Secret Code # 20 , Problem Set 6

6.3) $f(x) = -x^2 + 3x$

$f'(x) = -2x + 3 = 0$

$-2x = -3$

$\boxed{x = 3/2}$

$f''(x) = -2$ since negative slope decreasing and $3/2$ is max.

$g(x) = \ln(f(x)) = \ln(-x^2 + 3x)$

$\ln(x(-x+3))$

$\ln(x) + \ln(3-x)$

$g'(x) = \frac{1}{x} + \frac{1}{3-x} \cdot -1 = 0$

$\frac{1}{x} = \frac{1}{3-x}$

$3 - x = x$

$3 = 2x$

$\boxed{\frac{3}{2} = x}$

$g''(\frac{3}{2}) = \frac{-1}{x^2} + \frac{1}{(3-x)^2}$

$= -\frac{16}{36} + \frac{1}{36} = \frac{-15}{36} < 0$ so slope decreasing @ $x = \frac{3}{2}$ and $\therefore$ $x = 3/2$ is a maximum

6.4) $W = \frac{A!}{\prod_{i=1}^{m}(N_i!)}$ Stirling Approx: $\ln(N!) = n\ln(n) - n$

$$\ln(W) = \ln\left(\frac{A!}{\prod_{i=1}^{m}(N_i!)}\right) = \ln(A!) - \ln\left(\prod_{i=1}^{m}[N_i!]\right)$$

$$= \ln(A!) - \sum_{i=1}^{m} \ln(N_i!)$$

$$= A\ln(A) - A - \sum_{i=1}^{m}(N_i \ln(N_i) - N_i)$$

$$= A\ln(A) - A - \sum_{i=1}^{m} N_i \ln(N_i) + \underbrace{\sum_{i=1}^{m} N_i}_{A = \sum_{i=1}^{m} N_i}$$

$$= A\ln(A) \cancel{- A} - \sum_{i=1}^{m} N_i \ln(N_i) \cancel{+ A}$$

$$\boxed{\ln(W) = A\ln(A) - \sum_{i=1}^{m} N_i \ln(N_i)}$$

6.5) $$\left(\frac{\partial \ln(W)}{\partial N_i}\right)_{N_j} = \frac{\partial}{\partial N_i} A\ln(A) - \frac{\partial}{\partial N_i} \sum_{i=1}^{m} N_i \ln(N_i)$$

$$\frac{\partial}{\partial N_i}\left(\cancelto{0}{N_1 \ln(N_1)} + \cancelto{0}{\ldots} + \underbrace{N_i \ln(N_i)} + \cancelto{0}{\ldots} + \cancelto{0}{N_m \ln(N_m)}\right)$$

$$\frac{\partial}{\partial N_i}\underbrace{\left[\sum_{i=1}^{m} N_i \cdot \ln\left(\sum_{i=1}^{m} N_i\right)\right]} - \frac{\partial}{\partial N_i} \underbrace{\sum_{i=1}^{m} N_i \ln(N_i)}$$

$$\left[\cancel{\sum_{i=1}^{m} N_i} \times \frac{1}{\cancel{\sum_{i=1}^{m} N_i}} \cdot 1 + \ln\left(\sum_{i=1}^{m} N_i\right) \cdot 1\right] - \left[\cancel{N_i} \cdot \frac{1}{\cancel{N_i}} + \ln(N_i) \cdot 1\right]$$

$$[\cancel{1} + \ln(A)] - [\cancel{1} + \ln(N_i)]$$

$$\boxed{\left(\frac{\partial \ln(W)}{\partial N_i}\right)_{N_j} = \ln(A) - \ln(N_i)}$$

6.6)

$N_1 + N_2 + N_3 = A = 20$

Plot $\ln(W)$ as function of N's.

6.7) $N_1 + N_2 + N_3 = A = 20$

$\varepsilon_1 = 0, \quad \varepsilon_2 = 2, \quad \varepsilon_3 = 4$

$\varepsilon_1 \times N_1 + \varepsilon_2 \times N_2 + \varepsilon_3 N_3 = E_T = 20$

$\cancel{\varepsilon_1 \times (A - N_2 - N_3)} + \varepsilon_2 N_2 + \varepsilon_3 N_3 = E_T = 20$

$N_2 + 4N_3 = E_T = 20$

$N_2 + 4N_3 = 20$

$N_1 + N_2 + N_3 = 20$

$\ln(W) = A\ln(A) - (N_1 \ln N_1 + N_2 \ln N_2 + N_3 \ln N_3)$

$N_1 = 20 - N_2 - N_3$

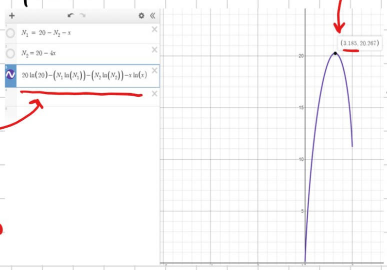
$N_2 = 20 - 4N_3$ $\Rightarrow$ $N_1 = 20 - (20 - 4N_3) - N_3 = 3N_3$

$N_2 = 20 - 4N_3$

$A = 20$

$\ln(W) = 20\ln(20) - N_1 \ln(N_1) - (N_2 \ln(N_2)) - N_3 \ln(N_3)$

$\hookrightarrow$ Plot:



Because intersection of plane w/ surface defines 2D line, maximize for N_3^* then solve for N_1^* and N_2^*

$N_3^* = 3.185$ is max

$N_2^* = 20 - 4(3.185) = 20 - 16 = 7.26$

$N_1^* = 20 - N_3^* - N_2^* = 20 - 3.185 - 7.26 = 9.555$

(integers only)

$N_3^* = 3$

$N_2^* = 20 - 4(3) = 8$

$N_1^* = 20 - 8 - 3 = 9$

Maximized @ $(N_1^*, N_2^*, N_3^*) = (9, 8, 3)$

$\hookrightarrow$ (Verified in notebook.) $\ln(W) = 20.20826$.

6.8A) A canonical Ensemble because replicas vary in energy unlike microcanonical ensembles.

6.8B) Notebook

6.8C) $Q = \sum_{i=1}^{7} \Omega_i e^{-\hat{E}_i/RT}$

$= 1 + 3e^{-1000/RT} + 6e^{-2000/RT} + 7e^{-3000/RT} + 6e^{-4000/RT} + 3e^{-5000/RT} + e^{-6000/RT} = 9.504$

where $T = 300$ K

$R = 8.3145$ J/mol K

6.9B) $Q = \sum_{i=1}^{3} \Omega_i e^{-\hat{E}_i/RT} = 1 + e^{-1000/RT} + e^{-2000/RT}$

$q_i = \dfrac{e^{-\hat{E}_i/RT}}{Q}$

6.10B) $Q = (1 + e^{-1000/RT} + e^{-2000/RT})^3$ See notebook!