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fluids probed by Inelastic X-Ray Scattering**

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The terahertz dynamics of simplest fluids probed by Inelastic X-Ray Scattering

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Abstract: More than two decades of Inelastic X-Ray Scattering (IXS) studies on noble gases and alkali metals are reviewed to illustrate the advances they prompted in our understanding of the terahertz dynamics of simplest systems. The various literature results outline a remarkably coherent picture of common and distinctive behaviours of liquids and their crystalline counterparts. Furthermore, they draw a consistent and comprehensive picture of the evolution of collective modes at the crossover between the hydrodynamic and the single particle regime, their coupling with fast (sub-ps) relaxation processes and their gradual disappearance upon approaching microscopic scales. The gradual transition of the spectrum towards the single particle limit along with its coupling with collisional relaxations will be discussed in some detail. Finally, less understood emerging topics will be discussed as the occurrence of polyamorphic crossovers, the onset of non-hydrodynamic modes and quantum effects on the spectrum, as well as recent IXS results challenging our vision of the supercritical phase as an intrinsically homogeneous thermodynamic domain.

Keywords: Inelastic X-ray Scattering, Inelastic Neutron Scattering, Noble Gases, Relaxation Phenomena, Liquid and Supercritical Systems

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1. Introduction

Despite many decades of thorough scrutiny, the collective dynamics of molecules in fluid and glassy systems still eludes a comprehensive understanding. This difficulty mostly owes to the lack of large-scale symmetries in the structure of these materials and the often exceptionally complex movements of their microscopic constituents. In this respect, dealing with monatomic fluids provides a substantial simplification both for the absence of intramolecular degrees of freedom and for the straightforward and short-range character of inter-atomic interactions. All these features are crucial to develop rigorous theoretical models, to simplify the interpretation of experimental results as well as to reliably approximate their dynamic and static response in computer simulations [1].

Among various variables conveying insight on the dynamic behaviour of these systems, density fluctuations are a particularly well-suited subject to study, as several independent investigation methods can directly probe them. Indeed, the most significant advances in the field of the dynamics of liquids arose from the critical comparison of either simultaneous or independent experimental and computational studies. In fact, both spectroscopy measurements and Molecular Dynamics (MD) simulations directly probe density correlations through their Fourier and Laplace transform, the dynamic structure factor, $S(Q, \omega)$ [2]. The latter is a unique function of the energy, $\hbar\omega$, and the momentum, $\hbar Q$, exchanged between the probe and the sample in a scattering measurement, with $\hbar$ being the reduced Planck constant.

When discussing the evolution of the $S(Q, \omega)$ shape across various dynamic regions, it is useful to take the average interatomic separation (d) and mean inter-collision time (τ_{coll}) as references and consider how the probed distance, $L = 2\pi/Q$ and time window, $t = 2\pi/\omega$, respectively compare with these parameters:

- (1) When $L \gg d$ and $t \gg \tau_{coll}$, the system appears as a continuous and isotropic medium, whose dynamic response is probed by averaging over a large number of microscopic interactions. In this limit, any detailed information on the microscopic structure and internal degrees of freedom of the sample is lost, and the hydrodynamic theory for continuous and homogeneous media gives a consistent account of the dynamic response. This theory stems from the conservation laws of the density of mass, momentum and energy and eventually leads to predict [3] the presence of three sharp features dominating the spectrum: the Rayleigh peak, arising from entropy fluctuations diffusing at constant pressure (P), and the two Brillouin side peaks, connected to pressure waves propagating at constant entropy.
- (2) In the opposite limit ($L \ll d$ and $t \ll \tau_{coll}$) the probed dynamic event reduces to the free recoil of the single atom induced by the collision with the probe particle (e.g. a photon or a neutron) and before any successive interactions with first neighbouring atoms. Here, the shape of the spectrum mirrors the momentum distribution of the struck particle in its initial state, which, for a classical system, is determined by the Maxwell-

Boltzmann distribution. In the reciprocal space probed by a scattering experiment, this distribution leads to derive a Gaussian spectrum [4] centred on the recoil energy.

Although the $S(Q, \omega)$ shape is well-known in these two limits, no sound theory predicts its evolution in between them. The investigation of this crossover is particularly insightful in the mesoscopic regime probed by high-frequency spectroscopic techniques, as Inelastic X-Ray (IXS) and Neutron Scattering (INS), which both probe distances and timescales comparable with first interatomic separations and cage oscillation periods respectively.

At these scales, thermodynamic and transport parameters are no longer constant coefficients, but rather space and time-dependent local variables of the fluid, as a reflection of the non-homogeneous, non-stationary nature of matter.

Clearly, at these mesoscopic scales a mere hydrodynamic description of density fluctuations loses physical significance, however, a suitably generalised hydrodynamic theory of density fluctuations can still hold validity for dense fluids. To understand this point, it is useful to recognise that, at the densities typical of the liquid phase, individual atoms are so closely packed that the only short-time movements they can experience are extremely short-ranged cage vibrations, or rattling movements, in some aspects resembling lattice vibrations in crystalline materials. Since these very rapid oscillations typically span the sub-nanometer, sub-picosecond space-time window, at the scales covered by IXS and INS, the probed dynamic response still results from an average over many microscopic interactions. This requisite is essential for a suitably generalised hydrodynamic theory to hold validity and for spectral modes to still keep a “collective” character.

Indeed, the persistence of collective generalised modes at mesoscopic scales was one of the breakthrough experimental results achieved in the 1960s in the field of the Physics of Liquids.

Historically, the study of $S(Q, \omega)$ in liquids at mesoscopic scales has been for many decades an exclusive domain of INS, whose development dates back to the mid-1950s [5]. Conversely, IXS is still a relatively young technique, which only came to light toward the end of the past millennium [6-9]. Its development owed to the advent of new generation synchrotron sources with unprecedented brilliance and the parallel advances in crystal optics fabrication.

This lag mainly stems from the exceptionally small relative energy resolution, $\Delta E/E$, required by IXS measurements of collective excitations in disordered systems. Specifically, being a conventional IXS spectrometer operated at ≈ 20 keV, it demands a $\Delta E/E$ at least as small as 10^{-7} to properly resolve such collective excitations, typically ranging in the meV window. Conversely, neutrons at low to moderate temperatures have ≈ 10 meV energies, which enable INS measurements to resolve meV even at moderate $\Delta E/E$ values ($\approx 10^{-1}$) [10]. Furthermore, for materials with atomic number $Z < 4$, photoelectric absorption dominates over IXS scattering and this makes this technique scarcely efficient for high Z samples. Finally, the IXS cross section rapidly decays upon increasing Q severely hampering investigations approaching the single particle limit.

Despite these difficulties, in the last decades, the superior performance of X-Ray sources has substantially improved the level of statistical accuracy typically attainable by IXS measurements. These advances paved the way for new detailed and physically informative studies of the spectral shape, which nowadays represent ideal test benches for present and future theories of fluid dynamics.

In summary, the development of Inelastic X-Ray Scattering (IXS) has substantially expanded the potentialities of modern spectroscopy, thus providing an unprecedented detailed mapping of the whole lineshape evolution and improving our knowledge of all dynamical processes occurring in a fluid from macroscopic to microscopic scales.

This progress, coupled with the promise of new-generation IXS spectrometers to cover “no man’s lands” of the dynamic plane, pave the way towards a totally new class of investigations in more complex metamaterials, as block copolymers and fully programmable superlattices of nanoparticles. Future IXS investigations on these materials are deemed to shed insight on the implementation of THz scale acoustic manipulations by structural engineering. The fundamental and applicative potentialities of this field are enormous, yet still largely unexplored (for a general review see, e.g. Ref. [11]). The exploration of this new Science frontier poses both practical and theoretical challenges, which can only be tackled by counting a more sound knowledge of the dynamic behaviour of simple prototypical systems, which stresses the need for systematic review efforts in the field.

Although, on the theoretical side, several excellent monographs are available, the experimental point of view is mostly outlined by a large number of specific, rather than comprehensive, research reports. . However few notable exceptions exist in literature and amongst them is worth mentioning a review of THz spectroscopy results on liquid metals [12] and a general review more concerned with instrumental aspects of IXS technique [13]. Other general accounts of IXS results are reported for water [13] and glass formers [6].

Given these grounds, this paper aims at providing an overview of various IXS results on simplest prototypical liquids, as noble gases and liquid alkali metal, while discussing relevant advances and still open issues. Rather than aiming at being exhaustive, it selectively discusses few “big themes” emerging from the body of available IXS results and is organised as follows: § 2 proposes a theoretical derivation of IXS cross section; § 3 illustrates common and complementary aspects of the two THz spectroscopic techniques currently available: IXS and INS. § 4 discusses the evolution of the spectral shape of simple fluids at the departure from the hydrodynamic regime, also introducing some broadly used models describing such a lineshape crossover. § 5 reviews the Q and ω dependence of transport parameters from the hydrodynamic to the single particle region. Finally, § 6 outlines some IXS results representing emerging or less “conventional” application of IXS studies in simple fluids. Finally, perspectives of this field of research disclosed by the advent of new generation spectrometers are briefly illustrated in § 7.

2. General introduction to the IXS technique

The main scope of this Section is to illustrate the derivation of IXS cross section, thus introducing the key dynamic variable measured by this technique: the dynamic structure factor. Before handling analytical details explicitly, some preliminary remarks on the general layout of an IXS spectrometer may be useful.

In an IXS measurement, a beam of X-Ray with a narrow angular divergence and a well-defined energy and polarisation impinges on a sample and, after the impact, is scattered all over the solid angle. A small number of the scattered photons is then intercepted and counted by the detector. Along its travel from the source to the detector, the X-Ray photon beam passes through various elements filtering its energy (monochromators), divergence (collimators) and, if needed, polarisation (polarizers), both before and after the scattering from the sample. The general layout

of an IXS spectrometer is rather straightforward, and, broadly speaking, it represents an implementation of the familiar triple-axis concept [5]: the first axis locates at the monochromator crystal, and rotations around it are used to select the energy of incident photons. Rotations of the spectrometer arm around the second axis, which locates at the sample position, are instead used to change the momentum transfer. Finally, the third axis is the one of the analyser crystal, and rotations around it define the energy scattered photons, $\hbar\omega_f$. Figure 1 schematically illustrates this general layout.

At variance of traditional neutron triple-axis spectrometers, in IXS instruments energy scans are usually performed by changing the lattice parameter, or d -spacing, of one of the energy-selecting units, (most often the monochromator) through the control/scan of their temperature. The main rationale behind the use of temperature-based scans is that, otherwise, the rocking of analyser/monochromator element around the Bragg reflection would cause an intolerable degradation of the energy resolution of the instrument.

Since, at a given reflection angle, the energy of the Bragg peak is determined by the d -spacing of the reflecting crystal, the difference in the d -spacings of the monochromator and analyser crystals fixes the value, $\hbar\omega$, of the energy gained/lost by X-Ray photons in the scattering event. Due to the energy conservation of the scattering process, $\hbar\omega$ also corresponds to the energy lost/gained by the target sample. Therefore, for a fixed scattering geometry, a change of the d -spacing difference between monochromator and analyser crystal ultimately provides an ω -scan of the intensity at a given Q value. Such an ω -distribution of the scattered intensity is customarily referred as the spectral density, or spectrum, of the sample.

Figure 1: A schematic layout of a typical IXS spectrometer.

2.1 The IXS cross section

It is safe to assume that, in a scattering process, the interaction time between probe and target system is much shorter than any other timescale relevant for the experiment. Assuming that the scattering source can be described by a point sitting at the origin, infinitely massive and at rest, the electrical field scattered at a position $\mathbf{r}$ is a solution of the inhomogeneous Helmholtz equation [15]:

$$(\nabla^2 + k^2)\mu(\mathbf{r}) = -\delta(\mathbf{r}), \quad (1)$$

where " ∇^2 " is the Laplacian operator, while $k = |\mathbf{k}|$ is the wavenumber of the incident electromagnetic wave. Downstream from the sample, the outgoing wave is the sum of a plane wave, transmitted with no deviation, and a spherical one. If the incident beam has small cross section and divergence, a spherical wave of the form:

$$\psi_{sc} \propto \frac{e^{ikr}}{r} \quad (2)$$

uniquely describes the state the scattered photons at any finite scattering angles. One readily recognises that the scattering event partly removes the incident photons from their plane wave initial state and re-radiated them in a spherical wave, which appears as a straightforward manifestation of the Huygens' principle [16]. The photon fan deviated at an angle 2θ to within a solid angle $d\Omega$ is finally intercepted by a detector having a sensitive area $dA = r^2 d\Omega$ sufficiently small - and distance from the sample large enough - to safely approximate the spherical wave impinging on it as a plane wave. The scattering event thus ultimately causes a transition of the photons between two plane wave states. Furthermore, the scattered photons, before reaching the detector, pass through the analyser, which filters out their energy within a narrow bandwidth dE_f . Therefore, the intensity measured by the instrument can be cast in the following general form:

$$I \propto I_0 h \sigma_s \left(\frac{\partial^2 \sigma}{\partial \Omega \partial E_f} \right) d\Omega dE_f, \quad (3)$$

Here I_0 is the photon flux impinging upon the sample, n the number density of scattering units, and h the transverse size of the beam illuminating the sample, here assumed constant across the sample thickness t_s . Eq. 3 contains the double differential scattering cross-section, defined as:

$$\frac{\partial^2 \sigma}{\partial \Omega \partial E_F} = \frac{\text{Rate of photons scattered into } d\Omega \text{ with final energy between } E_F \text{ and } E_F + dE_F}{I_0 \partial \Omega \partial E_F}. \quad (4)$$

It is worth noticing that being typical IXS measurements performed in transmission geometry, part of the scattered intensity is absorbed by the sample itself. The intensity reduction experienced by the photon beam after crossing a sample slab of infinitesimal thickness dx is:

$$dI = I(x) - I(x + dx) = -I n \sigma dx \Rightarrow \int_0^{t_s} \frac{dI}{I} = \int_0^{t_s} n h dx.$$

From which it follows that:

$$I \propto I_0 n h L \exp(-\mu t_s) \left(\frac{\partial^2 \sigma}{\partial \Omega \partial E_f} \right) d\Omega dE_f, \quad (5)$$

where it was introduced the photo-absorption coefficient $\mu = 1/\lambda_a$, with λ_a being the photo-absorption length of the sample at the given incident energy. The sample length, L , maximising the scattering intensity is determined by superimposing the condition $\partial I / \partial t_s = 0$, which yields $t_s = 1/\mu = \lambda_a$. Therefore, the optimal sample thickness should match the sample absorption length at the incident energy of the measurement.

It appears from Eq. 5 that the only non-trivial and in principle unknown factor defining the scattering intensity is the double differential cross-section $\partial^2 \sigma / \partial \Omega \partial E_f$. An analytical expression for this variable can be derived from the Hamiltonian describing the interaction between the electrons of the target system and the time-dependent electromagnetic field impinging on them. In the non-relativistic case and within the realistic assumption of negligible coupling of photons with the electron spin, such Hamiltonian reads as [9]:

$$H = H_{el} + H_{int}^{(1)} + H_{int}^{(2)}, \quad (6)$$

where the unperturbed Hamiltonian and the two leading perturbative terms in the sum respectively read as:

$$H_{el} = \sum_i \left[\frac{|\mathbf{p}_i|^2}{2M} + V(\mathbf{r}_i) \right] \quad (7)$$

$$H_{int}^{(1)} = -\frac{e}{2m_e c} \sum_i \{ \mathbf{A}(\mathbf{r}_i) \cdot \mathbf{p}_i \} \quad (8)$$

$$H_{int}^{(2)} = \frac{1}{2} r_0 \sum_i \mathbf{A}(\mathbf{r}_i) \cdot \mathbf{A}(\mathbf{r}_i). \quad (9)$$

Here the symbol $\{, \}$ represents the anticommutator operator, while $V(\mathbf{r}_i)$, $A(\mathbf{r}_i)$, $\mathbf{r}_i$ and $\mathbf{p}_i$ are the atom-electron potential, the vector potential, the position and the momentum of the i -th electron, respectively. Finally $r_0 = e^2/(m_e c^2)$ is the classical electron radius, with c , e , and m_e being the speed of light in vacuum, and the electron charge and mass, respectively.

The term linear in $A(\mathbf{r}_i)$ in Eq. 8 accounts, to the leading order, for one-photon processes such as absorption and emission, while it describes two-photon processes, as the scattering event, to the second order only. Conversely, the so-called Thomson term, i.e. the term quadratic in the vector potential (Eq. 9) reproduces the scattering event to the first order. Away from an electronic energy resonance, the Thomson term dominates over the second-order expansion of in Eq. 8, thus yielding the leading contribution to the scattering intensity. In the following, the double differential IXS cross section is derived assuming that this the Thomson term entirely describes the scattering process.

As mentioned, the collision with the sample causes a transition of the photon states between two distinct plane waves. Therefore, the scattering intensity could in principle be computed by counting all plane waves generated from the scattering of a single incident plane wave and pointing toward the 2θ direction to within a solid angle $d\Omega$. However, this procedure would pose a problem, since the normalisation integral of a plane wave diverges for long distances. This issue can be easily circumvented by normalising the plane waves within a cubic box of size L , and eventually considering the limit of diverging L . Within such a box, the following linear combination of normalised plane waves can be used to describe the vector potential [9]:

$$A(\mathbf{r}) = \sum_{k,\varepsilon} \sqrt{\left(\frac{2\pi\hbar}{\omega_k L^3}\right)} c\hat{\varepsilon} \left[\mathbf{a}_{k,\varepsilon}^+ \exp(i\mathbf{k} \cdot \mathbf{r}) + \mathbf{a}_{k,\varepsilon}^- \exp(-i\mathbf{k} \cdot \mathbf{r}) \right]. \quad (10)$$

Here the sign “+” and “-” in the exponents define the downstream and upstream plane wave propagation, respectively. The indexes k and ε label, the wave vector and the polarisation of the wave, identified by the unit vector $\hat{\varepsilon}$ and the vector $\mathbf{k}$, respectively. The parameters c , ω_k , $\mathbf{a}_{k,\varepsilon}^+$ and $\mathbf{a}_{k,\varepsilon}^-$ denote the in-vacuum light speed and angular frequency, the annihilation and the creation operators, respectively.

Coming back to the double differential scattering cross section, a general expression for this variable is given by:

$$\frac{d^2\sigma}{d\Omega dE_f} = \frac{dP_{i \rightarrow f}}{dt} \frac{1}{I_0} \frac{d^2n}{d\Omega dE_f}. \quad (11)$$

Here $dP_{i \rightarrow f}/dt$ is the probability rate per sample and probe units that a photon undergoes a transition between the initial and the final states (respectively labelled by the “ i ” and “ f ” suffixes), while $d^2n/d\Omega dE_f$ is the double differential density of photon states. Furthermore, in Eq. (11) it was introduced the photon flux as:

$$I_0 = \frac{c}{L^3}. \quad (12)$$

It is worth noticing that use of a cubic box of size L makes the count of the photon states particularly easy [17]; this computation eventually yields:

$$\frac{d^2 n}{d\Omega dE_f} = \frac{L^3}{8\pi^3} \frac{k_F^2}{\hbar c} \frac{dP_{i \rightarrow f}}{dt}. \quad (13)$$

Since the scattering event is prompted by a photons-sample interaction, it should be more appropriately described as a $|I, i\rangle \rightarrow |F, f\rangle$ transition, involving the combined photon-sample states. Here lower case and capital characters selectively label photon and sample states, respectively. Furthermore, before the scattering, the target sample is a many-body system at thermal equilibrium, rather than being in a well-defined initial quantum state. Furthermore, the final state of the sample cannot be determined either, since only initial and final states of the photons can, in principle, be measured. For these reasons, the probability rate is given by a sum over all possible (unknown) initial and final states of the sample:

$$\frac{dP_{i \rightarrow f}}{dt} = \sum_{I, F} \frac{dP_{F, i \rightarrow I, f}}{dt}, \quad (14)$$

with $P_{I, i \rightarrow F, f}$ being the probability of the $|I, i\rangle \rightarrow |F, f\rangle$ transition. The formula above is particularly useful, as the Fermi Golden Rule permits to express the probability rate under summation as:

$$\frac{dP_{i, F \rightarrow I, f}}{dt} = \frac{2\pi}{\hbar} \left| \langle F, f | H_{int}^{(2)} | I, i \rangle \right|^2. \quad (15)$$

The interaction term appearing in the above formula can be developed by inserting in it the expression of the Thomson term in Eq. 9 which contains the vector potential in Eq. 10. Explicitly:

$$\left| \langle F, f | H_{int}^{(2)} | I, i \rangle \right| = \left(\frac{r_0}{L^3} \right) (\hat{\mathbf{e}}_i^* \cdot \hat{\mathbf{e}}_f) \frac{2\pi\hbar c}{\sqrt{k_i k_f}} \sum_{j, m} \langle F | \exp(-i\mathbf{Q} \cdot \mathbf{r}_j) | I \rangle \langle I | \exp(i\mathbf{Q} \cdot \mathbf{r}_m) | F \rangle, \quad (16)$$

where $\hbar\mathbf{Q} = \hbar(\mathbf{k}_f - \mathbf{k}_i)$ represents the momentum gained by the photons. Furthermore, while deriving Eq. 16, it was considered that the frequency of the plane wave $\omega(k)$ is equal to ck_i and ck_f in the initial and the final photon states, respectively. It is worth noticing that the right-hand side of Eq. 16 depends on the sample's states only. By combining Eqs. 11-16, the double differential cross section eventually reduces to:

$$\frac{\partial^2 \sigma}{\partial \Omega \partial E_f} = r_0^2 \frac{k_f}{k_i} (\hat{\mathbf{e}}_i \cdot \hat{\mathbf{e}}_f)^2 \sum_{F,I} P_I \left| \langle I | \sum_j \exp(i\mathbf{Q} \cdot \mathbf{r}_j) | F \rangle \right|^2 \delta(\hbar\omega + E_I - E_F). \quad (17)$$

Here $\hbar\omega = E_f - E_i$ is the energy transferred from the photon to the sample, with the δ -function ensuring the overall energy conservation in the scattering process. Furthermore, the factor P_I defines the statistical population of the initial state.

The adiabatic approximation

It can be readily noticed that double differential cross section in Eq. 17 is the product of three factors: 1) the merely “electronic” factor r_0^2 ; 2) the factor $(k_f/k_i)(\hat{\mathbf{e}}_i^* \cdot \hat{\mathbf{e}}_f)^2$, which contains plane wave parameters of the incident and scattering photons and, finally, 3) the integral term, which directly relates to the target sample.

The latter term is particularly difficult to handle analytically, as, in principle, it encompasses electronic coordinates belonging to either the same or different atoms, which makes electronic and nuclear coordinates mutually intertwined. To disentangle them, further approximations must be adopted:

- The centre of mass of the electronic cloud is assumed to follow the nuclear motion as a slow drift with no delay (adiabatic approximation [17]). This approximation authorises to express the state of the sample as $|S\rangle = |S_n\rangle |S_e\rangle$, where the suffixes “n” and “e” labelling nuclear and electronic states respectively. This approximation becomes particularly accurate at energies smaller than electron energies in bound core states, i.e. for nearly all cases of practical interest for this review. In liquid metals, this approximation only excludes electron densities near the Fermi level.
- It is also safe to assume that the term $|S_e\rangle$ is unaffected by the scattering process. Therefore, the difference between the initial ($|I\rangle = |I_n\rangle |I_e\rangle$) and final ($|F\rangle = |F_n\rangle |F_e\rangle$) states of the sample is uniquely due to excitations associated with atomic density fluctuations.

Within the validity of these assumptions, the double differential cross section reduces to:

$$\frac{\partial^2 \sigma}{\partial \Omega \partial E_f} = r_0^2 \frac{k_f}{k_i} (\hat{\mathbf{e}}_i \cdot \hat{\mathbf{e}}_f)^2 \sum_{F_n, I_n} P_{I_n} \left| \langle I_n | \sum_j f_j(\mathbf{Q}) \exp(i\mathbf{Q} \cdot \mathbf{r}_j) | F_n \rangle \right|^2 \delta(\hbar\omega + E_I - E_F), \quad (18)$$

where it was introduced the atomic form factor of the j-th atom:

$$f_j(\mathbf{Q}) = \langle S_e | \sum_{\alpha=1}^Z \exp(i\mathbf{Q} \cdot \mathbf{r}_\alpha^j) | S_e \rangle \quad (19)$$

which only the coordinate of the electrons of the j-th atom. Assuming that all target atom scatter identically, i.e. that they have the same form factor, one can further simplify the expression of the double differential cross section:

$$\frac{d^2 \sigma}{d\Omega dE_f} = \frac{r_0^2}{\hbar} \left(\frac{k_f}{k_i} \right) (\hat{\mathbf{e}}_i^* \cdot \hat{\mathbf{e}}_f)^2 |f(\mathbf{Q})|^2 S(\mathbf{Q}, \omega), \quad (20)$$

where the variable $S(\mathbf{Q}, \omega)$ is the dynamic structure factor, defined as:

$$S(\mathbf{Q}, \omega) = \sum_{F_n, I_n} P_{I_n} \left| \langle I_n | \sum_j \exp(i\mathbf{Q} \cdot \mathbf{r}_j) | F_n \rangle \right|^2 \delta(\hbar\omega + E_I - E_F). \quad (21)$$

After simple manipulations based on the Heisenberg formalism [18] and using the integral definition of the Dirac's δ -function, one eventually obtains:

:

$$S(\mathbf{Q}, \omega) = \frac{1}{2\pi N} \int_{-\infty}^{\infty} \sum_{j,m} \langle \exp(-i\mathbf{Q} \cdot \mathbf{R}_j(t)) \exp(-i\mathbf{Q} \cdot \mathbf{R}_m(0)) \rangle \exp(-i\omega t) dt, \quad (22)$$

where the symbol $\langle \dots \rangle$ denotes a correlation function, which results from an average over the initial equilibrium state of the target system.

Notice that photon-electron coupling factor ($|f(\mathbf{Q})|^2$) vanishes upon increasing $\mathbf{Q}$, as the portion of electronic cloud involved in the scattering process becomes smaller upon decreasing the probed volume, Q^{-3} .

In Eqs. 20 and **Error! Reference source not found.** it was assumed that, for a homogeneous and isotropic system, as a liquid, the dynamic structure factor does not depend on the direction of the exchanged wave-vector, but uniquely on its amplitude $Q = |\mathbf{Q}|$.

2.2 Cross section and density correlation functions

Similarly to what discussed in Ref. [19] for INS, the double differential cross section of IXS can be now directly connected to the Fourier transform of the density-density correlation function. To see this explicitly, it is useful to define the variable density [2,20] at the mesoscopic scales probed by IXS. As mentioned, at these scales, the matter is no longer homogeneous, nor stationary, which suggests redefining the density as a proper function of both space and time. In particular, for a system composed of N atoms, the microscopic density can be represented as the sum of N Dirac δ -functions:

$$n(\mathbf{r}, t) = \sum_{i=1}^N \delta[\mathbf{r} - \mathbf{R}_i(t)], \quad (23)$$

where $\mathbf{R}_i(t)$ is the position of the i -th atom at the time t . According to the above formula, the integral of the $n(\mathbf{r}, t)$ over a given volume V , is equal to the number of atoms contained in such a volume. Specifically, in the macroscopic limit one has $n \int_V dV = N$, *i.e.* $n = N/V$, which is consistent with the macroscopic definition of the number density.

In the present context, it is more useful to deal with the density fluctuation from the equilibrium value:

$$\delta n(\mathbf{r}, t) = \sum_{i=1}^N \delta[\mathbf{r} - \mathbf{R}_i(t)] - n. \quad (24)$$

Furthermore, since a scattering experiment maps the reciprocal rather than the real space, it is convenient to introduce the space Fourier transform of the density:

$$n(\mathbf{Q}, t) = \sum_j \exp[i\mathbf{Q} \cdot \mathbf{R}_j(t)] \quad (25)$$

and the one of density fluctuation:

$$\delta n(\mathbf{Q}, t) = \sum_j \exp[i\mathbf{Q} \cdot \mathbf{R}_j(t)] - (2\pi)^3 n \delta(\mathbf{Q}). \quad (26)$$

Considering Eq. **Error! Reference source not found.**, one can make the following identification:

$$S(Q, \omega) = \tilde{S}(Q, \omega) = \frac{1}{2\pi N} \int_{-\infty}^{+\infty} e^{i\omega t} \langle \delta n^*(Q, 0) \delta n(Q, t) \rangle dt, \quad (27)$$

which holds validity as long as the term $\propto \delta(Q)\delta(\omega)$ (with $\delta(\omega) = 1/2\pi \int_{-\infty}^{+\infty} e^{i\omega t} dt$) in Eq. 26 is discarded. Indeed, since this term is irrelevant for an IXS measurement since it describes the forward elastic scattering.

All correlation functions we will be dealing with hereafter involve fluctuations of the variable from equilibrium, which rules out all constants terms (in the real space), or δ -functions (in the reciprocal space).

It is now useful to introduce few more correlation functions, which directly relate to the some of the topics discussed in this review. The first is the van Hove correlation function [19]:

$$G(r, t) = \frac{1}{N} \sum_{m=1}^N \sum_{j=1}^N \langle \delta[\mathbf{r} + \mathbf{R}_m(0) - \mathbf{R}_j(t)] \rangle = \frac{1}{N} \langle \delta n(\mathbf{r}, t) \delta n^*(\mathbf{r}, 0) \rangle. \quad (28)$$

This correlation function is often expressed as the sum $G(r, t) = G_s(r, t) + G_d(r, t)$, where:

$$G_s(r, t) = \frac{1}{N} \sum_m \langle \delta[\mathbf{r} + \mathbf{R}_m(0) - \mathbf{R}_m(t)] \rangle \quad (29)$$

$$G_d(r, t) = \frac{1}{N} \sum_{m=1}^N \sum_{j \neq m=1}^N \langle \delta[\mathbf{r} + \mathbf{R}_m(0) - \mathbf{R}_j(t)] \rangle. \quad (30)$$

where the suffix “s” and “d” respectively labelling the self and the parts of the van Hove function. These respectively consist of correlations between single particle’s densities at distinct times or between atomic pairs densities at distinct times respectively.

