

NON-INERTIAL ACCELERATIONS IN THE THEORY OF MOLECULAR DYNAMICS

M.W. EVANS

Dept. of Physics, University College of Swansea, Singleton Park,
Swansea SA2 8PP, WAles, (UK).

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ABSTRACT

By repeated use of differential operators in the rotating frame of reference it is shown that a large number of ways exist of correlating fundamental non-inertial acceleration terms in a molecular ensemble. The technique of computer simulation can be used to illustrate the time dependence of some of these new statistical correlations, which cannot be described with the conventional methods using diffusion equations. The effect of external fields can be conveniently built in to the rotating frame analysis, revealing many new correlations.

INTRODUCTION

The new rotating frame theory of molecular diffusion, recently applied to the molecular dynamics of an asymmetric top, is extended here to include new types of cross-correlation. Using the simple mathematics of frame transformation [1] the result is the generation of a very large number of possible auto and cross-correlations whose existence has not been explicitly realised. No spectral method can provide direct information on any of these and contemporary computer simulation on a very few. Standard diffusion theory, based on Fokker-Planck and Kramers equations [2,3] cannot be used to describe the simplest, even with considerable simplifying assumption. When the influence of external electric, magnetic, and electromagnetic force fields is included [4], or alternatively the extra torque due to the director potentials of liquid crystals, the number of possible cross-correlations (c.c.f.'s) is increased considerably. Similarly, consideration of cross-correlations between molecules results in the emergence, from the rotating frame method, of new possibilities when dealing with the collective

correlations of the molecular liquid state. These new cross-correlations all emerge from a very simple mathematical treatment. Out of the infinite number of possible auto and cross-correlation functions generated mathematically, the majority vanishes by symmetry for all t ; but a minority exists. Therefore, because the total number of possible correlations is infinite, the minority that exists also approaches infinity in number. The physical implications of this are that any theory which is intended to describe molecular diffusion must be capable of describing the time dependence of all the existing cross-correlation and auto-correlation functions (a.c.f.'s) self-consistently. Neither the diffusion theories [2,3] based on Kramers or Langevin nor the hydrodynamical approach [4] seems remotely capable of this as things stand at present. This leaves computer simulation as a numerical method which may be used to approximate the time dependence of the cross - and auto-correlation functions [5-10]. The general laws that may be expected to emerge from this fundamental approach may be those concerned with the specific effect on ensemble dynamics of external fields [4], and also of internal fields such as those caused by the director potential and the interaction of molecular force fields [11,12]. If we make the analogy between the classical correlation function and its quantum mechanical equivalent, an expectation value of a wave function [11], then the existence of the many different new a.c.f.'s and c.c.f.'s described here would mean the emergence of discrete spectral features, which under favourable experimental conditions, could be linked to specific types of cross-correlation. The liquid state at room temperature normally produces, however, a broad band, such as that in the far infra-red [11]. This work shows that the broad band absorption is composed of a very large number of discrete quantum features, sets of lines, each of which is associated, theoretically, with a particular type of lab. frame auto and cross-correlation in which rotational and translational wave functions are mutually influential [13,14]. There is much more to a broad band, therefore, than meets the eye.

DEVELOPMENT OF THE ROTATING FRAME THEORY

Consider a frame of reference, $m = (1,2,3)'$, which rotates with respect to the laboratory frame $f = (x,y,z)$ at the angular frequency, ω . Each frame has the same origin. Let \underline{r}_m be the position vector of the centre of mass of a molecule in each frame. Let $D_{f/m} \underline{r}_m$ be the linear velocity of the molecular centre of mass relative to (x,y,z) and $D_{m/m} \underline{r}_m$ that relative to $(1,2,3)'$. This defines the differential operators $D_{f/m}$ and $D_{m/m}$. Let us now examine the higher derivatives of \underline{r}_m in both frames.

VELOCITIES

The velocities in the fixed and rotating frames are linked through:

$$\mathcal{D}_{f\mathcal{L}}\mathcal{r} = \mathcal{D}_{m\mathcal{L}}\mathcal{r} + \omega \times \mathcal{r} \quad (1)$$

$$\mathcal{D}_{m\mathcal{L}}\mathcal{r} = \mathcal{D}_{f\mathcal{L}}\mathcal{r} - \omega \times \mathcal{r} \quad (2)$$

where it is understood that all the terms on the r.h.s. are defined with respect to frame (1,2,3)', and that on the l.h.s. with respect to frame (x,y,z). The angular frequency ω is the same in both frames because it is the rate at which one frame rotates with respect to the other.

