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GROUP THEORETICAL STATISTICAL MECHANICS APPLIED TO COUETTE FLOW

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In group theoretical statistical mechanics (gtsm) the ensemble average is treated with the rules of group theory in the laboratory frame (X, Y, Z) and the molecule-fixed frame (x, y, z) of the point group character tables. This allows the determination of non-vanishing averages, such as time correlation functions, at the field-on equilibrium. The effect of couette flow is evaluated on a range of ensemble averages by establishing the symmetry of the strain rate tensor in terms of the irreducible representations of the $R_h(3)$ rotation–reflection group in frame (X, Y, Z). This symmetry, which is also that of the pressure tensor, is $D_g^{(0)}+D_g^{(1)}+D_g^{(2)}$, consisting of an antisymmetric vorticity of symmetry $D_g^{(1)}$ and a symmetric strain rate component of general symmetry $D_g^{(0)}+D_g^{(2)}$. Thus, in addition to ensemble averages of symmetry $D_g^{(0)}$ in frame (X, Y, Z), the applied strain rate tensor allows new ensemble averages of $D_g^{(1)}$ symmetry and of $D_g^{(0)}+D_g^{(2)}$ symmetry. Depending on the number of off-diagonal elements in the strain rate tensor, up to six new elements of time correlation functions of the general type $\langle A(t)A^{T}(0)\rangle$ may appear by gtsm in frame (X, Y, Z), together with new bulk properties whose symmetry is included in $D_g^{(0)}+D_g^{(1)}+D_g^{(2)}$. The latter include thermal conductivity, thermal expansion and electric polarisability. The treatment is extended to the molecule-fixed frame (x, y, z) using the mapping rules of group theory.

1. Introduction

Over one hundred years ago, Neumann [1] realised that the symmetry of every physical property of an ensemble of molecules is determined by the point group of each molecular component. Neumann's principle was later re-stated by Curie [2]: "C'est la dissymétrie qui crée la phénomène", and has recently been put in the context of chirality and molecular symmetry by Barron [3]: "any type of symmetry exhibited by the point group of a system is possessed by every physical property of that system". Whiffen [4] has developed the Neumann principle to include thermodynamic ensemble averages, either in field-free thermodynamic equilibrium or in the presence of fields, by assuming that the ensemble average can be treated with the methods of group theory, both in frames (X, Y, Z) and (x, y, z). Various recent applications of Whiffen's methods, which we denote "group theoretical statistical mechanics", have been described by the present author, and these include the survey of rotation–translation cross correlation functions for most of the point groups of interest [5,6], the survey of rotation vibration coupling [7], and field effects [8]. Group theoretical statistical mechanics has also been applied to higher-order time correlation functions [8,9], and to show that the statistics of molecular diffusion processess are in general non-Gaussian [10]. A particularly interesting consequence has been the discovery [11,12] of the molecular dynamical origin of magneto and spin chiral dichroism [13–16], effects which have been predicted theoretically to exist at frequencies from the microwave to the ultraviolet.

In this paper we make the first application of group theoretical statistical mechanics to hydrodynamics and rheology, beginning with simple couette flow [17]. The group theoretical symmetry representation of the strain rate tensor in couette flow in an incompressible liquid is obtained in terms of the set of irreducible representations [18–20] of the three-dimensional rotation–reflection group, $R_h(3)$, of frame (X, Y, Z). Group theoretical

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statistical mechanics then implies that in a steady state in the presence of a strain rate, ensemble averages with the same symmetry as the strain rate tensor may exist in frame (X, Y, Z), and in the molecule-fixed frame (x, y, z). A justification of the application of group theoretical statistical mechanics in the steady state out of true thermodynamic equilibrium is given in terms of the thermodynamics of systems under shear given by H.J.M. Hanley and D.J. Evans [21,22]. Predictions are then made on the grounds of symmetry of new non-vanishing time cross correlations, new bulk ensemble averages, and of possible new effects in the molecule-fixed frame (x, y, z), observable by computer simulation.

