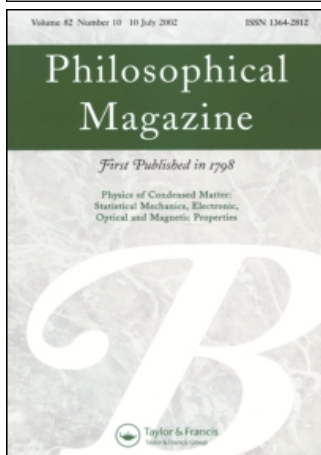


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Philosophical Magazine Part B

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713836176>

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Online Publication Date: 01 January 2002

To cite this Article: Scopigno, T., Ruocco, G., Sette, F. and Viliani, G. (2002) 'Short-time dynamics in simple disordered systems', *Philosophical Magazine Part B*, 82:2, 233 — 241

To link to this article: DOI: 10.1080/13642810208208545

URL: <http://dx.doi.org/10.1080/13642810208208545>

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Short-time dynamics in simple disordered systems

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ABSTRACT

The collective dynamics of a simple metal (lithium) have been numerically investigated by molecular dynamics and normal mode analysis. A generalized hydrodynamic framework allowed us to describe the system in different thermodynamic phases by the same model based on two relaxation processes. At the melting point we find good agreement with recent inelastic X-ray scattering results, while below the melting point, and ultimately in the glassy state, we find evidences of a 'harmonic' relaxation as recently found in Lennard-Jones systems.

The study of the collective dynamics in simple fluids provides unique information about the nature of the interatomic interactions on a microscopic level. From the experimental point of view, liquid metals can be considered as prototype of simple liquids and for this reason they have been extensively studied in the past by means of the inelastic neutron scattering (INS) technique (Copley and Rowe 1974, Morkel and Glaser 1986, Bodensteiner *et al.* 1992, Verkerk *et al.* 1992, Novikov *et al.* 1996). Recently, the interest in these systems has been renewed since the advent of the inelastic X-ray scattering (IXS) technique (Burkel 1991, Sinn *et al.* 1997, Scopigno *et al.* 2000a, 2001), as the complementarity of the two techniques allowed the experimental determination of the dynamic structure factor to be extended to systems with a dominant incoherent neutron scattering cross section and/or with high values of the sound velocity. From a general point of view, one of the most interesting outcomes of these studies is the presence of a relaxation process, usually detected as an increase in the sound velocity in the nanometre wave-vector region.

At the same time, theoretical and numerical studies have been devoted for more than 20 years to the understanding of the collective dynamics of these liquids. An

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idea suggested by molecular dynamics (MD) simulations, which has been recently demonstrated by IXS in the case of lithium (Scopigno *et al.* 2000b) and aluminium (Scopigno *et al.* 2001), is the existence of two different time scales driving the viscous decay of the high-frequency density fluctuations. These two time scales are believed to be associated with two different phenomena. The slower process is responsible for the highly correlated atomic motion. Its current understanding is provided by the same mode coupling approach which gives a satisfactory description of a large number of experimental and numerical results obtained in glass-forming systems (Casas *et al.* 1999). This process is usually referred to as the α -relaxation (structural relaxation) process. The faster process, less understood, is usually described in terms of uncorrelated binary collisions between particles (Sjögren 1980).

Recent theoretical (hard spheres) (Götze and Mayr 2000) and numerical (Lennard-Jones) (Ruocco *et al.* 2000b) studies on the high-frequency dynamics of model monatomic glasses have shown, even in a harmonic glass, the existence of a fast relaxation process. This process shows the typical phenomenology of relaxations, as the sound velocity increases with increasing wave-vector magnitude Q , in spite of the fact that all the diffusional degrees of freedom are frozen and anharmonicity is absent. This finding suggests the association of this relaxation process to the topological disorder (Ruocco *et al.* 2000b). According to this interpretation, the microscopic relaxation process should be a general property of disordered systems and, in particular, it must exist also in the liquid phase.

