Relaxation dynamics and acoustic properties in simple liquids

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Abstract

An overview of the relaxation dynamics in simple liquids is undertaken, in view of the recent experimental results achieved by means of inelastic X-ray and neutron scattering. We address some basic issues related to the extension of ordinary hydrodynamic in the Thz domain, such as the coupling of density and entropy fluctuations and the origin of anomalous acoustic dispersion within the general context of disordered systems dynamics. Specifically, we show that the Landau Placzeck ratio do not describe the quasielastic component of the dynamic structure factor and that the positive dispersion is a universal feature which can be understood in terms of a disorder induced relaxation process.
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1. Introduction

One of the major challenges in the field of simple liquids (liquid metals in particular) is the quest for a microscopic theory able to account for the dynamical properties at 'large' frequencies and wavevectors. The relaxation processes and the quasi-periodicity characterizing the dynamic and static structure, indeed, set a number of timescales and a lengthscales, respectively, which must be accounted for in order to gather a satisfactory picture of the microscopic dynamics. This no-man-land, in between the theory of continuous media and the single particle dynamics, can be approached through two conceptually different pathways, the solid like point of view and the liquid theory.

By the liquid point of view the approach consists in the extension of the simple hydrodynamics, describing the density fluctuations in the long wavelength limit, down to the lengthscale set by the mean interparticle distances. Such an extension stems from a generalization of the classical hydrodynamics assisted by the formalism of the memory function ruling the Langevin equation of motion of the density fluctuations, and relies on serious and sometimes not fully justified assumptions.

More specifically, in the special case of highly conductive systems, such an extension requires special care. As firstly envisaged by Faber [1], in a liquid metal – owing to the high (generalized) thermal conductivity, $D_T(Q)$ – the width of the quasielastic hydrodynamic mode (entropy fluctuations), $D_T(Q)Q^2$, may easily become larger than the Brillouin frequency $\omega = c(Q)Q$ as soon as $Q \approx \frac{c(Q)}{D_T(Q)}$. In principle, both the generalized sound velocity, $c(Q)$, and thermal diffusivity, $D_T(Q)$, are expected to decrease on approaching values comparable to the inverse mean interparticle distance, i.e. in coincidence with the first sharp rising edge of $S(Q)$. But assuming that the transition occurs when they are still Q-independent, one finds a crossover condition of $Q^* = \frac{c}{D_T}$ which, considering typical values of sound speed and thermal diffusivity of metals (a few thousands meters/second and ≈ 50 nm^2/ps, respectively), lies at wavevectors around 0.1–0.5 nm^{-1}. In other words, in the energy-wavevector domain probed by inelastic neutron or X-ray scattering experiment ($\omega \approx 1$ Thz, $Q \approx 1$ nm^{-1}) the

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thermal peak effectively overlaps with the Brillouin lines, the sound propagation turns from adiabatic to isothermal, and independent thermal fluctuations become impossible.

Beside the finite wavelength extension of the thermal relaxation, a second important generalization of the simple hydrodynamics involves the possible frequency dependence of viscosity or, in the language of the Mori–Zwanzig formalism [2], by the temporal decay of the longitudinal second order memory function [3,4].

This latter effect stems when the frequency of the observed density fluctuation become resonant with the inverse relaxation time ruling the viscosity decay. As in the case of the previously mentioned thermal effects, this condition sets an additional crossover between two different regimes, relaxed and unrelaxed, characterized by different sound velocities and attenuations. The whole phenomenology observed in this regime, is customarily rationalized in terms of a transition from a liquid like to solid like behavior.

2. Experimental results and discussion

The presence of relaxation processes in the microscopic dynamics heavily affects the density fluctuation spectra and, consequently, can be conveniently detected through inelastic scattering experiments. The main dynamical properties which are affected by such processes are, however, the sound velocity and attenuation. The two main effects, thermal and viscous, occurs over rather well separated timescales and, consequently, they are experimentally observed on probing quite different wavevectors: $Q \leqslant 1 \, \text{nm}^{-1}$ and $Q \approx 5 \, \text{nm}^{-1}$, respectively. For this latter reason, we will deal with the two cases separately, considering some evidences which gives significant hint to identify the role and the physical mechanism underlying the relaxation dynamics.