2. Symmetry of the strain rate tensor

The irreducible representations of the rotation–reflection point group $R_h(3)$ are denoted in frame (X, Y, Z) by $D_g^{(0)}, \ldots, D_g^{(n)}$ and $D_u^{(0)}, \ldots, D_u^{(n)}$ respectively, where the subscript g (gerade) denotes "even to parity reversal symmetry", and u (ungerade), denotes "odd to parity reversal symmetry". In this context, parity reversal is the operation $(X, Y, Z) \rightarrow (-X, -Y, -Z)$, carried out on each atom of each molecule of the system. The superscripts denote the order of the spherical harmonics [18]. In this notation, a simple scalar such as mass or energy is the totally symmetric representation $D_g^{(0)}$. A pseudoscalar such as Raman circular intensity difference [3] is $D_u^{(0)}$, a polar vector such as the position vector, $\boldsymbol{r}$, or the velocity, $\boldsymbol{v}$, is $D_u^{(1)}$, and an axial (or pseudo) vector such as molecular angular velocity, $\boldsymbol{\omega}$, is $D_g^{(1)}$.

In couette flow in an incompressible liquid (atomic or molecular), we are concerned with the relation [17], first derived by Newton, between the strain rate tensor, $\dot{\gamma}$, whose components are velocity gradients, and the shear stress tensor, denoted Π_{XY}. Newton's relation is

$$\Pi_{XY} = -\eta \frac{\partial v_X}{\partial Y} . \tag{1}$$

In a molecular dynamics computer simulation, the stress tensor is defined as the negative of the pressure tensor,

$$\Pi_{XY} = -P_{XY} = \frac{1}{A}\left(\sum_{i=1}^{N} m_i \bar{v}_{Xi} \bar{v}_{Yi} - \sum_{i=1}^{N-1} \sum_{j>1}^{N} \frac{r_{Xij} r_{Yij}}{r_{ij}} \frac{\mathrm{d}\phi(r_{ij})}{\mathrm{d}r} \right) . \tag{2}$$

Here $\bar{v}$ is the velocity in excess of the streaming flow velocity, r_{Xij} is the X component of $\boldsymbol{r}_{ij}$, the interparticle separation between particles i and j (atoms or centres of mass of molecules) and A is the area of the molecular dynamics cell. The quantity ϕ is the (scalar) potential energy between particles i and j. In eq. (1), η is the viscosity, which relates scalar elements of the shear stress tensor to counterparts in the strain rate tensor. Newton's relation (1) is a limit of the more general case, where the vicosity becomes dependent on the strain rate itself:

$$\boldsymbol{\Pi} = -2\eta(\dot{\gamma})\dot{\gamma} . \tag{3}$$

We can apply the symmetry arguments of group theoretical statistical mechanics in both cases in the steady state in the presence of shear, where the isotropic $R_h(3)$ symmetry is distorted by the shear. In general, the symmetry of the strain rate tensor is

$$\dot{\gamma} \equiv \boldsymbol{v}(\boldsymbol{r}^{-1})^{\mathrm{T}} , \tag{4}$$

which is a 3×3 tensor, with nine elements of the velocity gradient. This product is negative to time reversal symmetry, and has the D symmetry:

$$\Gamma(\boldsymbol{v})\Gamma(\boldsymbol{r}^{-1}) = D_u^{(1)} D_u^{(1)} = D_g^{(0)} + D_g^{(1)} + D_g^{(2)} , \tag{5}$$

where we have used the Clebsch–Gordan theorem:

$$\mathrm{D}^{(n)}\mathrm{D}^{(m)}=\mathrm{D}^{(n+m)}+\ldots+\mathrm{D}^{(|n-m|)}\,. \tag{6}$$

From eq. (2), we see that the pressure tensor, and thus the shear tensor, is also in general a 3×3 tensor with the D symmetry,

$$\Gamma(\bar{\boldsymbol{v}})\Gamma(\bar{\boldsymbol{v}})=\Gamma(\boldsymbol{r})\Gamma(\boldsymbol{r})=\mathrm{D}_{\mathrm{g}}^{(0)}+\mathrm{D}_{\mathrm{g}}^{(1)}+\mathrm{D}_{\mathrm{g}}^{(2)}\,, \tag{7}$$

the same as that of the strain rate tensor. It follows that the proportionality constant denoted by η in eq. (1), i.e. the viscosity, is a scalar component of $\mathrm{D}_{\mathrm{g}}^{(0)}$ symmetry. However, since this links different components of the stress and strain it may take on different magnitudes in general.

