Grand canonical potential

The **grand canonical potential** is obtained by performing the Legendre transform of U to replace S and N with T and μ. The corresponding Legendre transform is

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

Differentiating this relation we obtain:

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

Hence, $\Omega = \Omega(T, P, \{\mu_j\})$.

0.1 Maxwell relations

Internal energy U and entropy S are homogeneus function of the first order. A consequence of this fact is the relation called **Euler equation**:

$$U = TS - PV + \sum_{j} \mu_j N_j \tag{3}$$

Example 1: How to derive the Euler equation

Using the additive property of the internal energy U, we can derive a useful thermodynamic relation, the Euler equation.

$$U(\lambda S, \lambda V, \lambda N_1, \dots, \lambda N_m) = \lambda U(S, V, N_1, \dots N_m)$$

Let us differentiate this "extensivity condition" with respect to λ:

$$\frac{\partial U(\lambda S, \dots)}{\partial(\lambda S)} S + \frac{\partial U(\lambda S, \dots)}{\partial(\lambda V)} V + \sum_{i=1}^{m} \frac{\partial U(\lambda S, \dots)}{\partial(\lambda N_i)} N_i = U(S, V, N_1, \dots, N_m)$$

Setting $\lambda = 1$ in the above equation, we obtain:

$$\frac{\partial U}{\partial S} S + \frac{\partial U}{\partial V} V + \frac{\partial U}{\partial N_1} N_1 + \dots + \frac{\partial U}{\partial N_m} N_m = U$$

Using the definition of the intensive parameters, we arrive at the Euler equation:

$$U = TS - PV + \sum_{i=1}^{m} \mu_i N_i$$

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 2: Internal energy $U = U(S, V, N)$

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

where

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

It implies that

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

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 Maxweel 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

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

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

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

Example 3: Helmholz $A = A(T, V, N)$

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

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

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

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

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

Example 4: Gibbs $G = G(T, P, N)$

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

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

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

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

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

0.2 Response functions

Response functions are quantities that express how a system reacts when some external parameters are changed.

In fact, aim of most experiments is to measure the response of a thermodynamic system write respect to controlled variatious of thermodynamic variables. Any osservation is just the pertubation 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.*

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

- *Adiabatic compressibility.*

$$k_S = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{S,N} \underset{V=\left(\frac{\partial H}{\partial P}\right)_{S,N}}{=} -\frac{1}{V}\left(\frac{\partial^2 H}{\partial P^2}\right)_{S,N} \tag{11}$$

- *Isothermal compressibility.*

$$k_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{T,N} \underset{V=\left(\frac{\partial G}{\partial P}\right)_{T,N}}{=} -\frac{1}{V}\left(\frac{\partial^2 G}{\partial P^2}\right)_{T,N} \tag{12}$$

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

- *Molar heat capacity at constant pressure.*

$$c_P = \left(\frac{\delta Q}{\mathrm{d}T}\right)_{P,N} = T\left(\frac{\partial S}{\partial T}\right)_{P,N} \underset{-S=\left(\frac{\partial G}{\partial T}\right)_{P,N}}{=} -T\left(\frac{\partial^2 G}{\partial T^2}\right)_{P,N} \tag{13}$$

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

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

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

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

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

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

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

Let us illustrate a lemma useful for calculation:

Lemma 0.2.1. *Let x, y, z be quantities that satisfy the relation $f(x, y, z) = 0$. If w is a function of two any variables chosen between x, y, z, then:*

1. $\left(\frac{\partial x}{\partial y}\right)_w \left(\frac{\partial y}{\partial z}\right)_w = \left(\frac{\partial x}{\partial z}\right)_w$

2. $\left(\frac{\partial x}{\partial y}\right)_z = \frac{1}{\left(\frac{\partial y}{\partial x}\right)_z}$

3. $\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1$ *(concatenation relation or triple product rule).*

Example 5

The Maxwell relation

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

obtained from

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

$((T, P)$ equation) used with the response function α_P, permits to write

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

Example 6

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 $((T, V)$ equation)

$$dA = -S\,dT - P\,dV$$

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

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

Hence

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

0.2.1 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

$$\begin{cases} c_V \equiv \left(\frac{\delta Q}{\mathrm{d}T}\right)_V \geq 0 \\ c_P \equiv \left(\frac{\delta Q}{\mathrm{d}T}\right)_P \geq 0 \end{cases} \tag{19}$$

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

$$k_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T \geq 0 \tag{20}$$

Similar considerations for a magnetic system, gives

$$c_H \geq 0, \quad c_M \geq 0, \quad \chi_M \geq 0 \tag{21}$$

Remark. In diamangetic systems χ_M can also be negative.

