Journal of Molecular Liquids, 27 (1983) 11—18
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

THE LOW TEMPERATURE MOLECULAR DYNAMICS OF THE BROMOCHLOROFLUOROMETHANES - LABORATORY FRAME EFFECTS OF ROTATION/TRANSLATION COUPLING

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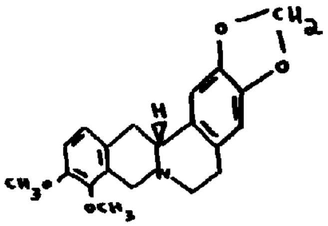
(Received 19 May 1983)

ABSTRACT

The racemic modification of molecular dynamical properties is simulated with a computer for the liquid bromochlorofluoromethanes near the melting points. The source of the laboratory frame modification is traced to <u>intrinsic</u> differences in the dynamical properties of enantiomer R and S. These show up only in a moving frame of reference, and are quantified in this paper by the moving frame correlation matrix $<\underline{v}(t)\underline{J}^T(0)>_m$, where $\underline{v}$ is the molecular centre of mass linear velocity and $\underline{J}$ its angular momentum; both vectors defined in the moving frame.

INTRODUCTION

The physical properties of a racemic mixture can be dramatically different from those of each component - the two enantiomers of an optically active molecular liquid. There is usually a distinct modification of the melting point, but a much smaller racemic modification of the boiling point of either enantiomer. In a propeller shaped molecule such as canadine:



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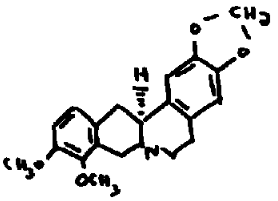

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the melting point of each enantiomer is 132°C but that of the mixture is no less than 42°C higher at atmospheric pressure. Canadine is an essentially rigid, polycyclic, natural product in which there is no hydrogen bonding to complicate the intermolecular potential energy surface. The spectral properties of each enantiomer are identical in the laboratory frame with the exception of their response to a symmetry-breaking variable such as circularly polarised radiation field. It is therefore difficult for the classical (phenomenological) theory of molecular diffusion [1] to explain why an equimolar mixture of two components, whose molecular dynamics appear to be identical, should behave differently and sometimes greatly so, over a significant range of temperature.

We have suggested recently [2,3], using computer simulation, that a cause of the racemic modification is the statistical correlation between the translation of the centre of mass of an individual molecule and *its own* rotational motion about this centre of mass. This type of statistical correlation may be quantified using matrices such as $\langle \underline{v}(t)\underline{J}^T(0)\rangle_m$ where the running-time averaging $\langle\ \rangle_m$ is over the vectors $\underline{v}$ and $\underline{J}$ *defined with reference to a moving frame*, for convenience that of the principal molecular moments of inertia in a rigid molecule. In this frame of reference we have detected for the first time an *intrinsic* difference in the physical properties of an R and S enantiomer [3]. This appears as a difference in some of the elemental cross-correlation functions of the 3 x 3 matrix $\langle \underline{v}(t)\underline{J}^T(0)\rangle_m$. (Each element is normalised by $\langle v^2\rangle^{\frac{1}{2}}\langle J^2\rangle^{\frac{1}{2}}$.) Typically, an element in enantiomer R is the mirror image, in its time dependence, of its counterpart in enantiomer S. The same element vanishes for all t in the racemic mixture. In an infinitely dilute gas these elements vanish for all t because there are no collisions through which angular and linear momentum may be exchanged. In a perfect molecular crystal, near zero Kelvin, they become infinite because the small remaining centre of mass translation of each and every molecule is identically correlated with its rotation. (The normalising factors $\langle v^2\rangle^{\frac{1}{2}}$ and $\langle J^2\rangle^{\frac{1}{2}}$ vanish at 0°K.) Near the boiling point, the magnitude of these elements diminishes rapidly, and increases strongly near the freezing point. This is evidence to the effect that the racemic modifications of the boiling point and freezing point are measures of rotation/translation coupling on a fundamental, molecular level.

In order to explore this hypothesis by computer simulation, we have to work with molecules smaller than canadine because of limitations on computer-power. Two convenient systems for this purpose are the 2 chlorobutanes and the bromochlorofluoromethanes [4]. The former system is one of those very rare cases in which both the boiling points and melting points of both enantiomers and mixtures are known accurately. Enantiomers and mixture boil at what appears to be the same temperature ($68^{o}C$), but there is a significant modification of about $9^{o}C$ to the melting points. The racemic mixture melts at $-131.3^{o}C$ and the laevorotator enantiomer at $-140.5^{o}C$ as reported by Timmermans and Martin [5] using ultra-pure reagents for their synthetic procedures. In this range of temperature, therefore, each enantiomer is a liquid but their equimolar, racemic mixture is a solid. The non-dichroic spectra and physical properties of the R and S enantiomers would b identical in all respects. The classical, phenomenological, theory of molecular diffusion would have to describe each enantiomer with exactly the same set of parameters (for example, the Debye relaxation time) and would not be able to tell them apart. The solidification upon equimolar solution would therefore be inexplicable in the laboratory frame of reference. The computer simulation methods developed recently can spot the differences in the moving frames of reference as described already, and ascribe the modification to rotation-translation coupling [2-4].

