Lecture 2.
Phonon Green's function. Mössbauer Effect and Neutron Scattering

Now we know the frequency spectrum of the lattice vibrations and corresponding eigenvectors. Our next step is to study lattice responses to (local, sudden) perturbation. The central place in these studies is occupied by the correlation function :

$$K_{jj'}^{\alpha\beta}(\mathbf{n}-\mathbf{n}', t-t') = \langle \mathbf{u}_j^{\alpha}(\mathbf{n},t)\mathbf{u}_j'^{\beta}(\mathbf{n}',t')\rangle, \quad \langle \hat{A}\rangle = \frac{\mathrm{Tr}\ \hat{A}\ e^{-\beta\mathcal{H}}}{\mathrm{Tr}\ e^{-\beta\mathcal{H}}}, \tag{1}$$

which is closely connected with the Green's function of the classical equation of motion. In order to clarify this connection and many other things, we concentrate first on the case of a single linear oscillator.

Green's Function of a Linear Oscillator

A linear oscillator has the Hamiltonian

$$\mathcal{H}(x,p) = \frac{p^2}{2m} + \frac{m\Omega^2 x^2}{2}, \tag{2}$$

and the Lagrangian

$$\mathcal{L}(x,\dot{x}) = [p\dot{x} - \mathcal{H}(x,p)]_{\dot{x}=\partial\mathcal{H}/\partial p} = \frac{m\dot{x}^2}{2} - \frac{m\Omega^2 x^2}{2}. \tag{3}$$

The classical equation of motion has the following form:

$$m\ddot{x} + m\Omega^2 x = 0. \tag{4}$$

We can introduce the Green's function according to the equation:

$$\left\{ \frac{d^2}{dt^2} + \Omega^2 \right\} G(t - t') = \delta(t - t') \tag{5}$$

which can be solved by the means of the Fourier transform

$$G(t) = \int_{-\infty}^{+\infty} \frac{d\omega}{2\pi}\, G(\omega)\; e^{-i\omega t}, \quad G(\omega) = \frac{1}{\Omega^2 - \omega^2}. \tag{6}$$

We can see from Eq (6) that the pole of the Green's function occurs at $\omega = \pm\Omega$. To make the Fourier transform in Eq (6) legitimate, we must remove the pole from the axis, or, alternatively, to shift the contour of integration. This leads to the introduction of two functions:

$$G^{R(A)}(\omega) \;=\; \frac{1}{\Omega^2 - \omega^2 \pm 2i\delta\;\omega}. \tag{7}$$

$$G^R(t) = \;\theta(t)\;\frac{\sin\Omega t}{\Omega}\;, \qquad\qquad G^A(t) = -\theta(-t)\;\frac{\sin\Omega t}{\Omega}\;, \tag{8}$$

which are called the retarded and advanced Green's functions and are analytic functions of the complex variable ω in the upper (lower) half-plane respectively.
Consider now a zero-temperature correlator

$$\mathcal{G}^R(t) = -\frac{i\hbar}{m}\theta(t)\langle\, \hat{x}(t)\hat{x}(0) - \hat{x}(0)\hat{x}(t)\,\rangle_0,\; \langle\, A\,\rangle_0 =< 0|\,\hat{A}\,|0> . \tag{9}$$

Since

$$\hat{x}(t) = \sqrt{\frac{\hbar}{2m\Omega}}\left[\hat{a}e^{-i\Omega t} + \hat{a}^+ e^{i\Omega t}\right],$$

this correlator is

$$\mathcal{G}^R(t) = -\frac{\hbar^2 \sin \Omega t}{m^2 \Omega}\theta(t)\langle \hat{a}\hat{a}^+ - \hat{a}^+\hat{a}\rangle_0 = -\frac{\hbar^2 \sin \Omega t}{m^2 \Omega}\theta(t) = -\,\frac{\hbar^2}{m^2} G^R(t). \tag{10}$$

Thus, we have found the connection between the Green's function G of the classical equation of motion and the zero-temperature correlator

$$\mathcal{G}(t) = -\frac{i\hbar}{m}\langle \hat{T}\left\{x(t)x(0)\right\}\rangle_0,\ \ \hat{T}\left\{A(t)B(0)\right\} = \begin{cases} A(t)B(0),\ t>0; \\ B(0)A(t),\ t<0. \end{cases} \tag{11}$$

Since

$$\mathcal{G}(t) = \mathcal{G}^R(t) + \mathcal{G}^A(t),$$

we obtain the relation

$$\mathcal{G}(t) = -\,\frac{\hbar^2}{m^2}\,\left\{G^R(t) + G^A(t)\right\}. \tag{12}$$

When we need to calculate the thermal average correlation, we have to recall that the density matrix $\rho(n)$ of the oscillator as a function of the occupation numbers n has the form

$$\rho(n) = \frac{e^{-\beta\hbar\Omega n}}{\sum_{k=0}^{\infty} e^{-\beta\hbar\Omega k}} = e^{-\beta\hbar\Omega n}\left[1 - e^{-\beta\hbar\Omega}\right] \tag{13}$$

This gives the Planck distribution for the mean occupation number $\langle n\rangle$:

$$\langle n\rangle = \sum_{n=0}^{\infty} n\ \rho(n) = \frac{1}{e^{\beta\hbar\Omega} - 1}, \quad \langle n\rangle + \frac{1}{2} = \frac{1}{2}\ \coth\frac{\hbar\Omega}{2T}. \tag{14}$$

