Lecture 16

08.03.2019

Thermal vibrations and Phonons

Quantum gas

Consider a system of $N = \sum_j n_j$ quantum particles with number n_j of particles in each quantum state ϵ_j

Bosons: $n_j = 0,1,2,\cdots$

Grand-canonical partition function:

Conditioned sum weighted by the Gibbs factor over all microstates with $\{n_j\}$ partition of particles between the energy levels $\{\epsilon_j\}$,

$$\Xi_{bosons} = \prod_j \sum_{n_j} e^{-\beta(\epsilon_j - \mu)n_j} = \prod_j \left(\frac{1}{1 - e^{-\beta(\epsilon_j - \mu)}} \right)$$

Quantum gas: Themodynamic properties

Landau free energy:

$$\Omega(\mathrm{T},\mathrm{V},\mu) = -PV = -kT\log\Xi$$

$$\Omega = kT\int d\epsilon D(\epsilon)\ln\left[1-e^{-\beta(\epsilon-\mu)}\right]$$

$D(\epsilon)d\epsilon \equiv$ number of quantum states with energy between ϵ and $\epsilon + d\epsilon$

Pressure:

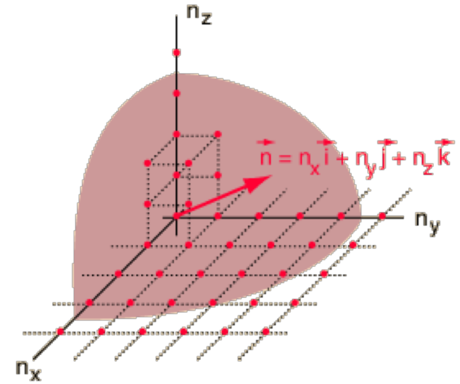
$$PV = -kT\int d\epsilon D(\epsilon)\log\left(1-e^{-\beta(\epsilon-\mu)}\right)$$

Average number of particles:

$$\langle N\rangle = \int d\epsilon\, D(\epsilon)\langle n\rangle_\epsilon = \int d\epsilon D(\epsilon)\frac{1}{e^{\beta(\epsilon-\mu)}-1}$$

Average energy*:*

$$\langle E\rangle = \int d\epsilon\, D(\epsilon)\langle n\rangle_\epsilon \epsilon = \int d\epsilon D(\epsilon)\frac{\epsilon}{e^{\beta(\epsilon-\mu)}-1}$$



Photon gas in a box: Blackbody radiation

Energy of a photon at a give frequency/wavenumber: $\epsilon = \hbar\omega = \hbar \mathrm{k} c = \frac{hc}{L} n, \quad k = |\vec{k}|,$ $n = |\vec{n}|$

Density of states:

$D(n)dn = 2\times 4\pi n^2 dn$ number of modes (quantum states) with state number between n and n+dn

$$D_\epsilon(\epsilon)d\epsilon = \frac{V}{\pi^2\hbar^3 c^3}\epsilon^2\, d\epsilon = D(n)dn$$

$$D_\omega(\omega)d\omega = \frac{V}{\pi^2 c^3}\omega^2 d\omega = D(n)dn$$

Landau free energy:

$$\Omega = kT\int d\omega D_\omega(\omega)\ln\left[1 - e^{-\beta\hbar\omega}\right], \qquad \mu = 0$$

Photon gas in a box: Blackbody radiation

Average energy of an EM mode with frequency $\boldsymbol{\omega}$ is the energy of a photon occupying that mode × the average number of photons

$$\langle\epsilon\rangle(\omega,T) = \hbar\omega\,\langle n\rangle(\omega,T) = \frac{\hbar\omega}{e^{\beta\hbar\omega}-1}$$

Average energy*:*

$$\frac{\langle E\rangle}{V} = \int d\omega\,\mathcal{E}(\omega,T) = \frac{1}{V}\int d\omega D_\omega(\omega)\,\langle\epsilon\rangle(\omega)$$

$$\frac{\langle E\rangle}{V} = \frac{\hbar}{\pi^2c^3}\int_0^\infty d\omega\,\frac{\omega^3}{e^{\beta\hbar\omega}-1} = \frac{\pi^2k^4}{15c^3\hbar^3}T^4$$

