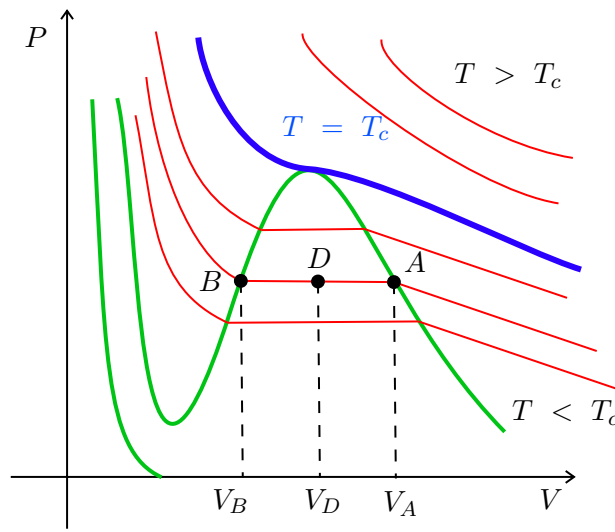## 0.1   Lever Rule

Consider the Figure 1, at all points between A and B the system is a mixsture 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:

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

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**:

$$\frac{x_A}{x_B} = \frac{v_B - v_D}{v_D - v_A} \tag{2}$$

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

$$T_1 = T_2, \quad P_1 = P_2, \quad \mu_1 = \mu_2 \tag{3}$$

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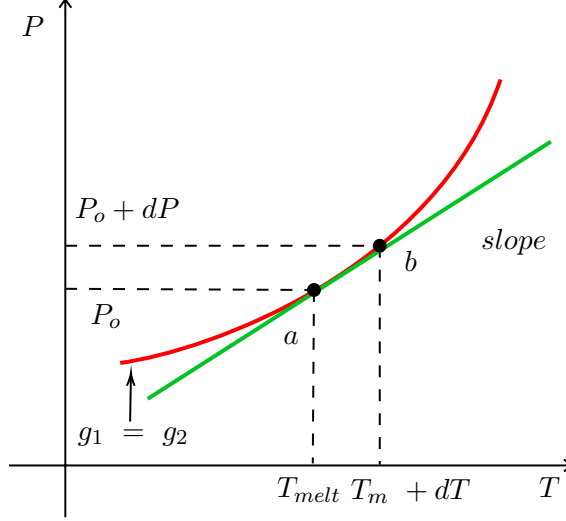
$$g_1(T, P) \equiv \frac{G_1}{N_1} = \mu_1 \tag{4a}$$

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

Therefore, on the coexistence line it should hold the relation

$$g_1(T, P) = g_2(T, P) \tag{5}$$

0.3 Clausius-Clapeyron equation

Suppose to know the position an 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. Rhe idea is to compute the slope of the tangent of the coexistence curve, i.e. $(\mathrm{d}P / \mathrm{d}T)$. 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

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

Hence, if a and b are very close:

$$\begin{cases} \mathrm{d}g_1 = g_1^{(b)} - g_1^{(a)} \\ \mathrm{d}g_2 = g_2^{(b)} - g_2^{(a)} \end{cases} \tag{7}$$

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

$$\Rightarrow \mathrm{d}g_1 = \mathrm{d}g_2 \tag{8}$$

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

$$\begin{cases} \mathrm{d}g_1 = -s_1 \, \mathrm{d}T + v_1 \, \mathrm{d}P = \mathrm{d}\mu_1 \\ \mathrm{d}g_2 = -s_2 \, \mathrm{d}T + v_2 \, \mathrm{d}P = \mathrm{d}\mu_2 \end{cases} \tag{9}$$

taking the difference, one obtains

$$- (s_2 - s_1) \, \mathrm{d}T + (v_2 - v_1) \, \mathrm{d}P = 0 \tag{10}$$

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

$$\left(\frac{\mathrm{d}P}{\mathrm{d}T} \right)_{coex} = \frac{(s_2 - s_1)}{(v_2 - v_1)} = \frac{\Delta s}{\Delta v} \tag{11}$$

Remark. Since $(\mathrm{d}P / \mathrm{d}T)_{coex}$ 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:

$$L_{12} = \Delta S T \tag{12}$$

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:

$$\left(\frac{\mathrm{d}P}{\mathrm{d}T}\right)_{coex} = \frac{s_2 - s_1}{v_2 - v_1} \tag{13}$$

