

THE LIQUID STATE AND ROTATION-TRANSLATION COUPLING

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ABSTRACT

Computer simulation is revolutionizing the field of liquid state dynamics and revealing the limited scope of the traditional approach of study by combined molecular spectroscopy and analytical modelling. The experiments produce composite profiles that are not easily deconvoluted in terms of the contributory relaxation processes while the theories are based on simplistic and subjective ideas. Little real progress has resulted from the immense effort expended in an attempt to elucidate the liquid state. Computer technology, however, is changing all this because the N-body problem is now being solved and new predictions are being made. For the first time we can explain why, in dynamical terms, a racemic mixture of lactic acid is a liquid at room temperature yet a single enantiomer of the same a solid. It emerges that molecular shape is critical in determining the dynamics of the condensed phase of matter.

HISTORICAL DEVELOPMENT AND THE STATE OF THE ART

"Understanding the liquid state has proven to be both a challenge and an embarrassment to generations of outstanding chemists and physicists". These are the now familiar words of Berne and Harp [1] and expressed rather precisely a situation that still existed in the early seventies. Obvious problems have frustrated the field of liquid state dynamics. The problems arise because a vast number of molecules interact and move cohesively.

The basics of the analytical theories of molecular diffusion reside in the pioneering works of Einstein [2], Langevin [3] and Debye [4]. It was natural

that these great innovators should use their intuition and logic to produce simplifying hypotheses, and develop molecular models, it was not possible to solve Newton's equations of motion for all the molecules in the ensemble - the real problem.

"In the last decades the field has changed out of all recognition and we are on the threshold of a great change in the very basis of the subject." [5]. The revolution has come in the form of computer technology for now at last Newton's equations are being solved - and for real molecules. Computer simulations of the dynamics of molecular liquids, approximate though they currently are, are already providing new insights. The revolution is such that unexpected predictions have been made [6] that demand we re-appraise the very basics of our subject. Misconceptions in the theoretical approaches and the limitations of traditional methods of study (the various spectroscopies) demand that future research proceeds by a concerted and coordinated effort in which the simulation precedes and even guides the experiment.

Little real progress has emanated from the thousands of experiments studied in isolation. The experiment produces a complex conglomerate of dynamical information that is not easily deciphered to obtain details of the motion that may then be used to test molecular models - prescriptions for a certain type of relaxation process only.

#### DEBYE AND ROTATIONAL RELAXATION

"To achieve simplicity we must identify the essentials, to express them clearly and pictorially and then to pursue their consequences with superb technical facility was Debye's style"[7].

Debye chose to study the rotational relaxation process and his theory worked well at the frequencies of study then available to the experimentalist. But the danger of considering a part only of a complete evolutionary and multi-source process was revealed when the region of study was extended to higher frequencies - when the far infra-red (tera Hertz frequencies) became accessible. Debye's low frequency processes are in fact a small part only of a total rotational relaxation which may span many decades of frequency, a couple only in "normal" isotropic liquids but ten or more in super-cooled systems (glasses). That is, the time evolution of a rotational relaxation process may be as small as picoseconds or as large as many years. The motion is a compendium of cooperative and individual motions, the final result a complex amalgam of the two, figure 1.

