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Symmetry analysis of non-equilibrium time correlation functions

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A symmetry analysis of non-equilibrium time correlation functions is introduced using the principles of group theoretical statistical mechanics and the new fluctuation dissipation theorem of Morriss and D. J. Evans. This approach permits a generalization of the customary Neumann or Curie theorem, providing a new microscopic approach to symmetry rules valid outside the linear regime.

1. Introduction

In this paper, two recent developments are used to give a new generally valid symmetry analysis of equilibrium and non-equilibrium time correlation functions, permitting a generalization of the customary Neumann or Curie theorem, and providing a new microscopic approach to symmetry rules valid outside the linear regime. The first development is the new fluctuation-dissipation theorem [1] of Morriss and Evans, which is valid both for linear and non-linear time correlation functions, and the second is the emergence [2–6] of the three principles of group theoretical statistical mechanics. In § 1 of this paper the three principles are given to introduce the fundamentals of symmetry in this context, and in § 3 a brief description is given of the Morriss–Evans theorem with examples of its application. Section 4 merges the two developments to give a new appreciation of non-linear fluctuation–dissipation processes.

2. The principles of group theoretical statistical mechanics

In considering fluctuation processes at thermodynamic equilibrium [7–15] and dissipation after the removal [16–20] of an applied external field of arbitrary strength it is possible to utilise the symmetry rules of group theory [21–23] in the laboratory frame (X, Y, Z) and in the molecule fixed frame (x, y, z). These rules provide [2–6] a set of three generally valid principles, the first of which is the Neumann or Curie principle [24–26] stated in terms of contemporary group theory.

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2.1. *Principle (1)*

The thermodynamic ensemble average $\langle ABC \ldots\rangle$ over the product of quantities $ABC \ldots$ exists at equilibrium if the product of symmetry representations of A, B, C, ... contains at least once the totally symmetric representation, $D_g^{(0)}$, of the $R_h(3)$ rotation–reflection point group in the laboratory frame (X, Y, Z).

2.2. *Principle (2)*

This thermodynamic average exists at equilibrium in the molecule fixed frame (x, y, z) of the point group character tables if the product of symmetry representations in the molecular point group contains the point group's totally symmetric representation at least once [24].

2.3. *Principle (3)*

If an ensemble of atoms or molecules is brought to a steady state out of true thermodynamic equilibrium by an externally applied field of arbitrary strength and given symmetry, extra ensemble averages may appear in the ensemble with the symmetry of the applied field.

In the laboratory frame (X, Y, Z) the irreducible representations of $R_h(3)$ are the D representations $D_g^{(0)}, \ldots, D_g^{(n)}$ and $D_u^{(0)}, \ldots, D_u^{(n)}$. The superscripts denote the order of the spherical harmonics and the subscripts g and u denote respectively even and odd to parity reversal symmetry. In this notation a scalar has the totally symmetric representation $D_g^{(0)}$; a pseudoscalar such as optical rotation angle is denoted $D_u^{(0)}$; a polar vector such as linear velocity is $D_u^{(1)}$; an axial or pseudovector such as angular velocity is $D_g^{(1)}$; a traceless symmetric tensor such as molecular quadrupole moment is $D_g^{(2)}$; and an odd parity traceless second rank tensor is $D_u^{(2)}$.

With these definitions it is possible to proceed to the symmetry description of the time correlation function, which in general is $\langle \mathbf{A}(0)\mathbf{B}^{\mathrm{T}}(t)\rangle$, where $\mathbf{A}$ and $\mathbf{B}$ are vector quantities representing molecular dynamical variables. In representing this product use is made of the Clebsch–Gordan theorem to expand the product of D representations into a sum of individual D components

$$D^{(n)}D^{(m)} = D^{(n+m)} + \ldots + D^{(|n-m|)}. \tag{1}$$

If $\mathbf{A}$ and $\mathbf{B}$ have the same parity symmetry the Clebsch–Gordan product is gerade, and it is ungerade if $\mathbf{A}$ and $\mathbf{B}$ have opposite parity reversal symmetries. Assuming the latter to be the case, with, for example, $\mathbf{A}$ representing molecular linear velocity, $\mathbf{v}$ (u) and $\mathbf{B}$ molecular angular velocity, $\boldsymbol{\omega}(g)$, we have

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

providing scalar, vector, and tensor components of the time correlation function $\langle \mathbf{v}(t)\boldsymbol{\omega}^{\mathrm{T}}(0)\rangle$.

