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Relative pair dynamics in simple supercooled liquids: Longitudinal contributions

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The pair dynamics of simulated argon samples is investigated at the melting (85 K), supercooled (55 K), and quenched (20 K) liquid states, and in the crystal (20 K) state. Tagged pairs, initially lying in a given shell, were divided into incoming and outgoing groups and followed along simulated trajectories. Over them, specific correlation functions $\Delta B(r_0;t)$, involving the pair separation vector projected along its initial value $\mathbf{r}_0$ (longitudinal dynamics), have been evaluated. More or less pronounced oscillations are detected according to the temperature of the thermodynamic states (and, obviously, their solid or liquid nature); for each state, they depend on the initial pair distance r_0, too. The oscillations vanish after few picoseconds (fast dynamics) in the case of crystal, whereas in the supercooled liquid they decay towards a plateau, whose height increases with the temperature. It is shown that the power spectrum of $\Delta B(r_0;t)$ practically yields the same density of states (DOS) produced by the pair velocity correlation function. The $\Delta B(r_0;t)$ functions obtained from the argon crystal at 20 K produce DOS curves dominated by two main frequency contributions, at about 40 and 60 cm^{-1} (Einstein and Debye frequency, respectively). Their shape is quite well reproduced by damped harmonic oscillator–like (DHO) functions vibrating at that frequencies. In liquid states, the $\Delta B(r_0;t)$ plateau, that forms after the fast DHO dynamics, accounts for the system diffusivity. The relaxation towards the plateau is modeled by an exponential function whose decay time is comparable with the average vibration period. Evidence that the liquid states conserve a certain memory of the vibrational modes of the crystal is obtained. In these states, the DHO functions at the Einstein and Debye frequencies plus an exponential function cannot reproduce the $\Delta B(r_0;t)$ shape. A pronounced shoulder, that forms around 0.5 ps, requires the contribution of a third DHO. In the DOS, it yields a band centered below 20 cm^{-1} that produces low frequency DOS excess in comparison with the DOS of the crystal. This contribution is present in liquid and supercooled high temperature states and survives near the temperature of the glass transition whereas the diffusion practically vanishes.

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I. INTRODUCTION

Recently, the study of fluid systems has devoted considerable emphasis to the interplay between collective and single-particle dynamics. For time smaller than a characteristic time τ_α (usually referred to as the time of the structural or α relaxation), the dynamics of a liquid should be described in terms of physical quantities typical of the solid state physics. So, one can use the concepts of phonons, normal modes, and others, especially when supercooled liquids or amorphous solids are considered. Many investigations on these systems have been recently performed, stimulated by progresses in the experimental probing of the terahertz frequency domain [1] and by improved performance of computing machines [2]. It has been shown that a fast sound installs in many liquids, the crossover from the normal to the fast dispersion curves being controlled by the τ_α value [1,3]. Various attempts of describing the dynamics of liquids via normal modes have also been performed [4–8]. The instantaneous modes are found to reproduce the dynamics at very short times, later producing unphysical divergences caused by the imaginary frequencies [6]. While the connection between imaginary frequencies and fluidity of the system is certain [4,5,9] (e.g., the diffusion coefficient) the exact relationships are not completely clear and object of current research [9–11]. All these theoretical, experimental, and computational progresses have also produced strong acceleration in the studies of vitreous systems and on the nonequilibrium thermodynamics [2,12,13]. For example, in several glasses, DOS intensity excess has been found in the terahertz region. The microscopic origin of the excess and its general presence in supercooled liquids are unclear.

Notwithstanding these efforts of the scientific community, one still searches for an adequate model to describe the dynamics in dense and supercooled simple liquids. The intriguing open problem is to obtain a satisfactory explanation of the microscopic mechanisms giving rise to the low frequency DOS intensity diffusion included. It is generally recognized that, in a supercooled or melting monatomic liquid, an atom undergoes quasiharmonic vibrations around an equilibrium point, and the jumps from one equilibrium position to another are responsible for diffusion. The study of the many particle potential energy landscape underlying a given thermodynamical state demonstrated the presence of local minima, the inherent structures [14], that the system visits during the diffusion. Zwanzig [15] developed a model for the velocity correlation function, in which a system in a local minimum is characterized by normal modes whose coherence is destroyed by the diffusive jumps. The normal mode density and a parameter of the model were evaluated in different ways, mainly through instantaneous [4,5] or quenched normal modes and cage relaxations [16,17]. Alternatively, one tries to obtain shoulder and double well landscape profiles [18] for the nondiffusive-anharmonic and diffusive modes, respectively. In water, for example, the relation between the fraction of double well modes and diffusion has been proved [19,20]. Generally, it is difficult to perform landscape profile classifications, since the instantaneous modes eigenvalues lose their physical meaning after few steps of dynamical evolution. To overcome this difficulty, a different approach has been followed by Wallace and coworkers [21–24], that developed the original idea of Frenkel: since the fusion has small effects over the heat capacity, the vibrational motions of liquids and solids should remain essentially the same. The strong increase of the diffusion coefficient is explained by the irregular distribution of the equilibrium points, as in an amorphous solid, and by their jumping which produces the ‘‘transit’’ of the system from one local minimum to another of same potential energy (random valleys). The transit must be local, i.e., involving a small number of near atoms, and fast (at limit instantaneous). Consequently, the set of normal modes which describe the vibrational dynamics of the system in random valleys varies very rapidly during diffusion. The attempt of modeling diffusive processes through specific distributions of normal modes plus damping was abandoned and the opposite picture of independent atom dynamics was chosen to describe the diffusion process. A reliable description of monatomic liquid metal velocity correlation function (VCF) was obtained.

In the present work, we deal with the relative pair dynamics of simple supercooled liquids probed by a specific correlation function $\Delta B(r_0;t)$ which depends on the initial pair separation r_0. Such a function has been used to explain the oscillations at short times observed over the time dependent relative distance $R^2(r_0;t)$ of water molecule pairs [25–27]. It is suitable for capturing vibrational modes and derive the corresponding translational density of state (DOS). In supercooled water, the fraction of nonharmonic motions is small [7] and the effect they produce over the DOS of the relative pair dynamics is small too. In this paper, we investigate the short time dynamics of three states of liquid argon, namely, the melting state, the supercooled state at 55 K, and the quenched state at 20 K (the temperature of the glass transition is around 17–18 K). This last state will be also referred to as amorphous state since the diffusion coefficient is nearly vanishing. The fluid argon has a considerable high quantity of nonharmonic modes; it is therefore suitable for understanding how these modes affect the short time dynamics. Indeed, while the idea of considering more or less damped phonons appears quite natural in ‘‘strong’’ liquids (as for the hydrogen bond dynamics in water), it could appear unreliable in the ‘‘fragile’’ ones (as for the noble gases). Our aim is to clarify the following points.

(1) How much the vibrational motions in liquid states are reminiscent of the phonon frequencies of the crystal.

(2) To state if the nonvibrational relaxations occur within the time of the fast dynamics or involve an higher time scale length.

