

Atomic Motion via Inelastic X-Ray Scattering

Cheiron School Beamline Practical - **Tuesday ONLY** at BL43LXU

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We will introduce students to the use of inelastic x-ray scattering, IXS, to investigate atomic motions. A short discussion of the technique and tour of the instrumentation will be followed by measurements of some simple materials. The notes below are meant to provide the students with a bit of guidance and background, and the "exercises" to provide some points for discussion. The Cheiron school audience is very broad, and the discussion below is probably too simple for some and may be too advanced for others. We will try to fill in the gaps during discussions.

1. Introduction

Atoms in materials are always in motion – be it long-range diffusive motion, as in liquids, or oscillatory, phonon, motions about equilibrium positions in a solid. Historically, the importance of this motion was noted because the thermodynamic behavior of materials (e.g. specific heat) made no sense until one postulated models of atomic motion – simple models include those suggested by Einstein and Debye. More recently, it has been understood that atomic motions are intimately connected to many facets of material behavior, including many structural phase transitions, and some important electronic ones. Perhaps most famous among these is the superconducting transition: superconductivity in most materials is driven by interaction of the atomic motions (phonons) and the electronic system. There are then strong reasons, both from the point of view of fundamental science, and for applied reasons (how does a new type of superconductor work?) to try to investigate dynamics.

In this practical we will investigate relatively simple atomic motion, longitudinal acoustic modes. These modes are the direct extrapolation of conventional sound – if you tap a crystal, sound will propagate through it, and, depending on the material properties, the sound will propagate with different speeds, and with different damping or attenuation. Consider striking a hard material, for example: naively (and correctly) one can expect the sound will propagate a long way, and relatively quickly. Meanwhile, a noise made in the water, will propagate much more slowly, and generally not so far.

We will look at microscopic sound in a hard material, diamond, and a liquid (an extreme version of a soft material), and see how these are different and how these differences reveal interesting information about the materials and may be related behavior, and how our to the simple macroscopic picture (sound velocity and damping) mentioned above.

2. The Method: Inelastic X-ray Scattering

X-rays have long been known to be sensitive to thermal motion via thermal diffuse scattering or Debye-Waller factors. The difficulty is that to measure atomic length scale correlations you should use x-rays that have a wavelength similar to the spacing between atoms ($\sim \text{\AA}$) and this then gives the x-ray energy in the keV region, with 1 \AA x-ray having an energy of 12.4 keV. Meanwhile, the energy scale of the atomic motions is typically ~ 0.001 eV. Thus, to measure atomic motions with x-rays, one requires energy resolution $\Delta E/E \sim 10^{-7}$, which is a severe requirement. Furthermore, as the cross section for inelastic scattering is small, one must be very careful to preserve the maximum possible flux.

[Exercise. **Neutrons vs X-Rays.** How much energy does a neutron with a 1 \AA deBroglie wavelength have? What is the required energy resolution ($\Delta E/E$) to measure \sim meV excitations with 1 \AA neutrons? Note that the answer to this question helps explain the fact that the field of inelastic *neutron* scattering developed some 40 years earlier than inelastic *x-rays* scattering.]

Beamline 43 of SPring-8 (BL43LXU) [1] is designed for measuring dynamics of atoms using x-rays. The beamline layout is shown in figure 1. Possibly the most notable fact at first glance is that is very large for a synchrotron radiation instrument. This in fact follows rather directly from Bragg's law, which also underlies many x-ray optics, thus we spend some time to discuss it here.