The representation $\mathrm{D}_{\mathrm{g}}^{(0)}+\mathrm{D}_{\mathrm{g}}^{(1)}+\mathrm{D}_{\mathrm{g}}^{(2)}$ of the strain rate tensor, the stress tensor and the pressure tensor reflects the fact that in general there is a symmetry component of symmetry $\mathrm{D}_{\mathrm{g}}^{(0)}+\mathrm{D}_{\mathrm{g}}^{(2)}$ and an antisymmetric component, generated by a vector product, of symmetry $\mathrm{D}_{\mathrm{g}}^{(1)}$. In the strain rate tensor, this reflects the fact [17] that the response to shear has an antisymmetric component of vorticity, of symmetry $\mathrm{D}_{\mathrm{g}}^{(1)}$, and a symmetric component of general symmetry $\mathrm{D}_{\mathrm{g}}^{(0)}+\mathrm{D}_{\mathrm{g}}^{(2)}$, which is a deformation. The mathematical treatment of these effects in a molecular liquid is formidably complicated, there are four conservation equations and eight constitutive equations, as derived by D.J. Evans [23]. The techniques of non-equilibrium computer simulation have been developed to deal with shearing in molecular liquids, mainly by D.J. Evans and co-workers [17,21–28]. The thermodynamics of systems under shear, sometimes far from equilibrium, have been developed by H.J.M. Hanley and D.J. Evans [21,22] and appear to be consistent with the results of nonequilibrium computer simulation. A system under shear is a steady state where $\mathrm{R}_{\mathrm{h}}(3)$ symmetry of true thermodynamic equilibrium is broken by the stress tensor, and the resulting strain rate tensor, both of symmetry $\mathrm{D}_{\mathrm{g}}^{(0)}+\mathrm{D}_{\mathrm{g}}^{(1)}+\mathrm{D}_{\mathrm{g}}^{(2)}$. Group theoretical statistical mechanics applied to this steady state reveals a great deal about the molecular dynamics which could otherwise be obscured by the dynamical complexity of the problem.

3. The laboratory frame (*X, Y, Z*)

The effect of a shearing field of symmetry $\mathrm{D}_{\mathrm{g}}^{(0)}+\mathrm{D}_{\mathrm{g}}^{(1)}+\mathrm{D}_{\mathrm{g}}^{(2)}$ in this frame is to make possible the existence of different ensemble averages with this symmetry, or of included symmetries such as $\mathrm{D}_{\mathrm{g}}^{(1)}$ or $\mathrm{D}_{\mathrm{g}}^{(0)}+\mathrm{D}_{\mathrm{g}}^{(2)}$. Examples of bulk properties with the latter symmetry are: electric polarisability, thermal and electric conductivity, thermoelectricity, thermal expansion, and magnetic susceptibility. Thus, we can say that shear has the effect of making the observed (field-free) polarisability in a given molecular liquid anisotropic, there are different components in different laboratory axes. Group theoretical statistical mechanics allows this conclusion to be drawn without the need for complicated calculations or computations. A liquid under shear should therefore exhibits dielectric loss and permittivity and other spectral features due to the appearance in frame (X, Y, Z) of electric polarisability of symmetry $\mathrm{D}_{\mathrm{g}}^{(0)}+\mathrm{D}_{\mathrm{g}}^{(2)}$ due to shear.

On the molecular scale, the strain rate tensor in response to the shearing effect of couette flow makes possible the existence of time correlation functions of overall symmetry $\mathrm{D}_{\mathrm{g}}^{(0)}+\mathrm{D}_{\mathrm{g}}^{(1)}+\mathrm{D}_{\mathrm{g}}^{(2)}$. The tensor symmetry of all time autocorrelation functions of the type $\langle \boldsymbol{A}(t)\boldsymbol{A}^{\mathrm{T}}(0)\rangle$, where $\boldsymbol{A}$ is a polar or axial vector, is given by this sum of D representations. Thus, group theoretical statistical mechanics tells us immediately that all nine elements of such correlation functions *may* exist in frame (X, Y, Z), depending on the number of components of the fluid velocity and the number of independent space variables in the couette flow. Where there is only one component of the velocity gradient in the couette flow, e.g., $\partial v_X/\partial Z$, then the shear-induced time correlation functions are of the type

