Mass and size effects on the memory function of tracer particles

G. R. Kneller and K. Hinsen
Centre de Biophysique Moléculaire, CNRS UPR 4301, Rue Charles Sadron, F-45071 Orléans Cedex 2, France

G. Sutmann
Central Institute for Applied Mathematics (ZAM) and John von Neumann Institute for Computing (NIC), Research Centre Jülich, D-52425 Jülich, Germany

(Received 2 October 2002; accepted 29 January 2003)

Using autoregressive modeling of discrete signals, we investigate the influence of mass and size on the memory function of a tracer particle immersed in a Lennard-Jones liquid. We find that the memory function of the tracer particle scales with the inverse reduced mass of the simulated system. Increasing the particle's mass leads rapidly to a slow exponential decay of the velocity autocorrelation function, whereas the memory function changes just its amplitude. This effect is the more pronounced the smaller and the heavier the tracer particle is. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1562620]

Diffusion of particles in liquids is one of the most fundamental transport processes studied in physical chemistry and biology. For many chemical reactions in liquids diffusion is the rate-limiting step. All measurable quantities relevant to diffusion of a tracer particle in a liquid can be expressed in terms of its (normalized) velocity autocorrelation function

$$\psi(t) \equiv \frac{\langle v(0)v(t)\rangle}{\langle v^2(0)\rangle}. \tag{1}$$

Here $v(t)$ is one Cartesian component of the velocity of the tracer particle and $\langle ... \rangle$ denotes a thermal average. As Zwanzig has shown,[1] one can derive a formal equation of motion for $\psi(t)$,

$$\frac{d\psi}{dt} = -\int_0^t d\tau \xi(t-\tau)\psi(\tau). \tag{2}$$

The kernel $\xi(t)$ is the memory function and (2) is called the memory function equation. The memory function can formally be expressed in terms of microscopic variables,[1,2]

$$\xi(t) = \frac{\langle \dot{v} \exp(i[1-\mathcal{P}]\mathcal{L}t)\dot{v}\rangle}{\langle v^2\rangle}, \tag{3}$$

where $\mathcal{L}$ is the Liouville operator of the system and $\mathcal{P}$ is a projector whose action on an arbitrary function in phase space, $\dagger$, is defined through

$$\mathcal{P}_\dagger = v\frac{\langle v_\dagger\rangle}{\langle v^2\rangle}. \tag{4}$$

In the past, various models for the velocity autocorrelation function (VACF) have been developed on the basis of the memory function equation (2). In the simplest case one sets $\xi(t) = \gamma\delta(t)$ which leads to an exponential form for the VACF, $\psi(t) = \exp(-\gamma t)$. This result is well-known from the Langevin theory of diffusion.[3,4] An overview over more involved models for $\xi(t)$ leading to the nonexponential VACFs of liquids can be found in Ref. 2.

An important question from a practical and theoretical point of view is to know how the nonexponential behavior of the VACF of a diffusing particle is related to its size and mass, in other words, at which point a simplified Langevin description of the tracer particle becomes appropriate. To answer this question, we use the information available from molecular dynamics (MD) simulations of liquids. The computation of memory functions from MD simulations has been described recently in Ref. 5, and we refer to this article for technical details and references. MD simulations yield trajectories of time dependent observables on a discrete time axis, $t = n\Delta t$, where Δt is the simulation time step or a multiple of it. The starting point to compute memory functions is thus a discrete version of Eq. (2),

$$\frac{\psi(n+1)-\psi(n)}{\Delta t} = -\sum_{k=0}^{n} \Delta t \xi(n-k)\psi(k). \tag{5}$$

In very much the same way as the Laplace-transformed memory function equation is used for the development of analytical models of $\psi(t)$, the z-transform of the discrete memory function equation (5) can be used for numerical studies. In particular, it can be solved for the z-transformed memory function,

$$\Xi_>(z) = \frac{1}{\Delta t^2}\left(\frac{z}{\Psi_>(z)} + 1 - z\right), \tag{6}$$

where $\Xi_>(z)$ is defined as

$$\Xi_>^{(\mathrm{AR})}(z) \equiv \sum_{n=0}^{\infty} \xi^{(\mathrm{AR})}(n) z^{-n}. \tag{7}$$