The Fourier transform of the van Hove function in Eq. 28 yields the intermediate scattering function:

$$F(Q, t) = \frac{1}{N} \int_V \langle \delta n(\mathbf{r}, t) \delta n^*(\mathbf{r}, 0) \rangle \exp(i\mathbf{Q} \cdot \mathbf{r}) d\mathbf{r} = \int_{-\infty}^{\infty} S(Q, \omega) \exp(i\omega t) d\omega, \quad (31)$$

which for $t = 0$ coincides with the static structure factor:

$$S(Q) = \frac{1}{N} \int_V \langle \delta \rho(\mathbf{r}, 0) \delta \rho^*(\mathbf{r}, 0) \rangle \exp(i\mathbf{Q} \cdot \mathbf{r}) d\mathbf{r} = \int_{-\infty}^{\infty} S(Q, \omega) d\omega. \quad (32)$$

As evident from the above equation, $S(Q)$ is the Fourier transform of the “static” ($t = 0$) value of the density fluctuations correlation, thus conveying direct insight on the structural properties of the fluid. Most importantly, $S(Q)$ can be measured by either X-Ray or neutron diffraction techniques, and the so-called pair distribution function [21]:

$$g(r) = \sum_{i \neq j} \langle \delta(r - R_i) \delta(R_j) \rangle \quad (33)$$

can be directly derived from it through:

$$g(r) = \frac{2}{\pi} \int_0^\infty [S(Q) - 1] Q \sin(Qr) dQ. \quad (34)$$

The pair distribution function represents the equilibrium probability distribution that a particle locates at a distance r from a tagged particle sitting at the origin, $r = 0$.

The incoherent contribution to the IXS spectrum

The treatment illustrated above and leading to Eq. 20 strictly applies to systems of N identical atoms within the validity of the Born–Oppenheimer approximation. For a system containing different atomic species, the derivation of the scattering cross section is similar, provided the system is isotropic. In the more general case of anisotropic molecules, a factorization between a merely electronic and a nuclear term is still possible and leads to the conclusion that the double differential cross section splits into two components: a coherent and an incoherent one. The former is proportional to the orientationally averaged value of the form factor, while the latter arises from mean squared fluctuations from it. To demonstrate this statement, it is useful to start from the expression of the intermediate scattering function of a molecular system:

$$F(Q, t) = \frac{1}{N \left(\sum_n f_n(Q) \right)^2} \left\langle \sum_{j,k} \sum_n \sum_m f_n(Q) f_m(Q) \exp\{iQ \cdot [r_m^k(t) - r_m^k(0)]\} \right\rangle \quad (35)$$

Where the i, j and n, m indexes label couples of molecules and nuclei respectively. Therefore, $f_n(Q)$ and r_n^i represent, respectively, the form factor and the coordinate of the n -th atom belonging to the i -th molecule. At this point, it is useful to introduce an “effective centre” of the i -th molecule:

$$R_i^c(t) = \frac{\sum_n f_n(Q) r_{n,i}^c(t)}{\left(\sum_n f_n(Q) \right)}, \quad (36)$$

where $\mathbf{r}'_{n,i}(t)$ is the coordinate of the n -th atom respect to the effective molecular centre, $\mathbf{R}_i^c(t)$. Using these coordinates, the $F(Q,t)$ reads as:

$$F(Q,t) = \frac{1}{N} \left\langle \sum_{j,k} \exp\{i\mathbf{Q} \cdot [\mathbf{R}_j^c(t) - \mathbf{R}_k^c(0)]\} \sum_n f_n(Q) f_m(Q) \exp\{i\mathbf{Q} \cdot [\mathbf{r}'_{n,i}(t) - \mathbf{r}'_{m,i}(0)]\} \right\rangle \quad (37)$$

This equation can be simply rearranged to obtain:

$$F(Q,t) = \frac{1}{N} \left\langle \sum_{j,k} \exp\{i\mathbf{Q} \cdot [\mathbf{R}_j^c(t) - \mathbf{R}_k^c(0)]\} \right\rangle F_1(Q) + F_2(Q,t). \quad (38)$$

It clearly appears that the first term in the above equation is proportional to the density fluctuation associated with the effective molecular centre of mass positions, while with $F_2(Q,t)$ is determined by the intramolecular degrees of freedom. We can safely assume that, in the mesoscopic region of interest here, these degrees of freedom essentially coincide with molecular orientation, i.e. that molecules behave as rigid roto-translators, without vibrational motions. The form factor with $F_1(Q)$ can be evaluated by performing an average over molecular orientations, uniquely determined by the intramolecular coordinate $\mathbf{r}'_{n,i}(t)$. This eventually yields:

$$F_1(Q) = \left\langle \sum_n f_n(Q) f_m(Q) \frac{\sin(Qr'_{n,i})}{Qr'_{n,i}} \frac{\sin(Qr'_{m,i})}{Qr'_{m,i}} \right\rangle = \overline{F(Q)} \quad (39)$$

The second term in Eq.38 can be cast in the form:

$$F_2(Q,t) = \left\langle \sum_{n \neq m} f_n(Q) f_m(Q) \exp\{i\mathbf{Q} \cdot [\mathbf{r}'_{n,j}(t) - \mathbf{r}'_{n,j}(0)]\} \right\rangle \quad (40)$$

Here both the considered n -th and m -th atoms belong to the same j -th molecule. Notice that for random orientation of the molecule one has:

$$\langle f_n(Q) f_m(Q) \rangle = \delta[F^2(Q)] \quad (41)$$

where $\delta[F^2(Q)] = \overline{F^2(Q)} - \delta_{nm} \overline{F(Q)}^2$ is the mean squared fluctuation of the form factor from its orientationally averaged value. Therefore:

$$F_I(Q, t) = \delta[F^2(Q)] \langle \exp\{i\mathbf{Q} \cdot [\mathbf{r}'_{n,i}(t) - \mathbf{r}'_{m,i}(0)]\} \rangle \quad (42)$$

Notice that the fluctuation $\delta[f^2(Q)]$ arises from the non-isotropic character of the electronic shape distribution and its coupling with single molecule orientation. Therefore, for a generic molecular system, one has:

$$\frac{\partial^2 \sigma}{\partial \Omega \partial \omega} = r_0^2 \left(\frac{k_i}{k_f} \right) (\hat{\mathbf{e}}_i^* \cdot \hat{\mathbf{e}}_f)^2 \left\{ \overline{F(Q)}^2 S_C(Q, \omega) + \delta[F^2(Q)] S_I(Q, \omega) \right\}. \quad (43)$$

The above formula shows that the scattering of the sample has both a coherent and an incoherent part, respectively, labelled by the “C” and “I” suffixes, namely:

$$S_C(Q, \omega) = \frac{1}{2\pi N} \int \sum_{-\infty}^{\infty} \langle \exp\{i\mathbf{Q} \cdot [\mathbf{R}_j^c(t) - \mathbf{R}_k^c(0)]\} \rangle \exp(-i\omega t) dt \quad (44)$$

$$S_I(Q, \omega) = \frac{1}{2\pi} \int \sum_{-\infty}^{\infty} \langle \exp\{i\mathbf{Q} \cdot [\mathbf{r}'_{n,i}(t) - \mathbf{r}'_{m,i}(0)]\} \rangle \exp(-i\omega t) dt \quad (45)$$

The coherent term contains both correlations involving either different ($j \neq k$) or the same ($j = k$) molecular centres at different times, while the incoherent term only relates to the same ($j = m$) molecular centre of mass at different times. An IXS measurement in principle probes both contributions and no simple method exists to single them out. However, the incoherent part is in general much smaller than for INS. The existence of the incoherent scattering can be understood by recognising that the electronic cloud seen by the probe depends on how the target molecules are oriented, therefore the scattering medium is perceived by the probe as non-uniform, i.e. changing erratically from a molecule to the next. Conversely, the average molecular orientation governs interference, or coherent, effects in the scattering of molecules. Accordingly, it can be deduced that the incoherent scattering relates to single-particle motions only, while the coherent stems from interference effects due to both collective and single-particle dynamics.

A closer comparison between various aspects of INS and IXS is the focus of the following paragraphs.

The multiple scattering

The theory described above holds validity when each scattered photon experience a single scattering event, i.e. it interacts only once with the target system. The single scattering intensity can be obtained inserting into Eq. 5 the double differential cross section in Eq. 20 (for a monatomic system), or the one in Eq. 43 (for a molecular system), i.e. in general:

$$\frac{\partial N_i}{\partial t} \propto I_0 n \sigma L \exp(-\mu t_s) \left(\frac{\partial^2 \sigma}{\partial \Omega \partial E_f} \right) d\Omega dE_f, \quad (46)$$

Where N_i is the number of photon scattered a single time. The intensity contribution from multiple scattering events cannot be cast in a known analytical form and its determination requires the use of computer simulation techniques. However, the single to double scattering events intensity ratio can be easily estimated for scattering geometries close to forward direction, i.e. for small scattering angle, which often the case in the experiments described in this review. In this approximation one has:

$$R_{1,2}(Q \rightarrow 0) \propto \frac{\pi \hbar n r_0^2}{Z^2 S(0)} \int_0^\pi d(2\theta) \left[f^2 \left(\frac{4\pi}{\lambda} \sin \theta \right) S \left(\frac{4\pi}{\lambda} \sin \theta \right) \right], \quad (47)$$

Where it was used $Q = (4\pi/\lambda) \sin \theta$. In all cases considered in this review the contribution is negligibly small.

The cross section of INS

The derivation of the scattering cross section for neutron scattering is illustrated in the monographs of Lovesey [4] and Squires [10] and only the final result is discussed here.

The first concern for an analytical derivation of the INS cross section is a proper description of the Hamiltonian of interaction between the incoming neutron beam and the target sample. A rigorous treatment of the problem would need a complete theory of the nucleon-nucleon, which currently is not available. However, experimental evidence proves that this interaction is very short-ranged and isotropic, and can be identified by a single unknown parameter, the scattering length of the i -th target nucleus, b_i .

In principle, the latter depends on the relative orientation of the spins of the neutron and the nucleus. Assuming for the sake of simplicity that the target nuclei are spinless, the only form of interaction potentially yielding an isotropic scattering in Born approximation has the form of a δ -function of space. An ideal candidate is the Fermi pseudopotential [22]:

$$V(\mathbf{r}) = \frac{2\pi\hbar^2}{m} \sum_{i=1}^N b_i \delta[\mathbf{r} - \mathbf{R}_i(t)]. \quad (48)$$

To derive an analytical expression for the double differential cross section, one can follow a perturbative method like the one illustrated in previous paragraphs. Eventually, this leads to:

$$\frac{\partial^2 \sigma}{\partial \Omega \partial E_f} = \left(\frac{k_i}{k_f} \right) N \left\{ \overline{b^2} S_c(Q, \omega) + \delta(b^2) S_1(Q, \omega) \right\}. \quad (49)$$

Where, $\delta(b^2) = \left| \overline{b^2} - \bar{b}^2 \right|$ is the mean square fluctuation of the scattering length of the target system.

2.3 A direct comparison between IXS and INS

In general, INS and IXS *methods* present some general analogies:

- They both can be used to investigate bulk rather than surface properties of materials.
- They probe density fluctuations through the Fourier transform of their autocorrelation function, $S(Q, \omega)$.
- They are “mesoscopic” probes.

Other similarities emerge from the comparison of the double differential cross section, expressed Eq. 49 and Eq. 43 for IXS and INS, respectively. Specifically:

- a) For both x-ray and neutron scattering the cross section depends on the ratio k_f/k_i . However, in the latter case, this factor does not depend on frequency and is essentially equal to 1.
- b) The role of the form in the IXS cross section is analogous to that of the scattering length in the INS. They define the coupling between the probe and the target sample, i.e. the photon-electron and neutron-nucleus interaction strengths, respectively. However, the form factor depends on the number of electrons in the target atoms, but not on the atomic mass. Therefore, as opposite to the scattering length, it is not sensitive to the isotopic composition of the sample.
- c) Another fundamental difference is that b is constant up to Q values comparable with the inverse of the nuclear size, while $f(Q)$ sharply decreases at high exchanged momenta. This trend severely limits the IXS count rates typically achievable at high Q 's

Overall, the two techniques present complementary advantages and disadvantage, making them ideally suited for certain applications and less to others, as thoroughly illustrated in § 2.4. Before entering in further details, it is useful to discuss some inherent constraints, customarily referred to

as kinematic limitations, which hamper IXS and INS techniques to a very different degree.

Kinematic limitations

The so-called kinematic limitations stem from the imposition of the energy and momentum conservation laws in the scattering process, which yields radically different results for either neutron or X-Ray scattering. Let's discuss the neutrons case first.

a) Neutron scattering

As mentioned, the momentum conservation law in the scattering event imposes $\mathbf{Q} = \mathbf{k}_f - \mathbf{k}_i$. This equality can be rearranged by taking the square of both members, thus obtaining:

$$Q^2 = k_f^2 + k_i^2 - 2k_i k_f \cos(2\theta). \quad (50)$$

Furthermore by dividing each member by k_i^2 , one has:

$$\left(\frac{Q}{k_i}\right)^2 = \left(\frac{k_f}{k_i}\right)^2 + 1 - 2\left(\frac{k_f}{k_i}\right)\cos(2\theta). \quad (51)$$

The energy conservation law $\hbar\omega = E_f - E_i$ can be instead manipulated by recognising that the (kinetic) energy of a neutron freely flying with velocity $v = \hbar k/m_n$ is:

$$E = \frac{\hbar^2 k^2}{2m_n}, \quad (52)$$

with m_n being the neutron mass. A simple algebraic manipulation eventually yields:

$$\frac{k_f}{k_i} = \sqrt{1 - \frac{\hbar\omega}{E_i}}. \quad (53)$$

Finally, after combining Eqs. 51 and 53 and taking the square root of both members, one eventually obtains:

$$\frac{Q}{k_i} = \sqrt{2 - \left(\frac{\hbar\omega}{E_i}\right) - 2 \cos(2\theta) \sqrt{1 - \frac{\hbar\omega}{E_i}}} . \quad (54)$$

Clearly, the portion of the dynamic (Q, ω) domain accessible by an INS measurement is limited by the condition that the arguments of the square roots are positive. In particular, the square root nested into the major one has a positive argument whenever $\hbar\omega \leq E_i$, which reflects the obvious constraint that the energy transferred from the neutron to the sample cannot exceed the energy carried initially by the former. Furthermore, the requirement for the argument of the main (larger) square root in Eq. 54 to be positive introduces further restrictions to the explored dynamic range, the relevance of this limitation will be discussed further below by using a practical example. Meanwhile it is useful to mention that the condition that the exchanged momentum defined in Eq. 54 is real-valued, introduces some parabolic boundaries delimiting the accessible portion of the (Q, ω) -plane.

a) X-Ray scattering

While for neutrons the dependence of energy on wavevector is quadratic (Eq. 52) for X-Ray it is linear:

$$E = \hbar ck . \quad (55)$$

As a consequence, the energy conservation in the scattering event can be written as:

$$\frac{k_f}{k_i} = 1 - \frac{\hbar\omega}{E_i} . \quad (56)$$

Combining the above equation with Eq. 50 one eventually obtains:

$$\frac{Q}{k_i} = \sqrt{2 - \left(\frac{\hbar\omega}{E_i}\right) - 2 \cos(2\theta) \left(1 - \frac{\hbar\omega}{E_i}\right)} . \quad (57)$$

In principle the accessible portion of the dynamic plane is subjected to the constraint that the argument under the square root is positive. However, this, in practice, does not represent a real limitation, as, for IXS, $\hbar\omega/E_i$ is $\approx 10^{-7}$, thus being much smaller than the other terms under the square root. Hence:

$$Q = k_i \sqrt{2[1 - \cos(2\theta)]} = 2k_i \sin(\theta) = \frac{4\pi}{\lambda} \sin(\theta), \quad (58)$$

where $k_i = 2\pi/\lambda_i$ with λ_i being the wavelength of the incident beam. Eq. 58 shows that, for IXS, Q and ω are uncoupled and, specifically, Q depends only on the scattering angle θ and on the incident wavelength, yet not on the energy. This implies that there are no inherent limitations of the (Q, ω) plane explorable by IXS, except the one arising from the finite energy resolution width, which prevents the access to small $\hbar\omega$ values.

Figure 2 illustrates a practical example of the relevance of kinematic limitations when performing an INS experiment. The plot refers to the case of two INS measurements carried out on heavy water in the mid-1980s. The inelastic peak position in the INS spectrum measured by Bosi et collaborators [23] with 36 meV incident energy is compared with the INS measurement of Teixeira collaborators on the same sample [24] yet at a higher incident energy (80 meV).

Furthermore, the plot displays the portion of the dynamic plane covered by the measurement in Ref. [23] (shadowed area) and the curve delimiting the dynamic region explored in Ref. [24], (dashed line).

Figure 2: The dispersion curves determined by INS measurements in heavy water by Bosi and collaborators [23] and by Teixeira collaborators [24] are reported as open circles and dots,

respectively. The thick solid and the dashed lines respectively demarcate the boundaries of the two experiments. The shadowed area represents the dynamic domain covered by the INS measurement by Bosi and collaborators.

A clear discrepancy readily emerges from a comparison of the two INS measurements. The INS measurement of Teixeira and collaborators [24] observed the presence of a high-frequency peak, back then misleadingly referred to as the “fast sound” mode. Conversely, the measurement of Bosi and collaborators [23] only evidenced the presence a low-frequency one, at those times identified as the finite- Q prosecution of the ordinary (macroscopic) sound mode.

The reason for such a disagreement owes partially to the restricted dynamic domain explored by Bosi and collaborators, which clearly excluded the high energy mode. On the other hand, the measurement of Teixeira and collaborators, due to the higher incident energy, was performed with an energy resolution too coarse to properly resolve the low-frequency peak.

It is worth noticing that, the inelastic peaks individually observed by the two experiments actually coexist in the spectrum of water at sufficiently high Q 's [25]. However, their assignment to a fast and a normal sound mode is incorrect [26]. Indeed, as demonstrated by successive computational [27] and experimental results [28] [12], the low-frequency peak arises from the presence of shear mode propagation, while the high-frequency one is the finite Q extension of the standard longitudinal sound mode.

The example in Figure 2 clearly shows that in this, as well as other, situations the explorable dynamic often resembles a “blanket too short”, which prevents the simultaneous coverage of high and low ω or Q values.

2.4 Complementary aspects of INS and IXS

The following paragraph proposes a succinct overview of the main advantages and disadvantage in the use of INS and IXS. These practical aspects need to be pondered carefully when planning an experiment on the THz dynamics of condensed matter systems.

2.4.1 Advantages of INS

- **Resolution shape**

Probably, the greatest advantage of INS is the narrow and sharp energy resolution function. Furthermore, the INS resolution can be easily tailored to the specific experimental needs, even though any improvement is usually achieved by shrinking the dynamic range covered. Although new concept IXS spectrometers [29] hold the promise of a substantially improved resolution and spectral contrast, it is highly unlikely that X-Ray probes can ever match the performance of current quasielastic neutron spectrometers.

- **Q -decay of the cross section**

For neutron scattering, no appreciable Q decay of the scattering length occurs up to Q values approaching the inverse of the nuclear size. These values are nearly a factor 10^3 larger than the Q 's at which typically $f(Q)$ halves its maximum ($Q = 0$) value. As a consequence, upon increasing Q , the IXS cross section decays much more rapidly than its INS counterpart. For this reason, INS spectrometers represent a unique tool to explore the

extremely high Q values belonging to the single particle regime [30]. The maximum Q values reached by IXS measurements thus far [31-34] is still orders of magnitude smaller than the values accessible by neutron scattering measurements.

- **Absorption**

At the typical energies of IXS measurements, the scattered intensity is primarily attenuated by the photoelectric absorption, which at low Q 's increases as Z^4 . This drastically reduces the efficiency of IXS measurements in high Z materials. Conversely, the relatively weak absorption cross section makes neutrons an ideal, nondestructive, probe of bulk properties of materials. This represents a decisive advantage when dealing with samples prone to radiation damage, as often the case of biological systems [35].

- **Single particle dynamics**

Although a large incoherent cross section represents a problem when investigating the collective dynamics, it is, of course, a strict requirement when focusing on single particle properties. For instance, the almost entirely incoherent cross section of hydrogen offers the unique opportunity of using INS as a probe of the single particle diffusion in highly hydrogenated compounds, as well as hydration patterns in proteins and other macromolecules [36].

- **Contrast variation**

The dependence of the neutron scattering cross section on the isotopic species offers the opportunity of modulating the scattering intensity by using isotope substitution methods. These techniques are extremely useful to optimise the contrast [37] while measuring, e.g., the spectrum of confined systems, or colloidal suspensions.

- **Partial scattering contributions in composite and molecular systems**

The isotope-specificity of INS cross section is a valuable resource to perform parallel INS measurements on chemically equivalent systems. As a possible application, an isotope manipulation can be used to determine partial correlation functions involving isolated atomic species in a molecular sample or a mixture [37]. This procedure is not possible with X-Ray probes as the X-Ray scattering does not depend on the isotopic composition of the sample, but rather on its chemical species (atomic number). Therefore, the X-Ray scattering intensity cannot be manipulated without altering the chemical properties of the sample.

2.4.2 Advantages of IXS

- **Virtual absence of kinematic limitations**

As discussed in previous paragraphs, INS techniques suffer from inherent kinematic constraints restricting the explorable portion of the dynamic plane. These limitations are

particularly penalising when dealing with systems having high sound velocity and when accessing to low Q values. Indeed, the parabolic boundaries defined by Eq. 54 (see also Figure 2) mainly exclude the high-frequency regions of the (Q, ω) plane and the accessible region becomes narrower at low Q 's. The development of IXS made possible spectroscopy measurements in previously forbidden portions of the dynamic plane.

- **Constant Q scans**

In INS measurements energy scans performed at a fixed scattering angle 2θ , in general, are not constant- Q measurements. In fact, while changing the energy (frequency), in general the Q does not stay constant, being these two variables connected through Eq. 54. Unfortunately, most line-shape models only predict the analytical form of constant- Q (rather than constant 2θ) cuts of $S(Q, \omega)$. The use of triple-axis spectrometry permits to circumvent this problem, by changing 2θ and E in a coordinated way, which keeps Q constant, according to Eq. 54. However, this method is rather time-consuming, as no more than one Q value can be measured in each scan. Conversely, time of flight (*ToF*) spectrometers can perform a fast mapping of $S(Q, \omega)$ surfaces with points sparse in the (Q, ω) plane. However, with this method, constant Q -cuts of $S(Q, \omega)$ can only be determined by interpolations performed with analytical models. This procedure may yield inconsistent results when $S(Q, \omega)$ surfaces are not sufficiently smooth or the sampled Q, ω values are too sparse. All these problems can be circumvented by using IXS techniques. Indeed, an IXS measurement at a fixed 2θ directly yields a constant Q cut of $S(Q, \omega)$, being Q a univocal function of the scattering angle.

- **Incoherent scattering**

As discussed above, the incoherent scattering contribution to the IXS signal arises from mean squared fluctuations of $f(Q)$, while for INS it relates to analogous fluctuations of the scattering length, b . The latter variable strongly depends on both the isotopic species and the relative orientation of the nuclear and neutron spin. This usually causes important mean square fluctuations of b , which drastically enhance the incoherent part of the neutron cross section ($\propto \langle b \rangle^2 - \langle b^2 \rangle$). Obviously, unless corrective methods are implemented, the large incoherent cross section of INS can be a serious drawback when investigating the collective dynamics, as, for instance, in all measurements discussed in this review. Concerning IXS, as discussed, mean squared fluctuations of $f(Q)$ arise from the anisotropy of molecular electronic clouds, which yield an incoherent contribution to the scattered intensity much smaller than in the INS case.

- **Incident flux on the sample**

Challenging requirements on the resolving power ($\Delta E/E \leq 10^{-7}$) severely hamper IXS count rates. Nonetheless, typical IXS spectrometers have incident fluxes much higher than that their INS counterparts. Typically, the former spectrometers can be operated with a 10^9 – 10^{10} photons/s photon flux within a focal spot as narrow as few hundreds of μm^2 , while for *ToF* spectrometers, a flux of $\approx 10^5$ photons/s is spread over a focal spot of a few square centimetres.

- **Multiple scattering**

The dominant contribution to the attenuation of the IXS signal is caused by the photoelectric absorption, which, on the bright side, also induces a substantial suppression of multiple scattering events. Therefore, for IXS measurements the multiple scattering intensity is often negligible compared to the single scattering signal; this is an invaluable advantage since the latter is the one $\propto S(Q, \omega)$, thus being of primary interest for scattering experiments.

- **Transverse beam size**

The incident beam of IXS spectrometers has an extremely narrow focal spot, usually few tens of square micrometre or even less. For this reason, IXS experiments can be performed on small-sized samples, thus potentially probing extreme thermodynamic conditions, such as high pressures [14] and low [38] or high temperatures [39].

3. Searching for the best-suited line-shape model: formal and qualitative considerations

Once the link between the IXS cross section and the dynamic structure factor $S(Q, \omega)$ has been shown, the various theoretical models predicting the shape of $S(Q, \omega)$ can now be briefly reviewed. First, it useful to introduce a general formalism from which most of these line-shape models can be easily derived.

3.1 The memory function formalism

The formalism of memory function stems from the expression of the equation of motion of an N -body system by means of the projection operators [3,40]. This paragraph briefly discusses the relevant analytical aspects of this formalism.

Let assume that a set of fluctuating variables $A_\nu(t)$ ($\nu = 1, \dots, k$) describes the time-dependent properties of the N constituents of an N -body system (with $k < N$), and that such a set has f degrees of freedom. One can introduce the column vector $A(t)$ as:

$$A(t) = \begin{bmatrix} A_1(t) \\ \vdots \\ A_k(t) \end{bmatrix}.$$

Assuming that the Hamiltonian H has no explicit dependence on time, the equation of motion of the $A(t)$ components has the form:

$$\frac{dA_v(t)}{dt} = [dA_v(t), H]_P = iLA_v(t). \quad (59)$$

Here $[...,...]_P$ are the Poisson brackets, while L is the Liouville operator [41]:

$$iL = \sum_{i=1}^f \frac{\partial H}{\partial p_i} \cdot \frac{\partial}{\partial r_i} - \frac{\partial H}{\partial r_i} \cdot \frac{\partial}{\partial p_i}.$$

A solution of Eq. 59 is $A(t) = \exp(iLt)iLA$, where it was used shorthand notation $A = A(0)$.

We can now introduce the matrix auto-correlation function of $A(t)$ as:

$$C(t) = (A(t), A^+) \quad (60)$$

Where A^+ is the Hermitian conjugate of A , i.e. the row vector $A^+(t) = [A_1^*(t) \dots A_k^*(t)]$. Eq. 59 can be rearranged by introducing the projection operators [3]:

$$\tilde{P} = (A, \dots) (A, A^+)^{-1} A = \sum_{\lambda, \nu} (A_\lambda, \dots) [(A, A^+)^{-1}]_{\lambda, \nu} \quad (61)$$

and

$$\tilde{Q} = I - \tilde{P}. \quad (62)$$

When $\tilde{P}$ and $\tilde{Q}$ act on a fluctuating variable, they project it, respectively, into the subspaces parallel and orthogonal to A . Here, the notion of orthogonality has a statistical nuance, i.e. two variables are dubbed orthogonal when uncorrelated. In fact, within the linear response theory, the concept of statistical average coincides with the one of scalar product [42]. Therefore, for two generic fluctuating vector variables A and B , one can make the identification $(A, B^+) = (A^+, B) \equiv \langle A^* \cdot B \rangle$, where it was used the hermiticity of the scalar product.

After some manipulations using the two projection operators defined in Eq. 59, the equation of motion of $A(t)$ can be cast in the following form:

$$\frac{dA(t)}{dt} = i\Omega \cdot A(t) - \int_0^t K(\tau) \cdot A(t-\tau) d\tau + f(t), \quad (63)$$

where the following vector and matrix variables have been introduced:

- The antisymmetric matrix $i\Omega = (iLA, A^+) \cdot (A, A^+)^{-1}$, which embodies the proper

frequency of the system, which characterises the oscillatory behaviour of $A(t)$.

- The fluctuating random force $f(t) = \exp(i\tilde{Q}L)\tilde{Q}LA$. Noticeably, due to the presence of the operator $\tilde{Q}$ one has $(f(t), A^+) = 0$, i.e. the random force is orthogonal to A . In practice the vector A , whenever possible, should include all slowly changing variables of a given system; the random force thus belongs to the subspace of rapidly changing variables, which is statistically uncorrelated to the subspace defined by A .
- $K(t) = (f(t), f^+)(A, A^+)^{-1}$ is the memory matrix or, for a single variable ($k = 1$), the memory function. As clear from Eq. 63, this kernel accounts for the ability of the variable $A(t)$ to keep a memory of all instants preceding the time t . Notice that the system's memory of a given instant τ can only have an effect on the dynamic variable at successive times, i.e. on $A(t - \tau)$.

