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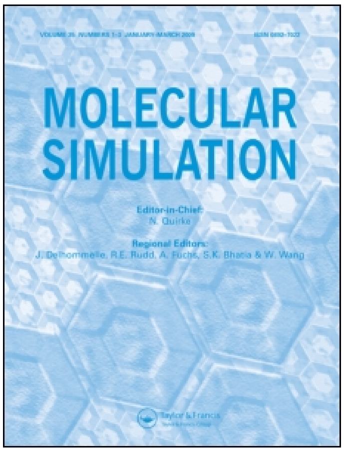

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ON THE ATOMIC VELOCITIES IN MOLECULAR AND LANGEVIN DYNAMICS SIMULATIONS OF SOFT-SPHERE SYSTEMS

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Time dependent probability distributions of the changes of direction of atomic velocities are considered in order to examine in detail the shape of the trajectories obtained through molecular simulations. We have analysed the atomic motions obtained from molecular dynamics simulations of soft-sphere systems at three very different states, i.e. a dilute fluid, a liquid at high density, and a solid. The methodology has also been used to check the reliability of the velocity evolution obtained when it is assumed that a single particle obeys the generalized Langevin equation and the effect of the other particles is represented by friction and random forces.

KEY WORDS: Molecular dynamics, Langevin dynamics, atomic trajectories, time-dependent properties, soft-spheres.

1. INTRODUCTION

Molecular dynamics is a computer simulation method ordinarily used for the calculation of classical trajectories of a set of a few hundred molecules representative of many-particle systems. Although Molecular Dynamics simulations provide detailed descriptions of the time evolutions of positions and velocities of individual particles, a great part of this information is removed when the microscopic configurations are averaged for the evaluation of correlation functions and macroscopic properties. These averages are generally performed in order to compare the Molecular Dynamics results with those obtained from theories or experiments. However, we think that more detailed analysis of the atomic motion should be undertaken [1, 2] because they may be very helpful for a deeper understanding of the behaviour of matter at a molecular level and for the development of theoretical approaches and microscopic models. Some studies along these lines have been reported recently. The individual trajectories in Lennard-Jones liquids were analysed in terms of their quasi-oscillations by Murthy and Singer [3, 4]. Lynden-Bell and coworkers [5] explained the cage effects in the translation velocities of molecular liquids by looking at the probability density of changes in direction of the velocity.

In this work, we analyse the changes in the direction of the atomic velocities as a function of time. In Section 2 we define the probability distributions used for these analyses and we discuss the results corresponding to the time evolution of particles in three representative soft-sphere systems. These probabilities are used in Section 3 for testing the reproduction of the motion of a tagged particle in a liquid when it is assumed that it obeys the Langevin or the generalized Langevin equations and the effects of the remaining particles are represented by friction and stochastic forces.

2. ANALYSIS OF THE CURVATURE OF THE ATOMIC TRAJECTORIES

A) Method

The quantity usually considered in the study of the time dependent properties of single particles is the velocity autocorrelation function

$$C(t) = \langle \mathbf{V}(t)\mathbf{V}(0)\rangle / \langle V0)^2\rangle \qquad (1)$$

However, this function only provides averaged information about the atomic motions. More detailed descriptions of the shape of the individual trajectories require the consideration of less averaged properties.

Following a method analogous to the one used by Lynden-Bell *et al.* [5] in their analysis of translational motions in molecular liquids, we have examined the time evolution of the angle θ formed by the velocity $\mathbf{V}(t)$ of a particle with an initial velocity $\mathbf{V}(0)$,

$$\theta(t) = cos^{-1}[\mathbf{U}(t)\cdot\mathbf{U}(0)] \qquad (2)$$

where $\mathbf{U}(t) = \mathbf{V}(t)/V(t)$. The probability, $W(\theta, t)\Delta\theta$, that θ is in the interval between θ and $\theta + \Delta\theta$ at time t has been evaluated by averaging over different particles and

