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GROUP THEORETICAL TREATMENT OF CLASSICAL n-TIME CORRELATION FUNCTIONS

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The methods of group theoretical statistical mechanics are used to investigate the set of n-time correlation functions in isotropic molecular liquids and in molecular liquids subjected to external electric and magnetic fields. It is found that the group theory corroborates the results of computer simulation where these are available, both for auto- and cross-correlation functions, in the field-off and field-on equilibrium conditions. Many more elements of the time correlation functions are allowed by symmetry in the presence of fields. For the first time, the symmetry and time dependence of higher-order n-time correlation functions are investigated by group theory. This results in a great simplification of the exploratory work of the computer simulator, because the group theory clearly distinguishes between those elements that vanish for all t and those that may exist in the laboratory frame (X, Y, Z) and the molecule-fixed frame (x, y, z). Group theoretical statistical mechanics reveal clearly that the statistics of a molecular liquid cannot be Gaussian in general, because three-time and higher-order correlation functions exist by symmetry. These should be observable in future computer simulation. Thus we arrive at the important conclusion that group theory applied to the dynamics of molecules in the liquid state invalidates a large number of literature theories of diffusion, including all those based on the Debye concept of "rotational" diffusion. These theories should be modified accordingly.

1. Introduction

The methods of non-equilibrium statistical mechanics [1–5] have recently been supplemented by a powerful new axiom, that the ensemble average can be treated using the methods of group theory [1]. The new methods of "group theoretical statistical mechanics" allow the determination of non-vanishing elements of time correlation functions, including cross-correlation functions (ccfs). The application of group theory very clearly reveals that certain elements vanish for all t at field-free equilibrium, that others exist for $0 < t < \infty$, and that still others appear when the molecular liquid is subjected to external force fields such as a magnetic field $\boldsymbol{H}$ or eletric field $\boldsymbol{E}$. Time correlation functions are Fourier transforms of spectra, and can also be integrated to provide transport coefficients. They are cornerstones of any detailed investigation of the condensed phase dynamics of molecular matter. The application of two-time autocorrelation functions (acfs) such as $\langle A(t) A^{\mathrm{T}}(0) \rangle$ is well known in the literature [6] on the various kinds of spectra of the liquid state, and it is slowly becoming apaparent that cross-correlation functions are important to the fundamental theory of liquid state chemical reactions [3,7], to the understanding of field effects [5], including electric, magnetic, and electromagnetic fields, and to the fundamental theory of molecular dynamics [1–5]. The detailed time dependences of some members of the set of non-vanishing time ccfs are known from computer simulations [8–12], and consideration of the properties of members of this set has recently been extended to cross-correlations between molecular translation, rotation, and vibration. In recent years the fundamental characteristics of molecular diffusion have been found to be non-Gaussian [13], non-Markovian [13,14], and non-linear [15]. The diffusion equations [16] used for the description of the molecular liquid state have therefore to be a class of stochastic non-linear partial differentials such as the Kramers equations. Consideration of their structures leads to the necessity of expanding our knowl-

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edge of time correlation functions as a class. In the treatment of non-Gaussian processes, for example [15], knowledge is required about three-time correlation functions such as $\langle \boldsymbol{v}(t_1)\boldsymbol{v}^{\mathrm{T}}(t_2)\boldsymbol{v}^{\mathrm{T}}(t_3)\rangle$, where $\boldsymbol{v}$ is the molecular linear centre of mass velocity, or $\langle \boldsymbol{\omega}(t_1)\boldsymbol{\omega}^{\mathrm{T}}(t_2)\boldsymbol{\omega}^{\mathrm{T}}(t_3)\rangle$, where $\boldsymbol{\omega}$ is the angular velocity. Fuller considerations take into account all members of the set of multi-time correlation functions $\langle \boldsymbol{A}(t_1)...\boldsymbol{A}^{\mathrm{T}}(t_n)\rangle$. Other branches of the theory of molecular dynamics [17–20] require consideration of cross-correlation functions of the type $\langle \boldsymbol{A}_{(1)}(t)\boldsymbol{A}^{\mathrm{T}}_{(2)}(0)\rangle$ between the same dynamical variable on different molecules. These latter may have the same symmetry, as in a pure molecular liquid, or different symmetry as in a solution of non-reacting or reacting molecules. Standard theories of molecular diffusion are usually severely restricted by the assumption that one mode of motion, such as translation, is independent of others such as whole molecule rotation and intra-molecular vibration within the diffusing molecule. If these restrictions are lifted it immediately becomes necessary to investigate ccfs, and therefore it becomes essential to know how many elements vanish for all t due to symmetry, and to classify those that do not vanish for the various molecular point groups. This lays the foundations for future theories and computer simulations of the class of non-vanishing time correlation functions in general, and for its utilisation in many circumstances of interest. For the purposes of group theoretical statistical mechanics this class is made as broad as possible, and includes members from two-, three- and n-time correlation functions, and equivalent cross-correlation functions, between molecular dynamical variables such as translation, rotation and vibration. In principle, consideration can be extended to quantum mechanics of molecular diffusion in the liquid state [21].

In this paper the methods of classification are developed for two-, three- and four-time correlation functions of the C_{2v} point group, representing a dipolar symmetry such as that of water or dichloromethane, and for the T_d non-dipolar point group exemplified by a solvent such as carbon tetrachloride. Vanishing and non-vanishing elements are classified for time correlations involving translation, rotation and normal modes of vibration, and the effect of fields such as $\boldsymbol{E}$ and $\boldsymbol{H}$ established in the laboratory frame (X, Y, Z) and the molecule-fixed frame (x, y, z) of the standard literature point group character tables [22–25]. The results serve as reference data for theories of diffusion in a particular context, such as the treatment of non-Gaussian molecular statistical mechanics, the theory of intermolecular correlation and chemical reactions in solution.

2. Field-free equilibrium. Laboratory frame (X, Y, Z)

2.1. Two-time acfs

In group theory [1] the symmetry of the frame (X, Y, Z), that of isotropic three-dimensional space is the rotation–reflection group $R_h(3)$, whose irreducible representations [23,24] are denoted $D_g^{(0)}, ..., D_g^{(n)}$ and $D_u^{(0)}, ..., D_u^{(n)}$. Here the subscripts g and u denote gerade and ungerade respectively, and the superscripts the order of the irreducible representation. In this notation, a scalar has symmetry $D_g^{(0)}$, a polar vector such as $\boldsymbol{v}$ is $D_u^{(1)}$, and an axial vector such as $\boldsymbol{\omega}$ is $D_g^{(1)}$. The statistical mechanical ensemble average $\langle A\rangle$, where A is a dynamical variable, will exist if the symmetry representation of A includes the totally symmetric representation (tsr) of the group $R_h(3)$, i.e. $D_g^{(0)}$. Therefore an average over a scalar will always exist in frame (X, Y, Z), an average over a vector such as $\boldsymbol{v}$ or $\boldsymbol{\omega}$ will vanish. The two-time autocorrelation function $\langle \boldsymbol{A}(t)\boldsymbol{A}^{\mathrm{T}}(0)\rangle$ exists in frame (X, Y, Z) because the product of representations $\Gamma(\boldsymbol{A}(t))\Gamma(\boldsymbol{A}(0))$ always contains the tsr $D_g^{(0)}$. This can be demonstrated with the Clebsch–Gordan theorem:

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

From (1) it is clear that the product of a symmetry representation $D^{(n)}$ with itself will always contain $D_g^{(0)}$, and that a two-time acf will exist in frame (X, Y, Z).

.2. *Two-time ccfs*

A time cross-correlation function $\langle \boldsymbol{A}(0)\boldsymbol{B}^{\mathrm{T}}(t)\rangle$ will exist in the laboratory frame (X, Y, Z) if the product of epresentations $\Gamma(\boldsymbol{A})\Gamma(\boldsymbol{B})$ contains the tsr at least once. If the tsr appears more than once, then more than one ndependent element of the ccf exists for $0<t<\infty$. For example, the ccf $\langle \boldsymbol{\omega}(t)\boldsymbol{v}^{\mathrm{T}}(0)\rangle$ vanishes for all t, i.e. the cf has no non-vanishing elements in frame (X, Y, Z). The time dependences of such ccfs have recently been studied in detail using computer simulation [8–12]. The results of group theoretical statistical mechanics and of computer simulation are entirely in agreement, i.e. the elements predicted by the former to exist for $0<t<\infty$ are indeed found to have a dependence upon time in several independent simulation algorithms.

