

THE EFFECT OF EXTERNAL ELECTRIC FIELDS ON MOLECULAR LIQUIDS AND INDUCED
TRANSLATIONAL MOTION

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ABSTRACT

A computer simulation is reported of the enantiomer S-CHBrClF subjected in the liquid state to intense external fields of force :
i) uniaxial electric field E_z ; ii) circularly polarised field at optical frequencies. The molecular dynamics are quantified in detail at field - on equilibrium in case i) using a range of auto correlation functions. The foremost result of the investigation is that the simple uniaxial field E_z makes the sample translate in a well defined direction. The direct effect of E_z on an isolated molecule of S-CHBrClF is purely rotational, but intramolecular rotation/translation coupling converts this rotation into coherent centre of mass translation. This gives rise to direct, laboratory frame, cross correlations of the type $\langle \underline{v}(t) \underline{J}^T(0) \rangle$ where \underline{v} is the molecular centre of mass translational velocity and \underline{J}^T the transposed molecular angular momentum vector. (The existence of these invalidates the classical theory of the Kerr effect.) The molecular dynamics of the hypothetical chiral ion S-CHBrClF⁻ are looked at with a view to corroborating the predictions by Baranova et al. concerning their response to electric field treatment. Despite the inherent instability of such an ensemble of like-charged ions the simulation can be used to produce a range of auto and cross-correlation functions with which to characterise the ionic dynamics. The effect of treating the ionic ensemble with a field E_z is reported briefly in terms of the non-vanishing ensemble averaged centre of mass velocity $\langle v_z \rangle$.

The induced translation in an electric field may be demonstrated on most liquids using a simple experimental set up. Its importance in optically active systems is such that it may be used to separate a racemic mixture into its enantiomers, the translational motion induced in the one enantiomer is necessarily, by symmetry, opposite to that induced in the other enantiomer. The observation therefore has technological importance. Other applications are discussed.

INTRODUCTION

One of the most subtle problems in liquid state physics is that of describing how the rotational motion of a molecule affects its own translation and vice versa. For convenience translation may be described through the centre of mass linear velocity, \underline{v} , and rotation through the molecular angular momentum, \underline{J} , or angular velocity, $\underline{\omega}$. One of the difficulties is that the simple, laboratory frame, cross-correlation function $\langle \underline{v}(t) \underline{J}^T(o) \rangle$ normally vanishes for all t because the parity reversal symmetry of \underline{v} and \underline{J} is different [1]. However, in a moving frame of reference, for convenience that of the principal molecular moments of inertia, these cross-correlations become visible by computer simulation for all dipolar and most non-dipolar molecular symmetries [2]. The description of molecular dynamics in the liquid state requires, therefore, a self consistent analysis, in terms of equations of motion, of correlation functions such as $\langle \underline{v}(t) \cdot \underline{v}(o) \rangle$, $\langle \underline{J}(t) \cdot \underline{J}(o) \rangle$ and $\langle \underline{v}(t) \cdot \underline{J}^T(o) \rangle_m$. (Here subscript m denotes averaging over vectors defined in the moving frame of reference.) Some attention is being given, now, to this problem with the methods of phenomenological theory, relying to a degree on the results of computer simulation for "numerical clues".

This attention is necessary because at least one fundamental phenomenon - the Pasteur racemic modification - depends for its description [3-5] on the detailed time evolution of $\langle \underline{v}(t) \underline{J}^T(o) \rangle_m$. This is different for an R and S enantiomer, and different again in mixtures of R and S enantiomers. In contrast, a.c.f.'s such as $\langle \underline{v}(t) \cdot \underline{v}(o) \rangle$ and $\langle \underline{J}(t) \cdot \underline{J}(o) \rangle$ are identical in the laboratory frame for R and S enantiomers but are different in this same frame for the racemic mixture. Another fundamental property of chiral molecules and perhaps all molecules in the liquid state is the propeller effect. This is,

self-evidently, the ability to translate in response to an applied torque. Baranova et al. [6,7] have described the appearance of bulk translation in two cases of interest: i) when an electric field is applied to a chiral ion; ii) when a circularly polarised, alternating field is applied to a racemic mixture of two uncharged enantiomers. Case i) is analogous in nature to the magnetically induced Faraday effect. In case ii) Baranova et al. [6] show theoretically that the two enantiomers slowly move in opposite directions, so that the applied field may be used to resolve pure enantiomers.

The purpose of this paper is to use the new molecular dynamics computer simulation techniques developed by Evans [8-12] to investigate the effect of an externally applied torque on the translational properties of chiral molecules and ions in the liquid state. These techniques consist of simulating the dynamical behaviour of an ensemble of molecules when subjected to an intense external field of force, which may be electric, magnetic, electromagnetic etc. in nature. Equilibrium properties such as orientational averages respond to energy pumped into the system in this way through various Langevin [9] or Kielich [12] functions, which are reproducible exactly with the computer simulation. A variety of dynamical properties may then be produced [11] which provide an insight to the competition between the strong aligning, external field and the natural, thermally induced, molecular dynamics. The field "decouples" the molecule from its thermal bath as in the reduced model theory by Grigolini and co-workers [13,14] and causes the appearance of rise and fall transients associated with the induction of birefringence. The relation between the rise and fall time scales may be used to provide clues to a profound and difficult analytical problem.

These techniques were developed with an ensemble of achiral, C_{2v} symmetry triatomics. In section 2 of this paper the modification necessary to the algorithm are described for a simple chiral symmetry, that of S-CHBrClF. Two types of force field are applied to 108 of these molecules:

- i) an electric field in the Z direction of the laboratory frame;
- ii) the electric field component of a circularly polarised electromagnetic field as defined by Baranova et al. [6].

