Journal of Statistical Physics, Vol. 60, Nos. 3/4, 1990

On the Description of Atomic Motions in Dense Fluids by the Generalized Langevin Equation: Statistical Properties of Random Forces

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Received June 1, 1989; final February 1, 1990

The suitability of the generalized Langevin equation (GLE) for a realistic description of the behavior of a system of interacting particles in solution is discussed. This study is focused on the GLE for a system of non-Brownian particles, i.e., the masses and the sizes of the solute particles are similar to those of the bath particles. The random and frictional forces on the atoms of the solute due to their collisions with the solvent atoms are characterized from molecular dynamics simulations of simple dense liquid mixtures. The required effective memory functions, which are dependent on the concentration of solute, are obtained by solving a generalized Volterra equation. The validity of the usual assumptions on the statistical properties of the random forces is carefully analyzed, paying special attention to their Gaussianity. The reliability of stochastic simulations based on the GLE is also discussed.

KEY WORDS: Generalized Langevin equation; random forces; time-dependent memory functions; molecular dynamics simulation; time correlation functions; computer experiments.

1. INTRODUCTION

The Langevin (LE) and generalized Langevin (GLE) equations are widely used in the statistical mechanical treatment of time-dependent phenomena in fluids. When applied to liquid solutions they allow us to replace the dynamical effects of the solvent on the solute by random and friction forces. The LE and GLE may also be used as substitutes for the classical Newton

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equation in computer simulations(1,2) at the McMillan–Mayer level of description,(3) i.e., when only the particles of solute are explicitly considered. These stochastic simulation methods—termed Langevin dynamics (LD) or generalized Langevin dynamics (GLD), depending on whether the LE or GLE is assumed—are very helpful when studying the atomic behavior of multicomponent systems, since the need for very expensive computational resources is obviated.

Although the LE was originally introduced from phenomenological arguments, its molecular foundations and ranges of validity are carefully analyzed in several papers.(4) The use of the LE is only justified when we deal with Brownian particles whose masses are much larger than those of the particles of the bath. If solute and solvent particles have similar sizes and masses, memory effects become important and a GLE must be considered. A simple derivation of the GLE for a single particle is achieved by applying the Mori projection method(5,6) to the components of the velocity. This formalism also provides a rigorous statistical mechanical definition of the different terms of the GLE. The random force $R(t)$ is the part of the total force that is initially orthogonal to the velocity and remains uncorrelated to $v(0)$ at all subsequent times, and the memory function $M(t)$ is defined from $R(t)$ according to the fluctuation-dissipation theorem.(6) In many cases (e.g., in LD or GLD simulations), more information about the random forces is required to characterize them and it is very usual to assume, as an additional hypothesis, a Gaussian distribution for $R(t)$. One of the aims of this paper is to assess the reliability of this hypothesis.

The derivation of the GLE for a system of interacting solute particles is not so simple. The application of the Mori projection technique to this case results in a GLE where the random forces have lost some of their characteristic properties and the memory functions are so complex that they are not easily modeled and used in computer simulation.(7) Moreover, in this derivation the forces among the solute particles would be due to the bare interactions, whereas in both theoretical studies and computer simulations of solutions at the McMillan–Mayer level of description the intersolute forces are ordinarily obtained from solvent averaged potentials $W(r)$. (A derivation of the GLE for a pair of solute particles interacting through a mean force potential is given elsewhere.(8) Alternatively, one can make the assumption that the effect of the solute–solute interactions is accounted for by merely adding a force term to the GLE.(9) The ability of GLD simulations to reproduce some of the solute properties (e.g., the radial distribution functions, the velocity autocorrelation functions, the self-diffusion coefficients, the shape of the atomic trajectories, etc.) when suitable memory functions and interaction potentials are used is discussed in previous works.(10–13) In this paper we analyze the GLE by studying the properties of the random forces on the assumption that the behavior of solute particles in realistic systems is described by the GLE. Moreover, we extend the test of the GLD simulation method to other solute properties, i.e., the acceleration–velocity cross-correlations and the Van Hove correlation functions.

In Section 2 we consider the case of single solute particles. We describe the procedure used for the determination of $R(t)$ values from an MD simulation. The $R(t)$ forces on single stationary solute particles are also evaluated and discussed. A method to obtain the concentration-dependent memory functions to be used in GLD simulations of interacting particles is proposed in Section 3. Section 4 is devoted to the study of statistical properties of the $R(t)$ forces for a system of interacting solute particles. In Section 5 the reliability of the GLD method is analyzed by comparing the results obtained in GLD simulations with the corresponding ones from MD simulations. Finally, some conclusions are drawn in Section 6.

