Solutions to Midterm Exam

(1)

5000	5000

W_{max}
most probable

4990	5010

$W_{max} + \delta W$

particles can be in BOX 1 or BOX 2
a priori probability $= \frac{1}{2}$

$$\ln\left[\frac{W_{max}+\delta W}{W_{max}}\right] = ?$$

no. of configurations

$$W_{n_1 n_2} = \frac{N!}{n_1!\, n_2!} \cdot \left(\frac{1}{2}\right)^{n_1} \cdot \left(\frac{1}{2}\right)^{n_2}$$

use Stirling's approximation

$$\ln W = N\ln N - N\ln 2 \quad - n_1 \ln n_1 - n_2 \ln n_2$$

Need Fluctuations from distribn of most probable state:

$$\ln(W + \delta W) = N\ln N - N\ln 2 - (n_1 + \delta n_1)\ln(n_1 + \delta n_1)$$
$$- (n_2 + \delta n_2)\ln(n_2 + \delta n_2)$$

subtracting:

$$\ln\left[\frac{W + \delta W}{W}\right] = -\delta n_1 \ln(n_1 + \delta n_1) - \delta n_2 \ln(n_2 + \delta n_2)$$
$$- n_1 \ln \frac{n_1 + \delta n_1}{n_1} - n_2 \ln \frac{n_2 + \delta n_2}{n_2}$$

To find W_{max}

$$\delta \ln W = 0 = \ln \delta n_1 + \ln \delta n_2 - \ln(n_1 \delta n_1)$$
$$- \ln(n_2 \delta n_2)$$

$$\delta n_1 + \delta n_2 = 0$$

$$\rightarrow \ln(n_1 \delta n_1) + \ln(n_2 \delta n_2) = 0$$

Substitute this into eqn for $\ln\left[\frac{W+\delta W}{W}\right]$:

$$\ln\left[\frac{W_{max}+\delta W}{W_{max}}\right] = -n_1 \ln\left(1+\frac{\delta n_1}{n_1}\right) - n_2 \ln\left(1+\frac{\delta n_2}{n_2}\right) - \delta n_1 \ln\left(1+\frac{\delta n_1}{n_1}\right) - \delta n_2 \ln\left(1+\frac{\delta n_2}{n_2}\right)$$

Introduce $\ln(1+x) \approx x - \frac{1}{2}x^2 + \frac{1}{3}x^3 - \ldots$ into these to get

$$\ln\left[\frac{W_{max}+\delta W}{W_{max}}\right] = -\overbrace{(\delta n_1 + \delta n_2)}^{zero} + \frac{1}{2}\left[\frac{(\delta n_1)^2}{n_1} + \frac{(\delta n_2)^2}{n_2}\right] - \left[\frac{(\delta n_1)^2}{n_1} + \frac{(\delta n_2)^2}{n_2}\right]$$

$$= -\frac{1}{2}\left[\frac{(\delta n_1)^2}{n_1} + \frac{(\delta n_2)^2}{n_2}\right]$$

Here $\delta n_1 = -10$ $\quad \delta n_2 = +10$
$n_1 = 5000$ $\quad n_2 = 5000$

$$\ln\left[\frac{W_{max}+\delta W}{W_{max}}\right] = -\frac{1}{2}\left[\frac{(10)^2}{5000} + \frac{(10)^2}{5000}\right] = -0.02$$

$$\frac{W_{max}+\delta W}{W_{max}} = e^{-0.02} = 0.9802$$

(2) a) $E_j = \sum_{i=1}^{N} n_i \epsilon$

b) $Q(T,N) = \sum_j \exp^{-E_j/kT} = \sum_{n_1, n_2, \ldots n_N = 0 \text{ or } 1} \exp\left[-\frac{1}{kT}\sum_{i=1}^{N} n_i \epsilon\right]$

The exponential factors into an uncoupled product

$$Q(T,N) = \prod_{i=1}^{N} \left\{ \sum_{n_i = 0 \text{ or } 1} \exp^{-n_i \epsilon/kT} \right\} = \prod_{i=1}^{N} \left(1 + \exp^{-\epsilon/kT}\right)$$

Alternately, use for independent particles

$$Q = q_1 \cdot q_2 \cdot q_3 \cdot \cdots q_N = \prod_{i=1}^{N} q = q^N$$

where $q = \sum_{\text{states}} e^{-\epsilon_i/kT} = 1 + e^{-\epsilon/kT}$

$$Q(T,N) = \left(1 + \exp^{-\epsilon/kT}\right)^N$$

$$A = -kT \ln Q = -NkT \ln\left(1 + \exp^{-\epsilon/kT}\right)$$

$$E = kT^2 \left(\frac{\partial \ln Q}{\partial T}\right)_V = NkT^2 \frac{\partial}{\partial T} \ln\left(1 + \exp^{-\epsilon/kT}\right)$$

$$= NkT^2 \left(\frac{\epsilon}{kT^2}\right) \frac{\exp^{-\epsilon/kT}}{1 + \exp^{-\epsilon/kT}} = N\epsilon \frac{e^{-\epsilon/kT}}{1 + e^{-\epsilon/kT}} = \frac{N\epsilon}{1 + e^{+\epsilon/kT}}$$

$$S = \frac{E - A}{T} = \frac{1}{T}\left[\frac{N\epsilon}{1 + e^{+\epsilon/kT}}\right] + Nk \ln\left(1 + e^{-\epsilon/kT}\right)$$

