2.2: Macroscopic Description of a Large Equilibrium System

The title of this section introduces two new terms. . . large and equilibrium. A system is large if it contains many particles, but just how large is “large enough”? A few decades ago, physicists dealt with systems of one or two or a dozen particles, or else they dealt with systems with about 10^{23} particles, and the distinction was clear enough. Now that computer chips have such small lines, systems of intermediate size are coming under investigation. (This field carries the romantic name of “mesoscopic physics”.) In practical terms, it is usually easy enough to see when the term “large” applies, but there is no rigorous criterion and there have been some surprises in this regard.

A similar situation holds for the term equilibrium. A system is said to be in equilibrium if its macroscopic properties are not changing with time. Thus a cup of tea, recently stirred and with churning, swirling flow, is not at equilibrium, whereas some time later the same cup, sedate and calm, is at equilibrium. But some of the properties of the latter cup are changing with time: for example, the height of water molecule number 173 changes rapidly. Of course this is not a macroscopic property, but then there is no rigorous definition of macroscopic vs. microscopic properties. Once again there is little difficulty in practice, but a rigorous criterion is wanting and some excellent physicists have been fooled. (For example, a mixture of hydrogen gas and oxygen gas can behave like a gas in equilibrium. But if a spark is introduced, these chemicals will react to form water. The gas mixture is in equilibrium as far as its physical properties are concerned, but not as far as its chemical properties are concerned.)

With these warnings past, we move on to the macroscopic description. As with the microscopic description, it has two parts: the first saying what the system is and the second saying what condition the system is in. For definiteness, we consider the helium-in-a-smooth-box model already introduced.

To say what this system is, we again list mechanical parameters. At first these are the same as for the microscopic description: the number of particles N, the mass of each particle m, and a description of the atom-atom interaction potential (e.g. the Lennard-Jones parameters a and b). But we usually don’t need to specify the atom-wall interaction or even the location of the walls. . . instead we specify only the volume of the container V. The reason for this is not hard to see. If we deal with a large system with typical wall-atom interactions (short range) and typical walls (without intricate projections and recesses) then very few particles will be interacting with the walls at any one instant, so we expect that the details of wall-atom interaction and container shape will be affect only a tiny minority of atoms and hence be irrelevant to macroscopic properties. There are of course exceptions: for example, in a layered substance such as graphite or mica, or one of the high-temperature superconductors, the shape of the container might well be relevant. But in this book we will not often deal with such materials.

Finally, what condition is the system in? (In other words, what corresponds to the dynamical variables in a microscopic description?) Clearly the “point in phase space”, giving the positions and momenta of each and every particle in the system, is far too precise to be an acceptable macroscopic description. But at the same time it is not acceptable to say we don’t care anything about microscopic quantities, because the energy of this system is conserved, so energy will be a feature of both the microscopic and macroscopic descriptions. In fact, for the helium-in-a-smooth-box model, energy is the *only* quantity that is conserved,[3] so it is the only item in the list of macroscopic descriptors. (Other systems, such as the earth-moon system, will have additional conserved quantities, and hence additional items in that list.)

What equilibrium is not

There’s a common misconception that at equilibrium, the sample is uniform. This might not be true: A mixture of ice and water at atmospheric pressure and temperature 0 C is at equilibrium but is not uniform. Or, consider a container of air 50 kilometers tall with its base on Earth at sea level: most of the molecules huddle at the bottom of the container, and the top is near-vacuum.

2.5 (Q) Three-body interactions: macroscopic

Even though three-body interactions do exist, they can usually be ignored in a macroscopic description. (Just as the wall-atom interaction does exist, but it can usually be ignored in a macroscopic description.) Why?

2.6 (Q,E) Lost in space

A collection of N asteroids floats in space far from other gravitating bodies. Model each asteroid as a hard sphere of radius R and mass m. What quantities are required for a microscopic description of this system? For a macroscopic description?

[3]The momentum and angular momentum of the helium atoms is not conserved, because there are external forces due to the box.