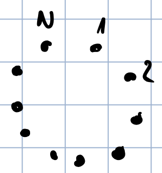
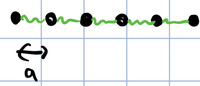
Previous lecture:

Physics of lattice vibrations (ions only)

"Prototype crystal" $d=1$ (more general case later on)





$L = Na$

• Periodic B.C

R_j - position of the j-th atom

$R_{N+1} = R_1$

$N \gg 1 \qquad N \approx 10^{23}$

Hamiltonian

- $T = \sum_{j=1}^{N} \frac{p_j^2}{2m}$
- $V = \sum_{j=1}^{N} \frac{k_s}{2}\left(R_{j+1} - R_j - a\right)^2$ (coupled harmonic oscillators)

$$H = \sum_{j=1}^{N}\left(\frac{p_j^2}{2m} + \frac{k_s}{2}\left(R_{j+1} - R_j - a\right)^2\right)$$

→ only nearest-neighbours interact.
→ small deviations from eq. positions.

$$R_j = \underbrace{\bar{R}_j}_{=\, ja} + \phi_j$$

$$\omega^2 := \frac{k_s}{m}$$

$$H = \sum_{j=1}^{N}\left(\frac{p_j^2}{2m} + \frac{m\omega^2}{2}\left(\phi_{j+1} - \phi_j\right)^2\right)$$

Fourier transform (discrete)

$$\begin{cases} \phi_j = \frac{1}{\sqrt{N}} \sum_q e^{iqR_j} \phi_q \\ p_j = \frac{1}{\sqrt{N}} \sum_q e^{iqR_j} p_q \end{cases}$$

$R_j = aj$!

$q \in \left]-\frac{\pi}{a}, \frac{\pi}{a}\right]$ (PBC)

$$H = \sum_{q \neq 0}\left(\frac{1}{2m} p_q p_{-q} + \frac{m\omega_q^2}{2} \phi_q \phi_{-q}\right) + \underbrace{\frac{1}{2m} p_0^2}_{H_0}$$

$$\begin{cases} a_q := \sqrt{\frac{m\omega_q}{2\hbar}}\left(\phi_q + \frac{i}{m\omega_q} p_q\right) \\ a_q^{+} := \sqrt{\frac{m\omega_q}{2\hbar}}\left(\phi_{-q} - \frac{i}{m\omega_q} p_{-q}\right) \end{cases}$$

$$H = H_0 + \sum_{q \neq 0} \hbar\omega_q\left(a_q^{+} a_q + \frac{1}{2}\right)$$

<u>Another point of view:</u> eom: $m\ddot{\phi}_j = k_s\left[\phi_{j+1}-\phi_j-(\phi_j-\phi_{j-1})\right]$

$\forall_{j\in\{1\dots N\}}\ m\ddot{\phi}_j = k_s\left[\phi_{j+1}-2\phi_j+\phi_{j-1}\right]$ – set of N (coupled) diff. eq. (linear)

Look for normal modes $\Rightarrow$ all atoms vibrate with the same wavevector and frequency.

$$\phi_j = A e^{i(qR_j-\omega_q t)} = A e^{i(qaj-\omega_q t)}.$$ Plug into eom $\to$ $\omega_q = 2\sqrt{\frac{k_s}{m}}\left|\sin\frac{qa}{2}\right|$

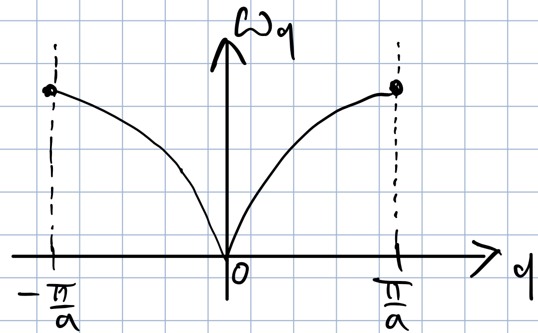
(dispersion relation)

Periodic BC: $\phi_{j+N}=\phi_j \to q=\frac{2\pi n}{L}$ $n\in\mathbb{Z}$.

