

## 0.1 Grancanonical potential

The two intensive variables to become independent are  $T$  and  $\mu$ . The corresponding Legendre transform is

$$\Omega = U - TS - \sum_{i=1}^r \mu_i N_i = A - \sum_{i=1}^r \mu_i N_i \quad (1)$$

Differentiating this relation we obtain:

$$\begin{aligned} d\Omega &= dU - S dT - T dS - \sum_{ij} d\mu_j N_j - \sum_{i=1}^r \mu_i dN_i \\ &= (\delta Q - T dS) - \delta W - S dT - \sum_{j=1}^r d\mu_j N_j - \sum_{j=1}^r \mu_j dN_j \end{aligned} \quad (2)$$

Hence,  $\Omega = \Omega(T, P, \mu_j)$ . Internal energy  $U$  and entropy  $S$  are homogeneous function of the first order. A consequence of this fact is the relation called **Euler equation**:

$$U = TS - PV + \sum_j \mu_j N_j \quad (3)$$

Instead, the **Maxwell relations** are relations between the mixed derivatives of the thermodynamic potentials. They can be obtained from the expressions of  $dU$ ,  $dH$ ,  $dA$ ,  $dG$  and  $d\Omega$  and from the Schwarz theorem on mixed partial derivatives. Due to Schwarz theorem, if a thermodynamic potential depends on  $t+1$  variables there will be  $\frac{t(t+1)}{2}$  independent mixed derivatives.

**Example 1** (Internal energy).

$$dU = T dS - P dV + \mu dN \quad (4)$$

where  $T = \left(\frac{\partial U}{\partial S}\right)_{V,N}$  and  $-P = \left(\frac{\partial U}{\partial V}\right)_{S,N}$ . It implies that

$$\frac{\partial^2 U}{\partial V \partial S} = \left(\frac{\partial T}{\partial V}\right)_{S,N} \underset{\text{Schwarz inequality}}{=} -\left(\frac{\partial P}{\partial S}\right)_{V,N}$$

therefore, we have the 1° *Maxwell relation* :

$$\left(\frac{\partial T}{\partial V}\right)_{S,N} = -\left(\frac{\partial P}{\partial S}\right)_{V,N}$$

All the 3 *Maxwell relations* obtained by the differential (4) with  $t=2$ , for which we have  $t+1=3$  and  $\frac{t(t+1)}{2}=3$  ( $[S, V, N]$ ), are

$$(S, V) : \quad \left(\frac{\partial T}{\partial V}\right)_{S,N} = -\left(\frac{\partial P}{\partial S}\right)_{V,N} \quad (5a)$$

$$(S, N) : \quad \left(\frac{\partial T}{\partial N}\right)_{V,S} = \left(\frac{\partial \mu}{\partial S}\right)_{V,N} \quad (5b)$$

$$(V, N) : \quad -\left(\frac{\partial P}{\partial N}\right)_{S,V} = \left(\frac{\partial \mu}{\partial V}\right)_{S,N} \quad (5c)$$

**Lecture 2.**  
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**Example 2** (Helmholz  $A = A(T, V, N)$ ).

$$dA = -S dT - P dV + \mu dN \quad (6)$$

In this case the 3 *Maxwell relations* ( $[T, V, N]$ ) are

$$(T, V) : \quad \left( \frac{\partial S}{\partial V} \right)_{T, N} = \left( \frac{\partial P}{\partial T} \right)_{V, N} \quad (7a)$$

$$(T, N) : \quad - \left( \frac{\partial S}{\partial N} \right)_{T, V} = \left( \frac{\partial \mu}{\partial T} \right)_{V, N} \quad (7b)$$

$$(V, N) : \quad - \left( \frac{\partial P}{\partial N} \right)_{V, T} = \left( \frac{\partial \mu}{\partial V} \right)_{T, N} \quad (7c)$$