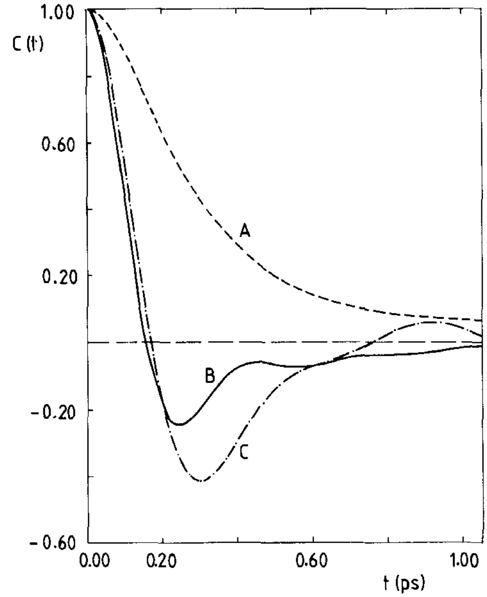

Figure 1 Velocity autocorrelation functions – – –state A ——state B –·–·–state C. Self-diffusion coefficients ($D = m^{-1}K_BT \int_0^\infty C(t)\,dt$) obtained from these C(t) functions: $D_A = 9.3 \times 10^{-9}$; $D_B = 4.1 \times 10^{-10}$; $D_C < 10^{-11}$ (D in m^2s^{-1})

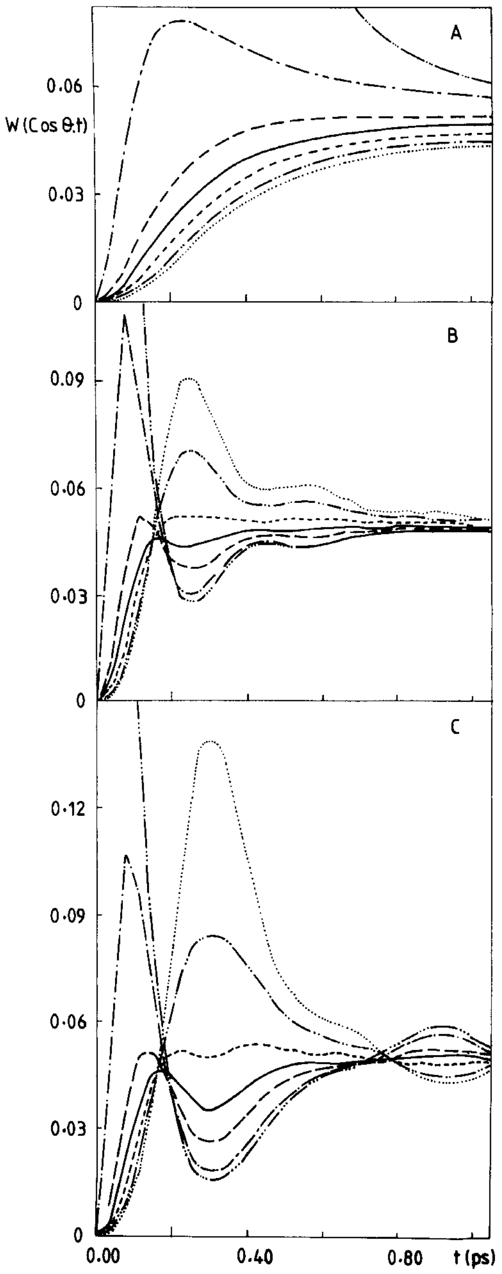

Figure 2 Time dependence of W(cosθ, t) at different values of cosθ: —··—cos$\theta = 1$, –·–·–cos$\theta = 0.7$, – – –cos$\theta = 0.3$, ———cos$\theta = 0$, - - - -cos$\theta = -0.3$, —·—cos$\theta = -0.7$, ·····cos$\theta = -1$

time origins. In this evaluation n_θ identical intervals $\Delta\theta$ between $\theta = 0$ and $\theta = \pi$ have been considered. Moreover we have also calculated the probability $W(cos\theta, t)\Delta cos\theta$ by assuming $n_{cos\theta}$ intervals between $+1$ and -1.