2.3. *Three-time acfs*

The theory of non-Gaussian processes [15] takes into consideration three-time and multi-time correlation functions, both for linear centre-of-mass diffusion, involving $\boldsymbol{v}$, and rotational diffusion involving the molecular angular velocity $\boldsymbol{\omega}$. The three- and odd-time acfs vanish for Gaussian processes and the even-time cfs reduce to products of two-time correlation functions. However, computer simulations [6,14,15] have shown clearly that the diffusion process is in general [13] non-Gaussian and non-Markovian, so that a method is needed to determine which elements of the possible multi-time cfs exist in frame (X, Y, Z), and also in the molecule-fixed frame (x, y, z). Group theoretical statistical mechanics [1–5] reveals immediately results such as the following two examples.

(1) Three-time and odd multi-time correlation functions involving a polar vector of $D_{\mathrm{u}}^{(1)}$ symmetry such as $\boldsymbol{v}$ vanish for all t, because the relevant product of representations does not contain $D_{\mathrm{g}}^{(0)}$. However, this does not imply that the diffusion process is in general Gaussian, because the even-time cfs of all orders will exist and will not in general reduce to products of two-time correlation functions. Evidence is available from several computer simulations [6,13–15] to show that the linear velocity's diffusion process is in general non-Gaussian.

(2) Three-time and odd multi-time correlation functions involving an axial vector of $D_{\mathrm{g}}^{(1)}$ symmetry such as $\boldsymbol{\omega}$ exist in general, because the products contain $D_{\mathrm{g}}^{(0)}$. This result, obtained on the grounds of symmetry alone, is in direct contradiction with diffusion equations that do not take into account the non-Gaussian nature of the molecular liquid state, such as the simple Smoluchowski and Fokker–Planck equations [14,15], but again in agreement with the indications of computer simulations in frame (X, Y, Z). These show that diffusion processes involving $\boldsymbol{\omega}$ are in general non-Gaussian, non-Markovian and non-linear.

2.4. *Three-time ccfs*

The existence of two-time ccfs such as $\langle \boldsymbol{A}(0)\boldsymbol{B}^{\mathrm{T}}(t)\rangle$ in frame (X, Y, Z) implies that of higher-order ccfs, and the set of non-vanishing three-time ccfs can be defined to exist for $0<t<\infty$ if the relevant product of representations contains the tsr at least once. For example, the three-time ccf may exist if the vectors making up the products are all gerade or all ungerade, but will always vanish for all t if the product of the three is of ungerade parity.

3. Field-free equilibrium. Molecule-fixed frame (x, y, z)

Ensemble averages of statistical mechanics can be written in terms of the molecule-fixed frame (x, y, z) as well as the laboratory-fixed frame (X, Y, Z). In fame (x, y, z) time cross-correlation functions can exist for $0<t<\infty$ which vanish for all t in frame (X, Y, Z). An example is $\langle \boldsymbol{v}(t)\boldsymbol{\omega}^{\mathrm{T}}(0)\rangle$, which was first discovered by computer simulation [8]. In frame (x, y, z) the symmetry of scalars, vectors and tensors is different for each molecular point group, thus implying the need for separate consideration of non-vanishing ccf elements for different types of molecule.

3.1. The C_{2v} point group

A diffusing molecule with C_{2v} symmetry is a dipolar asymmetric top. An example is the water molecule. The symmetry of a vector such as $\boldsymbol{v}$ or $\boldsymbol{\omega}$ is found by mapping the representation in frame (X, Y, Z), i.e. the $R_h(3)$ rotation–reflection group, onto C_{2v}. The methods for doing this are available in the literature [23]. A scalar in the point group C_{2v} has the totally symmetric representation A_1, the polar vector $\boldsymbol{v}$ maps onto $A_1+B_1+B_2$; and the axial vector $\boldsymbol{\omega}$ onto $A_2+B_1+B_2$. The product of representations of the time ccf $\langle \boldsymbol{v}(t)\boldsymbol{\omega}^T(0)\rangle$ is therefore

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

which shows that A_1 occurs twice. This implies [1–5] that two independent elements of the ccf exist in frame (x, y, z) for $0<t<\infty$. The results of computer simulation fully agree with this prediction, for C_{2v} diffusing asymmetric tops such as water and dichloromethane. Traditional theories of diffusion, based on Smoluchowski. Fokker–Planck and Kramers equations, have not yet been effective in reproducing such fundamental properties of the molecular liquid state, and much remains to be done in modifying the equations themselves and in finding effective numerical algorithms for their solution. The diffusion equations must ultimately be capable of predicting the non-vanishing ccfs of all orders, both in frame (X, Y, Z) and (x, y, z). In this context, group theoretical statistical mechanics is a powerful guide, for example, in the context of three-time acfs and ccfs in frame (x, y, z).

3.1.1. Time ccfs involving the molecular Coriolis acceleration, $2\boldsymbol{v}\times\boldsymbol{\omega}$

An example of a physically meaningful three-time ccf in frame (x, y, z) is that [26–30] between the molecular Coriolis acceleration $2\boldsymbol{v}\times\boldsymbol{\omega}$, and the same molecule's linear velocity $\boldsymbol{v}$ or angular velocity $\boldsymbol{\omega}$. The ccf under consideration may be defined as $\langle 2[\boldsymbol{v}(t)\times\boldsymbol{\omega}(t)]\boldsymbol{v}^T(0)\rangle$ or $\langle 2[\boldsymbol{v}(t)\times\boldsymbol{\omega}(t)]\boldsymbol{\omega}^T(0)\rangle$ in frame (x, y, z). It is clear from foregoing considerations that the second of these ccfs disappears in the laboratory frame (X, Y, Z) because the parity of $\boldsymbol{v}$ is ungerade and that of $\boldsymbol{\omega}$ is gerade. This is corroborated by computer simulation [31]. In the frame (x, y, z), computer simulations have revealed non-vanishing diagonal elements of the ccf between the Coriolis acceleration and the molecular linear velocity, $\boldsymbol{v}$, in frame (x, y, z) for $0<t<\infty$. All elements of $\langle 2[\boldsymbol{v}(t)\times\boldsymbol{\omega}(t)]\boldsymbol{\omega}^T(0)\rangle$ vanish in the simulation [31] for all t for C_{2v} symmetry in both frames. The following illustrates how group theoretical statistical mechanics reproduces this result precisely. As yet there is no equivalent procedure from the traditional theory of molecular diffusion.

3.1.2. Time ccf between Coriolis acceleration and linear velocity

The symmetry representation of the Coriolis acceleration in frame (x, y, z) is the product $\Gamma(\boldsymbol{v})\Gamma(\boldsymbol{\omega})$, so that the symmetry of the complete time ccf is $6A_1+7A_2+7B_1+7B_2$. This contains the tsr of the group C_{2v} six times, implying that there are six independent elements of the general triple product $\langle \boldsymbol{v}(t)\boldsymbol{\omega}^T(t)\boldsymbol{v}^T(0)\rangle$ that may have a finite time dependence for $0<t<\infty$. Thus, 21 out of the 27 possible elements of the tensor triple product $\langle \boldsymbol{v}(t)\boldsymbol{\omega}^T(t)\boldsymbol{v}^T(0)\rangle$ must vanish for all t in frame (x, y, z). To investigate the origin of the six non-vanishing elements we note that they come from the following triple products of irreducible representations:

$$B_1B_1A_1\equiv\langle v_x\omega_y v_z\rangle\equiv\langle(\boldsymbol{v}\times\boldsymbol{\omega})_z v_z\rangle,\quad B_2B_2A_1\equiv\langle v_y\omega_x v_z\rangle\equiv\langle(\boldsymbol{v}\times\boldsymbol{\omega})_z v_z\rangle,$$

$$A_1B_1B_1\equiv\langle v_z\omega_y v_x\rangle\equiv\langle(\boldsymbol{v}\times\boldsymbol{\omega})_x \boldsymbol{v}_x\rangle,\quad B_2A_2B_1\equiv\langle v_y\omega_z v_x\rangle\equiv\langle(\boldsymbol{v}\times\boldsymbol{\omega})_x v_x\rangle,$$

$$A_1B_2B_2\equiv\langle v_z\omega_x v_y\rangle\equiv\langle(\boldsymbol{v}\times\boldsymbol{\omega})_y v_y\rangle,\quad B_1A_2B_2\equiv\langle v_x\omega_z v_y\rangle\equiv\langle(\boldsymbol{v}\times\boldsymbol{\omega})_y v_y\rangle.$$

