

THE TRANSLATIONAL MOTION OF MOLECULES AT SHORT TIMES: A STUDY USING MOLECULAR
DYNAMIC SIMULATIONS AND THE MODEL OF ITINERANT OSCILLATION

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ABSTRACT

A newly developed version of the itinerant oscillator model for molecular translation in fluids is evaluated by means of data obtained from a molecular dynamics simulation of the fluid using an atom-atom potential. The data consists of:

- (i) Velocity (\underline{v}) and force (\underline{F}) autocorrelation functions.
- (ii) Mean square displacements of molecular centres of mass and even moments thereof.
- (iii) Autocorrelation of v^{2n} and F^{2n} (as a means of investigating the deviation of \underline{v} and \underline{F} from Gaussian behaviour).
- (iv) The van Hove function $G_s(\underline{R}, t)$.

The latter is matched against incoherent neutron scattering data observed by Dasannacharya and Rao [13] for liquid argon. The theoretical picture is realistic except that the neglect of cross-correlations and rotation-translation coupling is clearly affecting the agreement between the simulated and calculated mean square displacements. The self van Hove function $G_s(\underline{R}, t)$ exhibits complicated non-Gaussian behaviour which will be difficult to follow using the theory of Brownian motion.

INTRODUCTION

In recent articles [1-6] a model of the dynamical behaviour of a molecule in a fluid has been developed from Frenkel's [7] idea of oscillation about a temporary equilibrium position in the laboratory frame. The essential feature of the model (termed 'itinerant oscillator') is that a molecule may undergo harmonic oscillation

in a potential well within a cage of its nearest neighbours. This cage is assumed to undergo Brownian motion [8], so that the central molecule diffuses throughout the fluid.

The equations governing the translational version of this model are tractable in three dimensions [6,9,10], whilst their rotational counterparts (for molecular libration) can be solved only for molecules that contain a dipole whose axis rotates in a plane [1-5]. In this case the cage may be represented by a rigid annulus concentric and coplanar with the disk traced out by the motion of the dipole. Lastly, the more general case of joint translational and rotational motion has yet to be investigated. The particular advantage of such a treatment over one based on the Brownian translation of a free particle is that the velocity autocorrelation function ($C_v(t)$) is no longer an exponential. It is now at least capable of becoming negative, in closer accord with the indications given by simulations of molecular [11] and atomic [12] motions in the fluid state, and also in plastic crystals. In this paper we shall concentrate exclusively in studying translational movements using molecular dynamics and incoherent neutron scattering data [13] to measure quantitatively the validity of Frenkel's original idea [7]. In addition, the more general postulate [14] that the probability distribution underlying the motion of a molecule in a fluid is Gaussian is investigated by computing the a.c.f. of force ($C_F(t)$) and those of moments of the force (i.e. of $Mv(t)$, where v is the velocity of the encaged molecule, and M its mass). This exercise is repeated for the particle velocity v .

The van Hove self correlation function ($G_s(\underline{R}, t)$, where $\dot{\underline{R}} = \underline{v}$), has been evaluated elsewhere [6] for the itinerant oscillator, and here we compare the theoretical value with experimental neutron scattering results obtained for liquid argon by Dasannacharya and Rao [13]. This comparison is made possible by the development of an analytical link between $G_s(\underline{R}, t)$ and $C_v(t)$, phenomenological parameters being optimised by a least mean squares fitting of the latter to Rahman's molecular dynamics simulation of liquid argon [12]. This serves as a check for consistency between experiment [13], simulation [12], and analytical theory [6]. Finally, by simulating the speed a.c.f. and that of or the direction of v , it is shown that a constant speed approximation is adequate for most fluids at short and long times [15].

Theoretical background

Since this is set out fully in another paper [6] we discuss only briefly the nature of the phenomenological quantities mentioned above. It is assumed that the cage of neighbours is essentially rigid and that its fluctuations in space may be represented by the translational Brownian motion of a mass m . The position of m

relative to the origin at time t is denoted by a coordinate $\underline{r}(t)$. The vibrating atom or molecule is represented by a second particle of mass M inside the cage at $\underline{R}(t)$. This particle is attracted towards the cage by a restoring force proportional to the difference $[\underline{R}(t) - \underline{r}(t)]$. Finally, in order to obtain the simplest possible presentation of the theory it is assumed that the frictional force (and by inference the stochastic force) acting on M may be ignored, so that the equations of motion of the dynamical system comprising m and M are

$$m\ddot{\underline{r}}(t) + m\beta\dot{\underline{r}}(t) - M\omega_0^2[\underline{R}(t) - \underline{r}(t)] = m\dot{\underline{W}}(t) \quad (1)$$

$$M\ddot{\underline{R}}(t) + M\omega_0^2[\underline{R}(t) - \underline{r}(t)] = 0 \quad (2)$$

Here $\underline{W}(t)$ is a Wiener process, $m\beta\dot{\underline{r}}(t)$ is the frictional force acting on m and arising from the surroundings, and $M\omega_0^2$ is the spring constant. The three quantities regarded as phenomenological are β , Ω_0^2 and ω_0^2 , where

$$\Omega_0^2 = (M/m)\omega_0^2 \quad (3)$$

This is not the first attempt to develop an analytical theory for translational itinerant oscillation. However, other treatises by Sears [9], and by Damle et al [10] compare disadvantageously since the former suffers from mathematical inconsistencies [10], and the latter is rather too flexible and heuristic in the sense that six adjustable parameters were employed, four of which are independent.

