TECHNISCHE UNIVERSITÄT DRESDEN

DRESDEN concept

SFB 1143

Solid State Theory (SS2020)

Lecture 4: Lattice dynamics

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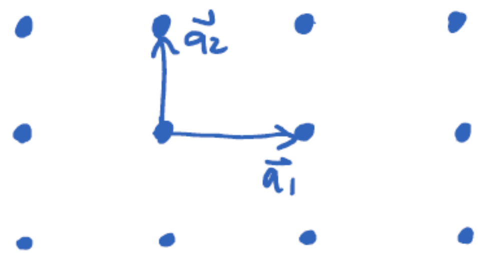
§ 1.3 Lattice structure

- Last lecture: Bravais and reciprocal lattices, unit cell, FBZ…

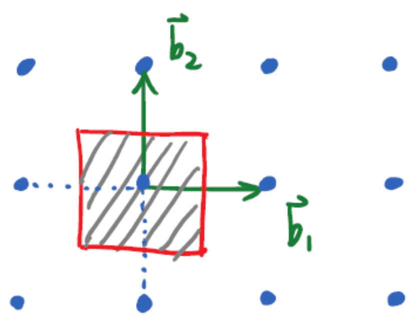


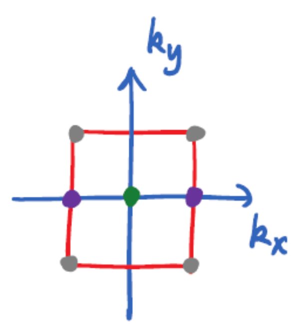
$$\vec{R}_n = n_1 \vec{a}_1 + n_2 \vec{a}_2 + n_3 \vec{a}_3$$

$$n \in \mathbb{Z}$$

$$\vec{G}_m = m_1 \vec{b}_1 + m_2 \vec{b}_2 + m_3 \vec{b}_3$$

$$\boxed{e^{i \vec{G}_m \cdot \vec{R}_n} = 1}$$





- Γ: $(0, 0)$
- M: $(\frac{\pi}{a}, \frac{\pi}{a})$
- X: $(\frac{\pi}{a}, 0)$

§ 1.3 Lattice structure

- The (discrete) Fourier transform is now easy to define:

$$f_j = \frac{1}{\sqrt{N}} \sum_{\mathbf{q}\in\mathrm{FBZ}} f_{\mathbf{q}}\, e^{i\mathbf{q}\cdot\mathbf{R}_j}$$

Label of unit cell, corresponding to $\mathbf{R}_j$

number of unit cells

Easy to motivate: $f_j = \sum_{\mathbf{q}} f_{\mathbf{q}}\, e^{i\mathbf{q}\cdot\mathbf{R}_j}$

use $e^{i(\mathbf{q}+\mathbf{G}_m)\cdot\mathbf{R}_j} = e^{i\mathbf{q}\cdot\mathbf{R}_j}$

§ 1.3 Lattice structure

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$$f_j = \frac{1}{\sqrt{N}} \sum_{\mathbf{q} \in \mathrm{FBZ}} f_{\mathbf{q}}\, e^{i\mathbf{q}\cdot\mathbf{R}_j}$$

Label of unit cell, corresponding to $\mathbf{R}_j$

number of unit cells

Inverse transformation: $$f_{\mathbf{q}} = \frac{1}{\sqrt{N}} \sum_{j} f_j\, e^{-i\mathbf{q}\cdot\mathbf{R}_j}$$

Useful identities: $$\boxed{\frac{1}{N} \sum_{j} e^{i(\mathbf{q}-\mathbf{q}')\cdot\mathbf{R}_j} = \delta_{\mathbf{q},\mathbf{q}'}} \qquad \boxed{\frac{1}{N} \sum_{\mathbf{q} \in \mathrm{FBZ}} e^{i\mathbf{q}\cdot(\mathbf{R}_j-\mathbf{R}_l)} = \delta_{jl}}$$

