Lecture 3
Wednesday 16th October, 2019.
Compiled: Thursday 17th October, 2019.

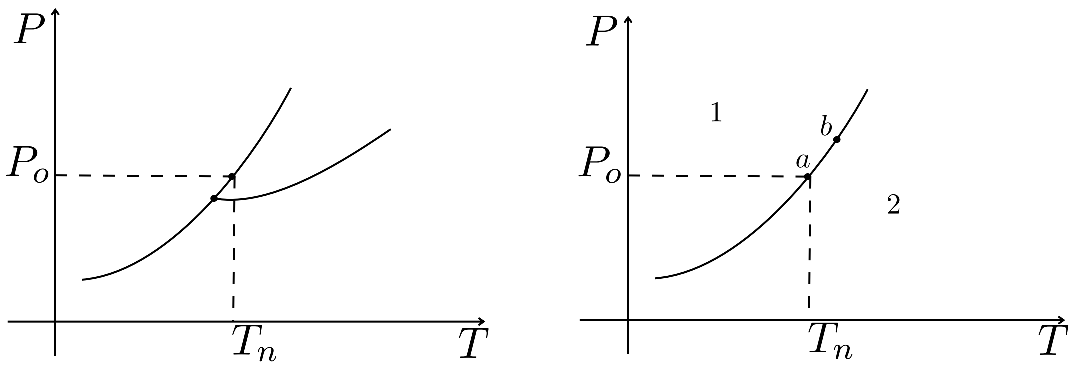

Figure 1: Description.

We know that because they are on the cohexistence line

$$\begin{cases} g_1^{(a)} = g_2^{(a)} \\ g_1^{(b)} = g_2^{(b)} \end{cases} \tag{1}$$

If close enough

$$\begin{cases} \mathrm{d}g_1 = g_1^{(b)} - g_1^{(a)} \\ \mathrm{d}g_2 = g_2^{(b)} - g_2^{(a)} \end{cases} \tag{2}$$

Therefore the *starting point* for *Clausius-Clapeyron* is

$$\mathrm{d}g_1 = \mathrm{d}g_2 \tag{3}$$

We have also:

$$\begin{cases} \mathrm{d}g_1 = -s_1\,\mathrm{d}T + v_1\,\mathrm{d}P \\ \mathrm{d}g_2 = -s_2\,\mathrm{d}T + v_2\,\mathrm{d}P \end{cases} \tag{4}$$

Taking the difference

$$-(s_2 - s_1)\,\mathrm{d}T + (v_2 - v_1)\,\mathrm{d}P = 0 \tag{5}$$

The splope is:

$$\left(\frac{\mathrm{d}P}{\mathrm{d}T}\right)_{coex} = \frac{(s_2 - s_1)}{(v_2 - v_1)} = \frac{\Delta s}{\Delta v} \tag{6}$$

Consider $L_{12} = \Delta s T$ the *latent heat*. Now, we go from gas to liquid (respectively region 1 and 2 in Figure **??** on the right), we have:

$$\left(\frac{\mathrm{d}P}{\mathrm{d}T}\right)_{coex} = \frac{s_2 - s_1}{v_2 - v_1} \qquad \overset{s_2 > s_1}{\underset{v_2 > v_1}{\Rightarrow}} \left(\frac{\mathrm{d}P}{\mathrm{d}T}\right)_{coex} > 0 \tag{7}$$

Melt:

$$\left(\frac{\mathrm{d}P}{\mathrm{d}T}\right)_{coex} = \frac{\delta Q_{melt}}{T_{melt}\Delta v_{melt}} \qquad \delta Q_{melt} = Q_{liq} - Q_{solid} > 0 \tag{8}$$

In general, $v_{liq} > v_{solid}$ which implies $\left(\frac{\mathrm{d}P}{\mathrm{d}T}\right)_{coex} > 0$, but there are cases when $v_{liq} < v_{solid}$ and $\rho_{liq} > \rho_{solid}$ (for instance the H_20, or also Silicon and Germanium).

