Computer simulation study of relative diffusion in simple liquids

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Abstract. Relative motions of particle pairs in a dense Lennard Jones liquid are investigated by molecular dynamics (MD) calculations. The relative velocities are split into their components parallel and perpendicular to the line of particles and the corresponding time correlation functions are calculated. The dependence of these correlation functions on the interparticle separation is discussed. Furthermore, the trajectories of a subset of particles of the same system are determined by generalized Langevin dynamics (GLD) simulation. The reliability of the atomic motion generated by the GLD method is verified by comparing the parallel and perpendicular relative velocity correlation functions resulting from GLD with those from MD.

1. Introduction

A proper understanding of the dynamic behaviour of particle pairs in liquids is of fundamental interest for both the theoretical treatment of microscopic processes in liquids (e.g. transport properties, chemical kinetics, etc) and the correct interpretation of experimental measurements (e.g. light absorption or scattering, NMR, vibrational relaxation, viscosity, etc). Molecular dynamics (MD) simulation is the tool which is commonly used for the study of relative diffusion in fluids at short time scales [1–6], since this kind of information cannot be obtained easily from experiments. The influence of separation on the relative velocity correlation functions has been analysed in earlier MD studies, but little attention has been paid to the orientational dependence of these functions, i.e. to the differences between the correlation functions for the components of the relative velocities parallel and orthogonal to the interparticle direction. Since the interparticle forces act along the line joining the particle pairs, it may be expected that the changes in the components of the relative velocities along this line should be greater than in other directions. Differences between parallel and orthogonal relative diffusion are discussed in section 2.

Theoretical and computer simulation treatments of the relative diffusion in liquids are frequently based on stochastic models using the generalized Langevin equation (GLE). The GLE is very helpful because it allows us to omit explicit consideration of some of the particles of the system (solvent), the effects of which are taken into account by

means of random and frictional forces. However, the GLE has only been derived rigorously for a single solute particle, and approximate extensions must be used for systems of interacting particles [7–11].

Generalized Langevin dynamics (GLD) is an economic method of computer simulation [12, 13], an alternative to MD, which is very useful for the study of complex systems or problems requiring very long simulations. In GLD, it is assumed that the solute particles obey a system of coupled GLEs which are numerically integrated. One of the difficulties in the use of this method is that suitable effective potentials $(W_{eff}(r))$ [14] and memories $(M_{eff}(t))$ [13, 15], which are dependent on the thermodynamic state of the system (density, temperature, concentration), should be used to obtain realistic trajectories of the solute atoms. Moreover, as the solvent effects on a given solute particle can be affected by the presence of other nearby solute particles, $W_{eff}(r)$ and $M_{eff}(t)$ would also be configuration dependent. Nevertheless, pair additive potentials and isotropic memory functions independent of the relative separations are commonly used in GLD simulations. The aim of section 3 is to discuss the reliability of the relative motions resulting from GLD simulations.

2. Relative velocity correlation functions in liquids

2.1. MD simulations

We simulated the trajectories of the atoms in liquid Kr at $T = 134.3\,\text{K}$ and $\rho = 1.7956 \times 10^{-2}\,\text{atoms/Å}^3$ ($T^* = 0.805$ and $\rho^* = 0.861$, in reduced units). MD simulations were carried out on a set of $N = 530$ particles in a cubic box with periodic boundary conditions. The interaction potential was a Lennard-Jones potential with a cutoff at 2.4σ. The Beeman algorithm with a time step of $10^{-2}\,\text{ps}$ was used for the numerical integration of the classical equations of motion. The radial distribution functions $g(r)$, the velocity autocorrelation functions of single particles $C(t)$ and the relative pair velocity autocorrelation functions $C_r(t)$ for the neighbouring particles ($\sigma \leqslant r \leqslant 2\sigma$) were determined from the configurations generated.