§ 1.4 Lattice dynamics for general 3D crystal

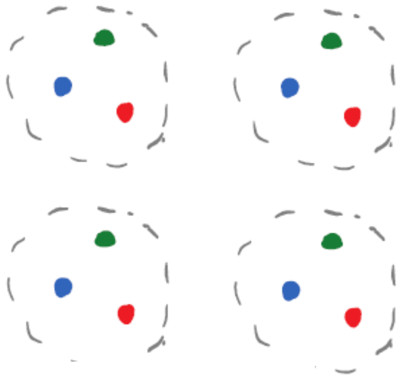
- Lattice dynamics in higher dimensions (d=2,3 => more realistic).

$$H_{ion} = \sum_i \frac{\vec{P}_i^2}{2M_i} + \frac{1}{2}\sum_{i \neq j} V(\vec{r}_i - \vec{r}_j)$$

§ 1.4 Lattice dynamics for general 3D crystal

- Lattice dynamics in higher dimensions (d=2,3 => more realistic).

N unit cells labeled by position $\vec{R}_\mu$ $(\mu=1,\cdots,N)$



α-th atom within the μ-th unit cell:

$\alpha=1,\ldots,r$

$$\vec{X}_{\mu\alpha} = \vec{R}_\mu + \vec{d}_\alpha$$

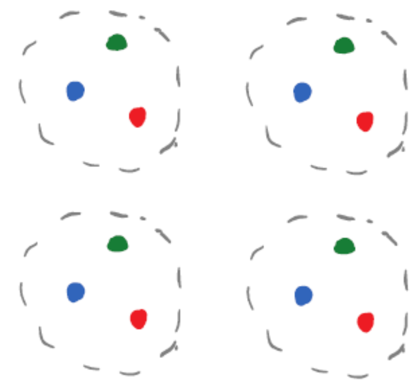
($\vec{X}_{\mu\alpha}$: equilibrium position)

relative positions for atoms within the same unit cell

§ 1.4 Lattice dynamics for general 3D crystal

- Lattice dynamics in higher dimensions (d=2,3 => more realistic).

N unit cells labeled by position $\tilde{R}_\mu$ $(\mu = 1, \cdots, N)$



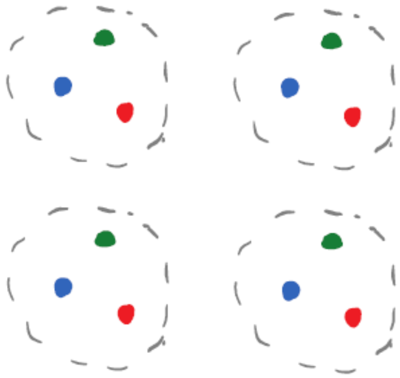
$\tilde{u}_{\mu\alpha}$: $u_{\mu\alpha i}$ $(i = x, y, z)$ (displacement)

potential energy:

$$V(\{u_{\mu\alpha i}\}) = V_0 + \frac{1}{2} \sum_{\mu\alpha i, \nu\beta j} \underbrace{D_{\mu\alpha i;\nu\beta j}}_{\text{dynamical matrix}} u_{\mu\alpha i} u_{\nu\beta j}$$

§ 1.4 Lattice dynamics for general 3D crystal

- It's just a minor generalization of the quantum diatomic chain (exercise discussed during the tutorial)



$$H = \sum_{\mu\alpha i} \frac{P_{\mu\alpha i}^2}{2M_\alpha} + \frac{1}{2} \sum_{\mu\alpha i, \nu\beta j} D_{\mu\alpha i;\nu\beta j}\, u_{\mu\alpha i} u_{\nu\beta j}$$

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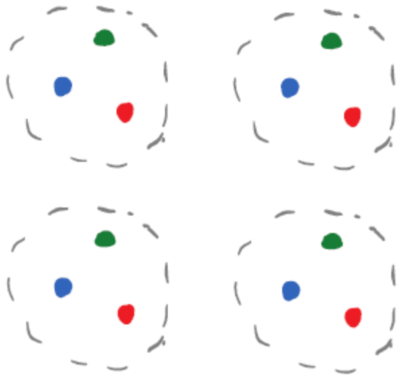

$$H = \sum_{\mu\alpha i} \frac{P_{\mu\alpha i}^2}{2M_\alpha} + \frac{1}{2} \sum_{\mu\alpha i,\nu\beta j} D_{\mu\alpha i;\nu\beta j}\, u_{\mu\alpha i} u_{\nu\beta j}$$

