Vibrations and Electronic Excitations in Solids

MSE 421 - Ceriotti

Vibrations in solids

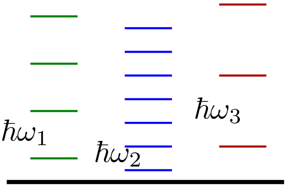
- Consider a solid with its atoms in their *equilibrium* positions $\mathbf{x}_i^{(0)}$. The energy for small displacements can be written as

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

  - 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

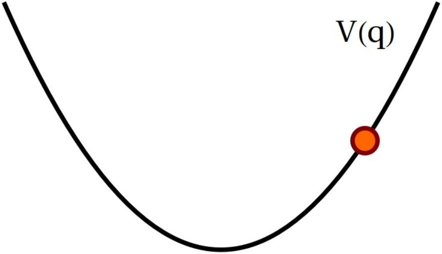


A classical oscillator

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

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

  - 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 $\partial \langle E \rangle / \partial T = k_B$

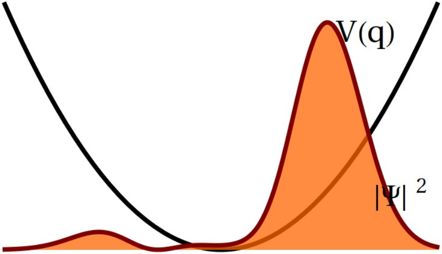


A quantum oscillator

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

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

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

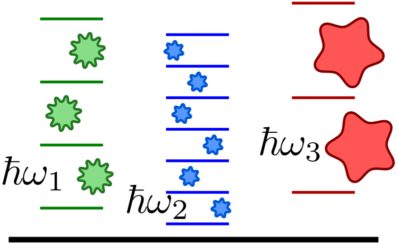


Energy levels or phonons?

- 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

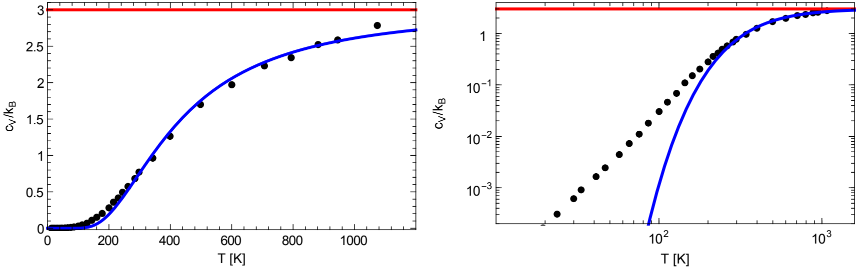
  $$\ln Q = \ln\left(1 - e^{-\beta\hbar\omega}\right)$$

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



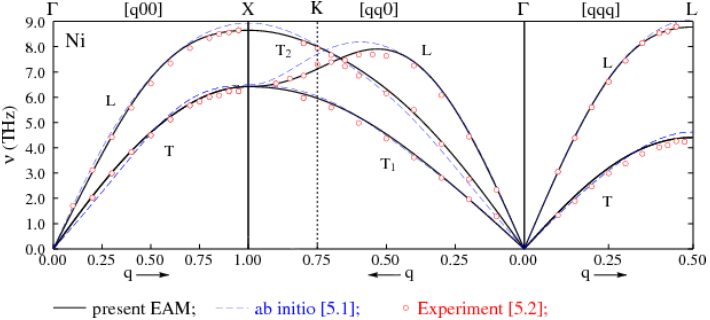
Heat capacity of an Einstein solid

- 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



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)

The Debye solid

- One should consider the contribution from different phonon frequencies!

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

- 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 $\hbar\omega/k_B T \to x; \qquad \mathrm{d}\omega \to k_B T/\hbar \mathrm{d}x$

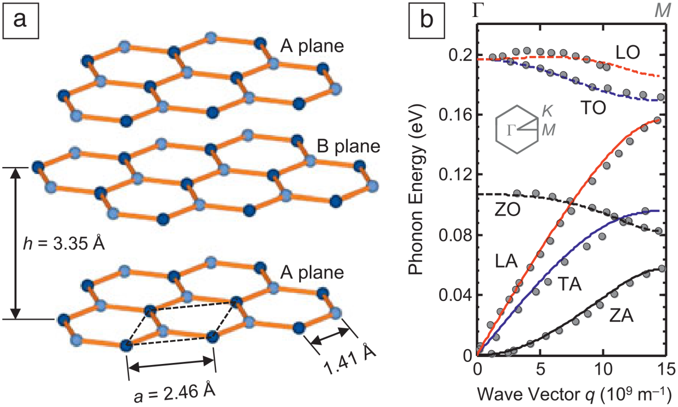
$$c_V(T) \propto \int_0^{\omega_D} \omega^2 \left[\frac{k_B T}{\hbar\omega} \sinh \frac{\hbar\omega}{2 k_B T}\right]^{-2} \mathrm{d}\omega$$

$$= \int_0^{\hbar\omega_D/k_B T} (k_B T/\hbar)^3\, x^2 \left[\frac{1}{x^2} \sinh x/2\right]^{-2} \mathrm{d}x$$