2. RANDOM FORCES ON A SINGLE PARTICLE

The application of the projection-operator formalism(5,6) to each component of the velocity vector shows that the motion of a single solute particle in a fluid may be described by the GLE

$$\dot{v}(t) = -\int_0^t M(t-t')\, v(t')\, dt' + m^{-1} R(t) \tag{1}$$

where the memory function $M(t)$ and the stochastic forces $R(t)$ obey the statistical relations

$$\langle R(t) \rangle = 0 \tag{2}$$

$$\langle R(t) \cdot v(0) \rangle = 0 \tag{3}$$

$$\langle R(t) \cdot R(0) \rangle = m k_B T M(t) \tag{4}$$

When the explicit values of $R(t)$ are required, a Gaussian distribution is ordinarily assumed

$$W(R) = (2\pi \langle R^2 \rangle)^{-1/2} \exp(-R^2/2\langle R^2 \rangle) \tag{5}$$

In order to test the reliability of Eq. (5), we have calculated the random forces on a single atom (solute) due to its interactions with the remaining atoms (solvent) in realistic systems. To do this we performed MD simulations of soft-sphere and Lennard-Jones dense fluids (see Appendix). The $R(t)$ forces were evaluated at each time step during the

MD simulations. If $F(t)$ is the total force on the solute particle, it follows from (1) that

$$R(t) = F(t) + \int_0^t M(t-t')\, v(t')\, dt' \qquad (6)$$

The total force at each instant as well as the previous velocities of the particles are directly obtained in the ordinary MD simulations without difficulty, but the determination of the $M(t)$ functions required the performance of previous MD simulations of the same systems. We obtained the velocity autocorrelation functions $C(t)$ from these auxiliary MD simulations and then $M(t)$ was calculated using the Volterra equation

$$\dot{C}(t) = -\int_0^t M(t-t')\, C(t')\, dt' \qquad (7)$$

Equation (7) was solved following the procedure proposed by Berne and Harp.(14)

Following the above procedure, the $R(t)$ forces on a single solute particle were evaluated during experiments 1 and 2 (details are given in the Appendix). As was expected from the definition of $R(t)$, we verified that Eqs. (2)–(4) were well fulfilled. However, some discrepancies were found when our results were compared with an exact Gaussian distribution (5) with the same variance $\langle R^2 \rangle$ (Fig. 1). The shapes of the curves corre-

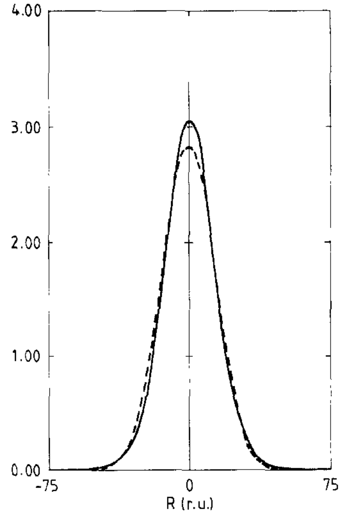

Fig. 1. Probability distribution of the random forces on a single particle: (—) from MD simulation (experiment 2); (- -) Gaussian distribution with the same variance, Eq. (5).

sponding to the distribution of frequencies of the $R(t)$ values resemble Gaussian functions, but slightly higher maxima are shown by the former. The central moments of the $R(t)$ distributions are compared with those corresponding to a normal distribution in Table I and we may observe noticeable quantitative deviations from $R(t)$ with respect to a Gaussian behavior. (β_2 from experiments shows noticeable differences with respect to the expected value for a normal distribution $\beta_2 = 3$).

We have also tested the Gaussianity of $R(t)$ by calculating the time correlation function

$$\varepsilon_2(t) = \langle R^2(t) \cdot R^2(0) \rangle / \langle R^4(0) \rangle \tag{8}$$

If $R(t)$ were Gaussian variables, $\varepsilon_2(t)$ would be written as(14,15)

$$\varepsilon_{2G}(t) = [1 + 2M_n^2(t)]/3 \tag{9}$$

where $M_n(t)$ is the normalized memory function

$$M_n(t) = \langle R(t) \cdot R(0) \rangle / \langle R^2(0) \rangle \tag{10}$$

The discrepancies between $\varepsilon_2(t)$ and $\varepsilon_{2G}(t)$ are clearly shown in Fig. 2 and they corroborate the quantitative non-Gaussianity of the $R(t)$ forces.