➢ Rescale: $P_{\mu\alpha i} \rightarrow \sqrt{M_\alpha} P'_{\mu\alpha i}$ and $u_{\mu\alpha i} \rightarrow \frac{1}{\sqrt{M_\alpha}} u'_{\mu\alpha i}$

$$H = \sum_{\mu\alpha i} \frac{\left(P'_{\mu\alpha i}\right)^2}{2} + \frac{1}{2} \sum_{\mu\alpha i,\nu\beta j} D'_{\mu\alpha i;\nu\beta j}\, u'_{\mu\alpha i} u'_{\nu\beta j}$$

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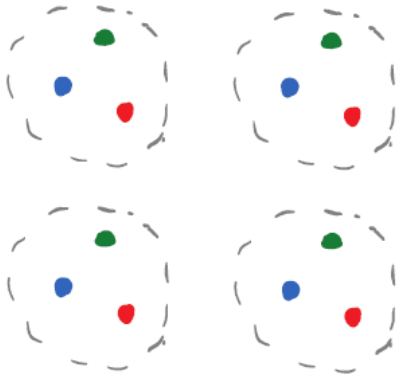

$$H = \sum_{\mu\alpha i} \frac{\left(P'_{\mu\alpha i}\right)^2}{2} + \frac{1}{2} \sum_{\mu\alpha i,\nu\beta j} D'_{\mu\alpha i;\nu\beta j}\, u'_{\mu\alpha i} u'_{\nu\beta j}$$

➢ Fourier transform:

$$u'_{\mu\alpha i} = \frac{1}{\sqrt{N}} \sum_{\mathbf{q}\in\mathrm{FBZ}} u'_{\mathbf{q}\alpha i}\, e^{i\mathbf{q}\cdot\mathbf{R}_\mu}$$

$$P'_{\mu\alpha i} = \frac{1}{\sqrt{N}} \sum_{\mathbf{q}\in\mathrm{FBZ}} P'_{\mathbf{q}\alpha i}\, e^{-i\mathbf{q}\cdot\mathbf{R}_\mu}$$

§ 1.4 Lattice dynamics for general 3D crystal

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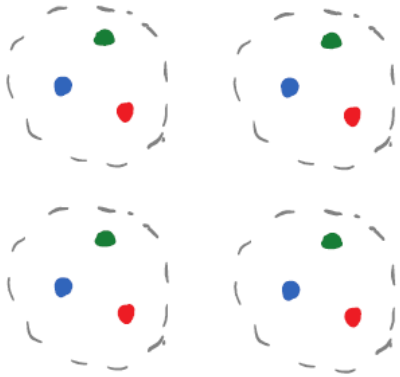

$$H = \sum_{\mu\alpha i} \frac{\left(P'_{\mu\alpha i}\right)^2}{2} + \frac{1}{2} \sum_{\mu\alpha i,\nu\beta j} D'_{\mu\alpha i;\nu\beta j}\, u'_{\mu\alpha i} u'_{\nu\beta j}$$

➢ Fourier transform:

$$H = \sum_{\mathbf{q},\alpha i} \frac{P'_{\mathbf{q},\alpha i} P'_{-\mathbf{q},\alpha i}}{2} + \frac{1}{2} \sum_{\mathbf{q},\alpha i,\beta j} D'_{\alpha i;\beta j}(\mathbf{q})\, u'_{\mathbf{q},\alpha i} u'_{-\mathbf{q},\beta j}$$

Translation symmetry of the dynamical matrix was used:

$$D'_{\alpha i;\beta j}(\mathbf{q}) \equiv \sum_{\nu} D'_{\mu\alpha i;\nu\beta j}\, e^{-i\mathbf{q}\cdot(\mathbf{R}_\mu - \mathbf{R}_\nu)}$$

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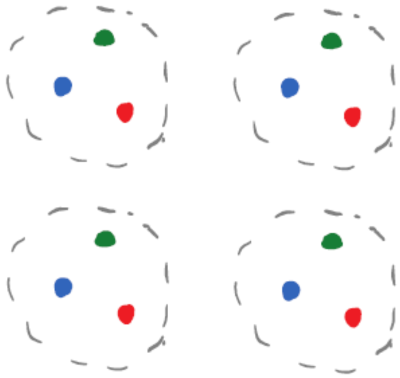


$$H = \sum_{\mathbf{q},\alpha i} \frac{P'_{\mathbf{q},\alpha i} P'_{-\mathbf{q},\alpha i}}{2} + \frac{1}{2} \sum_{\mathbf{q},\alpha i,\beta j} D'_{\alpha i;\beta j}(\mathbf{q})\, u'_{\mathbf{q},\alpha i} u'_{-\mathbf{q},\beta j}$$

