Inelastic x-ray scattering by liquid lithium near the melting point

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Inelastic x-ray scattering by liquid lithium near the melting point

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Abstract. The dynamic structure factor, $S(Q,\omega)$, and the static structure factor, $S(Q)$, of liquid lithium were investigated by means of inelastic x-ray scattering and small-angle x-ray scattering. Comparing our results to different molecular dynamics simulations we found a good agreement with MD simulations using an *ab initio* pair potential derived from the neutral pseudoatom method. However, measurements of the absolute cross section indicate that, in addition to coherent scattering, there is an incoherent scattering contribution for energy transfers of several meV.

Complementary to the inelastic neutron scattering technique, nowadays inelastic x-ray scattering experiments with sufficient energy resolution and flux have become possible by the use of synchrotron radiation [1, 2]. Especially for liquid or amorphous systems with a high sound velocity, like liquid lithium, this technique offers a larger accessible Q–ω space compared to that of neutron scattering [3–5].

In this paper we discuss measurements on liquid lithium at 220 °C, 40 °C above the melting point. The data were obtained in an inelastic x-ray scattering experiment at the European Synchrotron Radiation Facility (ESRF, beamline ID16) in Grenoble, yielding information about the shape of the dynamic structure factor, $S(Q,\omega)$, with an energy resolution of 11 meV. In addition, small-angle scattering data were taken at the Hamburger Synchrotron Labor (HASYLAB, beamline JUSIFA) leading to information about the absolute cross section.

In an x-ray experiment, the radiation is scattered off the electron density fluctuations in the sample. In a liquid metal, core and valence electrons contribute both to coherent and incoherent scattering. Following the analysis of Chihara [6] the nonresonant inelastic cross section for x-rays in the case of a liquid metal can be written as

$$\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega\ \mathrm{d}\omega}(Q,\omega) \propto \sigma_T N[(f_i(Q)+\rho_v(Q))^2 \mathrm{e}^{(1/2)\hbar\omega\beta} S(Q,\omega) + zS_v^0(Q,\omega) + (Z-z)S_i^{inc}(Q,\omega)] \tag{1}$$

with the Thomson cross section σ_T, the number of atoms N, the number of valence electrons z and the number of core electrons $(Z-z)$.

The dynamic structure factor $S(Q,\omega)$ is equal to the coherent dynamic structure factor known from inelastic neutron scattering describing the collective motions of the ions. The exponential factor in equation (1) (the detailed-balance factor) allows one to consider $S(Q,\omega)$ as a function symmetrical in ω [7].

The incoherent dynamic structure factors, $S_v^0(Q,\omega)$ and $S_i^{inc}(Q,\omega)$, arise from excitations of the electron gas—respectively from electron–hole excitations of the core

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electrons and from Compton scattering. For simple metals, $S_v^0(Q,\omega)$ can be replaced, as a first approximation, by the dynamic structure factor of a jellium [6]:

$$S_v^0(Q,\omega) \approx S_v^{jell}(Q,\omega). \tag{2}$$

In this approximation, no significant incoherent scattering for energy transfers below a few eV is expected.

As a consequence of this assumption, the intensity observed in an inelastic x-ray experiment with energy transfers well below an eV can be interpreted as coherent. For x-ray experiments on liquid metals without energy resolution, the incoherent scattering $S_v^0(Q,\omega)$ and $S_i^{inc}(Q,\omega)$ have to be taken into account as well; this is often referred to in the x-ray literature as the 'Compton correction'.

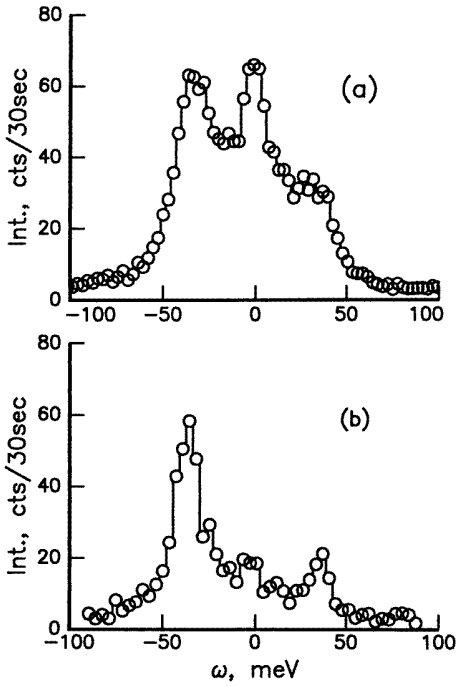

Figure 1. Inelastic x-ray scattering by liquid (a) and by solid lithium (b).