2.4. *The scalar component, $D_u^{(0)}$*

This represents the dot product, the trace of the matrix

$$\langle \mathbf{v}(0)\,.\,\boldsymbol{\omega}(t)\rangle = \langle v_X(0)\omega_X(t)\rangle + \langle v_Y(0)\omega_Y(t) + (v_Z(0)\omega_Z(t)\rangle. \tag{3}$$

2.5. *The vector component, $D_u^{(1)}$*

This is the cross product

$$\begin{aligned}\langle \mathbf{v}(0) \times \boldsymbol{\omega}(t)\rangle = {} & (\langle v_Y(0)\omega_Z(t)\rangle - \langle v_Z(0)\omega_Y(t)\rangle)\mathbf{i}\\ & + (\langle v_Z(0)\omega_X(t)\rangle - \langle v_X(0)\omega_Z(t)\rangle)\mathbf{j}\\ & + (\langle v_X(0)\omega_Y(t)\rangle - \langle v_Y(0)\omega_X(t)\rangle)\mathbf{k},\end{aligned} \tag{4}$$

where **i**, **j**, and **k** are respectively unit vectors in the X, Y, and Z axes of the laboratory frame (X, Y, Z). These off-diagonals are asymmetric in the relevant axis subscripts, i.e.

$$\langle v_X(0)\omega_Z(t)\rangle = -\langle v_Z(0)\omega_X(t)\rangle \tag{5}$$

and so on.

2.6. *The tensor component, $D_u^{(2)}$*

This is the traceless part of the generic tensor product

$$\begin{bmatrix} 0 & \langle v_X(0)\omega_Y(t)\rangle\mathbf{i}\mathbf{j}^{\mathrm{T}} & \langle v_X(0)\omega_Z(t)\rangle\mathbf{i}\mathbf{k}^{\mathrm{T}}\\ \langle v_Y(0)\omega_X(t)\rangle\mathbf{j}\mathbf{i}^{\mathrm{T}} & 0 & \langle v_Y(0)\omega_Z(t)\rangle\mathbf{j}\mathbf{k}^{\mathrm{T}}\\ \langle v_Z(0)\omega_X(t)\rangle\mathbf{k}\mathbf{i}^{\mathrm{T}} & \langle v_Z(0)\omega_Y(t)\rangle\mathbf{k}\mathbf{j}^{\mathrm{T}} & 0 \end{bmatrix}, \tag{6}$$

with off-diagonal components symmetric in the axis subscripts

$$\langle v_X(0)\omega_Z(t)\rangle = \langle v_Z(0)\omega_X(t)\rangle \tag{7}$$

in contrast to equation (5).

2.7. *Application of principles (1) and (3)*

With these definitions we may exemplify the application of Principles (1) and (3) to an atomic or molecular ensemble in the laboratory frame (X, Y, Z). (Principle (2) deals with frame (x, y, z) in molecular ensembles.)

Principle (1) means that no component of the tensor cross correlation function (c.c.f.) $\langle \mathbf{v}(0)\boldsymbol{\omega}^{\mathrm{T}}(t)\rangle$ exists at field free thermodynamic equilibrium because the right-hand side of equation (2) does not contain the totally symmetric representation $D_g^{(0)}$. This is what is found by computer simulation [27–30]. For the generic auto correlation function, however, the u subscript in equation (2) is replaced by a g subscript, and consequently the trace of $\langle \mathbf{A}(0)\mathbf{A}^{\mathrm{T}}(t)\rangle$ exists at thermodynamic equilibrium, being the time auto correlation function (a.c.f.) $\langle \mathbf{A}(0) \,.\, \mathbf{A}(t)\rangle$ whose symmetry is the totally symmetric representation $D_g^{(0)}$ of $R_h(3)$.