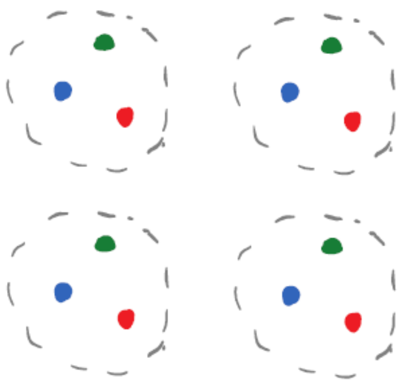
➢ Diagonalize $3r \times 3r$ matrix $D'(\mathbf{q})$:

$$H = \sum_{\mathbf{q}} \frac{(P''_{\mathbf{q}})^T P''_{-\mathbf{q}}}{2} + \frac{1}{2} \sum_{\mathbf{q}} (u''_{\mathbf{q}})^T \begin{bmatrix} [\omega_1(\mathbf{q})]^2 & \cdots & 0 \\ \vdots & \ddots & \vdots \\ 0 & \cdots & [\omega_{3r}(\mathbf{q})]^2 \end{bmatrix} u''_{-\mathbf{q}}$$

Dispersion relation

§ 1.4 Lattice dynamics for general 3D crystal

- It’s just a minor generalization of the quantum diatomic chain (exercise discussed during the tutorial)



$$H = \sum_{\mathbf{q},\alpha i} \frac{P'_{\mathbf{q},\alpha i} P'_{-\mathbf{q},\alpha i}}{2} + \frac{1}{2} \sum_{\mathbf{q},\alpha i,\beta j} D'_{\alpha i;\beta j}(\mathbf{q})\, u'_{\mathbf{q},\alpha i} u'_{-\mathbf{q},\beta j}$$

➢ Represent with bosonic operators:

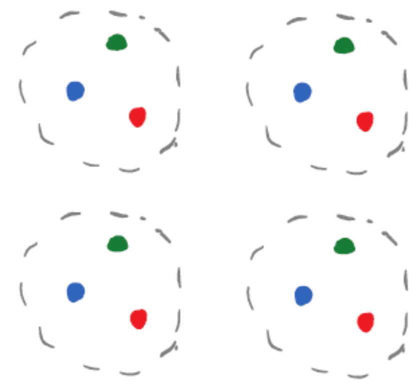
$$\boxed{H = \sum_{\mathbf{q}} \sum_{\gamma=1}^{3r} \hbar\omega_\gamma(\mathbf{q})\, (a^\dagger_{\mathbf{q}\gamma} a_{\mathbf{q}\gamma} + \frac{1}{2})}$$

$3r$ phonon modes!

§ 1.4 Lattice dynamics for general 3D crystal

- It's just a minor generalization of the quantum diatomic chain (exercise discussed during the tutorial)

$$H = \sum_{\mathbf{q},\alpha i} \frac{P'_{\mathbf{q},\alpha i} P'_{-\mathbf{q},\alpha i}}{2} + \frac{1}{2} \sum_{\mathbf{q},\alpha i,\beta j} D'_{\alpha i;\beta j}(\mathbf{q})\, u'_{\mathbf{q},\alpha i} u'_{-\mathbf{q},\beta j}$$



  - Represent with bosonic operators:

$\omega(\mathbf{q}) \to 0$ for $\mathbf{q} \to 0$

$$H_{3D} = \sum_{\vec{q},\, \nu=1,2,3} \hbar\omega_{\vec{q},\nu} \left(a^{+}_{\vec{q},\nu} a_{\vec{q},\nu} + \tfrac{1}{2} \right)$$ 3 acoustic

$$+ \sum_{\vec{q},\, \nu=4,\dots,3r} \hbar\omega_{\vec{q},\nu} \left(a^{+}_{\vec{q},\nu} a_{\vec{q},\nu} + \tfrac{1}{2} \right)$$ $3r-3$ optical

Phonon dispersions: theory vs experiment!

