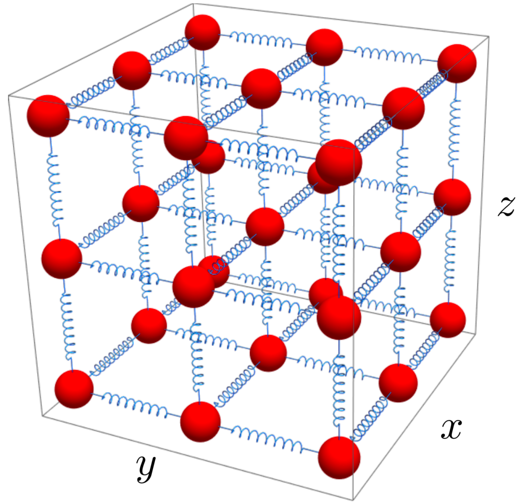
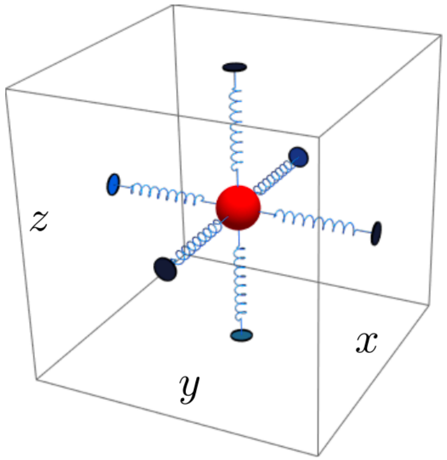
8. Einstein model of a simple solid

Simple model of a solid

- A model for the vibrational motion of the atoms in a crystal considers them attached to each other by springs.
- However this a (strongly) interacting system since energy is stored in interaction potentials between atoms.





- The Einstein model creates a weakly interacting system by ignoring interactions and assuming that each atom sits in its own harmonic potential

Simple model of a solid

- Let us first consider the model **classically**
- Each oscillator has energy $\varepsilon = \frac{1}{2}\kappa\vec{x}^2 + \frac{1}{2}m\vec{v}^2$
- Equipartition: In 3d there are 6 squared degrees of freedom, each carrying $\frac{1}{2}kT$ energy.
- Thus $\overline{E} = 3NkT$,

$$C_V = \frac{\partial \overline{E}}{\partial T} = 3Nk \quad \text{(Dulong-Petit law)}$$

- Dulong-Petit law holds experimentally for many monoatomic crystals, but not for Diamond.
- Einstein showed the anomaly for Diamond is due to it having a very large spring constant κ implying that one has to consider quantum effects

Statistical mechanics of the quantum h.o.

- Recall that for the 1d quantum harmonic oscillator the energy level are

$$\varepsilon \equiv \varepsilon_{1d} = \left(n + \frac{1}{2}\right)\hbar\omega \quad n = 0,1,2\ldots$$

(See Chapter 8 of quantum mechanics notes)

$$\varepsilon_{3d} = \left(n_x + n_y + n_z + \frac{3}{2}\right)\hbar\omega$$

- Einstein's model is a system of N $3d$ quantum oscillators all with the same frequency ω in thermal equilibrium; ω is chosen to fit the experimental data.
- Since they are independent (weakly interacting) we have the factorisation

$$Z = [Z(1)]^N = \left[Z_{1d}(1)\right]^{3N}$$

where $Z_{1d}(1) = \sum_{n=0}^{\infty} \exp\left(-\beta\hbar\omega\left[n + \frac{1}{2}\right]\right)$ is the partition function for a single 1d oscillator

Statistical mechanics of the quantum h.o.

- To evaluate the sum recall the geometric series $\sum_{n=0}^{\infty} a^n = \dfrac{1}{1-a}$, valid for $|a| < 1$

$$a = \exp(-\beta\hbar\omega) \Rightarrow \quad Z_{1d}(1) = \frac{\exp\left(-\frac{x}{2}\right)}{1-\exp(-x)} \quad \text{where} \quad x = \beta\hbar\omega$$

- Knowing Z, we can calculate all thermodynamic quantities of interest
- Now from the q.h.o. energy levels, we have $\overline{E} = 3N\overline{\varepsilon} = 3N\hbar\omega\left(\overline{n} + \dfrac{1}{2}\right)$

mean energy level

But we also have

$$\overline{\varepsilon} = -\frac{\partial}{\partial\beta}\ln Z_{1d}(1) = -\frac{dx}{d\beta}\frac{\partial}{\partial x}\ln Z_{1d}(1)$$

$$= -\hbar\omega\frac{\partial}{\partial x}\left[-\ln\left(1-\exp(-x)\right) - \frac{x}{2}\right]$$

$$= \hbar\omega\left[\frac{\exp(-x)}{1-\exp(-x)} + \frac{1}{2}\right]$$

Statistical mechanics of the quantum h.o.

