

## 10. LINEAR RESPONSE THEORY

### 10.1. Classical Linear Response Theory

Correlation functions provide a statistical description of the dynamics of molecular variables; however, it remains unclear how they are related to experimental observables. You have probably sensed this from the perspective that correlation functions are *complex*, and how can observables be complex? Also, correlation functions describe equilibrium dynamics, but from a realistic point of view, exerting external forces should move the system away from equilibrium. What happens as a result? These questions fall into the realm of nonequilibrium statistical mechanics, an area of active research for which formal theories are limited and approximation methods are the primary tool. Linear response theory is the primary approximation method, which describes the evolution away or toward equilibrium under perturbative conditions.

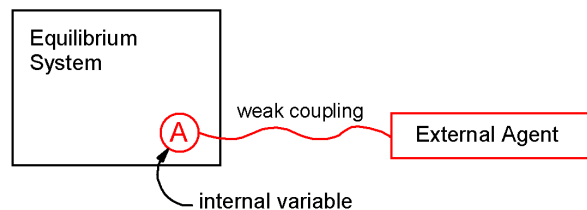
We will use linear response theory as a way of describing a real experimental observable. Specifically this will tell us how an equilibrium system changes in response to an applied potential. The quantity that will describe this is a response function, a real observable quantity. We will go on to show how it is related to correlation functions. Embedded in this discussion is a particularly important observation. We will now deal with a nonequilibrium system, but we will show that when the changes are small away from equilibrium, the equilibrium fluctuations dictate the nonequilibrium response! Thus knowledge of equilibrium dynamics is useful in predicting the outcome of nonequilibrium processes.

So, the question is “How does the system respond if you drive it away from equilibrium?” We will examine the case where an *equilibrium* system, described by a Hamiltonian  $H_0$  interacts weakly with an external agent,  $V(t)$ . The system is moved away from equilibrium by the external agent, and the system absorbs energy from the external agent.

How do we describe the time-dependent properties of the system? We first take the external agent to interact with the system through an internal variable  $A$ . So the Hamiltonian for this problem is given by

$$H = H_0 - f(t) A \quad (10.1)$$

Here  $f(t)$  is the time-dependent action of the external agent, and the deviation from equilibrium is linear in the internal variable. We describe the behavior of an ensemble initially at thermal equilibrium by assuming that each member of the ensemble is subject to the same interaction with the external agent, and then ensemble averaging. Initially, the system is



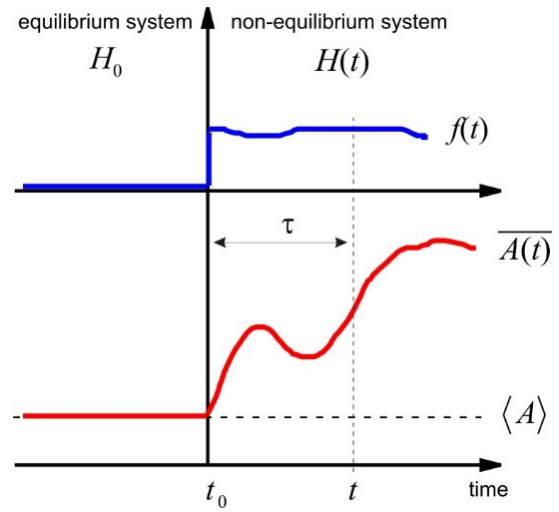
described by  $H_0$ . It is at equilibrium and the internal variable is characterized by an equilibrium ensemble average  $\langle A \rangle$ . The external agent is then applied at time  $t_0$ , and the system is moved away from equilibrium, and is characterized through a nonequilibrium ensemble average,  $\overline{A}$ .  $\langle A \rangle \neq \overline{A}(t)$  as a result of the interaction.

For a weak interaction with the external agent, we can describe  $\overline{A}(t)$  by performing an expansion in powers of  $f(t)$ .

$$\overline{A}(t) = (\text{terms } f^{(0)}) + (\text{terms } f^{(1)}) + \dots \quad (10.2)$$

$$\overline{A}(t) = \langle A \rangle + \int dt_0 R(t, t_0) f(t_0) + \dots \quad (10.3)$$

In this expression the agent is applied at  $t_0$ , and we observe the system at  $t$ . The leading term in this expansion is independent of  $f$ , and is therefore equal to  $\langle A \rangle$ . The next term in (10.3) describes the deviation from the equilibrium behavior in terms of a linear dependence on the external agent.  $R(t, t_0)$  is the linear response function, the quantity that contains the microscopic information on the system and how it responds to the applied agent. The integration in the last term of eq. (10.3) indicates that the nonequilibrium behavior depends on the full history of the application of the agent  $f(t_0)$  and the response of the system to it. We are seeking a quantum mechanical description of  $R$ .



## Properties of the response function

**1. Causal:** Causality refers to the common sense observation that the system cannot respond before the force has been applied. Therefore  $R(t, t_0) = 0$  for  $t < t_0$ , and the time-dependent change in  $A$  is

$$\delta \overline{A}(t) = \overline{A}(t) - \langle A \rangle = \int_{-\infty}^t dt_0 R(t, t_0) f(t_0) \quad (10.4)$$

The lower integration limit is set to  $-\infty$  to reflect that the system is initially at equilibrium, and the upper limit is the time of observation. We can also make the statement of causality explicit by writing the linear response function with a step response:  $\Theta(t - t_0) R(t, t_0)$ , where

$$\Theta(t - t_0) \equiv \begin{cases} 0 & (t < t_0) \\ 1 & (t \geq t_0) \end{cases} \quad (10.5)$$

**2. Stationary:** Similar to our discussion of correlation functions, the time-dependence of the system only depends on the time interval between application of the potential and observation. Therefore we write  $R(t, t_0) = R(t - t_0)$  and

$$\overline{\delta A(t)} = \int_{-\infty}^t dt_0 R(t - t_0) f(t_0) \quad (10.6)$$

This expression says that the observed response of the system to the agent is a *convolution* of the material response with the time-development of the applied force.

