2.3: Fundamental Assumption

Define microstate and macrostate.

There are many microstates corresponding to any given macrostate. The collection of all such microstates is called an “ensemble”. (Just as a musical ensemble is a collection of performers.)

Note: An ensemble is a (conceptual) collection of macroscopic systems. It is not the collection of atoms that makes up a macroscopic system.

(Terminology: A microstate is also called a “configuration” or a “complexion”. . . both poor terms. A macrostate is also called a “thermodynamic state”. A “corresponding” microstate is sometimes called an “accessible” or a “consistent” microstate.)

A system is said to be “isolated” if no energy goes in or out, and if the mechanical parameters (N, V, etc.) are also fixed. Most of the systems you deal with in classical mechanics classes, for example, are isolated.

The fundamental assumption of statistical mechanics is:

An isolated system in an equilibrium macrostate has equal probability of being in any of the microstates corresponding to that macrostate.

Conceptual difficulties:

1. What is equilibrium?
2. What is probability? (Any experiment is done on one system.)
3. May be false! (Can be motivated by the ergodic hypothesis, but this is just suggestive, and the ergodic hypothesis itself has not been proven and may be false. Cellular automata may violate this assumption. . . but do physical/biological systems? See for example Andrew I. Adamatzky, *Identification of Cellular Automata* (Taylor and Francis, 1995) and the essay review by Normand Mousseau, in *Contemporary Physics*, **37** (1996) 321–323; Stephen Wolfram, *A New Kind of Science* (Wolfram Media, 2002).)

Practical difficulties.

1. Gives way to find average values of microscopic quantities, such as

$$\langle\text{kinetic energy}\rangle, \ \langle\text{potential energy}\rangle, \ \langle\text{height}\rangle,$$

but not things like temperature and pressure.

2. Based on model. (In particular, infinitely hard smooth walls.)

3. For point particle model, requires infinitely thin sheet in phase space. Work instead with the volume of phase space corresponding to energies from E to $E+\Delta E$, and at the end of the calculation take the limit $\Delta E \to 0$.

To examine these practical difficulties in more detail, consider again the helium-in-a-smooth-box model. Suppose we want to find the number of microstates with energy ranging from E to $E+\Delta E$, in a system with N identical particles in a box of volume V.

Your first answer might be that there are an infinite number of points in phase space satisfying this criterion. This is true but it misses the point: A thimble and a Mack truck both contain an infinite number of points, but the Mack truck carries more because it has more volume. Clearly the microstate count we desire is some sort of measure of phase-space volume. I’ll call the region of phase space with energy ranging from E to $E+\Delta E$ by the name $\sigma(E, \Delta E)$, and call its volume

$$\int_{\sigma(E,\Delta E)} d\Gamma. \quad (\text{ Volume in phase space. }) \tag{2.3.1}$$

However, this volume isn’t precisely what we want. Permutation argument for N identical particles. (For a system with N identical particles, there are $N!$ points in phase space corresponding to the same microstate.) A better measure of the microstate count is thus

$$\frac{1}{N!}\int_{\sigma(E,\Delta E)} d\Gamma. \quad (\text{Delabeled volume in phase space.}) \tag{2.3.2}$$

There remains one more problem. We desire a count, which is dimensionless, and the above expression gives a phase-space volume, which has the dimensions of

$$(\text{angular momentum})^{3N}.$$

The solution to this problem is straightforward if clunky. Pick a quantity with the dimensions of angular momentum. Any quantity will do, so make an arbitrary choice. Call the quantity h_0. (Clearly, by the time we produce a measurable physical result at the end of a calculation, it had better be independent of our choice of h_0, just as the value of any measurable result in a classical mechanics problem has to be independent of choice of the potential energy zero.) Then define the microstate count as the dimensionless quantity

$$\Omega(E, \Delta E, V, N)=\frac{1}{h_0^{3N}} \frac{1}{N!} \int_{\sigma(E, \Delta E)} d\Gamma. \quad \text{(Dimensionless, delabeled volume in phase space.)} \tag{2.3.3}$$

In poker, there are 52 cards in a deck, so the probability of drawing any given card from a shuffled deck is 1/52. The number 52 plays a fundamental role in answering any question concerning probability in poker.

In statistical mechanics, there are Ω microstates corresponding to a macrostate, so the probability of encountering any given microstate is (if the fundamental assumption is correct) $1/\Omega$. The number Ω plays the same fundamental role in statistical mechanics that 52 does in poker.

2.7 Microstate count for a mixture

What expression corresponds to 2.3.3 for a collection of N_{He} Helium atoms and N_{Ar} Argon atoms?