Neutron Scattering for Condensed Matter Studies
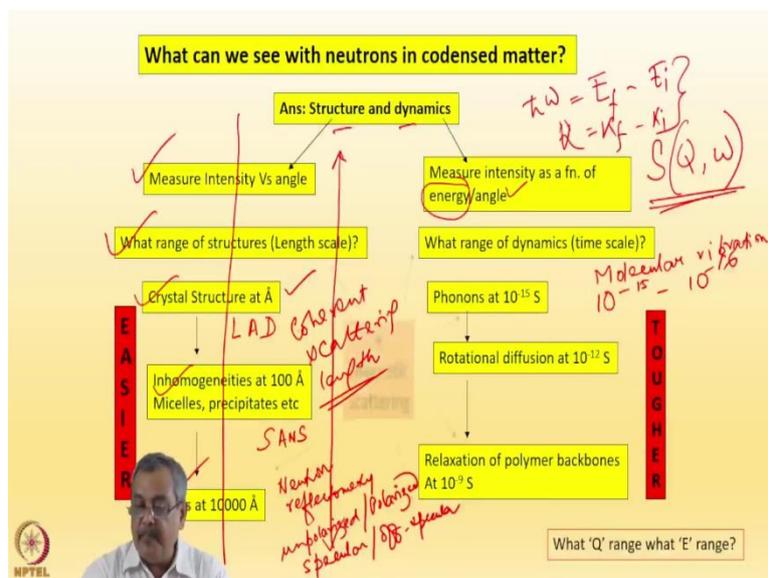## Professor Saibal Basu
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Week 10: Lecture 25B

Keywords: Inelastic neutron scattering, Scattering law, Fourier transform, Scattering cross-section, Correlation function, Phonon

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Earlier I had shown this tree to you, saying what we can see with neutrons in condensed matter regarding structure and dynamics. I have finished the structure part of the talk which is longer and possibly more used by people. Here, we measure intensity versus angle and when it comes to what range of structures, I mentioned crystal structures (at the beginning). I should also include liquid and amorphous diffractometer (LAD). These are all short-range structures. Crystal structures are at Å length scale (typically), liquid and amorphous diffraction also (study structure) in the Å range. Then I talked about SANS where you can see micelles, precipitates and inhomogeneities at typically about 10 nm to even micron size. Then lastly, I discussed neutron reflectometry: unpolarized/polarized specular and off-specular. With SANS, reflectometry, crystal diffraction, liquid and amorphous diffraction, we have completed the structure related studies from the tree.

I must mention here that because I was talking about structure which means spatial correlation either atom-atom in case of crystallography structure or inhomogeneities like micelles and others, so far, all these included coherent scattering lengths.

Now, we move forward to dynamics part, where we need to measure intensity of the scattered beam not only as a function of angle but also, we have to find out the energy of the scattered beam. So, we have $\hbar\omega = E_f - E_i$ which are the energy differences, $\boldsymbol{Q} = \boldsymbol{K_f} - \boldsymbol{K_i}$ which is the wave vector differences and we will be measuring what is known as scattering law $S(Q, \omega)$. For dynamics this scattering law $S(Q, \omega)$ is what we will be measuring. For dynamics not only Q but also energy of the scattered beam (is measured).

