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Principles of group-theoretical statistical mechanics

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Three principles are presented as the basis for group-theoretical statistical mechanics (GTSM), incorporating Neumann's (or Curie's) principle as the first. The second extends Neumann's principle to molecule fixed axes, (x,y,z), as defined in molecular point-group theory, and the third deals with the symmetry of applied fields and their effect on molecular ensembles in the field-on steady state. The power of GTSM is illustrated with reference to the set of field-induced n-time correlation functions in the laboratory frame (X,Y,Z) and frame (x,y,z).

INTRODUCTION

This Brief Report seeks to establish a link between ensemble averages and group theory in the laboratory frame (X,Y,Z) and the molecule fixed frame (x,y,z) of the point-group character tables. The aim is to reduce complicated problems of molecular dynamics in the condensed phases of molecular and atomic matter to simple considerations of the symmetry of point groups. These lead to methods of codifying the statistical dynamics of molecular ensembles in terms of ensemble averages that include the set of nonvanishing time cross-correlation functions of all orders, and the manner in which these are affected by applied external fields of all types and all orders. The combination of group theory and statistical mechanics is called group-theoretical statistical mechanics (GTSM) for ease of reference. Although GTSM does not lead to a detailed description of the time (or frequency) dependence of ensemble averages, it is a valuable guide to the set of time correlation functions which vanish for all t, thus simplifying considerably the task of investigation by computer simulation and analytical diffusion theory.

The fundamentals of GTSM are embodied in the following three principles, which allow great insight to the statistical mechanics of molecular ensembles.

Principle (1) (Neumann's or Curie's principle). Neumann's principle[1] in contemporary terms states that an ensemble average $\langle \mathbf{ABCD}\ldots \rangle$ exists in frame (X,Y,Z) if the product of representations $\Gamma(A)\Gamma(B)\Gamma(C)\ldots$ includes the totally symmetric representation of the $R_h(3)$ rotation-reflection point group of isotropic three-dimensional space.

Principle (2). This ensemble average exists in frame (x,y,z) if the product of symmetry representation contains the totally symmetric representation of the molecular point group at least once.

Principle (3). If an external field of force can be represented in frame (X,Y,Z) with an irreducible representation of the $R_h(3)$ point group, then the field may allow new ensemble averages in the field-on steady state in frame (X,Y,Z) with the symmetry of that irreducible representation.

EXAMPLES AND DISCUSSION

There is no rigorous proof of Neumann's principle, but no counter example is known to exist. It was succinctly restated[2] by Curie: "C'est la disymmetrie qui crée la phenomène," and recently reviewed by Barron.[3] For the sake of development it is taken as proven *a posteriori*. The totally symmetric irreducible representation[4] of the $R_h(3)$ point group is the scalar quantity $D_g^{(0)}$ so that according to Neumann, thermodynamic ensemble averages at field-free thermodynamic equilibrium are scalar quantities. Thus ensemble averages over the axial vector $D_g^{(1)}$, or the polar vector $D_u^{(1)}$, vanish in frame (X,Y,Z). Similarly, the time cross-correlation function (CCF) $\langle \mathbf{v}(0)\boldsymbol{\omega}^T(t)\rangle$ between a diffusing molecule's linear ($\mathbf{v}$) and angular ($\boldsymbol{\omega}$) velocity vanishes for all t in frame (X,Y,Z) for all molecular symmetries, including chiral, because the appropriate product of representations

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

does not contain $D_g^{(0)}$. Available computer simulations[5] support this application of Neumann's or Curie's principle (1).

The reason for promoting this principle as the first of GTSM is that its validity can be extended[6–9] to principles (2) and (3), from which useful conclusions can be drawn about the properties of CCF's and the structure of customary diffusion equations,[10–14] such as those of Fokker and Planck, Smoluchowski, and Klein or Kramers. Principle (2) shows which of the correlation functions must vanish in frame (x,y,z) and which may have a time dependence unconsidered in the traditional approach. An example is the CFF $\langle \mathbf{v}(t)\boldsymbol{\omega}^T(0)\rangle$, where principle (2) can be used to show the existence of

$$\langle v_x(t)\omega_y(0)\rangle \neq \langle v_y(t)\omega_x(0)\rangle ,$$

confirmed by several computer simulations of[15–20] C_{2v}

molecules. Other molecular symmetries have different existing and vanishing elements of CCF's of this type; rarely, if ever, are these considered in available diffusion theory. Principle (2) is therefore a considerable advance in our fundamental understanding of molecular diffusion.

