

Many atom systems, Boltzmann distribution

In a system of thermal equilibrium (constant temperature) the total energy (E) is distributed in such a way that **an average of $\frac{1}{2} kT$ energy corresponds to each degree of freedom** (equipartition theorem)

energy is constantly being redistributed among all particles and degrees of freedom.

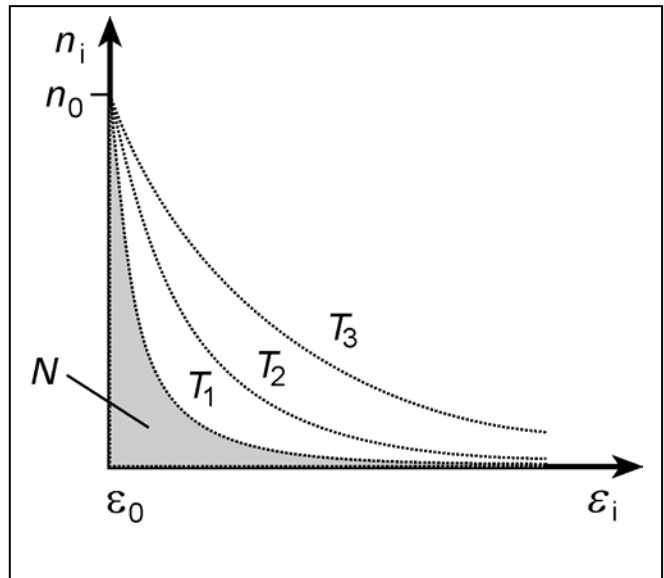
we could specify only the distribution of energy, by determining the numbers of particles (n_0, n_1, n_2, \dots) with energies ($\epsilon_0, \epsilon_1, \epsilon_2, \dots$)
A series of occupation numbers $\{n_0, n_1, n_2, \dots\} = \{n_i\}$ define state of the system.

in thermal equilibrium there is a series $\{n_i\}$ with the highest probability

$$E = \sum_i n_i \epsilon_i, \quad N = \sum_i n_i$$

$$n_i = n_0 e^{-\frac{\epsilon_i - \epsilon_0}{kT}}$$

Graphical representation of the Boltzmann distribution at various temperatures ($T_3 > T_2 > T_1$)



Phenomena based on Boltzmann distribution

a) The barometric formula

It is generally known that atmospheric density decreases with altitude. The density of the gas is given by the number of molecules per unit volume ($n = N/V$).

$$\epsilon_{\text{pot}} = mgh$$

$$\frac{n(h)}{n(0)} = e^{-\frac{mgh}{kT}}$$

b) Thermal emission of metals (electrons emitted due to heat)

delocalized electrons of common orbits in metals behave in many aspects like gases

The higher the temperature of the metal, the more electrons can leave the metal.

Their numbers are also determined by the Boltzmann distribution.

c) Nernst equation

voltage of U between points A and B

$$\varepsilon_{\text{pot}} = q_e U \quad (q_e \text{ is the elementary charge unit})$$

In thermal equilibrium the occupation numbers are given by the Boltzmann distribution:

$$\frac{n_A}{n_B} = e^{-\frac{qU}{kT}} \quad \frac{kT}{q} \ln \frac{n_A}{n_B} = U$$

This rule is analogous to the Nernst equation.

