Recapitulation and today's lecture

Last week, we finished Gibbs ensemble, we talked about partition functions for three types ensembles: (1) Microcanonical ensemble, (2) canonical ensemble, and (3) grand ensemble. We derived their partition functions as well as their relationships to the thermodynamic potentials. We also briefly talked about the Maxwell-Boltzmann distribution, where particles behave differently under different temperatures.

Today, we will discuss the stability and transition and the Phase Transition with two examples (1) Liquid/Gas and (2) Ferro/paramagnetic. We will also discuss the microscopic origin of the transition, order of the transition, and its relation with the partition function.

Stability and Transition

A phase transition occurs when a phase becomes unstable in a given thermodynamic condition described by the intensive variables (P, T, H, U, etc). Hence, at atmospheric pressure ($P = 1$ atm), ice is no longer a solid stable phase when the temperature is higher than $0°C$ Ic melts and we observe a solid/liquid transition.

We can predict the thermodynamic state of a material with the thermodynamic potentials obtained by the Legendre transformation. We can also calculate these thermodynamic potential via the physics statistics if we knew the partition function of the system. These potentials can be expressed with both intensive and extensive state variables, which characterize the system. The choice of the variable to study the system imposed the potential. If we work with the variables (T, V), we use the free energy F but if we work with the variables (P, T), we use the free energy G.

We can demonstrate in thermodynamics that a stable phase corresponds to a minimum of the potentials F and G. More generally, imagine a virtual transformation Δ of the thermodynamic quantities x from the equilibrium, we have a criterion of stability of the equilibrium condition which can be given by:

$$\Delta U + P\,\Delta V - T\Delta S \geq 0 \tag{1}$$

where ΔU, ΔS, and ΔV are the virtual variations of the internal energy U, the entropy S, and the volume V, from the equilibrium. It is the stability criterion of Gibbs-Duhem.

From this equation, we can deduce that a stable criterion is characterized by a minimum of the potential F (T and V are constant), G (at T and P are constant), ...

This condition which allows us to find a criterion of stability of the equilibrium must be examined in a strict manner. This criterion and its variants allow us to specify the equilibrium condition. Thus, important physic states of the matter, the glassy state for example, leads to state that the equilibrium of a system supposed stable, can be modified by application of a perturbation (thermal, mechanical, ...). We then must specify the situations in which the system is applicable to the Gibbs-Duhem criteria.

The equilibrium also corresponds to a maximum of the entropy and we then have for all the infinitesimal virtual variation: $\delta S = 0$. We have different situations: The conditions $\delta S = 0$ and $\Delta S < 0$ are satisfied whatever the virtual perturbation of the variables. Hence, if we perform Taylor expansion on ΔS at the equilibrium, we have:

$$\Delta S = \delta S + \frac{1}{2!}\delta^2 S + \frac{1}{3!}\delta^3 S + \frac{1}{4!}\delta^4 S + \cdots \tag{2}$$

where $\delta^2 S, \delta^3 S$, and $\delta^4 S$ are the differentials of second-, third-, and fourth-order terms with respect to the state variables. We then have $\delta^2 S, \delta^3 S, \delta^4 S, \cdots < 0$ for the equilibrium is stable.

The conditioned ($\delta S = 0, \delta^2 S < 0$) are checked for all the virtual perturbations but the condition $\Delta S < 0$ is not true for certain perturbations. We can have $delta^3 S, \delta^4 S > 0$; the equilibrium is called metastable

Certain perturbations satisfy the condition $\delta^2 S > 0$, the equilibrium is called unstable.

So we have introduced the notion of metastbility of an equilibrium, which can be intermediate state between the stability and instability. The condition $\delta^2 S = 0$ gives the metastable limit of the equilibrium. When a material from an initial stable equilibrium state is subjected to a transformation which satisfy to the condition. It gets from the metastability to the instablility, we observe a phase transition.

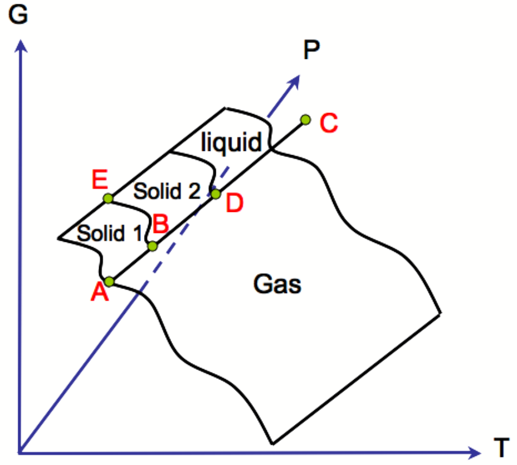

Figure 0-1: The surface of G as a function of P and T.

