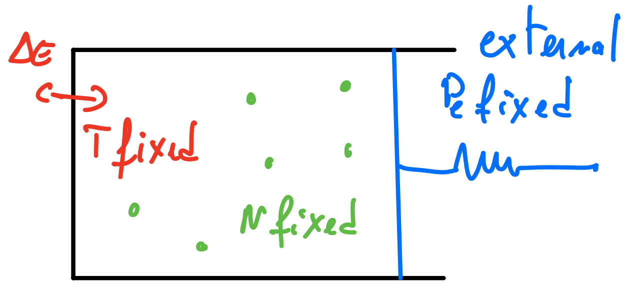
4.3) liquid gas phase transition in the isobaric ensemble

By changing ensemble, one shows that



$$P(\varphi) = \frac{1}{Z_I} e^{-\beta E(\varphi) - \beta P_e V(\varphi)}$$

where $Z_I(P,T,N) = \int_0^\infty dV\, e^{-\beta P_e V} Z_c(V,T,N) = \int_0^\infty dV\, e^{-\beta[P_e V + F(T,V,N)]}$

At large N, F is extensive, $F(N,V,T) \simeq N f(v,T)$; $v = \frac{V}{N}$ so that

$$Z_I = \int_0^\infty N\, dv\, e^{-\beta N [P_e v + f(v,T)]} = N \int_0^\infty dv\, e^{-\beta N \mu_L(v;T,P_e)}$$

where we call $\mu_L(v;T,P_e)$ the Landau chemical potential of the macrostate

with volume V / free volume $v = \frac{V}{N}$: $\mu_L(v,T,P_e) = P_e v + f(v,T)$

As $N \to \infty$ $Z_I \sim e^{-\beta N \mu_L(v^*;T,P_e)} = e^{-\beta N[Pv^* + f(v^*,T)]} = e^{-\beta[PV^* + F(V^*,N,T)]}$

As usual, $P(v) \underset{N\to\infty}{\sim} \delta(v - v^*)$ with $v^* = \underset{v}{\text{argmin}}\, \mu_L(v;T,P_e) = \underset{v}{\text{argmin}} [P_e v + f(v,T)]$

$$\Rightarrow \underbrace{P_e}_{P_{\text{external}}\text{ (imposed)}} = -\frac{\partial f}{\partial v}\Big|_{v^*} = -\frac{\partial F}{\partial V}\Big|_{V^*} = \underbrace{P_c}_{P_{\text{canonical}}\text{ (selected)}}$$

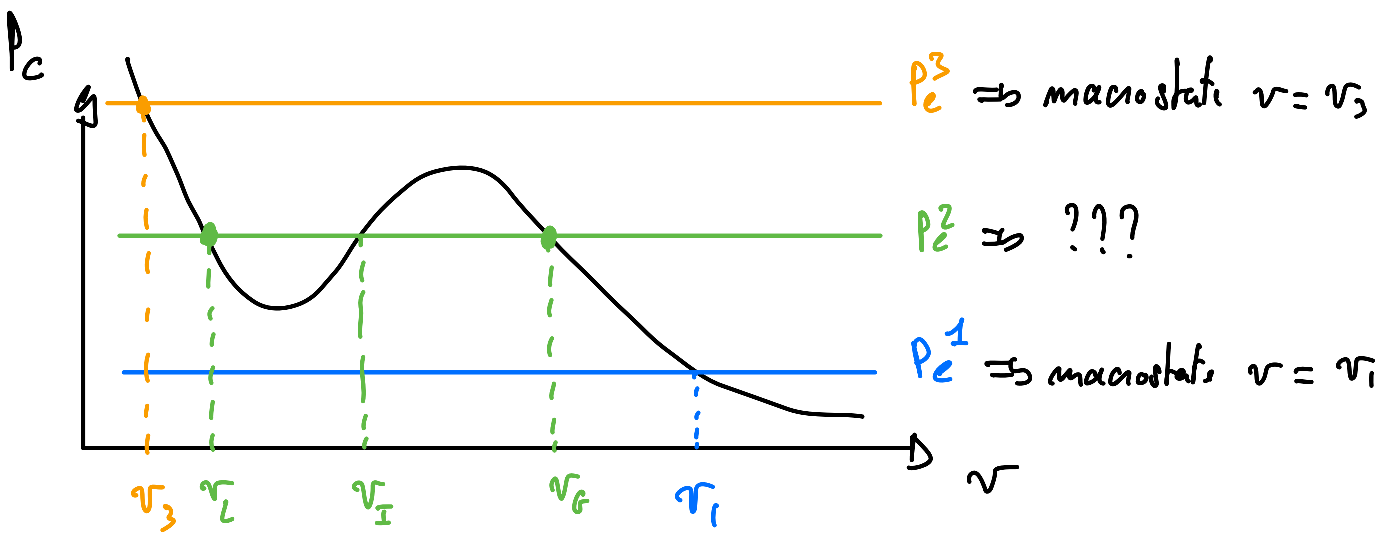
if there is a unique solution.