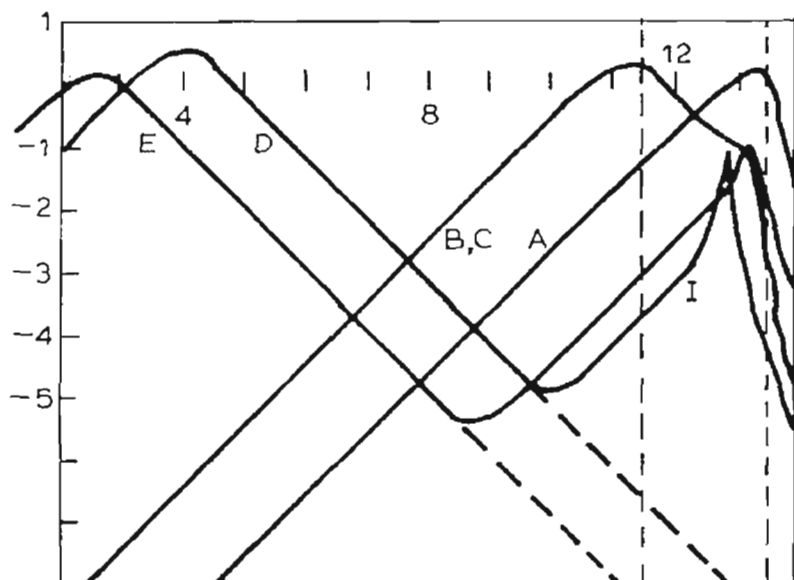


Fig. 1. Schematic of the diversity of loss features that are observed in the condensed phase of matter.

A — Water free from hydrogen bonding.

B,C — Liquids such as benzonitrile and plastic crystals (crystals retaining degree of orientational freedom), such as  $(\text{CH}_3)_3\text{CCl}$  where the far infra-red loss is resolved on the high frequency side of the Debye curve (both separated by only a few decades of frequency).

D The nematic phase of a liquid crystal spanning ten decades of frequency. Analytical theories predict a very sharp far infra-red loss which may not be realistic.

E Glass phase systems spanning fourteen or more decades of frequency.

Analytical theories must be able to reproduce this great diversity of molecular behaviour. In particular D and E are severe tests for any model.

A far infra-red spectrum, figure 2, is the high frequency adjunct of the low frequency Debye loss. Debye's theory does not predict this high frequency component, it suggested instead that all dipolar liquids are more or less opaque in the frequency range  $>10^{12}$  Hz including, of course, the visible. The complete spectra (zero-tera Hertz) are frequency distributions of the probability of occurrence of the events from which they originate and are statistical in nature. This frequency domain is linked to a temporal domain by Fourier's integral theorem so that these spectral functions may be transformed to correlation functions in the time domain which display more clearly the time evolution of the dynamical process. For dipolar liquids the auto-correlation function is normally exponential at long times, the times considered by Debye, and correspond to the loss of memory by the system of all previous events and the onset of a stochastic, random or Markov process. It is not so surprising therefore that Debye's theory, which ignored all dynamical coherence, worked well at these times.

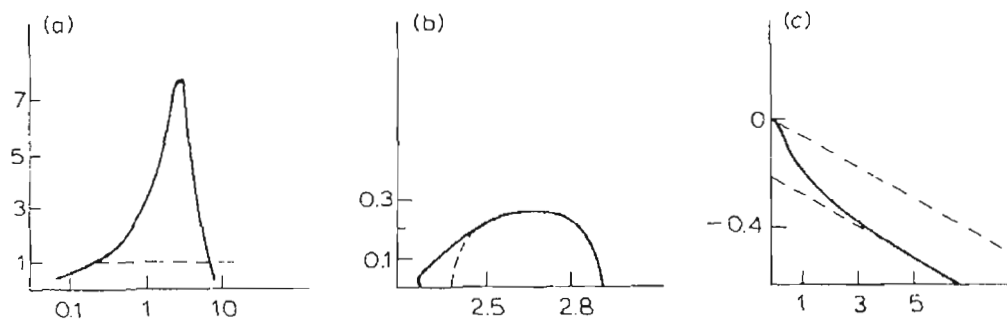


Fig. 2. A solution of  $\text{CH}_3\text{CN}$  in  $\text{CCl}_4$  showing the experimental measurements and the predictions of Debye theory in terms of  
 a)  $\alpha(\omega)$ , the absorption coefficient (Np/cm) and  
 b) the dielectric loss  $\epsilon''(\omega)$  and permittivity (the Cole-Cole arc), where  $\omega$  is the frequency.  
 c)  $\rho(t)$ , the orientational correlation function.