(3) The presence of a low frequency DOS excess was demonstrated for the longitudinal part of the translational dynamics of fast quenched 20 K argon [28]. Is the excess also present in the supercooled and melting states?

(4) The diffusive dynamics produces nonvanishing DOS intensity at zero frequency. It is interesting to know if the processes are entangled with contributions at high and/or low frequency (excess included) or evolve independently.

The investigations and arguments of the paper develop as follows. In Sec. II, the scheme of the molecular dynamics simulated experiments is presented; an introductory comparison between argon and water fluids and preliminary results on the relative square distance $R^2(r_0;t)$ are reported. In Sec. III A, some theoretical recalls, deriving the expression of $\Delta B(r_0;t)$ for the longitudinal pair dynamics, are reported in the purely vibrational case; results for the crystal at 20 K are presented. In Sec. III B, the presence of nonvibrational motions, increasing with temperature, is shown. To represent them, a phenomenological exponential relaxation is introduced. In Sec. III C, the relationship between $\Delta B(r_0;t)$ and the pair VCF is introduced. It is shown that the plateau of $\Delta B(r_0;t)$, formed when the short time dynamics ceases, is due to nonvibrational motions and to the system diffusivity. In Sec. IV A, models for the vibrational and nonvibrational dynamics are applied and the results of a best fitting procedure are reported. The attempt of showing that the liquid dynamics is reminiscent of the vibrational modes of the crystal is presented. In Sec. IV B, the connection between VCF, density of state, and diffusion is investigated for different temperatures and different initial pair separations. In Sec. IV C, the problem of the excess at low frequency is discussed. Section V reports final remarks and conclusions.

II. MOLECULAR DYNAMICS SIMULATIONS AND AN ARGON-WATER COMPARISON

In this work, the main quantities of interest are the correlation functions obtained from the interparticle center of mass (c.m.) vector $\mathbf{R}_{ij}$. In particular, we will study the time evolution of $\mathbf{R}_{ij}(t)$ along directions parallel to the zero time direction $\mathbf{R}_{ij}(0)$ (longitudinal dynamics). Let us to indicate with $\mathbf{u}_{ij}$ the unit vector of $\mathbf{R}_{ij}$, and define the functions

$$B(r_0;t)=\langle \mathbf{R}_{ij}(t)\cdot \mathbf{u}_{ij}(0)-R_{ij}(0)\rangle_0/\langle R_{ij}(0)\rangle_0, \tag{1}$$

$$R^2(r_0;t)=\langle R^2_{ij}(t)\rangle_0-\langle R^2_{ij}(0)\rangle_0, \tag{2}$$

where $\langle\ \rangle_0$ stands for average over tagged pairs which, at the initial time, have the c.m. distance $r_0=R_{ij}(0)$ ranging within the limits $r_a \leqslant r_0 \leqslant r_b$.

In the case of supercooled water, it has been shown [26] that both the Eqs. (1) and (2) contain contributions of vibrational modes and both can be also used to derive part of the translational DOS. The presence of such modes in the short time dynamics is detectable, for many initial pair separations r_0 [27], as a modulation superimposed to the smooth trend of the functions. In this work we investigate if this modulation affects the functions $B(r_0;t)$ and $R^2(r_0;t)$ also in the case of liquid argon and to what extent it represents a solidlike dynamics [29]. Molecular dynamics (MD) technique at con-

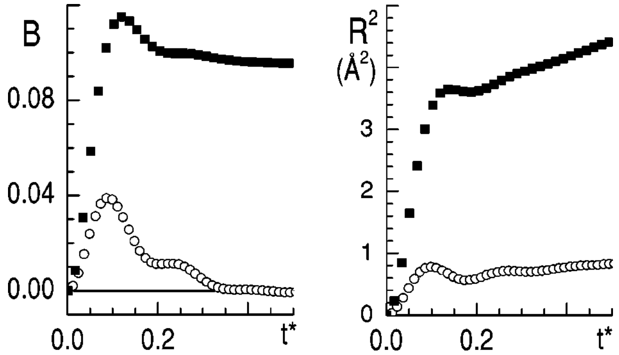

FIG. 1. $B(r_0;t)$ and $R^2(r_0;t)$ for pairs initially lying in the first half of the first coordination shell. Open circles—water in the supercooled state at 245 K ($r_0<2.72$ Å); full squares—supercooled argon at 55 K ($r_0<3.75$ Å). The reduced time is $t^*=t/\tau$ and $\tau=(M\sigma_0^2/RT)^{1/2}$, where σ_0^2 is evaluated from the position of the $g(r)$ first peak (3.75 and 2.72 Å for argon and water, respectively).

stant NVE conditions, Lennard-Jones potential and cubic box with periodic boundary conditions were used to produce microscopic configurations of an atomic system [30]. The parameters of the Lennard-Jones potential were those of argon: $\sigma=3.405$ Å, $\varepsilon=1.654\times10^{-21}$ J. The number of atoms was 1372 for the liquid at $T=85$ K, 4000 for the supercooled ($T=55$ K) and quenched (20 K) liquids, and for the crystal at $T=20$ K. All the runs were performed at the triple point density. For all the runs, after equilibration, the configurations were stored every four time steps, the time step being of 5 fs. The crystalline solid argon at 20 K was obtained by starting from the 0 K fcc lattice. The liquid configurations were produced via the standard technique of gently cooling high temperature disordered systems and equilibrating for a suitable time at the desired temperature. In particular, the quenched state at 20 K was obtained from the 55 K supercooled liquid by lowering the temperature by about 10 K, through velocity scaling at every 5 ps for 50 ps, in four runs, each one during 100 ps [31].

Equations (1) and (2) were computed for supercooled liquid argon (55 K) and compared with those of supercooled water. In Fig. 1 the results for $B(r_0;t)$ and $R^2(r_0;t)$ are shown. The limits r_a and r_b of the r_0 range select particles initially lying in the first half of the first coordination shell. To make the comparison easier, the time has been expressed in terms of reduced units. As is seen, oscillations are present over both the systems and have comparable periods. In argon, a greater damping seems however to be present [32]. To derive vibrational modes (see Sec. III later), at the initial time, one selects approaching (in) and departing (out) pairs of particles. Then, the correlation function

$$\Delta B(r_0;t)=[B^{(out)}(r_0;t)-B^{(in)}(r_0;t)]/2, \tag{3}$$

or similar expressions for $R^2(r_0;t)$, yields the vibrational modes. In Fig. 2, the functions $B(r_0;t)$, $B^{(out)}(r_0;t)$, and $\Delta B(r_0;t)$ are shown for pairs of supercooled argon atoms of the first coordination shell at 55 K. Note the relevant difference between the argon $B(r_0;t)$ of Figs. 1 and 2, the first one being signed by oscillations that are not present in the second one. This occurs because the modulations of the smooth $B(r_0;t)$ trend disappear for particular choices of the r_0 range, such as the first coordination shell [28]. It can be also seen that $\Delta B(r_0;t)$ shows a flat trend (a plateau) after few picoseconds. We will show that the short time dynamics is dominated by the vibrational motions, while the asymptotic trend is related to the system diffusivity. For this purpose, it is worthy to remember that we limit our study to the fast dynamics, i.e., to $t<5$ ps. Beyond this time and for low temperatures, the structural relaxations occur. In these cases, the true diffusion coefficient is reached only after the time τ_α, which can be very long at low temperatures, as in the case of water [33]. For this reason, it is more appropriate to relate the plateau height to the system diffusivity rather than to the diffusion coefficient itself.

