Zhi Chen HW#3 PHY 540

11) Consider degenerate ground state, as $T \Rightarrow 0$,

Find zero-temperature entropy of a 4-inch diameter, 0.5 mm thick n-type silicon wafer, doped with phosphorus atoms at a concentration of 10^{15} atoms per cm^3.

$$S = k_B \ln \Omega$$

$$V = \pi (2\,\text{inch} \;\; 2.54\,\text{cm/inch})^2 \; 0.05\,\text{cm}$$
$$\doteq 4.054\ \text{cm}^3$$

$n = 10^{15}$ phosphorus atom / cm^3

For $T \to 0$, $S = k_B \ln g_0$ ← degeneracy of states in ground level.

Combination: from n choose k objects:

$$\binom{n}{k} = \frac{n!}{k!(n-k)!}$$

$$\rho_{Si} = 2.33\ g/cm^3$$

then $M_{Si} = (2.33\ g/cm^3)(4.054\ cm^3)$

$$\doteq 9.446\ g \text{ of } Si$$

Each Si atom weigh $= 28.0855 \times 1.66 \times 10^{-24} g$

$\stackrel{!}{=} 4.6622 \times 10^{-23} g$

# of Si atom $= \dfrac{9.446 g}{4.6622 \times 10^{-23} g} = 2.026 \times 10^{23}$ # of Si

# of P atoms $= \left(10^{15} \frac{P\,atoms}{cm^3}\right)(4.054\ cm^3)$

$\stackrel{!}{=} 4.054 \times 10^{15}$ # of P atoms

Si: ${}^3P_0$: $2S+1=3$ $L=1$ $J=0$

or $S=1$

then $g_{0,Si} = (2S+1)(2L+1) = 9$

P. ${}^4S_{3/2}$: $2S+1=4$ $L=0$ $J=3/2$

$\hookrightarrow S = 3/2$

$$g_{0,P} = \left(2\left(\tfrac{3}{2}\right)+1\right)(2(0)+1) = 4$$

# of microstates: Combination at which P can be inserted into Si Wafer.

$$\Omega = \binom{n}{k} = \frac{n!}{k!\,(n-k)!}$$

For $n = 2.026 \times 10^{23}$ Si $k = 4.054 \times 10^{15}$ P

$$S = k_B \ln\left(\frac{n!}{k!\,(n-k)!}\right)$$

$$\overset{!}{=} k_B\left[\ln n! - \ln k! - \ln(n-k)!\right]$$

with Stirling: $\ln N! = N\ln N - N$

$$S = k_B\left[n\ln n - \cancel{n} - k\ln k + \cancel{k} - (n-k)\ln(n-k) + \cancel{n-k}\right]$$

$$\overset{!}{=} k_B\left[n\ln n - k\ln k - (n-k)\ln(n-k)\right]$$

$$\overset{!}{=} k_B\left[2.026\times10^{23}\ln(2.026\times10^{23}) - 4.054\times10^{15}\ln(4.054\times10^{15}) - (2.026\times10^{23} - 4.054\times10^{15})\ln(2.026\times10^{23} - 4.054\times10^{15})\right]$$

$$S = k_B\ 7.59\times10^{16}$$

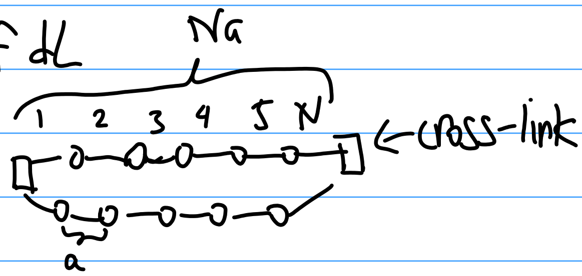
$$\overset{!}{=} (1.38\times10^{-23}\ J/K)\ 7.59\times10^{16}$$

$$\boxed{S \overset{!}{=} 1.047\times10^{-6}\ J/K}$$

12) First law of thermodynamics for rubber:

$$dE = TdS + f\,dL$$

properties of rubber band.



i) can be stretched to $5L_0$, L_0 is the relaxed length

2) With $L \uparrow$, $T \uparrow$

3) With $T \uparrow$, $f \uparrow$

4) $E \propto T$ but independent of L

Imagine 1-D chain, link can point forward or backward with $p = 1/2$

a) With $L_1 \cong 5L_0$, estimate average # of links N between successive ~~sulfer~~ - cross links.

