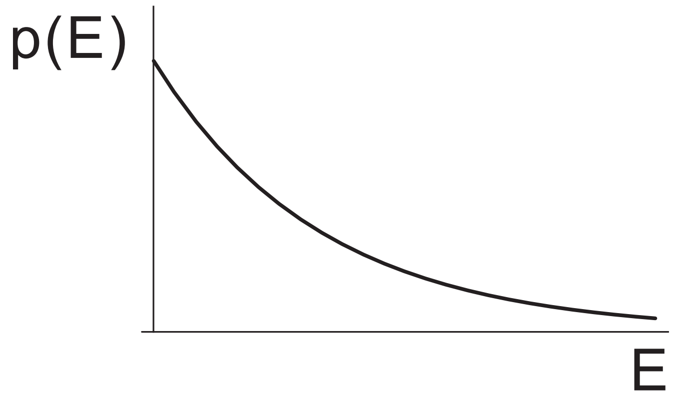
Canonical Ensemble



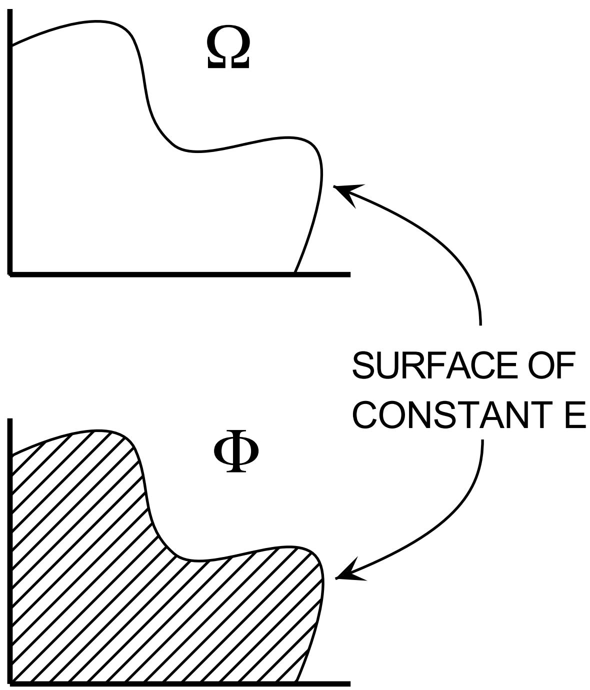
$$p(E) \propto e^{-E/kT} \quad \text{NOT!}$$

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

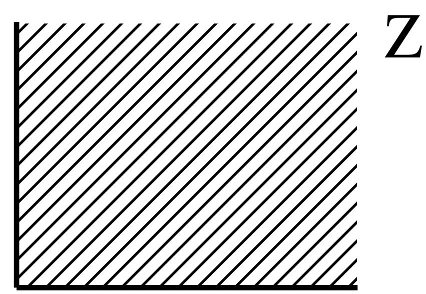
ADVANTAGES OF CANONICAL OVER MICROCANONICAL ENSEMBLE

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

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

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

$$p_1(\vec{p}, \vec{r}) = e^{-(p_x^2+p_y^2+p_z^2)/2mkT}/(Z_1 h^3)$$

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

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

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

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

Where $\lambda(T)$ (or $\Lambda(T)$) $\equiv h/\sqrt{2\pi mkT}$, the thermal de Broglie wavelength.

$$Z(T,V,N) = \frac{1}{N!}\left(\frac{V}{\lambda(T)^3}\right)^N$$

$$F = -kT \ln Z$$

$$= -kT\left[-N\ln N + N + N\ln\left(\frac{V}{\lambda(T)^3}\right)\right]$$

$$= -kTN\ln\underbrace{\left\{\frac{V}{N\lambda(T)^3}\right\}}_{\propto T^{-3/2}} -kTN$$

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

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N} = kN \ln\{\} - kTN \left(-\frac{3}{2}\ \frac{1}{\{\}}\ \frac{\{\}}{T}\right) + kN$$

$$= \underline{kN \ln\left\{\frac{V}{N\lambda(T)^3}\right\} + (5/2)Nk}$$

$$E = F + TS = \underline{(3/2)\ NkT}$$

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

$$\Delta S = 0 \Rightarrow \left\{ \frac{V}{N\lambda(T)^3} \right\} \text{ is constant } \Rightarrow \frac{V}{T^{3/2}} \text{ is constant}$$