Along this line, one may naturally investigate the presence and the evolution of this relaxation process in the different thermodynamic states of a given system. In particular, we recently studied whether in the case of a simple monatomic liquid it is possible to associate the fast relaxation process with the topological disorder and to improve our understanding of this phenomenon beyond the present belief based on uncorrelated binary collisions. As simple liquids have a strong tendency to crystallization over the typical experimental quenching rates (0.1 K s^{-1}), such a study has to be necessarily performed with numerical techniques, that is supercooling the system with much higher quenching rates, say 1 K fs^{-1} . Therefore, our study compares the dynamic properties of a monatomic system (lithium) in its liquid, supercooled, glassy and crystalline phases obtained by MD simulations. The existence of the two relaxation processes in all the disordered phases is testified by the analysis of quantities such as the sound velocity, acoustic attenuation and related relaxation times. The slow process, whose relaxation time seems to diverge at the glass transition, effectively behaves as the usual α relaxation observed in real glass formers. Most importantly, we find that the fast process is always present in the whole thermodynamic range and that its features do not change in the transition between the liquid and glass phases. This implies a crucial role of the topological disorder in driving this fast dynamic process even in the liquid phase. Moreover, it also indicates that even on the considered short time scale the atomic motion is highly correlated and cannot be described by uncorrelated binary interactions.

We performed MD simulations on a 2000-lithium-atom system interacting by the Price–Tosi pseudopotential. Lithium was chosen as an example of monatomic metals owing to the availability of high-resolution experimental data on the dynamic structure factor $S(Q, \omega)$ in the liquid phase, which has already shown the existence of the two relaxation processes (Scopigno *et al.* 2000b). The simulated system is liquid down to $T_m = 450 \text{ K}$, in good agreement with the experimental melting point. Below this temperature, it can be supercooled, attaining structural arrest at

$T_c \approx 260$ K, a value estimated from a power-law fit of the inverse diffusion coefficient. This value of T_c can be compared with that obtained from the depth ϵ of the effective interaction potential well; we estimated $T_c = 270$ K for the Price pseudo-potential using the relation $T_c \approx 0.47\epsilon$, valid for the monatomic Lennard-Jones potential (Angelani *et al.* 2000). Cooling further below T_c , by rapid quenching to avoid crystallization, the simulated lithium glass is ultimately obtained. Summing up, we studied the system in the 5–1100 K region. In the low- and high-temperature limits this system cannot be obtained experimentally because of crystallization or high chemical reactivity of the hot liquid. At any of the selected temperatures, the system has been stabilized for few hundred picoseconds and then the configurations, $\mathbf{u}_i(t)$, stored in order to calculate the dynamic structure factor $S(Q, \omega) = (1/N)FT \sum_{i,j} \langle \exp[-i\mathbf{Q} \cdot \mathbf{u}_i(t)] \exp[i\mathbf{Q} \cdot \mathbf{u}_j(0)] \rangle$. The numerical resolution $2\pi/\Delta t$, Δt being the acquisition length, was set to 1.3 ps^{-1} , while the ‘free spectral range’ (i.e. the accessible frequency window) $2\pi/\delta t$ where δt is the time spacing of the storage, was set to 120 ps^{-1} . Each $S(Q, \omega)$ at a fixed Q value was obtained as an average over different runs and \mathbf{Q} orientations in the simulation box.

In figure 1 a selection of spectra are reported for momentum transfer $Q = 4.0 \text{ nm}^{-1}$ and $Q = 10.0 \text{ nm}^{-1}$ at several temperatures, together with their best fit according to the model that will be discussed below.

The temperature dependence of the spectra reported in figure 1 shows two dominant features. One is the central line that becomes narrower with decreasing temperature, and with a width that becomes negligible at the glass transition. The other is the Brillouin component that shows a much reduced temperature dependence and maintains a significant linewidth even at very low temperatures, with no discontinuity around T_c .

