

0.1 Grancanonical potential

The two intensive variables to become independent are T and μ . The corresponding Legendre transform is

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

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

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

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

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

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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 α_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 χ_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.

0.4

Consider a fluid system and the variable $\frac{G}{N} \equiv g = g(T, P)$, where g is not anymore a function of N because we have divided for N . Suppose that α is in a given phase that can be *liquid*, *gas*, *solid*. Therefore g_α is a function of T, P , where new value of T and P corresponds to the minimum of g_α . Consider the surface g_α and g_β , we are looking for the lower one (see Figure 1) and there is a moment in which they coexist and the projection of the intersection is called projection line for which $g_\alpha(T, P) = g_\beta(T, P)$.

Now, we fix $P = P^*$, we have $g_\alpha(T, P^*)$ as shown in Figure 2a. Remember $c_P = -T \left(\frac{\partial^2 G}{\partial T^2} \right) \geq 0$, it is a concave function. At the triple point $g_{\text{solid}}(T_\alpha, P^*) = g_{\text{liq}}(T_\alpha)$ and $g_{\text{liq}}(T_b) = g_{\text{gas}}(T_b, P^*)$ (see Figure 2b).

If we define $s = -\left(\frac{\partial g}{\partial T} \right)_P$, we have $\Delta s T$ that is called the *latent heat* (Figure 3)

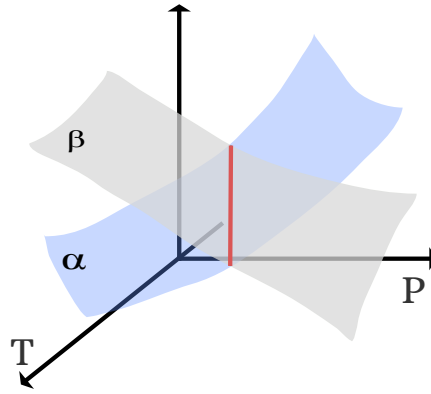


Figure 1: Description.

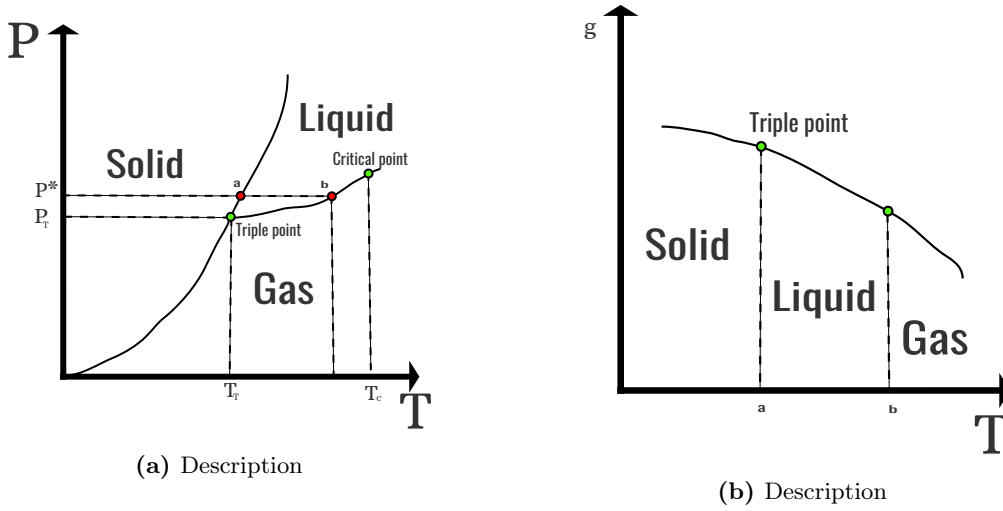


Figure 2: Description

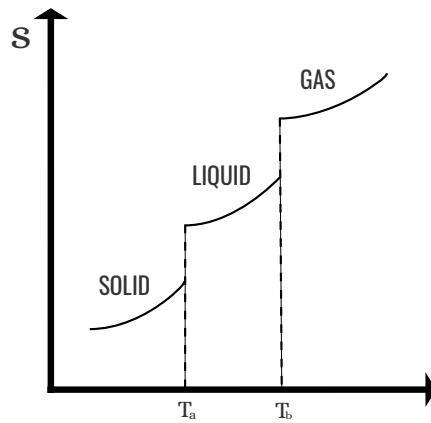


Figure 3: Description.

There are other cases in which we do not have this effect, as in Figure 4. This is different from the previous situation in which we had a jump.

