Introduction

Statistical physics studies microscopic system composed of several entities in interaction leading to a collective behavior at macroscopic scale. Statistical physics also bridges the gap between both microscopic and macroscopic worlds.

The thermodynamics developed until the beginning of the 20th century is going to be enough to derive the equilibrium behavior, but the statistical physics is going to get rid of his framework very restrictive via both probabilistic and statistics aspects.

Thermodynamics and kinetic theory of gas

At the beginning of the 20th century, statistic mechanics has been developed in order to brace diverse thermodynamic macroscopic properties of gas from their microscopic descriptions. For example, it is possible to determine the pressure P of a perfect gas from a movement of coming and going of one particle of this gas in a cubic box, which has the length of size L and the volume $V = L^3$. Following the direction of an axis, x, the particle that rebound on the right wall was recorded. A variation of this movement quantity:

$$\Delta P_x = -2\ v_x \tag{1}$$

This variation introduces an estimation of the force F that the wall exerts on the particle. At the time of rebound, the elastic collision occurs one time per coming and going (during a time-interval giving by $\Delta t = 2L/V_x$), F is then given by

$$F = \frac{\Delta P_x}{\Delta t} = -\frac{m\ v_x^2}{L} \tag{2}$$

The pressure P exerted by the particle on the wall is given by:

$$p = -\frac{F}{L^3} = \frac{m\ v_x^2}{L^3} = \frac{m\ v_x^2}{V} \tag{3}$$

For an isotropic gas, no direction is favored. We have

$$\begin{aligned} &\text{in average: } < v^2 >= 3\ < v_x^2 > \\ &\text{and then: } PV = \frac{m\ < v^2 >}{3} \end{aligned} \tag{4}$$

For N particles, we obtain

$$PV = \frac{N\ m\ < v^2 >}{3} = \frac{2U}{3} \tag{5}$$

For a perfect gas, the internal energy is the kinetic energy. Combing the last equation with the ideal gas law, $PV = Nk_bT$, we find the first equation of state for the perfect gas:

$$U = \frac{3}{2}Nk_bT \tag{6}$$

It gives the microscopic representation of the temperature, T. The temperature is a kind of measure of the agitation of the gas particles also called the energy of thermal agitation, $k_b T$.

Nevertheless, the particles of a real gas can enter into collision. They can also interact with themselves. Besides, they are characterized by the specific sizes and occupying a volume, forbidden to the other particles.

In a dense system, the study of collisions between particles allowed the description of an unperfect gas. We often are looking for corrections to idealize situations. For example, the state equation of perfect gas, $PV = Nk_b T$, becomes $(P + b)(V - a) = Nk_b T$ for a Van der Waals gas. The parameters a and b respectively depict the excluded volume and the short range alternation.

Interactions and Transitions

It is the more or less long range interactions which allow for the motion of different phases of the matter: In physics, they are systems including:

1. Coulomb interaction between charged particles. The Hamiltonian is written as:

$$H = \alpha \sum_i \sum_{j \neq i} \frac{Q_i Q_j}{r_{ij}^2} + \frac{1}{2} \sum_i m_i v_i^2 \tag{7}$$

   where the summation sums over all the pairs of ions i and j of charges Q_i and Q_j, and separated by a distance equals to r_{ij}.

2. Van der Waals interactions between molecules electrically neutral but having an intrinsic dipolar moments. The Hamiltonian is then:

$$H = \sum_i \sum_{j \neq i} [\frac{A}{r_{ij}^{12}} - \frac{B}{r_{ij}^{6}}] + \frac{1}{2} \sum_i m_i v_i^2 \tag{8}$$

All these potentials of interactions tend to agglutinate, arrange orient, or organize these microscopic entities in well defined structures. It is of course possible when the thermal agitation is weak with regard to the interaction energy. At high temperature, the system is disordered. By reducing the temperature of the system, a phase transition more or less ordered will occur.

