Sheet 1

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P1)

a) Number of micro states with Energy E_A in System A: $\Omega_A(E_A)$

All possible states in System B $\Omega_B(E-E_A)$

$\Rightarrow$ $\Omega_A(E_A)\Omega_B(E_B)$ All possible Kombinations for System A with System B

$\Rightarrow$ To get a probability we need to divide by the total number of possible States

All possible states in the whole system $\Omega_{A+B}(E)$

$$\Rightarrow P(E_A) = \frac{\Omega_A(E_A)\Omega_B(E_B)}{\Omega_{A+B}(E)}$$

b)

$$\ln(P_A(E_A)) \approx \ln(P(E_A^*)) + \frac{\partial \ln(P(E_A))}{\partial E_A}\Big|_{E_A^*}(E_A - E_A^*) + \frac{\partial^2 \ln(P(E_A))}{\partial E_A^2}\Big|_{E_A^*}(E_A - E_A^*)^2 + \dots$$

Leave out normalizing factor

$$P_A \propto \exp\left(\frac{\partial \ln(P(E_A))}{\partial E_A}\Big|_{E_A^*}(E_A - E_A^*) + \frac{\partial^2 \ln(P(E_A))}{\partial E_A^2}\Big|_{E_A^*}(E_A - E_A^*)^2\right)$$

$\Rightarrow$ by choosing E_A^* as max for $P(E_A^*)$

$$= \exp\left(\underbrace{P'(E_A^*)}_{=0}\frac{1}{P(E_A^*)}(E_A - E_A^*) + \frac{\partial^2 \ln(P(E_A))}{\partial E_A^2}\Big|_{E_A^*}(E_A - E_A^*)^2\right)$$

$$= \exp\left(\frac{\partial^2 \ln(P(E_A))}{\partial E_A^2}\Big|_{E_A^*}(E_A - E_A^*)^2\right)$$

$$= \exp\left(\frac{\partial^2}{\partial E_A^2}\ln\left(\frac{\Omega_A(E_A)\Omega_B(E-E_A)}{\Omega_{A+B}(E)}\right)\Big|_{E_A^*}(E_A - E_A^*)^2\right)$$

independent of E_A

$$= \exp\left(\frac{\partial^2}{\partial E_A^2}\left(\ln(\Omega_A(E_A)) + \ln(\Omega_B(E-E_A)) - \cancel{\ln(\Omega_{A+B}(E))}\right)\Big|_{E_A^*}(E_A - E_A^*)^2\right)$$

observe that $\ln(\Omega_A(E_A)) = \frac{S_A(E_A)}{k_B}$; $\ln(\Omega_B(E-E_A)) = \frac{S_B(E-E_A)}{k_B}$

$$\Rightarrow \dots = \exp\left(\frac{\partial^2}{\partial E_A^2}\left(\frac{S_A(E_A) + S_B(E-E_A)}{k_B}\right)\Big|_{E_A^*}(E_A - E_A^*)^2\right)$$

$$\Rightarrow \ldots = \exp\Big(\underbrace{\frac{\partial^2}{\partial E_A^2}\Big(\frac{S_A(E_A)+S_B(E-E_A)}{k_B}\Big)\Big|_{E_A^*}}_{= -\frac{1}{\sigma_{E_A}^2}}(E_A - E_A^*)^2\Big)$$

$$= \exp\Big(-\frac{(E_A - E_A^*)^2}{\sigma_{E_A}^2}\Big)$$

$$\frac{\partial E}{\partial E_A} = 1$$

c) $$\frac{1}{T} = \frac{\partial S(E)}{\partial E} \iff \frac{\partial}{\partial E}\frac{1}{T(E)} = \frac{\partial^2 S(E)}{\partial E^2}$$

$$\frac{\partial}{\partial E_A}\ln(P(E_A))\Big|_{E_A^*} = \frac{\partial}{\partial E_A}\Big(\ln(\Omega_A(E_A)) + \ln(\Omega_B(E_B)) - \ln(\Omega_{A+B}(E))\Big)\Big|_{E_A^*}$$

