Grand Potential

$\Omega = F - \mu' N = F - \mu n$

$$= -nRT - nRT \ln\left[\left(\frac{V}{V_0}\right)\left(\frac{n_0}{n}\right)\left(\frac{T}{T_0}\right)^{3/2}\right] + nRT \ln\left[\left(\frac{V}{V_0}\right)\left(\frac{n}{n_0}\right)\left(\frac{T}{T_0}\right)^{3/2}\right]$$

$$= -nRT$$

check: $\Omega = XY = -PV$ ✓

solve for ~~...~~ n as a function of μ

$$\frac{V}{V_0}\ \frac{n}{n_0}\ \left(\frac{T}{T_0}\right)^{3/2} = e^{-\frac{\mu}{RT}}$$

$$n = n_0 \frac{V_0}{V} \left(\frac{T}{T_0}\right)^{-3/2} e^{-\frac{\mu}{RT}}$$

$$\Omega = -n_0 \frac{V_0}{V} R \left(\frac{T}{T_0}\right)^{-3/2} T e^{-\frac{\mu}{RT}}$$

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I.5 Response functions

- thermodynamic quantities that are easiest to measure
- describe how a state variable changes as experimental parameters are tuned

I.5.1 Thermal response function (heat capacity)

$$\text{"}C = \frac{dQ}{dT}\text{"}$$

different heat capacities if different variables are kept constant while varying temperature.

a) $C_{X,\{N_j\}}$: change in heat as temperature is varied at constant X and $\{N_j\}$

$$dQ = dU - Y dX - \sum_j \mu_j' dN_j = \left(\frac{\partial U}{\partial T}\right)_{X,\{N_j\}} dT + \left[\left(\frac{\partial U}{\partial X}\right)_{T,\{N_j\}} - Y\right] dX + \sum_j \left[\left(\frac{\partial U}{\partial N_j}\right)_{T,X,\{N_{i\neq j}\}} - \mu_j'\right] dN_j$$

I.5.2 Mechanical Response function

isothermal susceptibility

$$\chi_T = \left(\frac{\partial X}{\partial Y}\right)_{T,\{N_j\}} = -\left(\frac{\partial^2 G}{\partial Y^2}\right)_{T,\{N_j\}}$$

adiabatic susceptibility

$$\chi_S = \left(\frac{\partial X}{\partial Y}\right)_{S,\{N_j\}} = -\left(\frac{\partial^2 H}{\partial Y^2}\right)_{S,\{N_j\}}$$

thermal expansivity

$$\alpha_{Y,\{N_j\}} = \left(\frac{\partial X}{\partial T}\right)_{Y,\{N_j\}}$$

Identities:

$$\chi_{T,\{N_j\}}\left(C_{Y,\{N_j\}} - C_{X,\{N_j\}}\right) = T\left(\alpha_{Y,\{N_j\}}\right)^2$$

$$C_{Y,\{N_j\}}\left(\chi_{T,\{N_j\}} - \chi_{S,\{N_j\}}\right) = T\left(\alpha_{Y,\{N_j\}}\right)^2$$

$$\frac{C_{Y,\{N_j\}}}{C_{X,\{N_j\}}} = \frac{\chi_{T,\{N_j\}}}{\chi_{S,\{N_j\}}}$$

Proof see problem set

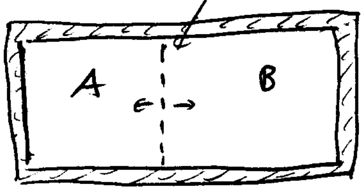
I. 6 Thermodynamic stability

Finite number of particles ⇒
thermodynamic variables (averages!) fluctuate spontaneously
During return to equilibrium entropy increases
⇒ equilibrium is stable if fluctuations decrease entropy

I.6.1 Local Equilibrium Conditions

PVT system movable porous membrane

isolated box, volume V_T



- two parts of the same gas
- solid/fluid in contact with its vapor

$$U_T = U_A + U_B \qquad \Delta U_T = 0$$
$$V_T = V_A + V_B \qquad \Delta V_T = 0$$
$$N_{j,T} = N_{j,A} + N_{j,B} \qquad \Delta N_{j,T} = 0$$
$$S_T = S_A + S_B$$

Entropy change:

$$\Delta S_T = \sum_{\alpha = A,B} \left[\left(\frac{\partial S_\alpha}{\partial U_\alpha}\right)_{V_\alpha, \{N_{j,\alpha}\}} \Delta U_\alpha + \left(\frac{\partial S_\alpha}{\partial V_\alpha}\right)_{U_\alpha, \{N_{j,\alpha}\}} \Delta V_\alpha + \sum_{j=1}^{\ell} \left(\frac{\partial S_\alpha}{\partial N_{j,\alpha}}\right)_{U_\alpha, V_\alpha, \{N_{k \neq j, \alpha}\}} \Delta N_{j,\alpha} \right]$$

$$= \left(\frac{1}{T_A} - \frac{1}{T_B}\right) \Delta U_A + \left(\frac{P_A}{T_A} - \frac{P_B}{T_B}\right) \Delta V_A - \sum_{j=1}^{\ell} \left(\frac{\mu'_{j,A}}{T_A} - \frac{\mu'_{j,B}}{T_B}\right) \Delta N_{j,A} + \ldots$$

