# Lattice heat capacity

evaluation of different models: Dulong-Petit, Einstein, Debye

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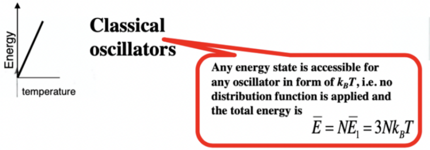
# Dulong-Petit model

- Classical oscillators
- Any energy is accessible
- Assume heat stored as vibrations



# Dulong-Petit model

- Equipartition of energy: Energy is shared equally amongst all energetically accessible degrees of freedom of a system (maximizing entropy by spreading out energy in the system).
- Predicts that each quadratic degree of freedom $f$ will have the energy $\frac{1}{2}k_B T$. The energy of the vibrational motion in x-direction, for instance, is:

  $$U_x = \frac{1}{2}mv_x^2 + \frac{1}{2}k_B \Delta x^2$$

  Considering $\mathrm{x}, \mathrm{y}$ and $\mathrm{z}$ direction we get $f = 2 \cdot 3 = 6$ and the total energy per atom (according to equipartition of energy) becomes

  $$E_{atom} = 6 \cdot \frac{1}{2}k_B T = 3k_B T$$

  For $N$ atoms we get

  $$E_{tot} = 3k_B TN$$

  And heat capacity

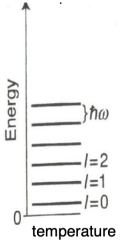
  $$C = \frac{dE}{dT} = 3k_B N$$

# Dulong-Petit

- Dulong-Petit only match with experiments for high temperatures ($T \geqslant 300\ \mathrm{K}$). That can be explained by the fact that all vibrational modes are fully activated/available at high temperatures, in which case equipartition theory can be used.
- This means for lower temperatures we must use quantum statistics and consider that not all vibrational modes are available, and that energy might be insufficient to excite the vibrational modes.

# Einstein model

- Quantum oscillators
- Discrete energy, not all energy levels are allowed
- Assume heat stored as vibrations




**Quantum oscillators**

**Not all energies are accessible, but only those in quants of $\hbar\omega n$, and Planck distribution is employed to calculate the occupancy at temperature T, so that**

$$E = 3N \cdot \langle n \rangle \cdot \hbar\omega$$

# Einstein model

- We can estimate the average energy for 3N oscillators: $< E_{tot} >= 3N < E_i >$ and each harmonic oscillator can have only discrete energy level: $E = n\hbar\omega$
- The energy for a single oscillator, in canonical ensemble is:

$$\langle E \rangle = \frac{\sum_{n=0}^{\infty} n\hbar\omega \exp\left[-n\hbar\omega / \left(k_B T\right)\right]}{\sum_{n=0}^{\infty} \exp\left[-n\hbar\omega / \left(k_B T\right)\right]} \tag{1}$$

# Einstein model

- For the ske of clarity we replaced $\frac{1}{k_B T} = \beta$. After some calculations :
$$\langle E \rangle = \frac{\sum_{n=0}^{\infty} n\hbar\omega \exp(-\beta n\hbar\omega)}{\sum_{n=0}^{\infty} \exp(-\beta n\hbar\omega)}$$
- $$\langle E \rangle = -\frac{\partial}{\partial\beta} \ln\left[\sum_{n=0}^{\infty} \exp(-\beta n\hbar\omega)\right]$$
$$= -\frac{\partial}{\partial\beta} \ln\left[\sum_{n=0}^{\infty} (\exp(-\beta\hbar\omega))^n\right]$$
- The argument $(-\beta\hbar\omega)$ inside the geometrical series is less than 1, hence converge to a finite value.
$$\langle E \rangle = -\frac{\partial}{\partial\beta} \ln \frac{1}{1-\exp(-\beta\hbar\omega)}$$
$$= \frac{\hbar\omega \exp(-\beta\hbar\omega)}{1-\exp(-\beta\hbar\omega)}$$
$$= \frac{\hbar\omega}{\exp(\beta\hbar\omega)-1}$$
- At the end each harmonic oscillator contributes with an average energy:
$$\langle E \rangle = \frac{\hbar\omega}{\exp\left[\hbar\omega/\left(k_B T\right)\right]-1}$$

# Einstein model

- Hence the total energy is:

$$E_{tot} = \langle E \rangle = \frac{\hbar\omega}{\exp\left[\hbar\omega / \left(k_B T\right)\right] - 1} \tag{2}$$

- The heat capacity follow as the derivative of the total energy:

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = 3Nk_B \left(\frac{\hbar\omega}{k_B T}\right)^2 \frac{e^{\frac{\hbar\omega}{k_B T}}}{\left(e^{\frac{\hbar\omega}{k_B T}} - 1\right)^2} \tag{3}$$

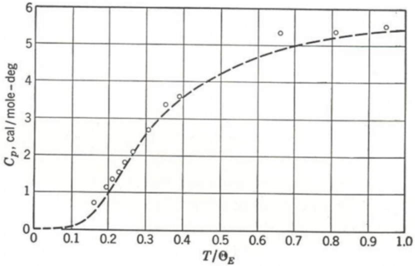



Fig. 6.2. Comparison of experimental values of the heat capacity of diamond and values calculated on the Einstein model, using $\Theta_E = 1320°K$. [After A. Einstein, Ann. Physik **22,** 180 (1907).]

