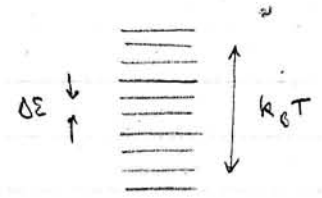
Lecture 6

Last time we saw that when $k_B T \gg \Delta\varepsilon$, we can treat ε levels as a continuum



This the classical regime. States are no longer discrete but continuous

Proof of the equipartition theorem

Suppose the energy is quadratic in "degrees of freedom", i.e. has the form:

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

Ex: $E = \frac{p^2}{2m} + \frac{1}{2} m\omega^2 x^2$ 1-D harmonic oscillator

$q_1 = p$, $q_2 = x$

In classical regime $\{q_1, q_2 \cdots q_N\}$ are continuous coordinates (not discrete) that define state of system

What is the partition function?

$$Z = \sum_i e^{-\beta E_i} \longrightarrow A \int_{-\infty}^{\infty} dq_1\, dq_2 \cdots dq_N \; e^{-\beta E(q_1, q_2 \cdots q_N)}$$

In classical regime, sum turns into an integral. Need normalization factor A to make Z dimensionally correct

$$p(E_i) = \frac{e^{-\beta E_i}}{Z} \longrightarrow \frac{A\, dq_1 dq_2 \cdots dq_N\, e^{-\beta E(q_1, q_2 \cdots q_N)}}{A \int_{-\infty}^{\infty} dq_1 dq_2 \cdots dq_N\, e^{-\beta E(q_1, q_2 \cdots q_N)}}$$

Notice that A cancels out in probability. For most quantities A will not matter. It will matter for entropy, though

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

$$\langle E_{q_1} \rangle = \frac{\int dq_1 \cdots dq_N \; a_1 q_1^2 \; e^{-\beta E_{q_1}} \; e^{-\beta E'(q_2 \cdots q_N)}}{\int dq_1 \cdots dq_N \; e^{-\beta E_{q_1}} \; e^{-\beta E'(q_2 \cdots q_N)}}$$

where we wrote $E = E_{q_1} + E'(q_2 \cdots q_N)$

$$\langle E_{q_1} \rangle = \frac{\int dq_1 \; E_{q_1} e^{-\beta E_{q_1}} \; \cancel{\int dq_2 \cdots dq_N \; e^{-\beta E'(q_2 \cdots q_N)}}}{\int dq_1 \; e^{-\beta E_{q_1}} \; \cancel{\int dq_2 \cdots dq_N \; e^{-\beta E'(q_2 \cdots q_N)}}}$$

$$= \frac{\int dq_1 \; E_{q_1} e^{-\beta E_{q_1}}}{\int dq_1 \, e^{-\beta E_{q_1}}}$$

$$= -\frac{\partial}{\partial \beta} \ln \left(\int e^{-\beta E_{q_1}} dq_1 \right) = -\frac{\partial}{\partial \beta} \ln Z_{q_1}$$

$$\int_{-\infty}^{\infty} dq_1 \; e^{-\beta E_{q_1}} = \int_{-\infty}^{\infty} dq_1 \; e^{-\beta a_1 q_1^2} = \sqrt{\frac{\pi}{a_1 \beta}}$$

Gaussian Integral (K+K Appendix A)

$$\therefore \langle E_{q_1} \rangle = -\frac{\partial}{\partial \beta} \left(\ln \beta^{-1/2} + \cdots \right) = \frac{1}{2} \frac{1}{\beta} = \frac{1}{2} k_B T$$

Works for any quadratic degree of freedom

$$\boxed{\langle E_{q_i} \rangle = \langle a_i q_i^2 \rangle = \frac{1}{2} k_B T}$$

Equipartition theorem

Key point is that equipartition works whenever I can treat states as continuum with $\Delta\varepsilon \ll k_B T$

Recall:

Einstein solid

N, 1-D harmonic oscillators

$$E_1 = \frac{p^2}{2m} + \frac{1}{2} m\omega^2 x^2$$

$$E_N = \frac{p_1^2 + p_2^2 \cdots p_N^2}{2m} + \frac{1}{2} m\omega^2 \left(x_1^2 + x_2^2 \cdots x_N^2\right)$$

$2N$ quadratic degrees of freedom

$$\therefore \quad U = \langle E_N \rangle = 2N \cdot \frac{1}{2} k_B T = N k_B T \quad \checkmark$$ agrees with high-T limit

Ideal gas

N, 3-D free particles

$$E_1 = \frac{p_x^2 + p_y^2 + p_z^2}{2m}$$

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

$3N$ quadratic degrees of freedom

$$\therefore \quad U = \langle E_N \rangle = 3N \cdot \frac{1}{2} k_B T = \frac{3}{2} N k_B T \quad \checkmark$$

