Gases and Solids

Last time

Open systems

Free energy

Today

Ideal gases

Simple solids

Next time

Defects in solids

Progress so far…

- Statistical mechanics:
  - Equilibrium is the most likely configuration
  - Partition function is a sum over microstates that summarises what we usually want to know about a system
- Thermodynamics:
  - All of classical thermodynamics—heat, work, entropy, free energy—can be derived from statistical mechanics
  - Once you know the partition function, you can forget about the microscopic details

Today

Two idealised systems that can provide us with a wealth of intuition about statistical mechanics:

- Ideal gases
- Simple solids

Preliminary: Partition function is multiplicative

The overall partition function of two isolated systems is the product of their partition functions (*homework*: show this)

$$q_{\text{total}} = q_1 q_2$$

Therefore, for *N* distinguishable components, we can write

$$Q = q^N$$

For *N* <u>*in*</u>distinguishable components (e.g., molecules in a gas), the result is

$$Q = \frac{q^N}{N!}$$

Ideal gas: Translational energy levels

Translation: only degree of freedom for an atomic gas

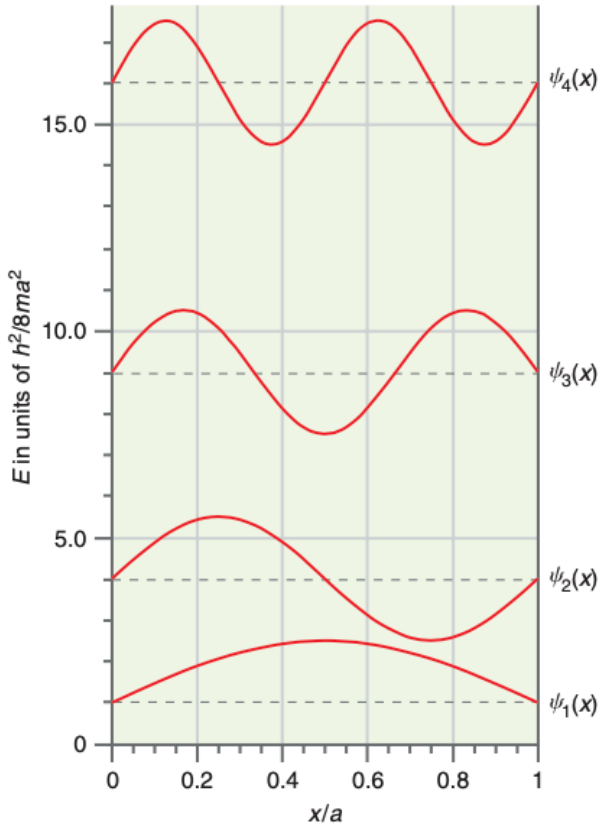
The energy levels of the 1D particle-in-a-box model:

$$\varepsilon_i = \frac{i^2 h^2}{8mL^2}$$

Energies depend on the size of the box. As *L* decreases and the particle is more confined, its energies increase.

A particle in a 3D box (a cube of side length *L*) requires three quantum numbers to specify the state:

$$\varepsilon_{i_x,i_y,i_z} = \frac{h^2}{8mL^2}\left(i_x^2 + i_y^2 + i_z^2\right)$$



Ideal gas: Partition function

In 1D, the molecular partition function is then

$$q = \sum_{i=1}^{\infty} e^{-\beta\varepsilon_i} = \sum_{i=1}^{\infty} e^{-\beta i^2 h^2/8mL^2}$$

This sum cannot be evaluated exactly.

But, if many states are occupied, we can replace the sum with an integral.

Can we do this? For helium in a 1 m^3 box,

$$\Theta_{\text{trans}} \sim \frac{h^2}{8mL^2k} \sim 10^{-18}\ \text{K}$$

Clearly, $T \gg \Theta$ for any sensible temperature

Ideal gas: Partition function

In 1D, the molecular partition function is then

$$q = \sum_{i=1}^{\infty} e^{-\beta\varepsilon_i} = \sum_{i=1}^{\infty} e^{-\beta i^2 h^2/8mL^2}$$

Replace sum with integral:

$$\approx \int_0^{\infty} e^{-\beta i^2 h^2/8mL^2}\, di$$

$$= \left(\frac{2\pi m}{h^2\beta}\right)^{1/2} L$$

In 3D,

$$q_{\text{trans}} = q_x q_y q_z = \left(\frac{2\pi m}{h^2\beta}\right)^{3/2} V$$

Ideal gas: Partition function

$$q_{\text{trans}} = q_x q_y q_z = \left(\frac{2\pi m}{h^2 \beta}\right)^{3/2} V$$

If we define the thermal wavelength as

$$\Lambda = \left(\frac{h^2 \beta}{2\pi m}\right)^{1/2}$$

we can write $$q_{\text{trans}} = \frac{V}{\Lambda^3}$$

Typical value for m^3 of gas: $$q_{\text{trans}} = 10^{30}$$

Ideal gas: Energy

We saw last week that

$$E = NkT^2 \frac{d \ln q}{dT}$$

This gives us

$$E_{\text{trans}} = NkT^2 \frac{d \ln q_{\text{trans}}}{dT} = \frac{3}{2} NkT = \frac{3}{2} nRT$$

Because $U = E$, we find that the internal energy of an ideal gas depends only on its temperature

Aside: Notice that *h* dropped out of the formula

Ideal gas: Equation of state

Finally, we want to find the equation of state for the ideal gas, i.e., the relationship between the macroscopic variables *p*, *V*, and *T*.