The most likely macrostate is the one whose canonical pressure is equal to the external pressure. Then

$$N\mu_L(v^*) = PV^* + F \underset{N\to\infty}{=} F - G = F - (F - \mu N) = \mu N$$

⇒ the chemical potential is the Landau chemical of the most likely macrostate.

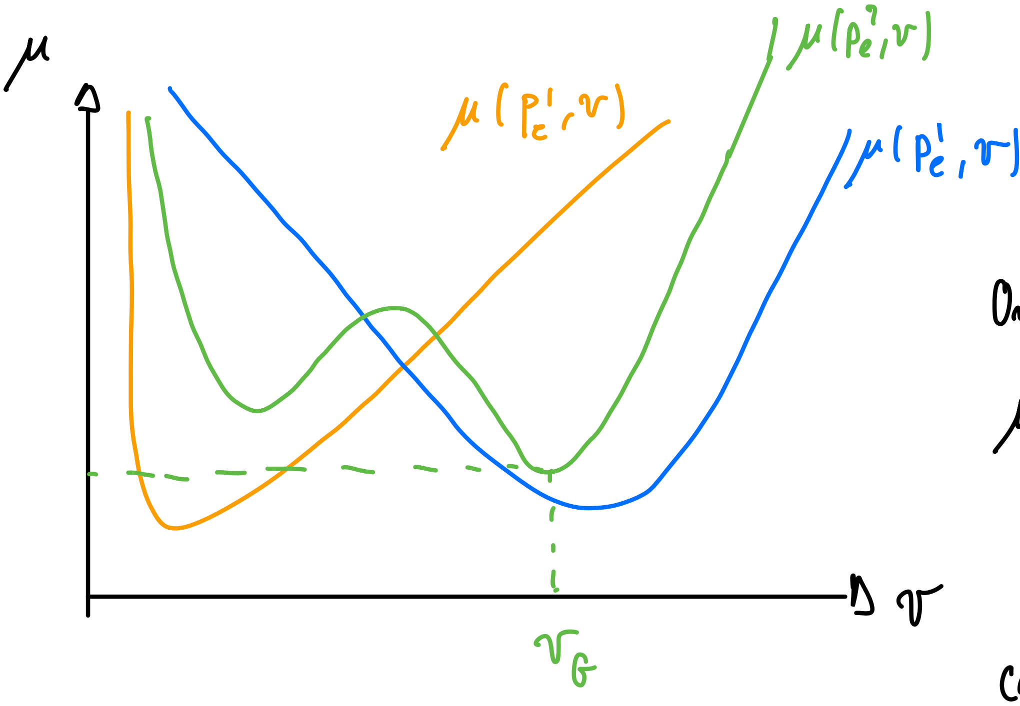
Summary: If one imposes an external pressure p_e & there is a unique solution $P_c(v) = p_e$, then one observes a homogeneous phase at fixed volume v ⇒ scenario for $T > T_c$. Q: What about $T < T_c$?



