

# Inelastic x-ray scattering from high pressure fluids in a diamond anvil cell

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We present an experimental setup to study terahertz dynamics in fluids under high pressure, employing inelastic x-ray scattering and diamond anvil cell techniques. The use of a carefully designed vacuum chamber and the minimization and control of sources of parasitic scattering allowed circumventing previous limitations due to important empty cell contributions to the scattering signal. The successful implementation of our setup is demonstrated in the case of supercritical fluid argon, for which a full viscoelastic analysis yields the dispersion relation of sound waves, the generalized heat capacity ratio, and longitudinal viscosity. Our results are in excellent agreement with available experimental observables and molecular dynamics simulations. © 2009 American Institute of Physics. [DOI: 10.1063/1.3076123]

The knowledge of thermophysical properties of materials at elevated pressure ( $P$ ) and temperature ( $T$ ) conditions is important in applied thermodynamics and geophysical/planetary science. Of particular interest is the study of fluid materials which, in the case of gaseous systems, are in the supercritical state where not much is known about the evolution of physical properties. Properties such as elastic moduli, dispersion relations and damping of acoustic waves, and viscosity and relaxation times are connected to the dynamics of density fluctuations<sup>1</sup> and can be determined, for example, by means of light scattering techniques.<sup>2-5</sup> The derived dynamical properties pertain to the hydrodynamic realm since the probe wavelength (a few hundreds of nanometers) is much larger than the coarse grained microscopic structure of any molecular system. Length scales comparable to the mean interparticle distances can be assessed by coherent inelastic neutron<sup>6-8</sup> and x-ray scattering (IXS).<sup>9-12</sup> The large size of neutron beams, however, limits such studies to relatively large samples, thus preventing the use of diamond anvil cells (DACs). These limitations can be overcome for IXS, since undulator based synchrotron x-rays can be focused down to small spot sizes in the micrometer range. A few remarkable efforts have been performed in this direction using moderate pressure cells (<0.2 GPa) for liquid metals.<sup>13,14</sup> Indeed, while studies on crystalline systems are routinely performed up to several tens of gigapascal windows,<sup>15</sup> experiments on liquids are scarce,<sup>16,17</sup> and a quantitative viscoelastic analysis of the IXS spectra has not been attempted, mainly due to problems of parasitic scattering from the sample environment and the diamonds, which is particularly critical in the study of light elements.

In this paper we present the apparatus for performing quantitative IXS measurements on fluid and solid samples in a DAC, which can be used to reach pressures of the order of 100 GPa and temperatures as high as 1000 K by resistive

heating. The comparison of the experimental spectra on fluid Ar with those obtained from molecular dynamics (MD) simulations, together with the generalized heat capacity ratio and the longitudinal viscosity obtained from the spectral analysis fully supports the quality of the measured spectra. This goal has been achieved because of the capability of quantitatively measuring the entire line-shape of the IXS spectrum which, especially in the quasielastic region, is a difficult task in the case of samples confined in a DAC, due to the presence of spurious scattering. These parasitic scattering sources are mainly (a) the air before and after the sample, (b) the diamond anvils, (c) the entrance and exit windows of the vacuum chamber (VC) containing the DAC, and (d) dust particles present on the diamond anvils. In order to minimize the first two contributions we developed a VC dedicated to IXS experiments with a membrane DAC (Fig. 1). The entrance window is made out of a 100  $\mu\text{m}$  thick mylar foil, is about 30 mm away from the sample, and allows

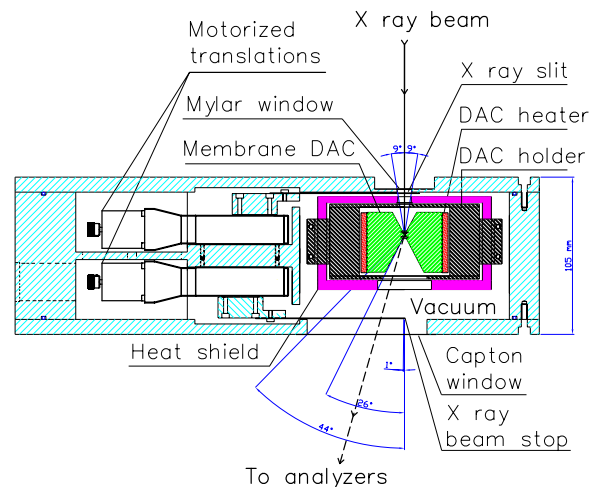


FIG. 1. (Color online) Schematic drawing of the VC.