The important step of the static phase was the description of phase transitions. A phase transition corresponds to an abrupt change of physics properties for precise values of certain external parameters (e.g., temperature). For example, if we reduce the temperature of water under $T = 0°C$, we observe a abrupt variation of density when the water becomes ice. Numerous phenomenons are linked to the phase transition.

Spin Model

In order to model the phase transition, the statistical physicist have developed spin models. Spins are microscopic entity, which are submitted to the thermal agitation. These spins are generally arranged in lattice. the minimization of the energy leads to a transition between an order of spins at low temperature and a disorder of spins at high temperature. Even though these models are simple to define, their behaviors are still studied. The numerical and theoretical study of spin models have motivated a lot of works in *Statistical Physics* during a major part of the 20th century and has been extended to study many phase transitions.

Aim of This Lecture

The statistic physics lectures are based on thermodynamics, classic mechanics, and quantum mechanics. The main purposes of this lecture are to provide the formalism based on the statistic physics to illustrate the importance of the concepts introduced in the domain and undertake the numerous applications.

Reminder in Thermodynamics

The statistical physics has been developed from concepts based on classical thermodynamics. This concept reminds briefly several fundamental notions necessary to a good understanding of the following lectures.

Extensive and Intensive Variables of Equilibrium

The thermodynamics is principally interested in by system at equilibrium. To describe thermodynamic system, we often use the internal energy, U, the volume, V, of the system and the number of the particles, N. Those variables are linked respectively to thermal, mechanical and osmotic equilibriums. The first principal states that they are sufficient to describe all thermodynamic equilibriums. Besides, these extensive variables are associated to conjugate intensive variables, T, P, and μ.

Boltzmann Entropy

The second principal state of thermodynamics states that an additional extensive variable is maximal at equilibrium. This is the entropy $S(U,\ V,\ N)$ which is a function of the extensive quantities. It gives information on the homogeneous state of the system. Boltzmann postulated that: $S = k_b ln \Omega$ where Ω is the number of microscopic states that the system can reach. The Boltzmann entropy will then bridge the gap between the microscopic and the thermodynamics variables. It is this precise aspect that will be studied in details in the following.