$L_1 = 5L_0 = Na$ find N # of links to reach

$L_0 = \frac{Na}{5}$ is the unstretched length of rubber band, which is the expected overall length traveled by random walk.

let $L_0^2 = \langle d^2 \rangle$ = Root-mean squared distance

$$\stackrel{!}{=} \sum_{i,n} P_i d^2$$

$$\stackrel{!}{=} \sum_{n=1}^{N} \frac{1}{2} a_n^2 + \frac{1}{2} (-a_n)^2$$

$$L_0^2 \stackrel{!}{=} N a^2$$

So $L_0 = \sqrt{N}\, a$

Then we know $L_0 = \frac{Na}{5}$

then $\frac{N\cancel{a}}{5} = \sqrt{N}\, \cancel{a}$

$$N^2 - 25N = 0$$

$$(N-25)N = 0$$

$\boxed{N = 25}$ or 0 ← discard 0 solution.

b) Unstretched $\Rightarrow$ Many state of same L_0
Stretched $\Rightarrow$ 1 state. (decrease in entropy), $\Delta S < 0$

Estimate ΔS for a single chain from relaxed length to maximum length.

$$S_{stretched} = k_B \ln(\Omega_{stretched} = 1) \stackrel{!}{=} 0$$

$$\Delta S = \cancel{S_{stretched}}^{=0} - S_{relax} \stackrel{!}{=} -S_{relax} \stackrel{!}{=} -k_B \ln \Omega_{relax}$$

Know $N = 25$ from part a)

$$\text{so } L_0 = \frac{L_1}{5} = \frac{Na}{5} = \frac{25a}{5} = 5a$$

we note that there are 5 net positive links

i.e. $p - n = 5$ where $p + n = N$

p: # of links in positive direction

n: # of links in negative direction.

$$\text{Then } \Omega_{relax} = \binom{N}{p} = \frac{N!}{p!(N-p)!} = \frac{N!}{p!\,n!}$$

Ω_{relax}: # of ways we can place positive links (or negative links)

Since $N = 25$, $p + n = N$

and $p - n = 5$

$\hookrightarrow p - (N - p) = 5$

$\hookrightarrow 2p - N = 5$

$$p = \frac{5 + 25}{2} = 15$$

$$\Omega_{Relax} = \frac{25!}{15!(25-15)!} = 3268760$$

$$\Delta S = -k_B \ln(3268760)$$

$$= -1.38 \times 10^{-23} \text{ J/K } (15)$$

$$\boxed{\Delta S = -2.07 \times 10^{-22} \text{ J/K}}$$

$dQ = TdS = 0$

c) Stretch rubber band adiabatically (stretch suddenly), then entropy is balanced by internal vibrational motion.

Estimate the increase in temperature of rubber band when it is adiabatically stretched

assume 13 atoms per monomer
and $N = 25$ So 25 monomers per chain.

Equipartition Theorem: $E = \frac{1}{2} k_B T$ per quadratic term.

For $m=13$ atoms in a single monomer, there are $\sim 3m$ vibrational modes with 2 quadratic terms for each mode.

