23.1: Ensembles of N-molecule Systems

When we begin our discussion of Boltzmann statistics in Chapter 20, we note that there exists, in principle, a Schrödinger equation for an N-molecule system. For any particular set of boundary conditions, the solutions of this equation are a set of infinitely many wavefunctions, $\Psi_{i,j}$, for the N-molecule system. For every such wavefunction, there is a corresponding system energy, E_i. The wavefunctions reflect all of the attractive and repulsive interactions among the molecules of the system. Likewise, the energy levels of the system reflect all of these interactions.

In Section 20.12, we introduce the symbol Ω_E to denote the degeneracy of the energy, E, of an N-molecule system. Because the constituent molecules are assumed to be distinguishable and non-interacting, we have

$$\Omega_E = \sum_{\{N_i\},E} W\left(N_i, g_i\right)$$

In the solution of the Schrödinger equation for a system of N interacting molecules, each system-energy level, E_i, can be degenerate. We again let Ω denote the degeneracy of an energy level of the system. We use Ω_i (rather than Ω_{E_i}) to represent the degeneracy of E_i. It is important to recognize that the symbol "Ω_i" now denotes an intrinsic quantum-mechanical property of the N-particle system.

In Chapters 21 and 22, we denote the parallel properties of an individual molecule by $\psi_{i,j}$ for the molecular wavefunctions, ϵ_i for the corresponding energy levels, and g_i for the degeneracy of the i^{th} energy level. We imagine creating an N-molecule system by collecting N non-interacting molecules in a fixed volume and at a fixed temperature.

In exactly the same way, we now imagine collecting $\hat{N}$ of these N-molecule, constant-volume, constant-temperature systems. An aggregate of many multi-molecule systems is called an ***ensemble***. Just as we assume that no forces act among the non-interacting molecules we consider earlier, we assume that no forces act among the systems of the ensemble. However, as we emphasize above, our model for the systems of an ensemble recognizes that intermolecular forces among the molecules of an individual system can be important. We can imagine specifying the properties of the individual systems in a variety of ways. A collection is called a ***canonical ensemble*** if each of the systems in the ensemble has the same values of N, V, and T. (The sense of this name is that by specifying constant N, V, and T, we create the ensemble that can be described most simply.)

The canonical ensemble is a collection of $\hat{N}$ identical systems, just as the N-molecule system is a collection of N identical molecules. We imagine piling the systems that comprise the ensemble into a gigantic three-dimensional stack. We then immerse the entire stack—the ensemble—in a constant temperature bath. The ensemble and its constituent systems are at the constant temperature T. The volume of the ensemble is $\hat{N}V$. Because we can specify the location of any system in the ensemble by specifying its x-, y-, and z-coordinates in the stack, the individual systems that comprise the ensemble are distinguishable from one another. Thus the ensemble is analogous to a crystalline N-molecule system, in which the individual molecules are distinguishable from one another because each occupies a particular location in the crystal lattice, the entire crystal is at the constant temperature, T, and the crystal volume is NV_{molecule}.

Since the ensemble is a conceptual construct, we can make the number of systems in the ensemble, $\hat{N}$, as large as we please. Each system in the ensemble will have one of the quantum-mechanically allowed energies, E_i. We let the number of systems that have energy E_1 be $\hat{N}_1$. Similarly, we let the number with energy E_2 be $\hat{N}_2$, and the number with energy E_i be $\hat{N}_i$. Thus at any given instant, the ensemble is characterized by a population set, $\{\hat{N}_1,\ \hat{N}_2,\ \ldots,\ \hat{N}_i, \ldots\}$, in exactly the same way that an N-molecule system is characterized by a population set, $\{N_1,\ N_2, \ldots,\ N_i, \ldots\}$. We have

$$\hat{N} = \sum_{i=1}^{\infty} \hat{N}_i$$

While all of the systems in the ensemble are immersed in the same constant-temperature bath, the energy of any one system in the ensemble is completely independent of the energy of any other system. This means that the total energy of the ensemble, $\hat{E}$, is given by

