

Lecture 3.
 Wednesday 16th
 October, 2019.
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0.1 Lever Rule

Consider the Figure 1, at all points between A and B the system is a mixture of gas and liquid. Points D has global density $P_D = P_A + P_B$ and therefore $v_D = \frac{1}{P_D}, v_A = \frac{1}{P_A}, v_B = \frac{1}{P_B}$ which implies:

$$v_D = \frac{N_A}{N}v_A + \frac{N_B}{N}v_B = x_A v_A + x_B v_B \quad (1)$$

Since $x_A + x_B = 1$ we have $(x_A + x_B)v_D = x_A v_A + x_B v_B$ and finally the **Lever Rule**:

$$\frac{x_A}{x_B} = \frac{v_B - v_D}{v_D - v_A} \quad (2)$$

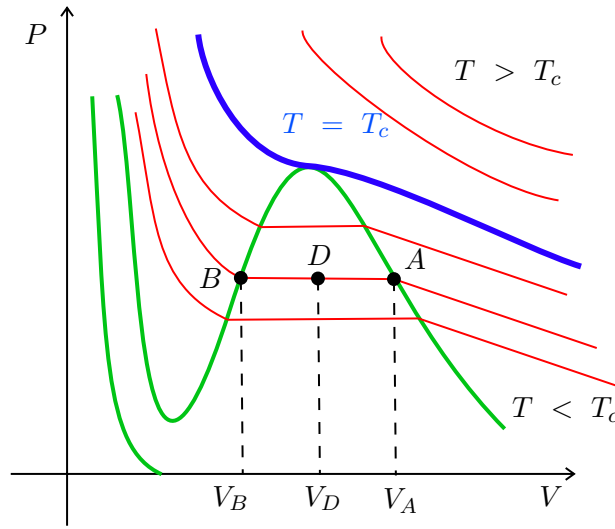


Figure 1: Description.

0.2 Thermodynamic of phase coexistence (one component system)

Consider a (P, V, T) system as a mixture of two species (1,2) at temperature T_1, T_2 , pressure P_1, P_2 and chemical potentials μ_1, μ_2 . The equilibrium condition is given by the maximum of the total entropy $S = S_1 + S_2$ and gives the conditions

$$T_1 = T_2, \quad P_1 = P_2, \quad \mu_1 = \mu_2 \quad (3)$$

this is the *coexistence condition* of the two phases. In terms of the Gibbs potential $G = U - TS + PV$, where U is given by the Euler equation $U = TS - PV + \mu_1 N_1 + \mu_2 N_2$, the Gibbs per mole is

$$g_1(T, P) \equiv \frac{G_1}{N_1} = \mu_1 \quad (4a)$$

$$g_2(T, P) \equiv \frac{G_2}{N_2} = \mu_2 \quad (4b)$$

Therefore, on the coexistence line it should hold the relation

$$g_1(T, P) = g_2(T, P) \quad (5)$$

0.3 Clausius-Clapeyron equation

Suppose to know the position on the coexistence line (for example the melt temperature T_m at the atmospheric pressure P_0 , as in Figure 2). Is it possible to find other points on the curve? For example T_m at lower or higher pressure?

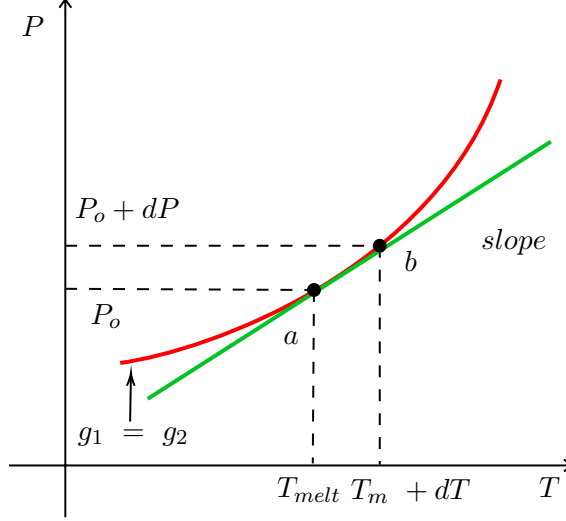


Figure 2: Description.

