Statistical Thermodynamics

From Micro to Macro

Consider an isolated ensemble of molecules confined to a recipient of constant volume V. This system is isolated, thus the number of particles is constant and equal to N. Furthermore, the system has a constant total energy E. If the system is at equilibrium, then the energy distribution in these conditions for this system has to be uniform: The probability of finding a molecule with energy $E' \neq E$ is always zero. Such a system is called a microcanonical ensemble (*1*).

In our molecular ensemble, all microstates are equally probably and thus the probability density of finding the ensemble in a given macrostate is simply

$$p = \frac{1}{\Omega}$$

where Ω is a function of E, N and V and gives the statistical weight of a configuration or macrostate. If an ensemble of molecules has several possible microstates, Ω represents the probability of reaching a macrostate composed of a combination of microstates (*2*). Note that even though the system has a constant energy E, there might be special constraints at the molecular level conditioning the distribution of molecules among their molecular levels. This does not restrain the system from having total energy E.

Ω consists on the total number of possible combinations we can use to distribute N particles among m accessible molecular levels, such that the total energy of the resulting ensemble is E and it can be calculated as

$$\Omega = \frac{N!}{n_0! n_1! ... n_m!} \tag{1}$$

n_i is the number of particles occupying the energy level i. Therefore, the statistical weight Ω measures how often a given set of microstates is visited by the molecular ensemble.

According to Boltzmann, the entropy of a system in a given configuration is given by the logarithm of Ω multiplied by a constant. This constant is defined as the Boltzmann constant.

$$S = k_B log(\Omega) \tag{2}$$

The microcanonical ensemble can be seen as a collection of an extremely large number of smaller isolated systems in many possible (accessible states) in a container with fixed volume and with a fixed energy (*3*). The microcanonical ensemble, also known as the NVE ensemble is defined by equation 1.2.

If instead of considering an isolated system we consider that our system is in thermal equilibrium with a heat bath at constant temperature (we fix the temperature to T instead of the energy to E), we obtain a canonical ensemble (*1*). This system can be seen as a collection of several microcanonical subensembles of different energy E_i. Note that the E_i refer to ensemble energies and have nothing to do with molecular energies. The volume is still fixed to V and the number of particles is also constant and has the value of N. The system is therefore closed. Because the energy is no longer fixed, its probability density is no longer uniform and different parts of the system might have different energy E_i. The number of ensembles with energy E_i is N_i and therefore the probability of finding an ensemble with total energy E_i is $p_i = \frac{N_i}{N}$. Since the total number of particles/ensembles is constant,

$$N=\sum\nolimits_i N_i \tag{3}$$

$$E=\sum\nolimits_i N_i E_i \tag{4}$$

One may similarly define the probability of finding the ensemble in a given macrostate. The problem is now instead that several possible macrostates are accessible. To determine the properties of the system we should characterize the most probable macrostate. Finding the most probable macrostate requires finding the maximum of Ω with respect to N_i given the particle and energy conservation laws. Because the number of particles is extremely high, we can instead maximize the logarithm of Ω with the same results. The function to maximize is thus

$$log\Omega = log(N!) - \sum\nolimits_i log(N_i!) \approx NlogN - N + 1 - \sum\nolimits_i N_i log(N_i) + \sum\nolimits_i N_i! - m$$

$$log\Omega = NlogN - \sum\nolimits_i N_i log(N_i) + 1 - m$$

If we solve the maximization problem under the constraints of equations 1.3 and 1.4 (using the method of Lagrange multipliers) we verify that

$$p_i=\frac{n_i}{N}=\frac{g_i e^{-\frac{E_i}{k_B T}}}{\sum_j g_j e^{-\frac{E_j}{k_B T}}} \tag{5}$$

where an extra factor g_i was added, which accounts for the degeneracy of the energy level i. The degeneracy simply takes in consideration that different energy levels might have the same energy and may therefore be all coupled together. We may therefore define degenerate states as those that are described by different set of quantum numbers n, l, ... and n', l', ... but that have the same energy.

The function p_i is the probability of finding a particle in a given energy level, and is known as the Boltzmann distribution.