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

Example Classical Harmonic Oscillator

$$\mathcal{H}_1(p,x) = \frac{p^2}{2m} + \frac{1}{2}Kx^2$$

$$p(p,x) = \frac{1}{\sqrt{2\pi mkT}}\,\mathrm{exp}[-\frac{p^2}{2mkT}]$$

$$\times\frac{1}{\sqrt{2\pi(kT/K)}}\,\mathrm{exp}[-\frac{x^2}{2(kT/K)}]$$

$$Z_1 = \frac{2\pi}{h}\sqrt{\frac{m}{K}}\,kT$$

Now assume there are N similar stationary oscillators so that we can extract thermodynamic information.

$$Z = Z_1^N \quad F = -kT \ln Z = -kTN \ln \left\{ \frac{2\pi}{h}\sqrt{\frac{m}{K}}kT \right\}$$

$$S = -\left(\frac{\partial F}{\partial T}\right)_N = kN \ln\{\} + kTN \frac{1}{\{\}} \frac{\{\}}{T}$$

$$= kN \ln \left\{ \frac{2\pi}{h}\sqrt{\frac{m}{K}}kT \right\} + Nk$$

This shows that an adiabatic path for a collection of classical harmonic oscillators is one of constant temperature.

$$E = F + TS = NkT$$

This shows that the heat capacity is a constant $C = Nk$ independent of temperature. This would be true even if the oscillators had a variety of different frequencies.

Canonical Ensemble

CLASSICAL

QUANTUM

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

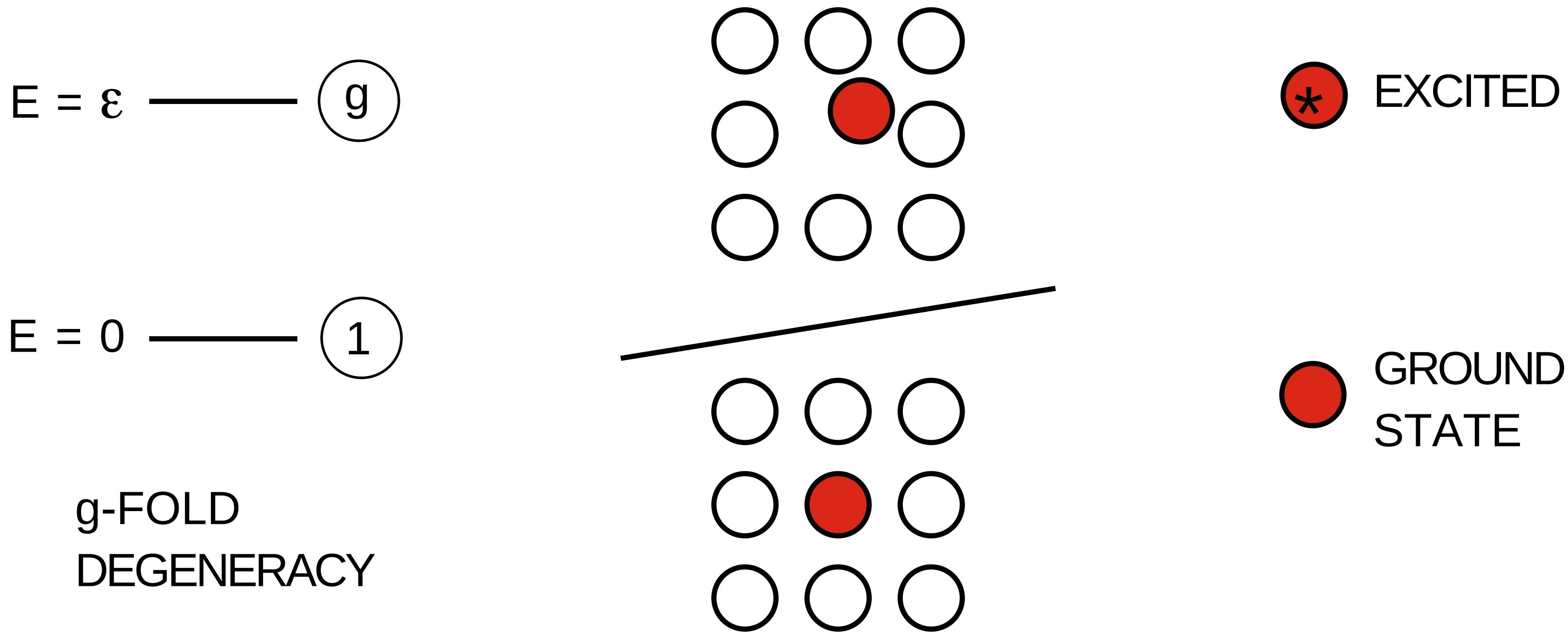
$$p(\text{ state}) = e^{-E_{\text{state}}/kT}/Z$$

$$Z = \int e^{-\mathcal{H}/kT}\{dp, dq\}/h^{\alpha}$$

$$Z = \sum_{\text{states}} e^{-E_{\text{state}}/kT}$$

where α depends on the dimensionality of the phase space.