$\omega_q=\omega_{-q}=\omega_{q+\frac{2\pi}{a}}$ $\qquad \phi_j^{(q)}=\phi_j^{q+\frac{2\pi}{a}} \to q$ may be restricted to $q\in\left]-\frac{\pi}{a},\frac{\pi}{a}\right]$ (FBZ)

$|q|\to 0 \Longrightarrow \omega_q \sim \underbrace{\sqrt{\frac{k_s}{m}}a}_{v_s}|q|$

(acoustic phonons) $\qquad v_s \to$ (Speed of sound)



General solution of eom: (combination of normal modes) $\phi_j = \frac{1}{\sqrt{N}}\sum_{q\in FBZ}\tilde{\phi}_q e^{iqR_j}$

$\hookrightarrow$ ($e^{-i\omega_q t}$ absorbed here)

Next step: $T=\frac{m}{2}\sum_j\dot{\phi}_j^2=\frac{m}{2}\sum_q\dot{\tilde{\phi}}_q\dot{\tilde{\phi}}_{-q}$

$V=\frac{k_s}{2}\sum_j(\phi_{j+1}-\phi_j)^2=\frac{m}{2}\sum_q\omega_q^2\tilde{\phi}_q\tilde{\phi}_{-q}$ $\Bigg\}\longrightarrow L=T-V$

$$p_q=\frac{\partial L}{\partial\dot{\tilde{\phi}}_q}=m\dot{\tilde{\phi}}_{-q}$$

$$\frac{\partial L}{\partial\dot{\tilde{\phi}}_q}=\frac{\partial}{\partial\dot{\tilde{\phi}}_q}\frac{m}{2}\sum_{q'}\dot{\tilde{\phi}}_{q'}\dot{\tilde{\phi}}_{-q'}= =\frac{m}{2}\sum_{q'}\left(\dot{\tilde{\phi}}_{q'}\delta_{q,-q'}+\dot{\tilde{\phi}}_{-q'}\delta_{q,q'}\right)= =\frac{m}{2}\dot{\tilde{\phi}}_{-q}\cdot 2=m\dot{\tilde{\phi}}_{-q}$$

Hamiltonian: $H=\left(\sum_q p_q\dot{\tilde{\phi}}_q-L\right)_{\dot{\tilde{\phi}}_{-q}=\frac{1}{m}p_q}$

$$H=\sum_{q\neq 0}\left(\frac{1}{2m}p_q p_{-q}+\frac{m\omega_q^2}{2}\phi_q\phi_{-q}\right)+\underbrace{\frac{1}{2m}p_0^2}_{H_0}$$

$$H=H_0+\sum_{q\neq 0}\hbar\omega_q\left(\overbrace{a_q^\dagger a_q}^{\hat{n}_q}+\frac{1}{2}\right)$$ $\to$ Sum of (independent) oscillators with frequencies ω_q and energies $\hbar\omega_q$; $q=\frac{2\pi}{L}n$.

$\{a_q, a_q^+\}$ obey bosonic c. r.

Eigenstates of H $\Leftrightarrow$ eigenstates of $\{\hat{n}_q\}$

$$|\psi\rangle = \prod_i \frac{(a_{q_i}^+)^{n_{q_i}}}{\sqrt{n_{q_i}!}} |0\rangle = |n_{q_1} n_{q_2} \dots n_{q_N}\rangle$$

$\hookrightarrow$ occupation number notation

Eigenenergies $E = E_0 + \sum_q n_q \hbar\omega_q$

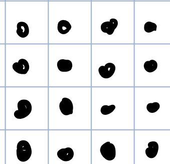
$$\hbar\omega_q \xrightarrow{q \to 0} 0 \quad \text{(no excitation gap)}$$

