

Time-Dependent Statistical Mechanics

9. Linear response theory in classical statistical mechanics

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1 Introduction

We now want to apply linear response theory in a very specific way to problems in equilibrium statistical mechanics. We imagine that we have a system that is in thermodynamic equilibrium at a specific temperature. We assume that it can be described by a canonical ensemble, in the sense that the measured values of properties are equal to the appropriate averages over a canonical distribution function.

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The Hamiltonian of the system will be called $H_0(\Gamma)$. It has no explicit time dependence. The system can come to equilibrium under the influence of this Hamiltonian, and the corresponding equilibrium distribution function is

$$P_{eq}(\Gamma) = (const.) \exp(-H_0(\Gamma)/k_B T)$$

If we prepare the system at equilibrium at time t_0 and measure a property A that corresponds to a function of Γ , namely $A(\Gamma)$ at time t , the corresponding ensemble average is

$$\langle A(t) \rangle_{eq} = \int d\Gamma A(t, \Gamma) P_0(\Gamma)$$

We have shown that this is in fact independent of t . Let's just call it $\langle A \rangle_{eq}$.

Suppose now we apply an additional time dependent field to the system. It could be something physical, like an electric field, or something very hypothetical, like a force that acts only on one type of molecule in the system. As a result of this external field, there is an additional term in the Hamiltonian. Let's assume it is of the form

$$H(\Gamma, t) = H_0(\Gamma) - g(t)B(\Gamma)$$

The field interacts with the property B of the system. (B might be the same as A or it might be different.) $g(t)$ is a time dependent amplitude that we can adjust. The minus sign is there for conventional reasons.

To see the meaning of this, suppose $g(t)$ were positive and were held constant for a long time, then there would be a new time-independent term in the Hamiltonian that would lower the energy of states that had positive values of B and raise the energy of states that have negative values of B . In general, such a term would, at any particular temperature, bias the system to be in states with larger values of B than it would have if there were no field applied. Similarly, negative values of f leads to a bias for smaller values of B .

As a result of having this field applied, the system is no longer at equilibrium. It follows that the measured value of A at time t is no longer $\langle A \rangle_{eq}$. The measured value of A at time t is given by the following statistical average

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

where $P(\Gamma, t)$ is the distribution function at time t . $P(\Gamma, t)$ is influenced by the time dependent field and is not in general equal to $P_{eq}(\Gamma)$. For times t before the field was turned on, $P(\Gamma, t) = P_{eq}(\Gamma)$.

We now ask the question: how does $A(t)_{exp} - \langle A \rangle_{eq}$ depend on $g(t)$ when $g(t)$ is very weak? On the basis of very general arguments, we might expect the following:

- The response is linear. Any type of perturbation theory for such a response will give a linear term. As long as the perturbation is small enough, the linear term should be a good approximation.
- The response is causal. The effect of $g(t)$ takes place only after, not before, it is turned up from zero.

- It is stationary. If we simply wait some time before applying the field to the equilibrium system, this should simply delay the response without changing its overall time dependence.
- It is stable. If the weak field is turned off, the system should return to equilibrium. If the field was very weak, it should not have pumped any appreciable energy into the system, so the temperature should remain unchanged.

In other words, the response in this case should have all the characteristics in our previous discussion of linear response.

Thus we expect that

$$A(t)_{calc} - \langle A \rangle_{eq} = \int_{-\infty}^t dt' \chi(t-t')g(t')$$

The response function χ that appears here should probably be denoted $\chi_{AB}(t)$, because it gives the response of A to a field that couples to B . Let's leave out the subscripts for simplicity. (We'll use them again if we need them to distinguish among various different response functions in the same problem.)

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Linear response experiment on a classical mechanical system

Part I. The system at equilibrium before we disturb it.

The Hamiltonian of the system when it is isolated is $H_0(\Gamma)$.

$$P_{eq}(\Gamma) = (const.) \exp(-H_0(\Gamma)/k_B T)$$

Prepare the system at equilibrium at time t_0 and measure a dynamical variable A at time t .

The corresponding ensemble average is

$$\langle A(t) \rangle_{eq} = \int d\Gamma A(t, \Gamma) P_{eq}(\Gamma)$$

We have shown that this is in fact independent of t . Let's just call it $\langle A \rangle_{eq}$.

Part II. Apply a time dependent field to the system for times greater than t_0 .

