NUMERICAL SOLUTION FOR ITINERANT LIBRATION IN TWO DIMENSIONS

E. KESTEMONT, F. HERMANS
Université Libre de Bruxelles, Pool de Physique, 1050 Brussels, Belgium

R. FINSY, R. VAN LOON
Vrije Universiteit Brussel, Faculteit van de Wetenschappen, 1050 Brussels, Belgium

and

G.J. EVANS and M.W. EVANS
Department of Chemistry, University College of Wales, Aberystwyth SY23 1NE, UK

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The planar itinerant oscillator model of molecular motion in a structured fluid, developed recently by Coffey et al., is simulated by invoking collisions between 120 rough annuli within which are harmonically bound disks carrying a dipole unit vector u. It is found that the *stochastic* equations of motion of the analytical treatment produce results which can be reproduced very accurately with the deterministic equations of motion used in the computer simulation. This implies that the simulation may be extended to problems beyond analytical tractability, such as itinerant libration in three dimensions, and libration combined with centre of mass oscillation. The use of a model such as this is considered as intermediate between simple brownian-motion theory and a full scale simulation of polyatomics.

1. Introduction

The use of molecular dynamics simulation to check and extend the analytical techniques available for the description of molecular motions in fluids is an innovation of the last decade or so [1]. In this letter we use the technique to simulate the system of ring/annulus itinerant libration developed recently by Coffey for angular motion of the asymmetric top [2]. The purpose of this intercomparison is to ascertain to what precision the numerical solution of the equations of motion used in the computational method reproduces the initial *stochastic* differential equations of the analytical approach. Knowing this the simulation may be extended to fields beyond analytical tractability. The assumptions inherent in a model of molecular motion may be exactly satisfied by (for example) rough sphere simulations, and therefrom analytical and simulated autocorrelation functions may be compared. In this way, O'Dell and Berne [3] have demonstrated clearly the limits of applicability of the J-diffusion model for spherical tops.

Similarly, the itinerant librator model of molecular motion may be simulated by a two-dimensional molecular dynamics system consisting of rough rings within which are disks, bound harmonically [4]. Exchange of linear and angular momentum occurs when two rings collide. This may be compared with the system devised analytically by Coffey [2] where the annulus of moment of inertia I_1 is subjected to brownian motion with friction coefficient ζ. It is established in this letter that the analytical results varying ζ may be simulated very precisely with the computer, so that the latter may be used to extend the formalism to three dimensions [5], or to include, for example, the effects of rotation/translation coupling [6].

2. Computational details

We consider an assembly of 120 particles (i.e. disks/annuli) of total mass m, and diameter D. The motion of the annulus is perturbed by collisions, between which the centre of each particle moves along a straight line at constant velocity and total angular momentum. The rotational motion of the annulus and disk is governed by:

$$I_1\ddot{\theta}_1(t) = -\gamma[\theta_1(t) - \theta_2(t)] \,, \tag{1}$$

$$I_2\ddot{\theta}_2(t) = \gamma[\theta_1(t) - \theta_2(t)] \,. \tag{2}$$

Here I_1 and I_2 are the moments of inertia of the annulus and the disk; θ_1 and θ_2 specify the position of a point on the rim of the annulus and the position of the dipole on the disk. γ is the restoring torque constant between ring and disk. The dipole on the inner disk is supposed vanishingly small so that dipole–dipole coupling is neglected.

When a collision occurs, an energy transfer takes place between rotational and translational degrees of freedom, depending on the dimensionless quantity [7]:

$$\tau = 4I_1/mD^2 \,.$$

In this letter we seek to establish how closely τ may be used to simulate the frictional torque $\zeta\dot{\theta}_1(t)$ and $\lambda(t)$, the *random* couple of the brownian motion assumed analytically. In the molecular dynamics the change of linear and angular velocities at a collision between particles A and B are given by the following set of equations [4]:

$$\boldsymbol{\upsilon}'_A = \boldsymbol{\upsilon}_A + [\tau/(1+\tau)]\,[\boldsymbol{\upsilon} + (1/\tau)\boldsymbol{k}(\boldsymbol{k}\cdot\boldsymbol{\upsilon})] \,, \tag{3}$$

$$\boldsymbol{\upsilon}'_B = \boldsymbol{\upsilon}_B - [\tau/(1+\tau)]\,[\boldsymbol{\upsilon} + (1/\tau)\boldsymbol{k}(\boldsymbol{k}\cdot\boldsymbol{\upsilon})] \,, \tag{4}$$

$$\boldsymbol{\omega}'_A = \boldsymbol{\omega}_A - [2/(1+\tau)D]\,\boldsymbol{k}\times\boldsymbol{\upsilon} \,, \tag{5}$$

$$\boldsymbol{\omega}'_B = \boldsymbol{\omega}_B - [2/(1+\tau)D]\,\boldsymbol{k}\times\boldsymbol{\upsilon} \,. \tag{6}$$

Here $\boldsymbol{\upsilon}_A$ and $\boldsymbol{\upsilon}_B$ are the translational velocities and $\boldsymbol{\omega}_A$ and $\boldsymbol{\omega}_B$ are the angular velocities of the annulus, that of the inner disk being unaffected by the collision. The primed variables correspond to the situation just after the collision. $\boldsymbol{k}$ is the unit vector directed from the centre of the B particle to that of A at the time of collision. $\boldsymbol{\upsilon}$ is the relative velocity of the points in contact:

$$\boldsymbol{\upsilon} = \boldsymbol{\upsilon}_B - \boldsymbol{\upsilon}_A - \tfrac{1}{2}D\boldsymbol{k}\times(\boldsymbol{\omega}_A + \boldsymbol{\omega}_B) \,. \tag{7}$$

Initially the 120 particles are arranged in 12 rows of 10 at the nodes of a triangular lattice whose dimensions are chosen to obtain the desired density d expressed as the number of particles per unit surface. Periodic boundary conditions are used and initially the translational and angular velocities and the orientation of the two parts of each particle are randomly distributed. Reduced units of $I_1/kT = 1, D = 1, \alpha = \gamma/kT$ and $R = I_1/I_2$ are used.

After the system has reached equilibrium it is followed for up to 1024 time intervals of $\Delta t = 0.05(kT/I_1)^{-1/2}$. The two components of the unit vector parallel to the dipole, the two components of the derivative of this vector, the angular velocity of the disk and the torque on it are recorded for each particle for subsequent calculation of correlation functions.

3. Discussion

In figs. 1A–H we present some autocorrelation functions and response functions for the above system as a simulation of the fluid envisaged by planar itinerant libration. The analytical curves for least mean squares best fit behave similarly and are inseparable by eye for various values of ζ. This justifies the use of simulation in two dimensions and therefore future computation in three dimensions for itinerant libration or itinerant centre of mass oscillation may be contemplated. The analytical treatment thus far of three dimensional itinerant libration is so involved [5] as to be almost impractical, and this implies that the equivalent task for combined libration/oscillation, as in real fluids, would be even more so. These physical systems are of interest in being approximants of the Mori continued fraction expansion of the Liouville equation, so that a simulation of combined (roto-translational) properties would be helpful in the description of neutron inelastic scattering. Berne and Montgomery [6] have calculated the correlation function for coupled rotation/translation in a fluid of rough spheres in the Chandler binary collision approximation and in the small-step diffusion limit. The coupled autocorrelation functions:

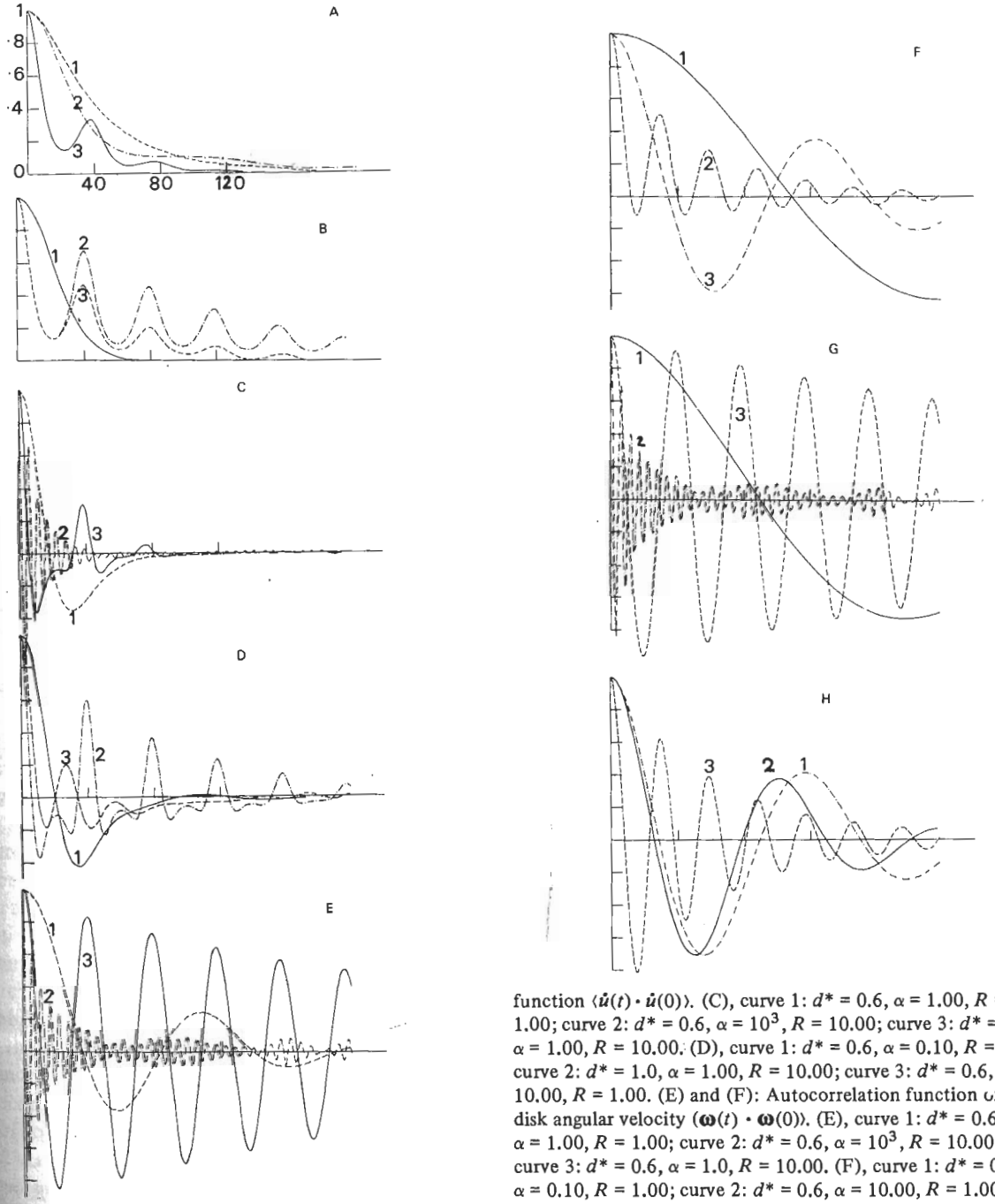

Fig. 1. (A) and (B): Autocorrelation functions of orientation of the disk dipole unit vector u. (A), curve 1: reduced density $(d^*) = 0.6$, $\alpha = 10^3$, $R = 10.00$, $\tau = 0.50$ in this and all following curves of the figure; curve 2: $d^* = 0.8$, $\alpha = 1.0$, $R = 1.00$; curve 3: $d^* = 0.6$, $\alpha = 1.0$, $R = 10.00$. (B), curve 1: $d^* = 0.6$, $\alpha = 0.1$, $R = 1.00$; curve 2: $d^* = 1.0$, $\alpha = 1.0$, $R = 10.00$; curve 3: $d^* = 0.8$, $\alpha = 1.0$, $R = 10.00$. (C) and (D): Autocorrelation function $\langle \dot{u}(t) \cdot \dot{u}(0) \rangle$. (C), curve 1: $d^* = 0.6$, $\alpha = 1.00$, $R = 1.00$; curve 2: $d^* = 0.6$, $\alpha = 10^3$, $R = 10.00$; curve 3: $d^* = 0.6$, $\alpha = 1.00$, $R = 10.00$. (D), curve 1: $d^* = 0.6$, $\alpha = 0.10$, $R = 1.00$; curve 2: $d^* = 1.0$, $\alpha = 1.00$, $R = 10.00$; curve 3: $d^* = 0.6$, $\alpha = 10.00$, $R = 1.00$. (E) and (F): Autocorrelation function of the disk angular velocity $\langle \boldsymbol{\omega}(t) \cdot \boldsymbol{\omega}(0) \rangle$. (E), curve 1: $d^* = 0.6$, $\alpha = 1.00$, $R = 1.00$; curve 2: $d^* = 0.6$, $\alpha = 10^3$, $R = 10.00$; curve 3: $d^* = 0.6$, $\alpha = 1.0$, $R = 10.00$. (F), curve 1: $d^* = 0.6$, $\alpha = 0.10$, $R = 1.00$; curve 2: $d^* = 0.6$, $\alpha = 10.00$, $R = 1.00$; curve 3: $d^* = 0.8$, $\alpha = 1.00$, $R = 1.00$. (G) and (H): Autocorrelation function of the disk torque $\langle \dot{\boldsymbol{\omega}}(t) \cdot \dot{\boldsymbol{\omega}}(0) \rangle$. (G), curve 1: $d^* = 0.6$, $\alpha = 0.10$, $R = 1.00$; curve 2: $d^* = 0.6$, $\alpha = 10^3$, $R = 10.00$; curve 3: $d^* = 0.6$, $\alpha = 1.0$, $R = 10.00$. (H), curve 1: $d^* = 0.8$, $\alpha = 1.0$, $R = 1.00$; curve 2: $d^* = 0.6$, $\alpha = 1.0$, $R = 1.00$; curve 3: $d^* = 0.6$, $\alpha = 10.00$, $R = 1.00$. Abscissa: time steps in reduced units.