The above equation is, of course, only useful if $\Psi_>(z)$ and the inverse z-transform of $\Xi_>(z)$ can be computed. As it has been shown in Ref. 5, this can be achieved by describing the underlying time series $v(n)$ as an autoregressive (AR) stochastic process of order P,

$$v(t)=\sum_{n=1}^{P} a_n^{(P)} v(t-n\Delta t)+\epsilon_P(t). \tag{8}$$

Multiplying (8) with $v(t-n\Delta t)$ and performing a thermal average yields a set of linear equations for the predictor coefficients, $a_n^{(P)}$ $(n=1,...,P)$. The resulting linear equations, which read $\Sigma_{n=1}^{P} a_n^{(P)} \psi(|k-n|\Delta t)=\psi(k\Delta t)$ $(k=1,...,P)$, are known as the Yule–Walker equations.[6] They require the knowledge of $\psi(t)$, which can be computed from the MD trajectory. The square amplitude σ_P^2 of the white noise $\epsilon_P(t)$ is given by $\sigma_P^2=1-\Sigma_{n=1}^{P} a_n^{(P)} \psi(n\Delta t)$. In our studies we use the Burg algorithm,[6–8] which takes the time series $v(k\Delta t)$ as input and estimates $\psi(t)$ as well as σ_P^2 implicitly. Within the AR model the (unilateral) z-transformed discrete VACF has the simple form[5]

$$\Psi_{>}^{(\mathrm{AR})}(z)=\sum_{j=1}^{P} \beta_j \frac{z}{z-z_j}, \quad |z|>|z_j|, \tag{9}$$

where the coefficients β_j are given by

$$\beta_j=\frac{1}{a_P^{(P)}} \frac{-z_j^{P-1}\sigma_P^2}{\Pi_{k=1,k\neq j}^{P}(z_j-z_k)\Pi_{l=1}^{P}(z_j-z_l^{-1})}, \tag{10}$$

and z_j are the zeros of the characteristic polynomial

$$p(z)=z^P-\sum_{k=1}^{P} a_k^{(P)} z^{P-k}. \tag{11}$$

In the following $p(z)$ is assumed to have P distinct zeros which fulfill the stability criterion $|z_k|<1$. The latter is guaranteed by the Burg algorithm. The memory function in the time domain is now obtained by inserting (9) into (6) and computing $\xi(n)$ from (7) by polynomial division.[9] The latter step is motivated by the definition (7) of $\Xi_{>}^{(\mathrm{AR})}(z)$. Within the AR model the zeros of $p(z)$, i.e., the poles of $\Psi_{>}^{(\mathrm{AR})}(z)$, also determine the VACF on the positive time axis. Inverse z-transformation of (9) yields

$$\psi(n)=\frac{1}{2\pi i} \oint_C dz\, z^{n-1} \Psi_{>}^{(\mathrm{AR})}(z)=\sum_{j=1}^{P} \beta_j z_j^n \tag{12}$$

for $n\geqslant 0$. The integration contour is any closed path containing all poles of $\Psi_{>}^{(\mathrm{AR})}(z)$.

Applying the method described above, we have computed the memory function of a tracer particle immersed in liquid argon at a temperature of 90.0 K. The interactions between the fluid particles are described by a Lennard-Jones potential and those between the tracer particle and the fluid by distance-shifted version of the same potential