Plancks distribution: spectral energy density

$$\mathcal{E}(\omega,T) = \frac{\hbar}{\pi^2c^3}\frac{\omega^3}{e^{\beta\hbar\omega}-1}$$

Average number of particles:

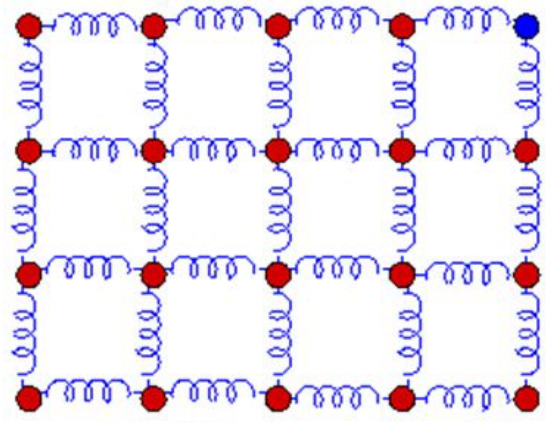
$$\langle N\rangle = \int d\epsilon\,D(\epsilon)\langle n\rangle_\epsilon = \frac{V}{\pi^2c^3}\int_0^\infty d\omega\,\frac{\omega^2}{e^{\beta\hbar\omega}-1} = \left(\frac{\boldsymbol{kT}}{\boldsymbol{\hbar c}}\right)^{\boldsymbol{3}}\frac{\boldsymbol{I_2}}{\boldsymbol{\pi^2}}$$

Radiation Pressure

$$PV = -\frac{kTV}{\pi^2c^3}\int d\omega\,\omega^2\log\left(1-e^{-\beta\hbar\omega}\right) = -F(T,V) = \frac{V\pi^2}{45\hbar^3c^3}(kT)^4$$

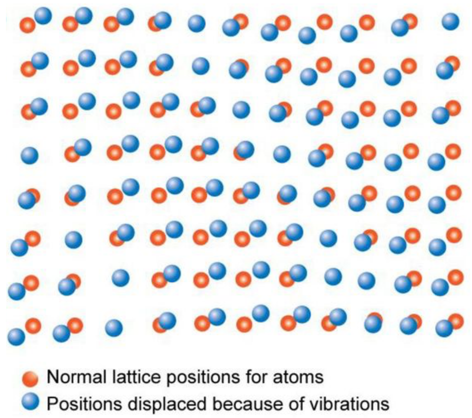
Solid state material: crystal

Harmonic solids: atoms in a crystal held at lattice sites by elastic forces



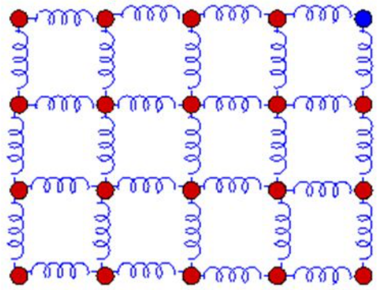
Lattice vibrations: sum of harmonic oscillators

$$H = \frac{1}{2}\sum_{i=1}^{3N}(p_i^2 + \omega_i^2 q_i^2)$$



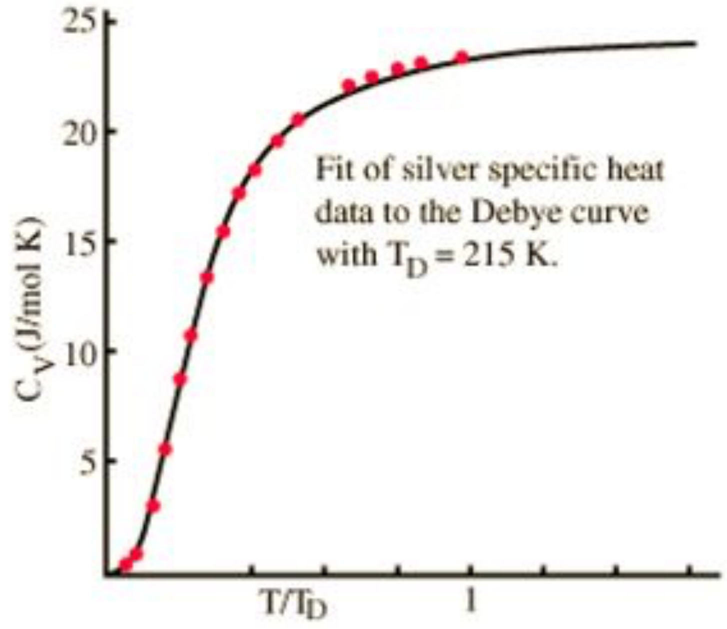
Virial theorem: $\mathrm{U} = 6\mathrm{N}\frac{kT}{2} = 3NkT$

