

# Time-Dependent Statistical Mechanics

## 1B. An introduction to ensemble averages in nonequilibrium statistical mechanics

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September 24, 2009

At this point we want to discuss just one aspect of the use of statistics and probability in statistical mechanics. Consider a typical experimental situation that we want to describe using the fundamental mechanics of the atoms and molecules. For simplicity here, we shall assume that the molecules in the material being studied move according to classical mechanics.

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If we regard the system as a classical mechanical system, then each degree of freedom has a coordinate and a momentum. For simplicity, let's consider that the system is an atomic liquid containing  $N$  identical atoms in thermodynamic equilibrium at a certain temperature  $T$  and volume  $V$ . We prepare the system, and then start the experiment at  $t = 0$ . Then the mechanical state of the system at  $t = 0$  is specified by listing all of the coordinates and momenta:  $\mathbf{r}^N, \mathbf{p}^N$ . The subsequent motion of the system is governed by Hamilton's equations. Suppose there is something we want to calculate about the future behavior of the system, e.g.

$$\sum_{i=1}^N (\mathbf{r}_i(t) - \mathbf{r}_i(0))^2$$

for some specific value of  $t$ , e.g. 600 seconds. (Suppose we could do this.) We would get a certain answer. You may recognize this as something related to diffusion, but we'll come to this a little later.

Suppose we did it again. The initial state at  $t = 0$  would be different, but I claim we would get essentially the same answer.

We do it again. We would get the same answer.

Why is it that we always get the same answer?

The reason has to do with what is sometimes called the Law of Large Numbers. Here is an analogy.

Suppose you collected all the students of Stanford University, about 14,000 of them. You picked one student at random and measured his or her height. Then you pick another student at random and measure his or her height. The answer would be different each time you did it, and there would be a reasonable spread in heights. Most would be between about 5.2 feet and 6.2 feet, but there would be some shorter and taller. So the answer would be typically

$$5.7 \pm 0.5 \text{ feet}$$

with about a 10% fluctuation from one measurement to another.

Now suppose you did things somewhat differently. You picked 100 students at random and added their heights together. The answer would typically be about

$$570 \pm 5 \text{ feet}$$

The average is 100 times larger than the previous one, but the error is only about 10 times as large.

So when you measure the total height of 100 people, the fractional variation from measurement to measurement is about 1%.

If you did it for 1000 people, you would get

$$5700 \pm 16 \text{ feet}$$

or a typical fluctuation of about 0.3%.

**Basic principle.** Many (but not all) of the mechanical quantities we are interested in calculating have the property that the spread in their values is very small on a fractional basis. The quantities that have this property are typically those involving a large number of contributions, each of which involves a small number of particles.

If we get the same answer for all initial states, suppose we calculate the average of

$$\sum_{i=1}^N (\mathbf{r}_i(t) - \mathbf{r}_i(0))^2$$

over the statistical distribution of initial states appropriate for a system of  $N$  particles in volume  $V$  at temperature  $T$ . You may recall from previous courses that this distribution is called the canonical distribution. The average over this distribution will be denoted

$$\left\langle \sum_{i=1}^N (\mathbf{r}_i(t) - \mathbf{r}_i(0))^2 \right\rangle_{NVT}$$

This is usually called a canonical average (or a canonical ensemble average).

**Basic principle (continued).** If a mechanical quantity has the property described above, every measurement of it will give almost exactly the same answer and will be almost exactly equal to the canonical ensemble average of that mechanical quantity.

**Important points.** Ensemble averages of mechanical quantities play an important role in equilibrium statistical mechanics. Ensemble averages are also important in the theory of nonequilibrium statistical mechanics.

There are several reasons:

- Any time we can express something of interest to equilibrium ensemble averages, we are relating that thing of interest to other variables about which a lot is known.
- Some times it is in fact easier to calculate ensemble averages than to calculate the quantity being averaged.
- For reasons that will become clear, we often find that *equilibrium* averages of certain properties, such as the one we have been considering, play an important role in the theory of *time dependent* and *nonequilibrium* phenomena, such as diffusion and chemical reaction rates.
- The results of many spectroscopic and scattering experiments can be expressed in terms of ensemble averages of a special type, namely correlation functions.

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