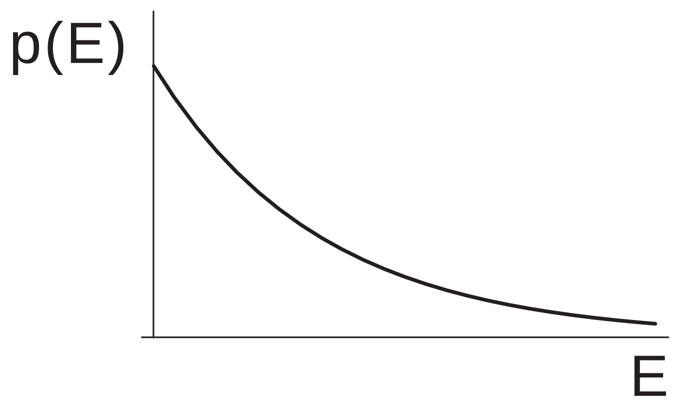
Canonical Ensemble



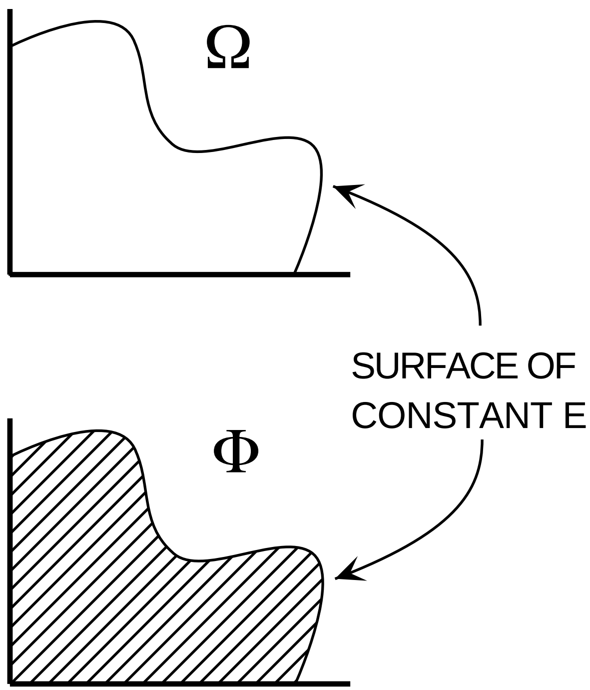
$$p(E) \propto e^{-E/kT} \quad \text{NOT!}$$

$$p(\{p,q\}) \propto e^{-\mathcal{H}(\{p,q\})/kT}$$

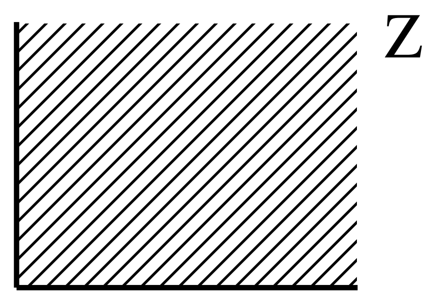
ADVANTAGES OF CANONICAL OVER MICROCANONICAL ENSEMBLE

1) ONE INTEGRATES OVER ALL PHASE SPACE

MICROCANONICAL



CANONICAL



2) SEPARATION

let $\mathcal{H} = \mathcal{H}_a + \mathcal{H}_b$, then $e^{-\mathcal{H}/kT} = e^{-\mathcal{H}_a/kT} e^{-\mathcal{H}_b/kT}$

$\Rightarrow p(\{p,q\}) = p(\{p,q\}_a)\ p(\{p,q\}_b)$ (a & b are SI)

$\Rightarrow Z = Z_a\, Z_b \Rightarrow F = F_a + F_b \Rightarrow S = S_a + S_b$ etc.

$\Rightarrow$ For N similar, non-interacting systems

$$Z = (Z_1)^N\,, \quad F = NF_1\,, \quad S = NS_1$$

$\Rightarrow$ For N indistinguishable particles

$$Z = \frac{(Z_1)^N}{N!}\,, \quad \text{correct Boltzmann counting}$$

Example Non-interacting classical monatomic gas

$$\mathcal{H} = \sum_{i=1}^{N} \frac{\vec{p_i} \cdot \vec{p_i}}{2m} = \sum_{i=1}^{N} \mathcal{H}_i \quad \Rightarrow \quad Z = \frac{(Z_1)^N}{N!}$$

$$\mathcal{H}_1(\vec{p}, \vec{r}) = \frac{p_x^2 + p_y^2 + p_z^2}{2m}$$

$$p_1(\vec{p}, \vec{r}) = e^{-(p_x^2+p_y^2+p_z^2)/2mkT}/Z_1$$

Gaussian $p_x \Rightarrow < \vec{p} \cdot \vec{p} > = < p_x^2 + p_y^2 + p_z^2 > = 3mkT$

$< \mathcal{H}_1 > = 3/2\, kT$

$$Z_1 = \int e^{-(p_x^2+p_y^2+p_z^2)/2mkT} \ \frac{dp_x dp_y dp_z dx dy dz}{h^3}$$

$$= (2\pi mkT)^{3/2} L_x L_y L_z / h^3 = V \left(\frac{2\pi mkT}{h^2}\right)^{3/2}$$

$$Z(T,V,N) = \frac{1}{N!} V^N \left(\frac{2\pi mkT}{h^2}\right)^{3N/2} = \frac{1}{N!} \left[V \underbrace{\left(\frac{2\pi mkT}{h^2}\right)^{3/2}}_{\text{units of cm}^{-3}} \right]^N$$

$$= \frac{1}{N!} \left[\frac{V}{v_0} \left(\frac{2\pi mkT}{h^2}\right)^{3/2} v_0 \right]^N$$

$$
\begin{aligned}
F &= -kT \ln Z \\
&= -kT \left[-N \ln N + N + N \ln(V/v_0) + \frac{3N}{2} \ln\left(\frac{2\pi mkT v_0^{2/3}}{h^2} \right) \right]
\end{aligned}
$$

use $N = N \ln e = \frac{3N}{2} \ln(e^{2/3})$

$$
= -kT \left[N \ln \frac{V}{N v_0} + \frac{3N}{2} \ln\left(\frac{2\pi e^{2/3} mkT v_0^{2/3}}{h^2} \right) \right]
$$

$$P = -\left(\frac{\partial F}{\partial V}\right)_{T,N} = (-1)(-kTN)\,\frac{1}{\frac{V}{Nv_0}}\,\frac{1}{Nv_0} = \underline{\frac{NkT}{V}}$$

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N} = k[\quad] + kT\left(\frac{3N}{2}\,\frac{1}{()}\,\frac{()}{T}\right)$$

$$= \underline{\frac{3N}{2}\,k + k\left[N\ln\frac{V}{Nv_0} + \frac{3N}{2}\ln\left(\frac{2\pi(ev_0)^{2/3}mkT}{h^2}\right)\right]}$$

$$E = F + TS = \underline{\frac{3}{2}\,NkT}$$

Find the adiabatic path, $\Delta S = 0$.

$$\ln \frac{V}{N v_0} - \ln \frac{V_0}{N v_0} = -\frac{3}{2}(\ln T - \ln T_0)$$

$$\ln \frac{V}{V_0} = -\frac{3}{2} \ln \frac{T}{T_0} \Rightarrow \underline{\frac{V}{V_0} = \left(\frac{T}{T_0}\right)^{-3/2}}$$