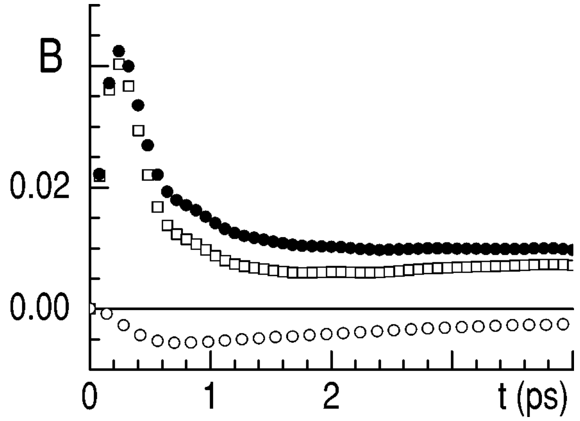

FIG. 2. $B(r_0;t)$ (open circles), $B^{(out)}(r_0;t)$ (open squares), and $\Delta B(r_0;t)$ (full circles) for pairs of supercooled argon atoms initially lying in the first coordination shell ($r_0<3.75$ Å), at $T=55$ K.

III. THEORETICAL RECALLS AND PRELIMINARY RESULTS

For atomic systems characterized by weak interactions (such as the Lennard-Jones ones), the effects of nonvibrational motions can be non-negligible. So, also at the melting point, $T\cong85$ K, the diffusive contributions can affect significantly the correlation function $\Delta B(r_0;t)$. To have only vibrational modes, supercooling is necessary. For liquid argon, the diffusive contributions become practically negligible (see Fig. 4 later) at the temperature of 20 K, the glass transition temperature being around 17 K. In this work the independence between vibrational and diffusive motions is assumed; the two dynamics are discussed separately in Secs. III A and III B.

A. The vibrational approximation

For a crystalline or amorphous solid the diffusion is vanishing and the fast microscopic dynamics is due to vibrational motions only. In this case, after a small time interval from the initial observation time, the c.m. position of an atom i, along the Cartesian axis α, can be written as

$$x_{i\alpha}(t)=x_{i\alpha}(0)+\sum_{n} a_{i\alpha,n}\chi_n(t), \tag{4}$$

where $x_{i\alpha}(0)$ is the initial position and $a_{i\alpha,n}$ is the component of the nth mode χ_n along $i\alpha$. The interparticle c.m. separation vector $\mathbf{R}_{ij}$ can be written as

$$\mathbf{R}_{ij}(t)=\mathbf{R}_{ij}(0)+\sum_{n} \mathbf{A}_{ij,n}\chi_n(t), \tag{5}$$

where $\mathbf{A}_{ij,n}$ is the vector of components $A_{ij\alpha,n}=a_{j\alpha,n}-a_{i\alpha,n}$. If we consider only vibrational nearly harmonic motions [34], the correlation function $B(r_0;t)$ of Eq. (1) becomes

$$B_h(r_0;t)=\left\langle \sum_{n} A^{p}_{ij,n}\chi_n(t)\right\rangle_0 \Big/ \langle R_{ij}(0)\rangle_0, \tag{6}$$

where $A^{p}_{ij,n}$ is the projection of $\mathbf{A}_{ij,n}$ over $\mathbf{u}_{ij}(0)$. $B_h(r_0;t)$ yields the average of the normal modes projected over the space directions $\mathbf{u}_{ij}(0)$. The $\chi_n(t)$ kinematic equation is

$$A^{p}_{ij,n}\chi_n(t)=Q_{ij,n}\cos(\omega_n t)+V_{ij,n}\sin(\omega_n t)/\omega_n, \tag{7}$$

where $Q_{ij,n}=\mathbf{A}_{ij,n}\cdot\mathbf{u}_{ij}(0)\chi_n(0)$, $V_{ij,n}=\mathbf{A}_{ij,n}\cdot\mathbf{u}_{ij}(0)\dot{\chi}_n(0)$, and ω_n and $\dot{\chi}_n(0)$ are the frequency and the initial velocity of the nth mode, respectively. The average over $V_{ij,n}$ vanishes for the equilibrium distribution of the initial velocities. With the same arguments used in Ref. [25], one can introduce selection in the pair velocity at the initial time and obtain two particle groups, the approaching (in) and departing (out) ones, whose dynamics is followed along the simulated trajectories. The averages of $Q_{ij,n}$ and $Q^{(out)}_{ij,n}$ coincide because they depend on the coordinate distribution only. Then by subtracting $B^{(out)}_h(r_0;t)$ from $B_h(r_0;t)$ one has [25]

$$\Delta B_h(r_0;t)=\sum_{n} \langle V^{(out)}_{ij,n}\sin(\omega_n t)/\omega_n\rangle_0/\langle R_{ij}(0)\rangle_0, \tag{8}$$

which contains the mode dynamics. Equation (8) can be written as

$$\begin{aligned}\Delta B_h(r_0;t)&=\sum_{n}\left\langle V_{ij,n}\int \delta(\omega-\omega_n)\frac{\sin(\omega t)}{\omega}d\omega\right\rangle_0 \Big/ \\ &\qquad \langle R_{ij}(0)\rangle_0 \\ &=\int D_h(r_0;\omega)\frac{\sin(\omega t)}{\omega}d\omega,\end{aligned} \tag{9}$$

where $D_h(r_0;\omega)$ is the power spectrum given by the Fourier transform (FT)

$$D_h(r_0;\omega)=\int \Delta B_h(r_0;t)\,\omega\sin(\omega t)dt. \tag{10}$$

We will refer to $D_h(r_0;\omega)$ as to a vibrational DOS since it plays as a density of state; in Sec. IV B we will show that it practically coincides with the usual definition of the vibrational DOS derived from the pair VCF. In a solid, the index n in Eqs. (8) and (9) runs over the main phonon contributions. However, even in a case of a perfect argon crystal, since $\mathbf{u}_{ij}(0)$ does not select a fixed crystallographic direction, the pure phonon contributions are expected to broaden and mix. To represent the resulting contribution to the DOS, we will use a phenomenological expression (DHO-like form) given by