Thermodynamic limit $L \to \infty$
$N \to \infty$

$$\frac{N}{L} = \frac{1}{a} = \text{const.}$$

$$\Delta q = \frac{2\pi}{L} \xrightarrow{L \to \infty} 0$$

Lattice vibrations - a more general case in $d=3$



$j = 1 \dots N$

Periodic lattice (not necessarily cubic)

$$H = \sum_{j=1}^{N} \frac{\bar{p}_j^{\,2}}{2m} + U(\bar{R}_1 \dots \bar{R}_N)$$

$\bar{R}_j$ - position of the j-th atom

$(\bar{R}_1^{(0)}, \bar{R}_2^{(0)}, \dots \bar{R}_N^{(0)})$ - equilibrium position corresponding to the minimum of U

$$\vec{R}_j = \bar{R}_j^{(0)} + \bar{u}_j$$

$$\bar{u}_j = \sum_\alpha u_j^\alpha \bar{e}_\alpha$$

$\hookrightarrow$ displacement vector

$$U(\bar{R}_1 \dots \bar{R}_N) = U_0 + \frac{1}{2} \sum_{ij} \sum_{\alpha\beta} u_i^\alpha \left.\frac{\partial^2 U}{\partial u_i^\alpha \partial u_j^\beta}\right|_{\bar{u}_j = 0\ \forall_j} u_j^\beta + \dots$$

Discrete Fourier transform

$$f(\bar{R}_j^{(0)}) = \frac{1}{\sqrt{N}} \sum_{\bar{k} \in BZ} f(\bar{k}) e^{i\bar{k}\bar{R}_j^{(0)}} \qquad f(\bar{k}) = \frac{1}{\sqrt{N}} \sum_{j=1}^{N} f(\bar{R}_j^{(0)}) e^{-i\bar{k}\bar{R}_j^{(0)}}$$

$$\delta_{\bar{R}_j^{(0)}, 0} = \frac{1}{N} \sum_{\bar{k} \in BZ} e^{i\bar{k}\bar{R}_j^{(0)}} \qquad \delta_{\bar{k}, 0} = \frac{1}{N} \sum_{j=1}^{N} e^{-i\bar{k}\bar{R}_j^{(0)}}$$

$$D^{ij}_{\alpha\beta} := \left.\frac{\partial^2 U}{\partial u_i^\alpha \partial u_j^\beta}\right|_{\bar{u}_j = 0 \,\forall j}$$

(notation)

$$D^{ij}_{\alpha\beta} = D_{\alpha\beta}(\underbrace{\bar{R}_i^{(0)} - \bar{R}_j^{(0)}}_{:= \bar{R}_{ij}})$$

$$D_{\alpha\beta}(\bar{R}) = D_{\alpha\beta}(-\bar{R})$$

(lattice symmetry)

$$D^{ij}_{\alpha\beta} \longmapsto \bar{\bar{D}}(\bar{R}_{ij})$$

$$\bar{u}_j = \bar{u}(\bar{R}_j^{(0)})$$

EOM: $m\ddot{u}_j^\alpha = -\frac{\partial U}{\partial u_j^\alpha}$ $\qquad -m\ddot{\bar{u}}_j = \sum_i \bar{\bar{D}}(\bar{R}_i^{(0)} - \bar{R}_j^{(0)})\bar{u}_i$

$\left(\sum_i = \sum_{\bar{R}_i^{(0)}}\right)$

Look for harmonic solutions:

$$\bar{u}(R_j^{(0)}, t) = \bar{\epsilon}\, e^{i(\bar{k}\bar{R}_j^{(0)} - \omega t)}$$

$$-m(-\omega^2)\bar{\epsilon}\, e^{i\bar{k}\bar{R}_j^{(0)}} \cancel{e^{-i\omega t}} = \sum_{\bar{R}_i^{(0)}} \bar{\bar{D}}(\bar{R}_i^{(0)} - R_j^{(0)})\epsilon\, e^{i\bar{k}\bar{R}_i^{(0)}} \cancel{e^{-i\omega t}}$$

$$m\omega^2\bar{\epsilon} = \sum_{\bar{R}_i^{(0)}} \bar{\bar{D}}(\bar{R}_i^{(0)} - \bar{R}_j^{(0)})\bar{\epsilon}\, e^{i\bar{k}(\bar{R}_i^{(0)} - R_j^{(0)})}$$

