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Last time:

Canonical formalism.

$$F(N,V,T) = -kT \ln Z_N(V,T)$$

$$Z_N(V,T) = \sum_r e^{-\beta E_r}$$

Notice that

$$dF = -S\,dT - P\,dV + \mu\,dN$$

then $P = -\left.\frac{\partial F}{\partial V}\right|_{T,N}$

$$P = -\left.\frac{\partial F}{\partial V}\right|_{N,T} = kT\,\frac{\partial \ln Z_N}{\partial V} =$$

$$= kT\,\frac{\partial Z_N/\partial V}{Z_N} = \frac{kT}{Z_N}\frac{\partial}{\partial V}\sum_r e^{-\beta \epsilon_r} =$$

$$= -\frac{kT}{Z_N}\sum_r \beta\,\frac{\partial \epsilon_r}{\partial V}\,e^{-\beta\epsilon_r} = -\frac{\cancel{kT}}{\cancel{kT}}\,\frac{\sum_r \frac{\partial \epsilon_r}{\partial V} e^{-\beta\epsilon_r}}{\sum_r e^{-\beta\epsilon_r}}$$

$$\Rightarrow \quad PdV = -\sum_r \overbrace{\frac{e^{-\beta\epsilon_r}}{\sum_r e^{-\beta\epsilon_r}}}^{P_r}\, d\epsilon_r =$$

$$= -\sum_r P_r\, d\epsilon_r = -dU$$

We see that the change in the average energy U of the system during a process that changes ε_r (energy levels) leaves the probabilities constant, i.e., $dS = 0$.

Entropy:

$$P_r = \frac{e^{-\beta \varepsilon_r}}{Z_N}$$

$$\langle \ln P_r \rangle = \langle -\beta \varepsilon_r - \ln Z_N \rangle = -\beta \langle \varepsilon_r \rangle$$

$$- \langle \ln Z_N \rangle = -\beta U + \frac{F}{kT} = \beta (F - U)$$

$$\langle \ln P_r \rangle = \beta (F - U) = \beta (U - TS - U) =$$

$$= -\frac{1}{kT} TS = -\frac{S}{k}$$

then $S = -k \langle \ln P_r \rangle = -k \sum_r P_r \ln P_r$

S is totally dependent on P_r.

S is determined by the probability distribution.

At $T=0$ $P_r = 1$ for ground state, 0 for all other states

$S_{T=0} = -k \, 1 \ln 1 \equiv 0$ (third law).

As T increases S increases because there are many more accessible states. The system becomes more disordered and we know less about its actual state.

- For microcanonical ensemble

$$P_r = \frac{1}{\Omega} \quad \text{where } \Omega = \#\text{ of accessible states.}$$

and 0 for states that are not accessible.

Then

$$S = -k \sum_r P_r \ln P_r = -k \sum_r \frac{1}{\Omega} \ln \frac{1}{\Omega}$$

$$= -k \frac{\cancel{\Omega}}{\cancel{\Omega}} \ln \frac{1}{\Omega} = \boxed{k \ln \Omega}$$

Partition function in terms of the density of states:

If ϵ_r is degenerate with degeneracy g_r we can write:

$$Z_N(V,T) = \sum_r g_r e^{-\beta \epsilon_r}$$

now ϵ_r are all different.

and

$$P_r = \frac{g_r e^{-\beta \epsilon_r}}{\sum_r g_r e^{-\beta \epsilon_r}}$$

If we have a macroscopic system with $\Delta E \ll 1$ we may consider E as continuous.

Then we define a continuous probability distribution:

$P(E)\,dE$: probability that the system has energy between E and $E+dE$

$$P(\epsilon)\,d\epsilon \propto e^{-\beta\epsilon}\,\underbrace{g(\epsilon)}_{\text{density of states}}\,d\epsilon$$

Normalized:

$$P(\epsilon)\,d\epsilon = \frac{e^{-\beta\epsilon}g(\epsilon)\,d\epsilon}{\int_0^\infty e^{-\beta\epsilon}g(\epsilon)\,d\epsilon}$$

$$\therefore \quad Z_N(V,T) = \int_0^\infty e^{-\beta\epsilon}g(\epsilon)\,d\epsilon$$

You see that $Z_N(\beta)$ is the Laplace transform of $g(E)$.

Laplace transform $F(s)$ of $f(t)$ is given by:

$t \geq 0$

$$F(s) = \int_0^\infty e^{-st} f(t)\, dt$$

s is complex

$s = \sigma + i\omega$

In our case $s \longrightarrow \beta$

$t \longrightarrow E$

Then $g(\epsilon)$ can be obtained as the anti laplace transform of Z_N.

