CHAPTER III :

1st and 2nd order transformations

First- and Second-
Order Transformatio

III.1. General Introduction :

Phase transformations (or phase transitions) describe the passage of a system from one physical state to another: solid, liquid, gas, plasma, liquid crystal, magnetic phase, superconductor, etc. During a transition, the physical properties of the system change abruptly or gradually, depending on the type of transformation.

There are two main fundamental categories:

- **First-order transitions**
- **Second-order transitions**

III.2. Classification of phase transitions:

Phase transitions are classified according to several criteria:

III. 2.1. According to the order of discontinuity:

This is the historical thermodynamic classification introduced by Ehrenfest (see next section).

III. 2.2. According to the physical nature of the transition:

- **Structural transitions** : change in atomic arrangement (e.g., metal melting, martensitic transition).
- **Magnetic transitions:** ferro → paramagnetic (Curie transition).
- **Electrical transitions** : ferroelectric → paraelectric.
- **Superconducting transitions:** passage to the superconducting state.

- **Fluid phase transitions:** gas → liquid, liquid → solid.

III. 2.3. Depending on the presence of a latent (latent heat):

- With latent heat ⇒ **1st order** transition.
- Without latent heat ⇒ **2nd order** transition.

III. 2.4. According to the continuity of the transformation:

- **Discontinuous transitions** : jumps in entropy, volume, density.
- **Continuous transitions:** no abrupt jumps, but critical behaviors.

III.3. Current classification of phase transitions:

III.3.1. 1st order transitions:

When water begins to boil, it undergoes a phase transition from liquid to gas. For each of the two phases considered separately, the equation of state is a well-defined, continuous, regular function with continuous derivatives. However, during the transition from liquid to gas, one function abruptly changes to another. Such a transition is called **a first-order transition.**

- **Gibbs enthalpy**

Phase transitions in the **P-T diagram** are described by the Gibbs enthalpy.

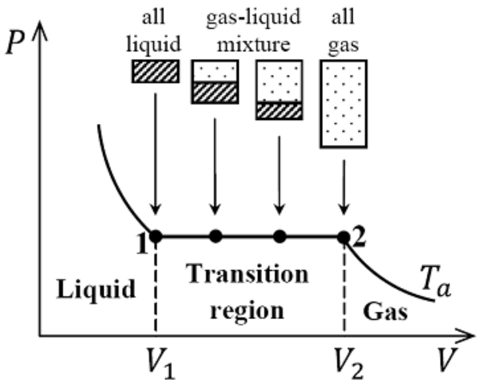
G(T,P,N)

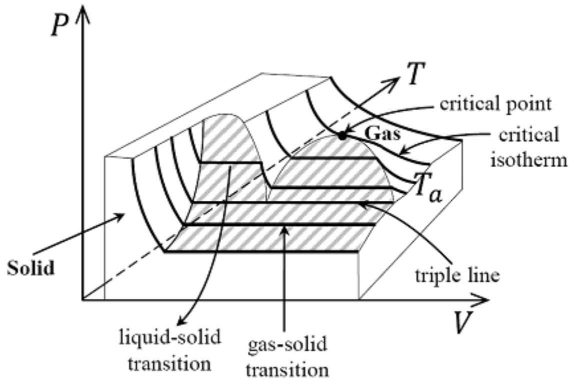
The function G (T, P, N) **remains continuous** across the phase boundary during a first-order transition.

On the other hand, the entropy S and the volume V, which are given by the derivatives:

$$S = -\left(\frac{\partial G}{\partial T}\right)_P \qquad V = -\left(\frac{\partial G}{\partial P}\right)_T \qquad dG = -SdT + VdP + \mu dN$$

Contrary, **they are discontinuous.**





- **Latent heat.**

Let us consider, instead of the **P-T diagram, the P-V** diagram , which is a projection of the equation of state of water.

