Homework Phy 4523.

Chapter 1.

1. V.d W eq'n $\left(P + \frac{a}{V^2}\right)(V-b) = \theta R$

seek form $P = G(\theta, V)$

$$P + \frac{a}{V^2} = \frac{\theta R}{V-b} \quad \therefore \quad \boxed{P = -\frac{a}{V^2} + \frac{\theta R}{V-b}}$$

2. $Q = dU + PdV$ $U(T,V) =$ fn of state

$$\therefore dQ = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV + PdV$$

$$= \left(\frac{\partial U}{\partial T}\right)_V dT + \left[P + \left(\frac{\partial U}{\partial V}\right)_T\right] dV$$

3(a) $\frac{\partial}{\partial z}(10y + 6z) = 6 = \frac{\partial}{\partial y}(6y)$ $\therefore$ exact.

(b), (c) inexact

4 (a) $\frac{d}{dz}\left(y^\alpha z^\beta \cdot 12z^2\right) = 12(2+\beta)\, y^\alpha z^{(1+\beta)}$

$\frac{d}{dy}\left(y^\alpha z^\beta \cdot 18yz\right) = 18 z^{1+\beta}(1+\alpha)\, y^\alpha$

$\rightarrow$ exact differential if $\beta = \frac{1}{2}(3\alpha - 1)$

4(b). $\frac{d}{dz}\left(y^{\alpha} z^{\beta} 2 e^{-z}\right) = 2y^{\alpha}\left[\beta z^{\beta-1} e^{-z} + z^{\beta}(-1) e^{-z}\right]$

$\frac{d}{dy}\left[y^{\alpha} z^{\beta}(-y e^{-z})\right] = -z^{\beta} e^{-z}\left[(1+\alpha) y^{\alpha}\right]$

Need

$2\left[\beta z^{\beta-1} + z^{\beta}(-1)\right] = (-) z^{\beta}(1+\alpha)$

$2\left[\beta z^{-1} - 1\right] = -(1+\alpha)$ No solution

6. $dQ = dQ)_V + dQ)_P$

$= C_V (dT)_V + C_P (dT)_P$

$PV = nRT \Rightarrow (dT)_V = V dP/nR \quad (dT)_P = P dV/nR$

$\Rightarrow dQ = \left(C_V V dP + C_P P dV\right)/nR$

7. $P = aV^{-\gamma}$

$W = -\int_{V_1}^{V_2} P dV = -\int a V^{-\gamma} dV = (-a) \left.\frac{V^{-\gamma+1}}{1-\gamma}\right|_{V_1}^{V_2}$

$= \frac{a}{\gamma-1} \left(V_2^{(1-\gamma)} - V_1^{(1-\gamma)}\right)$

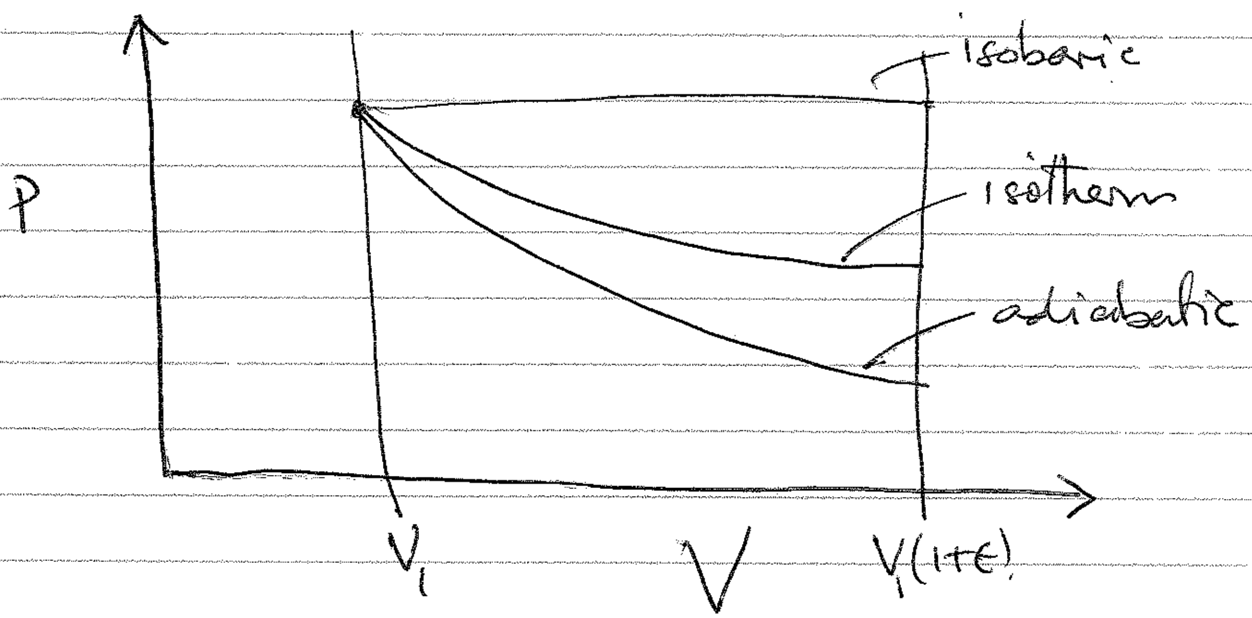
8. $PV^{\gamma-1} = \text{const}$ $\gamma - 1 = 1/3$