In order to analyse the orientational dependence of the relative velocity correlation functions we decomposed the relative velocities into components parallel and orthogonal to the line joining the particle pairs (Tildesley and Madden [16] used a similar procedure for the study of diffusion in molecular liquids). In addition to the orientational dependence of the relative diffusion, we analysed its spatial dependence by computing the time correlation functions restricted to different initial interparticle separations [3]. We proceeded as follows. We divided the radial region around each particle at time $t = 0$ into 10 zones of equal width, $\Delta r = 0.1\,\sigma$, and the relative pair velocity autocorrelation functions, restricted to pairs of particles within every zone ($i = 1, \ldots, 10$), were determined

$$C_r(t; i) = \frac{\langle V_{\alpha\beta}(t) \cdot V_{\alpha\beta}(0); i\rangle}{\langle V_{\alpha\beta}(0)^2; i\rangle} \qquad (\alpha, \beta = 1, \ldots, N) \qquad (2.1)$$

where $V_{\alpha\beta}(t) = v_\alpha(t) - v_\beta(t)$ and the statistical averages are restricted to particle pairs within the ith zone. Moreover, the relative velocities of each pair of particles were resolved into two components, one along the interparticle vector and the other orthogonal to it. Projections were performed onto the initial interparticle vector $r_{\alpha\beta}(0)$ since the relaxation times of the velocities in dense liquids are short compared with the time
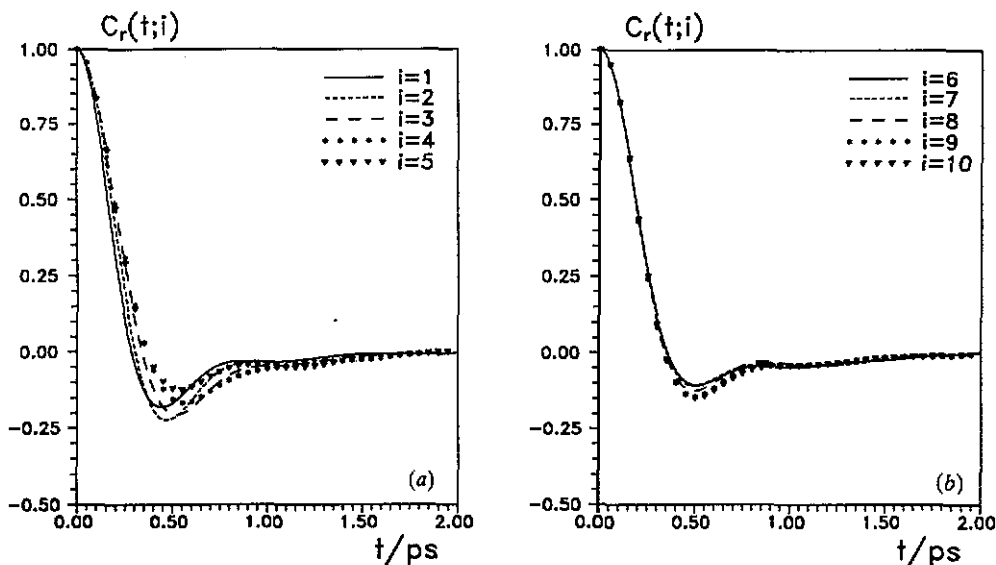
Figure 1. The normalized relative pair velocity autocorrelation functions for the different initial interparticle separations: (*a*) zones 1 to 5; (*b*) zones 6 to 10.

that it takes for the relative position of particles to change considerably. We calculated the restricted time correlation functions for the parallel $(C_r^p(t; i))$ and orthogonal $(C_r^o(t; i))$ components of the relative velocities

$$C_r^p(t; i) = \frac{\langle V_{\alpha\beta}^p(t) V_{\alpha\beta}^p(0); i \rangle}{\langle V_{\alpha\beta}^p(0)^2; i \rangle} \tag{2.2}$$

$$C_r^o(t; i) = \frac{\langle V_{\alpha\beta}^o(t) \cdot V_{\alpha\beta}^o(0); i \rangle}{\langle V_{\alpha\beta}^o(0)^2; i \rangle} \tag{2.3}$$

where $V_{\alpha\beta}^p(t) = V_{\alpha\beta}(t) \cdot u_{\alpha\beta}(0)$, $V_{\alpha\beta}^o(t) = V_{\alpha\beta}(t) \times u_{\alpha\beta}(0)$ and $u_{\alpha\beta}(0)$ is a unitary vector along the initial interparticle separation, $u_{\alpha\beta}(0) = r_{\alpha\beta}(0)/r_{\alpha\beta}(0)$. The mean correlation functions for the relative velocities $(C_r(t))$ and for their parallel $(C_r^p(t))$ and orthogonal $(C_r^o(t))$ components were determined by averaging the functions corresponding to the different zones.

