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SINGLE PARTICLE ROTOTRANSLATION IN COMPUTER DIATOMICS

MYRON EVANS

Edward Davies Chemical Laboratories, University College of Wales, Aberystwyth, Dyfed, SY23 1NE (Gt. Britain)

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ABSTRACT

The interaction of rotation and translation in dipolar molecules is investigated by means of a molecular dynamics simulation of the mixed autocorrelation functions of energy (moments) and speed. The forms of these autocorrelation functions are sensitive to shape anisotropy as measured by three interatomic distances, one of which corresponding to N_2.

INTRODUCTION

In this note we present some calculations by molecular dynamics simulation of rototranslational autocorrelation functions of interest to a fully self-consistent theory of the molecular dynamical evolution in liquids. The rotations and translations cannot be considered separately (as in the theory of inelastic neutron scattering) because there are strong mutual interactions. These have been discussed for loaded rough hard spheres by Chandler [2] who finds analytically a strong retardation of rotational diffusion by translational effects and vice-versa. Condiff and Dahler [3] have discussed the problem using statistical mechanics based on the work of Kirkwood et al. [4] and Rice et al. [5] and find that the rototranslational effects vanish only in two extremes:

(a) unloaded hard spheres;

(b) symmetrical hard spherocylinders.

With the computing power available now it is possible to investigate the problem more thoroughly and with more acceptable intermolecular potentials, using the Lennard-Jones type, for example, with attractive as well as repulsive components. It is possible to examine the problem directly in a molecule such as N_2 by computing the mixed autocorrelation functions:

(a) $\langle |\underline{v}(t)||\underline{\omega}(o)| \rangle$, the linear ($|\underline{v}|$) and angular ($|\underline{\omega}|$) speed autocorrelation functions.

(b) $\langle v^{2n}(o)\omega^{2n}(t) \rangle$, the kinetic energy autocorrelation functions and their even

moments (2n).

These are chosen for computational convenience because they represent more clearly the nature of the interaction than the simple mixed autocorrelation function $\langle \underline{v}(o).\underline{\omega}(t) \rangle$. For N_2 symmetry the latter is very small (but not necessarily vanishingly so [6]) and would need enormously long runs for its proper definition. This is because N_2 can be reasonably approximated by a symmetric spherocylinder if the electrodynamics (e.g. quadrupole-quadrupole interaction) are neglected. The purpose of computing such functions (which are, apparently, unrelated to experimental data) may be demonstrated using a formalism for the N-body dynamical evolution such as that embodied in the Fokker-Planck type equation [7]

$$\frac{\partial f}{\partial t} = - \frac{\partial}{\partial \underline{A}} \cdot \left(\dot{\underline{C}}_{\underline{A}} \underline{C}_{\underline{A}}^{-1} \underline{A} f \right) + \frac{1}{2} \frac{\partial}{\partial \underline{A}} \cdot \left(\underline{C}_{\underline{A}} \frac{d}{dt} (\underline{M}^{-1}) \underline{C}_{\underline{A}}^{T} \frac{\partial f}{\partial \underline{A}} \right)$$

Here $\underline{A}$ is a column vector of linearly independent dynamical variables, $C_{\underline{A}}(t)$ is the correlation function $\langle \underline{A}\, \underline{A}^{T}(o) \rangle$, $\underline{M}$ a variance-covariance matrix and $f(\underline{A}(t); t | \underline{A}(o))$ a conditional probability density function. If rotational motion and translational motion are mutually intercorrelated statistically then $\underline{A}$ is defined as:

$\underline{A} \equiv \begin{bmatrix} \underline{p} \\ \underline{L} \end{bmatrix}$, where $\underline{p}$ is the linear and $\underline{L}$ the angular momentum of the rigid molecule. Eqn.(1) may then be solved [7] for f in terms of the autocorrelation functions $\langle \underline{p}\underline{p}^{T}(o) \rangle$; $\langle \underline{L}\underline{L}^{T}(o) \rangle$, $\langle \underline{p}\underline{L}^{T}(o) \rangle$, and $\langle \underline{L}\underline{p}^{T}(o) \rangle$. The self-consistency of any theory for these four autocorrelation functions may then be elucidated with the use of molecular dynamics simulations by building up from f the energy and speed autocorrelation functions described already.

A framework for such efforts is provided phenomenologically by using successive approximents of the Mori continued fraction [8] based on

$$\dot{\underline{A}}(t) = - \int_{o}^{t} d\tau \hat{\phi}(t - \tau) \underline{A}(\tau) + \underline{F}_{\underline{A}}(t)$$

which defines the autocorrelation matrix as

$$C_{\underline{A}}(t) = \hat{\mathcal{L}}_{a}^{-1} [s + \hat{\phi}_{\underline{A}}(s)]^{-1}$$

in the usual way. Here $\hat{\phi}_{\underline{A}}$ is the memory operator and $\underline{F}_{\underline{A}}$ is Mori-propagated, using projection operators.

The molecular dynamics results are therefore useful in themselves and since they are the first of their kind (as far as we are aware) are communicated briefly as follows. They were computed using atom-atom interactions with 256 molecules arranged initially on an α nitrogen lattice. Running time-averages were developed and used to build up the results over a restricted range of 1000 to 1600 time steps.