EXAMPLE 2 LEVEL SYSTEM: STATES OF AN IMPURITY IN A SOLID



LOCATION

INTERNAL

ENERGY LEVELS

PHYSICAL DIFFERENCE

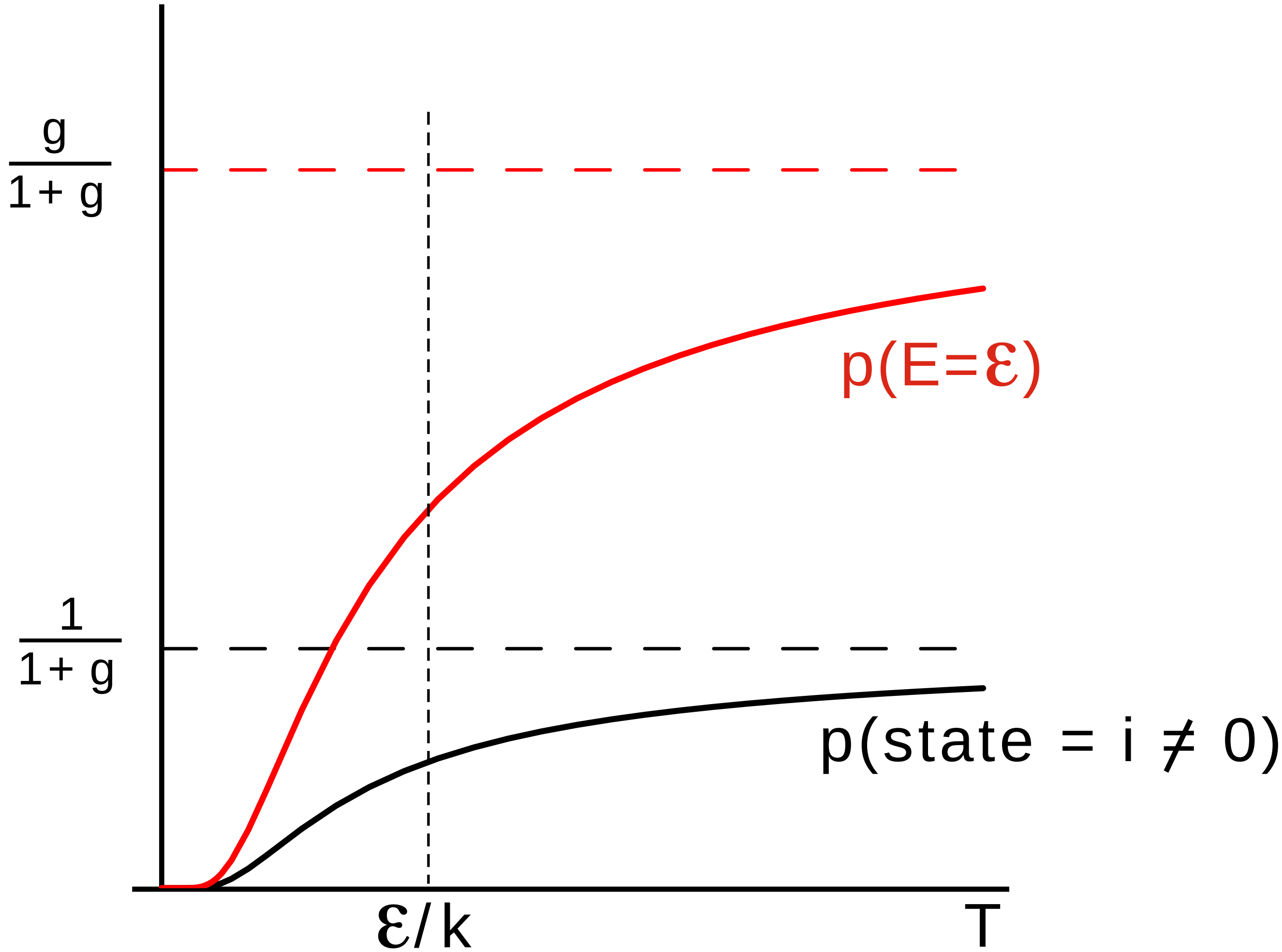
STATES: $\underbrace{|0>}_{E=0}, \quad \underbrace{|1>, \quad \cdots \quad |g>}_{E=\epsilon}$

$$Z_1 = \sum_{\text{states}} e^{-E_{\text{state}}/kT} = 1 \times e^0 + g \times e^{-\epsilon/kT} = 1 + ge^{-\epsilon/kT}$$

$$p(\text{state}) = e^{-E_{\text{state}}/kT} / Z_1$$

$$= \frac{1}{1 + ge^{-\epsilon/kT}} \qquad \text{for } |0>$$

$$= \frac{e^{-\epsilon/kT}}{1 + ge^{-\epsilon/kT}} \qquad \text{for } |i> \quad i = 1, \cdots g$$