$$\langle v_X(t)v_Z(0)\rangle=-\langle v_X(0)v_Z(t)\rangle\,, \tag{8}$$

which is "time antisymmetric" and of $\mathrm{D}_{\mathrm{g}}^{(1)}$ symmetry, and

$$\langle v_X(t)v_Z(o)\rangle = \langle v_X(0)v_Z(t)\rangle\,, \tag{9}$$

which is "time symmetric" and of traceless $D_g^{(2)}$ symmetry. (Very recent computer simulations [29–31] have corroborated these symmetry based arguments with the actual time dependence of the new cross correlations in atomic (Lennard-Jones) fluids.) The observed time dependence of the shear-induced cross correlation function is therefore "time asymmetric", being *a weighted sum of (8) and (9).* (This new symmetry predicted phenomenon has also just been observed in computer simulation [30].) The time antisymmetric component of the shear-induced cross correlation function $\langle \boldsymbol{v}(t)\boldsymbol{v}^{\mathrm{T}}(0)\rangle$ of atomic velocity, $\boldsymbol{v}$, for example, takes its antisymmetry from the fact that $D_g^{(1)}$ denotes "vector part of", i.e. $\langle \boldsymbol{v}(t)\times\boldsymbol{v}(0)\rangle$. This vanishes at $t=0$, but is finite at finite $t<\infty$. For an applied shear resulting in a strain rate of type $\partial v_X/\partial Z$ this cross correlation function reduces to (see appendix):

$$D_g^{(1)}:\quad \langle \boldsymbol{v}(t)\times\boldsymbol{v}(0)\rangle \equiv \langle v_X(t)v_Z(0)\rangle \boldsymbol{j} - \langle v_Z(t)v_X(0)\rangle \boldsymbol{j}\,. \tag{10}$$

With a strain rate of type $\partial v_X/\partial Z$ there is no diagonal component, and the trace ($D_g^{(0)}$) of the complete matrix vanishes. The symmetric deformation induced by shear is therefore of $D_g^{(2)}$ symmetry, representing the time symmetric cross correlation function:

$$D_g^{(2)}:\quad \langle \boldsymbol{v}(t)\boldsymbol{v}^{\mathrm{T}}(0)\rangle \equiv \langle v_X(t)v_Z(0)\rangle \boldsymbol{i}\boldsymbol{j}^{\mathrm{T}} + \langle v_Z(t)v_X(0)\rangle \boldsymbol{j}\boldsymbol{i}^{\mathrm{T}}\,. \tag{11}$$

Thus, group theoretical statistical mechanics (and recent corroborative computer simulations) has revealed new cross correlation functions [29–31] which appear in response to shear produced by couette flow. These appear to be unknown in conventional rheology. By extending our arguments to the pressure tensor and its various time correlation functions, we can argue by symmetry alone that shear produces the Weissenberg effect [32], the pressure generated perpendicular to the plane of shear. We conclude that the Weissenberg effect is caused by atomic or molecular cross correlation functions, and that the latter can be observed experimentally with Weisenberg effect apparatus [32].

In this context, we note that non-zero strain rates of "diagonal" type do not appear in simple couette flow of type $\partial v_X/\partial Z$, but is can be shown from first principles that both diagonal and off-diagonal strain rate components exist in flows in two or three dimensions past objects. In flow past a disk in two dimensions, for example, the following four strain rates are generated:

$$\partial v_X/\partial Z = [2v_0 X/(X^2+Z^2)]\sin[2\tan^{-1}(Z/X)]\,, \tag{12}$$

$$\partial v_X/\partial X = -[2v_0 Z/(X^2+Z^2)]\sin[2\tan^{-1}(Z/X)]\,, \tag{13}$$

$$\partial v_Z/\partial X = [2v_0 Z/(X^2+Z^2)]\cos[2\tan^{-1}(Z/X)]\,, \tag{14}$$

$$\partial v_Z/\partial Z = -[2v_0 X/(X^2+Z^2)]\cos[2\tan^{-1}(Z/X)]\,. \tag{15}$$