But what is *p*?

p is the generalised force conjugate to the volume, i.e., the work done on an expanding gas has to be

$$dW = -pdV$$

From before,

$$dU = \sum_i n_i \, d\varepsilon_i + \sum_i \varepsilon_i \, dn_i$$

Work Heat

Ideal gas: Equation of state

$$-pdV = dW = \sum_i n_i d\varepsilon_i \qquad \Rightarrow \qquad p = -\sum_i n_i \frac{d\varepsilon_i}{dV}$$

Recall that

$$\varepsilon_{i_x,i_y,i_z} = \frac{h^2}{8mL^2}\left(i_x^2 + i_y^2 + i_z^2\right) = \frac{h^2}{8m}\left(i_x^2 + i_y^2 + i_z^2\right)V^{-2/3} = aV^{-2/3}$$

constant w.r.t. V

Therefore:

$$\frac{d\varepsilon_i}{dV} = -\frac{2}{3}aV^{-5/3} = -\frac{2}{3}\varepsilon_i V^{-1}$$

Overall:

$$p = \sum_i n_i \frac{2}{3}\varepsilon_i V^{-1} = \frac{2}{3}V^{-1}E = \frac{NkT}{V} = \frac{nRT}{V}$$

This *derives* the ideal gas law from purely microscopic principles!

Ideal gas: Equation of state, version 2

Like everything else, p can be obtained once you know the partition function

$$dA = -SdT - pdV \qquad \Rightarrow \qquad p = -\left(\frac{\partial A}{\partial V}\right)_T$$

$$A = -kT \ln Q = -kT \ln \frac{q^N}{N!}$$

$$p = -\left(\frac{\partial}{\partial V}\left(-kT \ln \frac{q^N}{N!}\right)\right)_T = NkT\left(\frac{\partial}{\partial V} \ln q\right)_T$$

$$= NkT\left(\frac{\partial}{\partial V} \ln\left(\frac{V}{\Lambda^3}\right)\right)_T = \frac{NkT}{V}$$

Ideal gas: Heat capacity

The heat capacity is the amount of heat that needs to be supplied to an object to increase its temperature by one unit:

$$C = \frac{dQ}{dT}$$

For an ideal, monoatomic gas at constant volume:

$$C_V = \left(\frac{dQ}{dT}\right)_V = \left(\frac{dU}{dT}\right)_V = \left(d\frac{\left(\frac{3}{2}NkT\right)}{dT}\right)_V = \frac{3}{2}Nk = \frac{3}{2}nR$$

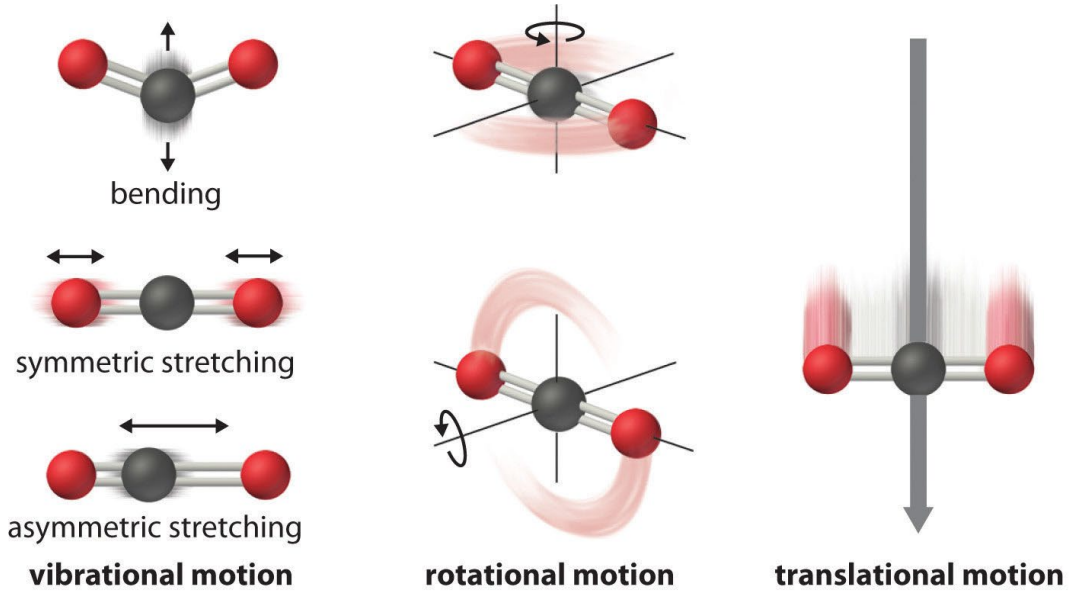
Homework: Show that, at constant pressure, $C_P = \frac{5}{2}Nk$