ACCELERATIONS

The frame relations now involve two applications of the operators $\mathcal{D}_{f\mathcal{L}}$ and $\mathcal{D}_{m\mathcal{L}}$ providing the forward and backward transformations.

$$\mathcal{D}_{f\mathcal{L}}^2 \equiv \mathcal{D}_{f\mathcal{L}}(\mathcal{D}_{f\mathcal{L}}\mathcal{r}) = \mathcal{D}_{m\mathcal{L}}^2\mathcal{r} + 2\omega \times \mathcal{D}_{m\mathcal{L}}\mathcal{r} + (\mathcal{D}_{m\mathcal{L}}\omega) \times \mathcal{r} + \omega \times (\omega \times \mathcal{r}) \quad (3)$$

$$\mathcal{D}_{m\mathcal{L}}^2 \equiv \mathcal{D}_{m\mathcal{L}}(\mathcal{D}_{m\mathcal{L}}\mathcal{r}) = \mathcal{D}_{f\mathcal{L}}^2\mathcal{r} - 2\omega \times \mathcal{D}_{f\mathcal{L}}\mathcal{r} - (\mathcal{D}_{f\mathcal{L}}\omega) \times \mathcal{r} + \omega \times (\omega \times \mathcal{r}) \quad (4)$$

The eqn (4) introduces into the lab frame the Coriolis acceleration, the centripetal acceleration and the non-uniform acceleration. These appear whenever the Newton equations are written in a non-inertial context [1]. For molecular dynamics they are important [6-9], and cannot be approximated out of existence as in standard diffusion theory [2,3]. Naturally, they have quantum mechanical counterparts, which may, under "particle in the box" conditions [13,14], result in discrete, observable infra red absorptions and other spectral features.

DERIVATIVES OF ACCELERATION

In this case the operators are applied three times in the forward and back transforms, producing:

$$\begin{aligned} \mathcal{D}_{f\mathcal{L}}^3 &= \mathcal{D}_{m\mathcal{L}}^3\mathcal{r} + \mathcal{D}_{m\mathcal{L}}(2\omega \times \mathcal{D}_{m\mathcal{L}}\mathcal{r}) + \mathcal{D}_{m\mathcal{L}}((\mathcal{D}_{m\mathcal{L}}\omega) \times \mathcal{r}) + \mathcal{D}_{m\mathcal{L}}(\omega \times (\omega \times \mathcal{r})) \\ &+ \omega \times \mathcal{D}_{m\mathcal{L}}^2\mathcal{r} + \omega \times (2\omega \times \mathcal{D}_{m\mathcal{L}}\mathcal{r}) + \omega \times ((\mathcal{D}_{m\mathcal{L}}\omega) \times \mathcal{r}) + \omega \times (\omega \times (\omega \times \mathcal{r})) \quad (5) \end{aligned}$$

$$\begin{aligned}
 D_{mr}^3 = & D_{fr}^3 \ddot{r} - D_{fr}(2\omega \times D_{fr}\dot{r}) - D_{fr}((D_{fr}\omega) \times \dot{r}) + D_{fr}(\omega \times (\omega \times \dot{r})) - \omega \times D_{fr}^2 \ddot{r} \\
 & + \omega \times (2\omega \times D_{fr}\dot{r}) + \omega \times ((D_{fr}\omega) \times \dot{r}) - \omega \times (\omega \times (\omega \times \dot{r})) \quad (6)
 \end{aligned}$$

Eqn (6) shows the existence of many higher order accelerations for each molecule in the laboratory frame (x,y,z). The a.c.f.'s of all of these exist in frame (x,y,z) and some of the c.c.f.'s between the terms are allowed by symmetry. Furthermore, making use of the results:

$$\langle D_{mr}^2(t) \cdot D_{mr}^3(o) \rangle \neq 0; \quad t \neq 0 \quad (7)$$

$$\langle D_{fr}^2(t) \cdot D_{fr}^3(o) \rangle \neq 0; \quad t \neq 0 \quad (8)$$

it becomes clear that many new cross-correlations are generated in frame (1,2,3)' and (x,y,z).

EXTERNAL TORQUES

If the molecular ensemble is treated with an external field [2,4,12] the acceleration term $D_{fr}\omega$ in frame (x,y,z) must be rewritten as the sum of the intrinsic acceleration and a term due to the effect of the field.

ELECTRIC FIELD

The extra angular acceleration due to the electric field is:

$$-\mu \times E / I_E$$

where μ is the molecular dipole, and E the external field strength. Here I_E in the denominator is the equivalent inertia due to the effect of E on the molecule. The total angular acceleration is therefore:

$$D_{fr}\omega = \frac{\mu \times E}{I_E} \quad (9)$$

Substituting this in eqns (2), (4) and (6) immediately produces a range of new lab. frame cross-correlation functions involving the field acceleration. Taking into account polarisability effects [2,3] the effective field on each molecule is:

$$E = E_o + E \cdot \alpha \cdot E + EEE \cdot \gamma + \dots \quad (10)$$

where α is the molecular polarisability, γ the hyper-polarisability, and so on.

Similar considerations hold for the torque $-\mu \times H$ generated by a static external magnetic field, although in this case the situation is affected by the inevitable presence of Lorentz forces.