But, paramagnet

We found $U = -N\mu B \tanh \frac{\mu B}{k_B T}$

When $k_B T \gg \mu B$ $\quad U = -N\frac{(\mu B)^2}{k_B T}$ $\quad \times$

Here energy is not quadratic + quantum effects are dominant. Equipartition does not work

Maxwell velocity distribution

For an ideal gas, what is the probability $f(v)$ that a given gas molecule has speed between v, $v+dv$?

$$E = \frac{1}{2}mv^2 = \frac{1}{2}m\left(v_x^2 + v_y^2 + v_z^2\right)$$

From the derivation of equipartition theorem, we can write:

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

That's not exactly what we want. We want this in terms of speed $v = \sqrt{v_x^2 + v_y^2 + v_z^2}$. Switch to spherical coordinates:

$$\left(\begin{array}{l}\text{Prob. that velocity} \\ \text{has magnitude } v, \text{ direction } \theta, \phi\end{array}\right) = \frac{v^2 dv\, d\Omega\; e^{-\beta E}}{\int v^2 dv\, d\Omega\; e^{-\beta E}}$$

where $d\Omega = \sin\theta\, d\theta\, d\phi$ (solid angle)

We don't care about direction θ, ϕ, so integrate over it:

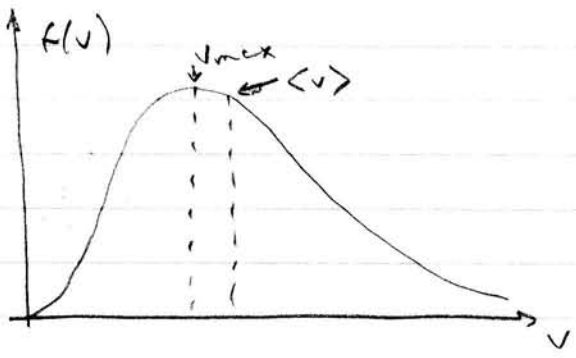
$$P(v) = f(v)\,dv = \frac{v^2 dv\; e^{-\beta E}}{\int_0^{\infty} v^2 dv\, e^{-\beta E}} = \frac{v^2 dv\; e^{-\beta \frac{1}{2}mv^2}}{\int_0^{\infty} v^2 dv\, e^{-\beta \frac{1}{2}mv^2}}$$

Evaluate denominator. Notice that:

$$\int_0^{\infty} v^2 dv\; e^{-\alpha v^2} = -\frac{\partial}{\partial \alpha}\int_0^{\infty} dv\, e^{-\alpha v^2} = -\frac{\partial}{\partial \alpha}\,\frac{1}{2}\sqrt{\frac{\pi}{\alpha}} \qquad \alpha = \frac{m}{2k_B T}$$

$$= \frac{1}{4}\frac{\sqrt{\pi}}{\alpha^{3/2}} = \frac{\sqrt{\pi}}{4}\left(\frac{2k_B T}{m}\right)^{3/2} = \frac{1}{4\pi}\left(\frac{2\pi k_B T}{m}\right)^{3/2}$$

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



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

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

$$v_{max} = \sqrt{\frac{2k_B T}{m}}$$

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

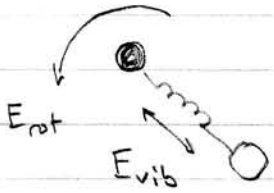
For N_2 at 300 K $v_{max} = 422$ m/s = 1000 mph !!

Ideal gas (re-revisited)

So far we've considered a monatomic ideal gas

What happens for something more complicated with internal degrees of freedom?

Consider diatomic gas with distinguishable atoms like CO



$\longrightarrow E_{trans}$

$$E = E_{trans} + E_{rot} + E_{vib}$$

$$z_{molecule} = \sum_{E\ (\text{all states})} e^{-\beta E} = \sum_{E_{trans}} e^{-\beta E_{trans}} \sum_{E_{rot}} e^{-\beta E_{rot}} \sum_{E_{vib}} e^{-\beta E_{vib}}$$

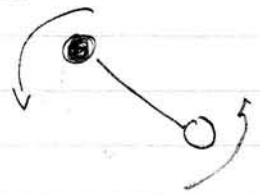
$$= z_{trans}\, z_{rot}\, z_{vib}$$

True as long as there is no coupling between degrees of freedom

Last time we showed:

$$E_{trans} = \frac{\hbar k^2}{2m} \qquad Z_{trans} = n_Q V \qquad U = \frac{3}{2} N k_B T$$

Rotational states of CO



Ignore rotation about C–O axis

In QM J, J_z are quantized ($\bar{J}$ = total angular momentum)

$$E_{rot} = E_J = \frac{|\bar{J}|^2}{2I} = \frac{j(j+1)\hbar^2}{2I} \equiv \varepsilon\, j(j+1)$$

I ↑ moment of inertia

E_{rot} depends on j but for each J there are $2j+1$ allowed values of J_z with same energy ⇒ degenerate states

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

Look at high-T limit $k_B T \gg \varepsilon$ ($\varepsilon \sim$ spacing between levels)