**Figure 1:** From the picture we see a good agreement for medium-high temperature, however for $t \to 0$ the Einstein specific heat goes to 0 faster than expected

# Debye Model

- 3N normal modes of oscillations.
- Spectrum of frequency from $\omega = 0 to \omega_D$ (due to the limit on number of modes, fixed degree of freedom )
- Treat solid as continuous elastic medium (ignore details of atomic structure)
- Normal modes: An oscillation in which all particles move with the same frequency and phase.

## Debye Model Title

- Each mode of oscillation contributes a frequency-dependent heat capacity, and we should integrate over all possible $\omega$:

$$C_V(T) = \int_0^{\omega_D} D(\omega) C_E(\omega, T) d\omega$$

- Allowed number of $\mathrm{k}$ -values with modules less than $\mathrm{k}$ (inside sphere with radius $\mathrm{k}$ ):

$$N(k) = \left(\frac{L}{2\pi}\right)^3 \frac{4\pi}{3} k^3$$

- The velocity of sound $v$ is taken as constant and we have

$$\omega = vk$$

- Which yields

$$N(\omega) = \left(\frac{L}{2\pi}\right)^3 \frac{4\pi}{3} \frac{\omega^3}{v^3} = \frac{V\omega^3}{6\pi^2 v^3}$$

# Debye Model

- Now we can calculate the density of states

$$\text{DOS}(\omega) = \frac{dN(\omega)}{d\omega} = \frac{V\omega^2}{2\pi^2 v^3}$$

- If there are $\mathrm{N}$ primitive cells in the sample, the total number of acoustic phonon modes is $N$. The cut off frequency $\omega_D$ is determined from $N(\omega)$ to be

$$N(\omega) = N \Leftrightarrow \omega_D^3 = \frac{6\pi^2 v^3 N}{V}$$

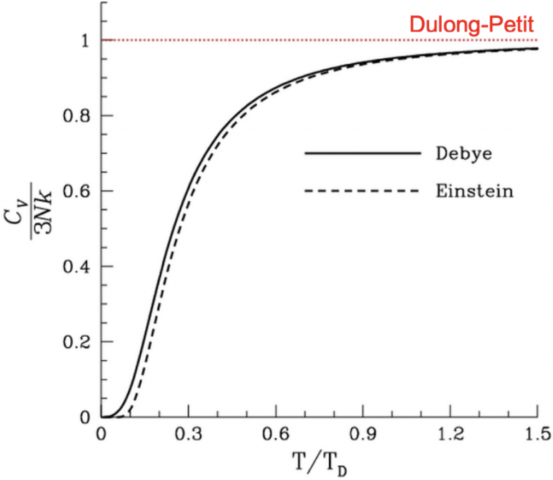
- We define the Debye temperature $\theta_D$ as the temperature of a crystal's highest normal mode of vibration, that is the highest temperature that can be achieved due to a single normal vibration. This is found as

$$E_{\text{max}} = \hbar\omega_D = k_B\theta_D$$

where : $\theta_D = \frac{\hbar\omega_D}{k_B} = \frac{\hbar v}{k_B}\left(\frac{6\pi^2 N}{V}\right)^{\frac{1}{3}}$

- The total thermal energy (considering 3 polarizations for acoustic modes) is then
$$U = 3\int D(\omega)n(\omega)\hbar\omega d\omega = 3\int_0^{\omega_D} \frac{V\omega^2}{2\pi^2 v^3}\frac{\hbar\omega}{e^{\frac{\hbar\omega}{k_B T}}-1}d\omega$$
- Where we used that average occupancy of energy levels in equilibrium is given from Planck distribution:
$$\langle n\rangle = \frac{1}{e^{\frac{\hbar\omega}{k_B T}}-1} = n(\omega)$$
- We then find the heat capacity to be
$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = \frac{3V\hbar^2}{2\pi^2 v^3 k_B T^2}\int_0^{\omega_D}\frac{\omega^4 e^{\frac{\hbar\omega}{k_B T}}}{\left(e^{\frac{\hbar\omega}{k_B T}}-1\right)^2}d\omega$$
- Substitute $x = \frac{\theta_D}{T} = \frac{\hbar\omega}{k_B T}$ :
$$C_V = 9Nk_B\left(\frac{T}{\theta_D}\right)^3\int_0^{x_D}\frac{x^4 e^x}{(e^x-1)^2}dx$$
- Here we can see the good behaviour at low temperatures that Einstein cannot predict.

# Comparisons



# Comparisons

- Debye temperature is related to stiffens of material (stiffer materials have higher Debye temperature). For temperatures above the Debye temperature all the phonons are activated and it will follow the classical model by Dulong-Petit.

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- however, at very very low temperature we need to take into account also the heat capacity from the FEFG, that goes linear with the temperature.