a) $\mathcal{U} = \sum_{i,z}' p_{i,z} E_{i,z}$ ; $\langle V \rangle = \sum_{i,z}' p_{i,z} V_z$

Nebenbedingungen:

① Wahrscheinlichkeit: $\sum_{i,z}' p_{i,z} - 1 = 0$

② Energie $\mathcal{U}$: $\sum_{i,z}' p_{i,z} E_{i,z} - \mathcal{U} = 0$

③ Volumen $\langle V \rangle$: $\sum_{i,z}' p_{i,z} V_z - \langle V \rangle = 0$

zu maximierende Entropie:

$S = -k \sum_{i,z}' p_{i,z} \ln p_{i,z}$

Maximierung mit Nebenbedingungen:

$\longrightarrow$ Lagrangemultiplikatoren $\lambda_1$, $\lambda_2$ und $\lambda_3$

$$\frac{\partial}{\partial p_{j,z'}} \Big\{ -k \sum_{i,z}' p_{i,z} \ln p_{i,z} + \lambda_1 \Big( \sum_{i,z}' p_{i,z} - 1 \Big) + \lambda_2 \Big( \sum_{i,z}' p_{i,z} E_{i,z} - \mathcal{U} \Big) + \lambda_3 \Big( \sum_{i,z}' p_{i,z} V_z \Big) \Big\} \overset{!}{=} 0$$

$$-k \sum_{i,z}' \frac{\partial p_{i,z}}{\partial p_{j,z'}} \ln p_{i,z} - k \sum_{i,z}' p_{i,z} \frac{\partial \ln p_{i,z}}{\partial p_{j,z'}} + \lambda_1 \sum_{i,z}' \frac{\partial p_{i,z}}{\partial p_{j,z'}} + \lambda_2 \sum_{i,z}' \frac{\partial p_{i,z}}{\partial p_{j,z'}} E_{i,z} + \lambda_3 \sum_{i,z}' \frac{\partial p_{i,z}}{\partial p_{j,z'}} V_z$$

$$= -k \ln p_{j,z'} - k + \lambda_1 + \lambda_2 E_{j,z'} + \lambda_3 V_{z'} = 0$$

$$\Rightarrow \ln p_{j,z'} = \left( \frac{\lambda_1}{k} - 1 \right) + \frac{\lambda_2}{k} E_{j,z'} + \frac{\lambda_3}{k} V_{z'}$$

$$p_{j,z'} = \exp\left\{ \frac{\lambda_1}{k} - 1 \right\} \exp\left\{ \frac{\lambda_2}{k} E_{j,z'} + \frac{\lambda_3}{k} V_{z'} \right\}$$

$$= \frac{1}{Z} \, e^{-\beta E_{j,z'} - \gamma V_{z'}}$$

mit $\beta = -\frac{\lambda_2}{k}$, $\gamma = -\frac{\lambda_3}{k}$, $Z = e^{-\left(\frac{\lambda_1}{k} - 1\right)}$

$\sum_{i,z}' p_{i,z} = 1 \Rightarrow Z = \sum_{i,z}' \exp\left( -\beta E_{i,z} - \gamma V_z \right)$

b) $S = -k \sum'_{i,z} p_{i,z} \ln p_{i,z}$ , $p_{i,z} = \frac{1}{Z} \exp\left(-\beta E_{i,z} - \gamma' V_z\right)$

$$\Rightarrow S = -k \sum'_{i,z} p_{i,z} \left(-\beta E_{i,z} - \gamma V_z - \ln Z\right)$$

$$= k\beta \sum'_{i,z} p_{i,z} E_{i,z} + k\gamma' \sum'_{i,z} p_{i,z} V_z + k \ln Z$$

$$= k\beta\, \mathcal{U} + k\gamma' \langle V \rangle + k \ln Z$$

jetzt: $\beta = \frac{1}{kT}$ , $\gamma' = \gamma/\beta = \gamma' kT$

$$\Rightarrow S = \frac{\mathcal{U}}{T} + \frac{\gamma'}{T} \langle V \rangle + k \ln Z$$

c) $G = -kT \ln Z$

aus b): $k \ln Z = S - \frac{\mathcal{U}}{T} - \frac{\gamma' \langle V \rangle}{T}$

$$G = -kT \ln Z = \mathcal{U} + \gamma' \langle V \rangle - TS$$

d) ① $G(T, \gamma', N) = -kT \ln Z$

② $G = \mathcal{U} + \gamma' \langle V \rangle - TS$

$$= \mathcal{U}(S, N, \langle V \rangle) + \gamma' \langle V \rangle - TS$$

Totales Differential von ①:

$$dG = \left(\frac{\partial G}{\partial T}\right)_{\gamma', N} dT + \left(\frac{\partial G}{\partial \gamma'}\right)_{T, N} d\gamma' + \left(\frac{\partial G}{\partial N}\right)_{T, \gamma'} dN$$