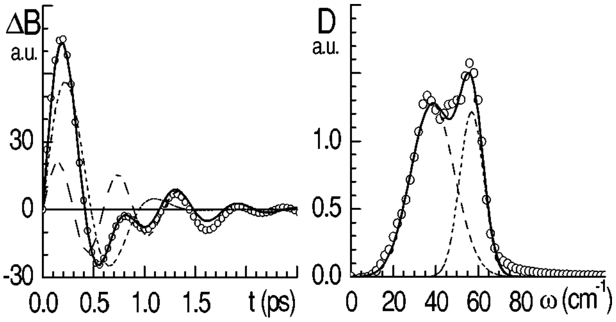

FIG. 3. $\Delta B(r_0;t)$ and the related DOS $D(r_0;\omega)$ both in arbitrary units, for pairs of crystalline argon atoms at $T=55$ K, initially lying in the first coordination shell. Long and short dashed curves represent the contributions of two DHO vibrating at the frequencies of about 40 and 60 cm^{-1}. Solid curve and points represent the fit of Eq. (11) and the MD data, respectively.

$$\Delta B_h(r_0;t)=\sum_{n} x_n\sin(\omega_n t)\exp-(t/\tau_n)^2, \tag{11}$$

where n runs over few principal frequencies ω_n, and x_n and τ_n are parameters. In a solid, one expects that ω_n is nearly equal to the main frequencies of the phonon branches. For the fcc argon crystal and along a specific crystallographic direction, one expects three different frequencies corresponding to the three dispersion curves (eventually degenerate along particular directions). In Fig. 3, $\Delta B(r_0;t)$ and $D(r_0;\omega)$ are shown for solid argon at the temperature of 20 K and for pairs of the first coordination shell. The fit with two DHO reproduces satisfactorily the strong oscillations of $\Delta B(r_0;t)$; the corresponding broadened lines in the DOS are at about 40 and 60 cm^{-1}, the Einstein and Debye frequencies, respectively. These results for the perfect crystal justify the use of the DHO line shape and suggest its application to the dynamics of supercooled liquid states. In such cases, to compare $\Delta B(r_0;t)$ and $D(r_0;\omega)$ due to different thermodynamic states, it is worth introducing the normalized quantities

$$\Delta B^*(r_0;t)=\frac{\Delta B(r_0;t)}{\int_0^\infty D(r_0;\omega)d\omega},$$

$$D^*(r_0;\omega)=\frac{D(r_0;\omega)}{\int_0^\infty D(r_0;\omega)d\omega}. \tag{12}$$

The meaning of this kind of normalization is discussed in Sec. III C, later.

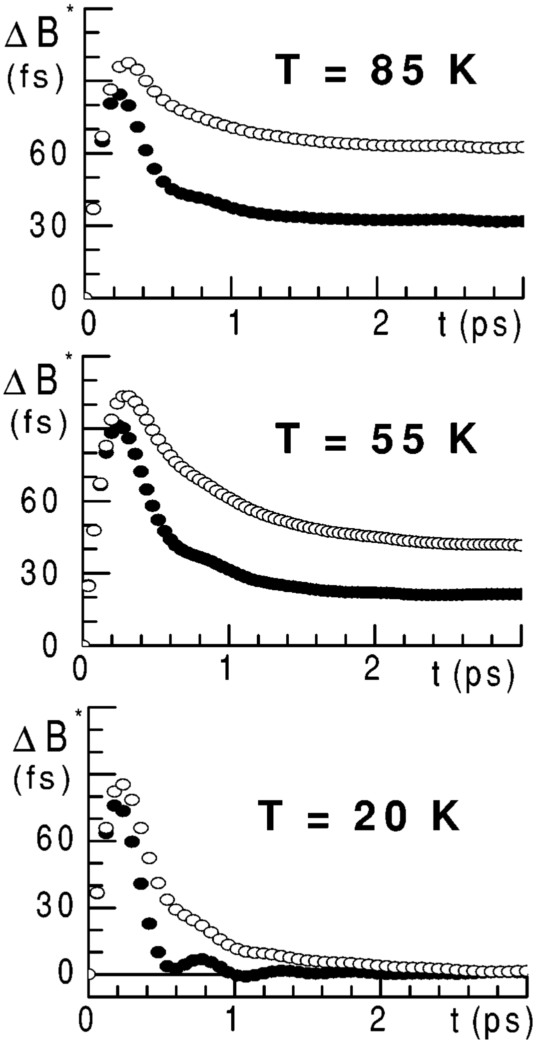

FIG. 4. $\Delta B^*(r_0;t)$ for pairs of atoms initially lying in the first coordination shell (full circles) and in the range 18.8 Å $<r_0<19.1$ Å (open circles).

B. The nonvibrational contributions

Figure 4 shows $\Delta B^*(r_0;t)$ for three argon thermodynamic states and two different initial separation r_0, in the first coordination shell and in the shell 18.8 Å$<r_0<19.1$ Å. As is seen, all the $\Delta B^*(r_0;t)$ always reach an asymptotic trend that vanishes for the state at 20 K. Since the plateau height vanishes also in the crystal (see Fig. 3), the asymptotic plateau is attributable to nonvibrational contributions.

We assume that $\Delta B(r_0;t)$ is the sum of vibrational, nearly harmonic, $\Delta B_h(r_0;t)$, and nonvibrational, $\Delta B_{nh}(r_0;t)$, contributions:

$$\Delta B(r_0;t)=\Delta B_h(r_0;t)+\Delta B_{nh}(r_0;t). \tag{13}$$

Equations (10) and (11), and the arguments around them hold within the vibrational approximation. For the nonvibrational contributions, we will assume an exponential relaxation; this is justified mainly by a criterion of simplicity [35]. We write

$$\Delta B_{nh}(r_0;t)=A(r_0)[1-\exp-(t/\tau_e)]. \tag{14}$$

Its power spectrum is

$$D_{nh}(r_0;\omega)=\omega\int_0^\infty A(r_0)[1-\exp-(t/\tau_e)]\sin(\omega t)dt$$
$$=A(r_0)/[1+(\omega\tau_e)^2]. \tag{15}$$

Equation (14) yields $A(r_0)$ for $t\to\infty$, that is, the plateau height of $\Delta B(r_0;t)$. In the case of liquid water and for the longitudinal dynamics, it has been shown that $A(r_0)$ is related to the relative pair diffusion coefficient [35]. Here, we will show this to hold for the longitudinal dynamics of supercooled argon too.

C. The connection with the velocity correlation function

Equation (9) defines by itself the longitudinal part of the translational DOS and it is exact in the limit of a pure vibrating system. It is worth, however, to connect this part with the usual DOS definition derived from the VCF. Moreover, in the case of the nonvibrational dynamics, the physical meaning of the power spectrum, defined by Eq. (15), is not clear. In this section, these two points are addressed by assigning the relation between the $\Delta B(r_0;t)$ correlation function and specific VCF.