Further sections of this paper deal with the results of applying intense force fields of this type to the S enantiomer of CHBrClF near the melting point of 158K. Section 3

deals with the foremost result of this paper - that an intense uniaxial electric field produces a net translation in a sample of optically active molecules: in this case S (and R) CHBrClF. The direction of translation reverses with the electric field direction and is opposite for the R enantiomer. Therefore it is not necessary to use a circularly polarised field in the manner of Baranova et al. to resolve the enantiomers. A sufficiently strong uniaxial field suffices. In section 4 we discuss the details of the laboratory frame molecular dynamics of our optically active species under the influence of a very strong electric field and quantify for the first time a laboratory frame cross-correlation function of the type $\langle \underline{v}(t) \underline{J}^T(0) \rangle$. The existence of this function means that rotation/translation coupling is directly observable in an ensemble of optically active molecules, which is, inter alia, the reason why chiral molecules translate when treated with an electric field. Another interesting consequence with a strong electric field is that the translational statistics [15] are changed from those of a 3-D ensemble to those of a 1-D ensemble, i.e. the second moment, kinetic energy, a.c.f. $\langle v^2(t)v^2(0) / v^4 \rangle$ no longer reaches a 3-D Gaussian limit of 3/5 as $t \rightarrow \infty$ but instead goes to the 1-D limit of 1/2 because the molecules are constrained to drift translationally in one direction while continuing to be influenced by a stochastic background (the thermal bath at equilibrium). In section 5 the moving frame is used to investigate the detailed nature of rotation/translation coupling in the presence of the strong electric field and to explain the opposite behaviour of the two enantiomers in terms of the elemental cross-correlation functions of $\langle \underline{v}(t) \underline{J}^T(0) \rangle_m$. In section 6 we investigate the velocity drift with a circularly polarised field of the type used by Baranova et al. [6] and in section 7 sketch out the dynamics of an ensemble of charged chiral molecules [7], in this case the hypothetical ion CHBrClF⁻, indicating the probable effect of an electric field. Finally in section 8 we describe the experimentally observed induced translation in achiral molecules and discuss technological applications of this effect.

Section 2: Simulation Algorithm

The essential features of this algorithm are fully described elsewhere in the literature. The equations of motion for 108 molecules of S and R type, (or a mixture of 54 R or S) are integrated with a

method developed by Ferrario and Evans [16]. At the appropriate stage in the algorithm the effect of an electric field may be introduced in at least two ways.

- i) By defining the dipole moment vector $\underline{\mu}$ in the laboratory frame. The direct effect of an external electric field \underline{E} on the molecular dynamics is then well-known to be the introduction of an extra torque $-\underline{\mu} \times \underline{E}$. Therefore, in the absence of intermolecular interaction, an electric field can only rotate an uncharged molecule [17]. If we consider additionally [18] molecular polarisability, $\underline{\alpha}$, or hyperpolarisability, $\underline{\gamma}$, there is again no mechanism through which the field can produce molecular translation in the absence of intermolecular interaction. Therefore, for the sake of clarity, we restrict this method in this paper to the dipole moment and associated torque ($-\underline{\mu} \times \underline{E}$).
- ii) All higher order polarisability terms can be included exactly if the electrostatic characteristics of each molecule are broken up into a set of partial charges q_i located at the atomic sites. The net effect on each atom of each molecule of an electric field E_z in the Z axis of the laboratory frame is then: $-E_z q_i$. The terms $-E_z q_i$ are inserted in the appropriate place inside the forces loop of the algorithm. In an uncharged molecules the effect of the terms $-E_z q_i$ in the absence of intermolecular interaction is again to rotate the molecule. In the presence of intermolecular forces the net force on each atom of each molecule is supplemented by the externally applied term $-E_z q_i$. If the chiral molecule under consideration is charged, then the electric field will have a direct translational as well as rotational effect because the molecule is no longer electrically neutral.

The strength of the Z component E_z of the field \underline{E} can be increased arbitrarily in the computer simulation. This has the advantage for a theoretician of clarifying the definition of the complete problem. Using the numerical technique of computer simulation it is no longer necessary or desirable to restrict our consideration to low field strengths, whose energetic effect is much smaller than the thermal kT . In this paper we do the opposite: minimise kT by looking at the liquids just above the melting point and employ a field strength E_z sufficient to nearly saturate the Langevin function. This maximises the chances of seeing most clearly the phenomenon at hand, that of electric field induced translation. We shall see later that the phenomenon which is established at high field

strengths in the simulation is also present at electric field strengths available in the laboratory. Therefore the spirit of our computer simulation has been, as always, to provide numerical guidelines for the theoretician and experimentalist. The present simulation is not an attempt to replace real experiment with a "computer experiment" but is used to verify and explain a reported [21] experimental observation.

The algorithm employs the standard methods of temperature rescaling and uses a fixed input volume related to the size of the molecular dynamics "cube". Therefore the initial effect of applying E_z (i.e. switching it on instantaneously) is to increase the rotational temperature far above the field-off mean level of $158 \pm 25\text{K}$. However, the rescaling routine quickly reduces the temperature again to the field-off level, and maintains it there even though the energy constantly being pumped in to the system via the field E_z greatly exceeds kT , the system as a whole being at a point on the Langevin function close to saturation. During the non-equilibrium rise-transient process, shortly after the field is applied, the rotational temperature can be very high. At equilibrium in the presence of the field it is maintained at the field-off level. Once field-on equilibrium is reached correlation functions of various kinds may be calculated by running-time averaging if the system is statistically stationary. The next section deals with the translational characteristic of the system at field-on equilibrium.

Section 3: Translation Induced by an Electric Field

One of the indications of the transformation of the rotational torque $-\mu \times E$ into translational energy is illustrated in fig. (3.1) through the behaviour of the translational temperature (T_t) after field application. The rescaling routine E_z reduces T_t to $158 \pm 25\text{K}$ from an initial level which is very much greater. This is a clear sign that the rotational kinetic energy supplied by E_z is almost instantaneously transformed into translational kinetic energy (or temperature). These modes of motion are therefore inextricably inter related in the thermal bath of 10^8 S-CHBrClF molecules.

The most straightforward way of monitoring the development of bulk translation is to construct the averages $\langle v_x \rangle_{10^8}$, $\langle v_y \rangle_{10^8}$ and $\langle v_z \rangle_{10^8}$,

where $\langle \rangle_{108}$ means a simple average over the 108 molecules at each time step after the field E_z is switched on. (It is also useful to calculate $\langle v_x^2 \rangle_{108}$, $\langle v_y^2 \rangle_{108}$ and $\langle v_z^2 \rangle_{108}$ to obtain an idea of the magnitude of the translational effect.)

At field-off equilibrium we should have $\langle v_x \rangle_{108} = \langle v_y \rangle_{108} = \langle v_z \rangle_{108} = 0$, and this condition is illustrated for S CHBrClF in fig. (3.2).

