

The Group Theory of Molecular Diffusion and Chemical Reactions in the Liquid State of Matter

M. W. Evans*

Department of Chemistry, Bourne Laboratory,
Royal Holloway and Bedford New College,
University of London,
Egham, Surrey TW20 0EW,
U.K.

*Also at
I.B.M., Data Systems Division,
Neighborhood Road,
Kingston, New York 12401,
U.S.A.
and
Honorary Research Fellow,
Dept. of Physics,
University of Lancaster,
Lancaster LA1 4YB, U.K.

Abstract

By assuming that the ensemble average of statistical mechanics reduces according to group theory several new results are obtained concerning the nature of time cross correlation functions (c.c.f.'s) in the isotropic liquid state of matter. In the laboratory frame (X, Y, Z) group theory allows the possibility for several time c.c.f.'s between transport processes of appropriate symmetry. These provide new Green Kubo coefficients that can be investigated in principle by computer simulation and observed experimentally. The rule governing time cross correlation between translational, rotational, and vibrational dynamical variables of a diffusing molecule are deduced both in frame (X, Y, Z) and in the molecule fixed frame (x, y, z) of the point group character tables. The rules are valid for all molecular point groups. The group theoretical considerations are extended to cross correlations between physical properties of different molecules, on preparation for considering by group theory the symmetry of a chemical reaction in solution.

Introduction

The well developed axioms of group theory have recently been applied¹⁻⁵ to the molecular liquid state with the important additional principle that the ensemble average ($\langle \dots \rangle$) reduce according to the rules of point group theory. The existence of elements of ensemble averages such as time correlation functions has been determined using products of irreducible representations of the individual molecular dynamical components making up the time correlation function. This allowed an independent check on numerous computer simulations by the present author and co-workers⁶⁻¹⁵ and by the Brussels School¹⁶. The results of group theory and simulation were in detailed agreement, both in the presence and absence of fields applied to the sample at equilibrium.

In this paper the methods of group theoretical statistical mechanics are applied to produce new results in several different areas. Firstly, scalars, vectors, and tensors representing physical quantities are labelled with the appropriate irreducible representation (i.r.) in the three dimensional rotation - reflection group $R_h(3)$ of isotropic three dimensional space. The existence of a set of non-vanishing time cross correlation functions (c.c.f.'s) in the laboratory frame (X, Y, Z) is then deduced using the products of irreducible representations ($D_g^{(n)}$ and $D_u^{(n)}$) of the point group $R_h(3)$. In this way several new cross transport coefficients are shown to exist on the basis of symmetry, using the fundamental new axiom, i.e. that $\langle \dots \rangle$ behaves according to point group theory.

Secondly, tables are given for the symmetry of some simple time c.c.f.'s in several molecular point groups, referring to the molecule fixed frame (x, y, z). Several general results emerge from these tables concerning the nature of time c.c.f.'s in frame (x, y, z) between the molecular centre of mass velocity (\mathbf{v}) and angular velocity (ω) and normal modes of vibration (\mathbf{Q}) in the liquid state of molecular matter.

Thirdly the scope of group theoretical statistical mechanics (g.t.s.m.) is extended to include the symmetry of chemical reactions in the liquid state, with a view to explaining by symmetry some of the phasing mechanisms

in molecular reactions, a subject of great contemporary interest to computer simulations¹⁷⁻²⁵ of liquid state chemical reactions.

Laboratory Frame (X, Y, Z). New C.c.f.'s and Cross Transport Effects

Referring to Table 9.1, p. 82, of ref. (26) it is possible to associate with any physical property of a diffusing molecule, or ensemble of molecules, a D label. The symmetry of a scalar quantity in this context is²⁶⁻³⁰ the totally symmetric representation (t.s.r.) $D_g^{(0)}$. Molecular linear velocity is an odd parity (u) polar (or true) vector quantity and molecular angular velocity an even parity (g) axial (or pseudo) vector. If we examine the symmetry of a vector quantity **A** and of another one **B** a time *t* later the existence of their time cross-correlation function

$$C_{AB}(t) = \langle A(t)B^T(0) \rangle \quad (1)$$

is determined by the product of symmetry representations

$$\Gamma(A)\Gamma(B) \quad (2)$$

The product (2) must contain as one of its irreducible representations the t.s.r. $D_g^{(0)}$ for C_{AB} to exist on the interval $0 < t < \infty$. On the basis of this simple rule, (principle (1) of g.t.s.m.¹⁻⁵), we may reach immediately the following deductions.