Principle (3) is exemplified as follows. If an electric field **E** is applied to an initially isotropic molecular liquid, it makes possible the existence of field-on equilibrium averages with the same D symmetry as the electric field. This is the irreducible representation $D_u^{(1)}$ of the $R_h(3)$ point group. This is true whatever the field strength, and a well-known example is dielectric polarization.[21] Much less well appreciated, but clear from principle (3), is that **E** also induces[22–25] CCF's of $D_u^{(1)}$ symmetry in frame (X,Y,Z); for example,

$$\langle v_i(0)\omega_j(t)\rangle = -\langle v_j(0)\omega_i(t)\rangle \ , \tag{2}$$

which vanishes only when $\mathbf{E}=0$. This is true whatever the strength of the applied electric field **E**, which in general also promotes the set of ungerade CCF's of the type

$$\langle A_i(0)B_j(t)\rangle = -\langle A_j(0)B_i(t)\rangle \ . \tag{3}$$

Computer simulation should be used to obtain the time dependence of these CCF's and their frequency dependence by Fourier transformation. None of this is customarily considered in diffusion theory, for example, the itinerant oscillator.[26–30]

In another example of principle (3), simple Couette flow[31–34] in a molecular or atomic liquid with shear strain $\partial v_X/\partial Z$, we have the applied field symmetry[9]

$$\Gamma(\partial\mathbf{v})\Gamma(\partial\mathbf{r}^{-1}) = D_u^{(1)}D_u^{(1)} = D_g^{(0)}+D_g^{(1)}+D_g^{(2)} \ . \tag{4}$$

According to principle (3), this may induce field-on averages of the type $D_g^{(0)}$, $D_g^{(1)}$, and $D_g^{(2)}$. In general, therefore, Couette flow makes visible in frame (X,Y,Z) all nine elements of the generic gerade autocorrelation function (ACF) $\langle \mathbf{A}(0)\mathbf{A}^T(t)\rangle$. If **A** denotes the atomic or molecular linear velocity **v**, and we restrict the shear strain to the simple $\partial v_X/\partial Z$, then the $D_g^{(0)}$ component, representing the trace, disappears, leaving for the antisymmetric and symmetric components

$$\langle v_X(0)v_Z(t)\rangle = -\langle v_X(t)v_Z(0)\rangle \quad \text{for } D_g^{(1)} \tag{5}$$

and

$$\langle v_X(0)v_Z(t)\rangle = \langle v_X(t)v_Z(0)\rangle \quad \text{for } D_g^{(2)} \ , \tag{6}$$

respectively, representing shear-induced vorticity and deformation. The result visible in computer simulation[9] is a weighted sum of (5) and (6), and is a new type of time-asymmetric velocity CCF unknown to traditional rheology. Analogous time asymmetric CCF's of the stress tensor, also previously unknown, have been derived using principle (3) and confirmed with computer simulation. These provide a new and simple explanation for the experimentally well-known Weissenberg effect, pressure induced perpendicular[31] to a shearing plane. (This causes important practical problems, such as roller fracture in the print industry.) The full range of applicability of principle (3) can be considered when considering effects inherently nonlinear in the applied field strength.

HIGHER POWERS OF THE ELECTRIC FIELD

According to principle (3), the D symmetries of **EE**, **EEE**, ..., **E** $\cdots$ **E** (factored n times) will induce time correlation functions and other ensemble averages of the same D symmetry in frame (X,Y,Z). The full D symmetries of the first two terms are

$$\Gamma(\mathbf{E})\Gamma(\mathbf{E}) = D_g^{(0)}+D_g^{(1)}+D_g^{(2)} \ , \tag{7}$$

and

$$\Gamma(\mathbf{E})\Gamma(\mathbf{E})\Gamma(\mathbf{E}) = D_u^{(0)}+3D_u^{(1)}+2D_u^{(2)}+D_u^{(3)} \ , \tag{8}$$

respectively. Here (7) has the same symmetry as the right-hand side of (4), and consequently **EE** may cause the same type of ensemble averages to appear. (Note that **EE** is the complete product of the two vectors **E** and **E**.) For **EEE** the D signature in (8) is ungerade, i.e., odd to even parity reversal, producing a number of new CCF's at field-on equilibrium, which are not considered customarily in, for example, the theory of the Kerr effect. The latter is seriously deficient because of its neglect of these CCF's. The presence of the pseudoscalar symmetry $D_u^{(0)}$ in (8) implies, through principle (3), the existence in (X,Y,Z) of diagonal elements of the odd-parity CCF of the general type

$$\langle \mathbf{A}(0)\mathbf{B}^T(t_1)\mathbf{C}^T(t_2)\rangle \ ,$$

or three-time ACF of the type

$$\langle \mathbf{A}_u(0)\mathbf{A}_u^T(t_1)\mathbf{A}_u^T(t_2)\rangle \ ,$$

where **A** denotes a vector of symmetry $D_u^{(1)}$. There are three $D_u^{(1)}$ terms in (8), implying the existence in (X,Y,Z) of three independent vector triple products; for example,