On the other hand we have also considered the time evolution of the plane of the trajectories. Firstly, we have evaluated the vectors $\mathbf{N}(t)$ perpendicular to the plane determined by the velocities of a particle at two consecutive time-steps

$$\mathbf{N}(t) = \mathbf{A}(t)/A(t), \quad \text{with } \mathbf{A}(t) = \mathbf{V}(t) \times \mathbf{V}(t + \Delta t) \tag{3}$$

We have determined the probabilities $W(\phi, t)\Delta\phi$ and $W(cos\phi, t)\Delta cos\phi$, where

$$\phi(t) = cos^{-1}[\mathbf{N}(t)\cdot\mathbf{N}()] \tag{4}$$

In this case, the probabilities are symmetric with respeet to $\phi = \pi/2$ and $cos\phi = 0$ and we have only considered n_ϕ equal intervals between $\phi = 0$ and $\phi = \pi/2$ and $n_{cos\phi}$ identical intervals between 0 and 1.

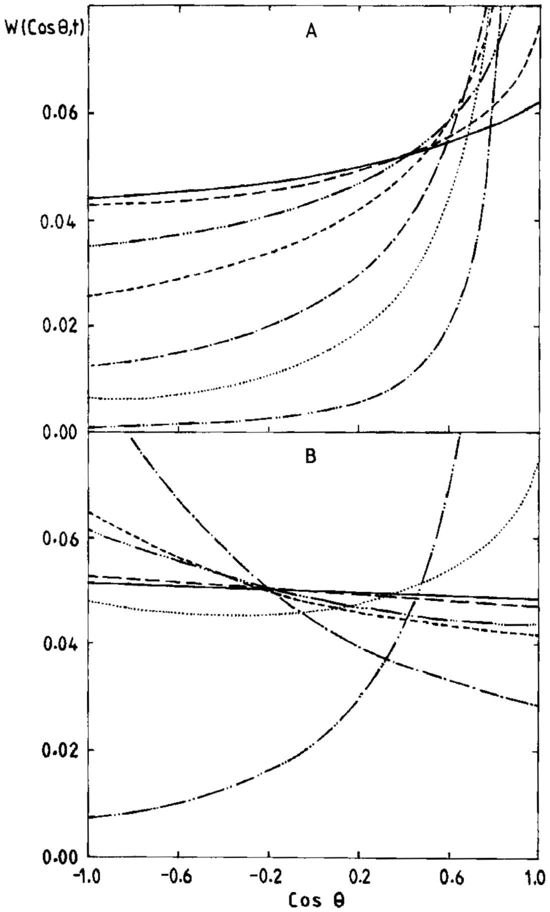

Figure 3 Probability distributions of $\cos\theta$ (states A, B) at different times: —··—t = 10τ, ·····t = 20 τ, —·—·—t = 30 τ, ----t = 50 τ, —··—t = 70 τ, ———t = 110 τ, ——t = 140 τ

B) Application

The probability distributions defined in the preceeding paragraphs have been evaluated from the configurations obtained in Molecular Dynamics simulations of soft-sphere systems at three different thermodynamic states, i.e. a dilute fluid (state A), a dense liquid (state B) and an F.C.C. crystal (state C). Details concerning the simulated systems and computational methods are summarized in the Appendix. The corresponding $C(t)$ functions and seld-diffusion coefficients are shown in Figure 1.