1) All time auto-correlation functions (a.c.f.'s) exist in frame (X, Y, Z) because the product

$$\Gamma(A)\Gamma(A) \quad (3)$$

always contains the t.s.r. by the Clebsch Gordan Theorem

$$D^{(n)}D^{(m)} = D^{(n+m)} + \dots + D^{(|n-m|)} \quad (4)$$

2) All time c.c.f.'s in frame (X, Y, Z) between an odd parity (ungerade) property and an even parity (gerade) property will vanish for all *t* at isotropic equilibrium, because (2) can never contain the t.s.r.

3) Similarly, the c.c.f. between a property purely of rank *n* and a property purely of rank *m* ($n \neq m$) disappears for all *t* in frame (X, Y, Z) from eqn (4).

4) Thus we arrive at the general rule that time c.c.f.'s between a property **A** and a property **B** can exist if and only if

a) **A** and **B** have the same parity (g or u);

b) the D representations of **A** and **B** separately contain terms of the same rank;

c) the existence of the c.c.f. is not precluded by a gross symmetry law independent of group theory, such as time reversal symmetry.

Examples

1) The time c.c.f. $\langle v(t)\omega^T(0) \rangle$ vanishes for all t in (X, Y, Z) for all molecular point groups in an isotropic environment because the linear velocity is ungerade and the angular velocity is gerade.

2) The c.c.f.'s $\langle v(t)\mu^T(0) \rangle$ and $\langle v(t)\dot{\mu}^T(0) \rangle$ exist for $0 < t < \infty$. Here μ is the molecular dipole moment and $\dot{\mu}$ its time derivative, the molecular rotational velocity³¹. These three vectors all have the same (ungerade) symmetry in the laboratory frame.

3) Electric polarisability, thermal and electric conductivity, thermal expansion, thermoelectricity and magnetic susceptibility are all bulk physical properties which are symmetric second rank tensors with D signature

$$\Gamma(\mathbf{A}) = D_g^{(0)} + D_g^{(2)} \quad (5)$$

Elasticity is a bulk property which is a symmetric fourth rank tensor represented by

$$\Gamma(\mathbf{B}) = 2D_g^{(0)} + 2D_g^{(2)} + D_g^{(4)} \quad (6)$$

Let us assume that the bulk property is a sum over the equivalent individual molecular properties in the isotropic liquid state. It follows that the symmetry representations or product thereof must contain the t.s.r. in frame (X, Y, Z) if they are to survive thermodynamic averaging. The symmetry rules apply to bulk properties as well as single molecule properties.

For example, the product

$$\Gamma(\mathbf{A})\Gamma(\mathbf{B}) = (D_g^{(0)} + D_g^{(2)})(2D_g^{(0)} + 2D_g^{(2)} + D_g^{(4)}) \quad (7)$$

contains $D_g^{(0)}$ four times. It follows that four independent time c.c.f.'s can exist in the isotropic liquid between the liquid's elasticity tensor and 1) the tensor of electric polarisability; 2) of thermal conductivity; 3) electric conductivity; 4) thermoelectricity; 5) thermal expansion; 6) magnetic susceptibility.

Two are diagonal elements and two are off-diagonal. Integrals over these time c.c.f.'s result in new kinetic (diffusion) coefficients which can always be computer simulated and sometimes be measured experimentally. The equivalent molecular properties (c.c.f.'s between single molecule equivalents of the bulk properties) are also cross-correlated in the isotropic liquid. The application of fields breaks $R_h(3)$ symmetry and makes possible the existence of many new c.c.f.'s.

4) If we examine the product

$$\Gamma(\mathbf{A})\Gamma(\mathbf{A}) = (D_g^{(0)} + D_g^{(2)})^2 \quad (8)$$

the t.s.r. is included twice, which means that two independent c.c.f.'s may exist between any two bulk or molecular physical properties with the symmetry $D_g^{(0)} \neq D_g^{(2)}$, e.g. between thermal conductivity and magnetic susceptibility; or electric polarisability and thermal expansion; or electric conductivity and magnetic susceptibility and so forth. One component of this set is always diagonal and the other always off-diagonal.

5) Two diagonal and one off-diagonal c.c.f. elements exist between the first electric hyperpolarisability ($D_u^{(1)} + D_u^{(3)}$) of an isotropic liquid and 1) its piezoelectricity tensor and 2) its electrooptic Kerr effect tensor (both $2D_u^{(1)} + D_u^{(2)} + D_u^{(3)}$).