Naturally, the question arises what is the range of dynamics that we can study using neutrons. I just mentioned here we can measure phonons with typical time scales of 10^{-15} s, rotational diffusions (10^{-12} s) and very slow dynamics such as relaxation of polymer backbones (10^{-9} s). We can also measure the faster dynamics of molecular vibration and this will have. As we go higher in energy, the dynamics becomes faster because time scales are shorter which is inverse to the energy, the energy changes are larger. When I go to longer time scales then we go to energy differences which are smaller, so we are going to slower processes. Hence, slower processes have smaller energy transfer and faster processes have higher energy transfer. This is true not only in this case, we might extend it all the way up to nuclear physics where you do scattering experiments at very high energy transfer because they are looking at time scales which are significantly shorter than what you are doing here.
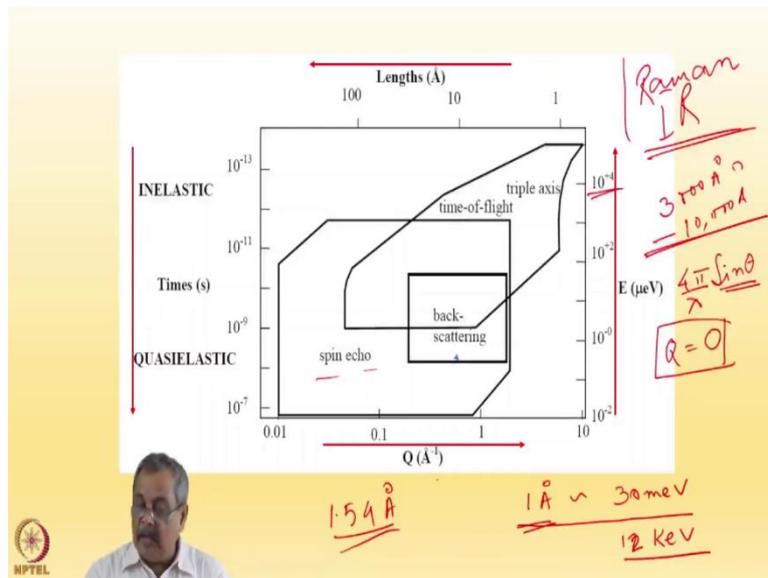
The discussion on inelastic neutron scattering for dynamics will target the questions on study of Q range and energy range. But before that, let me just bring it to your notice that in case of thermal neutrons the wavelength is around 1 Å and the energies around 30 meV and neutrons penetrate very deeply in material. You can span a very large part of the Q-ω space.

For example, if I am doing Raman scattering or infrared absorption spectroscopy, I can find out the vibrational energy levels of a molecule. But the fact remains that here the wavelengths are typically around 3000 Å to 10,000 Å of the impinging (light) radiation and using the relation, $Q = \frac{4\pi}{\lambda} \sin \theta$ we get that this kind of experiment with such large wavelengths, Q is close to 0. whereas in case of neutrons I can span a very large part of Q range. That is the advantage of neutron over x-rays (or light). In case of x-rays with wavelength around 1 Å, the energy (of the x-rays) is too large, it is around 12 keV (for ~1 Å x-rays). So there the problem is that we cannot span the energy range (mentioned earlier).

Hence, in case of neutrons I can span the Q values as well as energy ranges from sub μeV to 100s of meV using various spectrometers like back scattering, time of flight, triple axis, spin echo etc. I cannot describe all of them to you but I will target to explain to you the function of the major inelastic neutron spectrometers at Dhruva and at other parts in the world.

Master formula

$$\left(\frac{d^2\sigma}{d\Omega dE}\right)_{K\lambda \to K'\lambda'} = \frac{K'}{K}\left(\frac{m}{2\pi\hbar^2}\right)^2 \sum_{\lambda\sigma} p_\lambda p_\sigma \sum_{\lambda'\sigma'} \left|\langle K',\lambda'|\hat{V}|K,\lambda\rangle\right|^2 \delta(\hbar\omega + E_\lambda - E_{\lambda'})$$

We can bring in time through the δ function

$$\delta\left(\hbar\omega + E_\lambda - E_{\lambda'}\right) = \frac{1}{2\pi\hbar}\int_{-\infty}^{\infty} dt\, e^{-it(\hbar\omega + E_\lambda - E_{\lambda'})/\hbar}$$

Not assuming a δ fn potential

and $\hat{V}(r) = \sum_j \hat{V}_j(r - R_j)$ $\longrightarrow$ $\hat{V}_j(Q) = \int d^3r\, e^{iQ\cdot r}\hat{V}_j(r)$

