

We start this chapter with a definition of probability that enables us to define the average value of a physical property of a system. We then consider systems in thermal equilibrium, the definition of entropy, and the definition of temperature. The second law of thermodynamics will appear as the law of increase of entropy. This chapter is perhaps the most abstract in the book. The chapters that follow will apply the concepts to physical problems.

FUNDAMENTAL ASSUMPTION

The fundamental assumption of thermal physics is that a closed system is equally likely to be in any of the quantum states accessible to it. All accessible quantum states are assumed to be equally probable—there is no reason to prefer some accessible states over other accessible states.

- * A closed system will have constant energy, a constant number of particles, constant volume, and constant values of all external parameters that may influence the system, including gravitational, electric, and magnetic fields.
- * A quantum state is accessible if its properties are compatible with the physical specification of the system: the energy of the state must be in the range within which the energy of the system is specified, and the number of particles must be in the range within which the number of particles is specified. With large systems we can never know either of these exactly, but it will suffice to have $\delta U/U \ll 1$ and $\delta N/N \ll 1$.

Unusual properties of a system may sometimes make it impossible for certain states to be accessible during the time the system is under observation. For example, the states of the crystalline form of SiO_2 are inaccessible at low temperatures in any observation that starts with the glassy or amorphous form: fused silica will not convert to quartz in our lifetime in a low-temperature experiment. You will recognize many exclusions of this type by common sense. We treat all quantum states as accessible unless they are excluded by the specification of the system (Figure 2.1) and the time scale of the measurement process. States that are not accessible are said to have zero probability.

Of course, it is possible to specify the configuration of a closed system to a point that its statistical properties as such are of no interest. If we specify that the