The equation of motion for the correlation matrix $C(t) = (A(t), A^+)$ can be readily derived from Eq. 63 by taking the scalar product of each member with the variable A :

$$\frac{dC(t)}{dt} = i\Omega \cdot C(t) - \int_0^t K(\tau) \cdot C(t - \tau) d\tau. \quad (64)$$

Here $C(t) \equiv (A(t), A^+)$ is the autocorrelation function of the variable A . Notice that, the term $f(t)$ in Eq. 63 does not appear in the above equation owing to its orthogonality to A . Eqs. 63 and 64 are known as the Langevin equations for the variable A and its autocorrelation C , respectively. These integrodifferential Volterra type equations [43] can be easily solved via Laplace transform, so as to convert the convolution integral into a product. With this manipulation, Eq. 64 reads as:

$$\frac{\tilde{C}(s)}{C(0)} = [sI - i\Omega + \tilde{K}(s)]^{-1}, \quad (65)$$

where

$$\tilde{C}(s) = \int_0^\infty C(t) \exp(-st) dt$$

and

$$\tilde{K}(s) = \int_0^\infty K(t) \exp(-st) dt$$

are the Laplace transforms of the correlation and memory function, respectively.

It can be noticed that the random force is a stochastic variable belonging to a subspace orthogonal to A . At this stage it is useful to introduce the new projection operators:

$$\tilde{P}_I \equiv \frac{(f, \dots)}{(f, f)} f \quad \tilde{Q}_I = I - \tilde{P}_I, \quad (66)$$

which can be used to derive generalised Liouville equation for the random force:

$$\frac{df(t)}{dt} = +i\Omega_I f(t) - \int_0^t K_I(\tau) f(t-\tau) d\tau + f_I(t). \quad (67)$$

Here the new random force acting on $f(t)$ is $f_I(t) = \exp(i\tilde{Q}_I L) \tilde{Q}_I L f$, while the new memory function reads as $K_I(t) = (f_I(t), f_I^+) (f, f^+)^{-1}$.

The memory function $K(t) = (f(t), f^+) (A, A^+)^{-1}$ is, in turn, a normalised correlation function of the variable $f(t)$, and, as such, it obeys to a Langevin equation. Once the latter is Laplace transformed one obtains an equation similar to Eq. 65, namely:

$$\frac{\tilde{K}(s)}{K(0)} = [sI - i\Omega_I + \tilde{K}_1(s)]^{-1}, \quad (68)$$

Here, $K_I(t)$ can be seen the new memory function for both the variable $f(t)$ and its normalised correlation function $K(t)$. The link between $\tilde{C}(s)$ and $\tilde{K}_1(s)$ can be derived by inserting Eq. 68 into Eq. 64, which leads to:

$$\frac{\tilde{C}(s)}{C(0)} = \left[sI - i\Omega + \frac{K(0)}{sI - i\Omega + \tilde{K}_1(s)} \right]^{-1}. \quad (69)$$

Again, it can be recognised that the time evolution of $f_1(t)$ obeys to a Langevin equation and so does its normalised correlation function $K_1(t)$. This suggests following an iterative approach to derive an expression linking the correlation function to memory functions of increasing (iteration) order. This procedure eventually leads to the following recursive formula:

$$\frac{\tilde{C}(s)}{C(0)} = \left[sI - i\Omega + \frac{K(0)}{sI - i\Omega + \frac{K_1(0)}{sI - i\Omega + \frac{K_2(0)}{sI - i\Omega + \dots}}} \right]^{-1}, \quad (70)$$

customarily referred to as the continued fraction expansion of the correlation function.

The case of a single dynamic variable is the one of interest for this review. In this instance, of course, all matrices reduce to scalar variables; furthermore, time-reversal requirements impose Ω_i

= 0 for any value of the iteration index i , hence:

$$\frac{\tilde{C}(s)}{C(0)} = \left[s + \frac{K(0)}{s + \frac{K_1(0)}{s + \frac{K_2(0)}{s + \dots}}} \right]^{-1} \quad (71)$$

The $t = 0$ values of the i -th order memory function $K_i(t)$ can be determined by superimposing the sum rule fulfilment to the spectrum $C(\omega) = \text{Re}[\tilde{C}(s = i\omega)]$. This, for the few lowest orders of the continuous fraction development yields:

$$K_1(0) = \langle \omega^2 \rangle \quad (72)$$

$$K_2(0) = -\frac{\ddot{K}_1(0)}{2K_1(0)} = \frac{\langle \omega^4 \rangle}{\langle \omega^2 \rangle} - \frac{\langle \omega^2 \rangle}{\langle \omega^0 \rangle} \quad (73)$$

$$K_3(0) = -\frac{\ddot{K}_2(0)}{2K_2(0)} = \frac{1}{\Delta_2} \left[\frac{\langle \omega^6 \rangle}{\langle \omega^2 \rangle} - \left(\frac{\langle \omega^4 \rangle}{\langle \omega^2 \rangle} \right)^2 \right] \quad (74)$$

Here $\langle \omega^n \rangle = i^n \left[\frac{d^n C(t)}{dt^n} \right]_{t=0} = \int_{-\infty}^{+\infty} \omega^n C(\omega) d\omega$ is the n -order moment of the spectrum $\text{Re} \tilde{C}(s)$.

Notice that, for a classical system, time-reversal requirements impose that all odd moments vanish. In principle, all considerations valid for the first-order memory function can be repeated at any iteration level, n , for the n -order memory function K_n [44]. A problem to face when dealing with high-order iterations of the continued fraction formula is the demanding calculation of the corresponding spectral moments as well as the loose interpretation of memory functions involved. As evident from Paragraph 2.2, the fluctuating variables of interest here are the density fluctuations, as their Fourier-Laplace transform of its correlation function, the dynamic structure factor $S(Q, \omega)$, is directly measured by both IXS and INS.

Writing Eq. 71 for the density-density correlation function and truncating it to the 2nd order, one has:

$$\frac{\tilde{F}(Q, s)}{S(Q)} = \left[s + \frac{\omega_0^2}{s + \tilde{m}_L(Q, s)} \right]^{-1} \quad (75)$$

Where $\tilde{F}(Q, s)$ and $\tilde{m}_L(Q, s)$ are the Laplace transforms of the intermediate scattering function, while is the second-order memory function of density fluctuations, respectively. Notice that $m_L(Q, t)$ is also the first-order one of the variable currents (microscopic velocities).

In Eq. 75 $\omega_0^2 = Q^2 k_B T / [MS(Q)]$ is the normalised second moment $\langle \omega^2 \rangle / \langle \omega^0 \rangle$, while for the 0-th

moment it was used $\langle \omega^0 \rangle = S(Q)$. The $S(Q, \omega)$ can be easily derived from Eq. 75 through:

$$\frac{S(Q, \omega)}{S(Q)} = \frac{1}{\pi} \text{Re} \left[\frac{\tilde{F}(Q, s = i\omega)}{S(Q)} \right] = \frac{1}{\pi} \text{Re} \left[i\omega + \frac{\omega_0^2}{i\omega + m_L(Q, s = i\omega)} \right]^{-1}.$$

The last term of the above formula can be developed to obtain eventually:

$$\frac{S(Q, \omega)}{S(Q)} = \frac{1}{\pi} \frac{\omega_0^2 m_L'(Q, \omega)}{[\omega^2 - \omega_0^2 - \omega m_L''(Q, \omega)]^2 + \omega^2 [m_L'(Q, \omega)]^2}, \quad (76)$$

where $m_L'(Q, \omega)$ and $m_L''(Q, \omega)$ are, respectively, the real and imaginary parts of the Fourier transform of $m_L(Q, t)$. Clearly, Eq. 76 shifts the problem of the choice of the most appropriate model from $S(Q, \omega)$ to $m_L(Q, \omega)$ (or $m_L(Q, t)$).

The theoretical framework illustrated above is usually referred to as the memory function or Zwanzig-Mori formalism [45,46] (see also Ref. [20]). Many models currently used to describe the spectrum of disordered systems can be derived from this theoretical framework, upon suitable choices of the memory function.

This treatment of the lineshape is entirely classical in nature. Quantum effects are usually treated within the assumption that they come into play when considering the statistical population of states having different ω 's, through the so-called detailed balance principle [47]. Among all possible methods to comply with this principle, one of the most commonly adopted consists in the multiplication of the classical $S(Q, \omega)$ profile by a frequency dependent factor. Explicitly:

$$S(Q, \omega) = \frac{\hbar\omega}{k_B T} \left[\frac{1}{1 - \exp(-\hbar\omega/k_B T)} \right] S_c(Q, \omega) \quad (77)$$

Here $S_c(Q, \omega)$ is the “classical” or symmetric, part of the spectrum, which the remainder of this review deals with, unless otherwise specified.

3.2 A model for the line-shape

The exact analytical form of the spectrum is in general unknown, except at two extreme regions of the dynamic plane, namely either at Q, ω 's either infinitesimal (hydrodynamic limit) or extremely high (single particle limit). Along the crossover between these two limits density fluctuations become strongly coupled with molecular degrees of freedom. This makes the interpretation of $S(Q, \omega)$ particularly complex, yet especially informative of the various dynamical process occurring in a fluid at mesoscopic scales.

All models developed in the attempt to describe the gradual departure of the $S(Q, \omega)$ from the simple hydrodynamic regime have to cope with inherent limitations. These restrict their

applicability either to specific sample conditions (e.g. either low or high density), or dynamic windows (e.g. either low or high Q, ω values). Most of these models are phenomenological in character and do not provide a quantitative prediction of the Q -dependence of transport parameters. This is indeed, such a Q -dependence is usually determined *a posteriori* only, as a result of a best-fitting procedure of the spectra measured at different Q 's. The superimposition of the sum rule fulfilment or other external constraints to the model is often used to improve the physical soundness of the line-shape modelling.

While choosing the most appropriate model for the line-shape, a crucial factor to consider is the number of free parameters contained in such model, which must be minimised to prevent statistical correlation between best-fit results. Often, such a number is decreased by adopting ad hoc approximations, as suited to the sample and dynamic range considered.

3.2.1 The Simple Hydrodynamic spectrum

As well assessed experimentally, the hydrodynamic theory for continuous media consistently describes the dynamics of density fluctuations in simple liquids at quasi-macroscopic distances and timescales. This theoretical approach starts from the expression of the conservation laws of (density of) mass, momentum and energy in a fluid [3,48]. These laws are described by few independent linear equations, which, however, do not form a complete set until complemented by two constitutive equations: the Navier-Stokes equation and the heat transfer one. The Fourier-Laplace transforms of this complete set of equations yields the hydrodynamic matrix, whose eigenvalues define the modes dominating the spectral shape (see Ref. [3] for a detailed derivation). The resulting (linearized) hydrodynamic spectrum has the following form:

$$S(Q, \omega) = A_h^H \frac{z_h^H}{\omega^2 + (z_h^H)^2} + A_s^H \left[\frac{z_s^H}{(\omega - \omega_s^H)^2 + (z_s^H)^2} + \frac{z_s^H}{(\omega + \omega_s^H)^2 + (z_s^H)^2} \right] + A_s^H b_s^H \left[\frac{(\omega - \omega_s^H)}{(\omega - \omega_s^H)^2 + (z_s^H)^2} - \frac{(\omega + \omega_s^H)}{(\omega + \omega_s^H)^2 + (z_s^H)^2} \right] \quad (78)$$

With $b_s^H = [A_h^H z_h^H / (1 - A_h^H) + z_s] / \omega_s^H$.

Here ω_s^H , and z_s^H indicate, respectively, the shift and the width of the symmetric inelastic modes, while z_h^H is the width of quasi-elastic one. The superscript “H” here labels the linearized hydrodynamic value of the corresponding parameter. All coefficients in Eq. 78 are Q -dependent, although such dependence is not mentioned in the used shorthand notation. A similar notation will be adopted hereafter, unless otherwise stated.

Eq. 78 has three main components, namely - from left to right:

- (1) The central or Rayleigh peak (Lorentzian term $\propto A_h^H$) which relates to entropy (heat) fluctuations diffusing at constant pressure (P).
- (2) The two Brillouin side peaks (term $\propto A_s^H$), connected to P -fluctuations propagating at constant entropy, and
- (3) An additional contribution (term $\propto A_s^H b^H$) asymmetric around the Brillouin peaks position and having negative tails. This term sharpens the large ω -decay of the Lorentzian

contributions 1) and 2), thus enabling the convergence of spectral moments $\int_{-\infty}^{+\infty} \omega^n S(Q, \omega) d\omega$ with $n \leq 2$.

The various shape parameters appearing in Eq. 78 are involved functions of the hydrodynamic frequencies: $c_s Q$, $D_T Q^2$ and ΓQ^2 (with $\Gamma = 1/2[(\gamma - 1)D_T/\gamma + \nu_L]Q^2$). Here c_s , γ , D_T/γ are the sound velocity, the constant pressure-to-constant volume specific heats ratio and the thermal diffusivity, respectively, while $\nu_L = \eta_L/\rho$ is the kinematic longitudinal viscosity, with ρ and η_L being the density and the longitudinal viscosity. At long wavelengths [49], the latter can be expressed as $\eta_L = \eta_b + 4/3\eta_s$ with η_s and η_b being the shear and the bulk components of the viscosity, respectively.

However, at low Q 's, the condition $D_T Q^2, \Gamma Q^2 \ll c_s Q$ is fulfilled for most fluids, which suggests performing a series development of the eigenvalue equation hydrodynamic matrix in the small variables $D_T Q^2$ and ΓQ^2 (see Ref. [3]) This eventually leads to the following low- Q identities:

$$\left\{ \begin{array}{l} \omega_s^H = c_s Q \end{array} \right. \quad (79)$$

$$\left\{ \begin{array}{l} z_s^H = \frac{\Gamma Q^2}{2} = \frac{[(\gamma - 1)D_T + \nu_L]Q^2}{2} \end{array} \right. \quad (80)$$

$$\left\{ \begin{array}{l} z_h^H = D_T Q^2 \end{array} \right. \quad (81)$$

Furthermore, within the same low Q approximation, one has $A_s^H = 1/\gamma$ and $A_h^H = (\gamma - 1)/\gamma$.

It is important to keep in mind that the above equations are valid as long as the condition $D_T Q^2, \Gamma Q^2 \ll c_s Q$ is fulfilled. This condition means that the lifetime of the diffusive mode, $2\pi/(D_T Q^2)$, and that of the acoustic modes, $2\pi/(\Gamma Q^2)$, are both much longer than the acoustic period ($2\pi/c_s Q$). Therefore, at extremely low Q 's, the spectrum is dominated by few long living, or quasi-conserved, collective excitations, customarily referred to as hydrodynamic modes; this spectral shape is commonly called the Rayleigh-Brillouin spectrum.

The profile in Eq. 78 can be retrieved in its complete form. i.e. without the approximations of Eqs. 79-81, by using the following expression for the memory function:

$$m_L(Q \rightarrow 0, t) = \omega_0^2 (\gamma - 1) \exp(-D_T Q^2 t) + \nu_L Q^2 \delta(t) \quad (82)$$

The first term on the right-hand side of Eq. 82 accounts for the thermal contribution to the time decay of the memory function. For infinitesimally low Q 's, this term gives rise to the Rayleigh peak and contributes to the width of the Brillouin peaks (see Eq. 80) through the $(\gamma - 1)D_T$ factor.

The second term on the right-hand side of Eq. 82 accounts instead for the “viscous” decay of the memory function.

The presence of a δ -function of time reflects the circumstance that, in the hydrodynamic limit, viscous dissipation processes affecting density fluctuations become extremely fast.

Figure 3 displays a typical shape of the Rayleigh-Brillouin triplet from a liquid along with its three individual spectral components.

Figure 3: A typical Rayleigh-Brillouin triplet spectrum of a liquid (Eqs. 78-81). The individual contributions to the total shape are represented by shaded areas and thick lines as indicated in the legend.

3.2.2 The Generalised Hydrodynamics model

As mentioned, beyond the continuous limit the transport coefficients become local rather than global parameters of the fluid, i.e. they become dependent on spatial coordinates, or, in the reciprocal space, on the exchanged wave-vector Q .

Owing to the lack of a rigorous theory predicting such a Q -dependence, the various theoretical attempts to extend the hydrodynamic description at finite Q values, mostly prescribe merely phenomenological recipes. In particular the so-called Generalised Hydrodynamics (GH) models rely on the assumption that the departure from the Rayleigh-Brillouin shape is smooth enough to leave the formal structure of the hydrodynamic spectrum (Eq. 78) unaltered, namely:

$$S(Q, \omega) = \frac{S(Q)}{\pi} \left\{ \frac{A_h z_h}{\omega^2 + z_h^2} + A_s \left[\frac{z_s}{(\omega - \omega_s)^2 + z_s^2} + \frac{z_s}{(\omega + \omega_s)^2 + z_s^2} \right] + A_s b \left[\frac{(\omega - \omega_s)}{(\omega - \omega_s)^2 + z_s^2} - \frac{(\omega + \omega_s)}{(\omega + \omega_s)^2 + z_s^2} \right] \right\}, \quad (83)$$

yet they assume that the relevant shape parameters have an unknown Q -dependence. Such a Q -dependence is usually determined only *a posteriori* by best fitting the GH model of Eq.83 to the line-shapes measured (or computed) at various Q values.

As shown in the following, the line-shape profile in Eq. 83 can also be derived by a kinetic theory approach, through the series development of the spectrum of density fluctuation in the basis of the eigenstates of the Enskog operator (see Eq.105).

3.2.3 The pure viscoelastic model

The core hypothesis of all viscoelastic models is that transport parameters relevant for the spectral shape acquire an ω -dependence, consisting in a transition from a liquid-like low-frequency regime and a solid-like high-frequency one. This crossover is usually called “viscoelastic” since “viscous” (liquid-like) and “elastic” (solid-like) aspects of the dynamic response coexist in it. The simplest way to account for such viscoelastic effects on $S(Q, \omega)$ is to assume the following exponential decay of the memory function:

$$m_L(Q, t) = \tau [c_\infty^2 - c_0^2] Q^2 \exp(-t/\tau) \quad (84)$$

where τ is the relaxation time. In this model, hereafter referred to as pure viscoelastic, the sound velocity is generalised as a frequency dependent variable, systematically increasing from its zero-frequency value, c_0 , to the infinite frequency one, c_∞ . At the lowest Q 's Eq. 84 can be consistent with the hydrodynamic memory function (Eq. 82), under two conditions:

- 1) At very low Q 's, the time decay becomes extremely rapid, i.e. $\lim_{Q \rightarrow 0} m_L(Q, t) \propto \delta(t)$.
- 2) The thermal decay of the memory function (exponential term in Eq. 82) has negligible strength, or, equivalently, $\gamma \approx 1$.

Notice that, within the above conditions, the low Q consistency with the hydrodynamic expression in Eq. 82 further imposes $\nu_L = \tau [c_\infty^2 - c_0^2]$, in agreement with the Maxwell treatment of viscoelasticity.

The simple viscoelastic model in Eq. 84, introduced by Lovesey [50] in the early 1970s, assume a more precise physical meaning after the superimposition of the first three sum rules to $S(Q, \omega)$, which links the model parameters to the structural and thermodynamic properties of the sample. Explicitly:

$$c_o^2 Q^2 = \frac{\langle \omega^2 \rangle}{\langle \omega^0 \rangle} = \frac{k_B T}{MS(Q)} Q^2 \quad (85)$$

$$c_\infty^2 Q^2 = \frac{\langle \omega^4 \rangle}{\langle \omega^2 \rangle} = \frac{k_B T}{M} Q^2 + \Omega_0^2 - \Omega_Q^2 \quad (86)$$

$$A_2 = (c_\infty^2 - c_o^2) Q^2 = \frac{\langle \omega^4 \rangle}{\langle \omega^2 \rangle} - \frac{\langle \omega^2 \rangle}{S(Q)}, \quad (87)$$

where $\langle \omega^0 \rangle = S(Q)$, while k_B is the Boltzmann constant. Furthermore, the Einstein frequency, Ω_0 , and his finite Q generalisation Ω_Q are defined by:

$$\Omega_0^2 = \frac{n}{M} \int d\mathbf{r} g(r) (\hat{\mathbf{Q}} \cdot \nabla)^2 V(r) \quad (88)$$

and

$$\Omega_Q = \frac{n}{M} \int d\mathbf{r} g(r) \cos(\mathbf{Q} \cdot \mathbf{r}) (\hat{\mathbf{Q}} \cdot \nabla)^2 V(r). \quad (89)$$

∇_Q^2 the projection of the Laplacian operator along the direction of $\mathbf{Q}$ and $V(r)$ the interatomic potential.

On a general ground, the viscoelastic model interpolates between the viscous and the elastic behaviours through the sum rules defined above. In fact, it assumes that the sound velocity c_s undergoes a transition from the 0-frequency (viscous) value, $c_0 = \omega_0/Q = \sqrt{B/\rho}$ with B being the bulk modulus, as appropriate for a liquid, to the infinite frequency (elastic) one $c_\infty = \omega_\infty/Q = \sqrt{M_e/\rho}$, where M_e is the elastic modulus, as adequate for solids. Notice that $M_e = B + 4/3G$ with G the shear modulus, which is obviously >0 , thus indicating that the sound velocity increases along the viscous-to-elastic crossover.

Eqs. 85 and 86 define the values of B and M_e linking them to the second and fourth normalised spectral moment, respectively.

In particular, Eq. 85 extends to finite Q 's the macroscopic ($Q = 0$) compressibility result [21] which ultimately leads to express the isothermal sound velocity as $c_T = \sqrt{K_B T / MS(0)}$ considering that within the validity of the pure viscoelastic model, $\gamma = 1$, thus $c_T = c_s$.

The instantaneous loss of memory characteristic of a viscous (liquid-like) system limit can be accounted for by a Markovian ($\propto \delta(t)$) term in the memory function (see Eq. 82). Conversely, the freezing of all dissipative channels, characteristic of the elastic response, is best described by a memory function constant in time.

The single exponential model in Eq. 84, customarily referred to as pure viscoelastic [51] or Debye [52] model, represents the simplest interpolation the two limiting behaviours of the memory function.

From a physical point of view, a viscoelastic behaviour originates from the coupling between density fluctuations and a relaxation phenomenon having characteristic timescale τ .

To understand this point, one can recognise that a spontaneous or a scattering-generated density fluctuation induces a time-dependent perturbation of the local equilibrium of the fluid. As a response to this disturbance, decay channels are activated to redistribute the energy from the fluctuation toward some internal degree of freedom having characteristic time-scale τ . These rearrangements ultimately drive the system to relax in a new local equilibrium after a time lapse comparable with τ .

Let assume, for instance, that the density fluctuation has the form of an acoustic wave propagating throughout the fluid. Two different regimes can thus be identified, depending on how the period of such an acoustic wave, T , compares with τ .

1) when $T \gg \tau$, dissipative processes affecting the acoustic wave are extremely rapid and drive “instantaneously” the system to equilibrium. Under these conditions, the slow acoustic oscillations propagate over successive equilibrium states of the system (viscous limit). 2) Conversely, when acoustic oscillations are extremely rapid ($T \ll \tau$), internal degrees of freedom of the system become too slow to dissipate their energy, and the acoustic wave propagates without energy losses (elastic limit).

When the acoustic period is intermediate between the values characteristic of the elastic and viscous regime, i.e. when $T \approx \tau$, the response of the fluid embodies both viscous and the elastic aspects, thus being customarily quoted to as viscoelastic.

Due to the progressive decrease in acoustic dissipation, the energy of the acoustic wave increases systematically across the viscoelastic transition and so does the sound velocity, while the viscosity follows the opposite trend.

Therefore, fingerprints of relaxation phenomena can be directly found by looking at the frequency dependence of transport parameters. Indeed, the first theoretical descriptions of viscoelastic effects on the spectral shape moved from the assumption of a frequency dependence of bulk [53], or shear viscosity [54].

A practical example of the viscoelastic behaviour of sound velocity induced by the coupling with a relaxation process is proposed by Figure 4, which refers to the case of glycerol [55]. The plot compares independent results obtained in complementary frequency windows such as:

- i) Ultrasound (*US*) absorption measurements, spanning the 10-150 MHz range [56,57];
- ii) Brillouin (visible) Light Scattering (*BLS*) and Brillouin Ultra Violet Scattering (*BUVS*) measurements, spanning the 1.5-20 GHz range.
- iii) IXS measurements, covering the THz region.

The plot indicates that the value of sound velocity dramatically increases upon increasing the frequency of the spectroscopic method. Another remarkable feature emerging from the plot is that the inflexion point of the curves moves towards higher frequencies while increasing the temperature, which reflects the increasingly rapid internal rearrangements of the fluid. This trend is paradigmatic of the broad class of relaxation processes customarily referred to as structural relaxations, characterised by a strongly temperature-dependent time-scale. Structural relaxations are dominating in highly viscous systems as glass formers or associated fluids.

When describing the effects of relaxation phenomena in the line-shape, the pure viscoelastic hypothesis is often an oversimplified assumption; for instance, stretched exponentials [58,59], or other continuous distributions of time-scales [60] seem more realistic options. Indeed, sound

velocity data in Figure 4 proved that the Cole-Davidson profile (solid lines through data) give a more precise description of experimental values than the simple viscoelastic model.

Figure 4: The sound velocity of glycerol measured at different frequencies by complementary techniques and various temperatures, as shown in the legend. The dashed lines are best fits to data obtained assuming a continuous distribution of relaxation time-scales [60]. Data are redrawn from Ref. [60], which also includes US measurements from Refs. [56] and [57].

Nonetheless, the single exponential hypothesis turns out to be particularly useful as a model for the spectral shape in the THz window, owing to a two-fold reason: 1) it has the smallest number of free parameters, and 2) its Fourier transform can be handled analytically. The former is a key advantage, as the inclusion of an excessive number of free parameters in the model would enhance the statistical correlation of best fitting results. This problem is often exacerbated by common difficulties faced when fitting IXS spectra, such as the highly-damped character of spectral modes, the resolution limitations, and the limited count rate.

The spectral signature of a relaxation process

A clear signature of a relaxation process is the onset a further quasi-elastic component in the spectral shape. This additional spectral feature is usually referred to as the “Mountain peak” after the name of Raymond Mountain, who theoretically predicted its onset [61] at low Q ’s. In the low Q , ω limit, the width of the Mountain peak reduces to $1/\tau_c$, where $\tau_c = (c_\infty/c_0)^2 \tau$ [62] is the relaxation time of the compliance function $J = M^{-1}$ where M is the longitudinal modulus [64]. A

scheme of the evolution of the spectral shape expected when a relaxation is active is sketched in Figure 5, which shows three spectral shapes typically observed at decreasing temperatures and for a fixed Q value belonging to the continuous limit.

Figure 5: *Schematic representation of the T evolution of the line-shape at a fixed low Q value when a relaxation is active. The temperature decreases from the top to the bottom plot (see text).*

The plots show that the visibility of viscoelastic effects on the spectrum depends on how the inelastic shift ω_s compares with the width of the mountain peak. In this case, the viscoelastic crossover manifests itself as a function of temperature, which ranges from the high T (small τ_c) viscous regime to the low T (large τ_c values) elastic one. One readily notices that:

- i) In the high T 's (viscous) limit, the *Brillouin* peaks stay at their fully relaxed (low frequency) position, $c_0 Q$. The quasi-elastic contribution coincides with the Rayleigh peak; the relaxation mode has the form of a flat background, being its width $1/\tau_c \gg \omega_s$.

- ii) Upon lowering T , τ_c increases up to enter in the viscoelastic window, $\omega_s \approx 1/\tau_c$, the *Brillouin* peaks progressively broaden, while enhancing their overlap with the tail of the Mountain peak, which in turn gradually widens.
- iii) At lower T 's, a new limiting (elastic) regime is joined. Here the Brillouin peaks are extremely narrow, which reflects the virtual absence of viscous dissipation characteristic of the elastic limit. Also, the infinitely slow relaxation processes yield an extremely narrow Mountain peak, which becomes indistinguishable from the Rayleigh mode.

3.2.4 Molecular Hydrodynamics models

As compared with Generalised Hydrodynamics models (GH) which generalise transport and thermodynamic coefficient as Q -dependent variables only, the so-called Molecular Hydrodynamics (MH) models also take into account the ω -dependence. As mentioned when discussing the pure viscoelastic model, the ω -dependence is primarily brought about by the coupling of density fluctuations with an active relaxation process. Although both GH and MH models are merely phenomenological in spirit, the consistency with the simple hydrodynamic result in the $Q \rightarrow 0$ limit and the fulfilment of sum rule introduces rigorous physical constraints on the Q and ω behaviour of spectral parameters.

Within the MH framework, the memory function can be expressed as:

$$m_L(Q, t) = \frac{c_s^2(Q)Q^2}{\gamma(Q)S(Q)} (\gamma(Q) - 1) \exp(-D_T(Q)Q^2 t) + \nu_L(Q, t)Q^2 \quad (90)$$

The two terms on the right-hand side of the equation are (from left to right):

- (1) **The Q -generalized thermal contribution.** The first term extends the hydrodynamic expression of the thermal decay in Eq. 82 to finite Q 's. All transport and thermodynamic coefficients in this term are a finite- Q generalisation of the hydrodynamic transport and thermodynamic coefficients appearing in the simple hydrodynamic model.
- (2) **The Q - and ω -generalized viscosity contribution.** In the second term, $\nu_L(Q, \omega)$, denotes a Q and t dependent longitudinal kinematic viscosity ν_L . This term in principle accounts for all relaxation processes leading to the mentioned viscoelastic transition.

To become suitable for practical use, the expression in Eq. 90 still need an ansatz for $\nu_L(Q, t)$, which accounts for all relaxation phenomena affecting the viscosity. In principle, these may arise from the coupling of density fluctuations with internal molecular rearrangements, which can be as diverse and complex as the sample's internal degrees of freedom are.