The mean square of the oscillations is

$$\langle x^2\rangle = \frac{\hbar}{2m\Omega}\sum_{n=0}^{\infty}(2n+1)\,\rho(n) = \frac{\hbar}{2m\Omega}\ \coth\frac{\hbar\Omega}{2T} = \frac{2}{m}T\sum_{n=-\infty}^{+\infty}\frac{1}{\Omega^2 + \omega_n^2}, \tag{15}$$

where a so-called Matsubara frequency $\omega_n = 2\pi nT/\hbar$ is introduced. Using this notation, Eq (15) can be rewritten in the form:

$$\langle x^2 \rangle = \frac{2}{m} T \sum_{n=-\infty}^{+\infty} G(-i\omega_n). \tag{16}$$

Phonon Green's Function

The phonon Green's function $G_{jj'}(\mathbf{n}, \mathbf{n}'; t, t')$ can be understood as the Green's function of the Schrödinger's equation for the wave function of displacements $\mathbf{u}_j(\mathbf{n}, t)$ at all nuclear sites. In exactly the same way as in the previous section, the phonon Green's function can be expressed through a thermal average. For the given Matsubara frequency ω_n and quasi-momentum $\mathbf{q}$, the Green's function $G(\omega_n, \mathbf{q})$ is:

$$\begin{aligned} G_{jj'}^{\alpha\beta}(\omega_n, \mathbf{q}) &= \langle u_j^{\alpha}(\mathbf{n}, \tau) u_j'^{\alpha}(\mathbf{n}', \tau') \rangle_{\omega_n\ \mathbf{q}} = \\ &= \sum_s \frac{\hbar}{\omega_s(\mathbf{q})\sqrt{M_j M_j'}}\ e_j^{\alpha}(\mathbf{q}, s)[e_j'^{\beta}(\mathbf{q}, s)]^* G_s(\omega_n, \mathbf{q}); \\ G_s(\omega_n, \mathbf{q}) &= \frac{1}{\omega_n^2 + \omega^2(\mathbf{q})}. \end{aligned} \tag{17}$$

The analytic continuation from the positive (negative) integer values of ω_n to the imaginary axis, $\omega_n \to i\omega \pm \delta$, generates the retarded (advanced) phonon Green's function. The summation over ω_n gives the thermodynamic mean square of fluctuations $\langle \mathbf{u}(\mathbf{q})\mathbf{u}(-\mathbf{q}) \rangle$.

Mössbauer effect

Solid state research employs experimental methods of other branches of physics: high-frequency spectroscopy, nuclear physics, electron and x-ray diffractometry, etc. The γ-ray resonance spectroscopy (the Mössbauer effect) is one of most effective ways of diagnostics. An excited nucleus at one of the lattice sites undergoes a transition with the emission of monochromatic γ-rays of energy E_γ. Another nucleus, being in the ground state, absorbs these rays. If either the emitter or absorber has a special local atomic surrounding, the latter could shift and split the emission (absorption) line and destroy the resonance. Moving the sample with a certain velocity $\mathbf{v}$, the one can restore (through the Doppler effect) the condition of the resonance and realize in this way the local field spectroscopy.
An obstacle on this way is caused by the recoil. Indeed, if a classical nucleus of mass M emits a γ-quantum of energy E_γ, it loses the momentum $p_\gamma = E_\gamma/c$ and, therefore, loses the recoil energy $E_R = E_\gamma^2/2Mc^2$, which destroys the resonance condition. Fortunately, quantum mechanics restricts simultaneous fixation of both the position and the momentum of the nucleus. Therefore, when a given nucleus experiences a recoil, being in the crystalline lattice, it does not loose a fixed momentum or energy, but emits (absorbs) a certain number of phonons. The probability of emitting no phonons (recoil-less γ-ray emission) is finite. This recoil-less process (which secures the condition of resonance) is called the Mössbauer effect. Our goal in this section will be to find out the probability of this process.

Let the nucleus is be at the atomic site $\mathbf{n}, j$ and emit a γ-quantum with the wave vector $\mathbf{k}$. Then the amplitude of the process is

$$A \exp\left[i\mathbf{k}\mathbf{u}\right],$$

where $\mathbf{u}$ is an operator in the space of occupation numbers of phonons. The probability of the recoil-less decay W is equal, therefore, to

$$W = |A|^2 \sum_i \rho_i | < i|e^{i\mathbf{k}\mathbf{u}}|i > |^2 = W_0 \; w, \tag{18}$$

where ρ_i denotes the density matrix, W_0 stands for the decay probability in vacuum, and the Debye-Waller suppression factor w is equal to

$$w = exp\left[-k^\alpha k^\beta \langle u^\alpha u^\beta \rangle\right]. \tag{19}$$

Since

$$\langle u_j^\alpha u_j \beta \rangle = \frac{\hbar}{M_j} \sum_{s,\mathbf{q}} e_j^\alpha(s,\mathbf{q})[e_j^\beta(s,\mathbf{q})]^* \frac{n(s,\mathbf{q}) + 1/2}{\omega_s(\mathbf{q})}$$

Eq (19) describes all the most important features of the effect:

- the Mössbauer effect has a finite probability, which is maximal at zero temperature
$$w \sim \exp\left[-\frac{E_R}{\hbar}\langle\frac{1}{\omega}\rangle\right].$$
- At high temperature $T \geq \omega_D$ the effect is suppressed and becomes strongly temperature dependent:
$$w \sim \exp\left[-\frac{2E_R T}{\hbar^2}\langle\frac{1}{\omega^2}\rangle\right].$$

- The effect is isotropic in cubic crystals and has an anisotropy in anisotropic ones: the suppression factor is larger when the γ-ray emission is observed along those crystallographic directions, which coincide with the polarization of the most rigid modes.

In practice, the radio-active nucleus is often the nucleus of an impurity. Since the vibration of impurities involves local modes (see problems), the probability of the Mössbauer effect on these nuclei can have peculiar temperature dependence, specific for the given host and impurity.