2.2. Results and discussion

The $C_r(t; i)$ functions resulting from the MD simulations are shown in figure 1. We can see that there is a dependence of $C_r(t; i)$ on the initial separation which is greater when the particles are closer. From $i = 1$ to $i = 5$, the $C_r(t; i)$ minima become shallower (except for $i = 1$ and 2) and their positions are shifted towards higher values of t. It should be noted that these zones correspond to pairs made up of a given particle and its neighbours in the first coordination shell. For the last zones ($i = 5$ to $i = 10$), when the initial separation increases, the minima are slightly deeper but their positions are not significantly shifted. Our results are in agreement with those found by Posch *et al* [3] for a
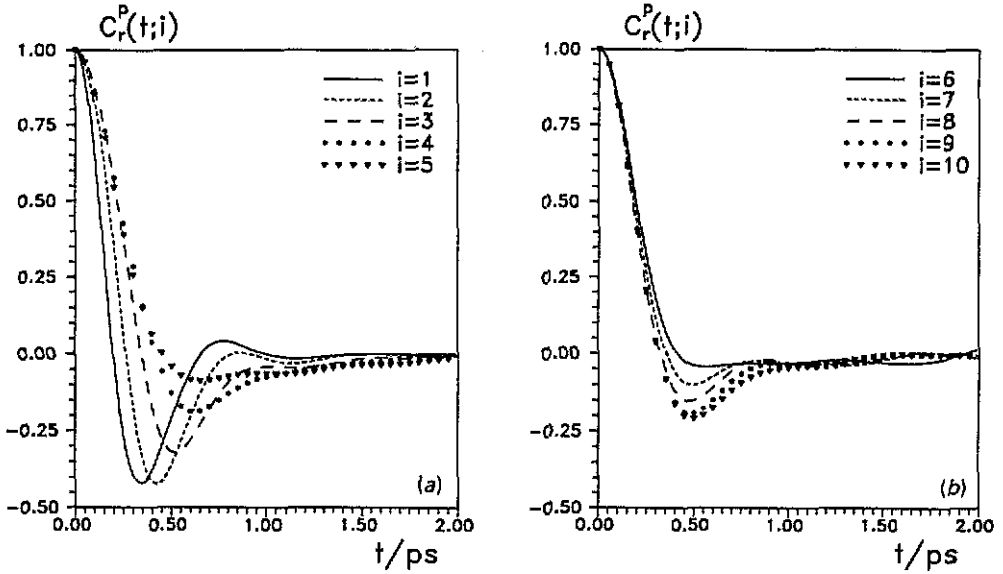
Figure 2. The same as figure 1, but for the components of the relative velocities parallel to the initial interparticle directions.

liquid of similar characteristics. Nevertheless, the changes of $C_r(t; i)$ with i are rather small and the existence of a minimum for $i = 2$ which is deeper than for $i = 1$ cannot be interpreted easily. These results suggested the convenience of considering properties which could provide more detailed and suitable descriptions of the relative motions. For this reason, we computed $C_r^p(t; i)$ and $C_r^o(t; i)$.

As may be observed in figures 2 and 3, there is a marked dependence of the $C_r^p(t; i)$ functions on the initial separation even for the last zones. In contrast, small differences may be observed among the $C_r^o(t; i)$ functions. Moreover, $C_r^o(t; i)$ are very close to the functions averaged over the different zones (figure 4). These results corroborate the suitability of our decomposition of the relative velocities.

The evolution of $C_r^p(t; i)$ with the initial separation is consistent with the changes of mean force between the particles. This force is obtained as the gradient of the mean force potential (figure 5) defined from $g(r)$ by the expression

