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The Group Theory of Shear Induced Pair Radial Distribution Functions in Atomic Liquids

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Abstract

Angular resolution of the pair radial distribution function in computer simulations of shear induced thickenening in atomic (Lennard–Jones) liquids has revealed the presence of anisotropic local structure which is explained on the basis of group theoretical statistical mechanics. This explains the observed structural asymmetry from the basic assumption that the symmetry of allowed ensemble averages in the steady state in the presence of shear is the same as that of the applied strain rate. The computer simulation results are reproduced from group theory by assuming that the crystal like lattice arrangement of atoms which appear in the simulations under shear can be described by some of the thirty two crystallographic point groups, namely hexagonal, trigonal, and triclinic. The hexagonal lattice symmetries C_{3h} and C_{6h}; the trigonal symmetry S_6; and the triclinic symmetry $C_i(S_2)$ are found to support the crystal-like structures necessary to explain the observed angular resolution of the pair radial distribution function.

Introduction

The non-equilibrium molecular dynamics computer simulations of Heyes and co-workers [1–5] have revealed a number of significant new phenomena of non-Newtonian rheology in atomic liquids using a battery of new numerical techniques. Among the most interesting of these is in the context of shear thinning and thickening. Simulations have shown [3] that as the shear rate is increased the atoms of the liquid ensemble form structurally arrested states with crystal-like symmetries. The point group of the ensemble is therefore changed from the well-known [6–8] rotation–reflection group $R_h(3)$ of three dimensional isotropic space to that of the shear induced lattice. In this communication we use the recently developed axioms [9–12] of group theoretical statistical mechanics (g.t.s.m.) to explain the observed [3] symmetry of angularly resolved pair radial distribution functions (r.d.f.'s) in non-equilibrium simulations of Lennard–Jones ensembles. It is shown that only a small number of lattice symmetries [13] support the observed anisotropy under shear, and explains why shear is able to produce this anisotropy.

Part 1 states the three principles of g.t.s.m.; part 2 states the problem to which these axioms are applied; and part 3 discusses the results obtained from this application of g.t.s.m. to shear induced structurally arrested states in atomic liquids.

1. The principles of group theoretical statistical mechanics

A long series of conventional [14–20] and non-equilibrium [1–5] computer simulations has led to the recent emergence of three principles of the application of point group theory to statistical mechanics. This has become known as group theoretical statistical mechanics (g.t.s.m.). The first of these is Neumann's Principle [21], also known as Curie's Principle [22, 23]. The second has emerged from the application of point group theory in the molecule fixed frame (x, y, z) by Whiffen [24] to some of the present author's computer simulation results. Frame (x, y, z) is as conventionally defined in the character table [6–8, 13], and the third principle deals with the effect of external fields, again in response to the copious evidence of computer simulation.

1.1. *Principle 1*

The thermodynamic ensemble average $\langle \boldsymbol{ABC}\ldots \rangle$ over the product $\boldsymbol{ABC}\ldots$ exists in the laboratory frame (X, Y, Z) if the product of symmetry representations $\Gamma(\boldsymbol{A})\Gamma(\boldsymbol{B})\Gamma(\boldsymbol{C})\ldots$ contains the totally symmetric representation (t.s.r.) of the three dimensional rotation-reflection point group $R_h(3)$.

1.2. *Principle 2*

This ensemble average exists in the molecule fixed frame (x, y, z) if the product of symmetry representations in this frame contains at least once the totally symmetric representation (t.s.r.) of the molecular point group.

1.3. *Principle 3*

The ensemble average in frame (X, Y, Z) is changed by the application of an external field of force in such a way that the symmetry of new steady state ensemble averages is that of the applied field itself.

Principle (1) shows, for example, that some time cross correlation functions (c.c.f.'s) exist at thermodynamic equilibrium, and exposes the limits of conventional diffusion theory, where all time c.c.f.'s are customarily ignored or assumed simply to vanish for all t. The members of the set of non-vanishing c.c.f.'s in frame (X, Y, Z) are selected by Principle (1) for all molecular symmetries. Powerful evidence for the role of c.c.f.'s in non-Newtonian rheology has emerged from the recent simulations of Evans and Heyes [25–27].

