}$ and $D_u^{(0)}, ..., D_u^{(n)}$. The superscripts denote the order of the spherical harmonics and the subscripts denote gerade (even) or ungerade (odd) to parity reversal symmetry, the parity reversal operation being (X, Y, Z) to $(-X, -Y, -Z)$. A D representation with superscript 0 is a scalar (subscript g) or pseudoscalar (subscript u); one with superscript 1 is a vector (u) or pseudovector (g); with superscripts 2 and so on, higher order g or u tensors. In this language of D representations, the three principles can be stated as follows. The first,[25] is Neumann's Principle of 1885, restated in particularly clear terms by Pierre Curie who stated that "symmetry determines the phenomenon".[26]

Principle 1: Neumann's Principle. The thermodynamic equilibrium ensemble average $\langle ABC...D \rangle$ over the product $ABC...$ of scalar, vector, or tensor quantities exists in the laboratory frame (X, Y, Z) if the product of symmetry representations of A, B, C... contains the totally symmetric representation, $D_g^{(0)}$, of the $R_h^{(3)}$ point group at least once.

Principle 2. This average exists in the molecule-fixed frame of the point group character tables, frame (x, y, z), of the product of representations contains at least once the totally symmetric representation of the molecular point group itself.

Principle 3. If an external force field of given D symmetry is applied to a molecular ensemble, bringing this into a steady state, then extra ensemble averages are created in frame (X, Y, Z) with the same D symmetry as that of the applied field or field combination.

In this paper, we are particularly concerned with the application of principle 3 in electrorheology, where an electroshearing field (electric field and shear applied with spinning electrodes) combination is applied to a molecular or atomic ensemble. An electric field E is a polar vector of $D_u^{(1)}$ symmetry, and a shear has been shown recently to have the D symmetry $D_g^{(0)} + D_g^{(1)} + D_g^{(2)}$.[17] A combination of the two fields in electroshearing, applied by using spinning electrodes, will have the product of these D symmetries, which is

$$E \times shear = D_u^{(1)}(D_g^{(0)} + D_g^{(1)} + D_g^{(2)})$$
$$= D_u^{(1)} + (D_u^{(0)} + D_u^{(1)} + D_u^{(2)}) + (D_u^{(1)} + D_u^{(2)} + D_u^{(3)})$$

$$(1)$$

Here we have used the Clebsch–Gordan theorem to split the symmetries into three combinations, each of which may be used to say something about the symmetry of the applied field combination and thus of the induced ensemble averages according to principle 3. The overall parity symmetry of the electroshearing combination is ungerade, meaning that only thermodynamically averaged quantities with this parity symmetry are allowed in the frame (X, Y, Z) by the applied field combination. The overall time reversal symmetry of the combination is dependent on the product of the individual symmetries of the electric field and shear. If the former is a static field, its time reversal symmetry is positive, but the time reversal symmetry of an alternating electric field is negative. The time reversal symmetry of shear is a product of that of position, r (+), and linear velocity, v (−), and is therefore negative. The time reversal symmetries in electroshearing are therefore as follows: (i) negative overall with a static electric field; (ii) positive overall with an alternating, or time-dependent, electric field.

Note that the overall symmetries deduced in (i) and (ii) appear from the fact that the time reversal (T) symmetry of a static electric field is positive, and that the T symmetry of a time-varying electric field can be negative under certain circumstances, for example when there is a sinusoidal time dependence. The T symmetry of velocity v is negative, and that of position, r, is positive, so that T(Evr) is negative for static E and positive for sinusoidally time varying E.

The overall parity and D symmetry of electroshearing is given by eq 1 and the time reversal symmetry has just been given. The symmetries of the various possible field combinations can now be discussed in terms of the general triple vector product of the individual fields involved. This is Evr, made up of the general product of the electric field E and the product vr of the shear field. In couette flow, there are no v·r components of the shear field; i.e., this is made up of off-diagonal elements only. This means that in electroshearing with rotating electrodes, there can be no effective field combination of the type E(v·r). The field combinations available all involve $v \times r$ or vr^T. From eq 1, the possible individual field combinations are as follows: (1) The symmetry product $D_u^{(1)}D_g^{(1)}$ gives the three possible combinations E·(v × r); E × v × r; and E × vr^T. (2) The symmetry product $D_u^{(1)}D_g^{(2)}$ gives the three further possible combinations E × vr^T, $E(vr^T)^T$, and Evr. Therefore, depending on the relative geometry of the applied fields, different field D symmetries are possible in general. If electroshearing is carried out with a simple arrangement of rotating electrodes, then the electric field is parallel to the vector r × v, so that only a few of the combinations in (1) and (2) are possible. These exclude E(v·r) and E × v × r. However, all the other possible field combinations may have an effect. For example, E·(v × r) is maximized in rotating electrodes, both for static and alternating electric fields. The next section deals with the possible consequencies of principle 3 applied to the different field combination D symmetries possible when electroshearing in rotating electrodes.