$\Delta U_A = -\Delta U_B$
$\Delta V_A = -\Delta V_B$
$\Delta N_{j,A} = -\Delta N_{j,B}$

stability of the equilibrium $\Rightarrow$ $(\Delta S_T) \leq 0$

ΔU_A, ΔV_A, $\Delta N_{j,A}$ can have both signs

$$\Rightarrow \boxed{T_A = T_B \qquad P_A = P_B \qquad \mu'_{j,A} = \mu'_{j,B}}$$

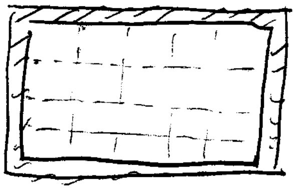
Similar arguments:

wall not movable: only $T_A = T_B$ $\quad \mu'_{j,A} = \mu'_{j,B}$

wall not permeable: only $T_A = T_B$ $\quad P_A = P_B$

etc..

I.6.2 Local Stability Conditions

M cells:  $V_T, S_T, U_T, \{N_{j,T}\}$

$P^\circ, T^\circ, \{\mu_j^\circ\}$ identical in all cells (see I.6.1)

cell α: $V_\alpha, S_\alpha, U_\alpha, \{N_{j,\alpha}\}$ $\quad \Delta U_\alpha = U_\alpha - U_\alpha^\circ \quad \Delta V_\alpha = V_\alpha - V_\alpha^\circ \quad \Delta N_{j,\alpha} = N_{j,\alpha} - N_{j,\alpha}^\circ$

equilibrium quantities

$$S_\alpha(U_\alpha, V_\alpha, \{N_{j,\alpha}\}) = S_\alpha^\circ(U_\alpha^\circ, V_\alpha^\circ, \{N_{j,\alpha}\}^\circ) + \left(\frac{\partial S_\alpha}{\partial U_\alpha}\right)^\circ_{V,\{N_j\}} \Delta U_\alpha + \left(\frac{\partial S_\alpha}{\partial V_\alpha}\right)^\circ_{U,\{N_j\}} \Delta V_\alpha + \sum_{j=1}^{\ell} \left(\frac{\partial S_\alpha}{\partial N_{j,\alpha}}\right)^\circ_{U,V,\{N_{k\neq j}\}} \Delta N_{j,\alpha} + \text{higher order terms}$$

$$\Delta S_T = \sum_{\alpha=1}^{M} S_\alpha(U_\alpha, V_\alpha, \{N_{j,\alpha}\}) - S_\alpha^\circ(U_\alpha^\circ, V_\alpha^\circ, \{N_{j,\alpha}\}^\circ)$$

$$= \underbrace{\sum_{\alpha=1}^{M}\left[\left(\frac{\partial S_\alpha}{\partial U_\alpha}\right)_{V,\{N_j\}} \Delta U_\alpha + \left(\frac{\partial S_\alpha}{\partial V_\alpha}\right)_{U,\{N_j\}} \Delta V_\alpha + \sum_{j=1}^{\ell}\left(\frac{\partial S_\alpha}{\partial N_{j,\alpha}}\right)_{U,V,\{N_{k\neq j}\}} \Delta N_{j,\alpha}\right]}_{=0 \text{ according to I.6.1}} + \text{higher order terms}$$

$\Rightarrow$ have to look at second derivatives!

$$\left(\frac{\partial^2 S_\alpha}{\partial U_\alpha^2}\right)_{V,\{N_j\}} \Delta U_\alpha \Delta U_\alpha + \left(\frac{\partial}{\partial V_\alpha}\left(\frac{\partial S_\alpha}{\partial U_\alpha}\right)_{V,\{N_j\}}\right)^{0}_{U,\{N_j\}} \Delta U_\alpha \Delta V_\alpha + \sum_{j=1}^{\ell}\left(\frac{\partial}{\partial N_{j,\alpha}}\left(\frac{\partial S_\alpha}{\partial U_\alpha}\right)_{V,\{N_j\}}\right)^{0}_{U,V,\{N_{k\neq j}\}} \Delta N_{j,\alpha} \Delta U_\alpha$$