**Example 3** (Gibbs  $G = G(T, P, N)$ ).

$$dG = -S dT - V dP + \mu dN \quad (8)$$

In this case the 3 *Maxwell relations* ( $[T, P, N]$ ) are

$$(T, P) : \quad - \left( \frac{\partial S}{\partial P} \right)_{T, N} = \left( \frac{\partial V}{\partial T} \right)_{P, N} \quad (9a)$$

$$(T, N) : \quad - \left( \frac{\partial S}{\partial N} \right)_{T, P} = \left( \frac{\partial \mu}{\partial T} \right)_{P, N} \quad (9b)$$

$$(P, N) : \quad \left( \frac{\partial V}{\partial N} \right)_{P, T} = \left( \frac{\partial \mu}{\partial P} \right)_{T, N} \quad (9c)$$

## 0.2 Response functions

Aim of most experiments is to measure the response of a thermodynamic system write respect to controlled variations of thermodynamic variables. In fact, any observation is just the perturbation of a system and looking for the response. A list of the commonly used response functions is the following:

- *Thermal expansion coefficient at constant pressure.*

$$\alpha_P \equiv \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_{P, N} \quad (10)$$

- *Molar heat capacity at constant pressure.*

$$c_P = \left( \frac{\delta Q}{dT} \right)_P = T \left( \frac{\partial S}{\partial T} \right)_P - S = \left( \frac{\partial G}{\partial T} \right)_P - T \left( \frac{\partial^2 G}{\partial T^2} \right)_P \quad (11)$$

- *Adiabatic compressibility.*

$$k_S = - \frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_{S, N} = - \frac{1}{V} \left( \frac{\partial^2 H}{\partial P^2} \right)_{S, N} \quad (12)$$

- *Isothermal compressibility .*

$$k_T = - \frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_{T, N} = - \frac{1}{V} \left( \frac{\partial^2 G}{\partial P^2} \right)_{T, N} \quad (13)$$

*Remark.* Remember that  $k_T$  it is the second derivative of the Gibbs potential write respect to pressure.

- *Specific heat at constant volume.* Consider a quasi static transformation.

$$c_V = \left( \frac{\delta Q}{dT} \right)_{V,N} = T \left( \frac{\partial S}{\partial T} \right)_{V,N} = \left( \frac{\partial(-\partial A/\partial T)_{V,N}}{\partial T} \right)_{V,N} = -T \left( \frac{\partial^2 A}{\partial T^2} \right)_{V,N} \quad (14)$$

- *Magnetic suscettibility* ( $d=1$ ) for a magnetic system  $(\vec{M}, \vec{H}, T)$ .

$$\chi_T = \left( \frac{\partial M}{\partial H} \right)_T \underset{M=-\frac{\partial G}{\partial H}|_T}{=} - \left( \frac{\partial^2 G}{\partial H^2} \right)_T \quad (15)$$

More generals,  $\vec{M}, \vec{H}$  we have

$$\chi_{\alpha\beta} = \left( \frac{\partial M_\alpha}{\partial H_\beta} \right)_T, M_\alpha = - \left. \frac{\partial G}{\partial H_\alpha} \right|_T \Rightarrow \chi_{\alpha\beta} = \left. \frac{\partial^2 G}{\partial H_\beta \partial H_\alpha} \right|_T \quad (16)$$

Note that the response functions, when used with the Maxwell relations, allow to express observables usually inaccessible to experiments with measurable quantities.

**Example 4** (The Maxwell relation).

$$\left( \frac{\partial S}{\partial P} \right)_{T,N} = - \left( \frac{\partial V}{\partial T} \right)_{P,N}$$

obtained from

$$dG = -S dT + V dP$$

and the response function  $\alpha_P$  permit to write

$$\underbrace{\left( \frac{\partial S}{\partial P} \right)_{T,N}}_{\substack{\text{inaccessible} \\ \text{to experiments}}} = \underbrace{-V\alpha_P}_{\text{measurable}} \quad (17)$$

**Example 5.** Let us start with the Maxwell relation

$$\left( \frac{\partial S}{\partial V} \right)_{T,N} = \left( \frac{\partial P}{\partial T} \right)_{V,N}$$

obtained from

$$dA = -S dT - P dV + \mu dN$$

From some property of multi-variable differential calculus one has the **triple product rule**:

$$\left( \frac{\partial P}{\partial T} \right)_{V,N} \left( \frac{\partial V}{\partial P} \right)_{T,N} \left( \frac{\partial T}{\partial V} \right)_{P,N} = -1 \quad (18)$$