Table 1

Best Fit Parameters in Reduced (Dimensionless) Units

d^*	T^*	Number Density (p^*)	ω_0^{2*}	Ω_0^{2*}	β^*
0.200	2.00	0.80	62.1	172.1	24.7
0.329	2.00	0.80	102.1	175.3	18.8
0.400	2.00	0.80	133.5	182.9	16.8

Computation

The algorithm developed recently by Tildesley and Streett [16], and by Wegdam et al, [11] for the solution, using Newton's equations, of the motion of 256 interacting double Lennard-Jones potentials is used here to evaluate the following statistical quantities.

- (i) The velocity and force autocorrelation functions.
- (ii) The mean square displacement, $\langle [\underline{R}(t) - \underline{R}(0)]^2 \rangle$ of the encaged molecule.
- (iii) Autocorrelations of v^{2n} and F^{2n} to investigate the deviation from Gaussian distribution of velocity and force.
- (iv) Even moments of the mean square displacement, in order to investigate the non-Gaussian nature of $G_s(\underline{R}, t)$.
- (v) The a.c.f.'s of the modulus and direction of velocity, to investigate the nature of speed conservation in the dense fluids.

It was found that stability in the computed translational energy: rotational energy ratio was attained at high densities after about 800 time increments of 5×10^{-15} secs. These first steps were rejected and the next 400 used to calculate the statistical quantities of interest. An interatomic distance of d^* (in reduced units defined by Cheung and Powles [17], for example) of 0.3292 corresponds to the 'real' molecule N_2 . Here we have used $d^* = 0.2, 0.3292$ and 0.4 in order to investigate the effect of geometrical elongation on the molecular motions. No difference in the calculated a.c.f.'s could be discerned by comparing runs of 200 and 400 steps, their being so short-lived. For the more general calculation of cross-correlation and multi-particle c.f.'s, stability is not attained usually until 3000 or 4000 steps have been used and rejected. Using the two-centre potential builds in an anisotropic repulsion core, but the dispersive part is cut off at 3.2σ (where σ is the bond length) so that the whole of the potential is representative of both geometrical and electrostatic anisotropy. Naturally, here we are interested only in the centre of mass translation of the molecules. However, this is clearly affected to a greater or lesser extent depending on the facility with which the dumbell shaped molecules may rotate.

RESULTS

The computed a.c.f.'s of force, velocity (and of its modulus and direction) are shown in Fig. (1) with the least mean squares best fit of the analytical to the simulated $C_F(t)$. Here ω_0^2 , Ω_0^2 and β are optimised, and tabulated below. Rahman's velocity a.c.f. and power spectrum [12] are matched in Fig. (2), where is

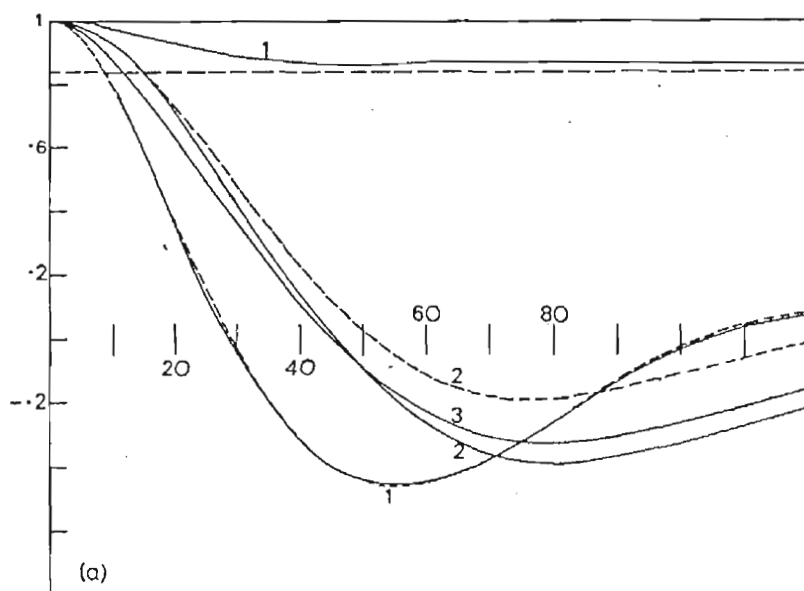
illustrated the $G_s(\underline{R}, t)$ function predicted therefrom. At constant temperature, ω_0^2 is proportional to the mean square force $\langle F^2 \rangle$ on the inner particle M, which may be computed independently. The latter is plotted in Fig.(3) against the former (found by least mean squares fitting), the two curves being normalised at $d^* = 0.3292$, so that the underlying trend is brought out more clearly. In Fig.(4) the computed mean square displacements are plotted against those calculated analytically from $C_F(t)$, and the non-Gaussian deviations in $G_s(\underline{R}, t)$ investigated by simulating the Rahman $a_n(t)$ functions (see below) for $n = 2, 3, 4$. In Fig.(5) the non-Gaussian nature of force and velocity is investigated using a.c.f.'s of their even powers. If the velocity were a Gaussian variate the following relations [15] hold