In the presence of a Z axis static electric field, computer simulations [27–30] have shown the existence of

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

whose symmetry signature is $D_u^{(1)}$. Principle (3) links this result to the symmetry of the electric field **E**, a $D_u^{(1)}$ polar vector: the induced thermodynamic average in the field-on steady state has the symmetry $(D_u^{(1)})$ of the inducing field itself, and this is true irrespective of the field strength. The $D_u^{(1)}$ symmetry average (8) vanishes only when $\boldsymbol{E} = \mathbf{0}$.

In the presence of shear, inducing a strain rate $\partial v_X/\partial Z$ of symmetry $D_g^{(0)} + D_g^{(1)} + D_g^{(2)}$ [31–33], Principle (3) means that ensemble average such as time correlation functions will appear with the same overall symmetry. These are exemplified by the time *asymmetric* velocity c.c.f.'s [31–33]

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

which comprised a weighted sum of time antisymmetric $D_g^{(1)}$ components and time symmetric $D_g^{(2)}$ components:

$$D_g^{(1)}\colon \langle v_X(0)v_Z(t)\rangle = -\langle v_Z(0)v_X(t)\rangle, \tag{10}$$

$$D_g^{(2)}\colon \langle v_X(0)v_Z(t)\rangle = \langle v_Z(0)v_X(t)\rangle \tag{11}$$

A third example of Principle (3) is the illustration of the expected symmetry effect of a chiral influence, recently defined by Barron [34] as an external influence which is odd to parity reversal and even to time reversal symmetry. In magneto-chiral dichroism [35–37] for example, the chiral influence is a combination of the magnetic field $\mathbf{B}(D_g^{(1)})$ and the propagation vector $\mathbf{k}(D_u^{(1)})$ of unpolarised or linearly polarized electromagnetic radiation. The symmetry signature of this chiral field is given by the product of symmetry representations

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

being again a sum of scalar, vector and tensor components, all odd to parity reversal and even to time reversal. In principle, therefore, a chiral influence allows the existence of ungerade time c.c.f.'s of the types (3), (4), and (6). If the applied chiral influence is made up of two co-linear vectors, only the trace of the field induced c.c.f., equation (3), will be expected, otherwise, vector and tensor types (4) and (6) will also be induced by principle (3).

3. New fluctuation dissipation theorems

The set of field induced time cross-correlation functions just exemplified will be accompanied by a set of new fluctuation-dissipation theorems which are new generalized Green–Kubo relations. This is a direct consequence of the Morriss–Evans theorem [1], recently derived by Morriss and Evans in the context of non-equilibrium molecular dynamics computer simulation. It was derived by these authors from first principles, and can be stated through the equation

$$\langle B(t)\rangle = \langle B(0)\rangle - \frac{F_e}{kT}\int_0^t \langle B(s)J(0)\rangle\, ds, \tag{13}$$

where $B(t)$ is an arbitrary time dependent phase variable of the ensemble and where F_e and J are respectively the applied force field and dissipative flux, defined by

$$\frac{dH_0}{dt} = -JF_e \tag{14}$$

The theorem, equation (13), generalizes the traditional Green–Kubo relations to arbitrary applied field strength, and therefore takes them outside the area of linear-response theory. They link the non-equilibrium value of the phase variable, (the left-hand side of equation (13)) to the integral over a time correlation function between the dissipative flux $J(0)$ in the equilibrium state and B at a time s after the external field F_e has been turned on.

