Recap from last time

$$Pr(v) = 4\pi \left(\frac{m}{2\pi k_B T}\right)^{3/2} v^2 e^{-\left(\frac{m(v^2)}{2k_B T}\right)}$$
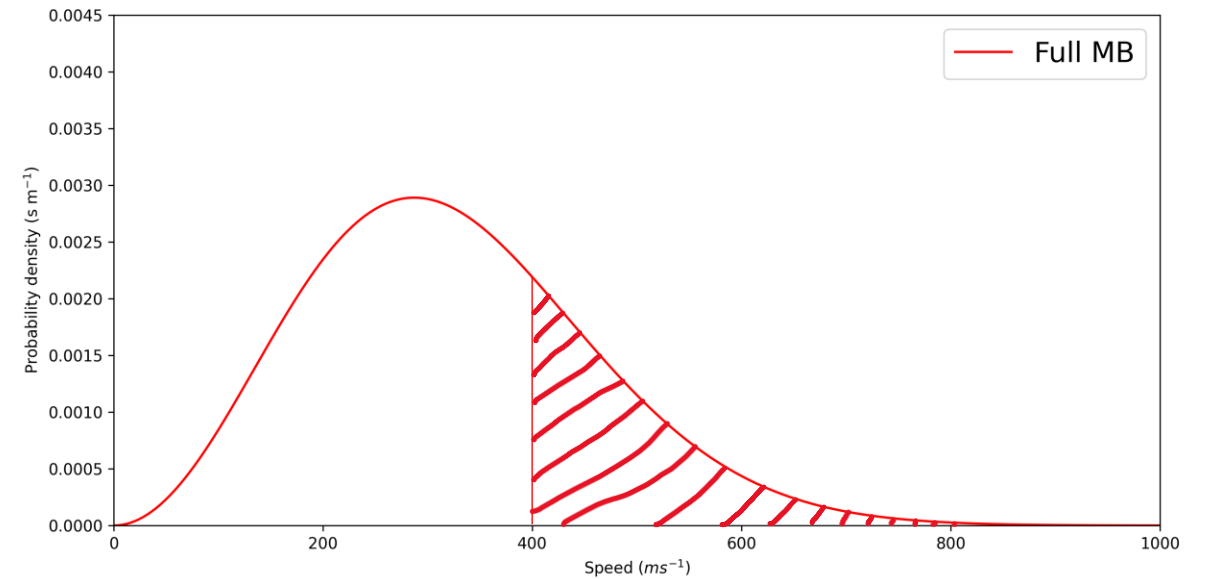
What is the probability of finding a particle with a speed greater than 400 ms^{-1} $(Pr(v > 400 \, m/s))$?