The Hamiltonian becomes time dependent

$$H(\Gamma, t) = H_0(\Gamma) - g(t)B(\Gamma)$$

The field interacts with the property B of the system. (B might be the same as A or it might be different.)

$g(t)$ is a time dependent amplitude that we can control.

The minus sign is there for conventional reasons.

Measure A as a function of t .

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

where $P(\Gamma, t)$ is the distribution function at time t . $P(\Gamma, t)$ is influenced by the time dependent field and is not in general equal to $P_{eq}(\Gamma)$. For times t before the field was turned on, $P(\Gamma, t) = P_{eq}(\Gamma)$.

Question: How does $A(t)_{exp} - \langle A \rangle_{eq}$ depend on $g(t)$ when $g(t)$ is very weak?

On the basis of very general arguments, we might expect the following:

The response is linear, causal, stationary, and stable.

In other words, the response in this case should have all the characteristics in our previous discussion of linear response.

Thus we expect that

$$A(t)_{exp} - \langle A \rangle_{eq} = \int_{-\infty}^t dt' \chi(t-t')g(t')$$

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2 Classical result for the response function

2.1 The time derivative of a dynamical variable

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A dynamical variable is a function of Γ . E.g. $A(\Gamma)$ or $A(Q^N, P^N)$. It gives the value of some property A when the system is in state Γ .

Time dependence of a dynamic variable in an isolated system. Suppose the system is isolated and the Hamiltonian is just $H(\Gamma)$. Suppose the system is at a specific Γ . How rapidly is A changing with time?

By the chain rule

$$\frac{d}{dt}A(Q^N, P^N) = \sum_{i\alpha} \left(\frac{\partial A}{\partial Q_{i\alpha}} \dot{Q}_{i\alpha} + \frac{\partial A}{\partial P_{i\alpha}} \dot{P}_{i\alpha} \right) = \sum_{i\alpha} \left(\frac{\partial A}{\partial Q_{i\alpha}} \frac{\partial H}{\partial P_{i\alpha}} - \frac{\partial A}{\partial P_{i\alpha}} \frac{\partial H}{\partial Q_{i\alpha}} \right)$$

It is understood that all the things on the right are to be evaluated at the same point in phase space as the left hand side is to be evaluated.

Thus the time derivative of a dynamical variables in an isolated system is also a dynamical variable.

Write this as

$$\dot{A}(Q^N, P^N) = \sum_{i\alpha} \left(\frac{\partial A}{\partial Q_{i\alpha}} \frac{\partial H}{\partial P_{i\alpha}} - \frac{\partial A}{\partial P_{i\alpha}} \frac{\partial H}{\partial Q_{i\alpha}} \right)$$

This formula holds for any dynamical variable A .

2.2 Calculation of the response function

The response function χ is a property of the equilibrium system and is independent of $g(t)$, if the response is really linear. Can we obtain a microscopic interpretation of χ ?

The answer is: “Of course, yes.” Here we shall do it under the assumption that the system is classical.¹

Since there is a single χ function, we can calculate it in a variety of ways and we should in principle get the same answer. Let’s take one of the most straightforward ways.

To obtain $\chi(t)$, consider the special case that $g(t) = g_0\delta(t)$. Then if we calculate $A(t)_{calc} - \langle A \rangle_{eq}$ and then divide by g_0 , we should get $\chi(t)$ directly.

¹In a homework set, you dealt with a similar problem in the case of the dynamics being Brownian motion. Later in the course we will consider the case of the system being quantum mechanical.

Solution of the Liouville equation

For negative times, the system was in equilibrium.

For $t < 0$, $P(\gamma, t) = P_{eq}(\Gamma)$. Then, consider the Liouville equation to get the distribution function at later times.

