Physics 460/560 Lecture 6

- Anharmonic effects

$r_n = r_n^{(0)} + x_m$

$$U(\{r_n\}) = U_0 + \frac{1}{2}\sum_{n,m} \frac{\partial^2 U}{\partial r_n \partial r_m}\Big|_{\{r_n^{(0)}\}} x_n x_m$$

$$+ \frac{1}{3!}\sum_{n,m,\ell} \underbrace{\frac{\partial^3 U}{\partial r_n \partial r_m \partial r_\ell}\Big|_{\{r_n^{(0)}\}}}_{V_{nm\ell}} x_n x_m x_\ell$$

$$+ \cdots$$

$$x_n = \frac{1}{\sqrt{L}} \sum_k Q_k e^{ikna}$$ → insert in 3rd order term:

$$\sum_{n,m,\ell} V_{nm\ell}\, x_n x_m x_\ell = L^{-3/2} \sum_{kqp} Q_k Q_q Q_p \sum_{nm\ell} V_{nm\ell}\, e^{i(kn+qm+p\ell)a}$$

what do we know about $V_{nm\ell}$?

Translational invariance

$$\Rightarrow V_{nm\ell} = V(n-\ell, m-\ell)$$

$$\frac{1}{L^{3/2}}\sum_{nm\ell} V(n-\ell, m-\ell)\, e^{i(kn+gm+p\ell)a}$$

$$= \frac{1}{L^{3/2}}\sum_{nm\ell} V(n-\ell, m-\ell)\, e^{i[k(n-\ell)+g(m-\ell) + (k+g+p)\ell]a}$$

[Let $n' = n-\ell$, $m' = m-\ell$:]

$$= \frac{1}{\sqrt{L}}\sum_{n'm'} V(n', m')\, e^{i(kn'+gm')a}\; \underbrace{\frac{1}{L}\sum_{\ell} e^{i(k+g+p)\ell a}}_{\delta_{p,-k-g}}$$

Define $\frac{1}{\sqrt{L}}\sum_{n'm'} V(n', m')\, e^{i(kn'+gm')a} = \tilde{V}(k,g)$

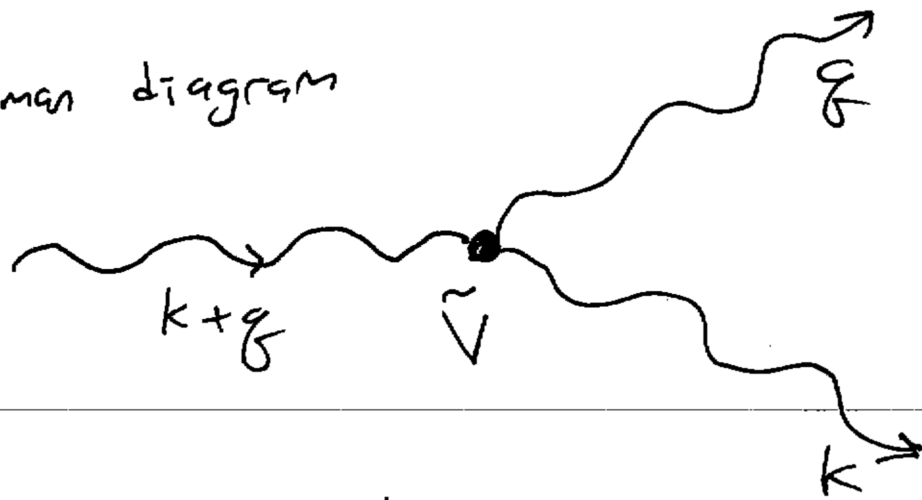
The cubic term in U becomes

$$\frac{1}{3!}\sum_{k,g} Q_k Q_g Q_{-k-g}\, \tilde{V}(k,g).$$

Since $Q_k = \sqrt{\frac{\hbar}{2m\omega_k}}\,(a_k + a_{-k}^{+})$, this term induces processes such as:

$$a_k^{+} a_q^{+} a_{k+q}$$

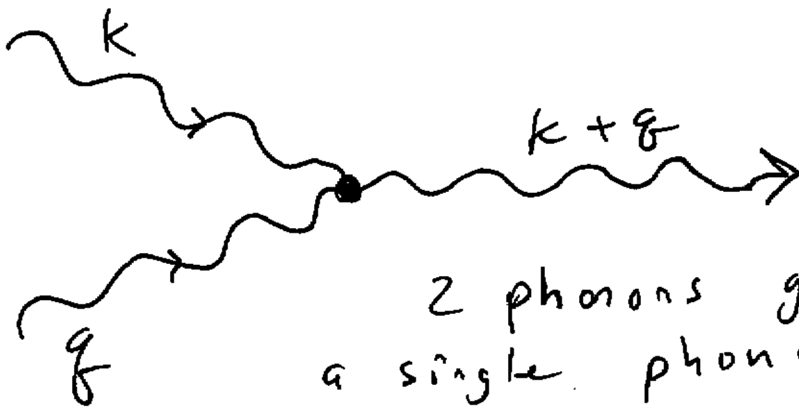
Feynman diagram



One phonon decays into two, conserving crystal momentum,

or

$$a_{k+q}^{+} a_k a_q$$



2 phonons generate a single phonon, etc.

Anharmonic effects are most important in crystals made of very light ions, since the ions vibrate with larger amplitudes.

- <u>3D crystal</u> e.g. simple cubic

Equilibrium positions of atoms/ions:

$$\vec{R}_{\vec{n}} = \vec{n}\, a \qquad \vec{n} = (n_x, n_y, n_z)$$

Actual positions:

$$\vec{r}_{\vec{n}} = \vec{R}_{\vec{n}} + \vec{x}_{\vec{n}}$$

$$U(\{\vec{r}_{\vec{n}}\}) \simeq U(\{\vec{R}_{\vec{n}}\}) + \frac{1}{2} \sum_{\vec{n},\vec{m}} \sum_{\mu\nu=1}^{3}$$

$$\times\, x_{\vec{n}}^{(\mu)} \left(C_{\vec{n}\vec{m}}\right)_{\mu\nu} x_{\vec{m}}^{(\nu)},$$

where

$$\left(C_{\vec{n}\vec{m}}\right)_{\mu\nu} = \left.\frac{\partial^2 U}{\partial r_{\vec{n}}^{(\mu)} \partial r_{\vec{m}}^{(\nu)}}\right|_{\{\vec{R}_{\vec{n}}\}}$$

- What symmetries does $(C_{\vec{n}\vec{m}})_{\mu\nu}$ possess?

1. Translational invariance:

$$(C_{\vec{n}\vec{m}})_{\mu\nu} = (C(\vec{n}-\vec{m}))_{\mu\nu}$$

2. Inversion symmetry:

$$(C(\vec{n}))_{\mu\nu} = (C(-\vec{n}))_{\mu\nu}$$

3. $(C(\vec{n}))_{\mu\nu} = (C(-\vec{n}))_{\nu\mu}$

This follows from the definition of C as the matrix of 2nd derivatives of U.

2. + 3. $\Rightarrow$ $(C(\vec{n}))_{\mu\nu} = (C(\vec{n}))_{\nu\mu}$

Let us write $(C(\vec{n}))_{\mu\nu} = C_{\mu\nu}(\vec{n})$.

The last symmetry implies that $C_{\mu\nu}$ is a real symmetric matrix.