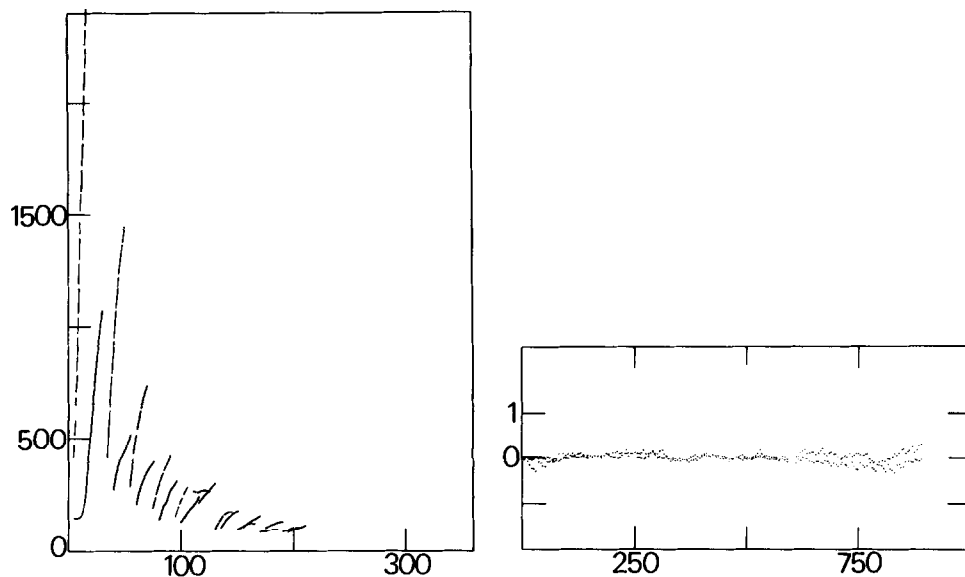


Fig. 3.1 Rescaling the translation (—) and rotational (---) temperatures to input level (158K) after field application. Note that the rotational kinetic energy added to the 108 molecules by the external field is converted almost instantaneously into translational kinetic energy (i.e. temperature).

Ordinate: temperature/K; Abcissa: time/ps.

Fig. 3.2 Behaviour of $\langle v_x \rangle$, $\langle v_y \rangle$ and $\langle v_z \rangle$ (in program units) over about 5.0 ps at equilibrium.

Ordinate: $10^{14} \langle v_z \rangle$;

Abcissa: time/ps.

The effect on S-CHBrClF of switching on the field (via the torque $-\underline{\mu} \times \underline{E}$) is illustrated in two ways in figs. (3.3) and (3.4). The orientational rise transient in fig. (3.3) is the response of $\langle e_{3z} \rangle_{108}$ to the field as a function of time. Here \underline{e}_3 is a unit vector in the axis of the I_3 principal molecular moment of inertia and e_{3z} its Z component in the laboratory frame. The transient is saturated in less than 1.0 ps (200 time steps) - about the same length of time as it takes the rescaling subroutine (the "thermostat") to reduce the temperature again to its field off level.

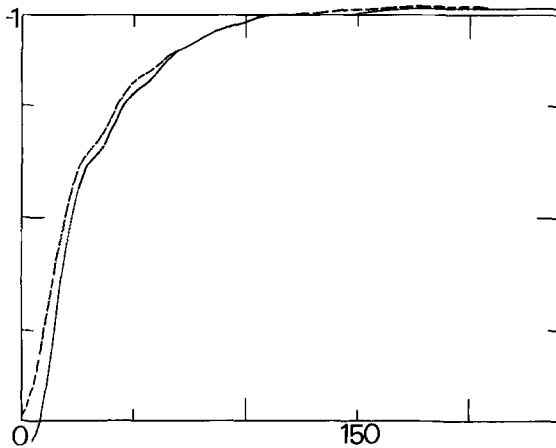


Fig 3.3 $\langle e_{3z} \rangle$ rise transient; ——— for a field E_z ;
 - - - - - $\langle e_{3z} \rangle$ for a field $-E_z$.
Ordinate: $\pm e_{3z}$; Abscissa: time/ps.

The main result of this paper appears after the orientational rise transient is saturated and after the temperature has been reestablished. This is illustrated in fig. (3.4) as a slowly developing drift away from their field-off values of all three components of $\langle \underline{v} \rangle_{108} = \underline{i} \langle v_x \rangle_{108} + \underline{j} \langle v_y \rangle_{108} + \underline{k} \langle v_z \rangle_{108}$. Here \underline{i} , \underline{j} and \underline{k} are unit vectors in the x, y and z lab. frame axes. Therefore the mean velocity of the 108 molecules slowly increases with time after the field is switched on. The mean square velocity $\langle v^2 \rangle_{108}$ is, at the same time, maintained constant, being directly proportional to the translational temperature. The time scale of this drift is much longer than the orientational transient rise time. It

is clear that all three components of $\langle \underline{v} \rangle_{108}$ are increasing in magnitude at 5.0 ps into field - on equilibrium, and show no signs of returning again to zero. In figs (3.4 band C) we have taken advantage of the

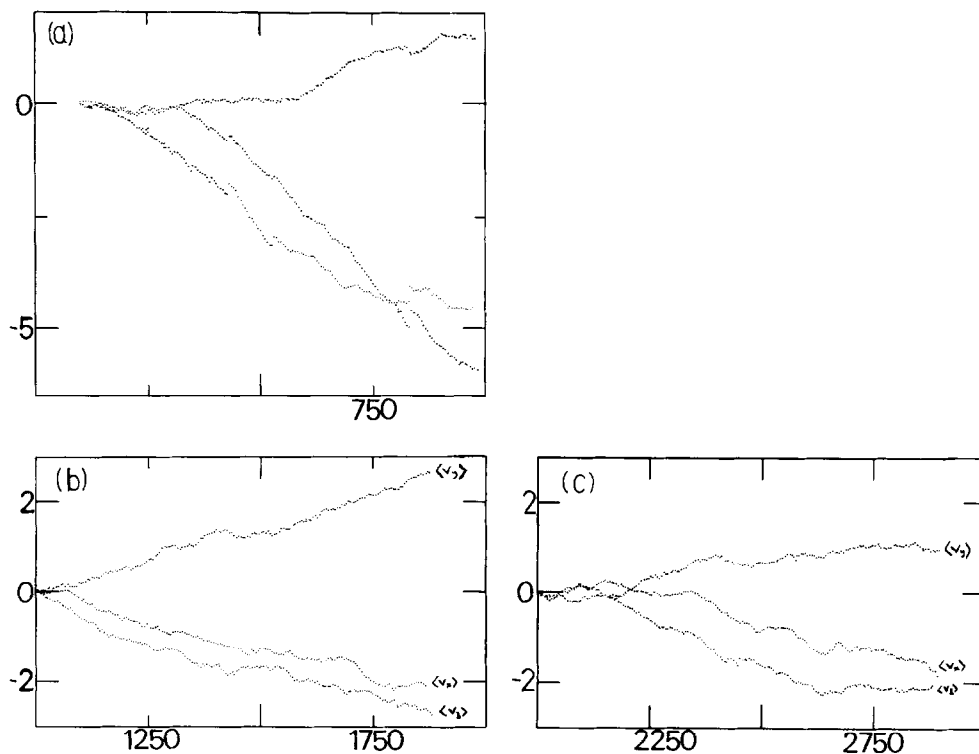


Fig. 3.4 (A) Illustrating the electric field induced translation with (1) $\langle v_x \rangle$; (2) $\langle v_y \rangle$; (3) $\langle v_z \rangle$ over a time scale of about 5.0 ps. The drift from zero level may be judged with reference to the "base line" of fig. 3.2.

