IP326. Lecture 6. Tuesday, Jan. 22, 2019

● <u>Equilibrium Time Correlation Functions</u>

In Lecture 2, we introduced a few of the kinds of experiments that we were interested in interpreting in statistical mechanical terms. One of these, we said, is carried out according to the following recipe:

– Prepare the system in some specific way.
– Allow the system to equilibrate.
– When the system has equilibrated, set the time to 0.
– Allow the system to evolve for a time t and measure A at this time; denote its value is $A(t)$.
– Allow the system to evolve to time t' and measure another property, say B, at this time, denoting it $B(t')$.
– Multiply the two measured values together.
– Repeat these steps a number of times and average the data. The result is $\overline{A(t)B(t')}_{\text{exp}}$.

We've asserted that the theoretical analogue of this result is the equilibrium time correlation function of A and B. That is,

$$\begin{aligned}\overline{A(t)B(t')}_{\text{exp}} &= \langle A(t)B(t')\rangle \\ &= \int d\Gamma A(t;\Gamma)B(t';\Gamma)P(\Gamma)\end{aligned}$$

or equivalently, using f_0 to denote the equilibrium phase space density distribution,

$$\langle A(t)B(t')\rangle = \int d\Gamma f_0(\Gamma)A(t;\Gamma)B(t';\Gamma)\,. \tag{1}$$

The functional form of f_0 will usually be known from equilibrium statistical mechanics; it is determined by the nature of the external constraints on the system (such as constant T, V, N.)

Although it hasn't been said so explicitly, A and B in Eq. (1) need not be real, and if they happen to be complex (as they often are – we'll consider specific examples later), their time correlation functions have to be defined more generally. This more general definition is based on a mathematical object in quantum mechanics called the scalar product, and it represents the dynamical variable $A^*(t)$ as a "bra" vector $\langle A(t)|$, and the variable $B(t')$ as a "ket" vector $|B(t')\rangle$. So from now on, we'll write the equilibrium ensemble average of these two variables as $\langle A(t)\,|\,B(t')\rangle$, and understand it to mean

$$\langle A(t)\,|\,B(t')\rangle \equiv \int d\Gamma f_0(\Gamma)A^*(t;\Gamma)B(t';\Gamma) \tag{2}$$

where the asterisk on A denotes complex conjugation. By defining the TCF in this way, we ensure that when $B = A$ and $t' = t$, the TCF is real, just as the corresponding experimental quantity is. As we'll see, the above bra-ket notation makes it easy to derive various results for TCFs by manipulations of the kind common in quantum mechanics.

● Various Operator Identities

1. Because iL is real, it immediately follows that

$$(iL)^* = iL$$

and

$$\left(e^{\pm itL}\right)^* = e^{\pm itL}$$

Now consider the average $\langle A \,|\, LB \rangle$, where A and B are both measured at the initial time $t = 0$. By definition

$$\langle A \,|\, LB \rangle = \int d\Gamma f_0(\Gamma) A^*(\Gamma) L B(\Gamma) \tag{3}$$

Since $iL = \dot{\Gamma} \cdot \partial / \partial \Gamma$, it follows that $L = -i\dot{\Gamma} \cdot \partial / \partial \Gamma$, and so

$$\langle A \,|\, LB \rangle = -i \int d\Gamma f_0(\Gamma) A^*(\Gamma) \dot{\Gamma} \cdot \frac{\partial}{\partial \Gamma} B(\Gamma)$$

If we integrate this expression by parts, and discard the surface terms, we get

$$\langle A \,|\, LB \rangle = i \int d\Gamma B(\Gamma) \frac{\partial}{\partial \Gamma} \cdot \dot{\Gamma} f_0(\Gamma) A^*(\Gamma)$$

$$= i \int d\Gamma B(\Gamma) \left\{ f_0(\Gamma) A^*(\Gamma) \frac{\partial}{\partial \Gamma} \cdot \dot{\Gamma} + A^*(\Gamma) \dot{\Gamma} \cdot \frac{\partial}{\partial \Gamma} f_0(\Gamma) + f_0(\Gamma) \dot{\Gamma} \cdot \frac{\partial}{\partial \Gamma} A^*(\Gamma) \right\}$$

$$= i \int d\Gamma B(\Gamma) \left\{ 0 + 0 + f_0(\Gamma) \dot{\Gamma} \cdot \frac{\partial}{\partial \Gamma} A^*(\Gamma) \right\}$$

$$= -\int d\Gamma B(\Gamma) f_0(\Gamma) L A^*(\Gamma) \tag{4}$$

Now because iL is real, L is purely imaginary, which means $L^* = -L$, so we can write Eq. (4) as

$$\langle A \mid LB \rangle = \int d\Gamma f_0(\Gamma)[LA(\Gamma)]^* B(\Gamma)$$

$$= \langle LA \mid B \rangle \tag{5}$$

So L acts like a Hermitian operator: it can be interchanged between the bra and ket in much the same way as the corresponding operator in quantum mechanics is moved around in the scalar product.