Rather than the absolute time points, we can define a time-interval  $\tau = t - t_0$ , so that we can write

$$\overline{\delta A(t)} = \int_0^{\infty} d\tau R(\tau) f(t - \tau) \quad (10.7)$$

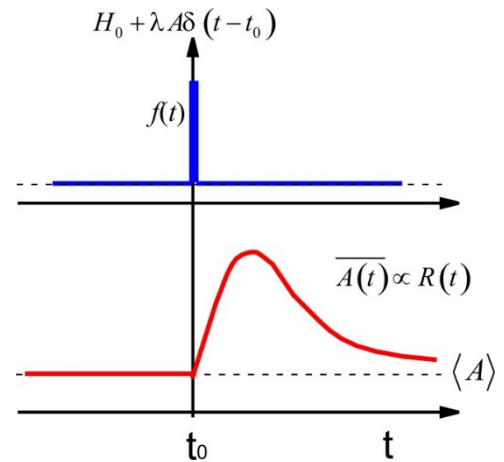
**3. Impulse response:** Note that for a delta function perturbation:

$$f(t) = \lambda \delta(t - t_0) \quad (10.8)$$

We obtain

$$\overline{\delta A(t)} = \lambda R(t - t_0) \quad (10.9)$$

Thus,  $R$  describes how the system behaves when an abrupt perturbation is applied and is often referred to as the impulse response function. An impulse response kicks the system away from the equilibrium established under  $H_0$ , and therefore the shape of a response function will always rise from zero and ultimately return to zero. In other words, it will be a function that can be expanded in *sines*. Thus the response to an arbitrary  $f(t)$  can be described through a Fourier analysis, suggesting that a spectral representation of the response function would be useful.



### The susceptibility

The observed temporal behavior of the nonequilibrium system can also be cast in the frequency domain as a spectral response function, or susceptibility. We start with eq. (10.7) and Fourier transform both sides:

$$\begin{aligned}\overline{\delta A(\omega)} &\equiv \int_{-\infty}^{+\infty} dt \overline{\delta A(t)} e^{i\omega t} \\ &= \int_{-\infty}^{+\infty} dt \left[ \int_0^{\infty} d\tau R(\tau) f(t-\tau) \right] e^{i\omega t}\end{aligned}\quad (10.10)$$

Now we insert  $e^{-i\omega\tau} e^{+i\omega\tau} = 1$  and collect terms to give

$$\overline{\delta A(\omega)} = \int_{-\infty}^{+\infty} dt \int_0^{\infty} d\tau R(\tau) f(t-\tau) e^{i\omega(t-\tau)} e^{i\omega\tau} \quad (10.11)$$

$$= \int_{-\infty}^{+\infty} dt' e^{i\omega t'} f(t') \int_0^{\infty} d\tau R(\tau) e^{i\omega\tau} \quad (10.12)$$

or 
$$\overline{\delta A(\omega)} = \tilde{f}(\omega) \chi(\omega) \quad (10.13)$$

In eq. (10.12) we switched variables, setting  $t' = t - \tau$ . The first term  $\tilde{f}(\omega)$  is a complex frequency domain representation of the driving force, obtained from the Fourier transform of  $f(t')$ . The second term  $\chi(\omega)$  is the susceptibility which is defined as the Fourier–Laplace transform (single-sided Fourier transform) of the impulse response function. It is a frequency-domain representation of the linear response function. Switching between time and frequency domains shows that a convolution of the force and response in time leads to the product of the force and response in frequency. This is a manifestation of the convolution theorem:

$$A(t) \otimes B(t) \equiv \int_{-\infty}^{\infty} d\tau A(t-\tau) B(\tau) = \int_{-\infty}^{\infty} d\tau A(\tau) B(t-\tau) = \mathcal{F}^{-1}[\tilde{A}(\omega)\tilde{B}(\omega)] \quad (10.14)$$

Here  $\otimes$  refers to convolution,  $\tilde{A}(\omega) = \mathcal{F}[A(t)]$ ,  $\mathcal{F}[\dots]$  is a Fourier transform, and  $\mathcal{F}^{-1}[\dots]$  is an inverse Fourier transform.

Note that  $R(\tau)$  is a real function, since the response of a system is an observable. The susceptibility  $\chi(\omega)$  is complex:

$$\chi(\omega) = \chi'(\omega) + i\chi''(\omega) \quad (10.15)$$

Since 
$$\chi(\omega) = \int_0^{\infty} d\tau R(\tau) e^{i\omega\tau} \quad (10.16)$$

