Thermodynamics of the van der Waals gas; liquid-gas coexistence & Maxwell construction

Van der Waals eqn of state:

$$p = \frac{Nk_BT}{V-Nb} - a\left(\frac{N}{V}\right)^2$$

$$p = -\frac{\partial F}{\partial V} \Rightarrow F(T,V_2) - F(T,V_1) = \int_{V_1}^{V_2} dV \left(a\left(\frac{N}{V}\right)^2 - \frac{Nk_BT}{V-Nb}\right)$$

$$= aN^2\left(-\frac{1}{V}\right)\Big|_{V_1}^{V_2} - Nk_BT\ln(V-Nb)\Big|_{V_1}^{V_2} =$$

$$= -\frac{aN^2}{V_2} + \frac{aN^2}{V_1} - Nk_BT\ln\frac{V_2-Nb}{V_1-Nb}$$

For $V_1 \to \infty$ at fixed N, T - the gas becomes ideal, and

$$F(T,V_1) \approx F_{ideal}(T,V_1) = Nk_BT\{\ln N - \ln V_1 -$$

$$-\frac{3}{2}\ln T + \frac{3}{2}\ln\frac{h^2}{2\pi mk_B} - 1\} = Nk_BT\{\ln\frac{N\lambda^3}{V} - 1\}$$

$$\boxed{\begin{aligned} F(T,V_2) \approx -\frac{aN^2}{V_2} - Nk_BT\ln(V_2-Nb) + Nk_BT \times \\ \times\{\ln N - \frac{3}{2}\ln T + \frac{3}{2}\ln\frac{h^2}{2\pi mk_B} - 1\} \end{aligned}}$$

$$\boxed{F(T,V) = -\frac{aN^2}{V} - Nk_BT\ln(V-Nb) + \underbrace{f_{\text{lina}}(T,N)}_{\text{but NO } V}}$$

Quick derivation

$$\boxed{F(T,V) = \lim_{V_1\to\infty}\left(F_{\substack{ideal\\gas}}(T,V_1) + \int_{V_1}^{V} dV'\left(a\frac{N^2}{V'^2} - \frac{Nk_BT}{V'-Nb}\right)\right)}$$

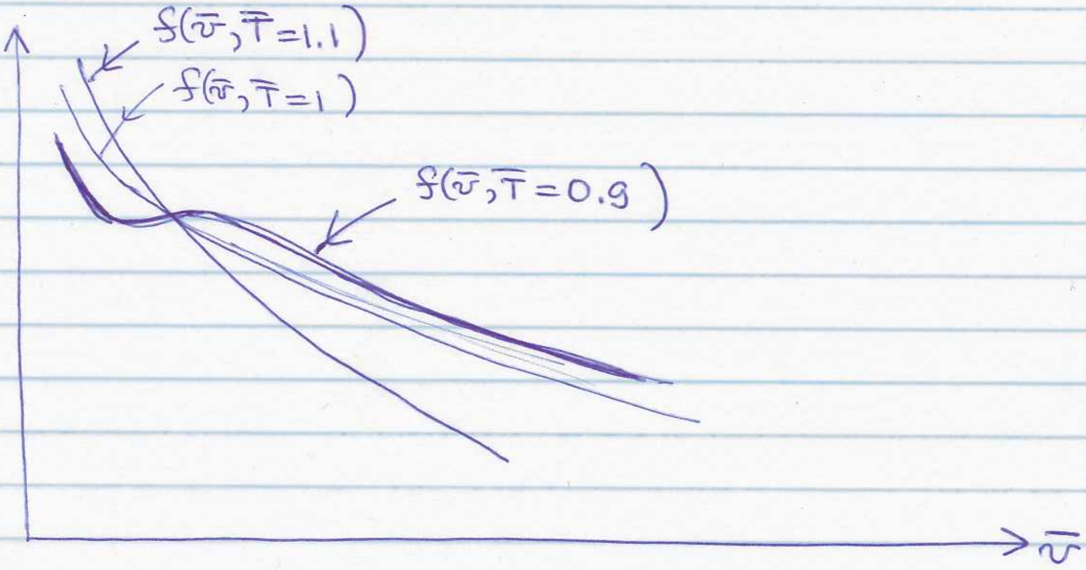
$$\boxed{F_{vdW}^{(N,V,T)} = -a\frac{N^2}{V} + Nk_BT\left\{\ln\left(\frac{N\lambda^3(T)}{V-Nb}\right) - 1\right\}}$$