However, common wisdom suggests opting for a model, which has a limited number of free parameters and is compatible with the small Q hydrodynamic result, such as the following:

$$\nu_L(Q, t) = \tau [c_\infty^2 - c_0^2] Q^2 \exp(-t/\tau) + 2\Gamma_0 \delta(t). \quad (91)$$

This time decay is defined by the following two terms:

- **The viscoelastic contribution.** This term is analogous to the one defining the simple viscoelastic model for the memory function (Eq. 84) and leading to the transition on increasing ω from c_0 to c_∞ .
- **The instantaneous contribution.** The last term accounts for the coupling of density fluctuations with the ultrafast vibrational dynamics here approximated by an instantaneous, or Markovian, decay $\propto \delta(t)$. Typically, the amplitude $2\Gamma_0$ is reported to have quadratic Q -dependence and is insensitive to thermodynamic changes [63].

When modelling IXS spectra, the relaxation time τ is sometimes expressed as $\tau = (c_0/c_\infty)^2 \tau_c$ and the compliance relaxation timescale τ_c is the free parameter to be optimised by the best fit procedure. This allows IXS best fit results to keep consistency with the natural outcome of low Q, ω spectroscopic results, since, as mentioned, the width of the Mountain peak is equal to $1/\tau_c$ at small Q 's [61,62].

The number of free parameters in the model is often lowered by fixing some of them to the respective $Q = 0$ values, as obtained using macroscopic thermodynamic and transport coefficients reported in the literature. In more fortunate cases, Q -dependent values derived from MD simulations in literature can be used instead. Most often, the adopted model is obtained as a suitable approximation of Eqs. 90 and 91, as appropriate to the specific sample and thermodynamic conditions probed by the experiment.

Although these approximations have in principle an unpredictable impact on the fitting outcome, a very consistent picture emerges from the whole body of IXS works proposing MH analyses of the spectral shape.

These involve a variety of samples broader than those interest for this review and including noble gases [65-67], diatomic liquids [66,68], liquid metals [11,69-71], hydrogen-bonded systems [72,73], and glass formers [55,74-76].

All finite Q extensions of the hydrodynamic result discussed so fail to predict the onset of non-hydrodynamic modes in the spectrum reported by an increasing number of experimental and computational works.

An example of this inadequacy is the emergence of a low-frequency inelastic peak in the spectrum of systems as diverse as liquid water [27,28,77,78], tetrahedrally arranged glasses [79,80], glass formers [81], liquid metals [82-86], complex biophysical samples [87-89], and mixtures [90]. A concise review of the experimental evidence for this additional spectral feature is proposed in Ref. [91].

The onset of this low-frequency mode is customarily ascribed to a shear mode propagation in the sample. In principle, the assignment of a shear, or transverse, polarisation to a spectral mode could seem surprising, as $S(Q, \omega)$ couples primarily with longitudinal movements only. Indeed, in a liquid, the presence of shear waves contributions to $S(Q, \omega)$ can only originate via the so-called longitudinal-transverse coupling [27,28,92], that is a mixing between acoustic modes having orthogonal polarisations. At present, no known analytical model of the memory function can account for such a coupling and the additional low-frequency spectral feature is described empirically by adding single excitation profile to the line-shape model. A more rigorous description should be based on a proper expression of the memory function able to reproduce the double-excitation feature in a time domain much shorter than the structural relaxation time and over mesoscopic distances. Furthermore, to be consistent with the low Q hydrodynamic

result, the memory function model should adequately account for the evolution of the transverse mode from a low- Q overdamped shoulder to a high- Q well-resolved peak. To make the situation even worse, at low to intermediate Q 's it is often hard to distinguish the highly damped transverse mode from the Mountain peak, which is fingerprints the presence of viscoelastic effects on the line-shape. The evidence of a shear mode in the spectrum simple monatomic materials will be discussed in ¶ 6.3 in further detail.

3.2.5 The Damped Harmonic Oscillator model

In many situations, relaxation phenomena occur over timescales much shorter than those typical of the probed density fluctuations. This being the case, the so-called Markovian hypothesis, i.e. an instantaneous time-decay, can be used for the memory function. A significant example is provided by the dynamic response in the hydrodynamic regime. On the other hand, in the elastic limit, infinitely slow relaxation processes can be accounted for by inserting in the memory function a term constant in time, reflecting the lack of acoustic dissipation typical of this regime. In general, a model for the memory function should include both elastic and viscous contributions, which account for the coupling of density fluctuations with both extremely fast and extremely slow degrees of freedom. Hence:

$$m_L(Q, t) = \nu_{L,\infty} Q^2 + 2\Gamma_0 \delta(t) = (c_\infty^2 - c_0^2) Q^2 + 2\Gamma_0 \delta(t) \quad (92)$$

The corresponding spectral shape can be obtained by inserting the above equation into Eq. 76, to eventually get:

$$\frac{S(Q, \omega)}{S(Q)} = (1 - f_Q) \frac{\Gamma_0^2 \omega_\infty^2}{(\omega^2 - \omega_\infty^2)^2 + 4\Gamma_0^2 \omega^2} + 2\pi f_Q \delta(\omega) \quad (93)$$

Where $f_Q = 1 - (c_\infty/c_0)^2$ is the so-called non-ergodicity parameter [28,93]. The first term on the right-hand side is the so-called Damped Harmonic Oscillator (DHO) model profile [94], which accounts for the two inelastic (Stokes and anti-Stokes) peaks in the spectrum, while the additional term $\propto \delta(\omega)$ describes the elastic peak. As clear from the memory function in Eq. 92, the DHO provides an accurate description of the spectral shape at frequencies much higher than those proper of the hydrodynamic limit. In this elastic limit, the viscous relaxation is essentially “frozen”, thus yielding a flat contribution to the memory function in Eq. 92. For this reason, the model in Eq. 93 is broadly used to fit the THz spectral shape of highly viscous systems as glass formers at the melting or in supercooled phase [6].

The term $\propto \delta(t)$ in Eq. 92 describes rapid time decays of the memory function originated by the coupling of density fluctuations with extremely fast microscopic degrees of freedom (typically in the 10^{-13} s window). The physical nature of these degrees of freedom depends, of course, on the system considered. In glass formers, they are often identified with intramolecular vibrations, in monatomic fluids are instead ascribed to interatomic collisions. In some cases, discussed further below, the presence of an instantaneous decay of the memory function has been associated to the intrinsic disorder of the fluid, or equivalently to the circumstance that intermolecular vibrations cannot be represented as plane waves.

3.2.5 Kinetic Theory models and generalised hydrodynamic

The memory function models discussed so far aim at a merely phenomenological extension of the hydrodynamic description to finite Q 's. Following a more rigorous approach, such an extension could be performed, for instance, from the knowledge of the collision cross section. This would require expressing density fluctuations as a function of both atomic positions and velocities, as prescribed by kinetic theory (KT) approaches. Unfortunately, a rigorous theory of these so-called phase-space correlation functions could rigorously work for hard sphere models, for which, indeed, interparticle interactions only consists of mutual collisions.

The use of hard sphere systems as a model for real fluids, relies on the existence of a theory, albeit approximate, in principle valid for hard spheres, as the so-called revised Enskog theory (RET) [95], which generalises the original Enskog theory developed in the 1920s [96]. The aim of this approach is to derive the correlation function matrix associated to the generic fluctuating variable $\delta\alpha_j(t)$ of the j -th atom, which for an N -particle system reads as:

$$C_{k,j}(t) = \langle \delta\alpha_j(0)\delta\alpha_k(t) \rangle_N = \langle \delta\alpha_j(0) \exp(iL_{\text{HS}}^N t) \delta\alpha_k(0) \rangle_N, \quad (94)$$

where it was introduced the hard sphere Liouville operator:

$$L_{\text{HS}}^N = \sum_{i=1}^N p_i \cdot \frac{\partial}{\partial \mathbf{r}_i} + \sum_{\substack{i \neq j=1 \\ i < j}}^N \mathbf{T}_{ij}. \quad (95)$$

Here T_{ij} is an operator accounting for inter-particle collisions. One can now introduce the first three normalised phase-space variables for the N -particle system as:

$$\delta n_Q = \frac{1}{\sqrt{N}} \sum_{j=1}^N \phi_1(\mathbf{v}) \exp(i\mathbf{Q} \cdot \mathbf{r}_j) \quad (96)$$

$$\delta u_Q = \frac{1}{\sqrt{N}} \sum_{j=1}^N \phi_2(\mathbf{v}) \exp(i\mathbf{Q} \cdot \mathbf{r}_j) \quad (97)$$

$$\delta T_Q = \frac{1}{\sqrt{N}} \sum_{j=1}^N \phi_3(\mathbf{v}) \exp(i\mathbf{Q} \cdot \mathbf{r}_j) \quad (98)$$

which represent the normalised phase-space counterparts of the hydrodynamic variable density, velocity, and temperature fluctuations. These N -body variables contain the respective single-particle functions of velocity:

$$\phi_1(v) = \frac{1}{S(Q)}; \quad (99)$$

$$\phi_2(v) = \sqrt{\frac{M}{k_B T}} \frac{\mathbf{Q} \cdot \mathbf{p}}{Q} \quad (100)$$

$$\phi_3(v) = \frac{1}{\sqrt{6}} \left(3 - \frac{Mv^2}{k_B T} \right). \quad (101)$$

The core idea of RET is to replace the N -particle correlation functions in Eq. 94 by the single particle correlations defined as:

$$C_{jj}^E(\mathbf{Q}, t) = \langle \phi_j(\mathbf{v}_1) \exp[iL_E(\mathbf{Q}, \mathbf{v})] \phi_j(\mathbf{v}_1) \rangle, \quad (102)$$

where the single-particle generalised Enskog operator:

$$L_E(\mathbf{Q}, \mathbf{v}_1) = i\mathbf{Q} \cdot \mathbf{v}_1 - ng(\sigma) \bar{A}_Q + nA_Q \quad (103)$$

replaces the N -particle operator L_{HS}^N in Eq. 95. Here, $g(\sigma)$ is the pair distribution function corresponding to two hard spheres at contact. The first term is the Fourier transform of the free streaming term (first term of Eq. 95). The second term accounts for binary collision and acts on a generic function $h(\mathbf{v}_1)$ which depends on velocity as $\bar{A}_Q h(\mathbf{v}_1) = A_Q h(\mathbf{v}_1) - \langle A_Q h(\mathbf{v}_1) \rangle$, where the binary collision operator, also appearing in the original Boltzmann equation, is given by:

$$A_Q h(\mathbf{v}_1) = \sigma \int d\hat{\sigma} \int d\mathbf{v}_2 \phi(\mathbf{v}_2) \mathbf{v}_2 \cdot \hat{\sigma} \theta(\mathbf{v}_2 \cdot \hat{\sigma}) \{ h(\mathbf{v}_1) - h(\mathbf{v}_1') - \exp(i\mathbf{Q} \cdot \hat{\sigma}) [h(\mathbf{v}_2) - h(\mathbf{v}_2')] \}.$$

Here the vector $\sigma = \sigma \hat{\sigma}$ is used to define the hard sphere collision, its amplitude being equal to the distance of the two hard spheres at contact, and the direction -- identified by the unit vector $\hat{\sigma}$ -- parallel to the line connecting them.

The third term on the right-hand side of Eq. 103 has no analogue in the original Boltzmann equation, and it contains the static structure factor $S(Q)$, i.e., the “mean field” in which the binary collisions take place. Its explicit form is defined through:

$$A_Q h(\mathbf{v}_1) = \frac{1}{n} \left[1 - \frac{1}{\sqrt{S(Q)}} \right] \int d\mathbf{v}_2 \phi(\mathbf{v}_2) i\mathbf{Q} \cdot (\mathbf{v}_1 + \mathbf{v}_2) h(\mathbf{v}_2).$$

The eigenvalues of the operator $L_E(\mathbf{Q}, \mathbf{v})$ have been computed numerically in the literature [85,86]. The first three of them correspond to eigenmodes extending to finite Q 's the hydrodynamic modes. In the basis of the eigenmodes the Enskog operator reads as:

$$L_E(\mathbf{Q}, \mathbf{v}) = \sum_h |\varphi_h(\mathbf{Q}, \mathbf{v})\rangle \lambda_h(\mathbf{Q}) \langle \varphi_h(\mathbf{Q}, \mathbf{v})|, \quad (104)$$

Where $|\varphi_h(\mathbf{Q}, \mathbf{v})\rangle$ and $\lambda_h(\mathbf{Q})$ are the h -th eigenmode and associated eigenvalue, respectively. In this basis, the dynamic structure factor can be expressed as:

$$S(\mathbf{Q}, \omega) = \frac{I}{\pi} S(\mathbf{Q}) \text{Re} \left\langle \frac{I}{i\omega - L_E(\mathbf{Q}, \mathbf{v})} \right\rangle = \frac{I}{\pi} S(\mathbf{Q}) \text{Re} \left\{ \sum_h \left[\frac{A_h(\mathbf{Q})}{i\omega + \lambda_h(\mathbf{Q})} \right] \right\}, \quad (105)$$

where $A_h(\mathbf{Q})$ is the amplitude of the h -th eigenmode.

In general, the eigenvalue $\lambda_h(\mathbf{Q})$ has both imaginary and real components, representing respectively the damping and the propagating frequency of the h -th mode. Eq. 105 is known as the development of the dynamic structure factor as a sum of generalised Lorentzian terms, i.e. Lorentzian function having complex amplitudes and widths.

It is important to stress that a third-order ($h = 0, \pm 1$) truncation of the above series reproduces the linear hydrodynamic result analytically isomorph to Eqs. 78 and 83.

Historically, the KT was developed in the attempt of providing a rigorous account of the microscopic dynamics of fluids, within the hypothesis of uncorrelated collisions (see, e.g., the comprehensive reviews in Refs. [97] and [98]). Intuitively, it can be recognised that the close-contact nature of these interactions rules out the possibility of long-range correlations, thus restricting the domain of validity of KT to hard-sphere-like systems i.e. systems in which extremely short-range (repulsive) interactions are dominating. Furthermore, the hypothesis of uncorrelated collisions applies to very dilute gases only, since, at high densities, particles' collisions are no longer statistically independent and so-called “ring collisions” play a non-negligible role.

Despite the advances prompted in the mid-1970s by the development of RET, KT approaches have been for long trapped in an impasse, due to the impossibility of expressing transport parameters as power series in the density [98], at variance of what routinely done for thermodynamic coefficients. New motivations in the field came from the use of computer studies, and, in particular, from a breakthrough MD result obtained by Alder and Wainwright [99] on model systems composed of hard spheres and hard disks. This work showed that the velocity autocorrelation function decays as $t^{-1/2}$ and as $t^{-3/2}$ in the respective cases. This unexpectedly slow time-decay owes to the presence of vortices in the molecular flow due to correlated collision events.

3.2.7 The Mode Coupling approach

From the theoretical point of view, the presence of the vortices evidenced in the work of Alder and Wainwright can be accounted for by a local formulation of Mode Coupling Theory (MCT) [100-102], which allows handling the Q dependence of transport parameters it involves rather complex and system-dependent Q -integrations [103].

Both the *KT* and MCT approaches can be derived in the framework of the memory function formalism [62]. Concerning MCT the core ideas behind the derivation of the memory function

can be found in Ref [104] and are also discussed in Ref. [62]. Formally, one can start from the expression of the memory function:

$$\mathbf{K}(t) = \frac{(f, f^*(t))}{(\mathbf{A}, \mathbf{A}^+)} \quad (106)$$

Hence, recalling that the random force $f(t) = \exp(i\tilde{\mathbf{Q}}\mathbf{L}t)\tilde{\mathbf{Q}}\mathbf{L}\mathbf{A}$ the memory matrix reads as:

$$\mathbf{K}(t) = \frac{(\tilde{\mathbf{Q}}\dot{\mathbf{A}} \exp(i\tilde{\mathbf{Q}}\mathbf{L}t)\tilde{\mathbf{Q}}\dot{\mathbf{A}}^+(t))}{(\mathbf{A}, \mathbf{A}^+)} \quad (107)$$

Its Laplace transform is:

$$\tilde{\mathbf{K}}(s) = \frac{1}{(\mathbf{A}, \mathbf{A}^*)} (\mathbf{A} \left| \frac{1}{s + i\tilde{\mathbf{Q}}\mathbf{L}\tilde{\mathbf{Q}}} \right| \mathbf{A}^+(t)) \quad (108)$$

To make the expression of the memory function explicit, it is important to identify a variable responsible for the time decay of the memory function. Although this choice is in principle unlimited, it is reasonable to choose a variable which strongly couples with $\mathbf{A}$, as for instance $\mathbf{B} = \mathbf{A}\dot{\mathbf{A}}$ and to correspondingly introduce the new projection operator:

$$\wp_2 = \frac{(\mathbf{B}, \dots)}{(\mathbf{B}, \mathbf{B}^*)} \mathbf{B} \quad (109)$$

The resolvent operator in Eq. 108 can be approximated as:

$$\frac{1}{s - i\tilde{\mathbf{Q}}\mathbf{L}\tilde{\mathbf{Q}}} \cong \wp_2 \frac{1}{s - i\tilde{\mathbf{Q}}\mathbf{L}\tilde{\mathbf{Q}}} \wp_2,$$

which allows writing the memory function as:

$$\tilde{\mathbf{K}}(s) = \frac{1}{(\mathbf{A}, \mathbf{A}^+)} \mathbf{V}(\mathbf{B} \left| \frac{1}{s + i\tilde{\mathbf{Q}}\mathbf{L}\tilde{\mathbf{Q}}} \right| \mathbf{B}^+(t)) \mathbf{V}^+ \quad (110)$$

Here we have introduced the so-called vertex interaction operator:

$$\mathbf{V} = \frac{(\dot{\mathbf{A}}, \mathbf{B}^+)}{(\mathbf{B}, \mathbf{B}^+)} \mathbf{B},$$

which plays the role of an effective interaction term. A further approximation can be performed to factorise the time-dependent memory function:

$$\begin{aligned} (\dot{A}A|exp i\tilde{Q}L\tilde{Q}t|A^+ \dot{A}^+) &\cong (\dot{A}|exp iLt|\dot{A}^+) (A|exp iLt|A^+) + (\dot{A}|exp iLt|A^+) (A|exp iLt|A^+) \\ &= J(t)C(t) + |f(t)|^2, \end{aligned} \quad (111)$$

where $C(t)$ is the regular time correlation function, while $J(t)$ is the time correlation function of the variable $\dot{A}$. Mostly, this factorization consists in completely discarding the operator $\tilde{Q}$. With the above factorization, the mode coupling memory function can be, finally, written as:

$$\tilde{K}(s) = \frac{1}{(A, A^*)} V \int ds' [\tilde{J}(s') \tilde{C}(s-s') + \tilde{f}(s') \tilde{f}^+(s-s')] V^+. \quad (112)$$

This memory function is expressed as a frequency convolution of the random force and the two correlation functions $\tilde{J}(s)$ and $\tilde{C}(s)$ representing the modes which couples with a coupling constant essentially determined by the vertex V . Eq. 112 clearly unveil the non-linear character of the MCT approach.

The KT and MCT predictions for the spectrum of simple monatomic fluids were subjected to experimental scrutiny by some INS works performed until the late 1980s. In particular, the work of Postol and Pelizzari on supercritical Ar [105] provided the first experimental test of the RET predictions on the THz spectrum of density fluctuations. Unfortunately, no quantitative agreement could be found, although the low density (10.5 atoms/nm^3) and high temperature (295 K) made the sample an ideal benchmark to test *KT* predictions. A later work by de Schepper and collaborators on Ar [106] aimed at testing the development of $S(Q, \omega)$ as a sum of Lorentzian terms as prescribed by the *KT*. The effect of spectral rule fulfilment was also considered by comparing the results obtained imposing the fulfilment of sum rules of increasing order [107]. A similar analysis was repeated in a successive work on Ar at different pressures [108], where non-analytic dispersion relations predicted by the *MCT* were compared with experimental dispersion curves. It was found that experimental results were accurately predicted by *MCT*, although for $Q > 4 \text{ nm}^{-1}$ this theory does not provide a satisfactory account of the observed behaviour of quasielastic and inelastic linewidths of the spectrum. Other attempts to experimentally validate the *MCT* predictions were much later performed on glass forming systems, however, the discussion of these results goes beyond the scope of the current review.

3.2.8 The Generalized Collective Modes approach

An analytical account of non-hydrodynamic effects on the Q -dependence of transport parameters is, in principle, provided by the Generalised Collective Mode (GCM) theory [109-111]. In its essence, the GCM theory stems from the assumption that, at short time-scales, the hydrodynamic variables can no longer be treated as slow, quasi-conserved, quantities and the coefficients governing their short-time expansion, i.e. their n -order time derivatives, must be explicitly considered when computing the hydrodynamic matrix. The *GCM* approach deals specifically with these further non-hydrodynamic variables, whose fluctuations give rise to new spectral modes, sometimes referred to as kinetic.

Examples of these non-hydrodynamic modes in liquids are structural relaxations, shear and heat waves, optic-like excitations in binary liquid mixtures, and so on.

Literature works based on GCM analysis of the Q -dependence of transport parameters relevant for the spectral shape can be found, e.g. in Ref. [112]. The results of this work suggest that the deviation from the hydrodynamic sound dispersion behaviour can be either “positive” or “negative”, depending on the ratio between the high-frequency (elastic) and the isothermal speed of sound. A series of IXS measurements on different liquid and supercritical fluids was reviewed against the *GCM* predictions in Ref. [113], thus providing an experimental validation of this approach at least up to intermediate Q values.

More recently, a GCM analysis of IXS measurements has been proposed and found to give a correct description of the spectrum at low Q values [114]. However, these results suggested that the accuracy of the GCM prediction up to Q values typically covered by IXS needs some form of Q -generalization of transport parameters.

3.3. The Single Particle regime

As mentioned, an analytically rigorous prediction for the line-shape exists only in two extreme regions of the dynamic plane, namely at the smallest Q, ω values (hydrodynamic regime) and at the highest ones (single particle regime). In the latter limit, the probed dynamic event reduces to the free recoil of the single struck atom after the collision with the probe and before any further interaction with the surrounding atomic cage. At these short times, the equation of motion of the j -th atom simply reads as $\mathbf{R}_j(t) = \mathbf{v}_j t$.

This merely ballistic behaviour can be readily understood for hard sphere model systems, in which microscopic interactions have a genuinely collisional nature, i.e. they are instantaneous and localised in space. In a real fluid, these interactions span finite distance and time intervals, thus in principle, the atom cannot experience an entirely free recoil. Nonetheless, if the energy transferred in the scattering event is much larger than the energy of any local interaction, for short times the struck atom is freed from these interactions after the strong impulse received from the probe. In this so-called Impulse Approximation (IA) regime, it is safe to assume that no sizable external force acts on the isolated photon-target atom system.

The initial state of the struck atom is characterised by a distribution of momenta, any of which yields a sizable contribution to the scattering intensity. In some respect, the atom behaves like a moving source, which generates a “Doppler broadened” scattering and its momentum distribution defines the shape of the scattered intensity.

Since for extremely high Q 's the probed distances are much smaller than first neighbouring atoms' separations, correlations between distinct atoms vanish in this limit. This so-called incoherent approximation holds validity when the “coherent” oscillations of $S(Q)$ damp out, and $S(Q)$ joins its extremely high Q unit value. The dynamic response is here fully described by the self component of the van Hove function in Eq.29. From a space Fourier transform of the van Hove function, one can derive the self component of intermediate scattering function:

$$F_s(Q, t) = \frac{1}{N} \left\langle \sum_{i=1}^N \exp[iQ \cdot (\mathbf{R}_i(t) - \mathbf{R}_i(0))] \right\rangle \quad (113)$$

The Fourier transform of $F_s(Q, t)$ is $S_s(Q, \omega)$, the “self” part of dynamic structure factor. In the IA regime, one has $S(Q \rightarrow \infty, \omega) = S_s(Q \rightarrow \infty, \omega)$.

The computation of the spectrum in the incoherent limit is particularly simple for a classical monatomic liquid. For classical atoms, the probability distribution for the velocity v is given by a Maxwell-Boltzmann distribution, which is a Gaussian function of the atomic velocity. As shown, e.g. in Ref. [4], Fourier transforming in both Q and ω eventually leads to the following Gaussian shape for the dynamic structure factor:

$$S_{IA}(Q, \omega) = \left(\frac{M}{2\pi k_B T Q^2} \right)^{1/2} \exp \left[-\frac{M\hbar^2}{2\pi k_B T Q^2} (\omega - \omega_r)^2 \right] \quad (114)$$

where the suffix “IA” labels the Impulse Approximation value of $S(Q, \omega)$. The profile in Eq. 114 is a Gaussian centred at the recoil frequency $\omega_r = Q^2/2M$ and having a width proportional to the mean kinetic energy of the tagged particle.

Summarising, the whole line-shape evolution between the hydrodynamic and the single particle regime is schematically sketched in Figure 6.

Figure 6: Sketch of the evolution of the spectral shape from a liquid sample across various Q windows characterised by different behaviour the $S(Q)$ profile, plotted in semilogarithmic scale. Courtesy of F. Bencivenga.

At small Q 's, the spectral shape rapidly evolves from the Rayleigh-Brillouin profile toward a more complex triplet structure, in which the dominant modes become increasingly damped. In

particular, when the momentum transfer becomes comparable with the inverse of the interparticle separation, one probes the so-called “mesoscopic regime” roughly indicated by the arrow.

A black area approximately locates the, so called kinetic regime, where the lineshape has nearly lost any signature of inelastic modes.

The Gaussian profile centred at the recoil frequency is reached asymptotically as the Q -oscillations of the $S(Q)$ damp off joining the limiting unit value.

Once both practical and theoretical aspects of IXS technique have been discussed, it is now time to focus on experimental results, particularly focusing on some relevant topics related to the THz dynamics of simplest liquids. As mentioned in the introductory Section, this review primarily deals with IXS studies on noble gases and alkali metals, although it occasionally discusses for reference spectroscopic results obtained with complementary methods and in slightly more complex samples.

These experimental results are discussed following a partially chronological order, with a narration splitting into four main parts:

- 1) Part I deals with a period roughly extending from the early 1960s to the mid-1990s, to be identified, for the sake of this review, as the period preceding the development of IXS.
- 2) Part II aims at illustrating some relevant topic addressed by IXS technique since its development in the mid-1990s.
- 3) Part III illustrates some less conventional or emerging research issues in the field of IXS investigation of simple, with especial attention to those holding the promise of exciting future developments.
- 4) A final part will illustrate the opportunities disclosed in the field by the development of next generation IXS instruments.

4. Part I: Experimental results before the advent of IXS

4.1 Preliminary remarks: measuring the spectral shape by Brillouin Light Scattering

The hydrodynamic shape of the spectrum defined by Eqs. 78 was predicted since the seminal work of Brillouin [115] and the successive theoretical formulation of Landau and Plazeeck in the early 1930s [116] (see also the review in Ref. [61]). However, first experimental confirmations of such theoretical shape could only be achieved much later [117], owing to the fine resolving power ($\Delta E/E < 10^{-7}$) and, consequently, the complex interferometric techniques typically required for similar measurements in liquids.

The first Brillouin study on inert gases dates back to the experiment of Fleury and Boon on Ar and Ne along the coexistence line [118]. The shape of a typical spectrum of Ar measured in such work is displayed in Figure 7. The corresponding non-convoluted hydrodynamic spectrum is also included in the plot for comparison as derived from Eqs. 78-81 using thermo-physical and transport properties derived from existing databases [119] and bulk viscosity data in the literature [120]. This spectral profile provides the best estimate of the true $S(Q, \omega)$ shape and, as expected,

it is dominated by three extremely sharp and well-separated peaks, which is consistent with the condition of the validity of the Rayleigh-Brillouin (Eqs. 78-81), namely $D_T Q^2, \Gamma Q^2 \ll c_s Q$.

Among various results, Fleury and Boon found that, in the probed GHz window, the sound velocity of Ar is nearly .4 % lower than the one measured by ultrasound (US) absorption in the MHz range [121]. This result may seem surprising since as discussed in ¶ 5.2, the behaviour of a liquid becomes more solid-like upon a frequency increase, this trend is usually reflected by an enhancement of sound velocity instead of the decrease observed by Fleury and Boon.

Figure 7: *The Rayleigh-Brillouin spectrum of Ar measured along the coexistence line by Brillouin light scattering measurement in Ref. [118]. The hydrodynamic spectrum reconstructed using tabulated thermo-physical properties [119], and bulk viscosity measurements [120] is reported for comparison as a solid line. The spectral shape is redrawn with permission from in Ref. [118].*

A similar “negative dispersion” was also later reported for water [122], which seems even more surprising when considering the frequency increase reported afterwards by GHz [123,124] measurements in the supercooled phase and the successive ones [125,72] at higher temperatures. Despite some initial surprise, it was later recognised [126] (see also Ref. [62], page 263) that this apparent negative sound dispersion has no real physical significance, but is rather due to the slightly smaller value expected for the sound velocity when extracted from the BLS spectrum (hypersonic speed) rather than measured by US (ultrasonic speed). This weak ($< 1\%$) discrepancy becomes observable only when the competing viscoelastic effects are absent; to some degree the ability to detect this small effect highlights the precision reached by BLS measurements already in the late sixties.

As discussed, the Rayleigh-Brillouin spectrum features the dynamic response of a simple fluid at extremely low Q and ω values. More specifically, this dynamic regime is met whenever the probed distances become much larger than interatomic separations and any possible structural heterogeneity (cluster, cooperatively arranging region), while the probed times are much longer than the timescale of any internal degrees of freedom of the fluid.