To investigate the origin of the residual Brillouin linewidth at low temperatures, we compared in figure 2 the spectra obtained by MD at 5 and 300 K in a crystal produced by thermalizing a perfect bcc lattice, with the corresponding disordered phase, as obtained by a rapid quench from a temperature above T_m . As clearly shown, the sound attenuation of the liquid or glass is significantly larger than in the crystalline counterpart, evidence that strongly indicates the dominant role of the disorder in controlling the high-frequency acoustic properties. It is worth pointing out how anharmonicity effects introduce only a negligible effect, as shown by the comparison between the crystalline linewidth at the two temperatures (figure 2) and by the coincidence of the dynamic structure factors as obtained by molecular dynamics and by the one-phonon approximation (Ruocco *et al.* 2000b).

On the contrary, the linewidth in the glass and in the cold liquid can be associated with a relaxation process, as the observation of the positive dispersion of the sound velocity demonstrates. This effect, expected to take place at frequencies such that $\omega\tau \approx 1$ (τ being the relaxation time), is shown in the insets of figure 2, where we report the quantity $\dot{c}_1(Q) = \omega_1(Q)/Q$ with ω_1 the maximum of the current correlation spectra $J(Q, \omega) = \omega^2/Q^2 S(Q, \omega)$. The positive dispersion of sound, correctly reproduced by the simulations of the glass and cold liquid phases, is missing in the crystal, thus supporting the relaxation hypothesis.

On the basis of a raw qualitative analysis, figure 1 reveals the presence of at least two relaxation processes driving the high-frequency collective dynamics of the considered system: a slower process, strongly temperature dependent, which shows up mostly in the width of the central line, and a faster process, strongly temperature independent, which gives rise to the width of the inelastic feature. These simulations

