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The Inter-relation of Rotational and Translational Motion in Molecular Dynamics.

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Abstract

A review of the recent source literature on the statistical correlation between rotation and translation in condensed molecular matter rveals the extent to which computer simulation now provides fundamental new insights in this branch of molecular physics.Cross correlation functions of this type have been discovered in the frame of the molecular principal moments of inertia and direct in the lab. frame in the presence of a parity breaking external electric field.The non-inertial linear velocities and accelerations exist in both frames for a simultaneously rotating and translating molecule, and are shown to lead to major new insights into statistical cross correlation on the single molecule level.The relation between molecular dynamics and hydrodynamics is discussed in terms of these new correlations.

Introduction

The traditional approach to the problem of describing the diffusion of molecules in an ensemble has been to consider the translational[1] motion of the molecular centre of mass and the rotational motion of the same molecule as if they were statistically uncorrelated for all t.This leads to a very limited theoretical appreciation of the complete problem because the information fundamentally available is is restricted to autocorrelation functions[2] (a.c.f.'s) of the linear centre of mass velocity (v) or of the angular velocity (ω) depending on the type of motion under consideration.The traditional approach leaves out of consideration all the various statistical cross correlations between vectors such as these, and related vectors such as the molecular centre of mass position, r , the net force on a molecule at time t (F) ; the net torque , Tq , and the orientational unit vectors e_1, e_2 and e_3 in the principal molecular moment of inertia axes 1, 2, and 3.This review article intends to show that the existence of these cross correlation functions is important for the complete theoretical understanding of a range of problems in condensed matter physics, and conversely that the theory of molecular diffusion should be extended to take account of the new results now available from computer simulation and to be described in this article.There is no analytical theory available yet which is capable of describing the rapid accumulation of new and basic results from computer simulation. Those that are based on the theories of rotational or translational diffusion and extended therefrom[3-10] contain too many parameters and therefore too many unknowns to be determined by the limited amount of experimental data available.This is the result of attempting to extend theories and equations which are themselves approximations to the full N body problem at hand.The so -called "roto translational" theory of molecular diffusion[10] is therefore the result of approximating the approximate, and is unlikely to be fully developed from first considerations without self defeating empiricism.

In this situation the only method available at present of tackling the problem of how to describe the interrelation between rigid molecule centre of mass translation and rigid molecule rotation is computer simulation.This method also has to rely on a set of approximations[11], for example the parameterisation of the intermolecular pair potential, but this type of approximation is checked by access to independent data (e.g. measurement of second virial coefficient and crystal structure). Once the intermolecular pair potential is reasonably accurately defined the computer simulation method can proceed, with limitations of speed and accuracy in the computer system used, to produce a wide variety of cross correlation functions self consistently from the given model pair potential.There are other approximations built in to the computer simulation method, such as pairwise additivity, periodic boundary conditions, and limited sample size, so that it is always necessary to check the accuracy of the simulation method against a range of experimental data[12] before reliance can be put on the time dependence and normalised amplitude of the cross correlation functions themselves.However it remains true that the cross correlation functions can be produced by computer simulation from a given pair potential , and this is the only contemporary theoretical method of deriving cross correlation functions from first principles.

Having obtained the necessary information about time cross correlation functions in this way the next step is to attempt to devise a direct experimental method for their investigation.There are numerous experimental ways at looking at a.c.f.'s through the Fourier transform of different types of spectra[13-15], but the direct experimental determination of cross correlation functions is much more difficult. In this review article we attempt to describe two new methods for this purpose.It must also be bourne in mind that the experimental determination of a.c.f.'s relies significantly on the hidden assumption that a.c.f.'s can, indeed, be separated from c.c.f.'s in the data reduction process.Computer simulations have now shown that this is never the case , single molecule cross correlations always contribute in some way to the final spectrum, and the true time dependence of the a.c.f.'s can only be obtained experimentally with a theory that is capable of taking into account fully the role played by cross correlations of all kinds.Linear response theory, for example, usually deals with a.c.f.'s alone , and is applicable, naturally, only when the sample is disturbed by an external electric field.However, it is precisely under these conditions that cross correlations between the molecular centre of mass linear velocity, and the angular velocity, appear in the lab. frame directly.The existence of c.c.f.'s such as

$$< \mathbf{v}(t)\omega^{T}(0) >$$

in the laboratory frame was first detected[16] with computer simulation and its description recquires the extension of linear response theory and the Onsager reciprocal relations.There have been several attempts to take account of this in hydrodynamic "media" with two or more bodies in the medium[9] but no satisfactory solution to the problem has yet emerged on a single molecule level. Therefore the simulations bring into doubt the validity of basic linear response theory, due to the existence of field induced cross correlations in the laboratory frame (x, y, z).

This one example illustrates the fundamental importance to molecular dynamics, linear response theory, and spectroscopy in general of cross correlation functions of the fundamental single molecule type

$$< \mathbf{A}(t)\mathbf{B}^{T}(0) >$$

between the vector A at time t and a vector **B** of the same molecule at t = 0.In this review the considerations leading to the computation of cross correlation functions of various kinds are detailed in sections (2) to (8) below.Section (2) deals with frames of reference; section (3) with non inertial accelerations, new accelerations in rotating and moving frames of reference; section (4) with the definition of matrix elements in cross correlation functions; section (5) with a description of the basic techniques of computer simulation and the development of array processors, section (6) with simple c.c.f.'s in frames (1, 2, 3) and (x, y, z) , section (7) with the behaviour of more complex c.c.f.'s in condensed and gaseous media; and section (8) with applications in this context and development of supercomputers and parallel processors.

Section 2 : Definition of Frames of Reference

To see the time dependence of cross correlation functions the definition of frame of reference is basically important.It was realised only in the early eighties[17] that in this respect the correct frame to use is the frame of the principal molecular moments of inertia (1, 2, 3).To define a molecular vector such as the molecular centre of mass velocity, or the molecular angular velocity, in the frame (1, 2, 3) it is necessary to transform its components from frame (x, y, z) to frame (1, 2, 3) using the transformation relations

$$A_1 = A_x e_{1x} + A_y e_{1y} + A_z e_{1z} \tag{1}$$

$$A_2 = A_x e_{2x} + A_y e_{2y} + A_z e_{2z} \tag{2}$$

$$A_3 = A_x e_{3x} + A_y e_{3y} + A_z e_{3z} \tag{3}$$

where the subscripts refer to the axes of the appropriate frame of reference, and where the unit vectors e are defined along the principal molecular moment of inertia axes 1, 2 and 3.