2.1. Thermal effects

A direct observation of the isothermal regime through deviation of the sound velocity from its adiabatic value have not been reported yet. A first obvious reason is that the resonance condition is expected in a region which lies outside the experimental windows available at present. Moreover, most of metallic systems investigated so far (such as alkali metals) are characterized by specific heat ratio very close to unit and, consequently, the quantitative differences between the adiabatic and isothermal value would be hardly noticeable. Looking at the sketch reported in Fig. 1, however, one can argue that in metallic system with very high specific heat ratios the sound velocity might in principle take values below the adiabatic one on approaching the low Q edge of an IXS experiment ($Q \approx 1 \, \text{nm}^{-1}$).

There are, however, several experimental indications suggesting the existence of such an isothermal regime. First, the ratio of the inelastic to the elastic spectral compo-
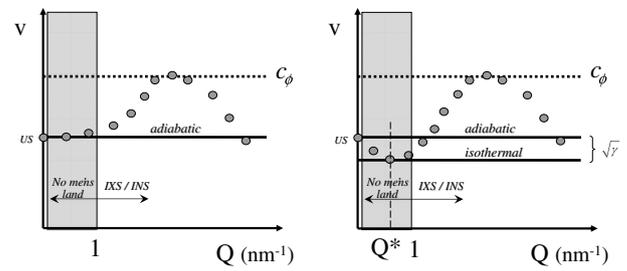

Fig. 1. Sketch of the expected behavior of the sound velocity for an ordinary liquid (left panel) and for a conductive liquid (right panel), respectively.

nent markedly departs from the prediction of the Landau-Placzek ratio, holding in the adiabatic regime (for instance light scattering experiments in transparent media). In Fig. 2, for instance, we report the (generalized) specific heat ratio estimated by inelastic to the elastic ratio of liquid lithium spectra [5–7], i.e. assuming that this latter entirely stems from non propagating entropy fluctuations as it happens in an ordinary adiabatic hydrodynamics. As can be noticed, the obtained result markedly departs from a direct numerical estimate [8], thus indicating the failure of the hydrodynamic prediction.

A second hint comes from the thermal contribution to the sound attenuation, Γ_{th}, which cannot be described by the hydrodynamic expression

$$\Gamma_{\text{th}} = \frac{Q^2}{2}[(\gamma - 1)D_{\text{T}}] \tag{1}$$

where ρ and D_{T} are density and thermal diffusivity, respectively. It has, in fact, to be replaced with an expression involving the isothermal sound velocity c_{t}

$$\Gamma_{\text{th}} = (\gamma - 1)c_{\text{t}}^2/D_{\text{T}} \tag{2}$$

which is constant in the low Q limit (where $S(Q)$ is almost flat) having no explicit Q dependence. This latter expression, in fact, has been shown to describe appropriately
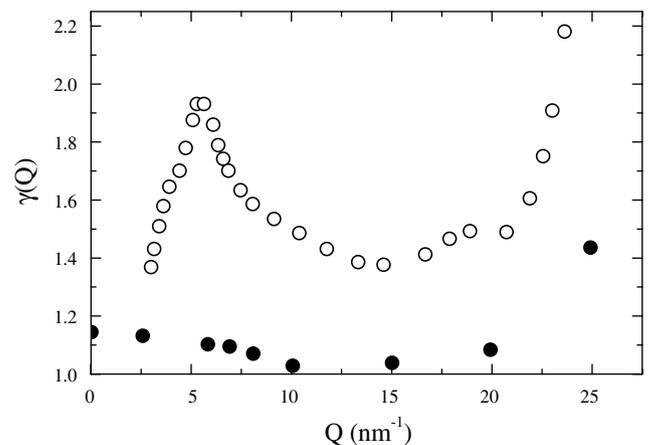

Fig. 2. Comparison between the generalized specific heat ratio $\gamma = c_{\text{p}}/c_{\text{v}}$ as obtained by the proposed model (○) and by direct numerical calculation (●).

the thermal contribution to the Brillouin linewidth when the isothermal condition $\omega \ll D_T Q^2$ holds [9].

A third issue concerns the weird temperature and wave-vector dependencies which are obtained assuming the persistence of an entropic contribution outside the strict hydrodynamic regime [5,7,10]: as a consequence of such an assumption, the generalized thermal diffusivity turns out to be heavily dependent on the wavevector even in the region where the $S(Q)$ is almost constant, and its temperature dependence is also abnormally fast upon undercooling the melt in molecular dynamics simulations [11].