We now employ principle 3 to predict the presence of ensemble averages of $D_u^{(0)}$ symmetry in achiral media induced in electroshearing by a combination of alternating electric field and shear vorticity of this symmetry.

The rotation of plane polarized light is one possible consequence of applying the field combination E·(v × r) to the sheared liquid by using an alternating electric field. This is because this particular field combination has positive time reversal symmetry and negative parity reversal symmetry, with the overall D symmetry $D_u^{(0)}$. This satisfies the requirements for the field combination being chiral.[27] There is a possibility therefore of a new kind of "Faraday effect" where the latter's magnetic field is replaced by a combination of electric field and shear that satisfies the requirements of overall

(23) Evans, M. W.; Heyes, D. M. *Phys. Scr.* **1990**, *41*, 304.
(24) Evans, M. W. *Chem. Phys. Lett.* **1989**, *158*, 375.
(25) Neumann, F. E. *Vorlesungen uber die Theorie Elastizität des Festen Korper und des Lichtäthers*; Teubner: Leipzig, 1885.
(26) Curie, P. *J. Phys (Paris)* **1894**, *3*, 393.

(27) Barron, L. D. *Chem. Soc. Rev.* **1986**, *15*, 189.

parity conservation and reversality recently discussed by Barron.[27] In order to see this effect, the electric field vector **E** must be parallel to the vector generated by the cross product **v** × **r**. In a liquid being sheared by rotating plates, the latter is perpendicular to the plane of shear, and thus parallel to an alternating electric field applied by using the rotating plates as electrodes. If the liquid is being sheared in the X–Z plane by a simple strain rate, $\partial v_X/\partial Z$, the electric field is applied in the Y axis of the laboratory frame. In terms of molecular dynamics, the combined influence of the shear and electric field introduces into the laboratory frame new ccf's that radically change the nature of dielectric and far infrared spectra normally observed in a static (nonsheared) liquid. This opens up the experimental possibility of studying the nature of non-Newtonian effects such as shear thickening and thinning with dielectric and far infrared methods. The dielectric effects,[18] would be especially dramatic when the rate of shear is adjusted to the range of frequencies of the applied electric field (e.g., radio and MHz). This is obtainable in the laboratory by using the correct viscosity range in the sample under investigation. Some experimental evidence for these effects is already available in the literature,[18] but much investigation needs to be done.

The ccf induced by the $D_g^{(1)}$ shear of the type $\partial v_X/\partial Z$ has recently been found by a nonequilibrium molecular dynamics simulation[17] to be

$$\langle v_X(t)\, v_Z(0) \rangle = -\langle v_X(0)\, v_Z(t) \rangle \tag{2}$$

a time-antisymmetric ccf, which vanishes at $t = 0$. A static or alternating electric field has been found by computer simulation,[20,21] to induce similar time ccf's in the laboratory frame between a diffusing molecule's angular velocity, ω, and its own linear velocity, **v**. If the electric field is applied in the Y axis, the induced ccf's are

$$\langle v_X(t)\, \omega_Z(0) \rangle = -\langle \omega_X(0)\, v_Z(t) \rangle \tag{3}$$

A combination of both electric field and shear vorticity, embodied in the results, (2) and (3), can result in chiral effects, the rotation of the plane of polarized radiation across the whole frequency range of dielectric and far infrared spectroscopy. On a molecular dynamical level, this is due to the presence of the ccf $\langle \omega(t) \cdot v(0) \rangle$ between the velocity and angular velocity of a diffusing molecule. This ccf is a pseudoscalar of positive time reversal symmetry and negative parity symmetry, and is induced by electroshearing with an alternating or otherwise time-dependent electric field. The ccf's of this type, and of the types shown in (2) and (3), should be observable in a computer simulation of electroshearing in liquids and colloids. There is therefore much scope for experimental investigation of the chiral influence of electroshearing across the complete dielectric and far infrared range of about fourteen frequency decades.

The thermal conductivity, the Green–Kubo integral over the Irving–Kirkwood heat flux tensor, **J**, has the D symmetry of eq 1, i.e., the same D symmetry as that of a combination of electric field and shear. Thus all possible field combinations in electroshearing contribute in principle to the thermal conductivity. However, in looking for an experimental effect of this kind, it is necessary to use a static electric field and an overall negative time reversal symmetry of the combination of electric field and shear. This is because the time reversal symmetry of **J** is itself negative. Thus, principle 3 predicts that the application of a static electric field with spinning electrodes to a molecular liquid will result in measurable changes in the thermal conductivity. In this case, both the shear-induced vorticity and the shear-induced deformation will contribute to the change in thermal conductivity.