However, the real and imaginary contributions are not independent. We have

$$\chi' = \int_0^{\infty} d\tau R(\tau) \cos \omega\tau \quad (10.17)$$

and 
$$\chi'' = \int_0^{\infty} d\tau R(\tau) \sin \omega\tau \quad (10.18)$$

$\chi'$  and  $\chi''$  are even and odd functions of frequency:

$$\chi'(\omega) = \chi'(-\omega) \quad (10.19)$$

$$\chi''(\omega) = -\chi''(-\omega) \quad (10.20)$$

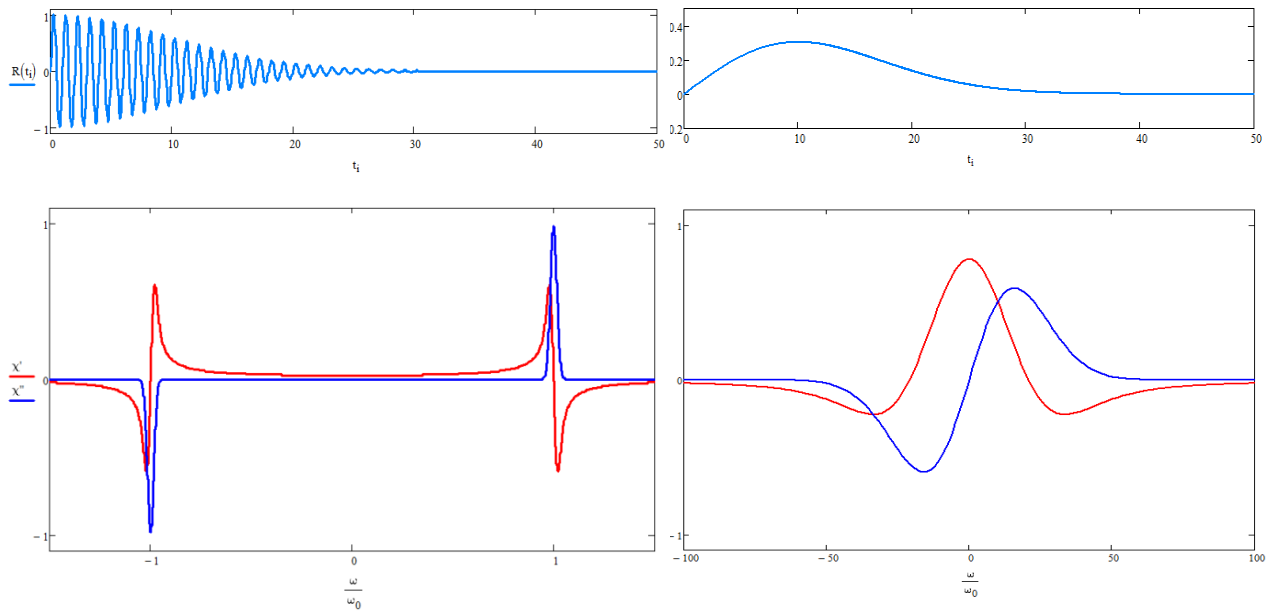
so that

$$\chi(-\omega) = \chi^*(\omega) \quad (10.21)$$

Notice also that eq. (10.21) allows us to write

$$\chi'(\omega) = \frac{1}{2}[\chi(\omega) + \chi(-\omega)] \quad (10.22)$$

$$\chi''(\omega) = \frac{1}{2i}[\chi(\omega) - \chi(-\omega)] \quad (10.23)$$



*Example of a high frequency underdamped response function oscillating as  $\sin(\omega_0 t)$  and corresponding susceptibility*

*Example of a low frequency overdamped response function and corresponding susceptibility*

### Kramers–Krönig relations

Since they are cosine and sine transforms of the same function,  $\chi'(\omega)$  is not independent of  $\chi''(\omega)$ . The two are related by the Kramers–Krönig relationships:

$$\chi'(\omega) = \frac{1}{\pi} \text{P} \int_{-\infty}^{+\infty} \frac{\chi''(\omega')}{\omega' - \omega} d\omega' \quad (10.24)$$

$$\chi''(\omega) = -\frac{1}{\pi} \text{P} \int_{-\infty}^{+\infty} \frac{\chi'(\omega')}{\omega' - \omega} d\omega' \quad (10.25)$$

These are obtained by substituting the inverse sine transform of eq. (10.18) into eq. (10.17):

$$\begin{aligned}\chi'(\omega) &= \frac{1}{\pi} \int_0^{\infty} dt \cos \omega t \int_{-\infty}^{+\infty} \chi''(\omega') \sin \omega' t d\omega' \\ &= \frac{1}{\pi} \lim_{L \rightarrow \infty} \int_{-\infty}^{+\infty} d\omega' \chi''(\omega') \int_0^L \cos \omega t \sin \omega' t dt\end{aligned}\quad (10.26)$$

Using  $\cos ax \sin bx = \frac{1}{2} \sin(a+b)x + \frac{1}{2} \sin(b-a)x$ , this can be written as

$$\chi'(\omega) = \frac{1}{\pi} \lim_{L \rightarrow \infty} \text{P} \int_{-\infty}^{+\infty} d\omega' \chi''(\omega') \frac{1}{2} \left[ \frac{-\cos(\omega' + \omega)L + 1}{\omega' + \omega} - \frac{\cos(\omega' - \omega)L + 1}{\omega' - \omega} \right] \quad (10.27)$$

If we choose to evaluate the limit  $L \rightarrow \infty$ , the cosine terms are hard to deal with, but we expect they will vanish since they oscillate rapidly. This is equivalent to averaging over a monochromatic field. Alternatively, we can average over a single cycle:  $L = 2\pi / (\omega' - \omega)$  to obtain eq. (10.24). The other relation can be derived in a similar way. Note that the Kramers–Krönig relationships are a consequence of causality, which dictate the lower limit of  $t_{\text{initial}} = 0$  on the first integral evaluated above.