Bragg's law governing x-ray diffraction from crystalline materials states

$$\lambda = 2d \sin(\Theta_B)$$

where d is the spacing between the planes of the crystal lattice, and Θ_B the Bragg angle the incident radiation

BL43LXU: Quantum NanoDynamics

See: <http://user.spring8.or.jp/sp8info/?p=3138>

High-Resolution, Non-Resonant Inelastic X-Ray Scattering

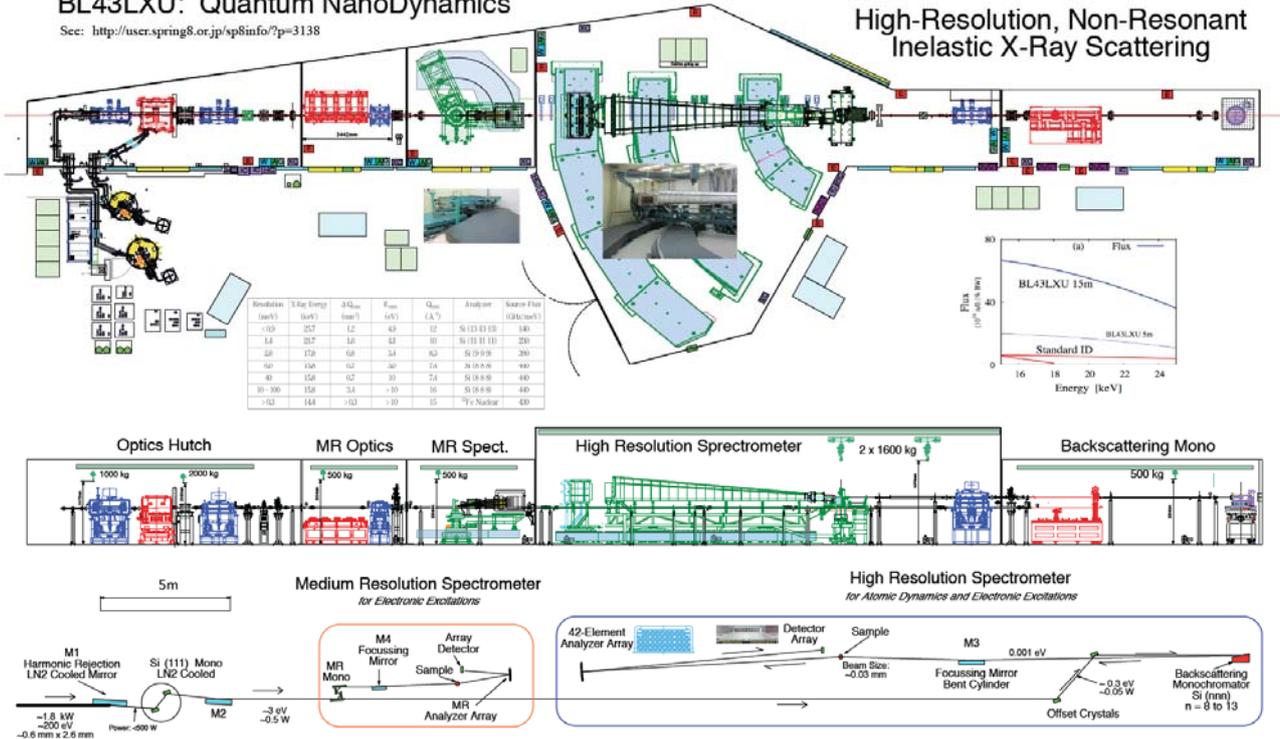


Figure 1. Schematic of BL43LXU. The top figure shows the hutches outlines, as viewed from above, while the lower part shows the beam path through the beamline. The part shown is about 50 m long.

planes. Differentiation of Bragg's law immediately gives

$$\Delta\lambda = 2\Delta d \sin(\Theta_B) + 2d \cos(\Theta_B) \Delta\Theta$$

which relates small changes in the various quantities. Assuming the lattice constant of the material is now fixed ($\Delta d=0$) then this may be re-written as

$$\Delta\Theta = \tan(\Theta_B) \frac{\Delta\lambda}{\lambda}$$

This makes it immediately clear that in order to achieve a maximum angular acceptance for our optics, large $\Delta\Theta$, for a fixed energy resolution, it is desirable to operate at Bragg angles near to 90 degrees ($\Theta_B=\pi/2-\delta$, $\delta\ll 1$). In fact we typically operate with $\delta \sim 0.3$ mrad. The scattered angle is then twice delta, so it is clear one needs very long path lengths (~ 10 m) to separate the incident and reflected beams from an optic. This explains the large size of the beamline.

