

Lecture 6 – Equipartition theorem



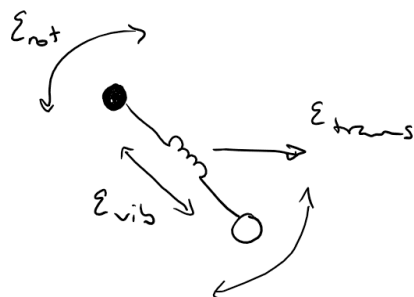
LAST TIME: We introduced the partition function $Z(T) = \sum_i e^{-\epsilon_i/k_B T}$

Z counts microstates, weighing each by a Boltzmann factor. For a system with energy levels $\epsilon_0 < \epsilon_1 < \epsilon_2 \dots$ each term in Z gets progressively smaller.

In low-temperature limit, $k_B T$ is less than the spacing between energy levels, and only first few terms contribute significantly to sum. In high-temperature limit $k_B T$ is much greater than spacing between levels, then many terms contribute.

TODAY: Can we make general statements about behavior of systems at high temperature?

Ex: diatomic ideal gas (CO)



So far we've considered a monatomic ideal gas. How do we treat more complex gas with internal degrees of freedom?

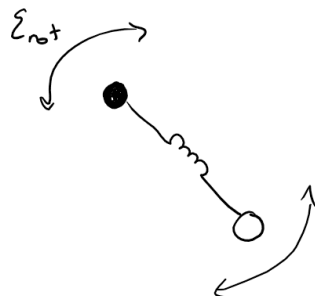
Consider diatomic ideal gas with distinguishable atoms like CO

Molecule has translational, rotational, vibrational degrees of freedom: $\epsilon_{mol} = \epsilon_{trans} + \epsilon_{rot} + \epsilon_{vib}$

As long as there is no coupling between degrees of freedom:

$$\begin{aligned} Z_{mol} &= \sum_{\text{All states}} e^{-\beta \epsilon_{mol}} = \sum_{\epsilon_{trans}} e^{-\beta \epsilon_{trans}} \sum_{\epsilon_{rot}} e^{-\beta \epsilon_{rot}} \sum_{\epsilon_{vib}} e^{-\beta \epsilon_{vib}} \\ &= Z_{trans} Z_{rot} Z_{vib} \end{aligned}$$

We showed last time: $\epsilon_{trans} = \frac{\hbar^2 k^2}{2m}$, $Z_{trans} = n_Q(T)V$, $U_{trans} = \frac{3}{2} N k_B T$



Rotational states of CO:

Treat molecule as quantum rigid rotor, ignoring rotation about C-O axis.

Review of quantum rigid rotor and angular momentum:

In quantum mechanics, total angular momentum \vec{J} is quantized such that its magnitude $J = |\vec{J}| = \sqrt{j(j+1)}\hbar$, with $j = 0, 1, 2, \dots$ and one component $J_z = m_j\hbar$, with $m_j = -j, -j+1, \dots, j-1, j$. For each value of j there are $2j+1$ values of m_j .

The energy of a rigid rotor is given by

$$\varepsilon_{rot} = \frac{|\vec{J}|^2}{2I} = \frac{j(j+1)\hbar^2}{2I} = \varepsilon j(j+1)$$

where I is the moment of inertia of the rotor.

Question 1: Determine the rotational partition function

Z is a sum over all quantum states, i.e. over quantum numbers j and m_j . However, the energy depends only on j , so each Boltzmann factor must be multiplied by the degeneracy from all possible values of m_j for each j :

$$Z_{rot} = \sum_{J, J_z} e^{-\beta \varepsilon_{rot}} = \sum_{j=0}^{\infty} (2j+1) e^{-\beta \varepsilon j(j+1)}$$

Low-T limit ($k_B T \ll \varepsilon$):

$$Z_{rot} = 1 + 3e^{-2\beta\varepsilon} + 5e^{-6\beta\varepsilon} + 7e^{-12\beta\varepsilon} + \dots$$