d) Equilibrium and rates of chemical reactions

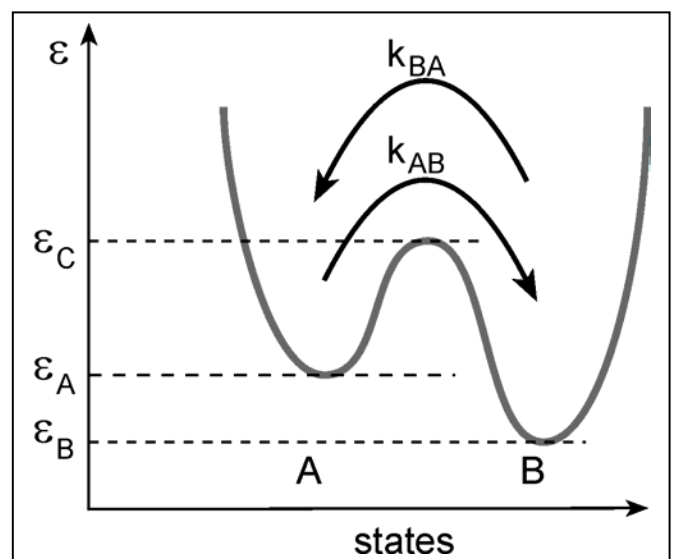
In equilibrium, the distribution of the two states is given by:

$$\frac{n_A}{n_B} = e^{-\frac{\varepsilon_A - \varepsilon_B}{kT}}$$

The ratio $n_A/n_B = K$ is called the equilibrium constant.

reaction requires a certain amount of activation energy,

which depends on the size of the energy barrier (ε_C)



therefore for the reaction rates:

$$k_{AB} = \text{const.} \cdot e^{-\frac{\varepsilon_C - \varepsilon_B}{kT}}$$

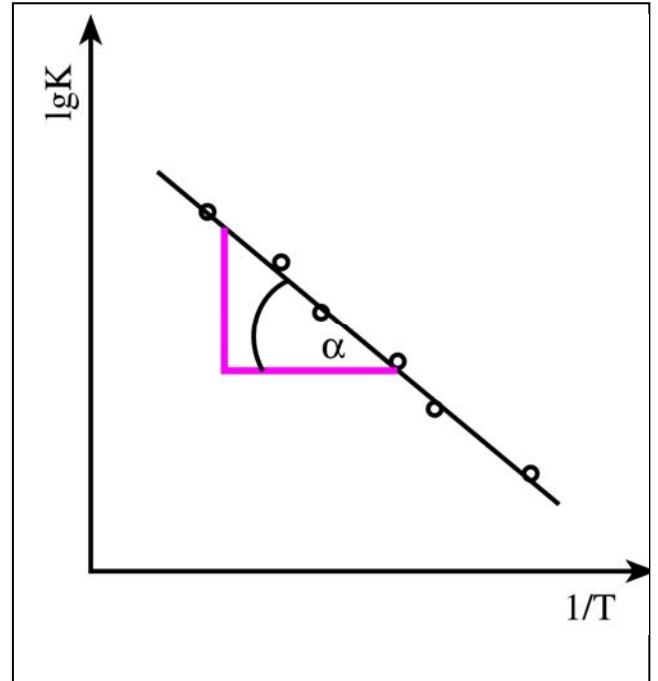
$$k_{BA} = \text{const.} \cdot e^{-\frac{\varepsilon_C - \varepsilon_A}{kT}}$$

and

$$\frac{k_{AB}}{k_{BA}} = K$$

Arrhenius plot

The energy difference of the states can be obtained from the slope of the line fitted to the measurement data:



Ideal Gases

The model of an ideal gas is thought of as a **large number (N) of spherical particles with identical masses moving randomly**, while colliding completely elastically with each other and the walls of the container. All other **interactions**, and **the total volume of the molecules** relative to the size of the container **can be ignored**

$$\frac{1}{2} m \overline{v^2} = \frac{3}{2} kT$$

(The averaging is denoted by a bar – this has to be done after calculating squares.)

These formulae can also be considered as one definition of **temperature**. In this model, the **pressure of the gas** originates in the collision of particles with the container.

$$pV = NkT$$

Real Gases

we have to **take into account**

1. **the intrinsic volumes of the molecules**, and that the
2. **molecules** (approaching the wall) before collision slightly **slowed down by the attraction of others**

if the volume of a single molecule is denoted by b : $p(V-Nb) = NkT$

Applying this correction we would get smaller pressure due to the attraction effect mentioned above.