[Exercise. **Acceptable angular divergence.** Assume you use a Bragg reflection near backscattering, $\delta = 0.3$ mrad at an x-ray energy of 21.747 keV. What is the contribution to the energy resolution if the x-ray beam divergence is 80 micro-radians. How about if $\delta = 1$ mrad]

[Exercise. **Perfect silicon.** The intrinsic energy resolution of a Bragg reflection, $\Delta E/E$, is

given by $1/N$, where N is the number of planes reflecting radiation. To achieve meV resolution at 21.7 keV, how many planes are needed? In backscattering ($\delta = 0$), how thick (mm) does the crystal have to be? How many materials do you think might have the required level of perfection?]

[Exercise. **Temperature scans.** Assume white radiation is incident on a silicon Bragg reflection optic. What is the fractional energy change ($\Delta E/E$) of the reflected beam if the temperature of the optic is changed by 1 degree C? Note the thermal expansion of silicon is isotropic, with an expansion coefficient of $\alpha = 2.6 \times 10^{-6}/K$ near room temperature (ie: a change of 1K in temperature leads to a fractional expansion of 2.6 ppm.) How much do you think one can *practically* change the reflected energy using temperature in this way?]

3. The Dynamic Structure Factor, $S(Q,\omega)$

Naively, one might think that to understand the dynamics of a material, one should measure the positions, as a function of time, of all the atoms in the sample of interest. Certainly this information is *sufficient* to "know" the dynamics of a material. However, this may not help you to *understand* the

dynamics, as it is a huge amount of information, and one would need a fast computer to somehow process it and answer meaningful questions. Also, while this information can be measured in some special cases for slow motion, it is, now, nearly impossible to measure for the fast motions we discuss here. Thus, most often people measure *correlations* of motions in atoms, and not the detailed motion of atoms. It turns out, in fact, that these correlations are the natural direct result of a standard scattering experiment.

Scattering theory in physics is highly developed. The reader is directed to such classic texts as Squires [2] for a treatment, as well as the original literature (the seminal paper by van Hove [3], is in fact very readable and clear). In short, within some very simple approximations - that the scattering is weak, that the scatterer is far from the detector and far from the source, etc - the scattered intensity is directly related to the density-density correlation of a material. Thus scattering experiments naturally answer the question: "If I slightly perturb one atom, how does the perturbation propagate to other atoms in the material".

We now introduce some standard terminology. The scattered intensity at some particular angle and energy transfer in our measurements is proportional to the double differential cross section,

$$\left(\frac{d^2\sigma}{d\Omega dE} \right)_{k\alpha \rightarrow k'\beta} = r_e^2 (\epsilon_\alpha^* \cdot \epsilon_\beta) S(\mathbf{Q}, \omega)$$

$$\mathbf{Q} \equiv \mathbf{k}' - \mathbf{k}$$

$$E = \hbar\omega = E' - E''$$

This introduces the dynamical structure factor of a material, $S(\mathbf{Q}, \omega)$, which is related to the cross section through a scale factor describing the interaction of electrons and light: the product of the classical radius of the electron, r_e , and the usual polarization factor for Thomson (dipole) scattering*. We also define the momentum transfer, \mathbf{Q} , as the difference between the incident and scattered wave vectors. The dynamic structure factor (sometimes also called the scattering law), is then related to the equilibrium density-density correlations of the material by

$$S(\mathbf{q}, \omega) = \frac{1}{2\pi\hbar} \int_{-\infty}^{+\infty} dt e^{-i\omega t} \int_{-\infty}^{+\infty} d^3r d^3r' e^{i\mathbf{q}\cdot(\mathbf{r}-\mathbf{r}')} \langle \rho(\mathbf{r}, 0) \rho^+(\mathbf{r}', t) \rangle$$

which explicitly shows the dependence on the density-density operator.