- This implies that the mean energy level is $\bar{n} = \dfrac{\exp(-x)}{1-\exp(-x)} = \dfrac{1}{\exp(x)-1}$ $\quad x = \beta\hbar\omega = \dfrac{\hbar\omega}{kT}$

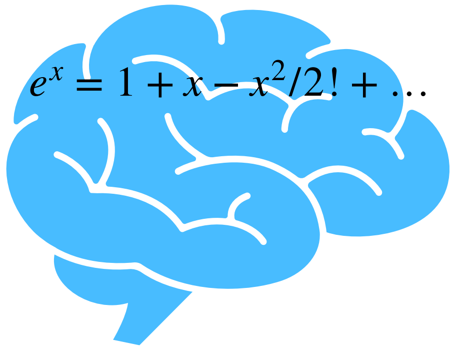
- Hence $\bar{E} = 3N\hbar\omega\left[\dfrac{1}{\exp(x)-1} + \dfrac{1}{2}\right]$

- The constant volume heat capacity is: $C_V = \left(\dfrac{\partial \bar{E}}{\partial T}\right) = \left(\dfrac{\partial x}{\partial T}\right)\left(\dfrac{\partial \bar{E}}{\partial x}\right)$

$$C_V = -3N\frac{\hbar\omega}{kT^2}\frac{d}{dx}\left[\frac{1}{\exp(x)-1}\right] = 3Nk\frac{x^2\exp(x)}{(\exp(x)-1)^2}$$

- Consider the high T limiting behaviour of $\overline{E}$ and C_V

- When $x = \dfrac{\hbar\omega}{kT}$ is small, $e^x \approx 1 + x$



$e^x = 1 + x - x^2/2! + \ldots$

$$\overline{E} = 3N\hbar\omega \left[\frac{1}{\exp(x) - 1} + \frac{1}{2}\right]$$

$$\approx 3N\hbar\omega \left[\frac{1}{x} + \frac{1}{2}\right]$$

$$\approx 3NxkT \left[\frac{1}{x} + \frac{1}{2}\right]$$

$$\overline{E} \approx 3NkT + \frac{3}{2}N\hbar\omega$$

$$C_V = \left(\frac{\partial \overline{E}}{\partial T}\right)_V \approx 3Nk$$

- When $x = \dfrac{\hbar\omega}{kT}$ is large,

$$\overline{E} = 3N\hbar\omega \left[\frac{1}{\exp(x) - 1} + \frac{1}{2}\right]$$

$$\approx 3NxkT \left[\exp(-x) + \frac{1}{2}\right]$$

$$C_V = 3Nk\frac{x^2 \exp(x)}{(\exp(x) - 1)^2}$$

$$\approx 3Nkx^2 \exp(-x)$$

High and low temperature behaviour

- Define a characteristic temperature where $x = \beta\hbar\omega = 1$, i.e. excitation energy $\hbar\omega = kT$

$$T^\star = \frac{\hbar\omega}{k}$$

- $T^\star$: temperature below which quantum effects (with typical energy $\sim \hbar\omega$ dominate over classical effects with typical energy $\sim kT$

T

$T \gg T^\star, x \ll 1$

$$\bar{n} \approx \frac{1}{1 + x\ldots - 1} \approx \frac{1}{x} = \frac{kT}{\hbar\omega} \qquad \bar{E} \approx 3NkT + \frac{3}{2}N\hbar\omega$$

$$C_V = \left(\frac{\partial \bar{E}}{\partial T}\right)_V \approx 3Nk \quad \text{(Dulong-Petit)}$$

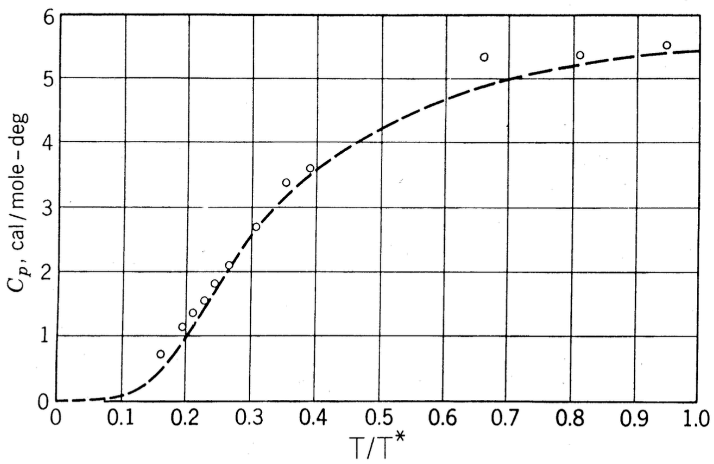
$T \ll T^\star, x \gg 1$

$$\bar{n} \approx \exp(-x) \qquad \frac{C_V}{3Nk} \approx x^2 \exp(-x)$$

Most oscillators are in the ground state; $C_V \ll 3Nk$.

High and low temperature behaviour

- $x = \hbar\omega/kT$ is small (high T): recover the 'classical' results where Planck's constant does not appear in the thermodynamic quantities (except as an arbitrary additive constant). Quite generally high T is the classical limit where equipartition holds.
- $x = \hbar\omega/kT$ is large (low T): quantum effects, in particular the effect of a discrete gap between the ground state and first excited state, become important. Furthermore the model neglects low-frequency collective effects of particle motion ('phonons').



The measured heat capacity of diamond, plotted as a function of $T/T^{\star}$, with $T^{\star} = 1320K$, compared with the Einstein model prediction.