$$C_{2v}(t) = \frac{3}{5} \left[1 + \frac{2}{3} C_v^2(t) \right],$$

$$C_{4v}(t) = (225 + 600 C_v^2(t) + 120 C_v^4(t)) / 945$$

and so on.

Here, $C_{2v}(t)$, for example, is defined as $\langle v^2(t)v^2(0) \rangle / \langle v^4(0) \rangle$, the kinetic energy a.c.f. Both $C_{2v}(t)$ and $C_{4v}(t)$ were calculated using $C_F(t)$ for optimisation. They were also simulated independently using the atom-atom algorithm, and the two sets of functions are compared in Fig.(5), where is also shown the three a.c.f.'s. $\langle F^2(t)F^2(0) \rangle / \langle F^4(0) \rangle$, which ought to decay to a constant were the force a Gaussian variate.



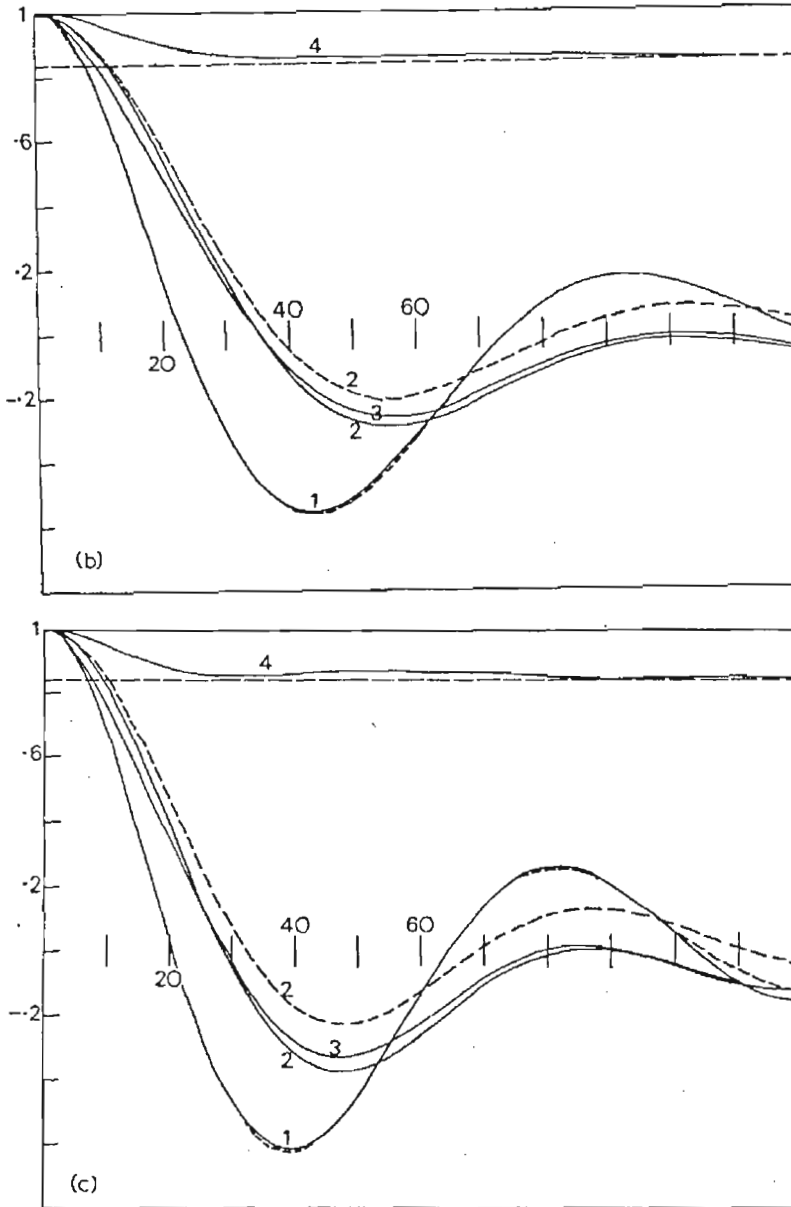


Fig. 1.

(a) — (1) Atom-atom simulation of the force a.c.f. $C_F(t)$ for a reduced interatomic separation $d^* = 0.20$, ($p^* = 0.8$, $T^* = 2.0$).

— (2) Simulated velocity a.c.f.

— (3) Simulated a.c.f. of the direction of velocity.

— (4) Simulated speed a.c.f., the horizontal line is $8/(3\pi)$.

- - - (1) l.m.s. best fit of the itinerant oscillator to the simulated $C_F(t)$.

