8. Boltzmann Distribution and Canonical Ensemble

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Statistical Thermodynamics

A field of physical chemistry which derives macroscopic properties (thermodynamic variables) from microscopic properties obtained from quantum mechanics.

The two scopes are linked, but can look quite different due to the averaging process arising from central limit theorem.

In this course, we focus on the behavior of the molecules in equilibrium at constant temperature.

Eventually, we will learn about the foundation for estimating thermodynamic quantities of the molecules from the properties calculated by using quantum chemistry.

Microscopic vs. Macroscopic

Two molecules in a equally divided container
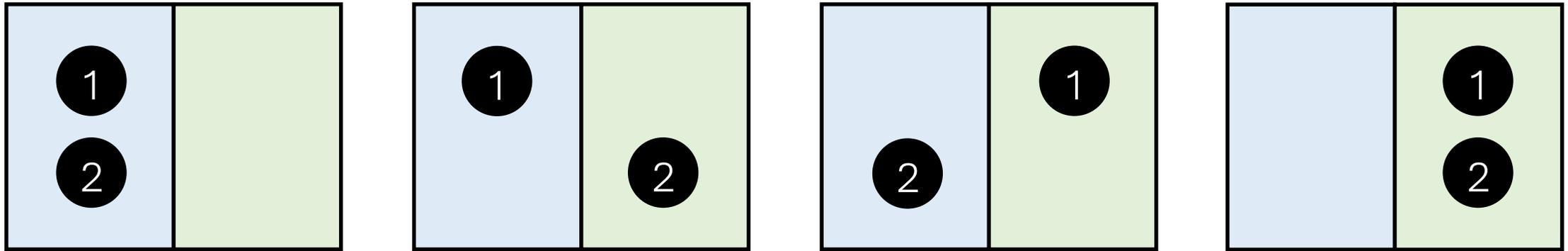
The most probable configuration is the one with equal distribution.

Nevertheless, the probability of all molecules being in the left container is still

$$\left(\frac{1}{2}\right)^2 = \frac{1}{4},$$

which is not highly unlikely.

Microscopic vs. Macroscopic

How about 1 mole of molecules? The probability of all molecules in the left container will be

$$P(N_A, 0) = \frac{\text{(number of selected configuration)}}{\text{(number of all configurations)}} = \frac{1}{2^{N_A}} \sim \frac{1}{10^{1.81 \times 10^{23}}},$$

which would be a vanishingly small quantity.

How about only a slight asymmetry by 0.1%, of the ratio of 0.501 : 0.499? The probability would be calculated as

$$P(0.501N_A, 0.499N_A) = \frac{x}{y},$$

where $x = {}_{N_A}C_{0.501N_A}$ and $y = 2^{N_A}$.

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Microscopic vs. Macroscopic

Such a quantity involving powers and factorials can be calculated by using the logarithm and Stirling's approximation,

$$\ln N! \sim N \ln N - N.$$

As the combination is calculated as

$$_nC_r = \frac{n!}{r!(n-r)!},$$

we have

$$\ln P(0.501N_{\mathrm{A}}, 0.499N_{\mathrm{A}}) = \ln {}_{N_{\mathrm{A}}}C_{0.501N_{\mathrm{A}}} - \ln 2^{N_{\mathrm{A}}}$$

$$= \ln N_{\mathrm{A}}! - \ln(0.501N_{\mathrm{A}})! - \ln(0.499N_{\mathrm{A}})! - N_{\mathrm{A}}\ln 2$$

$$\sim N_{\mathrm{A}}(-0.501\ln 0.501 - 0.499\ln 0.499 - \ln 2)$$

$$\sim -1.20 \times 10^{18},$$

$$\log_{10} P(0.501N_{\mathrm{A}}, 0.499N_{\mathrm{A}}) \sim -1.20 \times 10^{18}/\ln 10 = -5.23 \times 10^{17}.$$

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Microscopic vs. Macroscopic

Therefore the probability of the asymmetry by 0.1 % is

$$P(0.501 N_{\mathrm{A}}, 0.499 N_{\mathrm{A}}) \sim \frac{1}{10^{5.23 \times 10^{17}}},$$

which is still extremely small to be observed during the timescale of the universe ($\sim 10^{17}$ s).