### Example: Driven harmonic oscillator

One can classically model the absorption of light through a resonant interaction of the electromagnetic field with an oscillating dipole, using Newton's equations for a forced damped harmonic oscillator:

$$\ddot{x} - \gamma \dot{x} + \omega_0^2 x = F(t) / m \quad (10.28)$$

Here the  $x$  is the coordinate being driven,  $\gamma$  is the damping constant, and  $\omega_0 = \sqrt{k/m}$  is the natural frequency of the oscillator. We originally solved this problem is to take the driving force to have the form of a monochromatic oscillating source

$$F(t) = F_0 \cos \omega t \quad (10.29)$$

Then, equation (10.28) has the solution

$$x(t) = \frac{F_0}{m} \left( (\omega^2 - \omega_0^2)^2 + \gamma^2 \omega^2 \right)^{-1/2} \sin(\omega t + \delta) \quad (10.30)$$

with 
$$\tan \delta = \omega_0^2 - \omega^2 / \gamma \omega \quad (10.31)$$

This shows that the driven oscillator has an oscillation period that is dictated by the driving frequency  $\omega$ , and whose amplitude and phase shift relative to the driving field is dictated by its detuning from resonance. If we cycle-average to obtain the average absorbed power from the field, the absorption spectrum is

$$\begin{aligned}
 P_{\text{avg}}(\omega) &= \langle F(t) \cdot \dot{x}(t) \rangle \\
 &= \frac{\gamma \omega^2 F_0^2}{2m} \left[ (\omega_0^2 - \omega^2)^2 + \gamma^2 \omega^2 \right]^{-1/2}
 \end{aligned} \tag{10.32}$$

To determine the response function for the damped harmonic oscillator, we seek a solution to eq. (10.28) using an impulsive driving force  $F(t) = F_0 \delta(t - t_0)$ . The linear response of this oscillator to an arbitrary force is

$$x(t) = \int_0^\infty d\tau R(\tau) F(t - \tau) \tag{10.33}$$

so that time-dependence with an impulsive driving force is directly proportional to the response function,  $x(t) = F_0 R(t)$ . For this case, we obtain

$$R(\tau) = \frac{1}{m\Omega} \exp\left(-\frac{\gamma}{2}\tau\right) \sin \Omega \tau \tag{10.34}$$

The reduced frequency is defined as

$$\Omega = \sqrt{\omega_0^2 - \gamma^2/4} \tag{10.35}$$

From this, we evaluate eq. (10.16) and obtain the susceptibility

$$\chi(\omega) = \frac{1}{m(\omega_0^2 - \omega^2 - i\gamma\omega)} \tag{10.36}$$

As we will see shortly, the absorption of light by the oscillator is proportional to the imaginary part of the susceptibility

$$\chi''(\omega) = \frac{\gamma\omega}{m \left[ (\omega_0^2 - \omega^2)^2 + \gamma^2 \omega^2 \right]} \tag{10.37}$$

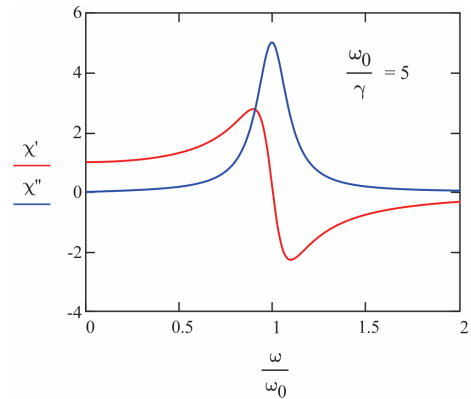
The real part is

$$\chi'(\omega) = \frac{\omega_0^2 - \omega^2}{m \left[ (\omega_0^2 - \omega^2)^2 + \gamma^2 \omega^2 \right]} \tag{10.38}$$

For the case of weak damping  $\gamma \ll \omega_0$  commonly encountered in molecular spectroscopy, eq. (10.36) is written as a Lorentzian lineshape by using the near-resonance approximation

$$\omega^2 - \omega_0^2 = (\omega + \omega_0)(\omega - \omega_0) \approx 2\omega(\omega - \omega_0) \tag{10.39}$$

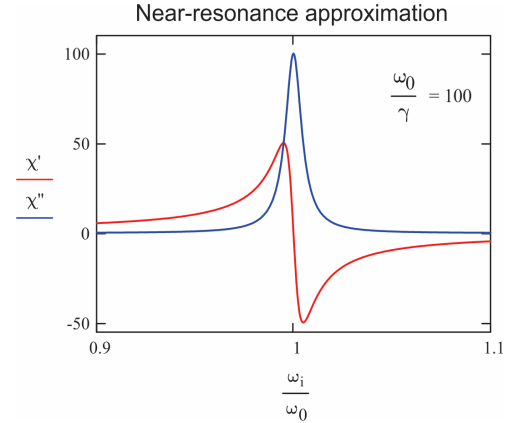
$$\chi(\omega) \approx \frac{1}{2m\omega_0} \frac{1}{\omega - \omega_0 + i\gamma/2}. \tag{10.40}$$



Then the imaginary part of the susceptibility shows asymmetric lineshape with a line width of  $\gamma$ , full width at half maximum.

$$\chi''(\omega) \approx \frac{1}{2m\omega_0} \frac{\gamma}{(\omega - \omega_0)^2 + \gamma^2/4} \quad (10.41)$$

$$\chi'(\omega) \approx \frac{1}{m\omega_0} \frac{(\omega - \omega_0)}{(\omega - \omega_0)^2 + \gamma^2/4} \quad (10.42)$$



### Nonlinear response functions

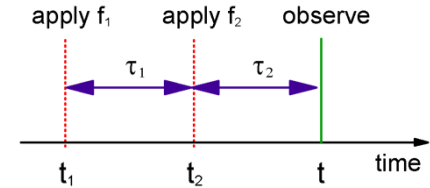
If the system does not respond in a manner linearly proportional to the applied potential but still perturbative, we can include nonlinear terms, i.e. higher expansion orders of  $\overline{A(t)}$  in eq. (10.3).