Then $dE = 25(3)(13)(2)\frac{1}{2} k_B dT$
$= 975 k_B dT$

Since $dS = 0 = \Delta S_{config} + \Delta S_{vib} = 0$

$\Delta S_{vib} = -\Delta S_{config}$

$\Delta S_{vib} = 2.07 \times 10^{-22}$ J/K

$$\int dS = \frac{dE}{T} = 975\, k_B \int_{T_i}^{T_f} \frac{dT}{T}$$

$$\Delta S_{vib} = 975\, k_B \ln\left(\frac{T_f}{T_i}\right)$$

$$T_f = T_i \exp\left\{ \frac{\Delta S_{vib}}{975\, k_B} \right\}$$

Let $T_i \cong 300\,K$
room temp

$$T_f = 300 \exp\left\{ \frac{2.07\times10^{-22}}{(975)\,1.38\times10^{-23}} \right\}$$

$$= 304.65\ K$$

$$\boxed{\Delta T = T_f - T_i = 304.65 - 300 = 4.65\,K}$$

d) $f = -T\left(\frac{\partial S}{\partial L}\right)_T = \frac{k_B T L}{a^2 N}$ Need

we know $S = k_B \ln \Omega$ where $\Omega = \frac{N!}{p!\,(N-p)!}$

we know $L = (p-n)a$

$N = p+n$

so $p = \frac{N}{2} + \frac{L}{2a}$ and $N-p = \frac{N}{2} - \frac{L}{2a}$

$$S_{final} = k_B \ln\left(\frac{N!}{\left(\frac{N}{2}+\frac{L}{2a}+1\right)!\left(\frac{N}{2}-\frac{L}{2a}-1\right)!}\right)$$

$$\overset{!}{=} k_B \ln\left(\frac{N!}{\left(\frac{N}{2}+\frac{L}{2a}\right)!\left(\frac{N}{2}+\frac{L}{2a}+1\right)\left(\frac{N}{2}-\frac{L}{2a}\right)!\left(\frac{1}{\frac{N}{2}-\frac{L}{2a}}\right)}\right)$$

$$\overset{!}{=} k_B\left[\underbrace{\ln\left(\frac{N!}{\left(\frac{N}{2}+\frac{L}{2a}\right)!\left(\frac{N}{2}-\frac{L}{2a}\right)!}\right)}_{S_{init}} + \underbrace{\ln\left(\frac{\frac{N}{2}-\frac{L}{2a}}{\frac{N}{2}+\frac{L}{2a}+1}\right)}_{\Delta S}\right]$$

$$S_{fin} - S_{init} = \Delta S = k_B \ln\left(\frac{\frac{N}{2}-\frac{L}{2a}}{\frac{N}{2}+\frac{L}{2a}+1}\right)$$

$$\overset{!}{=} k_B\left[\ln\left(\frac{N}{2}\left(1-\frac{L}{Na}\right)\right) - \ln\left(\frac{N}{2}\left(1+\frac{L}{Na}+\frac{2}{N}\right)\right)\right]$$

$$\overset{!}{=} k_B\left[\cancel{\ln\frac{N}{2}} - \cancel{\ln\frac{N}{2}} + \ln\left(1-\frac{L}{Na}\right) - \ln\left(1+\frac{L}{Na}+\frac{2}{N}\right)\right]$$

taylor $\ln(1+x) \cong x - \frac{x^2}{2}$ assume $x \ll 1$ and $\frac{L}{Na} \ll 1$ since small stretch

$$\overset{!}{=} k_B\left(-\frac{L}{Na} - \frac{L}{Na} - \frac{2}{N}\right)$$

$$\Delta S \overset{!}{\simeq} -k_B \frac{2L}{Na}$$ assume $N \gg 2$, ignore $\frac{2}{N}$ term

then $\quad f = -T\left(\frac{\partial S}{\partial L}\right)_T$

$$\stackrel{!}{\simeq} -T\frac{\Delta S}{\Delta L}$$

with $\Delta L = 2a$

$$\stackrel{!}{=} \frac{-T}{2a}\left(-k_B\frac{2L}{Na}\right)$$

$$\boxed{f \stackrel{!}{\simeq} \frac{k_B T L}{a^2 N}}$$

13) a) Derive general expression for $\bar{\Omega}_N(E)$ of a molecule with N vibrational modes

$$\rho_i(E_i) = \frac{1}{\hbar w_i} = \text{const}$$

constant.