In complex molecular fluids, the departure from the hydrodynamic regime can be observed even at the “quasi-macroscopic” scales probed by BLS and it is primarily revealed by a systematic increase (decrease) of the sound velocity (longitudinal viscosity) upon increasing Q . Furthermore, viscoelastic effects are revealed by an often elusive lineshape effect as the rise of an additional weak spectral component: the mentioned Mountain mode. Its presence was reported, for instance, by a BLS works in CCl_4 [127,128], neopentane [129] and cyclohexanol [130]. In these measurements, the Mountain peak has been connected to a relaxation process arising from the coupling between vibrational and translational degrees of freedom [131], back at those times referred as thermal relaxation.

A different kind of relaxation thoroughly studied by early BLS studies is the so-called structural relaxation, commonly observed in glass forming systems. A case extensively studied is the one of glycerol, which represents a prototype of intermediate glass former within the Angell classification [132]. Relaxation phenomena in glycerol have been investigated both by US [133,134] and BLS [135,136] techniques. This relaxation, sometimes referred to as α -relaxation [101,137], is characterised by a decay time which strongly depends on temperature, changing from $\approx 10^{-12}$ s in the non-supercooled liquid phase up to about 100 s close to the glass transition temperature. The typical phenomenology of this relaxation process will be discussed further below in this review.

A method to account for the effects of relaxation phenomena on the lineshape is to introduce a suitable time (frequency) dependence of transport coefficients or, equivalently, by adding a new relaxing variable to the set of dynamic variables entering in the hydrodynamic equations [61]. The viscoelastic theory in its original formulation was mostly used to describe the dynamic behaviour of highly viscous fluids as glass forming systems [64]. The extensions of a viscoelastic description to simplest fluids [138-140] indicates that the viscoelastic behaviour is an intrinsic property of all liquid aggregates, although its dynamic range and related phenomenology are, of course, strongly system-dependent.

4.2 A generalised Brillouin triplet at mesoscopic scales

Upon increasing Q the lifetime of inelastic modes gradually shortens, which reflects the decreasing ability of the system to support the propagation of high-energy, $E (= \hbar c_s Q)$ sound waves. Furthermore, acoustic oscillations gradually lose their collective character upon decreasing their wavelength, $2\pi/Q$, as they involve smaller volumes and thus fewer atoms. In this respect, a bare hydrodynamic theory of density fluctuations becomes certainly inappropriate for wavelengths $2\pi/Q$, comparable or shorter than the first neighbouring atoms separation, d , as in this mesoscopic *regime* the very notion of “collective mode” loses physical significance. This corresponds to the Q -range typically explored in IXS and INS measurements. However, the use of the mean free path λ as a reference leads to different conclusions. Indeed, dense fluids are so tightly packed, that λ values in these systems typically range in the Å window, thus possibly becoming even smaller than the atomic size. Under these conditions, the only short-time movements permitted to single atoms are very rapid rattling oscillations having a sub-ps period, T_r .

Consequently, at the low to intermediate Q ’s probed by IXS and INS measurements, the conditions $2\pi/Q \ll \lambda$ and $2\pi/\omega \ll T_r$ are still fulfilled, which implies that the dynamic response is still averaged over many elementary dynamical events, as in principle required for the validity of a suitably generalised hydrodynamic theory.

Given these grounds, in the early 1960s, the persistence of a triplet spectral shape down to mesoscopic scales appeared a hypothesis intriguing, yet plausible and worth intensive scrutiny. Therefore, several INS experiments carried out in the mid-1960s aimed at seeking for signatures of hydrodynamic-like excitations in the THz spectrum of simple fluids. These works were pioneered by some INS measurements on dense Ne, Ar, and D₂ [141] bearing evidence for “extended hydrodynamic” peaks in the spectrum. Furthermore, the authors found that at the lowest Q ’s, the frequency shift of these peaks approached from above the linear hydrodynamic dispersion, which suggested to interpret these spectral features as the high Q relics of Brillouin peaks. This conclusion seemed, at least partially, refuted by the INS work by Kroô and collaborators on Ar [142], which instead reported no evidence for distinct inelastic features. Nonetheless, the presence of phonon-like excitations emerged indirectly from a comparison between liquid and solid phase spectra. Likewise, inconsistencies in these two early INS measurements owed to the different incident wavelength used, which made the results hardly comparable.

In the same period, Sköld and collaborators [143] measured the INS spectrum of Ar in both liquid ($T = 94$ K and 102 K) and solid ($T = 68$ K and 78 K) phases. The authors observed a linear Q -dependence of the inelastic shift at the lowest Q ’s, the slope being consistent with the adiabatic sound velocity. Furthermore, they showed that, at higher Q ’s, the sound dispersion curve of the liquid sample vaguely resembles the phonon dispersion curve of the solid, thus suggesting that the local pseudo-periodicity of the liquid structure gives rise to quasi-periodic zones reminiscent of the Brillouin zones of a crystal.

Identifiable inelastic peaks in the $S(Q, \omega)$ were observed up to Q values as large as 16 nm^{-1} in an INS work on liquid lead [144]. A successive INS measurement on the same sample [145] also suggested clear resemblances between the sound dispersion in fluids and the phonon dispersion in crystalline solids. Most importantly, this work proved the occurrence, in the liquid phase, of a typical solid-like behaviour as the ability to support a shear wave propagation, as revealed by the onset of a shear mode in the INS spectrum.

Previous INS measurements in superfluid He [146], also showed the presence of a solid-like

dynamic response, which manifested itself through well-resolved THz modes having a sinusoidal phonon-like Q dispersion. However, the quantum character of this system makes the interpretation of this result not straightforward.

4.3 Clear evidence of extended Brillouin peaks at mesoscopic scales

One of the first convincing proofs of the persistence of distinct inelastic peaks in the THz spectrum of a fluid was obtained by INS measurements on supercritical neon [147,148] and liquid Rb [150]. The INS spectra measured in the two experiments are respectively reported in Figure 9 and Figure 8 .

The measurements on Ne by Bell and collaborators spanned an unusually low Q interval ($0.6 \text{ nm}^{-1} \leq Q \leq 1.4 \text{ nm}^{-1}$), which further reduced the dynamic gap with low Q spectroscopic methods as *BLS* (Q less than few 10^{-2} nm^{-1}). In Figure 9 the spectra measured in Refs. [147] and [148] are compared with more recent INS measurements on supercritical Ar [149] further extending the explored Q range ($0.35 \text{ nm}^{-1} \leq Q \leq 1.25 \text{ nm}^{-1}$) toward the small Q range covered by *BLS*. The INS spectra of liquid Rb reported in Figure 8 cover Q values larger by nearly one order of magnitude the range of neon and argon INS measurements in Figure 9, however they display broad inelastic shoulder up to the highest Q value (10 nm^{-1}).

It can be noticed that all spectral shapes reported in Figure 9 and Figure 8 exhibit a hydrodynamic-like triplet profile, consisting of a dominating quasi-elastic mode and two acoustic excitations (spectra taken from Ref. [149] are only reported on the Stokes side).

One readily notices that, while for neon inelastic modes become highly damped already at $Q = 1 \text{ nm}^{-1}$, for liquid Rb they are still discernible up to a Q value as high as 10 nm^{-1} .

Likewise, this different behaviour stems from the different amplitude of the repulsive part of interatomic potentials [151], which is much stronger in noble gases than in liquid metals.

In this respect, noble gases more closely resemble the ideal model of hard spheres. The first neighbouring atoms' distance, d can be used to get a more quantitative assessment of these differences. Indeed, it was estimated [152], that in hard sphere models inelastic peaks survive until $Qd = 0.5$, in liquid Ar until $Qd \approx 1$ and in liquid Rb until $Qd \approx 4$.

Figure 8: *INS spectra of liquid Rb. All spectra are redrawn from Ref. [150].*

4.4 The key role of thermodynamic conditions

The presence of distinct peaks in the spectrum reminiscent of Rayleigh-Brillouin hydrodynamic shape suggested to perform [148] a best fit analysis of the spectral shape using the generalised hydrodynamic model in Eq. 78.

The values of the transport parameters extracted from such a line-shape analysis are reported in Figure 10 after normalisation by the corresponding hydrodynamic predictions, as derived from Eqs. 79-81 using the information included in the original references, or using tabulated thermo-physical properties [119] and bulk viscosity data [120]. Furthermore, in Figure 10 the corresponding values derived from more recent INS measurements in Ar [149] are also reported for comparison. The inclusion of these more recent measurements is particularly helpful since their higher statistical accuracy, and dense Q -grid probed, enables a very precise determination of the Q -dependent parameters. It can be readily noticed that, apart from lowest Q data of Ref. [149], all normalised data are very close to 1. This demonstrates good consistency between INS measurements and hydrodynamic predictions, which is indeed surprising, given the mesoscopic

scales covered by this spectroscopic technique. Also, the highly-damped character of the spectral modes measured in these INS works (see Figure 9) would suggest a failure of the simple hydrodynamic predictions in Eqs. 79-81, which implicitly assumes the presence of strongly underdamped modes in the spectrum, i.e. $D_T Q^2, I Q^2 \ll c_s Q$.

This finding leads to the unexpected conclusion that these “extended hydrodynamic” modes follow a simple hydrodynamic trend up to Q and ω values exceeding the ones covered by BLS by almost two orders of magnitude.

At this stage, a question may naturally arise on the Q value at which the breakdown of the simple hydrodynamic behaviour occurs. A significant amount of successive IXS results proves that the answer strongly depends on the thermodynamic conditions of the sample.

In this respect, it is worth noticing that data reported in Figure 10 refer to supercritical samples only. In supercritical conditions, viscoelastic effects leading to a non-hydrodynamic behaviour are in principle much weaker. As shown in the following, THz spectroscopy results in the liquid phase outline an entirely different picture.

Figure 9: Typical INS spectra of Ar measured by Bell and collaborators [147] (left plot) and by Bafle and collaborators [149] (right plot) at the indicated Q values. The intensities are vertically shifted for clarity.

An example of the Q -dependence of sound velocity in a liquid noble gas can be found in Figure 11. Data refer to INS measurements on liquid Ar at various pressures [108]. One can readily notice that at low to intermediate Q 's, the sound velocities measured at THz scales largely exceed the hydrodynamic value, c_s .

This is the mentioned PSD effect, namely the frequency increase of sound velocity caused by a viscous-to-elastic transition. In fact, from low to moderate Q 's, an increase of Q corresponds to an increase in the acoustic frequency $\omega_s = c_s Q$.

The comparison between Figure 10 and Figure 11 proves that the onset of non-hydrodynamic effects in the sound dispersion strongly depends on the thermodynamic conditions of the sample. Upon looking at Figure 11, one readily notices a gradual lowering of PSD upon increasing the pressure, which is consistent with the expectation that the difference between liquid-like and solid-like behaviour, i.e. the amplitude of the viscous-to-elastic transition, tends to vanish upon approaching solidification.

Figure 10: Shape parameters of the $S(Q, \omega)$ reported in Refs. [147] and [149] for Ne and Ar respectively and at the indicated thermodynamic conditions. Data are normalised to the corresponding hydrodynamic values as derived from Eqs. 79-81. Transport parameters in those equations are extracted from original works, from a database of the National Institute of Standards and Technology [119] and bulk viscosity data in Ref. [120].

4.5 The dynamic response at short wavelengths

Overall, INS measurements performed until the mid-1990s demonstrated that when the probed wavelength $2\pi/Q$ approaches the typical adjacent atoms' separations, the propagation of collective excitations becomes strongly coupled with the local structure of the fluid. A variable particularly helpful to characterise such a coupling is the static structure factor, $S(Q)$, can g. An example of $S(Q)$ profile measured by X-Ray diffraction [153] in a simple monatomic liquid (liquid Cs) is illustrated in Figure 12, or, in a wider Q -range, in Figure 18.

Figure 11: The Q -dependence of the generalised sound velocity of liquid Ar determined from best-fit values of ω_s Eq. 83 at the pressure values indicated in each plot. carried out. The corresponding hydrodynamic value. i.e. the adiabatic sound velocity c_s is also reported as dashed horizontal line. Data are extracted from INS measurements of Ref. [108]

It is readily noticed that $S(Q)$ reaches a sharp maximum at $Q = Q_m \approx 2\pi/a$, where a is a distance close to the average first neighbouring atoms separation d^i . Beyond the first diffraction peak, $S(Q)$ displays oscillations around the unit value which gradually damp out upon increasing Q .

The so-called single particle limit, corresponding to $S(Q) = 1$ is reached only asymptotically at infinitely high Q values.

In Figure 12, the $S(Q)$ profile measured by X-Ray diffraction in liquid caesium is compared with the Q dependence of the inelastic shift, ω_s , extracted from the INS spectrum [154].

Figure 12: In the lower plot the extended sound velocity of liquid Cs is reported (line+open circles) as derived from INS measurements in Ref. [154], with the straight line representing the hydrodynamic value. The amplitude of the Positive Sound Dispersion (PSD), is roughly indicated for reference. The upper panel displays the sound dispersion (line+dots) in Ref. [154] along with the static structure factors $S(Q)$ therein derived from INS spectra (line+open circles) or measured by X-Ray diffraction [153].

The reported curves show the following noteworthy features:

- 1) At low and intermediate Q values ω_s as a steep Q -dependence whose linear slope $c_s = \omega_s/Q$ (see bottom plot) slightly exceeds the hydrodynamic value, i.e. the adiabatic sound velocity, also reported for reference as a horizontal line.
- 2) A maximum in the dispersion curve ω_s occurs at $Q = Q_m/2$, as typically seen in crystalline materials at the edge of the first Brillouin zone.
- 3) At higher Q values, the dispersion curve bends down to a sharp minimum at $Q = Q_m$. This minimum is a clear manifestation of the destructive interference between the scattering-excited acoustic wave and the pseudo-periodicity of the local structure.

Naively, the analogy with the case of a linear chain (see the bottom plot in Figure 15) suggests ascribing this minimum to the coexistence of both an acoustic wave “transmitted through” and one “reflected from” a structural “node” at the position of first neighbours’ cage. Clearly, for the linear chain, the Q dispersion exhibits cusp behaviour at the structure node due to the opposite dispersion slope (propagation speed) $\pm c_s$ of the two waves. In any event, the presence of a dispersion minimum reveals the effect of the local order in the sound propagation of a liquid, which stresses some resemblance between a liquid and its crystalline counterparts. Not unexpectedly, the sharpness of such a minimum is usually observed to enhance upon approaching solidification.

While giving a closer look at the lower panel of Figure 12, it is interesting to compare the amplitude of the positive sound dispersions of this alkali metal with the one, much stronger, previously discussed for a noble gas (Figure 11). In this respect, the squared Einstein frequency Ω_0 was often considered as a rough predictor of the amplitude of PSD [20]. As readily inferred from Eq. 88, Ω_0 depends on the average value of the Laplacian of the interatomic potential. The main contribution to this Laplacian comes from the region where the potential has the steepest variation with r , i.e. the repulsive range. For this reason, the PSD is more pronounced in systems, as noble gases, for which this repulsive part is especially harsh.

4.6 Evidence of a propagation gap

In the mid-1980s several neutron scattering measurements on noble gases reported the presence of a “propagation gap” in the sound dispersion curve [155,156], that is a Q region centred at the position the first diffraction peak, where the inelastic shift vanishes.

The occurrence of a propagation gap at the position of the first $S(Q)$ maximum was predicted by KT calculations [157] and also experimentally observed by INS measurements in molten salts [158] and liquid He [159,160]. Cohen and collaborators investigated this effect in the framework of the GET [161] and interpreted it as the prevalence of elastic force over dissipative ones. For sufficiently small Q ’s, elastic forces prevail thus always enabling the propagation of sound waves. At larger Q ’s, dissipative forces become dominating and prevent the sound mode from propagating. At even higher Q values lying beyond the position of the first diffraction peak, the free streaming term of the Enskog operator (first term in Eq. 103) has increasing relevance, eventually overwhelming dissipative forces and restoring sound propagation.

However, the actual physical significance of the gap raised some scepticism [162,163] as it locates around the position of first diffraction peak, where the spectrum reduces to a narrow featureless peak, which makes the use of a triple peak model (Eq. 83) somehow questionable [162]. Indeed, lineshape analyses performed with different models [65] do not lead to the observation of similar effects. However, when comparing the dispersion curve obtained by various models, one has to face the problem of possible inconsistencies in the definitions of the extended acoustic frequency. In more recent times these inconsistencies have been the focus of a thorough analytical scrutiny [94].

5. Part II: The development of IXS

Until the mid-90s INS was the only spectroscopic method available to study the THz spectrum of disordered systems. As discussed in § 3, this technique is intrinsically hampered by kinematic constraints, which limit the accessible region of the dynamic plane. These limitations become particularly penalising 1) upon accessing to small Q 's, where the collective character of the dynamics becomes dominating and 2) when dealing with samples having large sound velocity.

A work of Burkel and collaborators on liquid lithium pioneered high-resolution IXS studies on simple systems. The measurements were performed using the X-Ray spectrometer INELAX at DESY synchrotron at HASYLAB, Hamburg [7,164].

Despite the low Z , liquid lithium is a sample well-suited for IXS measurements, owing to the high sound velocity. Furthermore, in lithium, as in many other liquid metals, $\gamma \approx 1$, which makes the ratio of inelastic to elastic intensity, or Landau-Placzek ratio, particularly high, at least in the hydrodynamic limit. Both these factors improve the visibility of collective excitations in the spectrum. These characteristics make inelastic peaks in the spectrum of liquid lithium, and liquid metals in general, exceptionally well-defined even with relatively coarse energy resolution available in the early development of IXS.

The spectral shape of lithium measured in Ref. [164] seemed consistent with the one predicted by earlier MD results, thus providing some validation of the potential used in those computations. although the statistical accuracy of the measurement did not authorise definitive conclusions.

Substantial progress was achieved a few years later, after the development of ID16 beamline at the European Synchrotron Radiation Facility in Grenoble, France, an IXS spectrometer with an unprecedented narrow (1.5 meV) energy resolution bandwidth. A detailed description of this spectrometer can be found, e.g., in Refs. [165] and [166].

In the first operative phase of ID16, IXS investigations in monatomic systems were rather sporadic, being the mainstream interest of the user community primarily focused on associated or highly viscous systems, as water [167-169] and glass formers [6]. However, the first IXS measurement on liquid lithium was one of the first breakthrough results obtained with this novel experimental method. Among various results, the unprecedented statistical accuracy of the measurement enabled a clear-cut discrimination between alternative hypothesis on the nature of the interatomic potential of the sample. Specifically, it was found that the so-called neutral pseudo-atom potential [170] provides a more accurate prediction of the spectral shape than the empty core potential proposed by Ashcroft [171].

5.1. The Q -evolution of the shape parameters in dense noble gases

One of the advantages of dealing with inert gases is their large compressibility, which offers the opportunity of spanning wide density spans even with moderate P and T increases. This permits to explore substantial variations of the interparticle distance and, consequently, of the strength of microscopic interactions. Furthermore, the considerably smaller transverse size of the beam enables to perform IXS measurements on small-sized samples, thus potentially disclosing the access to more extreme thermodynamic conditions. Across the years this new opportunity revitalised the interest toward the study of the dispersive behaviour of dense fluids in wide thermodynamic regions extending from the liquid to the supercritical region.

Indeed, as discussed, the comparison between the dynamic response of simple systems below and

largely above critical point evidenced some striking differences. These are illustrated in Figure 13, which displays the dispersion curves either measured or simulated in supercritical Ne [172] and He [173], respectively. The neon sample was kept at $T = 294$ K, $P = 3$ Kbar ($n = 29.1$ atoms/nm³), while helium was at $T = 25.5$ K, $P = 0.8$ Kbar ($n = 30.6$ atoms/nm³). Both systems were in deeply supercritical conditions being ($T_c = 44.5$ K, $P_c = 27.7$ bar) and ($T_c = 5.2$ K, $P_c = 2.26$ bar) the respective critical points of the two samples. Dispersion curves measured in the liquid phase are reported in the upper plots for comparison as derived from INS measurements in neon at ($T = 35$ K, $P = 80$ bar, $n = 33.4$ atoms/nm³) and helium at ($T = 4$ K, $P = 1$ bar, $n = 19.5$ atoms/nm³) discussed in Refs. [173] and [159], respectively.

Let's first discuss the results obtained for the supercritical samples (dots). The MD simulations on neon yield much less scattered results, thus enabling a more precise estimate of the Q -threshold (Q_H) defining the validity domain of the extended hydrodynamic behaviour. A comparison between the computational results and the corresponding simple hydrodynamic prediction leads to estimate $Q_H \approx 8$ nm⁻¹. The simple hydrodynamic predictions are reported for comparison as solid lines and have been obtained inserting in Eqs. 79-81 transport coefficients extracted from the *NIST* database as well as from bulk viscosity data in Ref. [119]. The latter is not too distant from the value $Q \approx 10$ nm⁻¹ for which $Q\lambda_E \approx 1$ -1.5, with λ_E being the Enskog mean free path of the sample. $\lambda_E = 2/\pi n d^2 g(d)$, where d is the diameter of the hard spheres. Beyond this Q value, the spectrum enters in the so-called kinetic regime, i.e. in the domain of validity of KT approaches.

Briefly, the sound dispersions curves in liquid and supercritical samples differ in two main aspects:

- 1) The evidence of a strong positive sound dispersion (PSD) in the liquid phase for Q smaller than about 12 nm⁻¹.
- 2) The occurrence of a propagation gap in the liquid phase, which correspond to the clear minimum in supercritical samples.

Concerning the first point, it is tempting to infer that the PSD effect is somehow distinctive of the liquid phase. However, the reality is more complex, as a sizable PSD was found in some supercritical regions as well, as extensively discussed in the rest of this review.

It is worth stressing that the onset of a large PSD is often associated with a considerably high value of the Einstein frequency previously introduced in Eq.88. For Lennard-Jones systems an approximate expression of the Einstein frequency is given by $\Omega_0 \propto T^{\frac{1}{2}} n^2 p q$, with p and q being the exponent of the Lennard-Jones potential [20]. Unfortunately, this formula does not provide an accurate prediction of the dispersive trends shown in Figure 13. In fact, it leads to estimate that the two supercritical samples have an Einstein frequency larger by a factor 2.2 (neon) and 6.2 (helium) than that of their liquid counterparts, although their dispersion bears no evidence of PSD effects.

Figure 13: *Best-fit shape parameters of the linearized hydrodynamic model in Eq. 83 (open circles) in supercritical neon (left column) and helium (right column). Data refer to the results of MD simulations and IXS measurements in Ref. [172] and [173] respectively. Dispersion curves measured by INS in liquid neon [174] and helium [159] are also reported for comparison (dots) in the left and right plots respectively (blue dots). In each plot, the solid lines represent the hydrodynamic prediction with Eqs. 79-81 in which the relevant thermodynamic and transport parameters have been derived from the NIST database [119] and bulk viscosity data from Ref. [120].*

5.2 Generalities on the role of $S(Q)$

In a scattering experiment, the access at high Q values enables the study of the dynamics over short distances where fast dynamic events, as “in cage” rattling, are dominant. At high Q ’s far exceeding the hydrodynamic regime the dynamic response can be described starting from a short-time expansion of the intermediate scattering function in Eq. 31 [20], which, for a classical system contains even powers of the time. Explicitly:

$$F(Q, t) = S(Q) - \langle \omega^2 \rangle (t^2/2) + \langle \omega^4 \rangle (t^4/24) + \dots, \quad (115)$$

where it was used $F(Q, 0) = S(Q)$. After dividing both members of the equation by $S(Q)$, the

leading term of the short time expansion becomes the normalised second moment $\omega_0^2 = \langle \omega^2 \rangle / S(Q) = k_B T Q^2 / [MS(Q)]$. Assuming that the shape of $S(Q, \omega)$ is a single featureless peak, as approximately the case for $Q \approx Q_m$, the parameter ω_0^2 gives a reasonable measure of its width. Therefore, one can expect that the overall width of the spectrum reaches a minimum at Q_m , i.e. at the position of the first sharp $S(Q)$ maximum. This effect, customarily referred to as the de Gennes narrowing [175], reveals an overall increase of the lifetime of density fluctuations plausibly induced by the interference of density fluctuations with the first neighbouring atomic arrangement. Interestingly, this narrowing has also a visible impact on the incoherent spectrum, which directly relates to the single atom diffusion. This topic was thoroughly investigated in an INS work by Sköld [176] in the late 1960's, which addressed the problem of a quantitative comparison between the shape of the coherent and the incoherent spectrum of Ar. To interpret the outcome of its INS measurements, Sköld proposed a modification of the Vineyard model of continuous diffusion [177], also known as convolution approximation. The Vineyard's model relies on the assumption that coherent and incoherent components of the spectrum are linked through the formula $S_c(Q, \omega) = S(Q)S_i(Q, \omega)$. Although at sufficiently high Q 's this approximation provides a consistent prediction of experimental results, at low Q 's it clearly violates the sum rules requirements originally derived by Placzek [178] and later, for classical systems, by de Gennes [175].

To amend to this problem, Sköld modified the Vineyard approximation by assuming instead $S_c(Q, \omega) = S(Q)S_i(Q/\sqrt{S(Q)}, \omega)$. The core idea behind this hypothesis is that the static structure factor $S(Q)$, identifies the number of atoms effectively taking part to the coherent scattering, such a number becoming equal to one in the single particle regime. One can thus replace the momentum $\hbar Q$ with the momentum "effectively" gained by the system $\hbar Q / \sqrt{S(Q)}$. The factor $\sqrt{S(Q)}$ here describes the inertial response of the target system to the perturbation induced by the scattering event. Although the Sköld model was primarily conceived to set a quantitative link between coherent and incoherent spectral shapes, it expresses a concept which turns out to be useful for the scope of the present discussion. Specifically, the idea that $S(Q)$ embodies the inertial response of the target system, naturally explains the slowing down of the dynamic response (de Gennes narrowing) at $Q = Q_m$, where $S(Q)$ reaches its first sharp maximum.

In this perspective, it would be interesting to check if any available experimental result suggests a $1/S(Q)$ -dependence of shape parameters - ω_s, z_s and z_h -. defining the Generalised Hydrodynamic model in Eq. 83. This being the case, the Q dependencies of these parameters beyond the simple hydrodynamic regime could, in principle, be described by replacing Q by $Q_{eff} = Q\sqrt{S(0)/S(Q)}$ in Eqs. 79-81. Namely:

$$\left\{ \begin{array}{l} \omega_s = c_s Q_{eff} \end{array} \right. \quad (116)$$

$$\left\{ \begin{array}{l} z_s = \frac{[(\gamma-1)D_T + \nu_L]}{2} Q_{eff}^2 \end{array} \right. \quad (117)$$

$$\left\{ \begin{array}{l} z_h = D_T Q_{eff}^2 \end{array} \right. \quad (118)$$

To check the validity of this approximation. Figure 14 displays the Q -dependencies of the generalised sound velocity, kinematic longitudinal viscosity, and thermal diffusivity:

$$c_s(Q) = \frac{\omega_s}{Q}, \quad \nu_L(Q) = \frac{2z_s}{Q^2} - (\gamma(Q)-1) \frac{z_h}{Q^2}, \quad D_T(Q) = \frac{z_h}{Q^2}. \quad (119)$$

derived using best-fit values of ω_s , z_s and z_h obtained from the MD simulation in Refs. [172], [179] and compares them with the normalised generalised transport variables deduced from Eqs. 116-118, i.e.:

$$c_s(Q) = \sqrt{\frac{S(\theta)}{S(Q)}} c_s, \quad \nu_L(Q) = \frac{S(\theta)}{S(Q)} \nu_L, \quad D_T(Q) = \frac{S(\theta)}{S(Q)} D_T \quad (120)$$

The latter are here derived using the $S(Q)$ reported in Ref. [65] and the values of c_s , ν_L and D_T obtained from the *NIST* database [119] and bulk viscosity data [120].

The values of the generalised hydrodynamic variables determined using either Eqs. 119 or Eqs. 120 are compared in the three plots of Figure 14. It clearly appears that the two determinations yield fairly consistent results, although some discrepancy can be noticed in the values generalised thermal diffusivity $D_T(Q)$ at intermediate Q 's.

This result is particularly interesting, as it suggests that in the considered deeply supercritical conditions ($T/T_c = 6.6$ and $P/P_c = 10.8$) the Q -dependence of transport parameters is mainly described, beyond the hydrodynamic limit, by a $[Q^2/S(Q)]^{n/2}$ law, with $n = 1$ and 2 for the inelastic shift and the inelastic widths respectively.

5.3 Semi-quantitative considerations on the Q -dependence of shape parameters

As noticed in earlier paragraphs, the dependence of the inelastic shift on $Q/\sqrt{S(Q)}$ is consistent with a finite Q extension of the compressibility theorem [21]. In fact, the later can be easily rearranged to obtain $c_s = \sqrt{\gamma} c_T = \sqrt{\gamma k_B T / MS(\theta)}$, which lends itself to the following finite- Q generalisation:

$$\omega_s = c_s(Q)Q = \sqrt{\frac{\gamma k_B T}{MS(Q)}}Q = c_s Q_{eff} \quad (121)$$

Here it was assumed that the only Q -dependent parameter in Eq. 121 is $S(Q)$, while γ can be treated as a macroscopic non-local (Q -independent) parameter. Although the soundness of this assumption can hardly be proven on a rigorous ground, from the simulation result of Ref. [139], it can be deduced that the relative variation of $\sqrt{\gamma}$ in the Q range considered in Figure 14 is of the order of few percent. It is also important to notice that Eq. 121 does not provide a good prediction of the Q -dependence of sound velocity when viscoelastic effects become sizeable.