ELECTROMAGNETIC FIELD

The electromagnetic field vector is, as usual,

$$E_{em} = E_0 \exp(i(\omega t - k \cdot R)) \quad (11)$$

and from eqns (2), (4), and (6) would automatically generate new cross correlations through, for example, the Buckingham effect, i.e. a torque and birefringence generated by an electromagnetic field applied to a molecular ensemble [12].

None of the available theories of molecular diffusion, hydrodynamical or otherwise, go nearly into enough detail to produce these new correlation functions analytically. However the relatively primitive methods of computer simulation we now have available can be used to illustrate their

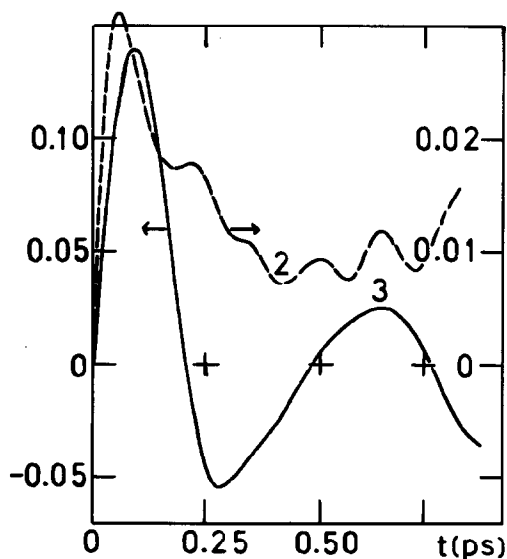


Fig. 1. Some diagonal elements of the cross-correlation function $\langle \mu(t) \times (\mu(t) \times \chi(t)) \cdot \mu(0) \times \chi(0) \rangle / [\langle \omega^2 \rangle \langle \omega^2 \rangle^{\frac{1}{2}} \langle v^2 \rangle]$

in the moving frame of reference (1,2,3)

2. (2,2) element.

3. (3,3) element.

existence numerically, and also to pinpoint the exact effects [4] on cross-correlation of an external field of force applied to the sample. With the increase in speed and power of computers the link up with hydrodynamics can be made [15,16,17], and it would be possible to see how the results of this letter fit in to the overall hydrodynamic scheme. In the meantime, for gaseous hydrogen selenide, the results of a simulation with only 108 molecules illustrates in fig. (1) the existence of a simple cross-correlation function, one out of many which has not seen the light of day before. This is:

$$\frac{\langle \psi(t) \times (2\psi(t) \times \chi(t)) \cdot 2\psi(0) \times \chi(0) \rangle}{4\langle \omega^2 \rangle \langle \omega^2 \rangle^{\frac{1}{2}} \langle v^2 \rangle} \quad (12)$$

This cross-correlation, implied by eqns (5) and (3), exists in the moving frame defined by the three principal molecular moments of inertia, but vanishes by symmetry in frame (x,y,z) for all t. The a.c.f.'s of the components exist however in frame (x,y,z) and are illustrated in fig. (2).

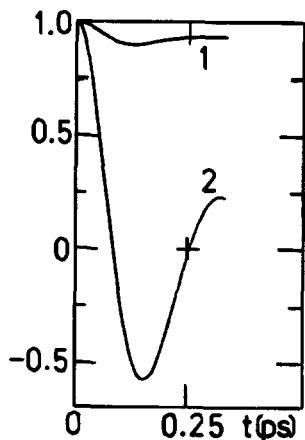


Fig. 2. Autocorrelation functions of the force $2m\psi(t) \times (\psi(t) \times \chi(t))$, in (1) the laboratory frame and (2) the moving frame of reference.

CROSS-CORRELATIONS BETWEEN DIFFERENT MOLECULES

If the analysis leading to eqns (2) to (6) is repeated for the time-dependent intermolecular separation of two molecules:

$$\rho_i(t) = \mathbf{r}_{i1}(t) - \mathbf{r}_{i2}(t) \quad (13)$$

we obtain varieties of cross-correlation which depend on ρ_i and contain the position vectors \mathbf{r}_{i1} and \mathbf{r}_{i2} of the two molecules in question. A

straightforward piece of algebra leads to the implied existence of cross-correlation functions such as

$$\langle 4(\varphi(t) \times \chi_2(t)) \cdot (\varphi(o) \times \varphi(o) \times \chi_1(o)) \rangle$$

and

$$\langle 4(\varphi(t) \times \chi_1(t)) \cdot (\varphi(o) \times \varphi(o) \times \chi_2(o)) \rangle$$

(14)

which correlate and define statistically the way that the dynamics of molecule (1) depend on those of molecule (2). None of these seems to have been explored in any detail, although they implicitly play a role in the construction of the theory of N particle diffusion. Having got as far as eqn (14) it is natural to extend the logic to three and more particles, thus greatly expanding the number of a.c.f.'s and c.c.f.'s which have a theoretical existence in the molecular condensed states of matter. With the use of supercomputers [15] the nature of these cross-correlation functions could be explored in considerable detail, with a view to unifying the hydrodynamic and molecular theory of the condensed phases.

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