It is also possible to use principle 3 to predict the presence in the laboratory frame of individual ensemble averages of the type ⟨A⟩, i.e. over a single molecular dynamical quantity that may be related to macroscopic observables. Such averages may exist only if they have positive time reversal symmetry. Therefore, in order to see them in electroshearing, we need the use of an alternating electric field applied with the spinning electrodes. Examples of such quantities, which are ungerade to parity reversal symmetry and which are positive to time reversal symmetry are ⟨M⟩, the

thermodynamic average of the dipole moment of the collection of diffusing molecules, and that over the linear acceleration, the time derivative of **v**. This means that one or more components of the dipole auto correlation function exist for all t, signaling an effect of electrorheology on the dielectric complex permittivity. The existence of a nonvanishing acceleration implies that electroshearing introduces a net body force into the sample.

By the D symmetries of various properties in the laboratory frame (X, Y, Z), it is possible to anticipate from principle 3 some other possible effects of electroshearing with overall positive time reversal symmetry. For example, the gyration tensor of optical activity has the symmetry $D_u^{(0)} + D_u^{(2)}$ which is included in the sum in (1). This again leads to the expectation of effects such as the rotation of the plane of polarized radiation and a Raman circular intensity difference, for example, in response to electroshearing with an alternating electric field. Also, the molecular hyperpolarizability has the D symmetry $D_u^{(1)} + D_u^{(3)}$, which is again included in eq 1. By principle 3, therefore, we expect a possible nonvanishing hyperpolarizability to appear in frame (X, Y, Z) in response to electroshearing with an alternating applied electric field. The symmetry of electroshearing envelopes that of the hyperpolarizability tensor in the laboratory frame of reference. Finally, the D symmetry of piezoelectricity and the electrooptic Kerr effect is the sum $2D_u^{(1)} + D_u^{(2)} + D_u^{(3)}$, which appears as part of the D symmetry on the right side of eq 1. Considerations of symmetry therefore allow an electrooptic Kerr effect in an electrosheared liquid, involving the rotation of the polarization of a probe laser. This effect should be especially interesting in liquid crystals and related functional fluids. With the right type of material, electroshearing also envelopes the symmetry of piezoelectricity, the presence of which could be used to probe the nature of the material between the spinning electrodes.

We have discussed some of the potential applications of the ER effect, in addition to its main effect in the viscosity of the fluid. In this report, we apply molecular simulation to the ER effect to gain insights into its molecular origins and in particular the time correlation functions thereby induced in the fluid.

3. Simulation Method

In these simulations, we generate the positions of model colloidal particles subject to an electric field in the y direction and to laminar shear flow, dv_x/dy. The molecular configurations are generated at fixed time intervals, h, by using the BD technique.[28] First we will describe the basics of BD and then the method of including the electric field and shear.

The strict Langevin BD method employed here[28] treats the suspending medium on two independent levels. The background fluid acts to dampen out the velocities of the colloidal particles. The force on the particles by the solvent opposes the velocity through a friction coefficient, β. The discrete nature of the solvent is taken into account by a random force **R** acting upon the colloidal particles. The value of the random force on each particle changes with time in order to represent the net effect of the collisions of the solvent molecules on the colloidal particle. In each time interval, there is an imbalance on either side of the colloidal particle, leading to the net force, **R**. This represents the net effect of the suspending medium over a fixed time interval (i.e., h):

$$\ddot{\mathbf{r}} = \mathbf{F}/m + \mathbf{R}/m - \beta \dot{\mathbf{r}} \tag{4}$$

where **r** is the position of an arbitrary macromolecule, **F** is the systematic component of the force derived from the pair interactions between the colloidal particles and m is the mass of the colloidal particle (assumed all the same here). The algorithm for updating the particle position is

$$r_x(t + h) = r_x(t) + (F_x(t) + R_x(t,h))h/m\beta + \gamma r_y(t) \tag{5}$$

$$r_y(t + h) = r_y(t) + (F_y(t) + R_y(t,h))h/m\beta \tag{6}$$

$$r_z(t + h) = r_z(t) + (F_z(t) + R_z(t,h))h/m\beta \tag{7}$$

where γ is the applied shear rate. Sliding (Lees–Edwards)

---

(28) Heyes, D. M. J. Non-Newtonian Fluid Mech. **1988**, 27, 47.