(Once again, we replace P by f to avoid confusion with momenta.)

$$\begin{aligned} & \frac{\partial f(Q^N, P^N)}{\partial t} \\ &= \sum_{i\alpha} \left(\frac{\partial H(t)}{\partial Q_{i\alpha}} \frac{\partial f(t)}{\partial P_{i\alpha}} - \frac{\partial H(t)}{\partial P_{i\alpha}} \frac{\partial f(t)}{\partial Q_{i\alpha}} \right) \\ &= \sum_{i\alpha} \left(\frac{\partial H_0}{\partial Q_{i\alpha}} \frac{\partial f(t)}{\partial P_{i\alpha}} - \frac{\partial H_0}{\partial P_{i\alpha}} \frac{\partial f(t)}{\partial Q_{i\alpha}} \right) - g_0 \delta(t) \sum_{i\alpha} \left(\frac{\partial B}{\partial Q_{i\alpha}} \frac{\partial f(t)}{\partial P_{i\alpha}} - \frac{\partial B}{\partial P_{i\alpha}} \frac{\partial f(t)}{\partial Q_{i\alpha}} \right) \end{aligned}$$

(This gives the time derivative of the distribution function for at each point in phase space. Note that everything on the right should be evaluated at the same point Q^N, P^N as the arguments on the left.)

We want to evaluate the second term on the right.

Precisely at the time 0, the value of $f(0)$ is what it was for slightly negative values of time, namely f_{eq} , which is of the form

$$f_{eq}(\Gamma) = (\text{const.}) \exp(-H_0(\Gamma)/k_B T)$$

Thus, at $t = 0$ we have

$$\begin{aligned} \frac{\partial f}{\partial P_{i\alpha}} &= -\frac{1}{k_B T} f_{eq}(\Gamma) \frac{\partial H_0}{\partial P_{i\alpha}} \\ \frac{\partial f}{\partial Q_{i\alpha}} &= -\frac{1}{k_B T} f_{eq}(\Gamma) \frac{\partial H_0}{\partial Q_{i\alpha}} \end{aligned}$$

So the delta function term in the Liouville equation is equal to

$$\begin{aligned} & -g_0 \delta(t) \sum_{i\alpha} \left(\frac{\partial B}{\partial Q_{i\alpha}} \frac{\partial f(t)}{\partial P_{i\alpha}} - \frac{\partial B}{\partial P_{i\alpha}} \frac{\partial f(t)}{\partial Q_{i\alpha}} \right) \\ &= g_0 \delta(t) \frac{1}{k_B T} f_{eq}(\Gamma) \sum_{i\alpha} \left(\frac{\partial B}{\partial Q_{i\alpha}} \frac{\partial H_0}{\partial P_{i\alpha}} - \frac{\partial B}{\partial P_{i\alpha}} \frac{\partial H_0}{\partial Q_{i\alpha}} \right) = g_0 \delta(t) \frac{1}{k_B T} f_{eq}(\Gamma) \dot{B}(\Gamma) \end{aligned}$$

Note that this is the time derivative of the dynamical variable B in the absence of the applied field when the system is at the point Γ in phase space. The fact that this is a time derivative in the *absence* of the field is confirmed by the presence on H_0 on the right. This is precisely the sum that appears in the previous expression for the delta function term contribution to the time derivative.

The Liouville equation becomes

$$\begin{aligned} & \frac{\partial f(Q^N, P^N)}{\partial t} \\ &= \sum_{i\alpha} \left(\frac{\partial H_0}{\partial Q_{i\alpha}} \frac{\partial f(t)}{\partial P_{i\alpha}} - \frac{\partial H_0}{\partial P_{i\alpha}} \frac{\partial f(t)}{\partial Q_{i\alpha}} \right) - g_0 \delta(t) \frac{1}{k_B T} f_{eq}(\Gamma) \dot{B}(\Gamma) \end{aligned}$$

Thus

$$\begin{aligned} f(\Gamma, 0+) &= f(\Gamma, 0-) + \frac{1}{k_B T} g_0 f_{eq}(\Gamma) \dot{B}(\Gamma) \\ &= f_{eq}(\Gamma) \left(1 + \frac{1}{k_B T} g_0 \dot{B}(\Gamma) \right) \end{aligned}$$

This gives us the distribution function of the ensemble just after the pulse was applied. Let's write this as

$$P(\Gamma, 0+) = P_{eq}(\Gamma) \left(1 + \frac{1}{k_B T} g_0 \dot{B}(\Gamma) \right)$$

The meaning of this is quite straightforward. There was a delta function force applied to the system at $t = 0$. If the amplitude g_0 is positive, then the force tended to encourage the system to have a larger value of B . Thus the pulse had the effect of increasing the probability of those states that have positive values of \dot{B} and decreasing the probability of those states that have negative values of \dot{B} . Thus the distribution, after the pulse, is moving in such a way that B is increased.

