Lecture 15

Canonical ensemble

For classical identical particles, define

$$Q_N(V,T) = \frac{1}{N!\,h^{3N}} \int e^{-\beta H}\, d\omega$$

Then $A = -kT \ln Q_N$

[Compare microcanonical: $\Sigma = \frac{1}{N!\,h^{3N}} \int_{E<H} d\omega$

$S = k_B \ln \Sigma$]

Let's apply to ideal gas

$$H = \sum_{i=1}^{N} \frac{|\vec{p}_i|^2}{2m}$$

$$Q_N = \frac{1}{N!\,h^{3N}} \int e^{-\frac{\beta}{2m}\sum_i |\vec{p}_i|^2}\, d^3q_1 \ldots d^3q_N\, d^3p_1 \ldots d^3p_N$$

Space integrals $\rightarrow V^N$

$$Q_N = \frac{V^N}{N!\,h^{3N}} \left[\int_0^\infty e^{-\frac{\beta p^2}{2m}}\, 4\pi p^2\, dp \right]^N$$

$$= \frac{V^N}{N!\,h^{3N}} (4\pi)^N \left(\frac{2m}{\beta}\right)^{3N/2} \Big[\underbrace{\int_0^\infty e^{-u^2} u^2\, du}_{\frac{\sqrt{\pi}}{4}} \Big]^N$$

$$= \frac{1}{N!} \left(\frac{V}{h^3}\right)^N \left(\frac{2\pi m}{\beta}\right)^{3N/2}$$

$$= \frac{1}{N!} V^N \left(\frac{2\pi m kT}{h^2}\right)^{3N/2}$$

$$\boxed{Q_N = \frac{1}{N!} \left(\frac{V}{\Lambda^3}\right)^N} \qquad \Lambda = \sqrt{\frac{h^2}{2\pi m kT}}$$

So $A = -kT\left[N \ln \frac{V}{\Lambda^3} - N \ln N + N \right]$

$$= -NkT\left[\ln \frac{V}{N\Lambda^3} + 1 \right]$$

$$\boxed{A = NkT\left[\ln \rho\Lambda^3 - 1 \right]} \qquad \rho = \frac{N}{V}$$

Then for instance,

$$S = -\left(\frac{\partial A}{\partial T}\right)_{N,V} = -Nk\left[\underbrace{\ln \rho\Lambda^3}_{\sim \ln T^{-3/2}} - 1 \right] - NkT\left(-\frac{3}{2}\frac{1}{T}\right)$$

$$= Nk\left[\frac{5}{2} - \ln \rho\Lambda^3 \right]$$

Sackur-Tetrode eqn ✓

and $P = -\left(\frac{\partial A}{\partial V}\right) = NkT\frac{1}{V}$ ✓

So we get all the ideal gas properties
without the evil N-dimensional integral!

Does it really work?

Might wonder whether canonical & microcanonical
predictions differ in their <u>fluctuations</u>

Micro-c. says energy $= E$ always

Canonical says $\langle \text{energy} \rangle = U$.

But if E varies from system to system,
might expect to observe.

Can calculate

Have $$U = \langle E \rangle = \frac{\sum_r E_r e^{-\beta E_r}}{\sum_r e^{-\beta E_r}}$$

$$\frac{\partial U}{\partial \beta} = -\frac{\sum_r E_r^2 e^{-\beta E_r}}{\sum_r e^{-\beta E_r}} + \frac{\left[\sum_r E_r e^{-\beta E_r}\right]^2}{\left[\sum_r e^{-\beta E_r}\right]^2}$$

$$= -\langle E^2 \rangle + \langle E \rangle^2$$

So variation in E

$$\Delta E^2 \equiv \langle E^2 \rangle - \langle E \rangle^2 = -\frac{\partial U}{\partial \beta}$$

$$= kT^2 \frac{\partial U}{\partial T}$$

$$= kT^2 C_V$$

and $$\frac{\Delta E}{U} = \frac{\sqrt{kT^2 C_V}}{U}$$

Note $C_V \propto N$

$U \propto N$

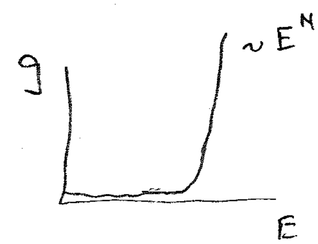
So $$\frac{\sqrt{C_V}}{U} \propto \frac{1}{\sqrt{N}} \to 0 \quad \text{as } N \to \infty$$

See that actual range of E's likely to be occupied is very small

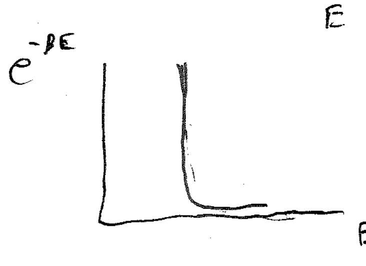
Why?

$$P(E) \propto g(E)\, e^{-\beta E}$$

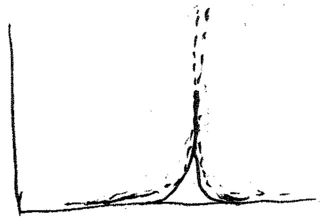
For large E, g grows very fast



$e^{-\beta E}$ decays very fast



Product has narrow peak



Pretty much, canonical ensemble is great.

