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CORRELATION BETWEEN ROTATION AND TRANSLATION IN CHIRAL ENSEMBLES: COMPARISON OF MOLECULE FIXED AND LABORATORY FRAME TIME CORRELATION FUNCTIONS

by
M.W. Evans,
Theory Center,
Cornell University,
Ithaca,
NY 14853
U.S.A.

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Abstract

A computer simulation of diagonal and off diagonal elements of the time correlation function between the linear and angular velocities of a chiral ensemble of R CHBrClF molecules shows that it vanishes in the noise of the simulation, despite the fact that its symmetry in the group of all rotations, R(3), is the totally symmetric irreducible representation. This is in distinct contrast to the result in the molecule fixed frame of the principal molecular moments of inertia, where all off diagonal elements of the same cross correlation function (c.c.f.) are easily measurable The c.c.f. is symmetry allowed in both frames, but is measurable in only one.

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Introduction

The Neumann/Curie Principle (1-7) states that an ensemble average <A> over the variable A exists if the latter's symmetry representation includes at least once the totally symmetric irreducible representation (t.s.r.) of the point group of the ensemble. In an ensemble of structurally achiral molecules, the thermodynamic average <B> over the pseudoscalar B of $D_u^{(0)}$ symmetry vanishes for all t because its D representation does not include $D_g^{(0)}$, the t.s.r. of $R_h(3)$, the point group of all rotations and parity inversions. Thus water, for example, does not rotate the plane of polarisation of a probe laser and i not optically active. In D representations of $R_h(3)$, the signature of true chirality (8,9) is the product of $D_u^{(1)}$ (polar vector such as linear velocity) and $D_g^{(1)}$ (axial vector such as angular velocity). The Clebsch Gordan theorem implies

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

in general. Therefore, if the two vectors are collinear, the signature of true dynamical chirality reduces to the pseudoscala $D_u^{(0)}$, provided that the product of the time reversal symmetries of the two vectors is positive (8,9). It follows that true dynamical chirality is not observable at field-free thermodynami equilibrium in structurally achiral ensembles.

If however the molecules of the ensemble are structurally chiral, such as (R) bromochlorofluoromethane, the parity inversion operation, P, generates a new and different ensemble, i.e. of (S) bromochlorofluoromethane molecules, and tl point group is R(3), the group of all possible rotations. The irreducible representations of R(3) are $D^{(0)}, \ldots, D^{(n)}$, which do not distinguish between g and u. The representation of scalar and pseudo-scalar quantity is the same, $D^{(0)}$, and it appears at first sight that an ensemble average over both A (scalar) and B (pseudoscalar) exists in R(3) according to the Neumann Curie principle. In R(3) the irreducible D representations do not distinguish between a scalar and pseudoscalar (both are $D^{(0)}$), or between a polar and axial vector ($D^{(1)}$). The signature of chirality in R(3) generated by the two vectors $\underline{v}$ and $\underline{\omega}$, the linear and angular velocities of a diffusing molecule, is

$$\Gamma(\underline{v})\Gamma(\underline{\omega}) = D^{(0)} + D^{(1)} + D^{(2)}$$

in which the product of time reversal (T) symmetries is positive.

In this paper computer simulation is used with an ensemble of 108 molecules of (R) bromochlorofluoromethane to construct the cross correlation function $\langle \underline{v}(t)\cdot\underline{\omega}(0)\rangle$ in frame (X, Y, Z) in order to test directly the Neumann/Curie principle in R(3). Here $\underline{v}$ and $\underline{\omega}$ are the molecular linear and angular velocities respectively and <> denotes the running time average over 6,000 time steps of 5.0 fs each.

Computer Simulation Methods

The equations of motion for an ensemble of 108 (R) bromochlorofluoromethane molecules were integrated with the code TETRA, fully described elsewhere (10-12) at a molar volume and temperature (293.0 K) corresponding to 1 bar of output pressure. The time step was set at 5.0 fs and data saved for analysis every two records over a production segment of 6,000 steps. The procedure was repeated for a contiguous segment of another 6,000 steps. For each segment the three components of the c.c.f. $\langle \underline{v}(t)\cdot\underline{\omega}(0)\rangle$ were evaluated in frame (X, Y, Z). If the .c.f. exists each element should have the same time dependence, because the sample is isotropic overall. The procedures were epeated for $\langle \underline{v}(t)\cdot\underline{J}(0)\rangle$ and $\langle \underline{F}(t)\cdot\underline{Tq}(0)\rangle$ where $\underline{J}$ is he molecular angular momentum, $\underline{F}$ the net force at instant t on a iven molecule, and $\underline{Tq}$ the net torque. Finally the complete omputation was repeated for molar volumes down to half of the riginal molar volume at 1 bar, keeping the temperature constant.

This was deemed to provide a thorough test for the existence of the c.c.f. elements in (X, Y, Z).

Results.

The three elements of $\langle \underset{\sim}{v}(t)\cdot\underset{\sim}{\omega}(0)\rangle$ were computed over two contiguous segments each of 6,000 time steps at 293 K, 1 bar output pressure. Comparison of the results shows that the c.c.f. vanishes in the noise of the computation. The same result appeared for the other c.c.f.'s over the complete range of state points investigated with 108 molecules of the (R) enantiomer.