Polyatomic gases

So far, we looked at monoatomic gases (only translational freedom)

Polyatomic gases can also vibrate and rotate, or have excited electronic states (see E&R ch. 31)

$$q = q_{\text{trans}} q_{\text{vib}} q_{\text{rot}} q_{\text{elec}}$$



Nevertheless, the ideal gas law, $pV = NkT$, is still true for ideal polyatomic gases.

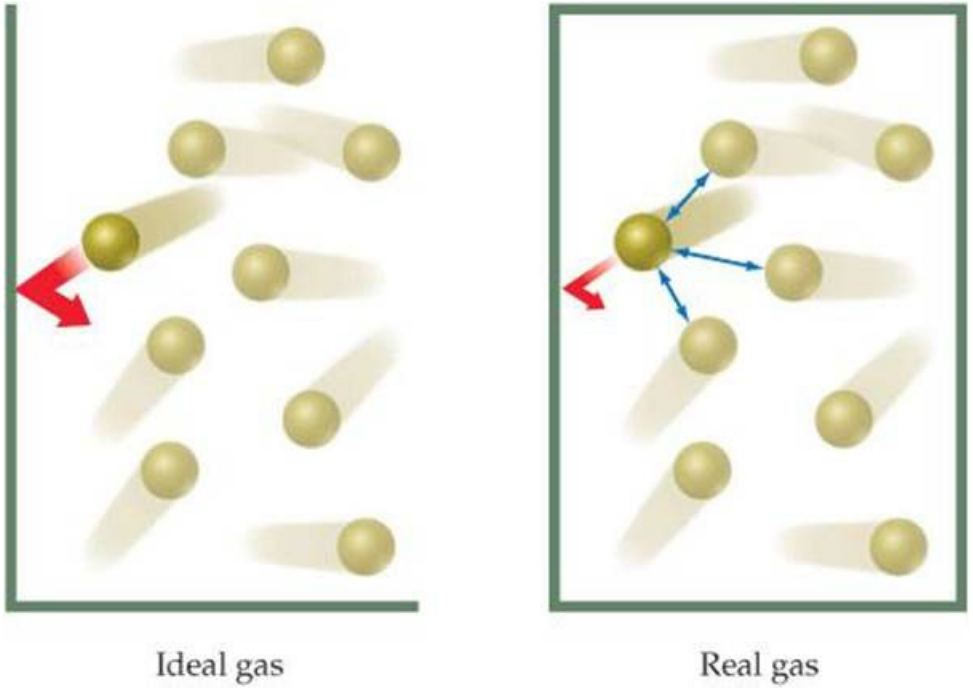
Mentimeter

Non-ideal gases

Real gases deviate from ideal behaviour because of interactions between the atoms (or molecules)

The interactions become important at high *p*, when the molecules can't avoid each other, and at low *T*, when energy-lowering interactions are more important than the entropy of expansion

More on this next week

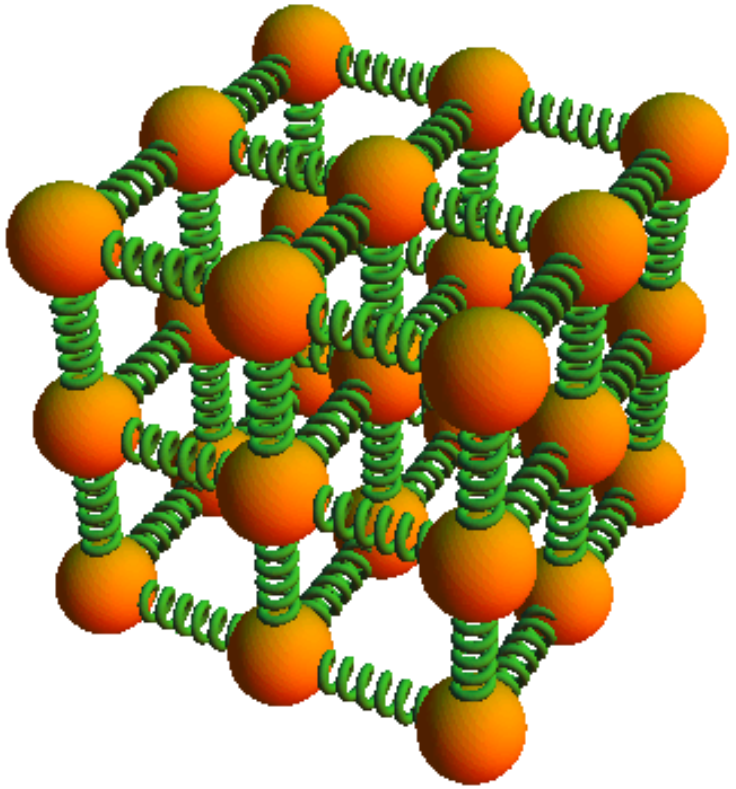


Simple solids

Vibration is the only possible degree of freedom in simple solids (e.g. Ar(s), metals).