Exercise 1

By using Maxwell relations show that

$$c_P - c_V = \frac{TV\alpha_P^2}{k_T} = \frac{1}{Vk_T}T\left(\frac{\partial V}{\partial T}\right)_P^2 \tag{22a}$$

$$c_H - c_M = \frac{T}{\chi_T}\left(\frac{\partial M}{\partial T}\right)_H^2 \tag{22b}$$

Solution. Let us start considering a system with a fixed number of particles (namely $\mathrm{d}N = 0$) and such that S is explicitly expressed in terms of T and V. Then:

$$\mathrm{d}S = \left(\frac{\partial S}{\partial T}\right)_V \mathrm{d}T + \left(\frac{\partial S}{\partial V}\right)_T \mathrm{d}V$$

Dividing by $\mathrm{d}T$ both sides keeping the pressure constant, and then multiplying by T:

$$T\left(\frac{\partial S}{\partial T}\right)_P - T\left(\frac{\partial S}{\partial T}\right)_V = T\left(\frac{\partial S}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_P$$

it implies

$$c_P - c_V = T\left(\frac{\partial S}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_P$$

Now, using the Maxwell relation $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$ and using the triple product rule we obtain

$$\left(\frac{\partial P}{\partial T}\right)_V = -\left(\frac{\partial P}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_P$$

we get:

$$c_P - c_V = -T\left(\frac{\partial P}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_P^2 = -T\alpha_P^2 V^2\left(\frac{\partial P}{\partial V}\right)_T = \frac{TV}{k_T}\alpha_P^2$$

It can be shown similarly for magnetic systems.

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

$$\begin{cases} c_P \geq c_V \geq 0 \\ c_H \geq c_M \geq 0 \end{cases} \tag{23}$$

For resuming, 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

Experimentally, any element or compound can be found, depending on the thermodynamic conditions in which it is, in different phases. When we say that a system is in a particular phase we mean that its physical properties (like density or magnetization) are uniform.

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

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

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 α as the phase of a one-component system (say α = 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

Let us suppose for example that the system can be found in two phases α and β (for example liquid and solid). Consider the surface g_α and g_β, we are looking for the lower one.

For given values of T and P the stable phase will be that with the lowest value of g: for example, if we have $g_\alpha(T, P) < g_\beta(T, P)$ then the system will be in phase α. Therefore there will be regions in (T, P) space were the most stable phase will be α and others in which it will be β. If we now plot the values of g as a function of T and T in (g, P, T) space for every phase of the system, we can determine the regions where the two phases will be the stable ones, namely we can determine the phase diagram of the system, as illustrated in Figure 1.1.

The very interesting region of this space (and the one on which we will focus our attention in this section) is the line where the surfaces of the two phases intersect: along this the two phases coexist, and when the system crosses it we say that it undergoes a *phase transition*. The coexistence line is the projection on the *(T,P)*

plane of the intersection between different surfaces, so the *coexistence condition* is:

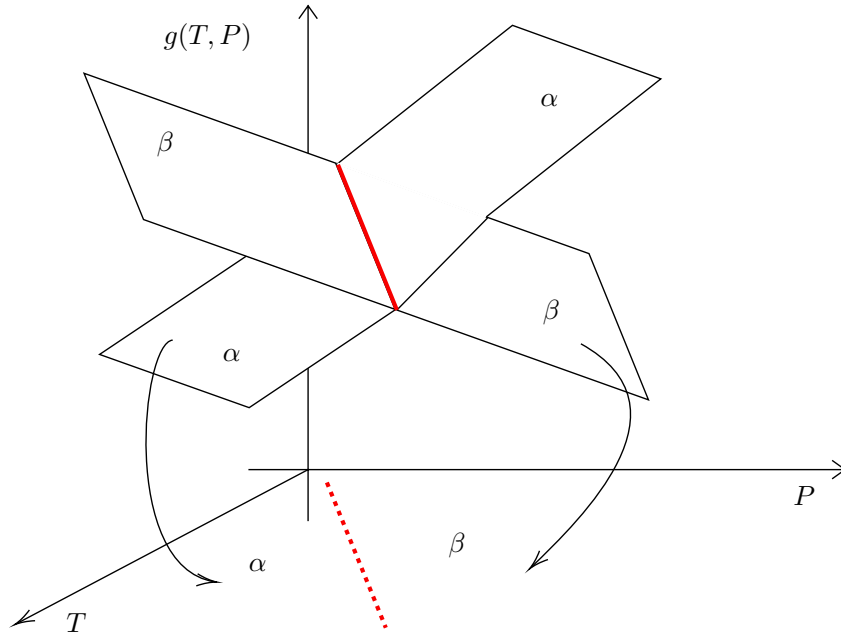$$g_\alpha(T, P) = g_\beta(T, P) \tag{1.2}$$

Figure 1.1: Phase diagram: stability of phases.

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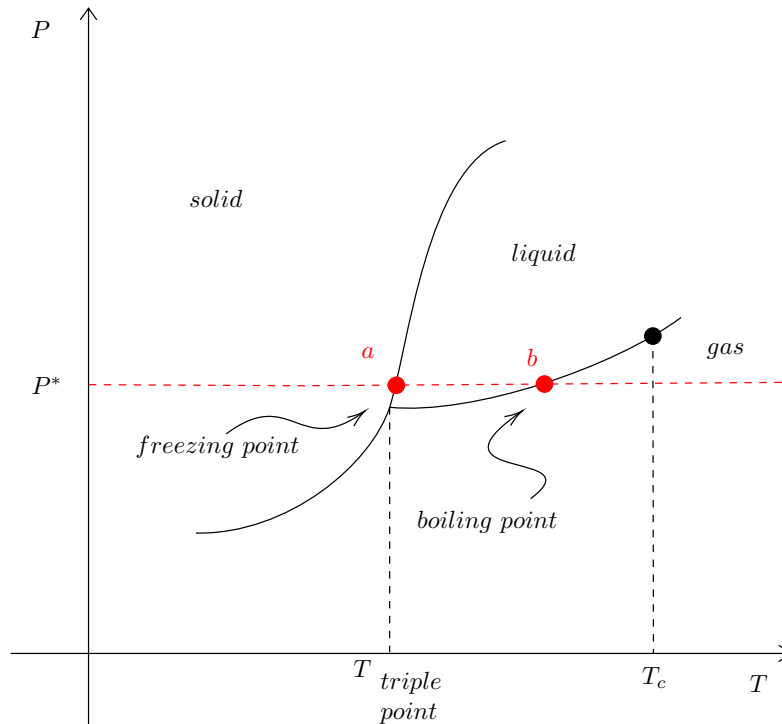

Figure 1.2: (T, P) projection.

The existence of a critical point has a very intriguing consequence: since the liquid-gas coexistence line ends in a point, this means that a liquid can continuously
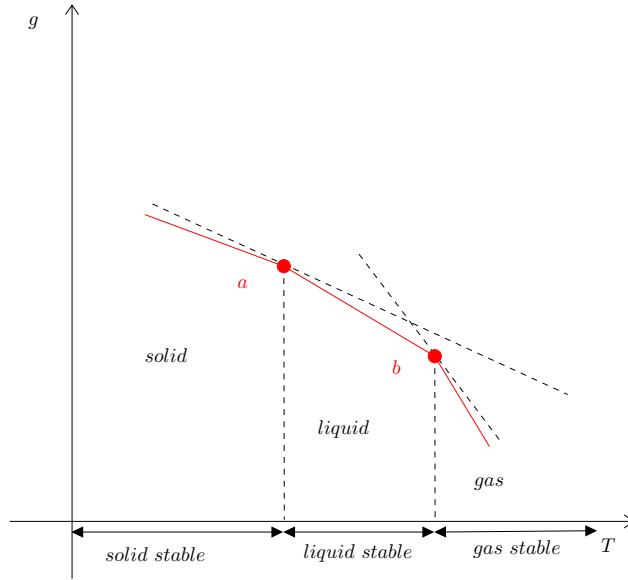
Figure 1.3: (g, T) projection at a fixed pression $P = P^*$. The red line is the coexistence line of the two phases α and β.

be transformed in a gas (or viceversa), and in such a way that the coexistence of liquid and gaseous phases is never encountered.