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the use of microscopes for visual inspection and pressure measurements. The exit window is made out of a 100  $\mu\text{m}$  thick capton foil with an angular opening of 45°. In order to eliminate the air scattering in front of the entrance window of the VC and from the entrance window itself, an 80  $\mu\text{m}$  wide slit is mounted inside the VC, close to the window. A beam stop, 500  $\mu\text{m}$  wide and with a concave section, stops the x-ray beam inside the VC, thereby preventing scattering from the exit window and from air outside the VC. Entrance slit and beam stop are made of 500  $\mu\text{m}$  thick tungsten foils and are motorized in order to allow a precise alignment with respect to the incident x-ray beam. Further features comprise a resistive heater, a ceramic heat shield, and temperature sensors for long-time stability studies at high  $P$ - $T$  conditions.

The setup has been tested by performing an experiment on fluid Argon at room  $T$  and high pressure, close to the melting line (1.2 GPa). Argon was chosen as it is a model system and has a reasonably strong IXS signal. The experiment was performed on beamline ID28 at the European Synchrotron Radiation Facility, using the silicon (9 9 9) setup with a total energy resolution of 3.0 meV. A ruby chip (5  $\mu\text{m}$  diameter) for pressure measurements<sup>18</sup> was placed very close to the edge of the cylindrical hole (200  $\mu\text{m}$  diameter and 100  $\mu\text{m}$  thick) in the stainless steel gasket. The empty cell spectrum was determined at the end of the experiment, after complete Ar removal by pressure release. It turned out that a very careful *ex situ* cleaning of the diamonds had to be performed, as the pressure release led to the deposition of small dust particles on the diamond culets, leading to parasitic elastic scattering. These small particles most probably are coming from the gasket and are sucked into the sample volume during the decompression. Furthermore, the crystallographic orientation of the two anvils was indispensable in order to avoid spurious elastic scattering from diamond Bragg reflections. In fact, an *in situ* check can be performed by monitoring the transmitted intensity. If a Bragg reflection is excited, a reduction in the transmitted intensity occurs due to energy conservation. A proper alignment therefore consists of avoiding any minima in the transmitted intensity. Taking these precautions, the residual empty cell contribution arises only from elastic scattering by impurities in the diamond anvils. In fact, the VC was tested without the DAC, showing that the intensity of the parasitic elastic scattering is completely negligible, i.e., less than 1 count/100 s at the lowest investigated  $Q$  transfer of 3.0  $\text{nm}^{-1}$ .

The experimental IXS spectra,  $I(Q, E)$ , at four selected values of exchanged momentum are shown in Fig. 2. They have been obtained from the raw measured spectra by the subtraction of the empty cell spectra. The IXS spectra are proportional to the convolution product of the dynamical structure factor,  $S(Q, E)$ , with the instrumental resolution function. The empty cell intensity has been scaled by the transmission of the sample (80%) and is at the most about 5% of the total intensity, a value in the range of the statistical errors. Figure 2 also shows the spectra obtained from MD simulations convoluted with the instrumental resolution function and scaled by an arbitrary factor in order to fit the experimental data. The overall agreement is very good. Minor differences in the high energy tails of the spectra are due to the finite simulation time.

Figure 3 reports the thermophysical parameters extracted from the experimental data using the viscoelastic model.<sup>1</sup>

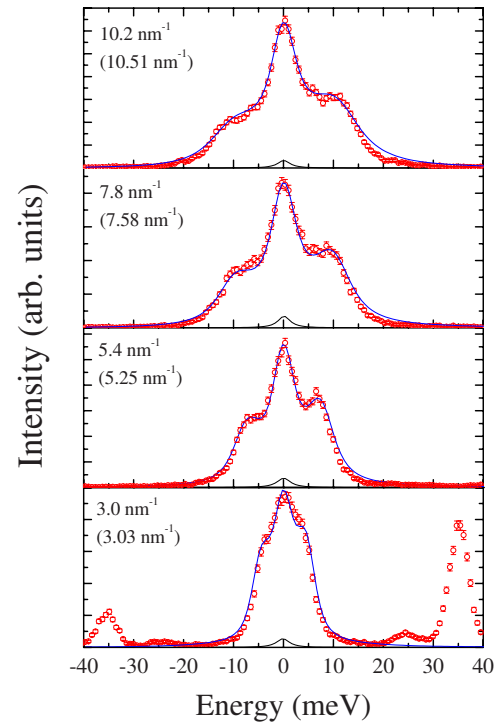


FIG. 2. (Color online) Representative IXS spectra of argon at 1.2 GPa and 295 K, at 4 selected  $Q$  values (empty dots) after subtraction of the empty cell contribution (black line). The blue line is obtained from MD simulations in similar  $P$ - $T$  conditions, at the  $Q$  values indicated in brackets. The inelastic features centered around 24 and 35 meV in the spectrum at  $Q=3 \text{ nm}^{-1}$  are the transverse and longitudinal phonons of diamond.