Since for liquid-gas :

$$\left(\frac{\mathrm{d}P}{\mathrm{d}T}\right)_{coex} > 0 \Rightarrow \frac{s_2 - s_1}{v_2 - v_1} > 0 \tag{14}$$

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:

$$\left(\frac{\mathrm{d}P}{\mathrm{d}T}\right)_{coex} = \frac{\delta Q_{melt}}{T_{melt} \Delta v_{melt}} \qquad \delta Q_{melt} = Q_{liq} - Q_{solid} > 0 \tag{15}$$

In general, $\Delta v_m = v_{liq} - v_{solid} > 0$ which implies $(\mathrm{d}P / \mathrm{d}T)_{coex} > 0$. There are cases, however, where $\Delta v_m = v_{liq} - v_{solid} < 0$ because $\rho_{liq} > \rho_{solid}$ (for instance the $H_2 0$, 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 coxistence ($0 < T < 4$). This implies that $\mathrm{d}P / \mathrm{d}T < 0$.

Example 1 (Melting point on Everest)**.**

Consider $T = 237K$ and $P = P_0$. If $\delta Q_m = 6.01 kJ/mol$ and $\Delta v = -1.7 cm^3 /mol$ we have:

$$\frac{\mathrm{d}P}{\mathrm{d}T} = \frac{\delta Q_m}{T \Delta v} = \frac{6.01 10^3 J/mol}{273 \cdot (-1.7 cm^3 /mol)} = -1.29 \cdot 10^4 J/m^3 = -1.29 bar/K \tag{16}$$

$$\Delta T = \frac{\Delta P}{(-1.29 Pa/K)} = \frac{(P_0 - P_{\text{Everest}})}{(-1.29 Pa/K)} = \frac{(1 - 0.36) atm}{(-1.29 Pa/K)} = -0.5 C \tag{17}$$

$$\Rightarrow T_m(\text{Everest}) = T_m(P_0) + 0.5 C \tag{18}$$

Example 2 (Boiling point on Everest)**.**

Consider $P_{\text{Everest}} = 0.36 atm$, $\rho(T = 100°C) = 0.598 kg/m^3$ and $L_{ge} = 2.257 \cdot 10^3 J/g$. The density of the vapour is about 1000 less than water, it implies that: $\Delta V = V_g - V_e \approx V_g = \frac{1}{\rho g}$. We have:

$$\frac{\mathrm{d}P}{\mathrm{d}T} = \frac{L_{ge}}{T \Delta V} = \frac{L_{ge} \rho_g}{T} = \frac{2.25 \cdot 10^3 J/g \cdot 0.593 kg/m^3}{373 K} = \frac{3.6}{K} \frac{10^3 J}{g} \frac{kg}{m^3} = 3.6 \cdot 10^3 Pa/K \tag{19}$$

$$\Rightarrow \Delta T \approx \Delta P/(3.6 10^3 Pa/K) = 18°C \rightarrow T_0 - T_{\text{Everest}} = 18°C C \Rightarrow T_{\text{Everest}} \approx 80°C \tag{20}$$
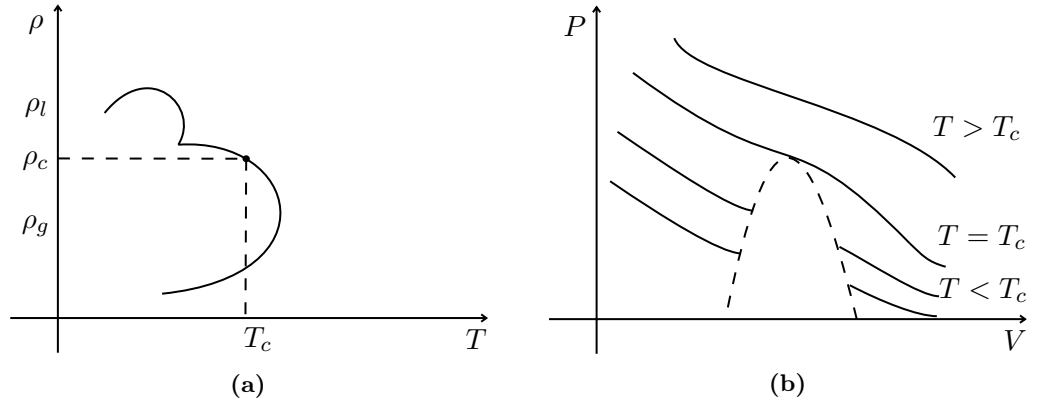
0.4 Order parameter of a phase transition

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

$$O_p \begin{cases} \neq 0 & T < T_c \\ = 0 & T \to T_c^- \end{cases} \tag{21}$$

When a phase transition implies a breaking of a phase symmetry, the order parameter is related to this symmetry. Therefore, the order parameter reflects the symmetry of the system. Recall that, at T_c the system has a symmetry broken.