Atoms in crystalline lattices can vibrate in all three dimensions

Therefore, a lattice of N atoms hosts $3N$ vibrations and $3N$ sets of energy levels.

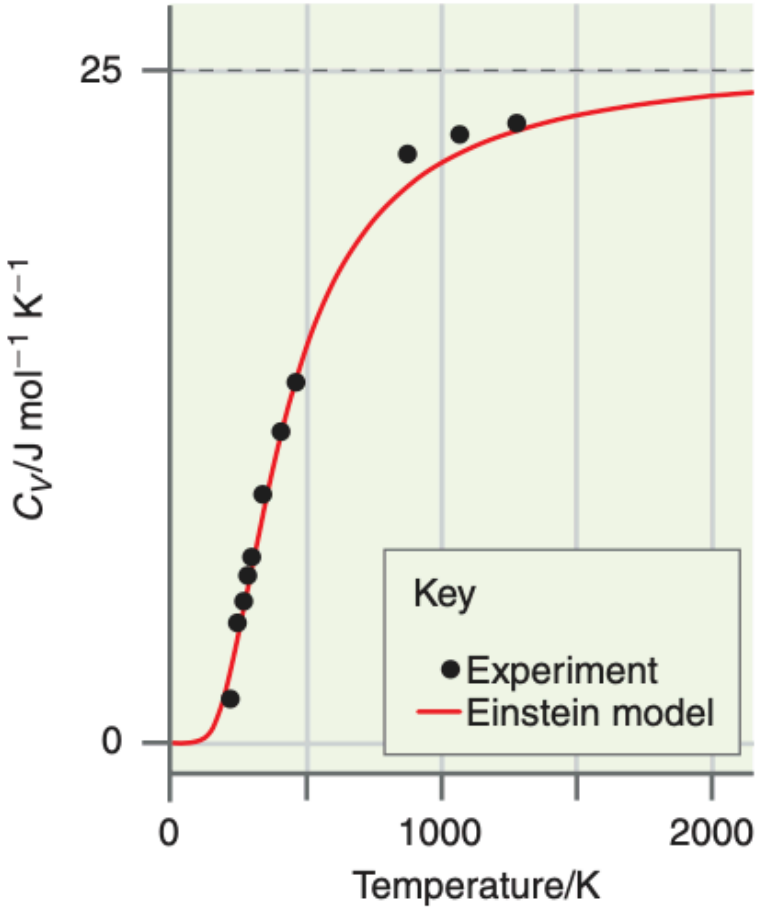


Simple solids: Einstein model

Einstein proposed a model (the "Einstein solid") to explain how the heat capacity of solids changes with temperature.

Two assumptions:

- Each atom is an independent 3D quantum harmonic oscillator
- All atoms oscillate with the same frequency

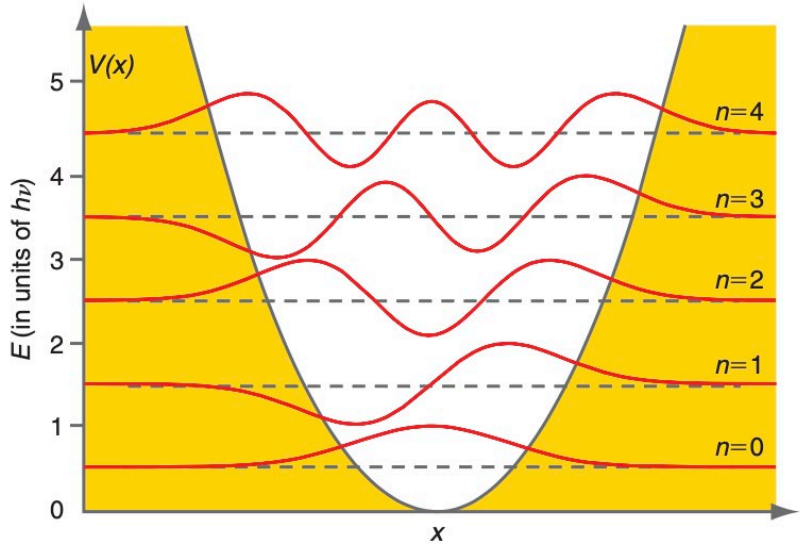


1D harmonic oscillator: Energy levels

In a harmonic oscillator, the energy levels are equally spaced

$$E_n = h\nu\left(n + \frac{1}{2}\right)$$

Ignoring the zero-point energy: $E_n = h\nu n$



The characteristic temperature for vibration is

$$\Theta_{\mathrm{vib}} = \frac{h\nu}{k}$$

Typical values of Θ_{vib}	
Ar (s)	40 K
Pb (s)	60 K
SO_2 (g) stretch	2000 K
H_2O (g) stretch	5000 K