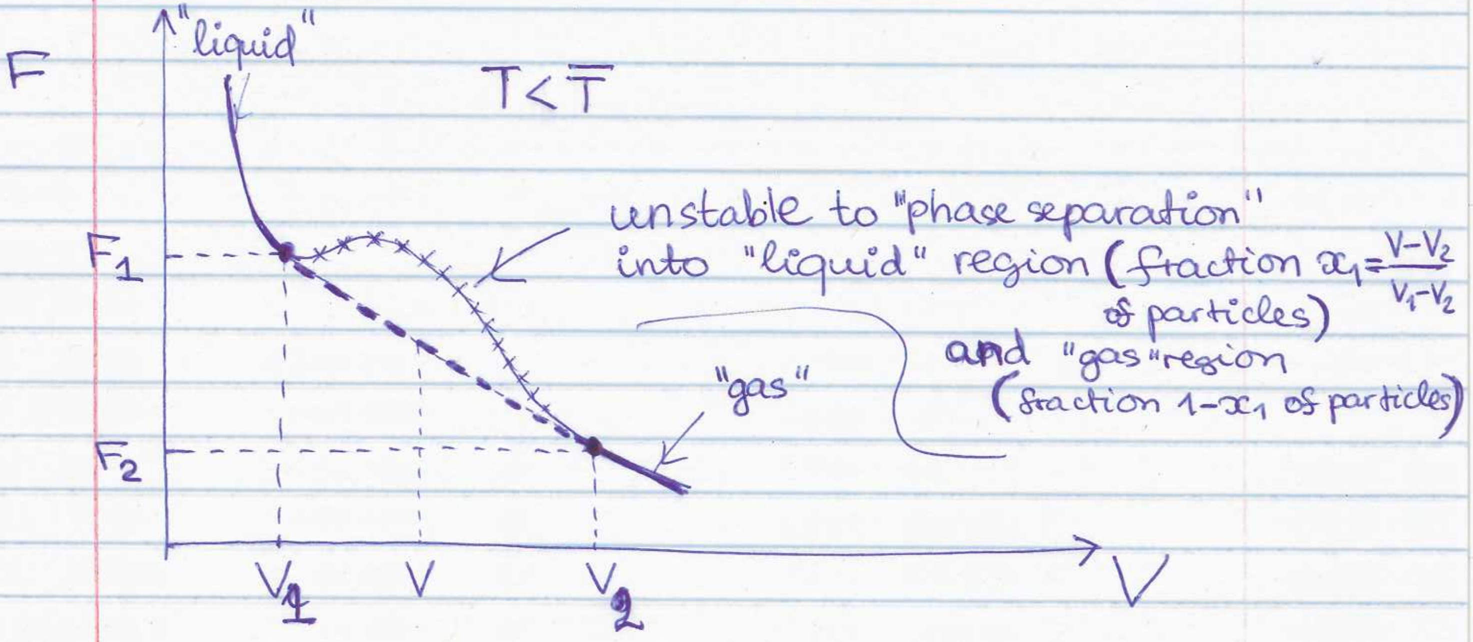
$$\frac{F(T,\overset{N,}{}V)}{N} = -\frac{a}{v}\ \text{[redacted]}\ k_BT\ln(v-b) + \text{func}(\text{[redacted]}T)$$

$$\boxed{f(v_{,T})} = -\frac{a}{v}\ \text{[redacted]}\ k_BT\ln(v-b) = -\frac{a}{3b\cdot\bar{v}}\ \text{[redacted]}\ \frac{8a}{27b}\bar{T}\ln(3\bar{v}-1)$$

+ const. indep of $\bar{v}$.

