

2.2: The Probability of An Energy Level at Constant N, V, and T

If only pressure–volume work is possible, the state of a closed, reversible system can be specified by specifying its volume and temperature. Since the system is closed, the number, N , of molecules is constant. Let us consider a closed, equilibrated, constant-volume, constant-temperature system in which the total number of molecules is very large. Let us imagine that we can monitor the quantum state of one particular molecule over a very long time. Eventually, we are able to calculate the fraction of the elapsed time that the molecule spends in each of the quantum states. We label the available quantum states with the wavefunction symbols, $\psi_{i,j}$.

We assume that the fraction of the time that a molecule spends in the quantum state $\psi_{i,j}$ is the same thing as the probability of finding the molecule in quantum state $\psi_{i,j}$. We denote this probability as $\rho(\psi_{i,j})$. To develop the theory of statistical thermodynamics, we assume that this probability depends on the energy, and only on the energy, of the quantum state $\psi_{i,j}$. Consequently, any two quantum states whose energies are the same have the same probability, and the g_i -fold degenerate quantum states, $\psi_{i,j}$, whose energies are ϵ_i , all have the same probability. In our imaginary monitoring of the state of a particular molecule, we observe that the probabilities of two quantum states are the same if and only if their energies are the same; that is, we observe $\rho(\psi_{i,j}) = \rho(\psi_{k,m})$ if and only if $i = k$.

The justification for this assumption is that the resulting theory successfully models experimental observations. We can ask, however, why we might be led to make this assumption in the first place. We can reason as follows: The fact that we observe a definite value for the energy of the macroscopic system implies that quantum states whose energies are much greater than the average molecular energy must be less probable than quantum states whose energies are smaller. Otherwise, the sum of the energies of high-energy molecules would exceed the energy of the system. Therefore, we can reasonably infer that the probability of a quantum state depends on its energy. On the other hand, we can think of no plausible reason for a given molecule to prefer one quantum state to another quantum state that has the same energy.

This assumption means that a single function suffices to specify the probability of finding a given molecule in any quantum state, $\psi_{i,j}$, and the only independent variable is the quantum-state energy, ϵ_i . We denote the probability of a single quantum state, $\psi_{i,j}$, whose energy is ϵ_i , as $\rho(\epsilon_i)$. Since this is the probability of each of the g_i -fold degenerate quantum states, $\psi_{i,j}$, that have energy ϵ_i , the probability of finding a given molecule in any energy level, ϵ_i , is $P(\epsilon_i) = g_i \rho(\epsilon_i)$. We find it convenient to introduce “ P_i ” to abbreviate this probability; that is, we let

$$P_i = \sum_{j=1}^{g_i} \rho(\psi_{i,j}) = P(\epsilon_i) = g_i \rho(\epsilon_i)$$

(the probability of energy level ϵ_i)

There is a P_i for every energy level ϵ_i . P_i must be the same for any molecule, since every molecule has the same properties. If the population set $\{N_1^*, N_2^*, \dots, N_i^*, \dots\}$ characterizes the equilibrium system, the fraction of the molecules that have energy ϵ_i is N_i^*/N . (Elsewhere, an energy-level population set is often called a “distribution.” Since we define a distribution somewhat differently, we avoid this usage.) Since the fraction of the molecules in an energy level at any instant of time is the same as the fraction of the time that one molecule spends in that energy level, we have

$$P_i = P(\epsilon_i) = g_i \rho(\epsilon_i) = \frac{N_i^*}{N}$$

As long as the system is at equilibrium, this fraction is constant. In Chapter 21, we find an explicit equation for the probability function, $\rho(\epsilon_i)$.

The energy levels, ϵ_i , depend on the properties of the molecules. In developing Boltzmann statistics for non-interacting molecules, we assume that the probability of finding a molecule in a particular energy level is independent of the number of molecules present in the system. While P_i and $\rho(\epsilon_i)$ depend on the energy level, ϵ_i , neither depends on the number of molecules, N . If we imagine inserting a barrier that converts an equilibrated collection of molecules into two half-size collections, each of the new collections is still at equilibrium. Each contains half as many molecules and has half the total energy of the original. In our model, the fraction of the molecules in any given energy level remains constant. Consequently, the probabilities associated with each energy level remain constant. (In Chapter 25, we introduce [Fermi-Dirac](#) and [Bose-Einstein](#) statistics. When we must use either of these models to describe the system, P_i is affected by rules for the number of molecules that can occupy an energy level.)

The number of molecules and the total energy are extensive properties and vary in direct proportion to the size of the system. The probability, P_i , is an intensive variable that is a characteristic property of the macroscopic system. P_i is a state function. P_i depends on ϵ_i . So long as the thermodynamic variables that determine the state of the system remain constant, the ϵ_i are constant. For a given macroscopic system in which only pressure–volume work is possible, the quantum mechanical energy levels, ϵ_i , are constant so long as the system volume and temperature are constant. However, the ϵ_i are quantum-mechanical quantities that depend on our specification of the molecule and on the boundary values in our specification of the system. If we change any molecular properties or the dimensions of the system, the probabilities, P_i , change.

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