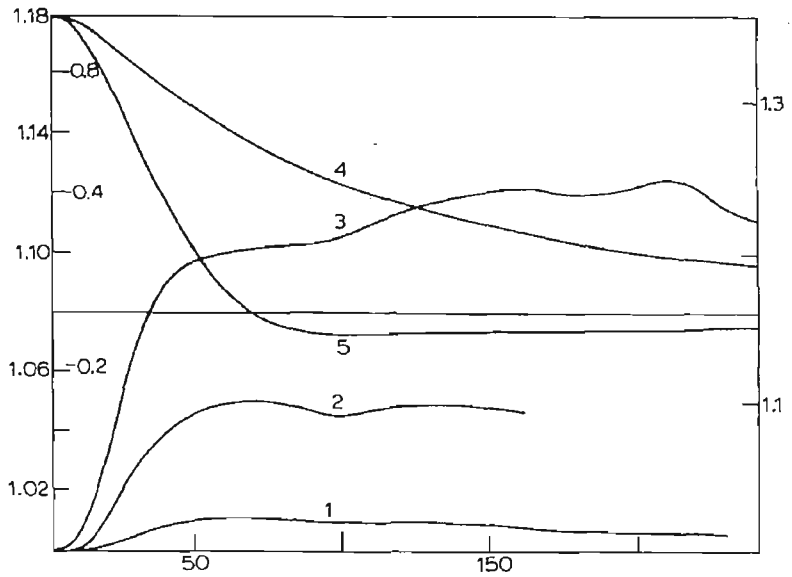

Fig.1. Molecular dynamics simulation of translation/rotation coupling for a diatomic molecule. (Interaction separation = 0.2 in reduced units V = centre of mass linear velocity, $\underset{\sim}{\omega}$ = angular velocity):

(1) $\left\langle |\underset{\sim}{v}(o)||\underset{\sim}{\omega}(t)| \right\rangle$; (2) $\left\langle V^2(o)\omega^2(t) \right\rangle$; (3) $\left\langle V^4(o)\omega^4(t) \right\rangle$ normalised to unity at t = o.

(4) Angular velocity autocorrelation function.

(5) Linear (centre of mass) velocity autocorrelation function.

Abscissa, time steps (of ca. 5 x 10^{-15} s).

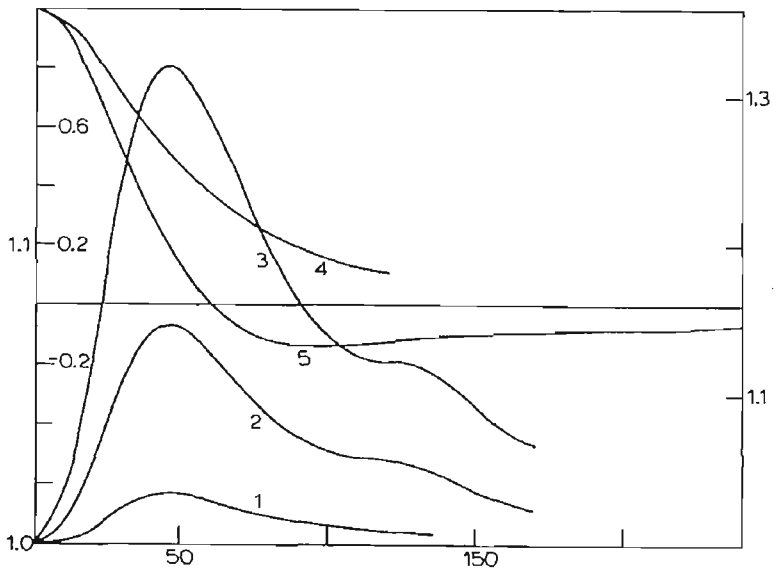

Fig.2. As for Fig. 1 , interatomic separation as for N_2.

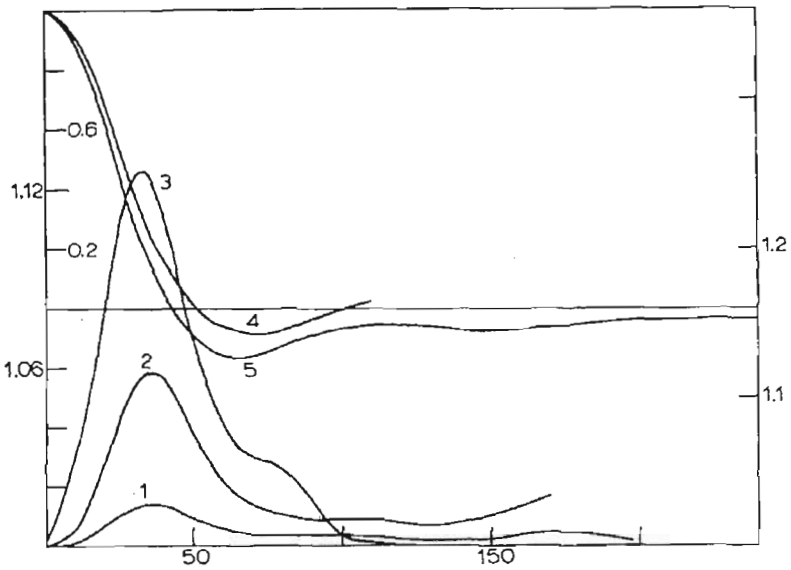

Fig.3. As for Fig. 1 , interatomic separation = 0.5.