Using the relations 1, 2 and 3 a general vector A can be defined in a frame of reference that both rotates and translates with the molecule as it diffuses. This special requirement is needed before it is possible to see the time dependence of a simple c.c.f. such as

$$C_{v\omega} = \frac{< \mathbf{v}(t)\boldsymbol{\omega}^T(0) >}{< v^2 >^{1/2} < \omega^2 >^{1/2}}$$

in the absence of an external electric field. This was first realised by Ryckaert et al[17], in 1981.The theoretical arguments[3-6] for the existence of single molecule c.c.f.'s prior to the appearance of this paper had not made clear the necessity of using the moving frame of reference (1, 2, 3) and they had not succeeded in illustrating the time dependence of this c.c.f.

Ryckaert et al. also provided arguments based on symmetry to show that it always vanishes for all t in the laboratory frame of reference (x, y, z) in an isotropic sample (i.e. in the absence of a parity breaking field of force such as an electric field E). When such a field is applied to the sample this c.c.f. appears directly[16] in the lab. frame (x, y, z). If the field is in the z axis the elements (x, y) and (y, x) exist; and so on by cyclical symmetry.A suitable combination of external electric field components would make all the off diagonal elements exist directly in the lab. frame, although for electric fields the diagonal elements always vanish.This was shown for the first time by Evans[16] in 1985, using strong static electric fields in a computer simulation of liquid dichloromethane.

Rigorously speaking, this result invalidates the basic assumption, often made in linear response theory, that

$$C_{v\omega} = 0$$

in the frame (x, y, z) for all t.We have discussed this point in the introduction.Also, it is worth pointing out that in all spectroscopic methods[2] the sample is perturbed by an external field, so that the methods of spectroscopy always promote its existence in the laboratory frame (x, y, z) whenever they employ a symmetry breaking field such as the static uniaxial electric field E.This is rarely, if ever, considered in the literature on linear response theory or spectroscopy in general.

The Rotating Frame of Reference.

Recently the use of a rotating frame of reference, (1, 2, 3), has led to the discovery by computer simulation[18-26] of a large number of higher order c.c.f.'s and to the first computation of the time dependence of a.c.f.'s and c.c.f.'s of non inertial accelerations, such as the Coriolis acceleration of a diffusing molecule which also exist in the moving frame (1, 2, 3) and the lab. frame (x, y, z).The rotating frame of reference (1, 2, 3)′ is defined for each molecule separately.It has its origin at the origin of the lab. frame (x, y, z) and rotates at the instant t with the angular velocity of the molecule.Frame (1, 2, 3) is therefore generated from (1, 2, 3)′ by a translation from the fixed origin of (1, 2, 3)′ to the moving origin of (1, 2, 3) at the molecular centre of mass.The advantage of considering frame (1, 2, 3)′ is that it allows the definition of the non- inertial accelerations in all three frames, and automatically introduces into consideration the position vector r of the molecular centre of mass.This immediately introduces into the analysis both the linear centre of mass velocity and the angular velocity through, for example, the Coriolis acceleration of the molecule

$$2\mathbf{v} \times \boldsymbol{\omega}$$

This simply reflects the fact that any rigid body motion has the effect of a translation followed by a rotation.

Using the three frames of reference, (x, y, z); (1, 2, 3); and (1, 2, 3)′; the technique of molecular dynamics computer simulation has been used in several recent papers[18-26] to reveal the existence of numerous cross correlation functions fundamental to any consideration of molecular diffusion processes.

Section 3 : The Non Inertial Accelerations

The nature of the non inertial accelerations becomes clear when we transform velocities or accelerations from the lab. frame (x, y, z) to the rotating frame of reference (1, 2, 3)′.The development hinges on the theorem of elementary dynamics which links the differential operator D_f in the lab frame to its equivalent in the rotating frame (1, 2, 3)′.If the differential operators act on r then the theorem is[27]

$$D_f\mathbf{r} = (D_m + \boldsymbol{\omega} \times)\mathbf{r} \tag{4}$$

and conversely

$$D_m\mathbf{r} = (D_f - \boldsymbol{\omega} \times)\mathbf{r} \tag{5}$$

In these relations it is understood that the operation

$$(D_m + \boldsymbol{\omega} \times)$$

in frame (1, 2, 3)′ is equivalent to the operation D_f in the lab frame (x, y, z), and conversely in eqn (5).Rewriting eqns (4) and (5) in terms of velocities gives

$$\{\mathbf{v}\}_{xyz} = \{\mathbf{v} + \boldsymbol{\omega} \times \mathbf{r}\}_{123'}$$

$$\{\mathbf{v}\}_{123'} = \{\mathbf{v} - \boldsymbol{\omega} \times \mathbf{r}\}_{xyz} \tag{6}$$

Eqn (6) shows that the linear centre of mass velocity in frame (x, y, z) is the equivalent of the sum

$$\{\mathbf{v} + \boldsymbol{\omega} \times \mathbf{r}\}$$

in frame (1, 2, 3)′, where $\boldsymbol{\omega}$ is the angular velocity of the rotating frame with respect to the lab frame.The converse (7) shows that the centre of mass velocity defined with respect to frame (1, 2, 3)′ is the difference

$$\{\mathbf{v} - \boldsymbol{\omega} \times \mathbf{r}\}$$

in the lab frame (x, y, z).It follows that whenever a body is rotating and translating simultaneously, terms such as $\boldsymbol{\omega} \times \mathbf{r}$ appear directly in the lab frame, as well as the rotating frame.It follows that they also exist in the principal molecular moment of inertia frame (1, 2, 3).Terms such as these are called "non inertial" because they are generated only when there is simultaneous rotation and translation so that the Newton equation, force is mass multiplied by linear acceleration, is modified by non-inertial linear accelerations which are real accelerations in frame (x, y, z), the frame of the observer.The non-inertial accelerations are generated by a second application of the differential operators in eqns (4) and (5), giving :

$$D_f^2\mathbf{r} = D_f(D_f\mathbf{r}) = (D_m + \boldsymbol{\omega} \times)(D_m\mathbf{r} + \boldsymbol{\omega} \times \mathbf{r}) = D_m^2\mathbf{r} + D_m(\boldsymbol{\omega} \times \mathbf{r}) + \boldsymbol{\omega} \times D_m\mathbf{r} + \boldsymbol{\omega} \times (\boldsymbol{\omega} \times \mathbf{r}) \tag{8}$$