For instance, consider the densities of liquid and gas and the related order parameter of the gas-liquid transition $\Delta \rho = \rho_l - \rho_g$, that is $\neq 0$ for $T \neq T_c$ but $\to 0$ when $T \to T_c$ (see Figure 3).

(a)   (b)

Figure 3: Description

In Figure 4 is shown the behaviour for a ferromagnetic system. Clearly $M \neq 0$ if $H \neq 0$. Recall that M is the order parameter of the paramagnetic-ferromagnetic phase transition:

$$H = 0 \Rightarrow \begin{cases} M \neq 0 & T < T_c \\ M \to 0 & T \to T_c^- \end{cases} \tag{22}$$

Consider *ferromagnetic system*, we have $\vec{M} \to \vec{H}$ (magnetic field), while for *ferro electric* we have $\vec{P} \to \vec{E}$ (electric field). For *liquid crystals* $Q_{\alpha\beta} \to \vec{E}, \vec{H}$, for *fluid* $V \to P$ (pressure) or $rho \to \mu$.

*Remark.* Note that $\rho = \frac{N}{V} = \frac{1}{v}$ hence either N or V varies.

0.5 Divergence of the responde functions at the critical point

While at the critical point the order parameter goes to zero continuously as $T \to T_c^-$, the responde function may develop divergences.

Example 3. In a fluid system since at $T = T_c$ the curve $P = P(V)$ develops an horizontal flex (Figure 3b), we have $k_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T \to \infty$. Similarly, in a magnetic since the curve is like Figure , we have $\chi_T = \left(\frac{\partial M}{\partial H}\right)_T \underset{T \to T_c}{\to} \infty$

0.6 Thermodynamic classification of the phase transitions

Thermodynamically one can distinguish two kinds of phase transitions:
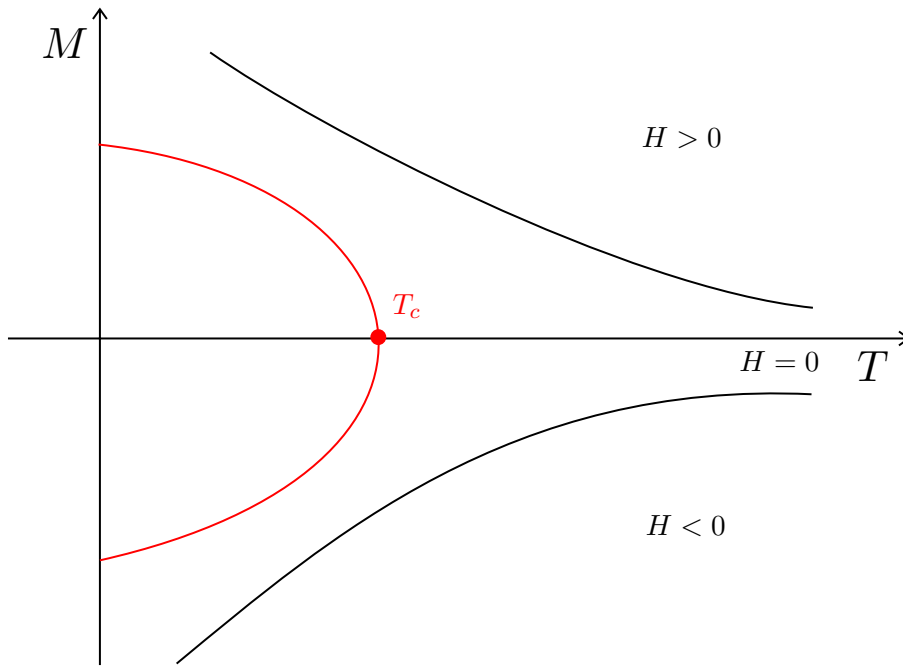
Figure 4: Description.