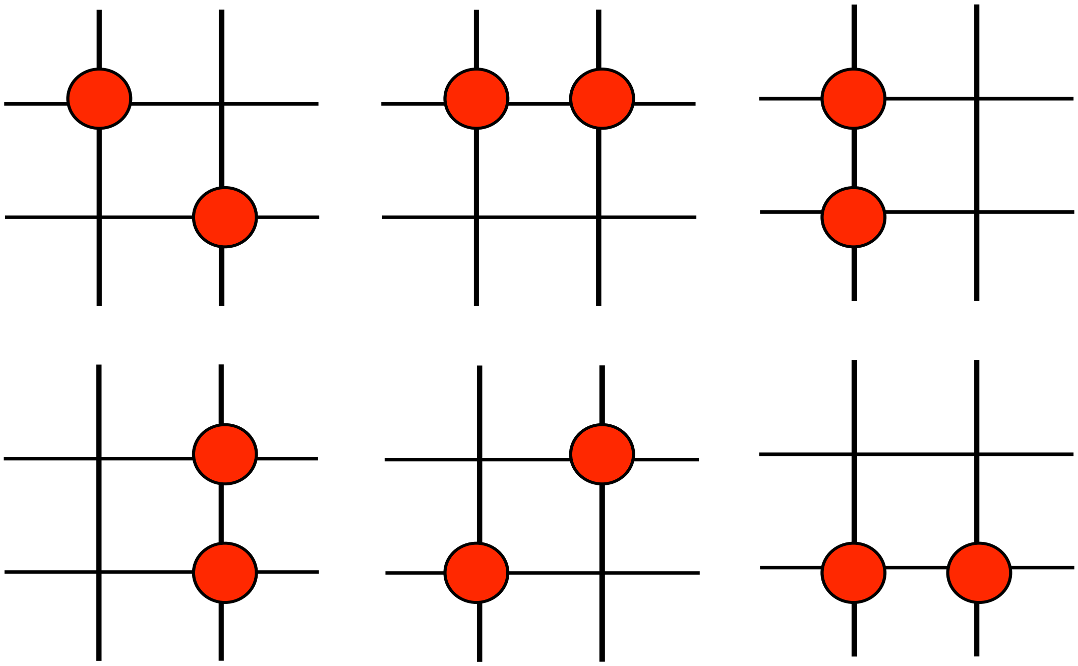

Figure 0-1: Number of possible arrangement for a two-particle system.

Equation of State

For every physical system, the energetic balance at thermal, mechanical and osmotic equilibriums leads to: $dU = TdS - PdV + \mu dN$. We can derive 3 equations of state:

$$T = (\frac{\partial U}{\partial S})_{V,\ N} \quad P = (\frac{\partial U}{\partial V})_{S,\ N} \quad \mu = (\frac{\partial U}{\partial N})_{S,\ V} \tag{9}$$

These equations are only true at equilibrium. For a perfect gas, the state equation can be written as: $U = \frac{3}{2}Nk_bT$.

Thermodynamic Potentials

It could be powerful to use intensive variables because the extensive variables are difficult to measure. We then use the Legendre transformation which allows to replace an extensive variable by its conjugate variable. The free energy is very often used: $F = U - TS$, which is a function of T, V, and N. The free energy leads to the following state equations:

$$S = (-\frac{\partial F}{\partial T})_{V,\ N} \quad P = (-\frac{\partial F}{\partial V})_{T,\ N} \quad \mu = (\frac{\partial F}{\partial N})_{T,\ V} \tag{10}$$

We could also use the free energy: $G = F + PV$, which is a function of T, P, and N. For this thermodynamic potential, we obtain the following 3 state equations:

$$S = (-\frac{\partial G}{\partial T})_{P,\ N} \quad V = (\frac{\partial G}{\partial P})_{T,\ N} \quad \mu = (\frac{\partial G}{\partial N})_{T,\ P} \tag{11}$$

We could also show that the free enthalpy is directly linked to the chemical potential μ via the Gibbs-Duhem relation $G = N\mu$ (for a single component).

Gibbs Ensemble

We have first to define a system composed of N microscopic entities. This system is in contact with a reservoir with which it is in thermodynamic equilibrium. the reservoir has for role to impose a temperature T to the system (like a thermostat). Besides, the reservoir allows or not both heat and matter exchange. The ensemble (system + reservoir) is completely isolated.