Conversely:

$$D_m^2\mathbf{r} = D_m(D_m\mathbf{r}) = D_f^2\mathbf{r} - 2\boldsymbol{\omega} \times D_f\mathbf{r} - (D_f\boldsymbol{\omega}) \times \mathbf{r} + \boldsymbol{\omega} \times (\boldsymbol{\omega} \times \mathbf{r}) \tag{9}$$

In eqn (8) it is clear that the single term in the fixed frame (x, y, z) is replaced by four terms in the rotating frame (1, 2, 3)′. Rewriting eqns (8) and (9) in terms of velocities and accelerations we obtain

$$\{\dot{\mathbf{v}}\}_{xyz} = \{\dot{\mathbf{v}} + 2\boldsymbol{\omega} \times \mathbf{v} + \dot{\boldsymbol{\omega}} \times \mathbf{r} + \boldsymbol{\omega} \times (\boldsymbol{\omega} \times \mathbf{r})\}_{123'} \tag{10}$$

$$\{\dot{\mathbf{v}}\}_{123'} = \{\dot{\mathbf{v}} - 2\boldsymbol{\omega} \times \mathbf{v} - \dot{\boldsymbol{\omega}} \times \mathbf{r} + \boldsymbol{\omega} \times (\boldsymbol{\omega} \times \mathbf{r})\}_{xyz} \tag{11}$$

Eqn (10) shows the appearance of the three non inertial linear accelerations in frame (1, 2, 3)′ and eqn (11) their presence in frame (x, y, z).They are : (1) the Coriolis acceleration of the complete rigid molecule; (2) its centripetal acceleration;$\boldsymbol{\omega} \times (\boldsymbol{\omega} \times \mathbf{r})$; (3) the linear acceleration $\dot{\boldsymbol{\omega}} \times \mathbf{r}$ due to its non uniform rotational motion.

It follows from the fundamental frame rotation relations (1-3) that these accelerations are real in frame (1, 2, 3).

The a.c.f.'s of these accelerations also exist in all three frames and have been illustrated for the first time recently using computer simulation for molecular symmetries including that of the spherical top, where the simple first order c.c.f.

$$< \mathbf{v}(t)\boldsymbol{\omega}^T(0) >$$

vanishes in all frames of reference.This result invalidates the Debye theory of rotational diffusion and all variations thereof.As far as we are aware there is no contemporary analytical theory capable of matching the computer simulation in this context.In addition, various higher order c.c.f.'s among the various non inertial linear velocities and accelerations also exist in the spherical top and all lower molecular symmetries. Therefore rotational and translational motion in the spherical top are as intricately bound together as in the asymmetric top and can never be "decorrelated" as in the numerous theories produced in the twentieth century on the entirely fictitious subject of rotational diffusion.Computer simulation has now shown clearly and conclusively that this is an illusion.

The process leading to eqns (10) and (11) may be extended to derivatives of non inertial linear accelerations by operating three times in each frame :

$$D_f^3\mathbf{r} = (D_m + \boldsymbol{\omega} \times)((D_m + \boldsymbol{\omega} \times)(D_m\mathbf{r} + \boldsymbol{\omega} \times \mathbf{r})) \tag{12}$$

$$D_m^3\mathbf{r} = (D_f - \boldsymbol{\omega} \times)((D_f - \boldsymbol{\omega} \times)(D_f\mathbf{r} - \boldsymbol{\omega} \times \mathbf{r})) \tag{13}$$

Eqns (12) to (14) show that when we take into account the derivatives of acceleration in this way the number of non inertial terms increases rapidly.Therefore the Taylor series expansion of any a.c.f. or c.c.f. in frame (1, 2, 3)′ would be equivalent in frame (x, y, z) to a sum involving a very large number of linear non inertial accelerations which are always present in frame (x, y, z) for a rotating and simultaneously translating body such as a diffusing molecule.

The number of possible a.c.f.'s and c.c.f.'s of the higher order non inertial terms also increases proportionately, providing a variety of new ways of looking in to the molecular dynamics of the liquid and condensed states of matter.For example, c.c.f's could be constructed between terms generated by

$$D_m, D_m^2, D_m^3, \ldots.$$

and therefore we see the emergence of a theoretically infinite number of possible a.c.f.'s and c.c.f.'s. No spectral method can give information on all of these.At present it may be possible to obtain the simple c.c.f.

$$< \mathbf{v}(t)\boldsymbol{\omega}^T(0) >$$

by field induced birefringence but no other c.c.f. can be obtained experimentally.Therefore any spectral investigation of molecular diffusion interpreted with "rotational diffusion" is an out of focus image of a mirage.The only valid method of interpretation is computer simulation unless theoretical progress is made away from the concept of "rotational diffusion" itself.

The c.c.f.'s referred to above exist in both frames (1, 2, 3) and (x, y, z) in symmetries including that of the spherical top.They might be of key importance in bridging the great gulf which exists at present between the theories of hydrodynamics and molecular diffusion.The former are more actively interested in the interrelation between rotation and translation on a macroscopic scale, because they have to deal from the outset with phenomena such as vortex flow which are neither exclusively rotational nor exclusively translational in nature.However the existence of molecules need not be postulated in hydrodynamics, so that no purely hydrodynamical theory will produce the simulation results referred to in this review.It follows that the simulation by computer of the "non inertial" c.c.f.'s and a.c.f.'s is real progress, which demands new fundamental theoretical methods in answer to the questions posed by the computer.Conversely, it is now possible[28] to produce hydrodynamic phenomena ,such as eddies, vortices, and stream lines, by computer simulation in two dimensions in an assembly of over 100,000 disks, and no theory of disk diffusion can yet match these results.The computer is asking questions which the theoreticians cannot answer.

Section 4 : Matrix Elements of Correlation Functions.