$$= \Delta U_\alpha \left[\left(\frac{\partial \frac{1}{T_\alpha}}{\partial U_\alpha}\right)^{0}_{V,\{N_j\}} \Delta U_\alpha + \left(\frac{\partial \frac{1}{T_\alpha}}{\partial V_\alpha}\right)^{0}_{U,\{N_j\}} \Delta V_\alpha + \sum_{j=1}^{\ell}\left(\frac{\partial \frac{1}{T_\alpha}}{\partial N_{j,\alpha}}\right)^{0}_{V,U,\{N_{k\neq j}\}} \Delta N_{j,\alpha}\right]$$

$$= \Delta U_\alpha \Delta \frac{1}{T_\alpha}$$

similar for ΔV_α and $\Delta N_{j,\alpha}$

$$\Rightarrow \Delta S_T = \frac{1}{2}\sum_{\alpha=1}^{M}\left[\Delta\left(\frac{1}{T_\alpha}\right)\Delta U_\alpha + \Delta\left(\frac{P_\alpha}{T_\alpha}\right)\Delta V_\alpha - \sum_{j=1}^{\ell}\Delta\left(\frac{\mu'_{j,\alpha}}{T_\alpha}\right)\Delta N_{j,\alpha}\right] + \text{third order terms}$$

use $\Delta\left(\frac{1}{T_\alpha}\right) = -\frac{1}{T^{0\,2}}\Delta T_\alpha$ and $\Delta U_\alpha = T^0 \Delta S_\alpha - P^0 \Delta V_\alpha + \sum_{j=1}^{\ell} \mu_j'^{\,0} \Delta N_{j,\alpha}$

$$\Delta S_T = -\frac{1}{2T^0}\sum_{\alpha=1}^{M}\left[\Delta T_\alpha \Delta S_\alpha - \Delta P_\alpha \Delta V_\alpha + \sum_{j=1}^{\ell}\Delta\mu'_{j,\alpha}\Delta N_{j,\alpha}\right] + \text{third order terms}$$

$$\underset{\substack{\uparrow \\ \text{choose } T,V,N_j \\ \text{as independent} \\ \text{variables}}}{=} -\frac{1}{2T^0}\sum_{\alpha=1}^{M}\Bigg\{\left(\frac{\partial S_\alpha}{\partial T_\alpha}\right)_{V,\{N_j\}}(\Delta T_\alpha)^2 + \underbrace{\left[\left(\frac{\partial S_\alpha}{\partial V_\alpha}\right)_{T,\{N_j\}} - \left(\frac{\partial P_\alpha}{\partial T_\alpha}\right)_{V,\{N_j\}}\right]}_{=0 \text{ Maxwell-relations}}\Delta T_\alpha \Delta V_\alpha$$

$$+ \sum_{j=1}^{\ell}\underbrace{\left[\left(\frac{\partial S_\alpha}{\partial N_j^\alpha}\right)_{T,V,\{N_{k\neq j}\}} + \left(\frac{\partial \mu'_{j,\alpha}}{\partial T_\alpha}\right)_{V,\{N_k\}}\right]}_{=0}\Delta T_\alpha \Delta N_{j,\alpha}$$

$$- \left(\frac{\partial P_\alpha}{\partial V_\alpha}\right)_{T,\{N_j\}}(\Delta V_\alpha)^2 + \sum_{j=1}^{\ell}\underbrace{\left[\left(\frac{\partial \mu_{j,\alpha}}{\partial V_\alpha}\right)_{T,\{N_k\}} - \left(\frac{\partial P_\alpha}{\partial N_{j,\alpha}}\right)_{T,V,\{N_{k\neq j}\}}\right]}_{=0}\Delta V_\alpha \Delta N_{j,\alpha}$$

$$+ \sum_{i=1}^{\ell}\sum_{j=1}^{\ell}\left(\frac{\partial \mu'_{j,\alpha}}{\partial N_{i,\alpha}}\right)_{T,V,\{N_{k\neq i}\}}\Delta N_{i,\alpha}\Delta N_{j,\alpha}\Bigg\}$$

$$\Delta S_T \le 0 \Rightarrow \left(\frac{\partial S}{\partial T}\right)_{V,\{N_j\}} \ge 0 \quad \Rightarrow \boxed{C_V \ge 0}$$

$$\left(\frac{\partial P}{\partial V}\right)_{T,\{N_j\}} \le 0 \quad \Rightarrow \boxed{K_T \ge 0}$$

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$$\sum_{i=1}^{\ell}\sum_{j=1}^{\ell}\left(\frac{\partial \mu_j'}{\partial N_i}\right)_{T,V,\{N_{k\neq i}\}}\Delta N_i \Delta N_j \ge 0 \Rightarrow \text{Matrix } \left(\frac{\partial \mu_j'}{\partial N_i}\right)_{T,V,\{N_{k\neq i}\}} \text{ positive definite}$$