0.1 Order parameter

Macroscopic observable that is equal to zero abote the critical temperature, and different from zero below:

$$O_p \begin{cases} \neq 0 & T < T_c \\ = 0 & T \to T_c \end{cases} \tag{9}$$

It reflects the symmetry of the system. Recall that, at T_c the system has a symmetry broken. For instance, for *ferromagnetic system* we have the conjugate $\vec{\mathbf{M}} \to \vec{\mathbf{H}}$, while for *ferro electric* we have $\vec{\mathbf{P}} \to \vec{\mathbf{E}}$. For *liquid crystals* $Q_{\alpha\beta} \to \vec{\mathbf{E}}, \vec{\mathbf{H}}$. Consider the density of liquid and gas, their difference is $\Delta\rho = \rho_l - \rho_g$, that is $\neq 0$ for $T \neq T_c$ but $\to 0$ when $T \to T_c$.

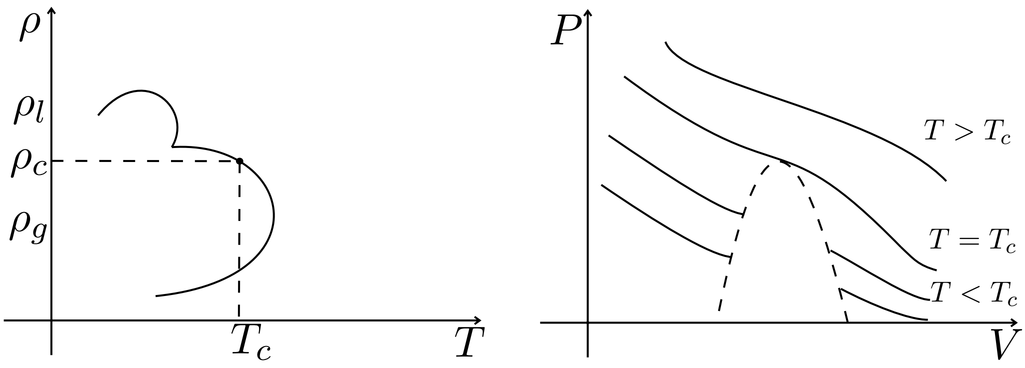

Figure 2: Description.

For a ferromagnetic system:

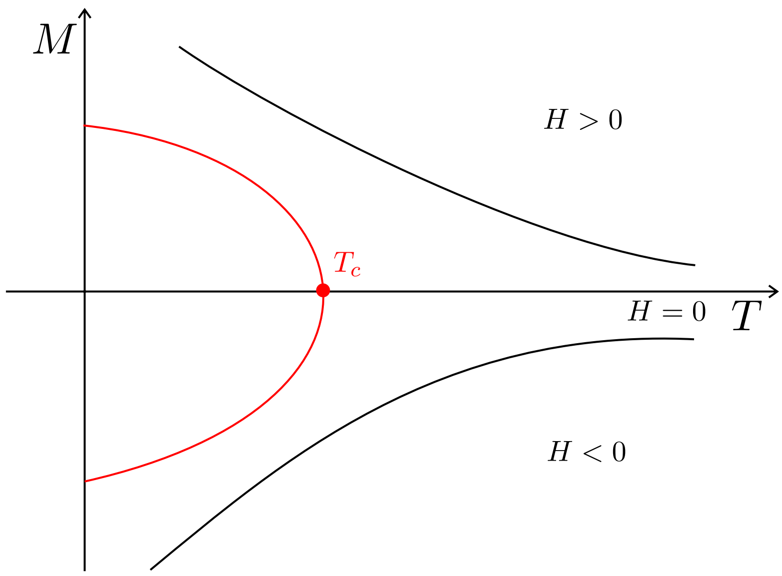

Figure 3: Description.

In general, when you are close to T_c, there are singolarities. How the curve diverges? What is the behaviour close to the critical point? Power Law, so which are the values of these critical exponents?

Define the adimensional parameter $t \equiv \frac{T - T_c}{T_c}$:

Definition 1 (**Critical Exponent** (or *Scale Exponent*))**.**

$$\lambda_{\pm} = \lim_{t \to 0^{\pm}} \frac{\ln |F(t)|}{\ln |t|} \tag{10}$$

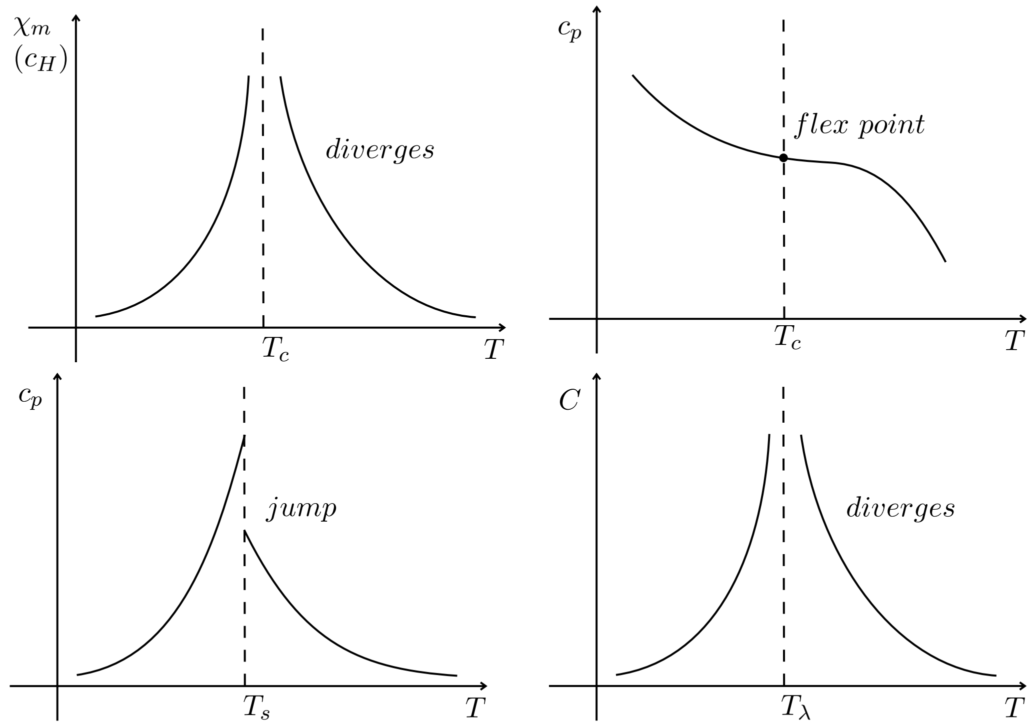

Figure 4: Description.

We note that it behaves like a power low and that

$$F(t) \overset{t \to 0^\pm}{\sim} |t|^{\lambda_\pm} \tag{11}$$

We can write:

$$F(t) = A|t|^{\lambda_\pm}(1 + bt^{\lambda_1} + \dots) \quad \lambda_1 > 0 \tag{12}$$

all other terms are less important.

Definition 2 (Exponent)**.**

- **Exponent** β : tells how the order parameter goes to zero. We have $M \overset{t \to 0^-}{\sim} (-t)^\beta$. No sense in going from above where it stays 0.
- **Exponent** $\gamma_\pm$: related to the response function. We have $\chi_T \overset{t \to 0^\pm}{\sim} |t|^{-\gamma_\pm}$. In principle $\gamma^+ \neq \gamma^-$, but they are the same in reality and we have $\gamma^+ = \gamma^- = \gamma$.
- **Exponent** $\alpha_\pm$: how specific heat diverges (second order derivative in respect of T), we have $c_H \sim |t|^{-\alpha_\pm}$.
- **Exponent** γ. We have $H \sim |M|^\delta sign(M)$. At the critical point how $\vec{\mathbf{M}}$ behaves when $\vec{\mathbf{H}} \to 0$? I fix $T = T_c$ and ask $\vec{\mathbf{M}}(\vec{\mathbf{H}}) =$? The result is $M \sim H^{1/\delta}$

The system displays correlation at very long distance, this one laught goes to the size of the system when $T \to T_c$. We are talking about long range correlation. The *correlation function* is $\xi \sim t^{-\nu}$.

Example 1. Consider a polymer done by N nanomer: ????

Consider the *Guggheneim experiment*, in which we have a liquid-gas. Different sets of data fit the same function if you rescale T/T_c We have