(B) The reestablishment of drift after resetting the mean velocities to zero at the end of the run illustrated in fig. 3.4a. Note that the rate of drift is slower.

(C) The same after run (B). The rate of drift is again slower.

In an undisturbed run the mean velocities would reach a final level, significantly different from zero, after about 15.0 ps. Contrast this time scale with that of $\langle e_{3Z} \rangle$ in fig. 3.3.

Ordinates and Abcissae as for fig. 3.3.

standard molecular dynamics subroutine which initially resets translational momenta to zero to force the mean velocities again to zero after the first 5.0 ps or so of the field-on simulation run. It is clear from fig. (3.5 (a) and (b)) that they thereafter immediately drift away again at a progressively reduced rate. The overall conclusion from fig. (3.4) is that the mean velocity $\langle v \rangle_{108}$ would, in an uninterrupted run, gradually increase to an equilibrium field-on value achieved probably about 30.0 ps after the field has been switched on. This contrasts with the 0.6 ps or so needed to saturate $\langle e_{3Z} \rangle_{108}$.

It is clear from these observations that we are looking at a propeller effect. The initial effect of the strong electric field is to force each molecule into a configurational alignment represented by $\langle e_{3Z} \rangle \doteq 1.0$. This constrains the natural (thermal) rotational motion into a "precessional" motion around the axis of \underline{E} (the lab. z axis) i.e. the natural spherical spatial distribution of the dipole $\underline{\mu}$ is changed into a narrow conical distribution around the z axis of the lab. frame. The axes of the molecular propellers are no longer randomly distributed and the translational effect caused by their rotation no longer averages to zero. This is analogous to the conclusion reached by Baranova et al. [6] using circularly polarised radiation but differs in one respect - in that a static rather than alternating field is sufficient to cause centre of mass translation.

Section (4): Field-on Dynamics

In this section we investigate the molecular dynamics of an S CHBrClF sample in the field-on case illustrated in fig. (4.1). In this figure we illustrate the final level reached by $\langle e_{3Z} \rangle$ and the field-on translational temperature T_{tr} fluctuating about the input value of 158K. The velocity drifts of figs. (3.4) imply that the sample is not stationary over an interval of time of the order of 30.0 ps., but the a.c.f.'s in which we are interested decay quite quickly (<0.5 p.sec) compared with the rate of drift. To a good approximation, therefore, it is valid to use running-time averaging when constructing these autocorrelation functions.

The most interesting result of this section is that of fig. (4.2), where we illustrate the field on, lab. frame auto-correlation functions $\langle \underline{v}(t) \cdot \underline{v}(0) \rangle / \langle v^2 \rangle$ and $\langle \underline{v}(t) \cdot \underline{v}(t) \underline{v}(0) \cdot \underline{v}(0) \rangle / \langle v^4 \rangle$. The velocity a.c.f. itself

exhibits the characteristically long negative tail but the kinetic energy a.c.f. reaches a $t \rightarrow \infty$ level of 0.5, rather than the 3 - D Gaussian result of $3/5$. It is significant in this context that the equivalent $t \rightarrow \infty$ limit for one dimensional statistics (i.e. $\langle \dot{x}^2(t)\dot{x}^2(0) \rangle$ rather than $\langle v^2(t)v^2(0) \rangle$) is $1/2$. Therefore the ensemble is "one dimensional" in translational nature i.e. there is a strong preference for molecules to drift in one well defined axis of the laboratory frame, as in fig. (3.4).

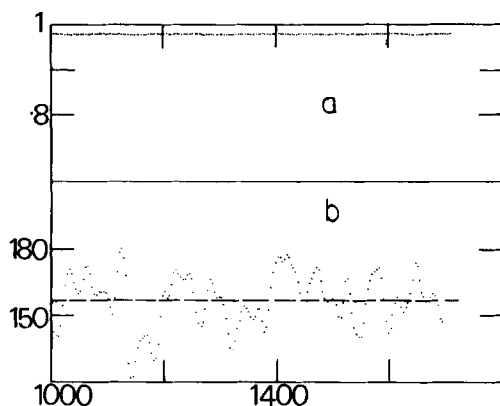


Fig. 4.1 (A) The final level attained by $\langle e_{3Z} \rangle$ (field-on equilibrium).

The Langevin function saturates at infinite field strength with

$\langle e_{3Z} \rangle = 1.0$.

(B) The translational temperature at field-on equilibrium (cf. fig. 3.1).

It fluctuates about $T_t = 158\text{K}$.

Ordinates: (a), $\langle e_{3Z} \rangle$; (b) translational temp/K.

Abcissa for both figs: time/ps.

Fig. (4.3) illustrates the field-on angular velocity and angular momentum a.c.f.'s and their second moments. There is a significant difference in the time dependence of these a.c.f.'s revealing the basic anisotropy in the rotational motion induced by the strong external torque. The oscillations in the angular velocity a.c.f. are the direct result of the external torque $-\underline{\mu} \times \underline{E}$, but the decay rate of the envelope of these oscillations is a result of the competition between the external field and the thermal motion of the molecular ensemble - the "decoupling effects" of Grigolini et al. [13,14].

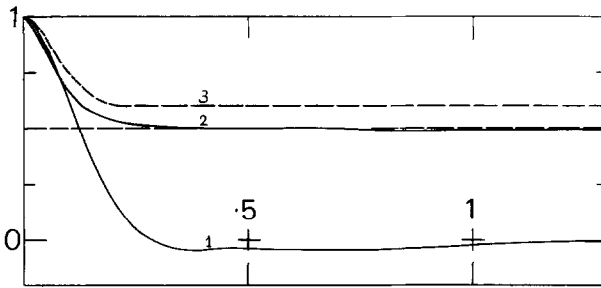


Fig. 4.2 (1) Centre of mass velocity a.c.f. $\langle \underline{v}(t) \cdot \underline{v}(0) \rangle / \langle v^2 \rangle$, field-on S CHBrClF.