- - - (2) $C_V(t)$ calculated from the optimised $C_F(t)$.

(b) $d^* = 0.3292$ (N_2).

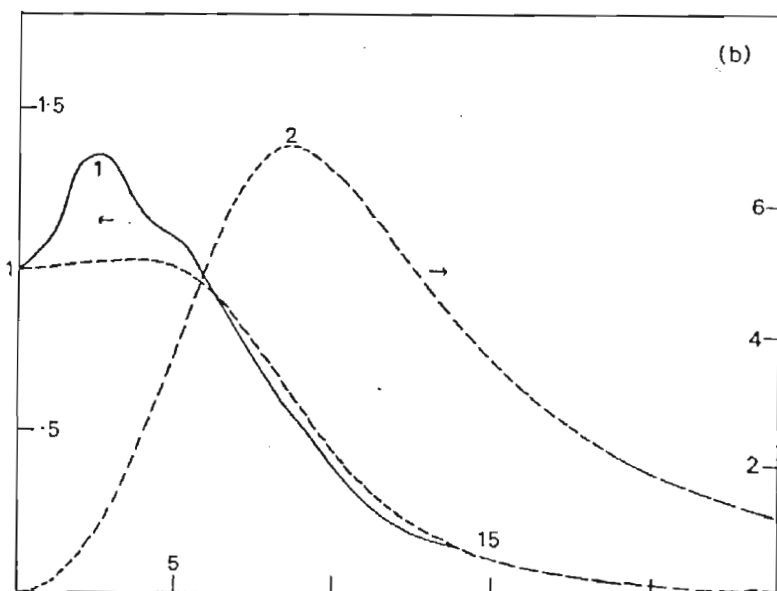
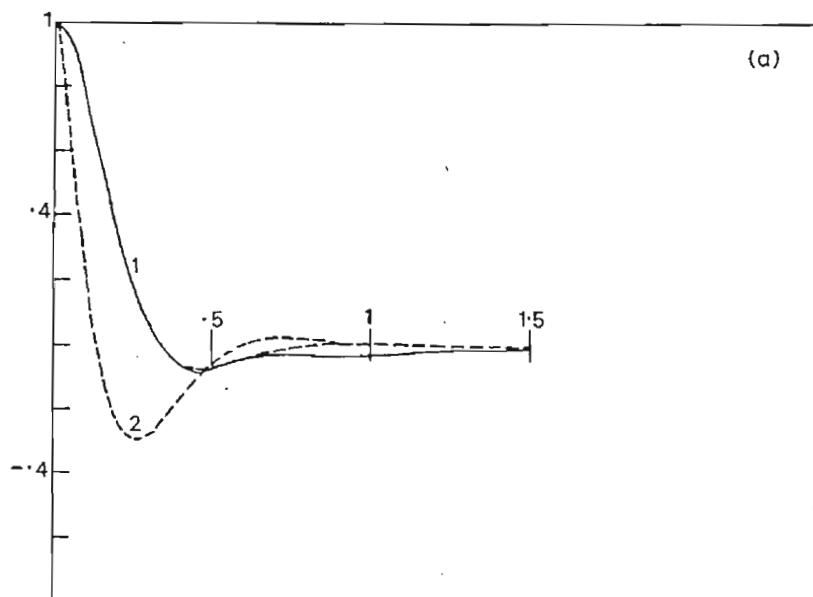
(c) $d^* = 0.40$.

Ordinate : $C(t)$; Abscissa: time steps of about 0.005 ps.

DISCUSSION

The classical theory of Brownian motion [8,14], where the centre of mass of a moving particle is assumed to be governed by Langevin's equation of 1906, namely, $\dot{\underline{v}}(t) + \tau^{-1}\underline{v}(t) = \dot{\underline{W}}(t)$, corresponds to: $C_v(t) = \exp(-t/\tau)$, where τ is a constant for the ensemble under consideration. Thus any negative parts in the observed or simulated $C_v(t)$ may not be reproduced.

The autocorrelation function, $C_v(t)$, of the itinerant oscillator is better behaved in that its series expansion in time contains odd terms only in t^5 and thereafter, but is still not ideal because a classical a.c.f. should retain the even terms



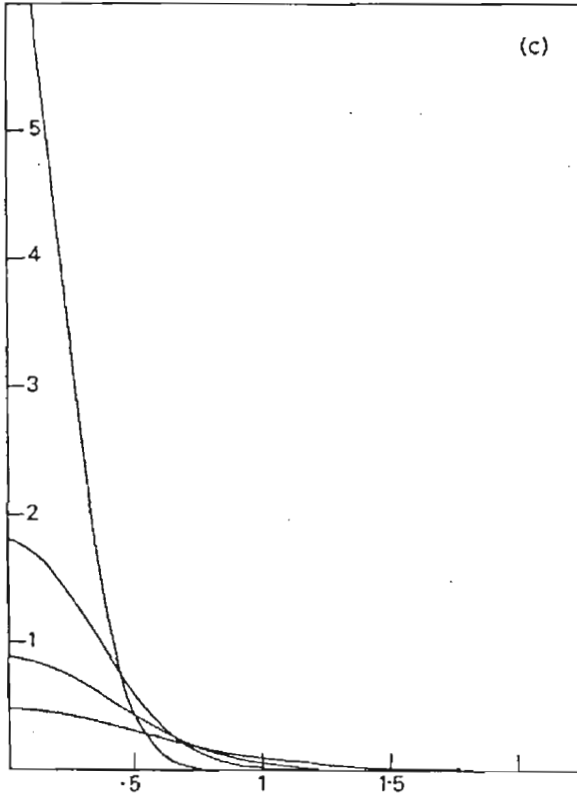


Fig. 2.