In response to an external influence, the molecular dynamics ensemble is governed by a new set of fluctuation dissipation theorems of the Morriss–Evans type. For example, if the external influence is a Z component of a static electric field, there is a torque $-\boldsymbol{\mu} \times E_Z$ between this and the molecular dipole moment $\boldsymbol{\mu}$. This is accompanied by an energy $\boldsymbol{\mu} \,.\, E_Z$. The Morriss–Evans theorem then reads

$$\langle B(t)\rangle = \langle B(0)\rangle - \frac{E_Z}{kT}\int_0^t \langle B(s)\dot{\mu}_Z(0)\rangle\, ds, \tag{15}$$

where $\dot{\mu}_Z$ is the Z component of the molecular rotational velocity [38]. The quantity $B(t)$ is in general any time dependent variable of relevance, for example, the molecular dipole moment itself or the molecular rotational velocity, its time derivative. In each case we recover generalizations of the traditional fluctuation dissipation theorems of dielectric relaxation

$$\langle \mu_Z(t)\rangle = -\frac{E_Z}{kT}\int_0^t \langle \mu_Z(s)\dot{\mu}_Z(0)\rangle\, ds, \tag{16}$$

$$\langle \dot{\mu}_Z(t)\rangle = -\frac{E_Z}{kT}\int_0^t \langle \dot{\mu}_Z(s)\dot{\mu}_Z(0)\rangle\, ds, \tag{17}$$

relating the transients on the left-hand sides to the non-equilibrium time correlation functions on the right-hand sides.

Furthermore, any cross correlation function which exists by principle (3) will be related through the Morriss–Evans theorem to its own field induced transient. This is a key result which generalizes the traditional Neumann or Curie principle (1) and provides new fluctuation dissipation relations valid outside the area covered by the traditional Green–Kubo approach. It also breaks new ground (§ 3) not covered by the Onsager–Casimir reciprocal principles, which are derived from considerations of time correlation functions.

For example, principle (1) allows the time cross-correlation function $\langle \mathbf{v}(t)\dot{\mu}_Z(0)\rangle$ to exist at field free equilibrium because the relevant product of representations contains $D_g^{(0)}$ once (the trace). In the presence of a Z axis static electric field this trace is supplemented by $D_u^{(1)}$ averages according to principle (3). The Morriss–Evans theorem (13) then allows the relations

$$\langle \mathbf{v}(t)\rangle = -\frac{E_Z}{kT}\int_0^t \langle \mathbf{v}(s)\dot{\mu}_Z(0)\rangle\, ds, \tag{18}$$

$$\langle \boldsymbol{\omega}(t)\rangle = -\frac{E_Z}{kT}\int_0^t \langle \boldsymbol{\omega}(s)\dot{\mu}_Z(0)\rangle\, ds, \tag{19}$$

for example for arbitrary electric field strengths, the integrands being, as usual, non-equilibrium time correlation functions. In the first example, equation (18), the symmetry signature of the non-equilibrium time c.c.f. $\langle \mathbf{v}(s)\dot{\mu}_Z(0)\rangle$ is

$$\Gamma(\mathbf{v}(s))\Gamma(\dot{\mu}_Z(0)) = D_u^{(1)}D_u^{(1)} = D_g^{(0)} + D_g^{(1)} + D_g^{(2)}, \tag{20}$$

which contains $D_g^{(0)}$ once. Consequently this c.c.f. exists: (1) at field free equilibrium; (2) at the field on steady state. Its transient (or non-equilibrium) counterpart also exists, with the same symmetry signature. In the second example, equation (19), the symmetry signature of the non-equilibrium time c.c.f. is

$$\Gamma(\boldsymbol{\omega}(s))\Gamma(\dot{\mu}_Z(0)) = D_g^{(1)}D_u^{(1)} = D_u^{(0)} + D_u^{(1)} + D_u^{(2)}, \tag{21}$$

which does not contain $D_g^{(0)}$ but contains $D_u^{(1)}$ once. By principle (1) the c.c.f. vanishes at field free equilibrium and by principle (3) its $D_u^{(1)}$ (vector) component exists in the presence of the $D_u^{(1)}$ electric field in the field on steady state. The Morriss–Evans relation (13) then follows for arbitrary electric field strength. In both examples (18) and (19) new transients appear on the left-hand sides which are not considered in traditional fluctuation dissipation and linear response theory, but which are symmetry allowed by principles (1) and (3) of group theoretical statistical mechanics. Further examples of this type, induced by a Z axis electric field, are

