
Vibrations and Electronic Excitations in Solids

MSE 421 - Ceriotti

Vibrations in solids

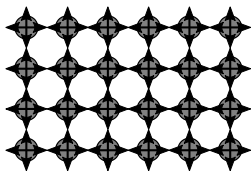
- Consider a solid with its atoms in their *equilibrium* positions $\mathbf{x}_i^{(0)}$. The energy for small displacements can be written as

$$V(\mathbf{x}) = V\left(\{\mathbf{x}_i^{(0)}\}\right) + \sum_i \left(\mathbf{x}_i - \mathbf{x}_i^{(0)}\right) \cdot \frac{\partial V}{\partial \mathbf{x}_i} + \frac{1}{2} \sum_{ij=1}^N \left(\mathbf{x}_i - \mathbf{x}_i^{(0)}\right) \frac{\partial^2 V}{\partial \mathbf{x}_i \partial \mathbf{x}_j} \left(\mathbf{x}_j - \mathbf{x}_j^{(0)}\right)$$

- This is a quadratic form in $3N$ dimensions, with the different coordinates coupled by $H_{ij} = \partial^2 V / \partial \mathbf{x}_i \partial \mathbf{x}_j$
- We can diagonalize $\mathbf{H}$ and re-write the potential in the basis of its eigenvectors, with the *normal-mode coordinates* u_k [when particles with different masses are present, work in mass-scaled coordinates and define the *dynamical matrix*]

$$V(\mathbf{u}) = V_0 + \frac{1}{2} \sum_k m \omega_k^2 u_k^2$$

- Each normal mode is a separate system, the thermodynamics of the solid can be seen as a combination of independent harmonic oscillators



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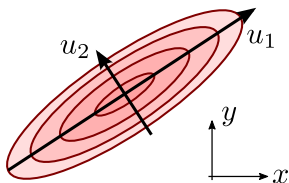
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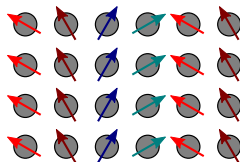
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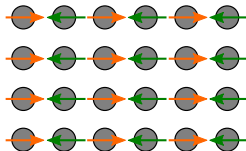
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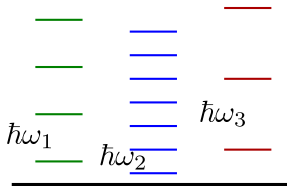
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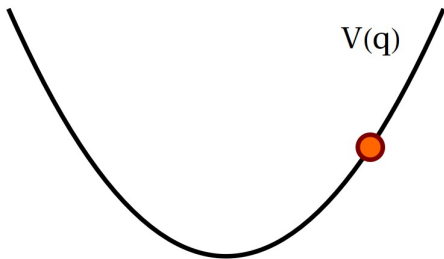


A classical oscillator

- Let's compute the canonical partition function of a harmonic oscillator of frequency ω

$$Q = \int dq dp e^{-\beta \left(\frac{1}{2} m \omega^2 q^2 + \frac{p^2}{2m} \right)} = \frac{2\pi}{\sqrt{m\omega^2\beta} \sqrt{\beta/m}} = \frac{2\pi}{\beta\omega}$$

- The free energy is $A = -k_B T \ln Q = \text{const.} + k_B T \ln \beta\omega$
- The mean energy is $\langle E \rangle = -\partial \ln Q / \partial \beta = 1/\beta$
- The heat capacity is $\partial \langle E \rangle / \partial T = k_B$

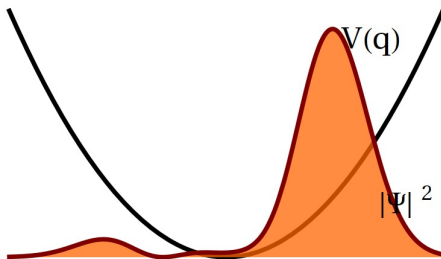


A quantum oscillator

- A quantum oscillator has energy levels $\hbar\omega \left(\frac{1}{2} + k\right)$

$$Q = \sum_k e^{-\beta\hbar\omega(\frac{1}{2}+k)} = e^{-\beta\hbar\omega/2} \sum_k e^{-\beta\hbar\omega k} = \frac{e^{-\beta\hbar\omega/2}}{1 - e^{-\beta\hbar\omega}} = \left[\sinh \frac{\beta\hbar\omega}{2} \right]^{-1}$$

- The free energy is $A = -k_B T \ln Q = \frac{\hbar\omega}{2} + k_B T \ln 1 - e^{-\beta\hbar\omega}$
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- The heat capacity is $\frac{\partial \langle E \rangle}{\partial T} = k_B \left[\frac{2}{\beta\hbar\omega} \sinh \frac{\beta\hbar\omega}{2} \right]^{-2}$

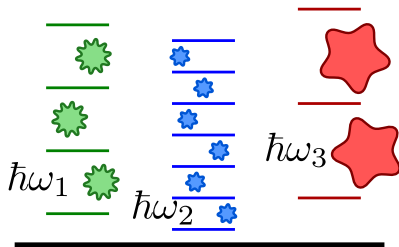


Energy levels or phonons?