— experimental

- - - classical theory predicting that the system is opaque at frequencies  $>10^{12}$  Hz.

Reproduced by permission from P. Desplanques, thèse d'Etat, University of Lille, 1973, p. 45.

Debye's philosophy, however simple and attractive, is not easily applied. Even if we isolate the "essentials" it is not straightforward to relate the variables to measurable quantities because it is not straightforward to assign the measured quantities to a particular relaxation process. Several types of relaxation can and do contribute to the decay of correlations measured in a particular experiment. Further these mechanisms contribute differently to correlation functions determined from different techniques.

#### ROTATIONAL RELAXATION EXTENDED. THE DIFFICULTIES ASSOCIATED WITH AN ANALYTICAL APPROACH

Rotational relaxation was extended and modified and soon a vast array of seemingly unrelated molecular models were incorporated into a general framework [8]. For the first time, at least, it was possible to follow, however approximately, the evolutionary dynamics over the complete time span, picoseconds to years, as nature demanded.

Hildebrand [9] was concerned about the way in which models were being tested. In particular he impressed the need for care in "force fitting" theories to experiment especially when computer quadratures are used. His words even now retain their significance. "A model should be regarded as suspect if it yields inferences in serious conflict with any of the pertinent properties of a system, regardless of how closely it can be made to agree with some, especially

if there are adjustable parameters. A model that is consistent with all properties, even if only approximately, can probably be made more precise, but if it is in irreconcilable conflict with any part of the evidence it is destined to be discarded, and in the meantime predictions and extrapolations based on it should be regarded as unreliable".

It is an unfortunate feature of molecular models that the more realistic they are made the greater is the number of adjustable parameters associated with them. So, for example, in Debye's days most of the work dealt with the measurement of spectroscopic line widths and relaxation times derived therefrom (yielding one single parameter to characterize the complicated process). In extended, rotational relaxation processes the number is increased to two or three or many more depending on the level at which we consider it acceptable to approximate the intermolecular potential. If one wishes to consider roto-translational relaxation then even in the simplest formalism the number of unknowns increases as the square of the number involved in the rotational relaxation process, approximated at the same level, because of the cross terms that are introduced. We now know that it is indeed essential to consider roto-translational motion - rotational and translational relaxation may be separated only in a few special liquids (e.g. those forming rotator phases).

#### THE MEASURED QUANTITIES AND CONTRIBUTIONS FROM OTHER MODES OF MOTION

Dynamic data are available using the techniques of infrared absorption, n.m.r. relaxation, light scattering, neutron scattering and our own experiment, zero-tera Hertz spectroscopy.

Infrared and zero-tera Hertz spectroscopy measures the auto-correlation function given classically by:

$$C_1(t) = \langle P_1[\underline{u}(0) \cdot \underline{u}(t)] \rangle = \langle \underline{u}(0) \cdot \underline{u}(t) \rangle$$

where  $P_1$  is the first Legendre polynormal and  $\underline{u}$  is a unit vector along the direction of the dipole transition moment.

The inverse Fourier transform of a Raman (or light scattering) band yields correlation functions of the type

$$C_2(t) = \langle P_2[\underline{u}(0) \cdot \underline{u}(t)] \rangle = \frac{1}{2} \langle 3[\underline{u}(0) \cdot \underline{u}(t)]^2 - 1 \rangle$$

where  $P_2$  is the second Legendre polynormal and  $\underline{u}$  is a unit vector along the symmetry axis of the linear or symmetric top molecule. Neutron scattering data contains information from all the molecule fixed tensors and is the most complicated to interpret.