Principle (2) rests on numerous careful computer simulations in the past few years. It means essentially that the set of non-vanishing c.c.f.'s in frame (x, y, z) may contain members that simultaneously vanish in (X, Y, Z). Both frames are needed for an elementary appreciation of molecular diffusion process. Principle (2) has successfully explained the data [24] from computer simulations, and in combination with principle (1) has pushed understanding of diffusion processes in molecular matter well beyond the conventional boundaries

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[28–32], which are defined almost always by the assumption that there exist no time c.c.f.'s of any kind, in either frame.

Principle (3) is a statement of how externally applied force fields of given symmetry set up extra ensemble averages at field-applied equilibrium. It is also valid in transient, non-equilibrium regimes. In both cases the overall symmetry of the new ensemble averages is that of the applied field. The following examples illustrate Principle (3) at work.

(1) It has been shown by conventional computer simulation that a static electric field applied [17–19] to a liquid of dipolar molecules in axis Z of frame (X, Y, Z) produces the result

$$\langle v_X(t)\omega_Y(0)\rangle = -\langle v_Y(t)\omega_X(0)\rangle \tag{1}$$

where $\boldsymbol{v}$ is the linear centre of mass velocity of a diffusing molecule and $\boldsymbol{\omega}$ its own angular velocity. The c.c.f.'s (1) vanish in frame (X, Y, Z) at field-off equilibrium but appear in response to the static field. This cannot be explained by the conventional theory of diffusion [28–30] or dielectric relaxation [31, 32]. However, it is a sample consequence of Principle (3) in that the irreducible representation in $\mathrm{R_h}(3)$ of the static electric field $\boldsymbol{E}$ is $\mathrm{D_u^{(1)}}$, that of a polar vector. The D symmetry of the complete nine-element tensor $\langle \boldsymbol{v}(t)\boldsymbol{\omega}(0)\rangle$ is

$$\Gamma(\boldsymbol{v})\Gamma(\boldsymbol{\omega}) = \mathrm{D_u^{(1)}D_g^{(1)}} = \mathrm{D_u^{(0)}} + \mathrm{D_u^{(1)}} + \mathrm{D_u^{(2)}} \tag{2}$$

the product of a polar and axial vector. The vector part, i.e., $\langle \boldsymbol{v}(t) \times \boldsymbol{\omega}(0)\rangle$, gives eq. (1), with $\mathrm{D_u^{(1)}}$ symmetry. The electric field has made possible the existence of the thermodynamic ensemble average (1) with the same symmetry as the field itself. Evans and Heyes [25–27] have shown recently that the D symmetry of the strain rate tensor of the shear is $\mathrm{D_g^{(0)}} + \mathrm{D_g^{(1)}} + \mathrm{D_g^{(2)}}$, which by Principle (3) sets up new ensemble averages, such as pair distribution functions or time correlation functions in frame (X, Y, Z) at the field on steady state. They found that this D symmetry is the same as that of the generic time a.c.f. $\langle A(t)A(0)\rangle$, with A representing atomic velocity for example. They then used state of the art non-equilibrium computer simulation to show the presence of new time c.c.f.'s with the overall symmetry of the strain rate. Principle (3) produces similar entirely novel results [25–27] for the time c.c.f.'s of pressure tensor components, revealing the fundamental origin of the Weissenberg effect of macroscopic non-Newtonian rheology [33], and explaining through c.c.f.'s the pressure set up in a sheared liquid in a direction perpendicular to the plane of shear. Further work by Evans and Heyes [27], using independent state of the art algorithms, showed that the new c.c.f.'s are also sensitive to the typical [34–38] macroscopic phenomena of non-Newtonian rheology, including the appearance of shear induced thickening and thinning, the appearance of string phases, and structurally arrested states. These all involve time c.c.f.'s in frame (X, Y, Z) for an atomic liquid, and also in frame (x, y, z) for a molecular liquid. Conventional methods of macroscopic rheology have failed to recognise this, in the same way that conventional diffusion theory has failed to recognise the role of c.c.f.'s at equilibrium. In both cases they are governed by Principle (3).