We also calculated the $R(t)$ forces that would correspond to a memoryless solute particle, i.e., when it is assumed that the solute particle obeys the ordinary LE. It is well known that this equation gives accurate results when applied to massive solute particles, but introduces important mistakes in the solute motions for short time scales when non-Brownian particles such as the ones in this work are considered. However, LE is very often used for non-Brownian solute particles in works only concerned with long-time properties such as the transport coefficients. In experiment 3 the

Table I. Central Moments of the Distributions of Random Forces on a Single Particle

Distribution parameters[a]	Simulation results[b,d]	Normal distribution[c,d]	Simulation results[b,e]	Normal distribution[c,e]
$\mu_1 = \langle R \rangle$	$< 10^{-12}$	0	$< 10^{-12}$	0
$\mu_2 = \langle R^2 \rangle = \sigma$	3.90×10^2	3.90×10^2	1.99×10^2	1.99×10^2
$\beta_1 = \langle R^3 \rangle = \sigma^3$	$< 10^{-3}$	0	$< 10^{-2}$	0
$\beta_2 = \langle R^4 \rangle = \sigma^4$	3.50	3	4.02	3

[a] μ_1 and μ_2 are expressed in reduced units.

[b] Results from a sample of 5×10^6 R values.

[c] Central moments for a Gaussian distribution with the same variance $\langle R^2 \rangle$ as the simulation results.

[d] Results corresponding to experiment 1.

[e] Results corresponding to experiment 2.

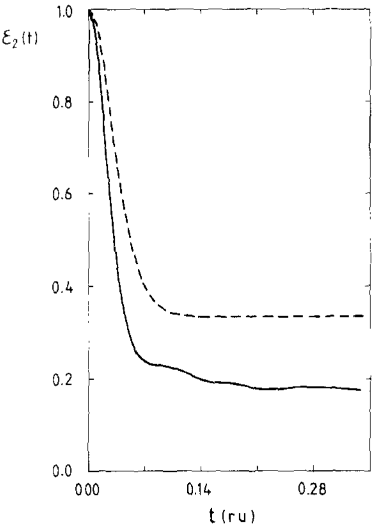

Fig. 2. The autocorrelation function $\varepsilon_2(t)$ of the $R(t)$ forces on a single particle: (—) from MD simulation (experiment 2); (- -) assuming the Gaussian approximation.

$R(t)$ forces were calculated from Eq. (6), but this time assuming that $M(t) = 2\gamma\delta(t)$, with $\gamma = k_B T/mD$ (D is the particle self-diffusion coefficient). The results show that Eq. (2) is fulfilled, but for small values of t the correlation between $R(t)$ and $v(0)$ is nonzero. Consistently with the assumed memory, the $R(t)$ autocorrelation function is a delta function which bears no relation to the real memory function. However, the deviations with respect to a Gaussian distribution are similar to those observed in the other experiments using the GLE.

On the other hand, we analyzed the possibility of obtaining the memory function from the force autocorrelation function on a stationary particle. The Brownian motion theory indicates that for an infinitely massive particle the random forces on a particle are essentially the same as the forces exerted on a fixed one.(4,16) So, the friction coefficients for particles with masses that are much larger (about a factor 100) than those of the solvent are close to those obtained from the forces on stationary particles.(17,18) In the case of light particles, time-dependent memory functions must be considered and a usual assumption(19,20) is that $M(t)$ might be approximated by

$$M'(t) = \langle R'(t) \cdot R'(0) \rangle / mk_B T \tag{11}$$

where $R'(t)$ is the force of the solvent on the fixed solute particle.

MD results for Na^+ and Cl^- in water(21,22) showed that $M'(t)$ functions obtained according to (11) and $M(t)$ functions deduced from the $C(t)$ functions of mobile ions are in good agreement and they only show noticeable differences at long times when collective effects are important. In experiments 4 and 5 (see Appendix) we considered simple dense fluids with a fixed particle. In these experiments the random forces $R'(t)$ coincide with the total forces of the bath on the stationary particle. Unlike the results for ions in water, our $M'(t)$ functions clearly differ from the $M(t)$ ones (Fig. 3). $M(t)$ and $M'(t)$ show clear disagreement and they only coincide at $t=0$. As in the work of Vogelsang and Hoheisel(18) for Lennard-Jones systems with finite massive solute particles, $M'(t)$ lies above $M(t)$ for short times. In our case $M'(t)$ remains above $M(t)$ even for long times [notice that an increase in the tail of $M'(t)$ as the mass of the solute increases may be observed in Fig. 3 of ref. 18]. We did not observe the agreement between $M(t)$ and $M(t')$ expected for large mass ratios.(18) The discrepancies between $M(t)$ and $M'(t)$ may be attributed to the differences in the relative motion between the solute and solvent particles when a mobile solute particle is replaced by a fixed one. It seems logical that such differences should be more important for the uncharged particles (as those in our experiments or in ref. 18) than for the entities constituted by ions and the water molecules of their hydration shells, which are kept together by strong Coulomb