1. Ones who develop latent heat.

2. Ones who do not develop latent heat. The entropy changes continuously at the transition.

0.6.1 Eherenfest classification

The *Eherenfest classification* is based on the behaviour of the derivatives of the thermodynamic potentials.

A phase transition is of order n if all the *n-1* derivatives are continuous and the nth derivative displays a finite discontinuity.

Example 4. For instance, the first order transition $S = -(\partial G/\partial T)_P$ has finite discontinuity.

Remark. There are first order transitions where S is continuous (no latent heat) but ρ is discontinuous ($v = (\partial G/\partial P)_T$).

Example 5. Second order transition. The specific heat displays a finite jump, see Figure 5c in the conductor-superconductor transition.
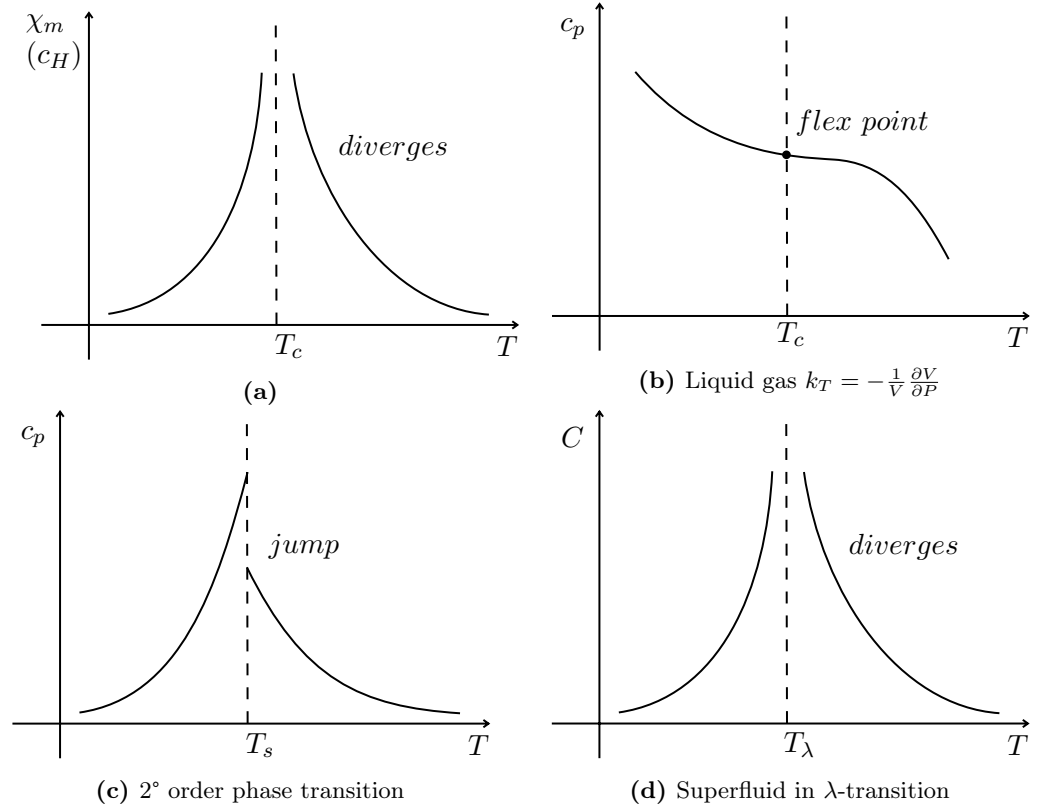
Second order transition but with divergence. Consider the fluid-superfluid transition (or λ transition) of the He_4 (Figure 5d).

0.6.2 Modern classification

A phase transition is of the first order if exists a finite discontinuity in either one or more partial derivatives of the thermodynamic potentials. If instead the first derivatives are all continuous but the second are either discontinuous or infinite one talks of continuous transitions. A critical point is a continuous transition.