Within this approach the spectra  $I(Q, E)$  are described in terms of the generalized isothermal sound velocity  $c_t(Q)$ , and of a thermal and a structural relaxation process, whose relaxation amplitudes and timescale can be obtained as a result of a fitting procedure to the experimental data. The generalized adiabatic sound velocity  $c_s(Q) = \sqrt{\gamma} \times c_t(Q)$ , with  $\gamma$  the heat capacity ratio, obtained by the experimental data, agrees very well with Brillouin measurements<sup>19</sup> in the long wavelength limit ( $Q \rightarrow 0$ ). The “apparent” sound velocity value, which is obtained by the frequency of the maxima of the longitudinal current correlation function<sup>1</sup>  $(\omega/Q)^2 S(Q, \omega)$ , with  $\omega = E/\hbar$ , exceeds the adiabatic value by  $\sim 20\%$ , (Fig. 3, upper panel). This is a typical feature reported in simple and complex liquids<sup>9,12</sup> and even in glass forming systems.<sup>10</sup> The heat capacity ratio in the hydrodynamic limit can be deduced from the Landau Placzek ratio, which depends on the relative intensity of the elastic and inelastic contributions:  $\gamma = [I_{el}/(2I_{in}) + 1]$ .<sup>1</sup> The  $I_{el}/(2I_{in})$  ratio has been calculated by fitting the energy spectra to the sum of three Lorentzian functions. In Fig. 3 (middle panel) we report values of  $\gamma$  deduced from the experimental data at the lowest  $Q$  values, as for  $Q$  higher than about 5  $\text{nm}^{-1}$  the hydrodynamic limit is no longer valid and the structural relaxation process modifies the spectral line shape. The result is in very good agreement with the determination of  $\gamma$  from the MD simulation, reported in the same panel. The  $\gamma$  at  $Q=0$  has also been measured up to 1 GPa (Ref. 20) and the extrapolated value at 1.2 GPa is equal to 1.32.

A further physical quantity, which can be extracted from the experiment, is the generalized ( $Q$  dependent) longitudinal viscosity, obtained from the time integral of the memory function corresponding to the viscoelastic model. The

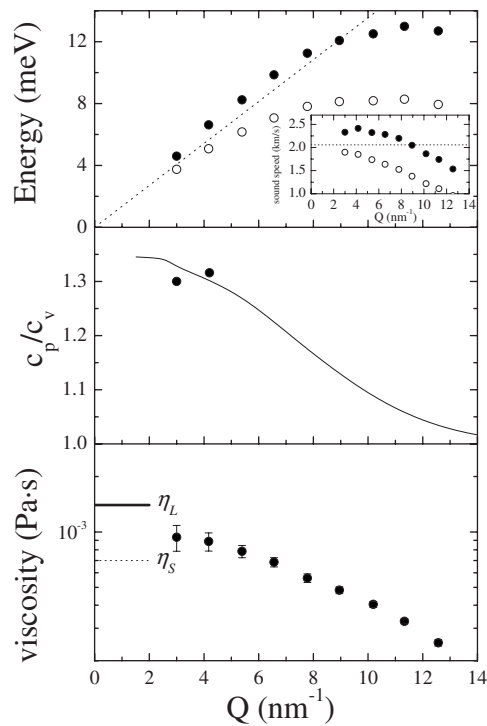


FIG. 3. Panel (a): Dispersion of the apparent (full dots) and adiabatic (open dots) energy of the collective modes (inset:  $Q$  evolution of the apparent and adiabatic sound velocity). The  $Q=0$  limit value of  $c_s$  obtained from Brillouin scattering experiments is represented by a dashed line, see Ref. 19. Panel (b):  $Q$  dependence of the heat capacity ratio estimated from static correlation functions, calculated in MD simulations (line), together with the two lowest  $Q$  values deduced by the Landau Placzek ratio. Panel (c):  $Q$  dependence of the generalized viscosity with exchanged momentum. The  $Q=0$  extrapolation lies between the shear ( $\eta_s$ ) and longitudinal ( $\eta_l$ ) hydrodynamic viscosity values.