$$W(r) = -k_B T \log[g(r)]. \tag{2.4}$$

The depth of the minima increases with the mean force, i.e. the backscattering is very sharp for $i = 1$ and 2, decreases from $i = 2$ to 6 and increases from $i = 6$ to 10. As for $C_r(t; i)$, the positions of the minima only are shifted for pairs within the first zones. For these pairs, the minima of $C_r^p(t; i)$ are largely determined by the collisions between the particles of the pair considered and, therefore, they are reached at shorter times when the particles are closer. For the pairs corresponding to the last zones, the influence of the separation on the position of the minima is negligible and they are located at the same position as the minima of the averaged functions represented in figure 4. This result confirms that the backscattering for particles in the second shell cannot be associated with the interactions between the particle belonging to the pair. It should be pointed out that, consistently with the $W(r)$ shape, the depth of the $C_r^p(t; i)$ minima for $i = 1$ and
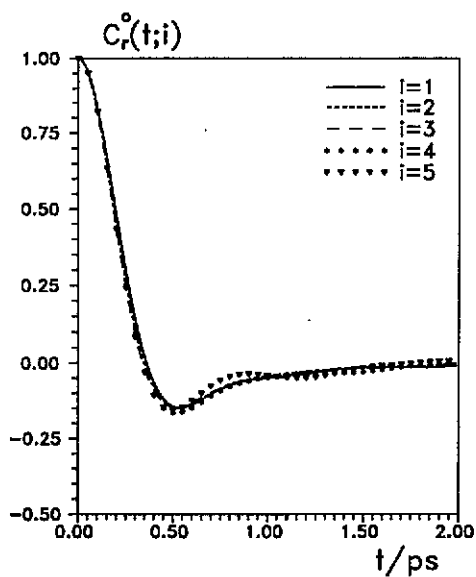
Figure 3. The same as figure 2(a), but for the orthogonal components of the relative velocities.
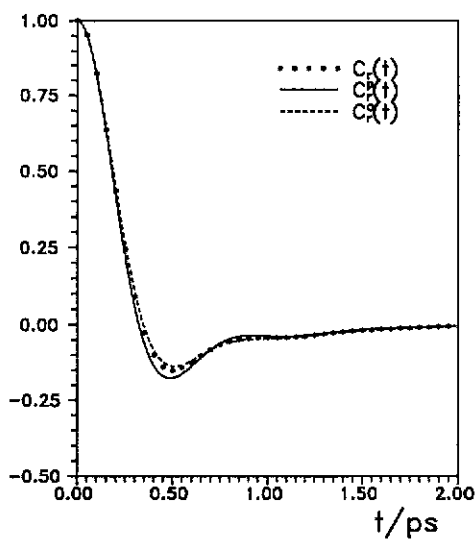

Figure 4. The normalized mean autocorrelation functions for the relative velocities $(C_r(t))$ and for their parallel $(C_r^p(t))$ and orthogonal $(C_r^o(t))$ components.
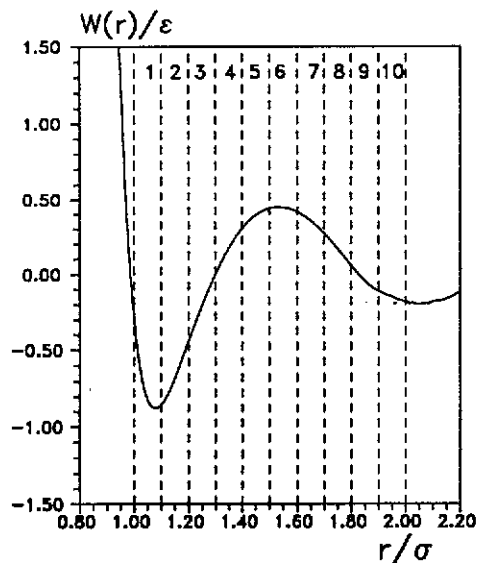

Figure 5. The mean force potential, equation (2.4). The separation intervals corresponding to the different zones ($i = 1$ to $i = 10$) are indicated.

$i = 2$ are similar. This shows that the $C_r(t; i)$ findings for $i = 1$ and 2 are the result of the combination of two functions ($(C_r^p(t; i)$ and $C_r^o(t; i))$ with their minima located at different positions.

3. Relative motions in GLD simulations

3.1. GLE for systems of interacting particles

As indicated in section 1, there is no rigorous deduction of a simple GLE for a system of interacting particles but different reasonable approximations have been proposed. Vesely and Posch [10] derived a GLE for two interacting particles which includes the cross memory terms and the intersolute forces. However, this formulation cannot easily be generalized to systems of N particles. An alternative treatment, frequently applied to the study of relative diffusion [3, 6] and chemical kinetics [17], is founded on the assumption that the time evolution of the relative position of two particles (or any other reaction coordinate) obeys a GLE, which incorporates an external force derived from a mean force potential. It should be pointed out that this GLE may be derived only when it is assumed that the coordinate is linearly coupled to a bath of harmonic oscillators. Moreover, this GLE is only useful for the study of specific problems directly related with the relative dynamics of particle pairs.