Each term becomes smaller and smaller. Only first term, corresponding to ground state, contributes. Excited states are “frozen out” at low temperatures.

$$Z_{rot} \approx 1 \text{ and } U_{rot} \approx 0$$

High-T limit ($k_B T \gg \varepsilon$):

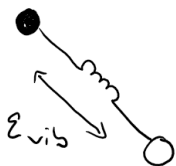
Here, we can treat energy levels as continuum. Turn sum in Z_{rot} to integral:

$$Z_{rot} \approx \int_0^{\infty} dj (2j+1) e^{-\beta \varepsilon j(j+1)} = \frac{1}{\beta \varepsilon} \int_0^{\infty} dx e^{-x} = \frac{1}{\beta \varepsilon},$$

using $x = \beta \varepsilon j(j+1)$, and $dx = \beta \varepsilon (2j+1) dj$

$$U_{rot} = -\frac{\partial}{\partial \beta} \ln Z_{rot} = +\frac{1}{\beta} = k_B T$$

(This is for 1 molecule. For N molecules, multiply by N)



Vibrational states of CO:

Treat as a 1-D quantum oscillator with frequency ω

$$\epsilon_{vib} = \hbar\omega \left(n + \frac{1}{2} \right), \quad n = 0, 1, 2, \dots$$

Question 2: Determine the vibrational partition function (and simplify answer)

Z_{vib} sums over all quantum numbers n :

$$Z_{vib} = \sum_n e^{-\beta \epsilon_{vib}} = e^{-\frac{1}{2}\beta\hbar\omega} \sum_{n=0}^{\infty} e^{-\beta\hbar\omega n}$$

That is an infinite series of the form

$$\sum_{n=0}^{\infty} x^n = \frac{1}{1-x}, \quad \text{valid for } |x| < 1$$

(true since $x = e^{-\beta\hbar\omega} < 1$). So:

$$Z_{vib} = \frac{e^{-\frac{1}{2}\beta\hbar\omega}}{1 - e^{-\beta\hbar\omega}}$$

Average energy of one molecule:

$$\begin{aligned} U_{vib} &= -\frac{\partial}{\partial \beta} \ln Z_{vib} = \frac{\partial}{\partial \beta} \left(\frac{1}{2}\beta\hbar\omega + \ln(1 - e^{-\beta\hbar\omega}) \right) \\ &= \frac{1}{2}\hbar\omega + \hbar\omega \frac{e^{-\beta\hbar\omega}}{1 - e^{-\beta\hbar\omega}} = \hbar\omega \left(\frac{1}{e^{\beta\hbar\omega} - 1} + \frac{1}{2} \right) \\ &= \hbar\omega \left(\langle n \rangle + \frac{1}{2} \right) \end{aligned}$$

where $\langle n \rangle = (e^{\beta\hbar\omega} - 1)^{-1}$ is the average value of the quantum number n .

Low-T limit ($k_B T \ll \hbar\omega$): $\langle n \rangle = (e^{\beta\hbar\omega} - 1)^{-1} \approx e^{-\beta\hbar\omega}$

$$U_{vib} \approx \hbar\omega \left(e^{-\beta\hbar\omega} + \frac{1}{2} \right)$$

Again, at low temperatures, excited states are “frozen” out and only ground state contributes $U_{vib} \approx \frac{1}{2}\hbar\omega$

High-T limit ($k_B T \gg \hbar\omega$): $\langle n \rangle = (e^{\beta\hbar\omega} - 1)^{-1} \approx (1 - \beta\hbar\omega)^{-1} = \frac{k_B T}{\hbar\omega}$