(2) $\langle \underline{v}(t) \cdot \underline{v}(t) \underline{v}(0) \cdot \underline{v}(0) \rangle / \langle v^4 \rangle$.

- - - 3-D Gaussian second moment, calculated from function (1).

Ordinate: Normalised a.c.f.; Abcissa: time/ps.

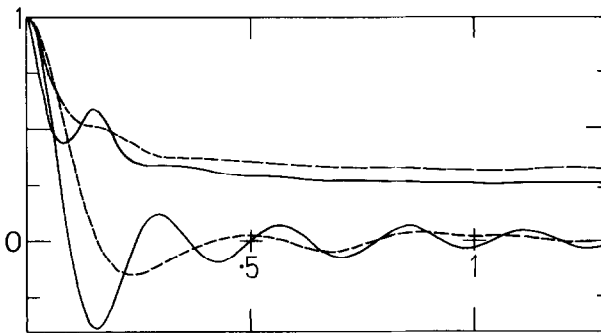


Fig. 4.3 As for fig. 4.2, — angular velocity a.c.f., - - - angular momentum a.c.f.

Ordinate: Normalised a.c.f.; Abcissa: time/ps.

Fig. (4.4) illustrates the different characteristics of the three rotational velocity a.c.f.'s $\langle \dot{\underline{e}}_1(t) \cdot \dot{\underline{e}}_1(0) \rangle$, $\langle \dot{\underline{e}}_2(t) \cdot \dot{\underline{e}}_2(0) \rangle$ and $\langle \dot{\underline{e}}_3(t) \cdot \dot{\underline{e}}_3(0) \rangle$. A Fourier transform of a suitable combination of these three functions produces a sharp, high-frequency far infrared spectrum.

In fig. (4.5), we illustrate the torque and force a.c.f.'s in the field-on case. In field-off simulations [19] these are usually almost

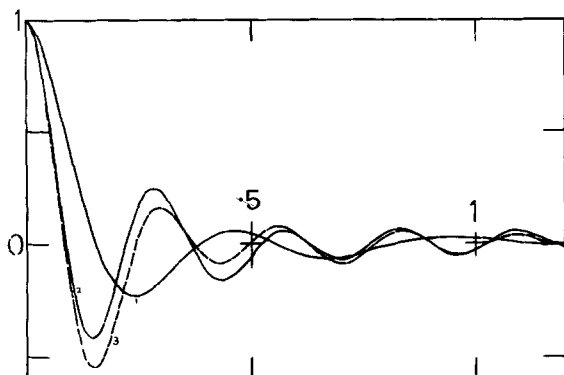


Fig. 4.4 As for fig. 4.2, rotational velocity a.c.f.'s

(1) $\langle \dot{\underline{e}}_2(t) \cdot \dot{\underline{e}}_2(0) \rangle / \langle \dot{\underline{e}}_2^2 \rangle$; (2) $\langle \dot{\underline{e}}_1(t) \cdot \dot{\underline{e}}_1(0) \rangle / \langle \dot{\underline{e}}_1^2 \rangle$;

- - - (3) $\langle \dot{\underline{e}}_3(t) \cdot \dot{\underline{e}}_3(0) \rangle / \langle \dot{\underline{e}}_3^2 \rangle$.

Ordinate: Normalised a.c.f; Abscissa: time/ps.

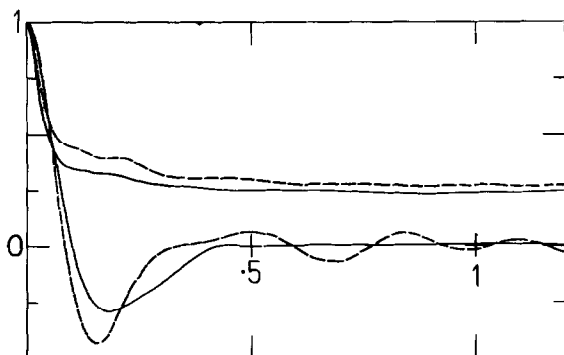


Fig. 4.5 As for fig. 4.2. — Force a.c.f. (lower curve); second moment (upper curve). - - - Torque a.c.f. (lower curve); second moment (upper curve).

Ordinate: Normalised a.c.f.; Abscissa: time/ps.

identical in their time-dependence, but the effect of the field is to induce oscillations in the torque a.c.f. leaving the force a.c.f. relatively more highly damped. The $t \rightarrow \infty$ levels reached by the second

moment a.c.f.'s are not the same. Finally in this section fig. (4.6) illustrates the (1,2) element of the laboratory frame cross-correlation function $\langle \underline{v}(t) \underline{\omega}^T(0) \rangle$. This is the first time that this type of direct cross-correlation has been observed. Its existence is direct proof of the propeller effect in one of the simplest types of chiral molecule. The electric field invalidates the parity reversal theorem [1] which normally implies that $\langle \underline{v}(t) \underline{\omega}^T(0) \rangle = 0$ in the laboratory frame and, de facto, the phenomenological theory must take into account the laboratory frame existence of this function when treating electric field induced translation. Such functions should also exist in the presence of magnetic and electro-magnetic fields and also for achiral molecules.

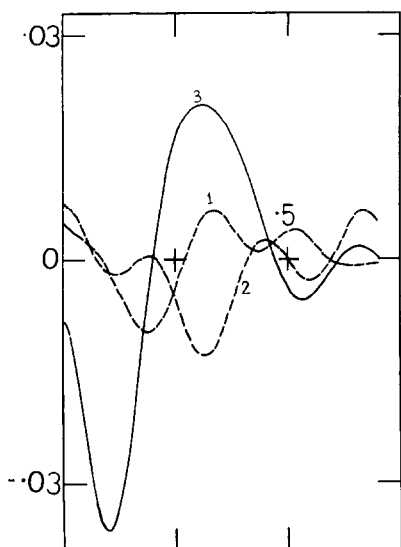


Fig. 4.6 Laboratory frame elements of $\langle \underline{v}(t) \underline{J}^T(0) \rangle$, where \underline{v}_T is the molecular centre of mass linear velocity and \underline{J}^T the transposed molecular angular momentum vector.

— Non-vanishing normalised (1,2) element. $(1,2) = \frac{\langle v_1(t) J_2(0) \rangle}{\sqrt{\langle v_1^2 \rangle \langle J_2^2 \rangle}}$

- - - (1) (3,2) element
 - - - (2) (3,1) element } exemplify cross elements which vanish into the background statistical noise, i.e. are too small in magnitude to be discernible.

Ordinate: Normalised a.c.f.; Abscissa: time/ps.

Section (5): Moving Frame Correlations in the Field-on Case.