Can prove useful result: <u>Equipartition Theorem</u>

Start with $\left\langle x_i \frac{\partial H}{\partial x_j} \right\rangle$

x_i = any of the $\{q, p\}$

$$\langle\ \rangle = \frac{\int x_i \frac{\partial H}{\partial x_j} e^{-\beta H} d\omega}{\int e^{-\beta H} d\omega}$$

Integrate numerator by parts;

$$u = x_i \qquad dv = \frac{\partial H}{\partial x_j} e^{-\beta H} = -\frac{1}{\beta}\frac{\partial}{\partial x_j} e^{-\beta H}$$

$$du = dx_i \qquad v = -\frac{1}{\beta} e^{-\beta H}$$

$$\int \rightarrow \int d\omega_{(j)} \left\{ -\frac{1}{\beta} e^{-\beta H} x_i \Big|_{x_{j1}}^{x_{j2}} + \frac{1}{\beta} \int \underbrace{\frac{\partial x_i}{\partial x_j}}_{\delta_{ij}} e^{-\beta H} dx_j \right\}$$

$d\omega_{(j)}$ ↑ all coords but x_j

x_{j1}, x_{j2} = boundary values of coordinate

Claim boundary terms vanish:

Cases: x_j = momentum : $x_j \rightarrow \pm\infty$

$H(x_{j1}) = H(x_{j2}) = \infty$

x_j = linear coord : $x_j \rightarrow$ walls of container

$H \rightarrow \infty$ since $V \rightarrow \infty$

x_j = angular coord: $x_{j1} = x_{j2}$

Two terms cancel

Left with $\frac{1}{\beta} \delta_{ij} \int e^{-\beta H} \, d\omega$

So $$\left\langle x_i \frac{\partial H}{\partial x_j} \right\rangle = \frac{1}{\beta} \delta_{ij} \frac{\int e^{-\beta H} \, d\omega}{\int e^{-\beta H} \, d\omega}$$

$$= \frac{1}{\beta} \delta_{ij}$$

$$\boxed{\left\langle x_i \frac{\partial H}{\partial x_j} \right\rangle = \delta_{ij} kT}$$

Now suppose H is a quadratic function of x_i

$$H = H(\{x_{j \neq i}\}) + A_i x_i^2$$

Then $$\left\langle x_i \frac{\partial H}{\partial x_i} \right\rangle = \langle x_i \, 2 A_i x_i \rangle$$

$$= 2 \langle A_i x_i^2 \rangle = kT$$

So $$\langle H \rangle = \langle H_{i \neq j} \rangle + \frac{1}{2} kT$$

Each coordinate that appears quadratically in H contributes $\frac{1}{2} kT$ to total energy

Ideal gas: $3N$ momenta $\Rightarrow U = \frac{3}{2} NkT$

Harmonic oscillators: $3N$ p's $+ 3N$ q's $\Rightarrow U = 3NkT$

Note however, that this an explicitly <u>classical</u> result

QM requires some corrections.

See how this works... look at harmonic oscillator in detail

Say $H = \sum_{i=1}^{N} H_i \qquad H_i = \frac{1}{2} m\omega^2 q_i^2 + \frac{p_i^2}{2m}$

Then $Q_1 = \frac{1}{h} \int_{-\infty}^{\infty} dq \int_{-\infty}^{\infty} dp \; e^{-\beta\left(\frac{1}{2} m\omega^2 q^2 + \frac{1}{2}\frac{p^2}{2m}\right)}$

$$= \frac{1}{h} \int_{-\infty}^{\infty} dq \; e^{-\left(\frac{\beta m\omega^2}{2}\right) q^2} \int_{-\infty}^{\infty} dp \; e^{-\left(\frac{\beta}{2m}\right) p^2}$$

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

$$= \frac{2\pi}{\beta h} = \frac{1}{\hbar\omega\beta}$$

We will mostly apply this analysis to study of modes in oscillating systems (phonons & photons, for example)

Modes are distinguishable, so lets take "particles" as distinguishable here.