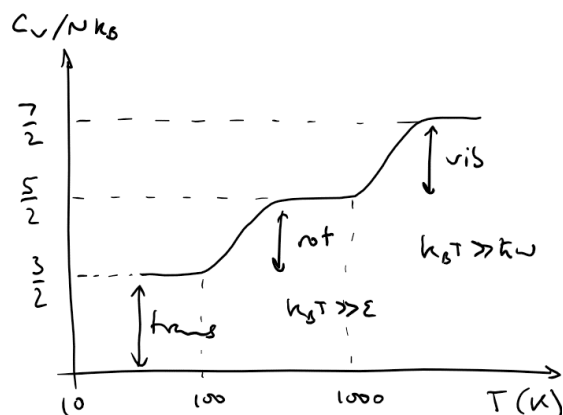
$$U_{vib} \approx \hbar\omega \left(\frac{k_B T}{\hbar\omega} + \frac{1}{2} \right) = k_B T + \frac{1}{2}\hbar\omega \approx k_B T$$

(Note: would get same answer turning Z_{vib} into integral: $Z_{vib} \approx e^{-\frac{1}{2}\beta\hbar\omega} \int_0^\infty dn e^{-\beta\hbar\omega n}$)

Behavior of diatomic gas apparent in measurements of heat capacity $C_V = \left(\frac{\partial U}{\partial T} \right)_V$

Ratio of heat added to (or removed from) system to change in temperature. Subscript V denotes constant volume.

$$U_{tot} = U_{trans} + U_{rot} + U_{vib}, \text{ so } C_V = C_V^{trans} + C_V^{rot} + C_V^{vib}$$



$$C_V^{trans} = \frac{3}{2} N k_B$$

$$C_V^{rot} = \begin{cases} 0 & \text{for } k_B T \ll \epsilon \\ N k_B & \text{for } k_B T \gg \epsilon \end{cases}$$

$$C_V^{vib} = \begin{cases} 0 & \text{for } k_B T \ll \hbar\omega \\ N k_B & \text{for } k_B T \gg \hbar\omega \end{cases}$$

Heat capacity for H_2

KEY CONCEPT: Equipartition theorem

Notice that in many cases of high-temperature limit, $U = \alpha N k_B T$ (e.g. Einstein model, ideal gas, rotations and vibrations in diatomic ideal gas)

Why is this and what determines the numerical factor α in U ?

- Key point is that $k_B T \gg$ spacing between energy levels
- We can treat energy levels as a continuum, i.e. Z turns into an integral

Suppose energy is quadratic in N "degrees of freedom":

$$\epsilon = a_1 q_1^2 + a_2 q_2^2 + \cdots + a_N q_N^2$$

where $\{q_1, q_2, \dots, q_N\}$ is a set of continuous variables that range from $-\infty$ to $+\infty$ and define the state of the system

(e.g. 1-D harmonic oscillator $\epsilon = \frac{p^2}{2m} + \frac{1}{2} m \omega^2 x^2$, $q_1 = p$ and $q_2 = x$)

Partition function Z can be turned into an integral

$$Z(T) = \sum_i e^{-\varepsilon_i / k_B T} \rightarrow A \int_{-\infty}^{\infty} dq_1 \int_{-\infty}^{\infty} dq_2 \cdots \int_{-\infty}^{\infty} dq_N e^{-\beta \varepsilon(q_1, q_2, \dots, q_N)}$$

↑

Need normalization factor A for
 Z to be dimensionally correct

Probabilities become

$$p(\varepsilon_i) = \frac{e^{-\beta \varepsilon_i}}{Z} \rightarrow \frac{A dq_1 dq_2 \cdots dq_N e^{-\beta \varepsilon(q_1, q_2, \dots, q_N)}}{A \int_{-\infty}^{\infty} dq_1 \int_{-\infty}^{\infty} dq_2 \cdots \int_{-\infty}^{\infty} dq_N e^{-\beta \varepsilon(q_1, q_2, \dots, q_N)}}$$