$$\Phi_N = \int_0^E dE' \int_0^{E'} dE_1 \int_0^{E_1} dE_2 \int_0 \cdots \int_0^{E_{N-2}} dE_{N-1} \prod_{i=1}^{N} \rho_i$$

$$= \prod_{i=1}^{N} \rho_i \int_0^E dE' \int_0^{E'} dE_1 \int_0^{E_1} dE_2 \cdots \int_0^{E_{N-2}} dE_{N-1}$$

$$= \prod_{i=1}^{N} \rho_i \int_0^E dE' \int_0^{E'} dE_1 \int_0^{E_1} dE_2 \cdots \int_0^{E_{N-3}} dE_{N-2} (E_{N-2})$$

$$= \prod_{i=1}^{N} \rho_i \int_0^E dE' \int_0^{E'} dE_1 \int_0^{E_1} dE_2 \cdots \int_0^{E_{N-4}} dE_{N-3} \frac{1}{2} E_{N-3}^2$$

as trend continuous and there is N # of integrals

$$= \prod_{i=1}^{N} \rho_i \frac{E^N}{N!}$$

$$= \prod_{i=1}^{N} \frac{1}{\hbar w_i} \frac{E^N}{N!}$$

$$\bar{\Omega}_N = \frac{d\Phi_N}{dE} = \frac{d}{dE}\left(\prod_{i=1}^{N} \frac{1}{\hbar w_i} \frac{E^N}{N!}\right)$$

$$= \frac{N}{N!} E^{N-1} \prod_{i=1}^{N} \frac{1}{\hbar w_i}$$

$$\boxed{\bar{\Omega}_N(E) = \frac{E^{N-1}}{(N-1)!} \prod_{i=1}^{N} \frac{1}{\hbar w_i}}$$

b) For $m=9$ atom, $N'=21$ DoF

consider only $N < N'=21$, $\hbar\omega_i < 1000\ cm^{-1}$

$$E = 3678\ cm^{-1}$$

$$\bar{\Omega}_{N=20} = \frac{E^{N-1}}{(N-1)!} \prod_{i=1}^{N} \frac{1}{\hbar\omega_i}$$

Since for $N>6$, $\hbar\omega > 1000\ cm^{-1}$, only do calculation up to $N=5$

$$\bar{\Omega}_{N=5} = \frac{(3678\ cm^{-1})^{5-1}}{(5-1)!} (251.31 \times 299.42 \times 417.2 \times 829.49 \times 911.66)^{-1}$$

$$\boxed{\bar{\Omega}_{N=5} = 0.3212\ cm}$$

c) Use Fermi Golden Rule to estimate the rate that the bright state decays and the vibrational energy is redistributed among other normal modes.

$$\Gamma_{i \to bath} = \frac{2\pi}{\hbar} \left| \langle bath | \hat{H}' | ZOBS \rangle \right|^2 \Omega(E)$$

Estimate $\left| \langle bath | \hat{H}' | ZOBS \rangle \right|^2$:

know IVR happens at $\sim 25ps$. or $\Gamma \sim \frac{1}{25ps}$

$$\langle bath | \hat{H}' | ZOBS \rangle = \sqrt{\frac{\hbar}{2\pi} \frac{\Gamma_{i \to bath}}{\Omega(E)}}$$

with
$\hbar = 5.31 \times 10^{-12}\ cm^{-1}\ s$

$$\stackrel{!}{=} \sqrt{\frac{5.31 \times 10^{-12}\ cm^{-1}\ s}{2\pi} \frac{\frac{1}{25 \times 10^{-12} s}}{0.3212\ cm}}$$