Hence

$$\begin{aligned} \left( \frac{\partial P}{\partial T} \right)_{V,N} &= \frac{-1}{\left( \frac{\partial V}{\partial P} \right)_{T,N} \left( \frac{\partial T}{\partial V} \right)_{P,N}} = - \frac{\left( \frac{\partial V}{\partial T} \right)_{P,N}}{\left( \frac{\partial V}{\partial P} \right)_{T,N}} \\ &= \frac{-V\alpha_P}{-Vk_T} = \frac{\alpha_P}{k_T} \end{aligned} \quad (19)$$

### 0.3 Response functions and thermodynamic stability

Now, we analyze the concept of **thermal stability**. If one injects heat in a system either at constant volume or at constant pressure, its temperature will inevitably increase

$$\begin{cases} c_V \equiv \left( \frac{\delta Q}{dT} \right)_V \geq 0 \\ c_P \equiv \left( \frac{\delta Q}{dT} \right)_P \geq 0 \end{cases} \quad (20)$$

*Remark.* The thermal capacities are *non-negative functions*!

It is useful also the concept of **mechanical stability**. If one compress a system by keeping  $T$  constant, we would expect that it shrinks

$$k_T = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T \geq 0 \quad (21)$$

Similar considerations for a magnetic system, gives

$$c_H \geq 0, \quad c_M \geq 0, \quad \chi_M \geq 0 \quad (22)$$

*Remark.* In diamagnetic systems  $\chi_M$  can also be negative.

**Exercise 1.** By using Maxwell relations show that

$$c_P - c_V = \frac{TV\alpha^2}{k_T} = \frac{1}{Vk_T} T \left( \frac{\partial V}{\partial T} \right)_P^2 \quad (23a)$$

$$c_H - c_M = \frac{T}{\chi_T} \left( \frac{\partial M}{\partial T} \right)_H^2 \quad (23b)$$

A consequence is that since the right hand terms are non negative it follows that

$$\begin{cases} c_P \geq c_V \geq 0 \\ c_H \geq c_M \geq 0 \end{cases} \quad (24)$$

For reasuming, we have seen the thermodynamic of a phase, where the equilibrium state can be described by the maximum of the entropy. If we have a given phase, we can look for the Gibbs function. If we have more phases, we want to change between these phases.

# Chapter 1

## Equilibrium phases and thermodynamics of phase transitions

### 1.1 Equilibrium phases as minima of Gibbs free energy

Equilibrium states are given by *maxima* of the entropy and *minima* of internal energy, or by *minima* of thermodynamics potentials such as  $A$  and  $G$ . Let us consider for example the Gibbs potential per particle of a fluid system

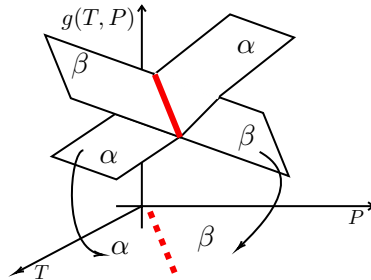
$$\frac{G}{N} \equiv g = g(T, P) \quad (1.1)$$

that depends on two intensive variables  $T$  and  $P$  and is not anymore a function of  $N$  because we have divided for  $N$ . Let us define  $\alpha$  the phase of a one-component system (say  $\alpha = \text{gas or liquid}$ ). Therefore, the thermodynamic properties are described by surfaces of function  $g_\alpha(T, P)$  and for all equilibrium phase we have a surface on the space  $(T, P, g)$ . For each value of  $T$  and  $P$  the thermodynamically stable phase is the one for which  $g_\alpha(T, P)$  is minimum.