- An alternative view on the problem is to consider each excitation as one *quasiparticle*, occupying the energy level $\hbar\omega$, and subtracting the *zero-point energy* $\hbar\omega/2$
- In this sense, each vibrational modes contributes to the overall partition function a term

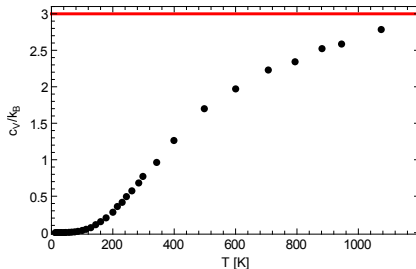
$$\ln Q = -\ln(1 - e^{-\beta\hbar\omega})$$

that is equivalent to the partition function for bosons, with the chemical potential set to zero - so-called *phonons*



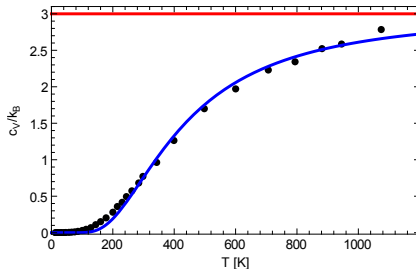
Heat capacity of an Einstein solid

- Heat capacity of diamond. Classical value (Dulong-Petit) $3k_B$
- $3N$ quantum oscillators at frequency ω_E (Einstein solid). Looks good...
- ... but wrong behavior at low T



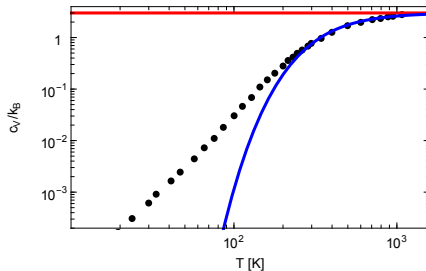
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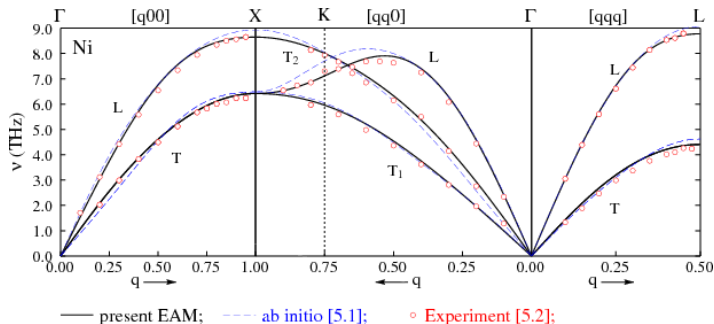
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Vibrations in a real solid

- How do vibrations look like in a solid? We can investigate with inelastic neutron scattering, or with various spectroscopies.

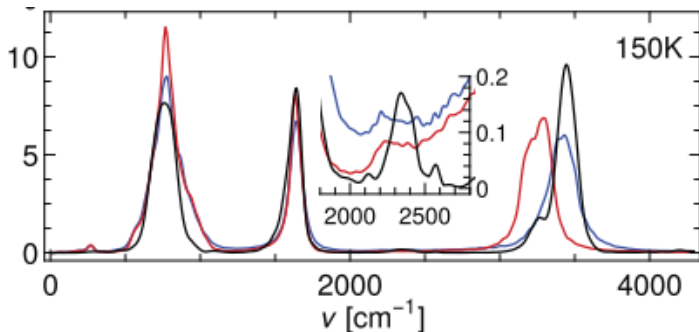


Phonon dispersion curves in Nickel

PRB 83, 134118 (2011); Phys. Rev. 136 A1359 (1964), Phys. Rev. B 59, 3393 (1999)

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Calculated vibrational density of states in hexagonal ice
JCP 140, 234116 (2014)

The Debye solid

- One should consider the contribution from different phonon frequencies!

$$c_V(T) = \int_0^{\omega_D} g(\omega) c_V^{QHO}(\omega, T) d\omega \quad \text{Debye solid}$$