The negative correction depends on the attraction by other particles on a molecule approaching the wall, and the number of molecules hitting the wall per unit time. Both are proportional to the number of molecules per unit volume, $n = N/V$.

Thus

$$p = \frac{NkT}{V - Nb} - an^2$$

where a is a constant specific for the substance, and indicative of the strength of intermolecular forces

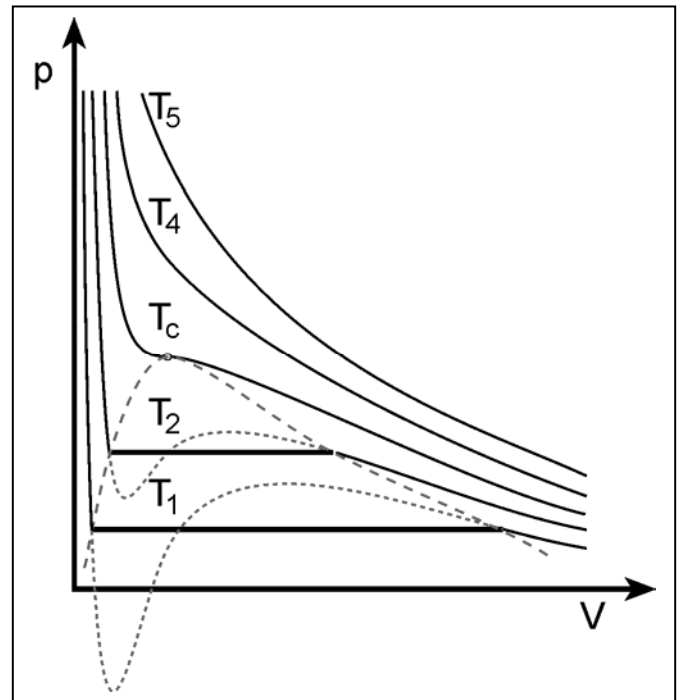
Van der Waals state equation
for real gases:

$$\left(p + a \frac{N^2}{V^2} \right) (V - Nb) = NkT$$

Van der Waals isotherms ($p(V)$ diagram; $T_1 < T_2 < T_c < T_4 < T_5$).

(Inside the dashed line both phases (liquid and vapor) are present.)

In order to liquefy a gas, it must be cooled under the so-called critical temperature (T_c).



Solid State Materials

Crystalline States

most important property is **large-scale periodic order**
(highest level of order)

Ideal crystals are an infinite periodic spatial sequence of identical structural elements. The geometric properties and the symmetry of the crystal is **defined by the lattice** (the crystal structure is made by putting the right ‘building blocks’ into the lattice at each vertex). The lattice consists of basic units called **elementary cells**.