$$(\rho_l - \rho_c) \sim (-t)^\beta \tag{13}$$

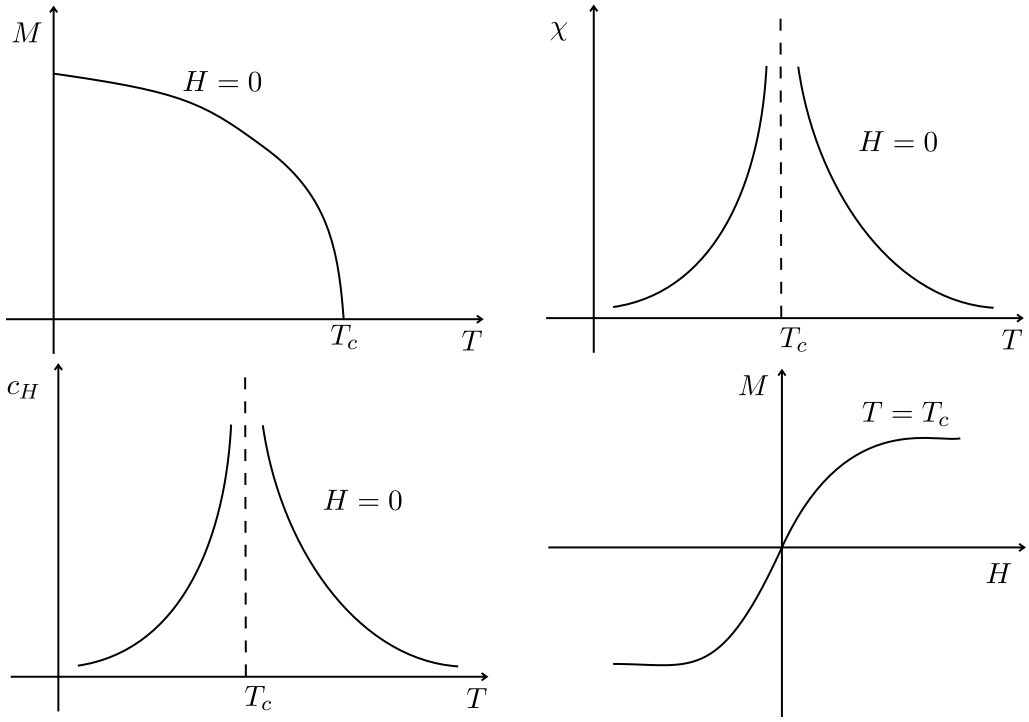

Figure 5: Description.

We have $\beta \sim 1/3 \approx 0.335$. If you do the same for a string ferromagnetic is $1/3$ too.

$$\begin{cases} k_T(c_p - c_v) = Tv\alpha^2 = Tv\frac{1}{v^2}\left(\frac{\partial v}{\partial T}\right)_P^2 = t\frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_P^2 \\ \chi_T(c_H - c_M) = T\left(\frac{\partial M}{\partial T}\right)^2 \end{cases} \tag{14}$$

We have $c_M \geq 0, \chi_T \geq 0$ and $c_H \geq \frac{T}{\chi_T}\left(\frac{\partial M}{\partial T}\right)^2$ because $c_H = T$. If $T \to T_c^-, H = 0$ we have:

$$\begin{cases} c_H \sim (-t)^{-\alpha} \\ \chi_T \sim (-t)^{-\gamma} \end{cases} \tag{15}$$

Therefore $M \sim (-t)^\beta$, which implies $\frac{\partial M}{\partial T} \sim (-t)^{\beta-1}$. Finally we obtain the **Rush-Brook inequality**:

$$\alpha + 2\beta + \gamma \geq 2 \tag{16}$$

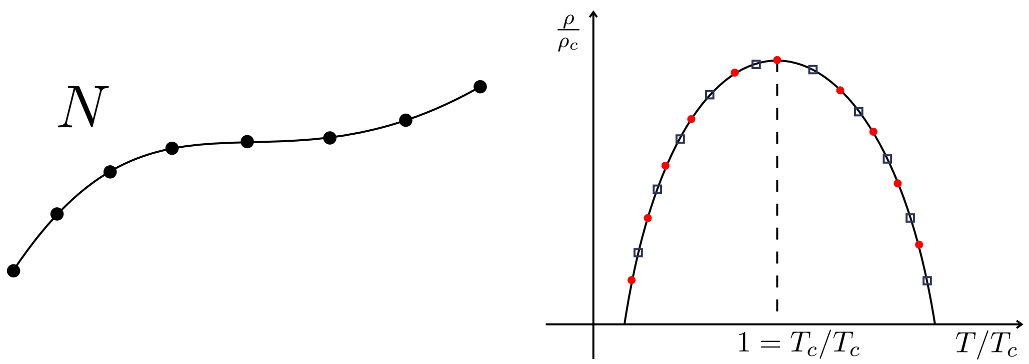

Figure 6: Description.