$$Pr(v > 400 \, m/s) = \int_{v_0}^{\infty} Pr(v) \, \mathrm{d}v$$

As $v \to 0$, $v^2 \to 0$, $e^{-\left(\frac{m(v^2)}{2k_BT}\right)} \to 1$

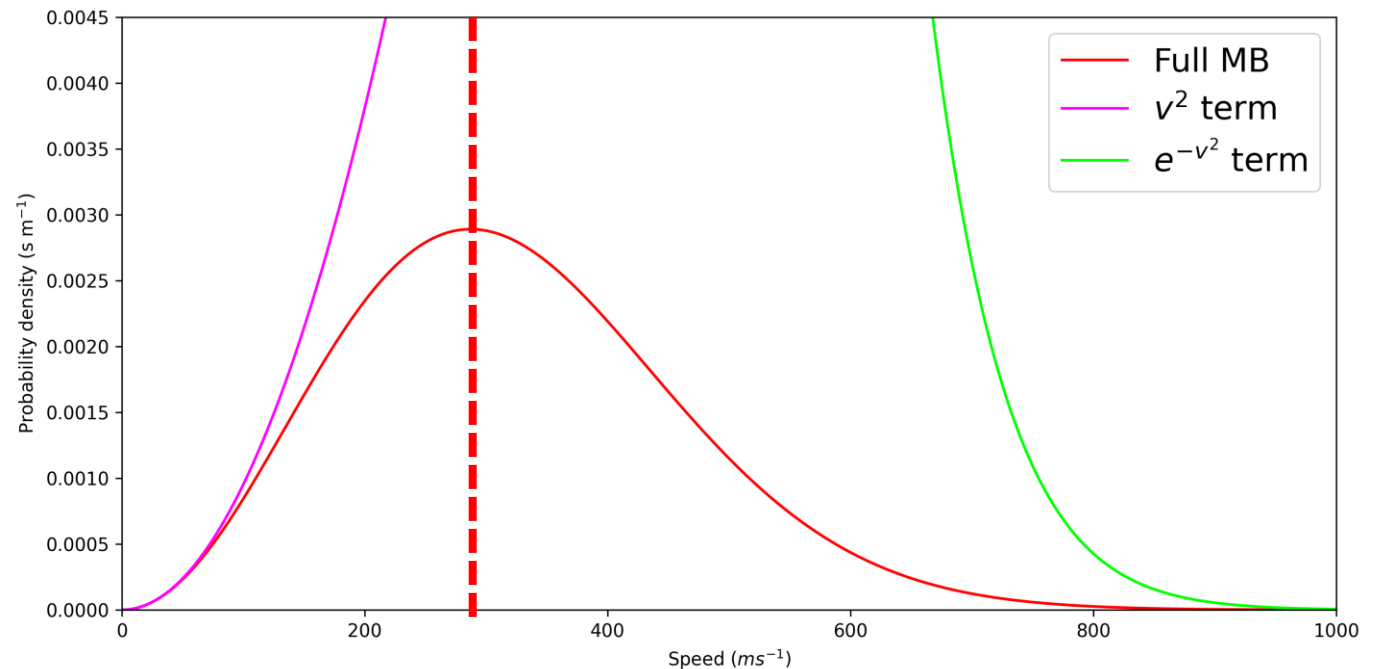As $v \to \infty$, $v^2 \to \infty$, $e^{-\left(\frac{m(v^2)}{2k_BT}\right)} \to 0$

$$Pr(v) = 4\pi\left(\frac{m}{2\pi k_BT}\right)^{3/2} v^2 e^{-\left(\frac{m(v^2)}{2k_BT}\right)}$$

Hence, as $Pr(v)$ is given by the product of these two terms:

$Pr(0) \to 0$

$Pr(\infty) \to \infty$

Results in a peak of most likely probability

Recap from last lecture

These all provide bridges between the microscopic and macroscopic worlds

Most probable speed when $\dfrac{\mathrm{d}Pr(v)}{\mathrm{d}v} = 0$

=> $\quad v_m = \sqrt{\dfrac{2k_BT}{m}}$

Average speed: $\langle v \rangle = \int_0^\infty Pr(v)v\,\mathrm{d}v$

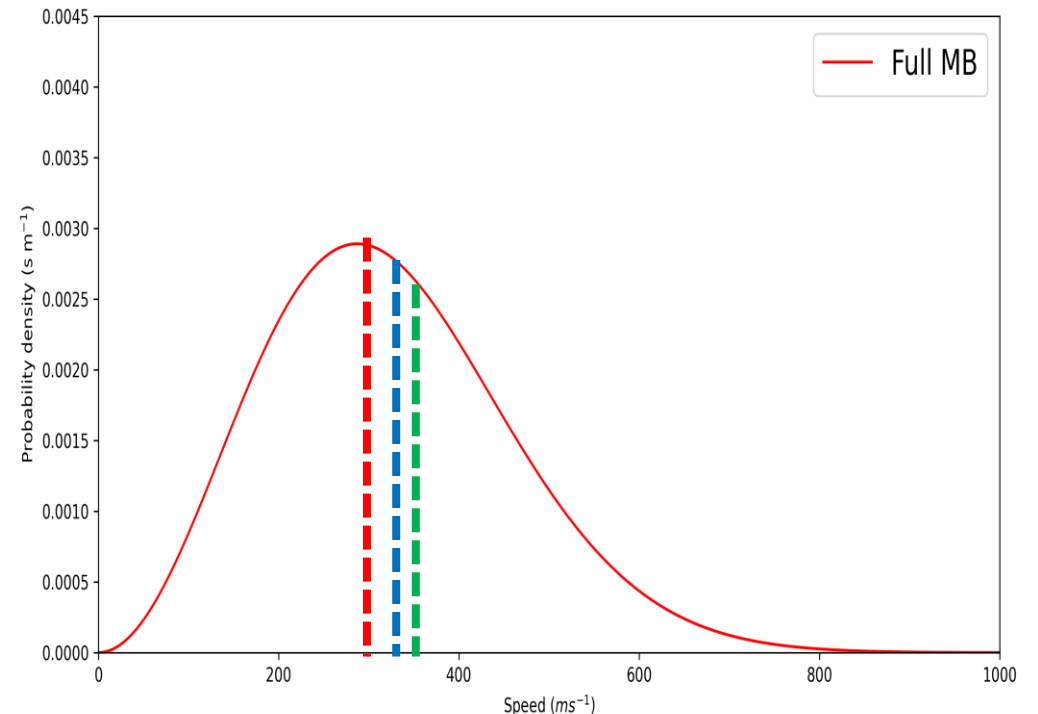=> $\langle \vec{v} \rangle = \sqrt{\dfrac{8k_BT}{\pi m}} = \dfrac{2}{\sqrt{\pi}}v_m$