1D harmonic oscillator: Partition function

The partition function of a harmonic oscillator can be calculated exactly

$$q_{\mathrm{vib}} = \sum_{n=0}^{\infty} e^{-\beta n h\nu} = e^0 + e^{-\Theta_{\mathrm{vib}}/T} + \left(e^{-\Theta_{\mathrm{vib}}/T}\right)^2 + \left(e^{-\Theta_{\mathrm{vib}}/T}\right)^3 + \ldots$$

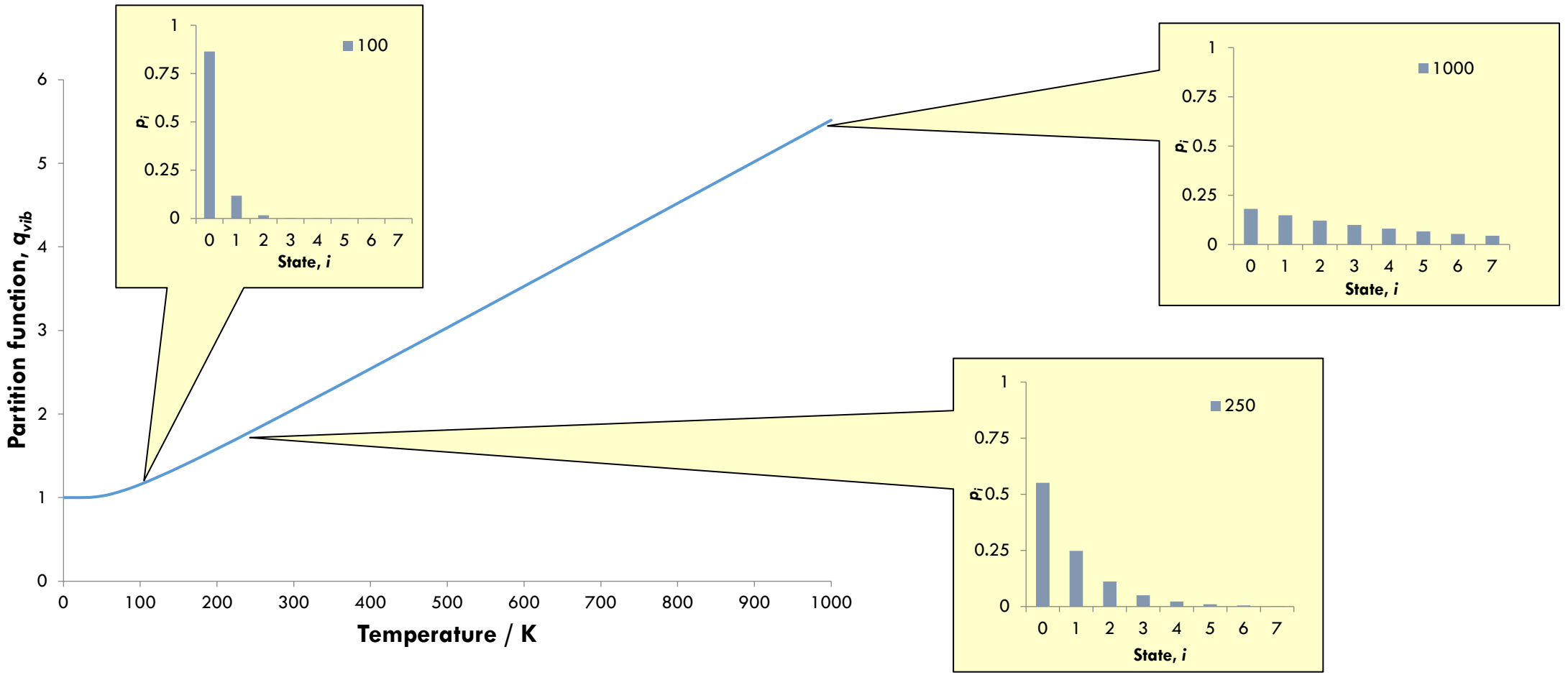
This is a geometric series, so we can sum it up:

$$\sum_{n=0}^{\infty} x^n = \frac{1}{1-x} \text{ if } |x| < 1$$

$$q_{\mathrm{vib}} = \frac{1}{1 - e^{-\Theta_{\mathrm{vib}}/T}}$$

1D harmonic oscillator: Partition function

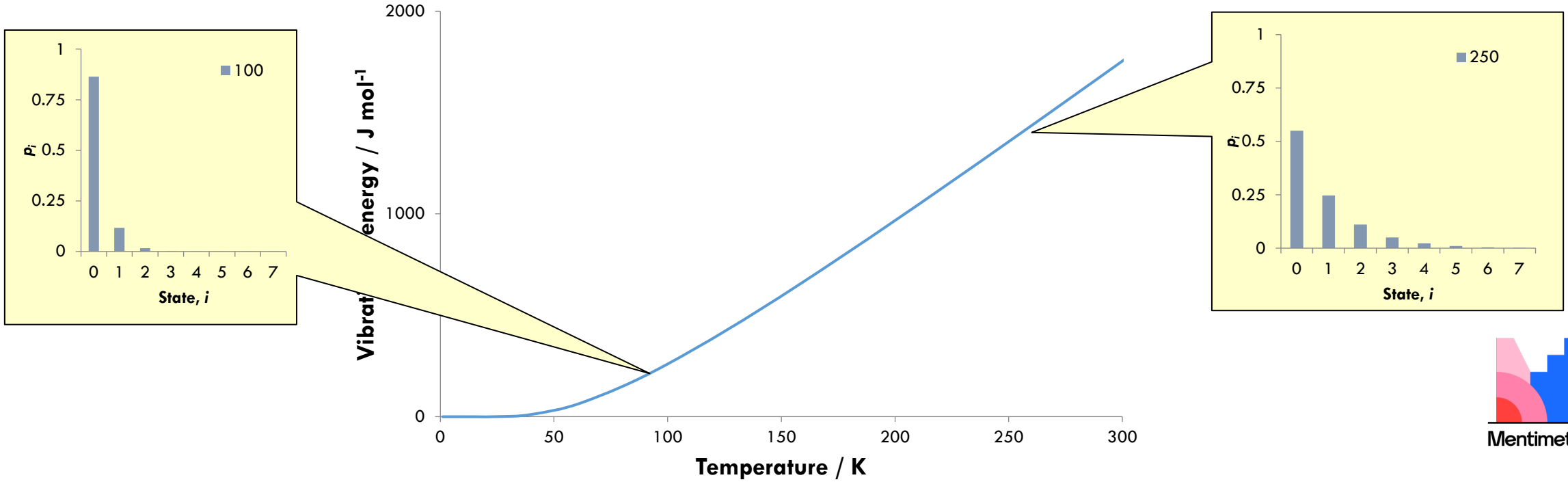
Here is how the energy is partitioned for an oscillator with Θ = 200 K



1D harmonic oscillator: Vibrational energy

The energy (above the zero-point energy) is then

$$E = NkT^2 \frac{d \ln q}{dT} = NkT^2 \frac{d}{dT} \ln \left[1 - \exp\left(-\Theta_{\text{vib}}/T\right)\right]^{-1} = \frac{Nk\Theta_{\text{vib}}}{\exp\left(\Theta_{\text{vib}}/T\right) - 1}$$



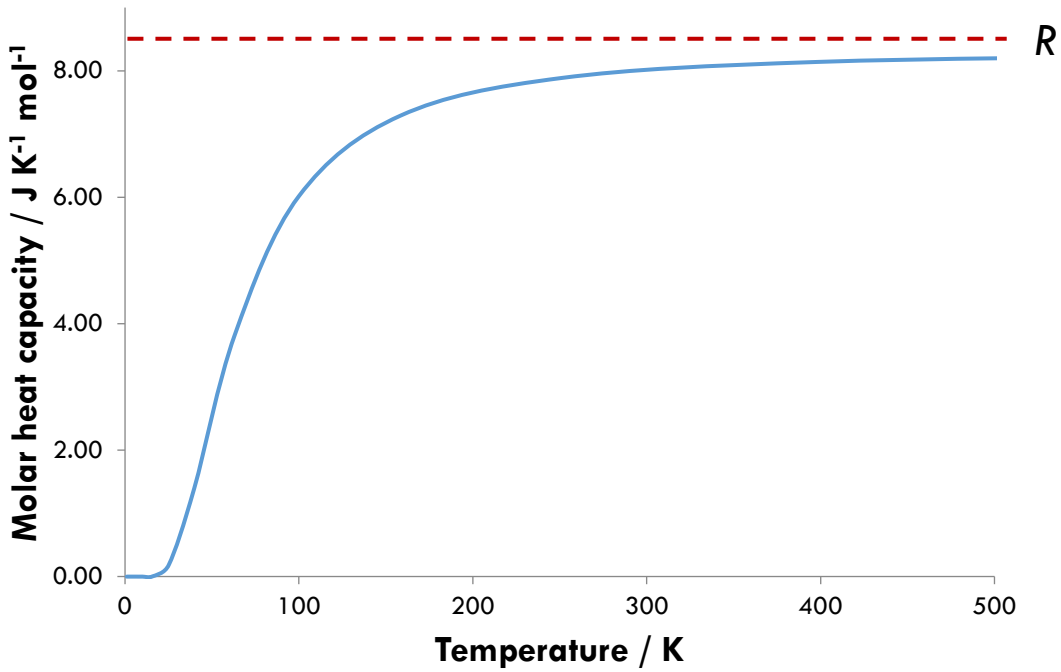
Mentimeter

1D harmonic oscillator: Heat capacity

The heat capacity increases with T as the molecules are able to absorb more energy

$$C_V = \left(\frac{dE}{dT}\right)_V$$

$$= Nk\left(\frac{\Theta_{\text{vib}}}{T}\right)^2 \frac{\exp\left(\Theta_{\text{vib}}/T\right)}{\left(\exp\left(\Theta_{\text{vib}}/T\right)-1\right)^2}$$