The answer is yes for small deviations of T and P from a . The idea is to compute the slope of the tangent of the coexistence curve, i.e. (dP / dT) . This is given by the Clausius-Clapeyron equation. Both at a and b the two phases 1 and 2 coexist. This means that at the coexistence line

$$\begin{cases} g_1^{(a)} = g_2^{(a)} \\ g_1^{(b)} = g_2^{(b)} \end{cases} \quad (6)$$

Hence, if a and b are very close:

$$\begin{cases} dg_1 = g_1^{(b)} - g_1^{(a)} \\ dg_2 = g_2^{(b)} - g_2^{(a)} \end{cases} \quad (7)$$

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

$$\Rightarrow dg_1 = dg_2 \quad (8)$$

From the molar version of the Gibbs-Duhem relation we have

$$\begin{cases} dg_1 = -s_1 dT + v_1 dP = d\mu_1 \\ dg_2 = -s_2 dT + v_2 dP = d\mu_2 \end{cases} \quad (9)$$

taking the difference, one obtains

$$-(s_2 - s_1) dT + (v_2 - v_1) dP = 0 \quad (10)$$

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

$$\left(\frac{dP}{dT} \right)_{coex} = \frac{(s_2 - s_1)}{(v_2 - v_1)} = \frac{\Delta s}{\Delta v} \quad (11)$$

Remark. Since $(dP/dT)_{coex}$ is finite, the equation explains why a first order transition is characterised by discontinuous changes in entropy and volume (or density). ΔS gives the heat L_{12} that is exchanged with the environment:

$$L_{12} = \Delta ST \quad (12)$$

0.3.1 Application of C-C equation to the liquid-gas coexistence line

Now, we go from gas to liquid (we call it respectively region 2 and 1), we have:

$$\left(\frac{dP}{dT}\right)_{coex} = \frac{s_2 - s_1}{v_2 - v_1} \quad (13)$$

Since for liquid-gas :

$$\left(\frac{dP}{dT}\right)_{coex} > 0 \Rightarrow \frac{s_2 - s_1}{v_2 - v_1} > 0 \quad (14)$$

and since $v_2 > v_1$, we have $s_2 > s_1$. The gas has more entropy as it should be. When going from a low-temperature phase to a high-temperature phase entropy always increases $\Delta S > 0$, because $c_P \equiv T(\partial S/\partial T)_P > 0$.

The sign of ΔV is more uncertain though. To see this point let us consider the C-C equation at the solid-liquid (now solid is region 1 and liquid region 2) coexistence curve. At the melt temperature:

$$\left(\frac{dP}{dT}\right)_{coex} = \frac{\delta Q_{melt}}{T_{melt} \Delta v_{melt}} \quad \delta Q_{melt} = Q_{liq} - Q_{solid} > 0 \quad (15)$$

In general, $\Delta v_m = v_{liq} - v_{solid} > 0$ which implies $(dP/dT)_{coex} > 0$. There are cases, however, where $\Delta v_m = v_{liq} - v_{solid} < 0$ because $\rho_{liq} > \rho_{solid}$ (for instance the H_2O , or also Silicon and Germanium). The paradigmatic example is the freezing of water where $v_{ice} > v_{liq}$ since ice is less dense than liquid water at the coexistence ($0 < T < 4$). This implies that $dP/dT < 0$.

Example 1.

Example 2.

0.4 Order parameter

The *order parameters* are macroscopic observable that are equal to zero above the critical temperature, and different from zero below:

$$O_p \begin{cases} \neq 0 & T < T_c \\ = 0 & T \rightarrow T_c^- \end{cases} \quad (16)$$

It reflects the symmetry of the system. Recall that, at T_c the system has a symmetry broken. Consider *ferromagnetic system*, we have $\vec{M} \rightarrow \vec{H}$, while for *ferro electric* we have $\vec{P} \rightarrow \vec{E}$. For *liquid crystals* $Q_{\alpha\beta} \rightarrow \vec{E}, \vec{H}$.

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 $\rightarrow 0$ when $T \rightarrow T_c$ (see Figure 3).

In Figure 4 is shown the behaviour for a ferromagnetic system.

