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THREE PRINCIPLES OF GROUP THEORETICAL STATISTICAL MECHANICS

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Three new principles are introduced from the application of group theory to statistical mechanics at thermodynamical equilibrium and in the field-on steady state. They are illustrated with reference to computer simulations in the laboratory frame (X, Y, Z) and in the molecule fixed frame (x, y, z) of the point group character tables. The principle governing the effect of applied external fields is illustrated with reference to an appplied vortex and shear in conventional and non-equilibrium molecular dynamics computer simulations.

1. Introduction

The use of computer simulation in the past decade has transformed our appreciation of the molecular dynamics of liquids and gases. Conventional computer simulation has revealed the existence and nature of members of the set of non-vanishing time cross correlation functions (ccf's), both in the field-on steady state [1] and at thermodynamic equilibrium [2,3]. In conventional diffusion theory [4], all members of these sets are assumed to vanish for all t, whereas computer simulation shows that each non-vanishing ccf has a distinctive and characteristic time dependence. The field-on and field-off sets contain different members, the field-on set being larger than its field-off counterpart. For example, a static electric field $\boldsymbol{E}$ applied in the Z axis of the laboratory frame (X, Y, Z) to a molecular ensemble results in the appearance [1] of the ccf's

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

where $\boldsymbol{v}$ is the diffusing molecule's linear velocity and $\boldsymbol{\omega}$ its own angular velocity. These ccf's vanish in frame (X, Y, Z) when $\boldsymbol{E}=\boldsymbol{0}$, and were first discovered [1] by computer simulation in 1985, seventy years after Debye's (1913) rotational diffusion theory [5], based on the supposition that all time ccf's vanish for all t. In the intervening period, conventional diffusion theory had branched in many directions [4], but had been utterly unable to anticipate the result (1). The latter is now known to be just one example out of many non-vanishing time ccf's in frame (X, Y, Z) which characterise molecular diffusion in all known molecular symmetries. Furthermore, the set of non-vanishing ccf's in frame (x, y, z) of the standard literature point group character tables [6–8] is different in nature from that in (X, Y, Z). Certain members that exist [2,3] at thermodynamic equilibrium in (x, y, z) vanish in (X, Y, Z). In general the (x, y, z) set contains more members, both at thermodynamic equilibrium and in the field-on steady state. Conventional diffusion theory had again been unable to anticipate this result, and still cannot deal with the numerical data without considerable difficulties of over parameterisation.

Recently, the newer methods of non-equilibrium molecular dynamics computer simulation [9–12] have added to the set of field on time ccf's in the steady state characterised by shear [13], and strain rate response. New time ccf's have been discovered [14–16], using SLLOD and profile unbiased algo-

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rithms, which in general are time asymmetric, being a weighted sum of time antisymmetric ccf's characterising vorticity, and time symmetry counterparts generated by shear deformation. These new ccf's have been shown [14–16] to be the fundamental cause of the Weissenberg effect [17], the pressure generated in a direction perpendicular to the plane of shear, and are therefore measurable experimentally. Conventional theory of rheology had not anticipated their existence, even in a qualitative manner.

The failure of conventional theory is due to the neglect of time cross correlation functions, and it is clearly important to develop symmetry arguments to anticipate their presence in a molecular liquid. This Letter provides three new principles with which to guide computer simulation by the application of group theory to statistical mechanics, referred to for convenience and brevity as "group theoretical statistical mechanics" (gtsm).

Principle (1). The thermodynamic ensemble average $\langle \mathrm{ABC}... \rangle$ over ABC... exists if the product of representations $\Gamma(\mathrm{A})\Gamma(\mathrm{B})\Gamma(\mathrm{C})$... contains the totally symmetric representation (tsr) of the three-dimensional rotation reflection group $\mathrm{R_h}(3)$ of isotropic atomic or molecular ensembles.

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

Principle (3). If an external field of force is applied to a molecular ensemble which subsequently reaches a steady state in the presence of that field, new ensemble averages may be created whose symmetry is that of the applied field.

2. Examples and discussion

2.1. Principle (1)

This principle is a restatement in terms of group theory of the Neumann principle [18], also known as the Curie principle [19]. It uses the language of group theory [6–8] applied to frame (X, Y, Z) in isotropic, three-dimensional, space. In these terms the irreducible representations of $\mathrm{R_h}(3)$ represent scalars ($\mathrm{D}_\mathrm{g}^{(0)}$); pseudoscalars ($\mathrm{D}_\mathrm{u}^{(0)}$); polar vectors ($\mathrm{D}_\mathrm{u}^{(1)}$); axial vectors ($\mathrm{D}_\mathrm{g}^{(1)}$) and tensors ($\mathrm{D}_\mathrm{g}^{(2)}$, $\mathrm{D}_\mathrm{u}^{(2)}$, etc.). The tsr is $\mathrm{D}_\mathrm{g}^{(0)}$), the representation of a scalar. This principle shows that the time ccf $\langle \boldsymbol{\mu}(t)\boldsymbol{v}^\mathrm{T}(0) \rangle$, for example, between a molecule's electric dipole moment, $\boldsymbol{\mu}$, and its own linear velocity, $\boldsymbol{v}$, exists in frame (X, Y, Z) because the product of representations

