Characteristic times in the nanometer-picosecond translational collective dynamics of molecular liquids

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Molecular-dynamics calculations of the translational dynamic structure factor in liquid CO_2 and CD_4 are analyzed by means of the generalized Langevin equation for the intermediate scattering function in the second-order memory function approximation. We give a rigorous general relation among the decay times of the memory and the lifetimes of the modes of the density-density correlation function. The comparison of the various characteristic times among them and with the collision time, carried out as a function of the wave vector, reveals strong relationships between the memory relaxation and the density-density correlation modes, some of which have purely "collisional" and other "collective" character. We show that essential information about the life time of structural properties in a molecular liquid at nanometer dimensions can be obtained if the time behavior of the correlation function is considered in addition to that of the memory function.

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Experimental and computer simulation studies of translational collective dynamics of dense fluids approaching the molecular space-time scales have received continuous attention in the last decades due to the great interest in understanding relaxation processes in the high-frequency regime [1–4]. A generally accepted data interpretation is still lacking though. The aim of this Rapid Communication is to shed light on relaxation phenomena in liquids by showing that a clear interpretation can be given of the characteristic times involved in the description of the dynamic structure factor $S(Q,\omega)$ at high wave vector Q.

Molecular fluids have also been extensively studied [4] through spectroscopic and molecular-dynamics (MD) simulation methods. For such systems it can be argued [5] that the correlation relevant to translational dynamics is the one between the molecular centers of mass. Here we consider the case of CO_2 and CD_4 in their dense liquid state. Indeed, we recently reported [5–7] accurate analyses of their translational dynamics as represented by the carbon-carbon (CC) partial dynamic structure factor $S_{CC}(Q,\omega)$ since in both molecules the carbon atom occupies the barycentric position. Such data were calculated by means of MD simulation with experimentally validated anisotropic intermolecular potentials [8,9]. This is the unique mean we have up to now to determine the purely translational part of the total $S(Q,\omega)$ in molecular fluids. In the following, all dynamical quantities will refer to the center-of-mass–center-of-mass correlation although we shall omit the subscript CC to simplify the notation.

$S(Q,\omega)$ spectra are usually analyzed and interpreted in terms of a generalized Langevin equation of motion for the intermediate scattering function $F(Q,t)$, which acquires a hierarchical nature through the definition of a sequence of memory functions [1]. The closure of the equation hierarchy is typically carried out at the level of the second-order memory function $M(Q,t)$, for which a simple time evolution is assumed as an "ansatz" defining the model interpretation.

$M(Q,t)$ is customarily built with one or more time exponentials and/or a $\delta(t)$ function. This choice reflects the physically sound concept that memory decays in first approximation exponentially, with $\delta(t)$ possibly modeling a situation where the decay is very fast compared to the fluid time scale set by $F(Q,t)$. We will not consider here memory functions containing other forms of time dependence.

When $M(Q,t)$ is modeled as said above, $F(Q,t)$ will show the presence of properly defined collective modes; one or more of them are nonpropagating modes decaying exponentially with time, while two others consist of exponentially damped oscillations corresponding to propagating excitations. Consistently, the spectrum $S(Q,\omega)$ is the sum of a number of quasielastic Lorentzian lines plus two inelastic ("Brillouin") lines [6].

It is worth noting, however, that the presence of a $\delta(t)$ term in $M(Q,t)$ leads to an infinite fourth frequency moment of $S(Q,\omega)$ [6]. This can limit considerably the spectral range in which the data can be theoretically reproduced at the level of the second-order memory function, which otherwise has the capability of giving a finite fourth moment as well. Indeed, as shown below, a memory modeled with one exponential and a δ term, such as the one corresponding to linearized hydrodynamic theory [6], will not be proven adequate for the cases under study although any valid model is bound to recover the hydrodynamic theory of fluids in the $Q \rightarrow 0$ limit.

