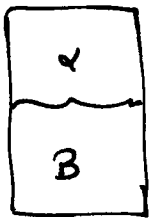
Equilibrium Conditions



$$\max\left[S^\alpha(E^\alpha, V^\alpha, N^\alpha) + S^\beta(E^\beta, V^\beta, N^\beta)\right]$$

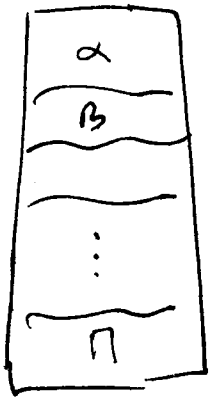
$$dS^\alpha + dS^\beta = 0$$

$$\frac{1}{T^\alpha}dE^\alpha + \frac{p^\alpha}{T^\alpha}dV^\alpha - \frac{\mu^\alpha}{T^\alpha}dN^\alpha + \frac{1}{T^\beta}dE^\beta + \frac{p^\beta}{T^\beta}dV^\beta - \frac{\mu^\beta}{T^\beta}dN^\beta = 0$$

Isolated total system, $dE^\alpha + dE^\beta = 0$, $dV^\alpha + dV^\beta = 0$, $dN^\alpha + dN^\beta = 0$

$$\Rightarrow \left(\frac{1}{T^\alpha} - \frac{1}{T^\beta}\right)dE^\alpha + \left(\frac{p^\alpha}{T^\alpha} - \frac{p^\beta}{T^\beta}\right)dV^\alpha + \left(\frac{\mu^\alpha}{T^\alpha} - \frac{\mu^\beta}{T^\beta}\right)dN^\alpha = 0 \Rightarrow$$

$T^\alpha = T^\beta \quad p^\alpha = p^\beta \quad \mu^\alpha = \mu^\beta$ (1-component)



For multiphase equilibrium, involving Π phases, C components

$$T^\alpha = T^\beta = \cdots = T^\Pi$$
$$p^\alpha = p^\beta = \cdots = p^\Pi$$
$$\mu_1^\alpha = \mu_1^\beta = \cdots = \mu_1^\Pi$$
$$\vdots$$
$$\mu_C^\alpha = \mu_C^\beta = \cdots = \mu_C^\Pi$$

$(\Pi - 1)\cdot(C+2)$ equations

$\Pi \cdot (C+1)$ independent intensive variables

$$F = -(\Pi - 1)(C+2) + \Pi(C+1) = -\Pi C + C - 2\Pi + 2 + \Pi C + \Pi$$

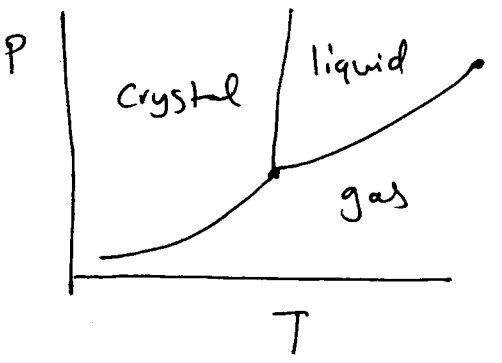
F "degrees of freedom" – number of independent intensive variables

$$\Rightarrow \boxed{F = C - \Pi + 2}$$ Gibbs phase rule

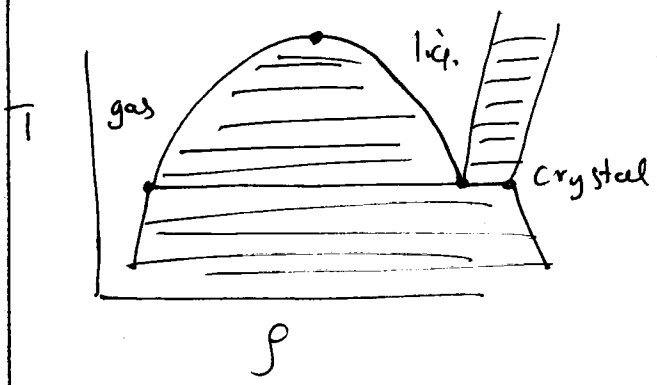
If there are chemical reactions in the system, these also provide equations linking the chemical potentials of the reactants + products: $F = C - \Pi + 2 - R$

R = independent reactions

Clapeyron Equation



The phase rule suggests that on a (P,T) plane for C=1 1-phase regions have 2 degrees of freedom (areas), 2-phase have 1 (lines) and 3-phase 0 (points).



For other properties (e.g., density ρ) there are discontinuities going from one phase to another.

The slope $\left(\frac{dP}{dT}\right)_{\alpha\text{-}\beta \text{ coexistence}}$ is connected to fundamental properties:

$$d\mu^{\alpha}(T,P) = d\mu^{\beta}(T,P) \qquad \mu = g \text{ for } C=1$$

$$\Rightarrow -s^{\alpha}dT + v^{\alpha}dP = -s^{\beta}dT + v^{\beta}dP \Rightarrow$$

$$\left(\frac{dP}{dT}\right)_{\alpha\text{-}\beta \text{ coexistence}} = \frac{s^{\beta}-s^{\alpha}}{v^{\beta}-v^{\alpha}} = \frac{\Delta s}{\Delta v}$$

no assumptions or approximations!