$$= \Big(\frac{\partial}{\partial E_A}\frac{S_A(E_A)}{k_B} + \frac{\partial}{\partial E_B}\frac{S_B(E_B)}{k_B} - \cancel{\frac{\partial}{\partial E_A}\ln(\Omega_{A+B}(E))}\Big)\Big|_{E_A^*}$$

$$\frac{1}{k_B}\Big(\frac{1}{T_A(E_A^*)} + \frac{1}{T_B(E_A^*)}\Big) \stackrel{!}{=} 0$$

$$\iff T_A(E_A^*) = T_B(E_A^*)$$

I used that

$$\frac{\partial^2 S_B(\overbrace{E-E_A}^{E_B})}{\partial E_A^2} = \frac{\partial^2 S_B(E_B)}{\partial E_B^2}$$

$$\boxed{E_A = E - E_B \qquad \frac{\partial^2 E_A}{\partial E_B^2} = 1 \Rightarrow \partial E_A^2 = \partial E_B^2}$$

Express $\sigma_{E_A}^2$:

$$\sigma_{E_A}^2 = -\frac{k_B}{\frac{\partial^2}{\partial E_A^2}(S_{A+B}(E_A))\Big|_{E_A^*}} = -\frac{k_B}{\frac{\partial^2}{\partial E_A^2}\big(S_A(E_A) + S_B(\underbrace{E-E_A}_{E_B})\big)\Big|_{E_A^*}} = -\frac{k_B}{\frac{\partial^2 S_A(E_A)}{\partial E_A^2}\Big|_{E_A^*} + \frac{\partial^2 S_B(E_B)}{\partial E_B^2}\Big|_{E_A^*}}$$

d)

$$C_A = \frac{\partial E_A}{\partial T} \qquad T_A = \frac{\partial E_A}{\partial S_A} \Rightarrow \frac{\partial S_A}{\partial E_A} = \frac{1}{T_A}$$

$$\Rightarrow \frac{\partial^2 S_A}{\partial^2 E_A} = \frac{\partial}{\partial E_A}\Big(\frac{1}{T_A}\Big) = -\frac{1}{T^2}\frac{\partial T}{\partial E_A} = -\frac{1}{T^2}\frac{1}{C_A}$$

$$\left.\begin{aligned} &\iff C_A = -\frac{1}{\frac{\partial^2 S_A}{\partial^2 E_A}}\frac{1}{T_B^2} \\ &\Rightarrow C_B = -\frac{1}{\frac{\partial^2 S_B}{\partial^2 E_B}}\frac{1}{T_B^2} \end{aligned}\right\} \Rightarrow \sigma_{E_A}^2 = \frac{k_B}{\frac{1}{C_A(E_A^*)T_A^2(E_A^*)} + \frac{1}{C_B(E_A^*)T_B^2(E_A^*)}}$$

e) $\langle E_A \rangle = E_A^* \propto N$

$$\frac{\sigma_{E_A}}{E_A^*} = \sqrt{\frac{k_B}{\frac{1}{C_A (E_A^*) T_A^2 (E_A^*)} + \frac{1}{C_B (E_A^*) T_B^2 (E_A^*)}}} \frac{1}{E_A^*}$$

$$= \sqrt{\frac{k_B T_A^2}{\frac{1}{C_A} + \frac{1}{C_B}}} \frac{1}{E_A^*}$$

$A << B$

f) $$\sigma_{E_A}^2 = \frac{k_B}{C_A (E_A^*) T_A^2 (E_A^*) + C_B (E_A^*) T_B^2 (E_A^*)} \overset{T_A = T_B}{=} \frac{k_B}{T_A^2 (C_A + C_B)}$$

$$= T_A^2 k_B \frac{1}{1/C_A + 1/C_B} \qquad C_A << C_B \Rightarrow \frac{1}{C_A} >> \frac{1}{C_B}$$