boundary conditions are employed at the BD cell boundaries to maintain continuity of the shear velocity profile across all space.[28] The random force is taken from a normal distribution with standard deviation, $\langle R_\alpha^2(t,h) \rangle$, where

$$\langle R_\alpha^2(t,h) \rangle = 2mk_BT\beta/h \qquad (8)$$

where $\alpha = x$, y, or z. The colloid–colloid particle potential, $\phi(r)$, has the form

$$\phi(r_{ij}) = \epsilon(\sigma/r_{ij})^{12} + (\mu_y^2/r_{ij}^3)(1 - 3r_{yij}^2/r_{ij}^2) \qquad (9)$$

where the first term represents the core–core repulsion and is called the soft-sphere potential. The y component of the separation between particles i and j, r_{ij}, is r_{yij}. The second term is, to first order, the intermolecular interaction due to the external field induced dipoles, μ_y. Therefore

$$F_x = 12(r_{xij}/r_{ij})\epsilon\sigma^{12}/r_{ij}^{13} + 3\mu_y^2(r_{xij}/r_{ij}^5)(1 - 3r_{yij}^2/r_{ij}^2) - \\ 6(\mu_y^2/r_{ij}^3)(r_{xij}r_{yij}^2/r_{ij}^4) \quad (10)$$

$$F_y = 12(r_{yij}/r_{ij})\epsilon\sigma^{12}/r_{ij}^{13} + 3\mu_y^2(r_{yij}/r_{ij}^5)(1 - 3r_{yij}^2/r_{ij}^2) + \\ 6(\mu_y^2/r_{ij}^3)(r_{yij}/r_{ij}^2 - r_{yij}^3/r_{ij}^4) \quad (11)$$

$$F_z = 12(r_{zij}/r_{ij})\epsilon\sigma^{12}/r_{ij}^{13} + 3\mu_y^2(r_{zij}/r_{ij}^5)(1 - 3r_{yij}^2/r_{ij}^2) - \\ 6(\mu_y^2/r_{ij}^3)(r_{zij}r_{yij}^2/r_{ij}^4) \quad (12)$$

The BD simulations were performed on a cubic unit cell of volume V containing $N = 108$ macroparticles. To help establish scaling relationships, the calculations were performed in reduced units, i.e., $k_BT/\epsilon \rightarrow T$, and number density, $\rho = N\sigma^3/V$. Time is in $\sigma(m/\epsilon)^{1/2}$, shear rate is in $(\epsilon/m)^{1/2}/\sigma$, viscosity is in $(m\epsilon)^{1/2}/\sigma^2$ and stress is in $\epsilon\sigma^{-3}$. Calculated quantities are mostly given in terms of these units. The effective hard-sphere diameter, σ_{HS}/σ, of the soft-sphere potential is[29]

$$\sigma_{HS}/\sigma = 0.9359/T^{12} \qquad (13)$$

The fluid density of the hard-sphere fluid at fluid–solid coexistance is $\rho_{HS} = 0.9428N\sigma_{HS}^3/V$. Therefore, the coexistence fluid density in soft-sphere units is 1.15.[30]

Most of the simulations reported here were conducted at $\rho = 1.1$, $\epsilon = 298k_B$, and $T = 1.0$. The solids volume fraction is $\phi = (\pi/6)\rho_{HS}$, where $\rho_{HS} = (0.902)^3\rho$, hence $\phi = 0.472$, which is a fluid state close to the phase boundary. Other material parameters were chosen to be those of an experimental system at the solvent density and particle density of 1000 kg m^{-3}, the viscosity of the suspending fluid (0.001 P), the temperature (298 K), and the size of the particle $\sigma = 1$ µm. The time step in the simulation is equivalent to 1 ms.