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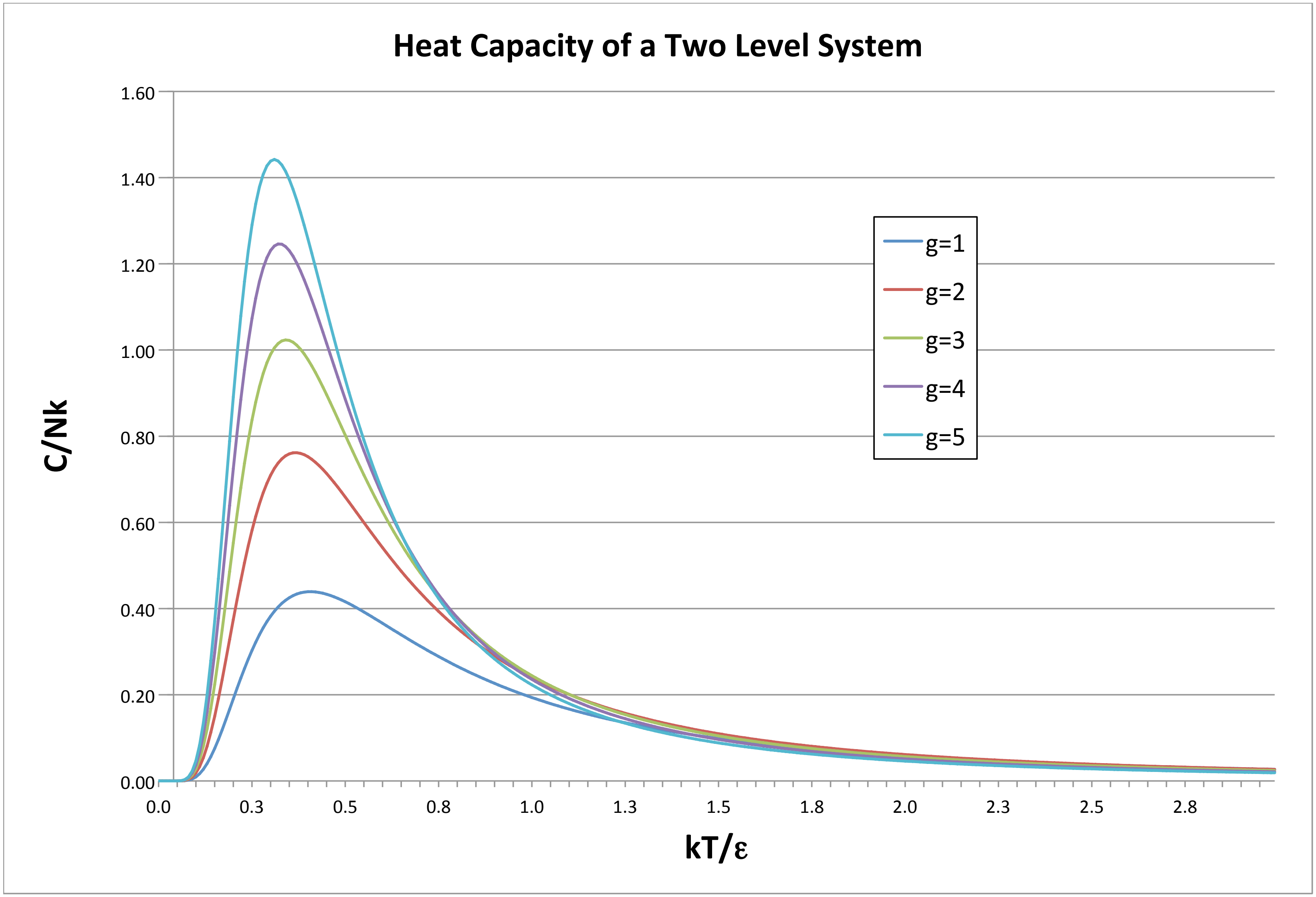
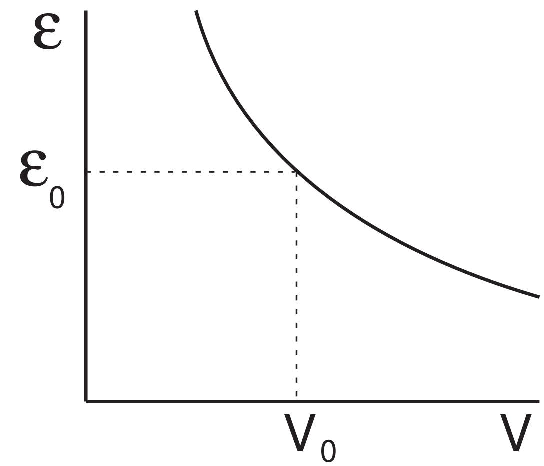

