Time-Dependent Statistical Mechanics 6. Averages of time dependent quantities in classical statistical mechanics

H.C.A.

October 1, 2009

We continue to focus on ensembles of systems that all have the same value of N and V. It will be convenient to have a single symbol to represent Q^N, P^N. Let's use Γ. Thus each value for Γ corresponds to a point in phase space and a possible mechanical state of the system of N molecules.

Lecture 4 10/1/09

1 Time dependence of phase points

Let's define $\gamma(t; \Gamma, t')$ to be the location in phase space at time t of a system that was at Γ at time t'. $\gamma(t; \Gamma, t')$ is in principle calculated by starting a system at Γ at time t' and integrating the equations of motion for the coordinates and momenta forward in time until time t.

If the Hamiltonian is independent of time, and $\gamma(t; \Gamma, t')$ is calculated, the result depends on $t - t'$ but for fixed $t - t'$ it does not depend on t'. Only the time interval and the starting point are relevant for solving the differential equations when the Hamiltonian is independent of time. Thus we have

$$\gamma(t; \Gamma, t') = \gamma(t - t'; \Gamma, 0)$$

***(slide)*

Phase space (for a mechanical system)

A high dimensional Cartesian space with one axis for each coordinate $Q_{i\alpha}$ and one for each momentum $P_{i\alpha}$ in the system.

Phase point

A point in phase space.

Specified by a set of values of all the coordinates and momenta: Q^N, P^N.

Corresponds to a possible instantaneous state of the system.

Let Γ be the generic symbol for (Q^N, P^N), a phase point.

Time dependence of phase points

Let $\gamma(t; \Gamma, t')$ to be the location in phase space at time t of a system that was at Γ at time t'.

If we choose (Γ, t') and keep them fixed, then

> $\gamma(t; \Gamma, t')$ as a function of t traces out a smooth curve in phase space

The special case of a time independent Hamiltonian

$\gamma(t; \Gamma, t')$ depends on $t - t'$. Thus we have

$$\gamma(t; \Gamma, t') = \gamma(t - t'; \Gamma, 0)$$

Liouville equation

Suppose we have a probability distribution in phase space $f(\Gamma, t)$.

The probability density satisfies the Liouville equation.

Special solution: If the probability distribution is the equilibrium canonical distribution time initially $f(\Gamma, t_0) = P_{eq}(\Gamma)$ and if the Hamiltonian has no time dependence, then the solution of the Liouville equation for all later times is

$$f(\Gamma, t) = P_{eq}(\Gamma) \quad \text{for all } t$$

(end of slide)

2 Dynamical variables

A *dynamical variable* is a mechanical quantity (as opposed to a statistical quantity like a distribution function) that is a function of Γ; i.e. a function of the mechanical state of the system. For example, the kinetic energy $T(\Gamma)$ is a dynamical variable. So is the potential energy $V(\Gamma)$. And the total energy $H(\Gamma)$. Other examples include things like the x component of momentum of particle 13, the y coordinate of molecule 3900, the polar angle θ for rigid rod number 6000001. A more complicated example is the number of molecules whose center of mass is within 5 Angstroms of a specific point in space.

Let's use $A(\Gamma)$, $B(\Gamma)$, ..., as the symbols for generic dynamical variables.

For example, let's consider a system of point particles. Consider the kinetic energy of the system. This is a physical quantity. The formula for evaluating it when the system is in state $\Gamma = \mathbf{r}^N \mathbf{p}^N$ is

$$T(\Gamma) = T(\mathbf{r}^N, \mathbf{p}^N) = \sum_{i=1}^{N} \frac{\mathbf{p}_i \cdot \mathbf{p}_i}{2m}$$

Now suppose we evaluate the physical quantity, the kinetic energy, at time t for a system that was in state Γ at time t_0. Then the appropriate thing to calculate is

$$T\left(\gamma(t; \Gamma, t_0)\right)$$

Let's write this as $T(t, \Gamma)$.

$$T(t, \Gamma) \equiv T\left(\gamma(t; \Gamma, t_0)\right)$$

This is an example of a time dependent dynamical variable. Its physical meaning, to repeat, is the value of the kinetic energy at time t for a system that was in state Γ at time t_0.