Considering the product $B_1B_1A_1$ for example, it represents $\langle v_x\omega_y v_z\rangle$ because in the product of representations $\Gamma(\boldsymbol{v})\Gamma(\boldsymbol{\omega})\Gamma(\boldsymbol{v})$, B_1 refers to $\boldsymbol{v}$, the second B_1 to $\boldsymbol{\omega}$ and A_1 to $\boldsymbol{v}$. The existing element of the time ccf $\langle 2[\boldsymbol{v}(t)\times\boldsymbol{\omega}(t)]\boldsymbol{v}^{\mathrm{T}}(0)\rangle$ in frame (x, y, z) represented by the product $B_1B_1A_1$ is therefore $\langle 2v_x\omega_y v_z\rangle$. Similarly, the existing element represented by $B_2B_2A_1$ is $\langle 2v_y\omega_x v_z\rangle$. Proceeding in this way it can be seen that the non-vanishing elements of $\langle 2[\boldsymbol{v}(t)\times\boldsymbol{\omega}(t)]\boldsymbol{v}^{\mathrm{T}}(0)\rangle$ are the diagonal elements $\langle 2[\boldsymbol{v}(t)\times\boldsymbol{\omega}(t)]_i v_i(0)\rangle$; $i=x, y, z$. In general these have a different time dependence in frame (x, y, z) because they are independent by symmetry, and this is exactly what is found by computer simulation, both in liquid water [32] and in liquid dichloromethane [31].

3.1.3. ccf between Coriolis acceleration and angular velocity

This ccf is a special case of the tensor triple product $\langle \boldsymbol{v}(t)\boldsymbol{\omega}^{\mathrm{T}}(t)\boldsymbol{\omega}^{\mathrm{T}}(0)\rangle$ with 27 elements in general. In the point group C_{2v} the product of representations $\Gamma(\boldsymbol{v})\Gamma(\boldsymbol{\omega})\Gamma(\boldsymbol{\omega})$ is $7A_1+6A_2+7B_1+7B_2$, indicating that there are seven occurrences of the tsr A_1. However, only two of these have a meaningful Cartesian representation from the C_{2v} point group character table, and these are the triple products $B_1B_2A_2$ and $B_2B_1A_2$, equivalent to $\langle\omega_y v_y\omega_z\rangle$ and $\langle\omega_x v_x\omega_z\rangle$ in the general triple product $\langle\boldsymbol{\omega}(t)\boldsymbol{v}^{\mathrm{T}}(t)\boldsymbol{\omega}^{\mathrm{T}}(0)\rangle$. These elements do not occur in the ccf $\langle 2[\boldsymbol{\omega}(t)\times\boldsymbol{v}(t)]\boldsymbol{\omega}^{\mathrm{T}}(0)\rangle$ which is therefore zero for all t. Again this is precisely what is found for all nine elements of the ccf by separate computer simulation, both in liquid water and liquid dichloromethane. The five other triple products of representations that give A_1 are $A_1A_2A_2$, $A_1B_1B_1$, $B_2A_2B_1$, $A_1B_2B_2$, and $B_1A_2B_2$. If these are investigated with reference to the literature point group character table it is found that none is a valid element of the ccf $\langle 2[\boldsymbol{\omega}(t)\times\boldsymbol{v}(t)]\boldsymbol{\omega}^{\mathrm{T}}(0)\rangle$. In $A_1A_2A_2$ for example, A_1 referring to $\boldsymbol{\omega}$ has no R representation in the C_{2v} point group character table, i.e. is an irreducible representation that cannot refer directly to rotation.

3.1.4. Three-time acfs

Molecule-fixed frame (x, y, z). The theory of molecular diffusion must encompass the existence of three-time and multi-time autocorrelation functions in frame (x, y, z) as well as frame (X, Y, Z). The great majority of theories assume at present that three-time autocorrelation functions vanish as a consequence of the Gaussian view [14] of statistical mechanics. It is straightforward to use group theoretical statistical mechanics to show that this approximation is not valid in general. Consider for example the three-time acfs $\langle\boldsymbol{v}(t_1)\boldsymbol{v}^{\mathrm{T}}(t_2)\boldsymbol{v}^{\mathrm{T}}(t_3)\rangle$ and $\langle\boldsymbol{\omega}(t_1)\boldsymbol{\omega}^{\mathrm{T}}(t_2)\boldsymbol{\omega}^{\mathrm{T}}(t_3)\rangle$, each of which has 27 elements in general. The respective products of representations in C_{2v} symmetry are $7A_1+6A_2+7B_1+7B_2$ and $6A_1+7A_2+7B_1+7B_2$. Therefore there are seven and six occurrences respectively of A_1. In the former case the seven non-vanishing elements are found as follows:

$$A_1A_1A_1\equiv\langle v_z(t_1)v_z(t_2)v_z(t_3)\rangle,\quad A_1B_1B_1\equiv\langle v_z(t_1)v_x(t_2)v_x(t_3)\rangle,\quad B_1A_1B_1\equiv\langle v_x(t_1)v_z(t_2)v_x(t_3)\rangle,$$

$$B_1B_1A_1\equiv\langle v_x(t_1)v_x(t_2)v_z(t_3)\rangle,\quad B_2A_1B_2\equiv\langle v_y(t_1)v_z(t_2)v_y(t_3)\rangle,\quad A_1B_2B_2\equiv\langle v_z(t_1)v_y(t_2)v_y(t_3)\rangle,$$

$$B_2B_2A_1\equiv\langle v_y(t_1)v_y(t_2)v_z(t_3)\rangle,$$

and in the latter the six non-vanishing elements are

$$A_2B_1B_2\equiv\langle\omega_z(t_1)\omega_y(t_2)\omega_x(t_3)\rangle,\quad A_2B_2B_1\equiv\langle\omega_z(t_1)\omega_x(t_2)\omega_y(t_3)\rangle,\quad B_1A_2B_2\equiv\langle\omega_y(t_1)\omega_z(t_2)\omega_x(t_3)\rangle,$$

$$B_1B_2A_2\equiv\langle\omega_y(t_1)\omega_x(t_2)\omega_z(t_3)\rangle,\quad B_2A_2B_1\equiv\langle\omega_x(t_1)\omega_z(t_2)\omega_y(t_3)\rangle,\quad B_2B_1A_2\equiv\langle\omega_x(t_1)\omega_y(t_2)\omega_z(t_3)\rangle.$$

Any theoretical approach which is implicitly or explicitly Gaussian in nature implies that *all* the above three-time acf elements must vanish for all t. Clearly, if computer simulation corroborates their existence, as seems likely, the Gaussian view must be discarded in favour of something more realistic.

Laboratory frame (X, Y, Z). Irrespective of molecular symmetry, the three-time autocorrelation function of linear velocity vanishes in the laboratory frame for all t because the relevant product of representations,

$$\Gamma(\boldsymbol{v})\Gamma(\boldsymbol{v})\Gamma(\boldsymbol{v})=D_u^{(1)}D_u^{(1)}D_u^{(1)}$$

cannot contain the tsr $D_g^{(0)}$. In contrast the three-time acf of molecular angular velocity contains $D_g^{(0)}$ once:

$$\Gamma(\boldsymbol{\omega})\Gamma(\boldsymbol{\omega})\Gamma(\boldsymbol{\omega})=D_g^{(1)}D_g^{(1)}D_g^{(1)}=D_g^{(0)}+3D_g^{(1)}+2D_g^{(2)}+D_g^{(3)},$$

so that one independent element exists for all molecular symmetries in frame (X, Y, Z). This is the trace element

$$\langle \omega_X(t_1)\omega_X(t_2)\omega_X(t_3)\rangle = \langle \omega_Y(t_1)\omega_Y(t_2)\omega_Y(t_3)\rangle = \langle \omega_Z(t_1)\omega_Z(t_2)\omega_Z(t_3)\rangle, \qquad (2)$$

which should therefore be observable by computer simulation. The Gaussian view of molecular statistical mechanics leaves this out of consideration, i.e. implicitly assumes that it vanishes for all t. There is no way therefore of obtaining the time dependence of (2) from a simple Gaussian diffusion equation such as the Debye diffusion equation.