$$\sum_{\bar{R}^{(0)}} \bar{\bar{D}}(\bar{R}^{(0)})\, e^{-i\bar{k}\bar{R}^{(0)}} = \bar{\bar{D}}(\bar{k})$$

$$m\omega^2\bar{\epsilon} = \bar{\bar{D}}(\bar{k})\bar{\epsilon}.$$

For each $\bar{k}$ there is a basis in which $\bar{\bar{D}}(\bar{k})$ is diagonal (one may show that $\bar{\bar{D}}(\bar{k})$ is symmetric)

$\lambda \in \{1, 2, 3\}$. $\qquad K_{\bar{k}\lambda}$ ← eigenvalues

$$\bar{\bar{D}}(\bar{k})\bar{\epsilon}_{\bar{k}\lambda} = K_{\bar{k}\lambda}\bar{\epsilon}_{\bar{k}\lambda}.$$

Identified classical eigenmodes of the 3d lattice characterized by $(\bar{k}, \lambda)$.

$$u_{\bar{k}\lambda}(\bar{R}^{(0)}, t) = \epsilon_{\bar{k}\lambda}\, e^{i(\bar{k}\bar{R}^{(0)} - \omega_{\bar{k}\lambda} t)}$$

$$l_{\bar{k}\lambda} := \sqrt{\frac{\hbar}{m\omega_{\bar{k}\lambda}}} \qquad \omega = \sqrt{\frac{K_{\bar{k}\lambda}}{m}}.$$

Next step: introduce creation/annihilation operators for each eigenmode

$$\begin{cases} u_{\bar{k}\lambda} = \dfrac{l_{\bar{k}\lambda}}{\sqrt{2}} \,\epsilon_{\bar{k}\lambda} \left(a_{\bar{k}\lambda} + a^{+}_{-\bar{k}\lambda}\right) \\ p_{\bar{k}\lambda} = \dfrac{\hbar}{l_{\bar{k}\lambda}} \dfrac{i}{\sqrt{2}}\, \epsilon_{\bar{k}\lambda}\left(-a_{\bar{k}\lambda} + a^{+}_{-\bar{k}\lambda}\right) \end{cases}$$

(in full analogy to the 1-d chain)

$$H \longrightarrow \sum_{\bar{k}\lambda} \hbar\omega_{\bar{k}\lambda}\left(a^{+}_{\bar{k}\lambda} a_{\bar{k}\lambda} + \frac{1}{2}\right) = H_{PH}$$

Typically we get $\omega^2_{\bar{k}\lambda} \sim k^2$ for k small (acoustic phonons).

For T small the system's behaviour is dominated by phonons with $|\bar{k}|$ small.

Thermodynamic properties (e.g. c_v)

T fixed $\qquad u = \frac{1}{V}\langle E\rangle$

$$P_{ST} = \frac{1}{Z} e^{-\beta E_{ST}} \qquad \beta = \frac{1}{k_B T}$$

Microscopic state $\{n_{\bar{k}_1\lambda_1} \dots n_{k_N\lambda_N}\}$

$$\langle E\rangle = \sum_{\text{States}} P_{ST}\cdot E_{ST}$$

$$\langle E\rangle = \sum_{n_{\bar{k}_1\lambda_1}} \sum_{n_{\bar{k}_2\lambda_2}} \dots \sum_{n_{\bar{k}_N\lambda_N}} \frac{1}{Z} E(\{n_{\bar{k}\lambda}\})\, e^{-\beta E(\{n_{\bar{k}\lambda}\})} = -\frac{\partial}{\partial\beta}\ln Z$$