(a) ——— Rahman $C_V(t)$, simulated [12] for liquid argon.

- - - (1) Itinerant oscillator, best fit.

- - - (2) $C_F(t)$ estimated from the $C_V(t)$ best fit.

Ordinate: $C(t)$; Abscissa: time/ps.

(b) ——— Rahman simulated normalised velocity power spectrum.

- - - - (1) Velocity power spectrum calculated from the itinerant oscillator best fit to $C_V(t)$.

- - - (2) Itinerant oscillator normalised force spectrum.

Ordinate Intensity; Abscissa frequency/THz.

(c) Plot of $G_S(\underline{R}, t)$ calculated for the itinerant oscillator from fitting the Rahman $C_V(t)$ function.

Ordinate: $G_S(\underline{R}, t)/\underline{A}^{-3}$; Abscissa: $\underline{R}/\underline{A}$

only [15]. However, as Fig.(1) shows, negative regions in $C_F(t)$ and $C_V(t)$ are dealt with fairly satisfactorily, albeit that the $C_V(t)$ obtained analytically by fitting the simulated $C_F(t)$ is always slightly different from the simulated $C_V(t)$. Again, the characteristic long negative tail in the computed $C_V(t)$ of both Rahman and ourselves is not reproduced at all. This means that the low frequency peak in the

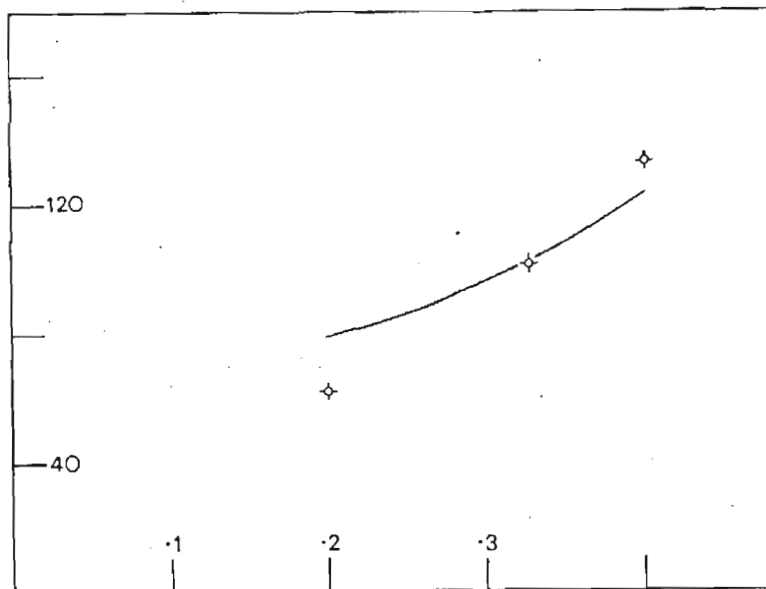
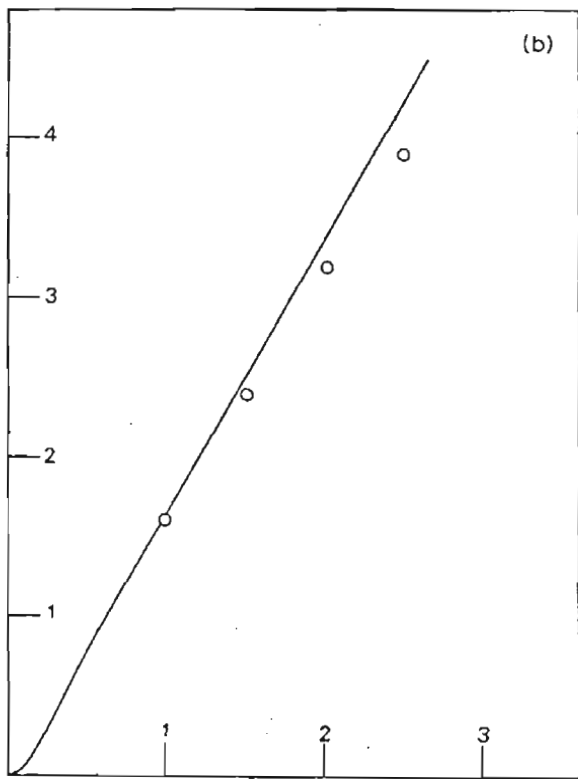
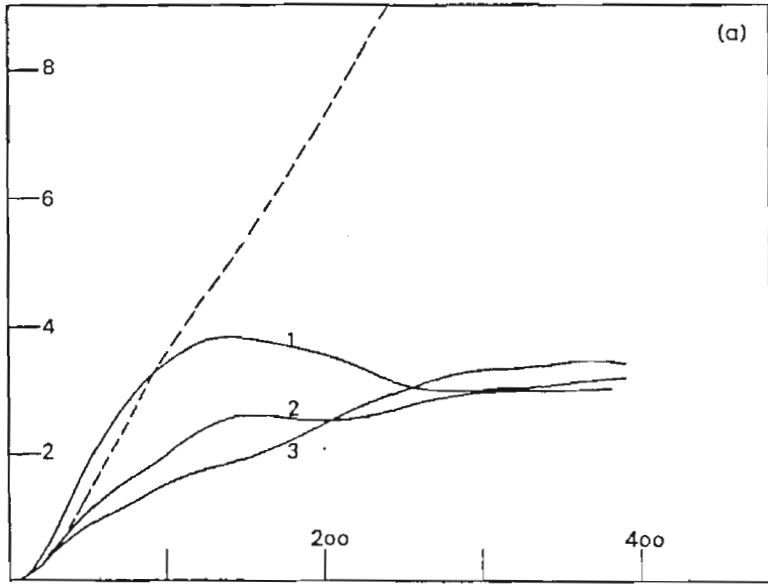