Two phases 1 and 2 coexisting at a temperature T $_0$ have different entropies S1 and S2. The system must therefore absorb or release heat, called latent heat ΔQ $_L$.

$$\Delta Q_L = T_0\left(S_2 - S_1\right)$$

- **During a first-order phase transition.**
  - **Clausius-Clapeyron equation**

We denote discontinuities across the phase boundary by

$$\Delta G = G_2\left(T, P, N_2\right) - G_1\left(T, P, N_1\right)$$

$$\Delta S = S_2 - S_1 = -\left(\frac{\partial(\Delta G)}{\partial T}\right)_P$$

$$\Delta V = V_2 - V_1 = -\left(\frac{\partial(\Delta G)}{\partial P}\right)_T$$

Where we assume that S2 > S1 .

- **Cyclical chain rule:**

The discontinuities ΔG, ΔS and ΔV are functions of V, T and P, which are themselves related by the equation of state:

$f(P,V,T) = 0$.

Therefore, there must exist a function $\breve{f}$ such that:

$$\breve{f}(\Delta G, T, P) = 0$$

This condition allows us to apply the cyclic rule. We then obtain:

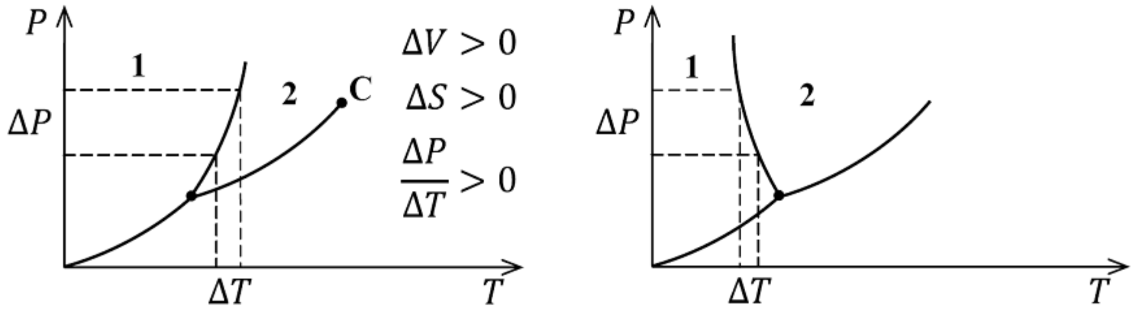
$$\left(\frac{\partial(\Delta G)}{\partial T}\right)_P \left(\frac{\partial T}{\partial T}\right)_{\Delta G} \left(\frac{\partial P}{\partial(\Delta G)}\right)_T = -1$$

- **Vapor pressure:**

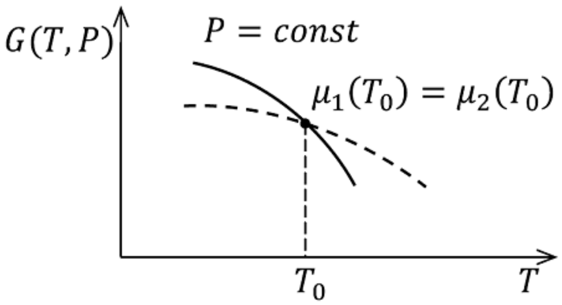
We note that P is the **vapor pressure** (*Dampfdruck* in German) for the liquid-gas transition. It varies with temperature along the phase transition line as follows:

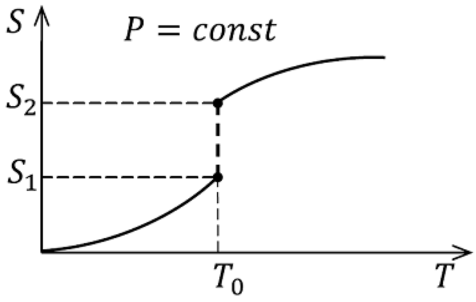
$$\frac{dP}{dT} \equiv \left(\frac{dP}{dT}\right)_{\Delta G = 0}$$

Where we used ΔG=0 when the two phases are in equilibrium with each other. Thus, $\left(\frac{dP}{dT}\right)_{\Delta G = 0}$ is **the slope of the transition line** in the **P-T diagram** .