At the triple point $g_{\text{solid}}(T_a, P^*) = g_{\text{liq}}(T_a)$ and $g_{\text{liq}}(T_b) = g_{\text{gas}}(T_b, P^*)$, as shown in Figure 1.3 (???).

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.

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 we have discontinuities, where $\Delta s T$ is called the *latent heat*. It is illustrated in Figure 1.4.

If there is a finite discontinuity in one or more of the first derivatives of the appropriate thermodynamic potential, the transition is called *first order transition*. In general, *a phase transition is signaled by a singularity in a thermodynamic potential*.

We can also fix the temperature $T = T^*$ and look at the variation of P, as shown in Figure 1.5.

Note that, we have $v = \left(\frac{\partial g}{\partial P}\right)_T > 0$:

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

so, also in this case we had a jump of the first order derivative of the thermodynamic potential g. It is illustrated in Figure 1.6.
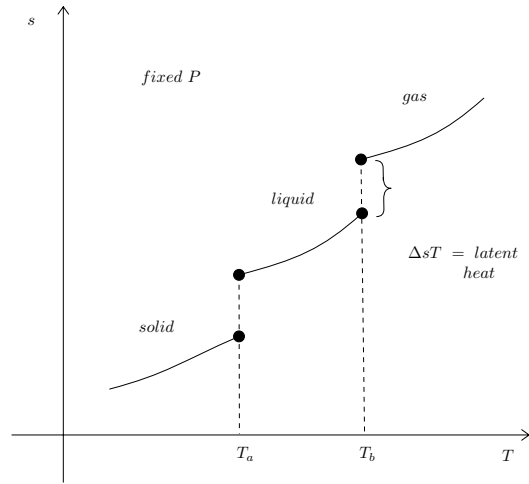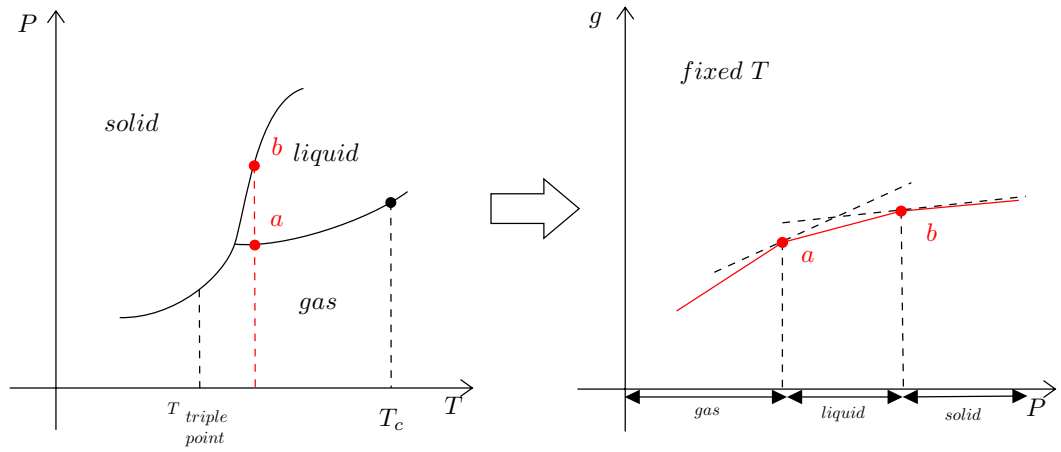
Figure 1.4: (s, T) projection.

Figure 1.5:   Left: (T, P) projection. Right: (g, P) projection at a fixed temperature $T = T^*$.
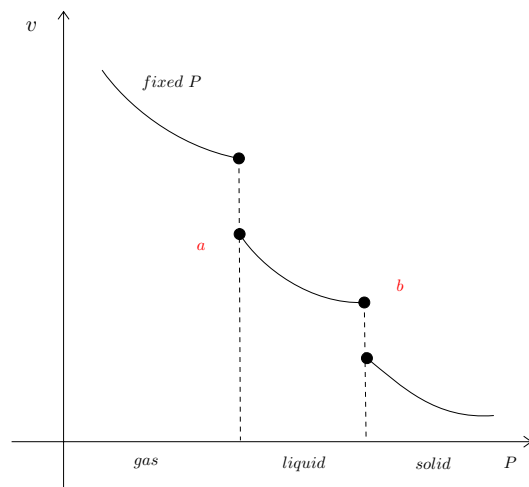

Figure 1.6: (v, P) projection.