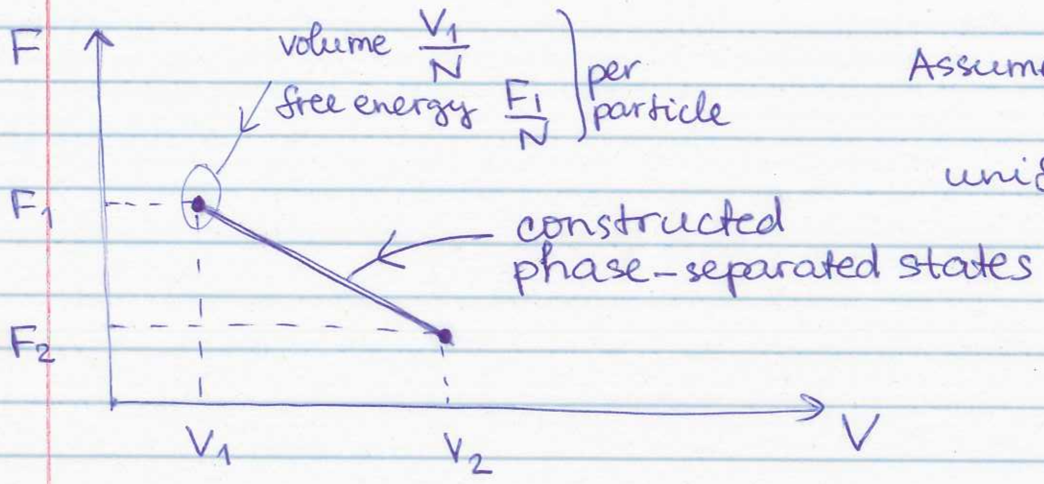
$$\boxed{= \frac{a}{3b}\left(-\frac{1}{\bar{v}}\ \text{[redacted]}\ \frac{8}{9}\bar{T}\ln(3\bar{v}-1)\right) + \text{const. indep of } \bar{v}}$$





N_{tot}

Thermodynamic variational principle: for fixed T, V, the stable state is the one minimizing the free energy $\Rightarrow$ implies F must be a convex fnctn of V.



Assume (V_1, F_1)
(V_2, F_2) are uniform states

Can construct a "phase-separated" state with fraction of particles

x_1 in state 1

x_2 in state 2

$$x_1 \cdot N + x_2 \cdot N = N$$
$$\Rightarrow x_1 + x_2 = 1$$

with: * free energy $F(x_1,x_2) = x_1 \cdot N \cdot \frac{F_1}{N} + x_2 \cdot N \cdot \frac{F_2}{N} = x_1 F_1 + x_2 F_2$

* total volume $V(x_1, x_2) = x_1 V_1 + x_2 V_2$

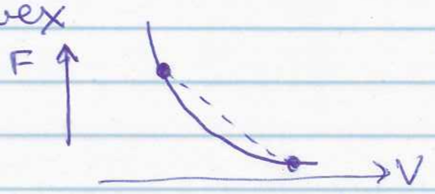
$$\begin{cases} F(x_1) = x_1 F_1 + (1-x_1) F_2 \\ V(x_1) = x_1 V_1 + (1-x_1) V_2 \end{cases} \qquad 0 \le x_1 \le 1$$

(V, F)

as we vary parameter $x_1 \in (0,1)$, this follows a straight line connecting (V_1, F_1) (when $x_1 = 1$) and (V_2, F_2) (when $x_1 = 0$)

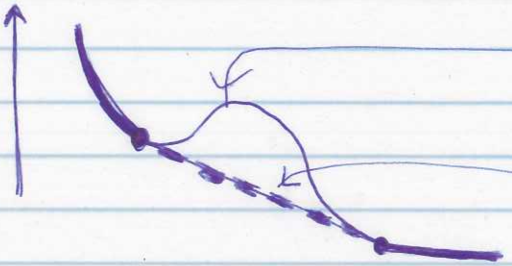
$$x_1 = \frac{V - V_2}{V_1 - V_2}$$

If we have a "guess" free energy curve (e.g. an upper bound variational curve) and if it is convex



, then we cannot lower the free energy any further.