For the purposes of computer simulation it is convenient to start with the bromochlorofluoromethanes and proceed to the structurally more complicated 2 chlorobutanes. We have already simulated the former system at a temperature about $10^{o}C$ below the boiling point [4], using principal cartesian coordinates reported in the literature [6] from an accurate electron diffraction study of the molecular structure. In this paper we extend our study to input temperatures near the freezing point of the racemic mixture (158 K) and into the supercooled states of enantiomers and mixture. The same, simple, model [4] is used for the pair potentia based on site-site components made up of atom-atom Lennard-Jones terms and partial charges for the electrostatic part of the total interaction potential. These site-site components are intrinsically the same in all three cases, i.e. an intermolecular carbon to carbon term in an R to R situation is the same as in the S to S, R to S or S to R cases. The total pair-potential is the sum of twenty five site-site terms in CHBrClF. The principal cartesian coordinates of the R and S enantiomers are different, but the laboratory frame autocorrelation functions from the computer simulation must be identical. This serves as a check on the above assumptions concerning the pair-potential and on the quality of the computer simulation.

The purpose of this low temperature simulation is to monitor the racemic modification in the laboratory frame as a function of $\langle \underline{v}(t)\underline{J}^{T}(0)\rangle_{m}$ in the moving frame using temperature as a variable. A computer simulation naturally goes into a supercooled, and eventually glassy, state as the temperature is lowered past the normal freezing point, and we use this property to monitor the observable (lab. frame) racemic modification in the supercooled liquids.

ALGORITHM AND COMPUTATIONAL METHOD

Theee are as described previously [4]. The input molar volumes at 158 K (the literature melting point of the racemic mixture) and at 100 K were estimated by a simple linear extrapolation of the recorded density of the racemic mixture at room temperature. The same simple site-site intermolecular potential was used as in the work at room temperature.

RESULTS AND DISCUSSION

Fig. (1) typifies the effect of mixing the two enantiomers on the molecular dynamics, in this case quantified with the centre of mass linear velocity autocorrelation functions in the laboratory frame. The a.c.f.s of the two enantiomers are almost identical, signalling good statistics in the simulation runs in both cases. The long negative tail of this a.c.f. is more oscillatory for the racemic mixture at the same input molar volume and temperature. The actual racemic modification of the melting point in the bromochlorofluoromethanes is unknown, but the simulations indicate a significant difference in the dynamical, and by implication, transport properties close to the melting point of the racemic mixture (158 K). The empirical and unrefined potential used in our simulation cannot be relied upon to indicate more than the fact that there is

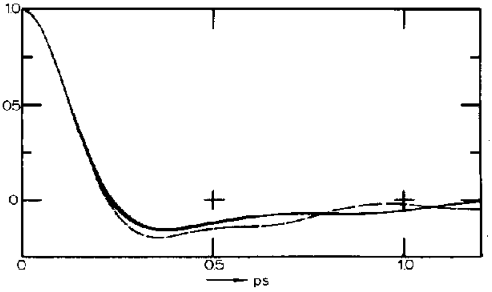


Fig. 1. Liquid HCBrClF at an input temperature of 158 K. Simulated centre of mass velocity a.c.f.'s in the laboratory frame, normalised to unity at $t = 0$.

R and S enantiomers.

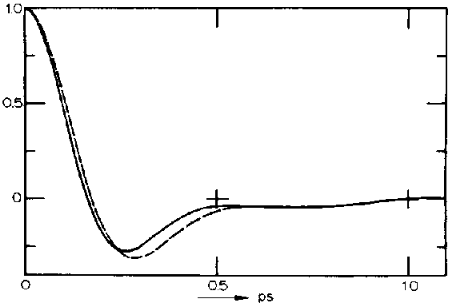
– – – – Racemic mixture at the same input molar volume and temperature.

Ordinate: $\langle \underline{v}(t).\underline{v}(0)\rangle / \langle v^2(0)\rangle$.

Abscissa: time/ps.

a dynamical modification. However, our results are clearly self-consistent given the model potential.

The modification of the laboratory frame angular velocity a.c.f. is shown in fig. (2) as a shift to longer times in the negative overshoot of the racemic a.c.f. A very similar pattern appears in a rotational velocity a.c.f. such as that of a principal axis unit vector ($\underline{e}_3$ (fig. 3)). This type of a.c.f. is related by Fourier transformation to a far infra-red spectrum, and fig. (3) suggests that the spectrum of the racemic mixture would peak at lower frequencies than that of either enantiomer.