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

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) $g(k) \propto k$, $g(\omega) \propto \omega$

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

$$T^2 \int_0^{\hbar\omega_D/k_B T} x^3 \sinh^{-2} x/2 \mathrm{d}x$$

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

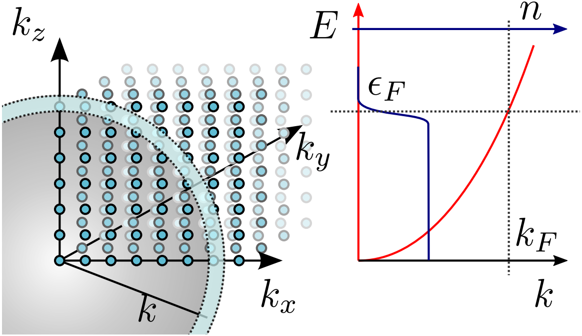
$$c_V^{2D,ZA}(T) \propto \int_0^{\omega_D} \left[\frac{k_B T}{\hbar\omega} \sinh \frac{\hbar\omega}{2k_B T}\right]^{-2} \mathrm{d}\omega \propto$$

$$T \int_0^{\hbar\omega_D/k_B T} x^2 \sinh^{-2} x/2 \mathrm{d}x$$

The free electron gas/1

- Free electrons are characterized by pure kinetic energy, with eigenstates labelled by a wavevector **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

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



The free electron gas/2

- The total number of electrons is set by

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

- At $T\to 0$, 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!

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

  - 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)

$$I=\int_{-\infty}^{\infty}\frac{H(\epsilon)}{1+e^{\beta(\epsilon-\epsilon_F)}}\mathrm{d}\epsilon \underset{x=\beta(\epsilon-\epsilon_F)}{=} \frac{1}{\beta}\int_{-\infty}^{\infty}\frac{H(x/\beta+\epsilon_F)}{1+e^{x}}\mathrm{d}x$$

$$=\frac{1}{\beta}\left[\int_{-\infty}^{0}\frac{H(x/\beta+\epsilon_F)}{1+e^{x}}\mathrm{d}x+\int_{0}^{\infty}\frac{H(x/\beta+\epsilon_F)}{1+e^{x}}\mathrm{d}x\right]$$

but

$$\frac{1}{1+e^{-x}}=\frac{e^x}{e^x+1}=\frac{e^x+1-1}{e^x+1}=1-\frac{1}{1+e^x},\ \text{so}$$

$$I=\frac{1}{\beta}\int_0^{\infty}H(-x/\beta+\epsilon_F)\,\mathrm{d}x+\frac{1}{\beta}\int_0^{\infty}\frac{H(x/\beta+\epsilon_F)-H(-x/\beta+\epsilon_F)}{1+e^x}=$$

$$=\int_{-\infty}^{\epsilon_F}H(\epsilon)\,\mathrm{d}\epsilon+\frac{1}{\beta}\int_0^{\infty}\frac{2H'(\epsilon_F)\,x/\beta}{1+e^x}\mathrm{d}x=$$

$$=\int_{-\infty}^{\epsilon_F}H(\epsilon)\,\mathrm{d}\epsilon+\frac{2H'(\epsilon_F)}{\beta^2}\int_0^{\infty}\frac{x}{1+e^x}\mathrm{d}x=\mathrm{const}+\frac{\pi^2}{6}H'(\epsilon_F)\,(k_BT)^2$$

The free electron gas/3

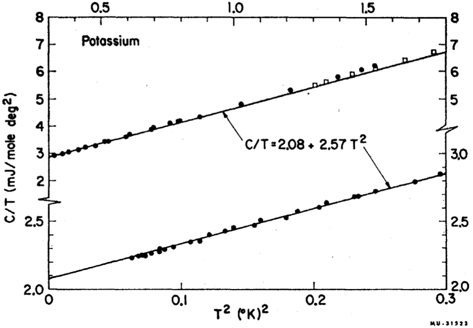
- Now, let's assume a general density of states $g\left(\epsilon\right)$, and finite T

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

- Applying the Sommerfeld expansion we get

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

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



Lien, Phillips, PRA (1964)