Since $h = g + Ts$ $\quad \Delta h = \cancel{\Delta g} + T\Delta s$

$\Delta g = 0$ @ coexistence

$$\therefore \left(\frac{dP}{dT}\right)_{\alpha\text{-}\beta \text{ coexistence}} = \frac{\Delta h}{T\Delta v}$$

Clapeyron equation

Under quite restrictive assumptions, this can be transformed further:

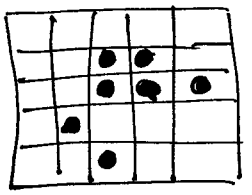
Assume: B = gas, follows $PV^B = RT$

α = liquid or solid, $v^B \gg v^\alpha$

Then $\left.\frac{dP}{dT}\right)_{LV}^{SVor} = \frac{h^B - h^\alpha}{T(V^B - V^\alpha)} \Rightarrow \left.\frac{dP}{dT}\right)_{vap} = \frac{\Delta h_{vap}}{T^2 R} P$

$\Rightarrow \frac{d\ln P}{d(1/T)} = -\frac{\Delta h_{vap}}{R}$ Clausius-Clapeyron Equation (= approximate)

Microscopic view



(E = −5ε)

Lattice-gas model, N particles, V sites

Nearest-neighbor attraction

Energy −ε

Energy = ? Assume each molecule has the same local environment

Energy per molecule: $e = -\frac{1}{2}\left(z\frac{N}{V}\right)\varepsilon$ (mean-field approx.)

$\frac{1}{2}$ to prevent double-counting

$\left(z\frac{N}{V}\right)$ average # of neighbors

$E = Ne = -\frac{\varepsilon z}{2}\left(\frac{N^2}{V}\right) = -\frac{\varepsilon z}{2}\rho^2 V$

Entropy S? $\Omega = \frac{V!}{N!(V-N)!} \Rightarrow S = k_B \ln \Omega =$

$= k_B\left[V\ln V - \cancel{V} - N\ln N + \cancel{N} - (V-N)\ln(V-N) + \cancel{V} - \cancel{N}\right]$

$= -k_B V\left[\ln\frac{V-N}{V} + \frac{N}{V}\ln\frac{N}{V-N}\right] = -k_B V\left[\ln(1-\rho) + \rho\ln\frac{\rho}{1-\rho}\right]$

Helmholtz free energy $A = E - TS$

$$\frac{A}{N} = -\frac{\varepsilon z}{2}\rho + k_B T \frac{1}{\rho}\left[\rho \ln\rho + (1-\rho)\ln(1-\rho)\right]$$

We can obtain the pressure from

$$P = -\left.\frac{\partial A}{\partial V}\right)_{T,N} = -N\frac{\partial \rho}{\partial V}\left(\frac{\partial (A/N)}{\partial \rho}\right)_T = \rho^2\left(\frac{\partial (A/N)}{\partial \rho}\right)_T =$$

$$= -\frac{\varepsilon z}{2}\rho^2 + k_B T \rho^2 \frac{\partial}{\partial \rho}\left[\ln\rho + \frac{1-\rho}{\rho}\ln(1-\rho)\right] =$$

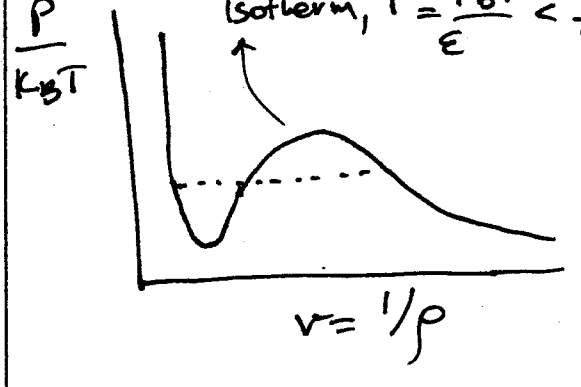
$$= -\frac{\varepsilon z}{2}\rho^2 + k_B T \rho^2\left[\frac{1}{\rho} - \frac{1-\rho}{\rho}\cdot\frac{1}{1-\rho} - \frac{1}{\rho^2}\ln(1-\rho)\right] \Rightarrow$$

$$\Rightarrow \boxed{P = -\frac{\varepsilon z \rho^2}{2} - k_B T \ln(1-\rho)}$$

recall unusual units of v, ρ (dimensionless) → P has units of energy/volume

or $$\frac{P}{k_B T} = -\frac{\varepsilon z}{k_B T}\frac{\rho^2}{2} - \ln(1-\rho) \quad (1)$$

Eq. (1) shows a "van der Waals loop" for $\frac{k_B T}{\varepsilon} \le \frac{z}{4}$



Recall Maxwell construction:

$$\left.\frac{\partial \mu}{\partial P}\right)_T = v \Rightarrow \Delta\mu = \int_{P_1}^{P_2} v\,dP$$

Criticality conditions:

$$\left.\frac{\partial P}{\partial \rho}\right)_T = 0 \quad \text{and} \quad \left.\frac{\partial^2 P}{\partial \rho^2}\right)_T = 0$$

Differentiation of P gives:

$$\left.\frac{\partial P}{\partial \rho}\right)_T = -\varepsilon z \rho_c + \frac{k_B T_c}{1-\rho_c} = 0 \quad (A) \qquad \left.\frac{\partial^2 P}{\partial \rho^2}\right)_T = -\varepsilon z + \frac{k_B T_c}{(1-\rho_c)^2} = 0 \quad (B)$$

Solving (B) $k_B T_c = \varepsilon z (1-\rho_c)^2 \xrightarrow{(A)} \varepsilon z \rho_c/(1-\rho_c) = \varepsilon z$

$$\Rightarrow \boxed{\rho_c = \frac{1}{2}}$$

expected because of symmetry between particles + holes

Substituting $\rho_c = 1/2$ in expression (4) confirms our statement about T_c:

$$\frac{k_B T_c}{\varepsilon} = z\rho_c(1-\rho_c) = \frac{z}{4}$$

In 3 dimensions, $z=6 \Rightarrow T_c^* = 1.5$

The true value (from simulations) is $T_c^* \simeq 1.12$

So mean-field theory overestimates T_c.

The reason is that it ignores correlations and fluctuations in the local environment.