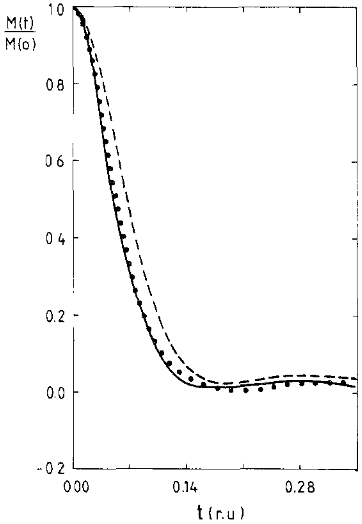

Fig. 3. Normalized memory functions for a single particle: (—) obtained from $C(t)$ of state B using Eq. (7); (···) from $R(t)$ forces in experiment 2; (- -) from $R'(t)$ forces on a stationary particle (experiment 5).

forces. Therefore, the results obtained for ions in aqueous solutions(21,22) cannot be directly extended to any system and the memories evaluated according to Eq. (11) must be used with caution.

3. EFFECTIVE MEMORY FUNCTIONS

As stated in Section 1, the derivation of the GLE for a single particle cannot be easily extended to a system of interacting solute particles. However, we may simply assume that each solute particle of the system moves according to the GLE

$$\dot{v}(t) = -\int_0^t M_{\text{eff}}(t-t')\, v(t')\, dt' + m^{-1}R(t) + m^{-1}F_{\text{eff}}(t) \tag{12}$$

where the systematic force $F_{\text{eff}}(t)$ due to the interaction with the other solute particles must be obtained from a solvent-averaged mean force potential and the random forces $R(t)$ obey the following statistical relations:

$$\langle R(t) \rangle = 0 \tag{13}$$

$$\langle R(t) \cdot v(0) \rangle = 0 \tag{14}$$

$$\langle R(t) \cdot F_{\text{eff}}(0) \rangle = 0 \tag{15}$$

$$\langle R(t) \cdot R(0) \rangle = mk_B T M_{\text{eff}}(t) - 2m \langle v(0) \cdot F_{\text{eff}}(0) \rangle\, \delta(t) \tag{16}$$

The GLD simulation method(2,23–25) is based on the assumption that solute particles move according to the GLE (12). $R(t)$ forces, which fulfill the relations (13)–(16), are usually generated from a Gaussian distribution. The second term on the right-hand side of the fluctuation-dissipation theorem (16) is ordinarily neglected. It was shown in previous papers(10,11) that effective memory functions $M_{\text{eff}}(t)$ and mean force potentials $W_{\text{eff}}(r)$ depending on the solute concentration must be used for the reproduction of the structural and dynamical properties of a set of interacting non-Brownian particles in solution. Next we describe a rigorous method to obtain the $M_{\text{eff}}(t)$ functions which should be used in GLD simulations in order to reproduce the dynamical behavior of the solute particles.

If we operate on Eq. (12) with $\langle v(0)\ldots\rangle / \langle v(0)^2 \rangle$ and we assume (14), we obtain

$$\dot{C}(t) = -\int_0^t M_{\text{eff}}(t-t')\, C(t')\, dt' + \theta(t) \tag{17}$$

where $\theta(t)$ is a time-dependent cross-correlation function between the systematic acceleration and the velocity at zero time of the particles which obey the GLE

$$\theta(t) = \langle a(t) \cdot v(0) \rangle / \langle v(0)^2 \rangle \tag{18}$$

A straightforward generalization of the algorithm(14) commonly employed to solve Eq. (7) may be used to invert the generalized Volterra equation (17) provided that $C(t)$ and $\theta(t)$ are known. An analogous procedure was used by Posch *et al.*(23) in their study of the relative dynamics of pairs of atoms.

In order to assess the reliability of this procedure, we performed MD simulations of simple liquids and we assumed that some particles of the simulated systems play the role of the solute, while the role of the solvent is attributed to the remaining particles. We determined the $M_{\mathrm{eff}}(t)$ functions by an iterative procedure as follows,

(i) $C(t)$ and $g(r)$ functions for solute particles are determinated from MD simulations of complete solute + solvent systems.

(ii) $W_{\mathrm{eff}}(r)$ is calculated from $g(r)$ according to the method proposed in ref. 10. An initial $M_{\mathrm{eff}}(t)$ function is chosen.

(iii) $\theta(t)$ is calculated using Eq. (18) during a GLD simulation with $M_{\mathrm{eff}}(t)$ and $W_{\mathrm{eff}}(r)$.

(iv) A new $M_{\mathrm{eff}}(t)$ is obtained by solving (17) with $C(t)$ of the complete system and $\theta(t)$ obtained in the preceding step. If the new $M_{\mathrm{eff}}(t)$ differs from the previous one, we go back to (iii), assuming the new $M_{\mathrm{eff}}(t)$.