Such a tendency to remain in the equilibrium (average) state naturally arises from the collective behavior of large number of particles.

It also demonstrates the irreversibility dictated by the 2nd law of thermodynamics - all systems eventually collapse to the equilibrium where energy and material are evenly distributed throughout the space.

Thoughts on Temperature

In the general chemistry course, we have learned about the Maxwell velocity distribution for ideal gas molecules.
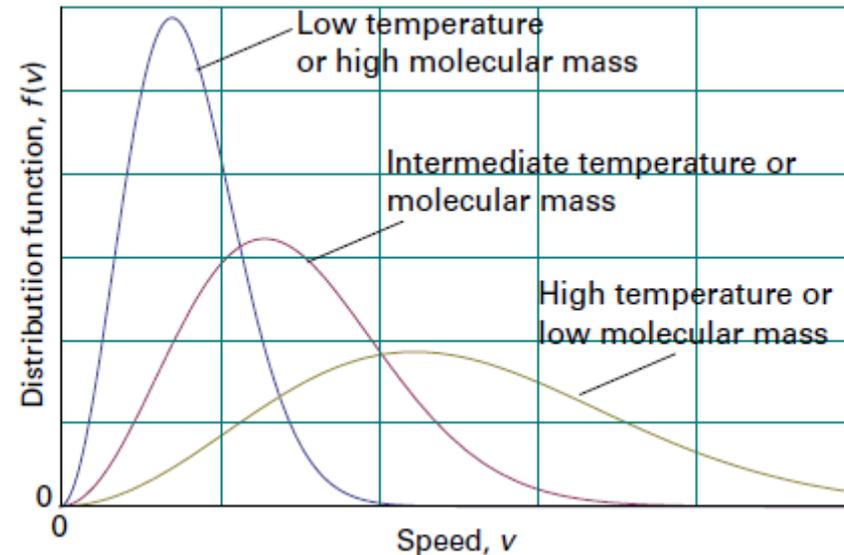
Atkins, 1B.4 (p. 15)

Question: suppose we can measure the velocity of individual molecules. Can we infer the temperature from the velocity of a single molecule?

Thoughts on Temperature

You can immediately see the answer is no, as the distribution at every temperature stretches across whole range of velocities.

Therefore, to find the temperature of gas, we need to collect the information for many different molecules.

It is generally not possible to gather information for all molecules in the system by measurement (as there are too many), although a small portion can still give a good estimate.

A same logic applies for other thermodynamic quantities: they must be calculated by using enough amount of information to represent the whole system, not just for one or a few different molecules.

Effect of Temperature: Boltzmann Distribution

Suppose there are many copies of a same molecule, and we know its energetic states by quantum mechanical calculations.

Boltzmann found that (Atkins, Ch. 12A) for every pair of two quantum states with energies E_1 and E_2, the ratio of probability of the molecules to be in the states is

$$\frac{P(E_2)}{P(E_1)} = e^{-\beta(E_2 - E_1)}$$

at a fixed temperature T, where

$$\beta = \frac{1}{k_{\mathrm{B}}T}$$

and $k_{\mathrm{B}} = 1.380649 \times 10^{-23} \ \mathrm{J\ K^{-1}}$ is the Boltzmann's constant.

Effect of Temperature: Boltzmann Distribution

The ratio $P(E_2)/P(E_1) = \exp[-\beta(E_2 - E_1)]$ implies that:

A state with a lower energy is more likely to be populated than a state with a higher energy.

The ratio exponentially decreases with $\Delta E = E_2 - E_1$.

At $T = 0$, $\beta \to \infty$ and $P(E_2)/P(E_1) = 0$ whenever $E_2 > E_1$.
This means that all molecules occupy the lowest-energy state (or states).

As T increases, the molecules start to populate higher-energy states.