Here, $-v_0$ is the mean flow velocity before reaching the disk. In this case, we clearly have a finite trace, of symmetry $D_g^{(0)}$, of the strain rate tensor:

$$\begin{pmatrix} \partial v_X/\partial X & \partial v_X/\partial Z \\ \partial v_Z/\partial X & \partial v_Z/\partial Z \end{pmatrix}.$$

Clearly, there are no strain rates in an atomic or molecular liquid at field-free equilibrium, and in that case all the shear-induced cross correlation functions vanish. In this context, the effect of shear on quantities of $D_g^{(0)}$ symmetry, such as the velocity autocorrelation function $\langle \boldsymbol{v}(t)\cdot\boldsymbol{v}(0)\rangle$, is to change its time dependence. This quantity (and all scalar quantities of symmetry $D_g^{(0)}$) exists both in the presence and absence of shear. Thus, bulk properties such as the electric polarisability, whose ensemble average is generally non-zero in field-free equilibrium, are affected by the shear and strain rate response in such a way that the $D_g^{(0)}$ component is changed in value and in such a way that the $D_g^{(1)}$ and $D_g^{(2)}$ components make them measurably anisotropic in the laboratory frame (X, Y, Z).

The strain rate tensor will also allow the existence in the laboratory frame of cross correlation functions of the type $\langle A(t)B^{T}(0)\rangle$ with $D_g^{(0)}+D_g^{(1)}+D_g^{(2)}$ symmetry, an example being that between the molecular dipole moment, μ, and the molecular linear velocity v, or between the molecular rotational velocity, $\dot{\mu}$, and its own linear velocity v. These cross correlation functions are assumed to vanish in most standard textbooks and conventional theory. Any molecular understanding of couette flow should include the computer simulation of these shear-induced cross correlation functions.

4. The molecule-fixed frame (*x*, *y*, *z*)

The frame (x, y, z) is that of the point group character tables [18–20], and ensemble averages may exist in (x, y, z) which vanish in the laboratory frame. A well known [10–12] example is $\langle \boldsymbol{v}(t)\boldsymbol{\omega}^{T}(0)\rangle$, the time cross correlation function between molecular linear and angular velocity. This vanishes for all t at field-free equilibrium in frame (X, Y, Z) because v and ω have opposite parity reversal symmetries. It also vanishes for all t in the presence of couette flow in the steady state, because the parity symmetry of the strain rate tensor is gerade and that of $\langle \boldsymbol{v}(t)\boldsymbol{\omega}^{T}(0)\rangle$ is ungerade. In frame (x, y, z), however, this is no longer true, and in the C_{2v} point group of water for example there are two non-vanishing elements of $\langle \boldsymbol{v}(t)\boldsymbol{\omega}^{T}(0)\rangle$ which are independent functions of time. This is well known from independent computer simulations by Evans et al. [4–12] and the Brussels School [10], but has recently been corroborated by the application of group theory by Whiffen [4]. The relevant symmetry representation in the C_{2v} point group of $\langle \boldsymbol{v}(t)\boldsymbol{\omega}^{T}(0)\rangle$ is

$$\Gamma(\boldsymbol{v})\Gamma(\boldsymbol{\omega})=(A_1+B_1+B_2)(A_2+B_1+B_2)$$

$$=A_1A_2+A_1B_1+A_1B_2+B_1A_2+B_1B_1+B_1B_2+B_2A_2+B_2B_1+B_2B_2=2A_1+3A_2+2B_1+2B_2\,. \qquad (16)$$

This is a product of the irreducible representations of $\boldsymbol{v}$ and $\boldsymbol{\omega}$ in the C_{2v} point group, and contains the totally symmetric representation, A_1, twice. In group theoretical statistical mechanics this means that two independent elements of $\langle \boldsymbol{v}(t)\boldsymbol{\omega}^{T}(0)\rangle$ exist in frame (x, y, z) out of a possible nine at field-free thermodynamic equilibrium. By examining the individual products which give the A_1 representation in (16), i.e. B_1B_1 and B_2B_2, we deduce from the C_{2v} point group character table that the non-vanishing elements are $\langle v_x(t)\omega_y(0)\rangle$ and $\langle v_y(t)\omega_x(0)\rangle$. This is exactly what is found by computer simulation [4–12] in C_{2v} symmetry environments such as water and dichloromethane in the liquid state. One element is positive, i.e. starts off with a positive time dependence, and the other is negative in this sense, with an independent (i.e. different) time development. Now we examine the effect of couette flow on functions such as $\langle \boldsymbol{v}(t)\boldsymbol{\omega}^{T}(0)\rangle$ in the frame (x, y, z).