Also:

$$\langle f \rangle = \sum_r f_r P_r = \frac{\sum_r f(\epsilon_r)\, g_r\, e^{-\beta \epsilon_r}}{\sum_r g_r\, e^{-\beta \epsilon_r}}$$

$$\xrightarrow[\text{cont.}]{} \frac{\int_0^\infty f(\epsilon)\, e^{-\beta \epsilon}\, g(\epsilon)\, d\epsilon}{\int_0^\infty e^{-\beta \epsilon}\, g(\epsilon)\, d\epsilon}$$

Examples:

Classical systems: phase space.

$$\therefore \quad \langle f \rangle = \frac{\int f(p,q)\, e^{-\beta H}\, d\omega}{\int e^{-\beta H}\, d\omega} \qquad d\omega = d^{3N}p\, d^{3N}q$$

We already found that we need to introduce a factor $\frac{1}{N!\,h^{3N}}$ to take care of the indistinguishability of the particles and of the minimum volume in phase space allowed by quantum mechanics.

Then

$$Z_N(V,T) = \frac{1}{N!\,h^{3N}} \int_{\text{all space}} e^{-\beta H(q,p)}\,d\omega \qquad (1)$$

Ideal gas: N identical particles

V : volume

T : equilibrium temp.

$$H(q,p) = \sum_{i=1}^{N} \frac{p_i^2}{2m} \qquad (2)$$

only kinetic energy

Plug (2) in (1):

$$Z_N(V,T) = \frac{1}{N!\, h^{3N}} \int e^{-\frac{\beta}{2m}\sum_{i=1}^{N} p_i^2} \prod_{i=1}^{N} d^3q_i \cdot d^3p_i =$$

$$\underbrace{\prod_{i=1}^{N} \int_0^L d^3q_i}$$

$$= \frac{V^N}{N!\, h^{3N}} \left[\int_0^\infty e^{-\frac{p^2}{2mkT}}\, \underbrace{4\pi}_{\int_0^\pi \cos\theta\, d\theta \int_0^{2\pi} d\varphi} p^2\, dp \right]^N =$$

tables

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

Now we obtain

$$F(N,V,T) = -kT \ln Z_N(V,T) =$$

using $\ln N! \sim N \ln N - N$

$$= -kTN\left[\ln\left\{\frac{V}{h^3}(2\pi m k T)^{3/2}\right\} - \ln N + 1\right]$$

$$= kTN\left\{\ln \frac{N h^3}{V(2\pi m k T)^{3/2}} - 1\right\} =$$

$$= kTN\left\{\ln\left[\frac{N}{V}\left(\frac{h^2}{2\pi m k T}\right)^{3/2}\right] - 1\right\}$$

This is the same that we obtained using micro-canonical.

Now you can obtain

$$\mu = \frac{\partial F}{\partial N}\Big|_{V,T}$$

$$P = -\frac{\partial F}{\partial V}\Big|_{N,T} = \frac{NkT}{V} \Rightarrow PV = NkT \text{ (eq. of state).}$$

$$S = -\frac{\partial F}{\partial T}\Big|_{N,V} = Nk\left[\ln\left\{\frac{V}{N}\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\right\} + \frac{5}{2}\right]$$

correct value because we corrected with $N!$

Also:

$$U = -\frac{\partial}{\partial \beta} \ln Z = -\frac{\partial \ln Z}{\partial T}\frac{\partial T}{\partial \beta} =$$

Notice that $Z_N \propto T^{\frac{3N}{2}}$

$\therefore$

$$\beta = \frac{1}{kT}$$

$$\frac{\partial \beta}{\partial T} = -\frac{1}{kT^2}$$

$$\frac{\partial T}{\partial \beta} = -kT^2$$

$$= +kT^2 \frac{\partial \ln Z}{\partial T} =$$

$$= +\frac{kT^2\, 3N\, T^{\frac{3N}{2}-1}}{2\, T^{\frac{3N}{2}}} =$$

$$= +\frac{3}{2} N k T$$

as expected.

Since the particles are non-interacting then

$$Z_N(V,T) = \frac{1}{N!}\left[\frac{V}{h^3}(2\pi m k T)^{3/2}\right]^N =$$

$$= \frac{\left[Z_1(V,T)\right]^N}{N!}$$

$Z_1(V,T)$ is the partition function for 1 single particle.

By taking the anti Laplace transform of Z_N we obtain $g(E)$:

$$g(E) = \mathcal{L}^{-1}(Z(\beta))$$

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

$f(t)$	$F(s)$
t^n	$\frac{n!}{s^{n+1}}$
E^n	$\frac{n!}{\beta^{n+1}}$

E '' t, β '' s

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

Notice that

$Z_N(V,T)$ can be evaluated if we know $g(E)$ as

$$Z_N(V,T) = \int_0^\infty e^{-\beta E} g(E)\, dE$$

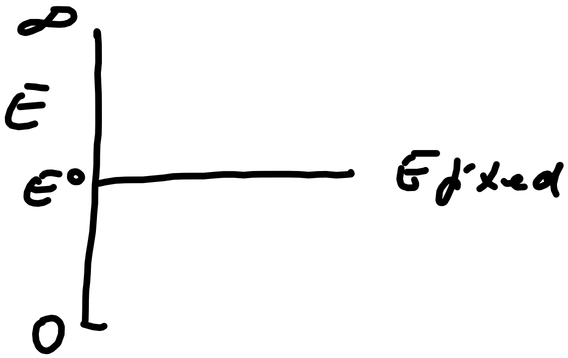
You can do the same for $Z_1(V,T)$ finding

that $a(\varepsilon) = \frac{2\pi V}{h^3}(2m)^{3/2}\,\varepsilon^{1/2}$.