Find $\underset{v}{\operatorname{argmin}} \left[p_e v + f(v,T) \right]$

$$Z = \frac{1}{N!\, \Lambda^{3N}} e^{\beta \frac{N^2 \varepsilon}{2V}} \left(V - \frac{N\Omega}{2} \right)^N \Rightarrow f = C^{st} - \frac{\varepsilon}{2v} - k_B T \ln\left(v - \frac{\Omega}{2} \right)$$

$$\mu = pv + f = \mu_0 + pv - \frac{\varepsilon}{2v} - kT \ln\left(v - \frac{\Omega}{2} \right)$$

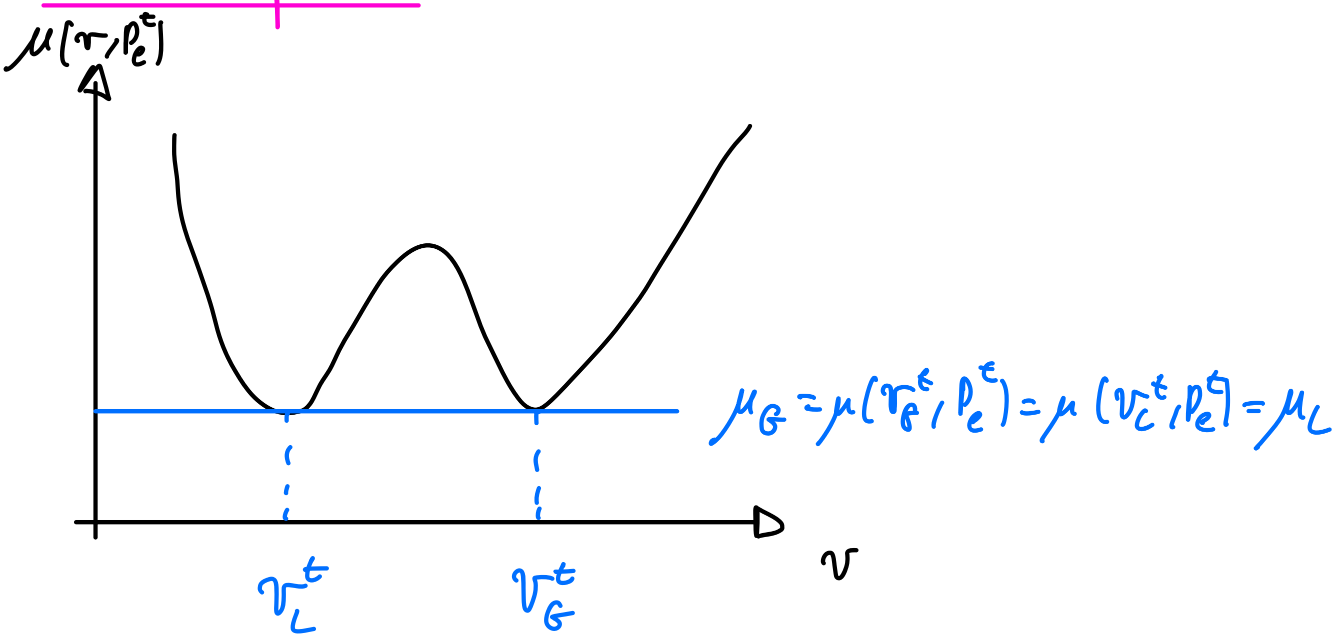


On this example, $\mu(P_e^2, v_G) < \mu(P_e^2, v_L)$

$\Rightarrow$ v_G wins & we observe the corresponding macrostate.

Large P $\Rightarrow$ small v win
Small P $\Rightarrow$ large v win
} how do we transition?