Newton + System = Conservation

unpolarized

$$= \frac{1}{2\pi\hbar}\int_{-\infty}^{\infty} dt\, e^{-i\omega t} \sum_{\lambda,\lambda'} p_\lambda \langle\lambda\left|\sum_j \hat{V}_j^\dagger(Q) e^{-iQ\cdot R_j}\right|\lambda'\rangle \times$$

$$\langle\lambda'\left|\sum_{j'} \hat{V}_{j'}(Q)\exp(itE_{\lambda'}/\hbar)\, e^{iQ\cdot R_{j'}}\exp(-itE_\lambda)/\hbar\right|\lambda\rangle$$

Handwritten annotations on slide:

$E_\lambda \quad K$
$E_{\lambda'} \quad K'$

$P_\lambda \sim e^{-E_\lambda/KT}$

$$\left|\langle\lambda\right| \qquad \left.|\lambda'\rangle\right|^2$$

$$\langle\lambda| \qquad |\lambda'\rangle\langle\lambda'| \qquad \rangle$$

$$\frac{\langle\lambda'|\, V_{j'}\, e^{iQ\cdot R_j}\,|\lambda\rangle}{|\lambda\rangle = e^{iE_\lambda t/\hbar}\,|\lambda\rangle}$$

$$e^{iE_\lambda t/\hbar}\,|\lambda\rangle$$

$$= e^{iHt/\hbar}\,|\lambda\rangle$$

$$\boxed{H|\lambda\rangle = E_\lambda|\lambda\rangle}$$

$$\langle\lambda'|\, V_{j'}(Q)\, e^{iHt/\hbar}\, e^{iQ\cdot R_{j'}}\, e^{-iHt/\hbar}\,|\lambda\rangle$$

$$\hat{A}(t) = e^{iHt/\hbar}\,\langle A|\, e^{-iHt/\hbar}$$

Before I go into the discussion, I want to take you back to the general theory that I discussed with you several lectures back at the beginning of the course. Please remember the scattering law $\frac{d^2\sigma}{d\Omega dE}$ that is what we tend to measure and written in terms of an initial state $K\lambda$ and specified by energy and momentum $(E_\lambda K)$ and the final state (E_λ, K'), for diffraction experiment $\lambda' = \lambda$. We put a delta function $\delta(\hbar\omega + E_\lambda - E_{\lambda'})$ (in the expression for scattering law) stating that in any scattering process the total energy (neutron plus system) which we were studying should be conserved. So the conservation (of energy) comes from this delta function.

In next step, we wrote the delta function as an integral over time, $\delta(\hbar\omega + E_\lambda - E_{\lambda'}) = \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} dt e^{-it(\hbar\omega + E_\lambda - E_{\lambda'})/\hbar}$ this delta function is a Fourier transform from time to energy space, that is integration over time of $e^{-it(\hbar\omega + E_\lambda - E_{\lambda'})/\hbar}$. $\hbar\omega$ is neutron energy change part and $E_\lambda - E_{\lambda'}$ is for the energy difference in the system between E_λ and $E_{\lambda'}$ states. In general, I can write the potential also as a Fourier transform over Q space of the spatial potential $\hat{V}_j(r)$ the potential at the jth site.

Using these expressions, we can write $\frac{d^2\sigma}{d\Omega dE}$ as a Fourier transform over time to go to $S(Q,\omega)$.

$$\left(\frac{d^2\sigma}{d\Omega dE}\right)_{K\lambda \to K'\lambda'} = \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} dt e^{-i\omega t} \sum_{\lambda\lambda'} p_\lambda \langle\lambda|\sum_j \hat{V}_j^+(Q)e^{-iQR_j}|\lambda'\rangle \times \langle\lambda'|\sum_{j'} \hat{V}_{j'}(Q)e^{\frac{itE_{\lambda'}}{\hbar}} e^{iQR_{j'}} e^{-itE_\lambda/\hbar}|\lambda\rangle$$