Root mean square speed:

$\langle v^2 \rangle = \int_0^\infty Pr(v)v^2\,\mathrm{d}v$

=> $\sqrt{\langle v^2 \rangle} = \sqrt{\dfrac{3k_BT}{m}} = \sqrt{\dfrac{3}{2}}v_m$

Average kinetic energy

In 3D, the average kinetic energy for gas molecules from Maxwell-Boltzmann (so assuming an ideal gas) is given by

$$\langle KE \rangle = \frac{1}{2} m \langle v^2 \rangle = \frac{3}{2} k_B T$$

We could show that in 1D (but we won't – you're all welcome) that the average kinetic energy is instead $\langle KE \rangle_x = \langle KE \rangle_y = \langle KE \rangle_z = \frac{1}{2} k_B T$

Remember our definition (from long, long ago) of heat capacity:

At a constant volume:

$$C_V = \left(\frac{\mathrm{d}U}{\mathrm{d}T} \right)_V = \frac{3}{2} k_B \text{ (per atom)}$$

$$C_V = \left(\frac{\mathrm{d}U}{\mathrm{d}T} \right)_V = \frac{3}{2} R \text{ (per mole)}$$

Heat capacities of (ideal) gases (lecture 10)

Recall that $\Delta Q = C \Delta T \rightarrow C = \dfrac{\mathrm{d}Q}{\mathrm{d}T}$ … for gas, need more careful treatment
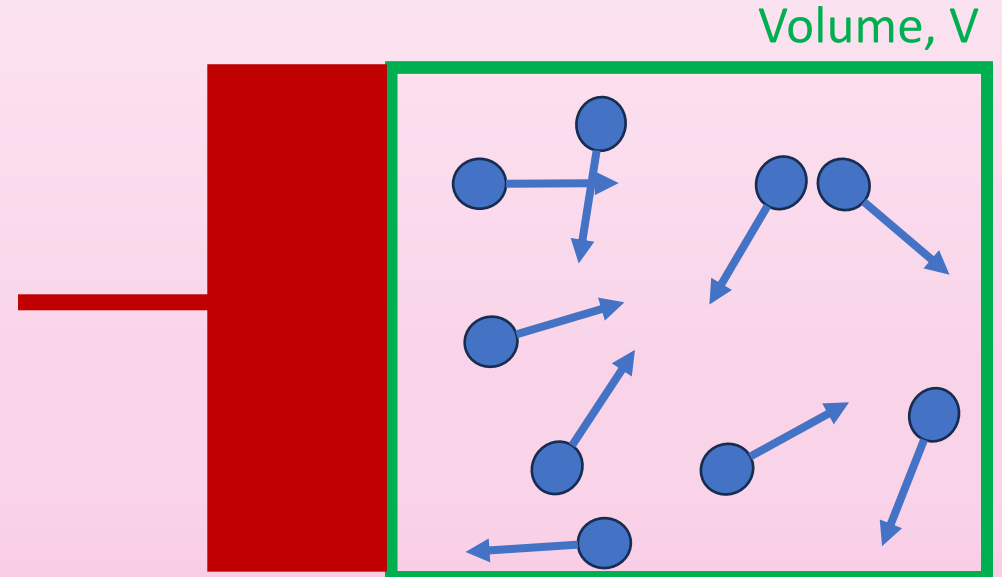
Molar heat capacity: $C = nc$

At a constant volume: $C_V = \left(\dfrac{\mathrm{d}U}{\mathrm{d}T}\right)_V$

At a constant pressure: $C_P = \left(\dfrac{\mathrm{d}H}{\mathrm{d}T}\right)_P$

Mayer's relation: $C_P = C_V + nR$

Thus it is clear that $C_P < C_V$

Volume, V

Molar heat capacity data (1 mole at 298 K)

