3.9: The Partition Function for a System of N Molecules

At a given temperature, the Boltzmann equation gives the probability of finding a molecule in any of the energy levels that the molecule can occupy. Throughout our development, we assume that there are no energies of interaction among the molecules of the system. The molecular partition function contains information about the energy levels of only one molecule. We obtain equations for the thermodynamic functions of an N-molecule system in terms of this molecular partition function. However, since these results are based on assigning the same isolated-molecule energy levels to each of the molecules, they do not address the real-system situation in which intermolecular interactions make important contributions to the total energy of the system.

As we mention in Sections 20.1 and 20.3, the ensemble theory of statistical thermodynamics extends our arguments to express the thermodynamic properties of a macroscopic system in terms of all of the total energies that are available to the macroscopic system. The molecular origins of the energies of the system enter the ensemble treatment only indirectly. The theory deals with the relationships between the possible values of the energy of the system and its thermodynamic state. How molecular energy levels and intermolecular interactions give rise to these values of the system energy becomes a separate issue. Fortunately, ensemble theory just reuses—from a different perspective—all of the ideas we have just studied. The result is just the Boltzmann equation, again, but now the energies that appear in the partition function are the possible energies for the collection of N molecules, not the energies available to a single molecule.