Here Fourier transfer over time is of a function which is a sum over the initial states(λ) and the final states (λ') : p_λ being the probability of the initial state which is $e^{-iE_\lambda/kT}$ for scattering experiments done at temperature kT. Second term on the R.H.S. of the above equation comes from the fact that the terms of form $|\langle\lambda|...|\lambda'\rangle|^2$ can be broken into $\langle\lambda|...|\lambda'\rangle \times \langle\lambda'|...|\lambda\rangle$ and we know that for a stationary state we can write, $|\lambda(t)\rangle = e^{-itE_\lambda/\hbar}|\lambda\rangle$ which gives time dependence. For an eigen function, $H|\lambda\rangle = E_\lambda|\lambda\rangle$, so we can use, $e^{-itE_\lambda/\hbar}|\lambda\rangle = e^{-itH/\hbar}|\lambda\rangle$. Hence, we can write, $\langle\lambda'|\sum_{j'} \hat{V}_{j'}(Q)e^{itE_{\lambda'}/\hbar}e^{-iQR_{j'}}e^{-itE_\lambda/\hbar}|\lambda\rangle$ as $\langle\lambda'|\sum_{j'} \hat{V}_{j'}(Q)e^{itH/\hbar}e^{iQR_{j'}}e^{-itH/\hbar}|\lambda\rangle$. Now, we know that for any quantum mechanical operator $\hat{A}(t)$ time dependence is given by $e^{itH/\hbar}|A|e^{-itH/\hbar}$. In our case, the operator is position operator $R_{j'}$. With this, we have

$$\frac{d^2\sigma}{d\Omega dE} = \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} dt e^{-i\omega t} \sum_{jj'} \overline{\hat{V}_j^+ \hat{V}_{j'}} \times \sum_\lambda \frac{e^{-\beta E_\lambda}}{Z} \langle\lambda|\sum_{jj'} e^{-iQR_j(0)} e^{iQR_{j'}(t)}|\lambda\rangle$$

$$p_\lambda = \frac{e^{-\beta E_\lambda}}{Z}; \quad \sum p_\lambda = 1$$

$$e^{-iEt/\hbar}\varphi = e^{-iHt/\hbar}\varphi; \text{ if } \varphi \text{ is an eigenfunction of } H$$

$$< \lambda^/ \left| \sum_{j^/} \widehat{V}_{j^/} e^{iE_\lambda t/\hbar} e^{iQ.R_{j^/}} e^{-iE_\lambda t/\hbar} \right| \lambda > =$$

$$< \lambda^/ \left| \sum_{j^/} \widehat{V}_{j^/}(Q) e^{itH/\hbar} e^{iQ.R_{j^/}} e^{-itH/\hbar} \right| \lambda >$$

I have plugged-in time dependence in the operator

$$\frac{d^2\sigma}{d\Omega dE^/} = \frac{1}{2\pi\hbar}\int_{-\infty}^{\infty} dt e^{-i\omega t} \sum_{jj^/} \widehat{V}_j^\dagger(Q)\widehat{V}_{j^/}(Q) \times \sum_\lambda exp(-\beta E_\lambda)/Z < \lambda \left| \sum_{jj^/} e^{-iQ.R_j(0)} e^{iQ.R_{j^/}(t)} \right| \lambda >$$

$$\frac{d^2\sigma}{d\Omega dE^/} = N\frac{K^/}{K}\left(\frac{m}{2\pi\hbar}\right)^2 \overline{V^2(Q)} \, S(Q,\omega)$$

$$S(Q,\omega) = \frac{1}{2\pi\hbar N}\int_{-\infty}^{\infty} dt \, exp(-i\omega t)\sum_{jj^/} < exp\left(-iQ.\widehat{R}_j(0)\right) exp\left(iQ.\widehat{R}_{j^/}(t)\right) >$$

Contains the dynamics of the system

So, from this expression, we can say that to get the scattering law we need the time correlation of the position operators. That means given a particle is at a point R at time 0, $R(0)$, where is it (or another particle) at time t or $R(t)$?