3.1.5. Four-time correlation functions

Utilisation of group theoretical statistical mechanics achieves a great simplification in the treatment of four-time correlation functions when these are looked at from the non-Gaussian viewpoint, i.e. are not simply products of two-time correlation functions.

Four-time autocorrelation functions. Molecule-fixed fame (x, y, z). The symmetry representation of $\langle \boldsymbol{v}(t_1)\boldsymbol{v}^{\mathrm{T}}(t_2)\boldsymbol{v}^{\mathrm{T}}(t_3)\boldsymbol{v}^{\mathrm{T}}(t_4)\rangle$ is $21A_1+20A_2+20B_1+20B_2$ and of $\langle \boldsymbol{\omega}(t_1)\boldsymbol{\omega}^{\mathrm{T}}(t_2)\boldsymbol{\omega}^{\mathrm{T}}(t_3)\boldsymbol{\omega}^{\mathrm{T}}(t_4)\rangle$ is $20A_1+21A_2+20B_1+20B_2$. Therefore it can be seen that only 21 elements and 20 elements respectively can exist out of a possible 81 in each case for C_{2v} symmetry. However, these are all independent in general and with a different time dependence in each case. Obviously, different results are obtained for different point groups.

Laboratory frame (X, Y, Z). For four-time velocity and angular velocity acfs the respective products of representations are:

$$D_u^{(1)}D_u^{(1)}D_u^{(1)}D_u^{(1)}=3D_g^{(0)}+6D_g^{(1)}+6D_g^{(2)}+3D_g^{(3)}+D_g^{(4)}$$

and

$$D_g^{(1)}D_g^{(1)}D_g^{(1)}D_g^{(1)}=D_u^{(1)}D_u^{(1)}D_u^{(1)}D_u^{(1)},$$

from which it can be seen that in each case there are three occurrences of the tsr for all molecular symmetries in frame (X, Y, Z). Therefore three independent elements of the four-time correlation functions may exist in the laboratory frame, with different time dependences, even for spherical top symmetry. For example, one of the three non-vanishing tsrs may indicate that the three diagonal elements exist of the higher order acf $\langle [\boldsymbol{v}(t)\cdot\boldsymbol{v}(t)][\boldsymbol{v}(0)\cdot\boldsymbol{v}(0)]\rangle$, well known from computer simulations of non-Gaussian processes [6,13–15], another may show the existence of the acf $\langle [\boldsymbol{v}(t)\cdot\boldsymbol{v}(0)]^2\rangle$, whose three diagonal elements have the same time dependence in isotropic three-dimensional space, and the third may indicate the existence of the elements

$$\langle v_X(t_1)v_X(t_2)v_X(t_3)v_X(t_4)\rangle = \langle v_Y(t_1)v_Y(t_2)v_Y(t_3)v_Y(t_4)\rangle = \langle v_Z(t_1)v_Z(t_2)v_Z(t_3)v_Z(t_4)\rangle$$

and so on.

3.2. Tetrahedral symmetry (T_d), spherical top

In the laboratory frame of reference the same symmetry considerations apply as in the case of the C_{2v} symmetry asymmetric top, but in the molecule-fixed frame (x, y, z) the individual characteristics of the two-, three- and four-time correlation functions are considered separately in this section for auto- and cross-correlations between dynamical variables of the same diffusing molecule.

3.2.1. Two-time correlation functions

In the molecule-fixed frame (x, y, z) the linear velocity, $\boldsymbol{v}$, or any polar vector such as an axis, $\boldsymbol{\mu}$, through the molecular centre of mass, maps onto the T_d symmetry representation T_2, and an axial vector such as $\boldsymbol{\omega}$ onto T_1. The time cross-correlation function $\langle \boldsymbol{v}(t)\boldsymbol{\omega}^{\mathrm{T}}(0)\rangle$ therefore vanishes for all t in frame (x, y, z) because

$$\Gamma(\boldsymbol{v})\Gamma(\boldsymbol{\omega})=\mathrm{T}_2\mathrm{T}_1=\mathrm{A}_2+\mathrm{E}+\mathrm{T}_1+\mathrm{T}_2$$

does not contain the tsr of the T_d point group, A_1. Autocorrelation functions such as those of $\boldsymbol{v}$ or $\boldsymbol{\omega}$ have one independent element represented by a single occurrence of A_1 in the respective products of representations,

$$\mathrm{T}_2\mathrm{T}_2=\mathrm{T}_1\mathrm{T}_1=\mathrm{A}_1+\mathrm{E}+\mathrm{T}_1+\mathrm{T}_2.$$

This means that the three diagonal elements of $\langle \boldsymbol{v}(t)\boldsymbol{v}^{\mathrm{T}}(0)\rangle$ and $\langle \boldsymbol{\omega}(t)\boldsymbol{\omega}^{\mathrm{T}}(0)\rangle$ in frame (x, y, z) have respectively the same time dependence for T_d symmetry. This is what is found by computer simulation [26]. Note that the cross-correlation function [9] $\langle \boldsymbol{v}(t)\boldsymbol{\mu}^{\mathrm{T}}(0)\rangle$ between an axis of frame (x, y, z) and $\boldsymbol{v}$ defined in this frame has the same characteristics. This fundamental property appears rarely if ever from the standard literature approach to the theory of molecular diffusion. For example it is unclear how, or impossible to, obtain the time dependence of $\langle \boldsymbol{v}(t)\boldsymbol{\mu}^{\mathrm{T}}(0)\rangle$ from the theory of the itinerant oscillator [33].

3.2.2. Three-time correlation functions

For the two-time correlation functions the results of computer simulation and group theoretical statistical mechanics provide detailed agreement, those elements that exist by symmetry in frame (x, y, z) are found to have a time dependence by computer simulationn. This is strong corroborative evidence for the inadequacy of contemporary diffusion equations whose inherent approximations prevent them from drawing anything but the roughest outline. A mathematically intricate but physically almost meaningless model such as the two-dimensional itinerant oscillator is not able to provide the time dependence [9] of $\langle \boldsymbol{v}(t)\boldsymbol{\mu}^{\mathrm{T}}(0)\rangle$, as mentioned already. Any data matching exercise with such a model is open to serious criticism stemming from the fact that much of the fundamental physics is missing. Any prediction from such a theory must be viewed with caution. This point is brought home with clarity by the combined use of group theoretical statistical mechanics and computer simulation.

As for the asymmetric top of C_{2v} symmetry, the ccf between the molecular Coriolis acceleration, $2\boldsymbol{v}\times\boldsymbol{\omega}$, and the linear velocity $\boldsymbol{v}$ can exist by symmetry in the laboratory frame (X, Y, Z). The great majority of diffusion theories restrict themselves to "pure" rotation or translation, and cannot describe this result, even in outline. In the molecule-fixed frame (x, y, z) the symmetry representation of the three-time ccf $\langle 2[\boldsymbol{v}(t)\times\boldsymbol{\omega}(t)]\boldsymbol{v}^{\mathrm{T}}(0)\rangle$ for T_d symmetry is

$$\Gamma(\boldsymbol{v})\Gamma(\boldsymbol{\omega})\Gamma(\boldsymbol{v})=\mathrm{T}_2\mathrm{T}_1\mathrm{T}_2=\mathrm{A}_1+\mathrm{A}_2+2\mathrm{E}+4\mathrm{T}_1+3\mathrm{T}_2,$$

showing one occurrence of the tsr. This comes from the product of triply degenerate Cartesian representations of the T_d point group character table, i.e.

$$\langle (v_x, v_y, v_z)(\omega_x, \omega_y, \omega_z)(v_x, v_y, v_z)\rangle,$$

meaning that the three diagonal elements of the ccf $\langle 2[\boldsymbol{v}(t)\times\boldsymbol{\omega}(t)]\boldsymbol{v}^{\mathrm{T}}(0)\rangle$ can exist in frame (x, y, z) with the same time dependence. Again this is exactly as found by computer simulation [26]. The latter also shows that the diagonal elements of the time ccf between the Coriolis acceleration and the same molecule's *angular* velocity vanish in both frames of reference for all t. In frame (x, y, z) the relevant product of representations is now

$$\mathrm{T}_1\mathrm{T}_2\mathrm{T}_1 \equiv \langle (\omega_x, \omega_y, \omega_z)(v_x, v_y; v_z)(\omega_x, \omega_y, \omega_z)\rangle,$$

but in this case the complete ccf vanishes in frame (X, Y, Z). In general, the six off-diagonal elements of $\langle 2[\boldsymbol{\omega}(t)\times\boldsymbol{v}(t)]\boldsymbol{\omega}^{\mathrm{T}}(0)\rangle$ exist in frame (x, y, z) on the basis of symmetry for the tetrahedral spherical top. (Recall that all elements vanish in frame (x, y, z) for C_{2v} asymmetric top symmetry.) No contemporary diffusion theory is capable of dealing with these subtleties, and this is a fundamental problem.