### 1.2 First order phase transition and phase coexistence

Consider the surface  $g_\alpha$  and  $g_\beta$ , we are looking for the lower one (Figure 1.1) and there is a moment in which they coexist. The coexistence line is the projection on the  $(T, P)$  plane of the intersection between different surfaces, so the **coexistence condition** is:

$$g_\alpha(T, P) = g_\beta(T, P) \quad (1.2)$$

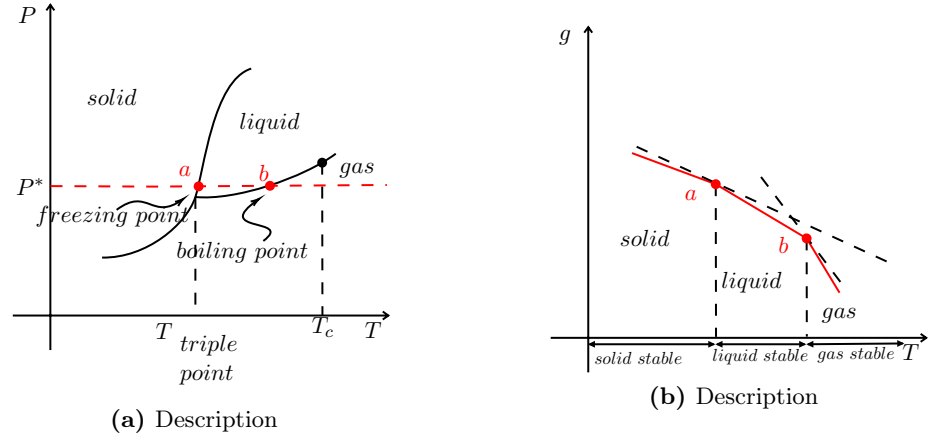


**Figure 1.1:** Description.

To fix the ideas, let us choose a given value of pressure  $P = P^*$  and study the behaviour of  $g(T, P^*)$  as a function of  $T$  when we go from solid to gas (Figure 1.2a).

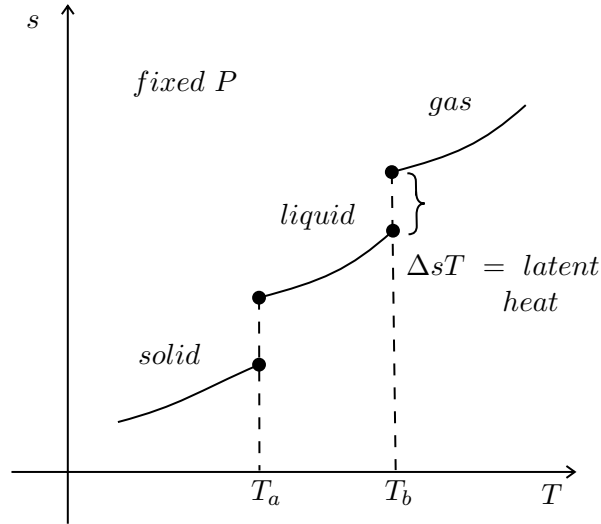
At the triple point  $g_{\text{solid}}(T_a, P^*) = g_{\text{liq}}(T_a)$  and  $g_{\text{liq}}(T_b) = g_{\text{gas}}(T_b, P^*)$  (see Figure 1.2b ). Note also that:

- At the coexistence points  $a$  and  $b$  of the two phases, one has  $g_\alpha(T) = g_\beta(T)$ .
- $g(T)$  is a continuous function of  $T$ .
- Note that,  $S = -\left(\frac{\partial G}{\partial T}\right)_V$  and  $c_P = -T\left(\frac{\partial^2 G}{\partial T^2}\right) > 0$ . This implies that  $g(T)$  is concave in  $T$  at fixed  $P$ .



**Figure 1.2:** Description

How about its derivatives? Since  $P$  is fixed we can vary  $T$  and look for  $s = -\left(\frac{\partial g}{\partial T}\right)_P$ . As we cross different phases (Figure 1.3) we have discontinuities, where  $\Delta s T$  is called the *latent heat*.