Let's look at second order:

$$\overline{\delta A(t)}^{(2)} = \int dt_1 \int dt_2 R^{(2)}(t; t_1, t_2) f_1(t_1) f_2(t_2) \quad (10.43)$$

Again we are integrating over the entire history of the application of two forces  $f_1$  and  $f_2$ , including any quadratic dependence on  $f$ .

In this case, we will enforce causality through a time ordering that requires (1) that all forces must be applied before a response is observed and (2) that the application of  $f_2$  must follow  $f_1$ . That is  $t \geq t_2 \geq t_1$  or



$$R^{(2)}(t; t_1, t_2) \Rightarrow R^{(2)} \cdot \Theta(t - t_2) \cdot \Theta(t_2 - t_1) \quad (10.44)$$

which leads to

$$\overline{\delta A(t)}^{(2)} = \int_{-\infty}^t dt_2 \int_{-\infty}^{t_2} dt_1 R^{(2)}(t; t_1, t_2) f_1(t_1) f_2(t_2) \quad (10.45)$$

Now we will call the system *stationary* so that we are only concerned with the time intervals between consecutive interaction times. If we define the intervals between adjacent interactions

$$\begin{aligned} \tau_1 &= t_2 - t_1 \\ \tau_2 &= t - t_2 \end{aligned} \quad (10.46)$$



Then we have

$$\overline{\delta A(t)^{(2)}} = \int_0^\infty d\tau_1 \int_0^\infty d\tau_2 R^{(2)}(\tau_1, \tau_2) f_1(t - \tau_1 - \tau_2) f_2(t - \tau_2) \quad (10.47)$$

### Readings

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## 10.2. Quantum Linear Response Functions

To develop a quantum description of the linear response function, we start by recognizing that the response of a system to an applied external agent is a problem we can solve in the interaction picture. Our time-dependent Hamiltonian is

$$H(t) = H_0 - f(t)\hat{A} = H_0 + V(t) \quad (10.48)$$

$H_0$  is the material Hamiltonian for the equilibrium system. The external agent acts on the equilibrium system through  $\hat{A}$ , an operator in the system states, with a time-dependence  $f(t)$ . We take  $V(t)$  to be a small change, and treat this problem with perturbation theory in the interaction picture.

We want to describe the nonequilibrium response  $\overline{A(t)}$ , which we will get by ensemble averaging the expectation value of  $\hat{A}$ , i.e.  $\langle \overline{A(t)} \rangle$ . Remember the expectation value for a pure state in the interaction picture is

$$\begin{aligned} \langle A(t) \rangle &= \langle \psi_I(t) | A_I(t) | \psi_I(t) \rangle \\ &= \langle \psi_0 | U_I^\dagger A_I U_I | \psi_0 \rangle \end{aligned} \quad (10.49)$$

The interaction picture Hamiltonian for eq. (10.48) is

$$\begin{aligned} V_I(t) &= U_0^\dagger(t) V(t) U_0(t) \\ &= -f(t) A_I(t) \end{aligned} \quad (10.50)$$

To calculate an ensemble average of the state of the system after applying the external potential, we recognize that the nonequilibrium state of the system characterized by  $|\psi_I(t)\rangle$  is in fact related to the initial equilibrium state of the system  $|\psi_0\rangle$  through a time-propagator, as seen in eq. (10.49). So the nonequilibrium expectation value  $\overline{A(t)}$  is in fact obtained by an equilibrium average over the expectation value of  $U_I^\dagger A_I U_I$ :

$$\overline{A(t)} = \sum_n p_n \langle n | U_I^\dagger A_I U_I | n \rangle \quad (10.51)$$

Again  $|n\rangle$  are eigenstates of  $H_0$ . Working with the first order solution to  $U_I(t)$

$$U_I(t-t_0) = 1 + \frac{i}{\hbar} \int_{t_0}^t dt' f(t') A_I(t') \quad (10.52)$$

we can now calculate the value of the operator  $A$  at time  $t$ , integrating over the history of the applied interaction  $f(t')$ :

$$\begin{aligned}
A(t) &= U_I^\dagger A_I U_I \\
&= \left\{ 1 - \frac{i}{\hbar} \int_{t_0}^t dt' f(t') A_I(t') \right\} A_I(t) \left\{ 1 + \frac{i}{\hbar} \int_{t_0}^t dt' f(t') A_I(t') \right\}
\end{aligned} \tag{10.53}$$

Here note that  $f$  is the time-dependence of the external agent. It does not involve operators in  $H_0$  and commutes with  $A$ . Working toward the linear response function, we just retain the terms linear in  $f(t')$

$$\begin{aligned}
A(t) &\cong A_I(t) + \frac{i}{\hbar} \int_{t_0}^t dt' f(t') \{ A_I(t) A_I(t') - A_I(t') A_I(t) \} \\
&= A_I(t) + \frac{i}{\hbar} \int_{t_0}^t dt' f(t') [A_I(t), A_I(t')]
\end{aligned} \tag{10.54}$$

Since our system is initially at equilibrium, we set  $t_0 = -\infty$  and switch variables to the time interval  $\tau = t - t'$  and using  $A_I(t) = U_0^\dagger(t) A U_0(t)$  obtain

$$A(t) = A_I(t) + \frac{i}{\hbar} \int_0^\infty d\tau f(t - \tau) [A_I(\tau), A_I(0)] \tag{10.55}$$