$$= T_A^2 k_B \frac{1}{1/C_A} = T_A^2 k_B C_A$$

First order correction for $\sigma_E^2 = T_A^2 k_B \left(\frac{1}{C_A} + \frac{1}{C_B}\right)^{-1}$

$$= T_A^2 k_B \left(\frac{1}{C_A} + 0\right)^{-1} - T_A^2 k_B \left(\frac{1}{C_A} + 0\right)^{-2} \left(\frac{1}{C_B}\right)$$

$$= T_A^2 k_B \left(C_A - \frac{C_A^2}{C_B}\right) = T_A^2 k_B C_A \left(1 - \frac{C_A}{C_B}\right)$$

P2

a) $H = \sum_i \vec{p}_i^{\,2}/2m$

$$Z = \frac{1}{N!}\frac{1}{h^{3N}} \iint d\vec{p}^{\,N} d\vec{r}^{\,N} \, e^{-\frac{H(p,r)}{k_B T}}$$

$$= \frac{1}{N!}\frac{1}{h^{3N}} \int d\vec{r}^{\,N} e^{-\frac{\overset{=0}{H(r)}}{k_B T}} \int d\vec{p}^{\,N} e^{-\frac{H(p)}{k_B T}}$$

$$= \frac{1}{N!}\frac{1}{h^{3N}} \int d\vec{r}^{\,N} \underbrace{\int d\vec{p}^{\,N} e^{-\vec{p}^{\,2}/2m k_B T}}_{\text{Spherical coordinates}\quad p_x^2 + p_y^2 + p_z^2 = r^2}$$

$$= \frac{1}{N!}\frac{1}{h^{3N}} V^N \left(\underbrace{\int_0^\pi \cos(\omega)\, d\omega}_{1} \underbrace{\int_0^{2\pi} d\varphi}_{2\pi} \underbrace{\int_0^\infty dr\, r^2 e^{-r^2/2m k_B T}}_{\frac{1}{4}\sqrt{\pi}\,(2m k_B T)^{3/2}} \right)^N$$

$$= \frac{1}{N!}\frac{1}{h^{3N}} V^N \left(2\pi \, \frac{1}{4} \, \pi^{\frac{1}{2}} (2m k_B T)^{3/2} \right)^N$$

$$= \frac{1}{N!}\frac{1}{h^{3N}} V^N \left(2 \cdot \cancel{\tfrac{1}{4}} \cdot \cancel{4}\,2 \cdot \sqrt{2} \cdot \pi^{3/2} (m k_B T)^{3/2} \right)^N$$

$$= \frac{V^N}{N!} \frac{1}{h^{3N}} \left(2\pi m k_B T \right)^{\frac{3N}{2}} \qquad \frac{1}{\lambda} := \left(\frac{1}{h^2} 2\pi m k_B T \right)^{1/2}$$

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

b) $$Z_A(N_A) = \frac{1}{N!}\frac{1}{h^{3N}} \left(\int e^{-\frac{p}{2m k_B T}} dp \right)^{3N} \left(\int_{V_A} dq^3 \right)^{N_A} \left(\int_{V_B} dq^3 \right)^{N_B} \binom{N}{N_A}$$

$$= \frac{1}{N!\, h^{3N}} P^{3N} V_A^{N_A} V_B^{N_B} \frac{N!}{N_A!\,(N-N_A)!}$$

$$= \lambda^{-3N} V_A^{N_A} V_B^{N_B} \frac{1}{N_A!\, N_B!} = \frac{(V_A/\lambda^3)^{N_A}}{N_A!} \frac{(V_B/\lambda^3)^{N_B}}{N_B!}$$

It would not hold without the rescaling.