6) Similarly, one off diagonal time c.c.f. element exists between the molecular or bulk gyration tensor of optical activity ($D_u^{(0)} + D_u^{(2)}$) and 1) the piezoelectricity tensor and 2) the electro-optic Kerr effect tensor of a chiral liquid.

7) Two off-diagonal c.c.f. elements exist between the bulk or molecular quadrupole moment ($D_g^{(2)}$) and the elasticity.

8) One off-diagonal c.c.f. element exists between the bulk or molecular quadrupole moment and all tensors of rank $D_g^{(0)} \neq D_g^{(2)}$ mentioned already.

There are many other cross-transport properties of this nature that may exist because their respective products of symmetry representations contain the t.s.r. in (X, Y, Z). These can be bulk or single molecule properties or mixtures of both types.

The Molecule-Fixed Frame (x, y, z)

It was first realised by computer simulation that many fundamental time c.c.f.'s exist in frame (x, y, z) that disappear in frame (X, Y, Z). Molecular point group theory is relevant in frame (x, y, z), fixed in the molecule itself and defined for all the molecular point groups in the literature character tables. Group theory can deduce whether or not a c.c.f. exists in frame (x, y, z). The following are examples of simple c.c.f.'s in frame (x, y, z) which link the rotational, translational and vibrational dynamics of a diffusing molecule for several point groups.

Molecular Translation and Rotation

The simplest type of c.c.f. linking these two types of diffusional motion is $\langle \mathbf{v}(t)\omega^T(0) \rangle$. This exists in frame (x, y, z) if the product of symmetry representations

$$\{\Gamma(\mathbf{v})\Gamma(\omega)\}_{(x,y,z)} \quad (9)$$

contains the t.s.r. of the molecular point group at least once. If it occurs more than once, more than one independent element of the c.c.f. exists in frame (x, y, z). The symmetry of any physical quantity is found by mapping²⁶⁻³⁰ that in $R_h(3)$ on to its equivalent in the molecular point group. The product (9) for example is obtained from this procedure applied to the linear and angular velocities and then using the literature rules for products of representations²⁶⁻³⁰.

This procedure is summarised for some molecular point groups in the Appendix, which also deduces from character tables the symmetry of the c.c.f. matrix between molecular linear and angular velocity in each point group. The results in the Appendix can be summarised in the second principle¹⁻⁵ of group theoretical statistical mechanics.

Principle 2

Ensemble averages in frame (x, y, z) exist at isotropic thermodynamic equilibrium if their symmetry representation contains the t.s.r. of the molecular point group at least once.

Examples

1) In $C_{\infty v}$ (linear dipolar) and C_{3v} (symmetric top) molecules the non-vanishing elements are

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

i.e. the time dependence is equal and opposite for $0 < t < \infty$.

2) In C_{2v} asymmetric tops such as water or dichloromethane there are two occurrences of the t.s.r. A_1 in the product (9), meaning

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

for $0 < t < \infty$. The time dependence is opposite in sign and unequal.

3) In C_{1h} asymmetric tops such as meta bromochlorobenzene there are four occurrences of the t.s.r. A' , meaning

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

for $0 < t < \infty$.

In the C_n chiral groups there are diagonal as well as off diagonal elements allowed by principle (2). These elements change sign from one enantiomer to its enantiomorph, and vanish in the racemic mixture. In the point group of lowest symmetry, C_1 , all nine elements may exist by symmetry. An example of a molecule of this type is bromochlorofluoromethane.

These examples provide a rich field of potential investigation of the individual time dependencies (frequency spectrum) of each independent element allowed by symmetry. They also prove a fundamental defect in the theory of rotational diffusion³², which assumes that all these elements vanish. Contemporary computer simulation provides detailed support for principle (2).

The Appendix summarises the symmetry of $\langle \mathbf{v}(t)\omega^T(0) \rangle_{(x, y, z)}$ for a number of dipolar and non-dipolar point groups. This table shows, for example, that

1) this c.c.f. vanishes for all t in non-dipolar achiral molecules;

2) elements may exist for $0 < t < \infty$ in the non-dipolar chiral point groups D_n . In D_3 for example

$$\begin{aligned} \langle v_x(t)\omega_y(0) \rangle &= - \langle v_y(t)\omega_x(0) \rangle \\ \langle v_z(t)\omega_z(0) \rangle &\neq 0 \end{aligned}$$

for $0 < t < \infty$. In general, these elements all switch sign from one enantiomorph to the other.