It is still not known what the precise effect of the external field is on the colloidal particles. We have modeled its effect as an induced point dipole at the center of each macromolecule that at all time, while the field is applied, points along the direction of the field (i.e., y, here). When the field is "turned off", the dipole moment is set to zero. We have deliberately kept the model as simple as possible in this preliminary study, in order to establish the minimum microscopic requirements for the ER effect. The value of this dipole moment, μ_y, that produced a strong ER effect in the simulations was 4.0 in reduced units. This is reasonable because experience gained in simulations of other non-Newtonian phenomena (e.g., shear thinning and thickening[31,32]) has revealed that a close competition between the hard-core repulsions and the perturbing force is required to produce these strongly non-Newtonian effects.[33,34] For the dipolar interactions to compete suc-
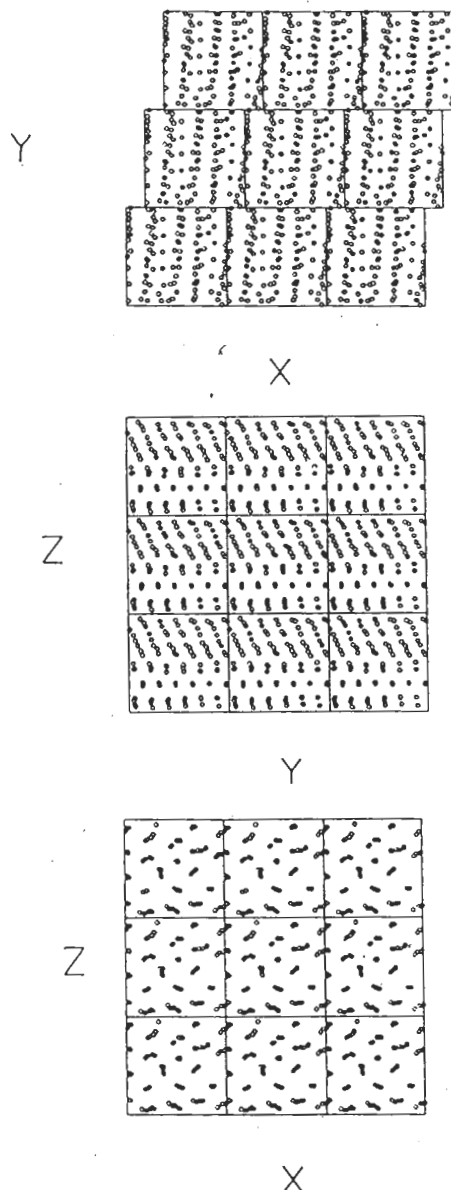

Figure 1. Projections of the model colloid particle centers on planes. All $N = 108$ particles are given at a reduced radius of 0.1σ to assist the presentation. The central square is the real BD cell. The surrounding eight squares are the image cells, appropriately shifted with Lees–Edwards boundary conditions in the xy plane. The streaming velocity is in the x direction. The velocity gradient is in the y direction. Parameters: $P_e = 0.001$; $\mu_y = 4$; $\eta_s = 0.02$ P; $T = 298$ K; mass of Brownian particle $= 0.636 \times 10^{-9}$ kg; $\sigma = 75$ µm; momentum relaxation time $\tau_p = 0.45 \times 10^{-4}$ s; $\tau_r = 0.48 \times 10^7$ s; $h = 966$ s; $E_Y = 75$ V/m; $\rho^* = 1.0$; $T^* = 1.0$.

cessfully with the short-range repulsions, the coefficient of the dipolar interaction must be of order unity in reduced units. The point dipole model is clearly a simplification but it is not possible at present to be more definite as to the charge reorganization caused by the applied electric field. Nor are practicable alternative simulation methods at present feasible for dense suspensions.[35] The shear rates are normalized by the time scale for local structural organization, τ_r, the time it takes a molecule to diffuse $\sigma/2$ at extreme dilution.

$$\tau_r = 3\pi\sigma^3\eta/4k_bT \qquad (14)$$

We consider reduced shear rates in terms of the Peclet number, $P_e = \tau_r\gamma/2$, of order unity.

Computations were carried out on a MICROVAX 2000 in the Chemistry Department of Royal Holloway & Bedford New College Computer Centre.

(29) Hammonds, K. D.; Heyes, D. M. *J. Chem. Soc., Faraday Trans. 2* **1988**, *84*, 705.
(30) Cape, J. N.; Woodcock, L. V. *J. Chem. Phys.* **1980**, *73*, 2420.
(31) Woodcock, L. V. *Mol. Sim.* **1989**, *2*, 253.
(32) Barnes, H. A. *J. Rheology* **1989**, *33*, 329.
(33) Heyes, D. M.; Kim, J. J.; Montrose, C. J.; Litovitz, T. A. *J. Chem. Phys.* **1980**, *73*, 3987.
(34) Heyes, D. M. *J. Chem. Soc., Faraday Trans. 2* **1986**, *82*, 1365.

(35) Ladd, A. J. C. *J. Chem. Phys.* **1989**, *90*, 1149.

4. Results and Discussion

In Figure 1 we show a typical example of the structural changes in the fluid when subjected to a shear flow and electric field. The field aligns the particles into bands or "strings" along the field lines. Long-range order forms spanning the BD cells. There are regions of high density and low density that alternate in the shear (xy) plane. These strings are of approximately one molecule in diameter, when viewed in plane of the electrode (xz). They are continually being formed (perpendicular to the plates). They then tilt in the x direction, become taut, and then break up. Strings of particles line up along the applied electric field, perpendicular to the shearing plates (which also serve as the electrodes). These resist shear flow as the shear flow tilts them and, as these macroparticles are the stress-carrying components of the suspension, the strings enhance the viscosity.

