Journal of Molecular Liquids, 40 (1989) 297–304
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

On the Material Frame Indifference Controversy: Some Results from Group Theory and Computer Simulation.

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(Received 2 February 1989)

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Abstract

Group theory and computer simulation are used to show that molecular and atomic scale time cross correlation functions have different symmetry properties in different frames of reference. Constitutive equations, written in any frame of reference, are approximations to classical molecular dynamics, and must therefore reproduce the results from group theory applied to ensemble averages such as time correlation functions, and corroborated by computer simulation. This may help to resolve some of the contemporary literature claims regarding material frame indifference and the implementation of "co- rotating" frames.

0167-7322/89/$03.50

Introduction

Recently, there have appeared at least two sets of literature controversies concerning the use of material frame indifference and co-rotating frames in constitutive equations. Eu[1] claims that constitutive equations for flow properties in molecular liquids as derived from kinetic equations are consistent with their counterparts in continuum mechanics only when the former are written in a co-rotating frame of reference. This has been criticised by Lodge et al.[2] who argue that the constitutive equations derived from kinetic equations can, under certain conditions, satisfy the objectivity principle. Eu[3] replied with the claim that the constitutive equations derived from the Boltzmann equation in a fixed frame of reference is not invariant to frame rotation and is therefore not objective. The term that makes the equation "unobjective" comes from the streaming term in the Boltzmann equation, and appears with a wrong sign. The constitutive equation is therefore qualitatively incorrect. Eu[1,3] claims that the cause of the trouble is the use of a fixed frame of reference, the original Boltzmann equation is accepted uncritically. The constitutive equation in Eu's co-rotating frame appears[3] to be thermodynamically and dynamically valid.

A related controversy has appeared between Ryskin[4,5] and Speziale[6] concerning material frame indifference. In this context, Ryskin[5] claims that there is no logical connection between frame indifference and the independence of motion of an observer, two fundamental principles of rheology. He claims that the school of rational mathematics has created confusion by using the latter principle in justification of the former. He further rejects the claim by Speziale[6] that invariance of constitutive equations under arbitrary translational acceleration of the reference frame is an exact consequecnce of the statistical description. Both authors appear to agree, however, that constitutive equations can only be special solutions of kinetic theory. They may satisfy the principle of material frame indifference even though kinetic theory itself contradicts it.

These argumants and controversies appear to be the result of attempts to create equations of motion for the problem of moving molecules in a medium such as a liquid where interactions between molecules create complicated individual trajectories. Clarification may be achieved by application of the newly developed principles of group theoretical statistical mechanics (g.t.s.m.)[7-12] and the numerical technique of computer simulation[13-20] to molecular dynamics in two frames of reference, one fixed in the laboratory and the other in the diffusing molecule. These are labelled (X, Y, Z) and (x, y, z) respectively, the latter being the standard reference frame of the point group character tables[21-23]. Using these two frames, one of which is rotated with respect to the other, it is argued by g.t.s.m. that thermodynamic ensemble averages may exist in one frame which disappear in the other, for example the time correlation function. Corroborative evidence for the symmetry arguments is provided with computer simulations of water and methyl chloride liquids. Further considerations of symmetry reveal the existence in frame (X, Y, Z) of atomic velocity cross correlation functions which appear not to have been considered by any form of constitutive equation. In an atomic liquid subjected to one dimensional couette flow, cross correlation functions (c.c.f.'s) of the type $< v_Z(t)\, v_X(0) >$ where v is the atomic velocity, have been generated recently by computer simulation[9,24], and are essentially fundamental atomic dynamical representations of what is known in rheology as the velocity generated by shear. Obviously there is no frame (x, y, z) in an atomic liquid, but if the method of Eu[1] is followed and a co-rottaing frame constructed such that its angular velocity is that of the vortex, then the observed time c.c.f. $< v_Z(t) v_X(0) >$ in the fixed frame (X, Y, Z) will vanish in the co-rottaing frame, and Eu's equations would not be able to account for this sheer induced c.c.f. in couette flow. This illustrates the need for caution in any rheological treatment of liquid dynamics. Neither Eu nor his critics are correct at the atomic and molecular level.