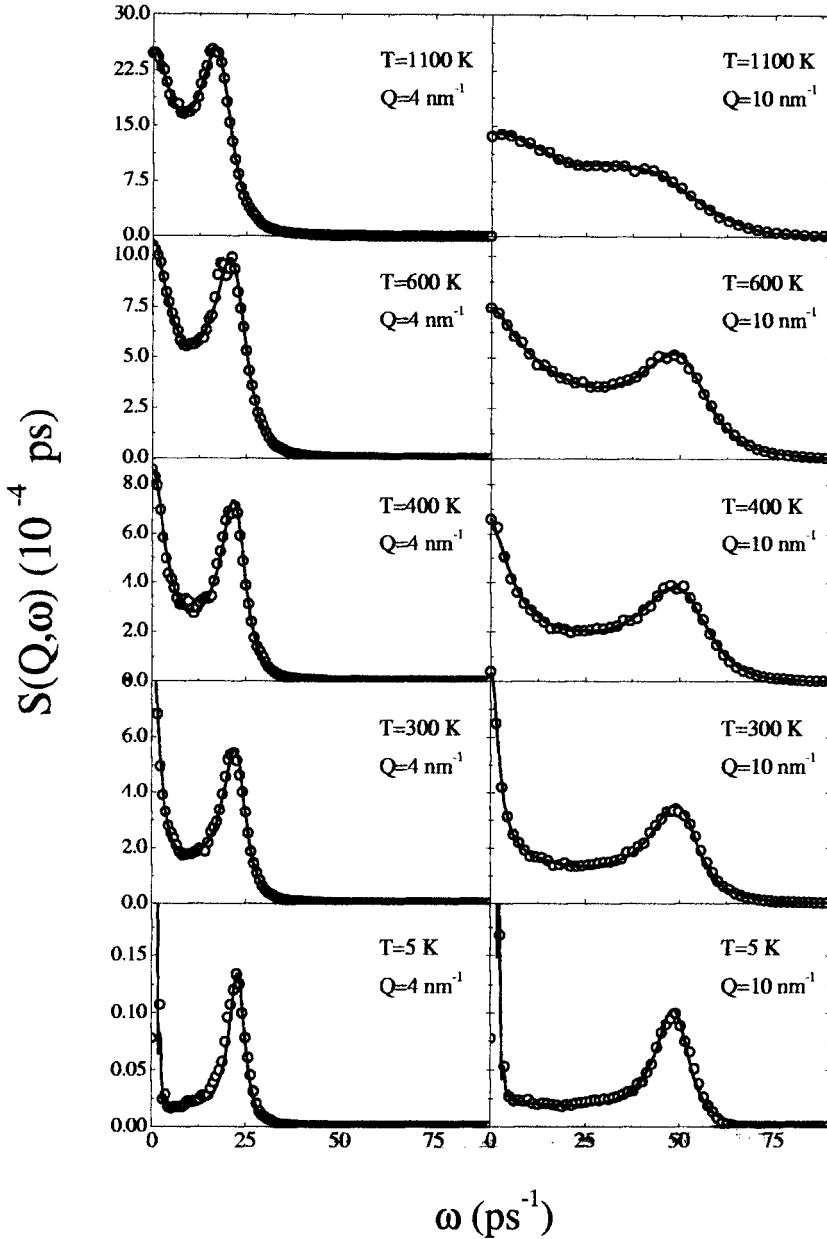


Figure 1. Dynamic structure factor of lithium (\circ) at $Q = 4.0 \text{ nm}^{-1}$ and $Q = 10.0 \text{ nm}^{-1}$ at different temperatures (and hence thermodynamic phases) and where the resolution full width at half-maximum is $\delta E_{\text{sim}} = 1.3 \text{ ps}^{-1}$ (which is negligible with respect to the intrinsic spectral widths): (—), best fit according to the model discussed in the text.

confirm, therefore, in a much wider temperature range the conclusions provided by the analysis of the IXS data on lithium (Scopigno *et al.* 2000b) and extend into the supercooled and glassy phase regions the theoretical predictions of dynamics ruled by two different time scales. Particularly interesting is the persistence of the fast relaxation processes, which are essentially identical in the liquid and in the glass.

