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THE BREAKDOWN OF MICROSCOPIC REVERSIBILITY IN A CHIRAL ENSEMBLE IN A TIME VARYING ENANTIOMORPHOUS INFLUENCE: A COMPUTER SIMULATION.

by

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Abstract

A computer simulation is used to investigate whether breakdown of microscopic reversibility occurs in an ensemble of (S)-CHBrClF molecules subjected to a time varying enantiomorphous external influence. Time correlation functions of the chiral ensemble in the field applied steady state are shown to obey the principle of stationarity to within 0.1%. Assuming that there is a link between stationarity and microscopic reversibility, it appears on this evidence that the latter is too small to appear above the noise of the simulation, even in a very strong enantiomorphic field.

Introduction

The interesting suggestion has been made recently (1) that conventional detailed balancing does not hold in chiral ensembles, and that in consequence, time-varying chiral, i.e. enantiomorphous, influences may result kinetically in absolute asymmetric synthesis. An example of such an influence is a collinear combination of static electric and magnetic fields, which is negative to time reversal (T), and thus is a falsely chiral influence according to the convention suggested by Barron (1-4). At field free thermodynamic equilibrium, Lifshitz and Pitaevskii (5) have suggested that in a chiral ensemble, detailed balancing is invalidated because parity inversion (P) generates the opposite enantiomer. In the presence of a time-varying

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enantiomorphous inflence, moreover, the T operator is also invalidated {1}, i.e. is not a symmetry operation. According to Barron, the product PT, however, remains valid, resulting in a new principle of enantiomeric detailed balancing in racemic mixtures.

The breakdown of conventional detailed balancing in this way implies that microscopic reversibility would not be necessary for the general validity of the Boltzmann H Theorem {1}, and it is therefore fundamentally important to devise quantitative methods of investigating irreversibility in chiral ensembles.

In this paper, this is attempted with a computer simulation of (S)-CHBrClF subjected to a time varying enantiomorphous influence consisting of two collinear Z axis electric fields, one static and one time dependent. The irreversibility at a fundamental level is assumed to be linked to statistical stationarity, which is investigated with the field applied scalar elements of the time cross correlation tensor

$$\langle F_i(t)\ v_i(0)\rangle = -\langle v_i(t)\ F_i(0)\rangle,$$

where F is the net force on a molecule, and v is the linear center of mass velocity of the same molecule, both defined in the laboratory frame (X, Y, Z).

1. Symmetry Considerations.

The point group of the chiral ensemble of (S)-CHBrClF is R(3) {6-10}, the group of all rotations, and the complete symmetry representation of an arbitrary combination of a static electric field ($\underset{\sim}{E}_o$) and a time varying field ($\underset{\sim}{E}(t)$) is, in R(3),

$$\Gamma\left(\underset{\sim}{E}_o\,\underset{\sim}{E}(t)\right) = D^{(0)} + D^{(1)} + D^{(2)} \quad ; \quad R(3) \quad \text{—} \ (1)$$

The combined T symmetry is negative. If $\underset{\sim}{E}_o$ is parallel to $\underset{\sim}{E}(t)$, both being in the Z axis, eqn. (1) reduces to

$$\Gamma\left(E_{oZ}\,E_Z(t)\right) = D^{(0)} \ ; \ R(3) \ \text{—} \ (2)$$

and the combination of electric fields is a time-varying enantiomorphous influence. The latter's symmetry signature in R(3) is $D^{(0)}$, which can be viewed as a pseudoscalar. (Note carefully that this argument is not valid in an ensemble of achiral molecules, whose point group (6-10) is $R_h(3)$, the group of all rotations and reflections. In this case

$$\Gamma\left(E_{0Z}E_Z(t)\right) = D_g^{(0)} \; ; \qquad R_h(3) \qquad -(3)$$

and the external influence is not enantiomorphous. Its representation, inter alia, is that of a scalar, $D_g^{(0)}$, and not a pseudoscalar, $D_u^{(0)}$. In R(3), the representations of a scalar and pseudoscalar quantity are both $D^{(0)}$, because P is not a valid symmetry operation of R(3).)

2. Quantitative Measurement of Microscopic Irreversibility.

To attempt a classical quantitative measurement of microscopic irreversibility its basic definition must be examined carefully. The quantum mechanical basis (1) for the conventional principle of microscopic reversibility and detailed balancing appears from the analysis by Barron to rest on time reversal symmetry in quantum mechanics. To find a classical counterpart with which to use conventional classically based molecular dynamics computer simulation, we consider the fundamental properties of the time cross correlation function, as discussed for example in ref. (11). In this context, we have the relations

$$\langle A(t)B(0)\rangle = \langle A(t+\tau)B(\tau)\rangle = \langle A(\tau-t)B(\tau)\rangle \qquad -(4)$$

and

$$\langle \dot{A}(t)B(0)\rangle = -\langle A(t)\dot{B}(0)\rangle \qquad -(5)$$

applying the principle of statistical stationarity (11). Here A and B are classical molecular dynamical variables, and < > denote running time averaging. A molecular dynamical process is statistically stationary if the time at which the process < > is started has no effect on the final result. It can be seen from eqn. (4) that a stationary process correlating A and B at field free thermodynamic equilibrium is positive to T. The same process involving time derivatives (eqn. (5)) is negative to T.