DISCUSSION

The nature of the *rototranslational functions* changes dramatically with increasing shape anisotropy (Figs. 1-4). The peaks and troughs reflect the influence of collision and become more or less clearly defined for molecules respectively longer than or shorter than N_2. The simulation was carried out at a reduced density of 0.643, a reduced temperature of 2.32 and for reduced bond lenghts of L^* = 0.20, 0.33 (N_2) and 0.50. The shape varies therefore from almost spherical to pronouncedly dumbell. The ranges of interaction mean that periodically, it becomes increasingly probable that the correlation between angular and linear speed, and the equivalent kinetic energies, is sharply increased after the arbitrary initial t = o in the more elongated molecules. In the almost spherical case correlation rises to a plateau level and remains beyond the limit of our simulation time. This is related to the fact that the elemental functions

$\left\langle \underline{v}(t).\underline{v}(o) \right\rangle$ and $\left\langle \underline{\omega}(t).\underline{\omega}(o) \right\rangle$ are longer lived.

For the case L^* = 0.33 and L^* = 0.50 it is possible to compute the cosine Fourier transforms of the mixed autocorrelation functions thus giving us the associated power spectra in the frequency domain (ω). The power spectra of r/t speed and r/t energy are illustrated in Fig.(4). Both spectra are finite at ω = o and thereafter decay similarly to the usual behaviour of autocorrelation functions such as $\left\langle \underline{\omega}(t).\underline{\omega}(o) \right\rangle$ in the time domain. The negative regions in the mixed kinetic-energy power spectrum

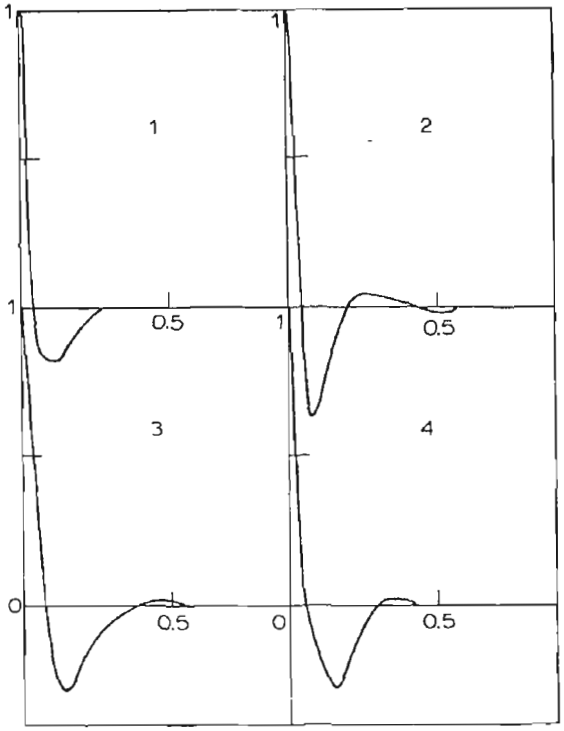

Fig. 4. Power spectra of the mixed autocorrelation functions:

(a) $$\int_0^\infty \left[\frac{\langle V^4(0)\omega^4(t)\rangle}{\langle V^4(0)\omega^4(0)\rangle} - 1 \right] \cos \omega t \, dt, \text{ for } N_2.$$

Abscissa = $10^{-12}\omega^*$ (in reduced units)

(b) $$\int_0^\infty \left[\frac{\langle |\underset{\sim}{V}(0)|\,|\underset{\sim}{\omega}(t)| \rangle}{\langle |\underset{\sim}{V}(0)|\,|\underset{\sim}{\omega}(0)| \rangle} \right] \cos \omega t \, dt \text{ for } N_2$$

(c) $$\int_0^\infty \left[\frac{V^4(0)\omega^4(t)}{V^4(0)\omega^4(0)} - 1 \right] \cos \omega t \, dt, \quad d^* = 0.5$$

(d) $$\int_0^\infty \left[\frac{\langle |\underset{\sim}{V}(0)|\,|\underset{\sim}{\omega}(t)| \rangle}{\langle |\underset{\sim}{V}(0)|\,|\underset{\sim}{\omega}(0)| \rangle} - 1 \right] \cos \omega t \, dt, \quad d^* = 0.5$$

come from the narrow half-width in time of the autocorrelation function peaks. They may be thought of physically as emission details rather than absorption, i.e. surges of rotation-translation time correlation rise to emission spectra in the frequency domain. Future simulations will probably be able to produce much more accurate r/t functions on the single molecule level, allowing a gradual extension of the methodology to mode-mode coupling on the many-particle levels coupling which produces spectral features discernible spectroscopically.

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