In general, if A denotes a physical quantity and $A(\Gamma)$ is the function associated with it, then $A(t, \Gamma)$ denotes the corresponding time dependent dynamic variable. $A(\Gamma)$ is the value of the physical quantity A when the state is Γ, and $A(t, \Gamma)$ is the value of the physical quantity A at time t when the state of the system was Γ at time t_0.

Note that

$$A(t_0, \Gamma) = A(\Gamma)$$

To define time dependent dynamical variables in a consistent way, we need to decide on a value of t_0 and use it consistently. We might use $t_0 = 0$, or some other time that is appropriate. Usually it is some time at the start of the experiment and after the system has been prepared.

(slide)

Dynamical variables

A *dynamical variable* is a mechanical quantity (as opposed to a statistical quantity like a distribution function) that is a function of Γ; i.e. a function of the mechanical state of the system.

It is a mechanical property of the system that depends on what mechanical state the system is in.

For example, the kinetic energy $T(\Gamma)$ is a dynamical variable.

So is the potential energy $V(\Gamma)$.

And the total energy $H(\Gamma)$.

Other examples include things like:

- the x component of momentum of particle 13,
- the y coordinate of molecule 3900,
- the polar angle θ for rigid rod number 6000001
- the number of molecules whose center of mass is within 5 Angstroms of a specific point in space.

Let's use $A(\Gamma)$, $B(\Gamma)$, $\ldots$, as the symbols for generic dynamical variables. They are values of the dynamical variables of a system when it is in state Γ.

Suppose we want to evaluate the property A at time t for a system that was in state Γ at time t_0. Then the appropriate thing to calculate is

$$A\left(\gamma(t; \Gamma, t_0)\right)$$

Let's write this as

$$A(t, \Gamma) \equiv A\left(\gamma(t; \Gamma, t_0)\right)$$

Note that

$$A(t_0, \Gamma) = A(\Gamma)$$

(end of slide)

3 An idealized experiment - measurement of a dynamical variable at a specific time

Let's consider an idealized experiment that correspond to the simple measurement of some dynamical variable at a specific time.

3.1 General case

Consider the following idealized experiment.

- Prepare a system in a specific way and set the time to t_0.
- Let the system evolve to time t.
- Measure the property A at time t.

Then repeat this procedure many times and average the results together. Let the result be called $A(t)_{exp}$.

If, in any one run, the system were in state Γ at time t_0, then the result of that run would be $A(t, \Gamma)$. Suppose that for the ensemble that is appropriate for the experiment, the distribution of initial states is $P(\Gamma)$. (We are back to using P rather than f for probability distributions.) Then the ensemble average that corresponds to the measurement is

$$A(t)_{exp} = \langle A(t, \Gamma) \rangle = \int d\Gamma \, A(t, \Gamma) P(\Gamma)$$

To reinforce the fact that the P that appears here is the initial distribution function we could write

$$A(t)_{exp} = \int d\Gamma \, A(t, \Gamma) P(\Gamma, t_0)$$

But there is an alternative form for the answer, which is the following.

$$A(t)_{exp} = \int d\Gamma' \, A(\Gamma') P(\Gamma', t)$$

Here, we are acknowledging that the state at time t, which is here given the name Γ', is a random variable that determines the measured A. We could just as well average over the distribution of that variable. The $P(\Gamma', t)$ that appears here is the solution of the Liouville equation that corresponds to the initial distribution $P(\Gamma, t_0)$. As long as we recognize that Γ' is a dummy integration variable, we can write

$$A(t)_{exp} = \int d\Gamma \, A(\Gamma) P(\Gamma, t)$$

(slide)

An idealized experiment - measurement of a dynamical variable at a specific time. Let's consider an idealized experiment that correspond to the simple measurement of some dynamical variable at a specific time.

- Prepare a system in a specific way and set the time to t_0.
- Measure the property A at time t.

Then repeat this procedure many times and average the results together.

Call the result $\overline{A(t)}_{exp}$.

(end of slide)

(slide)

Theoretical description of the experiment

If the system were in state Γ at time t_0, then the value of the measurement would be $A(t, \Gamma)$.

Let $P(\Gamma, t_0)$ = the probability distribution of mechanical states for the experiment at time t_0.