The curve corresponding to this limit condition of metastability is called *spinodal.* we can analitically determine the curve by writing the limi condition of metastability with other thermodynamic potentials: $\delta^2 G = 0, \delta^2 F = 0$.

In a case of a material composed of one chemical constituent and whom the molecules are isotropic, we can use the free energy G to describe its property, if we modify the equilibrium by physics with the variables (P, T). We can represent the function $G(P, T)$ by a surface in a space at 3-dimentsions; A state of the system (P and T fixed) corresponds to a point on his surface of coordinate (G, P, T). If we assume that the material can exist under two shapes of solid phases (solid 1 and solid 2), a liquid phase, and a gas phase. We will have four parts on this surface corresponding to four phases with the potential G_{S1}, G_{S2}, G_L, and G_g. That can be separated by lines. By definition, if we follow along these lines, we can find the equality of the potentials and the coexistence with the corresponding phases.

The direct application of Gibbs-Duhem criteria indicates that the stable equilibrium state corresponds to a phase which has the smallest potential (minimum of G). when crossing over these lines, the material undergoes a phase transformation. At point C, the liquid and gas phases are strictly identical. It is a singular point called *critical point.* At points B and D, three phases can coexist because the coexistence lines merge into a point, which is the intersection of the three surfaces. These are called *triple points.*

It is useful to project the surface shown in figure above on a plane (P, T) with the lines of coexistence AB, BE, BD, and DC. Hence, we obtain a phase diagram at equilibrium which represent in a plane with three different phases of the material.

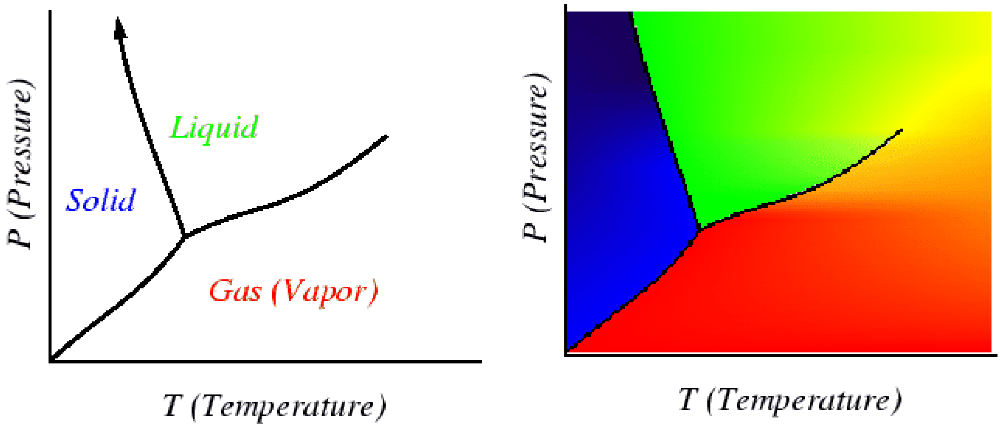

Figure 0-2: A single component phase diagram. On the right figure, the color represents a molar extensive quantities (i.e., blue is a low value of V and red is a large value of V) that apply to each phase at that particular P and T.

Phase Transition

Liquid-gas transition, ferromagnetic-paramagnetic transition are phenomenon called phase transition. A transition occurs when it exists a singularity in a thermodynamic function or in the derivative of these. The physics of transitions is a complex but very interesting domain which will be developed in this chapter.

Examples

(1) Liquid-Gas Transition

To illustrate the liquid-gas transition, we generally use a phase diagram (T, P). simple substances are capable of existing in phase of three types: solid, liquid and gas. The phase equilibrium lines separating these phases, appears typically as shown in Figure (0-2):

These lines, separate solid from liquid, liquid from gas, and gas solid from gas. The three lines meet at one common point T_r called *triple point.* At this unique temperature and pressure, arbitrary amount of all of phases can therefore coexist in equilibrium with each other. At point C, called critical point, the liquid-gas equilibrium line ends. The volume change ΔV between liquid and gas has then approached zero. Beyond point C, there is no further phase transformation since there exists only one fluid phase.

By crossing the vaporization line from high pressure to low pressure, we can observe an abrupt change from liquid state of density ρ_L to a gas state of density ρ_g. An important variation of density $\Delta\rho \equiv (\rho_L - \rho_g)$ appears in the system. The volume of the system is extended. This phase transition also go with a jump of entropy ΔS, which is expressed by the presence of a latent heat $L = T\Delta S$ necessary to the vaporization. In thermodynamics, we link the change of entropy to the shape of the curve of vaporization via the Clausius-Clapeyron relation:

$$\frac{dP}{dT} = \frac{L}{T\Delta V} = \frac{\Delta S}{\Delta V} \tag{3}$$

which is obtained by equaling the chemical potentials of both phases along the line of coexistence.