Gas	C_V (J mol^{-1} K^{-1})	C_P (J mol^{-1} K^{-1})	$C_P - C_V$ (J mol^{-1} K^{-1})
Helium (He)	12.52	20.79	8.27
Argon (Ar)	12.45	20.79	8.34
Krypton (Kr)	12.45	20.79	8.34
Xenon (Xe)	12.52	20.79	8.27
Hydrogen (H_2)	20.42	28.74	8.32
Nitrogen (N_2)	20.76	29.07	8.31
Oxygen (O_2)	20.85	29.16	8.31
Carbon monoxide (CO)	20.85	29.16	8.31

Remember that $R = 8.31$ J K^{-1}

Monatomic gases give $C_P = 5R/2$, $C_V = 3R/2$ Diatomic gases give $C_P = 7R/2$, $C_V = 5R/2$

Law of equipartition (much later… probably week 10)

Law of the equipartition of energy

"Any substance in equilibrium at a temperature T has an average energy of $\frac{k_B T}{2}$ for each **degree of freedom**"

A degree of freedom is defined as any term in the expression for the energy of the system which contains a squared position or velocity component...

For our ideal gas in 1D, we have $E(v_x) = \frac{1}{2}mv_x^2 = \frac{1}{2}k_B T$ $C_V = \frac{1}{2}R$

In 3D: $E\left(v_x, v_y, v_z\right) = \frac{1}{2}mv_x^2 + \frac{1}{2}mv_y^2 + \frac{1}{2}mv_z^2 = \frac{3}{2}k_B T$ $C_V = \frac{3}{2}R$

No gravity (mgh) term because the position term is linear

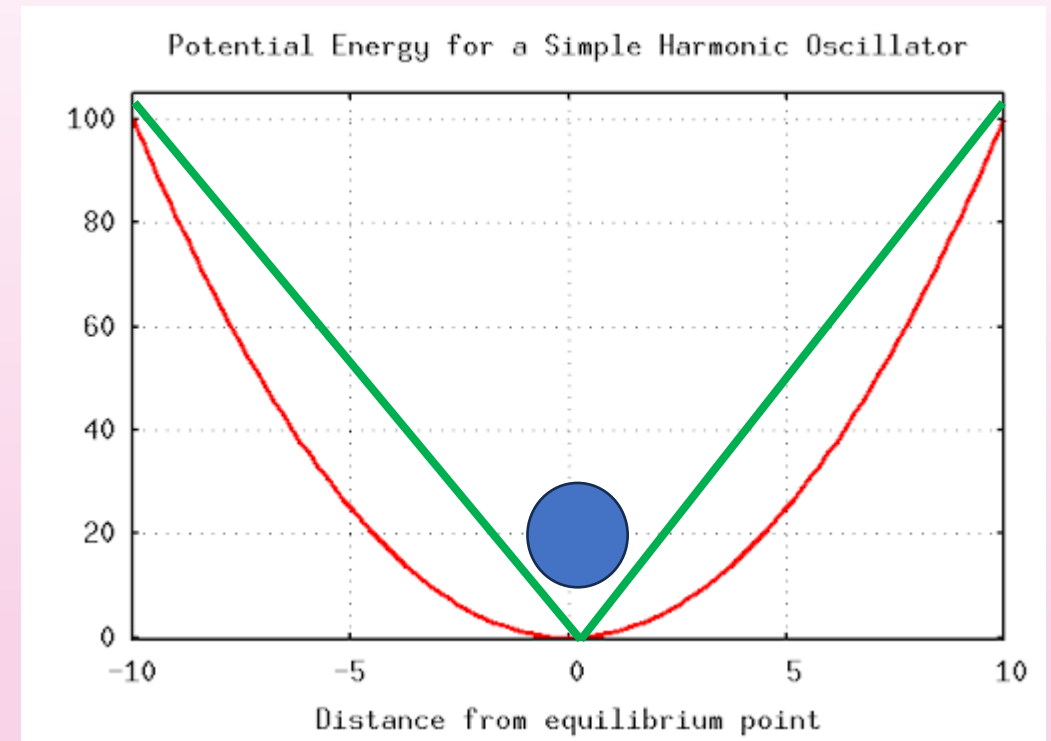# Other equipartition examples (1D)