Fig. 3. Plot of $K_0(o)$ and $\langle F^2 \rangle^*$ vs d^*
 $\diamond \omega_o^2$; — $\langle F^2 \rangle$; normalised at $d^* = 0.3292$. Abscissa: d^* .

computer argon velocity power spectrum does not appear analytically. Damle et al., [10] have forced an agreement with this spectrum by optimising their six parameters. At present, therefore, there is doubt as to whether the peak arises from uncoupled translational motion of some kind, or whether cross-correlations (collective motions or shearing) are mainly responsible. Both our treatment, and that of Damle et al., neglect this part of the total velocity correlation function, but Madden and Kivelson [19] have shown recently that the equivalent multi- and single-particle a.c.f.'s of angular velocity decay roughly on the same time scale. Confinement to auto-correlation is inevitable in simple Brownian theory, which means that intermolecular dynamical coherence cannot be investigated without some estimate of $G_d(\underline{R}, t)$, the van Hove distinct function. This is the probability of finding a particle at $\underline{R}(t)$ given the location of another at the origin initially. It is observable in fluids by coherent neutron or light scattering experiments [20] and its long range part may be thought of as being due to macroscopic density fluctuations. Obviously, a major problem of liquid-state theory is its calculation using the trajectories of individual molecules or atoms.

It is difficult to separate $G_s(\underline{R}, t)$ and $G_d(\underline{R}, t)$, but by use of incoherent, inelastic neutron-scattering, Dassannacharya and Rao [13] have estimated the former for liquid argon at 84.5 K, and found it to be Gaussian within experimental uncert-