The sum over all states in the denominator of the probability

$$Z' = \sum\nolimits_j g_j e^{-\frac{E_j}{k_B T}} = e^{-\frac{E_0}{k_B T}} \sum\nolimits_j g_j e^{-\frac{E_j - E_0}{k_B T}} \tag{6}$$

is the partition function, which is the thermodynamic state function of a canonical ensemble. This means that all thermodynamic state functions can be obtained by knowing Z'. At a certain temperature, the partition function measures how many states are accessible to the system. Depending on the temperature, the partition function can assume very large values.

If the first energy level is considered to be the reference (with zero energy) then,

$$Z' = g_0 + \sum\nolimits_j g_j e^{-\frac{E'{}_j}{k_B T}} \tag{7}$$

In this perspective, the partition function shows the ability of the system to populate states other than the state of lowest energy (*2*). This is naturally dependent on the difference of the energy levels with respect to the ground state and their degeneracy, and we may write $E_j^{'} = E_j - E_0$. The larger the density of states close to the ground state, the more more states can be populated, and the larger is the partition function.

Finally, if we consider a system with fixed volume and constant temperature but instead of fixing the number of particles we fix the chemical potential of all components (the number of particles is thus variable) we obtain a grand canonical ensemble (*1*). This system can exchange both heat and matter with the surroundings and it corresponds to an open system in the thermodynamical sense. The partition function is now given by

$$\Xi = \sum\nolimits_j g_j e^{-\frac{(E_j - \sum_k N_{j,k} \mu_k)}{k_B T}} \tag{8}$$

where μ_k is the chemical potential of the species k.

Note that in all three cases there are three variables being fixed (*1*) and if at least one of these constants cannot be fixed, the system cannot be at equilibrium and therefore cannot be fully described by time-independent state functions.

Even though from the definitions it might seem like a microcanonical ensemble is not related to the macrocanonical, it can be shown that all three ensembles are interrelated and can be used equivalently to solve different problems (*4*). This means that sometimes it might be convenient to solve a problem using a grand- or macrocanonical ensemble, whereas for some problems the micro- or the canonical ensembles are more practical. To aid this view, one can see the macrocanonical ensemble as a collection of canonical systems and a canonical ensemble as a collection of microcanonical ensembles. It is also possible to define even more ensembles, which might prove to be more practical to solve some specific problems. The three ensembles above mentioned are however the most common ones.

A Toolkit

The canonical partition function defined in the previous section is valid for systems of distinguishable particles. If however we have a system of identical particles we rewrite the canonical partition function as (*4*)

$$Z = \frac{Z'}{N!} \tag{9}$$

Note the distinction between Z' and Z: the former is the partition function for N distinguishable particles, whereas for the latter partition function the particles are considered indistinguishable. If we furthermore consider that there are no particle interactions we may furthermore write

$$Z = \frac{Q^N}{N!} \tag{10}$$

where Q refers to the partition function of a single molecule. Note that if there are subsets of indistinguishable particles the denominator becomes the product of the respective factorial terms. This means that if a system is composed by N_1 particles of molecule M_1 and N_2 particles of molecule M_2 then the denominator is $N_1!N_2!$ (instead of $N!$). Particle indistinguishability has to be accounted by brute force because it is a quantum mechanical concept. Classically, it would be possible to distinguish all particles.

Similarly to the partition function for N molecules, the single molecule partition function Q is given by

$$Q = \sum_j g_j exp[-\frac{\varepsilon_j}{k_B T}] \tag{11}$$

The index j runs through all the quantum mechanical energy levels of the single molecule. As discussed in another document (Quantum Mechanical Basis), the energy levels ε_j of a molecule can be split in four main contributions: translational; rotational; vibrational; electronic. Therefore

$$\begin{aligned} Q = &\sum_{j \in trans} g_j exp[-\frac{\varepsilon_j}{k_B T}] \sum_{k \in rot} g_k exp[-\frac{\varepsilon_k}{k_B T}] \sum_{l \in vib} g_l exp[-\frac{\varepsilon_l}{k_B T}] \sum_{m \in el} g_m exp[-\frac{\varepsilon_m}{k_B T}] \\ &= (q^{trans})(q^{rot})(q^{vib})(q^{el}) \end{aligned} \tag{12}$$