Before proceeding to a description of the results for various c.c.f.'s from computer simulation it is worth describing in this section the definition of the matrix products used in the construction of c.c.f.'s of the simple type

$$< \mathbf{A}(t)\mathbf{B}^T(0) >$$

The superscript T denotes vector transposition, so that the product

$$\mathbf{A}(t)\mathbf{B}^T(0)$$

is therefore a 3x3 matrix.For example, if **A** denotes **v**, the centre of mass linear velocity of an individual molecule, and **B** denotes ω, that molecule's angular momentum, then the running time average is also a 3x3 matrix

$$< \mathbf{v}(t)\mathbf{J}^T(0) > =$$

$$\begin{array}{lll} < v_1(t)J_1(0) & < v_1(t)J_2(0) & < v_1(t)J_3(0) > \\ < v_2(t)J_1(0) & < v_2(t)J_2(0) & < v_2(t)J_3(0)> \\ < v_3(t)J_1(0) & < v_3(t)J_2(0) & < v_3(t)J_3(0)> \end{array} \qquad (14)$$

where the subscripts show that the tensor product has been carried out in frame (1, 2, 3) of the principal moments of inertia of each molecule in the ensemble.Therefore the c.c.f. contains nine elements in general, each of which is a correlation function in its own right.However the diagonal elements of the moving frame matrix always disappear by symmetry for all point groups[17] so that only the off diagonal elements are considered. In the laboratory frame (x, y, z) the complete matrix vanishes for all t because the symmetry of v to parity reversal is negative while that of J is positive.The effect of an external electric field in this context is to break the parity invariance of the classical hamiltonian, so that elements of the c.c.f. appear in the lab. frame (x, y, z).

In isotropic (field free) media the six off diagonal elements in frame (1, 2, 3) provide a means of identifying the statistical cross correlation between v and J in terms of six different time dependencies.More elements are available in frame (x, y, z) in the presence of a parity breaking external field, such as an electric d.c. field, magnetic field, and electromagnetic (laser) field.In anisotropic media, such as crystals or internally anisotropic media such as liquid crystals, the (x, y, z) elements may be present in the isolated ensemble. The only systematic investigation of elements of the c.c.f. in frame (x, y, z) are those of Evans[16], who broke parity invariance in the hamiltonian with a d.c. z axis electric field applied to liquid dichloromethane in a computer simulation.The field promotes the existence of the (x, y) and (y, x) elements, which are mirror images in time dependence. For a d.c. electric field of the type

$$\mathbf{E} = E_x\mathbf{i} + E_y\mathbf{j} + E_z\mathbf{k} \tag{15}$$

all six off diagonal elements appear in the laboratory frame.

Higher Order Single Molecule C.c.f.'s

Cross correlation functions are fundamentally important to the dynamics of diffusing molecules in the condensed phases of matter.The use of the rotating frame of reference has revealed a method for systematic classification of the set of c.c.f.'s computed for the dynamical quantities defining the motion of a simultaneously rotating and translating molecule.These c.c.f.'s may exist in frames (1, 2, 3) and (x, y, z). Additionally the a.c.f.'s of the various non inertial linear velocities, accelerations and higher time derivatives thereof exist in both frames for all molecular symmetries.These correlation functions are the building blocks from which macroscopic phenomena can be constructed, and the next step in the development of the subject will be to define their role in flow phenomena with computer simulation. This is something that neither the molecular nor hydrodynamic theory of molecular liquids is capable of at present.

One of the simplest types of higher order c.c.f. is that between the Coriolis acceleration

$$2\mathbf{v}(t) \times \boldsymbol{\omega}(t)$$

of the complete molecule and its own centre of mass velocity.This exists in frame (1, 2, 3) but vanishes in frame (x, y, z) and is the 3x3 matrix

$$\mathbf{C}_1(t) = < \mathbf{v}(t) \times \boldsymbol{\omega}(t)\mathbf{v}^T(0) > \tag{16}$$

This has the following nine elements

$$\begin{array}{l}< (\mathbf{v}(t) \times \boldsymbol{\omega}(t))_1 v_1(0) > \; < (\mathbf{v}(t) \times \boldsymbol{\omega}(t))_1 v_2(0) > \; < (\mathbf{v}(t) \times \boldsymbol{\omega}(t))_1 v_3(0) > \\ < (\mathbf{v}(t) \times \boldsymbol{\omega}(t))_2 v_1(0) > \; < (\mathbf{v}(t) \times \boldsymbol{\omega}(t))_2 v_2(0) > \; < (\mathbf{v}(t) \times \boldsymbol{\omega}(t))_2 v_3(0) > \\ < (\mathbf{v}(t) \times \boldsymbol{\omega}(t))_3 v_1(0) > \; < (\mathbf{v}(t) \times \boldsymbol{\omega}(t))_3 v_2(0) > \; < (\mathbf{v}(t) \times \boldsymbol{\omega}(t))_3 v_3(0) > \end{array} \qquad (17)$$

The computer simulation work[18-22] on this matrix of correlation functions has shown that the off diagonal elements all vanish, whatever the symmetry of the molecule.This is in accord with the results of group theory as described by Ryckaert et al.[17] for frame (1, 2, 3).The diagonal elements on the other hand exist for all molecular symmetries, including the spherical top. The problem of isolating the non vanishing higher order c.c.f.'s from those which vanish by symmetry for all t is clarified by the finding that only diagonal elements of cross correlations of the type

$$< \mathbf{A}(t) \times \boldsymbol{\omega}(t)\mathbf{A}^T(0) >$$

exist in general, and then only on frame (1, 2, 3), vanishing in frame (x, y, z).Here **A** is a vector such as **v**, the molecular centre of mass velocity; or $\boldsymbol{\omega} \times \mathbf{r}$, the linear non uniform molecular velocity in frame (1, 2, 3), and so on. For this type of c.c.f. the application of an electric field changes the time dependence of the existing diagonal elements, but promotes neither the existence of off diagonal elements in frame (1, 2, 3) nor of any elements of the c.c.f. in frame (x, y, z).This is in contrast to the behaviour of the simple c.c.f.

$$< \mathbf{v}(t)\boldsymbol{\omega}^T(0) >$$

in response to an applied field.

Hydrodynamics : Irrotational and Vortex Fields

The increasing speed of digital computers means that a larger number of molecules per simulation can be used.The border line between molecular dynamics and hydrodynamics runs in the region where single molecule properties generate visible macroscopic phenomena such as whirlpools or vortices.These involve cooperative motion on a scale many orders of magnitude greater than that possible in contemporary computer simulation, which is just beginning to edge over the frontier line[28].The collective motion may be a vortex flow with respect to a given axis or a given origin in the liquid.This brings into consideration the position vector of the molecular centre of mass, because any vortex field is made up of molecules of a sample rotating with definite symmetry in respect of the lab frame origin.In contrast, in the theory of Brownian motion, often mistakenly applied to molecules, there is no order with respect to a point in the lab frame, and the position vector r can be dispensed with, for example in the Langevin equation.As mentioned already in this review the theory of Brownian motion applied to molecules by Debye is illusory, and gives no method of accounting properly for the role of the centre of mass vector r.As we have seen the latter appears naturally in a.c.f's and c.c.f.'s of the non inertial velocities, accelerations and higher derivatives, i.e. whenever there is rotation superimposed on translation, always the case in diffusing molecules.A whirlpool carries with it its own natural orbital angular momentum, quite foreign to the notion of Brownian motion on a molecular level.The problem here is how to identify and classify vortex fields on a molecular scale and to identify them from the various irrotational fields generated by the non inertial molecular velocities and accelerations .This seems an entirely new approach and may forge a much needed link between the theory of molecular diffusion, such as it is, and that of hydrodynamics, specifically the hydrodynamics of "structured" media.