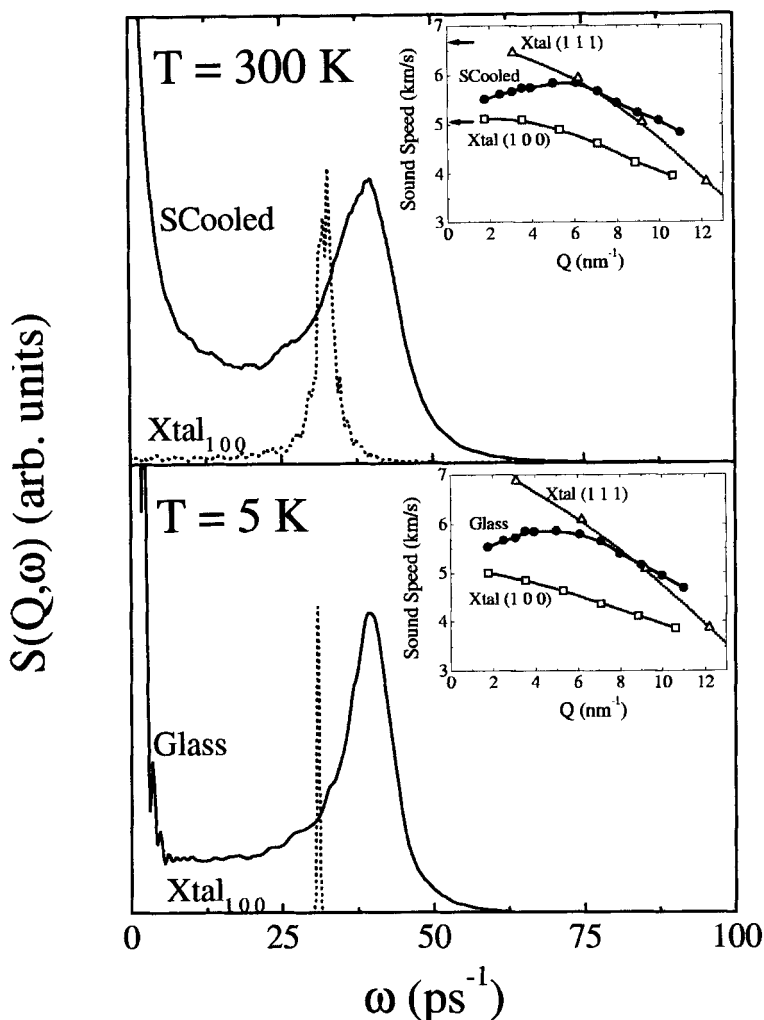


Figure 2. Dynamic structure factor below the melting point at $T = 5\text{ K}$ and $T = 300\text{ K}$. Glass and cold liquid phases (—) are compared with their crystalline counterparts (\cdots). The inset shows the speed of sound in different thermodynamic phases: (\bullet), glass and supercooled; (\square), crystal along (100); (\triangle), crystal along (111). The arrows indicate acoustic data at $T = 70\text{ K}$. Lines are guides for the eye only.

This result seems to be somewhat contradictory; in fact, in the liquid the fast relaxation process has been so far associated with uncorrelated binary collisions, while in the solid the atomic motion is dominated by long-range correlations. A quantitative description of this relaxation process may contribute to shedding light on this point.

For this reason, we first modelled the dynamic structure factor to find the temperature evolution of parameters characterizing the relaxation processes from the liquid down to the supercooled and glassy state. For this purpose, we adopted a model based on the memory function approach, introduced to represent the MD data on alkali metals (Levesque *et al.* 1973) and recently utilized to interpret the experimental data of liquid lithium (Scopigno *et al.* 2000b) and aluminium (Scopigno *et al.* 2001). Within this framework, the evolution of the density autocorrelation

function is described by a memory function through the Langevin equation for the density correlator ϕ :

$$\phi(Q, t) + \omega_0^2(Q)\phi(Q, t) + \int_0^t M(Q, t-t')\phi(Q, t') dt' = 0, \quad (1)$$

where $\omega_0^2(Q) = [k_B T / m S(Q)] Q^2$ with m the atomic mass and $S(Q)$ the static structure factor. By Fourier transformation, the dynamic structure factor is given by

$$\frac{S(Q, \omega)}{S(Q)} = \frac{\pi^{-1} \omega_0^2(Q) M'(Q, \omega)}{[\omega^2 - \omega_0^2 + \omega M''(Q, \omega)]^2 + [\omega M'(Q, \omega)]^2}. \quad (2)$$

The complex memory $M(Q, t)$ contains all the interaction details of the system. The dynamics of a simple liquid can be satisfactorily described by the two-time exponential *Ansatz* (Levesque *et al.* 1973):

$$M_L(Q, t) = \Delta_\alpha^2(Q) \exp\left(\frac{-t}{\tau_\alpha(Q)}\right) + \Delta_\mu^2(Q) \exp\left(\frac{-t}{\tau_\mu(Q)}\right), \quad (3)$$

where the subscripts α and μ indicate the α (structural) and the fast (microscopic) processes, respectively. We used equation (2) as a model function. Its convolution with the simulation resolution has been fitted to the MD spectra. The results of such procedure are shown in figure 1, where, together with the calculated dynamic structure factors at selected values of momenta and temperatures, we report their best-fit line-shapes.

A suitable way to investigate the relaxation pattern through the different thermodynamic phases is to look at the temperature evolution of the relaxation times $\tau_{\alpha, \mu}(Q, T)$, as obtained by the fitting procedure. At all the considered temperatures, the α process shows an almost flat Q dependence, with an apparent increase below $Q \approx 4 \text{ nm}^{-1}$, an artefact that occurs when the relaxation time is comparable with or higher than the inverse resolution, already observed in the analysis of the IXS spectra (Scopigno *et al.* 2000a). The microscopic process shows, instead, an effective slightly decreasing Q trend. In any case, both the time scales show similar Q dependences for each temperature (Scopigno *et al.* 2002). Considering now the temperature dependence of τ , the value of the structural relaxation time at large Q shows a sharp increase in the supercooled region and upon further cooling. On the contrary, the temperature behaviour of the fast microscopic μ process is very different. In fact, it gives basically a temperature-independent relaxation time in any of the considered phases.