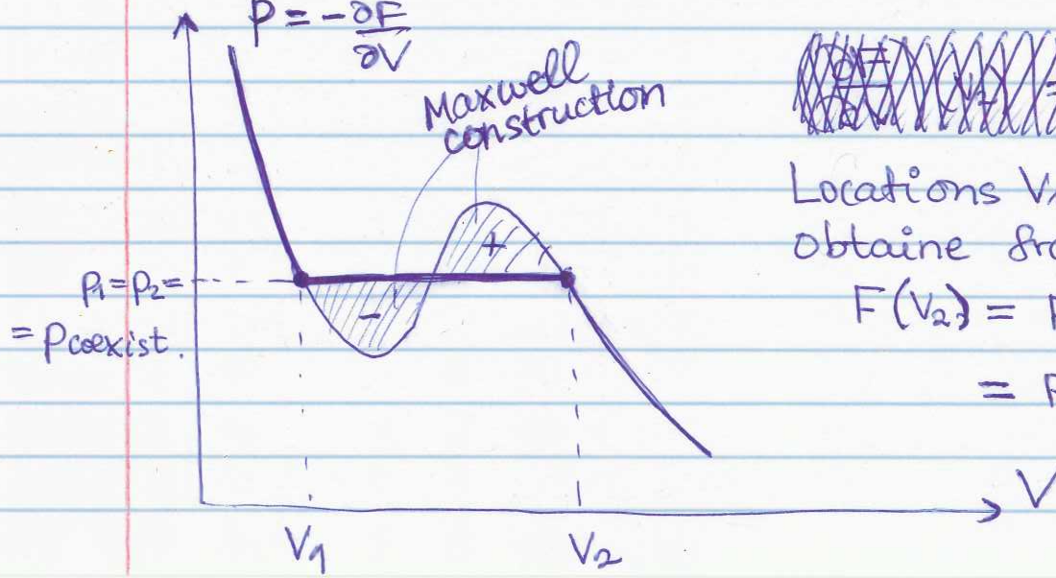
On the other hand, if by using some "uniform liquid" gas we obtained "trial free energy", then by further allowing phase separation we can lower the free energy to



Geometric construction: enveloping curve of all possible straight lines $(V_1, F_1) - (V_2, F_2)$.

Back to the van der Waals gas:

Along the phase-separated portion, the pressure $-\frac{\partial F}{\partial V}$ remains constant and equal that at the end points, $p = p_1 = p_2$ (the straight line segment is tangent to the "uniform liquid" portion at V_1 and "uniform gas" portion at V_2).