Deciphering details of the dynamics with these data is difficult. Since

one is dealing with an entity, the molecule, there exist both intra- and intermolecular motions. It is customary to deconvolute these processes, assuming no interaction between the two but this is not always acceptable. Intra- and intermolecular motions may become coupled and may severely distort infrared or Raman band shapes [10]. Even if these processes were separable further complications arise because the molecular centre of mass motion (translation), and motions around the centre of mass (rotations) are not always dynamically independent. They may become coupled and again severely distort spectral band shapes. Consider the far infra-red spectra of HD in liquid argon [11] - one of the most simple of liquid systems. The rotational and translational transitions of this light molecule are easily distinguished so that complications normally associated with the liquid phase, a broad featureless spectral profile, are reduced. The origin of the absorptions resides in the quadrupole moment which induces a dipole in the surrounding liquid environment. This induced dipole is modulated as the dipole rotates and transitions involving changes in these energies may be observed in the far infra-red. If we study  $H_2$  and  $D_2$  in the liquid argon the frequencies of the rotational transitions do not differ from those calculated for the unperturbed gas phase. The spectrum of HD in liquid argon shows larger half-widths, erratic frequency shifts, and additional absorptions arising from the relaxation of the rotational selection rules. The mechanism able to account for these anomalous characteristics follows from a consideration of rotation-translation coupling. Transitions corresponding to  $\Delta J = +2, +3$  and  $+4$  become allowed through the mixing of rotational wave functions, a direct consequence of the rotation/translation perturbation. These pronounced effects arise because of the slight asymmetric mass distribution of HD and is a striking example revealing the role of molecular shape in determining the molecular dynamics in an isotropic liquid.

However, spectral detail is normally not resolved in molecular liquids and it is not then possible to separate the various relaxation mechanisms contributing to a measured spectrum without making simplifying assumptions (e.g. without assuming the complete decoupling of rotation, translation and vibration).

It is not surprising therefore, that conclusions concerning the dynamics made from different experiments rarely agree and are sometimes contradictory [23].

#### THE FAILURE OF THE TRADITIONAL APPROACH

Calculated correlation times, the area under a correlation function (though the existence of other definitions adds testimony to the confused state of the

art) may be used to compare spectroscopic techniques. The results are normally disparate [5,23]. In fact basic concepts of the liquid state are inconsistent with each other and with the pertinent facts. Following Marcus [14], they include "holes, cells, clusters, cages, lattices, scaled particles, fluidised vacancies, hypernetted chains and molecules with solid-like degrees of freedom". This range of concepts reflects on the comparative failure of analytical modelling of the liquid state. As Hildebrand again reminds us [9], "simple liquids flow freely when expanded by only a few per cent over their intrinsic volume. There is no room for "holes" or "lattices" or jumps greater than a small fraction of their molecular diameter".

#### NEW PROGRESS AND COMPUTER SIMULATION

To proceed we should return to the basics. Our advantage over our predecessors is a distinct one because, for the first time, we can solve the equations of motion for an ensemble of real molecules.

The power of the technique is already observable. We do not have to make the same rash approximations concerning the details of the dynamics that plague molecular (and hydrodynamic theory). We postulate only a realistic inter-molecular potential (e.g. the Lennard Jones potential - this is orders of magnitude more realistic than potentials implied by various molecular models). We insert Lennard-Jones parameters for the molecule to be studied. We reproduce the dipole moment (if one exists) with del Re's point charges (or similar). The computer does the rest.

Questions are raised concerning some features of the algorithms. For example, it is suggested that the assumption of pair additivity is an oversimplification. We recall [9] that "the molar volume of  $V_t$  is defined as that volume at which soft molecules begin to be sufficiently separated between collisions to acquire fractions of their momentum in free space. At volumes smaller than  $V_t$  they are in fields of force not appropriately described by pair potentials. The role of temperature is only to determine volume. Values of  $V_t$  depend on the capacity of a molecular species to absorb collision momentum by bending, vibrating or rotating". Time will bring the necessary advancements and improvements but the foundations are already laid.