The slope ΔP/ΔT along the solid-liquid interface is **positive** when the substance contracts during solidification, which corresponds to the normal situation. However, **water expands when freezing** due to hydrogen bonds between molecules. In this case, ΔP/ΔT is **negative** .





III.4. Ehrenfest's classification of phase transitions:

There are many types of phase transitions. They can be classified using the thermodynamic properties of substances, in particular the behavior of the **chemical potential;** this is the **Ehrenfest classification.**

Many phase transitions (such as melting and vaporization) are accompanied by changes in entropy and volume. These changes influence the **slopes of the chemical potentials** of the two phases on either side of the phase transition:

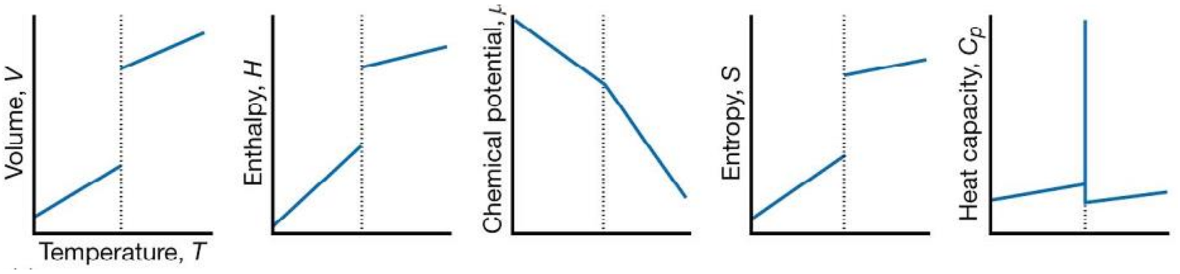
$$\left(\frac{d\mu_\beta}{dP}\right)_T - \left(\frac{d\mu_\alpha}{dP}\right)_T = V_{\beta,m} - V_{\alpha,m} = \Delta_{trs}V \quad \left(\frac{d\mu_\beta}{dT}\right)_P - \left(\frac{d\mu_\alpha}{dT}\right)_P = S_{\beta,m} - S_{\alpha,m} = -\Delta_{trs}S = -\frac{\Delta_{trs}H}{T}$$

Since $\Delta_{trs}V$ and $\Delta_{trs}H$ are non-zero for melting and vaporization, the slopes of the chemical potential plotted as a function of pressure or temperature are different on either side of the transition.

The **first derivatives** of the chemical potential with respect to pressure and temperature are therefore **discontinuous** during the transition. Such transitions are classified as **first-order transitions.**

Cp is the **slope** of a graph of H as a function of T. During a **first-order phase transition,** the enthalpy H changes from a finite amount for an infinitesimal variation of temperature to the transition temperature, the heat capacity becomes **infinite.**

The physical reason: the heat supplied is used to **affect the transition,** not to increase the temperature. Boiling water remains at the **same temperature,** even when heat continues to be supplied.

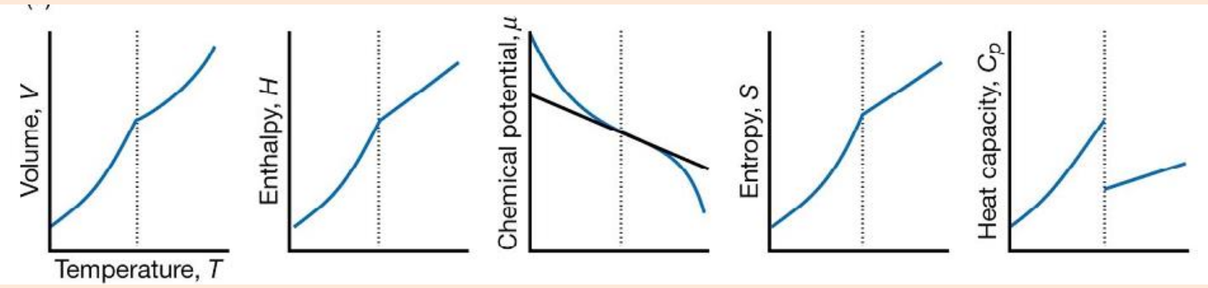


A **second-order transition:** The first derivative of the chemical potential μ is continuous, but its second derivative is discontinuous.