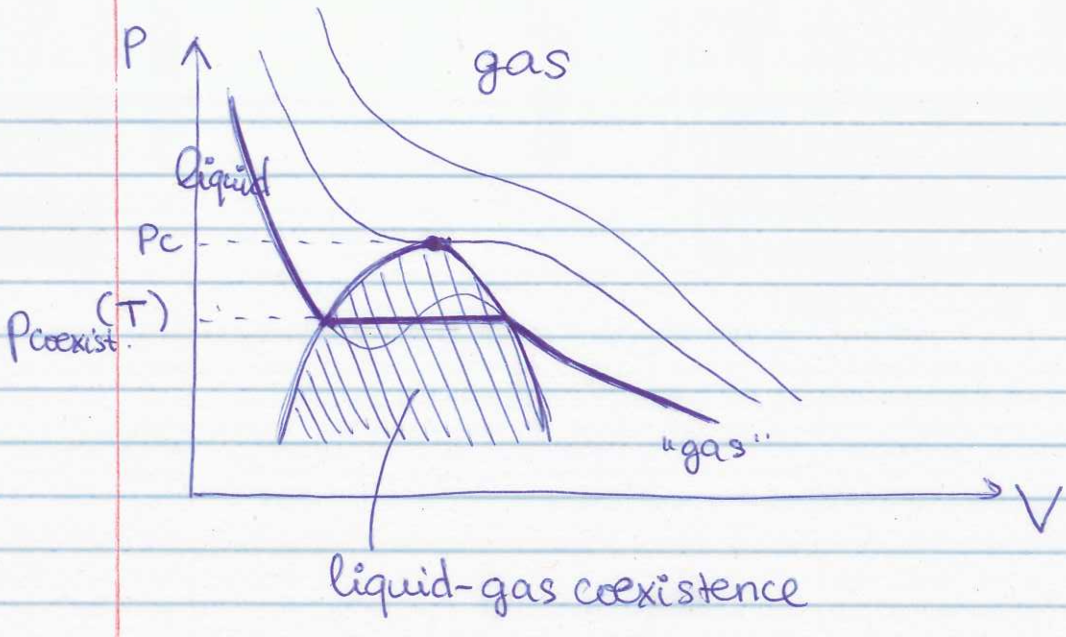


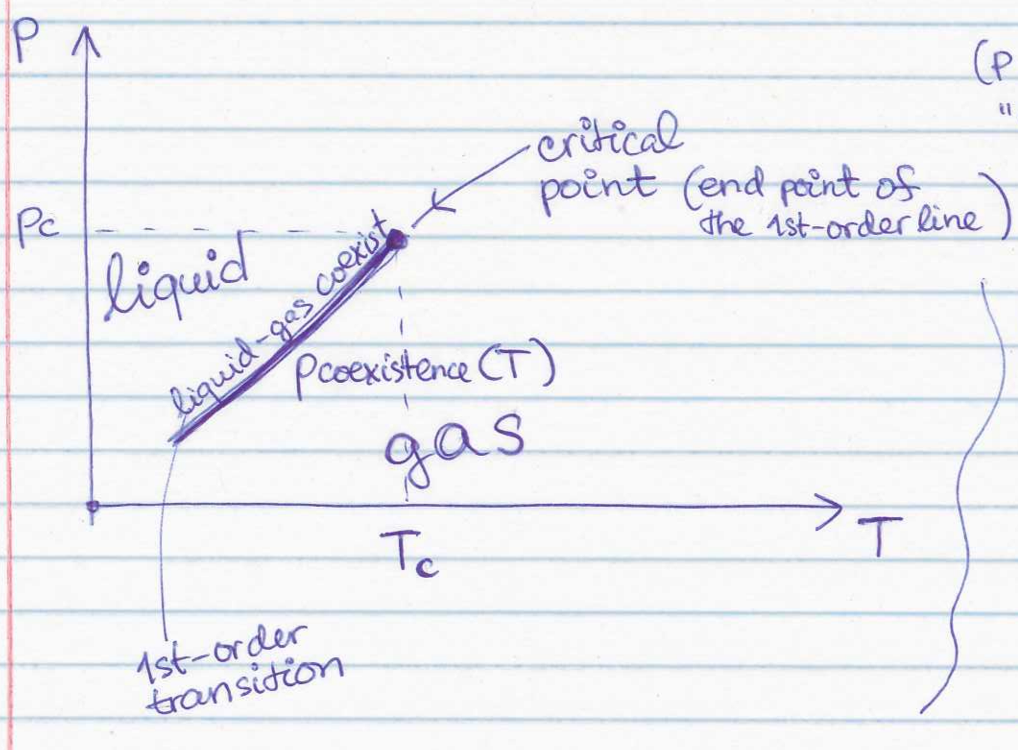
Locations V_1 and V_2 can be obtaine from:

$$F(V_2) = F(V_1) - p_{coex.} \cdot (V_2 - V_1);$$
$$= F(V_1) - \int_{V_1}^{V_2} p\, dV$$

Maxwell constr.

$$\Rightarrow \boxed{\int_{V_1}^{V_2} p\, dV = p_{coex.}(V_2 - V_1)}$$





(p,T) - both "intensive variables"

can motivate this by "walking" along the isotherm for $T > T_c$ and $T < T_c$

To think in terms of p,T variables, it is convenient to do Legendre transformation $V \to p = -\frac{\partial F}{\partial V}$