2. Crystal-Like arrested states at high shear rates, an excess of symmetry

Principle (3) may be applied to angularly resolved pair distribution functions, defined by

$$f_{\alpha\beta}(r) = \left(\sum_{i\neq j}^{N}\sum^{N}\langle R_{\alpha ij}R_{\beta ij}/R_{ij}^2\rangle\right)\Big/N \tag{3}$$

$$g_{\alpha\beta}(r) = 15Vf_{\alpha\beta}(r)/(V(r)N) \tag{4}$$

Here $R_{\alpha ij} = R_{\alpha i} - R_{\alpha j}$, where $R_{\alpha i}$ is the α cartesian component of the position of molecule i.

The angular component $f_{\alpha\beta}$ measures the anisotropic dispositions of molecules or atoms, and involves the ensemble average $\langle R_{\alpha ij}R_{\beta ij}\rangle$. Peaks in $g_{\alpha\beta}$ supply information on shear induced structurally arrested states. In eq. (4), V is the volume of the shell bounded by $r \pm \delta r/2$

$$V(r) = 4\pi r^2\delta r \tag{5}$$

For a shear resulting in a strain rate response of type $\partial v_X/\partial Z$. Principle (3) predicts the existence of the ensemble average $\langle R_{Xij}R_{Zij}\rangle$, but no other off-diagonal elements such as $\langle R_{Xij}R_{Yij}\rangle$ or $\langle R_{Yij}R_{Zij}\rangle$. This is simulated by Heyes [3] and is in satisfactory agreement with numerically derived data for low shear rates, but as the latter increase, off-diagonal elements of the angularly resolved pair r.d.f. appear [3] which are disallowed by Principle (3) in $\mathrm{R_h}(3)$. Heyes has explained this in terms of slow structural relaxation, outside the time window of the simulation. The applied shear has clearly led to lower symmetry in frame (X, Y, Z), a crystal-like environment has been generated from a shear induced phase change, taking the ensemble from $\mathrm{R_h}(3)$ to some other crystal-like point group of lower symmetry. The problem of how to apply group theoretical methods within this new group to explain the results actually observed by Heyes (Figs. (7) and (8) of Ref. [3]).

3. Application of G.t.s.m.

The $g_{\alpha\alpha}(r)$ in Figs. (7) and (8) of Ref. [3] emphasise pair correlations in the α direction and give relative nearest neighbour distances in the X, Y, and Z directions. Figure (7) shows a strain rate in reduced units of $\dot\gamma = 30$ and shows that the first peak in $g_{XX}(r)$ is 0.1σ further out than that of $g_{YY}(r)$ and $g_{ZZ}(r)$, where σ is a Lennard-Jones parameter. This trend becomes more pronounced at $\dot\gamma = 110$ where the separation is 0.15σ. Being a spherical average, however, $g(r)$ tends to obscure the strong anisotropic structural changes due to shearing.

As the shear rate is increased the system of molecules cannot adapt sufficiently rapidly to the shear distortions and the atoms overlap appreciably to form structurally arrested states. The stress grows and the diagonal elements of the pressure tensor take on metastable negative values. The asymmetric expansion coefficients $g_{\alpha\beta}(r)$ under this condition are shown in Fig. (8) of Ref. [3]. At a shear rate of 5 only the g_{XZ} component is statistically different from zero. However, Fig. (8) shows the appearance of statistically significant $g_{XY}(r)$ and $g_{YZ}(r)$ of GREATER magnitude than $g_{XZ}(r)$ at $\dot\gamma = 110$. This reflects slow structural relaxation times of the order of the simulation time. The ensemble in this state behaves like a solid in directions orthogonal to the streaming direction, but the atoms move within these "strings" fairly freely and the force autocorrelation function is more damped in the X than the Y and Z directions.