If we plot a diagram for the density ρ_L of a liquid phase and the density ρ_g of a gas phase along the curve of coexistence, we can see that the variation of density is canceled above the critical temperature T_c.

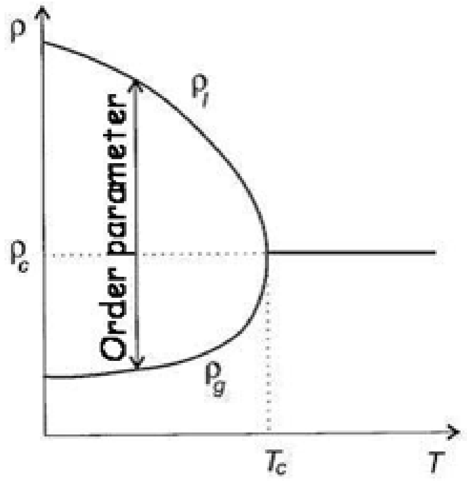

Figure 0-3: Densities of both liquid and gas phases along the curve of coexistence.

(2) Ferromagnetism paramagnetism transition

Another phase transition is observed in Ferromagnetic materials. These materials have a permanent magnetism in the absence of external magnetic field. This ferromagnetism can be observed in certain materials, such as iron, cobalt, and nichol. If we increase the temperature of a ferromagnetic materials above its critical temperature T_c, the ferromagnetism disappears to take place to the paramagnetism. If we cool this matter under T_c, a spontaneous magnetism can reappear again. This critical temperature is called the temperature of curie.

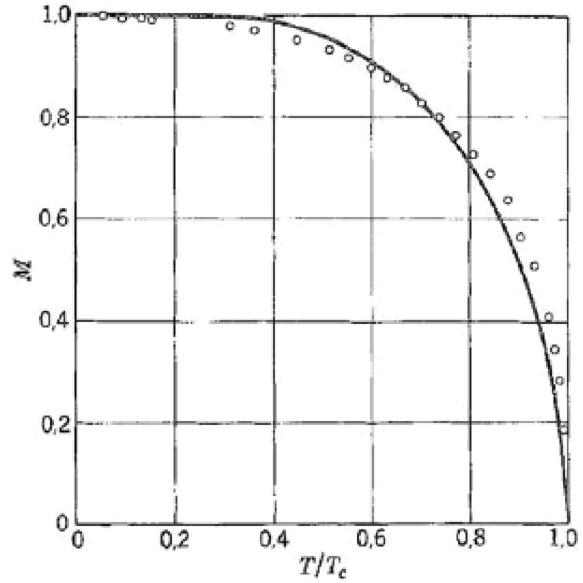

Figure 0-4: Magnetization of a rod of Ni as a function of the temperature.

To represent such transition, we can plot the magnetism M of a material as a function of the temperature. Under T_c, the magnetism is non-equal to 0 and can be negative and positive according to the averaged magnetism of the microscopic magnetic moments. When $T > T_c$, the magnetism is canceled. We obtain a diagram similar to the diagram obtained in the case of the variation of density $\Delta\rho$ of the gas-liquid transition. By crossing the temperature of curie, we will observe a jump of magnetism. In the other hand, we will observe a divergence of the magnetic susceptibility, χ, e.g., a divergence of the first derivative of M, H is the magnetic field. We have

$$\frac{M}{H} = \chi = \frac{\mathcal{C}}{|T - T_c|} \tag{4}$$

which is the law of Curie-Weiss. In the other hand, the entropy is continue in T_c. There will not be latent heat for such transition.

Microscopic Origin of the Transition

From previous examples, we can note that a phase transition is characterized by an abrupt change at the critical point. This microscopic quantity has two distinct values for both phases which surround the critical point. This quantity is chosen as order parameter to describe the transition. The order parameter is different for each case. It could be the density in the case of the liquid-gas transition, the magnetism M in the case of the ferromagnetic-paramagnetic transition.

What is the origin of the microscopic transition? We have seen that nothing happens for a perfect gas while a critical point appears for a Van der Waals (VDW) gas. The perfect gas is constituted of independent particles while the VDW gas is constituted of particles which interact with each other. In the same way, independent magnetic moments lead to the simple paramagnetism of curie while the magnetic moment of a crystal of N particles which interact with each others leads to a ferro-paramagnetic transition.

Interaction between microscopic entities are responsible of the transition. It is surprising to note that simple short range interactions are capable to induce a change of the state through all the system.

Order of Transition

Even though previous example are quantitively close, we are going to distinguish them. Ehrenfest suggested the following clarification. The first-order transition are those for which there is a discontinuity of at least one first derivative of the free energy. This implies a jump of entropy ΔS during the transition and the existence of a latent heat $L = T\Delta S$. The specific heat C_v and the compressibility k_T diverge.