In general, when you are close to T_c , there are singularities. 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:

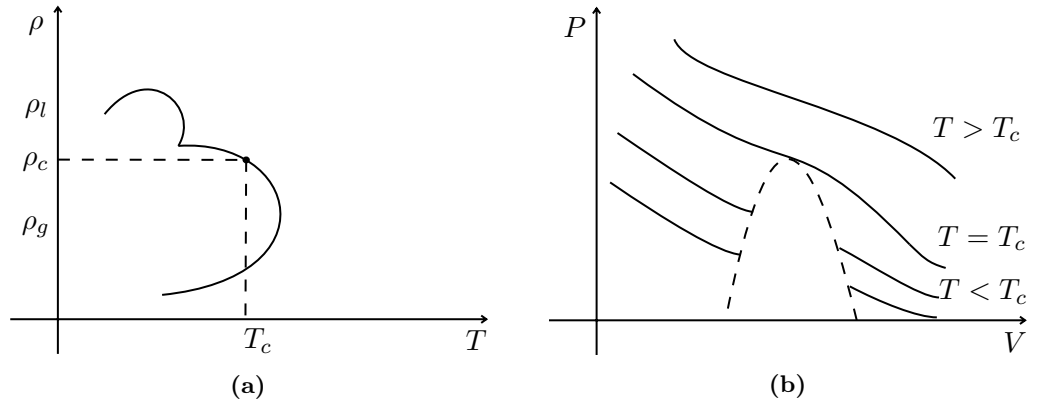


Figure 3: Description

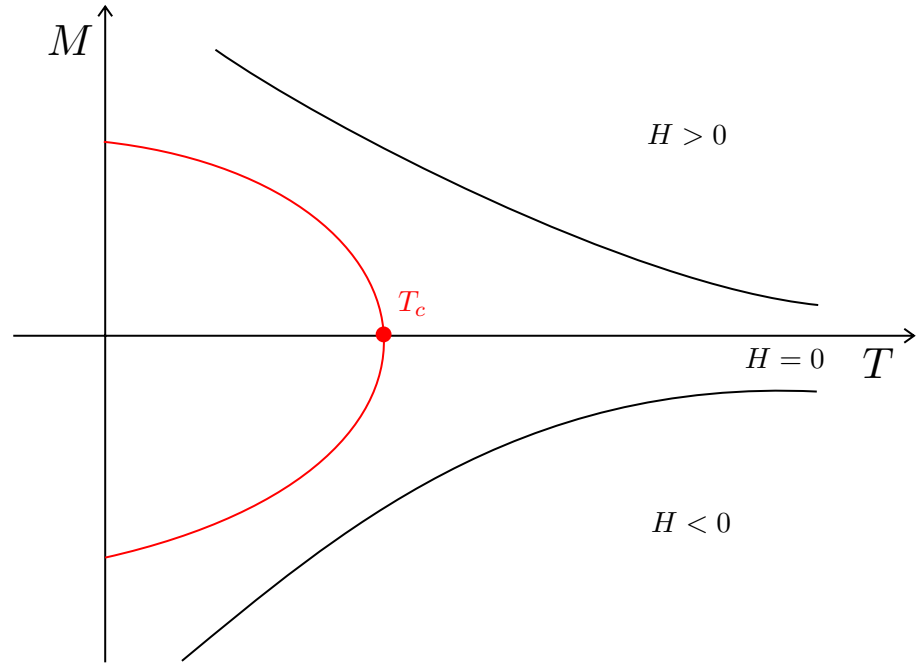


Figure 4: Description.

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:

$$\lambda_{\pm} = \lim_{t \rightarrow 0^{\pm}} \frac{\ln |F(t)|}{\ln |t|} \quad (17)$$

We note that it behaves like a power law and that

$$F(t) \stackrel{t \rightarrow 0^{\pm}}{\sim} |t|^{\lambda_{\pm}} \quad (18)$$

Therefore, we can write:

$$F(t) = A|t|^{\lambda_{\pm}}(1 + bt^{\lambda_1} + \dots) \quad \lambda_1 > 0 \quad (19)$$

where all other terms are less important.