Figs. (5.1), (5.2) and (5.3) illustrate the existence of all six off-diagonal elements of $\langle \underline{v}(t) \underline{J}^T(0) \rangle_m$ in the moving frame of reference for the S enantiomer. These elemental cross-correlation functions exhibit a by now familiar result: one pair of functions are antisymmetric for R and S enantiomers. The same function vanishes for all t in the racemic mixture. The effect of the field can be seen in the oscillations that these functions make about the time axis. The diagonal elements of $\langle \underline{v}(t) \underline{J}^T(0) \rangle_m$ vanish for all t even in the presence of the field.

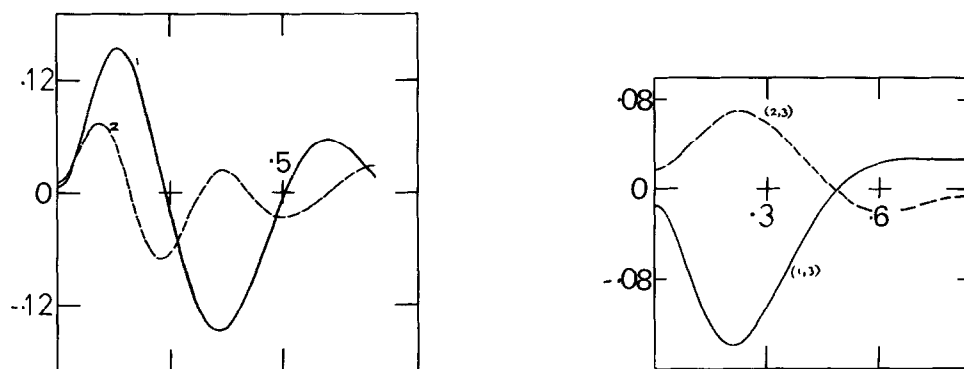


Fig. 5.1 Moving frame off-diagonal elements of $\langle \underline{v}(t) \underline{J}^T(0) \rangle_m$. Normalisation as in fig. 4.6. Field-on equilibrium.

— (3,1); - - - - (3,2).

Fig. 5.2 — (1,3); - - - - (2,3).

In fig. (5.4) the moving frame component a.c.f.'s of the centre of mass linear velocity are initially anisotropic, but go to what seems to be a common negative limit as $t \rightarrow \infty$. The hydrodynamic theory of the propeller effect, summarised by Hapel and Brenner [20] should ideally be extended to describe these correlation patterns, which are "signatures" of the details of the dynamical interconversion of rotation to translation on the picosecond, molecular scale. At present computer simulation is a unique source of information on these fundamental molecular dynamical processes.

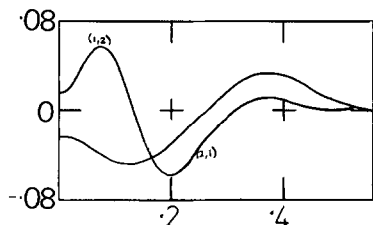


Fig. 5.3 — (1,2); - - - (2,1).

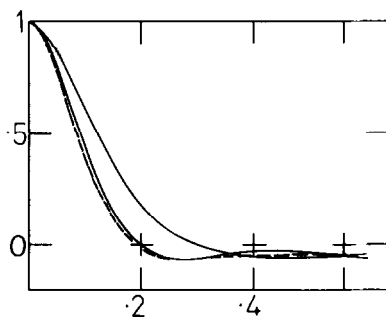


Fig. 5.4 Elements of the linear centre of mass velocity a.c.f., moving frame of reference. — (1) $\langle v_1(t)v_1(o) \rangle / \langle v_1^2 \rangle$
 — (2) $\langle v_2(t)v_2(o) \rangle / \langle v_2^2 \rangle$ - - - (3) $\langle v_3(t)v_3(o) \rangle / \langle v_3^2 \rangle$

Section 6: The Effect of a Circularly Polarised Electromagnetic Field on Molecular Translation.

The external electric field in this case take the form [6]:

$$E(\underline{e}_x \cos \omega t + \underline{e}_y \sin \omega t) \quad (6.1)$$

where \underline{e}_x and \underline{e}_y are unit vectors in the x and y directions of the laboratory frame of reference and ω the frequency of the applied alternating, circularly polarised field. E is the field strength. According to Baranova and Zeldovich [6], a field of this kind ought to produce a mean drift velocity

$$\langle \underline{v} \rangle = \frac{\omega a \rho d_o^2 |E|^2}{4(kT)^2 (1 + (\omega/\Gamma)^2)} \underline{e}_z \quad (6.2)$$

in the molecular ensemble. Here a is the effective radius of the molecule, ρ a dimensionless pseudoscalar coefficient, d_o an effective molecular dipole. The sign of ρ is different for an R and S isomer, so that $\langle \underline{v} \rangle$ is equal and opposite for each enantiomer. Γ is a friction coefficient.

The predictions of this theory were tested in the computer simulation using a field of the form (6.1) to interact with the partial charges situated at each atomic site in each molecule. The result of fig. (6.1) and (6.2), for a high frequency field, show that all three components of $\langle \underline{v} \rangle_{108}$ are affected by the field in a manner strikingly different from that illustrated in fig. (3.4) for an uniaxial electric field.

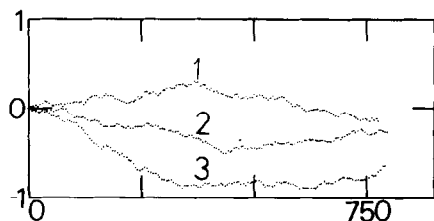


Fig. 6.1 Velocity drift with optical frequency circularly polarised field. (1) $\langle v_x \rangle$; (2) $\langle v_z \rangle$; (3) $\langle v_y \rangle$. In contrast to fig. 3.4, the drift seems to be periodic in nature.

Ordinate and Abcissa as for fig. 3.4.

Section 7: Equilibrium Dynamics of the Chiral Ion $S\text{CHBrClF}^-$

The purpose of simulating an ensemble of these artificial ions is to check the idea put forward by Baranova et al. [7] that an applied electric field produces in the ensemble a non-vanishing mean centre of mass velocity, i.e. a bulk translation.

Adding an extra negative charge to the fluorine atom produces an instability in the ensemble as illustrated in fig. (7.1). The translational temperature is very high and needs to be rescaled constantly. The total energy of the system is positive and the computed pressure large and positive. These results came from repulsion between 108 ions of like sign constrained in a constant volume. There is, however, no net centre of mass translation in this system. This can be rechecked readily by calculating $\langle v_x \rangle_{108}$; $\langle v_y \rangle_{108}$ and $\langle v_z \rangle_{108}$ over a sufficient time span (e.g. 2000 time steps).