$$\hat{E} = \sum_{i=1}^{\infty} \hat{N}_i E_i$$

Property	System	Ensemble
Quantum entity	***Molecule*** at fixed volume and temperature	***System*** comprising a collection of N molecules at fixed volume and temperature
Aggregate of quantum entities	***System*** comprising a collection of N molecules at fixed volume and temperature	***Ensemble*** comprising $\hat{N}$ systems each of which contains N molecules
Number of quantum entities in aggregate	N	$\hat{N}$
Wave functions/quantum states	ψ_i	Ψ_i
Energy levels	ϵ_i	E_i
Energy level degeneracies	g_i	Ω_i
Probability that an energy level is occupied	P_i	$\hat{P}_i$
Number of quantum entities in the i^{th} energy level	N_i	$\hat{N}_i$
Probability that a quantum state is occupied	$\rho\left(\epsilon_i\right)$	$\hat{\rho}\left(E_i\right)$
Energy of the aggregate's k^{th} population set	$E_k = \sum N_{k,i}\epsilon_i$	$\hat{E}_k = \sum \hat{N}_{k,i}\epsilon_i$
Expected value of the energy of the aggregate	$\langle E \rangle = N \sum P_i \epsilon_i$	$\left\langle \hat{E} \right\rangle = \hat{N} \sum \hat{P}_i E_i$

The population set, $\{\hat{N}_1,\ \hat{N}_2,\ \ldots,\ \hat{N}_i, \ldots\}$, that characterizes the ensemble is not constant in time. However, by the same arguments that we apply to the N-molecule system, there is a population set

$$\{\hat{N}_1^{\bullet},\ \hat{N}_2^{\bullet}, \ldots,\ \hat{N}_i^{\bullet}, \ldots\}$$

which characterizes the ensemble when it is at equilibrium in the constant-temperature bath.

We define the probability, $\hat{P}_i$, that a system of the ensemble has energy E_i to be the fraction of the systems in the ensemble with this energy, when the ensemble is at equilibrium at the specified temperature. Thus, by definition,

$$\hat{P}_i = \frac{\hat{N}_i^{\bullet}}{\hat{N}}.$$

We define the probability that a system is in one of the states, $\Psi_{i,j}$, with energy E_i, as

$$\hat{\rho}\left(E_i\right) = \frac{\hat{P}_i}{\Omega_i}$$

The method we have used to construct the canonical ensemble insures that the entire ensemble is always at the specified temperature. If the component systems are at equilibrium, the ensemble is at equilibrium. The expected value of the ensemble energy is

$$\left\langle \hat{E} \right\rangle = \hat{N} \sum_{i=1}^{\infty} \hat{P}_i E_i = \sum_{i=1}^{\infty} \hat{N}_i^{\bullet} E_i$$

Because the number of systems in the ensemble, $\hat{N}$, is very large, we know from the central limit theorem that any observed value for the ensemble energy will be indistinguishable from the expected value. To an excellent approximation, we have at any time,

$$\hat{E} = \left\langle \hat{E} \right\rangle$$

and

$$\hat{N}_i^{\bullet} = \hat{N}_i$$

The table above summarizes the terminology that we have developed to characterize molecules, N-molecule systems, and $\hat{N}$-system ensembles of N-molecule systems.

We can now apply to an ensemble of $\hat{N}$, distinguishable, non-interacting systems the same logic that we applied to a system of N, distinguishable, non-interacting molecules. The probability that a system is in one of the energy levels is

$$1 = \hat{P}_1 + \hat{P}_2 + \cdots + \hat{P}_i + \ldots$$

The total probability sum for the constant-temperature ensemble is

$$1 = \left(\hat{P}_1 + \hat{P}_2 + \cdots + \hat{P}_i + \ldots\right)^{\hat{N}} = \sum_{\{\hat{N}_i\}} \hat{W}\left(\hat{N}_i, \Omega_i\right) \hat{\rho}\left(E_1\right)^{\hat{N}_1} \hat{\rho}\left(E_2\right)^{\hat{N}_2} \ldots \hat{\rho}\left(E_i\right)^{\hat{N}_i} \ldots$$

where

$$\hat{W}\left(\hat{N}_i, \Omega_i\right) = \hat{N}! \prod_{i=1}^{\infty} \frac{\Omega_i^{\hat{N}_i}}{\hat{N}_i!}$$