We then adopt for $M(Q,t)$ a phenomenological time evolution made of two exponentials, which, as shown below, turns out to be the minimum required for an accurate description of the spectral data. This approach leads to the introduction of an extra relaxation mode in $F(Q,t)$, with respect to the hydrodynamic description, which appears to be necessary to correctly interpret the spectra of collective modes for Q in the range between $\sim 0.1Q_p$ and $\sim 0.8Q_p$. Here Q_p is the main peak position of the static structure factor $S(Q)$, i.e., the frequency integral of $S(Q,\omega)$. The de-

tailed analysis of the Q dependence of all the quantities which define either the memory model or the spectral distribution allows to disclose the existence of quantitative connections among the various times involved in the behavior of $M(Q,t)$ and $F(Q,t)$.

The so-called viscoelastic (VE) model for $M(Q,t)$ is

$$M(Q,t) = [\omega_L^2(Q) - \gamma(Q)\langle\omega_Q^2\rangle]\exp[-t/\tau(Q)] + [\gamma(Q) - 1]$$
$$\times \langle\omega_Q^2\rangle\exp[-t/\tau_T(Q)], \quad (1)$$

where $\langle\omega_Q^2\rangle$ is the normalized second frequency moment of $S(Q,\omega)$, $\omega_L^2(Q)$ is the ratio of fourth to second spectral moment, and $\gamma(Q)$ is a Q-dependent generalization of the thermodynamic specific-heat ratio γ_0. These parameters define the amplitudes of the two exponential terms of $M(Q,t)$, whose characteristic times are $\tau(Q)$ and $\tau_T(Q)$.

All the above quantities tend to their respective hydrodynamic expressions for $Q \to 0$ so that $\langle\omega_Q^2\rangle \sim c_s^2 Q^2/\gamma_0$, $\omega_L^2(Q) \sim c_L^2 Q^2$, and $\tau_T(Q) \sim 1/(\gamma_0 D_T Q^2)$, where c_L is the $Q \to 0$ limit of the infinite-frequency sound velocity, c_s is the adiabatic sound speed, and D_T is the thermal diffusivity. The $Q \to 0$ limit of $\tau(Q)$ is given by $\tau_0 = \nu/(c_L^2 - c_s^2)$, where ν is the kinematic longitudinal viscosity.

For ease of reference, we denote the two terms of the memory (1) as "viscous" and "thermal," extending to the whole Q range the meaning that they assume in the $Q \to 0$ limit where τ and τ_T are directly bound to viscosity and thermal diffusion, respectively, although such identifications become less stringent when a nonhydrodynamic regime is attained with increasing Q.

The general expression of the spectrum

$$S(Q,\omega) = \frac{S(Q)}{\pi}\mathrm{Re}\left[i\omega + \frac{\langle\omega_Q^2\rangle}{i\omega + \tilde{M}(Q,i\omega)}\right]^{-1}, \quad (2)$$

where $\tilde{M}(Q,z)$ is the Laplace transform of $M(Q,t)$, takes in the VE case the form [6]

$$S(Q,\omega) = \frac{S(Q)}{\pi}\left[I_1\frac{z_1}{z_1^2 + \omega^2} + I_2\frac{z_2}{z_2^2 + \omega^2} + I_s\frac{z_s + b_s(\omega + \omega_s)}{z_s^2 + (\omega + \omega_s)^2}\right.$$
$$\left. + I_s\frac{z_s - b_s(\omega - \omega_s)}{z_s^2 + (\omega - \omega_s)^2}\right] \quad (3)$$

made of two nonpropagating plus two propagating modes. The corresponding time correlation is

$$\frac{F(Q,t)}{F(Q,0)} = I_1 e^{-z_1 t} + I_2 e^{-z_2 t} + 2I_s e^{-z_s t}\frac{\cos(\omega_s t - \varphi)}{\cos\varphi}, \quad (4)$$

where b_s and φ are defined as in Ref. [6]. For the sake of simplicity the Q dependence of the parameters of $M(Q,t)$ and $S(Q,\omega)$ will not be indicated in the following.