An analysis of the new a.c.f.'s and c.c.f.'s in terms of field types can be pursued by taking the vector curl of each field (e.g. the non inertial linear velocity, acceleration, or higher time derivative).This shows which of the fields are vortex fields and which are irrotational on the molecular scale.It requires a leap of the imagination to link vortex fields on the molecular level with a macroscopic whirlpool, but the reasoning in this section is offered as one small step.The section is restricted to single molecule fields, but there is no conceptual difficulty in extending the analysis to fields involving more than one molecule, given the computer speed.

At this primitive stage of development it does seem clear however that the role of translation superimposed on rotation at the molecular level immediately introduces the position vector r, missing in Debye's idea[1] of rotational diffusion.The position vector r does not usually appear in the theory of uncoupled rotational or translational diffusion, which is therefore not capable of producing vortex fields of the right type for generating hydrodynamical properties from single molecule considerations, at least without assuming the intermediacy of a fluid medium, slip and stick boundary conditions, roto - translational friction coefficients[2] and so on. It is not really valid to assume the presence of such a medium when it is known that true molecules interact through an intermolecular potential and that a molecular liquid is , self evidently, made up of nothing but molecules.In other words the hydrodynamical principles are laws governing macroscopic properties whose origins are molecular dynamical. The computer power is now available to make the link between the two branches of physics, but only if the mutual influence of rotation and translation is recognised from the start.

Eqn (5) is the link between rotating frame velocity (l.h.s) and lab. frame velocity (r.h.s) The r.h.s. automatically uses two velocities :

$$\mathbf{v}_1 = \{\boldsymbol{\omega} \times \mathbf{r}\}_{xyz} \tag{18}$$

$$\mathbf{v}_2 = \{D_j\mathbf{r}\}_{xyz} \tag{19}$$

The velocity $\mathbf{v}_1$ depends on the position vector r and it is possible to show that the vector curl of $\mathbf{v}_1$ is ω,i.e.

$$\omega = 1/2\mathbf{Del} \times \mathbf{v}_1$$

For each molecule therefore the curl of the linear velocity is the angular velocity. The field $\nabla \times \mathbf{v}_1$ is therefore provided with the rotational property ω.In other words, vortex rotation occurs in regions in the the molecular ensemble where the curl does not vanish.For a given ω the velocity $\mathbf{v}_1$ is proportional to the position vector **r**.Therefore with respect to a given origin in the lab. frame (x, y, z) the further out from this origin the greater will be the velocity $\mathbf{v}_1$.This is charactersistic of a vortex field. In this picture, therefore, each molecule generates its own vortex field,or curl. In a computer simulation, the autocorrelation of the vortex field can be built up as

$$< \mathbf{Del} \times \mathbf{v}_1(t).\mathbf{Del} \times \mathbf{v}_1(0) >$$

in the laboratory frame (x, y, z) and in the moving frame (1, 2, 3). This is possible, and the running time average < > is well defined because the sample origin is fixed by the definitions

$$< \mathbf{r} > = \mathbf{0}$$

$$< \mathbf{r}(t).\mathbf{r}(0) > = 0$$

i.e. the sample is defined to be isotropic and the a.c.f. of the position vector vanishes in frame (x, y, z) at long times.The origin of the laboratory frame is therefore not arbitrary with respect to r for each molecule, but is defined in such a way as to ensure that the mean over the positions of all the molecules disappears in an isotropic sample.Therefore for velocities the use of the moving frame and introduction of the position vector r results in the appearance of an irrotational field and vortex field in the laboratory frame of reference.The various accelerations and their time derivatives can also be examined to see whether they are irrotational or vortex fields.This will show which of the new accelerations are potentially capable of generating a macroscopic vortex, and which are not.After this, it would be possible to show using c.c.f.'s generated by simulation whether the vortex fields are correlated to irrotational fields on the single molecule level.

Taking the vector curl of each acceleration term on the r.h.s. of eqn (9) in the laboratory frame, the only vortex field is that defined by

$$\mathbf{Del} \times ((D_f\omega) \times \mathbf{r})$$

The curl of the other three accelerations disappears in both frames of reference.Therefore the Newtonian field (the first term on the r.h.s. of eqn (9)) is an irrotational field and does not have a vector curl.This implies the natural result that translational diffusion does not generate a vortex on a single molecule level without the simultaneous presence of molecular rotation. The theory of translational diffusion cannot describe molecular vortex fields.Similarly the Coriolis acceleration has no vector curl, i.e. the curl operator in this context means differentiation with respect to the components of r.Since v and r are conjugate variables the differentiation of one with respect to the other produces zero.The Coriolis acceleration is therefore an irrotational field on a single molecule level. The only time the Coriolis acceleration generates a vortex is when the molecular centre of mass velocity v is a function of the molecular position in the lab frame.In this case there must be an external macroscopic force on the molecular ensemble which acts in such a way that there is a gain of fluid per unit volume per unit time. In hydrodynamic terms the fluid is compressible and the divergence of the fluid velocity does not vanish. In molecular terms, more molecules must move systematically into a given volume so that the external pressure on the molecular ensemble is increasing.

The vector curl of the molecular centripetal acceleration

$$\mathbf{Del} \times (\omega \times (\omega \times \mathbf{r}))$$

vanishes and this is not a vortex field.There remains the non uniform acceleration only. If the orbital velocity

$$\mathbf{v}_1 = \boldsymbol{\omega} \times \mathbf{r} \tag{21}$$

is differentiated with respect to time we obtain the "orbital" acceleration:

$$\dot{\mathbf{v}}_1 = \dot{\boldsymbol{\omega}} \times \mathbf{r} + \boldsymbol{\omega} \times \dot{\mathbf{r}} \tag{22}$$

which is a sum of the non uniform acceleration and the Coriolis acceleration. As we have seen, the vector curl of the Coriolis acceleration vanishes in the absence of a pressure gradient across the molecular ensemble, and this leads to the result

$$\dot{\boldsymbol{\omega}} = 1/2\mathbf{Del} \times \dot{\mathbf{v}}_1 \tag{23}$$

i.e. the vector curl of the orbital acceleration of each molecule is an angular acceleration, which is therefore an orbital angular acceleration involving the position vector r.A number of individual molecular accelerations of this nature could act cooperatively to result in a macroscopic vortex.