There is still the nuclear spin contribution to the energy, but this usually cancels out in statistical mechanical calculations and it is also very well separated from the four main energy contributions. Consequently, nuclear spin is neglected in our treatment here. Equation 1.12 is very practical, as it gives a prescription on how to obtain (single) molecule partition functions, which might be use to estimate thermodynamic properties of large ensembles of molecules. To build the connection between statistical mechanics and thermodynamics we must first as ourselves what is the average energy ($\bar{E}$) of the molecules in a given system. According to the definition we have

$$\bar{E}=\frac{\sum_j \varepsilon_j n_j}{\sum_j n_j}=\sum_j \varepsilon_j \frac{n_j}{\sum_k n_k}=\sum_j \varepsilon_j \frac{n_j}{N}=\frac{1}{Q}\sum_j \varepsilon_j exp[-\frac{\varepsilon_j}{k_B T}] \tag{13}$$

This expression can be easily rewritten into

$$\bar{E}=k_B T^2 \frac{\partial}{\partial T} log(Q) \tag{14}$$

The total energy of a system with N particles, its internal energy, can be defined from the average energy as

$$U=N\bar{E}=Nk_B T^2 \frac{\partial}{\partial T} log(Q)=k_B T^2 \frac{\partial}{\partial T} log(Q^N) = k_B T^2 \frac{\partial}{\partial T} log(Z) \tag{15}$$

From the internal energy we can get the heat capacity at constant volume,

$$C_V=2k_B T \frac{\partial}{\partial T} log(Z)+k_B T^2 \frac{\partial^2}{\partial T^2} log(Z) \tag{16}$$

Then using the second-law of thermodynamics, for a closed system

$$S - S_0 = \int_0^T \frac{C_V}{T'} dT' \tag{17}$$

which yields

$$S=k_B T \frac{\partial}{\partial T} log(Z)+k_B log(Z) \tag{18}$$

Since we are dealing with a system of non-interacting particles, we can define the heat capacity at constant pressure as

$$C_P=C_V + R = 2k_B T \frac{\partial}{\partial T} log(Z)+k_B T^2 \frac{\partial^2}{\partial T^2} log(Z) + R \tag{19}$$

According to the definition, we then have access to the system's enthalpy:

$$H=k_B T^2 \frac{\partial}{\partial T} log(Z)+k_B T V \frac{\partial}{\partial V} log(Z) \tag{20}$$

From these definitions we can then derive the Gibbs free energy and the Helmoltz energy

$$G{=}k_BTV\frac{\partial}{\partial V}log(Z){-}k_BTlog(Z) \tag{21}$$

$$A{=}-k_BTlog(Z) \tag{22}$$

Finally we still have the system's pressure

$$P{=}k_BT\frac{\partial}{\partial V}log(Z) \tag{23}$$

Note that the expressions above are valid for single molecules or for large molecular systems. Obtaining the thermodynamic limit requires one to rescale the values accordingly.

It is interesting to venture in the laws of classical thermodynamics using the concepts of statistical mechanics. As suggested in (*2*), and using our definition above for the internal energy, $U{=}\sum_i N_iE_i$, we can build the total differential for this quantity

$$dU{=}\sum\nolimits_i N_idE_i+\sum\nolimits_i E_idN_i$$

For reasons that will later become clearer, the first term can only come from pressure or volume changes in the system. It is thus associated with mechanical work. The second term accounts for changes in the energy level populations. This can be achieved using changes in temperature. This second term results from the system taking energy from the its surroundings, being associated with heat transfer.

Bibliography

1. G. Jeschke, *Lecture Notes: Advanced Physical Chemistry, Statistical Thermodynamics.* ETH, 2015.

2. A. Maczek and A. Meijer, *Statistical Thermodynamics.* Oxford, 2017.

3. E. Keszei, *Chemical Thermodynamics: An Introduction*, ch. Elements of Equilibrium Statistical Thermodynamics. Springer, 2012.

4. T. L. Hill, *An Introduction to Statistical Thermodynamics.* Dover, 1986.

5. M. D. Hanwell, D. E. Curtis, D. C. Lonie, T. Vandermeersch, E. Zurek, and G. R. Hutchison *J. Cheminf.*, vol. 4, p. 17, 2012.