Now let's calculate the average of A at time t for the ensemble. It is clearly equal to

$$\langle A(t) \rangle = \int d\Gamma P(\Gamma, 0+) A(t, \Gamma)$$

Note that in calculating $A(t, \Gamma)$, the usual mechanics of H_0 is all that is involved, because the applied field is zero for $t > 0$. So we get

$$\begin{aligned} \langle A(t) \rangle &= \int d\Gamma P_{eq}(\Gamma) \left(1 + \frac{1}{k_B T} g_0 \dot{B}(\Gamma) \right) A(t, \Gamma) \\ &= \int d\Gamma P_{eq}(\Gamma) A(t, \Gamma) + \frac{1}{k_B T} g_0 \int d\Gamma P_{eq}(\Gamma) \dot{B}(\Gamma) A(t, \Gamma) \\ &= \langle A \rangle_{eq} + \frac{1}{k_B T} g_0 \int d\Gamma P_{eq}(\Gamma) \dot{B}(\Gamma) A(t, \Gamma) \end{aligned}$$

Thus we find

$$\chi(t) = \frac{1}{k_B T} \int d\Gamma P_{eq}(\Gamma) \dot{B}(\Gamma) A(t, \Gamma) = \frac{1}{k_B T} \langle A(t, \Gamma) \dot{B}(0, \Gamma) \rangle = \frac{1}{k_B T} C_{A\dot{B}}(t)$$

Let's write this as

$$\chi_{AB}(t) = \frac{1}{k_B T} C_{A\dot{B}}(t)$$

If a delta function force

that couples to B and tends to increase the value of B

is applied at $t = 0$,

then the response of A at some time later

is (except for some constants) equal to

the time correlation function of A and \dot{B} at the time interval of interest

where the correlation function is the equilibrium correlation function in the absence of the applied field.

Note how simple this is. No minus signs, no numerical factors other than $1/k_B T$. A appears because this is the quantity whose response we are calculating. \dot{B} appears because a delta function force that couples to B has an effect on the distribution function that is proportional to $\dot{B}(\Gamma)$.

There is another version of this that is a little more common. To get it, we need to use a couple of properties of equilibrium correlation functions.

Some properties of classical equilibrium correlation functions:

Interchange of the two dynamical variables

$\langle A(t)B(t') \rangle$ is a function of $t - t'$. Therefore

$$C_{AB}(t) = \langle A(t)B(0) \rangle = \langle B(0)A(t) \rangle = C_{BA}(-t)$$

This holds for any A and B . (Note that this assumes we are dealing with classical mechanical systems.) Interchanging the two subscripts of a correlation function and changing the sign of the time leads to the same value of the correlation function.

A useful special case of this is

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

For classical mechanics, an autocorrelation function is symmetric under change of the sign of time.

An expression for the time derivative of a correlation function

$$\begin{aligned} \frac{d}{dt}C_{AB}(t) &= \frac{d}{dt} \int d\Gamma P_{eq}(\Gamma) A(t, \Gamma) B(\Gamma) = \int d\Gamma P_{eq}(\Gamma) \left(\frac{d}{dt} A(t, \Gamma) \right) B(\Gamma) \\ &= \int d\Gamma P_{eq}(\Gamma) \dot{A}(t, \Gamma) B(\Gamma) = C_{\dot{A}B}(t) \end{aligned}$$

$$\frac{d}{dt}C_{AB}(t) = C_{\dot{A}B}(t)$$

or

$$\dot{C}_{AB}(t) = C_{\dot{A}B}(t)$$

This holds for any A and B .

Another expression for the time derivative of a correlation function

Combining these two together, we get

$$\dot{C}_{AB}(t) = \frac{d}{dt}C_{AB}(t) = \frac{d}{dt}C_{BA}(-t) = -\dot{C}_{BA}(-t) = -C_{\dot{B}A}(-t) = -C_{\dot{B}A}(t)$$

or

$$\dot{C}_{AB}(t) = -C_{\dot{B}A}(t)$$

Thus we have

$$\chi_{AB}(t) = -\frac{1}{k_B T} \dot{C}_{AB}(t)$$

This is a relatively simple and elegant statement of our basic result:

the response of A

to a field that couples to B

is (except for factors) equal to

the time derivative of the correlation function of A and B *in the absence of the external field.*

This is the important formal result from the application of linear response theory to the problem of a weak external field applied to an equilibrium system.