Eqns (12) to (14) reveal the existence of many higher order terms in the moving and laboratory frames, some of which are vortex fields.The a.c.f.'s of all these terms can be constructed by computer simulation, and so can a large number of new c.c.f.'s between terms in both frames.Note that these are all essentially single molecule properties.We have not yet started to take into account cross correlations between molecules, because we are still at the point of establishing the single molecule dynamics. Essentially speaking, cooperativity of these single molecule a.c.f.'s and c.c.f.'s would lead to the evolution of hydrodynamical modes of collective motion from the equations of molecular dynamics.

The vortex fields on the r.h.s. of eqn (14) in the laboratory frame are those for which the curl exists, as usual. For example

$$\mathbf{Del} \times (\boldsymbol{\omega} \times (\boldsymbol{\omega} \times \mathbf{r})) = \boldsymbol{\omega} \times \dot{\boldsymbol{\omega}} \tag{24}$$

and the irrotational fields are those for which the curl disappears, e.g.

$$\mathbf{Del} \times (\boldsymbol{\omega} \times (\boldsymbol{\omega} \times (\boldsymbol{\omega} \times \mathbf{r}))) = \mathbf{0} \tag{25}$$

Analysis Involving the Inter Molecular Separation

Define the vector between the centres of mass of molecules 1 and 2 by

$$\mathbf{R} = \mathbf{R}_1 - \mathbf{R}_2 \tag{26}$$

If the two molecules are moving in such a way that this vector remains constant then the motion can be defined as cooperative. Assuming the motion of the two molecules is cooperative in this way then, and are also rotating about a common axis, the motion is that of a macroscopic vortex. The kinematic relation applies in this case to the intermolecular vector R, and may be written

$$\dot{\mathbf{R}} = \omega_l \times \mathbf{r} \tag{27}$$

where ω_l is the angular velocity generated by the cooperative orbital motion of the two molecules.In analogy with eqn (23) therefore

$$\omega_l = 1/2\mathbf{Del} \times \dot{\mathbf{R}} \tag{28}$$

i.e. the curl of R exists and this is therefore a vortex field.

More generally, if the vortex angular velocity defined in this way exists by dint of the cooperative motion of two molecules, then an indication of the existence of a macroscopic vortex from a computer simulation might be obtained through the existence of correlation functions of ω_l and its time derivatives

The existence of correlation functions of this type is therefore a direct test of the build up of a vortex using the dynamics of molecules , rather than the principles of fluid dynamics, which use no molecular concepts.

It is clear that this analysis, based on the cooperative motion of two molecules, can be extended to include the motion of many molecules, given the computer power. Note that the swirling motion represented by eqn (27), the kinematic equation for the intermolecular vector, need not be confined to a plane and may be approximately valid even when the intermolecular distance is not rigidly constant, but fluctuating as in a true molecular liquid.The existence of the a.c.f. of the orbital angular velocity is one way of testing for the existence of the cooperative vortex motion.

Section 5 : Simulation Methods: Array Processors

There are many fine review articles available now on computer simulation in condensed molecular matter, and the basic technique is accepted and used routinely in many laboratories.A useful description is provided by Fincham and Heyes[11] who mention the need for radically different computer architecture for future work with large numbers (of order 10,000) of relatively complex molecules.The borderline between molecular dynamics and hydrodynamics needs for its investigation many thousands of ineracting bodies, such as hard disks or molecules.To handle this amount of data requires specialised computer architecture.

The Simulation Program Code TETRA

The molecular dynamics computer simulation algorithm TETRA has been the mainstay of much of the work in the literature[2,15,16,18-26,29-37] on cross correlation functions.This section is a brief description of the algorithm, a typical constant volume algorithm for the simulation of small ensembles of polyatomic rigid molecules of any symmetry.The restricted speed, accessibility and storage capability of older computers such as the CDC 7600 has meant that all the simulation work to date on cross correlation functions has had to be carried out on small samples of 108 molecules, with a severely limited ration of time steps per segment. The use of new computer architectures is expected to change this out of all recognition in the next decade, enabling the use of samples of many thousands of molecules and many millions of time steps.

Equations of Motion in TETRA

A full description of TETRA is available in the original papers[35,38] and here we summarise the main features of its integration routine. With reference to the rotational equation of motion for the 108 molecules the first step is the calculation of the torque from the resultant forces on each atom.The resultant molecular torque is then integrated numerically for the angular momentum.The translational equation of motion in TETRA is integrated with a Verlet method. The code uses periodic boundary conditions and centre of mass to centre of mass cut off criteria. The number of atoms in each molecule and the number of molecules can be increased indefinitely provided the computer time is available. It incorporates corrections for long range forces and has facilities for using pair potentials of the site site type, with Lennard Jones atom atom and charge charge terms.For input temperature and molar volume the mean pressure is computed, together with relevant thermodynamic parameters such as the mean internal energy, total energy, and rotational and translational kinetic energy.

Implementation of TETRA in Parallel Processors

The implementation of a program such as TETRA on parallel processors requires the use of a computer architecture which is capable of processing in parallel several parts of the program simultaneously. The FORTRAN code is then executed in parallel, and the job makes explicit use of all the array processors.A precompiler has been evolved to introduce parallelism into the original source code, which is then prepared for use with the system such as the D.A.P. in the Univ. of London. An improvement to the speed and efficiency of a program such as TETRA can be obtained without an excessive amount of reprogramming of the original source code.Further descriptions of the I.C.L. D.A.P. can be found in the literature.