2.2. Viscous effects

The description of the viscosity relaxation effect, early reported in the molecular dynamics study of Lennard Jones systems, can be traced back to the so called viscoelastic model [12] which provides a formal substrate to the idea of a liquid to solid like dynamical transition experienced on increasing the frequency of the density fluctuation.

In studying the details of such relaxation process by instantaneous normal mode analysis, however, a new phenomenon – which become more and more evident on lowering the temperature, i.e. on increasing the value of the structural relaxation time, appears [11]. In the earlier MD study of Lennard Jones systems it has been soon realized that the viscous dynamics in the microscopic regime (i.e. at wavelength comparable with the inverse mean interparticle separation) proceeds through two distinct processes, characterized by two well separate time scales (τ_α and τ_μ). This belief has been recently substantiated by a number of IXS investigation, where the presence and the role of the two relaxation mechanisms has been widely discussed [9,6,13]. In particular, it has been pointed out that (for low temperatures or for high sound velocity systems) the slower, structural relaxation time (τ_α) satisfies the condition $\omega(Q)\tau_\alpha(Q) \gg 1$, while a faster, temperature independent microscopic relaxation process appears, characterized by a relaxation time which is comparable to the inverse Brillouin frequency. Consequently, the resonance condition ($\omega(Q)\,\tau_\mu(Q) = 1$) with this faster relaxation can be easily matched on probing the appropriate wavevector, while, as far as the structural relaxation is concerned, the liquid always responds in a solid like fashion. Interestingly, in simple liquids, the strength of the structural relaxation turns out to be one tenth of the whole relaxation amplitude [4,9], so that both the sound velocity and attenuation are mainly controlled by the faster relaxation process. The
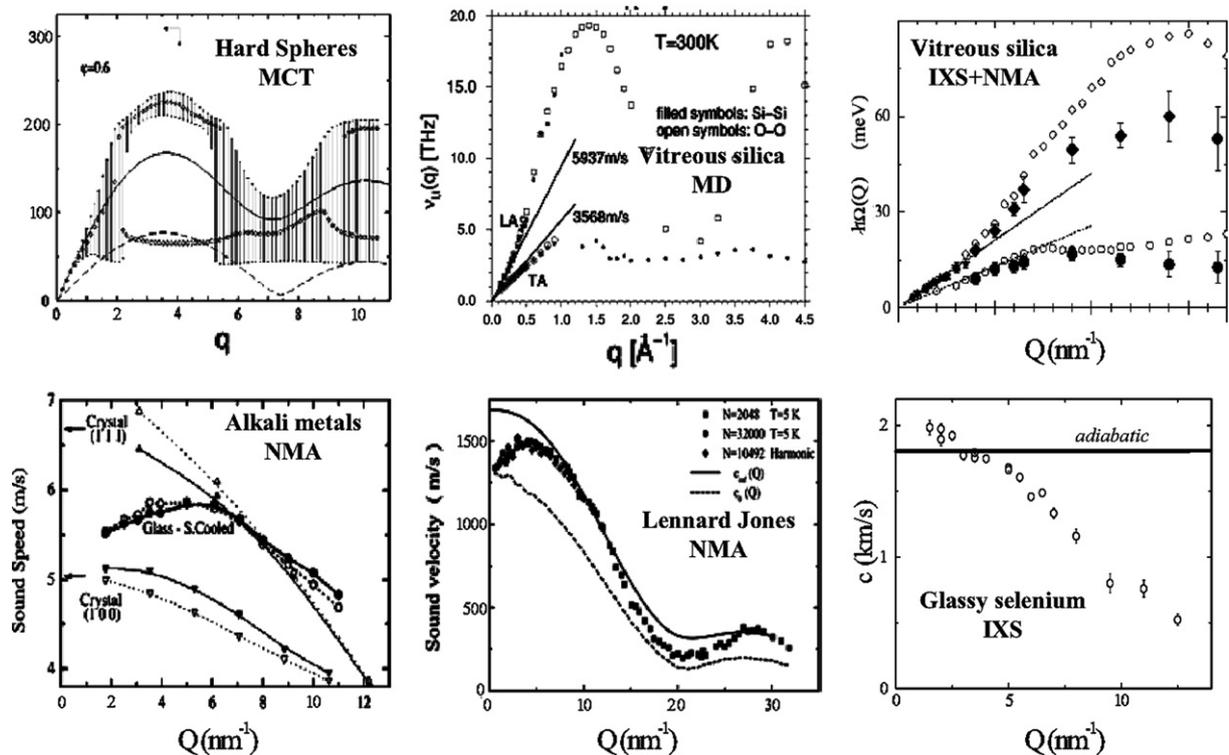