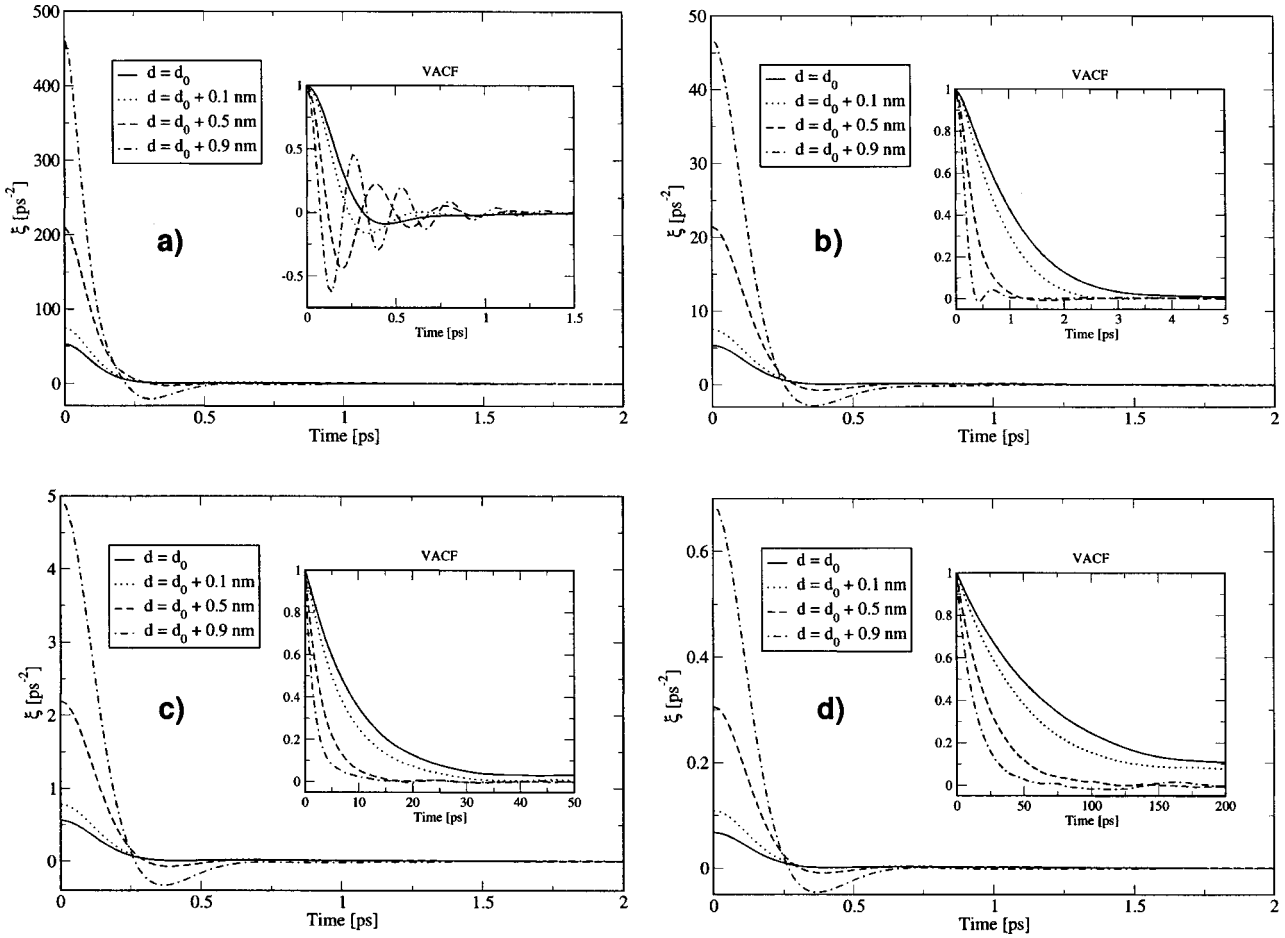

FIG. 1. Memory functions of the tracer particle for mass ratio $M/m=1$ (a), $M/m=10$ (b), $M/m=100$ (c), and $M/m=1000$ (d), respectively, and different particle sizes. The diameter of the tracer particle is $d=2^{1/6}\sigma+\delta$ with $\sigma=0.295\,99$ nm. The insets show the corresponding normalized velocity autocorrelation functions, $\psi(t)$.