One of the simplest methods of extending the GLE to a system of N interacting particles is to assume that the effects of the intersolute forces are accounted for by merely adding an extra term to the GLE for a single particle [9, 11]. Then, each solute particle moves according to a system of coupled GLEs

$$\dot{r}_{\alpha\mu}(t) = v_{\alpha\mu}(t)$$

$$m_\alpha \dot{v}_{\alpha\mu}(t) = -\int_0^t m_\alpha M_\alpha(t - t')v_{\alpha\mu}(t')\,\mathrm{d}t' + R_{\alpha\mu}(t) + F_{\alpha\mu}(r_{\alpha\beta}(t)) \tag{3.1}$$

$$\alpha, \beta = 1, \ldots, N \qquad \text{and} \qquad \mu = 1, 2, 3$$

where the index μ refers to the three Cartesian coordinates. The frictional force is written as a convolution in time of the velocity with the memory function $(M_\alpha(t))$. The force on the α particle due to its interaction with the remaining β particles $(F_{\alpha\mu}(r_{\alpha\beta}(t)))$ should be derived from a solvent averaged potential. Furthermore, it is also commonly assumed that the random forces $R_{\alpha\mu}(t)$ are related to $M_\alpha(t)$ through the fluctuation-dissipation theorem [9]

$$\langle R_{\alpha\mu}(t)R_{\beta\nu}(0)\rangle = \delta_{\alpha\beta}\delta_{\mu\nu}k_{\mathrm{B}}Tm_\alpha M_\alpha(t) \tag{3.2}$$

where k_{B} is the Boltzmann constant and T the temperature. It should be emphasized that equations (3.1) and (3.2) do not come from any careful derivation from the Liouville equation, but are assumed as a reasonable hypothesis.

3.2. GLD simulations

Generalized Langevin dynamics (GLD) is a computer simulation method [13] based on the hypothesis that a set of interacting particles in solution obey equations (3.1) and (3.2), i.e. the classical Newtonian equations are substituted by stochastic GLEs. Recent results [3, 11, 18] indicate that the atomic motions in liquids may be realistically simulated by the GLD method using memory functions which are non-local in time but local in space. However, Straub *et al* [6] observed that memories are strongly dependent on interparticle separation. The reliability of the relative motions obtained from GLD simulations using pair additive potentials and memory functions which are independent of the relative separations is discussed below.
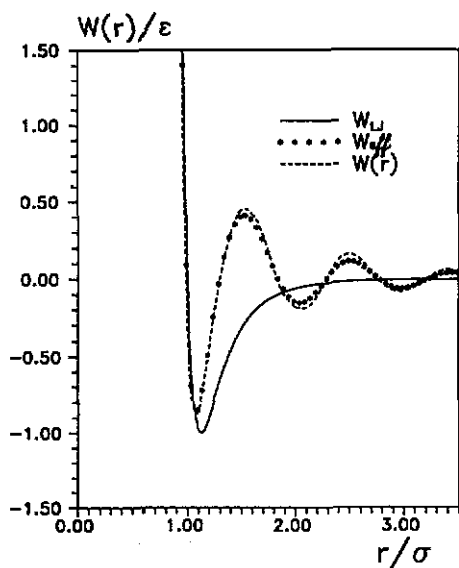
Figure 6. The effective mean force potential $(W_{eff}(r))$ used in GLD compared with the mean force potential $(W(r)$, equation (2.4)) and with the Lennard-Jones potential $(W_{LJ}(r))$.
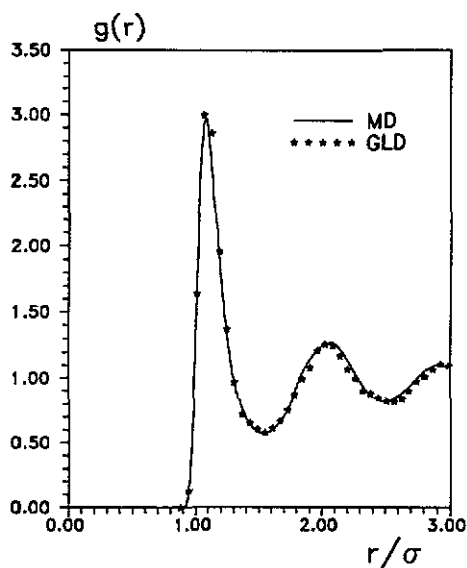
Figure 7. The radial distribution functions resulting from MD and GLD simulations.