Molecular Rotation and Vibration

The symmetry representations of normal modes of vibration in a diffusing molecule are expressed in frame (x, y, z) and thus depend on the molecular point group symmetry. Unlike their counterparts for rotation and translation they also depend on the number of atoms in the molecule. Having obtained the vibrational representation²⁶⁻³⁰ we may apply principle (2) to the evaluation of statistical cross correlation between vibration and rotation. The procedure as illustrated here is first approximation, because it is assumed that vibration does not significantly distort the molecular point group and that Coriolis and centripetal accelerations caused by rotational molecular motion do not affect and are not in turn affected by the molecular vibrational motion. This approximation can be refined considerably but is a useful illustrative guide.

Examples: Dipolar Molecules

1) Water

The representation in frame (x, y, z) of proper mode vibrations in water (C_{2v}) is

$$\Gamma(Q) = 2A_1 + B_2 \tag{10}$$

There are three proper modes: Q_1 , Q_2 , and Q_3 with symmetry A_1 , A_1 , and B_2 respectively, the symmetric stretch, symmetric bend, and asymmetric stretch. The existence of time c.c.f.'s in frame (x, y, z) such as

$$\langle Q_1(t)\omega^T(0) \rangle ; \langle Q_2(t)\omega^T(0) \rangle ; \text{ and } \langle Q_3(t)\omega^T(0) \rangle$$

is determined on the basis of principle (2) by the relevant products of representations. Of the three possible, only one contains the t.s.r.

$$\Gamma(Q_3)\Gamma(\omega) = B_2(A_2 + B_1 + B_2) = A_1 + A_2 + B_1 \quad (11)$$

In this case A_1 appears from the product B_2B_2 , which indicates that for $0 < t < \infty$ the non-vanishing elements of $\langle Q_3(t)\omega^T(0) \rangle$ are (x, y) and (y, x) which have unequal and opposite time dependence because the overall symmetry of the matrix must be ungerade. In liquid water therefore there are two time c.c.f.'s between the B_2 proper mode of vibration and the molecule's own angular velocity at this first level of approximation.

2) Ammonia

The symmetry representation of the normal vibrational modes is

$$\Gamma(Q) = A_1(Q_1) + A_1(Q_2) + E(Q_3) + E(Q_4) \quad (12)$$

from which

$$\Gamma(Q_3)\Gamma(\omega) = \Gamma(Q_4)\Gamma(\omega) = A_1 + A_2 + 2E \quad (13)$$

The A sub 1 t.s.r. in the product (13) is produced by EE , which means that

$$\langle Q_3(t)\omega^T(0) \rangle \quad \text{and} \quad \langle Q_4(t)\omega^T(0) \rangle$$

both contain equal and opposite non-vanishing elements $(x, y) = -(y, x)$ for $0 < t < \infty$. There is no time cross-correlation between the symmetric modes Q_1 and Q_2 and the molecule's angular velocity in frame (x, y, z) .

Examples, Non-Dipolar Molecules

1) Carbon Dioxide

In this case

$$\Gamma(Q) = \Sigma_g^+(Q_1) + \Sigma_u^-(Q_2) + \Pi_u(Q_3) \quad (14)$$

and no product of representations between Q_1 , Q_2 , and Q_3 contains the point group's t.s.r. Σ_g . There is therefore no time c.c.f. between vibration and rotation in liquid carbon dioxide.

Methane

Here

$$\Gamma(Q) = A_1(Q_1) + E(Q_2) + T_2(Q_3) + T_2(Q_4) \quad (15)$$

and again there is no time c.c.f. between the diffusing methane molecule's angular velocity in frame (x, y, z) and its normal modes of vibration.

3) Benzene

Here there are no less than thirty possible modes of proper vibration, singly and doubly degenerate. However, none of these form non-vanishing c.c.f.'s with the molecular angular velocity in frame (x, y, z) for the diffusing benzene molecule.

From considerations of this kind it can be concluded that in non-dipolar, achiral, molecules, c.c.f.'s between molecular proper modes of vibration and the same molecule's angular velocity vanish for all t in frame (x, y, z). In all dipolar molecules, time c.c.f.'s in frame (x, y, z) exist for $0 < t < \infty$ between at least one proper mode of vibration and angular velocity.