Section 1 of this paper deals with the fundamental symmetry arguments of g.t.s.m., and shows how thermodynamic ensemble averages may exist in one frame and vanish in another, according to frame definition, and applies the symmetry arguments of g.t.s.m. to time c.c.f.'s between the linear and angular velocities of a diffusing molecule. The symmetry arguments are applied at a fundamental molecular level, thus by-passing the need for approximation[25]. Section 2 applies the symmetry arguments to couette flow in atomic liquids, revealing the presence of new c.c.f.'s between orthogonal velocity components, and proving the inadequacy of standard constitutive equations in frame (X, Y, Z) and also in the co-rottaing frames of conventional rheology.

Section 1. Group Theory Applied to Molecular Dynamics

Group theory can be applied both in frame (X, Y, Z) and (x, y, z) and shows that thermodynamic averages are different in either frame. In frame (X, Y, Z) the relevant point group is the rotation-reflection group $R_h(3)$ whose irreducible representations are

$$D_g^{(0)},\ D_g^{(1)},\ \ldots,\ D_g^{(n)};\qquad D_u^{(0)},\ D_u^{(1)},\ \ldots,\ D_u^{(n)}$$

where the subscript g denotes even to parity reversal, and u odd. The superscripts denote the order of the spherical harmonics. Neumann's Principle[26] states that the thermodynamic ensemble average $<A>$ exists if A contains the totally symmetric representation, $D_g(0)$. An average over a product, such as a time correlation function, $<A(0)B(t)>$ exists if the product of the irreducible representations of A and B contains the totally symmetric representation at least once. Thus elements of the time correlation function $<v(t)v^T(0)>$ exists in frame (X, Y, Z) because the product of representations is

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

where the Clebsch-Gordan Theorem[21] has been used. The totally symmetric representation is the trace, the time auto correlation function $<v(t)\ .\ v\ (0)>$. If however we consider the time c.c.f. $<v(0)\ \omega^T(t)>$ with the same molecule's angular velocity, the product of representations is:

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

which does not contain the totally symmetric representation (t.s.r.). This c.c.f. vanishes in frame (X, Y, Z) in an isotropic liquid.

However, in frame (x, y, z) Neumann's Principle applies in the point group of the molecule. A thermodynamic ensemble average exists in this frame if it contains the t.s.r. of the point group. In the C_{2v} group for example this is A_1. The velocity maps from $D_u^{(1)}$ of frame (X, Y, Z) to $A_1 + B_1 + B_2$ of frame (x, y, z) and the molecular angular velocity from $D_g^{(1)}$ to $A_2 + B_1 + B_2$. The product of these irreducible representations in (x, y, z) is

$$\Gamma(v)\Gamma(\omega) = (A_1 + B_1 + B_2)(A_2 + B_1 + B_2) = 2A_1 + 3A_2 + 2B_1 + 2B_2 \tag{3}$$

showing two occurrences of the t.s.r. A_1. Thus two independent elemnts of the time c.c.f. between linear and angular velocity exist in frame (x, y, z), while all elements vanish in frame (X, Y, Z). On the molecular scale,

therefore, material frame indifference is not relevant. Similarly, in the C_{3v} point group of the methyl chloride molecule, for example, the product of representations is

$$\Gamma(v)\Gamma(\omega) = (A_1 + E)(A_2 + E) = A_1 - 2A_2 + 3E \tag{4}$$

showing one occurrence of the point group's t.s.r., A_1. The non vanishing elements are illustrated in this paper with computer simulation, and are