Equation (4) shows that the translational time correlation has a damped harmonic oscillator component. We recall [6] that this is true for the whole class of memory functions defined by exponential or δ functions and that the propagation (damped) frequency ω_s is related to two intrinsic properties of the oscillator, namely, the "self" (undamped) fre-

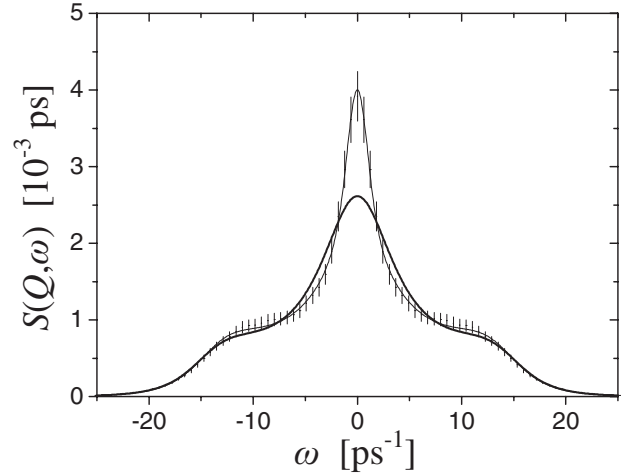FIG. 1. MD simulated center-of-mass $S(Q,\omega)$ of CD_4 at $Q = 8.2$ nm^{-1} (error bars). The thin line is the VE best fit, and the thick line is the best fit obtained with a hydrodynamiclike memory model (see text).

quency Ω and the damping coefficient z_s, by the relation $\omega_s = \sqrt{\Omega^2 - z_s^2}$, where $\Omega = \sqrt{\langle\omega_Q^2\rangle}/z_1 z_2 \tau\tau_T$ if model (1) is assumed.

MD $S(Q,\omega)$ data were calculated for 28 Q values between 2.0 and 15.9 nm^{-1} in CD_4 at $n = 16.6$ nm^{-3} and $T = 97.7$ K and for 58 Q values between 1.4 and 14.9 nm^{-1} in CO_2 at $n = 15.88$ nm^{-3} and $T = 221.9$ K, where n is the molecular number density and T the temperature. Details of the computer calculation method have already been given [5,8]. The analysis is based on fitting line shape [Eq. (3)] to MD spectra using as free parameters, besides $S(Q)$, either those of the memory [Eq. (1)] or directly those of Eq. (3) itself. In the latter case z_1, z_2, z_s, ω_s, and I_1 are fitted, while I_2, I_s, and b_s are derived from them [5]. For whatever choice of the fit parameters, all quantities in both Eqs. (1) and (3) can be obtained as functions of Q as explained in Refs. [5,6]. As an example, Fig. 1 shows one CD_4 spectrum together with the line yielding the best fit up to a frequency in the wings where the intensity decreases to $10^{-3} \times S(Q,0)$. The VE fit is very good at all Qs for both liquids. In Fig. 1 we also show the inadequacy of the best fit obtained with a simpler hydrodynamiclike $M(Q,t)$ model where the first exponential is replaced by a $\delta(t)$ term, which reduces the number of spectral lines to three [6].

Figure 2 displays Ω, z_s, and ω_s versus Q and shows that propagation is maintained ($\omega_s > 0$) up to $Q \sim 14$ nm^{-1} in CO_2 and $Q \sim 15.5$ nm^{-1} in CD_4. Beyond such Q values propagation is forbidden ($\omega_s = 0$) because Ω either stops increasing with Q (CO_2) or begins to decrease (CD_4) leading to $\Omega < z_s$ and bringing the oscillator into its overcritical damping state. When this happens, Eqs. (3) and (4) are modified as explained in Ref. [5].