§ 1.5 Heat capacity from lattice dynamics

- Use statistical mechanics to calculate the phonon contributions to the heat capacity of solids: Einstein vs. Debye

3D crystal, r atoms in a unit cell

$$H = \sum_{\vec{q}} \sum_{\nu=1\cdots 3r} \hbar\omega_{\vec{q},\nu} \left(a^{\dagger}_{\vec{q},\nu} a_{\vec{q},\nu} + \frac{1}{2} \right)$$

Finite temperature $T > 0$:

Bose-Einstein distribution

$$\langle a^{\dagger}_{\vec{q},\nu} a_{\vec{q},\nu} \rangle_T = \frac{1}{e^{\beta\hbar\omega_{\vec{q},\nu}} - 1}$$

See pages 1-5 in phonon4.pdf for calculation details in § 1.5 …

§ 1.5 Heat capacity from lattice dynamics

- Internal energy:

$$U(T) = \langle H \rangle_T = \sum_{\vec{q},\nu} \hbar\omega_{\vec{q},\nu} \left(\langle a^{\dagger}_{\vec{q},\nu} a_{\vec{q},\nu} \rangle_T + \frac{1}{2} \right)$$

$$= \sum_{\vec{q},\nu} \left(\frac{\hbar\omega_{\vec{q},\nu}}{e^{\beta\hbar\omega_{\vec{q},\nu}} - 1} + \frac{1}{2}\hbar\omega_{\vec{q},\nu} \right)$$

- Heat capacity at constant volume:

$$C_V(T) = \frac{\partial}{\partial T} U(T)$$

$$= \frac{\partial}{\partial T} \sum_{\vec{q},\nu} \frac{\hbar\omega_{\vec{q},\nu}}{e^{\hbar\omega_{\vec{q},\nu}/k_B T} - 1}$$

Experiments: $C_V \sim T^3$ at low temperature!

§ 1.5 Heat capacity from lattice dynamics

- Einstein model: $\omega_{\vec{q},\nu} = \omega_e$ (no dependence on $\vec{q}, \nu$)

$\omega_e \rightarrow$ averaged frequency

$$\Rightarrow C_V(T) = \frac{\partial}{\partial T} \sum_{\vec{q},\nu} \frac{\hbar\omega_e}{e^{\hbar\omega_e/k_BT}-1} = 3N_a k_B \left(\frac{\hbar\omega_e}{k_BT}\right)^2 \frac{e^{\hbar\omega_e/k_BT}}{\left(e^{\hbar\omega_e/k_BT}-1\right)^2}$$

$\vec{q},\nu \rightarrow$ $q = 1, \cdots, N$; $\nu = 1, \cdots, 3r$ ($N_a = Nr$: number of atoms)

$$\rightarrow \begin{cases} e^{-\hbar\omega_e/k_BT}, & k_BT \ll \hbar\omega_e \quad \text{(low temperature)} \ \times \\ 3N_a k_B, & k_BT \gg \hbar\omega_e \quad \text{(high temperature)} \ \checkmark \end{cases}$$

$3N_a k_B \rightarrow$ Dulong-Petit law (classical limit)

§ 1.5 Heat capacity from lattice dynamics

- Debye model: $\omega_{\vec{q},\nu} = \omega_{\vec{q}} = v_s|\vec{q}|$ $\quad \nu = 1, 2, 3$

  $\hookrightarrow$ acoustic phonon

Cut-off frequency ω_D

Debye temperature:

$$\hbar\omega_D = k_B T_D \quad \Rightarrow T_D = \frac{\hbar\omega_D}{k_B} \simeq 10^2 \sim 10^3\,K$$

(Check "Debye temperature table")

§ 1.5 Heat capacity from lattice dynamics

- Debye model: $\omega_{\vec{q},\nu} = \omega_{\vec{q}} = v_s|\vec{q}|$ $\quad \nu = 1, 2, 3$

  $\rightarrow$ acoustic phonon

Cut-off frequency ω_D

Density of states:

$$D(\omega) = \sum_{\vec{q}} \delta(\omega - \omega_{\vec{q}})$$

V: volume of the crystal

$$\overset{N\to\infty}{=} \frac{V}{(2\pi)^3} \int d\vec{q}\, \delta(\omega - \omega_{\vec{q}})$$