- Consider the low-frequency elastic vibrations.
 - Linear phonon dispersion $\omega(k) \propto k$ [slope depends on elastic constants!]
 - Density of states in 3D: $g(k) \propto k^2$, $g(\omega) \propto \omega^2$
- Just from a dimensional analysis, we can do the change of variables $\hbar\omega/k_B T \rightarrow x$; $d\omega \rightarrow k_B T/\hbar dx$

$$\begin{aligned} c_V(T) &\propto \int_0^{\omega_D} \omega^2 \left[\frac{k_B T}{\hbar\omega} \sinh \frac{\hbar\omega}{2k_B T} \right]^{-2} d\omega \\ &= \int_0^{\hbar\omega_D/k_B T} (k_B T/\hbar)^3 x^2 \left[\frac{1}{x^2} \sinh x/2 \right]^{-2} dx \end{aligned}$$

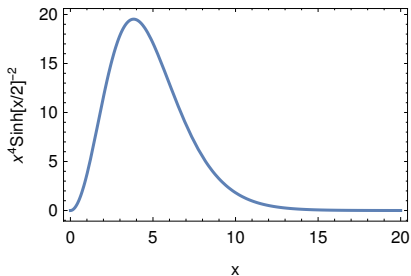
so for $T \rightarrow 0$ $c_V(T) \propto T^3 \int_0^\infty x^4 \sinh^{-2} x/2 dx$

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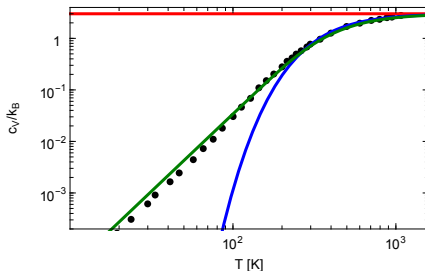
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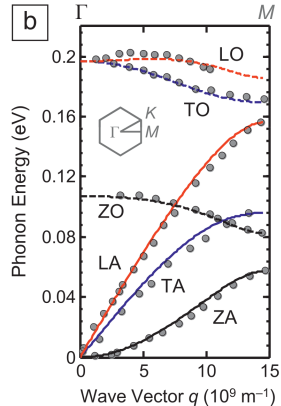
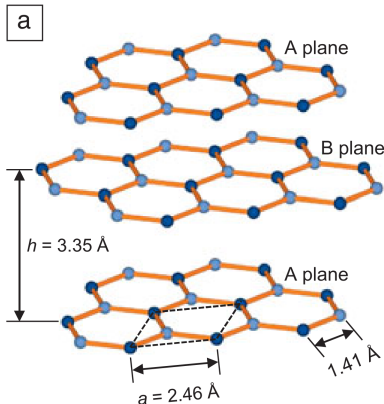
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$$c_V(T) \propto T^3$$

Thermal properties of graphene/1

- Graphene has very unusual thermal properties that can be understood based on its phonon dispersion curves. It contains two modes with $\omega(k) \propto k$, and one (out-of-plane, ZA) branch corresponding $\omega(k) \propto k^2$



Pop, Varshney, Roy, MRS Bulletin (2012)

Thermal properties of graphene/2

- Ignoring for a second the ZA modes, we have (2D, linear dispersion)
 $g(k) \propto k, g(\omega) \propto \omega$

$$c_V^{2D}(T) \propto \int_0^{\omega_D} \omega \left[\frac{k_B T}{\hbar \omega} \sinh \frac{\hbar \omega}{2k_B T} \right]^{-2} d\omega \propto$$
$$T^2 \int_0^{\hbar \omega_D / k_B T} x^3 \sinh^{-2} x / 2 dx$$

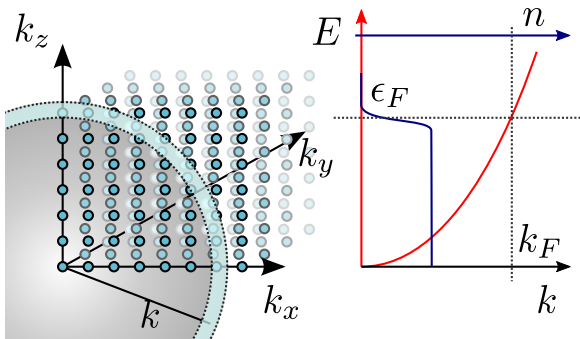
- How about the ZA branch? 2D, quadratic dispersion $\omega(k) \sim k^2$ so
 $d\omega = k dk, g(k) dk \propto k dk, g(\omega) \propto 1$

$$c_V^{2D,ZA}(T) \propto \int_0^{\omega_D} \left[\frac{k_B T}{\hbar \omega} \sinh \frac{\hbar \omega}{2k_B T} \right]^{-2} d\omega \propto$$
$$T \int_0^{\hbar \omega_D / k_B T} x^2 \sinh^{-2} x / 2 dx$$