Volume and entropy (and therefore enthalpy) **do not change** at the time of the transition.

The heat capacity Cp is **discontinuous** but does not become infinite.

Example: the conductor-superconductor transition in metals at low temperature.



- **Transition λ (lambda)**

This is a transition that **is not of the first order** , but for which the heat capacity becomes **infinite** at the transition temperature.

The system's heat capacity begins to increase well before the transition.

This type includes:

- Order/disorder transitions in alloys,
- The emergence of ferromagnetism,

- the fluid/superfluid transition in helium.

Summary:

The order of a phase transition depends on the **first derivative of the Gibbs enthalpy (G)** which exhibits a **discontinuity** when crossing the coexistence curve.

In other words:

We look at which derivative of G changes abruptly (or becomes infinite) during the transition from one phase to another.

The rank of this derivative indicates the order of the phase transition.

🔍 **Example to better understand**

- During a **first-order transition (melting, vaporization): The first-order** derivatives of G are discontinuous → entropy, volume.
- During a **second-order transition: The second-order** derivatives of G change abruptly → heat capacity, compressibility.

III.5. Landau's Theory:

The phases before and after a phase transition often have different symmetries. The high-temperature (HT) phase is generally more symmetrical than the low-temperature (LT) phase. This is referred to as symmetry breaking during the HT → LT transition.

To describe phase transitions with symmetry change, Landau introduced the notion of an (intensive) m-order parameter:

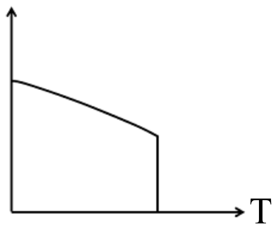
- $m=0$ in the high-temperature, symmetrical, disordered phase.
- $m\neq0$ in the low temperature phase, less symmetrical, ordered.

- **Order of a transition in the Landau sense** :

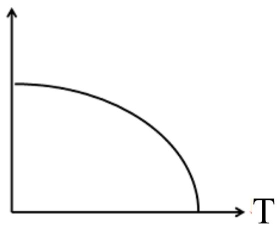
As in the case of Ehrenfest's classification, we can define the notion of order of a phase transition in the sense of Landau.

- First-order transitions are those for which the order parameter is discontinuous at the transition.
- Second-order transitions are those for which the order parameter remains continuous during the transition.

First order



Second order



Consider a phase transition with a change of symmetry for which we can define a parameter of order m. At a given temperature, the stable equilibrium state corresponds to a value of m that minimizes the free energy F(m , T). In the vicinity of the transition temperature T_0 , m is small. We can therefore expand F as:

$$F(m,T)=F_0(T)+A_0(T)m+A(T)m^2+B(T)m^3+C(T)m^4+\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots$$

Where F0 is the energy of the high-temperature phase .

- for T > T0, F must be minimal for $m=0$ and A(T) > 0.
- for T < T0, F must be minimal for $m\neq 0$ and A(T) < 0 (concavity)

The simplest choice is $A(T) = a(T - T_0)$ with a > 0

For a second-order transition, it can be shown that the odd terms are zero (A0 (T) = B(T) = 0) and that C(T) = c > 0, therefore:

$$F(m,T)=F_0(T)+a(T-T_0)^2+cm^4;\quad a\succ 0 \text{ and } c\succ 0$$

The value of m that minimizes F is a solution of

$$\frac{\partial F}{\partial m}=2a(T-T_0)^2+4cm^3=0$$

- for T > T $_0$, the only solution is m = 0
- For T < T0 , we have three solutions: a maximum at m = 0 and two minima $m=\pm\sqrt{\frac{a(T-T_0)}{2c}}$.
- In the vicinity of T0 , the order parameter behaves as $\sqrt{(T-T_0)}$