$\theta V^{\gamma-1} = \text{const.}$

$\theta R = \text{const.}$ $\therefore$ $300 R_1 = 1373 R_2$

$\therefore$ $R_2 = \frac{1500}{1373}$ nm $= 1.09$ nm

10.



$W = \int P dV =$ max. for isobaric, least for adiabatic

a) Isobaric $\int P dV = \epsilon P V_1 = \frac{\epsilon}{nRT_1}$

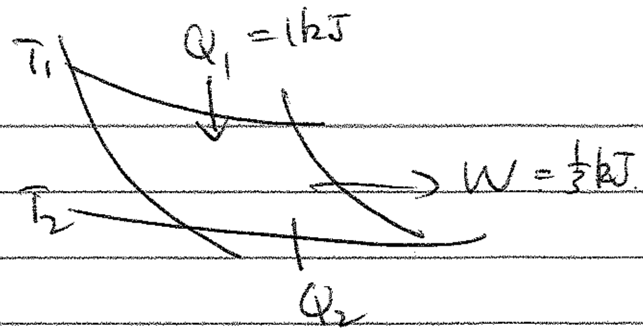
b) Isotherm $\int P dV = nRT \int \frac{dV}{V} = nRT \ln \frac{V_2}{V_1} = nRT\left(\epsilon - \frac{\epsilon^2}{2}\right)$

(c) Adiabatic $\int P dV = nRT \int \frac{dV}{V^{\gamma-1}} = \frac{nRT}{2-\gamma}\left[(1+\epsilon)^{2-\gamma} - 1\right]$

$= nRT\epsilon\left[1 + \frac{1-\gamma}{2}\epsilon^2\right] = \epsilon nRT\left[1 - \frac{3}{4}\epsilon\right].$

Homework Phy 4523

Chap. 2

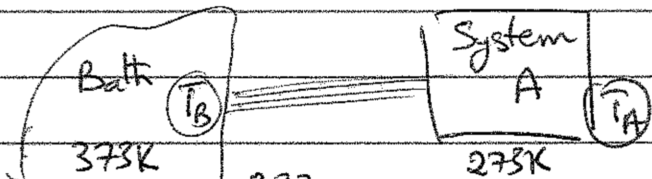


5. $\frac{Q_2}{T_2} = \frac{Q_1}{T_1}$

$\therefore Q_2 = Q_1 \frac{T_2}{T_1} = \frac{2}{3} kJ$

$\therefore W = 1/3\ kJ.$

8(a)



$x = T_B / T_A$

$\Delta S_{System} = \int_{273}^{373} \frac{dQ}{T} = c \ln \frac{373}{273} = 0.312C$

$\Delta S_{Bath} = \frac{-100C}{373} = -0.268C$

$\Delta S_{univ} = 0.044C$

(b) $\Delta S_{system} = \int_{273}^{323} \frac{cdT}{T} + \int_{323}^{373} \frac{cdT}{T} = C\left[\ln \frac{323}{273} + \ln \frac{373}{323}\right] = C \ln \frac{373}{273}$