Molecular Vibration and Centre of Mass Translation

Using methods closely analogous to those of the preceding section it is possible to investigate in frame (x, y, z) the properties of time c.c.f.'s between molecular centre of mass translational velocity and proper modes of vibration as the molecule diffuses in an isotropic liquid. Time c.c.f.'s between at least one proper molecular mode of vibration and centre of mass translation exist in frame (x, y, z) for all point groups. The non-vanishing elements are diagonals of the relevant c.c.f. tensor.

C.c.f.'s between Different Molecules : Molecular Mixtures

Before going on to consider the group theory of liquid state chemical reactions, it is necessary to extend consideration to ensemble averages over physical properties of two different molecules, of types (1) and (2), diffusing in a molecular mixture of these types.

In the laboratory frame (X, Y, Z) the ensemble average over property A of type (1) and B of type (2) exists if the product of representations

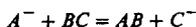
$$\Gamma(A_{(1)})\Gamma(B_{(2)})$$

contains $D_g^{(0)}$.

In the molecule fixed frame (x, y, z) there is no clear way of defining the combined point group symmetry of the two diffusing molecules of types A and B respectively.

Liquid State Chemical Reactions

Contemporary computer simulations³³ of chemical reactions in an isotropic liquid environment include details of the representative S_N2 scheme



in which there is clearly a symmetry change (molecular or atomic) between reactants (l.h.s.) and products (r.h.s). A recent review of computer simulations³³ of chemical reactions in solution has highlighted the progress made in understanding diatomic photodissociation in various solvents, together with simulations of

the A + BC (S_N2) reaction with weak and strong solvent interaction. Of importance in determining the course of the chemical reaction are interactions between individual reactants and solvent molecules, and the t_2 -like process of molecular line-shape theory, including phasing and dephasing of the molecular dynamics. For a reaction to take place, ordering must be achieved as well as energy flow. Both translational and rotational molecular motions must become properly phased for reaction to occur. Wilson points out³³ that these phasing processes can be studied in terms of cross correlation functions, both static (pair distribution functions) and dynamic (time correlation functions). The developments in this paper can be used to predict which of the time c.c.f. elements exist in frame (X, Y, Z) on the basis of a simple ansatz such that the c.c.f.'s between reactant and solvent molecules are maximised in magnitude if the initial instant, $t = 0$, of the running time average is taken at the top of the energy barrier for the reaction. In this situation the reacting molecules can either react to form products or fall back again into separate reactant molecules. In either case there is loss of energy, accompanied by loss of time correlation. Reactants are presumably formed if the statistical cross correlation is more favourable on that side of the energy barrier. Some cross correlations which are allowed by symmetry on the reactant side may be disallowed on the product side, both frames (X, Y, Z) and (x, y, z) being brought into consideration wherever feasible. In general the chemical reaction changes the number, time dependence, magnitude, and symmetry of the numerous possible time c.c.f.'s in the overall process. It can be imagined that there exist group theoretical principles which guide chemical reactions in the liquid state analogous to the well known principles of conservation of orbital symmetry in intramolecular contexts. A combination of computer simulation and group theory would be needed to establish this code and to find the key to chemical reactions in terms of statistical time cross correlations between reactants.

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Appendix: Symmetry of the Cross Correlation Function between Molecular Rotation and Translation in Some Molecular Point Groups

$$\begin{aligned}
 &9A (C_1) \\
 &5A + 4B (C_2) \\
 &3A + 3E (C_3) \\
 &3A + 2B + 2E (C_4) \\
 &3A + 2E_1 + E_2 (C_6) \\
 &4A + 5A'' (C_{1h}) \\
 \Gamma(v)\Gamma(\omega) = &2A_1 + 3A_2 + 2B_1 + 2B_2 (C_{2v}) \\
 &A_1 + 2A_2 + 3E (C_{3v}) \\
 &\Sigma^+ + 2\Sigma^- + 2\Pi + \Delta (C_{\infty v}) \\
 &2A_{1u} + A_{2u} + 3E_{2u} (D_{6h}) \\
 &\Sigma_u^+ + 2\Sigma_u^- + 2\Pi_u + \Delta_u (D_{\infty h}) \\
 &A_2 + E + T_1 + T_2 (T_d) \\
 &A_{1u} + E_u + T_{1u} + T_{2u} (O_h) \\
 &2A_1 + A_2 + 3E (D_3)
 \end{aligned}$$