If we look for example at the specific heat in Figure 5, 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

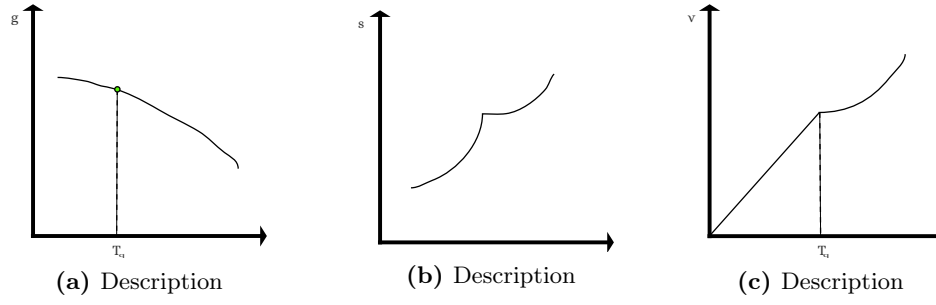


Figure 4: Description

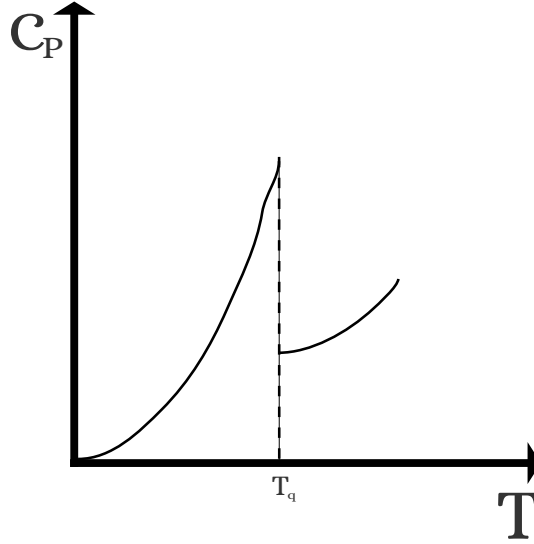


Figure 5: Description.

continuous transition. 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. 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. Usually critical points are end points of first order transition phases. Why there is no critical point between solid and liquid? 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.

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 7, where at the critical point the magnetization passes through zero.

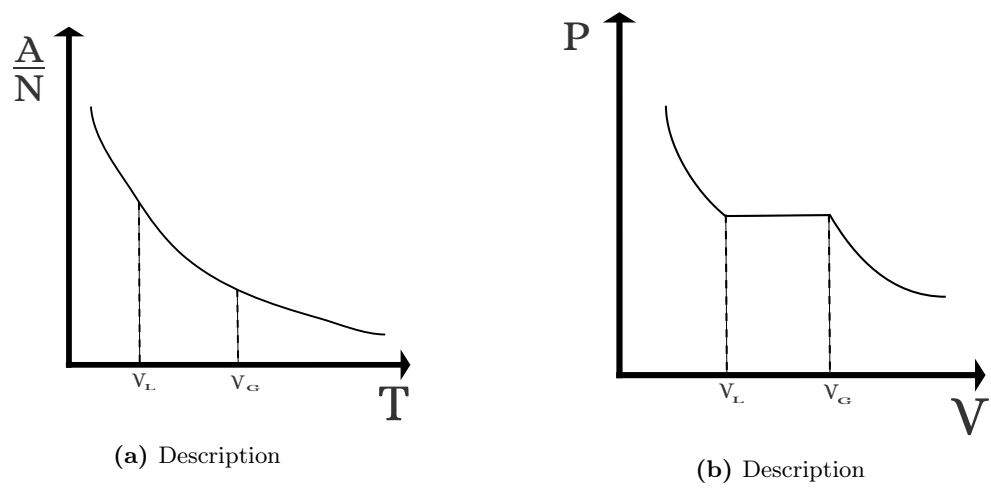


Figure 6: Description

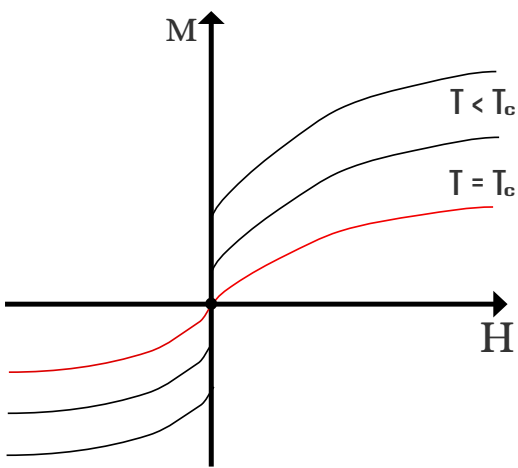


Figure 7: Description.