= Same as (a)

$\Delta S^1_{Bath} + \Delta S^2_{Bath} = -50C\left[\frac{1}{323} + \frac{1}{373}\right] = -0.155C$

$\Delta S_{Univ} = 0.023C$

(c) ΔS_{system} same

$\Delta S^1_{Bath} + \Delta S^2_{Bath} + \Delta S^3_{Bath} + \Delta S^4_{Bath} = -25C\left[\frac{1}{298} + \frac{1}{323} + \frac{1}{348} + \frac{1}{37\ldots}\right]$

$= -0.300$

$\Delta S_{Univ.} = +0.012C.$

8 (d) General Case

Bath T_B — Approach with large no. of steps each ΔT

No. of steps. $N = \frac{T_B - T_A}{\Delta T}$

$$\Delta S_{System} = \int_{T_A}^{T_A+\Delta T} \frac{dQ}{T} + \int_{T_A+\Delta T}^{T_A+2\Delta T} dQ/T + \cdots \int_{T_B-\Delta T}^{T_B} dQ/T = C \ln \frac{T_B}{T_A}$$

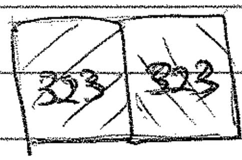
$$\Delta S_{Bath} = -\frac{NC\Delta T}{T_B} = -C(x-1) \rightarrow -C\delta x \quad \text{for } x \rightarrow 1+\delta x.$$

$$\Delta S_{System} = C \ln x \rightarrow +C\delta x \quad \text{for } x \rightarrow 1+\delta x$$

$$\Delta S_{Univ.} \rightarrow 0.$$

9. 

$C = \text{constant}$



$$\Delta S = \underbrace{\int_{373}^{323} \frac{C\,dT}{T}}_{\text{Blk A}} + \underbrace{\int_{273}^{323} \frac{C\,dT}{T}}_{\text{Blk B}} = C\ln\frac{323}{273} + C\ln\frac{323}{373}$$

$$= C\ln\left(\frac{323^2}{273\times 373}\right) = 0.024\,C.$$

10.
$$\Delta S = \int \frac{C\,dT}{T} = \int \frac{aT+bT^3}{T}\,dT = \int (a+bT^2)\,dT$$

$$= aT + \tfrac{1}{3}bT^3.$$

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16 $Q = 50W.$ $Q = C\Delta T$ $\Delta T = \frac{50}{.24} = 208$

$$\Delta S = \int \frac{dQ}{T} = C\ln\frac{T_F}{T_I} = 0.24\ln\frac{508}{300} = 0.127\ \text{J/K}.$$

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18 Maxwell relation #1

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \qquad S = S(V,T)$$

$$dS = \left(\frac{\partial S}{\partial V}\right)_T dV + \left(\frac{\partial S}{\partial T}\right)_V dT = \left(\frac{\partial P}{\partial T}\right)_V dV + \frac{C_V}{T}dT$$

or $$T\,dS = C_V\,dT + T\left(\frac{\partial P}{\partial T}\right)_V dV$$

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18. Maxwell relation #2

$$\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T$$

$S(P,T)$

$$dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP$$

$$= \frac{C_P}{T} dT - \left(\frac{\partial V}{\partial T}\right)_P dP$$

$$TdS = C_P dT - \left(\frac{\partial V}{\partial T}\right)_P dP$$

$$dU = TdS - PdV$$

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - P$$

$$= T\left(\frac{\partial P}{\partial T}\right)_V - P$$

using Maxwell relation #1.