We can now calculate the expectation value of  $A$  by performing the ensemble-average described in eq. (10.51). Noting that the force is applied equally to each member of ensemble, we have

$$\overline{A(t)} = \langle A \rangle + \frac{i}{\hbar} \int_0^\infty d\tau f(t - \tau) \langle [A_I(\tau), A_I(0)] \rangle \tag{10.56}$$

The first term is independent of  $f$ , and so it comes from an equilibrium ensemble average for the value of  $A$ .

$$\langle A(t) \rangle = \sum_n p_n \langle n | A_I | n \rangle = \langle A \rangle \tag{10.57}$$

The second term is just an equilibrium ensemble average over the commutator in  $A_I(t)$ :

$$\langle [A_I(\tau), A_I(0)] \rangle = \sum_n p_n \langle n | [A_I(\tau), A_I(0)] | n \rangle \tag{10.58}$$

Comparing eq. (10.56) with the expression for the linear response function, we find that the quantum linear response function is

$$\begin{aligned}
R(\tau) &= -\frac{i}{\hbar} \langle [A_I(\tau), A_I(0)] \rangle & \tau \geq 0 \\
&= 0 & \tau < 0
\end{aligned} \tag{10.59}$$

or as it is sometimes written with the unit step function in order to enforce causality:

$$R(\tau) = -\frac{i}{\hbar} \Theta(\tau) \langle [A_I(\tau), A_I(0)] \rangle \tag{10.60}$$

The important thing to note is that the time-development of the system with the applied external potential is governed by the dynamics of the equilibrium system. All of the time-dependence in the response function is under  $H_0$ .

The linear response function is therefore the sum of two correlation functions with the order of the operators interchanged, which is the imaginary part of the correlation function  $C''(\tau)$

$$\begin{aligned} R(\tau) &= -\frac{i}{\hbar} \Theta(\tau) \{ \langle A_I(\tau) A_I(0) \rangle - \langle A_I(0) A_I(\tau) \rangle \} \\ &= -\frac{i}{\hbar} \Theta(\tau) (C_{AA}(\tau) - C_{AA}^*(\tau)) \\ &= \frac{2}{\hbar} \Theta(\tau) C''(\tau) \end{aligned} \quad (10.61)$$

As we expect for an observable, the response function is real. If we express the correlation function in the eigenstate description:

$$C(t) = \sum_{n,m} p_n |A_{mn}|^2 e^{-i\omega_{mn}t} \quad (10.62)$$

then

$$R(t) = \frac{2}{\hbar} \Theta(t) \sum_{n,m} p_n |A_{mn}|^2 \sin \omega_{mn}t \quad (10.63)$$

$R(\tau)$  can always be expanded in sines—an odd function of time. This reflects that fact that the impulse response must have a value of 0 (the deviation from equilibrium) at  $t = t_0$ , and move away from 0 at the point where the external potential is applied.

## Readings

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### 10.3. The Response Function and Energy Absorption

Let's investigate the relationship between the linear response function and the absorption of energy from the external agent—in this case an electromagnetic field. We will relate this to the absorption coefficient  $\alpha = \dot{E}/I$  which we have described previously. For this case,

$$H = H_0 - f(t)A = H_0 - \mu \cdot E(t) \quad (10.64)$$

This expression gives the energy of the system, so the rate of energy absorption averaged over the nonequilibrium ensemble is described by:

$$\dot{E} = \frac{\partial \bar{H}}{\partial t} = -\frac{\partial f}{\partial t} \overline{A(t)} \quad (10.65)$$

We will want to cycle-average this over the oscillating field, so the time-averaged rate of energy absorption is

$$\begin{aligned} \dot{E} &= \frac{1}{T} \int_0^T dt \left[ -\frac{\partial f}{\partial t} \overline{A(t)} \right] \\ &= \frac{1}{T} \int_0^T dt \frac{\partial f(t)}{\partial t} \left[ \langle A \rangle + \int_0^\infty d\tau R(\tau) f(t-\tau) \right] \end{aligned} \quad (10.66)$$

Here the response function is  $R(\tau) = -i \langle [\mu(\tau), \mu(0)] \rangle / \hbar$ . For a monochromatic electromagnetic field, we can write

$$f(t) = E_0 \cos \omega t = \frac{1}{2} [E_0 e^{-i\omega t} + E_0^* e^{i\omega t}] \quad (10.67)$$

which leads to the following for the second term in (10.66):

$$\frac{1}{2} \int_0^\infty d\tau R(\tau) [E_0 e^{-i\omega(t-\tau)} + E_0^* e^{i\omega(t-\tau)}] = \frac{1}{2} [E_0 e^{-i\omega t} \chi(\omega) + E_0^* e^{i\omega t} \chi(-\omega)] \quad (10.68)$$

By differentiating (10.67), and using it with (10.68) in eq. (10.66), we have

$$\dot{E} = -\frac{1}{T} \langle A \rangle [f(T) - f(0)] - \frac{1}{4T} \int_0^T dt [-i\omega E_0 e^{-i\omega t} + i\omega E_0^* e^{i\omega t}] [E_0 e^{-i\omega t} \chi(\omega) + E_0^* e^{i\omega t} \chi(-\omega)] \quad (10.69)$$

We will now cycle-average this expression, setting  $T = 2\pi/\omega$ . The first term vanishes and the cross terms in second integral vanish, because  $\frac{1}{T} \int_0^T dt e^{-i\omega t} e^{+i\omega t} = 1$  and  $\int_0^T dt e^{-i\omega t} e^{-i\omega t} = 0$ .