$$\boxed{\langle bath | \hat{H}' | ZOBS \rangle \stackrel{!}{=} 0.3244\ cm^{-1}}$$

d) Estimate the temperature of ethanol molecule after OH stretch excitation and subsequent IVR, assuming ergodicity between the states

know $\quad S = k_B \ln \bar{\Omega}$

know $\quad \frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{V,N}$

$$\stackrel{!}{=} \frac{\partial}{\partial E} k_B \ln \bar{\Omega}$$

$$\stackrel{!}{=} k_B \frac{\partial}{\partial E} \ln \left(\frac{E^{N-1}}{(N-1)!} \prod_{i=1}^{N} \frac{1}{\hbar \omega_i} \right)$$

$$\stackrel{!}{=} k_B \frac{\partial}{\partial E} \left[\ln \left(E^{N-1}\right) + \ln \left(\frac{1}{(N-1)!} \prod_{i=1}^{N} \frac{1}{\hbar \omega_i} \right) \right.$$

$$\stackrel{!}{=} k_B \frac{1}{E^{N-1}} (N-1) E^{N-2}$$

$$\frac{1}{T} \stackrel{!}{=} \frac{k_B (N-1)}{E}$$

For $N=5$, $\quad T = \frac{E}{k_B (N-1)}$

$$\stackrel{!}{=} \frac{3678 \text{ cm}^{-1}}{(0.695 \text{ cm}^{-1} \text{K}^{-1})(5-1)}$$

$$\boxed{T \stackrel{!}{=} 1323 \text{ K}}$$

e) using canonical ensemble.

Consider low frequency modes as heat bath with Temp = T

Calculate the probability of finding vibration excitation $V=1$ in OH stretch and CH stretch mode, where $E = 3000\ cm^{-1}$

from part d

$$Q = \sum_{i}^{N=5} e^{-\beta E_i} \quad \text{where } E_i = \hbar \omega_i,\ \beta = \frac{1}{k_B T} = \frac{1}{(1323)(0.695)}$$

$$\stackrel{!}{=} \exp\left\{\frac{-251.31}{(1323)(0.695)}\right\} + \exp\left\{\frac{-299.42}{(1323)(0.695)}\right\} + \exp\left\{\frac{-417.2}{(1323)(0.695)}\right\}$$

$$+ \exp\left\{\frac{-829.49}{(1323)(0.695)}\right\} + \exp\left\{\frac{-911.66}{(1323)(0.695)}\right\}$$

$$Q \stackrel{!}{=} 2.8949$$

Probability to get $E = 3678\,cm^{-1}$

$$P_{E=3678} = \frac{1}{Q} e^{-\beta E} = \frac{1}{2.8949} \exp\left\{-\frac{3678}{(1323)(0.695)}\right\}$$

$$P_{E=3678\,cm^{-1}} \stackrel{!}{=} 6.326 \times 10^{-3}$$

$$\stackrel{!}{=} 0.6326\ \%$$

convert to percent

For CH stretch around $3000\,cm^{-1}$, the closest one is $E = 3006\,cm^{-1}$

$$P_{E=3006\,cm^{-1}} = \frac{1}{2.8949} \exp\left\{-\frac{3006\,cm^{-1}}{(1323)(0.695)}\right\} \times 100$$

$$\stackrel{!}{=} 1.314\ \%$$

f) For $\langle E \rangle = \sum_i \frac{E_i \exp\{-\beta E_i\}}{Q(T)} = 3678\ cm^{-1}$

discrete state, not continuous

Find $Q(T)$, then use $Q(T)$ to find Temperature.

$$Q(T) = \sum_i^N \exp\{-\beta E_i\} \quad \text{for } N \text{ particles}$$

$$\langle E \rangle = -\left(\frac{\partial \ln Q}{\partial \beta}\right)_{N,V}$$