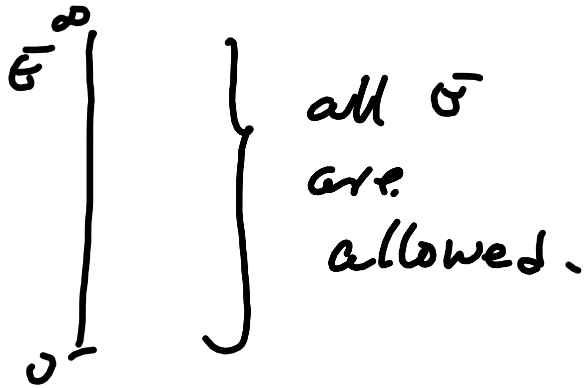
Energy fluctuations in the canonical formalism.

We will see that the fluctuations vanish as $N \to \infty$ then canonical and microcanonical are equivalent.

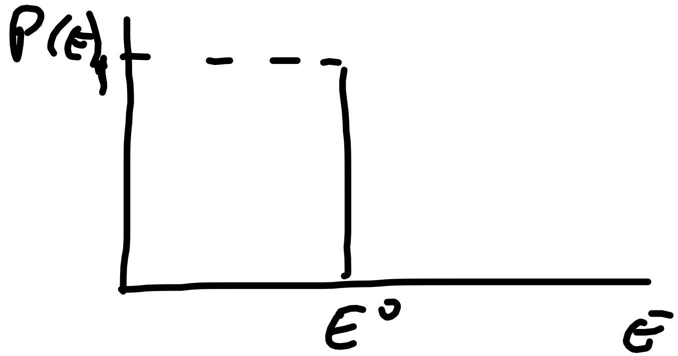
Microcanonical:



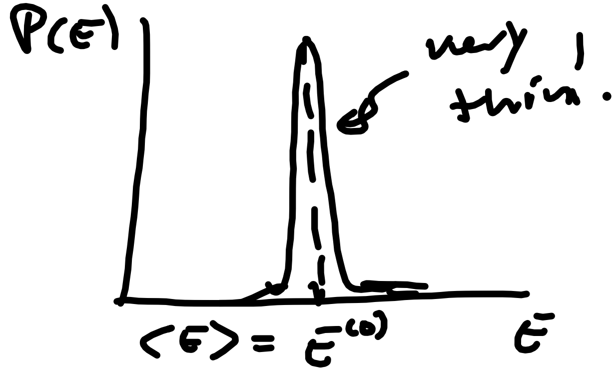
Canonical



Micro:



Canonical



In canonical:

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

$$\langle (\Delta E)^2 \rangle = \langle (E - \langle E \rangle)^2 \rangle =$$

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

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

with

$$\langle E^2 \rangle = \frac{\sum_r E_r^2 e^{-\beta E_r}}{\sum_r e^{-\beta E_r}}$$

$$\frac{\partial U}{\partial \beta} = \frac{\partial}{\partial \beta}\left[\frac{\sum_r E_r e^{-\beta E_r}}{\sum_r e^{-\beta E_r}}\right] = \underbrace{\frac{-\sum_r E_r^2 e^{-\beta E_r}}{\sum_r e^{-\beta E_r}}}_{-\langle E^2 \rangle} -$$

$$- \frac{(-)\left(\sum_r e^{-\beta\epsilon_r}\epsilon_r\right)^2}{\underbrace{\left(\sum_r e^{-\beta\epsilon_r}\right)^2}_{\langle E\rangle^2 = U^2}} = \langle E\rangle^2 - \langle E^2\rangle$$

$$\therefore \quad \langle(\Delta E)^2\rangle = -\frac{\partial U}{\partial\beta} = -\frac{\partial U}{\partial T}\frac{\partial T}{\partial\beta} =$$

$$= \frac{1}{k\beta^2}\frac{\partial U}{\partial T} = kT^2 \left.\frac{\partial U}{\partial T}\right|_V = kT^2 c_V$$

$$\frac{\sqrt{\langle(\Delta E)^2\rangle}}{\langle E\rangle} = \frac{\sqrt{kT^2 c_V}}{U} \propto \frac{1}{\sqrt{N}}$$ since $U \propto N$, $c_V \propto N$

$\rightarrow 0$ as $N \rightarrow \infty$!