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20. $$dU = TdS + \gamma dA$$

$F = U - TS$ $$dF = \gamma dA - SdT.$$

$F(S,A)$ function of state

Consider $$dF = \left(\frac{\partial F}{\partial S}\right)_A dS + \left(\frac{\partial F}{\partial A}\right)_S dA.$$

$$\frac{\partial}{\partial A}\left(\frac{\partial F}{\partial T}\right)_A = -\frac{\partial S}{\partial A} = \frac{\partial}{\partial T}\left(\frac{\partial F}{\partial A}\right)_T = \frac{\partial \gamma}{\partial T}$$

Hence $$\left.\frac{\partial S}{\partial A}\right)_T = -\left.\frac{\partial \gamma}{\partial T}\right)_A \qquad dS = -\left(\frac{\partial \gamma}{\partial T}\right)_A dA$$

$$\therefore\ dU = -T\left(\frac{\partial \gamma}{\partial T}\right)_A + \gamma dA.$$

$$= \left(\gamma - T\frac{\partial \gamma}{\partial T}\right)_A dA$$

$$U = \left[\gamma - T\left(\frac{\partial \gamma}{\partial T}\right)_A\right]A + \text{constant}$$

Chap. 3

10. Each throw is independent.

a) Probability of n up = $\underbrace{p \times p \times p \times \cdots}_{n \text{ times}}$

$= p^n.$

b) Probability of first throw being down

$= (1-p) \times \underbrace{p \times p \times p \times \cdots}_{(n-1) \text{ times}}$

$= (1-p)p^{n-1}$

(c) Probability of second time down on n^{th} throw.

$= \underbrace{p \times p \times \cdots (1-p) \cdots \times p}_{(1-p) \text{ anywhere in these } (n-1) \text{ steps}} \times (1-p)$

$= (n-1)(1-p)^2 p^{n-2}.$

3.11. Each throw is independent, each time probability of a head $p = \frac{1}{2}$.

(a) 8 heads. $P_{tot} = \left(\frac{1}{2}\right)^8$

$^nC_r = \frac{n!}{r!(n-r)!}$

(b) 7 heads. $P_{tot} = \left(\frac{1}{2}\right)^8 \, {}^8C_1$

$= 8/2^8$

Choosing r objects from n

(c) 6 heads. $P_{tot} = \left(\frac{1}{2}\right)^8 \, {}^8C_2$

$^8C_2 = \frac{8!}{6!\,2!}$

$= 28/2^8$

P at least 6 heads $= \frac{1}{2^8}[1+8+28] = \frac{37}{256}.$

3.13. let p_A, p_B, p_C be the probability that A, B or C be first to toss a coin if they proceed in order $A \to B \to C$.

$$p_A = 2p_B = 4p_C$$

But $p_A + p_B + p_C = 1$

or $(4 + 2 + 1)p_C = 1$ $\quad p_C = 1/7,\ p_B = \frac{2}{7},\ p_A = \frac{4}{7}$

17. P_1 all good for 1st choice $= \frac{95}{100}$

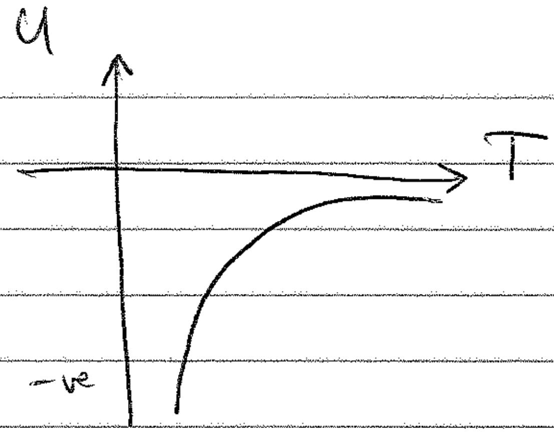
P_2 2nd $= 94/99$ etc.

$$P_{tot} = \frac{95}{100} \times \frac{94}{99} \times \frac{93}{98} \times \frac{92}{97} \times \frac{91}{96} \doteq \underline{0.7696}$$

