Boltzmann weight

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According to statistical mechanics, the probability that a system in thermal equilibrium occupies a state with the energy E is proportional to $\exp (- E / k_B T)$, where T is the absolute temperature and k_B is the Boltzmann constant. Of course, $k_B T$ has a dimension of energy. The exponential $\exp (- E / k_B T)$ is called the Boltzmann weight.

L. Boltzmann considered a gas of identical molecules which exchange energy upon colliding but otherwise are independent of each other. An individual molecule of such a gas does not have a constant velocity, so that no exact statement can be made concerning its state at a particular time. However, when the gas comes to equilibrium at some fixed temperature, one can make predictions about the average fraction of molecules which are in a given state. These average fractions are equivalent to probabilities and therefore the probability distribution for a molecule over its possible states can be introduced. Let the set of energies available to each molecule be denoted by $\{ \epsilon_l \}$. The probability, P_l, of finding a molecule in the state l with the energy ϵ_l is

$$\mathsf{P}_l = \frac{\exp (- \epsilon_l / k_B T)}{\sum_l \exp (- \epsilon_l / k_B T)} . \tag{a1}$$

This is called the Boltzmann distribution.

J.W. Gibbs introduced the concept of an ensemble (cf. also Gibbs statistical aggregate), which is defined as a set of a very large number of systems, all dynamically identical with the system under consideration. The ensemble, also called the canonical ensemble, describes a system which is not isolated but which is in thermal contact with a heat reservoir. Since the system exchanges energy with the heat reservoir, the energy of the system is not constant and can be described by a probability distribution. Gibbs proved that the Boltzmann distribution holds not only for a molecule, but also for a system in thermal equilibrium. The probability $\mathsf{P}(E_l)$ of finding a system in a given energy E_l is

$$P(E_l) = \frac{\exp (- E_l / k_B T)}{\sum_l \exp (- E_l / k_B T)} . \tag{a2}$$

With this extension, the Boltzmann distribution is extremely useful in investigating the equilibrium behaviour of a wide range of both classical and quantum systems [a1], [a2], [a3].

There are many examples of Boltzmann weights; some old and new ones are discussed below.

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