8.1. LINEAR RESPONSE THEORY

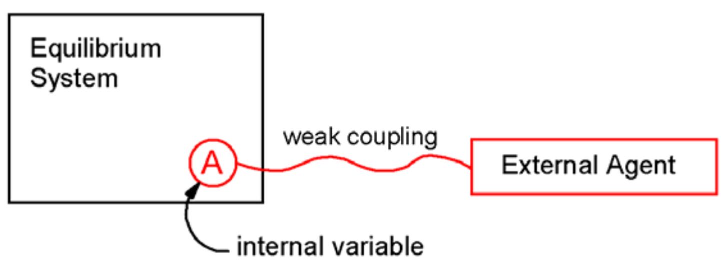
We have statistically described the time-dependent behavior of quantum variables in an equilibrium system through correlation functions. We have also shown that spectroscopic lineshapes are related to correlation functions for the dipole moment. But it's not the whole story. You have probably sensed this from the perspective that correlation functions are *complex*, and how can observables be complex?

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.

In this also is perhaps the more important type of 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 a knowledge of the equilibrium dynamics are useful in predicting non-equilibrium processes.

So, the question is "How does the system respond if you drive it 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 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

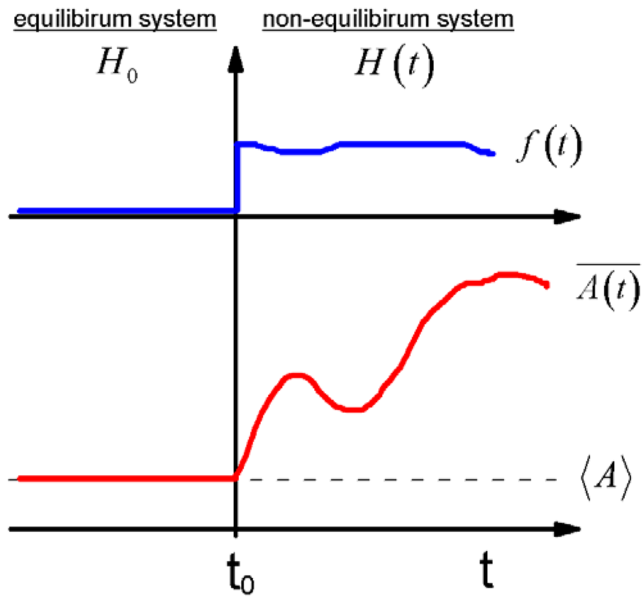


$$H = H_0 - f(t)\,A. \tag{8.1}$$

Here $f(t)$ is the time-dependence of external agent. 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 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 non-equilibrium 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 $f(t)$.



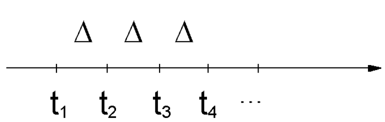
$$\overline{A(t)} = \left(terms\ f^{(0)} \right) + \left(terms\ f^{(1)} \right) + \ldots \tag{8.2}$$

$$\overline{A(t)} = \langle A \rangle + \int dt_0\ R(t,t_0)\ f(t_0) + \ldots \tag{8.3}$$

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 (8.3) 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 that describes how the system responds to the applied agent. The integration in the last term of eq. (8.3) indicates that the non-equilibrium 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*.

Rationalization for an expansion of $\overline{A(t)}$ in powers of $f(t)$:

Let's break time up into infinitesimal intervals:



$$t_i = i\Delta$$
$$f(t_i) = f_i$$

$$A(t_i) = A_i = A_i(\ldots, f_{i-2}, f_{i-1}, f_i)$$

Now, Taylor series expand about all $f_i = 0$

$$\overline{A(t_i)} = \underbrace{A_i(\ldots 0,0,0)}_{\langle A \rangle} \quad + \quad \sum_{j \le i} \left(\frac{\partial \overline{A}_i}{\partial f_j} \right)_{f_j = 0} f_j \quad + \quad \ldots$$

Value with no *f* applied

Sum over change due to force at all times of application

Linear (first-order) term:

$$\sum_j \left(\frac{\partial \overline{A}_i}{\partial f_j} \right)_{f_j = 0} f_j = \sum_j j\Delta \left[\frac{1}{j\Delta} \frac{\partial A_i}{\partial f_j} \right] f_j$$

$$\lim_{\Delta \to 0} (\ldots) = \int_{-\infty}^{t_i} dt_j R(t_j, t_i) f(t_j)$$

Properties of the Response Function

1. Causality: 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

$$\delta \overline{A(t)} = \overline{A(t)} - \langle A \rangle = \int_{-\infty}^{t} dt_0 \; R(t,t_0) \; f(t_0) \tag{8.4}$$

The lower integration limit has been 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

$$\Theta(t-t_0) \equiv \begin{cases} 0 & (t < t_0) \\ 1 & (t \ge t_0) \end{cases} . \tag{8.5}$$

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

$$\delta\overline{A(t)} = \int_{-\infty}^{t} dt_0 R(t-t_0)\, f(t_0) \tag{8.6}$$

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

$$\delta\overline{A(t)} = \int_{0}^{\infty} d\tau\, R(\tau)\, f(t-\tau) \tag{8.7}$$