4. $U(\{\vec{r}_{\vec{n}}+\vec{d}\}) = U(\{\vec{r}_{\vec{n}}\})$

The lattice potential is invariant under an overall translation $\vec{d}$.

$$\Rightarrow \quad 0 = \frac{1}{2}\sum_{\vec{n},\vec{m}}\sum_{\mu\nu} d_\mu \, C_{\mu\nu}(\vec{n}-\vec{m})\, d_\nu$$

$$0 = \sum_{\mu\nu} d_\mu d_\nu \underbrace{\sum_{\vec{n},\vec{m}} C_{\mu\nu}(\vec{n}-\vec{m})}_{N\sum_{\vec{n}} C_{\mu\nu}(\vec{n})}$$

$$\Rightarrow \quad \boxed{\sum_{\vec{n}} C_{\mu\nu}(\vec{n}) = 0}$$

The Hamiltonian is

$$H = \sum_{\vec{n}} \frac{\vec{p}_{\vec{n}}^{\,2}}{2m} + \frac{1}{2} \sum_{\vec{n},\vec{m}} x_{\vec{n}}^{(\mu)} C_{\mu\nu}(\vec{n}-\vec{m})\, x_{\vec{m}}^{(\nu)} .$$

Hamilton's equations are

$$\dot{x}_{\vec{n}}^{(\mu)} = \frac{\partial H}{\partial p_{\vec{n}}^{(\mu)}} = \frac{p_{\vec{n}}^{(\mu)}}{m}$$

$$\dot{p}_{\vec{n}}^{(\mu)} = -\frac{\partial H}{\partial x_{\vec{n}}^{(\mu)}} = \sum_{\vec{m}} \sum_{\nu} C_{\mu\nu}(\vec{n}-\vec{m})\, x_{\vec{m}}^{(\nu)}$$

Equation of motion:

$$m \ddot{x}_{\vec{n}}^{(\mu)} = - \sum_{\vec{m}} \sum_{\nu=1}^{3} C_{\mu\nu}(\vec{n}-\vec{m})\, x_{\vec{m}}^{(\nu)}$$

Ansatz: travelling wave

$$\vec{x}_{\vec{n}}(t) = \vec{\epsilon}\, e^{i\left(\vec{k}\cdot\vec{n}a - \omega t\right)}$$

$$M\omega^2 \epsilon^{(\mu)} = \sum_{\vec{m}} \sum_{\nu=1}^{3} \left\{ C_{\mu\nu}(\vec{n}-\vec{m})\, \epsilon^{(\nu)} \times e^{i\vec{k}\cdot(\vec{m}-\vec{n})a} \right\}$$

Let $\sum_{\vec{n}} C_{\mu\nu}(\vec{n}) e^{i\vec{k}\cdot\vec{n}a} \equiv \tilde{C}_{\mu\nu}(\vec{k})$.

Then

$$M\omega^2 \epsilon^{(\mu)} = \sum_{\nu=1}^{3} \tilde{C}_{\mu\nu}(\vec{k})\, \epsilon^{(\nu)}.$$

A solution exists if

$$\det\{ \underbrace{\tilde{C}(\vec{k})}_{3\times 3 \text{ matrix}} - M\omega^2 \mathbb{1} \} = 0$$

$\tilde{C}(\vec{k})$ is a real symmetric 3×3 matrix, since $C_{\mu\nu}(\vec{n}) = C_{\mu\nu}(-\vec{n})$. It follows that $\tilde{C}(\vec{k})$ has 3 real eigenvectors $\vec{\epsilon}_1, \vec{\epsilon}_2, \vec{\epsilon}_3$ which satisfy

$$\tilde{C}(\vec{k})\,\vec{\epsilon}_s = m\,\omega_s^2(\vec{k})\,\vec{\epsilon}_s$$

and can be normalized so that

$$\vec{\epsilon}_s(\vec{k})\cdot\vec{\epsilon}_r(\vec{k}) = \delta_{sr}\,.$$

- What is the frequency $\omega_s(\vec{k})$ for long wavelengths $(|\vec{k}a| \ll 1)$?