c)

$$P_A(N_A) = \frac{Z(N_A)}{Z} = \frac{1}{N_A!}\frac{1}{N_B!}\left(\frac{V_A}{\lambda^3}\right)^{N_A}\left(\frac{V_B}{\lambda^3}\right)^{N_B}\frac{N!}{\left(\frac{V}{\lambda^3}\right)^N}$$

$$= \frac{N!}{N_A!\,(N-N_A)!}\left(\frac{V_A}{\lambda^3}\right)^{N_A}\left(\frac{V-V_A}{\lambda^3}\right)^{N-N_A}\left(\frac{V}{\lambda^3}\right)^{-N}$$

$$= \binom{N}{N_A}\frac{{V_A}^{N_A}}{\lambda^{3N_A}}\frac{(V-V_A)^{N-N_A}\,\lambda^{3N}}{\lambda^{3(N-N_A)}\;V^N}$$

$$= \binom{N}{N_A}\frac{{V_A}^{N_A}}{\cancel{\lambda^{3N_A}}}\frac{(V-V_A)^{N-N_A}\;\cancel{\lambda^{3N}}\;\cancel{\lambda^{3N_A}}}{\cancel{\lambda^{3}}\qquad V^N}$$

Rescaling so that $V = 1$

$$\Rightarrow \binom{N}{N_A}\left(\frac{V_A}{V}\right)^{N_A}\frac{\left(\frac{V}{V}-\frac{V_A}{V}\right)^{N-N_A}}{(V/V)^N} = \binom{N}{N_A}\left(\frac{V_A}{V}\right)^{N_A}\left(1-\frac{V_A}{V}\right)^{N-N_A}$$

$$\Rightarrow \text{Binomial distributed}: \binom{n}{k} = p^k(1-p)^{n-k}$$

d)

$$P_A(N_A) = \frac{N!}{N_A!\,(N-N_A)!}\left(\frac{V_A}{V}\right)^{N_A}\left(1-\frac{V_A}{V}\right)^{N-N_A}$$

$$= \frac{\sqrt{2\pi N}\;N^N\cancel{e^{-N}}}{\sqrt{2\pi N_A}\;{N_A}^{N_A}\cancel{e^{-N_A}}\;\sqrt{2\pi(N-N_A)}\;(N-N_A)^{N-N_A}\;\cancel{e^{N_A-N}}}\left(\frac{V_A}{V}\right)^{N_A}\left(1-\frac{V_A}{V}\right)^{N-N_A}$$

$$= \frac{N^N}{{N_A}^{N_A}}\frac{1}{(N-N_A)^{N-N_A}}\sqrt{\frac{\cancel{2\pi}N}{\cancel{2\pi}N_A\;2\pi(N-N_A)}}\left(\frac{V_A}{V}\right)^{N_A}\left(1-\frac{V_A}{V}\right)^{N-N_A}$$

$$= \sqrt{\frac{N}{2\pi N_A(N-N_A)}}\;\frac{\left(1-\frac{V_A}{V}\right)^{N-N_A}}{(N-N_A)^{N-N_A}}\;\frac{{V_A}^{N_A}}{(N_AV)^{N_A}}\;\underbrace{\overbrace{N^{N_A}\;N^{N-N_A}}^{N^N}}$$

$$= \sqrt{\frac{1}{2\pi N\frac{N_A}{N}\left(1-\frac{N_A}{N}\right)}}\left(\frac{N\left(1-\frac{V_A}{V}\right)}{N-N_A}\right)^{N-N_A}\left(\frac{NV_A}{N_AV}\right)^{N_A}$$

now for $N \to \infty$ $\quad \frac{N_A}{N} \approx \frac{V_A}{V} := p$

$$\Rightarrow \sqrt{\frac{1}{2\pi N \frac{N_A}{N}\left(1-\frac{N_A}{N}\right)}} \left(\frac{N\left(1-\frac{V_A}{V}\right)}{N-N_A}\right)^{N-N_A} \left(\frac{N V_A}{N_A V}\right)^{N_A}$$