Concerning the width of the central peak, an expression can be obtained within a hard sphere model of the gas in the frame of the GET approach, as proposed e.g. in Ref. [180]. This model leads to predict $z_h = [D_E Q^2 / S(Q)] d(Q)$, where, in a first approximation, $d(Q) = [I - j_0(Q\sigma) - 2j_2(Q\sigma)]$ with $J_i(x)$ being i -order spherical Bessel function and σ is the hard sphere radius. The $d(Q)$ term has an oscillatory behaviour which partially compensates for the sharp Q -oscillations of the $I/S(Q)$ factor, thus smoothing out the overall Q -dependence of z_h . Furthermore, kinetic theory calculations of the second spectral moment of the extended heat (Rayleigh) mode lead to $\langle \omega^2 \rangle = D_T Q^2 / S(Q) = D_T Q_{eff}^2$ (see Ref. [181]).

Finally, no firm prediction exists on the possible direct Q_{eff}^2 dependence of the acoustic damping z_s , therefore data in panel c of Figure 14 appear, in this respect, particularly insightful.

As mentioned, the scenario outlined in Figure 14 is not universal, but rather typical of highly supercritical fluids. Indeed, the Q -dependencies of transport parameters observed in the liquid phase are completely different, as briefly discussed in the next paragraphs.

Figure 14: *The values of the generalised sound velocity (panel a), longitudinal kinematic viscosity (panel b) and thermal diffusivity (panel c) derived inserting in Eqs. 119 the values of α_k , z_s and z_h determined from the best of MD simulated spectra of Ne in Refs. [172] and [179] (dashed lines). The same generalised parameters are also reported as obtained from Eqs. 120 by inserting in it $S(Q)$ values derived from Ref. [65] and transport and thermodynamic coefficients available from the literature (dots). The hydrodynamic, $Q=0$, limiting values of the Q -generalized transport coefficients are reported as horizontal dashed lines for reference.*

5.3 Evidence of umklapp phenomena in a liquid

The analogy between the dynamic response of a liquid and a crystalline sample has been the focus of various IXS works on liquid metals. Among them, it is worth mentioning a work on liquid lithium [182], where a clear evidence of so-called umklapp processes [183] was reported. These are phonon scattering events in which the total momentum of the phonons is not conserved and are believed to be the main responsible for heat transfer in perfect crystals. As the latter systems have no impurities and anharmonicities, they can only sustain a constant heat flow if phonon scattering events transfer a momentum $\hbar\mathbf{G}$ to the whole crystal, with $\mathbf{G}$ being a reciprocal lattice vector. Conversely, in conventional phonon scattering processes the momentum carried by phonons is conserved, therefore these processes cannot cause a thermalization of the “phonon gas”,

since no fraction of the initial phonon momentum is transferred to the lattice.

A schematic representation of a umklapp scattering process is provided by the bottom plot of Figure 15, which shows the sound dispersion in the ideal case of a linear chain of atoms. The diffraction profile, also reported in the plot for reference, consists of infinitely sharp (Bragg) peaks having the form of a $\delta(Q-Q_N)$ functions, with Q_N being the position of the N -order Bragg spots.

In the scheme of the bottom of Figure 15, the umklapp scattering happens along the constant energy cuts at their intersections, identified by black spots, with the dispersion curve.

Therefore, a constant ω cut of the scattering intensity is expected to yield umklapp intensity peaks in correspondence to these points.

Upon assuming that acoustic-like excitations are in a linear, or extended hydrodynamic, dispersion regime, a peak in the $S(Q, \omega = \omega_0)$ scan is expected to occur at a wave-vector $Q_0 = \hbar\omega_0/c_s$. Furthermore, given the mentioned high Q resemblance between the liquid and crystalline solid, one should anticipate observing additional peaks at $Q_k = kG \pm Q_0$ with k being a generic integer number. However, since liquids obviously lack a large-scale order, it is reasonable to expect these peaks to be very broad and possibly visible only in systems having very sharp collective modes, as liquid metals.

Indeed these Umklapp peaks clearly appear in the constant energy (frequency) IXS scans from a lithium sample measured in Ref. [182] and reported in the upper plots of Figure 15. These features evidence a further aspect of the mentioned analogy between the high Q -dynamics of liquids and crystalline solids.

5.4 The role of the structural disorder

As extensively discussed throughout this review, viscoelastic approach generalises the hydrodynamic responses of a fluid to account for solid-like effects in the dynamic response, which gradually emerge at high frequencies. A slightly different point of view was recently proposed in two IXS works on Na [184] and Ga [83]. This approach stems from the notion that the continuous distribution of local structures characteristic of the disordered phase originates a distribution of elastic constants, which ultimately translate into the broadening of the dominating spectral features.

Along this line, the IXS work in Ref. [184] proposes a comparative analysis of the spectrum of sodium in the liquid and polycrystalline phases to single out the disorder-induced contribution to collective modes in the liquid phase.

The presence of a distribution of local, first neighbours, structures in the liquid phase is mirrored by the finite half-width, Δ , of the first sharp peak of $S(Q)$. Intuitively, the width Δ arises from a spread in the edge of the “Brillouin zones” (BZs) of a liquid, which is continuously distributed in the $Q_m \pm \Delta/2$ interval.

Figure 15: The two upper plots show the constant ω cuts of the IXS intensity measured on a sample of liquid lithium at 475 K (squares+line). The corresponding $S(Q)$ is also reported as a solid line as obtained from MD simulations of the sample at the melting ($T = 450$ K) and rescaled by an arbitrary intensity factor. The vertical arrows mark the position of the spectral features associated with the umklapp scattering (see text). All data are redrawn from Ref. [182]. The bottom plot reports a sketch of the sound dispersion and the diffraction pattern of a linear chain (see text).

This continuous distribution of lattice structures causes a spread in the phonon frequencies of a liquid, which ultimately shortens the lifetime of sound waves, or, equivalently, increases their damping z_s .

The link between structural and dynamical properties can be recognised, for instance, by considering that the Einstein frequency, ω_0 (see Eq.88), which provides a measure of the maximum phonon frequency in a solid, depends on the structure through both the pair distribution function and the Laplacian of the potential.

In Ref. [184] the effect of the intrinsic disorder of the sample was quantitatively estimated through the comparative fitting of IXS spectra from a liquid and a polycrystalline sample, with the following line-shape model:

$$S(Q, \omega) = \frac{\Gamma_0}{\omega^2 + \Gamma_0^2} + S_{\text{in}}(Q, \omega) \otimes G(\omega). \quad (122)$$

This model describes the effects of the distribution of local structures on the spectrum of the liquid as the sum of a Lorentzian central peak and the convolution (the “ $\otimes$ ” symbol in Eq. 122) between an inherent, crystal-like, inelastic profile, $S_{in}(Q, \omega)$, and a Gaussian broadening function, $G(\omega)$.

Conversely, the absence of disorder-induced broadening suggested to use, for the polycrystalline sample, a $\delta(\omega)$ -function approximation, for both $G(\omega)$ and the Lorentzian profile in Eq. 122.

The disorder-free scattering contribution, $S_{in}(Q, \omega)$, was described by a model including two DHO profiles (Eq. 93), accounting for the presence of modes with either longitudinal or transverse polarisation.

Interestingly, the results of this modelling indicates that $S_{in}(Q, \omega)$ has the same shape for the crystal and the liquid sample, which suggests that the spectral density of a fluid can be described as a continuous superposition of crystal-like phonon excitations which contribute to the spectrum via a Gaussian weighting function, as assumed in the convolution model of Eq. 122.

An example of the disorder contribution to the dispersion of collective excitations is provided by Figure 16, which reproduces a plot included in the original publication (Ref. [184]).

There the best fit value of the shift, ω_s of the high frequency (longitudinal) mode in the spectrum of liquid Na is reported as a function of the reduced momentum Q/Q_m . Notice a $\pm z_s$ error bar is associated with each point, where z_s is the damping of the inelastic component of the spectrum, $S_{in}(Q, \omega)$. The blue dashed lines defines the boundary of the $\omega_s \pm \Gamma_s$ band, where Γ_s is the total spectral halfwidth defined as $\gamma_s + W_G$, with W_G being the half-width of the Gaussian broadening function, $G(\omega)$ and γ_s is the inelastic halfwidth of $S_{in}(Q, \omega)$.

The graph also includes for reference the two phonon branches of the crystal corresponding to the highest and the lowest frequencies of the longitudinal acoustic phonon (ω^+ and ω^- respectively). The latter are plotted as a function of the reduced variables Q/Q^- and Q/Q^+ respectively, where $Q^\pm = Q_m \pm \Delta$ with Δ being the full width at half maximum of the first diffraction peak. Obviously, such dispersion curves define lower and upper limits of the dispersion compatible with the continuous distribution of structures of the liquid. The shaded area in between these two curves thus represents the “allowed region” for the dispersion curve of the liquid. Notably, this region almost coincides with the $\omega_s \pm \Gamma_s$ band within the overlapping values of the reduced wave-vector. From Figure 16, one is urged to conclude that two main factors determining the linewidth of a propagating collective mode in a liquid are:

- 1) The average short range order, which defines the frequency of the dominant mode of the liquid and its “disorder-free” damping, which is similar to that of the corresponding (poly)crystal.
 - 2) The inherent disorder, i.e. the continuous distribution of local structures revealed by the finite width of the first $S(Q)$ peak. This cause an additional broadening of inelastic modes in the liquid.
- Final consideration concern the comparison of the experimental dispersion curves with the computed value of the infinite frequency sound dispersion, ω_∞ also reported in the plot for comparison. The excellent agreement between ω_∞ and experimental dispersion demonstrates that all viscoelastic effects leading to the transition from the viscous to the elastic regime are already fully accomplished at frequencies (Q_s) lower than those covered by the IXS measurement in Ref. [184], which thus probe the essentially elastic or solid-like response of the sample. This led the authors to conclude that for the considered sample and thermodynamic conditions there’s no need to assume the presence of further high frequency, microscopic relaxations as those extensively

discussed in the remainder of this review.

It clearly appears that the line-shape interpretation discussed above follows a conceptual approach complementary to that of viscoelastic, or Molecular Hydrodynamics, models. In fact it describes the high-frequency spectrum of a liquid by generalising the response of a crystal, and specifically, by introducing in it the structural disorder. Conversely, viscoelastic approaches generalise the hydrodynamic response of a liquid by including in it solid-like, or elastic, aspects.

Figure 16: The sound dispersion curve of liquid Na (dots) is reported along with the highest and lowest energy acoustic branches of the polycrystalline phase (thick solid curves), as determined from phonon measurements along various crystallographic directions. The shaded area in between them yields a measure of the energy region allowed for the dispersion in the liquid compatible with the continuous distribution of structure (see text). The error bars are defined as $\pm \gamma_s$, where γ_s is the width of the inelastic mode of the $S_{in}(Q, \omega)$ profile in Eq. 122. The two dashed lines define the $\omega_k \pm \Gamma_s$ band, with Γ_s being the total spectral width, inclusive of the disorder contribution (see text). The computed value of the infinite frequency sound dispersion of the liquid is finally reported for comparison as a thick dash-dotted line. All curve are redrawn from data reported in Ref. [184].

These two approaches are not mutually exclusive as the “inherent disorder” interpretation described above mainly applies to the response of the liquid in the elastic limit, In this limit, the acoustic damping is dominated by static (Q -dependent) effects, like those stemming from the continuous distribution of structures, rather than the dynamic (ω -dependent) viscoelastic effects

which dominate at longer times and distances.

5.5 Toward the single particle limit

One of the most fundamental topics related to the dynamics of simple liquids, is the gradual transition, upon increasing Q , from the hydrodynamic to the single particle regime.

A variable well-suited to characterise this crossover is the extended sound dispersion, i.e. the curve describing the extended acoustic frequency as a function of Q . In the literature, the latter is often identified with the maxima positions of the longitudinal current spectrum $C_L(Q, \omega)$, i.e. correlation spectrum of the longitudinal components of atomic velocities.

Although this spectrum cannot be measured directly, it can be easily derived from the measurable variable $S(Q, \omega)$ through the simple relation $C_L(Q, \omega) = \omega^2 / Q^2 S(Q, \omega)$. From a physical point of view, the existence of a frequency, Ω , at which the correlation spectrum of atomic velocities reaches a maximum reveals the presence, at that given frequency, of a dominant mode in the collective dynamics of atoms. The actual interpretation of Ω as the dominant acoustic frequency extends to finite Q 's an assignment rigorously valid in the hydrodynamic limit only, where, indeed, $\Omega = \omega_s = c_s Q$.

Of course, the physical meaning of the frequency Ω becomes increasingly elusive as the single particle limit is approached, as the very concept of collective mode loses physical significance at much lower Q values.

The IXS measurement by Scopigno and collaborators in liquid lithium at 475 K [32] investigated the Q -dependence of Ω over an exceptionally wide Q -range unveiling important aspects associated to the crossover from the hydrodynamic to the single particle regime.

The result of such measurement is reported in Figure 17 and therein compared with the $S(Q)$ measured in liquid lithium [185] in a slightly narrower Q -range.

Figure 17: The maxima positions of the current spectra of liquid lithium at $T = 475$ K are reported as derived from IXS measurements in Ref. [69] (squares) and compared with the corresponding $S(Q)$ profile [170] (solid line).

The plot clearly shows that the “coherent” Q -oscillations of Ω and $S(Q)$ are essentially in phase opposition and gradually damp off as the incoherent limit, $S(Q) = 1$ is approached. Again, this Q dependence suggests that very loose Brillouin zone (BZ) can be observed even in a disordered system as a liquid. In this case, the washed-out character of the Q oscillations in both ω_s and $S(Q)$ profiles reflects the lack of long-range order characteristic of the liquid phase.

At this stage, it is worth giving a closer look at the evolution of the inelastic shift from hydrodynamic regime toward the single particle one.

This evolution is represented in Figure 18, where the maxima positions of the current spectra in Ref. [32] are compared with two opposite dispersive trends: 1) the low Q hydrodynamic linear dispersion and 2) the high Q single particle one. The latter is analytically determined by looking at the extremes of the current spectra identified by the equation $\partial/\partial\omega[\omega^2/Q^2 S_{IA}(Q, \omega)] = 0$, where $S_{IA}(Q, \omega)$ is the Gaussian shape characteristic of the single particle limit in Eq. 114. Aside of the trivial $\omega = 0$ solution, the maxima positions of the current are represented by the solid line in Figure 18.

Figure 18: The generalised sound dispersion of liquid lithium at $T = 475$ K reported in Ref. [32] is compared with the single particle and hydrodynamic limiting values (see text), respectively represented by the dashed and solid lines.

It can be clearly noticed that the inelastic shift evolves between the two extreme dispersive behaviours. Indeed, at high Q 's, the dispersion curve approaches from above the parabolic single particle trend in which both the $S(Q, \omega)$ and the longitudinal current have a maximum at the recoil frequency $\omega_r = \hbar Q^2 / 2M$.

Although a unified theory firmly predicting the whole crossover from the hydrodynamic to the single particle regime is not available, some phenomenological aspects associated with the spectral shape evolution in between these limits clearly emerge from the literature. These are clearly represented by Figure 19, which displays IXS spectra measured on lithium in Ref. [32] vertically shifted by an amount roughly proportional to the corresponding Q value.

It can be noticed that, at low Q 's, the Stokes intensity is dominated by a sharp, the extended Brillouin peak, which, upon Q -increase gradually transforms in a barely visible shoulder on the wings of a dominating central peak. Upon further Q -increase, the spectrum covers progressively larger ω -values, which, owing to the detailed balance factor (see Eq. 77), enhances the depletion of the anti-Stokes peak gradually increasing the asymmetry of the spectral intensity,. As a result the spectral intensity becomes increasingly skewed towards the Stokes side, also due to the parallel disappearance of the quasielastic mode. The centroid of the spectrum gradually moves

towards its limiting value $\omega_r = \hbar Q^2 / 2M$, while the spectrum gradually assumes a Gaussian shape. The $S(Q)$ profile is reported on the right plot and the vertical shift of the spectra by an amount roughly $\approx Q$ helps to locate the $S(Q)$ window mapped by each of them.

Figure 19: The left plot illustrates the transition of the spectral shape from the collective to the single particle regime in lithium at $T = 475$ K.. The thick dashed line serves as a guide to the eye roughly indicating the Q -evolution of the shift of the dominant inelastic feature on the Stokes side of the spectrum.. In the right plot the corresponding $S(Q)$ is reported for reference. The IXS spectra and the $S(Q)$ are redrawn from Ref. [32] and the former are here vertically shifted by an amount roughly equal to the corresponding Q value.

A complete representation of the various regimes of the $S(Q, \omega)$ is provided by Figure 20. The plot displays the IXS spectra of liquid neon and lithium measured in different Q windows along with the BLS measurement on Argon by Fleury and Boon. The static structure factor of lithium is also reported in the central plot for reference.

Figure 20: Overview of experimental spectra measured in several Q windows across the transition from the hydrodynamic to the single particle regime in monatomic fluids. Panel A) reports the Brillouin light scattering spectra of liquid Ar [117] Panel B) displays INS measurements on supercritical Ne [147] with the red line roughly indicating the linear dispersion of side peaks. Panel C) shows IXS spectra on liquid Ne [65,179] with corresponding best fitting line-shapes and individual spectral components. Finally, Panel D) displays IXS spectra of liquid Li from Ref. [32] along with the single particle Gaussian shape (solid line) predicted by Eq.114. The central panel reports the simulated $S(Q)$ of lithium.

One can recognise the various regimes of the line-shape discussed thus far. Namely:

- 1) At extremely low Q 's, the spectral shape is dominated by three long-lived, or quasi-conserved, modes: the two Stokes and anti-Stokes sound modes, which account for the propagation of acoustic waves at constant entropy and the heat diffusion mode, due to diffusive slowly relaxing thermal motions. At infinitesimally small Q 's these modes are collective and long-lived as they cover volumes ($\propto Q^{-3}$) containing many molecules and have a lifetime ($\propto Q^{-2}$) much longer than any microscopic timescale.
- 2) At Q values beyond the hydrodynamic limit, the three spectral modes become increasingly damped, gradually transforming into two broad side shoulders which disappear upon

approaching the position of the first $S(Q)$ maximum. At this Q value, the spectrum essentially reduces to a single quasielastic featureless peak.

- 3) At even higher Q 's, the coherent Q -oscillations of $S(Q)$ gradually damp off and the incoherent limit $S(Q)=1$ is approached. Correspondingly, the spectral shape transforms into the single particle Gaussian shape predicted by Eq. 114, as previously discussed in some detail.

5.6 The frequency-dependence of shape parameters: evidence for fast relaxation phenomena

In various works on noble gases reported by the literature it was observed that, in these systems, transport parameters experience important changes even upon relatively modest P or T variations. This primarily owes to the large compressibility of these systems, which enables to easily implement important changes in density, and thus, ultimately, of the interparticle interactions.

In particular, drastic changes are reported across the liquid-to-supercritical transition for both the frequency ω_s and damping z_s of the acoustic mode. Indeed, in the liquid phase, these parameters were found to respectively exceed and fall short of the hydrodynamic $Q=0$ limit, as reported by INS measurements in liquid Ne [65,173], Ar [106,186] and He [159,187,188]. Interestingly, any discrepancy with the hydrodynamic limit seemed to disappear when somehow extreme supercritical regions were reached [66,148,149,172,173,189].

This dependence on the aggregation phase is clearly illustrated in Figure 21, where it can be readily noticed that the shape parameters ω_s and z_s are, at the lowest Q 's, respectively larger and smaller than their hydrodynamic predictions (plots on the left column), both these dispersive effects completely disappear in deeply supercritical conditions (right column).

The trend followed by ω_s appears as a clear manifestation of the positive sound dispersion already introduced in preceding paragraphs as the main signature of a viscoelastic transition. The same viscoelastic effects can be inferred from the Q dependence of z_s . In fact, across a viscoelastic transition, the viscosity expectedly decreases upon increasing the acoustic frequency $c_s Q$, which reflect the gradual freezing of acoustic dissipation when approaching the elastic limit.

Overall, trend outlined in Figure 21 seems consistent with the conclusion that the acoustic propagation in the liquid phase bears evidence of an active relaxation process. The onset of relaxation phenomena in liquid and supercritical neon has been first investigated by IXS at the beginning of this millennium [68], based upon a line-shape modelling with a pure viscoelastic memory function (Eq. 84).

Microscopic vs. structural relaxations

Among various relaxations active in a fluid, structural relaxations are those connected to cooperative rearrangements of the structure following a scattering-induced, or a spontaneous density perturbation. These phenomena encompass dynamical events, which may span a very large timescale domain ranging, for instance, from slow structural arrangements of highly viscous glass formers to relatively fast process of breaking and forming of hydrogen bonds (HBs) in water at ambient temperature or warmer.

Figure 21: Left column: inelastic shift (panel a) and half width (panel c) of the inelastic peak in the spectrum of supercritical Ne at $T = 294$ K and $N = 29$ atoms/nm³ as derived from a best fit analysis with a Generalised Hydrodynamics model (Eq. 83). Open circles and dots represent IXS and MD data, respectively. Right column: the corresponding quantities are reported for liquid neon at $T = 35$ K and $N = 36.65$ atoms/nm³ (from Ref. [173]). In each plot, the solid lines indicate the corresponding simple hydrodynamic predictions. The latter were evaluated inserting in Eqs. 79-81) thermodynamic and transport coefficients derived from Ref. [119] and bulk viscosity data from Ref. [120].

Since these collective rearrangements are hindered by the viscous drag, the dependence of their timescale on thermodynamic conditions roughly parallels the one of viscosity.

Two successive IXS experiments at the end of the past millennium demonstrated the coupling of the THz spectrum of water with a relaxation process having a clear structural nature [72,125]. It is worth mentioning that a similar relaxation phenomenon in water was investigated by earlier BLS measurements in the supercooled phase [122,190] [123] as well as by a pioneering US absorption measurement in increasingly diluted water-glycerol mixtures [191].

The first of the two mentioned IXS works on water [125] was based on a longitudinal moduli analysis leading to the first quantitative determination of the relaxation timescale of water which, at ambient or higher T 's ranges in the ps window probed by IXS. This analysis was based upon the use of a simple DHO (see Eq. 93) modelling of the IXS spectrum of water. Conversely, the second IXS work [72] proposed a more detailed and physically informative description of the

spectral shape based upon an MH model of the memory function (see Eqs. 90 and 91). This enabled a full characterization of all relaxation parameters and relevant mesoscopic transport coefficients. In these two works, a wide T range was explored while adjusting the pressure to keep the density as close as possible to 1 g/cm^3 , as prescribed by the Equation of State [192]. The choice of moving the sample along a constant density path aimed at minimising the effects of free volume variations. The relatively small Q ($2 \div 6 \text{ nm}^{-1}$) and high T ($273 \text{ K} \leq T \leq 473 \text{ K}$) ranges probed in the experiment, authorised to exclude the presence of the additional low-frequency mode, commonly assigned to a shear mode (see ¶ 6.2 of this review); indeed, such a mode becomes visible at slightly larger Q 's and lower T 's only.

Among various results, the analysis performed in Ref. [72] enabled a direct derivation of both longitudinal kinematic viscosity $\nu_L = \eta_L / \rho$ and the compliance relaxation time τ_c .

In Figure 22 the $Q = 0$ extrapolated values of the parameters $\tau = (c_0/c_\infty)^2 \tau_c$ and $\nu_L = \eta_L / \rho$ reported in Ref. [72] are represented in Arrhenius plot.

The sharp temperature dependence and the parallelism of the curves, unmistakably reveal the structural nature of the observed relaxation process. Most importantly, the slope of such an Arrhenius behaviour leads to estimate an activation energy consistent with the known value of the hydrogen bond (HB) energy (see e.g. Ref. [193]), thus supporting the hypothesis that the observed relaxation is connected to structural rearrangement of the HB network.

Figure 22: The T dependence of the $Q = 0$ extrapolations of the generalised longitudinal viscosity (dots) and relaxation times (open circles). Data are from the IXS work discussed in Ref. [72].

While THz relaxation phenomena in water have a pronounced structural character, in liquid neon [65] as well as in other non-associated, weakly viscous fluids [66] they have a prevalently collisional nature. which likely connected with fast in cage collision in the 10^{-13} s range. Owing to their non-cooperative character, these collisional rearrangements are not appreciably slowed down by the viscous drag, and their time-scale is thus only weakly dependent on thermodynamic conditions.

At this stage, it is worth mentioning that significant variable to identify the physical origin of the relaxation process is the longitudinal viscosity. When using the pure viscoelastic (see Eq. 84) or the MH (see Eqs 90 and 91) model for the line-shape, best-fit values of viscoelastic parameters can be used to derive the longitudinal viscosity through $\eta_L = \rho\tau[c_\infty^2 - c_0^2]$.

A comparison between the η_L values so obtained in an inert gas and an associate fluid is proposed in Figure 23.

Figure 23: Longitudinal viscosity values derived from IXS measurements on water [72] and from joint IXS and INS on heavy water [78] are compared with the counterparts obtained for neon (data from Ref. [65]) both in liquid and supercritical conditions.

Specifically, the plot compares the Q -dependence of η_L , as derived from IXS measurements in neon [65] and water [72], as well as from a joint INS and IXS investigation on heavy water [78]. The plotted results show few noteworthy trends:

- 1) Viscosity curves of Ne are only weakly dependent on thermodynamic conditions, even though the macroscopic value of η_L estimated from thermodynamic [119] and bulk viscosity data [120] changes by more than 300% in the explored thermodynamic range.
- 2) Conversely, viscosity data of water in the same plot exhibit a T dependence as sharp as the one of macroscopic viscosity (see e.g. Ref. [194]). Indeed, their $Q = 0$ extrapolations were found consistent with corresponding values derived from literature [72]. The differences between the behaviours of water and neon data are likely connected to the existence of a HB network in the former system [122,123,190,195].
- 3) Highest T data of water seem to approach from above low- Q data of neon, consistently with the expected weakening of the HB network when moving toward supercritical conditions [196].
- 4) At high Q 's, the η_L values of both water and neon may join a common Q plateau characteristic of collisional relaxations, as suggested by extremely high-resolution INS measurements on deuterated water covering a wide Q -range also included in the plotⁱⁱ.

5.7 The adiabatic-to-isothermal crossover

Another interesting topic emerging from the whole body of IXS studies on simple systems is the transition of sound propagation from the adiabatic to the isothermal regime. To understand the physical aspects of this crossover, it is useful noticing that in most fluids acoustic waves propagate adiabatically over the long distances and times characteristic of the hydrodynamic limit.

In fact, at low Q , probed acoustic waves have a period $T_{aw} = \lambda/c_s$ (where $\lambda = 2\pi/Q$ is the exchanged wavelength) which diverges at long wavelengths. However, owing to the usually low thermal diffusivity, such a period is still much shorter than the time needed to achieve local thermalization $\tau_h = 2\pi/(D_T Q^2)$, where D_T is the thermal diffusivity. From the condition $\tau_h \gg T_{aw}$ it follows that virtually no thermal loss affects the density wave during the timespan of an acoustic oscillation. As a consequence, the acoustic wave propagates adiabatically, which means the compression-rarefaction zones associated with the acoustic oscillations have an internal temperature different from the one of the surrounding medium (**adiabatic** regime).

However, due to its Q^{-2} dependence, τ_h becomes rapidly shorter than T_{aw} (which grows only as Q^{-1}), hence at high Q values, the situation can be reversed and thermalization processes may become much faster than acoustic oscillations. Under these conditions, the acoustic wave joins a new propagation regime, in which its compression-rarefaction zones are always in thermal equilibrium with the propagation environment (**isothermal** regime).

Notice that the adiabatic sound propagation in the hydrodynamic limit is ubiquitously observed in non-metallic liquids. Conversely, the anomalously high thermal conductivity of liquid metals makes, thermalization process faster than typical acoustic oscillations; consequently, low-frequency sound propagation in liquid metals is isothermal, rather than adiabatic.

A parameter suitable to characterise the regime of acoustic propagation is the ratio between thermal and acoustic time-scales $R = D_T Q/c_s$. Clearly, the condition $R \approx 1$ marks the centre of the crossover between the adiabatic ($R \ll 1$) and isothermal ($R \gg 1$) regimes. In a scattering

experiment, the onset of the isothermal regime is observed when the momentum exchanged between the probe and the sample is low enough to ensure that the condition $R \gg 1$ holds validity.

This adiabatic-to-isothermal crossover can be directly characterised by looking at the evolution of the sound velocity between its adiabatic value (c_s) and the isothermal one ($c_s/\sqrt{\gamma}$). The relative amplitude of this effect is $(\sqrt{\gamma} - 1)/\sqrt{\gamma}$, thus being weak in systems having $\gamma \approx 1$, as liquid metals, yet sufficiently large in noble gases, for which γ values ≥ 2 are common. However, for noble gases, collective excitations in $S(Q, \omega)$ are usually highly damped and barely resolved, which causes a large uncertainty of sound velocity measurements.

A systematic observation of an adiabatic-to-isothermal (AI) crossover was reported in nitrogen [71] and several simple fluids [198] in both liquid and supercritical conditions. These systems had a high D_T and, most of all, a γ sensibly larger than unity. In particular, it was observed the AI transition gives rise to the expected negative sound dispersion, i.e. to the systematic decreases of the sound velocity from the adiabatic to the isothermal value. To investigate the nature of this negative sound dispersion, it is useful to take as a reference a parameter independent of the specific values of the limiting sound velocities, a particularly appropriate choice being:

$$M_T = [\omega_L^s - \omega_T^2] / [\omega_s^s - \omega_T^2]. \quad (123)$$

Where ω_s and ω_T are the adiabatic and isothermal value of the generalised sound frequencies, respectively given by $\sqrt{\gamma k_B T / MS(Q)}$ and $\sqrt{k_B T / MS(Q)}$ (in Ref. [71] the specific heats ratio was assumed Q -independent).

