Canonical ensemble

For classical identical particles, define

$$Q_N(v, T) = \frac{1}{N! h^{3N}} \int e^{-\beta \mathcal{H}} \, dv$$

Then $A = -kT \ln Q_N$

[Compare microcanonical: $\Sigma = \frac{1}{N! h^{3N}} \int_{E=0} e^{-\beta E} \, dv$]

$$S = k_B \ln \Sigma$$

Let's apply to ideal gas

$$H = \sum_{i=1}^{N} \frac{p_i^2}{2m}$$

$$Q_N = \frac{1}{N! h^{3N}} \int e^{-\beta \sum \frac{p_i^2}{2m}} \, d^3 q_1 \ldots d^3 q_N \, d^3 p_1 \ldots d^3 p_N$$

Space integrals $\Rightarrow V^N$

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

$$= \frac{V^N}{N! h^{3N}} \left( \frac{2m}{\beta} \right)^{3N/2} \left[ \int_0^\infty e^{-\frac{\rho^2}{2 \beta}} \, d\rho \right]^N$$

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

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

$$Q_N = \frac{1}{N!} \left( \frac{V}{\Lambda^3} \right)^N \quad \Lambda = \sqrt[3]{\frac{h^2}{2\pi m kT}}$$
So \[ A = -kT \left[ N \ln \frac{V}{N^3} - N \ln N + N \right] \]
\[ = -NkT \left[ \ln \frac{V}{N^3} + 1 \right] \]
\[ A = NkT \left[ \ln \rho A^3 - 1 \right] \quad \rho = \frac{N}{V} \]

Then for instance,
\[ S = -\left( \frac{\partial A}{\partial T} \right)_{N,V} = -Nk \left[ \ln \rho A^3 - 1 \right] - NkT \left( -\frac{2}{3} \frac{1}{T} \right) \]
\[ = Nk \left[ \frac{5}{2} - \ln \rho A^3 \right] \]

Sackur-Tetrode eqn \( \checkmark \)

and \[ P = -\left( \frac{\partial A}{\partial V} \right) = NkT \frac{1}{V} \checkmark \]

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 fluctuations

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 \( U = \langle E \rangle = \frac{\Sigma \sum e^{-\beta E}}{e^{-\beta E}} \)

\[
\frac{\partial U}{\partial \beta} = -\frac{\Sigma \sum E^2 e^{-\beta E}}{\Sigma e^{-\beta E}} + \left[ \frac{\Sigma \sum e^{-\beta E}}{\Sigma e^{-\beta E}} \right]^2
\]

\[
= -\langle E^2 \rangle + \langle E \rangle^2
\]

So variation in \( E \)

\[
\Delta E^2 = \langle E^2 \rangle - \langle E \rangle^2 = -\frac{\partial U}{\partial \beta}
\]

\[
= kT^2 \frac{\partial U}{\partial T}
\]

\[
= kT^2 C_U
\]

and \( \frac{\Delta E}{U} = \frac{\sqrt{kT^2 C_U}}{U} \)

Note \( C_U \propto N \)

\( U \propto N \)

So \( \frac{\sqrt{C_U}}{U} \propto \frac{1}{\sqrt{N}} \to 0 \) 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 \( \Rightarrow \)

\( e^{-\beta E} \) decays very fast.
Product has narrow peak

Pretty much, canonical ensemble is great.

Can prove useful result: **Equi-partition Theorem**

Start with \( \langle x_i \frac{\partial H}{\partial x_j} \rangle \) \( x_i \) any of the \( \xi_k, p^k \)

\[
\langle \rangle = \frac{\int x_i \frac{\partial H}{\partial x_j} e^{-\beta H} \, dw}{\int e^{-\beta H} \, dw}
\]

Integrate numerator by parts:

\( u = x_i \), \( dv = \frac{\partial H}{\partial x_j} e^{-\beta H} = -\frac{1}{\beta} \frac{\partial}{\partial x_j} e^{-\beta H} \)

\( du = dx_i \), \( v = -\frac{1}{\beta} e^{-\beta H} \)

\[
\int e^{-\beta H} \, dx_i \sum_{i \neq j} \left[ \frac{1}{\beta} e^{-\beta H} x_i \bigg|_{x_{i1}}^{x_{i2}} + \frac{1}{\beta} \int \frac{\partial x_i}{\partial x_j} e^{-\beta H} \, dx_j \right]
\]

all coors but \( x_j \)

\( x_{i1}, x_{i2} = \) boundary values of \( \text{coordinate} \)

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 \( U \rightarrow \infty \)
$x_j = \text{angular coord: } x_{j1} = x_{j2}$

Two terms cancel

Left with $\frac{1}{\beta} S_{ij} Se^{-\beta H} dw$

So $\langle x_i; \frac{\partial H}{\partial x_j} \rangle = \frac{1}{\beta} S_{ij} \frac{Se^{-\beta H} dw}{Se^{-\beta H} dw}$

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

$\langle x_i; \frac{\partial H}{\partial x_j} \rangle = S_{ij} kT$

Now suppose $H$ is a quadratic function of $x_i$:

$H = H(\sum x_i^2) + A_i x_i^2$

Then $\langle x_i; \frac{\partial H}{\partial x_i} \rangle = \langle x_i; 2A_i x_i \rangle$

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

So $\langle H \rangle = \langle H_{ij} x_j \rangle + \frac{1}{2} kT$

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

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

Harmonic oscillators: $3N$ positions and $3N$ momenta $\Rightarrow U = 3N kT$
Note however, that this is an explicitly classical result. QM requires some corrections.