The second-order phase transition exhibit discontinuities of the second derivative of the free energy. Thus, the entropy is continue but the first derivative of the entropy exhibits different values according to the phases. The specific heat C_v exhibits in general a discontinuous jump at the transition and the susceptibility χ diverges.

Order	**1**	**2**
Definition	discontinuity of $\frac{\partial F}{\partial T}$	discontinuity of $\frac{\partial^2 F}{\partial T^2}$
Properties	$\Delta S \neq 0$ latent heat $\Delta\rho \neq 0$ C_v diverge k_T (β) diverge	$\Delta S = 0$ no latent heat $\Delta\rho = 0$ jumps in C_v χ diverges
Examples	liquid-gas	ferro-para

The thermodynamics well describes the first-order phase transition via the Clausius-Clapeyron relation but but is not accurate for the second order. It can then be powerful to use statistical physics to describe the second-order phase transition.

The classification of Ehrenfest is very useful but not sufficient. Landau remarked that a phase transition without latent heat goes with a change of symmetry. Hence, in the case of a magnetic molecule, it doesn't have a permanent magnetic moment above the temperature of curie. Under this temperature, it has an oriented permanent magnetization in certain direction (ferro-magnetic state). This phenomenon is called a broken symmetry at the transition.

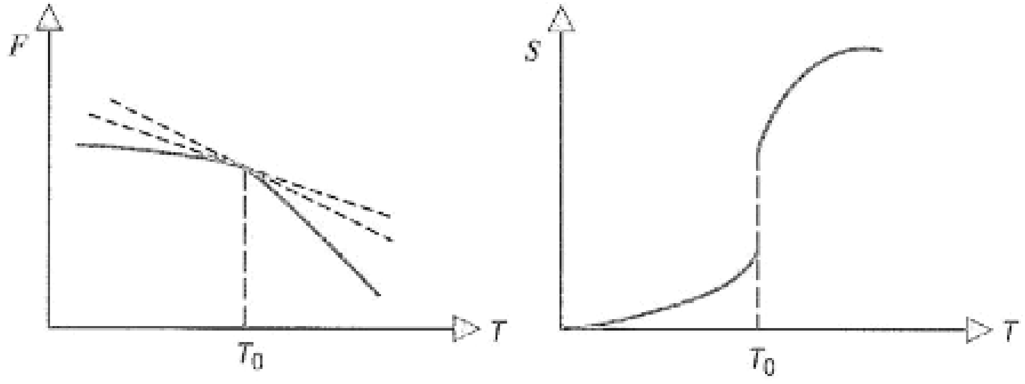

Figure 0-5: First-order transition in T_0, discontinuity of S.

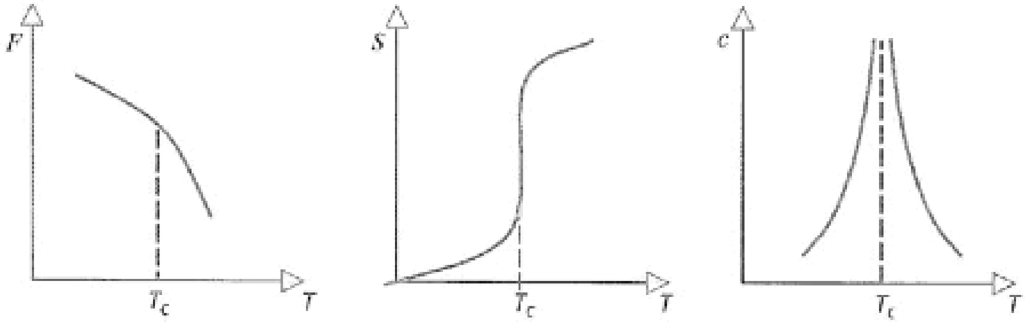

Figure 0-6: Second-order transition in T_c, discontinuity of C_v.

The question of symmetric is very important. In the study of the phase transition, Landau associated this phenomenon of the broken symmetry with the notion of order parameter. The order parameter is an extreme physical quantity, which equals to zero when the phase is more symmetric (or less ordered) and different to zero in the phase that is less symmetric (more ordered).

With this notion of order parameter, we can distinguish two types of transitions: the transition without order parameter for which the group of symmetry of both phases are such that no phases is strictly included in the other one; it is the first-order transition as described by Ehrenfest. Transitions for which we can define order parameter and that are such that the group of symmetry of the phase. The less symmetric is a under-group of the group of the symmetry of the phase the most symmetry. If the order parameter is discontinuous at the transition, it is a first-order transition, as defined by Ehrenfest, otherwise, (if it is continuous)it is a second-order transition.