We first introduce the function $F(r_0;t)$ satisfying the relation

$$F(r_0;t)=\frac{dB(r_0;t)}{dt}, \tag{16}$$

and search for a relation between $\Delta B(r_0;t)$ and the correlation function of the relative pair velocity $\mathbf{v}_{ij}$. If Eq. (16) is applied to the definition of $B(r_0;t)$ of Eq. (1), one has

$$F(r_0;t)=\langle \mathbf{v}_{ij}(r_0;t)\cdot\mathbf{u}_{ij}(0)\rangle_0/\langle R_{ij}(0)\rangle_0. \tag{17}$$

It is useful to write $\mathbf{v}_{ij}(r_0;t)$ in terms of radial and transverse parts with respect to the vector $\mathbf{u}_{ij}(t)$, i.e., $\mathbf{v}_{ij}(r_0;t)=v_{r,ij}(r_0;t)\mathbf{u}_r(t)+v_{t,ij}(r_0;t)\mathbf{u}_t(t)$, where $\mathbf{u}_r(t)\equiv\mathbf{u}_{ij}(t)$. Then Eq. (17) yields

$$F(r_0;t)=[\langle v_{r,ij}(t)\mathbf{u}_r(t)\cdot\mathbf{u}_r(0)\rangle_0$$
$$+\langle v_{t,ij}(t)\mathbf{u}_t(t)\cdot\mathbf{u}_r(0)\rangle_0]/\langle R_{ij}(0)\rangle_0$$
$$=F_{rr}(r_0;t)+F_{tr}(r_0;t). \tag{18}$$

The distinction between in and out groups of particles producing $\Delta B(r_0;t)$ yields

$$\Delta F(r_0;t)=\Delta F_{rr}(r_0;t)+\Delta F_{tr}(r_0;t). \tag{19}$$

In Fig. 5, $\Delta F_{rr}(r_0;t)$ and $\Delta F_{tr}(r_0;t)$, normalized to $\Delta F(r_0;0)$ (i.e., ΔF^*) and for pairs initially lying in the first coordination shell, are shown for supercooled argon at $T=55$ K. As is seen, the cross term $\Delta F^*_{tr}(r_0;t)$ is negligible so that the ΔF^* is entirely due to the radial part. This holds for all the thermodynamic states here investigated and for

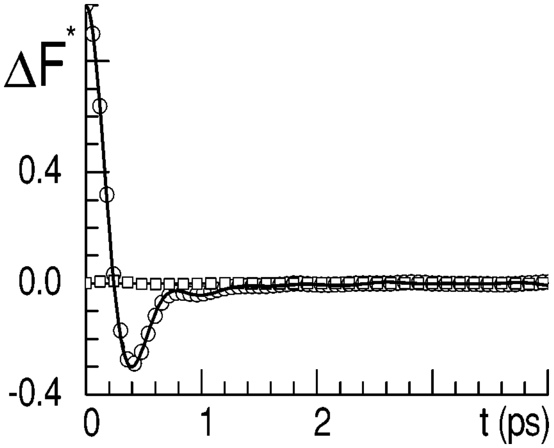

FIG. 5. Correlation functions for pairs of atoms ($T=55$ K) initially lying in the first coordination shell: $\Delta F^*_{rr}(r_0;t)$ (circles) and $\Delta F^*_{tr}(r_0;t)$ (squares) [Eq. (18) and (19)]. The relative radial VCF $V^*_r(r_0;t)$ (solid line) [Eq. (20)] is also shown.

every initial pair separation distance r_0 (see also Sec. IV B). In the same figure ΔF^* is compared with the relative radial VCF defined by

$$V^*_r(r_0;t)=\langle v_{r,ij}(r_0;t)v_{r,ij}(r_0;0)\mathbf{u}_{ij}(t)\cdot\mathbf{u}_{ij}(0)\rangle_0/\langle|v_{r,ij}(r_0;0)|^2\rangle_0. \tag{20}$$

The functions $\Delta F^*(r_0;t)$ and $V^*_r(r_0;t)$ are practically coincident. Consequently, the DOS obtained from the total $\Delta B(r_0;t)$ [Eq. (13)] corresponds to the part of the total translational DOS selected by the relative radial VCF. This justifies "*a posteriori*" the use of the name "density of states" given to the sin-FT of $\omega\Delta B(r_0;t)$. To obtain a physical meaning for the plateau height $A(r_0)$ [see Eq. (14)], we first note that one can write

$$\Delta F(r_0;t)=\frac{d\Delta B(r_0;t)}{dt}, \tag{21}$$

and

$$\Delta B(r_0;t)=\int_0^t \Delta F(r_0;t')dt'\approx\int_0^t V_r(r_0;t')dt'. \tag{22}$$

Second, the cos-FT of $\Delta F(r_0;t)$ is equal to the sin-FT of $\omega\Delta B(r_0;t)$, as one can prove by time cosine Fourier transforming both sides of Eq. (21) [36]. At this point the connection between the plateau height and the relative diffusion is established. Since for vibrational motions one has $D_h(r_0;0)=0$, from Eq. (15) and after trivial algebra one obtains

$$D^*(r_0;0)=\frac{A(r_0)}{\int_0^\infty D(\omega)d\omega}=\frac{2\mu}{\pi kT}\mathfrak{D}(r_0), \tag{23}$$

where μ is the reduced atomic mass and

$$\mathfrak{D}(r_0)=\frac{kT}{\mu}\int_0^\infty V^*_r(r_0;t)dt \tag{24}$$

is the relative radial pair diffusion coefficient. Equation (23) and the fact that $A(r_0)=D(r_0;0)$ demonstrate that in the normalized $\Delta B(r_0;t)$ function, i.e., $\Delta B^*(r_0;t)$ of Eq. (12), the plateau height is proportional to the pair diffusion coefficient. This also justifies the normalization to the DOS area introduced in Sec. III A.

IV. RESULTS AND DISCUSSIONS

We can now deal with the problem of handling thermodynamic states where both vibrational and nonvibrational modes are present. In fluid argon, the diffusional motions are expected to dominate for very high temperatures and/or low density. In the solid at low temperature, the vibrations are dominant. In the melting and supercooled liquids the two contributions can be comparable. Indeed, Fig. 4 shows that oscillating peak and the plateau, roughly representing the vibrational and the diffusional modes, respectively, have comparable intensity. In this case, we proceed by making some reasonable assumptions and then proving their reliability for different physical situations. First of all, the results of Sec. III for the 20 K crystal show that there are few main phonon frequencies in the DOS; if phononlike excitations survive in the liquid, their contribution should be centered at frequencies near to the solid ones. In other words, we assume that at very short times a low temperature liquid is frozen and a certain memory of the phonon frequencies is still present. If so, the dynamics will be composed by solidlike vibrational modes plus diffusive relaxations; the amount of such nonvibrational modes must give the plateau height. So, one expects that, when the system evolves from the glass transition to the melting, the density of states of the longitudinal dynamics could be described by two DHO centered around 40 and 60 cm^{-1}, as in the crystal, plus a function representing diffusive processes.