At the limit of $T \to \infty$, we have $\beta = 0$ and $P(E_2)/P(E_1) = 1$.
Therefore $P(E_1) = P(E_2)$ and every state has equal population.

A Side Note on Out-of-Equilibrium States

The relation $P(E_2)/P(E_1) = \exp[-\beta(E_2 - E_1)]$ need not be always satisfied: it is possible to put more population on a high-energy state.

However, such situation is not an equilibrium, and we cannot define the temperature (and other thermodynamic variables) in this case!

This is called population inversion, which is exploited for the operation of lasers.

Non-equilibrium statistical mechanics, a field which studies the systems out of equilibrium, is an active area of research still to nowadays.

https://en.wikipedia.org/wiki/Laser
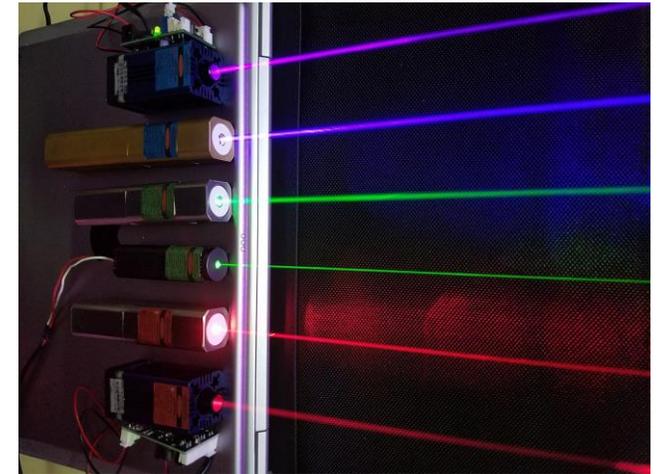
Effect of Temperature: Boltzmann Distribution

We still only know about the ratio between the probabilities. What are the absolute value of individual probabilities?

For simplicity, we first assume that there is no degeneracy and the energy of every state is different. Then we have

$$P_j = P_1 e^{-\beta(E_j - E_1)}.$$

The probabilities must be normalized, so the sum of the probabilities is equal to unity. Therefore

$$\sum_j P_j = P_1 \sum_j e^{-\beta(E_j - E_1)} = 1, \quad P_1 = 1/\left(\sum_j e^{-\beta(E_j - E_1)}\right) = 1/Q.$$

The normalization constant Q is called the partition function.

Effect of Temperature: Boltzmann Distribution

Starting from P_1, we can construct the occupation probabilities for higher-energy states,

$$P_j = e^{-\beta(E_j - E_1)}/Q.$$

In the case of degeneracy, the partition function is generalized to

$$Q = \sum_j^{\text{energy}} g_j e^{-\beta(E_j - E_1)} = \sum_k^{\text{state}} e^{-\beta(E_k - E_1)},$$

where g_j is the degree of degeneracy for the j-th lowest energy.

Example:

$$Q = 3 + 2e^{-\beta \Delta E},$$

$$P_{j=1} = 3/Q,$$

$$P_{j=2} = 2e^{-\beta \Delta E}/Q.$$

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Derivation of the Maxwell Velocity Distribution

Consider a group of ideal gas molecules in three dimensional free space, each moving in a straight line with a constant velocity of v which can be different for individual molecules.

Our objective is to find the probability distribution of v at a fixed temperature T based on the Boltzmann distribution.

As there is no external potential, a molecule only has the kinetic energy,

$$E = \frac{1}{2}mv^2 = \frac{1}{2}m(v_x^2 + v_y^2 + v_z^2),$$

where m is the mass of a molecule and v_x, v_y, and v_z are the velocities in x-, y-, and z-directions.