To be more quantitative in the assessment of the temperature dependence of the relaxation times, once it is observed that the Q dependences are similar for each temperature, we defined a Q -independent temperature coefficient $\gamma(T)$ through the relation $\tau(Q, T) = \gamma(T)\tau(Q, T_0)$. As arbitrary reference temperature we selected $T_0 = 1100 \text{ K}$, and we determined $\gamma(T)$ as the scaling factor that minimizes the mean square differences between each set of $\tau(Q, T)$ and the set at T_0 .

The result of such a procedure, for both the α and the μ processes, is reported in figure 3. As clearly seen, the relaxation time of the structural process increases about six times between T_0 and the lower available temperature ($T = 275 \text{ K}$). In the same plot we also report the quantity T/D , D being the diffusion coefficient determined in the simulations. As expected, this quantity follows a behaviour similar to that of the relaxation time of the α -process, thus confirming the validity of its identification with

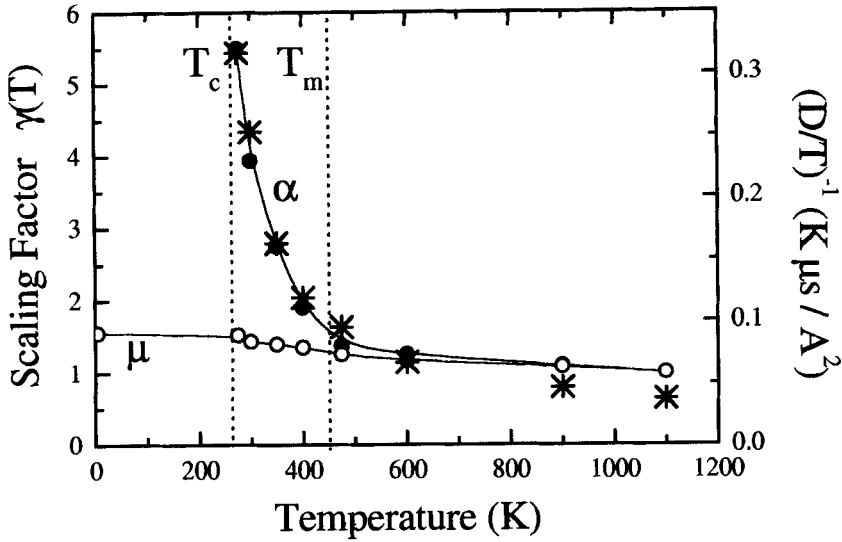


Figure 3. Temperature dependence of the relaxation times (\circ , \bullet) (left axis). In the same plot we also report the behaviour of the diffusion coefficient (\star) (right axis). Lines are guides for the eye only.

the structural relaxation process. On the contrary, the microscopic relaxation time exhibits a small variation in the whole temperature range with a total change of only 50% of the value at T_0 , and without any noteworthy behaviour around T_c . This demonstrates that the fast relaxation process is the same from the hot liquid down to the glass.

Once the glassy phase is attained, the Q dependence of the acoustic properties is entirely controlled by the microscopic process. The structural relaxation time, indeed, diverges, and the condition $\omega(Q)\tau_\alpha(Q) \gg 1$ holds for any values of Q . Both sound dispersion and attenuation behaviour are now ruled by the ratio of τ_μ to the characteristic time scale of the considered density fluctuation. For example, as seen in figure 2, the speed of sound undergoes an increase at around $Q = 3 \text{ nm}^{-1}$, where $\omega_1 \approx 20 \text{ ps}^{-1} \approx \tau_\mu^{-1}$. As far as sound attenuation is concerned, equation (1) predicts that, in the low-frequency (and therefore low- Q , as τ_μ has only a slight Q dependence) limit the acoustic damping Γ parameter tends to $\Gamma \rightarrow \Delta_\mu^2(Q)\tau_\mu(Q)^\dagger$. In figure 4, we reported the Brillouin width $\Gamma(Q)$ together with its low-frequency value as predicted by the Langevin equation. As clearly seen, for a Q value of up to 3 nm^{-1} where, as shown in the inset, the crossover condition $\omega(Q)\tau_\mu(Q) < 1$ is fulfilled, this low-frequency limit well represents the actual linewidth. At higher Q values, where $\omega(Q)\tau_\mu(Q) \approx 1$, the sound attenuation becomes progressively lower than $\Delta_\mu^2\tau_\mu$.