In this paper, we are not so much concerned with the general features of the electrorheological phase diagram, but more with bringing out new insights into the dynamics of these systems.

However, there are some properties that are routinely calculated during the simulation as means of monitoring the state of the modeled material. The shear viscosity of the suspension, η, is a useful macroscopic probe of the effect of shear rate and electric field on the model suspension. It is calculated as a running average of the shear stress divided by the shear rate as follows:

$$P_{xy} = (1/V)\sum_{i=1}^{N-1}\sum_{j\neq i}^{N} r_{xij}r_{yij}(d\phi/dr)/(2r_{ij}) \qquad (15)$$

where V is the (cubic) volume containing the N particles and where r_{xij} is the x component of the separation between particles i and j, r_{ij}.

$$\eta = -P_{xy}/\gamma \qquad (16)$$

Let η_s be the viscosity of the pure suspending medium. The relative viscosity, η_r is defined as

$$\eta_r = 1 + \eta/\eta_s \qquad (17)$$

The osmotic pressure, P, of the system is

$$P = (1/6V)\sum_{i}^{N-1}\sum_{j\neq i}^{N} r_{ij}(d\phi(r)/dr) \qquad (18)$$

The normal pressure components, P_{xx}, P_{yy}, and P_{zz} were evaluated as

$$P_{xx} = (1/V)\sum_{i=1}^{N-1}\sum_{j\neq i}^{N} r_{xij}r_{xij}(d\phi/dr)/(2r_{ij}) \qquad (19)$$

with obvious changes for the y and z components.

We have recently demonstrated that a shear rate, $\partial v_X/\partial Y$, induces new time-asymmetric cross correlation functions of velocity in the laboratory frame XYZ, which break the Onsager–Casimir symmetry,[17,36] i.e.

$$\langle v_X(0)\, v_Y(t)\rangle \neq \langle v_X(t)\, v_Y(0)\rangle \qquad (20)$$

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.

The result of eq 20 is given by the third principle of GTSM,[37] which states that an applied external field of given symmetry may induce new thermodynamic averages in an ensemble at field-applied steady state. These averages take the symmetry of the field itself. The D symmetry of the strain rate was shown to be

$$\Gamma(v)\Gamma(r)^{-1} = D_u^{(1)}D_u^{(1)} = D_g^{(0)} + D_g^{(1)} + D_g^{(2)} \qquad (21)$$

(36) Evans, M. W.; Evans, G. J.; Coffey, W. T.; Grigolini, P. *Molecular Dynamics*; Wiley/Interscience: New York, 1982.