Ideal gas in a harmonic potential:

$$C_V = R$$

$$E(v_x, x) = \frac{1}{2}mv_x^2 + \frac{1}{2}kx^2 = k_B T$$

Ideal gas in a linear potential:

$$E(v_x, x) = \frac{1}{2}mv_x^2 + Kx = \frac{1}{2}k_B T$$

$$C_V = \frac{1}{2}R$$

Potential Energy for a Simple Harmonic Oscillator

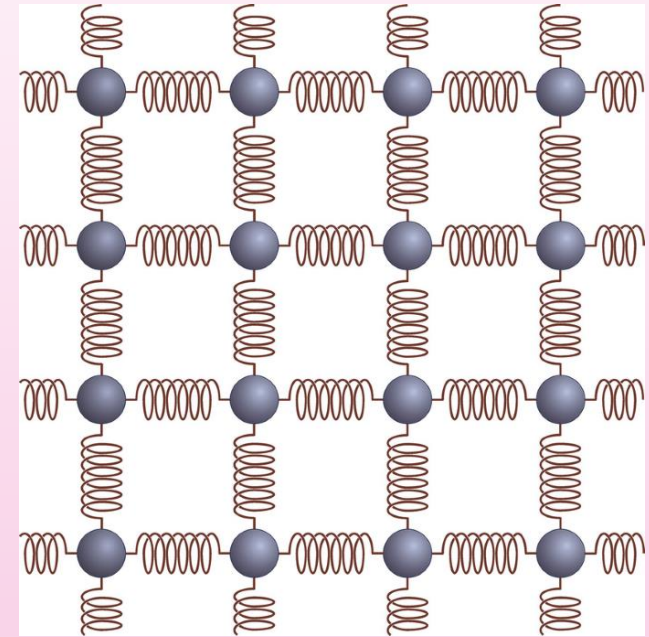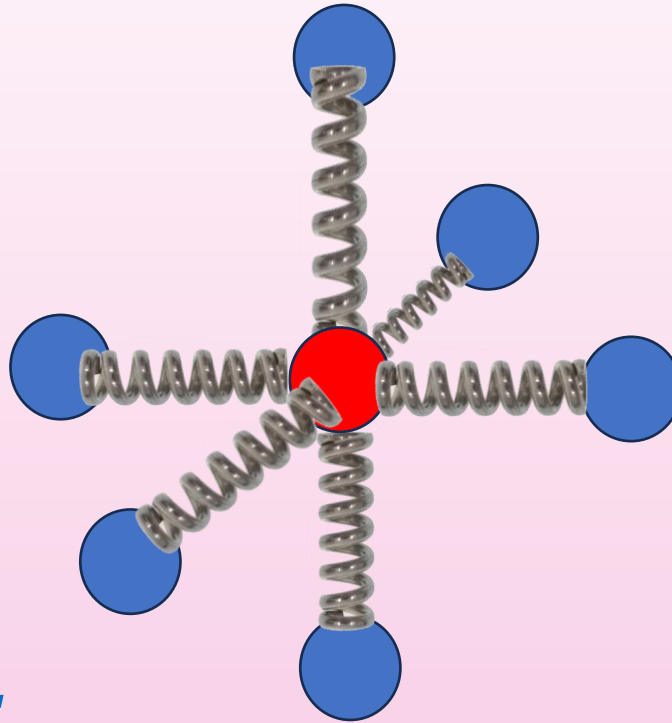Distance from equilibrium point

Dulong-petit heat capacity of solids

Each atom (mass m) is fixed, connected to its neighbours by interatomic forces (which we can treat like springs with spring constant K)

Each spring has vibrational energy

$$E = \frac{1}{2}mv_x^2 + \frac{1}{2}Kx^2 = k_B T$$

https://media.springernature.com/lw685/springer-static/image/chp%3A10.1007%2F978-3-031-18286-0_4/MediaObjects/318291_2_En_4_Fig5_HTML.png

Each atom connected to 6 springs (but each spring is shared by 2 atoms...)

$$E = 3k_B T \Rightarrow c_V = 3R$$

Dulong-petit heat capacity of solids

Element	Molar heat capacity C_v (J mol^{-1} K^{-1})
Bismuth	25.64
Gold	24.79
Platinum	25.04
Tin	25.30
Zinc	25.01
Gallium	24.60
Copper	25.14
Nickel	25.56
Iron	24.98
Calcium	24.67
Sulphur	25.30