It is worth pointing out how the quantity $\Delta_\mu^2(Q)\tau_\mu(Q)$ follows the ubiquitous Q^2 law customarily found for the acoustic attenuation in many glasses. Within the Langevin formalism, this behaviour directly derives from the relation between the area of the memory function and the longitudinal viscosity multiplied by Q^2 (Ruocco *et al.* 2000a).

\dagger As shown by Scopigno *et al.* (2000a), within the Langevin equation formalism it can be easily derived that, in the low-frequency limit $\omega \ll 1/\tau$, the inelastic part of the dynamic structure factor tends to a damped harmonic oscillator line shape, with a Brillouin linewidth given by the time integral of the memory function $M(t)$

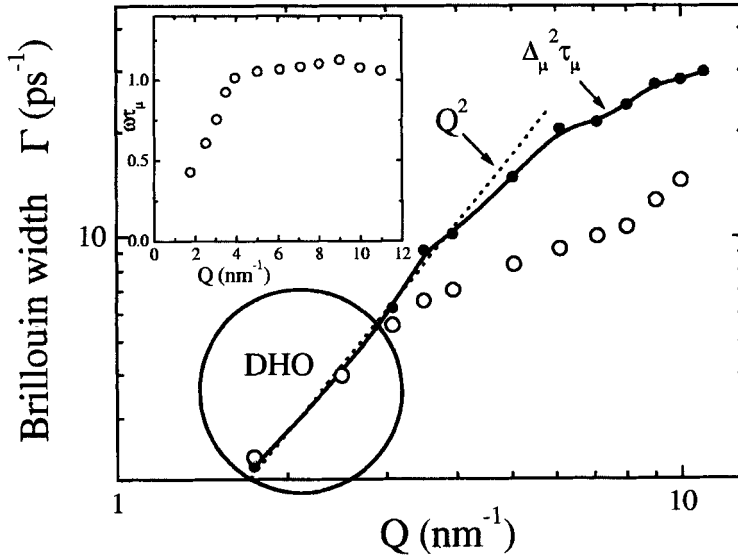


Figure 4. Acoustic attenuation in lithium simulated glass at $T = 5\text{ K}$ (DHO, damped harmonic oscillator): (○), Brillouin linewidth; (●), expected low-frequency limit. The inset shows the ratio of the microscopic relaxation time τ_μ to the density fluctuation time scale $1/\omega_1$.

In conclusion, we have shown how the dynamics of a simple monatomic system can be accounted for by a ‘two-relaxation’ scheme in a wide range of temperatures and thermodynamic states covering all the disordered phases: hot liquid, supercooled liquid and glass. The slower process is identified as the α process, which plays a key role in the glass transition of those systems capable to sustain strong supercooling. More interesting are the indications obtained from analysis of the faster process. On the basis of the comparison between glass and crystal, the equivalence of the fast relaxation process in the liquid and in the glass, and the consistency between the simulation and experimental results in the liquid, one can conclude that the origin of this process must be found in something common to liquid and glass; no better candidates other than topological disorder, can be hypothesized. On the considered fast time scale, indeed, corresponding to values of fractions of picoseconds, all the diffusion processes in the liquid are frozen and, over this snapshot time scale, one can say that the liquid and the glass are topologically identical. Along this line, one is then forced to conclude that, similarly to what has been found in other model glasses (Ruocco *et al.* 2000b), also in the liquid this fast relaxation process is intimately related to the topological disorder, while anharmonicity effects play only a secondary role. In fact, this work establishes the common origin of the fast relaxation process in the liquid and in the glass, recognizing its ultimate nature in the disorder.

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