Heat capacity of solids



Lattice vibrations: sum of harmonic oscillators

$$H = \frac{1}{2}\sum_{i=1}^{3N}(p_i^2+\omega_i^2 q_i^2)$$



Virial theorem: $\mathrm{U} = 6\mathrm{N}\frac{kT}{2} = 3NkT \rightarrow C_V = 3Nk$

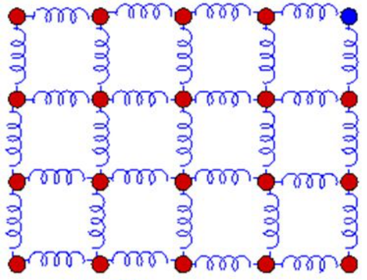
Dulong-Petit's law

Heat capacity: $C_V = \frac{\partial U}{\partial T} = 3Nk$ independent of T!

Puzzle of $C_V(T)$ *at low temperature*

Phonon gas: Einstein model

- Phonon: quanta of lattice vibrations (elastic waves) analogous to quanta of EM waves (photons)

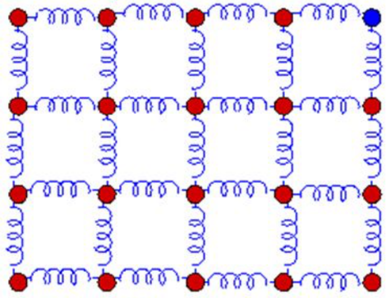


- Let us assume that all atoms vibrate with the same frequency, hence all phonons occupy the same mode and have the energy $\epsilon_\omega = \hbar\omega$

- By anology with photons, the average number of phonons for a given frequency mode ω follows the Bose-Einstein distribution

$$\langle n_\omega \rangle = \frac{1}{e^{\beta\hbar\omega} - 1}$$

Einstein model: thermodynamic propertieds



- Average energy of phonons with frequency ω

$$\langle E(\omega)\rangle = \hbar\omega\langle n_\omega\rangle = \frac{\hbar\omega}{e^{\beta\hbar\omega} - 1}$$

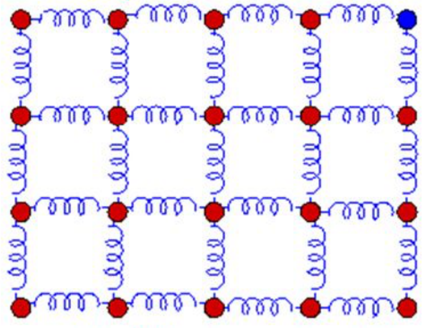
- Total energy of the solid:

$$\mathrm{U} = 3N\langle E(\omega)\rangle = \frac{3N\hbar\omega}{e^{\beta\hbar\omega - 1}}$$

- Heat capacity:

$$\mathrm{C_V} = \frac{\mathrm{dU}}{\mathrm{dT}} == 3Nk\left(\frac{\hbar\omega}{kT}\right)^2 \frac{e^{\beta\hbar\omega}}{\left(e^{\beta\hbar\omega - 1}\right)^2}$$