Transition pressure

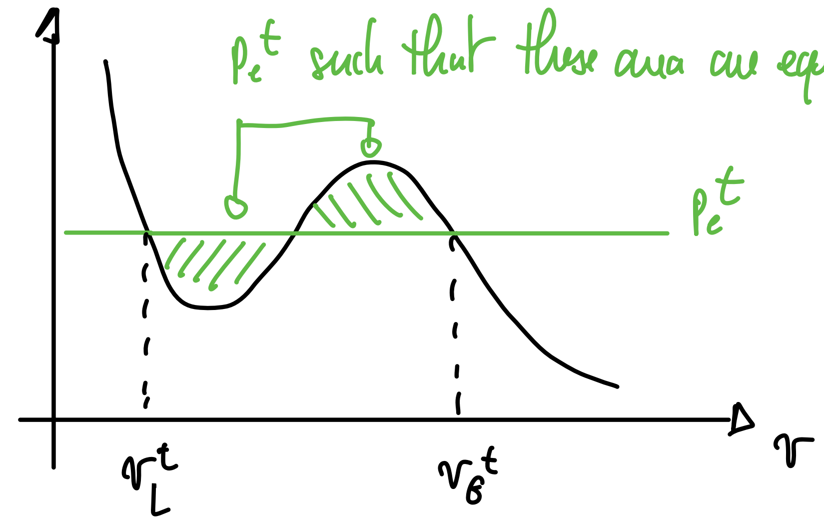


As P_e crosses through P_e^t, the system jumps from v_G^t to v_L^t

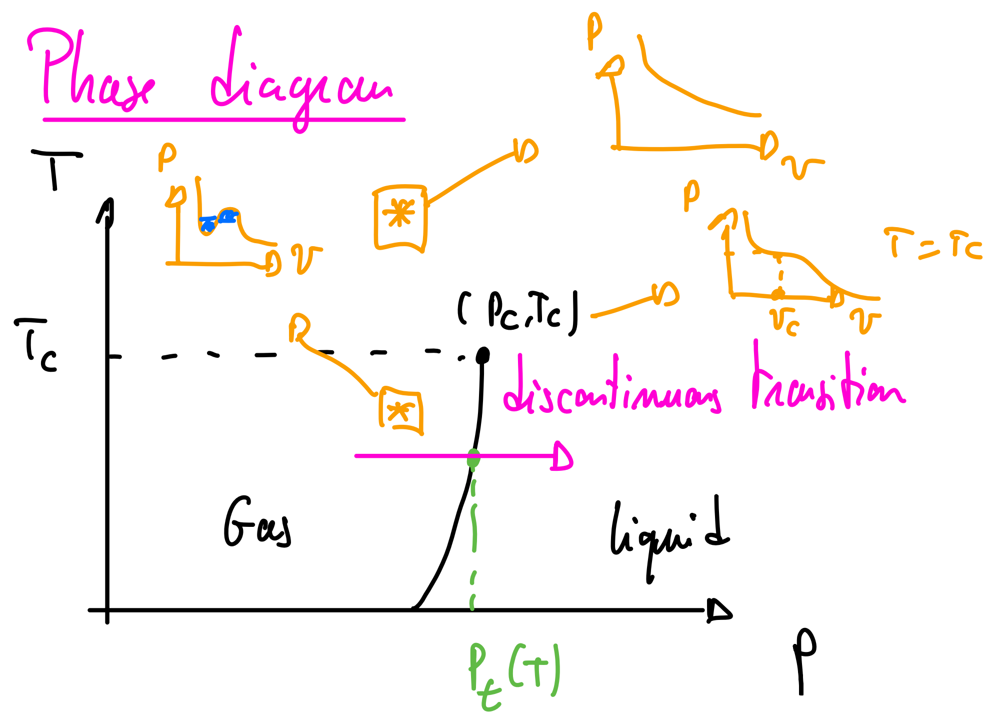
How do we find P_t?

