

1.7 Microscopic and Macroscopic Systems

It is useful, at this stage, to make a distinction between the different sizes of the systems that we are going to examine. We shall call a system *microscopic* if it is roughly of atomic dimensions, or smaller. On the other hand, we shall call a system *macroscopic* if it is large enough to be visible in the ordinary sense. This is a rather inexact definition. The exact definition depends on the number of particles in the system, which we shall call N . A system is macroscopic if $1/N^{1/2} \ll 1$, which means that statistical arguments can be applied to reasonable accuracy. For instance, if we wish to keep the relative statistical error below one percent then a macroscopic system would have to contain more than about ten thousand particles. Any system containing less than this number of particles would be regarded as essentially microscopic, and, hence, statistical arguments could not be applied to such a system without unacceptable error.

1.8 Classical and Statistical Thermodynamics

In this course, we are going to develop some machinery for interrelating the statistical properties of a system containing a very large number of particles, via a statistical treatment of the laws of atomic or molecular motion. It turns out that, once we have developed this machinery, we can obtain some very general results that do not depend on the exact details of the statistical treatment. These results can be described without reference to the underlying statistical nature of the system, but their validity depends ultimately on statistical arguments. They take the form of general statements regarding heat and work, and are usually referred to as *classical thermodynamics*, or just *thermodynamics*, for short. Historically, classical thermodynamics was the first type of thermodynamics to be discovered. In fact, for many years, the laws of classical thermodynamics seemed rather mysterious, because their statistical justification had yet to be discovered. The strength of classical thermodynamics is its great generality, which comes about because it does not depend on any detailed assumptions about the statistical properties of the system under investigation. This generality is also the principle weakness of classical thermodynamics. Only a relatively few statements can be made on such general grounds, so many interesting properties of the system remain outside the scope of classical thermodynamics.

If we go beyond classical thermodynamics, and start to investigate the statistical machinery that underpins it, then we get all of the results of classical thermodynamics, plus a large number of other results that enable the macroscopic parameters of the system to be calculated from a knowledge of its microscopic constituents. This approach is known as *statistical thermodynamics*, and is extremely powerful. The only drawback is that the further we delve inside the statistical machinery of thermodynamics, the harder it becomes to perform the necessary calculations.

Note that both classical and statistical thermodynamics are only valid for systems in *equilibrium*. If the system is not in equilibrium then the problem becomes considerably more difficult. In fact, the thermodynamics of non-equilibrium systems, which is generally called *irreversible thermodynamics*, is a graduate-level subject.

1.9 Classical and Quantum Approaches

We mentioned earlier that the motions (by which we really meant the translational motions) of atoms and molecules are described exactly by quantum mechanics, and only approximately by classical mechanics. It turns out that the non-translational motions of molecules, such as their rotation and vibration, are very poorly described by classical mechanics. So, why bother using classical mechanics at all? Unfortunately, quantum mechanics deals with the translational motions of atoms and molecules (via wave mechanics) in a rather awkward manner. The classical approach is far more straightforward, and, under most circumstances, yields the same statistical results. Hence, throughout the first part of this course, we shall use classical mechanics, as much as possible, to describe the translational motion of atoms and molecules, and will reserve quantum mechanics for dealing with non-translational motions. However, towards the end of this course, in Chapter 8, we shall switch to a purely quantum-mechanical approach.