In the relevant point group, R(3), the representation of the c.c.f. $\langle \underset{\sim}{v}(t)\cdot\underset{\sim}{\omega}(0)\rangle$ is, however, $D^{(0)}$, the totally symmetric representation. The Neumann/Curie principle as usually accepted allows it to exist in the laboratory frame (X, Y, Z). The same result is obtained from the principle for other c.c.f.'s of this type, such as $\langle \underset{\sim}{v}(t)\cdot\underset{\sim}{J}(0)\rangle$, $\langle \underset{\sim}{v}(t)\cdot\underset{\sim}{T_q}(0)\rangle$, $\langle \underset{\sim}{F}(t)\cdot\underset{\sim}{T_q}(0)\rangle$, $\langle \underset{\sim}{F}(t)\cdot\underset{\sim}{J}(0)\rangle$, which nevertheless vanish in the simulation. This shows that thermodynamic ensemble averages of $D^{(0)}$ symmetry which are nevertheless intrinsically pseudo-scalar in nature, such as the c.c.f. $\langle \underset{\sim}{v}(t)\cdot\underset{\sim}{\omega}(0)\rangle$, are vanishingly small and that true scalar quantities with the same irreducible representation, $D^{(0)}$, exist. The magnitudes of these laboratory frame cross correlation functions fall below the accuracy of the computation, and if this result is corroborated, it raises the POSSIBILITY that these pseudo-scalar ensemble averages are zero absolutely.

Note that a strong external influence, such as a static electric field, BREAKS R(3) symmetry and allows elements of these c.c.f.'s to be observed (10,11) according to the third principle of g.t.s.m. (4-6). According to the third principle, molecular ensemble averages are created in R(3) with this symmetry. If the external field is a strong right or left circularly polarised electromagnetic field, resulting in, field dependent, in general non-linear, birefringence, dichroism, and pseudo-scalar rotation of the plane of polarisation, the pseudo-scalar becomes an observable ONLY BECAUSE OF THE INFLUENCE OF THE CIRCULARLY POLARISED EXTERNAL FIELD OF FORCE, whose symmetry includes the pseudo-scalar $D^{(o)}$ in R(3). Thus, a strong circularly polarised field can result in absolute asymmetric synthesis, the gradual formation of one enantiomer (12-14) at the expense of another in a pro-chiral (racemic) mixture subjected to a circularly polarised laser.

Discussion

Under these circumstances, the absolute asymmetric synthetic process is accompanied by the appearance in frame (X, Y, Z) of the c.c.f. $\langle \underline{v}(t) . \underline{\omega}(0) \rangle$, which is therefore seen, according to Barron's rule, as the fundamental dynamical indicator of natural chirality (12-14). The influence of the indicator c.c.f is manifest also through associated spectral observables such as far infra red dichroism and birefringence. Experimental methods for far infra red dichroism are being developed (15). (In the molecule fixed frame (x, y, z), all elements of $\langle \underline{v}(t) \underline{\omega}(0) \rangle$ exist for C_1 molecular symmetry, and all change sign (16) between enantiomers. These switching elements vanish in the racemic mixture (17) and contribute indirectly to observable far infra red dichroism.)

Principle three also allows a straightforward explanation of literature effects of chiral ensembles such as the proposition by Baranova and Zeldovich (18) of resolution of the components of a racemic mixture with the rotating electric field of a right or left circularly polarised laser at radio frequencies. In this case principle three states that the D symmetry of the rotating electric field produces the same D symmetry of equal and opposite LINEAR velocity in each enantiomer (the "propeller" effect). (Both rotation and translation are negative to T). Thus, in R(3), a rotational external influence might produce translation, and vice-versa. A possible consequence of the latter is that the linear momentum imparted by a beam of unpolarised photons might result in the rotation of a chiral crystal suspended from a torsion wire, or of a chiral liquid in a thin-walled vessel. (This is different from the well known Beth effect {19}, where a circularly polarised laser rotates an achiral crystal or liquid, or Born effect {20}, where a rotating electric field does the same thing.) An unpolarised laser tuned to the precise rotational absorption line of a chiral molecule would have reverse effects for +M and -M transitions, where M is the quantum number of the molecular angular momentum in an axis of frame (X, Y, Z). This would be an example of linear photon momentum being converted into a rotational momentum, equal and opposite for two enantiomers. Both linear and angular momenta have $D^{(1)}$ symmetries in R(3).

Comparison with the Molecule Fixed Frame.

It has been shown by computer simulation {21-23}, using the same program, TETRA, that the same functions EXIST in the frame of the principal molecular moments of inertia. Some of these change sign between enantiomers and vanish in the racemic mixture {21-23}. The magnitude of the "propeller" correlations in the molecule fixed frame may therefore be several orders of magnitude greater than their counterparts in the laboratory frame, despite the fact that both types are allowed by symmetry. This could be of great importance in the dynamics of chiral bio-macromolecules such as D.N.A., composed of double (chiral) helices. A variety of C_3 symmetry molecules have been synthesised which are nearly perfect propellers, and it would be of interest in future simulations to look at the cross correaltion functions considered here in both frames of reference. It is known that certain micro-organisms undergo motile translation by rotational motion, which implies the existence of a cross correlation between linear and angular velocities direct in the laboratory frame, and also in a frame of reference fixed in the micro-organism or bio-macromolecule.

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