Einstein model: Heat capacity



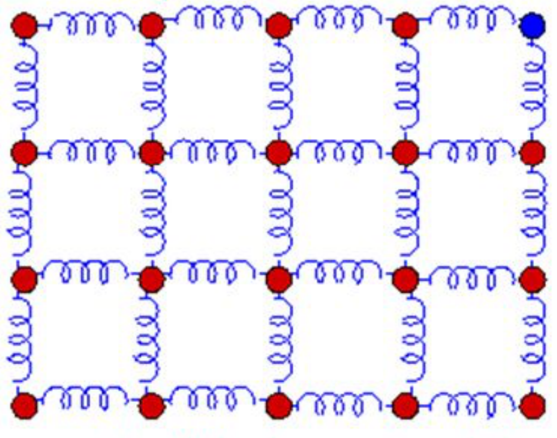
- Heat capacity:

$$C_V = \frac{dU}{dT} = = 3Nk \left(\frac{\hbar\omega}{kT}\right)^2 \frac{e^{\beta\hbar\omega}}{\left(e^{\beta\hbar\omega} - 1\right)^2}$$

- $C_V \approx \begin{cases} 3Nk\left(\frac{\hbar\omega}{kT}\right)^2 e^{-\beta\hbar\omega}, & kT \ll \hbar\omega \\ 3Nk\,, kT \gg \hbar\omega \end{cases}$

- Experimenatlly $C_V(T)$ goes to 0, but not exponentially

Phonon gas: Debye model



- The assumption that all atoms vibrate at the same frequency is relaxed!

  Atoms vibrate with different frequencies and a linear dispersion

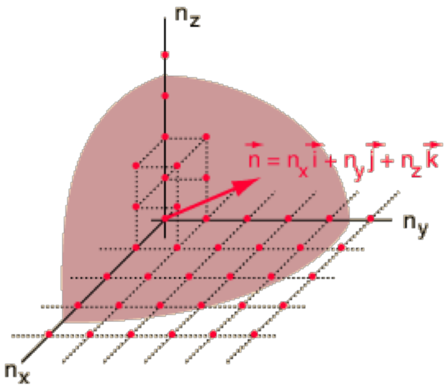
  $\omega = kv$, where v is the sound wave in the solid

- Density of elastic modes is analogous to the density of states for photons

(in the long-wavelength approximation, continuum elastic medium)

$$\sum_{\vec{n}} = \sum_{n_x}\sum_{n_y}\sum_{n_z} \approx_{N,L\to\infty} 3\int d\vec{n} = 3\int dn\, 4\pi n^2 = 3\frac{V}{(2\pi)^3}\int d\vec{k} = \int dk\, D(k)$$

$$D_n(n) = 3\times 4\pi n^2, \quad D(k) = 3\frac{V}{2\pi^2}k^2, \quad D_\omega(\omega) = 3\frac{V}{2\pi^2}\frac{\omega^2}{v^2}\frac{dk}{d\omega} = 3\frac{V}{2\pi^2}\frac{\omega^2}{v^3}$$



- Factor 3 accounts for three polarizations of the sound waves: 2 transverse and 1 longitudinal

Debye model: Density of states

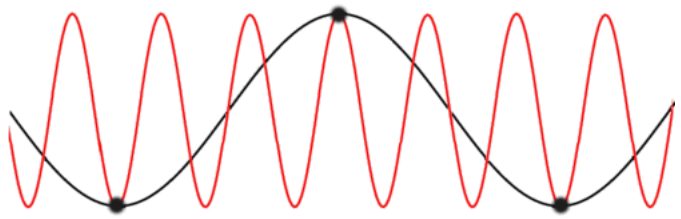
- Density of states for a phonon at a given frequency

