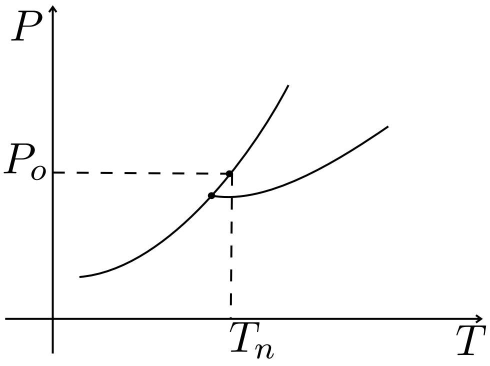
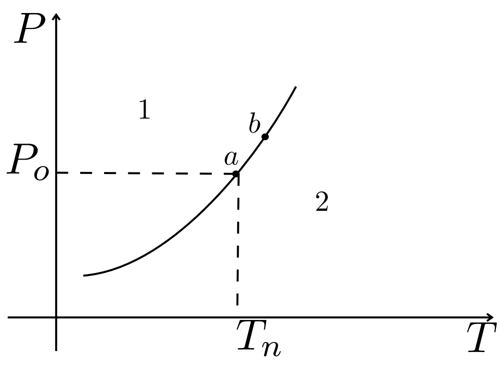
*Lecture 3*
*Wednesday 16th October, 2019.*
*Compiled: Thursday 17th October, 2019.*




**(a)** Coexistence plot.




**(b)** Zoom of the coexistence line.

**Figure 1**

We know that because they are on the cohexistence line

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

and, if they are 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

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

Consider 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, one obtains

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

The splope is called **Clausius-Clapeyron equation**:

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

Now, we go from gas to liquid (respectively region 1 and 2 in Figure 1b), 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 $\left(\mathrm{d}P / \mathrm{d}T\right)_{coex} > 0$, but there are cases when $v_{liq} < v_{solid}$ and $\rho_{liq} > \rho_{solid}$ (for instance the $H_20$, or also Silicon and Germanium).

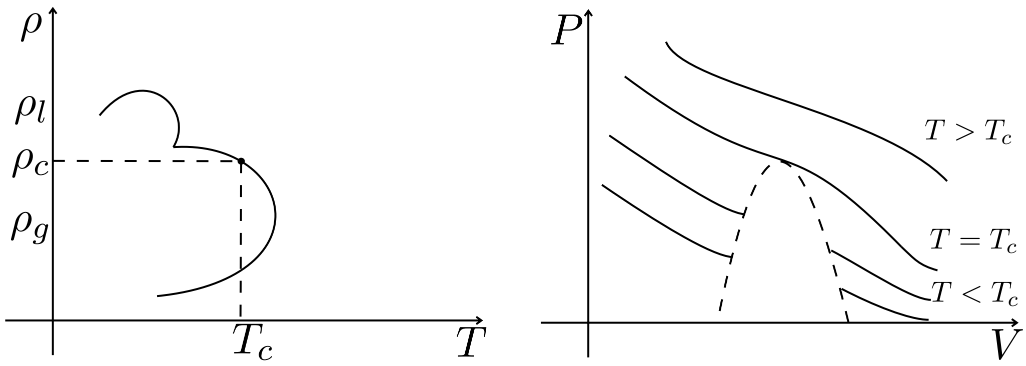
## 0.1 Order parameter

The *order parameters* are macroscopic observable that are equal to zero above 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. Consider *ferromagnetic system*, we have $\vec{\mathbf{M}} \to \vec{\mathbf{H}}$, 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 densities 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 $T \to T_c$.