$$C_l(\boldsymbol{q}, t) = \langle p_l(\boldsymbol{u}(t) \cdot \boldsymbol{u}(0)) \exp[i\boldsymbol{q} \cdot \Delta\boldsymbol{r}(t)] \rangle \qquad (8)$$

(in standard notation) were Fourier transformed and the resulting spectra compared with those calculated in the approximation:

$$C_l^{(u)}(\boldsymbol{q}, t) = \langle p_l(\boldsymbol{u}(t) \cdot \boldsymbol{u}(0)) \rangle \langle \exp[i\boldsymbol{q} \cdot \Delta\boldsymbol{r}(t)] \rangle , \qquad (9)$$

used almost universally in the theory of neutron scattering. It was found that the maximum deviation between $C_l(\boldsymbol{q}, t)$ and $C_l^{(u)}(\boldsymbol{q}, t)$ occurs for wavenumbers commonly found in thermal neutron scattering, and it was pointed out that the effect of the coupling would increase for structured molecules as opposed to rough spheres. It would therefore be useful to define the difference between eqs. (8) and (9) in the itinerant oscillator system, which applies to the motion in a plane of the asymmetric top dipole vectors encaged within a rigid cell of such molecules whose collective rotational motion sweeps out the annulus. The dynamical system is thus that of a structured fluid. Since we have shown in this letter that the itinerant librator system may be simulated very accurately, then future work will concentrate on combined libration/oscillation. It will also be possible to simulate probability density functions which are analytically almost intractable by classical methods [8], although less so with those of Davies et al. [9,10].

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