We used the GLD method for the simulation of the trajectories of a subset of particles of the system which was simulated by MD. It was assumed that these particles play the role of 'solute' whereas the other particles ('solvent') were not explicitly considered in the GLD simulation (in this case solute and solvent particles are identical). We performed GLD simulations of 92 atoms of Kr in the same box as in the MD simulation and the temperature was also kept at 134.3 K. The stochastic equations of motion (3.1) were numerically integrated using the algorithm described in [19]. As in MD, a time step of 10^{-2} ps was used. The $R_{i\alpha}(t)$ forces were assumed to be Gaussian [13].

The intersolute forces were calculated from the effective solvent averaged pair potential shown in figure 6. This $W_{eff}(r)$ was determined from the $g(r)$ function obtained in the MD simulation following the procedure proposed in a previous paper [14]. Although $W_{eff}(r)$ potentials are in general dependent on the solute concentration, the $W_{eff}(r)$ corresponding to the concentration in this work is close to the mean force potential at infinite dilution $W(r)$ (figure 6). The interactions were truncated at 3.4σ, which corresponds to the third $W_{eff}(r)$ maximum (it should be noted that the range of these interactions is greater than for the Lennard-Jones potential). As expected, the solute structure resulting from the GLD simulation with the $W_{eff}(r)$ potential is in accordance with the structure obtained by MD (figure 7). In order to discuss the influence of the intersolute forces on the relative diffusion, we carried out a complementary GLD simulation in identical conditions but truncating $W_{eff}(r)$ at its first minimum ($r = 1.12\sigma$).

The effective memory function used in the GLD simulations is shown in figure 3 of [15]. This $M_{eff}(t)$ was calculated from the $C(t)$ determined from the MD simulation according to a previously described procedure [13]. For the integration of the GLE, the Laplace transform of $M_{eff}(t)$ was fitted to a Mori continued-fraction expansion of 25
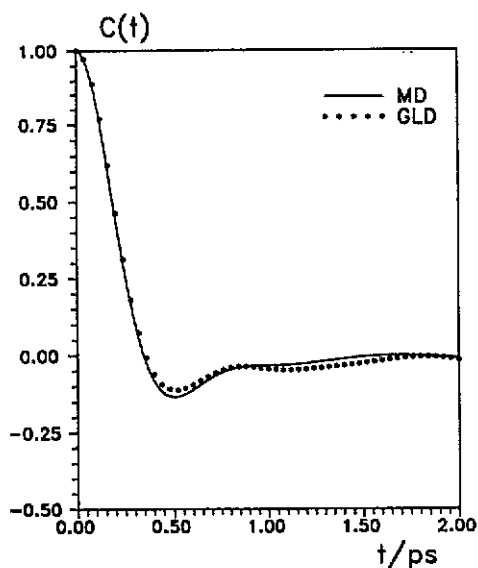
Figure 8. The normalized velocity autocorrelation functions for single particles resulting from MD and GLD simulations.

terms [15]. The $C(t)$ function resulting from GLD using $W_{eff}(r)$ and $M_{eff}(t)$ is in acceptable agreement with that from MD (figure 8). The differences between the two $C(t)$ functions may be attributed to defects in the fitting of $M_{eff}(t)$ to the Mori continued-fraction expansion.

3.3. Test of the GLD method

To perform the test of the GLD method we took as exact the results obtained from MD. It has already been shown (figures 7 and 8) that the structure $(g(r))$ and dynamics of single particles $(C(t))$ resulting from MD and GLD are in good agreement. However, this cannot be considered as a definitive test because the $W_{eff}(r)$ potential and the $M_{eff}(t)$ memory used in GLD were modelled by assuming that the $g(r)$ and $C(t)$ functions would be well reproduced by GLD. Hence, other correlation functions must be considered to perform a reliable test of the GLD method. In previous papers, we proved that properties such as the shape of the trajectories [18] or the van Hove functions [13] are acceptably reproduced by GLD, whereas noticeable discrepancies are observed in the case of collective properties (distinct time correlations) [20] which are strongly dependent on the hydrodynamic interactions (the effects of these interactions are not taken into account in the GLD simulations). In this section, the comparison between the MD and GLD results is extended to the relative motions of particles. This may be important for possible future applications of the GLD simulation method to the study of chemical reactions in solution.