The first step is to map the symmetry of the strain rate tensor on to the C_{2v} point group:

$$\Gamma(\dot{\gamma})=D_g^{(0)}+D_g^{(1)}+D_g^{(2)}\equiv 3A_1+2A_2+2B_1+2B_2\,. \qquad (17)$$

In general, the representation in C_{2v} contains three elements of type A_1, two of type A_2, two each of type B_1 and B_2. In group theoretical statistical mechanics this implies that ensemble averages in a liquid of C_{2v} molecules subjected to shear will, in the steady state, exist if they have any of the four types of symmetry. In the product of representations (17) there are the nine individual component products,

$$\begin{aligned}
&A_1A_2\equiv\langle v_z(t)\omega_z(0)\rangle,\quad (A_2);\quad A_1B_1\equiv\langle v_z(t)\omega_y(0)\rangle,\quad (B_1);\quad A_1B_2\equiv\langle v_z(t)\omega_x(0)\rangle,\quad (B_2);\\
&B_1A_2\equiv\langle v_z(t)\omega_z(0)\rangle,\quad (B_2);\quad B_1B_1\equiv\langle v_x(t)\omega_y(0)\rangle,\quad (A_1);\quad B_1B_2\equiv\langle v_x(t)\omega_x(0)\rangle,\quad (A_2);\\
&B_2A_2\equiv\langle v_y(t)\omega_z(0)\rangle,\quad (B_1);\quad B_2B_1\equiv\langle v_y(t)\omega_y(0)\rangle,\quad (A_2);\quad B_2B_2\equiv\langle v_y(t)\omega_x(0)\rangle,\quad (A_1);
\end{aligned} \qquad (18)$$

all of which give A_1, A_2, B_1, or B_2. In general, therefore, and without further physical discussion, all nine elements of $\langle v(t)\omega^{T}(0)\rangle$ *may* exist in frame (x, y, z) in the shear-on steady state. The elements (5) and (9), which also exist at field-free equilibrium, *do* exist in the presence of shear, albeit with a changed time dependence in each case, but the symmetry arguments can only say that the other seven elements *may* exist in the shear applied steady state. Definite proof requires further computer simulation. Couette flow may be characterised, therefore by complete correlation between molecular $\boldsymbol{v}$ and $\boldsymbol{\omega}$, for example in liquid water. This would be an unprecedented result arrived at from group theoretical statistical mechanics.

5. Rotation–vibration coupling

The symmetry representation of normal mode vibration [18–20] in frame (x, y, z) depends both on the molecular point group and on the number of atoms in the molecule. For the water molecule the symmetry representation of vibrational normal modes is

$$\Gamma(Q_i) = A_1(Q_1) + A_1(Q_2) + B_2(Q_3)\,, \tag{19}$$

so that there are three fundamentals. The symmetry representations of the three-time correlation functions between these normal modes and molecular angular velocity, for example, are

$$\begin{aligned}
\Gamma(Q_1)\Gamma(\omega) &= A_1(A_2 + B_1 + B_2) = A_2 + B_1 + B_2\,,\\
\Gamma(Q_2)\Gamma(\omega) &= A_1(A_2 + B_1 + B_2) = A_2 + B_1 + B_2\,,\\
\Gamma(Q_3)\Gamma(\omega) &= A_2(A_2 + B_1 + B_2) = A_1 + A_2 + B_1\,,
\end{aligned} \tag{20}$$

so that in field-free thermodynamic equilibrium only the third can exist, assuming that the mean rotational symmetry remains $A_2 + B_1 + B_2$. This is a reasonable assumption when vibration is a much faster process than rotation. If this assumption is not made, then the analysis is complicated considerably by the need to represent the rotational symmetry in a molecule framework distorted out of C_{2v} by vibration. In the classical picture this distortion is considerable only when we depart from the harmonic vibrator limit. The individual product of representations which produces A_1 is B_2B_2, so that the existing element is $\langle Q_{3y}(t)\omega_x(0)\rangle$.