* We have also dropped a phase space factor that is unity for x-ray, though not for neutrons.

Notably, the expression in terms momentum/frequency space, (\mathbf{q}, ω) , makes this quantity response to the normal modes in periodic materials: i.e. measuring $S(\mathbf{Q}, \omega)$ is exactly the appropriate way to investigate phonons in crystals.

[Exercise. **Correlation lengths.** The definition of is $\mathbf{Q}=\mathbf{K}'-\mathbf{K}$ where \mathbf{K} and \mathbf{K}' are the incident and scattered wave vectors, respectively, with their magnitude given by $|\mathbf{K}|=2\pi/\lambda$. By analogy to Bragg's law, write down an expression for the correlation length, d , probed at a momentum transfer of \mathbf{Q} . What is correlation length probed for $|\mathbf{Q}| = 2 \text{ nm}^{-1}$? 20 nm^{-1} ?]

4. Diamond

Diamond is well known as a jewel whose beauty of the crystal attracts people as shown, figure 2, but given its hardness, especially, it is also a useful material for industrial applications. This is related to the strong covalent bond based on the carbon sp^3 hybridized configuration. On the other hand, diamond is well known to be is easy to cleave in the $\{111\}$ direction, leading to beautiful gemstones, as seen in figure 2.

The physical properties of diamond are very useful for research of solid state physics. The hardness is useful, e.g., for making high pressure cells using "diamond anvils" (DAC) which are the best way of approaching (statically) the pressures in the center of the earth. Diamond also has excellent thermal conductivity (much better than copper) which makes it useful for some x-ray optical devices such high heat-load beamline monochromators.

The unit cell of diamond is shown in figure 3 and has



Figure 2. Photos of diamond crystals.

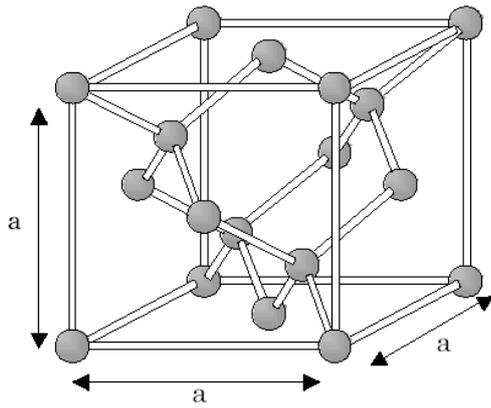


Figure 3. Diamond lattice cubic unit cell. The two atoms in a primitive unit cell are circled.

cubic symmetry, $Fd3m$, with 8 atoms/unit cell. The lattice constant is $a = 3.566 \text{ \AA}$. However, the primitive cell has only two atoms. The number of phonons possible at any momentum transfer is just 3 times the number of atoms per primitive cell, giving 6 phonon modes in diamond. The elastic properties are already known well. The longitudinal sound velocity is very fast, 18 km / sec, as compared to several km/s typical of a metal. The Debye temperature of diamond is very high, 2,200 K, several times higher than in usual metal. The high sound velocity and high Debye temperature mean that diamond is an extremely hard material.

The phonon dispersion was reported some years ago by inelastic neutron scattering, and is shown in figure 4 as a plot of the phonon frequencies at different momentum transfers - these are essentially the peak positions in measurements of $S(\mathbf{Q}, \omega)$. Modes that go to zero frequency at zero momentum transfer are acoustic, corresponding to the usual longitudinal and shear sound modes. Generally, for acoustic modes, the two atoms in a primitive cell will move together, in phase with each other, for acoustic modes. The high energy modes are optical modes, where the two atoms tend to move opposite each other. Recently, superconductivity was discovered in boron-doped (B-doped) diamond at low temperature [5]. Correlation between its superconductivity and phonon response has been demonstrated.