We applied this procedure to the systems described in experiments 1 and 2. The memories used to start the iterative procedure were obtained according to the semiempirical rule(11)

$$M_{\mathrm{eff}}(t) = (1 - x)\, M_{\mathrm{MD}}(t) \tag{19}$$

where x is the solute molar fraction and $M_{\mathrm{MD}}(t)$ is the memory function determined from the $C(t)$ which resulted from the MD simulation of the complete system. The integration algorithm used in GLD simulations to solve (12) is described in ref. 24. This method is based on the one proposed by Vesely(25) and it requires the knowledge of the coefficients of a finite Mori continued-fraction expansion of the Laplace transform of $M_{\mathrm{eff}}(t)$. The number of Mori coefficients to be used depends on the characteristics of $M_{\mathrm{eff}}(t)$,(11) but it is not usually possible to fit accurately the $M_{\mathrm{eff}}(t)$ Laplace transforms to a manageable number of Mori terms and truncation effects may result in some mistakes.

Although the determination of $M_{\mathrm{eff}}(t)$ would require, in general, an iterative procedure, we verified that, at least for the systems considered in this paper, the convergence was reached after the first step. This result corroborates the suitability of the semiempirical rule (19) used for the determination of the initial $M_{\text{eff}}(t)$ function.

The $C(t)$ functions corresponding to a set of interacting particles obtained from GLD simulations with $M_{\text{eff}}(t)$ are very close to the input $C(t)$ functions obtained from the MD simulations of the complete systems. This result not only confirms the ability of the procedure used for the determination of $M_{\text{eff}}(t)$, but it also suggests that although Eq. (12) is based on an ansatz, the dynamical properties of solute particles may be well reproduced by GLD simulations if the correct $M_{\text{eff}}(t)$ functions are used. In Fig. 4 we compare the $C(t)$ functions corresponding to the MD and GLD simulations of experiment 6, which is described in the Appendix. The agreement is very good for short times. The slight discrepancies observed for longer times should not be attributed to defects in the $M_{\text{eff}}(t)$ functions, but to the difficulties in the numerical treatment, mainly due to defects in the fitting of the Mori coefficients.

The behavior of the $C(t)$ functions resulting from GLD simulations is affected by two factors, i.e., the memory function $M_{\text{eff}}(t)$ introduced as a datum in order to model the individual motion of particles and the interparticle interactions whose effects are accounted for by the $\theta(t)$ function. If Eq. (17) is integrated, we obtain

$$C(t) = C(0) - C_M(t) + C_\theta(t) \tag{20}$$

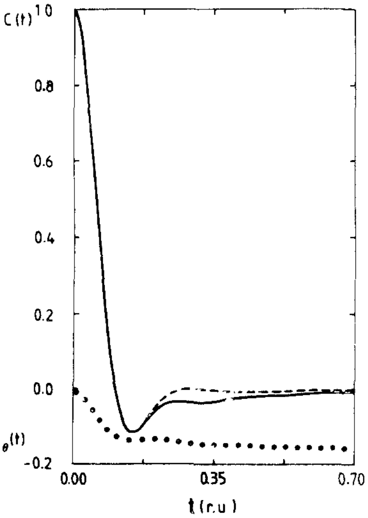

Fig. 4. Velocity autocorrelation function $C(t)$ from (—) MD and (- -) from GLD. (···) Time integral of the force–velocity cross-correlation function $C_\theta(t)$. Results from experiment 6.

where

$$C(0)=1 \tag{21}$$

$$C_M(t)=\int_0^t \int_0^{t''} M(t''-t')\,C(t')dt'\,dt'' \tag{22}$$

$$C_\theta(t)=\int_0^t \theta(t'')\,dt'' \tag{23}$$

We verified that $C_\theta(t)$ functions had simple shapes and that they quickly reached an almost constant value (see Fig. 4). Therefore, the influence of $\theta(t)$ functions is only significant at short times and their contribution to the $M_{\text{eff}}(t)$ functions is merely a small correction. Our results suggest that simple models for $\theta(t)$ are good enough for the determination of acceptable $M_{\text{eff}}(t)$ functions to be used in GLD computer simulations.

4. RANDOM FORCES ON INTERACTING PARTICLES

In the preceding section we confirmed that $C(t)$ functions of solute particles can be acceptably reproduced by computer simulations based on the numerical integration of the GLE. In this section we analyze the properties of the random forces which would replace the dynamical effects of the solvent on the solute if the motions of the solute particles are described according to the GLE.