As a simple example, let us say if a particle is moving in a linear path with a velocity $v = u + at$. In this problem, I can find out the velocity at a particular time and hence position at a particular time. But for many problems (and ensemble of particles) we have to take recourse to various kinds of modeling to get this correlation function because this correlation function and its Fourier transform will directly give me the $S(Q,\omega)$.

So now I write differential scattering cross-section $\frac{d^2\sigma}{d\Omega dE}$ in terms of scattering law in $S(Q,\omega)$ and this scattering law is given by the time Fourier transform of the correlation function and its ensemble average,

$$S(Q,\omega) = \frac{1}{2\pi\hbar N} \int_{-\infty}^{\infty} dt\, e^{-i\omega t} \sum_{jj'} \langle e^{-iQ\widehat{R}_j(0)} e^{iQ\widehat{R}_{j'}(t)} \rangle$$

Here angular brackets give me the ensemble average and this contains the dynamics of the system. So, we can study all dynamics in the system provided my energy range (experimental) allows that and I know some way of finding out $R_j(0)$ and $R_{j'}(t)$. Next part will be explaining how do we calculate such correlations.

As I mentioned earlier and let me repeat it again that if I consider this is in Q space then the second term here can be written as a Fourier transform of a (space-time) correlation function $G(r,t)$ in real space, so that we have relation,

$$S(Q,\omega) = \frac{1}{2\pi\hbar N}\int_0^\infty dt\, e^{-i\omega t}\int d^3 r\, e^{i\vec{Q}.\vec{r}} G(\vec{r},t)$$

Now a function in the real space-time $G(\vec{r},t)$ goes to an intermediate scattering function $I(Q,t)$ which it is Fourier transformed from 'r' to 'Q' and this goes to $S(Q,\omega)$ after Fourier transformation to 'ω' from 't'.

This is a double Fourier transform of the pair correlation function, $G(\vec{r}, t)$. So, ultimately, we have landed up at $G(\vec{r}, t)$. If a particle is at origin at time $t=0$ then correlation function defines the probability of finding the same particle (self-correlation) or another particle (pair-correlation) at time t at a position r.

But the time part also includes the dynamics and thus $G(\vec{r}, t)$ gives me dynamics of the system. If I take out the time then it becomes only a structural work (determination of structure) and if I include time then I have to find out how to get $G(\vec{r}, t)$ for the system.

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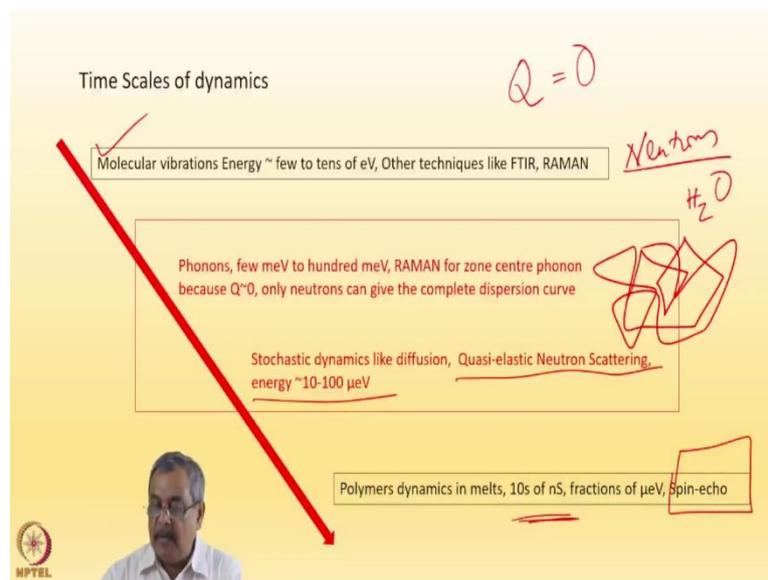
With this brief introduction to how we included time and dynamics in our formalism, I will take you to various time scales of dynamics which I also discussed briefly earlier. For molecular vibrations with few to tens of electron volts energy, other techniques like FTIR, Raman can be used but not for all Q values or not for all kinds of spatial correlation because Q range gives me spatial correlations whereas these above techniques study the system at close to $Q = 0$. These molecular vibrations can also be studied using neutrons.
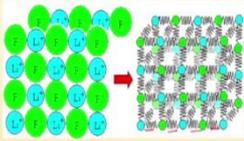
Next let us talk about phonons. Phonons are of energy few milli electron volts to hundreds of milli electron volts, Raman scattering can be used but again at $\sim Q = 0$ and because for phonons we use the Brillouin zone for finding out the dispersion relation of phonons in them so we can do Raman scattering for zone center phonons only. Whereas for phonon dispersion over the entire Brillouin zone we need to go to neutrons.