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

Let $x \equiv \beta\varepsilon j(j+1)$

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

$$= \frac{1}{\beta\varepsilon} \int_0^\infty dx\, e^{-x} = \frac{1}{\beta\varepsilon}$$

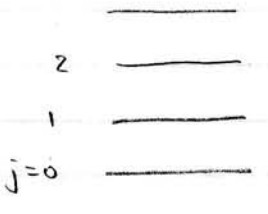
$$U_{rot} = -\frac{\partial}{\partial\beta} \ln Z_{rot} = +\frac{1}{\beta} = k_B T \qquad \text{(for } N \text{ molecules } U_{rot} = N k_B T\text{)}$$

Not surprising. E_{rot} has quadratic form, 2 degrees of freedom
Could get this result using equipartition theorem

What happens at lower T ?
Write out several terms of Z_{rot}

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

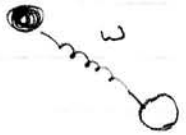
When $k_B T \lesssim \varepsilon$, each term becomes smaller and smaller only 1st few terms contribute. Excited states are "frozen out" as $T \downarrow$



When $k_B T \ll \varepsilon$, lowest level contributes $Z_{rot} \approx 1$

$U_{rot} = -\frac{\partial}{\partial\beta} \ln Z_{rot} \approx 0$ All particles in ground state

Vibrational states of CO



1-D harmonic oscillator

$$E_{vib} = E_n = \hbar\omega\left(n + \tfrac{1}{2}\right) \qquad n = 0, 1, 2, 3 \cdots$$

$$Z_{vib} = \sum_{n=0}^{\infty} e^{-\beta E_n} = \sum_{n=0}^{\infty} e^{-\beta\hbar\omega(n+1/2)}$$

$$= e^{-\frac{1}{2}\beta\hbar\omega} \sum_{n=0}^{\infty} e^{-\beta\hbar\omega n} \qquad \leftarrow \text{Series } \sum_{n=0}^{\infty} x^n = \frac{1}{1-x}$$

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

if $x < 1$

True for $x = e^{-\beta\hbar\omega}$

$$U_{vib} = -\frac{\partial}{\partial\beta} \ln Z_{vib} = \frac{\partial}{\partial\beta}\left[\tfrac{1}{2}\beta\hbar\omega + \ln\left(1 - e^{-\beta\hbar\omega}\right)\right]$$

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

$$\equiv \hbar\omega\left(\langle n\rangle + \tfrac{1}{2}\right)$$

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

At high T $(k_B T \gg \hbar\omega)$, $\langle n \rangle \approx \frac{k_B T}{\hbar\omega}$

$U_{vib} = \frac{\hbar\omega}{2} + k_B T \approx k_B T$ which we could have gotten by equipartition

At low T $(k_B T \ll \hbar\omega)$, $\langle n \rangle \approx e^{-\beta\hbar\omega}$

$U_{vib} = \frac{\hbar\omega}{2} + \hbar\omega\, e^{-\beta\hbar\omega}$ Again excited states "freeze out"
As $T \to 0$ all particles in ground state

$\Rightarrow U_{tot} = U_{trans} + U_{rot} + U_{vib}$

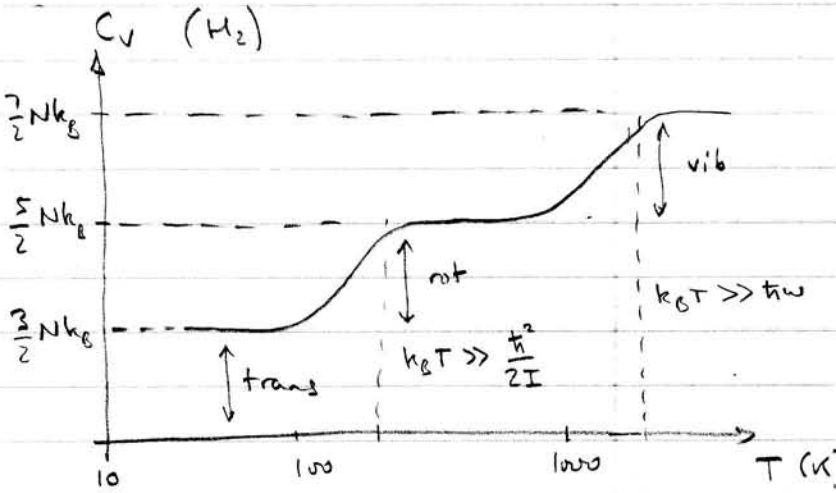
A convenient parameter is the heat capacity

$C_V \equiv \left(\frac{\partial U}{\partial T}\right)_V$ How much energy changes per temperature change

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

$C_V^{rot} = N k_B$ (high T)
$= 0$ $(T \to 0)$

$C_V^{vib} = N k_B$ (high T)
$= 0$ $(T \to 0)$



$C_V = C_V^{trans} + C_V^{rot} + C_V^{vib}$