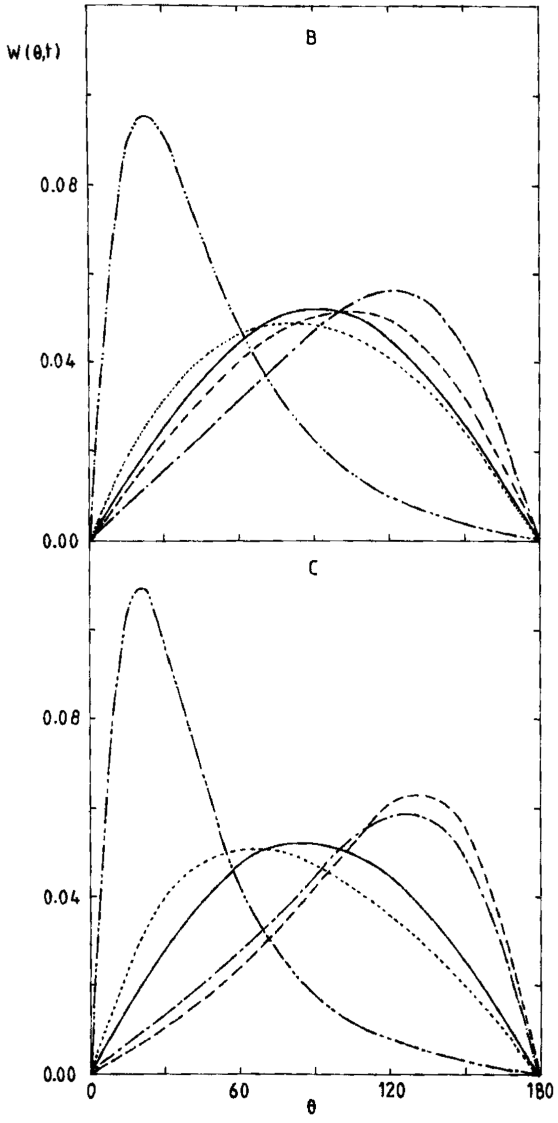

Figure 4 Probability distributions of θ (states B, C) at different times: —··—t = 10 τ, · · · ·t = 20 τ, —·—·—t = 30τ, – – –t = 50 τ, ——t = 140τ

While $C_A(t)$ shows a slow decay and does not take negative values, we can see significant minima (backscattering) in $C_B(t)$ and $C_C(t)$. This backscattering, which is deeper for the solid, is due to the cage effects induced by the collisions with the nearest neighbours (there are no attractive terms in the assumed potential). The more significant results obtained from the Molecular Dynamics simulations of the three systems considered are shown in the Figures 2–6.

We can see in Figures 2, 4 (B, C) that the characteristic solid-like behaviour of $C(t)$ functions of dense liquids is also shown by $W(\cos\theta, t)$ and $W(\theta, t)$ distributions. At the backscattering time-interval the probabilities for $\cos\theta < 0$ are bigger than those for $\cos\theta > 0$. Although these characteristics are shown by both the states B and C, they are more pronounced for the solid than for the liquid. Moreover, we can observe a long-time persistence of the correlations in the solid, with a second oscillation of $W(\cos\theta, t)$ corresponding to the $C_C(t)$ maximum.

Figures 2 and 3 (B, C) show that nearly equiprobable $\cos\theta$ distributions, (corresponding to $C(t) = 0$ values) are quickly reached ($t_B = 0.15$ ps, $t_C = 0.17$ ps). However, as has already been observed by Lynden-Bell *et al.* [5], the particles have been forgotten their original velocities and longer times ($t > 1$ ps) are required to obtain equiprobability distributions corresponding to uncorrelated velocities. For the dilute fluid (state A) the time evolution of $W(\cos\theta,t)$ toward the final equiprobability of $\cos\theta$ (Figures 2, 3; A) is slower and more orderly (there is no crossing among the curves). This behaviour is a result of the weaker interactions among particles in dilute systems.

With reference to the results of Figures 3 and 4, we emphasize the notorious differences between the $W(\cos\theta, t)$ and $W(\theta, t)$ distributions. It is due to the non-correspondence between the $\cos\theta$-intervals and the θ-intervals used for the evaluation of the probability distributions. For the present intervals, the $\cos\theta$-distribution for an

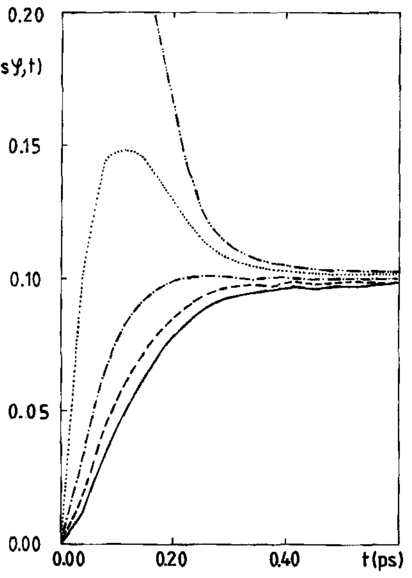

Figure 5 Time dependence of $W(\cos\phi, t)$ at the state B: —··—$\cos\phi = 1$, ·····$\cos\phi = 0.8$, —·—·—$\cos\phi = 0.6$, — — —$\cos\phi = 0.4$, ———$\cos\phi = 0$