Then there is something called stochastic dynamics. What are stochastic dynamics? The best example is a liquid, let us say in water, we consider one H_2O molecule and how it moves around. Stochastic dynamics like diffusion it can be studied using quasi-elastic neutron scattering which I will be discussing. These two techniques Inelastic scattering (phonons) and Quasi-elastic Neutron Scattering (stochastic/diffusion) I will be discussing initially. Then I will briefly touch upon molecular vibration and also a technique known as spin echo which is I should say one of the novel techniques to understand very slow dynamics. Tens of nanosecond time scale e.g. polymer chains moving in a melt and that kind of dynamics can be studied using spin echo.

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Now first let me discuss with you the phonons. You must be familiar with the fact that phonons are collective quantized oscillation of atoms in a crystalline material.

It is a lithium fluoride crystal and here we assume a spring between the atoms of the constituent crystal. It has to be a crystallographic structure when we talk about phonons and we consider that the atoms are bound by springs with each other.

Now I can write down the equation of motion for the sth atom in the system in terms of the elastic constant

$$m\frac{d^2u_s}{dt^2} = \sum_p C_p\left(u_{s+p} - u_s\right)$$

Here, $u_{s+p} - u_s$ is the relative displacement which is multiplied by the spring constant and summed over all the neighbors resulting in equation of motion for the sth atom for a monoatomic crystal.

Here, I assume two things: first one is that its time dependent is given by $e^{i\omega t}$ which means that there are vibrations which are quantized with energy $\hbar\omega$. If I consider a time dependence of $e^{i\omega t}$ then the above equation reduces to the equation in terms of displacement and ω^2, $-m\omega^2 u_s = \sum_p C_p (u_{s+p} - u_s)$, and also I assume a wave-like solution for the displacement of the atoms in the lattice. Wave-like nature of this displacement is the corner-stone of phonons in solid. So, the displacement of $(s+p)^{th}$ atom $u_{s+p} = ue^{i(s+p)Ka}$, where u is a constant and K is a (phonon) wave vector, a is the lattice spacing. Wave vector here is for the periodic spatial variation of this atomic displacement and this we have to find out.

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Substituting this in above equation we get, $-m\omega^2 u e^{isKa} = \sum_p C_p u\left(e^{i(s+p)Ka} - e^{isKa}\right)$ or $m\omega^2 = -\sum_p C_p\left(e^{ipKa} - 1\right)$. This is after summing over all neighbors. Now based on translational symmetry present in a crystal we get $C_p = C_{-p}$ that means if atoms are same distance away the spring constant remains same so I can break it up into, instead of summing over all atoms, I can do it over $p>0$ that we have relation reduced to, $m\omega^2 = -\sum_{p>0} C_p\left(e^{ipKa} + e^{-ipKa} - 2\right)$ or $\omega^2 = \frac{2}{m}\sum_{p>0} C_p(1 - \cos pKa)$

Now for nearest neighbor, instead of C_p we have C_1 and that gives me a solution which is,

$$\omega = \left[\frac{4C_1}{m}\right]^{1/2} \left|\sin\frac{Ka}{2}\right|$$

It is a sinusoidal curve relating ω and K. This is the derivation (of phonon dispersion) for a monatomic crystal with only nearest neighbor interaction. You can see that we have a wave like solution or dispersion relations following sine wave. Now question is that what sort of displacement we are talking about?