#### COMPUTER SIMULATION OF POLYATOMIC MOLECULAR LIQUIDS

A whole series of polyatomic molecular liquids have recently been simulated using site-site potentials including the three  $\text{CH}_2\text{Cl}_2$ ,  $\text{CH}_3\text{CN}$  and  $\text{CHCl}_3$ . Of the

three the spectral properties of  $\text{CHCl}_3$  are best reproduced. The calculated far infra-red spectrum, for example, agrees almost precisely with that measured, a pleasing result bearing in mind the comparative failure of analytical theories to reproduce this spectrum - even if recourse to "force fitting" highly parameterized models is adopted [12].

$\text{CH}_2\text{Cl}_2$  is not so well reproduced and  $\text{CH}_3\text{CN}$  is badly reproduced. The calculated far infra-red spectrum for the latter peaks at ca  $65 \text{ cm}^{-1}$  some  $35 \text{ cm}^{-1}$  displaced from the observed spectrum at ca  $100 \text{ cm}^{-1}$ .

#### THE INTERACTION OF ROTATION WITH TRANSLATION - MOLECULAR AND LABORATORY FRAMES OF REFERENCE

The simulation not only reveals this discrepancy but suggests why such a difference exists. In a rotating axes frame of reference (the molecular frame) strong cross correlation functions, involving the interaction of rotation with translation, are observed in the molecules in which the largest discrepancies occur. The effects of roto-translation must be investigated in this molecular frame [13] in "normal liquids" because they are concealed in the laboratory frame (the experimental frame) where we measure purely rotational functions.

Let us clarify. The simulation solves the equations of motion with a third order predictor method [16]. Rotation is integrated using as coordinates the angular momenta components and the three unit vectors along the principal axes of the molecular moment of inertia matrix (the molecular frame of reference). Frame transformation relationships may be used to calculate dynamical vectors in this molecular frame of reference from those in a laboratory frame of reference [13].

Parity and symmetry rules demand that some cross correlation functions must disappear in the laboratory frame - for example, the first moment roto-translational function  $\langle \underline{v}(t) \cdot \underline{J}^T(0) \rangle$  where  $\underline{v}$  is the centre of mass velocity and  $\underline{J}$  the angular momentum. Second moment cross-correlation functions are invariant to the frame of reference and may exist in the laboratory frame. However, it is not possible to measure these functions experimentally. So the direct observation of roto-translation effects are masked by the laws of physics. However, all the functions may be observed in the molecular frame in a molecular dynamics computer simulation which shows quite clearly that the auto (rotational) correlation functions measured in an experiment are affected to varying degrees by roto-translational interactions.



THE DIRECT OBSERVATION BY COMPUTER SIMULATION IN THE LABORATORY FRAME OF ROTO-  
TRANSLATIONAL INTERACTION IN LIQUIDS COMPOSED OF OPTICALLY ACTIVE MOLECULES

The simulation of 1,1 fluorochloroethane has revealed that the orientational autocorrelation functions of the  $P_1$  and  $P_2$  rank Legendre polynomials were the same for the R and S enantiomers but different for the racemic mixture. This was a consequence of the fact that the two elements of the molecular rotating frame matrix  $\langle \underline{v}(t) \cdot \underline{J}^T(0) \rangle$  are opposite in sign for each enantiomer (because of the reversed symmetries - mirror images) and consequently vanish in the racemic mixture, this being the only observable dynamical difference in the simulation. The effect is directly attributable, therefore, to the interaction of rotation with translation and is directly observed in this instance as differences in the far infra-red spectra of the enantiomers and racemic mixture. The effect of the interaction was large enough to shift the frequency of maximum absorption of the enantiomer at  $35 \text{ cm}^{-1}$  to ca  $65 \text{ cm}^{-1}$  in the racemic mixture (the phenomenological Debye loss time was approximately halved). These shifts are as large as those observed on cooling a liquid from near its melting point to close to its boiling point, is larger than we observe in dilution studies when a polar solute is dissolved in a non-polar and "non-interacting solvent" and is larger than the reported instances of the effects of external pressure on far infra-red profiles. It reveals a great difference in the molecular dynamics of the systems and the extreme importance of the R-T interaction.