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

Say \( H = \sum_{i=1}^{N} H_i \) where \( H_i = \frac{1}{2} m w^2 q_i^2 + \frac{p_i^2}{2m} \).

Then \( Q_1 = \frac{1}{\hbar} \int_{-\infty}^{\infty} dq_i \int_{-\infty}^{\infty} dp_i e^{-\beta \left( \frac{1}{2} m w^2 q_i^2 + \frac{1}{2} \frac{p_i^2}{m} \right)} \)

\[ = \frac{1}{\hbar} \int_{-\infty}^{\infty} dq_i \int_{-\infty}^{\infty} dp_i e^{-\beta \left( \frac{1}{2} \frac{p_i^2}{m} \right)} \]

\[ = \frac{1}{\hbar} \left( \frac{2\pi}{\beta m w^2} \right)^{1/2} \left( \frac{2\pi m}{\beta} \right)^{1/2} \]

\[ = \frac{2\pi}{\beta \hbar} = \frac{1}{\hbar w \beta} \]

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

Modes are distinguishable, so let's take "particles" as distinguishable here.

Then \( Q_N = (Q_1)^N = (\hbar w \beta)^N \)

and \( A = -kT \ln Q_N = N kT \ln \frac{\hbar w}{kT} \).
Get \( S = -\frac{\delta A}{\delta T} = -[Nk \ln \frac{2\omega}{kT} + NkT \left( -\frac{1}{T} \right)] \)

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

and \( U = A - TS \)

\[
U = NkT \quad \text{as expected}
\]

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

Do it and compare:

Know energy levels \( E_n = (n + \frac{1}{2}) \omega \) \( n = 0, 1, 2, \ldots \)

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

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

\[
= e^{-\frac{\beta \omega}{2}} \cdot \frac{1}{1 - e^{-\omega \beta}}
\]

\[
= \frac{1}{e^{\beta \omega / 2} - e^{-\beta \omega / 2}}
\]

\[
Q_1 = \frac{1}{2 \sinh \frac{\beta \omega}{2}}
\]

\( Q_N = Q_1^N = e^{-N \frac{\beta \omega}{2}} \left[ 1 - e^{-\beta \omega} \right]^{-N} \)
Then \( A = -kT \left( \hat{E} - N \frac{k_B w}{2} - N \ln (1 - e^{-\beta t w}) \right) \)

\[
A = N \hat{E} \frac{k_B w}{2} + kT \ln (1 - e^{-\beta t w})
\]

Not same as classical result \( A_{cl} = N kT \ln \beta t w \)

Expect to recover classical result in limit \( kT \gg \beta t w \)

\[e^{-\beta t w} \approx 1 - \beta t w + \frac{1}{2} (\beta t w)^2\]

\[
A \rightarrow N \hat{E} \frac{k_B w}{2} + kT \ln \left[ \beta t w - \frac{1}{2} (\beta t w)^2 \right]
\]

\[
= N \hat{E} \frac{k_B w}{2} + \frac{1}{2} \left[ \ln \beta t w + \ln (1 - \frac{1}{2} (\beta t w)^2) \right] \\
\approx -\frac{1}{2} \beta t w
\]

\[= N \hat{E} \frac{k_B w}{2} + kT \ln \beta t w - \frac{t w}{2^2}
\]

\[= N kT \ln \beta t w = A_{cl}
\]

So that is fine.

But difference matters if \( kT \ll \beta t w \)

For instance,

\[
\mathcal{L} = \frac{\partial}{\partial \beta} (\beta A)
\]

\[
\approx \frac{\partial}{\partial \beta} \left[ N \hat{E} \frac{k_B w}{2} + kT \ln (1 - e^{-\beta t w}) \right]
\]

\[= \frac{N t w}{2} + \frac{t w}{1 - e^{-\beta t w}}
\]
More complicated temp dependence than classical system
See that equipartition 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 x translation $(x, y, z)$
2 x rotation $(\theta, \phi)$
2 x vibration (both $p$ & $q$ contribute)

Expect $U = \frac{3}{2} N k T$ from equipartition

But vibrational frequency usually pretty big

$\nu = 2\pi \times 10^{14}$ Hz
So \( \frac{\hbar \omega}{k} \approx 5000 \text{K} \)

For \( T \) smaller than this, no vibrational excitation
and \( U \approx \frac{5}{2} N k_b T \)
as observed

Rotational level spacing is \( \sim 100 \times \) smaller

Freeze out at \( \sim 50 \text{K} \)

But most diatomic gases liquify by that temp.