We next discuss in detail the Q dependence of the time decay constants relevant for the collective dynamics. Besides τ_T and τ, we consider the life times of the modes of $F(Q,t)$ or $S(Q,\omega)$ defined as $\tau_1 = 1/z_1$, $\tau_2 = 1/z_2$, and $\tau_s = 1/z_s$. In Eqs. (61a) and (68a) of Ref. [6] we showed that, with the assumption of the memory model (1), the rigorous relation
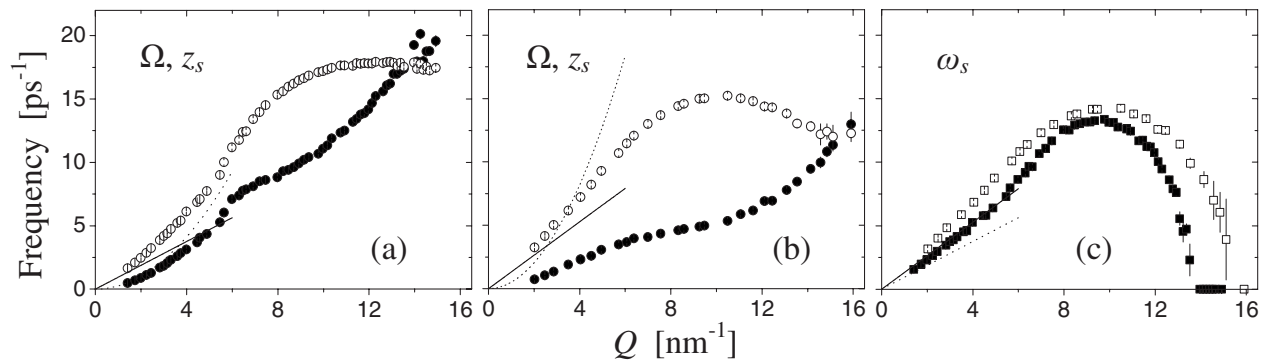
FIG. 2. Parameters of the damped harmonic oscillator representing the propagating modes. (a) Ω (open circles) and z_s (full circles), with the respective lowest-order hydrodynamic behaviors $c_s Q$ (solid line) and $[(\gamma_0 - 1)D_T + \nu]Q^2/2$ (dotted line). Data refer to CO_2. (b) The same as in (a) for CD_4. (c) Dispersion curve ω_s for CO_2 (full squares) and CD_4 (open squares) with the respective lowest-order hydrodynamic behavior $c_s Q$ (dotted line for CO_2, solid line for CD_4). For the values of c_s, γ_0, D_T, and ν see Refs. [5,11].

$$1/\tau_T + 1/\tau = 1/\tau_1 + 1/\tau_2 + 2/\tau_s \qquad (5)$$

is obeyed, which highlights that the parallel decay of the memory into two channels implies the parallel decay of the correlation into four channels, with conservation of the total decay frequency.

Figure 3 shows the Q dependence of the various τs and, for comparison, the value of the Enskog mean free time t_E which provides an estimate of the collision time in a liquid taking into account its structural properties. For a fluid of hard spheres with diameter d, $t_E = \sqrt{m/\pi k_B T}/[4nd^2 g(d)]$, where m is the molecular mass, k_B is the Boltzmann constant, and $g(d)$ is the pair distribution function at contact. In our real molecular systems, an effective diameter d has been estimated by fitting at best the hard sphere $S(Q)$ [10] to MD results, obtaining $d = 0.354$ nm and $t_E = 0.107$ ps for CO_2 and $d = 0.379$ nm and $t_E = 0.056$ ps for CD_4.

From the results displayed in Fig. 3 we can observe the following:

(a) An overall deviation from hydrodynamics sets on at rather low Q. The departure is larger in CD_4 than in CO_2 and a transition to clear nonhydrodynamic behavior definitely takes place around $Q \sim 3$ and ~ 5 nm^{-1}, respectively. Thus,

when the wavelength of the probed fluctuations becomes of the order of 1–2 nm, corresponding to volumes containing a few tens of molecules, all relaxations in both memory and correlation function change character.

(b) τ_1/γ and τ_T, which are prescribed by theory to have the same hydrodynamic limit [6], actually coincide at all Qs. This fact highlights a close relation between the thermal memory relaxation and the correlation mode labeled as 1.

(c) τ_T and τ differ by at least one order of magnitude in the whole Q range, therefore describing two distinct processes in the memory relaxation, with the thermal one decaying much more slowly than the viscous one. The latter appears to be directly related to binary collisions since $\tau \lesssim t_E$, while the slow relaxation of the thermal process suggests that more collisions, therefore more molecules, are involved in the decay of the correlation.