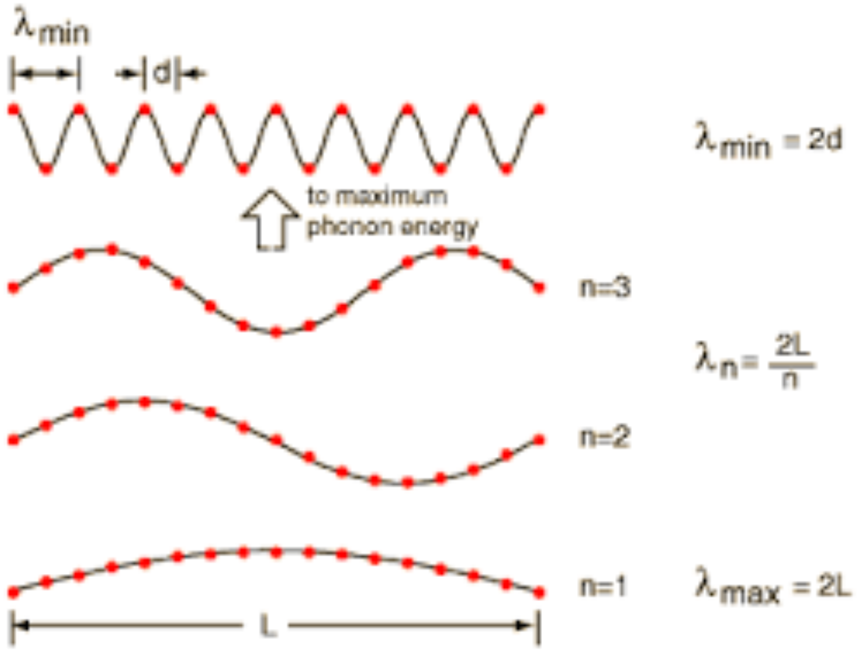
$$D(\omega) = 3\frac{V}{2\pi^2}\frac{\omega^2}{v^3}$$

- Spectrum of possible wavelengths in a solid is bounded by the system size $\lambda_{max} = L \rightarrow \infty$ and the lattice distance $\lambda_{\min} = 2d$

- This means that

- $\omega \in [0, \omega_D]$, $\omega_D = \frac{\pi v}{d}$ upper bound on the allowed frequencies

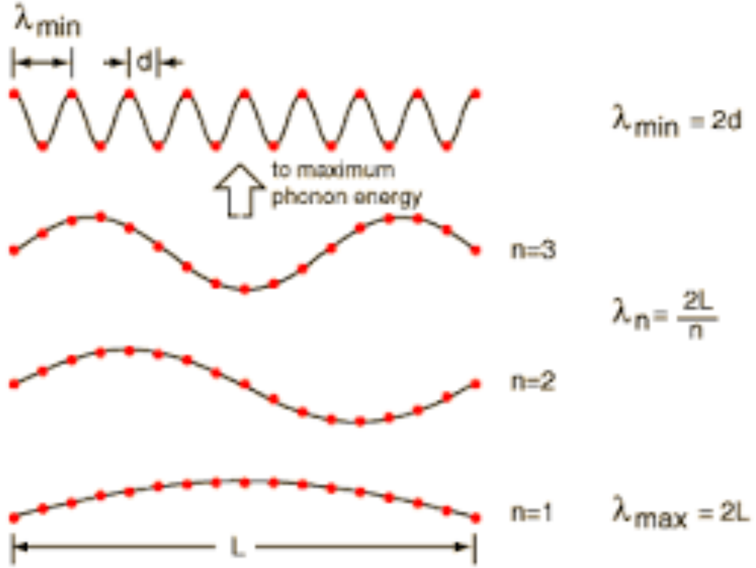




Debye frequency

Density of elastic modes is analogous to the density of states for photons

$$D(\omega) = 3\frac{V}{2\pi^2}\frac{\omega^2}{v^3}, for \;\; 0 \leq \omega \leq \omega_D$$



- Total number of modes: $3N$ normal modes (in 3D) for N atoms

$$3N = \int_0^{\omega_D} d\omega\, D(\omega) = 3\frac{V}{2\pi^2 v^3}\int_0^{\omega_D} d\omega\, \omega^2$$

Debye frequency $\omega_D = v\left(\frac{6\pi^2 N}{V}\right)^{\frac{1}{3}} \rightarrow \omega_D = \frac{2\pi v}{\lambda_{\min}} = v(6\pi^2\rho)^{\frac{1}{3}}, \quad \rho = \frac{N}{V}$