In order to explain Fig. (8) of Ref. [3] it is necessary to assume that the overall point group of at least some part of the ensemble is no longer $R_h(3)$ of the isotropic liquid, distorted by shear, but is that of a shear-induced crystal-like structure. From the "snap-shots" of the simulation provided by Heyes [3] this appears to be hexagonal, trigonal, or triclinic, an overall triangular lattice which produces

$$f_{XX} \neq f_{YY} \neq f_{ZZ} \neq f_{XZ} \neq f_{XY} \neq f_{YZ} \neq 0 \tag{5}$$

To find the symmetry of the applied shear within each of these crystal-like point groups it is necessary to map $D_g^{(0)} + D_g^{(1)} + D_g^{(2)}$ on to the appropriate irreducible representation within that crystal-like point group. These representations for thirty five point groups of interest, including the crystalline point groups, are shown in tabular form. The following are examples of this procedure for shear induced crystal-like point groups.

3.1. *Hexagonal* C_{3h} *(Hermann Mauguin* $\bar{6}$*)*

In this crystal point group, one of the hexagonal crystal symmetries, the symmetry of shear is

$$D_g^{(0)} + D_g^{(1)} + D_g^{(2)} = A^{II}A^{II} + E^{I}A^{II} + A^{II}E^{I} + E^{I}E^{I} \tag{6}$$

which allows ensemble averages of the type

$$\langle R_{Xij}R_{Xij}\rangle \neq \langle R_{Yij}R_{Yij}\rangle \neq \langle R_{Zij}R_{Zij}\rangle; \tag{7a}$$

$$\langle R_{Xij}R_{Yij}\rangle \neq \langle R_{Xij}R_{Zij}\rangle \neq \langle R_{Yij}R_{Zij}\rangle \tag{7b}$$

using Principle (3) within the C_{3h} point group rather than the $R_h(3)$ point group. Equation (7) predicts angularly resolved pair distribution functions with the property (5). Thus both the digonal and off-diagonal elements have a different r dependence if the structurally arrested state has the crystal symmetry C_{3h} or $\bar{6}$. Comparison of this result with available computer simulations by Heyes can be made by examining the numerical data in Figs. (7) and (8) of Ref. [3]. These show that at strain rates $\dot{\gamma} = 110$ and $\dot{\gamma} = 30$ in normalised units the diagonal elements g_{YY} and g_{ZZ} are almost equal but discernably different, the third, g_{XX}, being distinctly different from the other two. In Fig. (8) of Ref. [3] the amplitudes of the off-diagonal elements g_{XY} and g_{YZ} are greater than the third element g_{XZ}, all three being distinctly different.

Our calculations, based on Principle (3) applied to the various point groups show that the hexagonal point group $C_{6h}(6/m)$ also gives this result, along with the trigonal S_6 and the triclinic S_2. Other hexagonal or in general triangular type lattices are either disqualified on the basis of being chiral, or produce degeneracies, in the sense that one or more angularly resolved pair r.d.f. elements are equal.

4. Discussion

Shear thickening is accompanied by the appearance of structurally arrested states in which the crystal-like symmetry supports six different angularly resolved radial pair distribution functions. These are rationalised with group theoretical statistical mechanics.

More generally, the methods developed in this paper, based on the three principles of group theoretical statistical mechanics, can be applied to structural and dynamical properties of atomic and molecular ensembles both in the laboratory frame (X, Y, Z) and in the molecule fixed frame (x, y, z). The methods can deal with angularly removed pair, triplet, quadruplet and N order distribution functions for atom atom interactions, for example, in molecular liquids such as water. The presence of structurally arrested states is indicated by the presence of a component which is not allowed by the three principles of g.t.s.m. applied to angularly resolved functions in the presence of shear. For example, in simple atomic ensembles the angularly resolved quadruplet radial distribution function has a maximum of 729 scalar components, but g.t.s.m. shows that only fifteen of these can have an independent existence at equilibrium. These break down further into different symmetries, providing a wealth of information on the equilibrium structure. When shear is applied, a further 36 independent components of $D_g^{(1)}$ symmetry and 40 components of $D_g^{(2)}$ symmetry become visible when the ensemble has not become structurally arrested. In the latter condition, the overall point group changes as described in the text, providing a rich variety of extra information.

The same methods can be applied to dynamical ensemble averages, and in molecular ensembles we have available two frames of reference, (x, y, z) and (X, Y, Z). Averages in the former are governed by principle two and in the latter by principle three.