The free electron gas/1

- Free electrons are characterized by pure kinetic energy, with eigenstates labelled by a wavevector $\mathbf{k}$ (plus spin), and energy $\hbar^2 \mathbf{k}^2 / 2m_e$
- If we consider a cubic volume $V = L^3$ with periodic boundary conditions, accessible states are quantized and characterized by $\mathbf{k} = (n_x, n_y, n_z) \frac{2\pi}{L}$
- For large L , sums over energy levels can be approximated as integrals

$$\sum_{\mathbf{n}\sigma} \cdot = \underbrace{2}_{\text{spin}} \frac{V}{8\pi^3} \int \cdot d\mathbf{k} = \frac{V}{4\pi^3} \int \cdot 4\pi k^2 dk$$



The free electron gas/2

- The total number of electrons is set by

$$\langle N \rangle = \frac{V}{\pi^2} \int \frac{1}{e^{\beta(\hbar^2 k^2 / 2m - \epsilon_F)} + 1} k^2 dk$$

- At $T \rightarrow 0$, the Fermi function becomes a step function switching from 1 to 0 for $\hbar^2 k_F^2 = 2m\epsilon_F$, so

$$\frac{\langle N \rangle}{V} = \rho = \frac{1}{\pi^2} \frac{1}{3} k_F^3 \quad \rightarrow \quad k_F = \sqrt[3]{3\pi^2 \rho}$$

- We can write the energy density as a function of ρ !

$$\langle E \rangle = \frac{V}{\pi^2} \int_0^{k_F} \frac{\hbar^2 k^2}{2m} k^2 dk = \frac{V}{\pi^2} \frac{\hbar^2}{2m} \frac{k_F^5}{5}, \quad \frac{\langle E \rangle}{V} = \frac{3\hbar^2 \sqrt[3]{9\pi^4}}{10m} \rho^{5/3}$$

- The energy of the FEG is a function of the density. This expression constitutes the basis for the Thomas-Fermi version of *density functional theory*

Sommerfeld expansion

- Let's derive in general a way to express integrals of the Fermi function (Sommerfeld expansion)

$$\begin{aligned} I &= \int_{-\infty}^{\infty} \frac{H(\epsilon)}{1 + e^{\beta(\epsilon - \epsilon_F)}} d\epsilon \stackrel{x = \beta(\epsilon - \epsilon_F)}{=} \frac{1}{\beta} \int_{-\infty}^{\infty} \frac{H(x/\beta + \epsilon_F)}{1 + e^x} dx \\ &= \frac{1}{\beta} \left[\int_{-\infty}^0 \frac{H(x/\beta + \epsilon_F)}{1 + e^x} dx + \int_0^{\infty} \frac{H(x/\beta + \epsilon_F)}{1 + e^x} dx \right] \end{aligned}$$

but

$$\begin{aligned} \frac{1}{1 + e^{-x}} &= \frac{e^x}{e^x + 1} = \frac{e^x + 1 - 1}{e^x + 1} = 1 - \frac{1}{1 + e^x}, \text{ so} \\ I &= \frac{1}{\beta} \int_0^{\infty} H(-x/\beta + \epsilon_F) dx + \frac{1}{\beta} \int_0^{\infty} \frac{H(x/\beta + \epsilon_F) - H(-x/\beta + \epsilon_F)}{1 + e^x} dx = \\ &= \int_{-\infty}^{\epsilon_F} H(\epsilon) d\epsilon + \frac{1}{\beta} \int_0^{\infty} \frac{2H'(\epsilon_F) x/\beta}{1 + e^x} dx = \\ &= \int_{-\infty}^{\epsilon_F} H(\epsilon) d\epsilon + \frac{2H'(\epsilon_F)}{\beta^2} \int_0^{\infty} \frac{x}{1 + e^x} dx = \text{const} + \frac{\pi^2}{6} H'(\epsilon_F) (k_B T)^2 \end{aligned}$$

The free electron gas/3

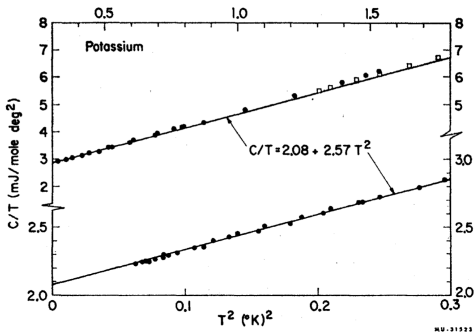
- Now, let's assume a general density of states $g(\epsilon)$, and finite T

$$\frac{\langle E \rangle}{V} = \int \frac{\epsilon g(\epsilon)}{1 + e^{\beta(\epsilon - \epsilon_F)}} d\epsilon$$

- Applying the Sommerfeld expansion we get

$$\frac{\langle E \rangle}{V} = \text{const} + \frac{\pi^2}{6} \epsilon_F H'(\epsilon_F) (k_B T)^2,$$

that is: the heat capacity in a metal at low temperature is $\propto T$



Lien, Phillips, PRA (1964)