We proceed in a way similar to that described in Section 2 for single particles. In this case the expression for the evaluation of the $R(t)$ forces on the solute particles is derived from (12) and it reads

$$R(t)=F(t)-F_{\text{eff}}(t)+m\int_0^t M_{\text{eff}}(t-t')\,v(t')\,dt' \tag{24}$$

$F(t)$ is the total force on the tagged solute particle and $F_{\text{eff}}(t)$ is the force due to its interaction with the other solute particles. $F_{\text{eff}}(t)$ forces were calculated from pair additive mean force potentials $W_{\text{eff}}(r)$ by following the procedure proposed in an earlier work$^{(10)}$ and used in Section 3. The method used to calculate $M_{\text{eff}}(t)$ was described in Section 3.

The results of experiments 7 and 8 (see Appendix for details) show that the $R(t)$ forces on a set of interacting particles evaluated according to (24) obey the statistical relations (13)–(16). The agreement between the $R(t)$ time autocorrelation functions and the corresponding $M_{\text{eff}}(t)$ functions (Fig. 5) confirms the reliability of the method proposed in Section 3 for the determination of $M_{\text{eff}}(t)$ functions. We observed that $\theta(0)$ and

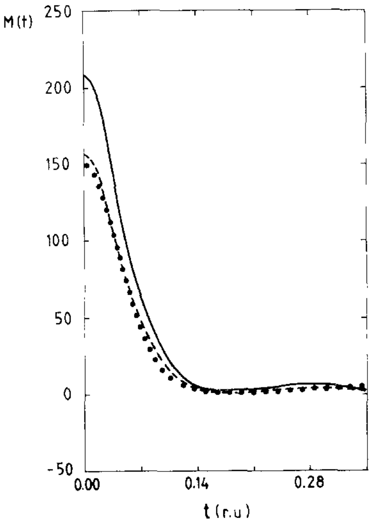

Fig. 5. (—) Memory function (experiment 8) from $C(t)$ of state B; (- -) effective memory function determined according to the method of Section 3; (···) from random forces on a set of interacting particles.

therefore the second term on the right-hand side of the fluctuation-dissipation theorem (16) was negligible. This last result is consistent with that obtained from Brownian dynamics simulations of *n*-butane.(26) Moreover, this should be true for all those systems whose particles have realistic motions, since $\dot{C}(0) = 0$ is a well-known property of the ordinary $C(t)$ functions for real systems and then it follows from (17) that $\theta(0) = 0$. We also analyzed the distribution of frequencies, the central moments, and the $\varepsilon_2(t)$ time correlation functions of the $R(t)$ values in experiments 7 and 8. We verified that their deviations from a Gaussian distribution are similar to those observed for single solute particles in Section 2.

5. TEST OF THE GLD SIMULATION METHOD

The results of the preceding section confirm that the microscopic behavior of a subset of interacting atoms may be consistently treated using the GLE (12) with $W_{\text{eff}}(r)$ and $M_{\text{eff}}(t)$. Moreover, the solute $g(r)$ and $C(t)$ correlation functions obtained from GLD simulations are in quite good agreement with those from MD simulations of the complete systems (see refs. 10 and 11 and Section 3). The self-diffusion coefficients D, which may be expressed as a time integral of $C(t)$, are also well reproduced by GLD simulations. Nevertheless, the simple comparison of $g(r)$ and $C(t)$ cannot be considered as a definitive test of the GLD method because these functions were precisely the ones we used to determinate $W_{\text{eff}}(r)$ and $M_{\text{eff}}(t)$. For this reason, other properties should be used for testing the GLD simulation method.

Previous papers proved the ability of GLD simulations for reproducing both the time-dependent probability distributions of the changes of direction of the atomic velocities$^{(12)}$ and the fractal behavior of the shape of the atomic trajectories.$^{(13)}$ In this work the comparison between the MD and GLD results is extended to the van Hove space- and time-dependent $G(r, t)$ function$^{(27)}$ and to the $\theta(t)$ cross-correlation function (18). To do that we performed MD and GLD simulations of a liquid mixture of soft spheres. Details of these simulations are given in the Appendix (experiment 9).

The van Hove correlation function $G(r, t)^{(27)}$ is the time-dependent generalization of the radial distribution function $g(r)$. This function is naturally separated into the self $[G_s(r, t)]$ and distinct $[G_d(r, t)]$ parts. We calculated these functions in experiment 9, and the results, which are represented in Figs. 6 and 7, show a good accordance between the time evolutions of the spatial correlations obtained in MD and GLD simulations.