1.2.1   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

$$\Delta s = \Delta v = 0$$

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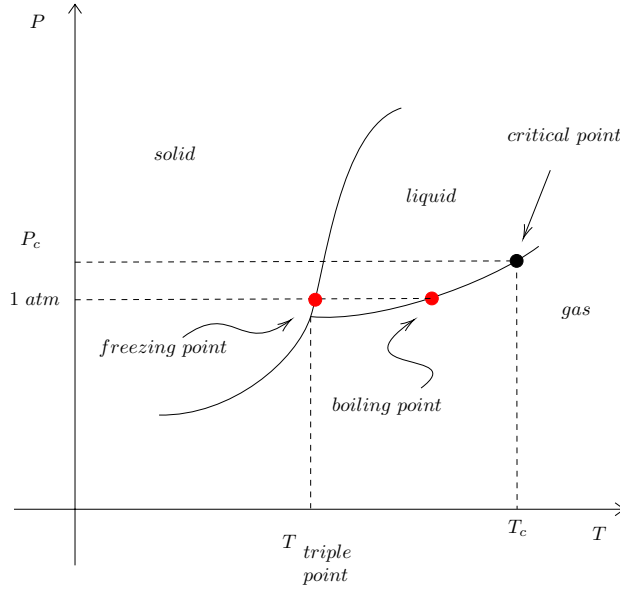

Figure 1.7:   Phase diagram of a fluid. All the phase transition are first-order except at the critical point C. Beyond C it is possible to move continuously from liquid to a gas. The boundary between the solid and liquid phases is thought to be always first-oder and not to terminate in a critical point.

1.2.2   Ferromagnetic system

A similar behaviour can be encountered in magnetic systems. We can have a magnetization different from 0 even when the is no magnetic field. Supposing $P \leftrightarrow H, V \leftrightarrow M$, we have $(P, T) \leftrightarrow (H, T)$.

The magnetization M has a jump at $H = 0$ for temperatures lower that the critical one; in this case since $M = -\frac{\partial F}{\partial H}$ we see that the first derivative of the free energy F with respect to H has a jump discontinuity. For instance, consider Figure 1.9. At the critical point the magnetization would pass through zero.
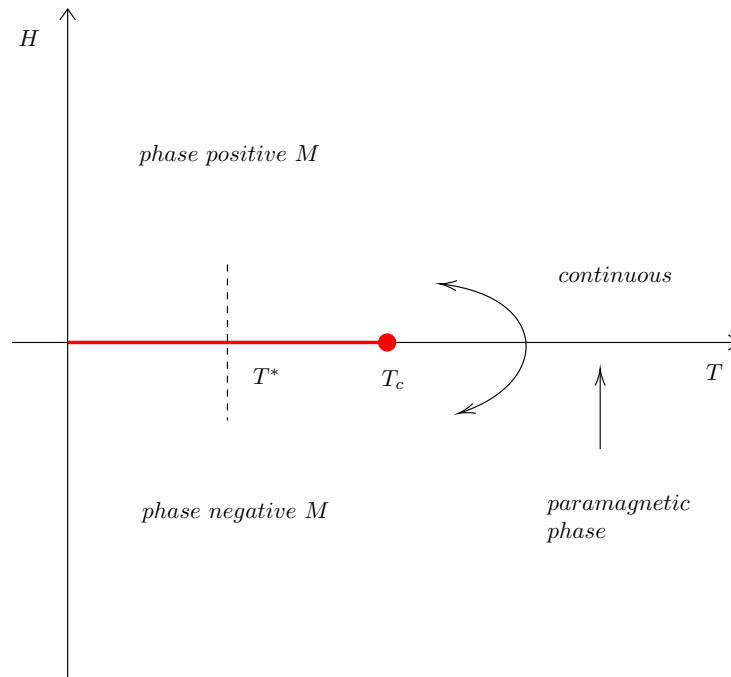
Figure 1.8: Phase diagram for a magnetic system in (T, H) space. A line of first-order transitions at zero field ends in a critical point at a temperature T_c.
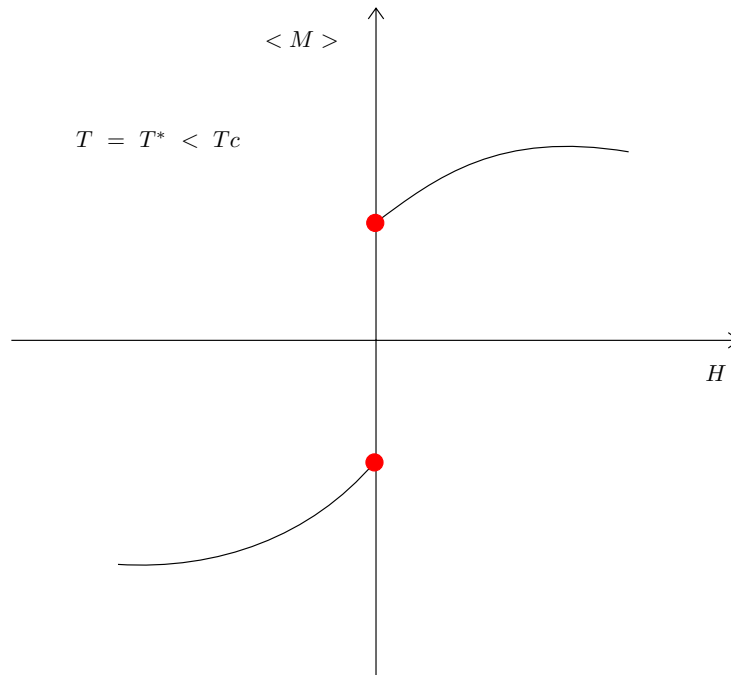