Application :

1- We can examine the behavior of entropy at the transition

$$S=-\frac{\partial F}{\partial T}=-\frac{\partial F_0}{\partial T}-am^2$$

- In the vicinity of T_0^+, $m=0$ and $S=-\left.\frac{\partial F_0}{\partial T}\right|_{T=T_0}$
- In the vicinity of T_0^-, $m=0$ and $S=-\left.\frac{\partial F_0}{\partial T}\right|_{T=T_0}-a^2\left(\frac{T_0-T}{2c}\right)$

Entropy therefore varies continuously during the transition. Consequently, there is no latent heat associated with the transition as expected for a second-order transition (in the usual sense).

2- We can examine the behavior of the heat capacity at the transition

$$C_V=T\left(\frac{\partial F}{\partial T}\right)_V \quad .;\quad S=\frac{\partial F}{\partial T}=-\frac{\partial F_0}{\partial T}-am^2$$

- In the vicinity of T_0^+, $m=0$ and $C_V=-T\left.\frac{\partial^2 F_0}{\partial T^2}\right|_{T=T_0}$

- In the vicinity of T_0^-, $m=0$ and $C_V = - T\left.\frac{\partial^2 F_0}{\partial T^2}\right|_{T=T_0} + a^2\left(\frac{T_0}{2c}\right)$

  Hence :

  $\Delta C_V = a^2\left(\frac{T_0}{2c}\right)$ →The heat capacity is discontinuous at the transition (second order), →as expected for a second-order transition in the Ehrenfest sense.

Conclusion:

Why is it important to know the order of a transition?

The order of a phase transition (1st, 2nd or nth order) provides essential information about:

- **The physical nature of the phase change**
- **The thermodynamic properties that change**
- **The behavior of matter near the transition**
- **Experimental and technological applications**

1. Understanding the quantities that change (ΔV, ΔS, ΔH, Cp…)

The order indicates **which derivatives of the Gibbs potential become discontinuous:**

- **1st order** → non-zero ΔV, ΔS, ΔH → **latent heat**
- **2nd order** → no latent heat, but discontinuity in Cp, compressibility…
- **nth order** → discontinuity in higher-order derivatives

This allows us to predict how the system reacts when the temperature or pressure is changed.

2. Predict the shape of the P–T, G–T, G–P curves

The fixed transition order:

- The **slope** of the transition lines (Clausius–Clapeyron)
- The presence or absence of a **jump** in the variables
- The infinite or non-infinite behavior of **Cp**

Without knowing the order, it is impossible to correctly draw the thermodynamic diagrams.

3. Predicting microscopic behavior

The order provides information about the **internal reorganization** of the material:

First-order transition:

- Sudden change in structure
- Coexistence of phases
- Nucleation & growth
- Latent heat

→ Important for solidification, fusion, distillation…

Second-order transition :

- Gradual but profound change
- Appearance of an **order parameter** (magnetization, superconductivity…)
- Critical fluctuations

→ Important for magnetic materials, superconductors, alloys…

III. 4. Industrial and scientific applications:

❖ Chemical and petrochemical industry:

- Distillation
- Extraction
- Synthesis and purification

→ We need to know the transition temperatures and the behavior of the phases.

❖ Metallurgy and alloys

- Transition from order to disorder
- Ferromagnetic ↔ paramagnetic
- Quenching, annealing, hardening

❖ Superconductors and advanced materials :

Second-order transition → essential for lossless electricity transmission.

❖ Cryogenics & Liquid Helium :

λ transition of helium → understanding of superfluids.

III. 5. Predicting critical phenomena :

- In the vicinity of a second-order transition, the fluctuations become enormous.
- Specific heat can diverge.
- The correlations become long (critical matter).

This allows us to understand **universal phenomena** in statistical physics.