3.1. Time correlation functions involving translation, rotation, and normal modes of vibration of a diffusing molecule

The symmetry representation of normal modes of vibration [22] in frame (x, y, z) depends [25] both on the molecular symmetry and the number of atoms in the molecule. In this section we restrict our consideration to a simple triatomic of C_{2v} symmetry, the water molecule, and a pentatomic of T_d symmetry, carbon tetrachloride. Group theoretical statistical mechanics is used to show that normal modes of vibration in these diffusing molecules are correlated in many different ways to the translation and rotation of the molecule as a whole. These effects show up [14] in infrared and Raman band shapes of the liquids, but at present very little is known about them, either from diffusion theory or computer simulation. Most theories decorrelate vibration from rotation and translation at the outset, and flexible model potentials for computer simulation [12] are not yet in general use.

The water molecule (C_{2v} symmetry). The symmetry representation of the normal modes of vibration of the water molecule is [25]:

$$\Gamma(Q_i)=2A_1+B_2.$$

There are three proper modes (fundamentals) with symmetry A_1 (symmetric stretch), A_1 (symmetric bend), and B_2 (asymmetric stretch). Each of these may be cross-correlated in frame (x, y, z) with molecular translation, rotation, or Coriolis acceleration, involving the latter simultaneously. If the normal modes are denoted by $\boldsymbol{Q}_1$, $\boldsymbol{Q}_2$, and $\boldsymbol{Q}_3$ it becomes possible to construct cross-correlation functions such as $\langle \boldsymbol{\omega}(t)\boldsymbol{Q}_1^{\mathrm{T}}(0)\rangle$, $\langle \boldsymbol{\omega}(t)\boldsymbol{Q}_2^{\mathrm{T}}(0)\rangle$ and $\langle \boldsymbol{\omega}(t)\boldsymbol{Q}_3^{\mathrm{T}}(0)\rangle$ whose existence in frame (x, y, z) for $0<t<\infty$ is determined by the respective products of representations $\Gamma(\boldsymbol{\omega})\Gamma(\boldsymbol{Q}_1)$, $\Gamma(\boldsymbol{\omega})\Gamma(\boldsymbol{Q}_2)$, and $\Gamma(\boldsymbol{\omega})\Gamma(\boldsymbol{Q}_3)$. Of these only the last product includes the totally symmetric representation of the C_{2v} point group, A_1. This appears from the product B_2B_2 providing the non-vanishing ccf elements $(x, y)=-(y, x)$ of $\langle \boldsymbol{\omega}(t)\boldsymbol{Q}_3^{\mathrm{T}}(0)\rangle$. In liquid water therefore there is a time ccf between the B_2 proper mode of vibration and the molecule's own angular velocity.

Similarly, the existence of time ccfs between the molecular linear velocity and normal modes of vibration can be established [5] using similar procedures. The method is illustrated with respect to establishing the various time cross-correlation functions between normal modes of vibration and the Coriolis acceleration. The appropriate products of representations are as follows for each of the fundamentals $\boldsymbol{Q}_1$, $\boldsymbol{Q}_2$, and $\boldsymbol{Q}_3$:

$B_1B_1A_1$ and $B_2B_2A_1$, i.e. $\langle (\boldsymbol{v}\times\boldsymbol{\omega})_z Q_{1z}\rangle$; $B_1B_1A_1$ and $B_2B_2A_1$, i.e. $\langle (\boldsymbol{v}\times\boldsymbol{\omega})_z Q_{2z}\rangle$;

$A_1B_2B_2$ and $B_1A_2B_2$, i.e. $\langle (\boldsymbol{v}\times\boldsymbol{\omega})_y Q_{3y}\rangle$.

Therefore cross correlations exist in liquid water between the molecular Coriolis acceleration and all three fundamentals.

The carbon tetrachloride molecule (T_d symmetry, spherical top). Here the vibrational symmetry representation is

$$\Gamma(\boldsymbol{Q}_i)=A_1(\boldsymbol{Q}_1)+E(\boldsymbol{Q}_2)+T_2(\boldsymbol{Q}_3)+T_2(\boldsymbol{Q}_4)$$

and using this it may be shown that there is no time cross-correlation function between molecular angular velocity and the normal modes of vibration of the same diffusing molecule. (In fact this is true [5] for all non-dipolar, achiral molecules.) However non-vanishing diagonal elements of the ccf between the linear velocity and fundamental vibrational modes can be shown to exist using the methods of group theoretical statistical mechanics. Normal-mode vibration in a diffusing molecule is never decorrelated from centre-of-mass translation [5], and also Coriolis acceleration. This is important in the theory of sound dispersion and light scattering [13], and more indirectly, in the fundamental theory [6] of absorption processes in the infrared, far infrared and lower frequencies. The newer methods of computer simulation, using flexible [12] ab initio potentials such as the MCYL, have already been used to investigate time cross-correlations involving intra-molecular vibration in the diffusing water molecule. Knowledge concerning these correlations from standard approaches is nearly non-existent at present, even in the classical context, because the relevant diffusion equations are cumbersome and insoluble. Some idea of the large gap that now exists may be obtained from the example of the rigid planar itinerant oscillator [16], which ignores all processes except planar rotation in simple symmetries. However, group theoretical statistical mechanics produces clear results about time correlation functions for all molecular symmetries and all physically meaningful dynamical processes, both in classical and quantum mechanics. The symmetry considerations simplify considerably the exploratory work of the computer simulator, obviating the need to simulate time correlations that vanish by symmetry, ~~but also suggesting,~~ conversely, the need to expand and deepen our knowledge of non-Gaussian, non-Markovian and non-linear processes. Nor is the group theoretical approach restricted to the isotropic state, the effect of symmetry-breaking processes such as externally applied force fields, can be taken into consideration as follows.

4. Equilibrium in the presence of fields

An electric field $\boldsymbol{E}$ breaks $R_h(3)$ symmetry and allows ensemble averages to exist in frame (X, Y, Z) which would otherwise vanish in the isotropic liquid. In terms [1] of irreducible representations $\boldsymbol{E}$ allows ensemble averages of $D_u^{(1)}$ symmetry to supplement averages of $D_g^{(0)}$ symmetry. Similarly $\boldsymbol{H}$ allows averages of $D_g^{(1)}$ symmetry to supplement the isotropic $D_g^{(0)}$ quantities. The new averages have the same D symmetry as the applied field itself, thus $\boldsymbol{E}$ is $D_u^{(1)}$ and $\boldsymbol{H}$ is $D_g^{(1)}$. Proceeding in this way E^2 allows averages with $D_g^{(0)} + D_g^{(2)}$ symmetry, E^3 with $D_u^{(1)} + D_u^{(3)}$ symmetry and so on. A combination of fields allows a combination of new averages and so on. Using these symmetries it is possible to evaluate in detail the effect of fields on multi-time correlation fucntions, referring to computer simulations where these are available.

4.1. Two-time correlation functions

One of the most well known results of treating a molecular liquid with an electric field $\boldsymbol{E}$ is to induce birefringence. As we have seen, the product of representations of an autocorrelation function of vectors such as $\boldsymbol{v}$, $\boldsymbol{\omega}$ or $\boldsymbol{\mu}$ (dipole) always contains the tsr of the $R_h(3)$ point group, $D_g^{(0)}$. For the dipole acf for example

$$\Gamma(\boldsymbol{\mu})\Gamma(\boldsymbol{\mu}) = D_u^{(1)} D_u^{(1)} = D_g^{(0)} + D_g^{(1)} + D_g^{(2)},$$

a product which also contains $D_g^{(1)}$. The latter is allowed in the presence of $\boldsymbol{H}$ and is indicative of birefringence. If $\boldsymbol{E}$ is applied in axis Z the acf $\langle \mu_Z(t)\mu_Z(0)\rangle$ is finite as $t \rightarrow \infty$, and is one of the trace elements with $D_g^{(0)}$ symmetry.