The $\theta(t)$ function (18) defined in Section 3 was also determined in experiment 9. As may be observed in Fig. 8, the agreement between the results is rather good, but we observe slight discrepancies around $t = 0.25$. Similar disagreements are shown by the $C(t)$ and they were also observed

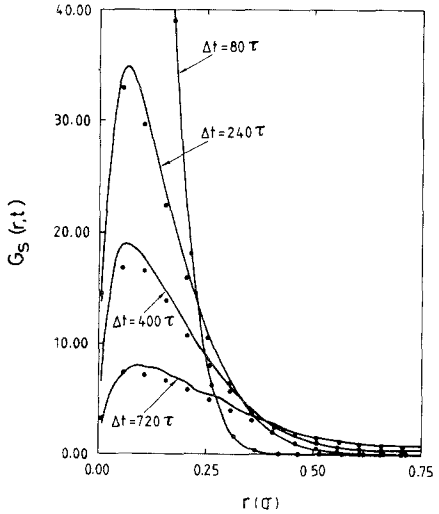

Fig. 6. Self part of the van Hove correlation functions at different times (experiment 9): (—) from MD simulation, (···) from GLD simulation.

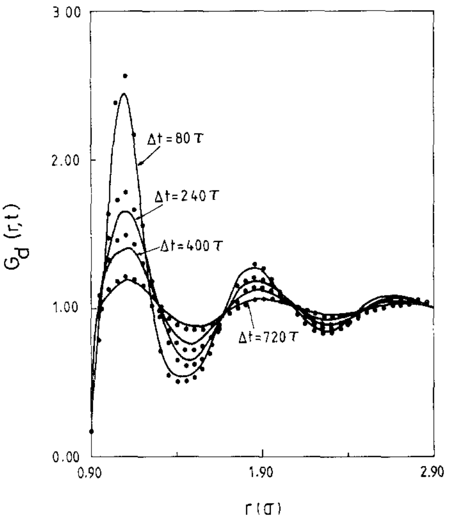

Fig. 7. Distinct part of the van Hove correlation functions at different times (experiment 9): (—) from MD simulation, (···) from GLD simulation.

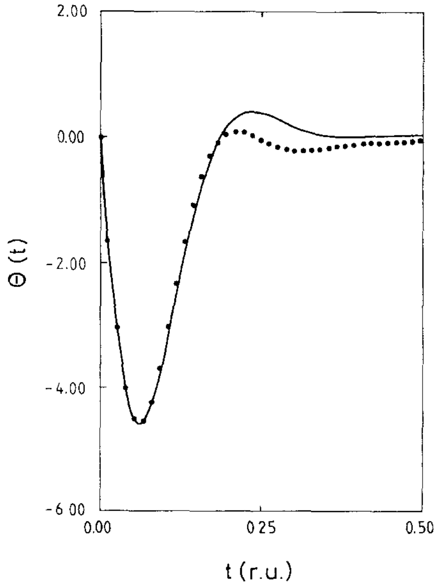

Fig. 8. Force–velocity cross-correlation functions in experiment 9 from (—) MD simulation, (···) from GLD simulation.

in experiment 6 (Fig. 4). These mistakes in GLD results are due to defects in the memory function actually used in the GLD simulation, which was obtained by fitting the $M_{\mathrm{eff}}(t)$ to a Mori continued-fraction expansion of three terms. In order to improve the GLD simulation method, we are developing an integration algorithm which will allow us to use $M_{\mathrm{eff}}(t)$ without the need for fitting them to a Mori expansion.

6. CONCLUDING REMARKS

MD simulations of realistic dense liquids have been used to characterize the $R(t)$ forces which appear when the GLD is used for the description of the atomic motions. Our results show that the distribution of frequencies of the $R(t)$ values resembles the ordinarily assumed Gaussian distribution, but some discrepancies appear when quantitative analyses are performed. It should be noticed that similar non-Gaussian features, which are associated with the nonlinearities of the microscopic interactions, were already observed from the analysis of the atomic velocities.(15,28)

Although the GLE for a system of interacting non-Brownian particles has not been theoretically demonstrated, the statistical properties of the $R(t)$ forces generated from MD simulations using the GLE are the ones ordinarily required for the random forces (13)–(15). Moreover, computer simulations based on the GLE and assuming a Gaussian distribution of $R(t)$ permit quite good reproductions of the analyzed structural and dynamical properties of the solute $[g(r), C(t), D, \theta(t), G(r, t),...]$. Nevertheless, reliable GLD simulations require the use of suitable $W_{\mathrm{eff}}(r)$ and $M_{\mathrm{eff}}(t)$ which are dependent on the solute concentration. As for $W_{\mathrm{eff}}(r)$,(10) the method that we propose for obtaining $M_{\mathrm{eff}}(t)$ requires MD simulations of the complete systems. In the case of complex systems, which are the most useful applications of the GLD method, these MD simulations may demand too expensive computations and approximate $W_{\mathrm{eff}}(r)$ and $M_{\mathrm{eff}}(t)$ models should be used. For this reason it turns out to be very practical to consider very simple systems, such as those in this work, for testing the GLD simulation method.