$$\langle \mathbf{A}(0)\times[\mathbf{A}(t_1)\times\mathbf{A}(t_2)]\rangle \ ,$$

$$\langle [\mathbf{A}(0)\times\mathbf{A}(t_1)]\times\mathbf{A}(t_2)\rangle \ ,$$

$$\langle \mathbf{A}(t_1)\times[\mathbf{A}(t_2)\times\mathbf{A}(0)]\rangle \ ,$$

so that principle (3) predicts the presence of scalar components of these vector quantities, such as

$$\langle A_Y(0)A_X(t_1)A_Y(t_2)\rangle, \quad \langle A_Y(0)A_Y(t_1)A_X(t_2)\rangle \ ,$$

$$\langle A_Z(0)A_X(t_1)A_Z(t_2)\rangle, \quad \langle A_Z(0)A_X(t_2)A_Z(t_1)\rangle \ ,$$

and so on. The field **EEE** may act through the first molecular hyperpolarizability to produce these new CCF's. None of these appears in customary diffusion theory, but can be investigated for time dependence with computer simulation.

HIGHER POWERS OF THE MAGNETIC FIELD B

The magnetic field B is an axial vector of D symmetry, so that the equivalents of (7) and (8) are

$$\Gamma(\mathbf{B})\Gamma(\mathbf{B}) = D_g^{(0)}+D_g^{(1)}+D_g^{(2)} \ , \tag{9}$$

$$\Gamma(\mathbf{B})\Gamma(\mathbf{B})\Gamma(\mathbf{B}) = D_g^{(0)}+3D_g^{(1)}+2D_g^{(2)}+D_g^{(3)} \ , \tag{10}$$

so that **BB**, for example, has the same D symmetry as **EE**, thereby inducing by principle (3) the same symmetry of time correlation function, and ensemble averages in general, in frame (X,Y,Z). Thus both **BB** and **EE** can produce time-asymmetric correlation functions under the proper circumstances. These are completely unknown to standard diffusion theory. The power **BBB** produces even-parity three-time correlation functions similar to the odd-parity equivalents produced by **EEE**.

ELECTROMAGNETIC FIELDS

Depending on polarization, there can be different types of electromagnetic field D symmetry. A circularly polarized electromagnetic field has the D symmetry

$$\Gamma(\mathbf{\Omega})\Gamma(\mathbf{k})=D_g^{(1)}D_u^{(1)}=D_u^{(0)}+D_u^{(1)}+D_u^{(2)} , \tag{11}$$

which is a product of the axial vector $\mathbf{\Omega}$, an axial type representing the spinning electric field component of the electromagnetic field, and the polar propagation vector $\mathbf{k}$. A plane or unpolarized laser on the other hand has the D symmetry

$$\Gamma(\mathbf{E})\Gamma(\mathbf{k})=D_g^{(0)}+D_g^{(1)}+D_g^{(2)} , \tag{12}$$

which is the product of the polar alternating electric field component $\mathbf{E}$ and $\mathbf{k}$. If powerful laser fields interact with molecular ensembles in (X,Y,Z), principle (3) can be used to establish the effect on molecular diffusion processes by considering quadratic and cubic terms in the electromagnetic field strength. The quadratic field symmetry for the circularly polarized field is

$$\Gamma(\mathbf{\Omega})\Gamma(\mathbf{k})\Gamma(\mathbf{\Omega})\Gamma(\mathbf{k}) = 3D_g^{(0)}+6D_g^{(1)}+6D_g^{(2)}+3D_g^{(3)}+D_g^{(4)} , \tag{13}$$

and for the linearly or unpolarized laser it would be

$$\Gamma(\mathbf{E})\Gamma(\mathbf{k})\Gamma(\mathbf{E})\Gamma(\mathbf{k}) = 3D_u^{(0)}+6D_u^{(1)}+6D_u^{(2)}+3D_\mu^{(3)}+D_u^{(4)} , \tag{14}$$

thus generating many types of new ensemble averages with component D symmetries. Similar considerations apply for the recently discovered phenomena[3,6–9] of magneto-chiral and spin-chiral dichroism and, indeed for any external field of force that can be described by a D signature.

PRINCIPLE (3) IN FRAME (x,y,z)

The principle may be extended to frame (x,y,z), or any other, by mapping the D symmetry of frame (X,Y,Z) onto the molecule fixed frame (x,y,z) of the molecular point group using the literature rules of point-group theory. The mapping is interestingly different for each frame (x,y,z), as defined by the appropriate molecular point group. This implies that the set of field-induced ensemble averages in frame (x,y,z) may have different properties for each point group, and this fact can be used in computer simulation as another pattern produced by the applied external field.

CONSEQUENCES

These examples summarize very briefly the fact that external fields set up ensemble averages, such as time correlation functions which take the D symmetry of the applied field, thus showing that molecular diffusion processes have an intricate symmetry of their own which appears as the field is applied.

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