~~Hmwk~~

~~Chap 4.~~

6. $S = S_0 - cU^2$



$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_V = -2cU$$

$$\text{or} \quad U = -\left(\frac{1}{2c}\right)\frac{1}{T}$$

8. $U = n\epsilon$

$$W = \frac{N!}{n!\,(N-n)!}$$

$$S = k_B \ln W = N\ln N - n\ln n - (N-n)\ln(N-n)$$

$$= N\left\{\ln N - \frac{n}{N}\ln n - \left(1-\frac{n}{N}\right)\ln(N-n)\right\}$$

$$= N\left\{\cancel{\ln N} - \frac{n}{N}\ln\frac{n}{N} + \cancel{\frac{n}{N}\ln N} - \left(1-\frac{n}{N}\right)\ln\left(1-\frac{n}{N}\right)\right.$$

$$\left. + \cancel{\left(1-\frac{n}{N}\right)\ln N}\right\}$$

$$= -N\left\{\frac{n}{N}\ln\frac{n}{N} + \left(1-\frac{n}{N}\right)\ln\left(1-\frac{n}{N}\right)\right\}$$

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_V = \left(\frac{\partial S}{\partial n}\right)_V\left(\frac{\partial n}{\partial U}\right)_V = \frac{1}{\epsilon}\frac{\partial S}{\partial n}$$

8 contd.

$$\frac{1}{k_B}\frac{\partial S}{\partial n} = -N\left\{\frac{1}{N}\ln\frac{n}{N} + 1 - \frac{1}{N}\ln\left(1-\frac{n}{N}\right) - 1\right\}$$

$$= \ln\left[\frac{n}{N}\Big/\left(1-\frac{n}{N}\right)\right]$$

let $x = \frac{n}{N}$

$$\frac{1}{k_B}\frac{\partial S}{\partial n} = \ln\left(\frac{x}{1-x}\right)$$

Hence

$$\frac{1}{T} = -\frac{k_B}{\epsilon}\ln\left(\frac{x}{1-x}\right) \quad \text{or} \quad \frac{x}{1-x} = e^{-\epsilon/k_BT}$$

$$\frac{1-x}{x} = e^{+\epsilon/k_BT} \quad \text{or} \quad \frac{1}{x} = 1 + e^{\epsilon/k_BT}$$

Hence $x = \dfrac{1}{1+e^{\epsilon/k_BT}}$

or $U = N\epsilon\Big/\left[1+e^{\epsilon/k_BT}\right].$

11.

$$S = Nk_B\left\{\ln A + \ln\left(\frac{mU}{2\pi\hbar^2 N}\right) + 2\right\}.$$

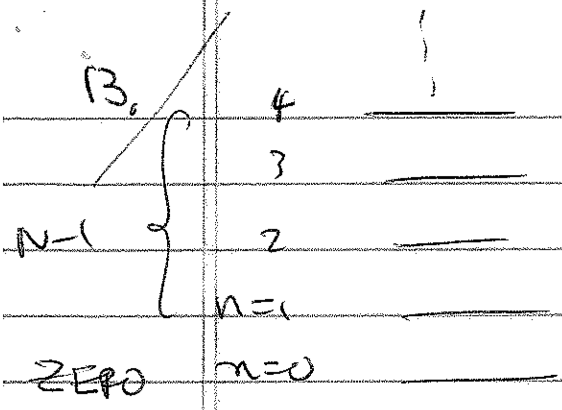
$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_V = Nk_B\left(\frac{m}{mU}\right)$$

$$U = Nk_BT$$

$$\mu = -T\left(\frac{\partial S}{\partial N}\right)_V = -Nk_BT\left\{\left(-\frac{1}{N}\right) - \frac{1}{N}\right.$$

$$\left. + k_B\left\{\ln\frac{A}{N} + \ln\left(\frac{mU}{2\pi\hbar^2 N}\right) + \cancel{2}\right\}\right.$$

$$\mu = k_B\left\{\ln\frac{A}{N} + \ln\frac{mU}{2\pi\hbar^2 N}\right\}$$



$$n = \frac{U}{\hbar\omega} = \text{\# quanta in level}$$

$$W = \frac{[(N-1)+n]!}{(N-1)!\, n!}$$

$$S = k_B \ln W$$

$$= k_B \left\{ (N-1+n)\ln(N-1+n) - (N-1)\ln(N-1) - n\ln n \right\}$$

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_V = \left(\frac{\partial S}{\partial n}\right)_V \left(\frac{\partial n}{\partial U}\right)_V = \frac{1}{\hbar\omega}\frac{\partial S}{\partial n}$$

$$\frac{1}{T} = \frac{k_B}{\hbar\omega}\left\{ \ln(N-1+n) - \ln n \right\}$$

$$\frac{\hbar\omega}{k_B T} = \ln\left(\frac{N-1+n}{n}\right) = +\ln\left\{\frac{N-1}{n} + 1\right\}$$

$$\frac{N-1}{n} + \cancel{1} = e^{\hbar\omega/k_B T} - 1$$

$$n = (N-1)\left[\frac{1}{e^{\hbar\omega/k_B T} - 1}\right]$$

or $$U = (N-1)\hbar\omega\left[\frac{1}{e^{\hbar\omega/k_B T} - 1}\right]$$

Chap 5.