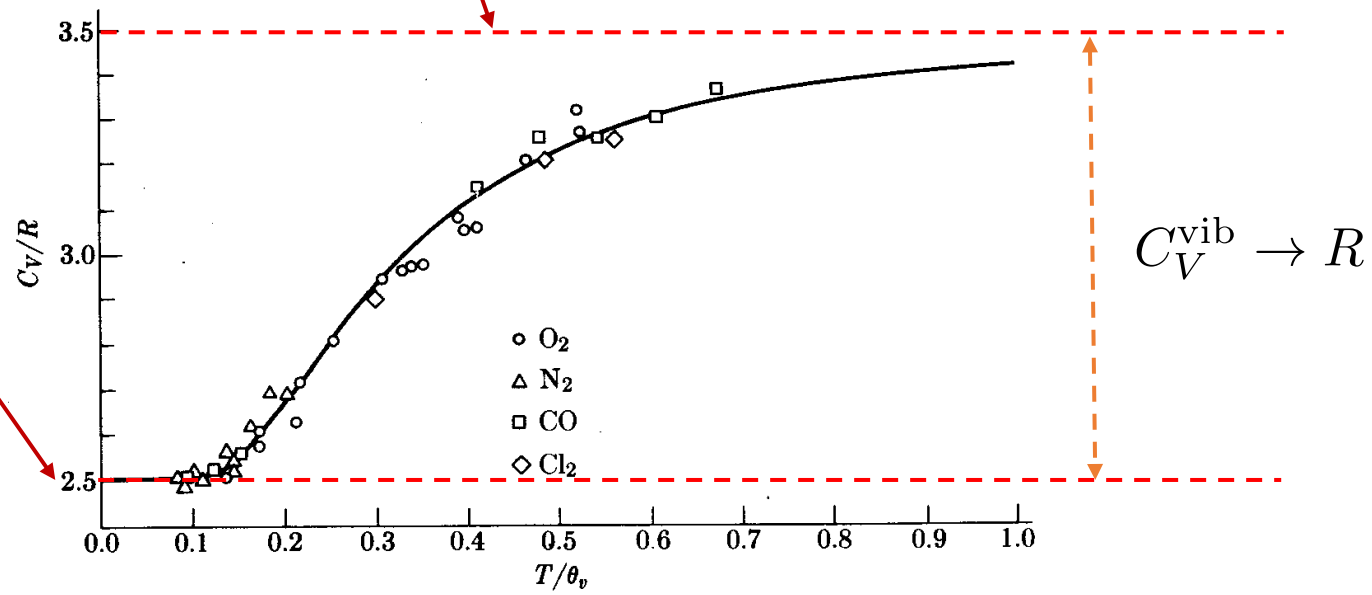


Mentimeter

1D harmonic oscillator: Molecular vibrations

The 1D harmonic oscillator provides a good description of the vibrational heat capacity of diatomic molecules

The heat capacity increases from
$5R/2$ (trans. + rot.) towards $7R/2$ (trans. + rot. + vib.)