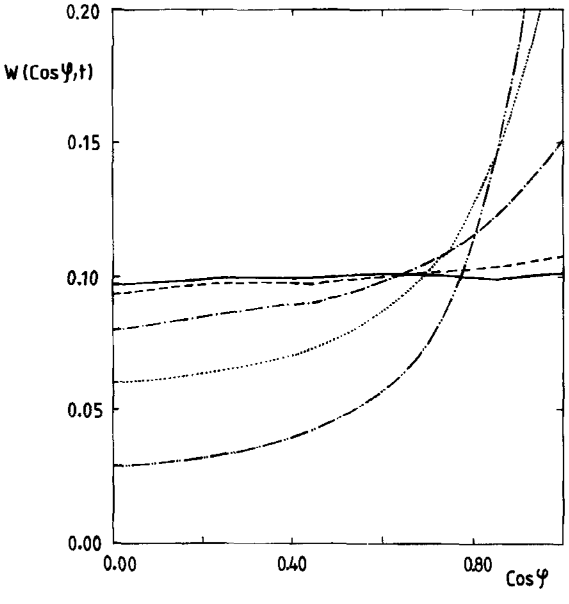

Figure 6 Probability distributions of $\cos\phi$ at the state **B**. —··—t = 10 τ, ·····t = 20 τ, –·–·–t = 30 τ, – – –t = 50 τ, ——t = 140 τ

isotropic distribution of directions must be constant but the corresponding θ-distribution must be a curve with a maximum at $\theta = \pi/2$. This behaviour is just that shown by the long time curves ($t = 140\tau$) in Figures 3 and 4.

Finally, we point out the orderly gas-like behaviour shown by the time evolution of the plane of the trajectories in the state B (Figures 5, 6). The weak interactions of atoms with the neighbours located perpendicularly to their direction of motion justifies the absence of noticeable cage effects for *cosθ* even at high densities. However, contrary to what happens with other distributions which do not show cage effects (e.g. *W*(*cosθ*, *t*) in dilute systems), the memory of the initial plane of the trajectory is rapidly lost. So we can observe that nearly equiprobable *cosθ* distributions are reached at shorter times ($t = 50\tau = 0.375$ ps) than those required in order that the corresponding C(t) function ($t > 1$ ps) vanishes. Analogous results have been found for *W*(*cosθ*, t) distributions in the states A and C.

3. TRAJECTORIES GOVERNED BY LANGEVIN EQUATIONS

Although Molecular Dynamics simulations of complex systems generally require very expensive computational resources, in many cases some species in the system are of primary interest and detailed information is not sought concerning the remainder. In such cases Brownian dynamics [6] or Langevin dynamics [7, 8] can be an interesting alternative to the conventional Molecular Dynamics technique. These stochastic methods are based in the determination of the time evolutions of the relevant particles of the system by using the ordinary [6, 7] or generalized Langevin [8] equations instead of the Newton equation and substituting the effects of the remaining particles by friction and random forces.

Recently, we have tested [7–10] the feasibility of reproducing by Langevin Dynamics or Generalised Langevin Dynamics methods the behaviour of a subsystem of "non-brownian" interacting particles, i.e. particles with similar masses and sizes to those considered implicitly. It has been shown that a satisfactory reproduction of the structure and time-dependent properties of the subsystem requires General Langevin Dynamics simulations using concentration-dependent effective potentials of mean force [9] and effective time-dependent memory functions [10].

In this work we have considered a subsystem comprizing a single particle. In this case, the projector-operator formalism leads to an exact generalized Langevin equation for the velocity components of the single particle (see for example [11])

$$m\dot{v}(t) = m\int_0^t M(t\text{-}t')\,v(t')\,\mathrm{d}t' + R(t) \tag{5}$$

where $R(t)$ is a random force related to the memory $M(t)$ through the fluctuation-dissipation theorem. Moreover, $M(t)$ is related to $C(t)$ according to the Volterra equation