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References

1. Heyes, D. M., Comp. Phys. Rep. **8** 71 (1988).
2. Hammonds, K. D. and Heyes, D. M., J. Chem. Soc., Faraday Trans. **2**, 84 705 (1988).
3. Heyes, D. M., *ibid.*, **82**, 1365 (1986).
4. Heyes, D. M. and Szczepanski, R., *ibid.* **83**, 319 (1987).
5. Heyes, D. M., Physica, **146A**, 341 (1987).
6. Urch, D. S., "Orbitals and Symmetry", Penguin, Harmondsworth (1970).
7. Flurry, R. L. Jr., "Symmetry Groups, Theory and Applications", Prentice Hall, Englewood Cliffs (1980).
8. Salthouse, J. A. and Ware, M. J., "Point Group Character Tables", Cambridge University Press, London (1972).
9. Evans, M. W., Chem. Phys. Letters **152**, 33 (1988).
10. Evans, M. W., Chem. Phys. **127**, 413 (1988).
11. Evans, M. W., Phys. Lett. A, **134**, 409 (1989).
12. Evans, M. W., Lie, G. C. and Clementi, E., *ibid.*, **130**, 289 (1988).
13. Phillips, F. C., "An Introduction to Crystallography", Longmans, London (1963).
14. Ryckaert, J. P., Bellemans, A. and Ciccotti, G., Mol. Phys. **44**, 979 (1981).
15. Evans, M. W. and Evans, G. J., in "Advances in Chemical Physics" (Edited by M. W. Evans, I. Prigogine, and S. A. Rice), Vol. 63, Wiley Interscience, New York (1985).
16. Coffey, W. T., Corcoran, P. and Evans, M. W., Proc. Roy. Soc. A, **410** 61 (1987).
17. Evans, M. W., Physica B&C, **131**, 273 (1985).
18. Evans, M. W., Lie, G. C. and Clementi, E., J. Chem. Phys. **88**, 5157 (1988).
19. Evans, M. W., Lie, G. C. and Clementi, E., Phys. Rev. A, **37**, 2551 (1988).
20. Evans, M. W. and Heyes, D. M., Phys. Scripta, **41**, 304 (1990).
21. Neumann, F. E., "Vorlesungen Uber Die Theorie Elastizitat Der Festen Korper Und Des Lichtathers." Teubner, Leipzig (1885).
22. Curie, P., J. Phys. (Paris), **3** 393 (1894).
23. Barron, L. D., Chem. Soc. Rev. **15**, 189 (1986).

24. Whiffen, D. H., Mol. Phys. **63**, 1053 (1988).
25. Evans, M. W. and Heyes, D. M., *ibid.*, **65**, 1441 (1988).
26. Evans, M. W. and Heyes, D. M., J. Chem. Soc., Faraday Trans., in press.
27. Evans, M. W. and Heyes, D. M., Mol. Phys. **69**, 241 (1990.
28. Wax, N. (ed.) "Collected Papers on Noise and Stochastic Processes". (Dover, New York (1954).
29. Scaife, B. K. P. (ed.) "Complex Permittivity". English Univ. Press, London (1971).
30. Buckingham, A. D. (ed.) "Organic Liquids, Structure, Dynamics and Chemical Properties", Wiley, New York (1979).
31. Williams, G., in "Dielectric and Related Molecular Processes", Vol. p. 151, Senior Reporter Mansel Davies, Chem. Soc., London (197
32. Brot, C., *ibid.*, p. 1.
33. Harris, J., "Rheology of non-Newtonian Flow", Longmans, Lond (1977).
34. Evans, D. J. and Morriss, G. P., Comp. Phys. Rep. **1** 297 (1984).
35. Morriss, G. P. and Evans, D. J., Phys. Rev. A, **35**, 792 (1987).
36. Evans, D. J. and Morriss, G. P., Phys. Rev. Lett. **56**, 2172 (1986).
37. Heyes, D. M., Kim, J. J., Montrose, C. J. and Litovitz, T. A., Chem. Phys. **73**, 3987 (1980).
38. Heyes, D. M., Montrose, C. J. and Litovitz, T. A., J. Chem. Sc Faraday Trans. **2**, 79 611 (1983).