In following simulations on other optically active liquids we observe that differences in the dynamics of the enantiomer and racemic mixture depend strongly on the molecular symmetry and, within a symmetry species, on the size of the atoms comprising the molecule. So, for example, if we replace the chlorine atom in the above molecule with a larger iodine atom (1,1-fluoroiodoethane), the dynamics are dominated by the enormity, and assumed sphericity, of this iodine atom. The differences between the dynamics of the enantiomers and racemic mixture are not so pronounced with only a small shift in the far infra-red peak frequency. The largest effects are observed in the molecules of lowest symmetry.

CONFIRMATION OF THE COMPUTER SIMULATION PREDICTION BY EXPERIMENT

All of this is a prediction of computer simulation. We have confirmed the prediction in the laboratory in a study of 3 methyl cyclohexanone [15]. The spectra of the enantiomer (+) 3 methyl cyclohexanone (a naturally occurring product) and its racemic mixture are displayed in figure (3). There is a

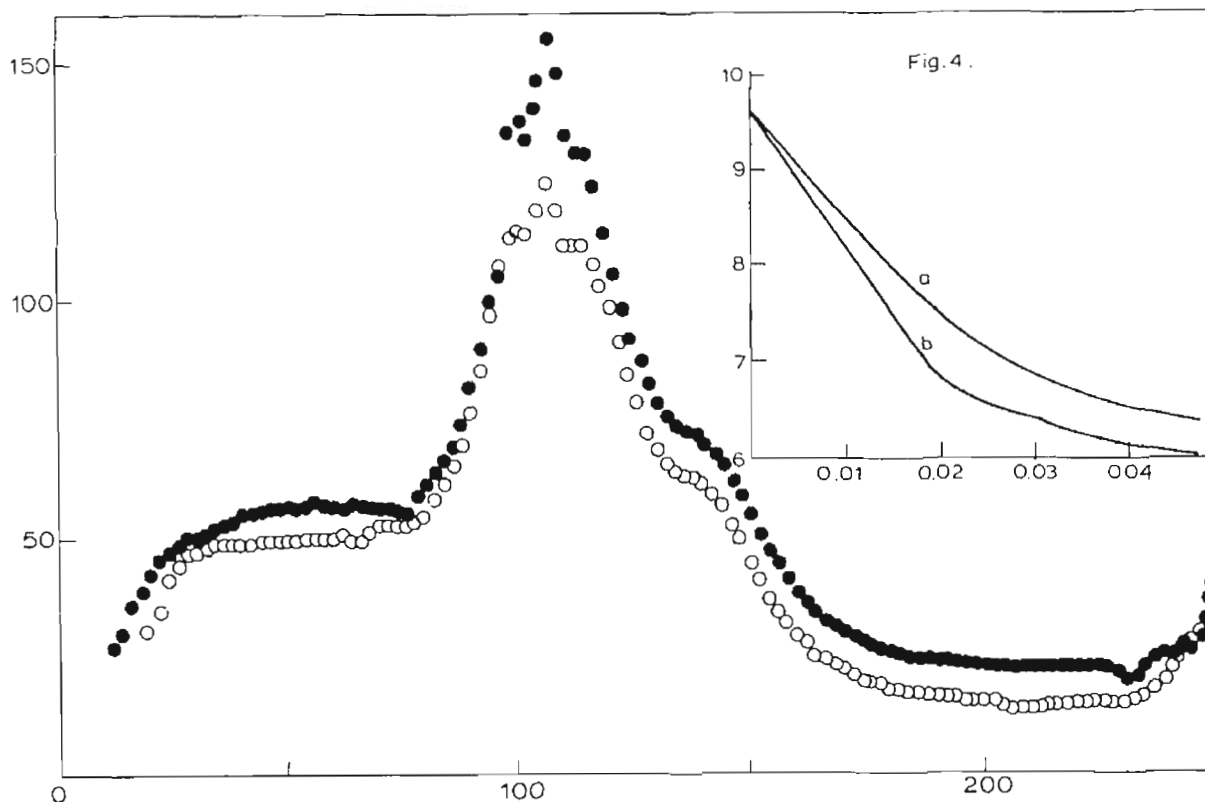


Fig. 3. The Far Infra-red Spectra of (+) 3 methyl cyclohexanone and a racemic mixture of methyl cyclohexanone.

a) results for a racemic mixture.

b) results for the enantiomer.

Ordinate:  $\alpha(\nu)/\text{nepers cm}^{-1}$ . Abcissae:  $\text{wavenumber/cm}^{-1}$ .

Fig. 4. (Inset in fig. 3) Variation of the Integral Transmission ( $50\text{-}250\text{ cm}^{-1}$ ) with pathlength of absorber for (+) 3 methyl cyclohexanone and a racemic mixture.

Ordinate: Integral Transmission/volts. Abcissae: Pathlength.

marked difference in the spectra, certainly in intensity. These are displayed more clearly in figure (4) (inset) where the integral transmission (the transmitted power over a complete frequency range) has been monitored for changes in sample thickness.