Figure 1.9: Plot of the Magnetization for $T = T^* < T_c$.

1.3   Second order phase transition

The transitions are classified in the first order transition and continuous transition. If the first derivatives are continuous but second derivatives are discontinuous or infinite the transition will be described as higher order, continuous or critical. This is different from the previous situation in which we had a jump for the first order derivative of a thermodynamic potential. Some examples are illustrated in Figure 1.10.

Let us suppose that

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

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

are continuous. This implies:

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

that is discontinuous. An example is *superconductivity*.

(a) Thermodynamic potential g.

(b) Continuous s.

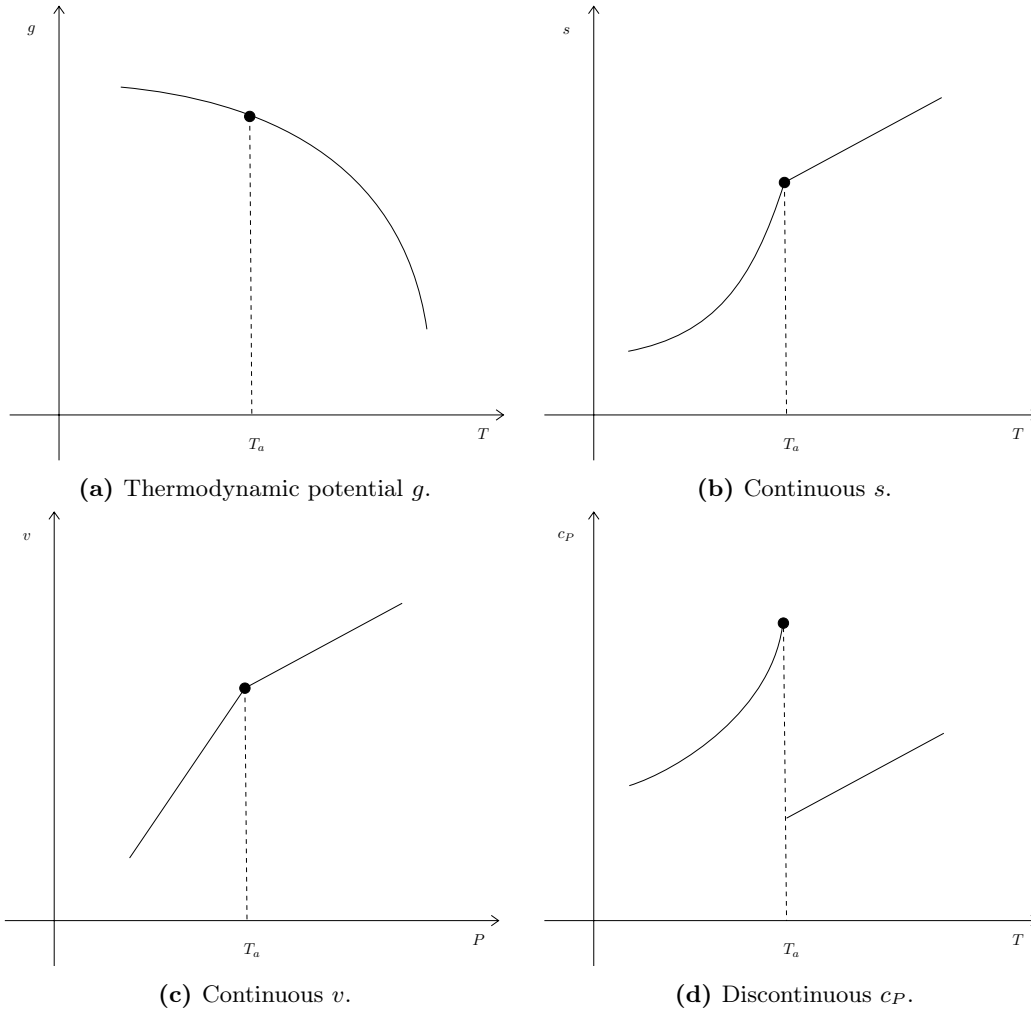**(c)** Continuous v.