$$= \sqrt{\frac{1}{2\pi N \underbrace{p(1-p)}_{:=\sigma^2}}} \left(\frac{1-\left(\frac{V_A}{V}\right)}{1-\frac{N_A}{N}}\right)^{N-N_A} \left(\frac{V_A}{\frac{N_A}{N} V}\right)^{N_A}$$

$$= \sqrt{\frac{1}{2\pi N \sigma^2}} \exp\left\{\frac{N}{N} \ln\left[\left(\frac{1-\frac{V_A}{V}}{1-\frac{N_A}{N}}\right)^{N-N_A} \left(\frac{V_A}{\frac{N_A}{N} V}\right)^{N_A}\right]\right\}$$

$$= \frac{1}{\sqrt{2\pi N\sigma^2}} \exp\left\{\frac{N}{N}\left((N-N_A)\ln\left(\frac{1-\frac{V_A}{V}}{1-\frac{N_A}{N}}\right) + N_A \ln\left(\frac{N\, V_A}{N_A\, V}\right)\right)\right\}$$

$$= \frac{1}{\sqrt{2\pi N\sigma^2}} \exp\left\{N\left(\left(1-\frac{N_A}{N}\right)\ln\left(\frac{1-p}{1-x}\right) + \frac{N_A}{N}\ln\left(\frac{p}{x}\right)\right)\right\} \quad \text{again } p = \frac{V_A}{V},\ x = \frac{N_A}{N}$$

$$= \frac{1}{\sqrt{2\pi N\sigma^2}} \exp\left\{-N\left(\underbrace{(1-x)\ln\left(\frac{1-x}{1-p}\right)}_{g(x)} + \underbrace{x\ln\left(\frac{x}{p}\right)}_{f(x)}\right)\right\} \; *$$

$\frac{N}{N_A} \approx \frac{V}{V_A}$

Taylor $x \approx p$:

$$T_g(x,p) = 0 \underbrace{-\ln\left(\frac{1-x}{1-p}\right)\Big|_{x=p}}_{=0} + \underbrace{\left[\cancel{(1-x)}\,\frac{\cancel{1-p}}{\cancel{1-x}}\,\frac{-1}{\cancel{1-p}}\right]_{x=p}}_{=-1}(x-p) +$$

$$+ \frac{1}{2}\left[\frac{1}{\cancel{1-p}}\,\frac{\cancel{1-p}}{1-x}\right]_{x=p}(x-p)^2 + \Theta(3) = (p-x) + \frac{1}{2(1-p)}(x-p)^2$$

$$T_f(x,p) = 0 + \left[\underbrace{\ln\left(\frac{x}{p}\right)}_{0} + \cancel{x}\frac{\cancel{p}}{\cancel{x}}\frac{1}{\cancel{p}}\right]_{p=x}(x-p) + \frac{1}{2}\left[\frac{1}{\cancel{p}}\frac{\cancel{p}}{x}\right]_{p=x}(x-p)^2 + \Theta(3)$$

$$= (x-p) + \frac{1}{2p}(x-p)^2$$

Combining $T_f + T_g$

$$= (\cancel{p} - x) + \frac{1}{2(1-p)}(x-p)^2 + (\cancel{x} - p) + \frac{1}{2p}(x-p)^2$$

$$= \left(\frac{1}{2(1-p)} + \frac{1}{2p}\right)(x-p)^2$$

$$= \left(\frac{\cancel{2}(1-p) + \cancel{2}p}{\cancel{2}(1-p)2p}\right)(x-p)^2$$

$$= \left(\frac{1-p+p}{2p(1-p)}\right)(x-p)^2$$

$$= \frac{1}{2\sigma^2}(x-p)^2$$

↳ Back into $P_1(N_A)$: *

$$\therefore = \frac{1}{\sqrt{2\pi N\sigma^2}} e^{\frac{N}{2\sigma^2}\left(\frac{N_A}{N} - \frac{V_A}{V}\right)^2}$$

→ This is a normal/gauss distribution

e) Damn I already have a Gauss Distribution, but cant find my mistake.