Recent computer simulations [34–37] have revealed that the time ccf $\langle \boldsymbol{v}(t)\boldsymbol{\omega}^{\mathrm{T}}(0)\rangle$ does not vanish in the presence of $\boldsymbol{E}_Z$. Thus $D_u^{(1)}$ of the product of representations

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

represents the non-vanishing elements $(X, Y) = -(Y, X)$ of the laboratory-frame ccf $\langle \boldsymbol{v}(t)\boldsymbol{\omega}^{\mathrm{T}}(0)\rangle$.

4.2. Three-time correlation functions

Symmetry considerations reveal that an electric field $\boldsymbol{E}$ allows the existence of ~~the three-time correlation func~~tion of molecular linear velocity, $\boldsymbol{v}$, directly in the laboratory frame. This result is ~~obtained through the product~~ of representations:

$$\Gamma(\boldsymbol{v})\Gamma(\boldsymbol{v})\Gamma(\boldsymbol{v}) = D_u^{(1)} D_u^{(1)} D_u^{(1)} = D_u^{(0)} + 3D_u^{(1)} + 2D_u^{(2)} + D_u^{(3)}$$

which contains $D_u^{(1)}$ three times, indicating the existence by symmetry of three independent elements of $\langle \boldsymbol{v}(t_1)\boldsymbol{v}^{\mathrm{T}}(t_2)\boldsymbol{v}^{\mathrm{T}}(t_3)\rangle$ in frame (X, Y, Z) in the presence of $\boldsymbol{E}$. It follows therefore that the statistical nature of linear diffusion cannot be Gaussian in the presence of an electric field. Clearly, all the odd-time correlation functions similarly exist in (X, Y, Z) in the presence of $\boldsymbol{E}$.

In contrast a magnetic field $\boldsymbol{H}$ does not allow three-time and odd-time correlation functions of molecular linear velocity.

Electric field-induced three-time correlation functions are so far unexamined by computer simulation, and much remains to be done in this area. The Fokker–Planck diffusion equation [6] for the probability density function of linear velocity will not produce the required result in this context, because its structure is implicitly Gaussian.

5. Some field-induced effects in the molecule-fixed frame (x, y, z)

5.1. The C_{2v} point group

There are many fundamental effects induced in this point group by electric and magnetic fields. This can be illustrated in the class of non-vanishing ccfs involving the linear velocity $\boldsymbol{v}$ and angular velocity $\boldsymbol{\omega}$ of the diffusing molecule. The first stage in the reasoning is to map the symmetry of the external field on to the C_{2v} point group. This provides the following:

$$\Gamma(\boldsymbol{E})=A_1+B_1+B_2, \quad \Gamma(\boldsymbol{H})=A_2+B_1+B_2,$$

$$\Gamma(\boldsymbol{E}^2)=A_1+(2A_1+A_2+B_1+B_2) \quad (\equiv D_g^{(0)}+D_g^{(2)}) \quad \text{(symmetric part)},$$

$$\Gamma(\boldsymbol{H}^2)=A_1+(2A_1+A_2+B_1+B_2) \quad (\equiv D_g^{(0)}+D_g^{(2)}) \quad \text{(symmetric part)},$$

$$\Gamma(\boldsymbol{E}^3)=(A_1+B_1+B_2)+(2A_1+A_2+2B_1+2B_2) \quad (\equiv D_u^{(1)}+D_u^{(3)}) \quad \text{(antisymmetric part)},$$

$$\Gamma(\boldsymbol{H}^3)=(A_2+B_1+B_2)+(A_1+2A_2+2B_1+2B_2) \quad (\equiv D_g^{(1)}+D_g^{(3)}) \quad \text{(antisymmetric part)}.$$

Thus, an electric field $\boldsymbol{E}$ allows ensemble averages of symmetry A_1, B_1, and B_2 to exist for C_{2v} in frame (x, y, z). A magnetic field allows ensemble averages of symmetry A_2, B_1, and B_2, and so on. It is clear that more elements of time correlation functions exist in field-applied equilibrium, whatever the nature of the field, than in field-free equilibrium. Furthermore, the *fundamental* nature of the molecular diffusion process is changed by a simple electric or magnetic field. The field-on and field-off dynamics are wholly different, and this difference expresses itself through time cross-correlation functions of all orders. None of this is accounted for in standard theory, such as that of dielectric relaxation [17], the dynamic Kerr effect [6], infrared and Raman band shapes [14,18], and in first approximations such as the various rotational diffusion models [33].

5.1.1. Two-time ccfs

Considering the ccf $\langle \boldsymbol{v}(t)\boldsymbol{\omega}^{\mathrm{T}}(0)\rangle$ the product of representations contains the individual products

$$\Gamma(\boldsymbol{v})\Gamma(\boldsymbol{\omega})=(A_1+B_1+B_2)(A_2+B_1+B_2)$$
$$=A_1A_2+A_1B_1+A_1B_2+B_1A_2+B_1B_1+B_1B_2+B_2A_2+B_2B_1+B_2B_2.$$

Of these, products which produce A_1, B_1 or B_2 will be finite ensemble averages in frame (x, y, z) in the presence of $\boldsymbol{E}$, and those which produce A_2, B_1 or B_2 in the presence of $\boldsymbol{H}$. These are in the presence of $\boldsymbol{E}$:

$$A_1B_1=B_1\equiv\langle v_z(t)\omega_y(0)\rangle, \quad A_1B_2=B_2\equiv\langle v_z(t)\omega_x(0)\rangle, \quad B_1A_2=B_2\equiv\langle v_x(t)\omega_z(0)\rangle,$$

$$B_1B_1=A_1\equiv\langle v_x(t)\omega_y(0)\rangle, \quad B_2A_2=B_1\equiv\langle v_y(t)\omega_z(0)\rangle, \quad B_2B_2=A_1\equiv\langle v_y(t)\omega_x(0)\rangle,$$

and in the presence of $\boldsymbol{H}$:

$$\mathrm{A}_1\mathrm{B}_1 = \mathrm{B}_1 \equiv \langle v_z(t)\omega_y(0)\rangle, \quad \mathrm{A}_1\mathrm{B}_2 = \mathrm{B}_2 \equiv \langle v_z(t)\omega_x(0)\rangle, \quad \mathrm{B}_1\mathrm{A}_2 = \mathrm{B}_2 \equiv \langle v_x(t)\omega_z(0)\rangle,$$

$$\mathrm{A}_1\mathrm{A}_2 = \mathrm{A}_2 \equiv \langle v_z(t)\omega_z(0)\rangle, \quad \mathrm{B}_2\mathrm{A}_2 = \mathrm{B}_1 \equiv \langle v_y(t)\omega_z(0)\rangle, \quad \mathrm{B}_1\mathrm{B}_2 = \mathrm{A}_2 \equiv \langle v_x(t)\omega_x(0)\rangle,$$

$$\mathrm{B}_2\mathrm{B}_1 = \mathrm{A}_2 = \langle v_y(t)\omega_y(0)\rangle,$$

so that there are no less than six independent elements of the tensor $\langle \boldsymbol{v}(t)\boldsymbol{\omega}^{\mathrm{T}}(0)\rangle$ in the presence of $\boldsymbol{E}$. The electric field-induced symmetry change is

$$\mathrm{C}_{2\mathrm{v}}: \begin{pmatrix} 0 & a_1 & 0 \\ -a_2 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}_{(x,y,z)} \quad +\boldsymbol{E}\rightarrow \begin{pmatrix} 0 & a_3 & b_1 \\ -a_4 & 0 & c_1 \\ -b_2 & -c_2 & 0 \end{pmatrix}_{(x,y,z)} .$$

The magnetic field allows the existence in frame (x, y, z) of seven new elements, including the diagonal elements, as well as the original field-free elements (x, y) and (y, x). Therefore in the presence of $\boldsymbol{H}$ the matrix is full, with nine independent cross-correlation functions. This fundamental field-induced change is important in any consideration of molecular diffusion processes in an aligning magnetic field, such as those in a room temperature nematic liquid crystal. Very few, if any, of the contemporary molecular theories [6] of liquid crystal behaviour take this into account.