Totales Differential von ②:

$$dG = \left(\frac{\partial \mathcal{U}}{\partial S}\right)_{N, \langle V \rangle} dS + \left(\frac{\partial \mathcal{U}}{\partial N}\right)_{S, \langle V \rangle} dN + \left(\frac{\partial \mathcal{U}}{\partial \langle V \rangle}\right)_{S, N} d\langle V \rangle$$

$$+ \left(\frac{\partial}{\partial \gamma'} \gamma' \langle V \rangle\right)_{\langle V \rangle} d\gamma' + \left(\frac{\partial}{\partial \langle V \rangle} \gamma' \langle V \rangle\right)_{\gamma'} d\langle V \rangle$$

$$- \left(\frac{\partial}{\partial T} TS\right)_S dT - \left(\frac{\partial}{\partial S} TS\right)_T dS$$

$$= \left[\left(\frac{\partial U}{\partial S}\right)_{N,\langle V\rangle} - T\right] dS + \left[\left(\frac{\partial U}{\partial \langle V\rangle}\right)_{S,N} + \gamma'\right] d\langle V\rangle$$

$$+ \langle V\rangle \, d\gamma' - S\,dT + \left(\frac{\partial U}{\partial N}\right)_{S,\langle V\rangle} dN$$

im totalen Differential von ① kommt kein $dS$ und $d\langle V\rangle$ vor:

$$\Rightarrow \left(\frac{\partial U}{\partial S}\right)_{N,\langle V\rangle} = T$$

$$-\left(\frac{\partial U}{\partial \langle V\rangle}\right)_{S,N} = \gamma'$$

$\gamma'$: Ableitung von Energie nach Volumen $\Rightarrow$ Druck $p$

(Einheiten: $\frac{[U]}{[\langle V\rangle]} = \frac{\text{kg}\,\frac{\text{m}^2}{\text{s}^2}}{\text{m}^3} = \frac{\text{kg}}{\text{s}^2\text{m}} = \frac{\text{N}}{\text{m}^2}$ )

e) Teilchenzahlen $N_1, N_2$ konst,

Entropie addiert sich: $S(U, \langle V\rangle) = S_1(U_1, \langle V\rangle_1) + S_2(U_2, \langle V\rangle_2)$

Gesamtsystem ist abgeschlossen:

$U = U_1 + U_2 = \text{const.} \Rightarrow dU_1 = -dU_2$

$\langle V\rangle = \langle V\rangle_1 + \langle V\rangle_2 = \text{const.} \Rightarrow d\langle V\rangle_1 = -d\langle V\rangle_2$

Im Gleichgewicht ist $S$ maximal: $dS = 0$

$$dS = \frac{\partial S_1}{\partial U_1} dU_1 + \frac{\partial S_1}{\partial \langle V\rangle_1} d\langle V\rangle_1 + \frac{\partial S_2}{\partial U_2} dU_2 + \frac{\partial S_2}{\partial \langle V\rangle_2} d\langle V_2\rangle$$

$$= \left(\frac{\partial S_1}{\partial U_1} - \frac{\partial S_2}{\partial U_2}\right) dU_1 + \left(\frac{\partial S_1}{\partial \langle V\rangle_1} - \frac{\partial S_2}{\partial \langle V_2\rangle}\right) d\langle V\rangle_1 = 0$$

$$S_i = \frac{U_i}{T_i} + \frac{p_i}{T_i}\langle V\rangle_i + k \ln Z_i \quad ; \quad i = 1,2$$

$$\frac{\partial S_i}{\partial U_i} = \frac{1}{T_i} \quad , \quad \frac{\partial S_i}{\partial \langle V\rangle_i} = \frac{p_i}{T_i}$$

$$\Rightarrow 0 = \underbrace{\left(\frac{1}{T_1} - \frac{1}{T_2}\right)}_{=0} dU_1 + \underbrace{\left(\frac{p_1}{T_1} - \frac{p_2}{T_2}\right)}_{=0} d\langle V\rangle_1 \Rightarrow \boxed{\begin{matrix} T_1 = T_2 \\ p_1 = p_2 \end{matrix}}$$