**(a)** Description **(b)** Description

**Figure 2:** Description

For a ferromagnetic system:

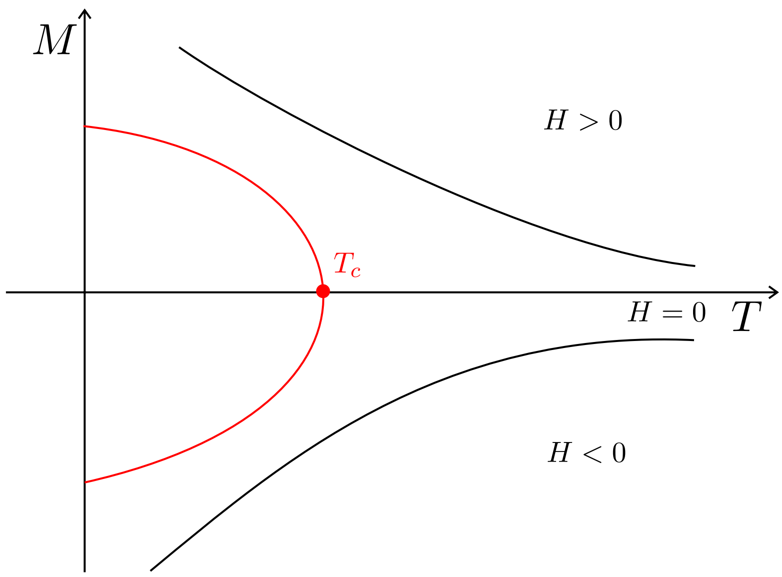
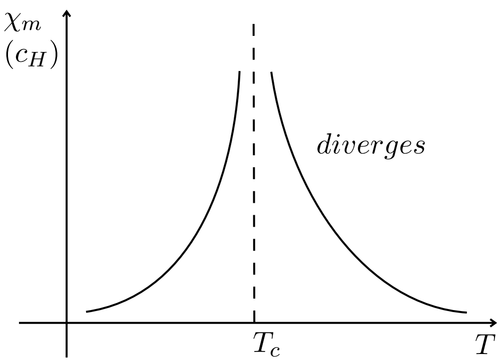


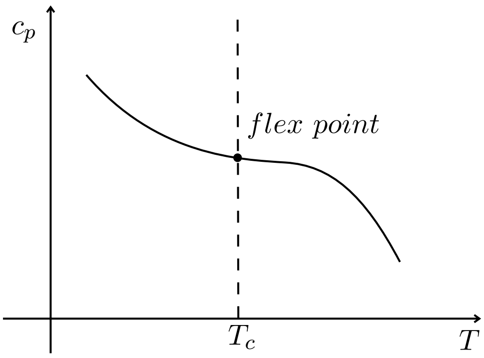

**Figure 3:** Description.

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 $t \equiv \frac{T - T_c}{T_c}$:




**(a)** Description

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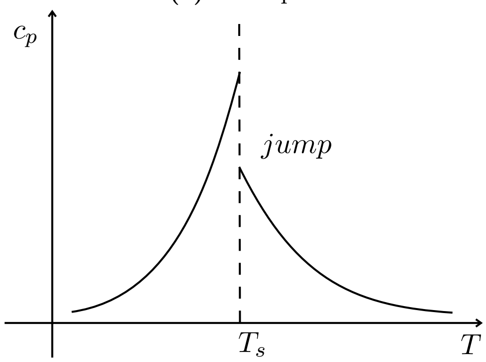
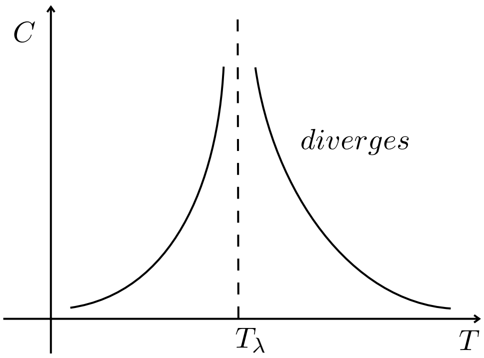



**(c)** Description




**(d)** Description

**Figure 4:** Description

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

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

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** $\beta$ : 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** $\gamma$. 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