0.7 Critical exponents

At the critical point response functions may diverge. How are these divergence? In general, when you are close to T_c, there are singolarities. Now, we can ask, how the

(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 5: Description

curve diverges? What is the behaviour close to the critical point? Power law, so which are the values of these critical exponents? The notion of *critical exponent* describes the behaviour of the order parameter and the responde functions in proximity of the critical point. In order to answer to these questions, let us define:

Definition 1 (**Critical Exponent** (or *Scale Exponent*))**.** Define the adimensional parameter measuring the distance from the critical point $t \equiv \frac{T-T_c}{T_c}$, the *Critical Exponent* λ associated to the function $F(t)$ is defined as:

$$\lambda_\pm = \lim_{t \to 0^\pm} \frac{\ln|F(t)|}{\ln|t|} \tag{23}$$

We note that it behaves like a power low and that one can also write the **power law**:

$$F(t) \overset{t \to 0^\pm}{\sim} |t|^{\lambda_\pm} \tag{24}$$

More generally, for $t \ll 1$:

$$F(t) = A|t|^{\lambda_\pm}(1 + bt^{\lambda_1} + \dots) \quad \lambda_1 > 0 \tag{25}$$

where all other terms are less important.

Definition 2 (Thermodynamic critical exponents)**.**

- **Exponent** β : tells how the order parameter goes to zero. Consider Figure 6a, we have $M \overset{t \to 0^-}{\sim} (-t)^\beta$. No sense in going from above where it stays 0.

- **Exponent** $\gamma_\pm$ (suscettibility): related to the response function. Consider

Figure 6b, we have $\chi_T \overset{t\to 0^\pm}{\sim} |t|^{-\gamma_\pm}$. In principle, the value of γ can depend on the sign of t i.e. $\gamma^+ \neq \gamma^-$, 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 6c, we have $c_H \sim |t|^{-\alpha_\pm}$.

- **Exponent δ**: in this case one consider the isotherm $T = T_c$ and look for the behaviour of M at the critical point at small H (or viceversa). The result is $M \sim H^{1/\delta}$. In Figure 6d, $H \sim |M|^\delta \text{sign}(M)$.

(a) Exponent β

(b) Exponent $\gamma_\pm$

(c) Exponent $\alpha_\pm$

(d) Exponent γ
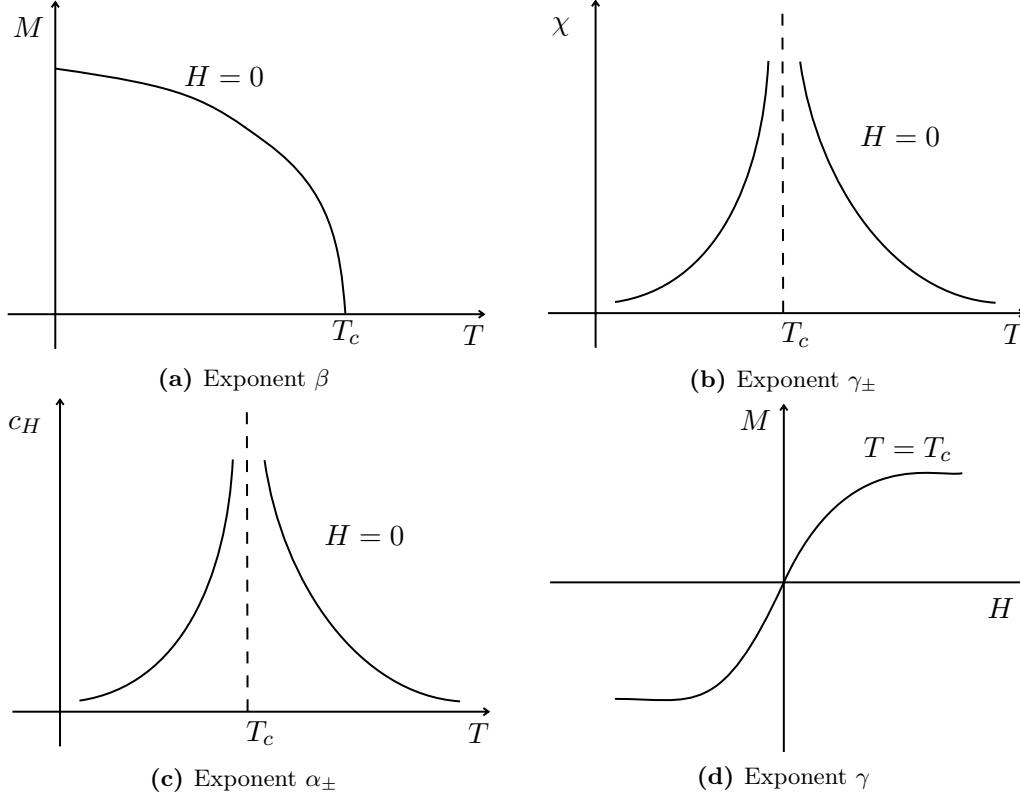
Figure 6: Description

0.7.1 Law of the corresponding states

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 7a.