P3)

Constraints: $\max\limits_{p_n} \frac{S}{k_B} = \max\limits_{p_n} -\sum_n p_n \ln(p_n)$; $\sum_n p_n = 1$; $\sum_n p_n E_n = E$

$$\mathcal{L} = -\sum_n p_n \ln(p_n) + \lambda_1 \left(\sum_n p_n - 1 \right) + \lambda_2 \left(\sum_n p_n E_n - E \right)$$

1. $$\frac{\partial \mathcal{L}}{\partial p_n} = -\left(\ln(p_n) + 1\right) + \lambda_1 + \lambda_2 E_n \overset{!}{=} 0$$

$$\Leftrightarrow \quad \ln(p_n) = \lambda_1 + \lambda_2 E_n - 1$$

$$\Leftrightarrow \quad p_n = e^{\lambda_1 + \lambda_2 E_n - 1} = e^{\lambda_1 - 1} e^{\lambda_2 E_n}$$

2. $$\frac{\partial \mathcal{L}}{\partial \lambda_1} = \sum_n p_n - 1 \overset{!}{=} 0$$

$$\Leftrightarrow \sum_n e^{\lambda_1 + \lambda_2 E_n - 1} - 1 = 0$$

$$\Leftrightarrow e^{\lambda_1 - 1} \sum_n e^{\lambda_2 E_n} - 1 = 0$$

$$\Leftrightarrow \lambda_1 = 1 + \ln \frac{1}{\sum_n e^{\lambda_2 E_n}}$$

$$\Leftrightarrow \lambda_1 = 1 - \ln\left(\sum_n \lambda_2 E_n\right)$$

$$\Rightarrow p_n = e^{1 - \ln\left(\sum_n \lambda_2 E_n\right) - 1} e^{\lambda_2 E_n}$$

$$= \frac{1}{\sum_n e^{\lambda_2 E_n}} e^{\lambda_2 E_n}$$

$\Rightarrow$ Boltzmann distribution wit $\lambda_2 = -\beta \Rightarrow \lambda_1 = 1 - \ln(Z)$

$$\Rightarrow p_n = \frac{1}{Z} e^{-\beta E_n}$$

b) $KL(p' \| p) = \sum_n p_n' \ln(p_n'/p_n) \geq 0$

$$= \sum_n p_n' \ln(p_n') - \sum_n p_n' \ln(p_n)$$

$$= -\frac{S'}{k_B} - \sum_n p_n' \ln\left(\frac{1}{Z} e^{-\beta E_n}\right)$$

$$= -\frac{S'}{k_B} - \sum_n p_n' (-\beta E_n - \ln(Z))$$

$$= -\frac{S'}{k_B} + \beta \sum_n p_n' E_n + \ln(Z) \underbrace{\sum_n p_n'}_{1}$$

with $\sum_n p_n' E_n = E'$,

$F = -k_B T \ln(Z)$

$$= -\frac{S'}{k_B} + \beta E' - \beta F$$

$F = E - TS$

$$\Leftrightarrow -\frac{S'}{k_B} + \beta E' - \beta E + \frac{S}{k_B} \geq 0$$

$$\Rightarrow \frac{S}{k_B} \geq \frac{S'}{k_B} + \beta E - \beta E'$$

$$\Rightarrow S \geq S' + \frac{1}{T}(\underbrace{E - E'}_{=0})$$

$=0$, because average energy is fixed

$$\Rightarrow S \geq S'$$

$\Rightarrow$ For any distribution p' the Entropi S is maximized by p.

c) $S \geq S' + \frac{1}{T}(E - E')$

$$\Leftrightarrow \frac{1}{T}E' - S' \geq \frac{1}{T}E - S$$

$$\Leftrightarrow E' - TS' \geq E - TS$$

$$\Leftrightarrow F' \geq F$$

$\Rightarrow p$ minimizes the free energy globally.