↑

Notice that normalization factor A cancels out

Let's calculate $\langle \varepsilon_{q_1} \rangle \equiv \langle a_1 q_1^2 \rangle$:

$$\langle \varepsilon_{q_1} \rangle = \frac{\int_{-\infty}^{\infty} dq_1 \int_{-\infty}^{\infty} dq_2 \cdots \int_{-\infty}^{\infty} dq_N a_1 q_1^2 e^{-\beta \varepsilon(q_1, q_2, \dots, q_N)}}{\int_{-\infty}^{\infty} dq_1 \int_{-\infty}^{\infty} dq_2 \cdots \int_{-\infty}^{\infty} dq_N e^{-\beta \varepsilon(q_1, q_2, \dots, q_N)}} = \frac{\int_{-\infty}^{\infty} dq_1 a_1 q_1^2 e^{-\beta \varepsilon_{q_1}} \int_{-\infty}^{\infty} dq_2 \cdots \int_{-\infty}^{\infty} dq_N e^{-\beta \varepsilon'(q_2, \dots, q_N)}}{\int_{-\infty}^{\infty} dq_1 e^{-\beta \varepsilon_{q_1}} \int_{-\infty}^{\infty} dq_2 \cdots \int_{-\infty}^{\infty} dq_N e^{-\beta \varepsilon'(q_2, \dots, q_N)}}$$

where we wrote $\varepsilon = \varepsilon_{q_1} + \varepsilon'(q_2, \dots, q_N)$.

$$\langle \varepsilon_{q_1} \rangle = \frac{\int_{-\infty}^{\infty} dq_1 \varepsilon_{q_1} e^{-\beta \varepsilon_{q_1}}}{\int_{-\infty}^{\infty} dq_1 e^{-\beta \varepsilon_{q_1}}} = -\frac{\partial}{\partial \beta} \ln \int_{-\infty}^{\infty} dq_1 e^{-\beta \varepsilon_{q_1}}$$

This is a Gaussian integral (K + K, Appendix A): $\int_{-\infty}^{\infty} dq_1 e^{-\beta a_1 q_1^2} = \sqrt{\frac{\pi}{\beta a_1}}$, so

$$\langle \varepsilon_{q_1} \rangle = -\frac{\partial}{\partial \beta} \ln(\beta^{-1/2}) + (\text{terms independent of } \beta) = \frac{1}{2} \frac{1}{\beta} = \frac{1}{2} k_B T$$

independent of a_1 !

Equipartition theorem – energy quadratic in a degree of freedom has average value:

$$\langle \varepsilon_{q_1} \rangle = \langle a_1 q_1^2 \rangle = \frac{1}{2} k_B T$$

Question 3: Use equipartition to evaluate average energies for the following systems:

a) N ideal gas particles in 3-D:

$$\varepsilon = \frac{p_{1x}^2 + p_{1y}^2 + p_{1z}^2}{2m} + \frac{p_{2x}^2 + p_{2y}^2 + p_{2z}^2}{2m} + \dots + \frac{p_{Nx}^2 + p_{Ny}^2 + p_{Nz}^2}{2m}$$

$3N$ quadratic degrees of freedom, so $U = \langle \varepsilon \rangle = \frac{3}{2} N k_B T$

b) N 1-D harmonic oscillators:

$$\varepsilon = \frac{p_1^2}{2m} + \frac{1}{2} m \omega^2 x_1^2 + \frac{p_2^2}{2m} + \frac{1}{2} m \omega^2 x_2^2 + \dots + \frac{p_N^2}{2m} + \frac{1}{2} m \omega^2 x_N^2$$

$2N$ quadratic degrees of freedom so $U = \langle \varepsilon \rangle = N k_B T$

Valid when $k_B T \gg$ spacing between energy levels.

Careful! Equipartition theorem cannot always be used.

Counter-example: spin- $\frac{1}{2}$ paramagnet

$$U = -N \mu_B \tanh \frac{\mu_B}{k_B T}$$

When $k_B T \gg \mu_B$, $U = -\frac{N(\mu_B)^2}{k_B T}$, not $\propto N k_B T$. Why does it fail?

Here, it's impossible to treat 2 energy levels of spin- $\frac{1}{2}$ particle in B field as a continuum.