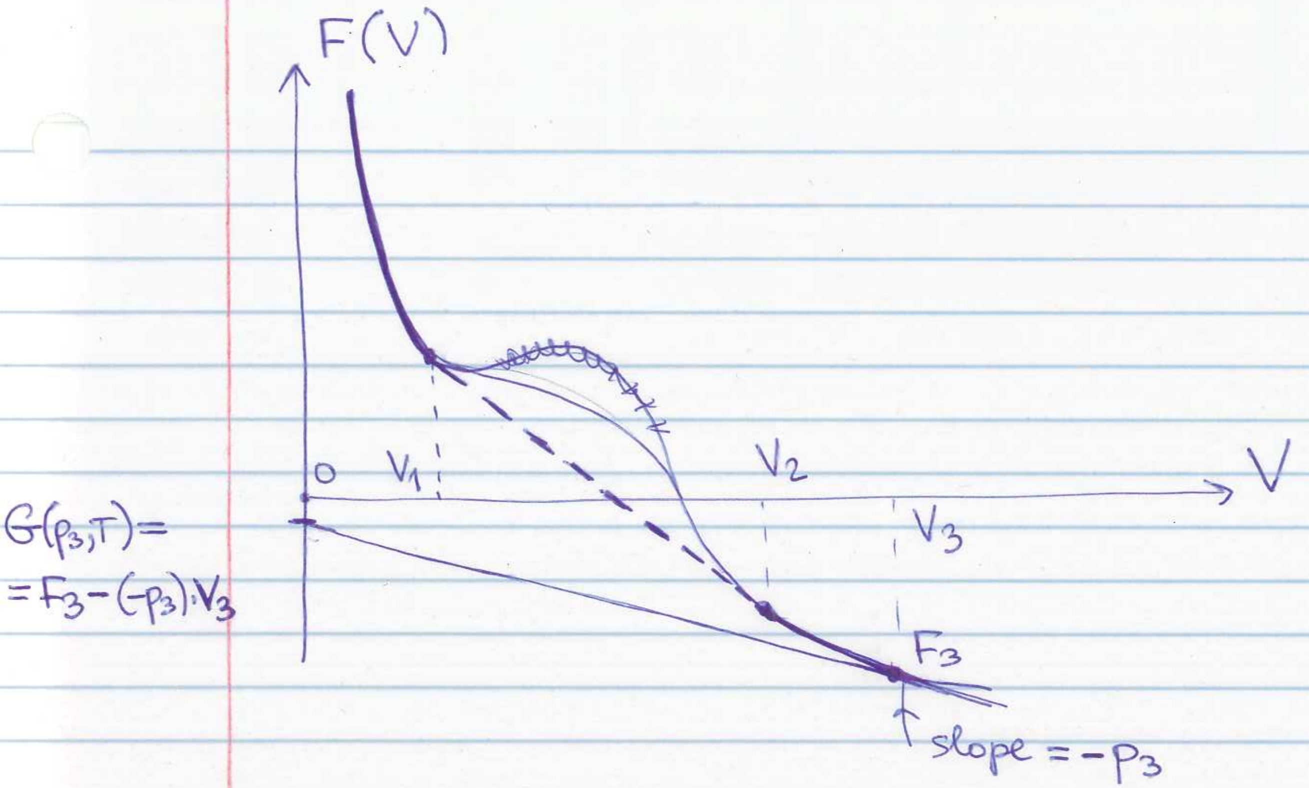
to Gibbs free energy

$$p = -\frac{\partial F}{\partial V};$$

$$G(p,T) = F(T,V) + pV;$$

$$G(p,T) = \min_V \{ F(T,V) + pV \}$$

Fixed T



slope @ V_1 = slope @ V_2 = $p_1 = p_2 = p_{\text{coexistence}}(T)$

$$G(p,T) \text{ has two branches : } \begin{cases} G_{gas}(p,T), & p<p_{coex.}(T) \\ G_{liquid}(p,T), & p>p_{coex.}(T) \end{cases}$$

$$G_{gas}(p_{coex.}(T),T) = G_{liq.}(p_{coex}(T),T)$$

Gibbs free energy per particle ≡ chemical potential

$\boxed{\mu_{gas}(p,T) = \mu_{liq}(p,T)}$ — defines a line in the p-T plane.

* Aside: coexistence of three phases, say solid, liquid, and gas: $\boxed{\mu_{gas}(p,T) = \mu_{liq}(p,T) = \mu_{solid}(p,T)}$ — defines a point in the p-T plane

"triple point"