$$\dot{c}(t) = -\int_0^t M(t\text{-}t')\,C(t)\,dt' \tag{6}$$

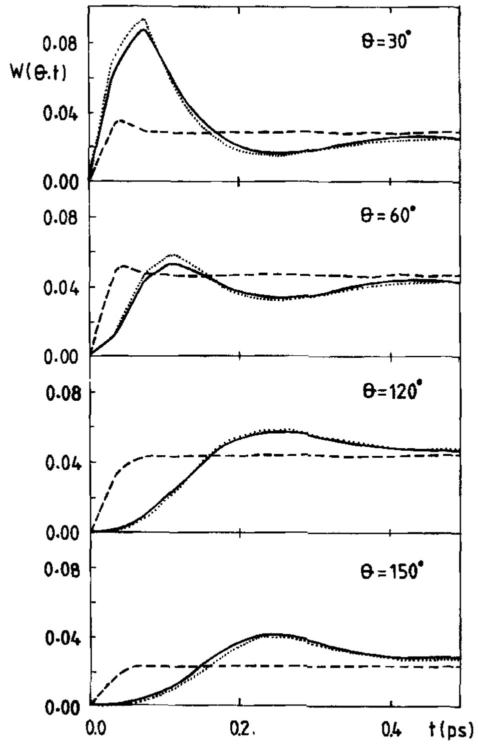

Figure 7 Time dependence of W(θ, t) probability distributions obtained from: LD– – –, GLD· · · ·, MD——— simulations

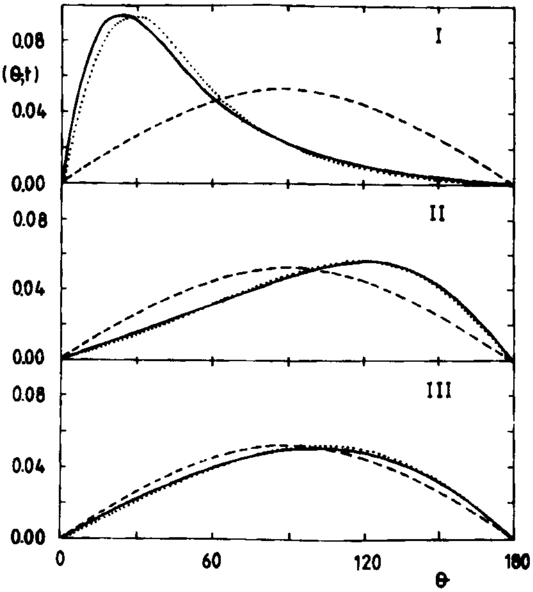

Figure 8 Probability distributions of θ at: $t = 10\tau$ (I); $t = 30\tau$ (II); $t = 50\tau$ (III) from LD — — —, GLD · · · · ·, MD——— simulations

For a given $C(t)$ the corresponding $M(t)$ function may be determined by numerical solution of the Volterra equation [12]. Using this memory function, we can simulate the time evolution of a single particle obeying equation (5) (Generalised Langevin Dynamics). Obviously, the similarity between the initial $C(t)$ and that calculated from the velocities of the particle obtained through numerical integration of the equation (5) is just a measure of the accuracy in the numerical procedure. But our interest now is focused on the ability of the Generalised Langevin Dynamics method to reproduce more detailed information about the atomic motions. That is why we have considered the probability distributions defined in the preceeding Section. We have checked the degree of resemblance between the results obtained from the Langevin equations and those obtained from the corresponding Molecular Dynamics simulations.

We have considered the same dense liquid (state B) already described in Section 2, being the single particle constituting the subsystem identical to the remainder. Now the properties calculated from the Molecular Dynamics simulation of the complete system are used as the "exact" results to be reproduced by Langevin Dynamics or Generalised Langevin Dynamics simulations of a single particle. Following the methodology described in the Appendix of [10] we have obtained the memory function corresponding to $C_B(t)$ by solving the Volterra equation and we have fitted this memory to two different models. Firstly we have assumed a delta function memory. In this case the discrepancies in the fitting are remarkable because $C_B(t)$ is not exponential (see Figure 1), and equation (5) is the usual Langevin equation (Langevin Dynamics simulation, B1). The second model, where non-white random forces are included, is based on a truncated Mori development of the Laplace transform $\tilde{M}_B(s)$ (Generalised Langevin Dynamics simulation, B2). A good reproduction of $M_B(t)$ (and therefore of $C_B(t)$) has required the use of a development including 25 Mori coefficients [10].