Compared with fig. (4.2) the decay of the centre of mass linear velocity auto correlation function of the chiral ions (fig. 7.2) is far slower. The second moment a.c.f. $\langle \underline{v}(t) \cdot \underline{v}(t) \underline{v}(0) \cdot \underline{v}(0) \rangle / \langle v^4 \rangle$ falls to a level which appears (beneath the periodic temperature rescaling) to be in

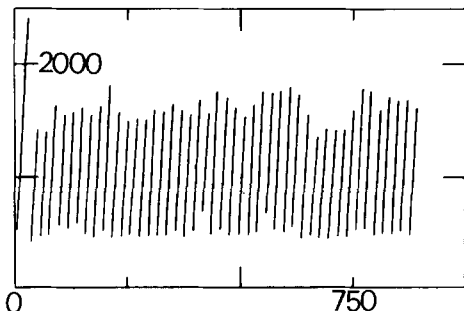


Fig. 7.1 Rescaling of the translational temperature $\langle T_{tr} \rangle$ for an ensemble of 108 CHBrClF^- ions.

Ordinate: $\langle T_{tr} \rangle$; Abscissa: time/ps.

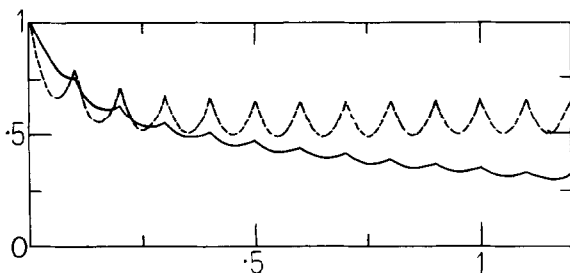


Fig. 7.2 $S \text{ CHBrCl F}^-$, centre of mass velocity a.c.f.'s. — first moment; - - - second moment. The periodicity in these functions can be traced to the temperature rescaling illustrated in fig. 7.1.

Ordinate: Normalised a.c.f.; Abscissa: time/ps.

the region of (0.56 ± 0.5) i.e. slightly lower than the Gaussian level for an equilibrium molecular ensemble of 0.6. It is instructive to look at the force autocorrelation function (fig. (7.3)). This is unaffected by the temperature rescaling process, (which is applied directly in the algorithm to the molecular linear and angular velocities), and decays

slowly to zero after an initial oscillation period of about 0.3 ps. The a.c.f. differs considerably from its molecular counterparts in that it never becomes negative. In contrast the torque a.c.f. quickly oscillates to zero (fig. (7.4)) with a deep negative overshoot. The behaviour of the

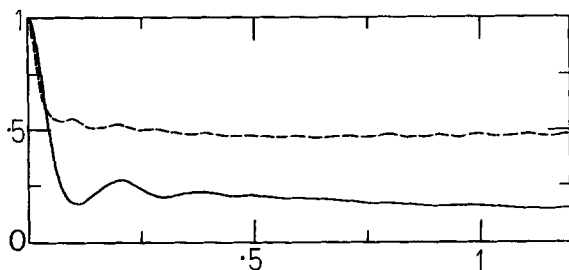


Fig. 7.3 As for fig. 7.2, force a.c.f.

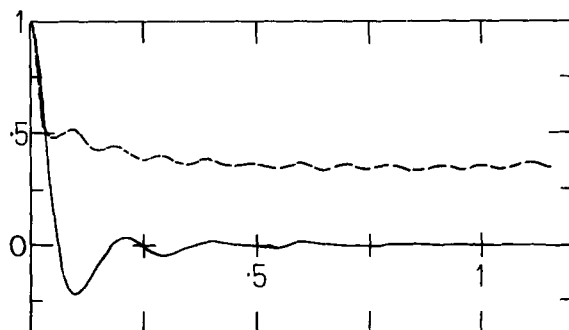


Fig. 7.4 As for fig. 7.2, torque a.c.f.

angular velocity a.c.f. (fig. (7.5)) is similar to that of the rotational velocity a.c.f.'s, typified by $\langle \dot{\underline{e}}_3(t) \cdot \dot{\underline{e}}_3(0) \rangle$ - both fall fairly quickly to zero. This contrasts with the angular momentum a.c.f. (fig. (7.6)), where the oscillations have disappeared. Finally, in fig. (7.7), the mixed, moving frame, autocorrelation functions $\langle \underline{v}(t) \underline{J}^T(0) \rangle_m$ seem not to vanish at $t = 0$. This behaviour is typified by the (3,2), (3,1) and (1,2) elements, which tail very gradually to zero as $t \rightarrow \infty$. This behaviour is quite different from that in equivalent molecular liquids [19].

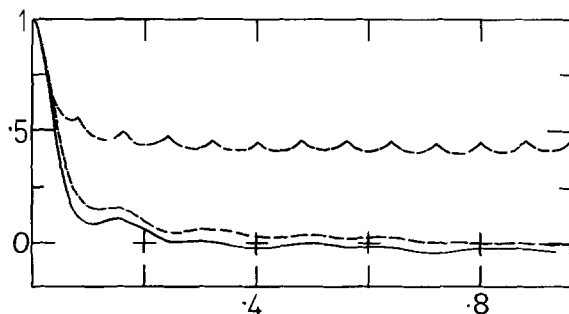


Fig. 7.5 — Rotational velocity a.c.f. $\langle \dot{e}_3(t) \cdot \dot{e}_3(0) \rangle / \langle \dot{e}_3^2(0) \rangle$.
 - - - - (1) Angular velocity a.c.f. - - - - (2) Second moment.
Ordinate: Normalised a.c.f.; Abscissa: time/ps.

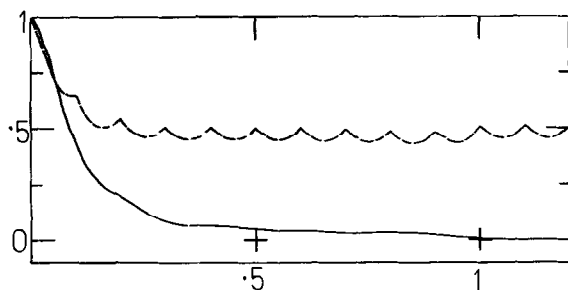


Fig. 7.6 As for fig. 7.2, angular momentum a.c.f.