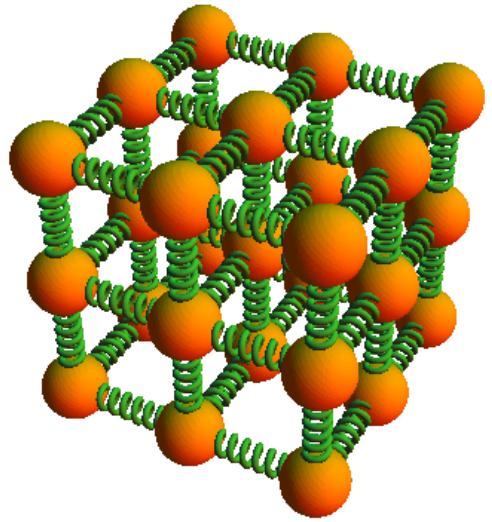
Simple solids: Einstein model

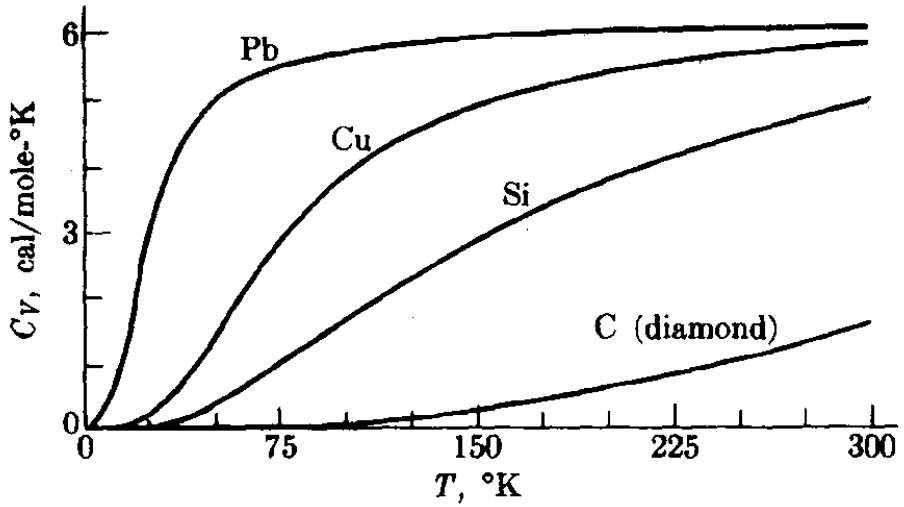
In solids, vibration is the only possible motion

Einstein model is based on two assumptions:

- Each atom is an independent 3D quantum harmonic oscillator
- All atoms oscillate with the same frequency

Because each atom can vibrate in 3 directions, it will contribute 3 times as much heat capacity as a single harmonic oscillator





Einstein model: Comparison to real solids

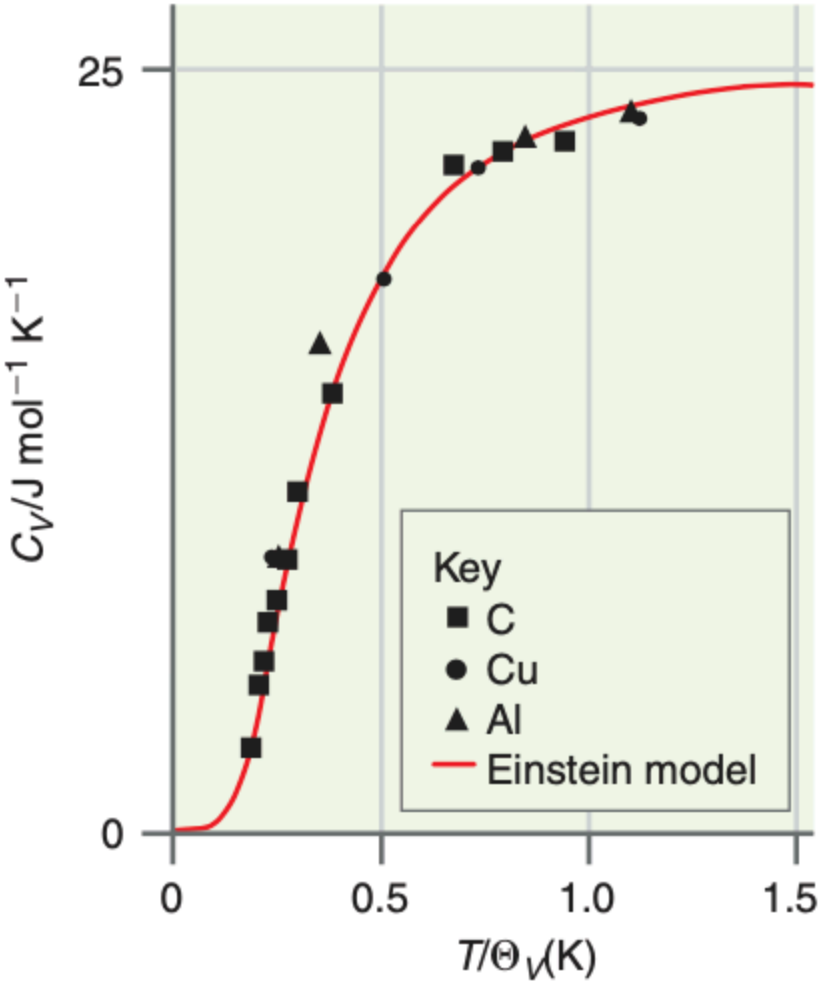
Einstein model fits the data well

Scaling T by Θ_{vib} brings all this molar heat capacities onto a single curve

At high T, the heat capacities approach $3R = 24.9$ J K^{-1} mol^{-1} (Dulong-Petit law)

The differences between different materials are all a result of the bond strengths, i.e., vibrational frequencies ν

Aside: the Einstein model fails at very low temperatures, when interactions become important and give rise to collective motion (phonons). A more accurate model is due to Debye.



Summary

Key points:

- The statistical mechanics of translation and vibration can be derived from quantum-mechanical models
- Statistical mechanics predicts the ideal gas law
- We can calculated the heat capacity, including the temperature dependence of the heat capacity of simple solids

Next time

Next time, we'll look at defects in solids, which are another example of a relatively simple system that we can explore using the tools developed so far.