7.

$$Z = e^{aT^3V}$$

$$F = -k_B T \ln Z = -a k_B T^4 V$$

$$P = -\left(\frac{\partial F}{\partial V}\right)_T = +a k_B T^4$$

$$-S = \frac{\partial F}{\partial T} = -4a k_B T^3 V$$

$$S = 4a k_B T^3 V$$

$$U = F + TS = 3a k_B T^4 V$$

12.

$$G = U_A + P_R V_A - T_R S_A$$

$$= F_A + P_R V_A + (T_A - T_R) S_A$$

$$\left(\frac{\partial G}{\partial V_A}\right)_T = 0 = \left(\frac{\partial F}{\partial V_A}\right)_T + P_R \sim$$

$$= -P_A + P_R \sim P_R = P_A$$

$$\left(\frac{\partial G}{\partial S_A}\right)_{V,P} = \left(\frac{\partial U_A}{\partial S_A}\right)_V - T_R = T_A - T_R = 0$$

$$\sim \boxed{T_A = T_R}$$

16 One particle

$$Z_1 = \sum_i e^{-\beta\epsilon_i}$$

$$= 1 + 3e^{-\beta\epsilon} + 3e^{-2\beta\epsilon} + e^{-3\beta\epsilon}$$

$$= \left(1 + e^{-\beta\epsilon}\right)^3$$

N particles

$$Z_N = \left(Z_1\right)^N = \left(1 + e^{-3\beta\epsilon}\right)^{3N}$$

$$F = -k_B T \ln Z_N = -3Nk_BT \ln\left(1 + e^{-\epsilon/k_BT}\right)$$

17.

$$Z = \left(\frac{V-Nb}{N}\right)^N \left(\frac{mk_BT}{2\pi\hbar^2}\right)^{\frac{3N}{2}} e^{N^2a^2/(Vk_BT)}$$

$$-F = k_BT\left\{ N\ln\left(\frac{V-Nb}{N}\right) + \frac{3N}{2}\left[\ln T + \ln\frac{mk_B}{2\pi\hbar^2}\right] + \frac{N^2a^2}{Vk_BT}\right\}$$

$$P = -\left(\frac{\partial F}{\partial V}\right)_T$$

$$= k_BTN\left(\frac{1}{V-Nb}\right) - \frac{N^2a^2}{V^2}$$

$$\text{or} \quad \boxed{\left(P + \frac{N^2a^2}{V^2}\right)\left(V-Nb\right) = Nk_BT}$$

17 contd. $U = k_B T^2 \left(\frac{\partial \ln Z}{\partial T}\right)$

$$= k_B T^2 \left\{ \frac{3N}{2} \cdot \frac{1}{T} - \frac{N^2 a^2}{V k_B T^2} \right\}$$

$$U = \frac{3}{2} N k_B T - \frac{N^2 a^2}{V}$$

21 $$U = -\frac{\partial}{\partial \beta} \ln Z$$

$$Z = \sum_i e^{-\beta \epsilon_i}$$

$$\frac{\partial}{\partial \beta} \ln Z = \frac{-\sum e^{-\beta \epsilon_i} \cdot \epsilon_i}{Z} = -\sum_i p_i \epsilon_i = \underline{-U}$$

<u>Harmonic Oscillator</u>

$$E_n = \left(n + \tfrac{1}{2}\right) \hbar\omega$$

$$Z = \sum_n e^{-\beta E_n}$$

$$= e^{-\beta \hbar\omega/2} \sum_{n=0}^{\infty} e^{-\beta n \hbar\omega}$$

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

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

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

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