$$U_{SS}=\sum_{i,j\in S} 4\epsilon\left(\left[\frac{\sigma}{r_{ij}}\right]^{12}-\left[\frac{\sigma}{r_{ij}}\right]^{6}\right), \tag{13}$$

$$U_{TS}=\sum_{j\in S} 4\epsilon\left(\left[\frac{\sigma}{r_{Tj}-\delta}\right]^{12}-\left[\frac{\sigma}{r_{Tj}-\delta}\right]^{6}\right). \tag{14}$$

Here "S" stands for "solvent" and "T" for "tracer particle." The interaction potential is determined by the Lennard-Jones parameters ϵ and σ (with $\epsilon=0.878\,64$ a.m.u.$\times$nm^2/ps^2, $\sigma=0.295\,99$ nm). The additional parameter δ allows to change the size of the tracer particle. Defining the particle size by the minimum of the Lennard-Jones potential, we have

$$d=d_0+\delta \quad \text{with} \quad d_0=2^{1/6}\sigma. \tag{15}$$

A system of 2048 particles in total has been simulated in the microcanonical NVE ensemble with a simulation time step of 20 fs. In order to obtain good statistics for the VACF of the tracer particle, long trajectories of up to 45 ns were created. This point is important if very heavy tracer particles are considered. For the subsequent analysis we fitted an AR process of order $P=80$ to each velocity trajectory of the tracer particle, using $\Delta t=20$ fs as sampling interval.

Figures 1(a)–1(d) show the memory functions of the tracer particle for mass ratios $M/m=1$, 10, 100, and 1000, respectively, where $m=39.95$ a.m.u. is the mass of an argon atom and M is the mass of the tracer particle. The insets show the corresponding VACFs computed from the AR model. All memory functions are given for the same time interval of 2 ps. This value is motivated by the AR model for $v(t)$, whose systematic part is defined in the time interval $[t-P\Delta t,t]$. Since $P=80$ and $\Delta t=20$ fs, we have $P\Delta t=1.6$ ps. Although $\xi(t)$ is defined on the whole positive time axis, values for $t>P\Delta t$ are to be considered as an extrapolation. We found that these extrapolated values tend rapidly to zero with increasing time. The most obvious result is that the mass of the tracer particle influences essentially the amplitude of its memory function, but the form of the latter is left almost unchanged. Only a slightly slower decay can be observed when passing from $M/m=1$ to 10. In contrast, the size of the tracer particle influences strongly its form. With increasing size, the VACF exhibits stronger oscillations. For a given size the scaling behavior of the memory function is nevertheless maintained.

The most interesting qualitative result for the VACF is that they approach rapidly an overdamped featureless exponential behavior with increasing mass, whereas the memory function changes just its amplitude. The form of the memory function is, in fact, irrelevant if the characteristic time scales of the memory function and the VACF can be clearly separated. This is exactly the assumption in the Langevin approximation, where the memory function is replaced by a Dirac delta distribution. The tendency to an exponential VACF is the more pronounced the smaller and heavier the tracer particle is. In contrast, increasing its size and reducing its mass enhances the vibrational component in the VACFs. To validate the VACFs obtained from the AR model we computed corresponding estimates directly from the MD trajectories and we found excellent agreement in all cases, confirming the results found in Ref. 5. In the statistically relevant time intervals the differences can be considered as zero. The behavior of the VACF can be qualitatively understood as follows: Differentiating the memory function equation (2) one obtains[2]