In Figure 24 the AI transition is reported as it emerges from the analysis of M_T values derived in Ref. [71] from a viscoelastic modelling of the IXS spectra of liquid N_2 . The model used for the memory function was the one defined by Eqs. 90 and 91, in which the transport and thermodynamic coefficients describing the thermal contribution were fixed to the values reported in Ref. [119].

It is important to stress that the decrease of sound frequency (negative sound dispersion) at the AI crossover in principle competes with the viscoelastic Q -increase of sound speed, i.e. the mentioned positive sound dispersion. In Refs. [71] and [197] the measured M_T values were thus corrected for PSD effects based upon the results of the performed viscoelastic modelling. After such correction, the values of M_T defined by Eq. 123 were found to evolve from 1 to 0 as the sound dispersion moved from the adiabatic to the isothermal regime.

Figure 24 shows the dependence of M_T on the parameter R , as determined in IXS measurements on nitrogen in Ref. [71]. One readily notices that $M_T(Q)$ stays in its adiabatic unit value until the value of M_T overcomes its threshold unit value demarcating the boundary between the adiabatic to the isothermal limit. A similar transition has been observed by IXS measurements on several supercritical systems [198].

5.8 Structural and microscopic relaxations in a liquid metal

The coexistence of structural and microscopic relaxations is often a reasonable hypothesis, which can be adequately accounted for by using at least two time-scales, in the time decay of the generalised viscosity (Eq. 91). Unfortunately, the related line-shape modelling would entail the use of many free parameters and could not be reliably performed in most IXS measurements on noble gases mentioned in this review.

Figure 24: The $M_T = [\omega_L^s - \omega_T^2] / [\omega_s^2 - \omega_T^2]$ is reported as a function of the parameter $R = D_T Q / c_s$ (see text) for $T = 171\text{K}$ (open circles) and 190 K (dots). The horizontal dashed line represents the adiabatic regime. Data are redrawn from Ref. [197].

Indeed, for these systems, the presence of highly damped spectral modes would unavoidably cause a strong statistical correlation between best-fit results. Conversely, in liquid metals, the presence of well resolved spectral features up to Q 's $\approx 2/3 Q_m$, allows best-fit routine to be reliably performed even with multiple time-scale models. Being aware of this advantage, an IXS work on liquid lithium [69] proposed a line-shape analysis based on a double timescale decay of the generalised viscosity (Eq. 91) plus a further “thermal” decay of the memory function (Eq. 90). The latter was assumed to have Q -independent coefficients, which were fixed to thermodynamic and transport coefficients derived from the literature.

As it readily appears from Figure 25, the two “viscous” time-scales derived from this line-shape analysis were separated by one order of magnitude across the whole Q -interval spanned. The fast timescale was found to range in the 10^{-13} s window, thus being comparable with the inverse of the

Einstein frequency, and essentially temperature independent. Both features have been previously observed in the dominant timescale of neon (see Figure 23). The authors of Ref. [69] assigned the long time-scale to a structural relaxation process responsible for the mentioned viscous-to-elastic transition, while the short one was connected with fast, vibration-like, microscopic degrees of freedom. They also ascribed the observed positive sound dispersion to the coupling of density fluctuations with the fast vibrational relaxation. In fact, the slowness of structural relaxations - revealed by the larger time-scale in Figure 25 - suggests that viscoelastic effects were likely active over times longer than those strictly probed by the measurement.

Interestingly, no clear temperature dependence can be observed for either of the two time-scales. This trend is somehow expected for the fast relaxation, due to the usually weak dependence of fast microscopic dynamics on thermodynamic conditions. Conversely, the absence of a neat T dependence of the slow time-scale is probably related to resolution limitation as well as, possibly, to the relatively mild viscosity changes happening within the explored T range.

Figure 25: The Q -dependence of the two dominant viscous relaxation timescales (open circles). Data are redrawn with permission from the IXS work on liquid lithium for $T = 475$ K (open circles) and $T = 600$ K (dots) discussed in Ref. [69].

It was mentioned that the line-shape analysis based on multiple timescale models primarily relies on the ability to determine the true spectrum of the sample. This at least requires that resolution limitations do not hamper the measurement, as usually the case of IXS measurements on liquid metals. An example of the well-resolved nature of the IXS intensity from a liquid metal sample is provided in Figure 26, which refers to liquid potassium [199]. It appears that the shape is dominated by relatively sharp features, whose intensity is asymmetrically distributed about the

elastic position ($\omega = 0$), owing to the detailed balance principle.

1) The Brillouin linewidth is dominated by the “microscopic” part of the viscosity, which does not relate to structural rearrangements, typically “frozen” at the high frequencies probed by IXS. Instead, it stems from a dephasing of density fluctuations caused by the non-plane wave character of atomic vibrations, which mirrors the intrinsic disorder of the liquid structure. For the same reason, the authors ascribed the positive sound dispersion to the occurrence of a disorder-related relaxation phenomenon, best observable when the probed wavelength overcomes the typical size of the local, first neighbour, order.

Figure 26: The IXS spectrum of liquid potassium at $Q = 6 \text{ nm}^{-1}$ compared with best-fit model line shapes (thick line) and instrumental resolution function (dashed line). Data are from Ref. [199].

In Ref. [199] a line-shape analysis performed with Molecular Hydrodynamics model (Eqs. 90 and 91) enabled the authors to conclude that, at variance of ordinary fluids, the positive sound dispersion in liquid metals consists in a Q -increase of the isothermal rather than the adiabatic sound velocity. As discussed in the previous paragraph, this owes to the anomalously high thermal conductivity of metallic fluids, which makes low-frequency sound propagation to occur in isothermal conditions.

5.9 Relaxation phenomena at the crossover between liquid and supercritical regions

An IXS study of the complex interplay between microscopic and structural relaxations across liquid and supercritical conditions is reported in Ref. [66]. In this work, IXS measurements were jointly performed in different fluids with increasing structural complexity, as:

- 1) a monatomic system (neon),
- 2) a diatomic one (nitrogen),
- 3) an associate liquid exhibiting a regular thermodynamic behaviour (ammonia),
- 4) an associated liquid exhibiting several thermodynamic, dynamic and structural anomalies (liquid water) .

The IXS spectral shapes were analysed by using an MH model as the one expressed by Eqs. 90-91. In this model, the parameters of the thermal decay of the memory function were fixed to the corresponding macroscopic values extracted from tabulated thermophysical properties. This strategy enabled a direct determination of all parameter relevant for the memory function; among them it is particularly interesting to discuss the case of the compliance relaxation time, τ_c .

To set a meaningful comparison between the τ_c values obtained in samples so different, these values were normalised to the average inter-collision time, τ_{coll} . A rough estimate of this parameter is readily achieved by approximating the sample with a hard sphere model obeying to the Maxwell-Boltzmann statistics, which yields:

$$\tau_{coll} = \sqrt{\frac{M}{16\pi D_{HS}^4 k_B T}}, \quad (124)$$

where D_{HS} is the hard sphere diameter. It is reasonable to expect that if the observed relaxation has a collisional, character, τ_c and τ_{coll} have comparable values and similar thermodynamic evolutions. In Figure 27 the reduced relaxation time $\psi = \tau_c / \tau_{coll}$ reported in Ref. [66] is plotted as a function of the dimensionless variable T_c/T for the various prototypical simple fluids mentioned above.

Figure 27: The ratio ψ between the relaxation τ_c and the microscopic collision τ_{coll} (see Eq. 124) timescales are reported as a function of T_c/T for the different systems indicated in the legend (notice that open stars are from Ref.[201]). The two straight lines through the symbols are guides to eye emphasising the drastic change in the temperature dependence of data. The inset reports the corresponding value of τ_c measured in the same work. All data are redrawn from Ref. [66].

In the inset, the values of the compliance relaxation time τ_c are also reported for reference. From a comparison of the data in the inset and those in the main plot, it appears that the normalisation for τ_{coll} brings all values into a single, system independent, master curve. At supercritical temperatures, this curve is well approximated by a horizontal line, which indicates a proportionality between the relaxation time and the inter-collision time. This behaviour suggests the prevalence of collisional relaxation processes above critical conditions in both non-associated (neon and nitrogen) and hydrogen-bonded (water and ammonia) systems. From this trend one is urged to infer a drastic weakening of the *HB* network beyond the critical point. Conversely, the steep T -dependence of Ψ in subcritical associated systems reveals a clear structural character of relaxation processes as well as its link with the existing *HB* network.

Summarising, Figure 27 demonstrates that structural relaxations are prevalent in associated liquids and that, beyond the critical point these relaxations are replaced by collision-dominated ones. This result seems particularly interesting, and may shed some insight into an issue as controversial as the actual persistence of *HBs* in supercritical phase [196,200].

It is finally worth mentioning that the interpretation of the liquids' dynamics as dominated by

structural and microscopic relaxation processes was questioned, for instance, by the mentioned IXS works on liquid Na [184] and Ga [83]. Indeed, the authors of these works suggest that the excess of intensity in the low-frequency part of the spectral shape, rather than arising from a relaxation process, stems from the onset of transverse modes in the spectrum (see § 6.2). According to this interpretation, the structural relaxation is the only phenomenon leading to the viscoelastic transition, and once the elastic limit is fully reached, there is no further faster relaxation step. A discussion of the onset of a transverse dynamic in the spectrum of simple systems is in the focus of § 6.1.

6. Part III: Less conventional applications of IXS

6.1 Probing the single particle regime

At the extremely high Q 's belonging to the so-called Impulse Approximation regime, the spectrum assumes a Gaussian shape for both classical and quantum systems [30]. In the quantum case, the width of the Gaussian shape is proportional to the quantum value of the single atom kinetic energy, $\langle K.E. \rangle$, rather than being proportional to $3k_B T / 2$, as in the classical case.

Common applications of extremely high Q scattering measurements are the determination of $\langle K.E. \rangle$ (see, e.g., Ref. [202]), which is generally unknown, or the investigation of other spectacular quantum effects on momentum distribution as, for instance, the occurrence of a Bose condensation [203].

For decades, studies of quantum effects in the spectrum of monatomic fluids have been an almost exclusive task of Deep Inelastic Neutron Scattering (DINS), owing to the direct access of this method to extreme Q values [30] where these effects are best observable. An IXS work on liquid neon [31] pioneered the use of a complementary technique such as IXS in this kind of studies. As a result, it was demonstrated that Deep Inelastic X-Ray Scattering (DIXS) enable to measure the spectrum in the single particle limit, offering an investigation method complementary and consistent with the more traditional DINS technique. Furthermore, it was found that the single particle kinetic energy extracted from the spectral shape gave clear evidence for quantum deviations.

An example of the gradual evolution of the IXS spectrum toward the single particle Gaussian shape is illustrated in Figure 28 as measured in Ref. [31]. It is worth noticing that the ω -shift of IXS lineshapes systematically enhances upon Q -increase, asymptotically reaching the value of the recoil frequency, which is indicated by a vertical arrow for the highest Q spectrum.

Figure 28 *The Q -evolution of the IXS spectrum of Ne toward the Gaussian shape centred at the recoil energy characteristic of the single particle regime. The IXS spectra, measured at the Q values indicated in the plot, are taken from Ref. [31]. The vertical arrow indicates the recoil energy computed for the highest Q spectrum.*

Owing to the large energy transfers involved in DIXS measurements, resolution requirements are much less stringent. Furthermore, the virtual absence of kinematic limitations allows in principle to cover the whole transition between the collective and the single particle regimes by using a single IXS spectrometer. This advantage is crucial since it allows to circumvent non-trivial problems of consistency to be faced when comparing results obtained with different instruments.

Given these grounds, one could wonder why DIXS measurements are still so sporadic in the literature. This likely owes to the significant intensity penalties suffered by IXS due to the rapid high Q decay of the form factor. Furthermore, the interest of this kind of studies was often focused to the onset of quantum effects, best observable in systems having light atomic mass, such as ^3He , ^4He , D_2 , H_2 , which are weak IXS scatterers. Finally, the highest Q 's reachable by DIXS are still below typical values covered by DINS measurements by more than an order of magnitude.

These fundamental and practical difficulties explain why DIXS experiments are still sporadic and this technique still in its infancy.

6.1.1 Final state effects

The Impulse Approximation regime can be reached only asymptotically at extremely high Q 's. Before fully joining this limit, the struck atom can no longer be considered a freely recoiling particle, as first neighbour interactions are non-negligible. It is usually safe to assume the latter to influence the final state of the struck particle only, while the initial (before scattering) state can still be considered free. Among various analytical treatments handling these “final state effects” explicitly, the so-called *additive approach* [204], is the one used in the very few extremely high Q *DIXS* measurements available [31,33,34]. This method stems from an expansion of the intermediate scattering function in time cumulants, in which only the first few lower order terms are retained. After Fourier transforming them, one obtains:

$$S(Q, \omega) = S_G(Q, \omega) + S_1(Q, \omega) + S_2(Q, \omega), \quad (125)$$

where: $S_G(Q, \omega)$ is the dominating Gaussian contribution, while $S_1(Q, \omega)$ and $S_2(Q, \omega)$ are the first two correction terms explicitly given, in the incoherent approximation limit, by:

$$S_G(Q, \omega) = \frac{1}{\sqrt{2\pi\mu_2}} \exp\left\{-\frac{\hbar^2 \omega_d^2}{2\mu_2}\right\} \quad (126)$$

$$S_1(Q, \omega) = -\frac{\mu_3}{8\mu_2^2} (\omega - \omega_d) \left(1 - \frac{\omega_d^2}{3\mu_2}\right) S_G(Q, \omega) \quad (127)$$

$$S_2(Q, \omega) = -\frac{\mu_4}{8\mu_2^2} \left(1 - \frac{2\omega_d^2}{\mu_2} + \frac{\omega_d^4}{3\mu_2^2}\right) S_G(Q, \omega) \quad (128)$$

Where the shift $\omega_d = \omega_r / S(Q)$ clearly tends to the recoil frequency in the incoherent ($S(Q) = 1$) limit. The lineshape parameters μ_2 , μ_3 and μ_4 are:

$$\mu_2 = \frac{4}{3\hbar^3} \omega_r \langle K.E. \rangle \quad (129)$$

$$\mu_3 = \frac{2}{3M} \omega_r \langle \nabla^2 V(r) \rangle \quad (130)$$

$$\mu_4 = -\frac{2}{M\hbar} \omega_r \langle F_Q^2 \rangle + 4\hbar^3 \left[\langle p_Q^4 \rangle - 3\langle p_Q^2 \rangle^2 \right] \quad (131)$$

Where p_Q and F_Q are the component along Q of the impulse of the single atom and force acting on it.

As a result of this perturbative treatment, deviations from a perfect Gaussian shape can be linked to the lowest order spectral moments through the above equations. These carries valuable insight on physically relevant variables as, e.g. the average force acting on the atom and the Laplacian of the potential, both providing a direct measure of the weight of quantum effects [31]. In particular it has been shown in Ref. [31] that only the first two lowest order corrections provide a sizable contribution to the spectral shape, the leading effect being an asymmetry of the $S(Q, \omega)$ respect to its centroid. Furthermore the value of the kinetic energy was found to exceed the classically predicted value by more than 20 %, consistently with previous determination in the literature.

6.2 The case of molecular systems

After the work of Monaco and collaborators on liquid neon [31], a successive DIXS work [33] aimed at investigating the next simplest case of a diatomic homonuclear system such as liquid iodine. In this case, the authors reported no signature of quantum effects, due both the larger molecular mass and the higher temperature of the sample.

Even in the absence of quantum deviations, the interpretation of the IXS spectrum of a molecular fluid can be overly complicated, owing to the coupling of the spectroscopic probe with all molecular degrees of freedom [205] as well as their mutual entanglement. Within the simplest assumption that all degrees of freedom are decoupled and belong to very different energy windows, the observed response strongly depends on how the exchanged energy, E compares not only with centres of mass translational energies, E_t , but also with intramolecular rotational and vibrational quanta, $\hbar\Omega_r$ and $\hbar\Omega_v$ respectively. These comparisons lead to defining three complementary *IA* regimes:

- When $E_t \ll E \ll \hbar\Omega_r, \hbar\Omega_v$ the struck molecule is “perceived” by the probe as a recoiling spherical particle. The energy of its translational recoil is $\hbar^2 Q^2 / 2M$, with M being the molecular mass. Here the scattered intensity carries direct insight on the purely translational momentum distribution of the molecular centres of mass.
- In an intermediate window ($E_t, \hbar\Omega_r \ll E \ll \hbar\Omega_v$), usually referred to as the *Sachs–Teller (ST)* regime [206], the molecule behaves as a freely recoiling rigid roto-translator. In this Sachs-Teller regime, the rotational part of the recoil can be written as $\hbar^2 Q^2 / 2M_{ST}$, in which the effective, or Sachs-Teller mass, M_{ST} , is determined by the eigenvalues of the molecular tensors of inertia. In this regime, the spectral density becomes proportional to the distribution of roto-translational momenta of the molecules. The DIXS work discussed in Ref. [31] demonstrated that the Sachs-Teller theory provides a consistent approximation of the spectral shape of a merely classical fluid as iodine at the largest Q values reachable by state of the art IXS spectrometers.
- Eventually, when the $E \gg \hbar\Omega_{r,v}$ condition is valid, the exchanged energy becomes overwhelmingly stronger than any intramolecular and intermolecular interaction. Therefore, the nucleus inside the molecule is freed from its bound state and, for short times, it experiences a free recoil. Under these conditions, the scattering intensity becomes proportional to momentum distribution of the single proton.

In principle, at larger exchanged energy and momentum, higher-level IA regimes occur. Eventually, when energies transferred in the scattering event become much higher than intranuclear interactions, sub-nuclear particles are liberated from nuclear bonds thus experiencing free recoils. The study of these phenomena is the typical domain of High Energy and Nuclear Physics.

6.3 The onset of a transverse dynamics in monatomic systems

The search for non-longitudinal modes in the THz dynamics of liquids has received growing attention in the last two decades, following the observation of an additional peak in the THz spectrum of density fluctuation of water [28,77,78,167,169]. A shear polarisation was assigned to such an acoustic mode based on independent IXS [28] and MD [27] results. Indeed, the ability of MD to selectively compute the correlation function of either longitudinal or transverse components of molecular velocities [27], led to the observation that the same collective modes dominate the spectra of these correlations. Indeed, the coupling of modes having longitudinal and transverse polarisation customarily referred to as L-T mixing [27,28,92] explains the emergence of a transverse mode in the $S(Q, \omega)$, which primarily couples with longitudinal movements only.

This effect becomes active only above a Q -threshold which, for instance, in water was found to be either 4 or $\approx 6 \text{ nm}^{-1}$, per Refs. [169] and [78] respectively. An L-T coupling was initially reported for several other tetrahedral systems, as amorphous GeO_2 [207] and GeSe_2 [208] which suggested that the L-T coupling is somehow connected to the tetrahedral geometry of the molecular arrangement.

However, this interpretation conflicts with the discovery of a similar L-T coupling in more tightly packed and non-associated systems, as Ga [82,83,86]. Indeed, liquid gallium seems a rather anomalous liquid metal since metallic and covalent bonds coexist in it [209] originating very short-lived Ga-Ga bonds, relics of the interatomic interactions in the crystalline form α -Ga. In this perspective, it is not surprising that several IXS measurements on liquids observed a merely a solid-like feature such as the ability to support a transverse mode propagation.

Specifically, the assignment of a transverse origin to the low-frequency mode in the spectrum of gallium stems from a comparison with measurements in the crystal [83] or with *ab initio* MD calculations [82,86]. In fact, this mode closely resembles the TA mode of the β -Ga crystalline phase, yet it has a larger damping dominated by both elastic anisotropy and structural disorder [83]. In Ref. [82] it was also hypothesised that the ability of liquid Ga in supporting a transverse mode is promoted by solid-like cage effect on the nanometer scale acting as a restoring force for the shear density waves.

This conclusion seems consistent with the anomalously high value estimated for the Poisson ratio of this element (0.42), which is comparable to that of rubber-like materials. Furthermore, an IXS work on sodium showed the presence in the spectrum of both longitudinal and transverse acoustic excitations at frequencies similar to the corresponding ones in the crystal phase [184]. The authors suggested that, at temperatures low enough, the continuous distribution of structure typical of the liquid phase – and responsible for the finite width of the first diffraction peak- can become so sharp to make the shear fluctuation underdamped ($R_t < 1$), thus enabling the propagation of transverse modes.

A study of transverse mode in Sn [85] suggested that inelastic excitation in this metal are strongly localised being their propagation length smaller than the Ioffe-Riegel distance (see, e.g., Ref. [210]). It is finally worth mentioning a very recent work in liquid Zn [211], in which a low-frequency spectral feature was observed and interpreted as a transverse mode. Its appearance was associated with the peculiar anisotropic interactions of this system. One of the main difficulties faced while investigating the onset of shear modes in the spectrum of a liquid sample is the limited ability of IXS and INS spectrometers to properly resolve the corresponding spectral features. One of the clearest examples of the emergence of a transverse peak on the low-frequency side of the spectrum can be found in

Figure 29. There, the IXS spectrum measured at $Q = 10 \text{ nm}^{-1}$ in Ga at 100°C [86] is reported along with the best fitting model line-shape including two DHO profiles and an additional quasi-elastic Lorentzian term.

Figure 29: The IXS spectrum of liquid Ga measured in Ref. [86] (open circles). The raw

measurement (open circles) is reported against the best fitting line-shape (solid line) obtained with a model composed of two DHO profiles accounting for inelastic collective modes plus a Lorentzian term accounting for the quasi-elastic central peak.

The shear mode contribution to the spectrum is particularly clear and has the form of two low-frequency side shoulders. Liquid metals are in principle ideal monatomic samples to observe the possible onset of shear modes, owing to the weaker central peak, which mitigates the problem of the large and slowly decaying resolution wings, often obscuring all low-frequency spectral features.

In most cases, even the best resolution attainable by state of the art IXS spectrometers is still barely adequate for the scope these studies. As discussed at the end of this review, a new-concept extremely high-resolution and high-contrast spectrometer will expectedly prompt substantial advances in the field. This measurement (open circles) is reported against the best fitting line-shape (solid line) obtained with a model composed of two DHO (Eq. 93) profiles accounting for inelastic collective modes plus a Lorentzian term describing the quasi-elastic central peak. The spectral contribution of the transverse mode is also indicated.

6.4 Seeking for thermodynamic boundaries

Experimental results discussed in previous paragraphs seem to suggest that the viscoelastic behaviour of the sound velocity, i.e. the discussed positive sound dispersion (PSD) is a universal dynamic signature of the liquid phase. In fact, the PSD has been observed in fluid systems as disparate as, for instance, hard sphere [212] and Lennard-Jones [213] model systems, noble gases [173] [65] and in diatomic [66,189], associated [72,125]) and glass forming [55,74,76] systems. Its disappearance at deeply supercritical conditions was [65] initially considered as an indication that supercritical fluids do not exhibit a high-frequency viscoelasticity.

A validity check for this conjecture would require a thorough investigation of the THz spectral shape of supercritical fluids at extreme P and T values. For many decades, this has been an almost prohibitive task, owing to various technical difficulties in reaching extreme thermodynamic condition, due to relatively large samples of typical THz inelastic measurements. Fortunately, the small transverse size of X-Ray beams makes possible IXS experiments on smaller samples thus paving the way to previously inaccessible thermodynamic conditions. Furthermore, the improved performance of undulators and crystal optics have dramatically enhanced the typical IXS count rates.

These advances paved the way toward a whole new class of IXS investigations on samples at extreme pressures, based upon the use of diamond anvil cells (DACs) [214].

Taking advantage of this opportunity, an IXS DACs measurement on deeply supercritical oxygen [189] demonstrated that a PSD of about 20% in amplitude is visible at temperatures nearly doubling T_c and for pressure exceeding P_c by more than two order of magnitude. The sound velocities extracted from the inelastic shift in the spectra measured in deeply supercritical Oxygen are reported in Figure 30 and therein compared with the value of the adiabatic sound velocity expected in the hydrodynamic limit.

Figure 30: *The Q -dependence of the generalised sound speed of supercritical oxygen at $T = 300\text{ K}$ at the three measured pressures (as indicated in the plot) each curve is compared with a horizontal line (see legend) corresponding to the adiabatic sound velocity expectedly joined at $Q = 0$. Data are taken from Ref. [189].*

The comparison evidence that the measured sound velocities exceed by nearly 20 % their respective hydrodynamic values for $Q \leq 10\text{ nm}^{-1}$ clearly demonstrating that a PSD survives even at the considered deeply supercritical conditions. ($T/T_c = 2$, $P/P_c > 100$). This result is especially relevant as it indicates that the disappearance of PSD effects in the supercritical region was an oversimplified conjecture, misled by the restricted thermodynamic regions back then accessible by IXS and INS experiments.

However, the result had also more general implications, as it suggests that the supercritical plane could present different dynamic domains:

1) liquid-like regions characterised by the onset of a high-frequency viscoelastic behaviour, as fingerprinted by a sizable PSD and 2) dense gas-like region where no viscoelastic effect is instead visible.

Another breakthrough result in this field is reported in a successive joint IXS and MD work on Ar [215] at extreme pressures, which showed the occurrence of a dynamic transition upon crossing a boundary in the supercritical domain. A dramatic reduction in the amplitude of PSD was, in fact, observed upon crossing the Widom line [216] and was interpreted as a crossover between a ‘liquid-like’ and a ‘gas like’ sub-regions of the supercritical phase. It is worth recalling here that Widom line is defined as the locus of specific heat maxima, which emanates from the critical point toward the supercritical domain with the same slope as the coexistence line, thus being often considered as its extension beyond the critical point.

The mere existence of a boundary in the thermodynamic plane challenges the long-standing vision of the supercritical phase as intrinsically uniform [217], thus disclosing unexplored scenarios and investigation opportunities.

Another significant result is the more recent observation that PSD effects are intimately related to the onset of a shear mode propagation.

Historically the first evidence of a shear mode propagation in a simple fluid dates back to two MD simulations carried out in the early 1970s on a Lennard-Jones, $L-J$, model representative of Ar in regular liquid phase and at the triple point [138,139]. It was observed that at sufficiently short wavelengths, the transverse current spectra of $L-J$ systems are dominated by a distinct inelastic feature, assigned to the propagation of shear waves. This feature was only visible in the transverse current spectrum, while no signature of it on the $S(Q, \omega)$ has even been reported

A more recent joint IXS and MD simulation work on deeply supercritical argon [218] proved the existence of a close link between a shear mode propagation and the presence of a sizeable PSD. In this study, IXS spectra were measured along an isobaric path (with $P = 1$ GPa) with T spanning the 300 K-436 K temperature range, while MD data spanned the same isobar within a larger T -interval (up to 800 K).

In this work, it was shown that the disappearance of the PSD in deeply supercritical conditions is accompanied by a parallel shear modes overdamping as indicated by the vanishing inelastic shift of the transverse mode (see Figure 31).

This trend confirms that the dynamic response of supercritical fluids is characterised by different regimes observable in distinct supercritical subdomains: a gas-like region and a liquid-like one. In the former regime, viscoelastic effects are absent, and the fluid cannot support transverse wave propagation. These merely elastic properties become instead visible upon crossing some thermodynamic boundary thereby accessing the liquid-like domain of the supercritical region.

Furthermore, in a joint IXS and MD work on deeply supercritical argon [219] the Frenkel line was identified as the crossover line between the two thermodynamic regions. The interpretation of the Frenkel line as a crossover line demarcating the presence/absence of transverse acoustic propagation was originally discussed in Ref. [220]. It was also previously predicted that the occurrence, across the Frenkel line, of both dynamic and structural crossovers accompanied by changes in phonon states [221-224].

Figure 31: The dispersion curves of deeply supercritical Ar at $P = 1$ GPa and at the T values indicated in the plots, are reported as evaluated from the maxima positions of MD simulated longitudinal (solid lines) and transverse (dots) current spectra. The corresponding hydrodynamic dispersions are also reported as dashed lines for comparison. Data in the figure are adapted from Ref. [218].

6.5 Polyamorphism phenomena in simple systems

Although pressure- or temperature-induced modifications of crystal structures and related effects on the lattice dynamics are well understood, transformations between distinct liquid or glassy phases with different local structures and densities are instead still elusive. This, of course, partially owes to the blurry concept of first neighbour order when applied non-crystalline systems, and, perhaps more importantly, to the difficult observation of these, so-called, poly(a)morphic (PA) transitions. In fact, several joint factors often hamper the study of these phenomena, as for instance, their occurrence in metastable thermodynamic conditions, where they are hidden by competing effects, as glass transition or crystal nucleation. Furthermore, when the density is the order parameter, extreme thermodynamic conditions are required to significantly alter this variable, due to the low compressibility of amorphous, non-gaseous, systems.

Nonetheless, the relevance and interest of PA liquid-liquid (or glass-glass) transitions has nowadays been fully acknowledged and their study represents an emerging area of science, whose industrial and basic science applications are still unexplored.

The idea that first order *liquid-liquid* transitions may occur in nature in single component substances originates from the interpretation of the anomalous thermodynamic behaviour of some materials, such as the pressure dependence of their melting curves [228], as also suggested by computer simulations [229,230].