A. The temperature dependence of ΔB and of the corresponding DOS

By combining the results of Secs. III A and III B, one can write $\Delta B^*(r_0;t)$ via the increasing function of Eq. (14) plus the DHO-like functions centered at the phonon frequencies of the crystal, Eq. (11). One has

$$\Delta B^*(r_0;t)=A^*(r_0)[1-\exp-(t/\tau_e)]+\sum_n x^*_n\sin(\omega_n t)\exp-(t/\tau_n)^2. \tag{25}$$

The reliability of Eq. (25) has been tested in detail for pairs argon atoms initially lying in the first coordination shell for different thermodynamic states. The first and second columns of Fig. 6 show the $\Delta B^*(r_0;t)$ functions and the corresponding DOS functions $D^*(r_0;\omega)$, respectively. For the argon crystal at 20 K (pictures at the top of Fig. 6), $A^*(r_0)$ vanishes and two DHO modes are sufficient to reproduce the global translational dynamics. In the other first column pic-

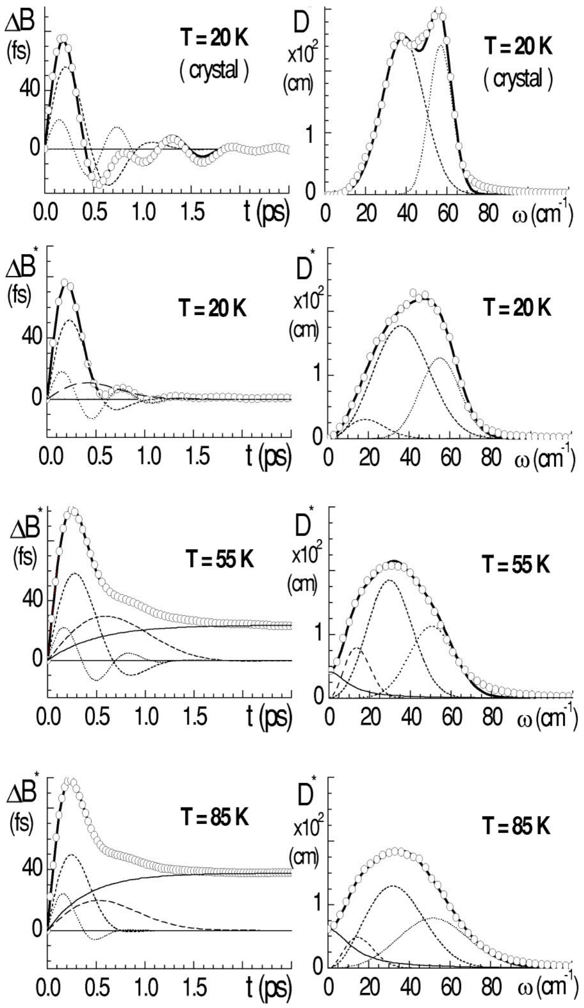

FIG. 6. $\Delta B^*(r_0;t)$ and the related DOS $D^*(r_0;\omega)$ for argon atoms initially lying in the first coordination shell: crystal at $T=20$ K, quenched liquid at $T=20$ K, supercooled liquid at $T=55$ K, and melting liquid at $T=85$ K. In each picture bold solid line and open circles represent the fit of Eq. (25) and the MD results, respectively; dotted and dashed lines represent the DHO [Eq. (11)] contributions; the thin solid line represents the contribution of nonvibrational motions. [Eqs. (14) and (15)].

tures, the presence of a plateau, whose intensity increases with the temperature, is evident; it is the sign of the relevance of the diffusive contributions. If one compares the behaviors of the crystal and of the melting and supercooled states, the above mentioned idea of describing the dynamics of the system with diffusion plus vibrations at the two main solid frequencies (40 and 60 cm^{-1}) fails in part. In fact, the phonon-like excitations are still a useful tool for reproducing the high frequency part of the DOS, but other contributions at low frequency appear as the crystalline state is left. In the amorphous state at 20 K the diffusion is negligible, but a contribution at low frequency is present. In the $\Delta B^*(r_0;t)$ function, it appears as a bump that prevents the first minimum to reach negative values as in the crystal. A global viewing of the $\Delta B^*(r_0;t)$ shapes of Fig. 6 can help the understanding of the short time dynamics. Three consecutive time regions can be identified: the first one is dominated by a strong peak between 0 and 0.5 ps, the second one by the shoulder between 0.5 and 1.0 ps, and the last one by the asymptotic behavior. From the $\Delta B^*(r_0;t)$ of the crystalline state, it is evident that the first peak contains two signals yielding the bands around 40 (Einstein) and 60 (Debye) cm^{-1} in the DOS; the Debye signal is responsible for the first minimum and successive modulations. Such modulations are still visible on the shoulders between 0.5 and 1.0 ps at 55 and 85 K. These results demonstrate that the description of the high frequency dynamics in terms of oscillations at the solid frequency is meaningful. However, the signal between 0.5 and 1.0 ps is absent in the crystal and seems to characterize the liquid states. It gives rise to a band below 20 cm^{-1} in the DOS (see Sec. IV C for further deepening). The plateau is reached within the times of the vibrational dynamics. As is shown in Fig. 6, the constant value, $A^*(r_0)$, is achieved after about 2 ps; this implies that the value of the time constant τ_e in Eq. (25) is lower than 1 ps. For supercooled argon at $T=55$ K and for liquid argon at $T=85$ K, the fitted value of τ_e is about 0.5 ps. In the quenched argon at $T=20$ K, $A^*(r_0)$ is nearly vanishing. However if one magnifies the vertical axis in the region around zero (see Fig. 7) a nonvanishing level is observed within the statistical noise. Figure 7 shows the exponential increase of Eq. (25) with $\tau_e=1$ ps. This shows that even if the τ_e value could increase at decreasing temperature, as in the case of water [30], for argon near to the state of an amorphous solid the nonvibrational dynamics decays with the times characteristic of the vibrational one. In terms of microscopic theory parameters, $A^*(r_0)$ can be related to the rate of elemental diffusive acts ("jumps" or "transits") while τ_e should represent the average duration of the single diffusive act. The τ_e values matches very well with the value of the transit times in the Wallace's theory [24] and this supports the assumption that the transits are fast.

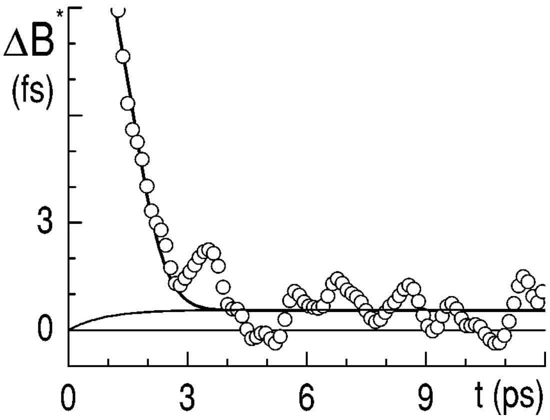

FIG. 7. $\Delta B^*(r_0;t)$ for pairs of argon atoms ($T=20$ K) initially lying in the first coordination shell. Bold solid line and open circles represent the fit of Eq. (25) and the MD results, respectively; the thin solid line represents the contribution of nonvibrational motions [Eq. (14)].