$$\ddot{\psi}+\xi(0)\psi+\int_0^t d\tau K(t-\tau)\dot{\psi}(\tau) \tag{16}$$

if one assumes that $\xi(t)$ obeys itself an equation of type (2), with $K(t)$ as kernel. If now $K(t)=\lambda\,\delta(t)$, i.e., if $K(t)$ decays much faster than $\xi(t)$, one obtains an exponential form for the memory function, $\xi(t)=\xi(0)\exp(-\lambda t)$, and $\psi(t)$ is the solution of the equation of motion for a damped harmonic oscillator, $\ddot{\psi}+\lambda\dot{\psi}+\xi(0)\psi=0$.[2,10,11] Note that $\xi(0)$ defines the frequency of the oscillator and λ the damping. Since all memory functions in our example decay on similar time scales, it is essentially $\xi(0)$ that determines the form of $\psi(t)$. If $\xi(0)$ is large, $\psi(t)$ exhibits the vibrations related to the rattling motion in the "cage" of nearest neighbors. If, in contrast, $\xi(0)$ is small, one obtains a purely exponential behavior. The approach to the exponential regime can be characterized by comparing the friction coefficient of the tracer particle, which is defined as $\gamma=\int_0^\infty dt\,\xi(t)$, with the corresponding value obtained from a fit of an exponential to the VACF, $\psi(t)\approx\exp(-\gamma t)$. Within the AR model, γ can be calculated as

$$\gamma=\sum_{n=0}^{\infty}\Delta t\,\xi(n)=\Delta t\,\Xi_{>}(1). \tag{17}$$

TABLE I. Relaxation constants γ for different mass ratios M/m and different sizes of the tracer particle. The particle diameter is $d=d_0+\delta$, with $d_0=2^{1/6}\sigma=0.3324$ nm. For each mass ratio the first line contains γ obtained from $\gamma=\Delta t\cdot\Xi_{>}^{(\mathrm{AR})}(1)$, and the second line contains γ obtained by fitting $\psi(t)\approx\exp(-\gamma t)$.

M/m	δ/nm = 0	0.1	0.5	0.9
1	7.3323	10.1861	21.2653	34.4472
	6.2288	8.1878	17.1468	28.6416
10	0.9314	1.2468	2.5204	4.9094
	0.9110	1.2131	2.7848	5.3593
100	0.1061	0.1483	0.3196	0.5721
	0.1024	0.1351	0.2975	0.5423
1000	0.0132	0.0203	0.0442	0.0792
	0.0131	0.0182	0.0422	0.0739

TABLE II. Scaling factors $\xi_M(0)/\xi_m(0)$ for different mass ratios M/m and different sizes of the tracer particle.

M/m	μ/m	δ/nm = 0	0.1	0.5	0.9
10	9.95	9.97	9.96	9.80	9.91
100	95.34	95.25	96.00	95.83	94.41
1000	671.81	788.94	686.10	686.46	679.15

TABLE III. Values of the memory function at $t=0$ compared to the negative curvature of the VACF, $-\ddot{\psi}(0)$. The latter has been obtained by numerical differentiation.

$\frac{M}{m}$	$\frac{\delta}{nm}$			
	0	0.1	0.5	0.9
1	53.2532	74.8534	210.4775	467.7310
	53.2721	74.7491	210.2601	467.7315
10	5.3438	7.5191	21.4838	47.2131
	5.2980	7.5034	21.2139	47.1845
100	0.5591	0.7797	2.1962	4.9542
	0.5283	0.7779	2.1960	4.9534
1000	0.0675	0.1091	0.3066	0.6887
	0.0587	0.1080	0.3105	0.6897

Table I shows the comparison for different masses and sizes of the tracer particle. The results show that the exponential fit is the better the smaller and the heavier the tracer particle is.

Since $\xi(0)$ is the essential parameter determining the form of $\psi(t)$, it is worthwhile to examine its scaling behavior in more detail. As Español and Zuñiga have shown,[12] the average square momentum of a tracer particle which is immersed in a solvent containing a *finite* number of particles, N, is given by $\langle p^2\rangle = k_B T\mu$, where $\mu=(M\cdot Nm)/(Nm+M)$ is the reduced mass of the system solute/solvent. Writing $v=p/M$ and $\dot{v}=F/M$, one obtains from (3)