5.1.2. Effect of electric and magnetic fields on three-time correlation functions

It has been shown already that a field $\boldsymbol{E}$ promotes the existence in the laboratory frame of the three-time correlation function of linear velocity, so that the overall linear diffusion process cannot be Gaussian in general. In frame (x, y, z) the effect of $\boldsymbol{E}$ depends as usual on molecular symmetry, and for the $\mathrm{C}_{2\mathrm{v}}$ point group many new elements appear both for auto- and cross-correlation functions in frame (x, y, z), supplementing those in frame (X, Y, Z). This effect is illustrated in this section with respect to cross-correlation functions between molecular Coriolis acceleration and linear and angular velocity, and the three-time autocorrelation functions of linear and angular velocity. Similar elements appear in the presence of a magnetic field $\boldsymbol{H}$.

Three-time acf of molecular angular velocity. Effect of E. This is a time correlation function which is almost never considered in the theory of electric fields applied to molecular liquids, for example, the theory of dielectric relaxation [6,17]. However, group theoretical statistical mechanics clearly reveal its properties, both at field-off and field-on equilibrium. These are obtained as usual in frame (x, y, z) by considering the relevant product of representations:

$$\Gamma(\boldsymbol{\omega})\Gamma(\boldsymbol{\omega})\Gamma(\boldsymbol{\omega}) = (\mathrm{A}_2+\mathrm{B}_1+\mathrm{B}_2)(\mathrm{A}_2+\mathrm{B}_1+\mathrm{B}_2)(\mathrm{A}_2+\mathrm{B}_1+\mathrm{B}_2)$$

consisting of 27 terms. In the absence of $\boldsymbol{E}$ we have seen already that there are 6 non-vanishing terms in general, coming from individual terms in the product which have overall symmetry A_1. In the presence of E, products which give A_1, B_1, and B_2 provide non-vanishing ensemble averages in general, so that all the terms of the general triple product $\langle \boldsymbol{\omega}(t_1)\boldsymbol{\omega}^{\mathrm{T}}(t_2)\boldsymbol{\omega}^{\mathrm{T}}(t_3)\rangle$ exist with the exception of

$$\langle \omega_z(t_1)\omega_z(t_2)\omega_z(t_3)\rangle, \quad \langle \omega_z(t_1)\omega_y(t_2)\omega_y(t_3)\rangle, \quad \langle \omega_z(t_1)\omega_x(t_2)\omega_x(t_3)\rangle,$$

$$\langle \omega_y(t_1)\omega_z(t_2)\omega_y(t_3)\rangle, \quad \langle \omega_y(t_1)\omega_y(t_2)\omega_z(t_3)\rangle, \quad \langle \omega_x(t_1)\omega_z(t_2)\omega_x(t_3)\rangle,$$

$$\langle \omega_x(t_1)\omega_x(t_2)\omega_z(t_3)\rangle.$$

In the presence of the electric field, $\boldsymbol{E}$, therefore, there are no less than 20 independent ~~elements of the three-time~~ acf of molecular angular velocity for $\mathrm{C}_{2\mathrm{v}}$ symmetry. For other molecular symmetries ~~there will be different~~ numbers of independent non-vanishign elements. Contemporary Gaussian theories, such as the original theory of rotational diffusion, fall well short of providing an adequate description of these. Indeed, for all dipolar

~~symmetries~~ rotational diffusion theory, and variations thereof such as the rotational itinerant oscillator, implicitly ~~assume that~~ all elements vanish for all t and for all $\boldsymbol{E}$. Contemporary computer simulation is expected to ~~provide a much~~ more ~~accurate description~~, and in particular, all elements that vanish by symmetry should vanish in the simulation. ~~We are left with~~ the familiar pattern that contemporary analytical theory lags far behind contemporary numerical simulation. Furthermore, the indications of group theoretical statistical mechanics challenge the most basic of accepted concepts in fluctuation–dissipation theory [14], which lies at the root of the theory of dielectric relaxation and non-equilibrium processes in general. This can be illustrated by reference to a statement of the fluctuation–dissipation theorem in the linear response approximation which asserts [14] that the equilibrium autocorrelation function (for example the two-time acf of orientation) has the same normalised time dependence as the fall transient from equilibrium in the presence of a field such as $\boldsymbol{E}$ to field-off equilibrium. It is difficult if not impossible to reconcile this theorem with the symmetry properties revealed by group theoretical statistical mechanics. There are many time correlation functions of all orders that display a time dependence by symmetry at field-on equilibrium but which vanish by symmetry at field-off equilibrium. Any fall transient from field-on to field-off equilibrium will reflect a profound change in the statistical mechanics of the molecular ensemble, and its time dependence can, in consequence, be only fortuitously the same as an equilibrium time correlation function. This in turn affects the validity of the Onsager reciprocal relations and related long-accepted concepts. The delicate and subtle processes that become visible by symmetry considerations, once we realise that the ensemble average is governed by group theory [1], are accessible to contemporary computer simulations but to no other established technique as yet. Once this is realised and generally accepted it becomes inevitable that less emphasis remains with the traditional "data-fitting" approach to molecular diffusion [33]. Thus, the illusory success of the Debye rotational diffusion theory and variations thereof has to be attributed to lack of appropriate, and appropriately discriminating, data.

Similar considerations lead to the conclusion that a magnetic field, $\boldsymbol{H}$, in general allows the existence of all 27 elements of the three-time acf of angular velocity at field-on equilibrium.

Three-time acf of molecular linear velocity. Effect of $\boldsymbol{E}$. Similar considerations lead to the conclusion that at field-on equilibrium ($\boldsymbol{E}\neq\boldsymbol{0}$) all the elements of the three-time autocorrelation function of molecular linear velocity exist in frame (x, y, z) for C_{2v} symmetry except for the following:

$$\langle v_z(t_1)v_x(t_2)v_y(t_3)\rangle,\quad \langle v_z(t_1)v_y(t_2)v_x(t_3)\rangle,\quad \langle v_x(t_1)v_z(t_2)v_y(t_3)\rangle,$$
$$\langle v_x(t_1)v_y(t_2)v_z(t_3)\rangle,\quad \langle v_y(t_1)v_z(t_2)v_x(t_3)\rangle,\quad \langle v_y(t_1)v_x(t_2)v_z(t_3)\rangle.$$

Therefore, the linear diffusion process at field-on equilibrium cannot be Gaussian and the 21 independent elements that exist in the presence of $\boldsymbol{E}$ provide a tapestry of information on the statistical nature of linear molecular diffusion.

A magnetic field, $\boldsymbol{H}$, in this context allows all 27 elements to exist independently, as in a magnetically aligned nematic liquid crystal.

Three-time ccfs in the presence of fields. The effect of an electric field or magnetic field on ccfs extends to elements of the time correlation function between the Coriolis acceleration and the molecular linear or angular velocity. The symmetry effect on the form, for example, by an applied force field $\boldsymbol{E}$ is as follows

$$C_{2v}:\quad \begin{pmatrix} a & 0 & 0 \\ 0 & b & 0 \\ 0 & 0 & c \end{pmatrix}_{(x,y,z)} \quad +\boldsymbol{E}\rightarrow \begin{pmatrix} a_1 & 0 & d \\ 0 & b_1 & e \\ f & g & c_1 \end{pmatrix}_{(x,y,z)}$$

In general, all the elements of the tensor triple product $\langle \boldsymbol{v}(t_1)\boldsymbol{\omega}^{\mathrm{T}}(t_2)\boldsymbol{v}^{\mathrm{T}}(t_3)\rangle$ become visible in a field $\boldsymbol{E}$ in frame (x, y, z) except for the following seven:

$$\langle v_z(t_1)\omega_z(t_2)v_z(t_3)\rangle,\quad \langle v_x(t_1)\omega_x(t_2)v_z(t_3)\rangle,\quad \langle v_y(t_1)\omega_y(t_2)v_z(t_3)\rangle,\quad \langle v_z(t_1)\omega_x(t_2)v_x(t_3)\rangle,$$
$$\langle v_x(t_1)\omega_z(t_2)v_x(t_3)\rangle,\quad \langle v_z(t_1)\omega_y(t_2)v_y(t_3)\rangle,\quad \langle v_y(t_1)\omega_z(t_2)v_y(t_3)\rangle.$$

5.2. The T_d point group

Considerations of field effects with the linear electric field $\boldsymbol{E}$ or magnetic field $\boldsymbol{H}$ in the laboratory frame (X, Y, Z) parallel those for C_{2v} symmetry. However, any molecule with T_d symmetry is non-dipolar, and consequently there is no torque generated between the molecular dipole moment and $\boldsymbol{E}$. Meaningful physical discussion is restricted therefore to the torque generated between the magnetic field $\boldsymbol{H}$ and magnetic dipole moment μ_H.