$$C_{2v}: < v_x(t)\omega_y(0) > \neq < v_y(t)\omega_x(0) > \tag{5}$$

$$C_{3v}: < v_x(t)\omega_y(0) > = - < v_y(t)\omega_x(0) > \tag{6}$$

Again for the C_{3v} point group the (X, Y, Z) frame elements vanish for all t. Statistical time correlation is different in the two frames for all point group symmetries. No constitutive equations have been derived that account for this general result. In conventional rheology, controversies are generated by the fact that the dynamical problem is not addressed at the fundamental molecular level. Reliance is put instead on intermediary equations which usually[1-4] make no reference to molecular structure. It appears that the available constitutive equations are assumed to hold for any molecular point group symmetry, and this cannot be correct. In g.s.m., briefly applied in this paper, this assumption is eliminated. In rheology, whatever the finer details of the argument, empiricism remains. Spencer[5] for example mentions the role of the Coriolis acceleration, which is supposed to vanish in the classical continuum limit. This is contested by Ryskin[6], with a proposed counter-example. At the more fundamental molecular level, Evans[7-9] has addressed the problem in detail using computer simulation, showing that the frame transformation (X, Y, Z) → (x, y, z) generates time c.e.f.'s involving the Coriolis, Eulerian, and centripetal molecular accelerations

$$(\dot{\mathbf{r}})_{(X,Y,Z)} \rightarrow (\dot{\mathbf{r}} + 2\boldsymbol{\omega} \times \mathbf{r} + \dot{\boldsymbol{\omega}} \times \mathbf{r} - \boldsymbol{\omega} \times (\boldsymbol{\omega} \times \mathbf{r}))_{(x,y,z)} \tag{7}$$

and so does the reverse transformation

$$(\dot{\mathbf{r}})_{(x,y,z)} \rightarrow (\dot{\mathbf{r}} - 2\boldsymbol{\omega} \times \mathbf{r} - \dot{\boldsymbol{\omega}} \times \mathbf{r} + \boldsymbol{\omega} \times (\boldsymbol{\omega} \times \mathbf{r}))_{(X,Y,Z)} \tag{8}$$

so that the simple translational Langevin equation, for example, becomes a much more complicated one in frame (x, y, z). Diffusion theory at the molecular level must be able to show why time c.e.f.'s may exist in frame (x, y, z) and not in frame (X, Y, Z) for the same ensemble. At present it is not capable of doing so and thus, constitutive equations are automatically deficient, being unable to account for molecular symmetry. This is the case both for the fixed frame arguments of Lodge et al. and the moving frame used by Eu.

Strain Rate Symmetry in Atomic Liquids

Recent work[9] on the symmetry of strain rate tensors applied in simple couette flow showed this to be represented by the sum of irreducible representations

$$D_E^{(2)} = D_E^{(1)} + D_E^{(2)}$$

This was shown to imply the existence of off-diagonal elements of the velocity correlation function. For a strain rate of the type $\partial v_X/\partial Z$ the time asymmetric c.c.f.

$$< v_X(t)v_Z(0) > \neq < v_X(0)v_Z(t) > \tag{9}$$

was obtained, being the sum of a time symmetric deformation component and a time antisymmetric vorticity component. These components and resulting time asymmetric c.c.f. appear in the laboratory frame (X, Y, Z). However, the vorticity in the rheological co-rotating frame vanishes if this is chosen so that its rotation coincides with the local angular velocity of the vortex!. The viewpoint of continuum fluid mechanics is therefore at odds with both computer simulation and g.t.s.m., the latter two being in agreement in all detail. The constitutive equations in either frame take no account of the existence of fundamental shear induced time c.c.f's, which computer simulation shows to be time asymmetric.

Illustration with Computer Simulation The presence of time c.c.f's in frame (x, y, z) of an isotropic liquid can be proven with computer simulation. In this section some c.c.f. elements are illustrated for the C_{2v} point group of water and the C_{3v} point group of methyl chloride in the isotropic liquid state (Figs. (1) and (2)). The simulations were carried out on the Cray 1s computer of the University of London Computer Centre in sep-

