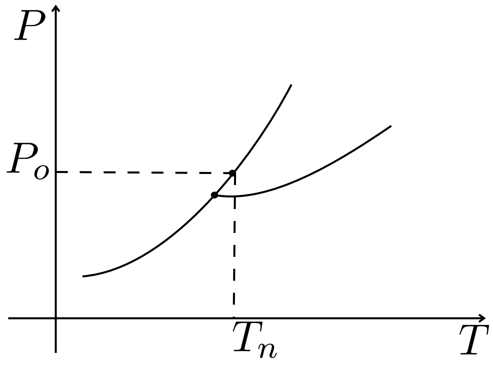
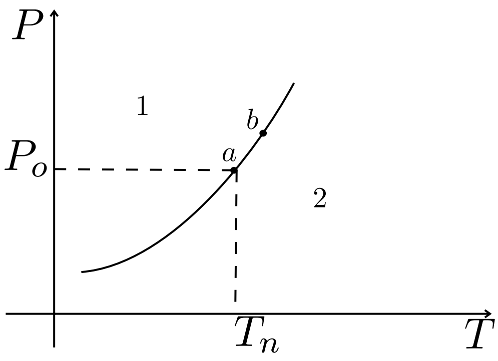
Lecture 3
Wednesday 16th October, 2019.
Compiled: Thursday 17th October, 2019.



(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**:

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

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 $(\mathrm{d}P\,/\,\mathrm{d}T)_{coex} > 0$, but there are cases when $v_{liq} < v_{solid}$ and $\rho_{liq} > \rho_{solid}$ (for instance the $H_2 0$, 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 $T \to T_c$ (see Figure 2).

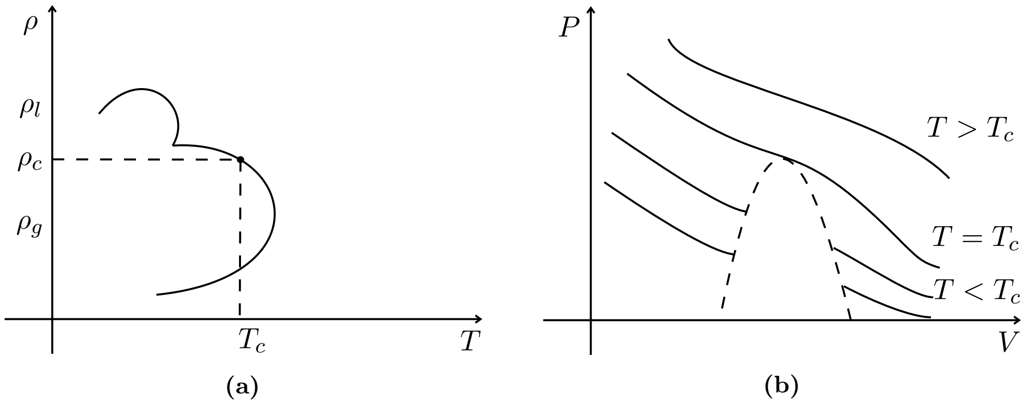


Figure 2: Description

In Figure 3 is shown the behaviour for a ferromagnetic system.