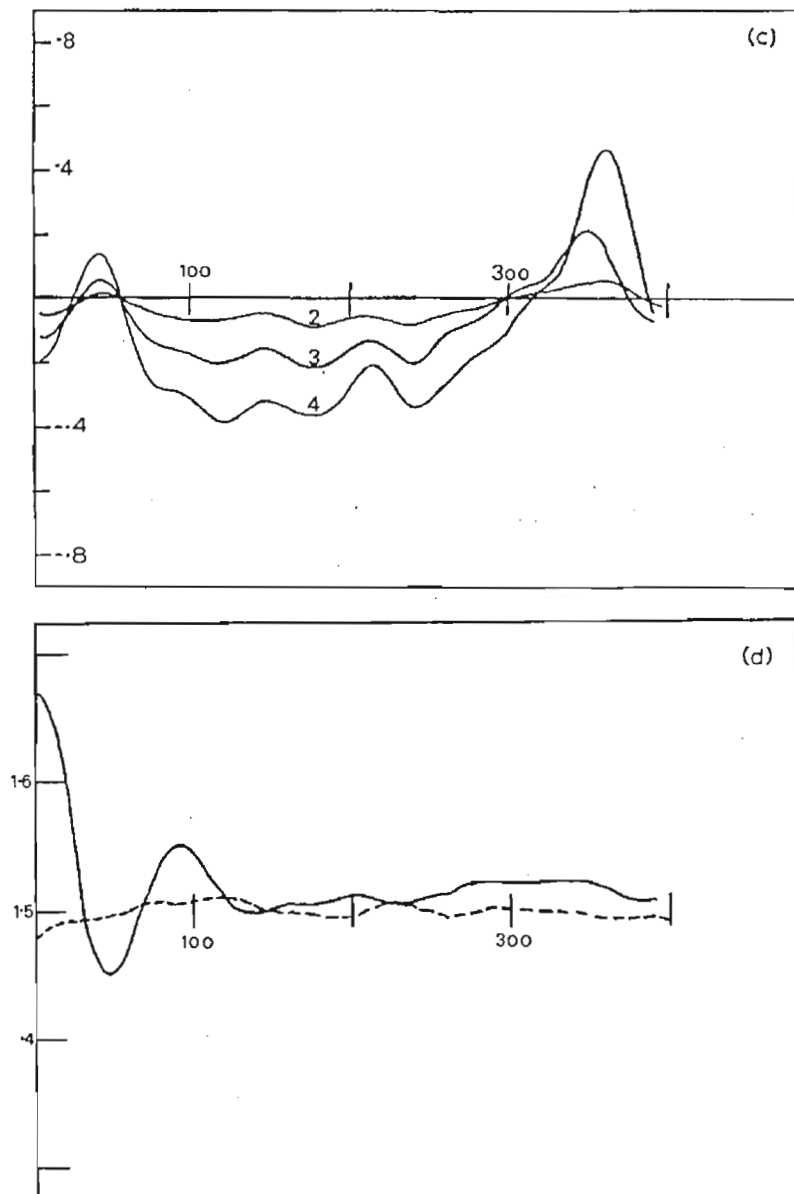


Fig. 4.

Mean square displacements

(a) — (1) $d^* = 0.20$

— (2) $d^* = 0.3292$

— (3) $d^* = 0.40$

- - - (3) i.o. mean square displacement calculated from the optimised $C_F(t)$.

Ordinate: $\langle R_1^2(t) \rangle^*$; Abscissa: time steps.

(b) Mean square displacements in liquid argon computed by Rahman.

— calculated from the itinerant oscillator fitting to Rahman's $C_V(t)$.

Ordinate: $\langle R_1^2(t) \rangle / \text{\AA}^2$; Abscissa: time/ps.

(c) Plot of $a_n(t)$ for $n = 2, 3, 4$, $d^* = 0.200$.

(d) Ratio of kinetic to rotational energy.

— after 800 steps.

- - - 200 - 600 steps.

Abscissae: Figs. 4(c) to 4(d), time steps.

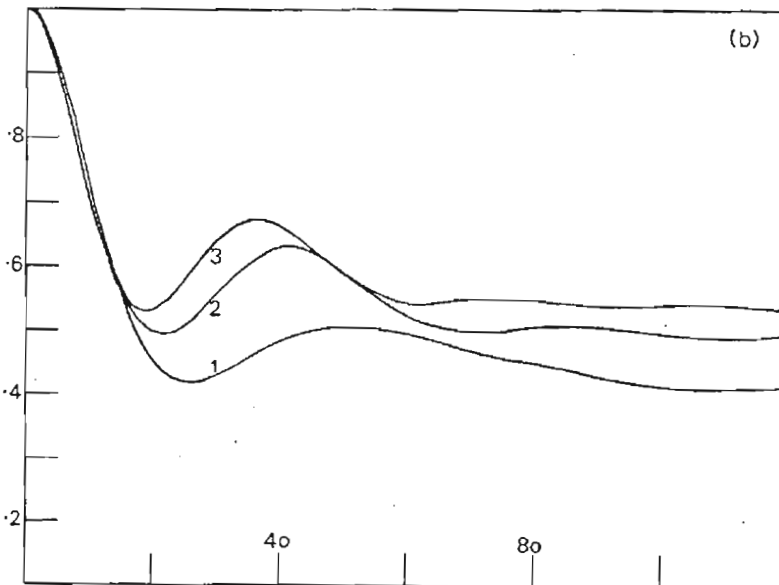
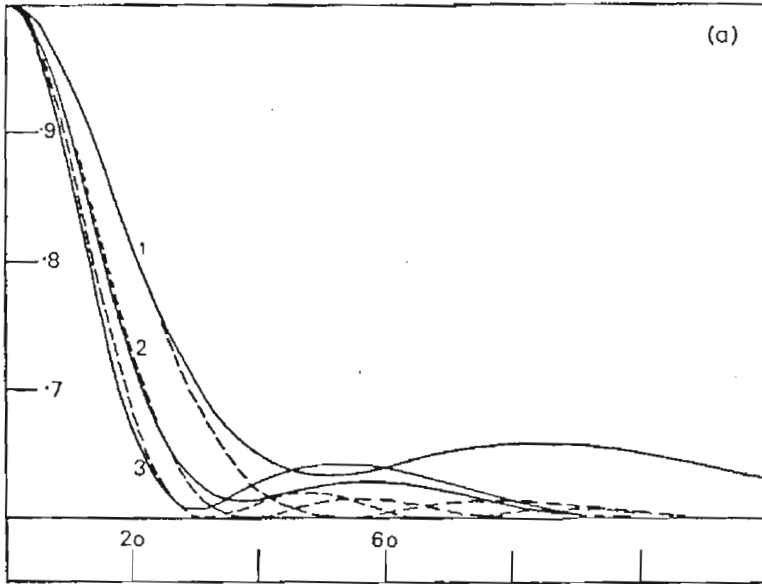


Fig. 5.