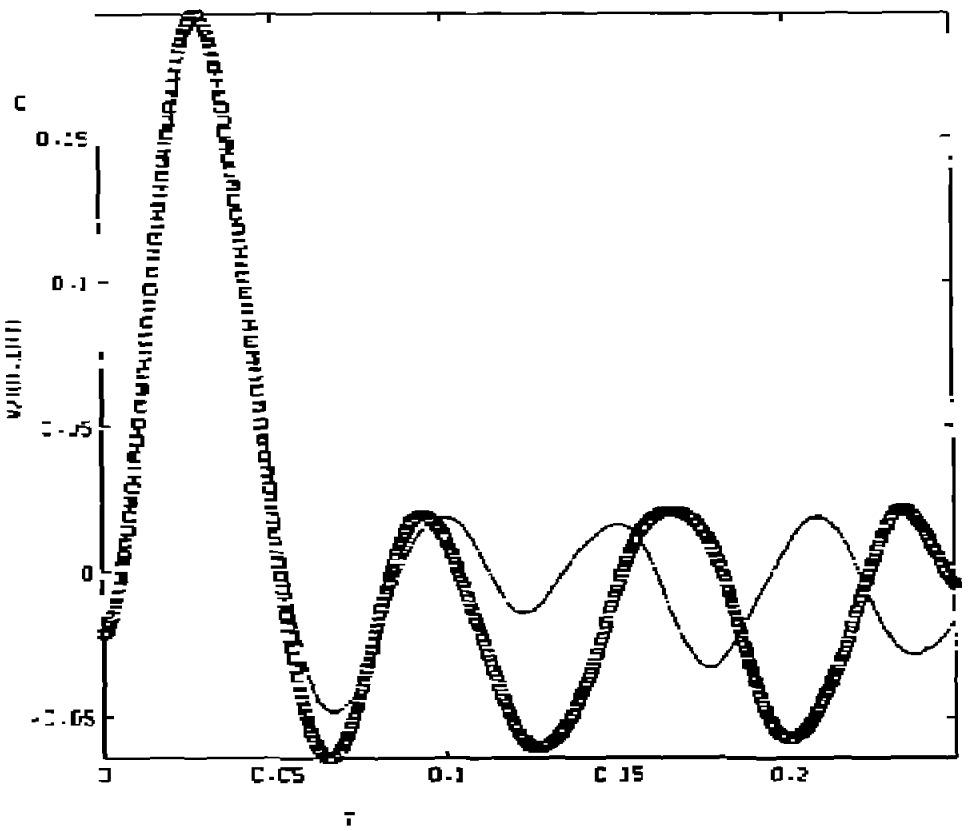

Fig. 1: Elements of the velocity / angular velocity cross correlation function from our computer simulation of liquid water.