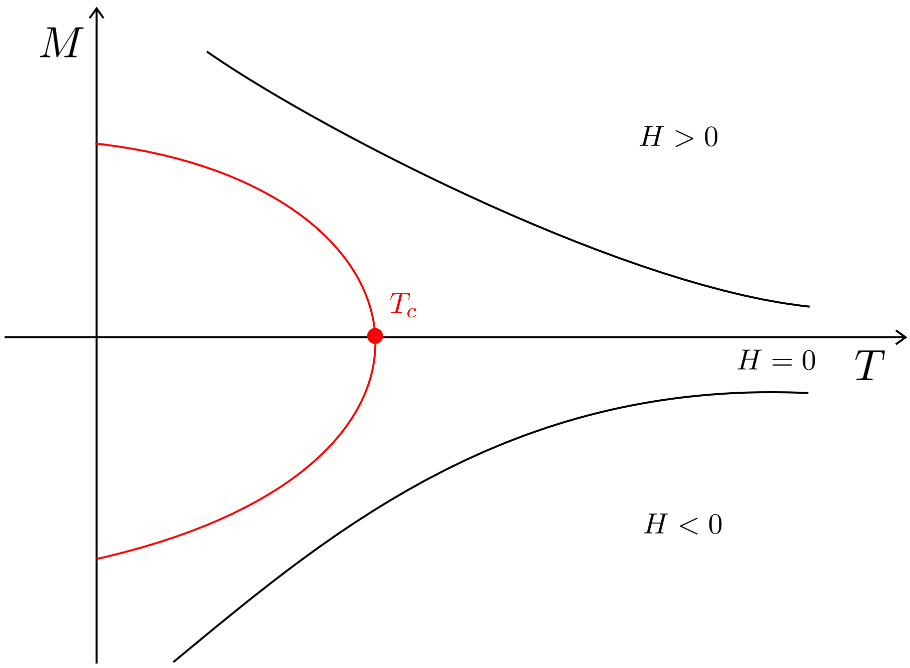
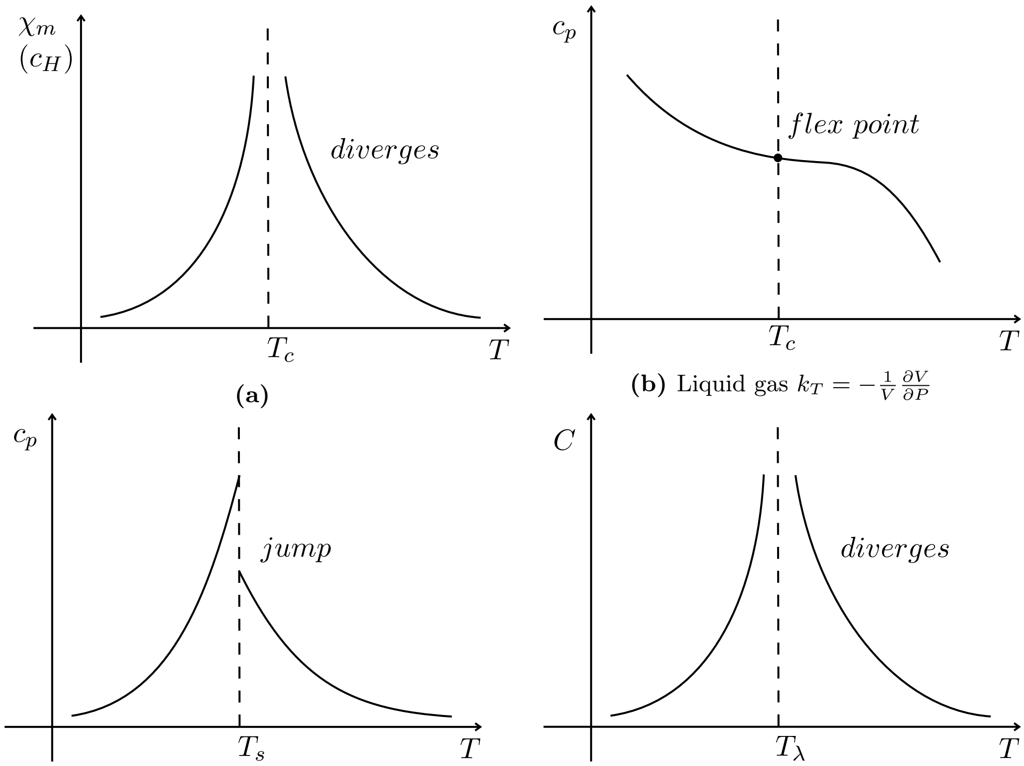


Figure 3: Description.

In general, when you are close to T_c, there are singolarities. Now, we can ask, how the curve diverges? What is the behaviour close to the critical point? Power law, so which are the values of these critical exponents? In order to answer to these questions, let us define:



(a)

(b) Liquid gas $k_T = -\frac{1}{V}\frac{\partial V}{\partial P}$

(c) 2° order phase transition

(d) Superfluid in λ-transition

Figure 4: Description

Definition 1 (**Critical Exponent** (or *Scale Exponent*))**.** Define the adimensional parameter $t \equiv \frac{T-T_c}{T_c}$, the *Critical Exponent* is defined as:

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

We note that it behaves like a power low and that

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

Therefore, we can write:

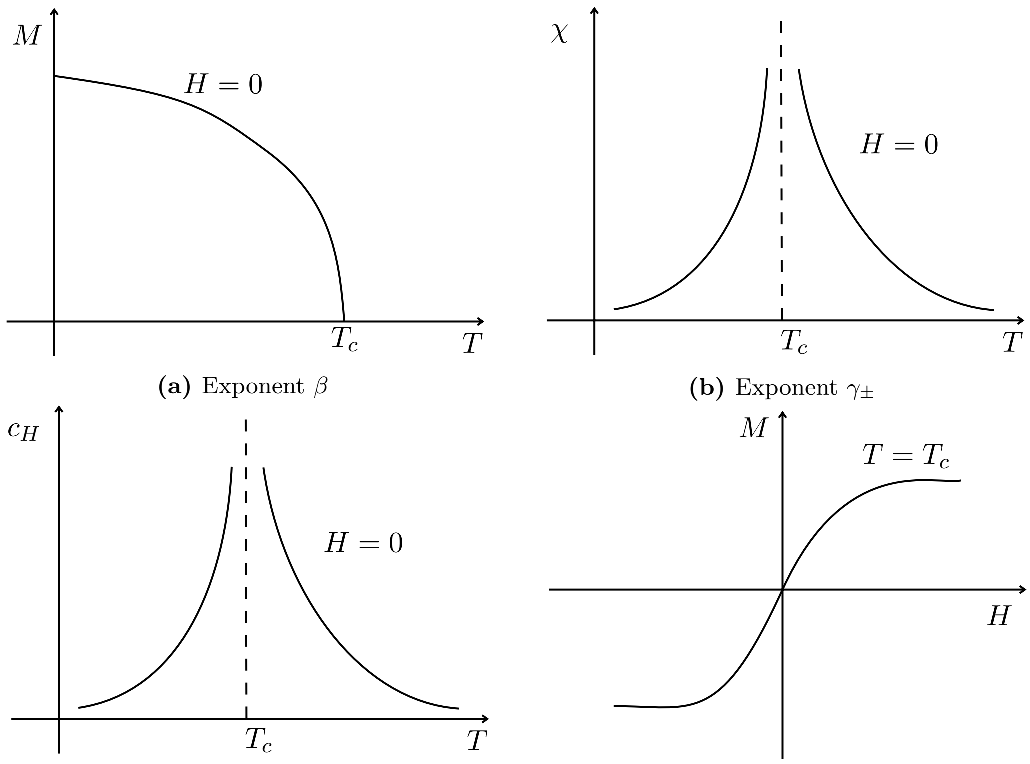
$$F(t) = A|t|^{\lambda_\pm}(1 + bt^{\lambda_1} + \dots) \quad \lambda_1 > 0 \tag{12}$$

where all other terms are less important.

Definition 2 (Exponent)**.**

- **Exponent** β : tells how the order parameter goes to zero. Consider Figure 5a, 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. Consider Figure 5b, 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). For instance see Figure 5c, we have $c_H \sim |t|^{-\alpha_\pm}$.

- **Exponent** γ. In Figure 5d, $H \sim |M|^{\delta}\text{sign}(M)$. Let us ask, how behaves $\vec{\mathbf{M}}$ at the critical point when $\vec{\mathbf{H}} \to 0$? First of all, we fix $T = T_c$ and ask what is the value of $\vec{\mathbf{M}}(\vec{\mathbf{H}})$. The result is $M \sim H^{1/\delta}$.



(a) Exponent β

(b) Exponent $\gamma_{\pm}$

(c) Exponent $\alpha_{\pm}$

(d) Exponent γ

Figure 5: Description

The system displays correlation at very long distance, these goes to the size of the system when $T \to T_c$. We are talking about long range correlation. The *correlation function* is $\xi \sim t^{-\nu}$. For instance, consider a polymer as in Figure 6a.

Consider the *Guggheneim experiment* (see Figure 6b), in which we have a liquid-gas. Different sets of data fit the same function if you rescale T/T_c We have

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

and $\beta \sim 1/3 \approx 0.335$. If you do the same for a string ferromagnetic is 1/3 too. Let us compute:

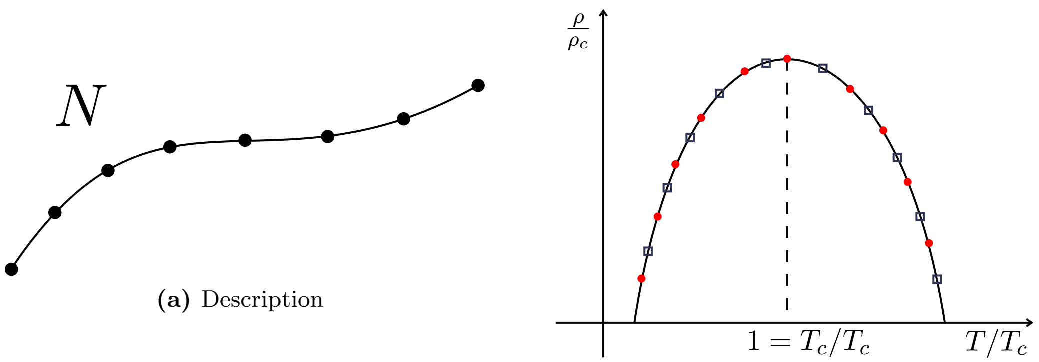
$$\begin{cases} k_T(c_p - c_v) = Tv\alpha^2 = Tv\frac{1}{v^2}\left(\frac{\partial v}{\partial T}\right)_P^2 = T\frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_P^2 \\ \chi_T(c_H - c_M) = T\left(\frac{\partial M}{\partial T}\right)^2 \end{cases} \tag{14}$$

with $c_M \geq 0, \chi_T \geq 0$ 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

Figure 6