At the same time, because $d\Gamma$ and $f_0(\Gamma)$ are both real, we can also write Eq. (4) as

$$\langle A \mid LB \rangle = \left(\int d\Gamma f_0(\Gamma) B^*(\Gamma) LA(\Gamma) \right)^*$$

$$= \langle B \mid LA \rangle^*$$

Therefore,

$$\langle A \mid LB \rangle^* = \langle B \mid LA \rangle \tag{6}$$

which expresses what happens when a time correlation function is complex conjugated.

2. Similarly, consider the average $\langle A | B(t) \rangle$. Written out in full this is

$$\langle A | B(t) \rangle = \int d\Gamma f_0(\Gamma) A^*(\Gamma) e^{itL} B(\Gamma)$$

Expanding out the exponential in series form, we get

$$\langle A | B(t) \rangle = \sum_{n=0}^{\infty} \frac{(it)^n}{n!} \int d\Gamma f_0(\Gamma) A^*(\Gamma) L^n B(\Gamma)$$

$$= \sum_{n=0}^{\infty} \frac{(it)^n}{n!} \int d\Gamma f_0(\Gamma) A^*(\Gamma) L L^{n-1} B(\Gamma)$$

$$= \sum_{n=0}^{\infty} \frac{(it)^n}{n!} \langle A | L L^{n-1} B \rangle \tag{7}$$

Using the Hermitian property of L, we can write Eq. (7) as

$$\langle A | B(t) \rangle = \sum_{n=0}^{\infty} \frac{(it)^n}{n!} \langle LA | L^{n-1} B \rangle$$

and then as

$$\langle A | B(t) \rangle = \sum_{n=0}^{\infty} \frac{(it)^n}{n!} \langle L^2 A | L^{n-2} B \rangle$$

until eventually, after $n-2$ additional repetitions of the above steps, we're left with

$$\langle A | B(t) \rangle = \sum_{n=0}^{\infty} \frac{(it)^n}{n!} \langle L^n A | B \rangle$$

which, when re-expressed as a phase space integral, translates to

$$\langle A | B(t) \rangle = \sum_{n=0}^{\infty} \frac{(it)^n}{n!} \int d\Gamma f_0(\Gamma) (L^n A(\Gamma))^* B(\Gamma) \tag{8}$$

Recall that *L* is purely imaginary, so $(L^n)^* = (-1)^n L^n$. When this result is substituted into Eq. (8), we find that

$$\langle A | B(t) \rangle = \int d\Gamma f_0(\Gamma) \left(e^{-itL} A^*(\Gamma) \right) B(\Gamma)$$

$$= \int d\Gamma f_0(\Gamma) \left(e^{-itL} A(\Gamma) \right)^* B(\Gamma)$$

Reverting to bra-ket notation again, we finally arrive at

$$\langle A | B(t) \rangle = \langle A | e^{itL} B \rangle = \langle e^{-itL} A | B \rangle \tag{9a}$$

or, alternatively,

$$\langle A | B(t) \rangle = \langle A(-t) | B \rangle \tag{9b}$$

3. The above identity has some interesting implications for a special time correlation function of the dynamical variable *A* called its *norm*, and defined as $\langle |A(t)|^2 \rangle$. What we mean by this definition is

$$\langle |A(t)|^2 \rangle = \langle A(t) | A(t) \rangle$$

$$= \int d\Gamma f_0(\Gamma) A^*(t) A(t)$$

$$= \int d\Gamma f_0(\Gamma)(e^{itL}A(\Gamma))^*(e^{itL}A(\Gamma))$$

$$= \langle e^{itL}A | e^{itL}A \rangle \tag{10}$$

From the identity in Eq. (9a), we can rewrite Eq. (10) as

$$\langle |A(t)|^2 \rangle = \langle e^{-itL}e^{itL}A | A \rangle$$

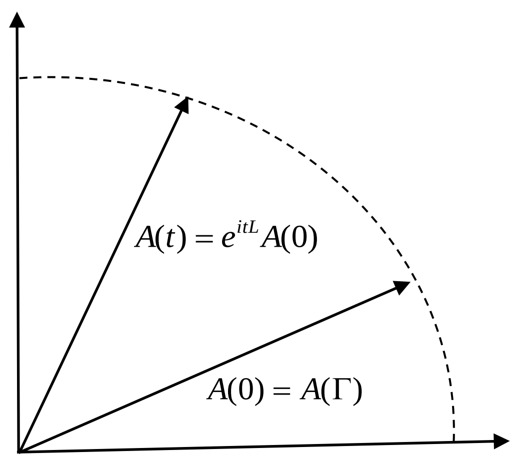
$$= \langle A | A \rangle$$

$$= \int d\Gamma f_0(\Gamma) A^*(\Gamma) A(\Gamma)$$

That is,

$$\langle |A(t)|^2 \rangle = \langle |A|^2 \rangle \tag{11}$$

What this relation says is that the ensemble average of the magnitude of the square of A at time t – in other words, its norm at time t – is unchanged from its norm at time 0. Since it is the action of the operator e^{itL} that takes A from its initial value $A(0) \equiv A$ to its final value $A(t)$ at time t, we say that e^{itL} is *unitary* or *norm preserving*. So e^{itL} has the character of a rotation operator, in that it leaves a dynamical variable's "magnitude" unchanged but changes its "orientation". This is illustrated in the figure below:



The mean square length of the vectors at 0 and t are, respectively, $\langle |A|^2 \rangle$ and $\langle |A(t)|^2 \rangle$.