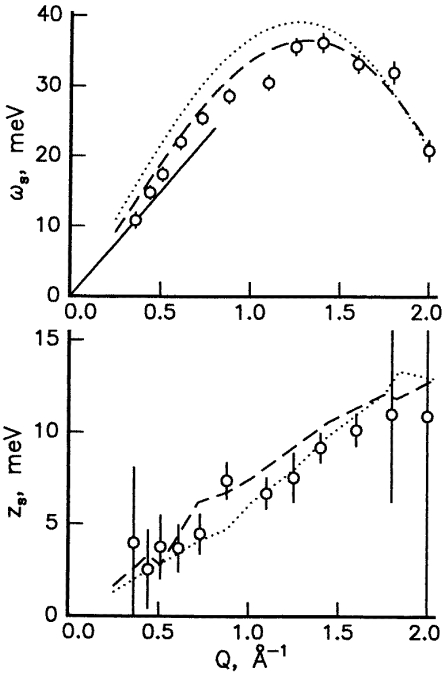

Figure 2. The dispersion, $\omega_s(Q)$, and half-widths, $z_s(Q)$, of the Brillouin lines. Open circles: inelastic x-ray scattering; dashed line: MD [10], using the NPA potential; dotted line: MD, using the empty-core potential; solid line: adiabatic sound velocity.

A typical data set obtained from inelastic x-ray scattering measurements on liquid lithium at $Q = 1.25$ Å^{-1} is shown in figure 1(a). The central peak (Rayleigh line) arises from entropy fluctuations in the liquid sample [8]. The intensity relation of the two lines at $\pm\omega_s$ (Brillouin lines) is given by the detailed-balance ratio.

In the solid state, the Rayleigh line disappears (figure 1(b)). The Brillouin lines become phononic excitations with a slightly higher ω_s and a weaker sound damping, corresponding to smaller linewidths.

A further analysis of $S(Q,\omega)$ was done in terms of the model of the extended hydrodynamic modes [9], using six adjustable parameters. The measured intensity was

described by a convolution of this model and the resolution function, leading to χ^2-values close to unity. We compared our results to molecular dynamics (MD) simulations [10], starting from two different assumptions for the pair potential: the empty-core potential [11] and an *ab initio* pair potential derived from the neutral-pseudoatom approximation (NPA potential) [12].

The dispersion of the Brillouin lines, ω_s, and the half-widths, z_s, are shown in figure 2. The dispersion relation from inelastic x-ray scattering is in better agreement with the MD data obtained with the NPA potential (the dashed line in figure 2(a)) than with the data starting from the empty-core potential (the dotted line). The increase of the Brillouin widths for $0.36 \leqslant Q \leqslant 2$ Å^{-1} is observed to be linear (figure 2(b)). Within the experimental error, no significant difference between the two MD data sets and the experimental data can be found.

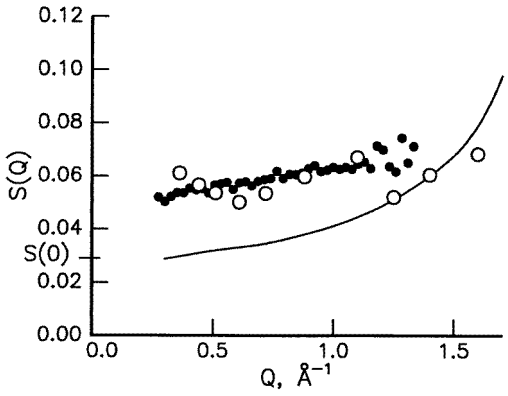

Figure 3. The static structure factor obtained from inelastic x-ray scattering (open circles), small-angle scattering (full circles) and MD, with the NPA potential (solid line).

However, looking onto the integrated intensities from the x-ray experiment, significant disagreement compared to the computer simulations exists for small momentum transfers Q. The MD data can be extrapolated for small Q to values close to the compressibility limit $S(Q = 0)$ (figure 3, solid line). A normalization of the integrated inelastic x-ray data to the high-Q limit yields in the limit of low Q roughly twice the compressibility value (the open circles in figure 3). However, this kind of normalization is not very precise due to mechanical instabilities in the inelastic x-ray set-up at the time of the experiment.

Therefore we additionally measured the absolute cross section with a small-angle scattering experiment. The data are corrected for empty-cell scattering, and are normalized to a reference scatterer. The correction for the incoherent scattering $S_v^0(Q, \omega)$ was obtained from experimental data on solid lithium [13], whereas that for incoherent scattering from the core electrons, $S_i^{inc}(Q, \omega)$, was taken from a Hartree–Fock calculation [14]. The multiple-scattering contribution was calculated using a similar method to that followed in reference [15]. The form factor for the valence electron, $\rho_v(Q)$, was corrected according to the NPA model [12]. The result (figure 3, full circles) confirms the observation from the inelastic x-ray data of an increased cross section at low Q.

A possible explanation for this extra intensity is that the assumption made in equation (2) is not justified for liquid lithium and an additional incoherent scattering with meV energy transfer is observed. A calculation from Rasolt [16] for liquid sodium and liquid aluminium indicates deviations from equation (2), which can change the x-ray cross section

significantly.

However, the possibility of systematical errors in the experimental determination of the absolute cross section is high, due to the low scattering power of the lithium atom. Improved measurements and data analysis related to this topic are still in progress.

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