$$\mu(v_G) = \mu(v_L) \Rightarrow \mu(v_G) - \mu(v_L) = \int_{v_G}^{v_L} dv \, \underbrace{\frac{d\mu}{dv}}_{P_e^t + \frac{\partial f}{\partial v} = P_e^t - P_c(v)} = 0$$

$$\Rightarrow \int_{v_G}^{v_L} dv \left[P_e^t - P_c(v) \right] = 0 \Rightarrow \text{Maxwell construction}$$

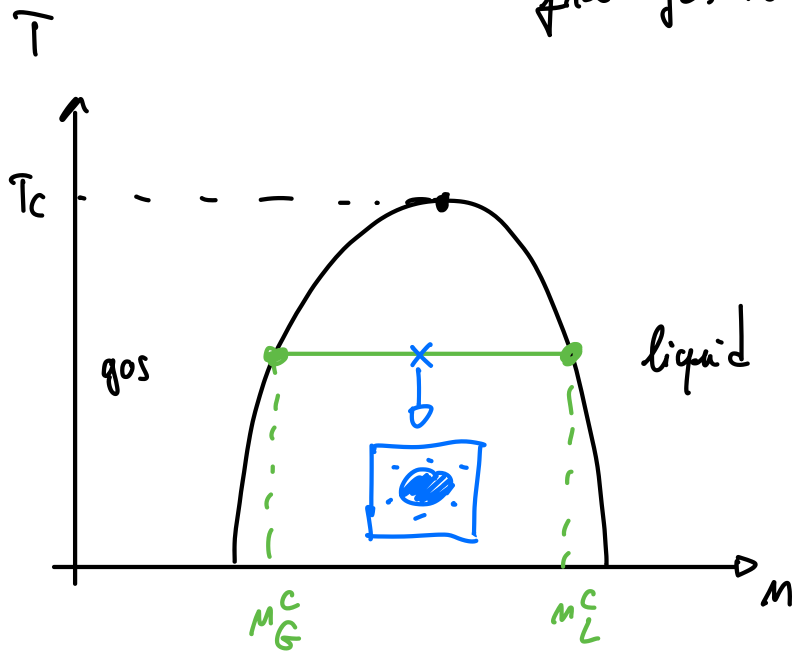


Phase diagram

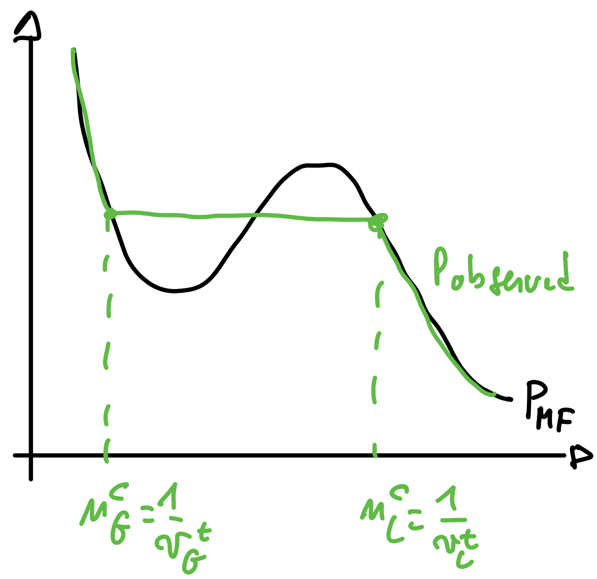


Canonical ensemble

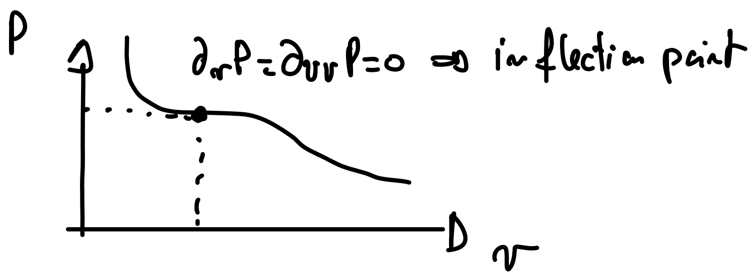
In the canonical ensemble, the system goes from gas to liquid through phase coexistence