Behavior of correlation functions for long times

$$C_{AB}(t) = \langle A(t)B(0) \rangle$$

As $|t| \rightarrow \infty$, $A(t)$ and $B(0)$ become statistically independent.

$$C_{AB}(t) \rightarrow \langle A(t) \rangle \langle B(0) \rangle = \langle A \rangle \langle B \rangle.$$

Correlation functions of fluctuations

$$\text{Define } \delta A(\Gamma) \equiv A(\Gamma) - \langle A \rangle. \quad \delta B(\Gamma) = B(\Gamma) - \langle B \rangle.$$

Consider

$$\begin{aligned} C_{\delta A \delta B}(t) = \langle \delta A(t) \delta B(0) \rangle &= \langle (A(t) - \langle A \rangle)(B(0) - \langle B \rangle) \rangle \\ &= C_{AB}(t) - \langle A \rangle \langle B \rangle - \langle A \rangle \langle B \rangle + \langle A \rangle \langle B \rangle \\ &= C_{AB}(t) - \langle A \rangle \langle B \rangle \end{aligned}$$

Therefore

$$C_{\delta A \delta B}(t) \rightarrow 0 \quad \text{as } |t| \rightarrow \infty$$

Let's carry this one step further.

Relaxation experiment

Consider the situation in which we turn on the external field that couples to B in the infinite past.

The system comes to equilibrium with the field.

Then we turn off the field at $t = 0$.

This is just a relaxation experiment. From our general discussion of linear response theory, we had,

$$S(t) = aR(t) = a \int_t^\infty dt' \chi(t') \quad \text{for } t > 0$$

In the notation of the present problem, for $t \geq 0$,

$$\begin{aligned} \langle A(t) \rangle - \langle A \rangle_{eq} &= g \int_t^\infty dt' \chi_{AB}(t') = g \int_t^\infty dt' \left(-\frac{1}{k_B T} \dot{C}_{AB}(t') \right) \\ &= -\frac{g}{k_B T} C_{AB}(t') \Big|_t^\infty = -\frac{g}{k_B T} (C_{AB}(\infty) - C_{AB}(t)) \\ &= -\frac{g}{k_B T} (\langle A \rangle \langle B \rangle - C_{AB}(t)) = \frac{g}{k_B T} C_{\delta A \delta B}(t) \end{aligned}$$

The final result is

$$\langle A(t) \rangle - \langle A \rangle_{eq} = \frac{g}{k_B T} C_{\delta A \delta B}(t) \quad \text{for } t \geq 0$$

If a constant field that couples to B has been on for a very long time and is turned off abruptly,

the relaxation of A to its equilibrium value as a function of time

is proportional to

the equilibrium time correlation function of the fluctuations of A and B .

More simply, the relaxation function is proportional to the equilibrium correlation function of fluctuations. This is a really remarkable result.

Much of what we have discussed so far in this course about time dependent statistical mechanics has been definitions and identities and hypotheses and simple models of dynamics, like Brownian motion. It is all very general,

but it was not clear what the consequences are. In some sense, this is the first really significant result that has come out of our discussion. It is a nontrivial and relatively simple statement about the relationship between an experiment in which relaxation is observed when an external field is turned off and the fluctuation properties of the same system at equilibrium in the complete absence of an external field.

It applies only to classical systems, but it can be generalized to quantum systems and other models for dynamics.

Linear response to a constant field (static response, zero frequency response). In the relaxation experiment, by the time we reached $t = 0$ the system has adjusted to the constant field and was holding constant (until we turned off the field).

From linear response theory we showed that

$$\langle A(0) \rangle = \langle A \rangle_{eq} + g_0 \chi'_{AB}(0)$$

where

$$\chi'(\omega) = \int_{-\infty}^{\infty} dt \chi_{AB}(t) \cos \omega t$$

There is another way of calculating $\langle A(0) \rangle$ for this experiment.

Since the field has been turned on for a long time, the system has had a chance to come to equilibrium in the presence of that field.

Let $P_{g_0}(\Gamma)$ be the equilibrium distribution function in the presence of a field of strength g_0 .

Then $P_0(\Gamma)$ would be the equilibrium distribution function in the absence of the external field.