In real measurement of crystalline sample, phonon measurements are carried out at higher Q position, where Q means the same as mentioned in previous section. Crystalline materials contain some periodicities strongly correlated with their crystal structure. This means that you can see the same phonon spectra in the equivalent q-position. To obtain phonon spectra more easily, you should chose the best Q position you can. The dynamic structure factor for a phonon mode, j, with frequency ω_{Qj} measured at a total momentum transfer \mathbf{Q} is given by [2]

$$S(\mathbf{Q}, \omega > 0)_j = N \frac{Z_j(\mathbf{Q})}{1 - e^{-\hbar\omega_{Qj}/k_B T}} \delta(\omega - \omega_{Qj}).$$

This means that $S(\mathbf{Q}, \omega)$ is proportionate to Q^2 . This suggests that you should measure phonon spectra at higher Q position, although the $f_d(\mathbf{Q})$ become small in general at large Q value.

$$Z_j(\mathbf{Q}) = \frac{1}{\omega_{Qj}} \left| \sum_{\substack{d \\ \text{Atoms} \\ \text{/Cell}}} \frac{f_d(\mathbf{Q})}{\sqrt{2M_d}} e^{-W_d} \mathbf{Q} \cdot \mathbf{e}_{\mathbf{q}j d} e^{i\mathbf{Q} \cdot \mathbf{d}} \right|^2$$

In the first measurement, you will carry out a crystalline material using pure diamond by inelastic x-ray scattering. The obtained phonon dispersion gives you the sound velocities in some directions. Experimental procedures are as follows:

- 1) Find several Bragg peaks of the sample for you to know the sample alignment.
 - 1-1) Calculate the angles of Bragg peaks from the lattice constant of diamond and the used x-ray wave length.
 - 1-2) Find Bragg reflections using diffractometer.
 - 1-3) Note the motor positions at each reflection.
- 2) Calculate the angle position to measure.
- 3) Move the motors to the calculated position in 2).
- 4) Measure inelastic x-ray scattering spectra.
- 5) Analyze the inelastic scattering spectra and plot the peak positions to the positions in the reciprocal space to obtain dispersion.
- 6) Determine the sound velocity from the obtained

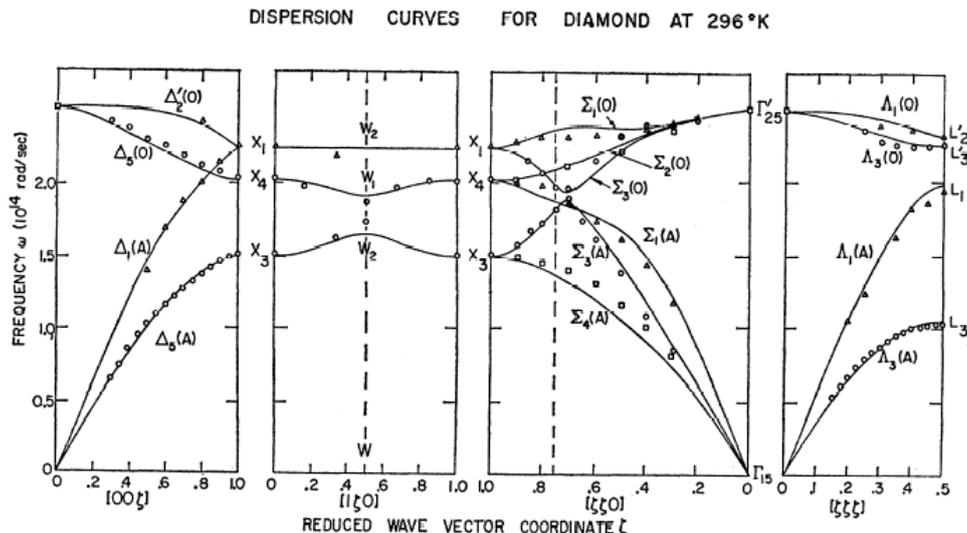


Figure 4. Phonon dispersion in diamond at room temperature investigated by inelastic neutron scattering. Markers show the experimental data points, and solid lines show the calculated results based on a shell model [4].

dispersion.