The rate of energy absorption from the field is

$$\begin{aligned} \dot{E} &= \frac{i}{4} \omega |E_0|^2 [\chi(-\omega) - \chi(\omega)] \\ &= \frac{\omega}{2} |E_0|^2 \chi''(\omega) \end{aligned} \quad (10.70)$$

So, the absorption of energy by the system is related to the imaginary part of the susceptibility. Now, from the intensity of the incident field,  $I = c|E_0|^2 / 8\pi$ , the absorption coefficient is

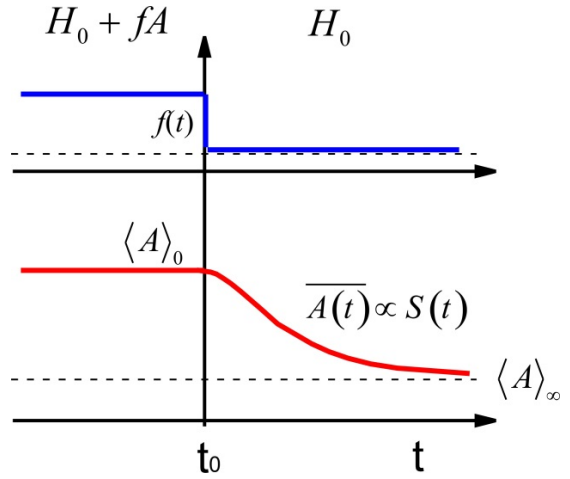
$$\alpha(\omega) = \frac{\dot{E}}{I} = \frac{4\pi\omega}{c} \chi''(\omega) \quad (10.71)$$

### Readings

1. McQuarrie, D. A., *Statistical Mechanics*. Harper & Row: New York, 1976.

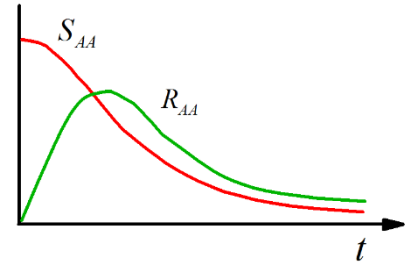
## 10.4. Relaxation of a Prepared State

The impulse response function  $R(t)$  describes the behavior of a system initially at equilibrium that is driven by an external field. Alternatively, we may need to describe the relaxation of a prepared state, in which we follow the return to equilibrium of a system initially held in a nonequilibrium state. This behavior is described by step response function  $S(t)$ . The step response comes from holding the system with a constant field  $H = H_0 - fA$  until a time  $t_0$  when the system is released, and it relaxes to the equilibrium state governed by  $H = H_0$ .



We can anticipate that the forms of these two functions are related. Just as we expect that the impulse response to rise from zero and be expressed as an odd function in time, the step response should decay from a fixed value and look even in time. In fact, we might expect to describe the impulse response by differentiating the step response, as seen in the classical case.

$$R(t) = \frac{1}{kT} \frac{d}{dt} S(t) \quad (10.72)$$



An empirical derivation of the step response begins with a few observations. First, response functions must be real since they are proportional to observables, however quantum correlation functions are complex and follow  $C(-t) = C^*(t)$ . Classical correlation functions are real and even,  $C(t) = C(-t)$ , and have the properties of a step response. To obtain the relaxation of a real observable that is even in time, we can construct a symmetrized function, which is just the real part of the correlation function:

$$\begin{aligned} S_{AA}(t) &= \frac{1}{2} \{ \langle A_I(t) A_I(0) \rangle + \langle A_I(0) A_I(t) \rangle \} \\ &= \frac{1}{2} \{ C_{AA}(t) + C_{AA}(-t) \} \\ &= C'_{AA}(t) \end{aligned} \quad (10.73)$$

The step response function  $S$  defined as follows for  $t \geq 0$ .

$$S(\tau) \equiv \frac{1}{\hbar} \Theta(\tau) \langle [A_I(\tau), A_I(0)] \rangle_+ \quad (10.74)$$

From the eigenstate representation of the correlation function,

$$C(t) = \sum_{n,m} p_n |A_{mn}|^2 e^{-i\omega_{mn}t} \quad (10.75)$$

we see that the step response function can be expressed as an expansion in cosines

$$S(t) = \frac{2}{\hbar} \Theta(t) \sum_{n,m} p_n |A_{mn}|^2 \cos \omega_{mn}t \quad (10.76)$$

Further, one can readily show that the real and imaginary parts are related by

$$\begin{aligned} \omega \frac{dC'}{dt} &= C'' \\ \omega \frac{dC''}{dt} &= -C' \end{aligned} \quad (10.77)$$

Which shows how the impulse response is related to the time-derivative of the step response.

In the frequency domain, the spectral representation of the step response is obtained from the Fourier–Laplace transform

$$S_{AA}(\omega) = \int_0^{\infty} dt S_{AA}(t) e^{i\omega t} \quad (10.78)$$

$$\begin{aligned} S_{AA}(\omega) &= \frac{1}{2} [C_{AA}(\omega) + C_{AA}(-\omega)] \\ &= \frac{1}{2} (1 + e^{-\beta\hbar\omega}) C_{AA}(\omega) \end{aligned} \quad (10.79)$$

Now, with the expression for the imaginary part of the susceptibility,

$$\chi''(\omega) = \frac{1}{2\hbar} (1 - e^{-\beta\hbar\omega}) C_{AA}(\omega) \quad (10.80)$$

we obtain the relationship

$$\chi''(\omega) = \frac{1}{\hbar} \tanh\left(\frac{\beta\hbar\omega}{2}\right) S_{AA}(\omega) \quad (10.81)$$

This is the formal expression for the fluctuation-dissipation theorem, proven in 1951 by Callen and Welton. It followed an observation made many years earlier (1930) by Lars Onsager for which he was awarded the 1968 Nobel Prize in Chemistry: “The relaxation of macroscopic nonequilibrium disturbance is governed by the same laws as the regression of spontaneous microscopic fluctuations in an equilibrium state.”