$$\Gamma(\boldsymbol{\mu})\Gamma(\boldsymbol{v}) = \mathrm{D}_\mathrm{u}^{(1)}\mathrm{D}_\mathrm{u}^{(1)} = \mathrm{D}_\mathrm{g}^{(0)} + \mathrm{D}_\mathrm{g}^{(1)} + \mathrm{D}_\mathrm{g}^{(2)} \tag{2}$$

contains $\mathrm{D}_\mathrm{g}^{(0)}$ once, representing the trace of $\langle \boldsymbol{\mu}(t)\boldsymbol{v}^\mathrm{T}(0) \rangle$ which is $\langle \boldsymbol{\mu}(t)\cdot\boldsymbol{v}(0) \rangle$. This ccf does not appear in conventional diffusion theory, but has been observed by computer simulation, for example in liquid water over its complete range of existence [20].

Both Neumann [18] and Curie [19] stated the principle [21] well in advance of Debye's rotational diffusion theory [5] (1913), but the concept of time correlation function did not appear [4] until the early 1920s, so that the mechanism of incorporating principle (1) into conventional diffusion theory was not available to Debye. As we have seen, further developments of the theory ignored the set of non-vanishing ccf's until revealed by computer simulation [1–3].

The principle may also be used to show that some ccf's such as $\langle \boldsymbol{v}(t)\boldsymbol{\omega}^\mathrm{T}(0) \rangle$ vanish in frame (X, Y, Z) at field-free thermodynamic equilibrium. The product of representations

$$\Gamma(\boldsymbol{v})\Gamma(\boldsymbol{\omega}) = \mathrm{D}_\mathrm{u}^{(1)}\mathrm{D}_\mathrm{g}^{(1)} = \mathrm{D}_\mathrm{u}^{(0)} + \mathrm{D}_\mathrm{u}^{(1)} + \mathrm{D}_\mathrm{u}^{(2)} \tag{3}$$

does not contain $\mathrm{D}_\mathrm{g}^{(0)}$.

2.2. Principle (2)

This conveniently summarises the results of numerous computer simulations by the Brussels School [3] and by Evans and co-workers [2]. It was first stated by Whiffen [22] in response to discussions with the present author. It relies on the mapping rules of group theory [6–8] to represent a ccf such as $\langle \boldsymbol{v}(t)\boldsymbol{\omega}^\mathrm{T}(0) \rangle$ in a *molecular* point group, in the frame (x, y, z) defined by the character table. It successfully and consistently explains the available simulation results, providing strong evidence for the validity and correctness of both approaches, and for the shortcomings of the conventional analytical theory. In the C_{2v} point group of water, for example, the product of representations of $\boldsymbol{v}$ and $\boldsymbol{\omega}$ is [22]

$$\Gamma(\boldsymbol{v})\Gamma(\boldsymbol{\omega})(C_{2v}) = (A_1+B_1+B_2)(A_2+B_1+B_2) = 2A_1+3A_2+2B_1+2B_2, \quad (4)$$

which contains the totally symmetric representation, A_1, twice, implying the existence of two independent elements:

$$\langle \omega_x(t)v_y(0)\rangle \quad \text{and} \quad \langle \omega_y(t)v_x(0)\rangle,$$

exactly as observed by computer simulations in liquid water [23] and liquid dichloromethane [24]. Similar calculations for the other molecular point groups show that in general the set of non-vanishing time ccf 's in frame (x, y, z) is larger than that in frame (X, Y, Z) at field free thermodynamic equilibrium. This is entirely consistent with the results of numerous simulations by Evans and co-workers [2] for various group symmetries from T_d to C_{3v} to chiral C_1; and with that of Ryckaert et al. [3] for $C_{\infty v}$ and $D_{\infty h}$. None of these ccf's can be described with conventional diffusion theory. Paradoxically, they are fundamental characteristics of statistical mechanics in molecular ensembles.

2.3. Principle (3)

This is stated for the first time in this communication, and supported by reference to conventional and non-equilibrium computer simulation. It is a deceptively simple looking statement and in order to gain a proper appreciation of how it should be used, the following examples are provided.