(37) Evans, M. W. *Phys. Lett. A* **1989**, *134*, 409; *Phys. Lett. A* **1990**, *146*, 185, 485.
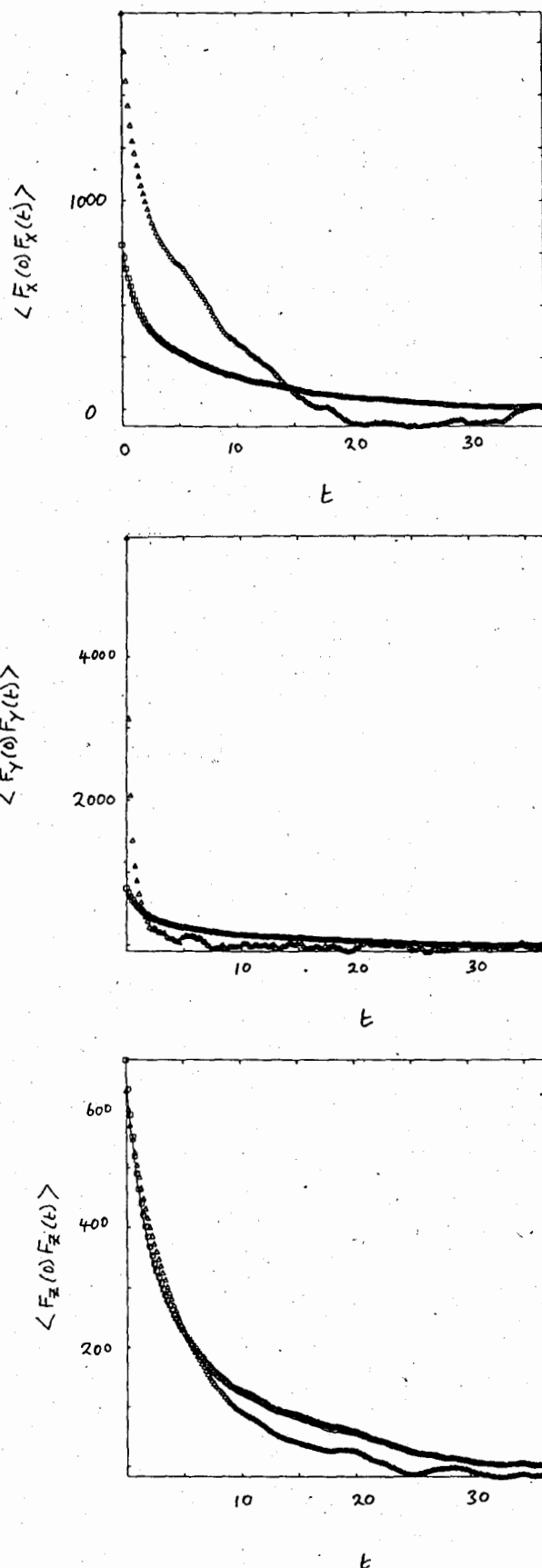
Figure 2. Force–time autocorrelation functions (a, top) $\langle F_X(0)\, F_X(t)\rangle$, (b, center) $\langle F_Y(0)\, F_Y(t)\rangle$, and (c, bottom) $\langle F_Z(0)\, F_Z(t)\rangle$ in reduced units for the (□) field-free case and (△) applied field case, $\mu_Y = 4$, for the simulation. Parameters: $\rho^* = 1.0$; $T^* = 1.0$; $P_e = 10$; equivalent hard-sphere volume fraction = 0.472; $\eta_s = 0.001$ P; $T = 298$ K; mass of Brownian particle = 0.636×10^{-9} kg; $\sigma = 1$ μm; momentum relaxation time $\tau_p = 0.167 \times 10^{-6}$ s; $\tau_r = 0.57$ s; $h = 0.11 \times 10^{-3}$ s.
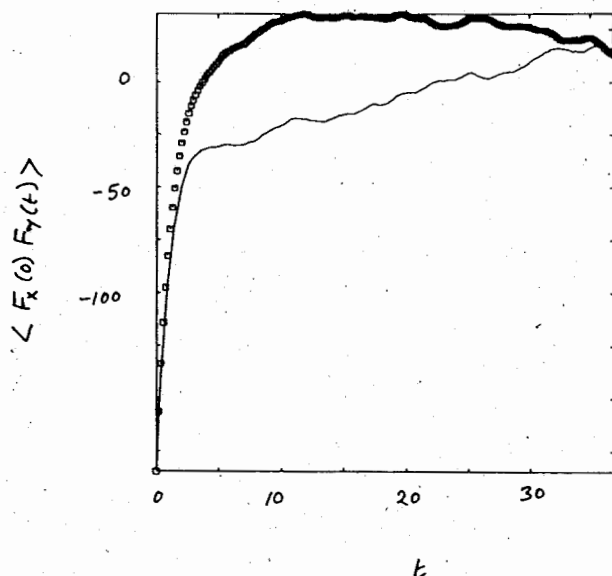
Figure 3. Force cross correlation function for the same system as in Figure 2 but without an electric field, i.e. $\mu_Y = 0$: (—) $\langle F_X(0) \, F_Y(t) \rangle$; (□) $\langle F_Y(0) \, F_X(t) \rangle$. This shows statistically significant time asymmetry.

The term, $D_g^{(0)}$, represents the trace or the diagonal sum of the cross correlation tensor, for example for velocity, $\mathbf{v}$

$$C_v(t) = \langle \mathbf{v}(0) \, \mathbf{v}^T(t) \rangle \qquad (22)$$

which has the same D symmetry as the strain rate tensor. When the latter has planar couette shear symmetry, the induced ccf of eq 22 is traceless. The vector and tensor parts of the symmetry signature represent, by principle 3, the time-antisymmetric and time-symmetric cross correlation functions (eq 1)

$$D_g^{(1)} \quad \langle v_X(0) \, v_Y(t) \rangle = -\langle v_Y(0) \, v_X(t) \rangle \qquad (23)$$

$$D_g^{(2)} \quad \langle v_X(0) \, v_Y(t) \rangle = \langle v_Y(0) \, v_X(t) \rangle \qquad (24)$$

respectively. Although they separately obey Onsager–Casimir symmetry, a $\partial v_X / \partial Y$ field in general produces a weighted sum of (23) and (24) to give the asymmetric result (1). This was noted in the previous study in this series.[17]