**Figure 1.3:** Description.

We can also fix the temperature  $T$  and look at the variation of  $P$  (Figure 1.4) and we have (Figure 1.5)  $v = \left(\frac{\partial g}{\partial P}\right)_T > 0$  :

$$\left(\frac{\partial^2 g}{\partial P^2}\right) = \left(\frac{\partial v}{\partial P}\right)_T = -vk_T < 0 \quad (1.3)$$

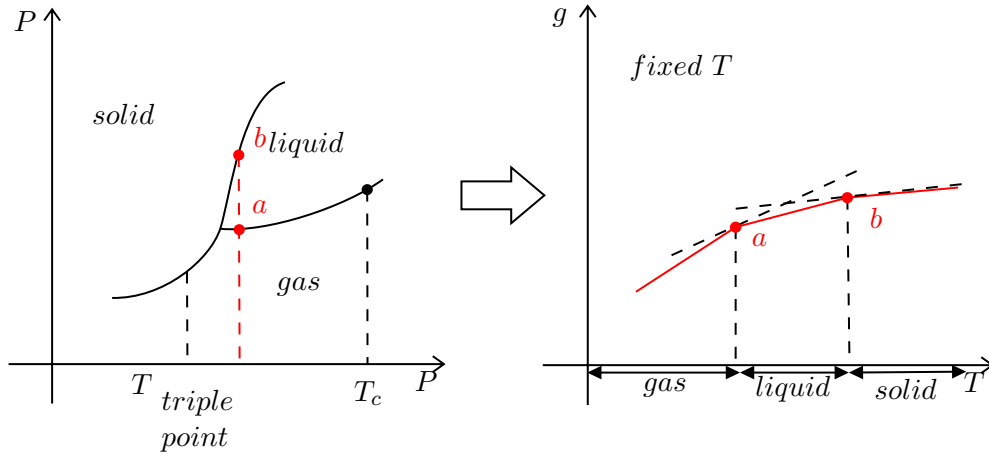


Figure 1.4: Description.

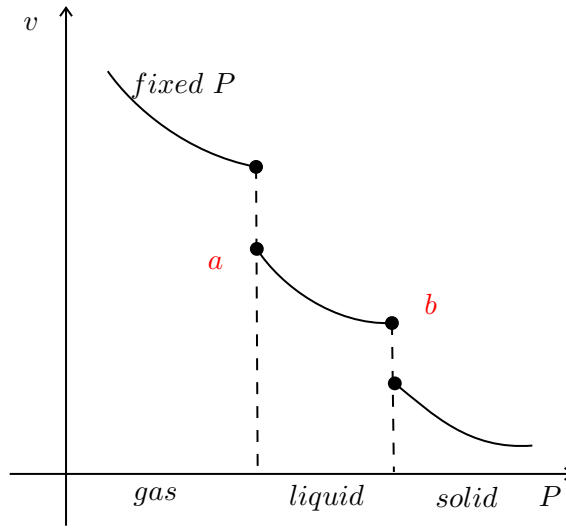


Figure 1.5: Description.

### 1.3 Second order phase transition

There are other cases in which we do not have these effects, as in Figure 1.6. This is different from the previous situation in which we had a jump:

$$\left(\frac{\partial g}{\partial T}\right)_P = -s \quad (1.4a)$$

$$\left(\frac{\partial g}{\partial P}\right)_T = v \quad (1.4b)$$

This implies:

$$\left(\frac{\partial^2 g}{\partial T \partial P}\right) = \left(\frac{\partial v}{\partial T}\right)_P = v_{\alpha P} \quad (1.5)$$

An example is *superconductivity*.

If we look for example at the specific heat in Figure 1.6d, it represent the transition from superconduction.

The critical point is special because there is not a jump, so we can go continuously from gas to liquid. The response function when we plot this point shows that the specific heat diverges. The transitions are classified in the first order transition and continuous transition. The superfluid transition is a transition where the second