B. Diffusion coefficient, density of states, and velocity correlation function

In Sec. III C, the connection between $\Delta B^*(r_0;t)$ and the pair VCF has been established. We can now test its validity

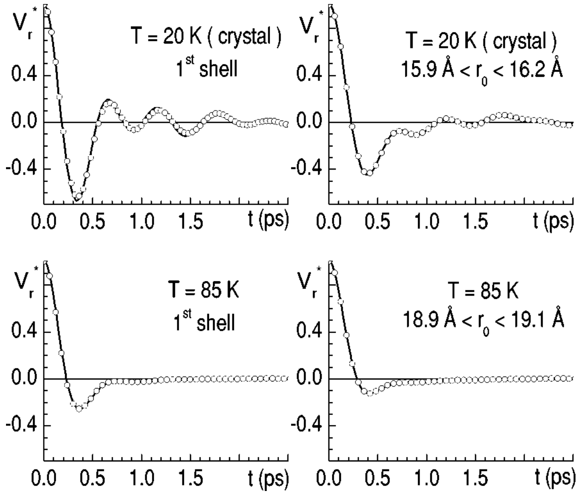

FIG. 8. Comparison between the VCF computed from the MD configurations by Eq. (20) (circles) and from the cos-FT of the DOS [this last one obtained from the sin-FT of $\omega\Delta B^*(r_0;t)$].

for the investigated thermodynamic states and for different r_0 ranges. In Fig. 8, the time radial VCF calculated by cosine Fourier transforming the DOS obtained from $\Delta B^*(r_0;t)$ is compared with that directly derived from the definition of Eq. (20). Only some limit cases are shown to demonstrate the very good level of agreement. As in the case of water [37], the equality $\Delta F^*(r_0;t)=V_r^*(r_0;t)$ holds well for supercooled and liquid states near the melting point. In this range of thermodynamic states, the correlation function $\Delta B^*(r_0;t)$ represents an independent way for deriving the DOS and studying the translational dynamics. To relate the plateau height to the system diffusivity, it is worth considering the connection of the $\Delta B^*(r_0;t)$ functions with the single-particle dynamics. For small values of r_0 (typically for the r_0 equal to few atomic diameters), the projection of the pair dynamics over the initial direction $\mathbf{u}_{ij}(0)$ is related to the local structure of the liquid. As r_0 increases, the two atoms of the pair move more and more independently and the longitudinal and transverse dynamics become equivalent. In this limit, $\Delta B^*(r_0;t)$ has to reflect the self-dynamics, and the nonvibrational dynamics must give the self-diffusivity. This effect is shown in Table I, where the values of $\mathfrak{D}(r_0)$ obtained from $A(r_0)$ [Eq. (23)] and from the time integral of the relative radial VCF [Eq. (24)] are reported. The agreement is good and the self-dynamics is completely reached for $r_0>16$ Å. This confirms the diffusive meaning of the plateau height for all the thermodynamic states here investigated. As expected, for large initial pair separations one obtains $\mathfrak{D}(r_0)$ equal to twice the time integral of the self-VCF. To summarize, the two parameters $A(r_0)$ and τ_e in Eq. (14) have the following physical meaning: in supercooled liquids, the plateau height $A(r_0)$, being proportional to $\mathfrak{D}(r_0)$, is related to the frequency of diffusive jumps (or transits), while τ_e represents the average time of a diffusive jump since it is determined by the rapidity of the system in reaching the plateau height.

C. Low frequency modes

In Ref. [28], we have studied the evolution of structural and dynamical properties of a fast quenched glassy argon at $T=20$ K as the crystallization proceeds. The obtained sample is "quasistable"; this means that it proceeds very slowly towards the crystalline state. Over narrow time windows, one can study the correlation functions in a condition of quasiequilibrium and all the quantities related to the fast vibrational dynamics appear measurable. In particular, the $\Delta B^*(r_0;t)$ functions are obtained over many 50-ps-time windows (Fig. 9). They remain practically unchanged for long time (500 ps), then evolve rapidly towards a stable state. It can be shown that the rapid change corresponds to a crystallization process [28]. In Fig. 9, the variations of the $\Delta B^*(r_0;t)$ functions are shown. As is seen, the main effect produced by the crystallization is the deepening of the first $\Delta B^*(r_0;t)$ minimum. This effect has been attributed to the disappearance of a low frequency (less than 20 cm^{-1}) mode present in the quenched state. This mode should represent the

TABLE I. Values of $\mathfrak{D}(r_0)$ for different initial pair separation in liquid argon states. For each temperature, the left and the right columns report the $\mathfrak{D}(r_0)$ values obtained from the plateau height [Eq. (23)] and from the time integral of relative radial VCF [Eq. (24)], respectively. The $\mathfrak{D}(r_0\rightarrow\infty)$ values obtained from the time integral of the self-velocity correlation function are reported in the last row.

	$\mathfrak{D}(r_0)$ (10^{-5} cm^2/s)		
r_0 (Å)	$T=85$ K	$T=55$ K	$T=20$ K
1st shell	1.70 1.60	0.40 0.35	≈ 0 ≈ 0
9.9–10.1	2.90 2.80	0.65 0.60	$\approx 10^{-2}$ $\approx 10^{-2}$
18.8–19.1	3.40 3.40	0.80 0.80	$\approx 10^{-2}$ $\approx 10^{-2}$
28.0–28.1		0.85 0.85	
$r_0\rightarrow\infty$	3.40	0.85	$\approx 10^{-2}$

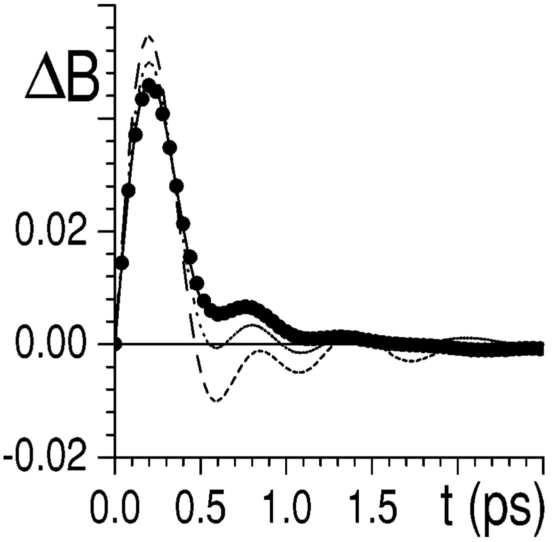

FIG. 9. The results of monitoring, at time windows of 50 ps, the time evolution of the 20 K fast quenched argon state via the dynamical behavior of $\Delta B(r_0;t)$ for $0<r_0<5.1$ Å. Circles—1st window (0–50 ps); solid line—average of $\Delta B(r_0;t)$ of the first eight time windows; short dashed curve—11th window; long dashed curve—12th window.

disorder of the higher temperature fluid conserved by the quenching process. As is seen in the DOS of Fig. 6, the same low frequency mode is present in the gently quenched state at 20 K as well as in the liquid states at 55 and 85 K. Furthermore, if one looks at the first column of Fig. 6 from bottom to top, i.e., from the melting to the crystal, one can see that the mode survives in the liquid at 20 K when diffusion disappears; it vanishes in the crystal at 20 K. This indicates that the low frequency mode dynamics is independent of the diffusive one. Consequently, the phenomenological separation between vibrations and relaxations of Eq. (13) is significant, since the two processes can be considered independent. However, the nature of the mode itself is not clear. It could be due to the disorder-favored leakage of the transverse dynamics along the longitudinal one or to a really new mode of vibration absent in the crystal. To clarify this point we are planning the study of the transverse dynamics in the normal, supercooled, quenched, and crystalline state.