$$\xi(0)=\frac{\langle F^2\rangle}{\mu k_B T}. \tag{18}$$

Since the average squared force on the tracer particle does not depend on its mass, it follows that $\xi(0)$ should scale with $1/\mu$. With the exception of $M/m=1000$ and $d=d_0$ the scaling behavior (Table II) follows the theoretical prediction and shows in particular that the appearance of the reduced mass instead of M in (18) is essential if the mass of the tracer particle represents a substantial fraction of the solvent mass. We attribute the exception to an insufficient thermalization of the tracer particle which is not only very massive, but also exposes only a very small surface to its neighbors. In this extreme case the thermalization process is extremely slow and probably not even achieved after several million time steps. Equation (18) also shows that the cage effect, i.e., the oscillations in the VACF, is enhanced with increasing size of the tracer particle. In this case the mean square force on the tracer particle is increasing since more solvent molecules interact with it.

We tested the validity of the initial value $\xi(0)$ by exploiting the relation $\xi(0)=-\ddot{\psi}(0)$. For this test we used a direct estimation of $\psi(n)$ from the MD trajectory and computed its negative curvature at $t=0$ by numerical differentiation, using the central difference scheme. Table III shows the results for different masses and sizes of the tracer particle. Again, except for $M/m=1000$ and the smallest size $d=d_0$, remarkable agreement is achieved in all cases.

This Communication has revealed that the exponential behavior of the VACF of a diffusing tracer particle is essentially attained by a change in amplitude of the memory function, and not by a change in form towards a Dirac distribution, as postulated in the Langevin model. The memory function is essentially scaled by the inverse reduced mass of the tracer particle. This illustrates nicely a conjecture of Español and Zuñiga[12] who demonstrated that the average square momentum scales with the reduced mass if the number of solvent particles is finite. The latter is an important point in computer simulations. With increasing mass of the tracer particle, the amplitude of the memory function becomes rapidly small, such that its form does not matter for $\psi(t)$, which becomes an exponential. The study has also shown that the size of a diffusing tracer particle does influence the amplitude and the form of the memory function. With increasing size the cage effect is enhanced and leads to stronger oscillations in $\psi(t)$. The paper has confirmed that the AR model is a reliable basis for computing correlation functions, and moreover a versatile tool to compute quantities such as the memory function, which cannot be computed directly from molecular dynamics computer simulations.

[1] R. Zwanzig, "Statistical Mechanics of Irreversibility," *Lectures in Theoretical Physics* (Wiley-Interscience, New York, 1961), pp. 106–141.
[2] J. P. Boon and S. Yip, Molecular Hydrodynamics (McGraw-Hill, New York, 1980).
[3] P. Langevin, Acad. Sci., Paris, C. R. **146**, 530 (1908).
[4] N. G. van Kampen, *Stochastic Processes in Physics and Chemistry*, revised edition (North-Holland, Amsterdam, 1992).
[5] G. R. Kneller and K. Hinsen, J. Chem. Phys. **115**, 11097 (2001).
[6] A. Papoulis, *Probability, Random Variables, and Stochastic Processes*, 3rd ed. (McGraw-Hill, New York, 1991).
[7] J. Burg, Ph.D. thesis, Stanford University, Stanford, 1975.
[8] J. Makhoul, IEEE Trans. Acoust., Speech, Signal Process. **25**, 423 (1977).
[9] Due to the fact the backtransform of $\Psi_>(z)$ is only defined for positive times, the second derivative (difference) of $\psi(n)$ must be multiplied by a factor of two in order to obtain the correct value. The same is thus true for the memory function. Note also that formally $\Sigma_j\beta_j=1$. Due to numerical inaccuracies this relation is not exactly fulfilled. It was found that renormalization of the $\{\beta_j\}$ leads to consistent and highly accurate results for the memory function.
[10] B. J. Berne, J. P. Boon, and S. A. Rice, J. Chem. Phys. **45**, 1086 (1966).
[11] J.-P. Hansen and I. R. McDonald, *Theory of Simple Liquids*, 2nd ed. (Academic, London, 1986).
[12] P. Español and I. Zuñiga, J. Chem. Phys. **98**, 574 (1993).