The theoretical average that corresponds to the average measurement is

$$\overline{A(t)}_{exp} = \langle A(t, \Gamma) \rangle = \int d\Gamma\, A(t, \Gamma) P(\Gamma, t_0)$$

Alternative form for the answer

$$\overline{A(t)}_{exp} = \int d\Gamma\, A(\Gamma) P(\Gamma, t)$$

The $P(\Gamma, t)$ that appears here is the solution of the Liouville equation that corresponds to the initial distribution $P(\Gamma, t_0)$.

Special case of an equilibrium system

Suppose the experiment of interest is performed on

- an equilibrium system
- with a time independent Hamiltonian
- that stays in equilibrium during the experiment.

The appropriate initial distribution is the canonical distribution. In this case, we have

$$P(\Gamma, t) = P(\Gamma, t_0) = P_{eq}(\Gamma)$$

Putting this into the second expression for $\langle A(t) \rangle$ gives

$$A(t)_{exp} = \int d\Gamma\, A(\Gamma) P_{eq}(\Gamma)$$

which is clearly a constant, independent of time, as expected.

(end of slide)

3.2 Special case of an equilibrium system

Suppose, however, that the experiment of interest is performed on an equilibrium system that stays in equilibrium during the experiment. That is, the system that is prepared is in an equilibrium state and its Hamiltonian is independent of time. Then we know that the result of the experiment will not depend on how long we wait before doing the measurement.

The theory should predict the same result. And it does, as we can now show.

The theory would say that we should use a canonical ensemble. If we use a canonical distribution initially and have a time independent Hamiltonian, we have $P(\Gamma, t) = P(\Gamma, t_0)$. Putting this into the second expression for $\langle A(t) \rangle$ gives

$$A(t)_{exp} = \int d\Gamma\, A(\Gamma) P(\Gamma, t_0)$$

which is clearly a constant, independent of time.

3.3 Comments

Many types of things that we want to calculate are of this type. In fact, much of equilibrium time-independent statistical mechanics is concerned with averages of this type.

4 Another idealized experiment - measurement of a time correlation function

The next idealized experiment does not correspond directly to something that one would go into the laboratory to do, but it is nevertheless closely related to real experiments. The reason for discussing it, however, is that theoretical analysis of such an experiment leads very directly to the idea of a time correlation function.

4.1 General case

Consider the following idealized experiment.

- Prepare a system in a specific way and set the time to t_0.
- Let the system evolve to time t_1.
- Measure the property A at time t_1.
- Let the system evolve to time t_2.
- Measure the property B at time t_2.
- Multiply the two measured numbers together.

Then repeat this procedure many times and average the results together. Let the result be called $(A(t_1)B(t_2))_{exp}$.

Let's use the fundamental postulate to calculate a theoretical value of this. If the initial state at time t_0 of the system were Γ, then the quantity measured would be equal to $A(t_1,\Gamma)B(t_2,\Gamma)$. The ensemble average of this is

$$(A(t_1)B(t_2))_{exp} = \langle A(t_1,\Gamma)B(t_2,\Gamma)\rangle = \int d\Gamma\, P(\Gamma)A(t_1,\Gamma)B(t_2,\Gamma)$$

There is an alternative form of this, as well. Let's regard the state of the system at time t_1, the time of the A measurement, as the fundamental random variable, and let's call it Γ'. In terms of that variable, the quantity measured in a run is $A(\Gamma')B(\gamma(t_2;\Gamma',t_1))$ and its ensemble average is

$$\int d\Gamma'\, P(\Gamma',t_1)A(\Gamma')B(\gamma(t_2;\Gamma',t_1))$$

4.2 Special case of a canonical ensemble

Suppose that the experiment of interest is performed on an equilibrium system. That is, the system that is prepared is in an equilibrium state and its Hamiltonian is independent of time.

Then we can simplify the latest expression by noting two things.

- $B(\gamma(t_2;\Gamma',t_1)) = B(\gamma(t_2-t_1;\Gamma',0))$. This is the case if the Hamiltonian is independent of time.
- $P(\Gamma',t_1) = P(\Gamma',t_0)$. The solution of the Liouville equation for this situation is independent of time.

