

Review

Thermodynamics -for understanding crystal growth-

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Abstract

To understand what entropy is, thermodynamical entropy was derived from Boltzmann's entropy formula. After defining the Helmholtz and the Gibbs free energies, we calculated the formation Gibbs free energies of an equilibrium and a non-equilibrium nucleus following Toshev's approach taking a water droplet as an example. It is demonstrated that the Gibbs free energy for the formation of a cluster takes the maximum as the cluster radius is increased. The cluster at this maximum is called critical nucleus.

Thermodynamics is also a useful tool to obtain the rate of crystal growth in a vapor phase. The partial pressures of all gaseous species are calculated by solving equations given by the law of mass action and the initial conditions. The mathematical formulas to give the growth rates in a closed tube and in a gas flow system are derived.

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1. Introduction

Crystal growth has had a huge impact on the present society through the inventions and the developments of electronic and optical devices. For further advancement in the art and science of crystal growth, understanding of crystal growth is essential [1]. Thermodynamics is one of the most important tools to understand crystal growth. To understand the growth of snow crystals in the sky, we should understand what the water vapor is in the sky, how the nucleation of ice crystal occurs under a certain temperature and how the growth of snows proceeds from their nuclei. All these matters are understood by employing fully or partly the thermodynamics. In the melt and the vapor growths of semiconductors, the state of surface or interface affects

strongly the growth. Depending on the temperature, the crystal surface changes from atomically smooth to completely atomically rough. Thermodynamics also can be applied to understand the state of the crystal surface. Including the above examples, thermodynamics is essentially important to solve the problems in crystal growth.

Thermodynamics and statistical physics treat common problems in the system of the many particles, where the former discusses from the macroscopic point of view while the latter does by starting from the microscopic view and ending at the macroscopic one. Therefore, many text books describe both thermodynamics and statistical mechanics in series in a single book. Traditionally, there are many good text books of thermodynamics and statistical mechanics. Among them, the book written by Sekerka [2] is one of the best books published recently.

The most important and sometimes the most difficult concept in thermodynamics is entropy. Hence, in this lecture, we start to explain entropy, which was defined by Boltzmann and then proceed to derive the thermodynamic entropy.

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Although thermodynamics can be applied to understand almost all problems of crystal growth, in this lecture, due to the time constraint, we restrict our subjects only to the nucleation and the rate of the growth in vapor phase. In addition to these two examples, thermodynamics is also applied to obtain phase diagram, to understand stoichiometry of the compounds, defect concentration etc. Good examples for the application of thermodynamics to understand the crystal growth and related problems between growth are found in Reference [3].

2. Entropy and heat

Vapor phase is composed of gaseous atoms or molecules. If one can assume them as independent particles, namely, if these particles have no attractive or repulsive forces between them, we can express the gas as ideal. Such particles are called free particles. A free particle moves straight until it hits a wall or another particle. Even under the free particle approximation, chemical reaction takes place when the particles hit each other.

In ideal gas approximation, if each particle has the same mass of m and if the velocity of the i -th particle is denoted by v_i , the kinetic energy of the i -th particle is given as,

$$\epsilon_i = mv_i^2 / 2. \tag{1}$$

When the number of the particles is expressed by N , the total kinetic energy of the ideal gas, U , is written as,

$$U = \sum_i^N \epsilon_i. \tag{2}$$

U is called the internal energy and is a sum of the kinetic energy of the particles. When the particles are kept under the temperature of T , under the assumption that the particles obey Boltzmann statistics, the average kinetic energy of the particle is given by $(3/2)kT$, where k is the Boltzmann constant. The calculation is carried out in standard text books of thermodynamics or statistical mechanics. Then, one gets,

$$U = 3NkT / 2. \tag{3}$$

When the total number of the particles is 1 mol, N should be the Avogadro constant and Nk is equal to the gas constant, R .

Another important quantity to express the behavior of many particles is entropy. To understand entropy, let us see Fig. 1. In room 1, the particles of A are contained separately from the particles of B in room 2 as shown in the figure. The rooms are separated by a board a-b. Once the board a-b is removed, everyone knows that these two kinds of particles start to mix and finally they are mixed completely as shown in Fig. 2. If the particles are free, there is no change

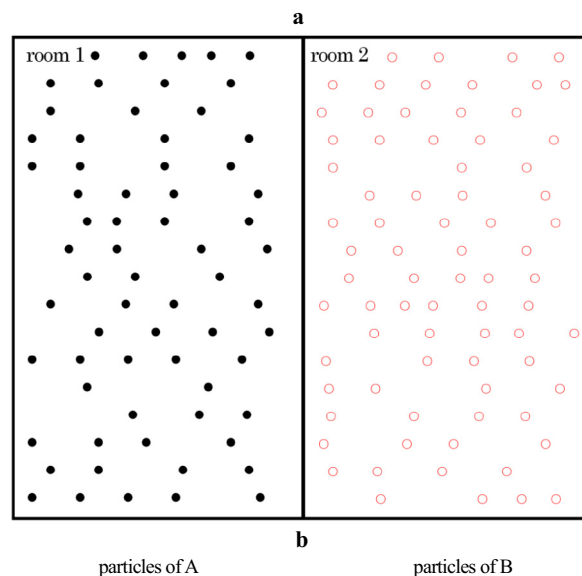


Fig. 1. Particles of A and B are separated by a board a-b and contained in different rooms.

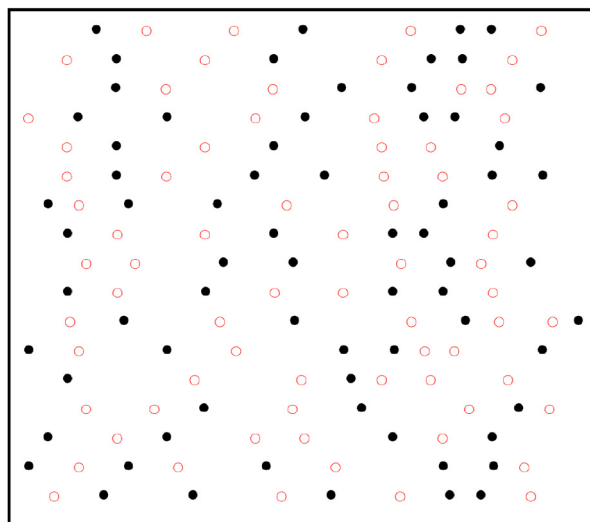


Fig. 2. After the removal of the board a-b, particles of A and B start to mix and finally they are mixed completely.

in internal energy, U , before and after the mixing. However, the state of the many particle system has changed very largely. The change is expressed by the increase of the entropy. The entropy, S , is defined by,

$$S = k \ln M, \tag{4}$$

where M is the number of the states. Equation (4) is known as Boltzmann's entropy formula.

For understanding the mixing phenomena, we take a simple example in which 2 particles each of A and B are

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