Time-Dependent Statistical Mechanics 1C. The basic postulate of equilibrium statistical mechanics and elementary properties of time correlation functions

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An experiment. Consider an experiment of the following type: Lecture 2 9/24/09

1. Prepare a molecular system and let it come to equilibrium under a certain set of conditions (e.g. and certain number of molecules N, a certain composition, a certain temperature T, a certain volume V).

2. When you are sure the system is equilibrated, start the clock (and set $t = 0$).

3. Perform one or more measurements at specific times.

4. Repeat the entire process, doing the same measurements at the same times.

5. Average the results of the various experiments.

The mechanical state of the system. The way the state is specified depends on the nature of the system and the nature of the dynamics. For the time being, consider only classical systems. Consider that the system evolves according to some classical mechanics.

- For Hamiltonian mechanics, the state of the system is the set of positions and momenta of all the particles.

- For Langevin dynamics, the state of the system is the set of positions and momenta of the Brownian particles.
- For Smoluchowski (diffusive) dynamics, the state of the system is the set of positions of the Brownian particles.

In general, let x denote a general state of the system. Let $x(t)$ denote the state of the system at time t.

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The mechanical state of the system. Suppose the system comes to equilibrium and evolves in time according to some classical mechanics.

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The probability distribution of states at equilibrium. Call this $P_{eq}(x)$. It could be a canonical distribution

$$P(x) = (const) \times \exp(-H(x)/k_B T)$$

or something more complicated or more simple, depending on the nature of the system and the way the equilibrium system is defined.

Dynamical variable. A dynamical variable is some function of the state of the system $A(x)$.

Examples:

- Velocity of particle i: $\mathbf{v}_i$
- Distance between particles i and j: $|\mathbf{r}_i - \mathbf{r_j}|$
- It could be any function of the mechanical variables that describe the state of the system.

Measurable quantities. In an idealized experiment, what we measure is the value of A at some time t. Thus we write this as $A(x(t))$.

Sometimes we write this more simply as $A(t)$.

We might measure $B(x(t'))$, sometimes written $B(t')$.

We might measure both, or additional measurables.

First type of experiment

Suppose we measure A at the initial time $t = 0$.

This is $A(x(0))$ or $A(0)$.

Let

$$\overline{A(0)} \equiv \text{the average of the result of several measurements of } A(0)$$

The theoretical quantity that this corresponds to this is

$$\langle A(0) \rangle \equiv \int dx\, P(x) A(x)$$

This is an equilibrium ensemble average of the type you studied when you learned about equilibrium statistical thermodynamics.

Fundamental postulate of equilibrium statistical mechanics. For this case, the postulate is

$$\overline{A(0)} = \langle A(0) \rangle \equiv \int dx\, P(x) A(x)$$

The measured value of a property is the ensemble average of that property. Here x, the dummy variable of integration, is the initial state of the system, i.e. the state at time 0.

We discussed the basis for this in the previous lecture. In fact, the quantity that is measured in reproducibly measured. Moreover, the probability distribution is highly peaked.

Another way of thinking about it is that an experiment is just like a theoretical calculation, with just a few small differences:

- a real experiment involves a finite number of runs,

  the theoretical calculation must average over an infinite number of initial states, so we use a probability distribution.

- in a real experiment, you must equilibrate the system well and reproducibly,

  in a theoretical calculation you must be sure you have the correct equilibrium probability distribution function.

- in a real experiment, there is statistical error, which is why you perform several runs and average the results

  in a theoretical calculation of an equilibrium ensemble average, there is no statistical error.

Second type of experiment. Suppose we measure A not at $t = 0$ but at some later time t.

We measure $A(x(t))$ or $A(t)$. For this case, the postulate is

$$\overline{A(t)} = \langle A(t) \rangle$$

How do we write the average on the right? It turns out that the way to express the answer depends on the nature of the dynamics. For the moment we don't want to commit ourselves, and a very general notation would be very confusing so we won't use one. For the moment, you probably have a clear idea of what the left side means. The right side is the theoretical analog in which we average $A(t)$ over its probability distribution which is determined in a complicated way by the probability distribution function of the $t = 0$ mechanical state.

A general characteristic of equilibrium averages.

$$\langle A(t) \rangle = \langle A(0) \rangle$$

or, in other words, $\langle A(t) \rangle$ is independent of t.

The meaning of this in terms of experiments is clear. If we set up an equilibrium system and measure a property, we will get the same result if we wait a certain period of time before making the measurement. The proof for any particular type of dynamics can be complicated.

Third type of experiment. Measure $A(t)$ and $B(t')$ from the same run and take their product. Then average this over runs. Then

$$\overline{A(t)B(t')} = \langle A(t)B(t') \rangle$$

The right side is the average of the product over the statistical distribution of initial states and over any statistical properties of the dynamics. This is an example of an equilibrium correlation function.

Some general properties of such averages for classical equilibrium situations.

A correlation function depends on the difference in the two time arguments.

$$\langle A(t)B(t') \rangle = \langle A(t+\tau)B(t'+\tau) \rangle$$

The meaning is similar to what we discussed. Only the interval between the two times is important, not the absolute values of each time.

We can define $C_{AB}(t)$, a function of one time variable, such that

$$\langle A(t)B(t') \rangle = C_{AB}(t-t')$$

Since $\langle A(t)B(t')\rangle = \langle B(t')A(t)\rangle$ for classical mechanics,

$$C_{AB}(t) = C_{BA}(-t)$$

If the time separation is very large,

$$\langle A(t)B(t')\rangle \to \langle A(t)\rangle\langle B(t')\rangle = \langle A(t)\rangle\langle B(0)\rangle \quad \text{as } |t - t'| \to \infty$$

We say that for large time intervals, $A(t)$ and $B(t')$ are statistically independent or uncorrelated.

Special case. Suppose $\langle A(0)\rangle = 0$ and $\langle B(0)\rangle = 0$. Then we have

$$\langle A(t)B(t')\rangle \to 0 \quad \text{as } |t - t'| \to \infty$$

$$C_{AB}(t) \to 0 \quad \text{as } |t| \to \infty$$

Lecture 2 9/24/09 continued in N4