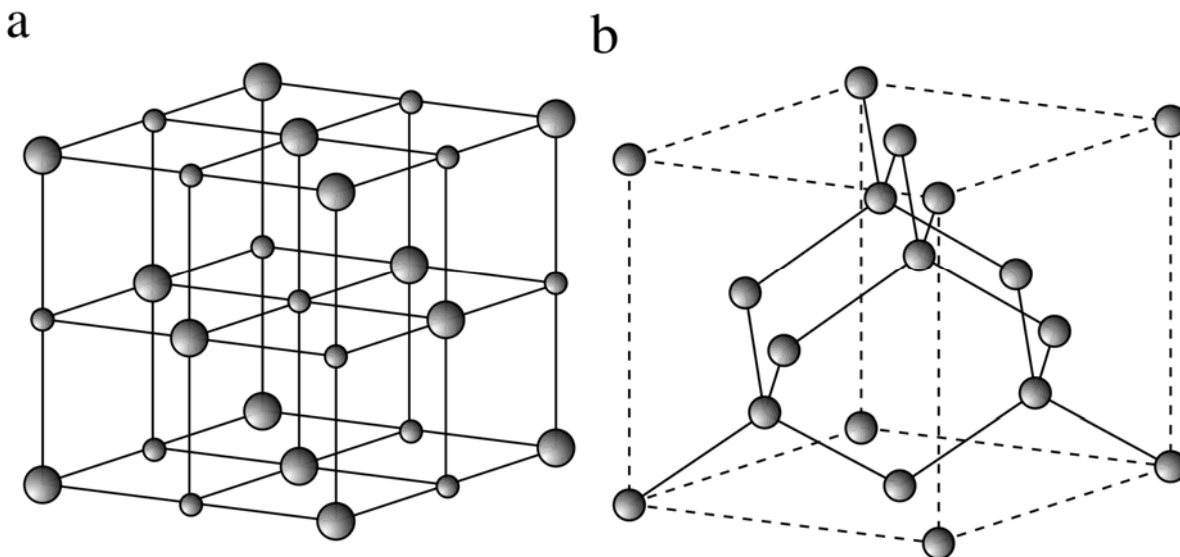


Fig. I.28. Elementary cells of NaCl (a) and Si (b) crystals.

Classification:

atomic, ionic, metallic, molecular lattice

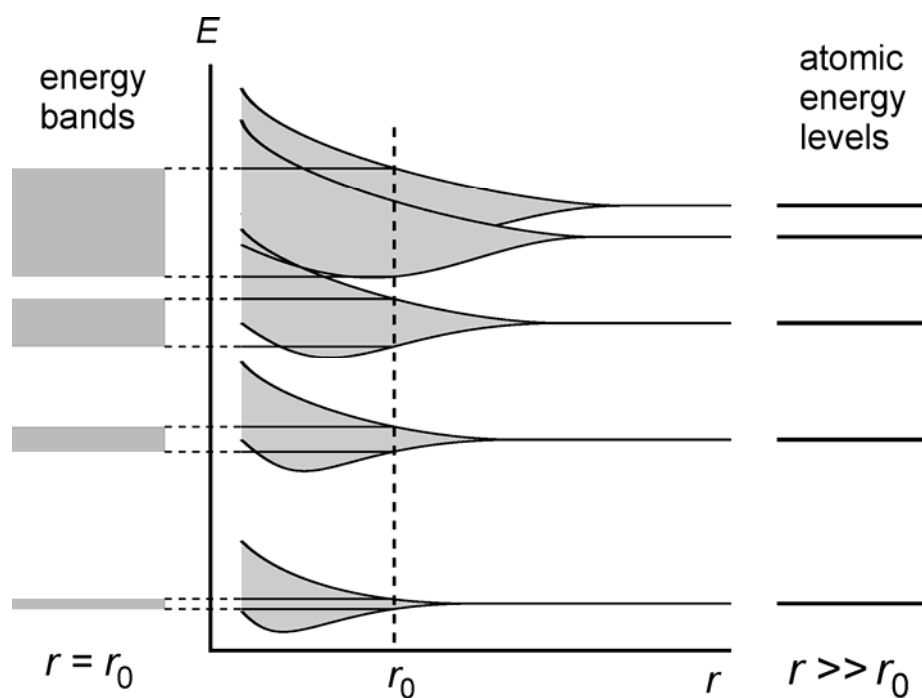
crystalline order in reality usually only extends to microscopic scales: microcrystals, monocrystals

Crystals are **anisotropic** substances, i.e. **they have distinguishable directions**. This can manifest, for instance, in the fact that within the crystal, light propagates with different velocities in different directions.

Energy Bands

As soon as the atoms get closer to form a crystal, and the state functions of atomic electrons start to overlap, **the Pauli principle comes into effect**. The tendency of the system to avoid identical quantum states is realized through **the ‘splitting up’ of the equal energies of interacting electrons into N close levels**.

As N is very large, the **multitude of close split levels forms in practice a continuous energy band**.



The formation of energy bands in crystals. Due to the decrease of atomic distances (r), the atomic energy levels are split up, and energy bands will form (r_0 denotes the equilibrium distance).