V. SUMMARY, FINAL REMARKS, AND CONCLUSIONS

The molecular dynamics technique has been used to simulate liquid argon at the melting temperature and for lower temperatures of supercooled states obtained at the fixed melting density. The structural relaxations are supposed separated in time with respect to the fast dynamics occurring in few picoseconds. In this time domain, the longitudinal dynamics has been investigated through the specific correlation function $\Delta B(r_0;t)$. Notwithstanding the fragile character of the argon fluid, $\Delta B(r_0;t)$ is able to provide useful information on the diffusive and vibrational dynamics, as in the case of water. It represents an approach to the translational dynamics of liquids independent and complementary to that of the velocity correlation function. The relationship connecting the two correlation functions has been derived and tested. As predicted by the theoretical considerations of Sec. III A, the vibrational dynamics can be represented by few DHO-like functions and constitutes the entire translational dynamics in crystal and amorphous solids (negligible diffusion). The addition of a simple diffusive mode allows a good description of the dynamics behavior at higher temperatures in the liquid states. Our main results are grouped in the following four points.

(1) The comparison between the $\Delta B(r_0;t)$ functions of the crystal and of the quenched state at 20 K has shown that two DHO functions at about 40 and 60 cm^{-1} are able to represent most part of the longitudinal translational dynamics of neighboring atoms. In the quenched liquid, another DHO is present at lower frequency. These DHO contributions continue to be very important at higher temperature, in the supercooled and melting liquid states. This suggests that the agreement between simulations and some theoretical predictions [22,23] could improve if contributions due to more than one average frequency are considered.

(2) The dynamics of the crystal differs from that of the quenched liquid at 20 K for a shallower first minimum in the $\Delta B(r_0;t)$ function. The difference is taken into account by a third DHO mode vibrating at lower frequency (less than 20 cm^{-1}) and characterizing the liquid state. In fact, it is also present in the dynamics of supercooled (55 K) and melting (85 K) liquids. Moreover, it practically coincides with the mode observed in the fast quenched 20 K argon state [28]. This mode vanishes as the crystallization of the system proceeds and is absent in the forming crystal. All these facts confirm the assignment of this mode to the short range disorder typical of the liquid and amorphous states. If the mode is completely new with respect to the crystal dynamics or represents a filtering of the transverse dynamics along the longitudinal one, can be clarified by future works.

(3) As the temperature increases, the fast dynamics cannot be described by only DHO functions. When the fast dynamics ceases, a plateau is observed. It is shown that its height is related to the system diffusivity. The sum of a phenomenological exponential relaxation representing diffusion and three DHO representing normal mode vibrations is able to reproduce the short time dynamics of the system for the different temperatures and different choice of the initial pair separation. A similar success was found in the case of water [37], where the ratio between vibrational and nonvibrational motions is strongly different. Therefore, the approach in terms of normal modes, reminiscent of the crystal dynamics, plus independent diffusive contributions appears to be realistic, at least in the case of dense low temperature fluids composed by simple molecules.

(4) The fast dynamics occurs in few picoseconds, typically for $t<3$ ps, owing to the damping effects. After this time, a nonvanishing plateau is present in the supercooled and melting states (see, for example, Figs. 2 and 4). In recent theories, the damping is attributed to the dephasing of modes when the system moves in a nearly harmonic valley; the system undergoes diffusion when it passes from one valley to another, as in the case of the transits [22,23]. In this theory, the transits are supposed to be local and of short time duration, at limit instantaneous. The parameter τ_e involved in the diffusive relaxation [Eq. (14)] should represent the average value of the transit times. As a matter of fact, we found $\tau_e \simeq 0.5$ ps at 55 K which compares fairly well with the recent evaluation [24] of 0.9 ps for the average value of the transit time for argon at 17.1 K. Values of τ_e comparable to the vibration periods were also found in the case of water [37]. Therefore, similar considerations about the transit time should hold in the case of molecular liquids characterized by strong orientational interactions.

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[29] The longitudinal dynamics is more sensitive to the variations of the pair distance r_0 and provides a more efficient tool than the transverse one for recognizing the similarity between liquid and solid neighbors arrangements. For these reasons, we report only the longitudinal dynamics results.

[30] The Daresbury Laboratory CCP5 program MDATOM by D. Fincham was used.

[31] Near the temperature of the glass transition, a one-Lennard-Jones (1LJ) system is in an out-of-equilibrium state, and shows the tendency to crystallizing. For obtaining metastable states in LJ systems, specific recipes must be used, such as the use of a binary mixture or the correction of the pair potential with the introduction of a many-body term (see Ref. [28], and references therein). In the studied 1LJ case, the dynamics probed by the simulation could be nonunique and dependent on the thermal history of the system. However, $\Delta B^*(r_0;t)$ we obtained for gently and very fast quenched states at 20 K are very similar.

[32] As noted in Ref. [21], liquid argon exhibits gaslike motions at low pressures; the liquidlike behavior is obtained under compression.

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[34] In this work all the vibrations are considered nearly harmonic and the terms vibrations and harmonic modes can be exchanged.

[35] The exponential form of Eq. (14) corresponds to an exponential relaxation of the diffusive contribution to the VCF. This implies independency in the microscopic mechanisms which produce diffusion [38] in agreement with many approaches to the theory of the liquid state.

[36] To emphasize the advantages of using $\Delta B(r_0;t)$ instead of VCF or the DOS, it is worth noting that $\Delta B(r_0;t) = \mathrm{IFTs}(D(r_0;\omega))/\omega$, where IFTs stand for the inverse sin-FT. Therefore, the direct determination of $\Delta B(r_0;t)$ provides an efficient tool for studying the low frequency dynamics. For example, from the observation of the DOS curves (see Fig. 6), one cannot realize the presence of the DHO mode at $\omega < 20\ \mathrm{cm}^{-1}$ in the total DOS. By contrast, the need of this mode is evident in the decomposition of $\Delta B(r_0;t)$. Moreover, the $\Delta B(r_0;t)$ correlation function allows the modeling of nondiffusive motions with simple DHO-like functions, as in Eq. (11). Indeed, even if these functions have nonvanishing time integrals, they yield VCF contributions with vanishing time integrals. This occurs because $\Delta B(r_0;t)$ behaves as a primitive function of the VCF [see Eq. (22)].

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