The critical exponents are more interesting than T_c since their values do not depend on microscopic details but only on few parameters such as the space dimension d and the symmetry of the system. One of the first experimental evidence of this universality was given by the work of Guggenheim on the coexistence curves of g different fluids: A, Kn, χ_e, Ne, N_2, CO_2 and O_2. By plotting T/T_c versus ρ/ρ_c (Figure 7b) he found that all the data collapse on the same curve, i.e. different sets of data fit the same function. Moreover for $t \to 0$:

$$(\rho_l - \rho_c) \sim (-t)^\beta \tag{26}$$

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

Remark. The law of corresponding states gives a universal liquid-gas coexistence curve.

The law is quite remarkable considering the spread in the values of critical parameters of the substances considered.

0.7.2 Thermodynamic inequalities between critical exponents

Rushbrocke inequality

Remember the relation between response functions:

$$\begin{cases} k_T(c_p - c_v) = Tv\alpha^2 = Tv\frac{1}{v^2}\left(\frac{\partial v}{\partial T}\right)_P^2 = T\frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_P^2 \\ \chi_T(c_H - c_M) = T\left(\frac{\partial M}{\partial T}\right)_H^2 \end{cases} \tag{27}$$

from the thermodynamic stability we have $c_M \geq 0, \chi_T \geq 0$. Hence from the previous relation we have

$$c_H \geq \frac{T}{\chi_T}\left(\frac{\partial M}{\partial T}\right)^2 \tag{28}$$

On the other hand, for $T \to T_c^-$ and $H = 0$ we have

$$\begin{cases} c_H \sim (-t)^{-\alpha} \\ \chi_T \sim (-t)^{-\gamma} \end{cases} \tag{29}$$

Therefore $M \sim (-t)^\beta$, which implies $\left(\frac{\partial M}{\partial T}\right)_{H=0} \sim (-t)^{\beta-1}$. Since the inequality is valid for all temperature T it follows

$$B(T_c - T)^{-\alpha} \geq B'T\frac{[(T_c - T)^{\beta-1}]^2}{(T_c - T)^{-\gamma}} \tag{30}$$

with $B, B' > 0$. Take the limit $T \to T_c^-$ we have:

$$\lim_{T \to T_c^-}(T_c - T)^{2-\alpha-2\beta-\gamma} \geq \frac{B'T}{B} > 0 \tag{31}$$

Since the left hand side must be strictly greater than zero we have the **RushBrook inequality**:

$$\boxed{\alpha + 2\beta + \gamma \geq 2} \tag{32}$$

Is obtained from the convexity property (in T and V) of the Helmolds free energy and from $A \sim t^{2-\alpha}$:
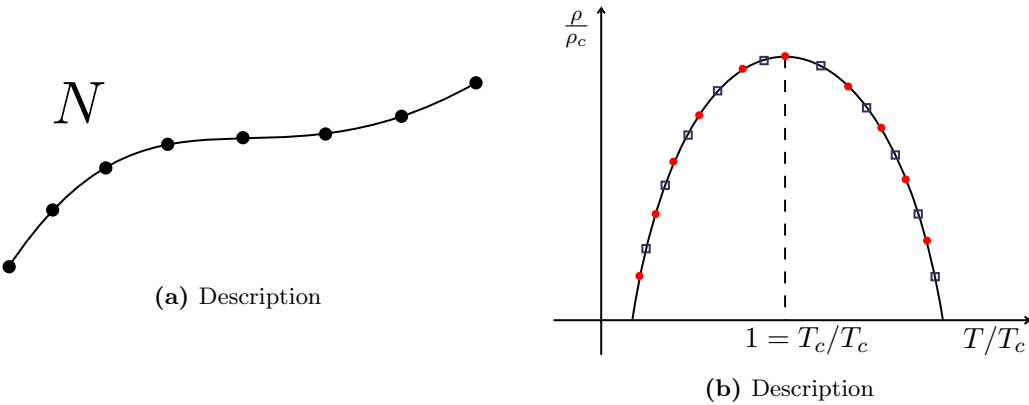
$$\Rightarrow \alpha + \beta(1 + \delta) \geq 2 \tag{33}$$

(a) Description

(b) Description

Figure 7