For particle i, we have

$$Q_i = \sum_j^\infty \exp\{-\beta(V_{i,j} + \tfrac{1}{2})\hbar W_i\}$$

but problem says ignore const energy $\frac{1}{2}\hbar W_i$

$$\overset{!}{=} \sum_j^\infty \exp\{-\beta V_{i,j} \hbar w_i\}$$

$$\overset{!}{=} \sum_j^\infty \exp\{-\beta \hbar w_i\}^{V_{i,j}}$$

geometric sum of infinite series: $\sum_{n=0}^\infty r^n = \frac{1}{1-r}$

$$Q_i \overset{!}{=} \frac{1}{1-\exp\{-\beta\hbar w_i\}}$$

Then total Q: $\quad Q = \prod_{i=1}^{21} Q_i = \prod_{i=1}^{21} \frac{1}{1-\exp\{-\beta\hbar w_i\}}$

Now solve for T using Python with

$$\langle E \rangle = -\frac{\partial}{\partial\beta}(\ln Q)_{N,V} = 3678\ cm^{-1}$$

$$\langle E \rangle = -\frac{\partial}{\partial \beta}\left(\ln\left[\prod_{i=1}^{21} \frac{1}{1-\exp\{-\beta\hbar\omega_i\}} \right]\right)$$

$$= -\frac{\partial}{\partial \beta}\left[\sum_{i=1}^{21} \ln\left(\frac{1}{1-\exp\{-\beta\hbar\omega_i\}} \right)\right]_{N,V}$$

Now solve for T using sympy with Eq:

$$3678 + \frac{\partial}{\partial \beta}\left[\sum_{i=1}^{21} \ln\left(\frac{1}{1-\exp\{-\beta\hbar\omega_i\}} \right)\right]_{N,V} = 0$$

See code: I get $\boxed{T \cong 870\,K}$

14) For canonical Ensemble: N, V, T: vary E,
use $A = -k_B T \ln Q$ as potential

For microcanonical Ensemble, N, V, E: use $S = k_B \ln \Omega$
as potential.

a) Show energy fluctuation: $\langle(\delta E)^2\rangle = k_B T^2 C_V$
and temperature fluctuation: $\langle(\delta T)^2\rangle = k_B T^2 / C_V$
the relative fluctuation scale as $\frac{1}{\sqrt{N}}$

We know energy is extensive, so it scales with
size of system:
i.e.

$$E_{tot} = \sum_i^N E_i$$

$$\langle E_{tot}\rangle = \sum_i^N \langle E\rangle = N\langle E\rangle$$

$$\text{so } \langle E\rangle \propto N$$

From 14.2) $\langle(\delta E)^2\rangle = k_B T^2 C_V \propto C_V$
and since C_V is also extensive
$C_V \propto N$

or $\langle(\delta E)^2\rangle \propto N$

$$\text{So } \boxed{\frac{\sqrt{\langle(\delta E)^2\rangle}}{\langle E\rangle} \propto \frac{\sqrt{N}}{N} \propto \frac{1}{\sqrt{N}}}$$

Temperature is intensive so it doesn't grow with N,
but $\langle(\delta T)^2\rangle = \frac{k_B T^2}{C_V} \propto \frac{1}{C_V} \propto \frac{1}{N}$

$$\text{so } \frac{\sqrt{\langle(\delta T)^2\rangle}}{\langle T\rangle} \propto \sqrt{\frac{1}{N}} \propto \frac{1}{\sqrt{N}}$$

b) Show: for large system with quasi-continuous energy spectrum, the partition function Q and density of states $\bar{\Omega}$ are related via laplace transform:

$$Q(\beta) = \int_0^\infty dE \, e^{-\beta E} \bar{\Omega}(E)$$

At large N, V system the description of microcanonical and canonical ensemble become equivalent

For canonical: $P_\nu = \dfrac{e^{-\beta E_\nu}}{Q}$

For microcanonical: $P_\nu = \dfrac{1}{\Omega} = \dfrac{1}{\bar{\Omega}\,\delta E}$