$Q \rightarrow 0$  limit of such estimate favorably compares to the hydrodynamic limit. This latter can be deduced on the basis of the experimentally determined shear viscosity (measured up to 1.0 GPa),<sup>21</sup> which has been shown to be approximately one-half of the longitudinal value.<sup>22</sup>

In conclusion, we developed an experimental methodology, which allows the x-ray measurement of the  $S(Q, E)$  of high pressure fluids in the DAC. The complete control of the empty cell signal, which has been minimized in the relevant spectral region, allows for an accurate determination of the line shape. This, in turn, enables the extraction of thermo-physical parameters in the terahertz frequency range, such as the dispersion of acousticlike excitations, the structural relaxation time, the generalized viscosity, and the heat capacity ratio. These advances will pave the way to the understanding of mesoscopic/microscopic dynamical properties of hot dense fluids, which is of paramount importance to unveil the rich physics of planetary systems. More generally, IXS

coupled to DAC techniques provides the opportunity to investigate dynamical properties of a large variety of high pressure elemental and compound fluids, both in the liquid and in the supercritical  $P$ - $T$  regions.

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<sup>1</sup>J. P. Boon and S. Yip, *Molecular Hydrodynamics* (McGraw-Hill, New York, 1980).

<sup>2</sup>B. J. Berne and R. Pecora, *Dynamic Light Scattering* (Wiley, New York, 1976).

<sup>3</sup>E. H. Abramson, L. J. Slutsky, M. D. Harrell, and J. M. Brown, *J. Chem. Phys.* **110**, 10493 (1999); E. H. Abramson, L. J. Slutsky, and J. M. Brown, *ibid.* **111**, 9357 (1999); E. H. Abramson, J. M. Brown, and L. J. Slutsky, *ibid.* **115**, 10461 (2001); F. Decremps, L. Belliard, B. Perrin, and M. Gauthier, *Phys. Rev. Lett.* **100**, 035502 (2008).

<sup>4</sup>K. Matsuishi, E. Gregoryanz, H. K. Mao, and R. J. Hemley, *J. Chem. Phys.* **118**, 10683 (2003).

<sup>5</sup>F. Li, Q. Cui, Z. He, T. Cui, C. Gao, Q. Zhou, and G. Zou, *Appl. Phys. Lett.* **88**, 203507 (2006).

<sup>6</sup>S. W. Lovesey, *Theory of Neutron Scattering from Condensed Matter* (Clarendon Press, Oxford, 1987).

<sup>7</sup>P. A. Egelstaff, *Nuovo Cimento D* **12**, 403 (1990).

<sup>8</sup>J. B. Suck, *Condens. Matter Phys.* **11**, 7 (2008).

<sup>9</sup>T. Scopigno, G. Ruocco, and F. Sette, *Rev. Mod. Phys.* **77**, 881 (2005).

<sup>10</sup>F. Sette, M. H. Krisch, C. Masciovecchio, G. Ruocco, and G. Monaco, *Science* **280**, 1550 (1998).

<sup>11</sup>G. Ruocco, F. Sette, U. Bergmann, M. Krisch, C. Masciovecchio, V. Mazzacurati, G. Signorelli, and R. Verbeni, *Nature (London)* **379**, 521 (1996).

<sup>12</sup>T. Scopigno, G. Ruocco, F. Sette, and G. Monaco, *Science* **302**, 849 (2003).

<sup>13</sup>D. Ishikawa, M. Inui, K. Matsuda, K. Tamura, S. Tsutsui, and A. Q. Baron, *Phys. Rev. Lett.* **93**, 097801 (2004).

<sup>14</sup>K. Tamura, M. Inui, K. Matsuda, and D. Ishikawa, *J. Non-Cryst. Solids* **353**, 3348 (2007).

<sup>15</sup>M. Krisch and F. Sette, in *Light Scattering in Solids IX, Novel Materials and Techniques*, edited by M. Cardona and R. Merlin (Springer, Berlin, Heidelberg, 2007).

<sup>16</sup>M. Krisch, P. Loubeyre, G. Ruocco, F. Sette, A. Cunsolo, M. D'Astuto, R. LeToullec, M. Lorenzen, A. Mermet, G. Monaco, and R. Verbeni, *Phys. Rev. Lett.* **89**, 125502 (2002).

<sup>17</sup>F. A. Gorelli, M. Santoro, T. Scopigno, M. Krisch, and G. Ruocco, *Phys. Rev. Lett.* **97**, 245702 (2006).

<sup>18</sup>H. K. Mao and P. M. Bell, *J. Geophys. Res.* **91**, 4673 (1986).

<sup>19</sup>M. Grimsditch, P. Loubeyre, and A. Polian, *Phys. Rev. B* **33**, 7192 (1986).

<sup>20</sup>R. B. Stewart and R. T. Jacobsen, *J. Phys. Chem. Ref. Data* **18**, 639 (1989).

<sup>21</sup>NIST Chemistry WebBook.

<sup>22</sup>N. Ailawadi, A. Rahman, and R. Zwanzig, *Phys. Rev. A* **4**, 1616 (1971).