20.3: The Population Sets of a System at Equilibrium at Constant N, V, and T

In developing Boltzmann statistics, we assume that we can tell different molecules of the same substance apart. We say that the molecules are ***distinguishable***. This assumption is valid for molecules that occupy lattice sites in a crystal. In a crystal, we can specify a particular molecule by specifying its position in the lattice. In other systems, we may be unable to distinguish between different molecules of the same substance. Most notably, we cannot distinguish between two molecules of the same substance in the gas phase. The fact that gas molecules are indistinguishable, while we assume otherwise in developing Boltzmann statistics, turns out to be a problem that is readily overcome. We discuss this in Section 24.2.

We want to model properties of a system that contains N, identical, distinguishable, non-interacting molecules. The solutions of the Schrödinger equation presume fixed boundary conditions. This means that the volume of this N-molecule system is constant. We assume also that the temperature of the N-molecule system is constant. Thus, our goal is a theory that predicts the properties of a system when N, V, and T are specified. When there are no intermolecular interactions, the energy of the system is just the sum of the energies of the individual molecules. If we know how the molecules are allocated among the energy levels, we can find the energy of the system. Letting N_i be the population of the energy level ϵ_i, any such allocation is a population set $\{N_1,\ N_2, \ldots, N_i, \ldots\}$. We have

$$N = \sum_{i=1}^{\infty} N_i$$

and the system energy is

$$E = \sum_{i=1}^{\infty} N_i \epsilon_i$$

Let us imagine that we can assemble a system with the molecules allocated among the energy levels in any way we please. Let $\{N_1^o,\ N_2^o, \ldots, N_i^o, \ldots\}$ represent an initial population set that describes a system that we assemble in this way. This population set corresponds to a well-defined system energy. We imagine immersing the container in a constant-temperature bath. Since the system can exchange energy with the bath, the molecules of the system gain or lose energy until the system attains the temperature of the bath in which it is immersed. As this occurs, the populations of the energy levels change. A series of different population sets characterizes the state of the system as it evolves toward thermal equilibrium. When the system reaches equilibrium, the population sets that characterize it are different from the initial one, $\{N_1^o,\ N_2^o, \ldots, N_i^o, \ldots\}$.

Evidently, the macroscopic properties of such a system also change with time. The changes in the macroscopic properties of the system parallel the changing energy-level populations. At thermal equilibrium, macroscopic properties of the system cease to undergo any further change. In Section 3.9, we introduce the idea that the most probable population set, which we denote as

$$\left\{N_1^{\bullet},\ N_2^{\bullet}, \ldots, N_i^{\bullet}, \ldots\right\}$$

or its proxy,

$$\{NP(\epsilon_1), NP(\epsilon_2), \ldots, NP(\epsilon_i), \ldots\}$$

(where $N = N_1^{\bullet} + N_2^{\bullet} + \ldots + N_i^{\bullet} + \ldots$), is the best prediction we can make about the outcomes in a future set of experiments in which we find the energy of each of N different molecules at a particular instant. We hypothesize that the most probable population set specifies all of the properties of the macroscopic system in its equilibrium state. When we develop the logical consequences of this hypothesis, we find a theory that expresses macroscopic thermodynamic properties in terms of the energy levels available to individual molecules. In the end, the justification of this hypothesis is that it enables us to calculate thermodynamic properties that agree with experimental measurements made on macroscopic systems.

Our hypothesis asserts that the properties of the equilibrium state are the same as the properties of the system when it is described by the most probable population set. Evidently, we can predict the system's equilibrium state if we can find the equilibrium $N_i^{\bullet}$ values, and *vice versa*. To within an arbitrary factor representing its size, an equilibrated system can be completely described by its intensive properties. In the present instance, the fractions $N_1^{\bullet}/N$, $N_2^{\bullet}/N$, ..., $N_i^{\bullet}/N, \ldots$ describe the equilibrated system to within the factor, N, that specifies its size. Since we infer that $P_i = P(\epsilon_i) = N_i^{\bullet}/N$, the equilibrated system is also described by the probabilities $(P_1, P_2, \ldots,\ P_i, \ldots)$.

Our hypothesis does not assert that the most-probable population set is the only population set possible at equilibrium. A very large number of other population sets may describe an equilibrium system at different instants of time. However, when its state is specified by any such population set, the macroscopic properties of the system are indistinguishable from the macroscopic properties of the system when its state is specified by the most-probable population set. The most-probable population set characterizes the equilibrium state of the system in the sense that we can calculate the properties of the equilibrium state of the macroscopic system by using the single-molecule energy levels and the most probable population set—or its proxy. The relationship between a molecular energy level, ϵ_i, and its equilibrium population, $N_i^\bullet$, is called the ***Boltzmann equation***. From $P_i = N_i^\bullet / N$, we see that the Boltzmann equation specifies the probability of finding a given molecule in energy level ϵ_i.

Although we calculate thermodynamic properties from the most probable population set, the population set that describes the system can vary from instant to instant while the system remains at equilibrium. The central limit theorem enables us to characterize the amount of variation that can occur. When N is comparable to the number of molecules in a macroscopic system, the probability that variation among population sets can result in a macroscopically observable effect is vanishingly small. The hypothesis is successful because the most probable population set is an excellent proxy for any other population set that the equilibrium system is remotely likely to attain.

We develop the theory of statistical thermodynamics for N-molecule systems by considering the energy levels, ϵ_i, available to a single molecule that does not interact with other molecules. Thereafter, we develop a parallel set of statistical thermodynamic results by considering the energy levels, $\hat{E}_i$, available to a system of N molecules. These N-molecule-system energies can reflect the effects of any amount of intermolecular interaction. We can apply the same arguments to find that the Boltzmann equation also describes the equilibrium properties of systems in which intermolecular interactions are important. That is, the probability, $P_i\left(\hat{E}_i\right)$, that an N-molecule system has energy $\hat{E}_i$ is the same function of $\hat{E}_i$ as the molecular-energy probability, $P_i = P\left(\epsilon_i\right)$, is of ϵ_i.

When we finish our development based on single-molecule energy levels, we understand nearly all of the ideas that we need in order to complete the development for the energies of an N-molecule system. This development is an elegant augmentation of the basic argument called the ***ensemble treatment*** or the ***ensemble method***. The ensemble treatment is due to J. Willard Gibbs; we discuss it in Chapter 23. For now, we simply note that our approach involves no wasted effort. When we discuss the ensemble method, we use all of the ideas that we develop in this chapter and the next. The extension of these arguments that is required for the ensemble treatment is so straightforward as to be (almost) painless.