Set them equal to each other for a large system.

$$\frac{1}{\bar{\Omega}\,\delta E} = \frac{e^{-\beta E_\nu}}{Q}$$

$$Q(\beta) = e^{-\beta E_\nu} \bar{\Omega}(E)\,\delta E$$

$\delta E \to dE$ as system gets large

$$\boxed{Q(\beta) = \int_0^\infty e^{-\beta E_\nu} \bar{\Omega}(E)\, dE}$$

and sum over all energies

c) As system size increases, $\bar{\Omega}(E) \uparrow$ rapidly but $e^{-\beta E} \downarrow$ rapidly, so the product $e^{-\beta E}\bar{\Omega}(E)$ is a sharply peaked

rewrite $\quad e^{-\beta E}\bar{\Omega}(E) = e^{\ln\bar{\Omega} - \beta E} = e^{W(E)}$

Show in limit $N \Rightarrow$ large, $W = \max$ at $E = \langle E \rangle$

$$\frac{\partial W}{\partial E} = 0 = \frac{\partial}{\partial E}\left(\ln\bar{\Omega} - \beta E\right)_{N,V,T}$$

$$\hookrightarrow \frac{\partial}{\partial E}\ln\bar{\Omega} - \beta = 0$$

$$\hookrightarrow \frac{\partial}{\partial E}\ln\bar{\Omega} = \beta$$

Since $\beta = \frac{1}{k_B T} = \frac{1}{k_B}\left(\frac{\partial S}{\partial E}\right)_{N,V}$ where $\left(\frac{\partial S}{\partial E}\right)$ is evaluated at $E = \langle E \rangle$, or thermal equilibrium this must mean $\frac{\partial}{\partial E}\ln\bar{\Omega}$ is also evaluated at $E = \langle E \rangle$

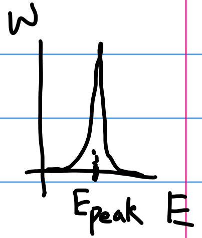
Another way to think is since:

From 14.1: $\langle E \rangle = -\left(\frac{\partial \ln Q}{\partial \beta}\right)_{N,V}$

$$\overset{!}{=} -\frac{\partial}{\partial \beta}\ln\left(e^{-\beta E}\bar{\Omega}(E)\,dE\right)$$

$$\overset{!}{=} \frac{\int_0^\infty E\, e^{-\beta E}\,\bar{\Omega}(E)\,dE}{\int_0^\infty e^{-\beta E}\,\bar{\Omega}(E)\,dE}$$

Since $e^{-\beta E}$ is decreasing rapidly and $\bar{\Omega}(E)$ is increasing rapidly, then



$\bar{\Omega}(E)\, e^{-\beta E}$ is close to a dirac-delta, centered at E_{peak}, or $\delta(E - E_{peak})$.

Then $$\langle E \rangle = \frac{\int_0^\infty E\, e^{-\beta E}\, \bar{\Omega}(E)\, dE}{\int_0^\infty e^{-\beta E}\, \bar{\Omega}(E)\, dE} \cong E_{peak}.$$

Since $E = E_{peak}$, where w is maximized

and we have $\langle E \rangle = E_{peak}$, we have $E = \langle E \rangle$

d) $$W(E) = \langle E \rangle + \delta E = -\beta E + \ln\bar{\Omega}(E)$$

$$\stackrel{!}{=} E_{peak} + \delta E$$

Expand $W(E)$:

$$W(E) = W(E=\langle E \rangle) + \cancel{\left(\frac{\partial W}{\partial E}\right)}\Bigg|_{E=\langle E \rangle} \delta E + \frac{1}{2}\left(\frac{\partial^2}{\partial E^2} W\right)(\delta E)^2$$