(a) — (1) Kinetic energy a.c.f., $d^* = 0.200$; atom/atom potential.

(2) $d^* = 0.3292$.

(3) $d^* = 0.400$

--- (1)

(2) As above, calculated by itinerant oscillation.

(b) $\langle F^2(t)F^2(0) \rangle / \langle F^4(0) \rangle$ Simulation only:

Ordinates: $C(t)$; Abscissae: time steps.

ainty. The Rahman simulation of $C_V(t)$ was carried out at 94.4 K; but the overall features of the experimental $G_S(\underline{R}, t)$ are reproduced fairly well by using ω_0^2 , Ω_0^2 and β estimated from Rahman's $C_V(t)$. (For details of the analytical link between $C_V(t)$ and $G_S(\underline{R}, t)$ the reader is referred to ref. [6]). For our dumbbell molecules, however, $G_S(\underline{R}, t)$ is distinctly non-Gaussian, as expressed by non-zero values of $a_n(t)$, defined by

$$a_n(t) = \frac{\langle [\underline{R}(t) - \underline{R}(0)]^{2n} \rangle}{\alpha_n \langle [\underline{R}(t) - \underline{R}(0)]^2 \rangle^n} - 1$$

where $\alpha_n = (2n + 1) \dots 5.3.1/3^n$.

The link with the van Hove function is [12]

$$\begin{aligned} \langle [\underline{R}(t) - \underline{R}(0)]^{2n} \rangle &= \int \underline{R}_1^{2n} G_S(\underline{R}_1, t) d\underline{R}_1 \\ &= \frac{1}{N} \sum_{i=1}^N [\underline{R}_i(t) - \underline{R}_i(0)]^{2n} \end{aligned}$$

in our simulation, where $N = 256$, and $\underline{R}_1 = \underline{R}(t) - \underline{R}(0)$. Berne and Harp, in their simulation [15] of CO with a modified Stockmayer potential, found $a_n(t)$ to be moderately sensitive to variations in N , becoming less significant as N was changed from 256 to 500 or thereabouts. Accordingly, it is expected that our simulation would over stress these deviations of $a_n(t)$ from zero to an unspecified extent. Further it is difficult to estimate the effect of our periodic boundary conditions on these functions. Berne has discussed [21] their effect on long tails in the auto-correlation of angular velocity. The complicated dependence of $a_n(t)$ ($n = 2, 3, 4$) upon time (stepped from an arbitrary $t = 0$ (Fig.4)) is not correlated with statistical noise in the ratio of rotational to kinetic energy, as is illustrated in Figs.4(e), (f) and (g). There seems little to be gained by attempting to follow these analytically with the techniques available at present except perhaps in the case of computer argon and other atomic fluids where the curves $a_n(t)$ are simpler in overall form. Work is continuing on the direct evaluation by molecular dynamics simulation of various p.d.f.'s, including $G_S(\underline{R}, t)$ and $G_D(\underline{R}, t)$.

The mean square displacement of argon atoms as simulated by Rahman is reproduced satisfactorily by a process of itinerant oscillation (Fig.4(b)), but Fig.4(a) shows clearly that the rate of diffusion calculated analytically for our more anisotropic molecules (packed at higher densities than Rahman's) is far too great. The calculated curve in Fig.4(a) is estimated, as usual, from the $C_F(t)$ fitting. Only at times close to the start are the simulated and analytical functions similar, there-

after the former flatten out and increase only slowly with a tendency to oscillate as in a clathrate solid. It seems, therefore, that an improved i.o. model should be capable of taking this high density behaviour in its stride, possibly by considering rotational constraints upon the centre of mass translation. These effects are discernible quite clearly in Fig.4(a) itself, since the simulations are all at the same reduced pressure and temperature, so that elongation of interatomic distance is the only variable. Fig.5(d) brings out the coupling through the fourth force-moment a.c.f., a function which for free translation falls at the time origin immediately to its long time limit. The fall-off is collision-free and thus the same for all elongations up to 10 time steps or so, but thereafter molecular interaction occurs and the three curves behave differently even though p^* and T^* are identical for each. In fact, throughout Fig.(5) the constant long time limits expected of Gaussian statistics are reached with difficulty (if at all) for both the second and fourth moment a.c.f.'s of velocity and force. There is little doubt, however, that this is due in part to statistical noise in the averaging (e.g. the simulated $C_{4v}(t)$ function for $d^* = 0.3292$ (fig.5(b)) falls below the theoretical limit of 0.2381), but in other instances these moment a.c.f.'s behave similarly to those computed by Berne and Harp for CO, in that a limiting value is approached at long times. The calculated moment a.c.f.'s are obtained, again, from fitting $C_F(t)$ and optimising ω_0^2 , Ω_0^2 and β , and follow the simulated functions at short times. Finally, it is clear that a.c.f.'s of molecular speed must be conserved fairly well in any system (decaying, as they do, to only $8/(3\pi)$ of their initial value), but even here Fig.1 shows up discernible effects of elongation on the translational motion, the decay being oscillatory and faster the longer the molecule.

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