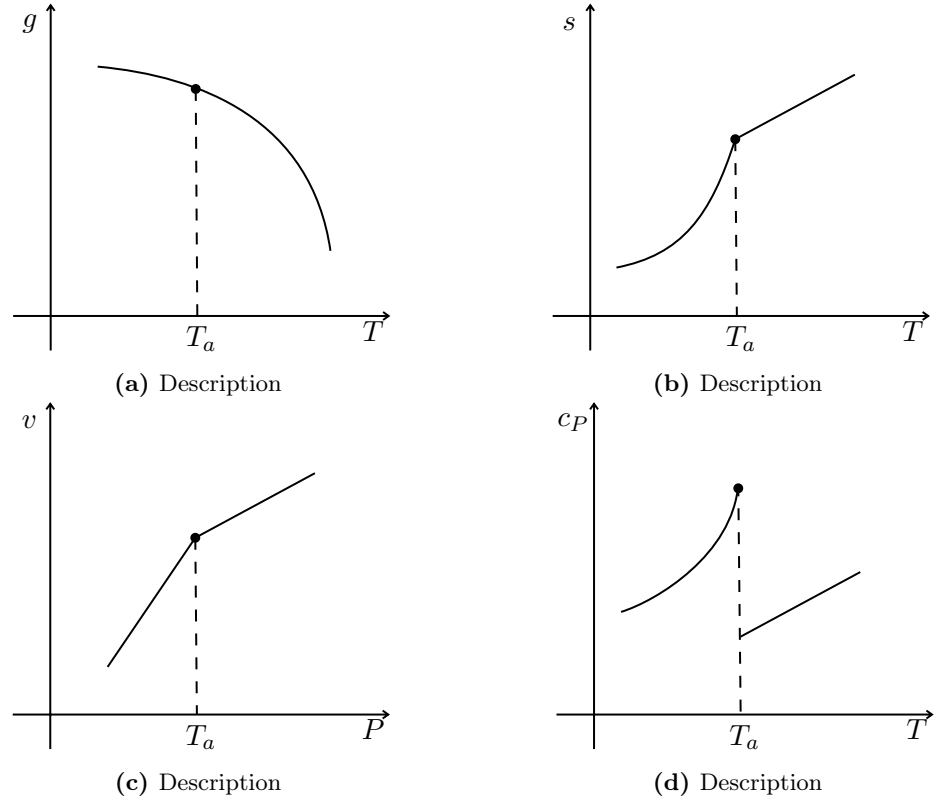


Figure 1.6: Description

derivative of the thermodynamic potential diverges. There are many phase transitions that can be classified in different ways. We note that at the coexistence line we increase  $V$ , but the pressure remains constant. At the coexistence line we see bubbles. It is the density that is changing locally, the bubbles become bigger and bigger and at the  $V_G$ , becomes a liquid.

## 1.4 Helmholtz free-energy

Consider  $A = A(T, V, N)$ , here  $P$  is replaced by  $V$  which is discontinuous at the first order transition. Moreover  $P > 0$  implies  $\partial A / \partial V < 0$  and

$$k_T = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T = -\frac{1}{V} \left( \frac{\partial P}{\partial V} \right)_T = \frac{1}{V} \left( \frac{\partial^2 A}{\partial V^2} \right)_T > 0 \quad (1.6)$$

$A$  is an overall convex function of  $V$ . The behaviour of  $A$  when there is a first order phase transition is as in Figure 1.7a. The linear sector becomes an horizontal one in the  $P = -(\partial A / \partial V)_T = P(V)$  curve (Figure 1.7b).

## 1.5 Critical points

At the critical point  $(P_c, T_c)$  the system can pass from the liquid to the gas phase (and viceversa) in a continuous way

$$\Delta s = \Delta v = 0 \quad (1.7)$$

Usually critical points are end point of first order transition phases. Why there is no critical point between solid and liquid? The crossover between phases having the same symmetry define the Landau point. There is a break of symmetry, for instance



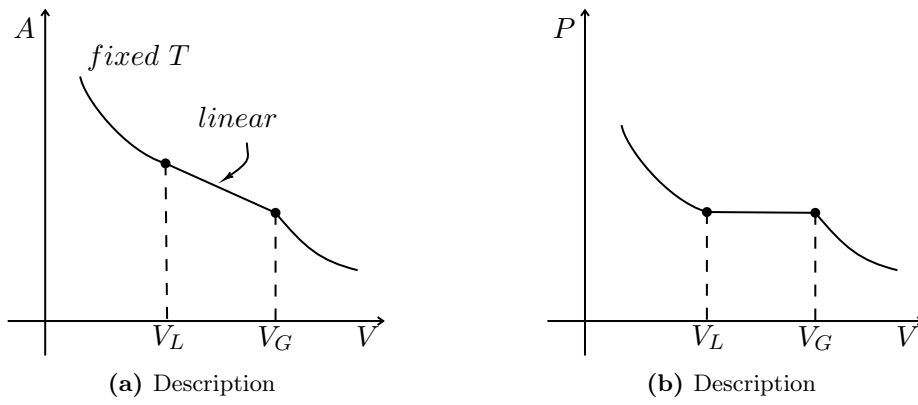


Figure 1.7: Description

we can think about the structure of the bravais lattice. Instead, from gas to liquid symmetries are not broken.