It is easy to show that the relation between the time correlation functions for the velocities and the relative velocities is [3, 4]

$$\langle V_{\alpha\beta}(t) \cdot V_{\alpha\beta}(0) \rangle = 2\langle v_\alpha(t) \cdot v_\alpha(0) \rangle - 2\langle v_\alpha(t) \cdot v_\beta(0) \rangle. \tag{3.3}$$

The last term in (3.3) corresponds to the cross correlations between the velocities of different particles. These correlations may be associated with the indirect dynamic interactions due to the coupling between the motions of different particles through the flows that they induce in the other neighbouring particles (hydrodynamic interactions
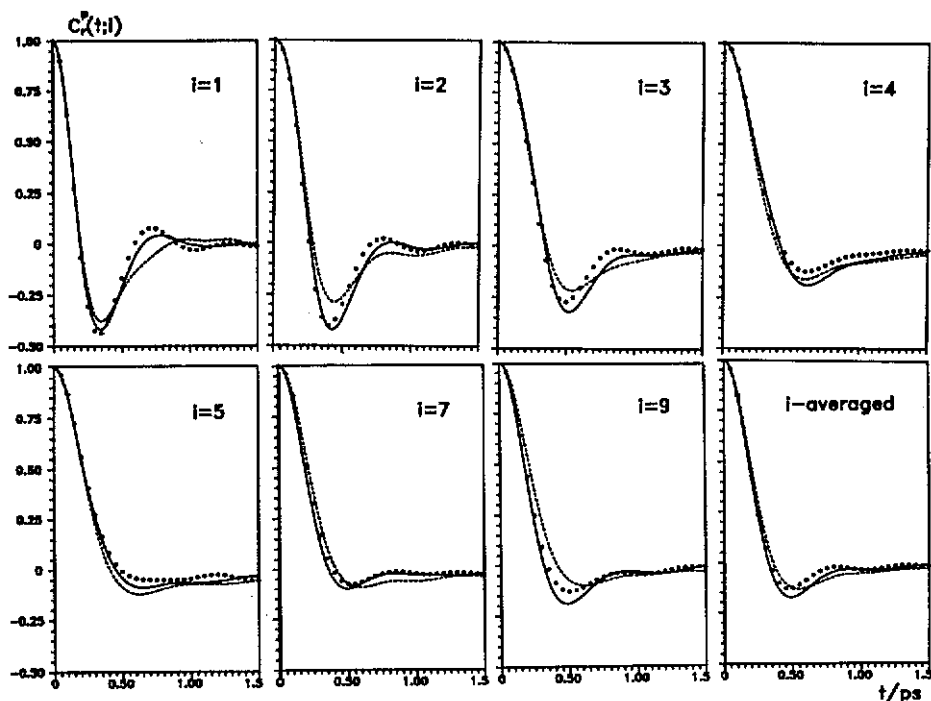
Figure 9. The normalized correlation functions for the parallel components of the relative velocities resulting from MD (———) and from GLD using the $W_{eff}(r)$ potential ($\cdots\cdots$) and a soft-sphere potential with the same repulsive part (– – –).

at microscopic scale). The effects of these indirect interactions were not included in the GLD simulations. However, the term corresponding to the cross correlations is markedly smaller than the other two terms in equation (3.3) [4] (the contribution of the cross velocity correlations to $C_r(t)$ is of the same order of magnitude as the discrepancies between the $C(t)$s in figure 8). Therefore, the normalized velocity autocorrelation functions $C(t)$ and $C_r(t)$ should be very similar, and it can then be expected that the $C_r(t)$ from GLD should be in accordance with that from MD. Nevertheless, the agreement between the $C_r(t)$s will not necessarily imply agreement between other, more detailed, functions such as $C_r^p(t; i)$ and $C_r^o(t; i)$.