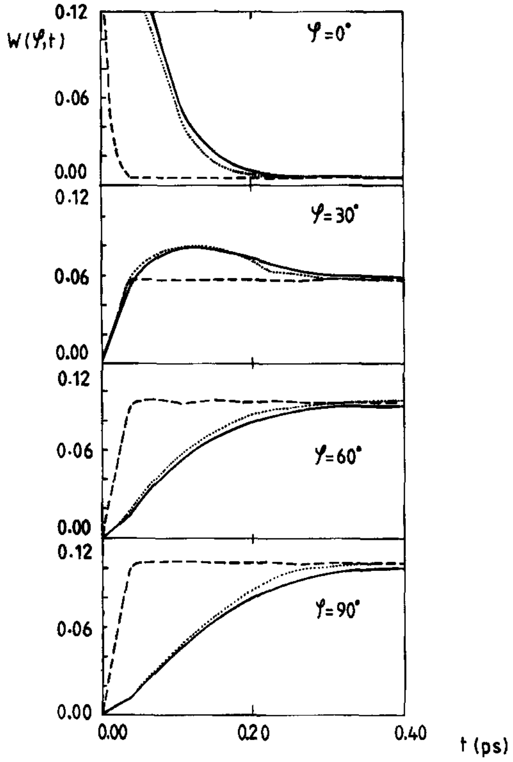

Figure 9 Time dependence of W(ϕ, t) probability distributions obtained from: LD— — —, GLD· · · ·, MD——— simulations

The probability distributions $W(\theta, t)$ and $W(\phi, t)$ obtained with both memory models are compared with the Molecular Dynamics models in the Figures 7, 8 and 9. We can see that the Langevin Dynamics results differ markedly from the Molecular Dynamics results. This is to be expected because the Langevin Dynamics method is only efficient for reproducing the long time behaviour of particles. On the other hand, the generalised Langevin Dynamics simulation, using a realistic memory, reproduces the more detailed properties studied in this work. We point out that these results are non-trivial because the information on the atomic motions at short time-scales (picosecond) is introduced in the Generalised Langevin Dynamics simulations only through the memory $M(t)$, which was deduced from the θ-averaged $C(t)$ function. The results shown in Figures 7–9 indicate that Generalised Langevin Dynamics may be considered as a reliable computer simulation method which allows us (when the suitable memory is used) a realistic reproduction of the main characteristics of the trajectories of a subset of representative particles of the considered system.

APPENDIX: COMPUTATION DETAILS

Mass of particles	$m = 6.625 \times 10^{-26}$ Kg(atomic mass of Ar)
interaction potential	short-range repulsive part of the

	Lennard-Jone (12-6) potential with $\sigma = 3.405\,\text{Å}$ and $\varepsilon = 119.8\,k_B$ (potential cutoff at 1.12σ)
temperature	$T = 115.6\,K$
density*	$\varrho = 2.7135 \times 10^{-2}\,A^{-3}$ (state A) $\varrho = 1.5075 \times 10^{-2}\,A^{-3}$ (states B and C)
number of particles	$N = 500$ (MD simulations) $N = 1$ (LD and GLD simulations)
integration time-step	$\tau = 7.5 \times 10^{-15}\,s$
number of equilibrium configurations	run A: 7.8×10^3: run B: 4.5×10^3 run C: 5×10^3: run Bl(LD): 1.8×10^6 run B2 (GLD): 1.3×10^6
integration algorithms**	MD: Beeman (velocities have been scaled to keep T = constant) LD: Allen [13] GLD: Guàrdia-Padró (modification of the algorithm proposed by Vesely [14] following the Beeman's scheme)
number of intervals	$n_\theta = 30$: $n_{cos\theta} = 20$ $n_\phi = 10$: $n_{cos\phi} = 10$

(*) Molecular Dynamics simulations of a dense liquid and a crystal with the same ρ and T have required the use of suitable initial configurations, i.e. a liquid configuration generated by succesive compressions of a slightly distorted f.c.c structure of low density (state B), and a slightly distorted f.c.c. structure of density ρ (state C). We have verified that throughout run C the crystal structure was preserved.

(**) More detailed discussions and references concerning the integration algorithms used in this work are given in references [7, 8].

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