If the shear strain rate is $\dot{\gamma} = \partial v_X / \partial Y$, the new cross correlations are of the type $\langle v_X(t) \, v_Y(0) \rangle$, $\langle P_{\alpha X}(t) \, P_{\alpha Y}(0) \rangle$, and $\langle P_{\alpha\alpha}(t) \, P_{XY}(0) \rangle$, where $\mathbf{v}$ is the atomic velocity in the XYZ frame and $P_{\alpha\beta}$ is the $\alpha\beta$ component of the pressure tensor. That is, $\langle P_{XZ}(0) \, P_{YZ}(t) \rangle$, $\langle P_{XY}(0) \, P_{XX}(t) \rangle$, $\langle P_{XY}(0) \, P_{YY}(t) \rangle$, $P_{XY}(0) \, P_{ZZ}(t) \rangle$, $\langle P_{XX}(0) \, P_{XX}(t) \rangle$, $\langle P_{YY}(0) \, P_{YY}(t) \rangle$, and $\langle P_{ZZ}(0) \, P_{ZZ}(t) \rangle$. This includes also these ccf's with time arguments reversed, which as noted can be different functions at nonequilibrium. We calculated these by the BD method. In Figure 2, we show the cartesian component force correlation functions, $\langle F_X(0) \, F_X(t) \rangle$, $\langle F_Y(0) \, F_Y(t) \rangle$, and $\langle F_Z(0) \, F_Z(t) \rangle$ for the sheared suspensions with and without an electric field (manifest in μ_Y). These forces here are solely between the model colloidal particles. We note that in the presence of the electric field the fluctuations in force increase in the shearing plane, in *both* the X and Y directions. There is virtually no effect in the Z direction. For the system considered, $P_e = 10$, $\rho = 1.1$, $T = 1.0$, $N = 108$, and dipole moment $\mu_Y = 0$ (4), we find that $\eta_r =$
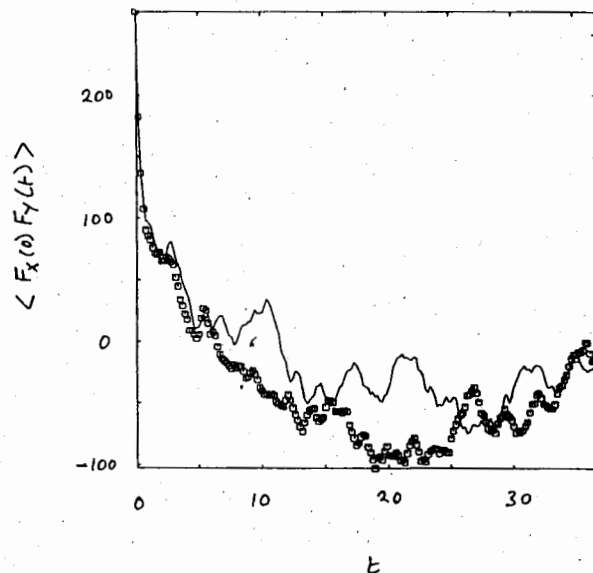

Figure 4. Same as for Figure 3, except that $\mu_Y = 4$. Note the change in sign of the functions from those in Figure 3.

1.74 (1.22), $P_{XX} - P_{YY} = 0.24$ (−38.46), $P_{YY} - P_{ZZ} = 1.33$ (44.22), $P = 25.95$ (34.71).

We observe that with shear but with $E_Y = 0$, $\mu_Y = 0$, the ccf $\langle F_X(0) \, F_Y(t) \rangle$ is statistically different from zero and $\langle F_Y(0) \, F_X(t) \rangle$ as predicted by GTSM above; see Figure 3. The $\langle F_X(0) \, F_Y(0) \rangle$ changes from being ≤ 0 to ≥ 0 on application of the electric field, a startling new phenomenon that captures a feature of dynamical relaxation in combined shear flow and applied electric field. This is evident in Figure 4.

This work has resemblence to parallel studies in the liquid crystal rheology and hydrodynamic theories of dielectric and magnetic colloidal dispersions, examples of which may be found in refs 38–40.

To summarize, we have successfully simulated the structural changes associated with the ER effect. We have characterized the molecular level dynamics of ER suspended particles, revealing that certain cross correlation functions are particularly sensitive to the precise values of electric field and shear rate.

(38) de Gennes, P. G. *The Physics of Liquid Crystals*; Clarendon: Oxford, UK, 1974; Chapter 5.

(39) Rosensweig, R. *Ferrohydrodynamics*; Cambridge University Press: New York, 1985.

(40) Hubbard, J. B.; Stiles, P. J. *J. Chem. Phys.* **1986**, *84*, 6955.