Between the gas & the liquid phase, pressure & chemical potential remain constants



4.4) Universality



Let us look at the behaviour close to P_c, T_c, μ_c

$$P(v) = P(v_c) + \left.\frac{\partial P}{\partial v}\right)_{T_c} (v - v_c) + \frac{1}{2} \frac{\partial^2 P}{\partial v^2} (v - v_c)^2 + \frac{1}{6} \frac{\partial^3 P}{\partial v^3} (v - v_c)^3 + \dots \quad (1)$$

At T_c, V_c, $\frac{\partial P}{\partial v} = \frac{\partial^2 P}{\partial v^2} = 0$

Mean-field

$$P = \frac{k_B T}{v - \frac{\Omega}{2}} - \frac{\varepsilon}{2 v^2}$$

$$P'(v) = 0 \iff -\frac{k_B T}{(v_c - \frac{\Omega}{2})^2} + \frac{\varepsilon}{v_c^3} = 0 \iff \frac{v_c^3}{\varepsilon} = \frac{(v_c - \frac{\Omega}{2})^2}{kT} \qquad (*)$$

$$P''(v) = 0 \qquad \frac{2 k_B T}{(v_c - \frac{\Omega}{2})^3} - \frac{3\varepsilon}{v_c^4} = 0 \iff \frac{v_c^4}{3\varepsilon} = \frac{(v_c - \frac{\Omega}{2})^3}{2 k_B T} \qquad (**)$$

$$\frac{(**)}{(*)} \Rightarrow \frac{v_c}{3} = \frac{v_c}{2} - \frac{\Omega}{4} \Rightarrow \boxed{v_c = \frac{3\Omega}{2}}$$

$$(*) \Rightarrow \boxed{kT_c = \Omega^2 \cdot \varepsilon \cdot \frac{8}{27\Omega^3} = \frac{8\varepsilon}{27\Omega}}$$

$$\boxed{P_c = \frac{k_B T_c}{v_c - \frac{\Omega}{2}} - \frac{\varepsilon}{2 v_c^2} = \frac{2\varepsilon}{27\Omega^2}}$$

Critical point:

Mean-field theory: v_c, T_c, P_c are 3 observables that depend on 2 parameters, ε & Ω

$\Rightarrow$ 1 dimensionless number

$$\frac{P_c v_c}{k_B T_c} = \frac{3}{8} \Rightarrow$$ parameter free! $\Rightarrow$ should be the same for all liquid gas phase separation

Experiments: Many systems lead to $\frac{P_c v_c}{k_B T_c} \in [0.28, 0.33]$

$\Rightarrow$ not universal but quite close.

Critical isotherm:

Mean-field theory: At $T = T_c$, $P - P_c \propto (v - v_c)^3$

Experiments $P - P_c \propto (v - v_c)^\delta$ with $\delta \simeq 5.0$ for all simple fluids $\Rightarrow$ universal!

Compressibility: $\kappa = -\frac{1}{v}\frac{\partial v}{\partial p}$

Mean field: $p'(v)\Big|_{v_c} = \frac{8a}{27 b^3} - \frac{k_B T}{b^2} = \frac{k_B(T_c - T)}{b} \Rightarrow \kappa \propto \frac{1}{T - T_c} \xrightarrow[T \to T_c]{} \infty$

Experiments: $\kappa \propto \frac{1}{|T - T_c|^{1,24}}$ for all simple fluids $\Rightarrow$ universal!

Three surprises

(i) Some observables are <u>universal</u>, behaving in the exact same way across a range of systems despite their microscopic differences

(ii) These universal behaviours are <u>not</u> quantitatively predicted by mean-field

(iii) The universal exponents are not simple number $(1, 1/2, \ldots)$

<u>Why?</u> Because fluctuations are important. $\rho(r) \simeq \rho_0$ is a brutal approximation, that fails close to the critical point.

<u>Can we predict all this?</u> Yes! Statistical field theory & 8.334.