Measuring Phonons with Neutrons

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Contents

- What even is a phonon anyway?
- How do they interact with neutrons?
- Things to think about for experiments.
- Going beyond the harmonic.
- Some examples.





Why Phonons?

- Not just background!
- Lattice dynamics is important for
 - Bonding
 - Heat transfer
 - Phase transitions
 - Some superconductors







- We are going to do everything within the harmonic approximation.
- So, connect a set of balls with springs of strength k. They sit at distance a apart when at rest.
- So, forces on atom n if displaced in x is

$$F = k(U_{n+1} - 2U_n + U_{n-1}).$$



- $\omega = \pm \sqrt{\frac{4k}{m}} \sin\left(\frac{Qa}{2}\right).$
- Our maximum frequency is related to the spring constant and mass.
- So strong bonds, high frequency.
- Light isotopes also are at high energy.









 $\frac{6\pi}{a}$

Q



































What about a diatomic chain?



- Atoms are distance a apart again (so a unit cell is 2a)
- Still connected together by spring constant k
- But now the mass is different.



The diatomic chain

$$\omega^2 = \frac{k}{Mm} \Big(M + m \pm \sqrt{M^2 + m^2 + 2Mm \cos Qa} \Big).$$

We now have two possible solutions at every wavevector.

The difference in mass opens a gap in the spectrum.

The mode at finite frequency at Q=0 is an "optic" mode.

But the fundamentals are the same as the monatomic chain.





How can we measure this?

- We need a suitable probe.
 - Typical excitation is 1-100 meV, 1-25 Thz, 10-800 cm-1.
 - Wavelength around 1 Å.
- Raman and IR are well suited for energy but not wavelength.
- Hard x-rays have the right wavelength but 10s KeV energies.
- $\frac{4k}{m}$ З 0 $\frac{2\pi}{a}$ $\frac{4\pi}{a}$ 6π n

• Soooo...



Neutrons are ideal!

- Neutrons have a well matched wavelength.
- They also have similar energies, this means it is easy to detect changes from excitations.
- But, neutrons are rare. We need really big samples!



Now to neutrons!



$$I(\vec{Q}, E) = \frac{N\hbar}{2} \sum_{\nu} \frac{1}{\omega(\vec{Q}, \nu)} \left| \sum_{j} \frac{b_{j}}{m_{j}^{1/2}} [\vec{Q} \cdot \vec{e_{j}}(\vec{k}, \nu)] e^{i\vec{Q} \cdot \vec{R_{j}}} T_{j}(\vec{Q}) \right|^{2} \times \left(\frac{[n(\omega(\vec{Q}, \nu), T) + 1]\delta(E + \hbar\omega(\vec{Q}, \nu)) + [n(\omega(\vec{Q}, \nu), T)]\delta(E - \hbar\omega(\vec{Q}, \nu))}{[n(\omega(\vec{Q}, \nu), T)]\delta(E - \hbar\omega(\vec{Q}, \nu))} \right).$$



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This is basically the structure factor we know and love!



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Delta functions say that you can only see a phonon where there is a phonon (duh) and N(w) is the bose factor because they are bosons. The only non-trivial bit is the +1 for energy transferred to the sample because you can always create a phonon, as well as interact with those already present.



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1/w and 1/m. i.e. it is less probably to excite a high frequency or heavy thing



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The only tricky bit. Phonons are strongest when the momentum transferred to the sample is parallel to the real space atomic motion.



One phonon scattering-key points

- Phonons are strongest when \vec{Q} is parallel to direction of atomic motion.
- Phonon intensity goes up with Q^2 .
- Phonons are weaker at high energy.
- Strong Bragg reflections often have strong phonons around them.
- Phonons can be stronger at high temperature (but care needed here).



Measuring a longitudinal acoustic phonon



We want to measure a longitudinal phonon along *OOL*.

Which peak would be best to measure around?



A moment on terminology

- When we introduced the chain, we only considered displacements along x. As a chain, the phonon can only propagate along x.
- This is termed a longitudinal mode. i.e. the displacements are along the chain direction. We could however have displaced along y or z instead. These would be termed a transverse mode and would not have the same dispersion.
- For 3d crystals along each direction in reciprocal space you will have 1 longitudinal and 2 transverse modes.





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Measuring a transverse acoustic phonon



What about a transverse phonon along 00l?



Measuring a transverse acoustic phonon



What about a transverse phonon along 00l?



Exploiting $Q \cdot e$, an example

- We were looking for a phonon around 12 meV.
- However, the background from the cryostat/mount was huge.
- Rotate sample 90°. Suppresses phonon but background unchanged





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Considering coverage

- Neutrons have mass. This can be inconvenient.
- The ideal case is to go out to very large Q. But to do so needs large neutron energy and we might not have the resolution.
- We need to plan. And we need to use our friend the scattering triangle.







Powders!

- Good news, powder experiments are simpler!
- Much simpler.
- With them we can extract the neutron weighted phonon density of states.
- But, going beyond that is hard.







Powders, what are we doing?

- We are averaging over a sphere at some |Q|.
- So, for small values of |Q| we are covering just a few (or even 1) Brillouin zones.
- But, for large |*Q*| we are covering many zones and will sweep through every point in the irreducible zone.
- This means for high |Q| we can no longer see the effect of $Q \cdot e$ and the signal is the same as incoherent scattering. This is called the incoherent approximation.