$q_D \rightarrow$ cut-off momentum ($\sim \frac{\pi}{a}$, a: lattice spacing)

$$= \frac{V}{(2\pi)^3} \int_0^{q_D} dq\, 4\pi q^2 \delta(\omega - v_s q)$$

$\rightarrow \delta(\omega - v_s q) = \frac{1}{v_s}\delta\left(\frac{\omega}{v_s} - q\right)$

$$= \frac{V}{(2\pi)^3} 4\pi \left(\frac{\omega}{v_s}\right)^2 \frac{1}{v_s}$$

for $0 \le \omega \le \omega_D$

§ 1.5 Heat capacity from lattice dynamics

- Debye model: $\omega_{\vec{q},\nu} = \omega_{\vec{q}} = V_s|\vec{q}|$ $\nu = 1, 2, 3$

  ↪ acoustic phonon

$$U_{acoustic}(T) = 3\sum_{\vec{q}}\left(\frac{\hbar\omega_{\vec{q}}}{e^{\hbar\omega_{\vec{q}}/k_BT}-1} + \frac{1}{2}\hbar\omega_{\vec{q}}\right)$$

$$= 3\int d\omega \underbrace{\sum_{\vec{q}} \delta(\omega - \omega_{\vec{q}})}_{= D(\omega)} \left(\frac{1}{e^{\hbar\omega/k_BT}-1} + \underbrace{\frac{1}{2}\hbar\omega}_{\text{zero-point energy dropped below (no T dependence)}}\right)$$

$$= 3\int_0^{\omega_D} d\omega \; \underbrace{N\frac{3\omega^2}{\omega_D^3}} \; \frac{\hbar\omega}{e^{\hbar\omega/k_BT}-1}$$

§ 1.5 Heat capacity from lattice dynamics

- Debye model: $\omega_{\vec{q},\nu} = \omega_{\vec{q}} = v_s|\vec{q}|$ $\quad \nu = 1, 2, 3$

$\hookrightarrow$ acoustic phonon

$$U_{acoustic}(T) = \frac{9N\hbar}{\omega_D^3}\left(\frac{k_B T}{\hbar}\right)^4 \int_0^{T_D/T} \frac{x^3}{e^x - 1}\,dx \qquad x = \frac{\hbar\omega}{k_B T}$$

$\hookrightarrow \omega_D = \frac{k_B T_D}{\hbar}$

$$= \frac{9N k_B T^4}{T_D^3} \int_0^{T_D/T} \frac{x^3}{e^x - 1}\,dx$$

$$= \begin{cases} 3N k_B T, & T \gg T_D \\ \frac{3\pi^4}{5} N k_B \frac{T^4}{T_D^3}, & T \ll T_D \end{cases}$$

$e^x - 1 \simeq x$

$\Downarrow$

$\int_0^{T_D/T} x^2\,dx = \frac{1}{3}\left(\frac{T_D}{T}\right)^3$

$\hookrightarrow \int_0^{\infty} \frac{x^3}{e^x - 1} = \frac{\pi^4}{15}$

§ 1.5 Heat capacity from lattice dynamics

- Debye model: $\omega_{\vec{q},\nu} = \omega_{\vec{q}} = v_s|\vec{q}|$ $\nu = 1, 2, 3$

  $\hookrightarrow$ acoustic phonon

$$C_{V,\text{acoustic}}(T) = \frac{\partial}{\partial T} U_{\text{acoustic}}(T)$$

$$= \begin{cases} 3Nk_B , & T \gg T_D \ \checkmark \\ \frac{12\pi^4}{5} Nk_B \left(\frac{T}{T_D}\right)^3 , & T \ll T_D \ \checkmark \end{cases}$$

§ 1.5 Heat capacity from lattice dynamics

- Debye model: $\omega_{\vec{q},\nu} = \omega_{\vec{q}} = v_s|\vec{q}|$ $\nu = 1, 2, 3$

  ↪ acoustic phonon

Lattice vibration contribution:

$C_V(T) \to A T^3$ for $T \to 0$ Debye's T^3 law !

agrees with experiments !

(quantum treatment of lattice vibrations necessary !)

Remark: AT^3 holds in 3D.

In 1D & 2D, one has AT and AT^2 at low T.