Fig. 3. Sound dispersion and velocities in several glassy systems. Top left: Hard spheres glass for packing fraction $\phi = 0.6$, analytical solution within MCT [16]. Longitudinal and transverse excitations energies are in units of 5×10^{-2} meV, wavevectors are in reduced units. Vertical bars are the FWHM of the excitations; Bottom left: Sound velocity (circles) in a metallic glass obtained quenching a model system modeled with Price–Singwi–Tosi pseudopotential [11], the crystalline counterpart along two symmetry direction (uptriangle and downtriangle) is also reported. Open and filled symbols correspond to different temperature in the glass and supercooled state, respectively; Bottom center: Lennard Jones glass obtained in a similar way [15], reported with the low and high frequency sound velocities; Top Center: vitreous SiO_2: Molecular dynamics [19] calculations of longitudinal and transverse sound branches. Top right: experimental determination by means of IXS scattering [17]. In both cases the transverse branch is also reported. Bottom right: glassy selenium [18], again the sound velocity exceeds the adiabatic value.

temperature independence of this latter process suggests to track its evolution upon in thermodynamic states other than the liquid phase. Unfortunately, this is almost impossible in bulk simple liquids, due to their strong crystallization tendency. As mentioned above, however, it is rather easy to perform numerical experiments producing supercooled and ultimately glassy states in monoatomic fluids interacting via density dependent effective potential, which have been shown to mimic the real properties of alkali metals [14]. In doing so, one effectively finds evidence for positive dispersion, quantitatively similar to the one observed in the liquid, in supercooled and glassy states while, as expected, this effect is completely swamped out looking at any branches of the crystalline state [11,15]. Motivated by this evidence, a number of experimental, numerical and theoretical results, summarized in Fig. 3, have been achieved in the last few years, showing the presence of positive dispersion in several glasses ranging from hard sphere analytical solution [16] to real glasses such as vitreous silica [17] or glassy selenium [18].

3. Conclusion

The collective dynamics of simple liquid metals, at wavelengths comprising a few atomic units, exhibit an extremely rich phenomenology. Although the ultimate scenario is still missing, there are a number of new evidences which necessarily have to be taken into account to raise the present degree of comprehension to a satisfactory level. Thinking in terms of characteristic wavelength of the density fluctuations or, equivalently, of exchanged momentum in an inelastic scattering experiment, three main regions can be identified below the Q position of the main peak of the static structure factor. Beyond the well known, hydrodynamic, small Q limit, a isothermal region should exist, around $0.1–0.5 \, \text{nm}^{-1}$, in which the sound velocity value decreases of a relative amount $\sqrt{\gamma}$, the thermal contribution to the sound attenuation saturates to the expression given by Eq. 2 (after the initial hydrodynamic Q^2 dependence), and the relative spectral components spreads over the Brillouin lines. As a matter of fact, the Q position where this phenomenon is expected to occur depends on the value of the thermal diffusivity, and it still has to be fully clarified whether it is the ionic or the whole thermal diffusivity which has to be taken into account.

On increasing the wavevector of about one order of magnitude, a further relaxation scenario appears. Rationalizing the experimental results in terms of generalized hydrodynamics, one finds that the usual picture based on the transition from a liquid like to a solid like response does not account alone for the reported phenomenology. As shown in Fig. 3, well established evidences such as the anomalous dispersion survives in the supercooled and ultimately in the glassy state [11,15]. In this respect, a predominant role of the topological disorder emerges, which can be casted in the framework of a 'fast' relaxation which heavily modifies the acoustic properties in the Thz region. The very nature of this relaxation process has still to be clarified at full, though it can be qualitatively understood in terms of the interaction of a plane-wave-like mode (the fixed Q excitation probed in an inelastic scattering experiment) with the real instantaneous eigenmodes of the inherent structure underlying the liquid dynamics. As these latter substantially departs from a plane wave, the single fourier component of the density fluctuation probed in a scattering experiment undergoes a relaxation decaying over the actual instantaneous eigenmodes.

Acknowledgment

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