1,1 fluorochloroethane has not been synthesized. But, if we consider a molecule of similar symmetry (i.e.  $C_s$  symmetry), e.g. lactic acid, then we do not even require recourse to our spectrometers to observe the differences. Differences in the dynamics are apparent even with the naked eye because, at room temperature, the enantiomer is a solid while the racemic mixture is a liquid!!

## THE IMPORTANCE OF MOLECULAR SYMMETRY IN DETERMINING LIQUID STATE DYNAMICS AND THE INABILITY OF MOLECULAR AND HYDRODYNAMIC THEORIES TO EXPLAIN THIS FUNDAMENTAL FEATURE

These observations have consequences for the liquid state in general. For the first time the importance of the molecular symmetry (and the size of the atoms comprising the molecule) in determining the liquid state molecular dynamics are revealed. Simulations show that very large rototranslation interactions exist in very simple liquids such as  $\text{CH}_3\text{CN}$  and  $\text{C}_2\text{H}_5\text{Cl}$  that are not optically active. It must have a pronounced influence on the details of the measured spectra but, as we have already said, is normally concealed in the laboratory frame. We do know that the simulated far infra-red spectra of  $\text{CH}_3\text{CN}$  peaks at a much lower frequency than the observed frequency of maximum absorption. This conforms with a recent suggestion by one of us (G.J.E.) that the spectral profile of this liquid is composite in nature, contributions also arising from the motions of dimers and higher aggregates of molecules. There is even a suggestion of spectral detail in the spectrum [19].

It is not then possible to analyse these data with the currently popular molecular models of the liquid state dynamics. Nor is it possible to analyse the spectra with hydrodynamical theories now that the influence of molecular shape is established. Molecular theories for roto-translational motion are either intracatable or contain many adjustable parameters, its development still being in an infancy. Hydrodynamic theories, by definition, do not consider the detailed molecular structure of the medium - let alone the structure of the molecules.