Section 6 : Simple Cross Correlation Functions

The many results obtained recently for c.c.f.'s such have been documented in the literature for several molecular symmetries coded into TETRA.The symmetry of the matrix

$$< \mathbf{v}(t)\mathbf{J}^T(0) >$$

depends on the point group of the molecule but some at least of the off diagonal elements exist for all dipolar molecules.All the off diagonal elements vanish however in spherical top molecules of T_d or O_h symmetry. In a linear dipolar molecule two of the off diagonal elements exist[17] and as the symmetry of the molecule decreases, more elements exist in the moving frame (1, 2, 3).A particularly interesting example is that of a chiral (optically active) molecule such as CHBrClF where all the off diagonal elements exist in general for both enantiomers, but where two of these elements have a mirror image time dependence[32] so that the complete matrix for both enantiomers has the following symmetry

$$\begin{tikzcd}
\underset{(R)}{\begin{bmatrix} 0 & + & + \\ - & 0 & + \\ - & + & 0 \end{bmatrix}} \arrow[dr] & & \underset{(S)}{\begin{bmatrix} 0 & + & - \\ - & 0 & + \\ + & + & 0 \end{bmatrix}} \arrow[dl] \\
& \underset{(RS)}{\begin{bmatrix} 0 & + & 0 \\ - & 0 & + \\ 0 & - & 0 \end{bmatrix}} &
\end{tikzcd}$$

It can be seen that two of the off diagonal elements of these matrices change sign, which implies that the time dependence of the off diagonal c.c.f.'s mirror images in one enantiomer its equivalent in the other.Therefore in the frame (1, 2, 3) the dynamical properties of two enantiomers are not identical. This was a result first discovered by computer simulation[32] and has led to the general and fundamental result that all enantiomers (mirror image pairs of molecules) have this dynamical property in frame (1, 2, 3) for these simple c.c.f.'s. When the two enantiomers are mixed in fifty fifty ratio, to form the racemic mixture, the switching off diagonal elements vanish for all t, giving the matrix symmetry illustrated above for the bromochlorofluoro methanes.

In other types of chiral molecule such as the trans 1, 2, dimethylcyclopropanes, the symmetry of the overall matrix is different[40]:

$$\begin{tikzcd}
\underset{(R)}{\begin{bmatrix} 0 & + & 0 \\ - & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}} \arrow[dr] & & \underset{(S)}{\begin{bmatrix} 0 & - & 0 \\ + & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}} \arrow[dl] \\
& \underset{(RS)}{\begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}} &
\end{tikzcd}$$

in that some of the off diagonal elements vanish in the noise of the computer simulation, leaving the two switching elements isolated and different in sign for each enantiomer. In the racemic mixture the two off diagonal elements vanish for all t, leaving a null matrix in this case for the c.c.f.

$$< \mathbf{v}(t)\mathbf{J}^T(0) >$$

Therefore in the special case of 1, 2, dimethyl cyclopropane the effect of this cross correlation on laboratory frame properties can be discerned by comparing the physical properties of the racemic mixture (where there is no cross correlation) with those of one enantiomer. A precise experimental determination of the liquid state properties of the enantiomer compared with those of the mixture can therefore be used as information on this correlation with the interpretative help of computer simulation.Furthermore the change of sign in the off diagonal elements is very specific to two elements and it seems that this is at the root cause of all dynamical differences between enantiomer and racemic mixture in the laboratory frame of reference.

Further information on the time dependence of the moving frame off-diagonal elements for a variety of molecular symmetries is available in the literature[35] on c.c.f.'s.

Laboratory Frame of Reference (x, y, z)

Two years after the discovery by computer simulation[31,32] of the property just described for enantiomers and racemic mixtures, the further discovery was made[16] of the existence of off - diagonal elements of this c.c.f. (or of the equivalent force-torque matrix) direct in the lab frame (x, y, z). The result of applying an electric field in the z axis of the lab. frame is, for example, to promote the existence of the (x, y) and (y, x) elements, which therefore has the symmetry:

$$\begin{bmatrix} 0 & + & 0 \\ - & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}_{(xyz)}$$

The cross-correlation function becomes directly visible in the laboratory frame whenever a molecular ensemble is perturbed by an external force field, specifically an electric field as above, or a magnetic or electromagnetic field , provided that these make the liquid sample anisotropic.It is precisely this perturbation that allows us[41] to see spectra, specifically dielectric spectra, i.e. permittivity dispersion and loss.In molecular dynamical terms the difference between a perturbed and isolated sample is that in the former case the c.c.f. exists for $t > 0$ and in the latter case vanishes for all t because the parity of v is opposite to that of J.This result is also true for alignment derived from the interaction between polarisability E^2 (e.g. when a sample is treated with an electro - magnetic field of force (a laser field) and alignment occurs via the Buckingham effect) .

The approximations inherent in fluctuation-dissipation theory now become more clearly defined.During the transient process a transition in the dynamics is taking place whereby

$$\begin{gathered} C_{tr} = 0 \\ \downarrow \\ C_{tr} \# 0 \end{gathered}$$

At field off equilibrium on the other hand the c.c.f. always vanishes, so that the time dependence of the orientational fall transient and the field off equilibrium orientational a.c.f. cannot be the same.In other words the spectroscopy of molecular diffusion always picks up information on c.c.f.'s such as these.

The implications of this have not been worked out fully in the literature on analytical theories for molecular diffusion as investigated by spectroscopic techniques, where the sample is always perturbed by a probe field. A simple theory for the effect of these lab frame c.c.f.'s has been given by Evans[16] based on Mori theory, and this reproduces self-consistently with the a.c.f.'s the major results of the simulation.

The classical cross correlation function has many of the properties of a quantum mechanical wave function and there is a quantum mechanical equivalent of

$$< \mathbf{v}(t)\boldsymbol{\omega}^T(0) >$$

There is therefore a translational influence on the rotational constants A ,B , and C.It is well known that the vibrational modes of a molecule influence the rotational constants (e.g. the Coriolis coupling of infra red and Raman spectra), but this is a purely intrmolecular effect.The translational influence should be observable directly in the presence of an electric field, because the c.c.f. then exists in the laboratory frame. There should be rorotranslational ("forbidden") energy levels generated by the quantum mechanical equivalent of the c.c.f. in the laboratory frame.These should be observable under the right conditions using precision infra red or Raman spectroscopy, and should be different in the presence and absence of an external electric field.

The latter also produces birefringence in the laboratory frame, and the theory[42] of field induced birefringence (e.g. of the Kerr effect) is invalidated by this effect if that theory does not account for centre of mass translational motion directly in frame (x, y, z).Theories of the Kerr effect based on "rotational diffusion" are incorrect because of the existence of c.c.f.'s in both frames; the usual c.c.f. in frame (1, 2, 3) and the field induced a.c.f. in frame (x, y, z).