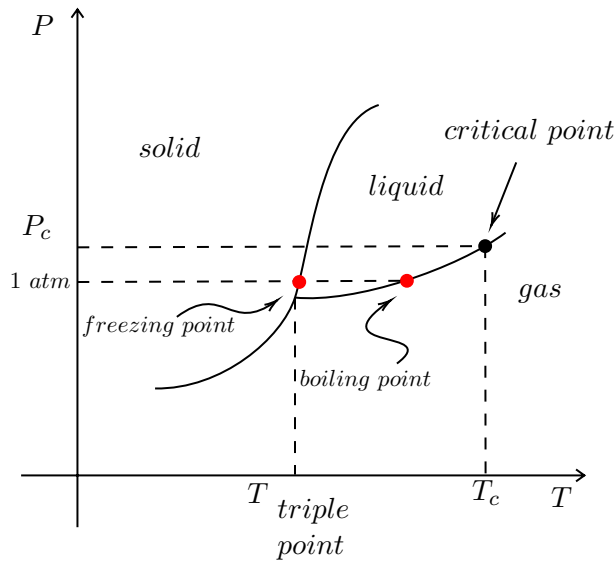
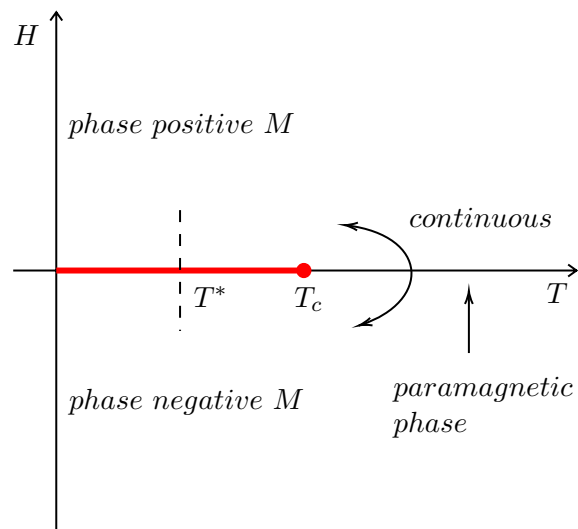


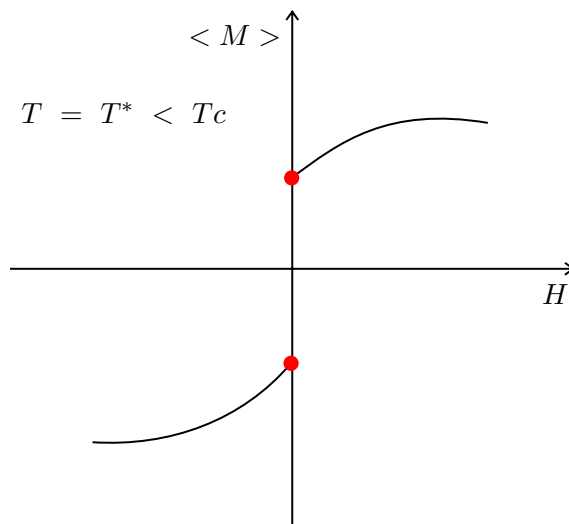
Figure 1.8: Description.

## 1.6 Ferromagnetic system

We can have a magnetization different from 0 even when there is no magnetic field. Supposing  $P \leftrightarrow H, V \leftrightarrow M$ , we have  $(P, T) \leftrightarrow (H, T)$ . We have two equilibrium states that are connected continuously, this is a first order transition. For instance consider Figure 1.10. At the critical point the magnetization would pass through zero.



**Figure 1.9:** Description.



**Figure 1.10:** Description.