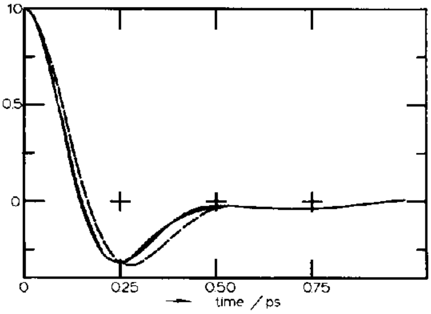
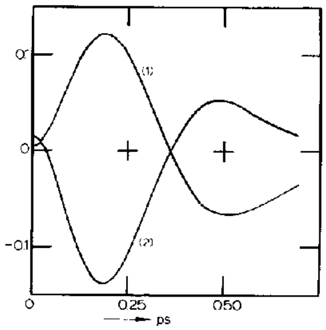


Fig. 2. As for fig. 1, molecular angular velocity a.c.f.'s.

Fig. 3. As for fig. 1, rotational velocity a.c.f.'s: $<\dot{\underline{e}}_3(t).\dot{\underline{e}}_3(0)>/<\dot{e}_3^2>$.

MOVING FRAME MATRIX $<\underline{v}(t)\underline{J}^T(0)>_m$

The (1,3) and (3,1) elements of this correlation matrix are illustrated for the enantiomers in figs. (4) and (5). They are mirror images in both cases. In consequence these cross correlation functions quantify the first observation of its kind of an intrinsic difference between the physical properties of an R and S enantiomer. Differences such as these are responsible for the visible (spectral and physical) racemic modification represented by figs. (1) to (3). The equivalent cross-correlation function to those in figs. (4) and (5) vanish for the racemic mixture. As reported elsewhere [4], there is less of a difference in the behaviour of the (2,1), (1,2), (3,2) and (2,3) elements between enantiomers and racemic mixture, but the overall symmetry of the complete matrix $<\underline{v}(t)\underline{J}^T(0)>_m$ changes.



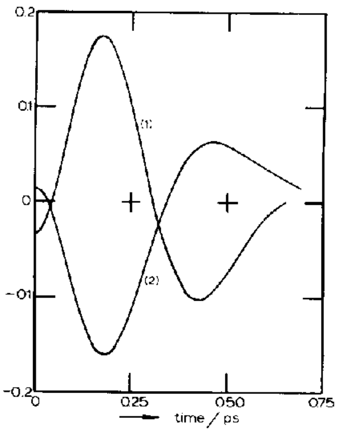


Fig. 4. Elements of $\langle \underline{v}(t)\underline{J}^T(0)\rangle_m$.

(1) (1,3) $\dfrac{\langle v_1(t)J_3(0)\rangle}{\langle v_1^2\rangle^{\frac{1}{2}}\langle J_3^2\rangle^{\frac{1}{2}}}$; R enantiomer.

(2) (1,3), S enantiomer. (1,3), racemic mixture vanishes for all t.

Ordinate: Corss elements.

Abscissa: time/ps.

Fig. 5. As for fig. 4, (3,1) elements.

(1) (3,1), S enantiomer.

(2) (3,1), R enantiomer.

(3,1) for the racemic mixture vanishes in the noise for all t.

The same patterns of behaviour are observable in the supercooled liquid state at 100 K. The amplitudes of the moving frame cross-correlation functions increase, but the same symmetry patterns are maintained as at 158 K and at room temperature [4].

PHENOMENOLOGICAL THEORY OF ROTOTRANSLATION

There have been sporadic attempts [7] to adapt the hydrodynamic theory, typified in the work of Condiff and Dahler [8], to describe the correlation between rotation and translation in the laboratory frame. However, $\langle \underline{v}(t).\underline{J}(0)\rangle$ in this frame vanishes [9] in an isotropic molecular liquid for all t and all molecular symmetries, including chiral symmetry, because of the parity difference between $\underline{v}$ and $\underline{J}$. Theories prior to the development of the moving frame trap of computer simulation [10] are restricted to the laboratory frame. There is no phenomenological theory yet available to describe the computed differences in $\langle \underline{v}(t)\underline{J}^T(0)\rangle_m$ described in this paper for chiral molecules. By implication the phenomenological theory cannot account for the well-known racemic modification of the physical properties of molecular liquids.

Apparently, this has not been realised since the inception of the phenomenological theory of molecular diffusion in 1905 by Einstein, and its adaptation by Debye for "rotational" motion in 1913.

The development of the existing theoretical methods [1] can take place by recourse to non-linear terms in the basic stochastic differential equations. Grigolini et al. [11,12] have shown recently that a non-linear term in the Langevin equation changes profoundly its mathematical properties with consequences which are still being explored. It is possible to adapt these non-linear structures to describe molecular diffusion in both frames of reference, and this is work in progress. There are, probably, parallel racemic modifications due to vibration/rotation coupling (infra-red, Raman) and vibration/translation coupling (acoustic dispersion).

ACKNOWLEDGEMENTS

The S.E.R.C. and C.C.P.5 are acknowledged for generous support.

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