(3) a) $A = -kT \ln Q$ is an extensive function

$$\frac{A_1}{A_2} = \frac{\ln Q(N_1, T, V)}{\ln Q(N_2, T, 1)}$$

since system 1 and 2 have the same T, same types of molecule and the same concentration, just different amounts

$$\frac{A_1}{A_2} = \frac{N_1}{N_2}$$

since $N_2 = N_1 N$

$$\therefore \frac{\ln Q(N_1, T, V)}{\ln Q(N_2, T, 1)} = \frac{N_1}{N_2} = \frac{N_1}{(N_1/N)} = V$$

$$\therefore \quad Q(N_1, T, V) = \left[Q(N_2, T, 1)\right]^V$$

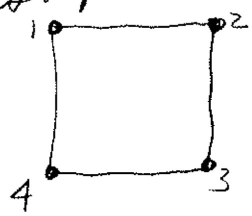
b) The analogous function for the grand canonical ensemble is the function $\bar{P}V$. Since the systems 1 and 2 are at same T, same concentration just different amounts, $\bar{P}_1 = \bar{P}_2$, same μ.
The fundamental relation for the grand ensemble is

$$\bar{P}V = kT \ln \Xi$$

$$\frac{\bar{P}_1 V_1}{\bar{P}_2 \cdot V_2} = \frac{kT \ln \Xi(\mu, T, V_1)}{kT \ln \Xi(\mu, T, V_2)}$$

$$\Xi(\mu, T, V_1) = \left[\Xi(\mu, T, V_2)\right]^{V_1/V_2}$$

(4) adsorption sites



sites distinguishable, atoms are not
energy of adsorption at a site $= -\epsilon$
energy of interaction between atoms on adjacent sites $= \omega$

For a given λ:

$$Z \equiv \sum_N \sum_j \lambda^N e^{-E_{jN}/kT}$$

$N=1$ $\quad E_j = -\epsilon \quad$ 4 such system quantum states

$N=2$ $\quad j$: (12) or (23) or (34) or (41) $\quad E_j = -2\epsilon + \omega \quad$ 4 such system quantum states
(13) or (24) $\quad E_j = -2\epsilon \leftarrow$ 2 such system quantum states

$N=3$ $\quad j$: one is empty $\quad E_j = -3\epsilon + 2\omega \quad$ 4 such system quantum states

$N=4$ $\quad E_j = -4\epsilon + 4\omega \quad$ only 1 system quantum state

$$Z = 4\lambda^1 e^{+\epsilon/kT} + 4\lambda^2 e^{+(2\epsilon-\omega)/kT} + 2\lambda^2 e^{+2\epsilon/kT} + 4\lambda^3 e^{(3\epsilon-2\omega)/kT} + \lambda^4 e^{(4\epsilon-4\omega)/kT}$$

$$\langle N \rangle = \left(\frac{\partial \ln Z}{\partial \ln \lambda}\right)_{T,V} = \frac{\lambda}{Z}\left(\frac{\partial Z}{\partial \lambda}\right)_{T,V}$$

$$= \frac{\lambda}{Z}\left\{4e^{\epsilon/kT} + 8\lambda e^{(2\epsilon-\omega)/kT} + 4\lambda e^{2\epsilon/kT} + 12\lambda^2 e^{(3\epsilon-2\omega)/kT} + 4\lambda^3 e^{(4\epsilon-4\omega)/kT}\right\}$$

$$\langle N \rangle = \frac{4\lambda e^{\epsilon/kT} + 8\lambda^2 e^{(2\epsilon-\omega)/kT} + 4\lambda^2 e^{2\epsilon/kT} + 12\lambda^3 e^{(3\epsilon-2\omega)/kT} + 4\lambda^4 e^{(4\epsilon-4\omega)/kT}}{4\lambda e^{\epsilon/kT} + 4\lambda^2 e^{(2\epsilon-\omega)/kT} + 2\lambda^2 e^{2\epsilon/kT} + 4\lambda^3 e^{(3\epsilon-2\omega)/kT} + \lambda^4 e^{(4\epsilon-4\omega)/kT}}$$

5. No. of ways n_1 molecules can be adsorbed on a surface that has S sites

$$\frac{s!}{(s-n_1)!\, n_1!}$$

No. of ways n_2 molecules can be adsorbed on the n_1 molecules in the first layer to make the second layer $=$

$$\frac{n_1!}{(n_1-n_2)!\, n_2!}$$

Total partition function for multilayer adsorption of N molecules

$$= Q(N,V,T) = \frac{s!}{(s-n_1)!\, n_1!} \cdot \frac{n_1!}{(n_1-n_2)!\, n_2!} \cdot \frac{n_2!}{(n_2-n_3)!\, n_3!} \cdots \times$$

$$\times\, q_1^{n_1} \cdot q_2^{n_2} \cdot q_3^{n_3} \cdots\cdots$$

$$\ln Q = s\ln \frac{s}{s-n_1} + n_1 \ln \frac{s-n_1}{n_1-n_2} + n_2 \ln \frac{n_1-n_2}{n_2-n_3}$$

$$+ n_1 \ln q_1 + n_2 \ln q_2 + \cdots$$

$$\Xi(V,T,\mu) = \sum_{N=0}^{\infty} e^{\frac{\mu N}{kT}} \cdot Q(N,V,T)$$