At sub Doppler resolution[43] (e.g. in Lamb dip and double resonance spectroscopy) c.c.f.'s invoving the velocity of the molecule relative to the laser beam are intrinsically important. If the linear velocity of the molecule is correlated to its own angular velocity the Doppler profile and inverse Lamb dip profile should:1) be different in the presence and absence of an electric field;2) be different for each rotational quantum transition in the presence of the field.

Translational absorption corresponds to $J = 0$ and can be seen[44] in the induced far infra red spectrum of a non dipolar species such as nitrogen.Analogous translational effects should be present in microwave line broadening and the various double resonance spectroscopies now available.

In summary

$$< \mathbf{v}(t)\boldsymbol{\omega}^T(0) >$$

is a fundamental c.c.f. which becomes measurable in the laboratory frame in the presence of an electric field, and its presence may be detected spectroscopically using techniques such as infra red / radio frequency double resonance of an enantiomer compared with its racemic mixture[43]. Recent results along these lines[43] have indicated that these spectra are not identical as expected from the classical theory of collision broadening.This excludes from consideration all statistical cross correlation effects because it was devised before the era of computer simulation.

Section 7 : Higher Order Cross Correlation Functions

Section 3, on the non inertial accelerations, has revealed the existence of many non inertial linear velocities and accelerations in frame (x, y, z).It follows that the a.c.f.'s of each of these exists in frame (x, y, z) and this has been verified recently using computer simulation. The pattern of non vanishing higher order c.c.f's between these terms, as mentioned already, takes the form

$$< \mathbf{A}(t) \times \omega(t)\mathbf{A}^T(0) >_{123} \tag{31}$$

where A is an appropriate dynamical vector.In this type of higher order c.c.f. the diagonal elements exist for t > 0 but the off diagonal elements vanish, in contrast to the simple c.c.f.'s of section (6).The effect[22] of an electric field[42] is to enhance the amplitude of these diagonal elements, but not to promote their existence in frame (x, y, z). Therefore this type of c.c.f. never appears direct in frame (x, y, z).

The Spherical Top

It has been noted already that the first order velocity to angular velocity a.c.f. vanishes in frames (1, 2, 3) and (x, y, z) in an isotropic liquid of spherical top molecules.However, the higher order c.c.f.'s of type (31) exist and this has been demonstrated recently with computer simulation[45].For T_d symmetry each diagonal element in frame (1, 2, 3) is identical; but in general the elements have a different amplitude and time dependence.The existence of diagonal elements of this type for the spherical top implies that the first theory of rotational diffusion, due to Debye must be invalidated rigorously despite its great elegance and usefulness to generations of dielectricians and spectroscopists. In natural philosophy this is always the fate of hypothesis.If it is not, then nothing has been learned by observation.In the spherical top the simulation methods now reveal the ever present statistical cross correlations between the molecular angular and linear momenta of type (31) and many others of higher order generated by the existence of the higher time derivatives of the non inertial linear accelerations. These higher order cross correlations remain almost wholly unexplored theoretically, but at the same time are fundamental to a realistic appreciation of molecular dynamics.

The cross correlation functions of type (31) are illustrated for liquid carbon tetrachloride in the the original literature[45].

The Asymmetric Top

A variety of higher order c.c.f.'s has been computed[18-24] for the C_{2v} top dichloromethane and also for the enantiomers and racemic mixtures of several chiral molecules[22]. In these papers the effect of an electric field was shown to be the promotion of changes in the time dependence of type (31) c.c.f.'s in frame (1, 2, 3), but not to affect the overall matrix symmetry.This is also true of chiral molecules, both of (R) and (S) type, and in this case there is no change of symmetry in the racemic mixture, again in contrast to the results of section (6).The actual time dependence of the higher order c.c.f.'s in this case is shown in the literature.Cross correlation functions among the various non inertial velocities and accelerations vanish for all t if they are not of type (31) in frame (1, 2, 3), in the presence and absence of an electric field.

Cross Correlation Functions in Molecular Gases

Recent molecular dynamics simulation work[46,47] has concentrated on the first and second order c.c.f.'s described above for molecular gases of C_{2v} symmetry such as hydrogen selenide, chlorine dioxide, and oxygen dichloride. The standard code TETRA was adapted for use with gases and the c.c.f.'s computed with running time averages as usual.The symmetry of the various known c.c.f. matrices described already does not change with the liquid to gas phase transition and this is probably also the case in liquid to solid phase transitions which can be investigated with constant pressure algorithms.However, the time dependence and normalised amplitude of the c.c.f. matrix elements are sensitive to phase transitions and can be used to study their dynamical effects in detail. This work is obviously still in its infancy, but promises to be a useful new technique.The molecular dynamics of a phase transition are are not always easy to follow with conventional techniques; the time dependencies in a.c.f.'s might be too similar just above and below the critical temperature; but the amplitude of the c.c.f.'s could be very different.

Section 8: Advances in Computer Architecture

In all the computations briefly mentioned in sections (1) to (7) the noise level of the c.c.f.'s , measured by the difference between two consecutive time segments, has often been high, and the sample necessarily restricted to 108 molecules because of the lack of computer speed and restricted access to mainframes such as the CDC 7600. Therefore all the computations mentioned in this article could be improved statistically and made much more accurate with access to improved architecture such as the IBM ICAP 1.Improved computer architecture would also allow attempts to be made at extending the computations to multi molecular cross correlations and to single molecule cross correlation functions between higher order non inertial accelaration derivatives and so on. The objective of this work would be to bridge the gap between classical molecular dynamics and the exact results of hydrodynamics by linking the behaviour of the various auto and cross correlation functions with flows and vortices generated from the equations of hydrodynamics in selected regions of a computer simulation sample of up to 50,000 molecules.

It is already possible on the ICAP1 system to reproduce certain hydrodynamic flow phenomena in samples of up to 160, 000 hard disks in two dimensions, and this is work in progress on the IBM architectures at Kingston.The use of molecules, rather than hard disks, would introduce into consideration many new possibilities of rotation to translation cross correlation, as this short review has attempted to show. On a multi molecular level these might have their equivalents in new hydrodynamic phenomena .

Another challenge to be met by conventional computer simulation is the description in molecular terms of phase transitions using the new cross correlation functions of single and multi molecular type to monitor the dynamical state of the system just above and below the phase transition. This could be useful to check whether the transition has indeed occurred, and what has been the effect on the molecular level.This work recquires large samples, constant pressure algorithms[11] and good parallel processor architecture for good statistics to be achieved.Therefore there is scope to take advantage in many ways of the speed currently offered by ICAP1, ICAP2, and ICAP3.

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