- 7) Comparison your results with those obtained by inelastic neutron scattering, for example, as shown in Fig. 3.

[Exercise. Check the line width of each peak in the spectra you measure: sometimes it can be broader than the resolution function. What does this mean?]

[Exercise. How is spectrum from diamond different from that of water?]

Note:

Reduced wave vector ($\zeta 0 0$) means reciprocal vector ($2\pi/a$) ($\zeta 0 0$), where a means the lattice constant of diamond. The slope of the dispersion provides the sound velocity in a direction.

4. Liquid

The second measurement will be the dynamic structure factor of a liquid. Below we will discuss the general liquid properties in terms of liquid water, however, the measurements, will be of polydimethylsiloxane (PDMS) $\text{CH}_3(\text{C}_2\text{H}_6\text{OSi})_n\text{Si}(\text{CH}_3)_3$, which is a silicone oil, in this case one that is used as a low-temperature cooling bath fluid. The dynamics of this material, to the best of our knowledge, have not yet been explored, so this measurement will provide new information, however, we expect many of the features (broad phonons, central peak, some diffusion) will be, broadly speaking, similar to those in water.

Figure 4, below, shows data from water at several momentum transfers. There is a strong central peak, with wings on the side that are the phonons, analogous to the longitudinal acoustic modes in diamond. Here however, one can note several differences:

1. The central (elastic) peak is strong compared to diamond – this results from the disorder of the material leading to enhanced scattering.
2. The central peak is NOT resolution limited. This is due to the diffusion of the molecules in the liquid (a glassy material, which is also disordered, would also have a strong central peak, but it would be resolution limited in this sample).
3. The phonon peaks are very broad. This indicates that the phonon modes have a short lifetime, again due primarily to the disorder.

[Exercise. **Sound Velocity.** Use the measured data to estimate the sound velocity? How does it compare with the low-frequency limit of about 1500 m/s in liquid water?]

[Exercise. **Diffusion and the Einstein relation.** Estimate the diffusion constant from the

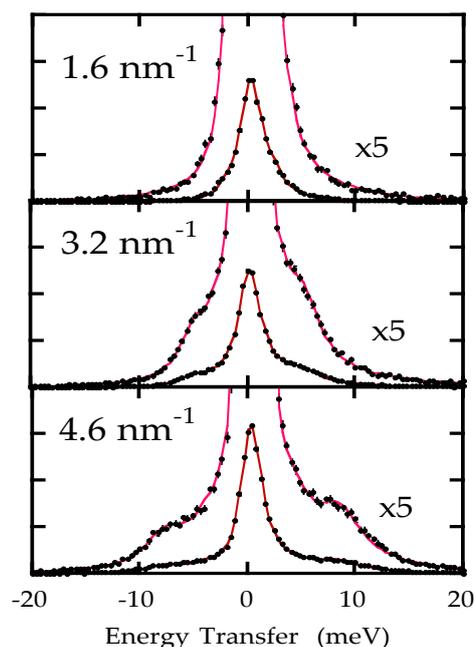


Figure 4. Inelastic scattering from water at the indicated momentum transfers. The red lines are fits to the data

linewidth of the central peak (do correct for the resolution!). Does it approximately obey the Einstein relation for Brownian motion? What is the diffusion coefficient?]

5. Conclusions

We have investigated the dynamics of two samples exemplifying crystalline material, diamond, and a disordered liquid. Both materials show acoustic modes at low momentum transfers, corresponding to approximate expectations from the fact that both materials propagate sound waves. However, while the water diamond has very well defined modes with a high sound velocity, characteristic of a hard solid, the water has highly damped modes characteristic of a soft material.

6. References.

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