$$Z = \sum_{\{n_{\bar{k}\lambda}\}} e^{-\beta\sum_{\bar{k}\lambda}\hbar\omega_{\bar{k}\lambda}(n_{\bar{k}\lambda}+\frac{1}{2})} = \prod_{\bar{k}\lambda}\left(\sum_{n_{\bar{k}\lambda}=0}^{\infty} e^{-\beta\hbar\omega_{\bar{k}\lambda}(n_{\bar{k}\lambda}+\frac{1}{2})}\right) = \prod_{\bar{k}\lambda}\frac{e^{-\frac{1}{2}\beta\hbar\omega_{\bar{k}\lambda}}}{1-e^{-\beta\hbar\omega_{\bar{k}\lambda}}}$$

$$\ln Z = -\sum_{\bar{k}\lambda}\left(\frac{\beta\hbar\omega_{\bar{k}\lambda}}{2} + \ln\left(1-e^{-\beta\hbar\omega_{\bar{k}\lambda}}\right)\right)$$

$$u = \frac{1}{V}\langle E\rangle = \frac{1}{V}\sum_{\bar{k}\lambda}\hbar\omega_{\bar{k}\lambda}\left(\frac{1}{2} + \frac{1}{e^{\beta\hbar\omega_{\bar{k}\lambda}}-1}\right)$$

(Bose-Einstein) $\quad \dfrac{1}{e^{\beta\hbar\omega_{\bar{k}\lambda}}-1} = \langle n_{\bar{k}\lambda}\rangle$

$$\left\{ \left.\begin{array}{l} V \to \infty \\ N \to \infty \\ \frac{N}{V} = \text{const} \end{array}\right\} \text{thermodynamic limit} \qquad \bar{k} = \frac{2\pi}{L}\vec{n} \quad \Delta^3 k = \frac{(2\pi)^3}{V} \xrightarrow{V\to\infty} 0 \qquad V = L^3 \quad \frac{1}{V}\sum_{k\lambda} f(\bar{k}) \longrightarrow \frac{1}{V}\frac{V}{(2\pi)^3}\int d^3k\, f(\bar{k})\cdot 3 \right\}$$

(*)

$$u \xrightarrow[\omega_{\bar{k}\lambda}\to\omega_{\bar{k}}]{V\to\infty} C_1 + \frac{3}{(2\pi)^3}\int d^3k \frac{\hbar\omega_{\bar{k}}}{e^{\beta\hbar\omega_{\bar{k}}}-1}$$

(simplifying assumption)

$$\left\{ \begin{array}{l} \text{Low-T limit } \beta \to \infty \\ \text{High-T limit } \beta \to 0 \end{array} \right\}$$

$$u \xrightarrow[\Longrightarrow\ \omega_{\bar{k}} \approx vk]{\beta\to\infty \text{ integral dominated by } k\approx 0} \quad C_1 + \frac{3}{(2\pi)^3}\int_0^{\Lambda} dk\, k^2 \int d\Omega \frac{\hbar v k}{e^{\beta\hbar v k}-1} \qquad \left(\Lambda \approx \frac{\pi}{a}\right)$$

(v direction indep. for simplicity)

scaling: $k' = \beta k \qquad \beta\Lambda \longrightarrow \infty$

$$u \longrightarrow C_1 + \beta^{-4} c_2(v,\hbar)$$

$$c = \frac{\partial u}{\partial T} \sim T^3 \quad \text{FOR } T \text{ SMALL.}$$

(universal power law behavior)
(for $d=3$)

High-T limit $\quad \frac{1}{e^{\beta\hbar\omega_{\bar{k}}}-1} \approx \frac{1}{\beta\hbar\omega_{\bar{k}}}$

$$u \xrightarrow{T\to\infty} C_1 + \frac{3}{(2\pi)^3}\underbrace{\int d^3k}_{\left(\frac{2\pi}{a}\right)^3} \frac{1}{\beta} = C_1 + C_3 T = C_1 + 3k_B T a^{-3}$$

$$u = \frac{U}{V} \qquad \tilde{u} = \frac{U}{N} = \left\{ \frac{V}{N} = a^3 \right\}$$

$$\tilde{u} = u a^{+3}$$

$$\tilde{u} = C_1' + 3k_B T$$

$$c = \frac{\partial \tilde{u}}{\partial T} = 3k_B.$$

(Dulong-Petit law).