=0 since
With $E=\langle E \rangle = E_{peak}$
first derivative =0

$$\stackrel{!}{=} -\beta\langle E \rangle + \ln\bar{\Omega}(E=\langle E \rangle) + \frac{1}{2}\frac{\partial}{\partial E}\left(\frac{\partial}{\partial E}\ln\bar{\Omega} + \beta\right)\delta E^2$$

$$\stackrel{!}{=} -\beta\langle E \rangle + \underbrace{\ln\bar{\Omega}(E=\langle E \rangle)}_{=\frac{S}{k_B}} + \frac{1}{2}\left(\frac{\partial}{\partial E}\ln\bar{\Omega}\right)\Bigg|_{E=E_{peak}} \delta E^2$$

$$\stackrel{!}{=} -\beta(\langle E \rangle - TS) + \frac{1}{2}\left(\frac{\partial}{\partial E}\ln\bar{\Omega}\right)\delta E^2$$

if $\langle E \rangle = E$, from previous part, we know

$$\ln\bar{\Omega} = \beta$$

then $$\frac{\partial}{\partial E}\beta = \left(\frac{\partial\beta}{\partial T}\right)_{N,V}\left(\frac{\partial T}{\partial E}\right)_{N,V}$$

$$C_V = \left(\frac{\partial E}{\partial T}\right)_{N,V} \qquad \stackrel{!}{=} \frac{\partial\left(\frac{1}{k_B T}\right)}{\partial T}\frac{1}{C_V}$$

$$\frac{\partial}{\partial E}\beta \stackrel{!}{=} -(k_B T^2 C_V)^{-1}$$

$$W(\langle E\rangle + \delta E) = -\beta(\langle E\rangle - TS) - \frac{1}{2}\frac{1}{k_B T^2 C_V}(E - \langle E\rangle)^2$$

And $Q(\beta) = \int_0^\infty dE\ e^{W}$

$$\stackrel{!}{=} \int_0^\infty dE\ e^{-\beta(\langle E\rangle - TS)}\ e^{-\frac{1}{2}\frac{1}{k_B T^2 C_V}(E-\langle E\rangle)^2}$$

with $u = \sqrt{\frac{1}{2}\frac{1}{k_B T^2 C_V}}\,(E - \langle E\rangle)$

$$du = \sqrt{\frac{1}{2}\frac{1}{k_B T^2 C_V}}\ dE$$

$$Q(\beta) = \sqrt{2 k_B T^2 C_V}\ e^{-\beta(\langle E\rangle - TS)}\left(\frac{1}{2}\underbrace{\int_{-\infty}^{\infty} du\ e^{-u^2}}_{\sqrt{\pi}}\right)$$

$$\boxed{Q(\beta) \stackrel{!}{=} \sqrt{\frac{k_B T^2 C_V \pi}{2}}\ e^{-\beta(\langle E\rangle - TS)}}$$

Since $A = -k_B T \ln Q$

$$S = \frac{\left[\langle E\rangle + k_B T \ln\left(\sqrt{\frac{k_B T^2 C_V \pi}{2}}\ e^{-\beta(\langle E\rangle - TS)}\right)\right]}{T}$$

$$\stackrel{!}{=} \left(\langle E\rangle + k_B T\left[\ln\left(\sqrt{\frac{k_B T^2 C_V \pi}{2}}\right) + -\beta(\langle E\rangle - TS)\right]\right)\frac{1}{T}$$

$$\stackrel{!}{=} \left[\cancel{\langle E\rangle - \langle E\rangle} + TS + \frac{1}{2}k_B T \ln\left(\frac{k_B T^2 C_V \pi}{2}\right)\right]\frac{1}{T}$$

$$\stackrel{!}{=} \underset{S \propto N}{S} + \frac{1}{2}k_B \ln\Big(\underbrace{\frac{k_B T^2 C_V \pi}{2}}\Big)$$

only extensive variable inside ln is C_V, so this term goes $\propto \ln(N)$. At large N, this is negligible.

So $S \cong S$