• Some Identities Involving Time Correlation Functions

As we've indicated earlier, TCFs are connected to several different measurable properties of equilibrium systems, but before making the nature of these connections precise, we'll first derive a number of exact mathematical relations that *all* TCFs satisfy by virtue of the properties of the Liouville operator.

1. Stationarity

Consider the following TCF:

$$C_{AB}(t_1, t_2) \equiv \langle A(t_1) | B(t_2) \rangle = \int d\Gamma f_0(\Gamma)(e^{it_1 L} A(\Gamma))^* e^{it_2 L} B(\Gamma)) \tag{12}$$

This can also be written as

$$C_{AB}(t_1, t_2) = \int d\Gamma f_0(\Gamma)(e^{it_2 L} B(\Gamma)) e^{it_1 L} A^*(\Gamma)$$

From the "adjoint" property of e^{itL} (see Eq. (9a)), we have

$$C_{AB}(t_1, t_2) = \int d\Gamma f_0(\Gamma)(e^{-it_1 L} e^{it_2 L} B(\Gamma)) A^*(\Gamma)$$

$$= \int d\Gamma f_0(\Gamma) A^*(\Gamma)(e^{-it_1 L} e^{it_2 L} B(\Gamma))$$

$$= \int d\Gamma f_0(\Gamma) A^*(\Gamma)(e^{i(t_2 - t_1)L} B(\Gamma))$$

$$= \langle A | B(t_2 - t_1) \rangle$$

$$= C_{AB}(t_2 - t_1)$$

This relation establishes mathematically what we'd argued earlier on physical grounds: that for systems in equilibrium, the TCF for a property defined by values of the dynamical variables *A* and *B* at two different times depends only on the *difference* between the two times, and not on their absolute values. So TCFs are stationary. Which means that without any loss of generality we can set t_1 to 0 and t_2 to *t*.

2. Interchange of Variables

Consider the TCF $\langle A(t_1) | B(t_2) \rangle$ again. From the stationarity of TCFs, we can write this immediately as $C_{AB}(t) = \langle A | B(t) \rangle$. Written out in full, the TCF is defined as

$$C_{AB}(t) = \int d\Gamma f_0(\Gamma) A^*(\Gamma) e^{itL} B(\Gamma)$$

$$= \left(\int d\Gamma f_0(\Gamma) A(\Gamma) e^{itL} B^*(\Gamma) \right)^*$$

$$= \left(\int d\Gamma f_0(\Gamma) (e^{-itL} A(\Gamma)) B^*(\Gamma) \right)^*$$

$$= \left(\int d\Gamma f_0(\Gamma) B^*(\Gamma) e^{-itL} A(\Gamma) \right)^*$$

$$= \langle B | A(-t) \rangle^*$$

$$= C_{BA}^*(-t)$$

So a TCF evaluated at the time t is equivalent to the complex conjugate of the TCF evaluated at the reversed time and at reversed order of the dynamical variables. If A and B happen to be real, then the above identity reduces to

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

3. <u>Derivatives of Time Correlation Functions</u>

Consider the TCF $C_{AB}(t)$, defined as

$$C_{AB}(t) = \int d\Gamma f_0(\Gamma) A^*(\Gamma) e^{itL} B(\Gamma)$$

Take its derivative with respect to time:

$$\frac{\partial C_{AB}(t)}{\partial t} \equiv \dot{C}_{AB}(t) = \int d\Gamma f_0(\Gamma) A^*(\Gamma) iLe^{itL} B(\Gamma)$$

In bra-ket notation this is

$$\dot{C}_{AB}(t) = \langle A | iLB(t) \rangle$$

$$= \left\langle A \middle| \frac{\partial B(t)}{\partial t} \right\rangle = \langle A | \dot{B}(t) \rangle$$

That is, $\dot{C}_{AB}(t) = C_{A\dot{B}}(t)$.

4. The special case of an autocorrelation function

Suppose $A = B$ and A is real. Then from the results derived earlier

$$C_{AA}(t) = C_{AA}(-t)$$

This means that autocorrelation functions are *even* functions of time (which can be an important consideration when constructing models of this quantity.)

Similarly, from the identity above,

$$\begin{aligned} \dot{C}_{AA}(t) &= \frac{\partial}{\partial t} C_{AA}(-t) \\ &= \frac{\partial}{\partial(-t)} C_{AA}(-t) \frac{d(-t)}{dt} \\ &= -\dot{C}_{AA}(-t) \end{aligned}$$

The dot here denotes the time derivative with respect to the argument of the function, which in this case is $-t$. So what the above relation implies is that the time derivative of an autocorrelation function is an *odd* function of the time.

Furthermore, suppose we evaluate this function at $t = 0$. The result is

$$\dot{C}_{AA}(0) = -\dot{C}_{AA}(0)$$

which can only be true if $\dot{C}_{AA}(0)$ is itself 0.