In the presence of a strain rate tensor the number of non-vanishing elements of the vibration to rotation cross correlation function may increase, in line with the discussion already made of translation–rotation coupling. Shearing may produce many new types of cross correlation, but this cannot be proven absolutely without computer simulation or experimental data.

6. Conclusions

Our discussion of group theoretical statistical mechanics applied to shear has been based on three principles, or axioms, which are reproduced here in conclusion.

Principle (1). The thermodynamic ensemble average $\langle ABC\ldots\rangle$ over $ABC\ldots$ exists in general if the product of representations $\Gamma(A)\Gamma(B)\Gamma(C)\ldots$ contains the totally symmetric representation $D_g^{(0)}$ of the rotation–reflection point group $R_h(3)$.

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

Principle (3). The ensemble average is changed by the application of an external field of force in such a way that the symmetry of the new steady state ensemble averages is determined by that of the applied field.

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Appendix. Some basic definitions

Some of the D notation used in the text may be unfamiliar to some readers and this appendix provides some basic definitions.

$D_g^{(0)}$ *(scalar) product of two vectors in a time correlation function.* $D_g^{(0)}$ symmetry refers to the product

$$\langle \boldsymbol{v}(t)\cdot\boldsymbol{v}(0)\rangle = \langle v_X(t)v_X(0)\rangle + \langle v_Y(t)v_Y(0)\rangle + \langle v_Z(t)v_Z(0)\rangle\,, \tag{A.1}$$

which produces a scalar. This is the conventional scalar (dot) product of two vectors contained within the ensemble average denoted by $\langle\ \rangle$.

$D_g^{(1)}$ *(vector) product of two vectors.* $D_g^{(1)}$ refers to the vector product, conventionally defined as

$$\langle \boldsymbol{v}(t)\times\boldsymbol{v}(0)\rangle = \begin{vmatrix} \boldsymbol{i} & \boldsymbol{j} & \boldsymbol{k} \\ v_X(t) & v_Y(t) & v_Z(t) \\ v_X(0) & v_Y(0) & v_Z(0) \end{vmatrix}\,,$$

where $\boldsymbol{i}, \boldsymbol{j}$, and $\boldsymbol{k}$ are unit vectors in the X, Y, and Z axes of (X, Y, Z). The vector product always has one positive component in one axis and one negative component. This implies the existence of

$$\langle v_X(t)v_Z(0)\rangle \quad \text{and} \quad -\langle v_Z(t)v_X(0)\rangle \quad \text{etc.},$$

which are antisymmetric.

$D_g^{(2)}$ *(tensor) product of two vectors.* In general the tensor product is

$$\langle \boldsymbol{v}(t)\boldsymbol{v}^{\mathrm{T}}(0)\rangle \equiv \begin{pmatrix} \langle v_X(t)v_X(0)\rangle \boldsymbol{ii}^{\mathrm{T}} & \langle v_X(t)v_Y(0)\rangle \boldsymbol{ij}^{\mathrm{T}} & \langle v_X(t)v_Z(0)\rangle \boldsymbol{ik}^{\mathrm{T}} \\ \langle v_Y(t)v_X(0)\rangle \boldsymbol{ji}^{\mathrm{T}} & \langle v_Y(t)v_Y(0)\rangle \boldsymbol{jj}^{\mathrm{T}} & \langle v_Y(t)v_Z(0)\rangle \boldsymbol{jk}^{\mathrm{T}} \\ \langle v_Z(t)v_X(0)\rangle \boldsymbol{ki}^{\mathrm{T}} & \langle v_Z(t)v_Y(0)\rangle \boldsymbol{kj}^{\mathrm{T}} & \langle v_Z(t)v_Z(0)\rangle \boldsymbol{kk}^{\mathrm{T}} \end{pmatrix},$$

whose symmetry is $D_g^{(0)} + D_g^{(2)}$. Excluding the diagonal elements leaves the symmetry $D_g^{(2)}$. The notation $\boldsymbol{ij}^{\mathrm{T}}$ means

$$\begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} (0\ 1\ 0) = \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

etc. This in general provides the symmetric result:

$$\langle v_X(t)v_Z(0)\rangle = \langle v_Z(t)v_X(0)\rangle\,.$$

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