Moreover, we can imagine instantaneously isolating the ensemble from the temperature bath in which it is immersed. This is a wholly conceptual change, which we effect by replacing the fluid of the constant-temperature bath with a solid blanket of insulation. The ensemble is then an isolated system whose energy, $\hat{E}$, is constant. Every system of the isolated ensemble is immersed in a constant-temperature bath, where the constant-temperature bath consists of the $\hat{N} - 1$ systems that make up the rest of the ensemble. This is an important feature of the ensemble treatment. It means that any conclusion we reach about the systems of the constant-energy ensemble is also a conclusion about each of the $\hat{N}$ identical, constant-temperature systems that comprise the isolated, constant-energy ensemble.

Only certain population sets, $\{\hat{N}_1,\ \hat{N}_2,\ \ldots,\ \hat{N}_i, \ldots\}$, are consistent with the fixed value, $\hat{E}$, of the isolated ensemble. For each of these population sets, there are $\hat{W}\left(\hat{N}_i, \Omega_i\right)$ system states. The probability of each of these system states is proportional to $\hat{\rho}\left(E_1\right)^{\hat{N}_1} \hat{\rho}\left(E_2\right)^{\hat{N}_2} \ldots \hat{\rho}\left(E_i\right)^{\hat{N}_i} \ldots$. By the principle of equal *a priori* probability, every system state of the fixed-energy ensemble occurs with equal probability. We again conclude that the population set that characterizes the equilibrium state of the constant-energy ensemble, $\{\hat{N}_1^{\bullet},\ \hat{N}_2^{\bullet}, \ldots,\ \hat{N}_i^{\bullet}, \ldots\}$, is the one for which $\hat{W}$ or $\ln \hat{W}$ is a maximum, subject to the constraints

$$\hat{N} = \sum_{i=1}^{\infty} \hat{N}_i$$

and

$$\hat{E} = \sum_{i=1}^{\infty} \hat{N}_i E_i$$

The fact that we can make $\hat{N}$ arbitrarily large ensures that any term, $\hat{N}_i^{\bullet}$, in the equilibrium-characterizing population set can be very large, so that $\hat{N}_i^{\bullet}$ can be found using Stirling's approximation and Lagrange's method of undetermined multipliers. We have the mnemonic function

$$F_{mn} = \hat{N} \ln \hat{N} - \hat{N} + \sum_{i=1}^{\infty} \left(\hat{N}_i \ln \Omega_i\ - \hat{N}_i \ln \hat{N}_i\ + \hat{N}_i\right) + \alpha\left(\hat{N} - \sum_{i=1}^{\infty} \hat{N}_i\right) + \beta\left(\hat{E} - \sum_{i=1}^{\infty} \hat{N}_i E_i\right)$$

so that

$$\left(\frac{\partial F_{mn}}{\partial \hat{N}_i^{\bullet}}\right)_{j \neq i} = \ln \Omega_i\ - \frac{\hat{N}_i^{\bullet}}{\hat{N}_i^{\bullet}} - \ln \hat{N}_i^{\bullet}\ + 1 - \alpha - \beta E_i = 0$$

and

$$\ln \hat{N}_i^{\bullet} = \ln \Omega_i - \alpha - \beta E_i$$

or

$$\hat{N}_i^{\bullet} = \Omega_i \exp(-\alpha) \exp -\beta E_i$$

When we make use of the constraint on the total number of systems in the ensemble, we have

$$\hat{N} = \sum_{i=1}^{\infty} \hat{N}_i^{\bullet} = \exp(-\alpha) \sum_{i=1}^{\infty} \Omega_i \exp(-\beta E_i)$$

so that

$$\exp(-\alpha) = \hat{N} Z^{-1}$$

where the partition function for a system of N possibly-interacting molecules is

$$Z = \sum_{i=1}^{\infty} \Omega_i \exp(-\beta E_i)$$

The probability that a system has energy E_i is equal to the equilibrium fraction of systems in the ensemble that have energy E_i, so that

$$\hat{P}_i = \frac{\hat{N}_i^{\bullet}}{\hat{N}} = \frac{\Omega_i \exp(-\beta E_i)}{Z}$$