There is no evidence from computer simulations (12 - 17) of the enantiomers and racemic mixture of CHClBrF and other chiral ensembles that stationarity does not apply in the enantiomers at field free equilibrium. This has been checked carefully by numerical methods based on Chebyshev polynomials (18, 19). Therefore any conjectured departures (1) from stationarity and resultant time reversal symmetry or anti-symmetry due to microscopic irreversibility are unlikely to be detected accurately by classical computer simulation at field free equilibrium in an enantiomer of CHBrClF. They are probably much too small. However, in the presence of external influences, which in a simulation can be made arbitrarily energetic, the possibility arises of utilising field induced time cross correlation functions (20 - 22) to check departures from stationarity in a very strong enantiomorphous influence.

A static electric field E_{oz} in the Z axis of (X, Y, Z) is known (20, 21) to produce the result

$$\langle v_X(t)\omega_Y(0)\rangle = -\langle v_Y(t)\omega_X(0)\rangle \quad - (6)$$

in the field applied steady state, which is further verified by the third principle of group theoretical statistical mechanics (7, 8). Here $\underline{v}$ is the molecular linear velocity and the symmetry in R(3) of the result (6) is $D^{(1)}$, positive to T. The third principle implies that the $D^{(1)}$ symmetry of the static electric field is imparted to the ensemble averages described in (6).

In a time varying enantiomorphous influence of the type (2), which has $D^{(0)}$ symmetry and is T negative, cross correlation functions of symmetry (6) are no longer supported by principle three. However, a c.c.f. of the right symmetry is

$$\langle v_i(t)F_i(0)\rangle = -\langle F_i(t)v_i(0)\rangle \quad — (7)$$

which is negative to T both on the grounds of reversality and the third principle. (Note that diagonal elements are used in (7), whereas off-diagonal elements are used in (6).) It appears, therefore, that quantitative DEPARTURES from the expected symmetry result (7) would measure the effect of microscopic irreversiblity in an enantiomer subjected to a time varying enantiomorphous influence, provided that there is a link between microscopic reversibility, in the sense implied by Barron {1}, and stationarity.

3. Computer Simulation Methods.

Classical molecular dynamics computer simulation was used with a sample of 108 (S)-CHClBrF molecules at 296 K, with a constant input molar volume adjusted for a mean computed pressure of one bar at field free equilibrium. The interaction potential was a Lennard-Jones site-site type, with partial charges {12-17}. The sample was subjected to an enantiomorphous influence consisting of a combination of a static and time varying electric field in the Z axis, producing the total torque {23, 24}

$$\underset{\sim}{T_q} = -\underset{\sim}{\mu} \times \left(\underset{\sim}{E_0} + \underset{\sim}{E}(t) \right) \quad — (8)$$

on each molecule, where $\underset{\sim}{\mu}$ is the molecular electric dipole moment. The sample was re-equilibrated to a steady state in the presence of $\underset{\sim}{T_q}$ and time correlation functions computed in the steady state to test eqn. (7) numerically. The additional energy imparted to the sample by $\underset{\sim}{T_q}$ was adjusted to make its effect on the time dependence of correlation functions clearly visible.

The integration time step was 0.05 ps, and contiguous segments of up to 6,000 time steps were used in constructing the field-on time correlation functions by running time averaging in the field applied steady state. The magnitude of $\underline{E}_0$ was adjusted to be half that of the electric field $\underline{E}(t)$, which was programmed in as cosinusoidal with a frequency adjusted to 20.0 THz.

4. Results and Discussion

In order to illustrate the accuracy of the simulation, the field-on cross correlation function

$$\langle v_x(t) F_x(0) \rangle = - \langle F_x(t) v_x(0) \rangle \quad — (9)$$

Provided that there is a link between non stationarity and he classical manifestation of microscopic irreversibility, there ppears, in conclusion, to be no unequivocal evidence for the atter in this simulation, either at field free equilibrium in he S enantiomer of CHBrClF, or in the presence of an arbitrarily trong enantiomorphous influence.

From the equivalence principle, it appears reasonable o assume that there is a classical equivalent to microscopic rreversibility as defined in quantum mechanics. It is not proven hat there is a link between classical reversibility and tationarity, but it seems reasonable to assume that one exists, ecause in the limit of complete irreversibility, the T operator f classical mechanics would be invalidated, time reversal ymmetry would not hold, and the process could not be tatistically stationary. We tentatively propose that a molecular nsemble which is statistically stationary at field free quilibrium must also be reversible on a microscopic scale.

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