The average of A over $P_{g_0}(\Gamma)$ is

$$\langle A \rangle_{g_0} = \int d\Gamma P_{g_0}(\Gamma) A(\Gamma)$$

Here $\langle \dots \rangle_{g_0}$ denotes the equilibrium average in the presence of a field of strength g_0 . This average must be the value of A just before we turned off the field at $t = 0$.

We want to evaluate this for small g_0 , which is consistent with the fact that we are interested in linear response.

We have

$$P_{g_0}(\Gamma) = (\text{const.}) \exp(-(H_0(\Gamma) - g_0 B(\Gamma))/k_B T)$$

This represents an equilibrium distribution *in the presence of a constant field of strength g_0* . Also, the equilibrium distribution in the absence of an external field is

$$P_0(\Gamma) = (\text{const.}) \exp(-H_0(\Gamma)/k_B T)$$

Then

$$\begin{aligned} P_{g_0}(\Gamma) &= (\text{const}) P_0(\Gamma) \exp(g_0 B(\Gamma)/k_B T) \\ &= \frac{P_0(\Gamma) \exp(g_0 B(\Gamma)/k_B T)}{\int d\Gamma' P_0(\Gamma') \exp(g_0 B(\Gamma')/k_B T)} \\ &= \frac{P_0(\Gamma) (1 + g_0 B(\Gamma)/k_B T)}{\int d\Gamma' P_0(\Gamma') (1 + g_0 B(\Gamma')/k_B T)} \\ &= \frac{P_0(\Gamma) (1 + g_0 B(\Gamma)/k_B T)}{(1 + g_0 \langle B \rangle_0 / k_B T)} \\ &= P_0(\Gamma) (1 + g_0 B(\Gamma)/k_B T) \left(1 - g_0 \langle B \rangle_0 / k_B T + O(g_0^2)\right) \\ &= P_0(\Gamma) \left(1 + g_0 (B(\Gamma) - \langle B \rangle_0) / k_B T + O(g_0^2)\right) \\ &= P_0(\Gamma) \left(1 + g_0 \delta B(\Gamma) / k_B T + O(g_0^2)\right) \end{aligned}$$

The effect of the applied field (for $g_0 > 0$) is to increase the probability of those states that for which δB is positive and decrease it for those states in which δB is negative.

The average value of A over this distribution is

$$\begin{aligned}
\langle A \rangle_{g_0} &= \int d\Gamma A(\Gamma) P_0(\Gamma) \left(1 + g_0 \delta B(\Gamma) / k_B T + O(g_0^2) \right) \\
&= \langle A \rangle_0 + \frac{g_0}{k_B T} \langle A \delta B \rangle_0 + O(g_0^2) \\
&= \langle A \rangle_0 + \frac{g_0}{k_B T} \langle \delta A \delta B \rangle_0 + O(g_0^2)
\end{aligned}$$

Comparison with the linear response theory result gives

$$\chi'_{AB}(0) = \frac{1}{k_B T} \langle \delta A \delta B \rangle_0 = \frac{1}{k_B T} \langle \delta A \delta B \rangle$$

The quantity on the left is often called a susceptibility. To see why, imagine that g_0 , the strength of the field that couples to B , is regarded as an additional thermodynamic variable. The derivative

$$\frac{\partial \langle A \rangle_{g_0}}{\partial g_0}$$

represent how ‘susceptible’ $\langle A \rangle_{g_0}$ is to changes in g_0 . From the equation above, it is easily seen that

$$\left. \frac{\partial \langle A \rangle_{g_0}}{\partial g_0} \right|_{g_0=0} = \chi'_{AB}(0) = \frac{1}{k_B T} \langle \delta A \delta B \rangle_0 = \frac{1}{k_B T} \langle \delta A \delta B \rangle$$

Thus we have the important result that the susceptibility of $\langle A \rangle_{g_0}$ to changes in g_0 , evaluated for $g_0 = 0$, is directly related to the static correlation function for fluctuations of δA and δB in equilibrium in the absence of the external field.

Another way of looking at it:

the response function $\chi(t)$ is a time dependent quantity

that describes the response of a system

that has been driven slightly out of equilibrium

by a small *time dependent* external field.

However, its zero frequency cosine transform (i.e. its time integral) is actually an equilibrium property and can be calculated from equilibrium statistical mechanics.

This is one of several such relationships between response functions and static equilibrium properties in classical statistical mechanics.

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