$$\langle \mathbf{v}(t) \,.\, \boldsymbol{\mu}(t)\rangle = -\frac{E_Z}{kT}\int_0^t \langle \mathbf{v}(s) \,.\, \boldsymbol{\mu}(s)\dot{\mu}_Z(0)\rangle \, ds, \tag{22}$$

$$\langle \mathbf{v}(t) \times \boldsymbol{\mu}(t)\rangle = -\frac{E_Z}{kT}\int_0^t \langle \mathbf{v}(s) \times \boldsymbol{\mu}(s)\dot{\mu}_Z(0)\rangle \, ds \tag{23}$$

and it is clear that there are many more. Each of these could be characterized by computer simulation and each contribute to the overall transient process. This shows that no molecular diffusion process is independent, as in the traditional approach: rotational, orientational, centre of mass translational, and vibrational diffusion processes are linked ineluctably at the fundamental molecular or atomic level through a well defined set of time cross-correlation functions and fluctuation-dissipation theorems which are generalized Green–Kubo relations.

4. Discussion

The combination of symmetry and fluctuation dissipation theory discussed in §§ 1 and 2 is valid in the non-linear regime, and the theory is not restricted to linear response. This has consequences for the Onsager–Casimir reciprocal relations [39–41], which require symmetry in the exchange of indices of quantities such as diffusion coefficients which are integrals over time correlation functions. Well known examples are provided in textbooks such as Landau and Lifshitz [42] which state that kinetic coefficients (γ) satisfy the Onsager–Casimir symmetry principle

$$\gamma_{ij} = \gamma_{ji}. \tag{24}$$

Traditional examples of these kinetic coefficients are the thermal conductivity and viscosity. However, these relations are valid only for a situation close to equilibrium, where a linear phenomenological relation exists between flux and force [43]. The master equation governing the fluctuation is a simple Fokker Planck equation, whose solution is governed by a gaussian distribution function. Onsager discussed [44, 45] the reciprocity of kinetic coefficients on the basis of microscopic reversibility, i.e. detailed balance as used in the derivation of the Boltzmann equation. For arbitrary applied field strengths, however, the Onsager–Casimir relations conflict with the results of this paper, as in the following example, because the Onsager coefficient has a non-vanishing antisymmetric part out of thermodynamic equilibrium, discussed by Tomita and Tomita [43]. These authors have provided a formal discussion of the breakdown of the Onsager–Casimir reciprocal relations in terms of 'a circulation of fluctuation', called 'the mean angular momentum of the probability fluid' which depends directly on the absence of microscopic reversibility as assumed by Onsager in an ensemble near to equilibrium. As pointed out by Tomita and Tomita [43], Onsager assumed the symmetry of his phenomenological coefficient by first considering time correlation functions. Our example, taken from the recent non-equilibrium computer simulation of M. W. Evans and Heyes [31–33], shows directly that in the presence of a strain rate of the type $\partial v_X/\partial Z$, time asymmetric cross-correlation functions appear in frame (X, Y, Z) in the field on steady-state, equations (9) to (11). Integration provides kinetic coefficients (i.e. cross-diffusion coefficients) that clearly are neither symmetric nor antisymmetric in the exchange of indices X and Z, in this case orthogonal cartesian components of the laboratory frame (X, Y, Z)

$$\int_0^\infty \langle v_X(0)v_Z(t)\rangle \, dt \neq \int_0^\infty \langle v_Z(0)v_X(t)\rangle \, dt. \tag{25}$$

Furthermore, the result (25) is independent of the strength of the applied force field, in this case a shear in couette flow. This unexpectedly leads to the result that the Onsager–Casimir reciprocal relations are never exactly valid in this case, even in the limit of linear response, when the strain rate is small and the response to shear is Newtonian. On the other hand, the results of this paper, i.e. a fusion of the Morriss–Evans theorem with principles (1) to (3), deals with the computer simulation results adequately for arbitrary applied field strength.

In conclusion, this paper has developed a new symmetry based method of generalizing the Neumann or Curie theorem for arbitrary applied field strength, allowing new insights to Green–Kubo and Onsager–Casimir theory of molecular and atomic ensembles.

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