The Boltzmann Distribution

A small system in thermal contact with a large system. We have considered thermal contact of two systems. Now consider a special case: a small system in thermal contact with a large system. To keep track of names, we will call the small system just the system, and call the large system the *reservoir*. The system and the reservoir are in thermal contact, exchanging energy. All other modes of interactions between the system and the reservoir are blocked: no exchange of molecules, or volume, or anything else.

The (small) system can be in any one of a set of states, $\gamma_1, \gamma_2, \gamma_3, ..., \gamma_s, ...$ These states need not be at the same energy level, because the system can draw energy from, or save energy to, the reservoir. Let the energy of these states of the small system be $U_1, U_2, U_3, ..., U_s, ...$ When the system equilibrates with the reservoir, the system still fluctuates among all these states. What is the probability for the system to be in each state?

The Boltzmann factor. To apply the fundamental postulate to answer the above question, we need an isolated system, which we will take to be the *composite* of the system and the reservoir. A state of the composite is specified by a state of the system and a state of the reservoir. When the system is in a specific state γ_s, the reservoir can be in a large number of states. Let configuration *s* of the composite constitute all states of the composite in which the (small) system is in state γ_s.

When isolated at a particular level of energy, U_R, the reservoir has a certain number of states, Ω_R. Because the reservoir is a large system, we may as well regard $\Omega_R(U_R)$ as a smooth function. The temperature of the reservoir, T_R, is defined by

$$\frac{\partial \log \Omega_R}{\partial U_R} = \frac{1}{T_R} .$$

The temperature of the reservoir does not change when the reservoir is in thermal contact with the other, much smaller, system, because the energy transferred between the reservoir and the small system is much smaller than the total amount of energy in the reservoir.

Let U_{tot} be the energy of the composite. When the system is in a specific state γ_s, the energy of the system is U_s, and the energy of the reservoir is $U_R = U_{tot} - U_s$. Because the temperature of the reservoir, T_R, is independent of the energy in the reservoir, $\log \Omega_R$ is linear in U_R, namely,

$$\log \Omega_R (U_{tot} - U_s) = \log \Omega_R (U_{tot}) - \frac{U_s}{T_R}.$$

Take exponential of both sides of the equation, and we obtain that

$$\Omega_R (U_{tot} - U_s) = \Omega_R (U_{tot}) \exp(-U_s / T_R).$$

Note that $\Omega_R (U_{tot})$ is the number of states of the reservoir at isolated energy U_{tot}. Upon losing energy U_s then isolated at energy $U_{tot} - U_s$, the reservoir reduces its number of states by a factor $\exp(-U_s / T_R)$, known as the *Boltzmann factor*.

Partition function. Note that $\Omega_R (U_{tot} - U_s)$ is also the number of states of the composite in the configuration that the small system is in state γ_s. Thus, the total number of states of the composite is

$$\Omega_{tot} = \sum \Omega_R (U_{tot} - U_s) = \Omega_R (U_{tot}) Z.$$

The sum is taken over all states of the system. The sum over all states,

$$Z = \sum \exp(-U_s / T_R),$$

is known as the *partition function*.

The probability for a system in thermal equilibrium with a reservoir to be in a specific state. As an isolated system in equilibrium, the composite is equally probable in each of the Ω_{tot} states. Consequently, the probability for the small system to be in state γ_s is $P_s = \Omega_R(U_{tot} - U_s)/\Omega_{tot}$, namely,

$$P_s = \frac{\exp(-U_s / T_R)}{Z}.$$

The probability depends on the energy of every state of the small system and the temperature of the reservoir, but is independent of any other characteristics of the system and the reservoir. This probability distribution is known as the *Boltzmann distribution*.

The probability for a system in thermal equilibrium with a reservoir to be in a configuration. A configuration of an isolated system is a subset of states of the isolated system. We now generalize this definition to a system in thermal equilibrium with a reservoir. A subset of the states of the system is called a configuration of the system.

Let configuration A consists of a subset of states of a system: $A = \{\gamma_i, \gamma_j, \gamma_s, ...\}$. The partition function of configuration A is the sum of the Boltzmann factors taken over all the states that constitute the configuration A:

$$Z_A = \sum_{\gamma_s \in A} \exp(-U_s / T_R).$$

The probability for the system to be in configuration A is

$$P_A = \frac{Z_A}{Z}.$$

Thermal fluctuation of an RNA molecule. As an example of configurations, consider a system consisting of a RNA molecule in a liquid, and the whole thing is equilibrated with a reservoir. Our experimental observation shows that the RNA molecule fluctuates between two conformations: a chain and a loop. Thus, all the states of the system are divided into two subsets (i.e., two conformations): one corresponding to each conformation. The fraction of time that the RNA molecule spends in each conformation is the probability of the conformation.

A matter of words. In speaking of a system equilibrated with a reservoir, to focus attention on the system, we often choose not to mention the reservoir, and simply say a *system held at a temperature*. This verbal change does not eliminate the need for the reservoir, for it is the reservoir that holds the small system at the temperature. We will regard the phrase "a system held at a temperature" synonymous to "a system in thermal equilibrium with a reservoir of a temperature".