The magnetic field $\boldsymbol{H}$ allows the existence of thermodynamic averages with symmetry $D_g^{(1)}$ and in consequence off-diagonal elements of any two-time autocorrelation function in frame (X, Y, Z) exist in the presence of $\boldsymbol{H}$. If the axial vector $\boldsymbol{H}$ is directed along the Z axis, the off-diagonal elements are $(X, Y) = -(Y, X)$, represented by the $D_g^{(1)}$ in the product of representations of the field-on acf. Similar elements can appear in the T_d symmetry group for the set of n-time correlation functions.

In the molecule-fixed frame the magnetic field $\boldsymbol{H}$ maps onto the symmetry representation T_1 of the T_d point group, so that ensemble averages in frame (x, y, z) with symmetry A_1 and T_1 do not vanish in general in the presence of $\boldsymbol{H}$. Thus the magnetic field does not affect the existence of n-time acfs or ccfs with ungerade symmetry in frame (X, Y, Z), and similarly in frame (x, y, z) will not affect them if their product of representations does not contain T_1. For example, the product of representations for $\langle \boldsymbol{v}(t)\boldsymbol{\omega}^T(0)\rangle$ is

$$\Gamma(\boldsymbol{v})\Gamma(\boldsymbol{\omega}) = T_2T_1 = A_2 + E + T_1 + T_2,$$

which includes T_1 once. Therefore the magnetic field has an effect in frame (x, y, z) of allowing non-vanishing elements of $\langle \boldsymbol{v}(t)\boldsymbol{\omega}^T(0)\rangle$ to exist for $0 < t < \infty$. In Cartesian representation, the product T_2T_1 is $(x, y, z)(R_x, T_y, R_z)$ from which the magnetic field symmetry change may be deduced as

$$T_d:\quad \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}_{(x,y,z)} \quad \xrightarrow{+\boldsymbol{H}} \begin{pmatrix} 0 & a & a \\ -a & 0 & a \\ -a & -a & 0 \end{pmatrix}_{(x,y,z)},$$

consistent with the fact that the overall symmetry of the matrix $\langle \boldsymbol{v}(t)\boldsymbol{\omega}^T(0)\rangle$ must be ungerade. There are no computer simulations available yet of magnetic field-induced symmetry changes in media such as nematic liquid crystals. For T_d symmetry, the time dependence of each of the magnetically allowed off-diagonal elements should be the same, because symmetry allows only one independent *type* of element. Liquid crystal molecules are likely to be of low symmetry, for example C_{1h}, or C_1, but plastic crystals [6] often contain T_d symmetry molecules, and are likely to be good examples of the above effect. The lower the symmetry of the molecule, the higher the number of independent field-induced time correlation functions.

Similar considerations lead to the conclusion that four independent T_1 elements of the three-time ccf can exist in general for $\langle \boldsymbol{v}(t)\boldsymbol{\omega}^T(t)\boldsymbol{v}^T(0)\rangle$, together with the original field-free A_1 element discussed already. The character table for T_d does not allow the precise allocation of these elements in this case because all come from the product

$$T_2T_1T_2 \equiv \langle (v_x, v_y, v_z)(\omega_x, \omega_y, \omega_z)(v_x, v_y, v_z)\rangle$$

of triply degenerate translational and rotational Cartesian representations. In this case extra information is needed, and this can be supplied in principle by computer simulation, but not by any of the traditional Gaussian diffusion theories. Similarly, the effect of a magnetic or electric field on cross-correlation and autocorrelation functions involving vibrational modes can be evaluated for all point groups using the appropriate products of representations.

5.3. *n-time correlation functions in molecular mixtures*

Finally we consider the properties of *n*-time correlation functions in mixtures of C_{2v} and T_d symmetry molecules [27]. The fundamental molecular dynamical processes of liquid mixtures and reactants involve phasing and dephasing processes [7] which have been considered recently by computer simulation and analytical theory. The role of time cross-correlation functions was found [7] to be critically important at certain stages in the chemical reaction process between molecules of different symmetry. The first stages towards an understanding of the symmetry rules governing such cross-correlation functions involve the use of group correlation tables [22,24] as well as point group character tables. There is a computer simulation available [27] of the molecular dynamics of water–carbon tetrachloride mixtures in which time cross-correlation functions were evaluated of the single molecule type, i.e. between a vector $\boldsymbol{A}(t)$ and a different type of vector $\boldsymbol{B}(0)$ belonging to the same (water) molecule.

In the laboratory frame (X, Y, Z) the same considerations apply without change to products of symmetry representations of vectors on different molecules, because the symmetry of linear velocity is the same, for example, for a water molecule or for a carbon tetrachloride molecule diffusing in frame (X, Y, Z). A time cross-correlation function will therefore exist or vanish between vectors on different diffusing molecules in frame (X, Y, Z) in an isotropic liquid. Thus the foregoing considerations of this paper apply without change to liquid mixtures for *n*-time correlation functions, and it is possible using group theoretical statistical mechanics to see which of these vanish in the phasing or dephasing stages of a chemical reaction.

In the molecule-fixed frame (x, y, z) on the other hand some means must be found to compare the symmetries of a given quantity in point group C_{2v} and point group T_d, in literature group correlation tables. A comprehensive collection of such tables is available in ref. [22] and allow a symmetry representation of one point group to be mapped onto another. For convenience the mappings from T_d to C_{2v} are listed as follows:

$$A_1(T_d) \equiv A_1(C_{2v}), \quad A_2(T_d) \equiv A_2(C_{2v}), \quad E(T_d) \equiv A_1 + A_2(C_{2v}),$$

$$T_1(T_d) \equiv A_2 + B_1 + B_2(C_{2v}), \quad T_2(T_d) \equiv A_1 + B_1 + B_2(C_{2v}).$$

5.3.1. *Two-time correlation functions*

As usual, the theory of chemical reactions or of molecular dynamics in liquid mixtures should in principle encompass time correlation functions of all orders in all frames of reference, including the frames (X, Y, Z) *and* (x, y, z).

To investigate the detailed symmetry of a two-time ccf such as $\langle \boldsymbol{v}_1(t)\boldsymbol{\omega}_2^{\mathrm{T}}(0)\rangle$ the first stage is to work out the product of representations. If, for example, $\boldsymbol{v}_1(t)$ refers to the molecule of C_{2v} symmetry and $\boldsymbol{\omega}$ to that of T_d symmetry the appropriate product will be:

$$\Gamma(\boldsymbol{v}_1)\Gamma(\boldsymbol{\omega}_2) = (A_1 + B_1 + B_2)_{C_{2v}}(T_1)_{T_d} = 2A_1 + 3A_2 + 2B_1 + 2B_2,$$

where $\boldsymbol{\omega}$ has been mapped from the T_d group onto the C_{2v} group. The resulting product of representations contains A_1 twice, and therefore two independent elements of the ccf exist in frame (x, y, z). In other words the linear velocity of the C_{2v} molecule can be statistically correlated with the angular velocity of the T_d molecule. In the case of two reactant species, molecules or radicals of given symmetry, these considerations would lead to the establishment of the role of time cross-correlation functions in the phasing stages of the reaction [7], as the two molecules maneouvre into a position favourable for reaction to take place.

5.3.2. *Three-time correlation functions*

If we exemplify this class by an investigation of the possible time correlation [26] between the Coriolis acceleration of the T_d molecule and the linear and angular velocities of the C_{2v} molecule we have the following products of representations, after appropriate mapping:

$$\Gamma((\nu\times\omega)_1)\Gamma(\nu_2)=(2A_1+3A_2+2B_1+2B_2)_{C_{2v}}(T_2)_{T_d}=6A_1+7A_2+7B_1+7B_2.$$

If, however, we map from the C_{2v} group onto the T_d group, the product of representations is

$$A_1+A_2+2E+4T_1+3T_2,$$

which is different, and contains a different number of occurrences of the appropriate tsr. The number of possible different (independent) elements of the cross correlation function is represented by the product with the higher number of occurrences of the tsr, but the time dependence of each element will be an average of the equivalents generated by ensembles of each component molecule taken separately.

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