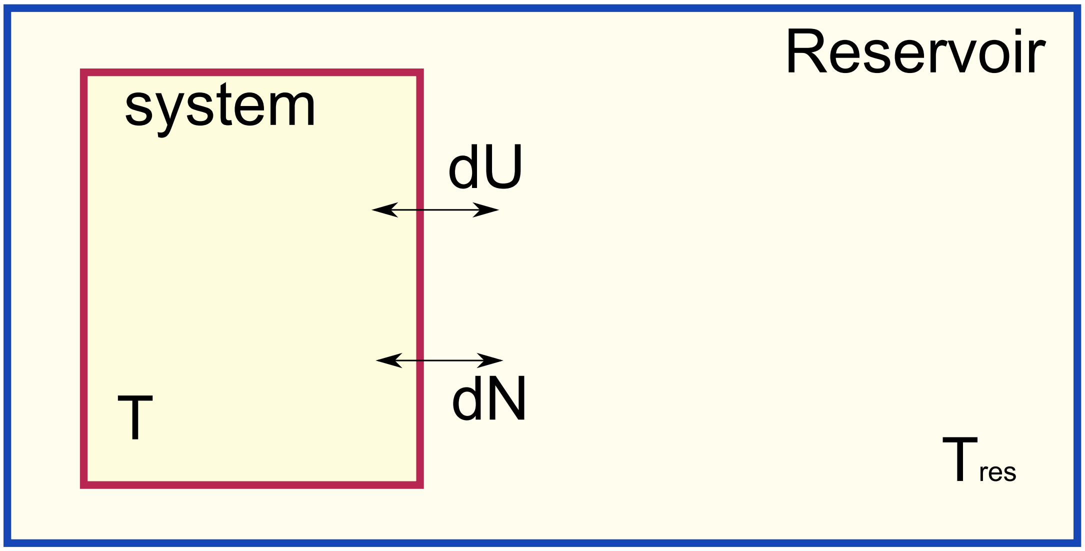

Figure 0-2: Example of system and resrvoir are in equilbrium

Phase Space

Atoms and molecules are properly described in terms of quantum mechanics. A description in terms of classical mechanics, although inadequate in general, may nevertheless sometimes be a useful approximation. It is, therefore, worth making a few comments about the specifications of the state of a system in classical mechanics.

We will start with a very simple case, a single particle in one dimension. This system can be completely described in terms of its position coordinates q and its corresponding momentum p. (This specification is complete since the laws of classical mechanics are such that a knowledge of q and p at any time permits prediction of the value of q and p at any other time.) It is possible to represent the situation geometrically by drawing Catesian axes labeled by q and p as shown here:

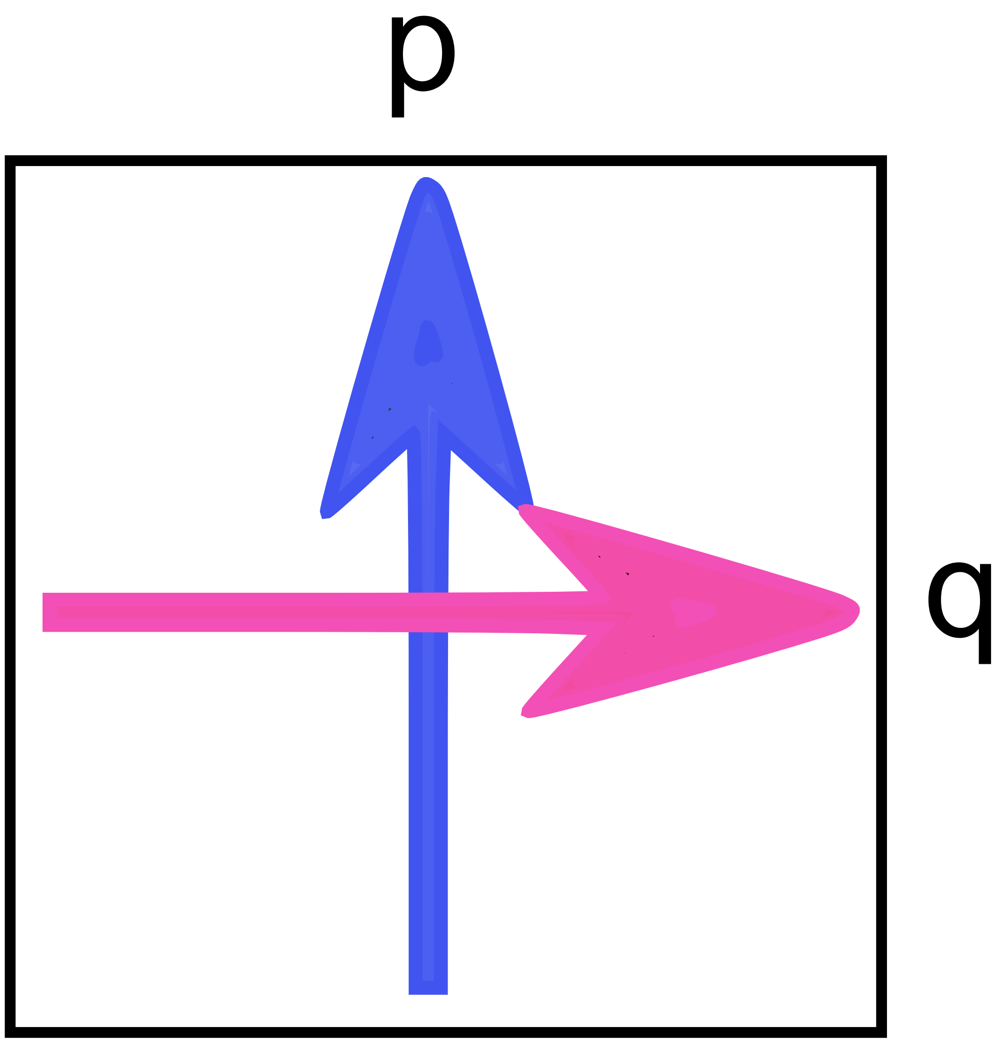

Figure 0-3: position coordinates q and its corresponding momentum p

Specification of q and p is then equivalent to specifying a point in this two-dimensional space (commonly called "phase space"). As the coordinate and momentum of the particle change in time, this representative point moves through this phase space.

In order to describe the situation in terms where the possible state of the particle are countable, it is convenient to subdivide the ranges of the variables q and p into arbitrary small discrete intervals. For example, one can choose fixed intervals of size δq for the subdivision of q, and fixed intervals of size δp for the subdivision of p. Phase space is then subdivided into small cells of equal size and of two-dimensional volume $\delta p \, \delta q = h_0$, where h_0 is some small constant having the dimension of angular momentum. The state of the system can then be specified by stating that this coordinate lies in some interval between q and $q + \delta q$ and its momentum lies into some interval between p and $p + \delta p$.

It may be remarked that quantum theory imposed a limitation on the accuracy with which a simultaneous specification of a coordinate q and its corresponding momentum $p$is possible. Indeed, this limitation was expressed by the Heisenberg uncertainty principle, which states that the uncertainties δq and δp in this two quantities are such that $\delta q \delta p \geq \hbar$, where $\hbar$ is the Planck's constant.

The generalization of the remarks to an arbitrary complex system is immediate. Such a system can be described by some of f coordinates $q_1, q_2, \cdots, q_f$ and f corresponding momentums $p_1, p_2, \cdots, p_f$ by a total of $2f$ parameters. The number f of independent coordinates needed for the description of the system is called "number of degrees of freedom" of the system. For example, if we are dealing with a system of N particles, then each particle is characterized by three position coordinates, so that $f = 3N$.

For example, we can take the harmonic oscillator of mass m and proper frequency ω_0 when the Hamiltonian is given by

$$H = \frac{p^2}{2m} + \frac{1}{2} m \omega_0^2 q^2 \tag{12}$$

The phase space is the place (p, q). We understand that every value of the internal energy U defines an <u>hyperspace</u> $H(q_1, q_2, \cdots, q_{3N}, p_1, p_2, \cdots, p_{3N}) = U$ in the phase space. If we know the internal energy with a certain <u>imprecision</u> δU, we will obtain an area $\Gamma(U)$ defined between two hypersurface of $H = U - \frac{1}{2}\Delta U$ and $H = U + \frac{1}{2}\Delta U$. This imprecision on the internal energy comes from small fluctuations of the system.

We need an infinite observation time to know U with a perfect precision. Thus, the trajectories of the system will take place in the area $\Gamma(U)$ of the phase space. We have to note that the calculations of the trajectories are impossible but what is important is the statistical measurements of these trajectories.

The classical mechanics considers a continue phase space. The area $\Gamma(U)$ contains an infinity of microscopic state. Nevertheless, the quantum physics is going to impose an elementary volume h^{3N} in the phase space. Hence, the accounting of the microstate Ω contains in this area $\Gamma(U)$ will be given by

$$\Omega(U) = \frac{1}{h^{3N}} \int_{\Gamma(U)} dp_i dq_i \tag{13}$$

This elementary volume h^{3N} comes from the ondulatory aspect of the matter.