Then $Q_N = (Q_1)^N = (\hbar\omega\beta)^{-N}$

and $A = -kT \ln Q_N = \boxed{NkT \ln \frac{\hbar\omega}{kT}}$

Get $S = -\frac{\partial A}{\partial T} = -\left[Nk \ln \frac{\hbar\omega}{kT} + NkT\left(-\frac{1}{T}\right)\right]$

$$\boxed{S = Nk\left[\ln \frac{kT}{\hbar\omega} + 1\right]}$$

and $U = A - TS$

$\boxed{U = NkT}$ as expected

But as long as particles are distinguishable, quantum calc isn't too hard

Do it and compare:

Know energy levels $\varepsilon_n = (n+\frac{1}{2})\hbar\omega$ $\quad n = 0, 1, 2\ldots$

So $Q_1 = \sum_{n=0}^{\infty} e^{-\beta(n+\frac{1}{2})\hbar\omega}$

$$= e^{-\frac{\beta\hbar\omega}{2}} \sum_{n=0}^{\infty} \left(e^{-\hbar\omega\beta}\right)^n$$

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

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

$$Q_1 = \frac{1}{2\sinh\frac{\beta\hbar\omega}{2}}$$

$$Q_N = Q_1^N = e^{-N\beta\hbar\omega/2}\left[1 - e^{-\beta\hbar\omega}\right]^{-N}$$

Then $A = -kT\left\{-N\frac{\beta\hbar\omega}{2} - N\ln\left(1-e^{-\beta\hbar\omega}\right)\right\}$

$$\boxed{A = N\left\{\frac{\hbar\omega}{2} + kT\ln\left(1-e^{-\beta\hbar\omega}\right)\right\}}$$

Not same as classical result $A_{cl} = NkT\ln\beta\hbar\omega$

Expect to recover classical result in limit $kT \gg \hbar\omega$

Then $e^{-\beta\hbar\omega} \approx 1-\beta\hbar\omega+\frac{1}{2}(\beta\hbar\omega)^2$

$$A \to N\left\{\frac{\hbar\omega}{2} + kT\ln\left[\beta\hbar\omega-\frac{1}{2}(\beta\hbar\omega)^2\right]\right\}$$

$$= N\left\{\frac{\hbar\omega}{2} + \frac{1}{\beta}\left[\ln\beta\hbar\omega + \underbrace{\ln\left(1-\frac{1}{2}\beta\hbar\omega\right)}_{\approx -\frac{1}{2}\beta\hbar\omega}\right]\right\}$$

$$= N\left\{\frac{\hbar\omega}{2} + kT\ln\beta\hbar\omega - \frac{\hbar\omega}{2}\right\}$$

$$= NkT\ln\beta\hbar\omega = A_{cl}$$

So that is fine.

But difference matters if $kT \lesssim \hbar\omega$

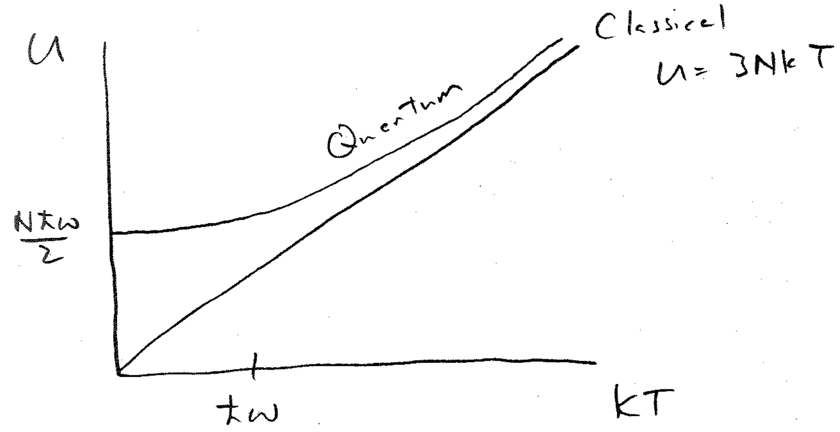
For instance,

$$U = \frac{\partial}{\partial\beta}(\beta A)$$

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

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

Plot:



More complicated temp dependence than classical system

See that equipartion theorem fails

General result:

If $kT \ll$ excitation energy for quantum motion then that degree of freedom is "frozen out"

$\Rightarrow$ doesn't contribute to thermodynamics

For instance, diatomic molecule

Degrees of freedom:

$3\times$ translation (x, y, z)

$2\times$ rotation (θ, ϕ)

$2\times$ vibration (both p & q contribute)

Expect $U = \frac{7}{2}NkT$ from equipartition

But vibrational frequency usually pretty big

$\omega \sim 2\pi \times 10^{14}$ Hz

So $\frac{\hbar\omega}{k} \approx 5000\,K$

For T smaller than this, no vibrational excitation

and $U \to \frac{5}{2} N k_B T$

as observed

Rotational level spacing is ~100x smaller

Freeze out at ~50K

But most diatomic gases liquify by that temp.