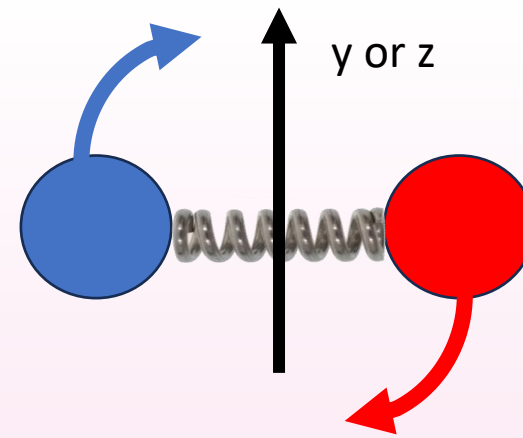$C_v = 3R = 24.9$ J mol^{-1} K^{-1} … good agreement from a quite basic model
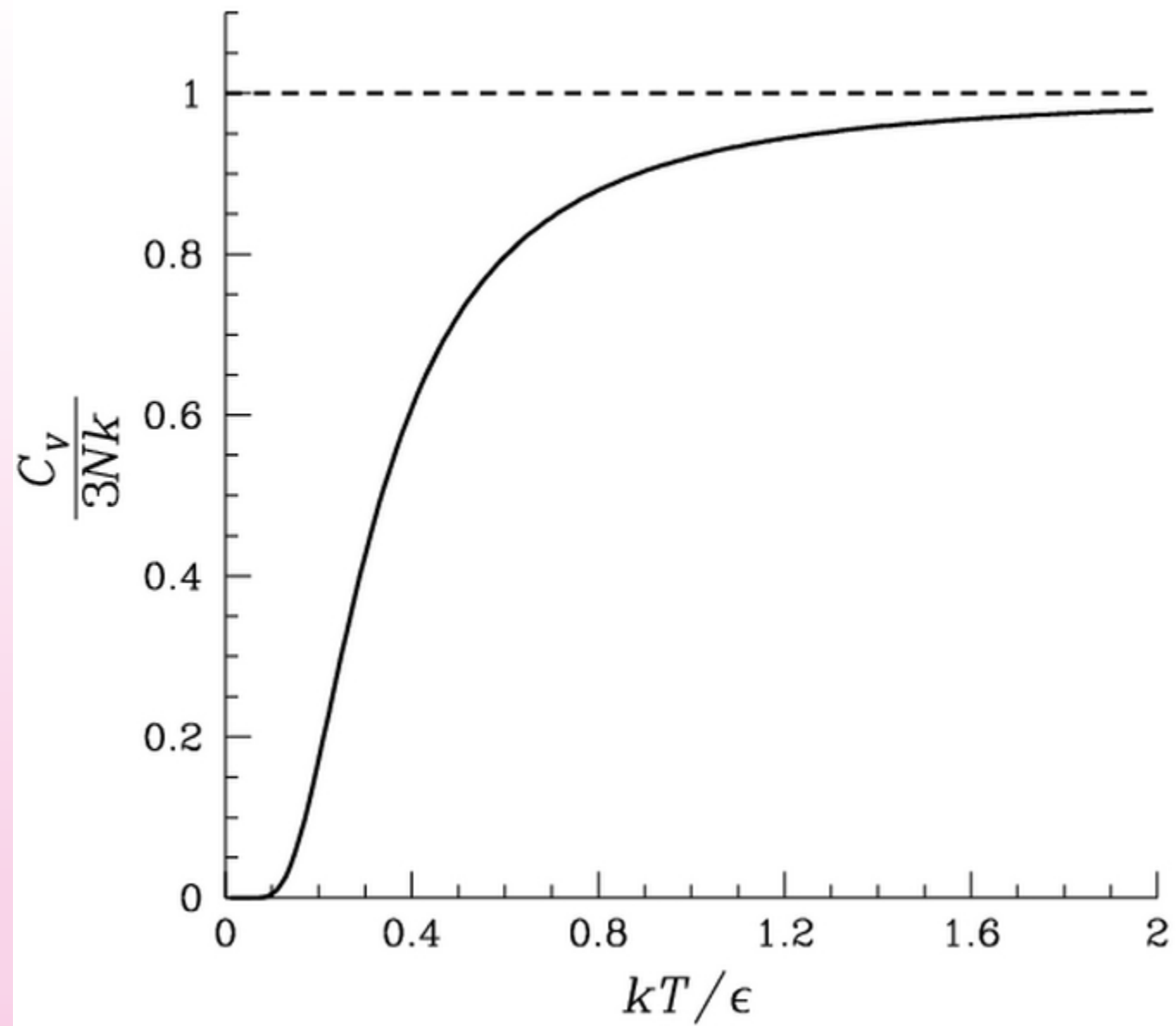
Diatomic molecules