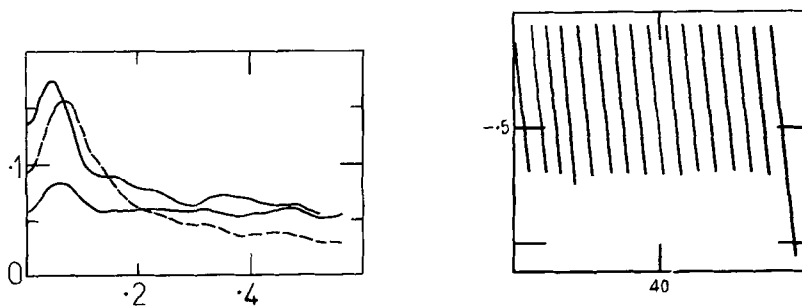


Fig. 7.7 Some off-diagonal elements of $\langle \underline{v}(t) \underline{J}^T(0) \rangle_m$, normalised as in fig. 5.1. (1) (3,2) element; (2) (3,1); (3) (1,2).
Ordinate: Normalised a.c.f.; Abscissa: time/ps.

Fig. 7.8 The effect of an electric field E_z on CHBrClF^- . Rescaling the drift in $\langle v_z \rangle$.

Ordinate: $10^4 \langle v_z \rangle$; Abscissa: time/ps.

The effect of an uniaxial electric field on the CHBrClF^- ion is illustrated in fig. (7.8). The drift in the direction of the field (lab. Z axis) in this case is very pronounced, because the field acts translationally on the net charge carried by each molecule. Therefore it ought to be straightforward to observe this effect experimentally, and to corroborate the theoretical predictions of Baranova et al.

Section 8: The Experimental Corroboration of the Induced Translational Effect on Achiral Molecular Liquids and Some Technological Applications.

A simple set up such as figure 8.1 demonstrates that a bulk translation of a liquid is induced by an external electric field [21]. Using two brass electrodes some 5 mm apart liquid (such as polar aniline) is drawn into the electrode gap. 1l cms of the liquid may be suspended in this way using a field up to 10 kV cm^{-1} . The effect is orders of magnitude stronger on some non-dipolar liquids. In CCl_4 , for example, the induced translation is such that fine droplets of liquid are expelled, at a fast rate, through the top of two electrodes some 13 cms long.

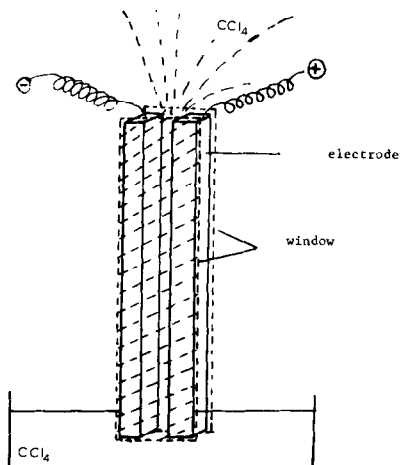


Fig. 8.1 Experimental electric field effect on molecular liquids.

It is well known of course that a dielectric is always drawn from a region of a weak field towards a region of stronger field. The dielectric liquid in our experiment is polarized when placed in an electric field and there is a net attraction into the field region. When in the

field our molecular dynamics simulation has shown that the rotational motion of the individual molecules is restricted and a subsequent conversion of these lost degrees of rotational freedom to translational motion occurs. Since the field is necessarily unidirectional the translational motion occurs in one direction, the total bulk sample moves.

It is not straightforward to compare in detail the computer simulation and experimental observations. In the former saturating electric fields are used as we have described. In the latter the fields on the bulk sample are relatively small compared with kT , the thermal energy. In fact the existence of the effect demonstrates the cooperative molecular nature of liquids. A simple energy calculation shows that fields of the present magnitude ($\sim 10^6 \text{ V cm}^{-1}$) cannot possibly reorient individual molecules in the bulk liquid. To observe an effect in the laboratory either the field must be large enough to overcome the natural thermal energies of the individual molecules, or, alternatively, enough molecules must be reoriented in unison so that the coupling energy is greater than kT . We conclude therefore that large aggregates or clusters of molecules must be reorientated in unison. This is not to resurrect the old swarm theories of Debye and Stewart [22], which assumed the existence of large, fixed groups of molecules with rigidly defined boundaries. The liquid is a continuous medium held together by strong attractive forces. Individual molecules are randomly arranged positionally but may have a significant rotational order on the local level [21], as demonstrated by various diffraction and structural studies. Hence, no molecule moves without the cooperation of its neighbours. Basic properties, such as the ability to fill and take the shape of a containing vessel, reflect this cooperative molecular nature.

We have demonstrated the problems that arise when one attempts to obtain single particle properties (e.g. single particle correlation times) using simplistic theoretical models to reduce and interpret experimental measurements on the bulk sample using spectroscopic probes of the dynamics. This conventional approach to the study of molecular liquids, and the numerous papers that have appeared in the literature, have, if anything, only served to confuse the issue and no overall viewpoint of the molecular dynamics of any of the liquids we have considered has been obtained [23]. There are many interesting and potentially more profitable experiments that should now be attempted [21,24].

Evans [25] has recently used this induced bulk translational effect on CCl_4 to grow crystals of camphor in a new, and potentially exciting, way. As we have said, Baranova [6,7] et al. have already suggested the use of the effect to separate enantiomers from a racemic mixture. Other applications of this field effect that have been suggested, or come to mind, include the separation of achiral liquid mixtures, liquid immersed motors (following the early work of Ricard Arno [26] in 1892 and Weiler in 1893 [27]), liquid pumps [28], the measurement of dielectric constants of liquids [29] and the separation of mixtures of particulate and granular materials [30]. An interesting recent paper [31] has suggested that the thermal decomposition of solids is modified in external electric fields.

Magnetization forces may also be used as the basis for the interaction with the liquids. It has already been suggested [32] that ferro-magnetic liquids can be synthesized by introducing a colloidal suspension of magnetizable particles into a carrier fluid. Colloidal suspensions tend to settle out over long periods of time, and in the presence of a magnetic field, the magnetized particles tend to flocculate. Colloidal suspensions have been synthesized that are stable over indefinite periods of time. There exists a vast Russian literature on various effects of magnetic fields on liquids including the magnetization of water [33]. This seems to have aroused little interest in the West. Yet, only recently, the Japanese, in the public press, announced the production of a new ship propelled, "at a faster rate than any other ship", using only a combination of magnetic and electric field effects on sea water.

In concluding, we believe we have traced the cooperative nature of liquids back to the actual molecules themselves and in particular to the interaction of a molecule's rotation with its translation. Because of this thermal energy may be transferred from one mode to another using suitable external perturbations. This allows us to use molecular liquid in technologically interesting and useful ways.

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