It follows that

$$(A(t_1)B(t_2))_{exp} = \int d\Gamma'\, P(\Gamma',t_0)A(\Gamma')B(\gamma(t_2-t_1;\Gamma',0))$$

This makes it clear that this quantity depends only on the time interval between the two measurements $t_2 - t_1$ and not on the time at which the first measurement is made. *(slide)*

Another idealized experiment - measurement of a *equilibrium* time correlation function

- Prepare a system *in equilibrium* and set the time to t_0.
- Measure the property A at time t_1.
- Measure the property B at time t_2.
- Multiply the two measured numbers together.

Then repeat this procedure many times and average the results together. Let the result be called $\overline{A(t_1)B(t_2))}_{exp}$.

Theoretical description of the experiment. If the initial state at time t_0 of the system were Γ, then the quantity measured would be equal to $A(t_1, \Gamma)B(t_2, \Gamma)$.

The average of this over an equilibrium distribution of initial states is

$$\overline{A(t_1)B(t_2))}_{exp} = \langle A(t_1, \Gamma)B(t_2, \Gamma)\rangle = \int d\Gamma\, P(\Gamma)A(t_1, \Gamma)B(t_2, \Gamma)$$

Alternative form for the answer.

$$\overline{A(t_1)B(t_2))}_{exp} = \int d\Gamma\, P(\Gamma, t_1)A(\Gamma)B(\gamma(t_2; \Gamma, t_1))$$

- $B(\gamma(t_2; \Gamma, t_1)) = B(\gamma(t_2 - t_1; \Gamma, 0)$

  the Hamiltonian is time-independent
- $P(\Gamma, t_1) = P(\Gamma, t_0) = P_{eq}(\Gamma)$

  the solution of the Liouville equation for this situation is independent of time.

Hence

$$\overline{A(t_1)B(t_2))}_{exp} = \int d\Gamma\, P_{eq}(\Gamma)A(\Gamma)B(\gamma(t_2 - t_1; \Gamma, 0))$$

This depends only on the time interval $t_2 - t_1$ and not on the individual times.

(end of slide)

5 Equilibrium time correlation functions

An equilibrium average of the form

$$C_{AB}(t_1 - t_2) = \langle A(t_1, \Gamma) B(t_2, \Gamma) \rangle_{eq} = \int d\Gamma \, A(t_1, \Gamma) B(t_2, \Gamma) P_{eq}(\Gamma)$$

is an example of an *equilibrium time correlation function*, and quantities of this type are very important for the concerns of this course. Sometimes we are interested in the case in which the two physical quantities are the same.

$$C_{AA}(t_1 - t_2) = \langle A(t_1, \Gamma) A(t_2, \Gamma) \rangle_{eq} = \int d\Gamma \, A(t_1, \Gamma) A(t_2, \Gamma) P_{eq}(\Gamma)$$

This is an example of an *equilibrium time autocorrelation function.*

We talked about the autocorrelation function of the velocity of a particle in connection with self-diffusion. Other correlation functions and autocorrelation functions are related to other physical properties of interest. There are two types of things that we will be concerned with.

- The formal properties of correlation functions, their symmetry properties, and relationships among correlation functions.
- The relationship between correlation functions and experimental observables.

(slide)

Equilibrium time correlation functions

An equilibrium average of the form

$$C_{AB}(t_1 - t_2) = \langle A(t_1, \Gamma)B(t_2, \Gamma)\rangle_{eq} = \int d\Gamma\, A(t_1, \Gamma)B(t_2, \Gamma)P_{eq}(\Gamma)$$

is an example of an *equilibrium time correlation function.* Sometimes we are interested in the case in which the two physical quantities are the same.

$$C_{AA}(t_1 - t_2) = \langle A(t_1, \Gamma)A(t_2, \Gamma)\rangle_{eq} = \int d\Gamma\, A(t_1, \Gamma)A(t_2, \Gamma)P_{eq}(\Gamma)$$

This is an example of an *equilibrium time autocorrelation function.*

There are two types of things that we will be concerned with.

- The formal properties of correlation functions, their symmetry properties, and relationships among correlation functions.
- The relationship between correlation functions and experimental observables.

(end of slide)

Lecture 4 10/1/09 continued in N8