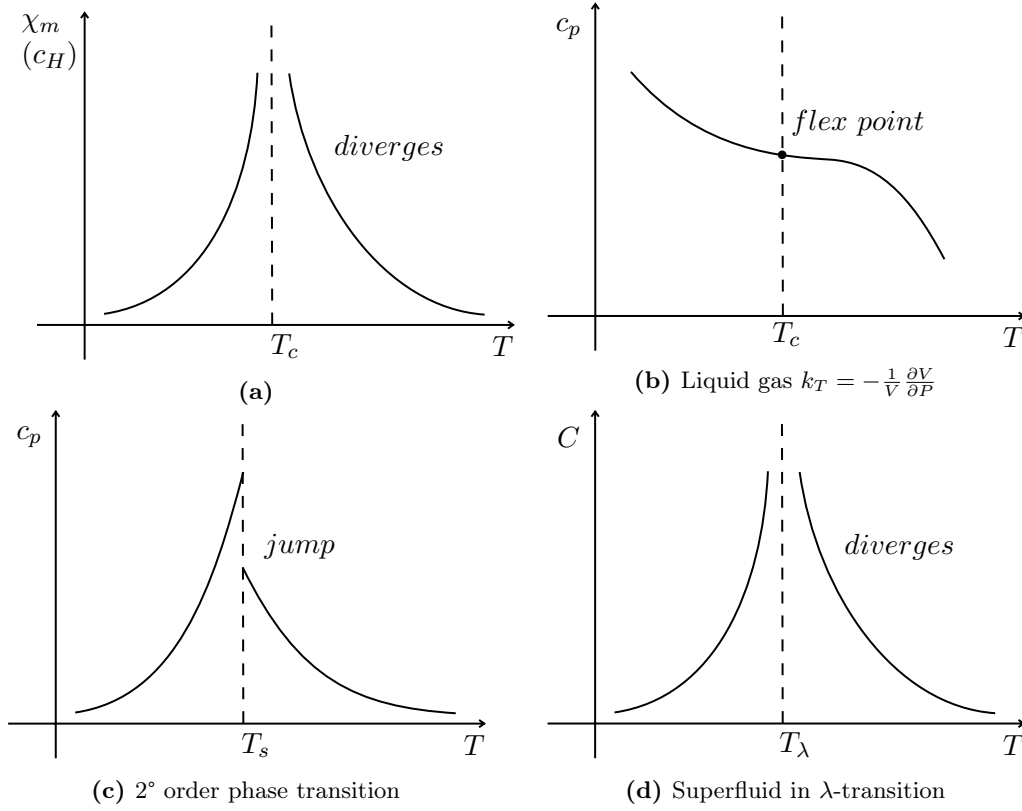


Figure 5: Description

Definition 2 (Exponent).

- **Exponent** β : tells how the order parameter goes to zero. Consider Figure 6a, we have $M \stackrel{t \rightarrow 0^-}{\sim} (-t)^\beta$. No sense in going from above where it stays 0.
- **Exponent** γ_\pm : related to the response function. Consider Figure 6b, we have $\chi_T \stackrel{t \rightarrow 0^\pm}{\sim} |t|^{-\gamma_\pm}$. In principle $\gamma^+ \neq \gamma^-$, but they are the same in reality and we have $\gamma^+ = \gamma^- = \gamma$.
- **Exponent** α_\pm : how specific heat diverges (second order derivative in respect of T). For instance see Figure 6c, we have $c_H \sim |t|^{-\alpha_\pm}$.
- **Exponent** γ . In Figure 6d, $H \sim |M|^\delta \text{sign}(M)$. Let us ask, how behaves \vec{M} at the critical point when $\vec{H} \rightarrow 0$? First of all, we fix $T = T_c$ and ask what is the value of $\vec{M}(\vec{H})$. The result is $M \sim H^{1/\delta}$.

The system displays correlation at very long distance, these goes to the size of the system when $T \rightarrow T_c$. We are talking about long range correlation. The *correlation function* is $\xi \sim t^{-\nu}$. For instance, consider a polymer as in Figure 7a.

Consider the *Guggenheim experiment* (see Figure 7b), in which we have a liquid-gas. Different sets of data fit the same function if you rescale T/T_c . We have

$$(\rho_l - \rho_c) \sim (-t)^\beta \quad (20)$$

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

$$\begin{cases} k_T(c_p - c_v) = Tv\alpha^2 = Tv\frac{1}{v^2} \left(\frac{\partial v}{\partial T}\right)_P^2 = T\frac{1}{v} \left(\frac{\partial v}{\partial T}\right)_P^2 \\ \chi_T(c_H - c_M) = T\left(\frac{\partial M}{\partial T}\right)^2 \end{cases} \quad (21)$$