(d) Discontinuous c_P.

Figure 1.10:   Example of a second order phase transition.

If we look for example at the specific heat c_P in Figure 1.10d, it represent the transition from superconduction.

The critical point is special beacause 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 superfluid transition is a transition where the second derivative of the thermodynamic potential diverges. There are many phase transitions that can be classified in different ways.

Remark. Note that at the coexistence line we increase V, but the pression remains constant. At the coexistence line we see bubbles. It is the density that is changing locally, the bubbles becames bigger and bigger and at the V_G , becames a liquid.

1.3.1   Helmholtz free-energy

(a) (V, A) projection for fixed T.   **(b)** (P, V) projection.
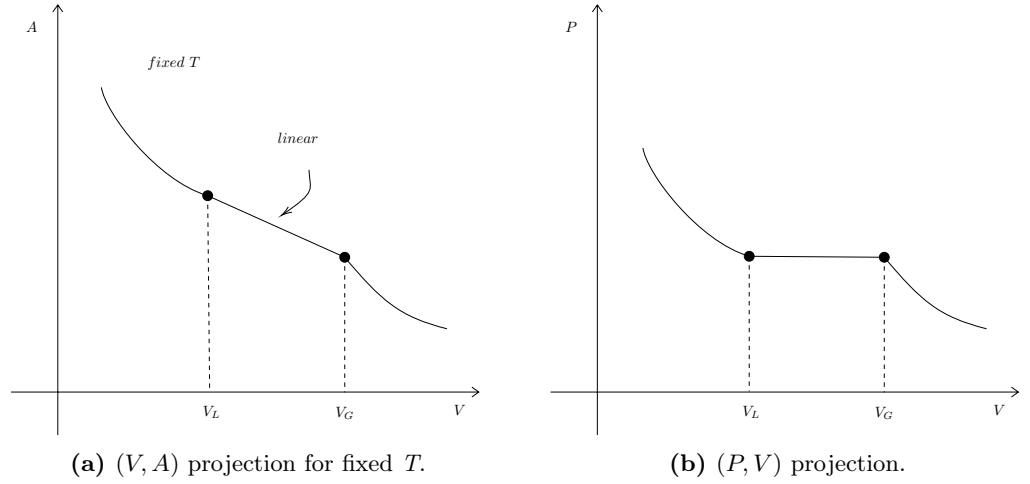
Figure 1.11: Helmholtz free-energy and phase transition.

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

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

so, A is an overall convex function of V. The behaviour of A when there is a first order phase transition is as in Figure 1.11a. The linear sector becomes an horizontal one in the $P = -(\partial A/\partial V)_T = P(V)$ curve (Figure 1.11b).