### MOLECULAR VERSUS HYDRODYNAMICAL APPROACHES BRIDGED?

Many of what are termed "hydrodynamical phenomena" may now be traced back to the molecules themselves because molecular symmetry alone demands that "the individual governs and is governed by the whole" [5]. Indeed some "hydrodynamical phenomena" are already being treated with molecular models. For example, consider the depolarized scattering spectrum of liquids such as aniline, quinoline and nitrobenzene. A feature appears in the spectrum which may be described as a deviation from a Lorentzian and the emergence of a dip in VH and HV geometries, commonly called the Rytov or "shear wave dip". Shear wave is a term introduced by the hydrodynamicist. They consider the liquid to be a continuous medium in which thermal fluctuations give rise to local inhomogeneities and thereby to

density and concentration fluctuations. Consequently they aim to explain liquid state behaviour in terms of macroscopic data such as the isothermal compressibility and concentration dependence of the osmotic pressure. These theories have been successfully applied to optically isotropic molecules but "there does not exist a set of hydrodynamic equations to describe the collective motions of a fluid containing optically anisotropic molecules" [17]. These theories cannot explain the Rytov or "shear wave dip". True the doublet was first predicted by Leontovich [24] on the basis of a hydrodynamic theory which was generalized and extended by Rytov [25]. But an essential requirement of this theory is that the phenomenological shear viscosity  $\eta_s$ , shear modulus,  $\mu_s$  and shear relaxation time  $\tau$  must satisfy the relation

$$\frac{\mu_s \tau}{\eta_s} = 1$$

Stegeman and Stoicheff [18] have observed that this ratio is less than unity for all the liquids they studied. As Berne and Pecora [17] point out "since these experiments several authors have formulated theories for the doublet in order to resolve this discrepancy and to place the somewhat hazy assumptions of the Leontovich-Rytov theories on a firmer statistical mechanical foundation". Currently popular theories are microscopic and not macroscopic in nature even though this shear dip does not appear to be related to a specific microscopic structure. Indeed it has now been observed in a number of molecular liquids including polar and non-dipolar liquids, planar and non-planar molecules, and both large and small molecules. It would be interesting to categorize this phenomena in terms of the group symmetry properties of the molecules comprising the liquid to ascertain whether it may be traced back to the molecules themselves and, in particular, to the interaction of rotation with translation.

#### FUTURE DEMANDS FOR THE SIMULATORS

We have not had the foresight to envisage some of the subtleties of the liquid state, particularly the pronounced role of the molecular shape in determining the dynamics. Analytical theory has tended to lead us into situations of increasing mathematical complexity. Molecular dynamics avoids this because the postulates are few.

It must ultimately be the aim of the simulators to explain the known phenomena that may be said to be currently beyond the scope of present day computers. For example it is necessary to explain such phenomena as the "Rytov dip", discussed above, critical opalescence and liquid crystalline

behaviour. The former is the intense scattering of light that occurs in the fluid critical region. It is already postulated that the marked increase in turbidity of the fluids near the gas-liquid critical point is a consequence of the fact that the pair correlation function becomes infinitely long ranged near its critical point. It should be possible to observe this in a simulation as an increase in roto-translational interaction in this region. And, of course, molecular reorientation in a liquid crystal must be strongly coupled to the translation which, as we know [20], is restricted by external potentials. All of this must be traceable to the geometrical anisotropy of the molecules. The anisotropy of the liquid crystal has some interesting implications for its molecular behaviour and new modes, attributed to a collective molecular origin, have recently been observed by one of us (G.J.E.) using far infra-red spectroscopy [21].

Gordon [22] once said "it becomes impractical to follow the dynamics at long times because of the complexity of the molecular trajectories", and so analytical theories evolved dependent on the methods of statistical mechanics in which the number of dynamical variables were reduced from Avogadro's order of magnitude, the real number involved, to only a few. Modern day simulations are doing just what we considered impossible then and follows the complete time evolution of the molecular trajectories. In so doing the very basis of our subject is being changed. At last we have moved from a model building era, with all the associated uncertainties and where the aim was to reproduce spectral profiles, to one in which predictions are being made. As computer power grows so the size of the molecules and the ensemble will grow. A complete solution of the liquid state dynamics, with all the implications (technical and biological) that must follow rests, literally, at our finger tips. A quiet revolution is in progress.

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