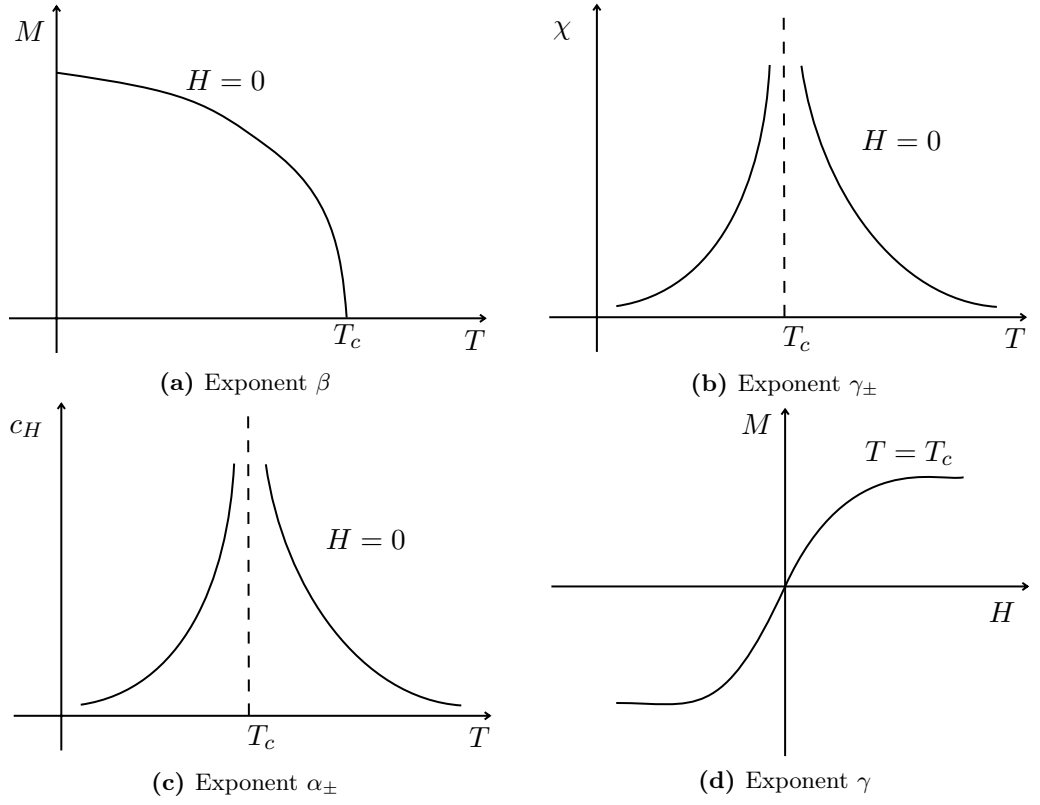


Figure 6: Description

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 $T \rightarrow T_c^-$, $H = 0$ we have:

$$\begin{cases} c_H \sim (-t)^{-\alpha} \\ \chi_T \sim (-t)^{-\gamma} \end{cases} \quad (22)$$

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

$$\alpha + 2\beta + \gamma \geq 2 \quad (23)$$

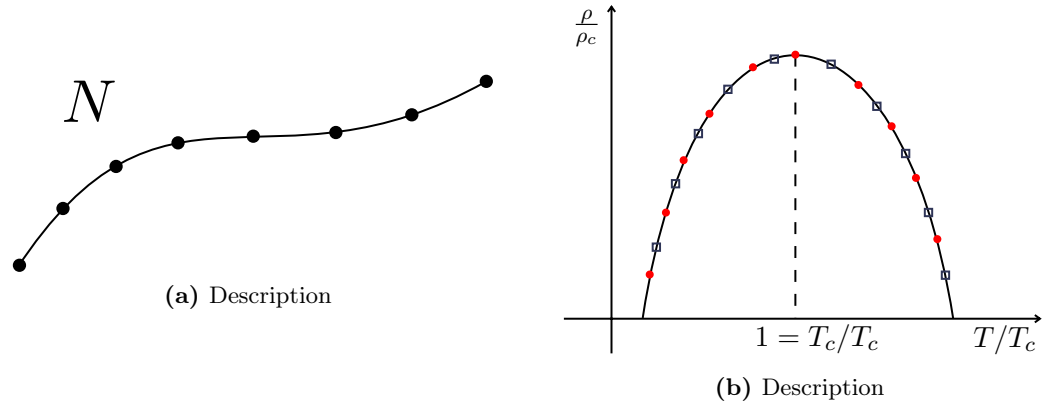


Figure 7