APPENDIX

The results shown in this paper were obtained by performing several computer experiments using the MD method with the Beeman algorithm(29) (in experiments 6 and 9 the GLD method was also used):

(i) State A corresponds to liquid Ar at $T^* = 0.965$ and $\rho^* = 0.931$.

The atoms interacted through a soft-sphere potential, i.e., a Lennard-Jones potential truncated at $2^{1/6}$. A time step of $\tau = 4.637 \times 10^{-3}$ was used.

(ii) State B corresponds to liquid Kr at $T^* = 0.80$ and $\rho^* = 0.812$. The interaction potential was a Lennard-Jones with a cutoff at 2.4. In this case the time step was $\tau = 3.543 \times 10^{-3}$.

(iii) State C corresponds to a liquid binary mixture of soft spheres at $\rho^* = 0.642$ ant $T^* = 0.481$. The solvent particles (75%) were Ar atoms and the mass and potential parameters of the solute particles (25%) were $m = 4m_{\mathrm{Ar}}$ and $\sigma = 1.25\sigma_{\mathrm{Ar}}$, $\varepsilon = 2\varepsilon_{\mathrm{Ar}}$, respectively ($m_{\mathrm{Ar}}, \sigma_{\mathrm{Ar}}$, and $\varepsilon_{\mathrm{Ar}}$ are the usual parameters for Ar). For the unlike interactions, the Lorentz–Berthelot rules were used. The time step was 2.623×10^{-3}. In this case, the reduced units are expressed in terms of ε, σ, and m.

In experiments 1 (state A) and 2 (state B) the system was made up of 100 atoms and during the MD simulations we used Eq. (6) for the calculation of $R(t)$ forces on each atom. We performed simulations of 6.500 time steps. Previous MD simulations of the same systems were performed for the determination of the $M(t)$ functions to be used in (6).

Experiment 3 was as experiment 2, but on the assumption that the solute particle obeyed the ordinary Langevin equation for Brownian particles, i.e., replacing in (6) the friction term by γv. The friction coefficient was calculated from the diffusion coefficient D of state B following the Einstein expression $\gamma = k_B T/mD$.

Experiments 4 and 5 were analogous to experiments 1 and 2, respectively, except that we kept one particle stationary. In experiments 4 and 5 we were only interested in the random forces on the stationary particle. So, longer simulations were required to achieve adequate average results. The total number of time steps in each experiment was 150.000.

In experiment 6 (state A) we considered 1025 particles and we assigned the role of solute to 125 of them and the role of solvent to the others. The $C(t)$ and $g(r)$ functions obtained from a previous MD simulation of the whole system were used for the determination of $M_{\mathrm{eff}}(t)$ and $W_{\mathrm{eff}}(r)$. A GLD simulation of the 125 solute particles was performed in order to determine $\theta(t)$ and to check the reliability of the GLD simulation method using $M_{\mathrm{eff}}(t)$ functions (see Section 3). The GLD simulation was performed according to the algorithm described in ref. 24. The Laplace transform of the $M_{\mathrm{eff}}(t)$ function was fitted to a Mori continued-fraction expansion of three terms.(11)

Experiments 7 and 8 were similar to experiments 1 and 2, respectively, but we assumed that 25 tagged particles played the role of the solute. Equation (24) was used for the calculation of $R(t)$ forces on these particles. $M_{\mathrm{eff}}(t)$ and $W_{\mathrm{eff}}(t)$ were deduced from the $C(t)$ and $g(r)$ functions resulting from a previous MD simulation of the same system in accordance with the method proposed in Section 3 and in ref. 10, respectively. $F_{\mathrm{eff}}(t)$ was calculated assuming that $W_{\mathrm{eff}}(r)$ potentials were truncated at 2.5.

Experiment 9 consisted of two simulations of a system in state C. The system was made up of 500 particles. We performed an MD simulation of the complete system and a GLD simulation of the 125 solute particles. The $M_{\mathrm{eff}}(t)$ and $W_{\mathrm{eff}}(r)$ required for the GLD simulation were calculated from the solute $C(t)$ and $g(r)$ obtained in the MD simulation according to Section 3 and ref. 10, respectively. The Laplace transform of $M_{\mathrm{eff}}(t)$ was fitted to a Mori continued-fraction expansion of three terms. $W_{\mathrm{eff}}(r)$ was truncated at 2.5 and the algorithm described in ref. 24 was used. The evolution of the system was studied over 160.000 time steps in the MD simulation and over 180.000 time steps in the GLD simulation. We point out that for the calculation of the $\theta(t)$ in the MD simulation we used the acceleration $a(t)$ derived from the $W_{\mathrm{eff}}(r)$ potential.

ACKNOWLEDGMENTS

We acknowledge the financial support of DGICYT, Project PS 87-0026-C02.

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