(a) With reference to result (1) of this Letter [1], principle (3) explains this by examining the D symmetry of the electric field vector, $\boldsymbol{E}$, in (X, Y, Z). This is $D_u^{(1)}$. The principle implies that ensemble averages of type $D_u^{(1)}$ may exist in frame (X, Y, Z). The D symmetry of $\langle\boldsymbol{\omega}(t)\boldsymbol{v}^{T}(0)\rangle$ is $D_u^{(0)}+D_u^{(1)}+D_u^{(2)}$, as we have seen, and this contains $D_u^{(1)}$ once. Principle (3) states that the $D_u^{(1)}$ part of $\langle\boldsymbol{\omega}(t)\boldsymbol{v}^{T}(0)\rangle$ exists in (X, Y, Z) in the presence of $\boldsymbol{E}$ at the field-on steady state. The $D_u^{(1)}$ part of $\langle\boldsymbol{\omega}(t)\boldsymbol{v}^{T}(0)\rangle$ is given by the vector product

$$\langle\boldsymbol{\omega}(t)\times\boldsymbol{v}(0)\rangle \equiv \boldsymbol{k}[\langle\omega_X(t)v_Y(0)\rangle - \langle\omega_Y(t)v_X(0)\rangle],$$

revealing two elements of $\langle\boldsymbol{\omega}(t)\boldsymbol{v}^{T}(0)\rangle$ mutually perpendicular to $\boldsymbol{E}$ applied in the Z (or $\boldsymbol{k}$) axis. This is again precisely what is revealed by computer simulation [1], a result which *invalidates* the conventional theory [4] of dielectric and Kerr effect relaxation.

(b) Evans and Heyes [14–16] have shown recently that the D symmetry of the strain rate tensor $\partial v_X/\partial Z$ of conventional Couette flow[17] is $D_g^{(0)}+D_g^{(1)}+D_g^{(2)}$, which by principle (3) allows the ensemble averages of this symmetry, or of included symmetries such as $D_g^{(1)}$ or $D_g^{(0)}+D_g^{(2)}$ to exist in the shear applied steady state. This D symmetry is that of the generic time correlation function $\langle\boldsymbol{A}(0)\boldsymbol{A}^{T}(t)\rangle$, where $\boldsymbol{A}$ is velocity, $\boldsymbol{v}$, for example. Non-equilibrium computer simulation showed the presence of new time ccf's of the following type at the shear on steady state [14–16]:

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

$$\langle v_X(t)v_Z(0)\rangle = \langle v_Z(t)v_X(0)\rangle, \quad D_g^{(2)}. \quad (5)$$

respectively a time antisymmetric type of $D_g^{(1)}$ symmetry which vanishes at $t=0$ and represents shear induced vorticity, and a time symmetric $D_g^{(2)}$ type representing shear induced deformation. The overall, computer simulated, time ccf of this type appears [14–16] to be *time asymmetric*, i.e.

$$\langle v_X(t)v_Z(0)\rangle \neq \langle v_X(0)v_Z(t)\rangle, \quad (6)$$

because it is a combination of the two types (5). This is yet again an entirely unexpected result in a non-newtonian [17] (and indeed simple newtonian) Couette flow with strain rate of type $\partial v_X/\partial Z$. A similar and again entirely novel result of principle (3) in this context is the first fundamental explanation of the Weisenberg effect through the prediction and subsequent computer simulation of new elements of the time ccf of the pressure tensor, explaining Weissenberg's well known observation [17] of positive or negative pressure in a direction perpendicular to the plane of shear. The new time ccf's are also sensitive to the onset of other well known non-newtonian phenomena such as convective and structural turbulence.

(c) Finally, an example is given of principle (3) applied in frame (x, y, z). Recent computer simulations by Evans, Lie and Clementi [25] of the effect of a vertex applied to liquid water revealed the effect on $\langle \boldsymbol{v}(t)\boldsymbol{\omega}^{\mathrm{T}}(0)\rangle$:

$$\begin{pmatrix} 0 & a_1 & 0 \\ b_1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \rightarrow \begin{pmatrix} \text{noise} & a_2 & c_2 \\ b_2 & \text{noise} & \text{noise} \\ d_2 & \text{noise} & \text{noise} \end{pmatrix} \qquad (7)$$

in frame (x, y, z). In this frame the symmetry of the applied vortex is $\mathrm{D}_{\mathrm{g}}^{(1)}$ mapped on to the $\mathrm{C}_{2\mathrm{v}}$ point group, giving the representation $\mathrm{A}_2+\mathrm{B}_1+\mathrm{B}_2$. To find the effect on $\langle \boldsymbol{v}(t)\boldsymbol{\omega}^{\mathrm{T}}(0)\rangle$ in frame (x, y, z) of an applied field of this symmetry we must consider the individual products on the r.h.s. of eq. (4) that give A_2, B_1 or B_2. By axiom (3), ensemble averages of this symmetry may exist, giving the possible overall symmetry effect:

$$\begin{pmatrix} 0 & a_1 & 0 \\ b_1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \xrightarrow[A_2+B_1+B_2]{} \begin{pmatrix} e_2 & a_2 & c_2 \\ b_2 & f_2 & h_2 \\ d_2 & i_2 & g_2 \end{pmatrix}. \qquad (8)$$

Both group theory and computer simulation leave possible the existence of the noise terms marked as such in (7). Again this result is unobtainable in conventional theory.

In conclusion, these are three out of many possible and incisive uses of the priciple labelled (3), put forward for the first time in this communication.

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