Debye model: Thermodynamics

- Density of elastic modes is analogous to the density of states for photons

$$D(\omega) = 3\frac{V}{2\pi^2}\frac{\omega^2}{v^3}, for\ \ 0 \leq \omega \leq \omega_D = v\left(\frac{6\pi^2 N}{V}\right)^{\frac{1}{3}}$$

- Total average energy of phonons

$$U(T,V) = \int_0^{\omega_D} d\omega\, D(\omega)\frac{\hbar\omega}{e^{\beta\hbar\omega}-1} = 3k\frac{V}{2\pi^2 v^3}\int_0^{\omega_D} d\omega\, \omega^2 \frac{\hbar\omega}{e^{\beta\hbar\omega}-1}$$

- Heat capacity

$$C_V(T) = \left(\frac{\partial U}{\partial T}\right)_V = \ 3k\frac{V}{2\pi^2 v^3}\int_0^{\omega_D} d\omega\, \omega^2 \left(\frac{\hbar\omega}{kT}\right)^2 \frac{e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega}-1)^2}$$

Debye model: Heat capacity

$$C_V(T) = 3k\,\frac{V}{2\pi^2 v^3}\int_0^{\omega_D} d\omega\,\omega^2\left(\frac{\hbar\omega}{kT}\right)^2\frac{e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega}-1)^2}$$

$$x = \frac{\hbar\omega}{kT}, \qquad T_D = \frac{\hbar\omega_D}{k}$$

$$C_V(T) = \ 3k\,\frac{V}{2\pi^2 v^3}\left(\frac{kT}{\hbar}\right)^3\int_0^{\frac{T_D}{T}} dx\,\frac{x^4 e^x}{(e^x-1)^2}$$

$$C_V(T) = 9Nk\,\left(\frac{T}{TD}\right)^3 F\left(\frac{T_D}{T}\right), \qquad F(y) = \int_0^y dx\,\frac{x^4 e^x}{(e^x-1)^2}$$

High T limit: $T \gg T_D \rightarrow y = \frac{T_D}{T} \ll 1$

$$F(y) = \int_0^y dx\,\frac{x^4 e^x}{(e^x-1)^2} = \int_0^y dx\,\frac{x^4}{x^2} = \frac{1}{3}y^3$$

$$\boldsymbol{C_V(T) \approx 3Nk, \qquad T \gg T_D}$$

Debye model: heat capacity

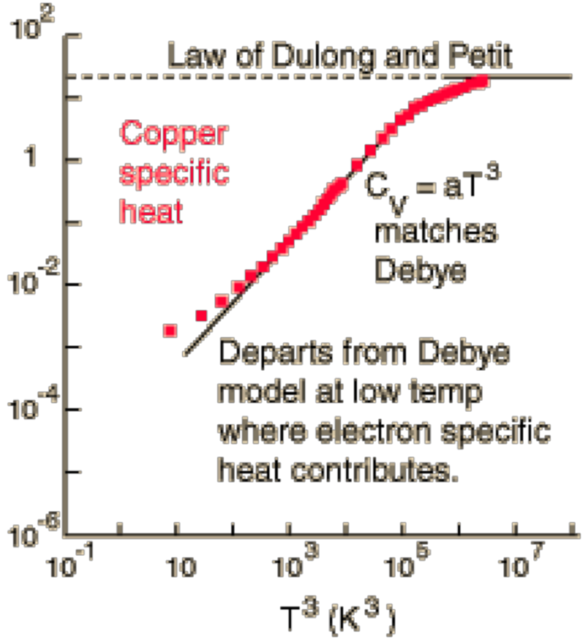
$$C_V(T) = 9Nk\left(\frac{T}{TD}\right)^3 F\left(\frac{T_D}{T}\right),$$

$$F(y) = \int_0^y dx\,\frac{x^4 e^x}{(e^x-1)^2}$$

Low T limit: $T \ll T_D$

$$F(y) \rightarrow_{y\rightarrow\infty} F(y) = \int_0^\infty dx\,\frac{x^4 e^x}{(e^x-1)^2} = \frac{4\pi^4}{15}$$

$$C_V(T) \approx \frac{12}{5} Nk\pi^4 \left(\frac{T}{T_D}\right)^3$$



after Rohlf