Unlike solids, diatomic molecules are connected by only one spring (2 DoF of vibrational energy)...

$$E_{vib} = \frac{1}{2}mv_x^2 + \frac{1}{2}Kx^2$$

2 DoF

They can also move (translational KE) around in the volume they occupy

$$E_{KE} = \frac{1}{2}mv_x^2 + \frac{1}{2}mv_y^2 + \frac{1}{2}mv_z^2$$

3 DoF

The two atoms may be able to rotate around the axis joining them (must be in a perpendicular direction)

$$E_{rot} = \frac{1}{2}I\omega_y^2 + \frac{1}{2}I\omega_z^2$$

2 DoF

7 degrees of freedom total... $E = \frac{7}{2}k_B T$ and $c_V = \frac{7R}{2}$

Molar heat capacity data (1 mole at 298 K)

Gas	C_V (J mol^{-1} K^{-1})	C_P (J mol^{-1} K^{-1})	$C_P - C_V$ (J mol^{-1} K^{-1})
Helium (He)	12.52	20.79	8.27
Argon (Ar)	12.45	20.79	8.34
Krypton (Kr)	12.45	20.79	8.34
Xenon (Xe)	12.52	20.79	8.27
Hydrogen (H_2)	20.42	28.74	8.32
Nitrogen (N_2)	20.76	29.07	8.31
Oxygen (O_2)	20.85	29.16	8.31
Carbon monoxide (CO)	20.85	29.16	8.31

Remember that $R = 8.31$ J K^{-1}

Diatomic gases give C_P = 7R/2, C_V = 5R/2

Experiment disagrees by 2 degrees of freedom!

Probability of energy population

Recall that the probability of measuring a given energy state is given by $Pr(E_i) \propto e^{-\left(\frac{E_i}{k_B T}\right)}$