Heat Capacity of a Two Level System
C/Nk
kT/ε
1.60
1.40
1.20
1.00
0.80
0.60
0.40
0.20
0.00
0.0
0.3
0.5
0.8
1.0
1.3
1.5
1.8
2.0
2.3
2.5
2.8
g=1
g=2
g=3
g=4
g=5

Assume

- N impurities $(N \gg 1)$
- $\epsilon = \epsilon_0 (V/V_0)^{-\gamma}$



$$Z = Z_1^N \qquad F(T,V,N) = -kT \ln Z = -NkT \ln Z_1$$

$$S = -\left(\frac{\partial F}{\partial T}\right)_V = Nk \ln Z_1 + NkT \left(\frac{g(\frac{\epsilon}{kT^2}) e^{-\epsilon/kT}}{1 + g e^{-\epsilon/kT}} \right)$$

$$S = Nk\ln(1 + ge^{-\epsilon/kT}) + gNk\left(\frac{\epsilon}{kT}\right)\frac{e^{-\epsilon/kT}}{1 + ge^{-\epsilon/kT}}$$

$$U = F + TS = N\frac{g\,\epsilon\,e^{-\epsilon/kT}}{1 + ge^{-\epsilon/kT}} = N\epsilon\,p(E = \epsilon)$$

$$P = -\left(\frac{\partial F}{\partial V}\right)_{T,N} = -\left(\frac{\partial F}{\partial \epsilon}\right)_T \underbrace{\left(\frac{\partial \epsilon}{\partial V}\right)_T}_{\frac{-\gamma\epsilon}{V}}$$

$$= NkT\,\frac{-(\frac{g}{kT})\,e^{-\epsilon/kT}}{1 + ge^{-\epsilon/kT}}\left(-\frac{\gamma\epsilon}{V}\right) = \underline{\frac{\gamma U}{V}}$$

ALTERNATIVE WAY OF FINDING U

Usually (but not always) $U = < \mathcal{H} >$.

If so, $U = \int \mathcal{H}(\{p, q\})\, p(\{p, q\})\, \{dp, dq\}$

But $Z = c \int e^{-\mathcal{H}(\{p,q\})\beta}\, \{dp, dq\} \qquad \beta \equiv 1/kT$

$$\left(\frac{\partial Z}{\partial \beta}\right)_{N,V} = c\int -\mathcal{H}(\{p,q\})e^{-\mathcal{H}(\{p,q\})\beta}\,\{dp,dq\}$$

$$-\frac{1}{Z}\left(\frac{\partial Z}{\partial \beta}\right)_{N,V} = \int \mathcal{H}(\{p,q\})\,\underbrace{\frac{e^{-\mathcal{H}(\{p,q\})\beta}}{\int e^{-\mathcal{H}(\{p',q'\})\beta}\,\{dp',dq'\}}}_{p(\{p,q\})}\,\{dp,dq\}$$

$$-\frac{1}{Z}\left(\frac{\partial Z}{\partial \beta}\right)_{N,V} = U$$

Example Monatomic Gas

$$Z = \frac{1}{N!} V^N \left(\frac{2\pi mkT}{h^2}\right)^{3N/2} = \alpha\, \beta^{-3N/2}$$

$$U = -\frac{1}{\alpha\, \beta^{-3N/2}} \left(-\frac{3N}{2}\frac{1}{\beta}\right) \alpha\, \beta^{-3N/2} = \underline{\frac{3}{2} NkT}$$

Example 2 Level System

$$Z = \left(1 + ge^{-\epsilon\,\beta}\right)^N$$

$$U = -\left(1 + ge^{-\epsilon\,\beta}\right)^{-N} N \left(1 + ge^{-\epsilon\,\beta}\right)^{N-1} \left(-\epsilon g e^{-\epsilon\,\beta}\right)$$

$$= \frac{gN\epsilon\, e^{-\epsilon/kT}}{1 + ge^{-\epsilon/kT}}$$

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Spring 2013