$$C_{\mu\nu}(\vec{k}) = \sum_{\vec{n}} C_{\mu\nu}(\vec{n})\, e^{i\vec{k}\cdot\vec{n}a}$$

$$= \frac{1}{2}\sum_{\vec{n}} C_{\mu\nu}(\vec{n})\left[e^{i\vec{k}\cdot\vec{n}a} + e^{-i\vec{k}\cdot\vec{n}a} - 2\right]$$

$$= \sum_{\vec{n}} C_{\mu\nu}(\vec{n})\left[\cos(\vec{k}\cdot\vec{n}a) - 1\right]$$

$$= -2\sum_{\vec{n}} C_{\mu\nu}(\vec{n})\,\sin^2\!\left(\frac{\vec{k}\cdot\vec{n}a}{2}\right)$$

$$= -2\sum_{\vec{R}} C_{\mu\nu}(\vec{R})\,\sin^2\!\left(\frac{\vec{k}\cdot\vec{R}}{2}\right)$$

Here we have used symmetries 2. and 4. For $|\vec{k}a| \ll 1$, we can approximate

$$-2 \sum_{\vec{R}} C_{\mu\nu}(\vec{R}) \sin^2\left(\frac{\vec{k}\cdot\vec{R}}{2}\right) \simeq$$

$$-\frac{k^2}{2} \sum_{\vec{R}} (\hat{k}\cdot\vec{R})^2 C_{\mu\nu}(\vec{R}),$$

provided $C_{\mu\nu}(\vec{R})$ falls off rapidly enough for large $|\vec{R}|$. Consequently, we have

$$\omega_s(\vec{k}) = c_s(\vec{k})\, k,$$

where $c_s^2(\vec{k})$ are the eigenvalues of the matrix

$$-\frac{1}{2M} \sum_{\vec{R}} (\hat{k}\cdot\vec{R})^2 C_{\mu\nu}(\vec{R}).$$

Thus the dispersion relation is linear for long wavelengths. In general, the speed of sound c_s will depend on the direction of propagation $\hat{k}$ as well as on the branch index s. It is straightforward to extend this result for a simple cubic lattice to any Bravais lattice.

$\Rightarrow$ All phonon modes in a monatomic Bravais lattice are acoustic, i.e., $\omega(\vec{k}) \propto k$ for $ka \ll 1$.

Quite generally, ω^2 is an eigenvalue of $\frac{1}{m}\tilde{C}(\vec{k})$. One can show that if the quadratic form

$$\frac{1}{2}\sum_{\vec{n}\vec{m}}\sum_{\mu\nu} x_{\vec{n}}^{(\mu)}\, C_{\mu\nu}(\vec{n}-\vec{m})\, x_{\vec{m}}^{(\nu)} > 0,$$

$\forall\ \vec{x}_{\vec{n}}$, then all eigenvalues of $\tilde{C}(\vec{k})$ are positive, so that ω is real. A negative eigenvalue of $\tilde{C}(\vec{k})$ implies an instability of the lattice, so we would not have expanded around the correct equilibrium configuration.

• The 3 branches

The 3 polarization vectors $\vec{\epsilon}_s(\vec{k})$ are mutually orthogonal, but their relation to the direction of propagation $\hat{k}$ is in general nontrivial.

In an isotropic medium, there is one longitudinal mode with $\vec{\epsilon} \parallel \hat{k}$ and two degenerate transverse modes with $\vec{\epsilon} \perp \hat{k}$. This is also true for waves travelling along certain symmetry axes in the simple cubic lattice.

• Quantum spectrum

The energy spectrum of the lattice is

$$E(\{n_{\vec{k}s}\}) = \sum_{s=1}^{3} \sum_{\vec{k}\in BZ} \hbar\omega_s(\vec{k})\left\{n_{\vec{k}s} + \tfrac{1}{2}\right\}$$

where $n_{\vec{k}s} = 0, 1, 2, \ldots \infty.$

We will not go through the trouble of deriving this for the 3D case. It is a special property of purely quadratic Hamiltonians that their normal mode frequencies are identical classically and quantum mechanically.