From the experimental side, the occurrence of a *liquid-liquid* phase transition driven by density and entropy rather than chemical composition, dates back to the first observation of a PA phenomenon in water [228] and of a similar transition in supercooled $Y_2O_3-Al_2O_3$ [231]. In water, a neutron diffraction study [232] demonstrated the occurrence of a continuous transition between a low-density aggregate (low-density water, LDW) and a high density one (high-density water, HDW). Such finding seems even more intriguing if one considers that a polymorphic transition takes place in the solid phase (between hexagonal Ice and Ice III) at nearly the same pressure. It can be anticipated that, upon approaching a liquid-liquid critical point, enhanced fluctuations between LDW and HDW structures would take place. Although far from critical conditions, this enhancement of density fluctuations is consistent with the observed small-Q growth of the $S(Q)$ of water [233] as well as of a large variety of polymers [234].

On a more general ground, the presence of a *liquid-liquid* coexistence line seems a rather common feature of many supercooled liquids, and there are also fundamental reasons to infer a possible universal behaviour [235, 236]. In fact these transitions are likely to occur in liquids having an intrinsically open molecular coordination environment, which fits the case of water [228], liquid silicon [237], germanium [238], and phosphorus [239,240], as well as amorphous SiO_2 [241] and GeO_2 [242] (see also Ref. [243] and references therein). The reason why PA transitions are more likely in open and often tetrahedrally-coordinated structures, is that a large free volume can accommodate substantial structural modifications even upon moderate thermodynamic changes.

In spite of a thorough experimental scrutiny, some general aspects of PA transitions are still obscure. This certainly includes dynamic effects, i.e. their possible influence on the propagation of collective modes in the $S(Q,\omega)$. These effects are supposedly more relevant at mesoscopic ($\approx$ nm) length-scales, where dynamic events become strongly coupled with local atomic arrangements. Evidence of PA transition was found in the IXS spectrum of liquid sulphur [244] and vitreous GeO_2 [245]. In both these works signatures of a PA crossover were observed by looking at the temperature and the pressure dependence of the sound velocity, respectively. These results are reported in Figure 32, where the presence of a slope discontinuity, or cusp-like behaviour can be noticed in the T and the P dependence of sound velocity (left and right plots, respectively). This trend is emphasised by the straight lines best fitting the data points before and after slope discontinuity it.

Figure 32: The sound velocity derived of sulphur ([244], left plot) and vitreous GeO₂ ([245] right plot), and reported as a function of T and P , respectively. The straight lines through the data are linear fits emphasising the slope change across a polyamorphic transition (at the pressure indicated by the vertical line).

In a joint *Ab Initio* Molecular Dynamics (AIMD) and IXS study in liquid Rb at 573 K [114] a similar trend of the sound velocity was also reported and ascribed to the occurrence of a liquid-liquid transition. The AIMD data were analyzed using GCM based models, which, among various results, led the authors to observe discontinuities in the slope of the pressure dependence of both the high-frequency sound velocity and the single atom diffusion, D . Notice that the flattening of the P dependence of D reveals the breakdown of the nearly-free electron behaviour a reduction in the core radius of Rb atoms as deduced from the relationship linking the particle size and diffusivity. Overall these findings provided a compelling evidence of a liquid-liquid phase transition in liquid Rb, thus extending the observation of PA phenomena to simplest systems as alkali metals.

Figure 33: The sound velocity (open symbols) in liquid Rb at 573 K is reported as a function of pressure as either measured by IXS (open squares) or simulated by *ab initio* MD, AIMD (full squares) in Ref. [114], the curves are compared with the pressure dependence of diffusion coefficient D (open circles) computed by AIMD methods [114]. Finally the star represents the zero pressure result obtained by INS [246]. The shaded area roughly indicates the crossover region (see text). All curves are redrawn from Ref. [114].

6.6 Gaining insight from spectral moments: the onset of quantum effects

The various theoretical descriptions of the dynamic structure factor discussed so far are mostly classical in character, being all based on the assumption that all involved operators are commuting and the correlation functions are even functions of time or, equivalently, that the spectral shape is symmetric in ω .

In this respect, it's worth distinguishing between two possible quantum effects on $S(Q, \omega)$:

- i) “diffraction” or “delocalization” effects, which arise from the non-commutative nature of Hamiltonian operators; and
- ii) exchange effects, reflecting the symmetry restrictions to be fulfilled by a many-body system of identical particles.

Both effects depend on the de Broglie wavelength $\lambda = \hbar(2\pi/mk_B T)^{1/2}$, however:

- Diffraction effects only emerge when λ matches the length-scales over which the interparticle potential varies appreciably.
- Exchange effects come into play when λ is comparable with first neighbours' separations and are observable only for small mass atoms or molecules, for which such a distance can be relatively small. The onset of these effects can only be observed at very low temperatures, and it often manifests itself through few “spectacular” quantum-mechanical effects, such as Bose condensation and superfluidity.

In general, the classical description of density fluctuation becomes inaccurate whenever the measurement matches the coherence window of quantum effects, which happens under two conditions:

- 1) The interatomic separation and cage oscillation period are respectively comparable with de Broglie wavelength, $\lambda_B = \hbar\sqrt{(2\pi/Mk_B T)}$ and timescale, $T_B = \lambda_B/c$. This implies that the sample itself exhibit a sizable quantum behaviour,
- 2) The probed distance, $2\pi Q^{-1}$, and timescale, $2\pi\omega^{-1}$ must, in turn, respectively match λ_B and T_B . Which means that the probe is properly tuned to observe the quantum behaviour of the sample.

For quantum fluids at few tenths of K , these conditions are usually fulfilled in Q, ω window exceeding by some decades the range covered by Brillouin visible Light Scattering and strongly overlapping with the dynamic domain of IXS and INS.

6.6.1 Analytically handling quantum effects

Based on the argument above, it is natural to anticipate that these quantum are revealed by the coefficient determining the short-time expansion of the Intermediate scattering function:

$$F(Q, t) = S(0) - i\langle\omega^1\rangle t + \langle\omega^2\rangle \frac{t^2}{2} - \langle\omega^3\rangle \frac{t^3}{3} + \dots \quad (132)$$

i.e. the n -order spectral moments. $\langle\omega^n\rangle = 1/i^n \left(\partial^n / \partial t^n \right) F(q, t) \Big|_{t=0}$. The time-dependence of density fluctuation results from the solution of the Heisenberg equation of motion:

$$\delta\dot{\rho}(Q, t) = i[\delta\rho(Q, t), H] = \frac{i}{\hbar} \sum_j \left[\exp[i\mathbf{Q} \cdot \mathbf{r}_j(t)], H \right] \quad (133)$$

where the *Hamiltonian*, H , for an N -particle system reads as:

$$H = \sum_i \frac{-\nabla_i^2}{2M} + \sum_{i \neq j} V(r_{ij}) \quad (134)$$

Therefore the n-order spectral moment can be calculated through:

$$\langle \omega^n \rangle = i^{-n} \frac{\partial^n}{\partial t^n} F(q, t) \Big|_{t=0} = \left(\frac{-I}{\hbar} \right)^n \langle \exp[-i\mathbf{Q} \cdot \mathbf{r}_k(0)] \dots \dots \dots [\exp[i\mathbf{Q} \cdot \mathbf{r}_k(0)], H] H \dots \dots \dots H \rangle \Big|_{t=0}.$$

Thus, for instance the first moment reads:

$$\langle \omega^I \rangle = \frac{I}{N} \sum_{j,k} \langle [\exp[i\mathbf{Q} \cdot \mathbf{r}_j(0)], H] \exp[-i\mathbf{Q} \cdot \mathbf{r}_k(t)] \rangle_{t=0} \quad (135)$$

The commutator reads as:

$$[\exp[i\mathbf{Q} \cdot \mathbf{r}_j(0)], H] = \exp[i\mathbf{Q} \cdot \mathbf{r}_j(0)] (\omega_r + v_{q,j}),$$

where $v_{Q,j} = i\hbar\mathbf{Q} \cdot \nabla_j / M$ is the velocity of the j-th atom projected along the direction of $\mathbf{Q}$ and it was introduced the recoil frequency $\omega_r = \hbar\mathbf{Q}^2 / 2M$. Hence, the first moment can be written as:

$$\langle \omega^I \rangle = \frac{I}{N} \sum_{j,k} \langle \exp[i\mathbf{Q} \cdot \mathbf{r}_{jk}(0)] (\omega_r + v_{q,j}) \rangle \quad (136)$$

At this stage it is convenient to split the first moment in self and distinct parts. The self part (j=k) is simply:

$$\langle \omega^I \rangle_s = \frac{\hbar\mathbf{Q}^2}{2M} + \sum_i \langle v_{Q,i} \rangle = \frac{\hbar\mathbf{Q}^2}{2M} \quad (137)$$

Where it was used the fact that $v_{Q,j}$ vanishes under thermal average, since the Hamiltonian is invariant under time reversal while it changes sign.

$$\langle \omega^I \rangle_d = \sum_{j,k} \langle \exp[i\mathbf{Q} \cdot \mathbf{r}_{jk}(0)] (\omega_r + v_{q,j}) \rangle \quad (138)$$

For a real operator one has that $\langle A \rangle = \frac{I}{2} \langle A + A^+ \rangle$, Therefore taking into account the commuting relation, one can rearrange the above equation as

$$\langle \omega^I \rangle_d = \sum_{j,k} \langle \{v_{q,j}, 2 \cos[\mathbf{Q} \cdot \mathbf{r}_{jk}(0)]\} \rangle = 0 \quad (139)$$

Where the symbol $\{A, B\} = AB + BA$ represents the anti-commutator of A and B Furthermore it was used the fact that the anti-commutator is $= 0$ since $v_{Q,j}$ change under time reversal, whereas $\cos[\mathbf{Q} \cdot \mathbf{r}_{jk}(0)]$ does not. Overall one has the exact relation:

$$\langle \omega^I \rangle = \omega_r \quad (140)$$

Similarly, an analytical expression can be derived for the second spectral moment, which eventually reads as:

$$\langle \omega^2 \rangle = \omega_r^2 [2 - S(Q)] + \omega_r \frac{Q^2}{2M} \left[\frac{4}{3} \langle K.E. \rangle + \frac{\hbar^2}{NM} \sum_{i \neq j} \nabla_i \nabla_j \cos(\mathbf{Q} \cdot [\mathbf{r}_i - \mathbf{r}_j]) \right] \quad (141)$$

where:

$$\langle K.E. \rangle = 3 \frac{I}{N} \sum_k \left\langle \frac{-(\mathbf{Q} \cdot \nabla_k)^2}{2M} \right\rangle = 3 \frac{Q^2}{N} \sum_k \left\langle \frac{p_q^2}{2M} \right\rangle \quad (142)$$

is the single particle mean kinetic energy. Notice that the classical limit one has simply $\langle \omega^2 \rangle = \langle \omega^2 \rangle_c = (k_B T / M) Q^2$. Furthermore, for an additive and pairwise interaction potential a $\hbar$ -expansion consistent to the $\hbar^2$ order yields:

$$\langle \omega^2 \rangle \approx \omega_r^2 + \omega_r \left[2k_B T + \frac{\hbar^2}{6k_B T} (\Omega_0^2 - \Omega_Q^2) \right] \quad (143)$$

which contains the Einstein frequency and its finite Q generalisation defined by Eqs. 88 and 89 respectively.

Using the same technique, one can evaluate the third spectral moment, which for additive pair potential reads as:

$$\langle \omega^3 \rangle = \omega_r^3 + 4\omega_r^2 \langle K.E. \rangle + (\Omega_0^2 - \Omega_Q^2) \quad (144)$$

Systematic INS studies of quantum deviations in the lowest order spectral mode in liquid Ne and Ar are discussed, for instance, in Refs. [155] and [186]. Results for argon are reported in Figure 34 which displays the first spectral moment normalised by the recoil frequency (lower panel) and the second spectral moment divided by its classical value. The plot includes for comparison a calculation obtained using the $\hbar^2$ -truncated expansion in Eq. 143, in which the Einstein frequency (Eq. 88) and its finite Q generalisation (Eq. 89) were computed using a Lennard-Jones potential. It can be readily shown that the normalised first spectral moment is, apart from the lowest Q values, very close to 1, which demonstrates that the exact expression of in Eq. 140 agrees nicely with experimental results. Furthermore, it can be noticed that the presence of relatively weak ($< 7\%$) quantum deviation is roughly predicted by the theoretical prediction (dashed line).

Figure 34: *Upper panel: the normalised second spectral moment of the INS spectra of liquid Ar at $T = 120$ K and $P = 11.5$ Mbar are reported as a function of Q . Data are normalised to their classical value (squares) and compared with the theoretical prediction of Eq. 143, as computed with a Lennard-Jones interaction potential. Lower panel: the corresponding first spectral moment normalised to its exact value ω_r is reported (squares). In both panels the horizontal solid line represents the unit value for reference. Data in the upper and lower panels are redrawn from Ref .*

[155] and [186], respectively.

6.1.2 IXS studies of quantum effects in simple liquids

Using a procedure similar to the one described above, the value of spectral moment can in principle be computed also from direct integration of the measured IXS intensity. However, such a computation is not easily performed on a rigorous basis, due to all spurious scattering and geometrical effects hampering the measurement, as well as the non-trivial contribution from the instrumental resolution. One can easily get rid of all artificial intensity effects —whenever ω -independent—by dealing with spectral moments' ratios.

Conversely, a correction for the resolution contribution would require a numerical deconvolution of the measured line-shape, which is in general ill-determined, unless the spectral shape has the form of a single featureless peak. In the IXS works mentioned above, spectral moments were instead computed from direct integration of best-fit (non-convoluted) model line-ensuring shape, multiplied by the detailed balance factor. The latter factor ensures that the considered lineshape has non-vanishing odd spectral models.

Three IXS works were performed following this strategy at the beginning of the new millennium, with the aim of investigating the onset of quantum effects on the spectrum of supercritical He [67] and liquid Ne [31,34]. While in the first work, quantum effects have been studied at moderate Q 's as a function of temperature and density; in the two IXS works on Ne, the impressively broad Q range covered enabled the coverage of the whole Q -transition from the classical (continuous) to the quantum (single particle) regimes. A key variable investigated in these works is directly linked to the second and first spectral moments through:

$$R_2 = \frac{\langle \omega^2 \rangle}{\langle \omega^1 \rangle} - \omega_r \quad (145)$$

By neglecting exchange effects and treating the atoms as distinguishable Boltzmann particles, eventually one obtains:

$$\lim_{Q \rightarrow \infty} R_2 = \frac{4}{3} \langle K.E. \rangle$$

$$\lim_{Q \rightarrow 0} R_2 = \frac{4}{3} \langle K.E. \rangle_C = 2k_B T$$

where it was used the classical expression of the mean single particle kinetic energy

$$\langle K.E. \rangle_C = \frac{3}{2} K_B T.$$

As a consequence of the above formulas one should be able, by changing Q , to follow the whole transition from the classic ($Q = 0$) to the quantum regime. Furthermore, from the measurement of the second spectral moment one should be able to achieve a straightforward measurement of

$\langle K.E. \rangle$. A measure of quantum deviation as a function of the temperature is provided by Figure 35 in which the values of R is reported after normalisation to its classical value as determined in Ref. [67]. It clearly appears from the plot that, as expected, the classical value is reached both at macroscopic distances and at high temperatures.

Figure 35: The spectral moment ratio of Eq. 145 of liquid He as a function of Q at the indicated thermodynamic condition. The unit classical value is reported as a dashed horizontal line. Data are redrawn from IXS measurements in Ref. [67].

Two joint IXS measurements and quantum Path Integral Monte Carlo (PIMC) simulations [247,248] studied these delocalization effects on the two isotopic molecular fluid H_2 and D_2 . The two sample were kept in corresponding states, i.e. thermodynamic states having the same values of the reduced variable T/T_c and n/n_c . The reason for this choice was the prediction that classical fluid in corresponding states [249,250] exhibit the same microscopic properties, any possible discrepancy being a possible indicator of sizable quantum effects. In this case, quantum deviations, if observable, were expectedly larger in H_2 than D_2 , owing to the lighter molecular mass.

The comparison between the dynamic and structural properties of the H_2 and D_2 samples emerging from Ref. [249] is summarised in Figure 36. The IXS spectrum of the two sample is compared in the left panel.

Figure 36: Panel a) IXS spectra from liquid H_2 at $T = 20$ K, $n = 21.24 \text{ nm}^{-3}$ (dots) and from liquid D_2 at $T=23$ K, $N = 24.61 \text{ nm}^{-3}$ / Panel b) static structure factors, $S(Q)$, obtained. From the spectral moments of the IXS best-fit line-shapes from H_2 (dots) and D_2 (open circles), compared with quantum PIMC simulations for H_2 (solid line) and D_2 (dashed line). Data are taken from Ref. [249].

The corresponding $S(Q)$ profiles evaluated either from the 0-th moments of IXS spectra or by quantum PIMC simulation is instead compared in the right panel. Aside from an overall good agreement between simulated and experimental $S(Q)$ profiles, the two plots highlight few noteworthy trends:

- 1) The spectrum of liquid hydrogen exhibits a more pronounced and well defined inelastic shoulder on the Stokes side. This shoulder reveals the presence of a relatively long living collective excitation, which in an earlier INS work was ascribed to the onset of a collective cage vibration of atoms due to a quantum delocalization effect [251].
- 2) Differences emerge from the comparison of the diffraction profiles of the two samples. Among them, it can be noticed a slight low- Q shift of the first diffraction peak of H_2 . This effect is a consequence of the higher quantum delocalization of H_2 molecules, which, as mentioned enables the molecular centroid to enter more deeply into the repulsive region of the interaction potential. The deeper penetration in a repulsive environment increases the average first neighbouring molecules' separation, thus shifting the first $S(Q)$ maximum to lower Q 's.

One of the controversial aspects of the discussed analysis of quantum effect is that the symmetric, part of the spectrum is estimated by using a viscoelastic model for the lineshape. This is a model entirely classic in nature as it stems from the assumption that all relevant operators are commuting quantities. In this respect, it is worth noticing that a quantum viscoelastic model can be used to incorporate quantum effects [225]. The presence of these effects is still compatible

with the choice of a single exponential *ansatz* for the memory function. Quantum deviations mainly manifest themselves as a global softening of the interaction potential.

From a physical point of view, this softening is brought about by the delocalized nature of the particle, whose centroid can thus experience larger overlaps with the region where the interatomic potential is repulsive.

It appears that IXS studies of quantum effects in the dynamic behaviour are nowadays in an impasse. In fact, a more rigorous calculation of these effects would require a direct determination of integrated intensity from raw data rather than model line-shape. This task can only be reliably accomplished through an absolute intensity measurement of $S(Q, \omega)$ or, as an alternative, by minimising the resolution contribution to the spectral moments of the experimental spectrum. This would require a resolution shape sharper and narrower than that of state-of-the-art IXS spectrometers.

7. Looking ahead: the contribution of next generation IXS instruments

As perhaps clear from what discussed thus far, the coverage of the whole evolution of the spectral shape between the hydrodynamic and the single particle regimes would require the bridging of the dynamic gap separating IXS and INS from lowest Q 's spectroscopic methods, as Brillouin Light Scattering. On the one hand, the access of INS to this Q, ω gap is severely challenged by inherent kinematic limitation while, on the other hand IXS measurements in the gap window are held back by the still limited energy and momentum resolution.

In most modern IXS spectrometers energy scans are implemented through the variation of the temperature difference between analyser and monochromator crystals [165]. This scheme has three main drawbacks:

- 1) It requires extremely accurate and somehow challenging temperature control (better than 10^{-4} K).
- 2) It can only be implemented at high incident energy, by using less intense, harmonics from the undulator sources; and, most importantly:
- 3) The corresponding resolution function has broad and slowly decaying, nearly Lorentzian, wings.

New optical schemes based on multiple bounce reflections from asymmetrically cut crystals provide a wealth of advantages over state of the art high-resolution IXS spectrometers. Namely:

- 1) They do not need the access to extremely high Bragg reflection orders, which would impose serious penalties to overall efficiency.
- 2) The multiple bounces dramatically increase the spectral contrast, i.e. the sharpness of the resolution function.
- 3) These assemblies are ideally operated at moderate energies at which many current synchrotron undulators perform best.
- 4) They offer a higher flexibility, including the opportunity of selecting nearly any energy and the capability of tailoring the resolution to specific experimental needs.

The working principle of one of such schemes has been demonstrated in recent works [252, 253] which also shows, as an example, a sub-meV measurement of the IXS spectrum of glycerol. Above

all, a novel beamline with a very narrow (sub-meV) and sharp (essentially Gaussian) resolution function [29] will be soon operative at the new synchrotron source NSLS II at Upton, NY. A schematic rendering of the spectrometer layout is proposed in Figure 37. The development of this new spectroscopic tool and its availability for the scientific community will enable a whole new class of IXS measurements in previously inaccessible or only partially accessible portions of the dynamic plane. This new opportunity is expected to improve the current understanding of the high-frequency dynamics of disordered systems.

Figure 37: A schematic layout of the new high-resolution IXS spectrometer soon available at NSLS II (from Ref. [29]).

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List of symbols used throughout the text

Fundamental constants		Φ	Photon flux
c	Speed of light in vacuum	L	Size of the normalisation box
$\hbar$	Reduced Planck constant	b	Neutron scattering length
r_0	Classical electron radius	H	Hamiltonian operator
k_B	Boltzmann constant	H_{el}	Unperturbed Hamiltonian ($\propto A(\mathbf{r})$)
m_n	Neutron mass	$H_{int}^{(1)}$	First perturbative term in the Hamiltonian ($\propto A(\mathbf{r})$)
μ	Absorption coefficient	$H_{int}^{(2)}$	Second perturbative term in the Hamiltonian (Thomson term)
Thermodynamic and transport properties		$E_i(E_f)$	Initial (final) photon energy
T	Temperature	$k_i(k_f)$	Initial (final) photon wavevector
P	Pressure	$\hat{\mathbf{e}}_i(\hat{\mathbf{e}}_f)$	Initial (final) unit photon polarization vector
n	Number density	$E_i(E_f)$	Initial (final) sample energy
ρ	Mass density	$\partial^2 \sigma / \partial \Omega \partial E_f$	Double differential cross section
d	Mean separation between first neighbouring atoms	$ I, i\rangle (F, f\rangle)$	Initial (final) combined photon-sample state
λ	Mean free path	$dP_{i,F \rightarrow I,f} / dt$	probability rate of the $ I, i\rangle \rightarrow F, i\rangle$ transition per sample and probe units.
τ_{coll}	Interatomic collision time	$d^2 n / d\Omega dE_f$	Double differential photon density of states
c_s	Adiabatic sound speed	$\hbar Q$	Momentum exchanged in the scattering event
c_T	Isothermal sound speed	$\hbar \omega$	Energy exchanged in the scattering event
Γ	Sound damping	P_i	Population of the initial state of the sample
η_L	Longitudinal viscosity	$f(Q)$	Atomic form factor
ν_L	Longitudinal kinematic viscosity	$f_m(Q)$	Form factor of the m-th
η_s	Shear viscosity		
η_b	Bulk viscosity		
D_T	Thermal diffusivity		
γ	Constant pressure to constant volume specific heats ratio		
Parameters of the IXS scattering theory			
$A(\mathbf{r})$	Vector potential		
$a^+(a^-)$	Creation (annihilation) operator		
$\hat{\mathbf{e}}_i(\hat{\mathbf{e}}_f)$	Initial (final) photon polarization unit vector		
2θ	Scattering angle		

	atom (for molecular systems)
Parameters defining the microscopic properties of the sample	
$\mathbf{R}_j(t)$	Position of the j-th nucleus (monatomic systems)
$\mathbf{R}_j^c(t)$	Coordinate of the effective centre of mass of the j-th molecule
$\mathbf{r}_{n,j}'(t)$	Coordinate of n-th nucleus belonging to the j-th molecules while taking the origin in $\mathbf{R}_j^c(t)$
$n(\mathbf{r}, t)$ and $(n(\mathbf{Q}, t))$	number density and its space Fourier transform
$\delta n(\mathbf{r}, t)$ and $\delta n(\mathbf{Q}, t)$	density fluctuation and its space Fourier transform
Correlations and spectral functions	
$S(Q, \omega)$	Dynamic structure factor
$S_{I,C}(Q, \omega)$	Incoherent ("I") and coherent ("C") components of $S(Q, \omega)$
$G(r, t)$	vanHove function
$G_{s,d}(r, t)$	self ("s") and distinct ("d") components of van Hove function
$F(Q, t)$ and $\tilde{F}(Q, s)$	Intermediate scattering function and its Laplace transform, with $s (= -i\omega)$
$S(Q)$	Static structure factor
$g(r)$	Pair distribution function
Memory function formalism	
L	Liouville operator

$\tilde{P} \ (\tilde{Q} = I - \tilde{P})$	Projection operator in the $\parallel A(t)$ space (corresponding projector in the $\perp A(t)$ space)
$C(t), \tilde{C}(s)$	Auto-correlation function, its Laplace transform
$C(t), \tilde{C}(s)$	Auto-correlation matrix, its Laplace transform
$K(t), \tilde{K}(z)$ $\mathbf{K}(t), \tilde{\mathbf{K}}(z)$	Memory functions, its Laplace transform
Memory matrices	
$f(t)$	Random force in the Langevin equation
Ω	Frequency matrix
$K_n(t)$ and $\mathbf{K}_n(t)$	n-order memory function and " memory matrix
$\langle \omega^n \rangle$	n-order spectral moment
$m_L(Q, t)$	Second order memory function in the density variable
$m_L(Q, \omega)$ $= m_L'(Q, \omega)$ $+ im_L''(Q, \omega)$	Complex frequency dependent second order memory function And its real and imaginary parts.
$V(r)$	Interatomic potential
Ω_0	Einstein frequency
Ω_Q	Finite Q generalisation of the Einstein frequency
Various spectral parameters	
Normalised second moment	
ω_s, ω_s^H	Generalised Hydrodynamics inelastic shift and its low Q approximation

z_s, z_s^H	Generalised Hydrodynamics inelastic halfwidth and its low Q approximation
z_h, z_h^H	Generalised Hydrodynamics quasielastic halfwidth and its low-Q approximation
b_s, b_s^H	Asymmetry factor of the hydrodynamic spectrum and its low-Q approximation
τ	Relaxation time
$c_\infty(\omega_\infty)$	Infinite-frequency sound velocity (sound frequency)
$c_0(\omega_0)$	Zero-frequency sound velocity (sound frequency)
τ_c	Compliance relaxation time
Γ_0	Strength of the instantaneous relaxation
$\nu_L(Q, t)$ and $\nu_L(Q, \omega)$	Generalised kinematic longitudinal viscosity and its Fourier transform
$\nu_{L,\infty}$ and $\nu_{L,0}$	Infinite and zero frequency kinematic longitudinal viscosity
f_q	Non-ergodicity parameter
$c_s(Q), \nu_L(Q), \eta_L(Q), D_T(Q), \gamma(Q)$	Finite Q-generalization of corresponding thermodynamic and transport parameters (see 2. Thermodynamic and transport properties)
Kinetic theory	
$\mathbf{L}_{HS}^N$	Liouville operator for a system of N hard spheres
$\phi_i(\mathbf{v})$	i-th single particle function of velocity
$L_E(\mathbf{Q}, \mathbf{v})$	Enskog operator

$\bar{\Lambda}_Q$	Binary collision operator
A_Q	Mean field operator in the Enskog equation
σ	Hard sphere collision vector
$ \varphi_i(\mathbf{Q}, \mathbf{v})\rangle$	i-th eigenstate of the Enskog operator
$\lambda_i(Q)$	i-th eigenvalue of the Enskog operator
Mode coupling theory	
$\wp_2$	Mode coupling projection operator
V	Mode coupling vertex
$L_E(\mathbf{Q}, \mathbf{v})$	Enskog operator
$\bar{\Lambda}_Q$	Binary collision operator
A_Q	Mean field operator in the Enskog equation
σ	Hard sphere collision vector
$ \varphi_i(\mathbf{Q}, \mathbf{v})\rangle$	i-th eigenstate of the Enskog operator
$\lambda_i(Q)$	Eigenvalue associated to the i-th eigenstate of the Enskog operator
$A_i(Q)$	Amplitude of the i-th eigenstate of the Enskog operator
Additional symbols introduced while discussing experimental results	
Q_m	Position of first S(Q) maximum
T_c and P_c	Critical temperature and pressure
Q_H	Q-threshold of hydrodynamic behaviour
λ_E	Enskog mean free path
p and q	Exponent of the Lennard-Jones potential
Q_{eff}	Effectively exchanged wavevector ($= Q/\sqrt{S(Q)}$)
$\mathbf{G}$	Reciprocal lattice vector

Q_N	Position of the N-order Bragg peak
Δ	Halfwidth of the first diffraction peak
$S_{in}(Q, \omega)$	Disorder-free (crystal-like) inelastic term of the model in Eq. 118
Γ_0	Halfwidth of the central Lorentzian peak of the model in Eq. 118
$G(\omega)$	Gaussian broadening function in the model in Eq. 118
W_G	Halfwidth of $G(\omega)$ in the model of Eq. 118
Γ_s	Total inelastic halfwidth of the model in Eq. 118
$C_L(Q, \omega)$	Longitudinal current spectrum
Ω	Position of $C_L(Q, \omega)$ maxima

τ_h	Thermalization time
R	Ratio between thermal and acoustic time-scales
ω_r	Recoil frequency
ω_d	S(Q)-normalized recoil frequency
$\langle K.E. \rangle$	Mean single particle kinetic energy
R'_2	Second spectral moment normalised to its classical value
p_Q	Component along the Q - direction of the single particle momentum
F_Q	Component along the Q - direction of the force acting on the single particle momentum

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ⁱ Notice that d is also equal to the position of the first maximum of the pair distribution function in Eq. 33.

ⁱⁱ In this measurements a slightly different model, including an additional DHO function (see 93) was used to account for the low frequency, transverse contribution appearing at high Q in the water spectrum.