(d) The memory fast decay time τ decreases smoothly with increasing Q and shows a plateau between $Q \sim 5$ and ~ 8 nm^{-1}, where correlation distances of the order of 1 nm are probed. Interestingly, in this Q range a clear change occurs in the relation of τ with the time decay of the correlation mode labeled as 2 and with the life time of the propagating modes. At high Q, we find $\tau \sim \tau_s/2$, indicating that the damping of the propagating modes changes continuously from a
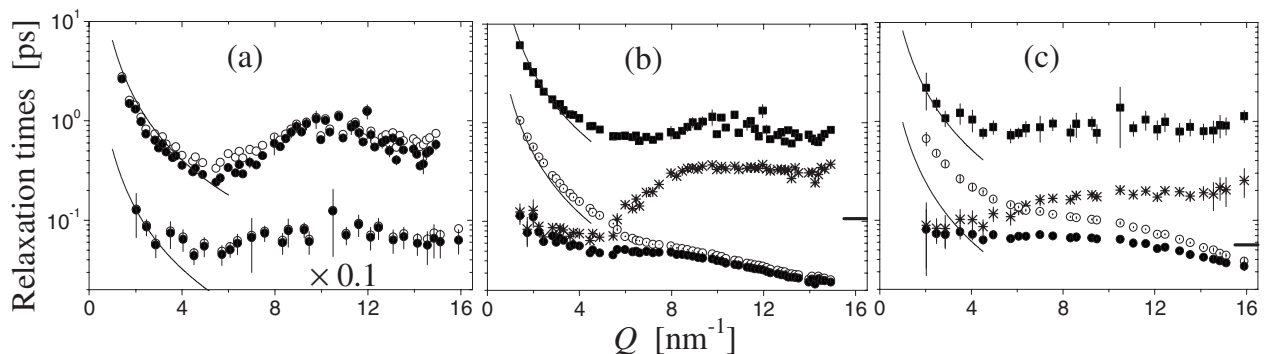

FIG. 3. Characteristic times of $M(Q,t)$ and $F(Q,t)$. (a) τ_T (dots with error bars) and τ_1/γ (open circles). CO_2 data are the upper curves; CD_4 plots are shifted downwards by one decade for graphical convenience. Solid lines give the lowest-order hydrodynamic behavior $1/(\gamma_0 D_T Q^2)$. (b) τ_1 (full squares), τ_2 (stars), $\tau_s/2$ (open circles), and τ (dots) for CO_2. Solid lines give the lowest-order hydrodynamic behavior $1/(D_T Q^2)$ of τ_1 and $1/[(\gamma_0 - 1)D_T + \nu]Q^2$ of $\tau_s/2$. The short line on the right side marks the value of t_E. (c) The same as in (b) for CD_4.

hydrodynamic character at low Q into a behavior dominated by the fast memory relaxation process which in turn is due to binary collisions as shown above.

(e) On the other hand, τ_2 behaves like τ at low Q, showing that the fast memory relaxation is reflected in the decay of a nonpropagating correlation mode but clearly increases, more evidently in CO_2, up to a practically constant value at high Q which is largely above the collision time, namely up to $\tau_2 \sim 3t_E$. Such a change to a "long" living nonpropagating mode in $F(Q,t)$ suggests the existence in the liquid of clusters with dimensions of order 1 nm^3 or less with life time τ_2 quite larger than the collision time. However, such microscopic structures do not affect the life time τ_s of propagating excitations, which remains of the order of t_E.

In conclusion, we have shown that a suitably modeled memory function explains in detail the translational dynamics of simple molecular liquids determined through the center-of-mass dynamic structure factor simulated with experimentally tested pair anisotropic potentials. For both studied liquids, a VE modeling proves adequate in the Q range up to $Q \sim Q_p$ and reveals strong relations among the charac-

teristic times of $M(Q,t)$ and $F(Q,t)$. The first nonpropagating correlation mode directly reflects the decay of the thermal part of the memory function. The second nonpropagating mode and the pair of propagating modes that give rise to the Brillouin spectral lines are both related in different Q ranges to the faster decay process in the memory, which is dominated by binary collisions. A transition from a collisional to a collective behavior of τ_2 is detected, which can be interpreted as the evidence that nanoscale clusters with life time of the order of a few tenths of picosecond do exist in the liquid. Such a transition occurs at Q values slightly larger than those where the onset of nonhydrodynamic behavior takes place.

Our approach also shows that the analysis of the Q dependence of the memory time constants provides only a limited picture of the evolution of structural properties at the nanometer scale, while a far deeper insight can be obtained if the time behavior of $F(Q,t)$ is also explored. In this way, for example, important information on structural relaxations contained in the second nonpropagating spectral mode can be evidenced.

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