Noting that  $\tanh(x) = (e^x - e^{-x}) / (e^x + e^{-x})$  and  $\tanh(x) \rightarrow x$  for  $x \gg 1$ , we see that in the high temperature (classical) limit

$$\chi''(\omega) \Rightarrow \frac{1}{2kT} \omega S_{AA}(\omega) \quad (10.82)$$



### Appendix: Derivation of step response function

We can show more directly how the impulse and step response are related. To begin, let's consider the step response experiment,

$$H = \begin{cases} H_0 - fA & t < 0 \\ H_0 & t \geq 0 \end{cases} \quad (10.83)$$

and write the expectation values of the internal variable  $A$  for the system equilibrated under  $H$  at time  $t = 0$  and  $t = \infty$ .

$$\langle A \rangle_0 = \left\langle \frac{e^{-\beta(H_0 - fA)}}{Z_0} A \right\rangle \quad Z_0 = \langle e^{-\beta(H_0 - fA)} \rangle \quad (10.84)$$

$$\langle A \rangle_\infty = \left\langle \frac{e^{-\beta H_0}}{Z_\infty} A \right\rangle \quad Z_\infty = \langle e^{-\beta H_0} \rangle \quad (10.85)$$

If we make the *classical* linear response approximation, which states that when the applied potential  $fA$  is very small relative to  $H_0$ , then

$$e^{-\beta(H_0 - fA)} \approx e^{-\beta H_0} (1 + \beta fA) \quad (10.86)$$

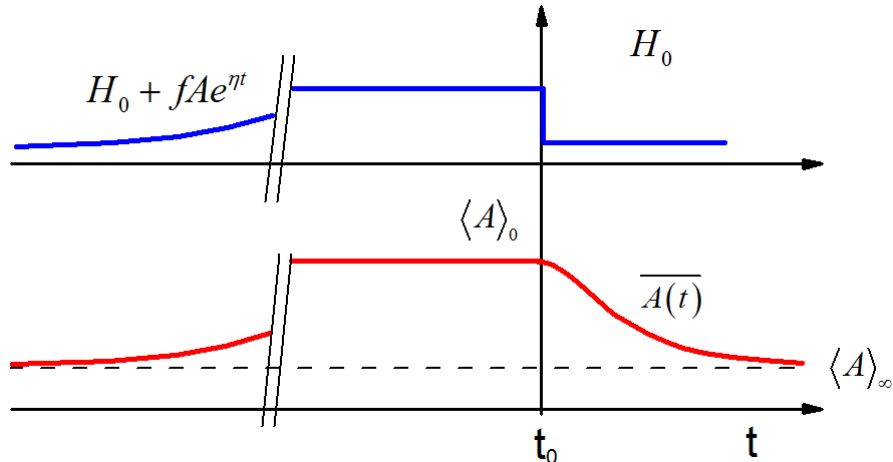
and  $Z_0 \approx Z_\infty$ , that

$$\delta A = \langle A \rangle_0 - \langle A \rangle_\infty \approx \beta f \langle A^2 \rangle \quad (10.87)$$

and the time dependent relaxation is given by the classical correlation function

$$\delta A(t) = \beta f \langle A(0) A(t) \rangle \quad (10.88)$$

For a description that works for the quantum case, let's start with the system under  $H_0$  at  $t = -\infty$ , ramp up the external potential at a slow rate  $\eta$  until  $t = 0$ , and then abruptly shut off the external potential and watch the system. We will describe the behavior in the limit  $\eta \rightarrow 0$ .



$$H = \begin{cases} H_0 + fA e^{\eta t} & t < 0 \\ H_0 & t \geq 0 \end{cases} \quad (10.89)$$

Writing the time-dependence in terms of a convolution over the impulse response function  $R$ , we have

$$\overline{\delta A(t)} = \lim_{\eta \rightarrow 0} \int_{-\infty}^0 dt' \Theta(t-t') R(t-t') e^{\eta t'} f \quad (10.90)$$

Although the integral over the applied force ( $t'$ ) is over times  $t < 0$ , the step response factor ensures that  $t \geq 0$ . Now, expressing  $R$  as a Fourier transform over the imaginary part of the susceptibility, we obtain

$$\begin{aligned} \overline{\delta A(t)} &= \lim_{\eta \rightarrow 0} \frac{f}{2\pi} \int_{-\infty}^0 dt' \int_{-\infty}^{\infty} d\omega e^{(\eta-i\omega)t'} e^{i\omega t} \chi''(\omega) \\ &= \frac{f}{2\pi} \int_{-\infty}^{\infty} d\omega PP\left(\frac{1}{-i\omega}\right) \chi''(\omega) e^{i\omega t} \\ &= \frac{f}{2\pi i} \int_{-\infty}^{\infty} d\omega \chi'(\omega) e^{i\omega t} \\ &= fC'(t) \end{aligned} \quad (10.91)$$

A more careful derivation of this result that treats the quantum mechanical operators properly is found in the references.

## Readings

1. Mazenko, G., *Nonequilibrium Statistical Mechanics*. Wiley-VCH: Weinheim, 2006.
2. Zwanzig, R., *Nonequilibrium Statistical Mechanics*. Oxford University Press: New York, 2001.