The non-zero vibrational energy states occur at large energies, and hence for a reasonable probability of the molecule being in that state, we can't have $k_B T \ll E_i$ (as it is at room temperature)
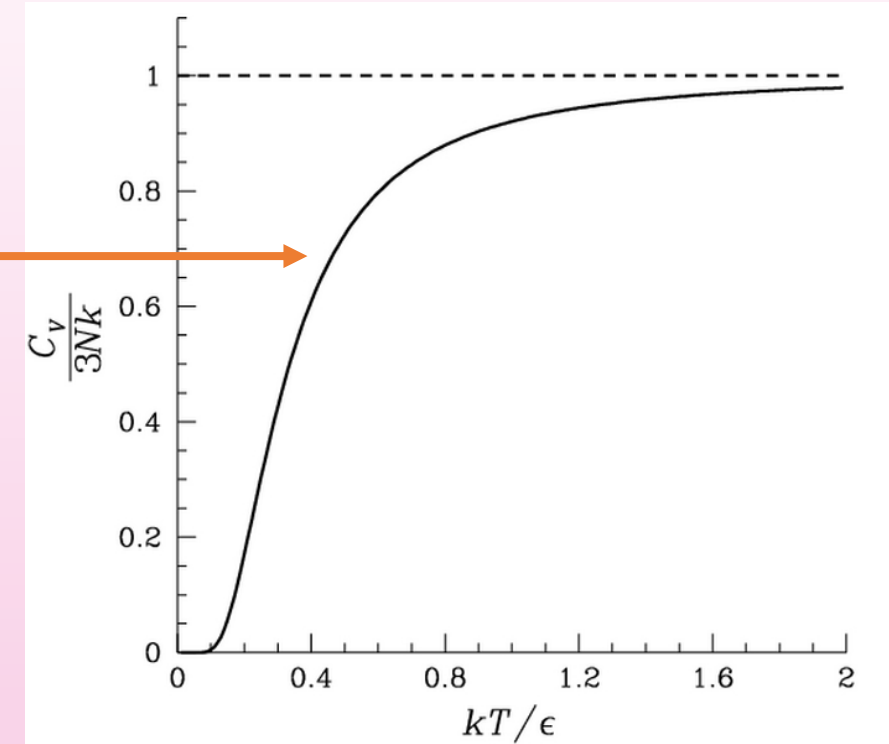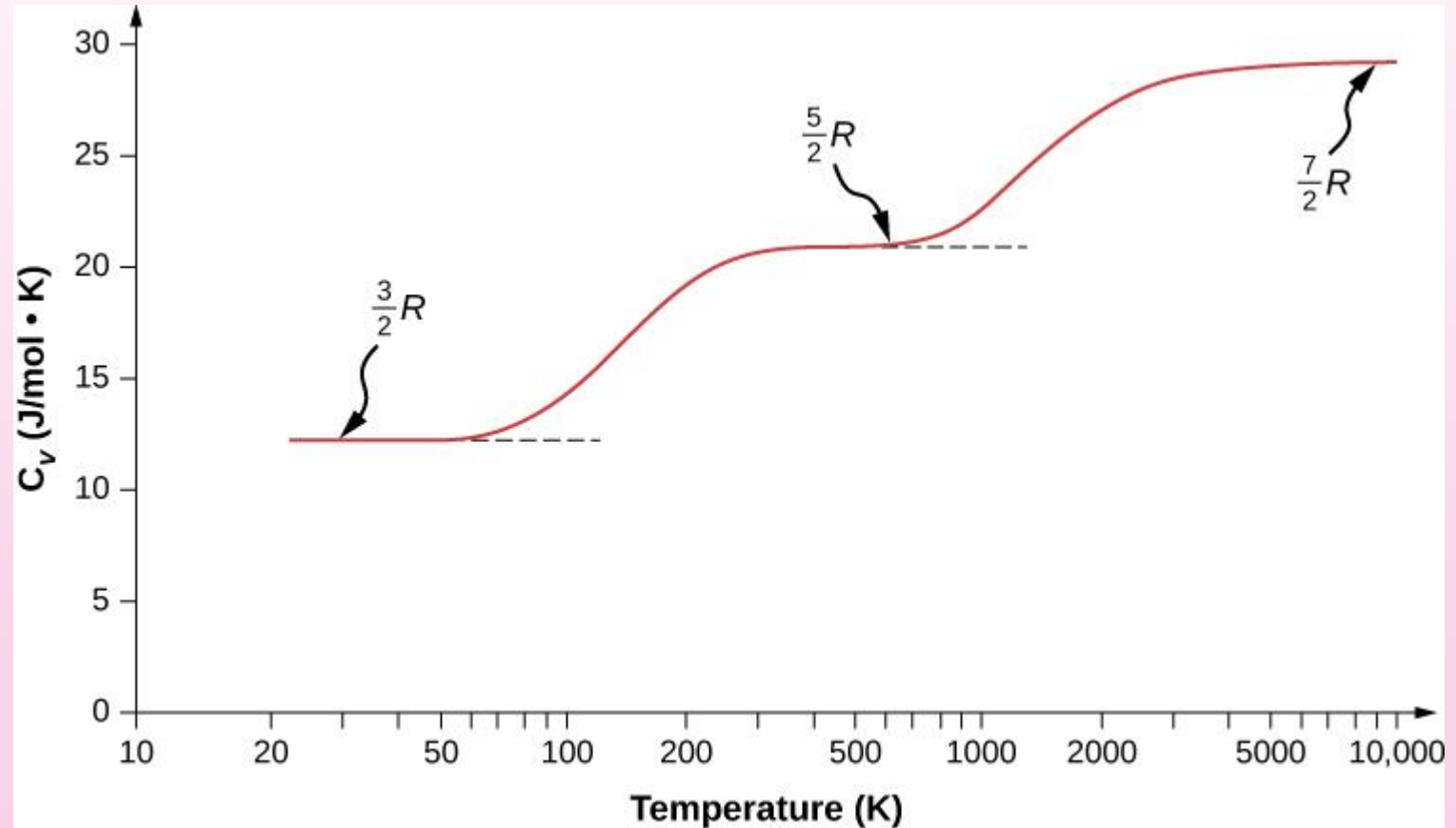
Probability of energy population

Degrees of freedom can be considered fully "excited" if
$$k_B T \gg E_1 - E_0$$

If $k_B T \ll E_1 - E_0$, the degree of freedom is said to be "frozen out"

Will look at the exact behaviour of these breakdowns in the 2nd year course "Quantum Approach to Solids"

Example question

We have 2 moles of a diatomic gas at a temperature of 20000 K.

What is do we expect the internal energy of the gas to be?

A: $\frac{7R}{2} \times 20000 \times 2 = 1.1$ MJ

What if instead, the molecules were rigid?

A: $\frac{5R}{2} \times 20000 \times 2 = 0.83$ MJ as no vibrational modes possible