

2.9: The Probabilities of the Population Sets of an Isolated System

In principle, the energy of an equilibrium system that is in contact with a constant-temperature heat reservoir can vary slightly with time. In contrast, the energy of an isolated system is constant. A more traditional and less general statement of the equal *a priori* probability principle focuses on isolated systems, for which all possible microstates necessarily have the same energy:

All microstates of an isolated (constant energy) system occur with equal probability.

If we look at the fraction of the molecules of an isolated system that are in each microstate, we expect to find that these fractions are approximately equal. In consequence, for an isolated system, the probability of a population set, $\{N_1, N_2, \dots, N_i, \dots\}$, is proportional to the number of microstates, $W(N_i, g_i)$, to which that population set gives rise.

In principle, the population sets of a constant-N-V-T system can be significantly different from those of a constant-N-V-E system. That is, if we move an isolated system, whose temperature is T , into thermal contact with a heat reservoir at constant-temperature T , the population sets that characterize the system can change. In practice, however, for a system containing a large number of molecules, the population sets that contribute to the macroscopic properties of the system must be essentially the same.

The fact that the same population sets are important in both systems enables us to make two further assumptions that become important in our development. We assume that the proportionality between the probability of a population set and $W(N_i, g_i)$, which is strictly true only for a constant-N-V-E system, is also true for the corresponding constant-N-V-T system. We also assume that the probabilities of a quantum state, $\rho(\epsilon_i)$, and a microstate, $\rho_{MS,N,E}$, which we defined for the constant-N-V-T system, are the same for the corresponding constant-N-V-E system.

Let us see why we expect the same population sets to dominate the macroscopic properties of otherwise identical constant-energy and constant-temperature systems. Suppose that we isolate a constant-N-V-T system in such a way that the total energy, $E = \sum_{i=1}^{\infty} N_i \epsilon_i$, of the isolated system is exactly equal to the expected value, $\langle E \rangle = N \sum_{i=1}^{\infty} P_i \epsilon_i$, of the energy of the system when its temperature is constant. What we have in mind is a *gedanken* experiment, in which we monitor the energy of the thermostatted system as a function of time, waiting for an instant in which the system energy, $E = \sum_{i=1}^{\infty} N_i \epsilon_i$, is equal to the expected value of the system energy, $\langle E \rangle$. When this occurs, we instantaneously isolate the system.

We suppose that the isolation process is accomplished before any molecule can experience an energy change, so that the population set that characterizes the system immediately afterwards is the same as the one that characterizes it before. After isolation, of course, the molecules can exchange energy with one another, and many population sets may be available to the system.

Clearly, the value of every macroscopic property of the isolated system must be the same as its observable value in the original constant-temperature system. Our microscopic description of it is different. Every population set that is available to the isolated system has energy $E = \langle E \rangle$, and gives rise to

$$W(N_i, g_i) = N! \prod_{i=1}^{\infty} \left(\frac{g_i^{N_i}}{N_i!} \right)$$

microstates. At the same temperature, each of these microstates occurs with the same probability. Since the isolated-system energy is $\langle E \rangle$, this probability is $\rho_{MS,N,\langle E \rangle}$. The probability of an available population set is $W(N_i, g_i) \rho_{MS,N,\langle E \rangle}$.

Since the temperature can span a range of values centered on $\langle T \rangle$, where $\langle T \rangle$ is equal to the temperature of the original constant-N-V-T system, there is a range of $\rho_{MS,N,\langle E \rangle}$ values spanning the (small) range of temperatures available to the constant-energy system. Summing over all of the population sets that are available to the isolated system, we find

$$1 = \sum_{\{N_i\}, E=\langle E \rangle, T=\langle T \rangle} W(N_i, g_i) \rho_{MS,N,\langle E \rangle} + \sum_{\{N_i\}, E=\langle E \rangle, T \neq \langle T \rangle} W(N_i, g_i) \rho_{MS,N,\langle E \rangle}$$

The addition of " $E = \langle E \rangle$ " beneath the summation sign emphasizes that the summation is to be carried out over the population sets that are consistent with both the molecule-number and total-energy constraints and no others. The total probability sum breaks into two terms, one spanning population sets whose temperature is exactly $\langle T \rangle$ and another spanning all of the other population sets. (Remember that the $\rho(\epsilon_i)$ are temperature dependent.)

The population sets available to the isolated system are slightly different from those available to the constant-temperature system. In our microscopic model, only population sets that have exactly the right total energy can occur in the isolated system. Only population sets that have exactly the right temperature can occur in the constant-temperature system.

Summing over all of the population sets that are available to the constant-temperature system, we partition the total probability sum into two terms:

$$1 = \sum_{\{N_i\}, E=\langle E \rangle, T=\langle T \rangle} W(N_i, g_i) \rho_{MS, N, \langle E \rangle} + \sum_{\{N_i\}, E \neq \langle E \rangle, T=\langle T \rangle} W(N_i, g_i) \rho_{MS, N, \langle E \rangle}$$

From the central limit theorem, we expect the constant-energy system to have (relatively) few population that fail to meet the condition $E = \langle E \rangle$. Likewise, we expect the constant temperature system to have (relatively) few population sets that fail to meet the condition $T = \langle T \rangle$. The population sets that satisfy both of these criteria must dominate both sums. For the number of molecules in macroscopic systems, we expect the approximation to the total probability sum

$$1 = \sum_{\{N_i\}, E} W(N_i, g_i) \rho_{MS, N, \langle E \rangle} \approx \sum_{\{N_i\}, E=\langle E \rangle, T=\langle T \rangle} W(N_i, g_i) \rho_{MS, N, \langle E \rangle}$$

to be very good. The same population sets dominate both the constant-temperature and constant-energy systems. Each system must have a most probable population set, $\{N_1^*, N_2^*, \dots, N_i^*, \dots\}$. If these are not identically the same set, they must be so close that the same macroscopic properties are calculated using either one.

Thus, the central limit theorem implies that the total probability sum, which we develop for the constant-temperature system, also describes the constant-energy system, so long as the number of molecules in the system is sufficiently large.

Now, two aspects of this development warrant elaboration. The first is that the probability of population sets that have energies and temperature that satisfy $E = \langle E \rangle$ and $T = \langle T \rangle$ *exactly* may actually be much less than one. The second is that constant-energy and constant-temperature systems are creatures of theory. No real system can actually have an *absolutely* constant energy or temperature.

Recognizing these facts, we see that when we stipulate $E = \langle E \rangle$ or $T = \langle T \rangle$, what we really mean is that $E = \langle E \rangle \pm \delta E$ and $T = \langle T \rangle \pm \delta T$, where the intervals $\pm \delta E$ and $\pm \delta T$ are vastly smaller than any differences we could actually measure experimentally. When we write $E \neq \langle E \rangle$ and $T \neq \langle T \rangle$, we really intend to specify energies and temperatures that fall outside the intervals $E = \langle E \rangle \pm \delta E$ and $T = \langle T \rangle \pm \delta T$. If the system contains sufficiently many molecules, the population sets whose energies and temperatures fall within the intervals $E = \langle E \rangle \pm \delta E$ and $T = \langle T \rangle \pm \delta T$ account for nearly all of the probability—no matter how small we choose δE and δT . All of the population sets whose energies and temperatures fall within the intervals $E = \langle E \rangle \pm \delta E$ and $T = \langle T \rangle \pm \delta T$ correspond to the same macroscopically observable properties.

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