We can use these ideas to derive Maxwell velocity distribution:

What is the probability for an ideal gas molecule to have speed in range v , $v+dv$?

$$\varepsilon = \frac{1}{2} m v^2 = \frac{1}{2} m (v_x^2 + v_y^2 + v_z^2)$$

From the derivation of the equipartition theorem:

$$\left(\begin{array}{l} \text{Prob. velocity has} \\ \text{components } v_x, v_y, v_z \end{array} \right) = \frac{dv_x dv_y dv_z e^{-\beta \varepsilon}}{\int_{-\infty}^{\infty} dv_x \int_{-\infty}^{\infty} dv_y \int_{-\infty}^{\infty} dv_z e^{-\beta \varepsilon}}$$

Actually, that's not exactly what we want. We want probability in terms of speed

$v = \sqrt{v_x^2 + v_y^2 + v_z^2}$. Switch to spherical coordinates:

$$\left(\begin{array}{l} \text{Prob. velocity has} \\ \text{magnitude } v, \text{ direction } \theta, \phi \end{array} \right) = \frac{v^2 dv d\phi \sin\theta d\theta e^{-\beta \varepsilon}}{\int_0^{\infty} v^2 dv \int_0^{2\pi} d\phi \int_0^{\pi} \sin\theta d\theta e^{-\beta \varepsilon}}$$

We don't care about orientation, so integrate over it

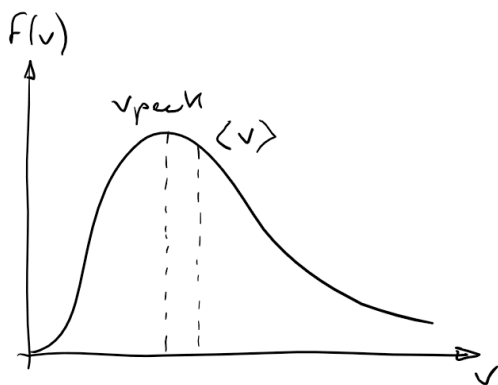
$$\left(\begin{array}{c} \text{Prob. velocity has} \\ \text{magnitude } v \end{array} \right) = \frac{v^2 dv e^{-\beta m v^2 / 2}}{\int_0^\infty v^2 dv e^{-\beta m v^2 / 2}}$$

Evaluate denominator, which is a Gaussian integral. Notice that:

$$\begin{aligned} \int_0^\infty v^2 dv e^{-\alpha v^2} &= -\frac{\partial}{\partial \alpha} \int_0^\infty dv e^{-\alpha v^2} = -\frac{\partial}{\partial \alpha} \frac{1}{2} \sqrt{\frac{\pi}{\alpha}} \\ &= \frac{1}{4} \frac{\sqrt{\pi}}{\alpha^{3/2}} = \frac{\sqrt{\pi}}{4} \left(\frac{2k_B T}{m} \right)^{3/2} = \frac{1}{4\pi} \left(\frac{2\pi k_B T}{m} \right)^{3/2} \end{aligned}$$

So, we get the Maxwell velocity distribution:

$$f(v)dv = 4\pi \left(\frac{m}{2\pi k_B T} \right)^{3/2} v^2 e^{-mv^2 / k_B T} dv$$



$$v_{peak} = \sqrt{\frac{2k_B T}{m}}, \text{ where } \left. \frac{df}{dv} \right|_{v=v_{peak}} = 0$$

$$\langle v \rangle = \int_0^\infty dv v f(v) = \sqrt{\frac{8k_B T}{\pi m}}$$

$$\langle v^2 \rangle = \int_0^\infty dv v^2 f(v) = \sqrt{\frac{3k_B T}{m}} *$$

For N_2 at 300K, $v_{peak} = 422 \text{ m/s} = 1000 \text{ mph}$ (faster than speed of sound)!

*Notice this agrees with equipartition theorem $\langle \frac{1}{2} m v^2 \rangle = \frac{3}{2} k_B T$