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The neutron weighted phonon density of states

$$PDOS_{neut}(E) = A \sum_{j} \left(\frac{b_j^2}{m_j}\right) PDOS_j(E),$$

- We normally correct the data for the effects of Bose statistics, $1/\omega$ and Q^2 .
- Then, in the incoherent approximation, the real Phonon Density of States (PDOS) is related to the PDOS we see via the above.
- This means we cannot obtain the true PDOS for anything other than a monoatomic system.



Choice of instruments



Back to our roots, Three Axis Spectrometer

- We are interested in how much energy was transferred to the sample.
- So we need to know neutron energy before and after the sample.
- One option is to use a monochromator before the sample and another after the sample.
- A Nobel prize winning idea (1994 in physics).





TAS pros and cons

Pros	Cons
High Flux	Small detector coverage
Perfect to focus on small region of Q , E space. i.e. dispersive excitations in single crystals	Not great for broad (disordered) excitations.
"Easy" to add polarisation	Struggle to access high energies





Time-of-flight: option 1 direct geometry

- We still need to know neutron energy before and after the sample.
- If we use a pulsed source, we could exploit the time structure to determine either Ei or Ef.
- But we need some optics to determine the other. A direct geometry instrument uses a "chopper" to fix Ei.

• TOF then gives you energy transfer.



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Direct geometry pros and cons

averaged flux
ghly focused studies
blarise



Indirect geometry pros and cons

Pros	Cons
Can have large detector arrays	Generally worse background
Better count rate than direct geometry for the same resolution.	Smaller dynamic range
Possible to have very good energy resolution.	Limited flexibility in setup.





Time-of-flight: option 2 indirect geometry

- We still need to know neutron energy before and after the sample.
- Again we use a pulsed source, we could exploit the time structure this time to determine Ei.
- Now we use some optics (a monochromator) to determine Ef.
- TOF then gives you energy transfer.







Indirect geometry pros and cons

Pros	Cons
Can have large detector arrays	Generally worse background
Better count rate than direct geometry for the same resolution.	Smaller dynamic range
Possible to have very good energy resolution.	Limited flexibility in setup.





Beyond the harmonic approximation

This is where all the "interesting" stuff happens. To discuss it properly would take a long time and not be terribly useful for most of you. What follows is somewhat of an oversimplification

- Phonon-phonon scattering (broadening)
- Thermal expansion
- Frequency shifts

Multiphonon signals (signal above the top of the dispersion)



Anharmonicity - Lifetimes

- Within the harmonic approximation phonons do not interact.
- Cubic terms in the potential allow three phonon processes. Quartic allow four etc. This allows creation and annihilation of phonons.
- In real space you can think of this as a sine wave (the phonon) multiplied by an exponential decay (a damping) where the decay rate is set by how frequently they scatter.



Anharmonicity - Lifetimes

- In real space you can think of this as a sine wave (the phonon) multiplied by an exponential decay (a damping).
- When we Fourier transform the sine wave becomes a delta function at the frequency of the mode.
- An exponential decay becomes a Lorenztian so what we observe is a Lorentzian centered at the phonon frequency.
- The broader the Lorentzian, the shorter the lifetime.





Anharmonicity - thermal expansion

- Think about the Lennard-Jones potential.
- If we just consider the harmonic part, we don't get any thermal expansion.
- You need an anharmonic potential to get expansion.





Image stolen from wikipedia

Anharmonicity-frequency shifts

- If we have lattice expansion, then you expect frequency shifts to lower energy due to thermal expansion (atoms move further apart, interactions weaken).
- But anharmonicity can also renormalize frequencies. If phonons can interact then every other phonon modifies the potential our atoms are in.
- This can actually cause phonons to move to higher frequency as we heat, and if you see it is indicative of very strong anharmonicity.



Anharmonicity - multiphonons

- Note, I mean multiphonon, not multiple scattering!
- Our neutron can create two (or more) phonons. But these don't necessarily have just frequency of the two modes.
- Instead, just like before they have a modification to their frequency.
- When measuring powders in particular multiphonon effects can be important to correct for.





Inelastic neutron scattering from $Ti_{0.68}Zr_{0.32}$. Image pinched from doi:10.1007/s003390201652. The thick line is total, thin line is 1 phonon and dashed is the multiphonon contribution.

Some examples



Metal-insulator transition in VO₂

- VO₂ undergoes a transition from insulating to metallic just above room temperature.
- This transition is accompanied by a structural one.
- What drives the transition? Lattice-electron coupling or strong electronic correlations...
- DOI:10.1038/nature13865





Rotating lone pairs low thermal conductivity

- Low thermal conductivity important in various applications.
- At elevated temperatures Pb lone pairs can start to rotate, dynamically shortening and lengthening bonds (i.e. a phonon).
- These are strongly anharmonic and lead to very strong phonon-phonon scattering





DOI:10.1021/jacs.3c02536.

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Phonons in a molecular QBit

- Spin-phonon coupling can cause decoherence in molecular bits.
- To minimize this you first need to understand the phonons.
- Not just validate calculations, but use those calculations to predict which have the strongest coupling





Summary

- Phonons are strongest when \vec{Q} is parallel to direction of atomic motion.
- Phonon intensity goes up with Q^2 .
- Phonons are weaker at high energy.
- You need to think about coverage
- There are lots of good books. I've always found "Structure and Dynamics" by Martin Dove to be a good introduction to phonon physics but others are available.