As may be seen in figure 9 the evolution of $C_r^p(t; i)$ with i is quite well reproduced by GLD. In the case of $C_r^o(t; i)$, the results are not significant, since the changes with i are rather small and the $C_r^o(t; i)$ functions are very close to $C_r(t)$. As we used a memory function which is isotropic and independent of the presence of neighbouring particles, the differences between the $C_r^p(t; i)$ and $C_r^o(t; i)$ functions as well as among the $C_r^p(t; i)$ functions for the different values of i would be associated with the interaction forces. This is consistent with the close relation observed between the $W(r)$ shape and the i-dependence of $C_r^p(t; i)$. In order to assess the influence of $W_{eff}(r)$, we carried out GLD simulations with the same memory but a soft-sphere potential ($W_{eff}(r)$ was truncated at its first minimum). In this case, the discrepancies between the $C_r^p(t; i)$ functions from GLD and MD for different separations are more marked (figure 9). This confirms that suitable $W_{eff}(r)$ potentials should be used for reproducing the changes in the relative

diffusion with the interparticle separation. It should be noted that the disagreements between MD and GLD with the soft-sphere potential become less apparent for $C_\Gamma^p(t)$. This confirms that more detailed functions such as $C_\Gamma^p(t; i)$ must be used for a reliable test of GLD. Moreover, $C_r(t; i)$ functions are less sensitive to the values of i than $C_\Gamma^p(t; i)$, because $C_r(t; i)$s also contain important contributions of $C_\Gamma^o(t; i)$s and these functions are almost independent of the interparticle separation.

Our results show that the relative motions in liquids at short time scales may be realistically reproduced from GLD simulations using suitable potentials and time-dependent memories, whereas the use of memory functions dependent on the interparticle separation is not essential. This conclusion is consistent with the results from other studies [3, 11] but seems to contradict the dependence of the memory on the separation observed by Straub *et al* [6]. However, the findings of Straub *et al* cannot be directly compared with those in this paper, since they assumed a GLE for the relative distance (not for the position of each particle). Moreover, they calculated $M(t)$, restricted to different separations, from MD simulations replacing the potential by a harmonic confining potential [21]. We would point out that, unlike theoretical studies, computer simulations using a GLE for each solute particle would be more advantageous than those considering a GLE for a reaction coordinate. The GLD method can supply more detailed information on systems of several solute particles (e.g. in chemical reactions between molecules) and GLD computer programs are very similar to ordinary MD programs.

4. Concluding remarks

The results presented in this study confirm that the dependence of relative diffusion on separation becomes more apparent when the relative velocities are resolved into components parallel and perpendicular to the initial interparticle vector. This indicates that the $C_\Gamma^p(t; i)$ functions may be very useful for checking the results of theoretical models or describing in detail the relative motions in liquids. We have employed these functions for testing the reliability of the GLD method. It has been corroborated that the $C_\Gamma^p(t; i)$ functions are more sensitive to the differences in relative motion than other, less detailed, correlation functions ($C_r(t; i)$, $C_\Gamma^p(t)$). Moreover, unlike $C_r(t; i)$ for $i = 1$ and 2, the evolution of the $C_\Gamma^p(t; i)$ functions (position and depth of the minima) with the interparticle separation reflect the characteristics of the mean force potential.

It has been shown that the GLD method, based on the approximate equations (3.1) and (3.2), may reproduce the main characteristics of relative motions in liquids at short time scales (it is well known that hydrodynamic interactions have a non-negligible effect on properties which occur over a relatively long time). The time correlation functions for the components of the relative velocities have been acceptably reproduced by GLD simulations using suitable $W_{eff}(r)$ pair-additive potentials and $M_{eff}(t)$ functions which are independent of the existence of other neighbouring solute particles. More refined stochastic simulations would require the use of more complex GLEs [8, 10] which cannot easily be used in computer simulations of systems of interacting particles (it should be remembered that the aim of the GLD method is to save computational resources).

Finally, we want to point out that the true purpose of GLD is the study of systems more complicated than that considered in this work (colloidal systems, macromolecules and chemical reactions in solution, etc). Then, the MD simulations required to obtain $W_{eff}(r)$ and $M_{eff}(t)$ would be very costly and other approximate methods should be probably employed. Nevertheless, the use of simple liquids which can be easily simulated

by MD is very helpful in order to investigate the possibilities and limits of the GLD method. The same procedure was employed in earlier papers [13–15, 18–20] for checking the ability of GLD to reproduce other properties.

Acknowledgment

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