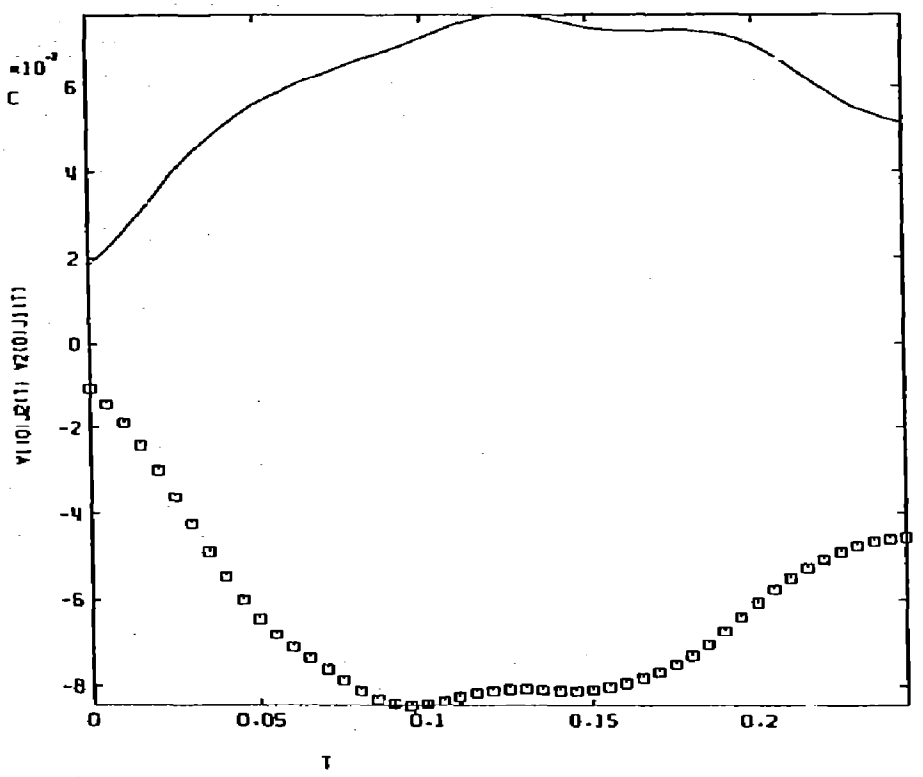

Fig. 2: The same for methyl chloride (one independent element in the molecule fixed frame (x, y, z).

ments of up to 3,000 time steps of 0.5 fs for water and 5.0 fs for methyl chloride. The intermolecular potentials in each case were Lennard-Jones atom-atom with point charges

$$\varepsilon/k(O-O) = 58.4K;\ \ \sigma(O-O) = 2.8\text{Å}$$
$$\varepsilon/k(H-H) = 21.1K;\ \ \sigma(H-H) = 2.5\text{Å}$$
$$q_q = -0.23|e|;\ q_O = 0.0;\ \ q_H = 0.23|e|$$
$$\varepsilon/k(Cl-Cl) = 175.0K;\ \ \sigma(Cl-Cl) = 3.35\text{Å}$$
$$\varepsilon/k(C-C) = 51.0K;\ \ \sigma(C-C) = 3.2\text{Å}$$
$$q_H = 0.063|e|;\ \ q_C = -0.056|e|;\ \ q_{Cl} = -0.131|e|$$

Figs. (1) and (2), although a little noisy, confirm the group theoretical reasoning of Section (1), i.e. for water there are two independent elements, and on for methyl chloride, of the type (x, y) = - (y, x). In frame (X, Y, Z) all elements vanish of this c.c.f., again in agreement with g.t.s.m.

We have proven in two ways, therefore, that material frame indifference does not extend to the fundamental molecular dynamics of a liquid, and is not a useful concept in computer simulation of flow phenomena. At the molecular level the classical continuum limit has no meaning, the concept of constitutive equations becomes redundant. The principle of material frame indifference, which requires that constitutive equations be of the same form in all frames of reference, becomes irrelevant, and even in the best of circumstances

Ryskin[5] has argued that it is a fallacy based on an assumed link between the idea of material behaviour being independent of the motion of an observer.

Computer simulation and g.t.s.m. show consistently that dynamical behaviour, and ensemble averages, are frame dependent, they are different in frames (X, Y, Z) and (x, y, z).

Atomic Liquids

In atomic liquids, a recent computer simulation and analysis with g.t.s.m. have shown clearly[9] that simple shear in couette flow is accompanied by the appearance in (X, Y, Z) of time asymmetric c.c.f.'s between orthogonal components of the peculiar velocity and pressure tensor (and therefore of the stress tensor). We have argued in Section (2) that the components of these new c.c.f.'s, (which were previously unknown to conventional rheology), are made up of vorticity and deformation, respectively time antisymmetric and symmetric. They would vanish if a corotating were constructed in the manner of Eu. This implies that atomic dynamics in a corotating frame, at the fundamental atomic level, would not be relevant to some of the data emerging from computer simulation. The relevance of constitutive equations is brought in to doubt because they have not been able to anticipate the existence of the new c.c.f.'s discovered in the computer simulations and group theoretical arguments of Evans and Heyes[9].

Acknowledgements

The S.E.R.C. is acknowledged for computer time, the Royal Society for the award of a 1983 Research Fellowship to DMH, and the Universities of London and Lancaster for honorary posts to MWE. I.B.M. is thanked for an award to MWE under the Visiting Scientist Program of Dr. Enrico Clementi.

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