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

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

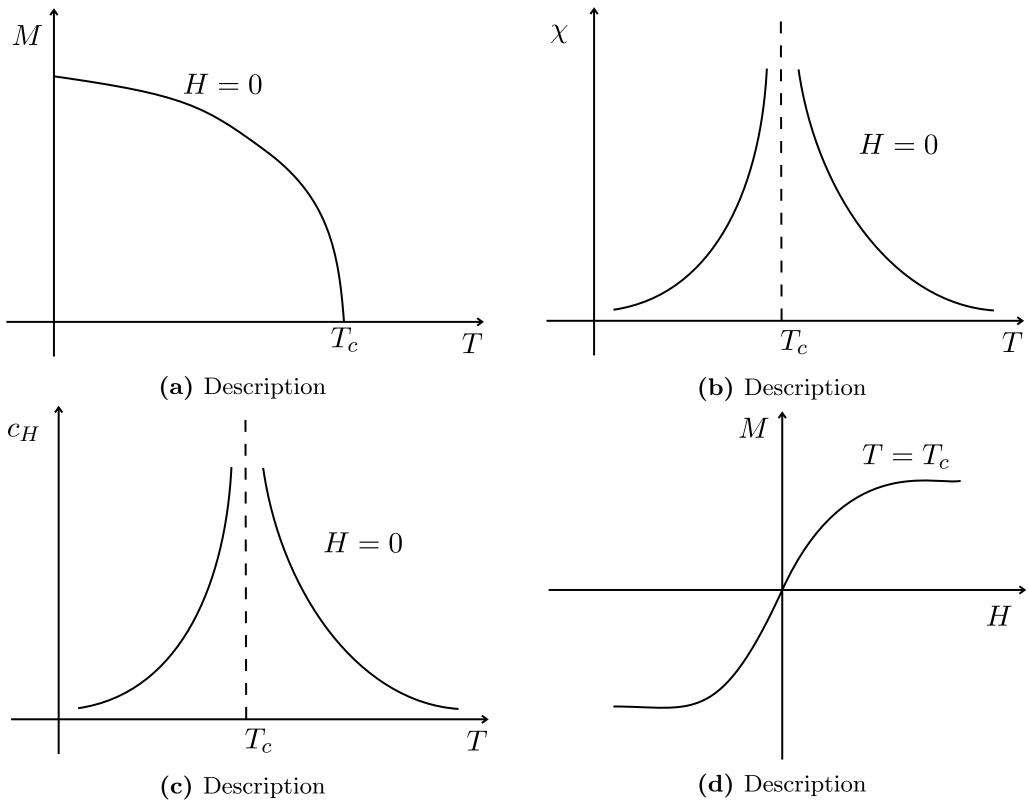
$$\begin{cases} k_T(c_p - c_v) = Tv\alpha^2 = Tv\frac{1}{v^2}\left(\frac{\partial v}{\partial T}\right)_P^2 = t\frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_P^2 \\ \chi_T(c_H - c_M) = T\left(\frac{\partial M}{\partial T}\right)^2 \end{cases} \tag{14}$$

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:

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

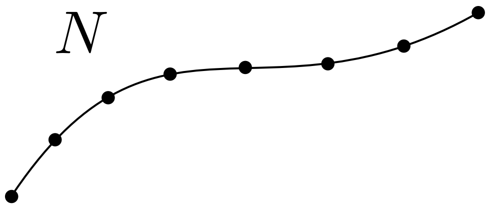
Therefore $M \sim (-t)^\beta$, which implies $\frac{\partial M}{\partial T} \sim (-t)^{\beta-1}$. Finally we obtain the **Rush-Brook inequality**:

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

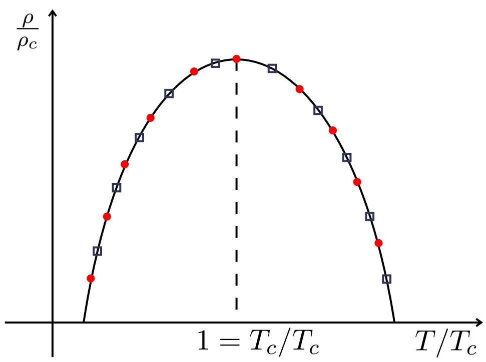



**(a)** Description **(b)** Description **(c)** Description **(d)** Description

**Figure 5:** Description




**(a)** Description




**(b)** Description

**Figure 6:** Description