Derivation of the Maxwell Velocity Distribution

The velocity is directly related to the energy, and not unique for individual molecules. We therefore need to use the formula

$$P(v_j) = g(v_j)e^{-\beta E(v_j)}/Q, \quad Q = \sum_j g(v_j)e^{-\beta E(v_j)},$$

where $E(v) = mv^2/2$ as we observed in the previous slide. As v is a continuous variable, the summation is replaced by integration:

$$P(v) = g(v)e^{-\beta mv^2/2}/Q, \quad Q = \int_0^\infty g(v)e^{-\beta mv^2/2}\,dv.$$

The value of $g(v)$, which is the number of molecules with velocity v, is proportional to the surface area of a sphere whose radius is v, as all points lying on this surface satisfy $v^2 = v_x^2 + v_y^2 + v_z^2$.

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Derivation of the Maxwell Velocity Distribution

Therefore, $g(v)$ follows the relation
$$g(v) = c(4\pi v^2),$$

where c is an unknown constant which will disappear in the final result.

We now have all the materials to evaluate the velocity distribution:
$$P(v) = 4c\pi v^2 e^{-\beta m v^2/2}/Q, \quad Q = 4c\pi \int_0^\infty v^2 e^{-\beta m v^2/2} \, dv.$$

The integral for Q can be calculated by using the integration formula
$$\int_0^\infty v^2 e^{-\alpha v^2} \, dv = \frac{\sqrt{\pi}}{4\alpha^{3/2}},$$

where $\alpha = \beta m/2$ in our case.

Derivation of the Maxwell Velocity Distribution

As a result, the integration gives

$$Q = c \left(\frac{2\pi}{\beta m} \right)^{3/2},$$

which can now be inserted in the probability distribution:

$$P(v) = 4\pi \left(\frac{\beta m}{2\pi} \right)^{3/2} v^2 e^{-\beta m v^2/2} = 4\pi \left(\frac{M}{2\pi RT} \right)^{3/2} v^2 e^{-Mv^2/2RT}.$$

This is Eq. (1B.4) in Atkins, p. 14. Here, we have converted the individual molecular mass to the molar mass $M = N_{\mathrm{A}} m$ by using $R = N_{\mathrm{A}} k_{\mathrm{B}}$.

The distribution has a maximum at a nonzero v. This is because, although the probability for individual states decreases with increasing v, such an effect is partially compensated by the increase in the $g(v)$.

Calculation of Statistical Quantities

The velocity distribution function

$$P(v) = 4\pi \left(\frac{M}{2\pi RT} \right)^{3/2} v^2 e^{-Mv^2/2RT}$$

can now be used to make statistical analysis on the speed, such as

$$\left. \frac{dP(v)}{dv} \right|_{v=v_{\mathrm{mp}}} = 0 \quad \rightarrow \quad v_{\mathrm{mp}} = \sqrt{\frac{2RT}{M}}, \qquad \text{most probable velocity}$$

$$v_{\mathrm{avg}} = \int_0^\infty vP(v)\,dv = \sqrt{\frac{8RT}{\pi M}}, \qquad \text{average velocity}$$

$$v_{\mathrm{rms}} = \left(\int_0^\infty v^2 P(v)dv \right)^{1/2} = \sqrt{\frac{3RT}{M}}. \qquad \text{root-mean-square velocity}$$

Ensembles

A group of molecules which form a fixed set of thermodynamic variables are called ensembles.

A good example is the ideal gas following Maxwell velocity distribution, which we have studied previously. In this case, the fixed variables are:

N : the number of molecules in the system,

V : the volume of the system,

T : the temperature of the system.

Such a group of molecules with fixed (N, V, T) are called a canonical ensemble or NVT ensemble, which must be constructed if we want to evaluate molar thermodynamic properties under constant V and T.

$$(N = N_{\mathrm{A}})$$

Ensembles

Four different types of ensembles are usually considered in the statistical thermodynamics.

Fixed (N, V, E) : microcanonical ensemble (NVE ensemble)

Fixed (N, V, T) : canonical ensemble (NVT ensemble)

Fixed (N, p, T) : isothermal-isobaric ensemble (NpT ensemble)

Fixed (μ, V, T) : grand canonical ensemble (μVT ensemble)

    μ : chemical potential

Note: NVT and NpT ensembles are identical for ideal gas, but they become generally different for real gas or liquid/solid systems.