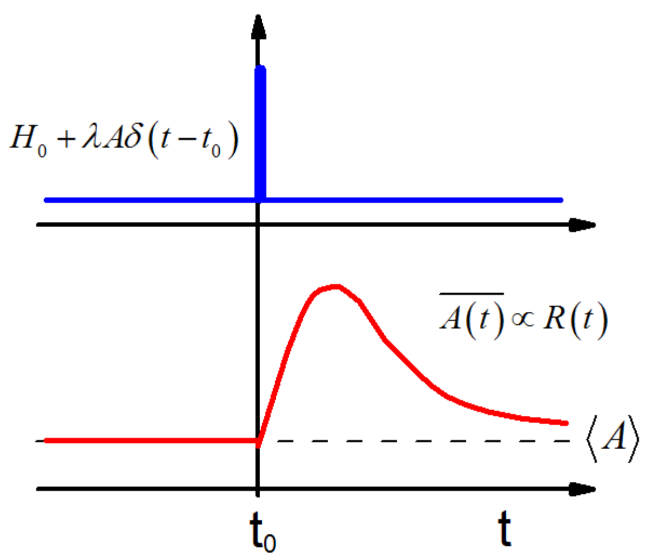
3. Impulse response. Note that for a delta function perturbation:

$$f(t) = \lambda\delta(t-t_0) \tag{8.8}$$

We obtain

$$\delta\overline{A(t)} = \lambda R(t-t_0)\,. \tag{8.9}$$

Thus, R describes how the system behaves when an abrupt perturbation is applied and is often referred to as the impulse response function.



FREQUENCY-DOMAIN REPRESENTATION: THE SUSCEPTIBILITY

The observed temporal behavior of the non-equilibrium system can also be cast in the frequency domain as a spectral response function, or susceptibility. We start with eq. (8.7) and Fourier transform both sides:

$$\delta\overline{A(\omega)} \equiv \int_{-\infty}^{+\infty} dt \left[\int_0^\infty d\tau\, R(\tau)\, f(t-\tau)\right] e^{i\omega t} \tag{8.10}$$

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

$$\delta\overline{A(\omega)} = \int_{-\infty}^{+\infty} dt \int_0^\infty d\tau\, R(\tau)\, f(t-\tau)\, e^{i\omega(t-\tau)}\, e^{i\omega\tau} \tag{8.11}$$

$$= \underline{\int_{-\infty}^{+\infty} dt'\, e^{i\omega t'}\, f(t')}\ \ \underline{\int_0^\infty d\tau\, R(\tau)\, e^{i\omega\tau}} \tag{8.12}$$

or

$$\delta\overline{A(\omega)} = \tilde{f}(\omega)\,\chi(\omega). \tag{8.13}$$

In eq. (8.12) 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:

$$A(t)\otimes B(t) \equiv \int_{-\infty}^{\infty} d\tau\, A(t-\tau)\, B(\tau) = \int_{-\infty}^{\infty} d\tau\, A(\tau)\, B(t-\tau) = \mathcal{F}^{-1}\left[\tilde{A}(\omega)\,\tilde{B}(\omega)\right] \tag{8.14}$$

where $\tilde{A}(\omega) = \mathcal{F}\left[A(t)\right]$, $\mathcal{F}[\cdots]$ is a Fourier transform, and $\mathcal{F}^{-1}[\cdots]$ is an inverse Fourier transform.

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

$$\chi(\omega) = \chi'(\omega) + i\chi''(\omega). \tag{8.15}$$

Since

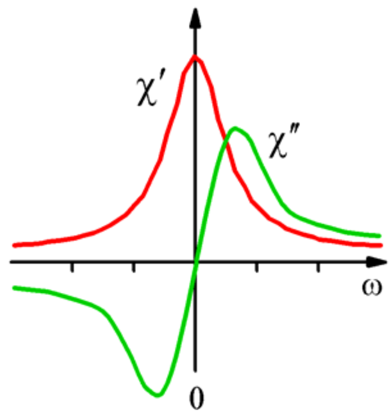
$$\chi(\omega) = \int_0^\infty d\tau\, R(\tau)\, e^{i\omega\tau}, \tag{8.16}$$

We have

$$\chi' = \int_0^\infty d\tau\, R(\tau) \cos\omega\tau \;=\; Re\left[\mathcal{F}\left(R(\tau)\right)\right] \tag{8.17}$$

and

$$\chi'' = \int_0^\infty d\tau\, R(\tau) \sin\omega\tau \;=\; Im\left[\mathcal{F}\left(R(\tau)\right)\right]. \tag{8.18}$$



χ' and χ'' are even and odd functions of frequency:

$$\chi'(\omega) = \chi'(-\omega) \tag{8.19}$$

$$\chi''(\omega) = -\chi''(-\omega) \tag{8.20}$$

so that $$\chi(-\omega) = \chi^*(\omega). \tag{8.21}$$

Notice also that eq. (8.21) allows us to write

$$\chi'(\omega) = \frac{1}{2}\left[\chi(\omega) + \chi(-\omega)\right] \tag{8.22}$$

$$\chi''(\omega) = \frac{1}{2i}\left[\chi(\omega) - \chi(-\omega)\right]. \tag{8.23}$$

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:

$$\chi'(\omega) = \frac{1}{\pi}\mathbb{P}\int_{-\infty}^{+\infty} \frac{\chi''(\omega')}{\omega' - \omega} d\omega' \tag{8.24}$$

$$\chi''(\omega) = -\frac{1}{\pi}\mathbb{P}\int_{-\infty}^{+\infty} \frac{\chi'(\omega')}{\omega' - \omega} d\omega' \tag{8.25}$$

These are obtained by substituting the inverse sine transform of eq. (8.18) into eq. (8.17):

$$\begin{aligned} \chi'(\omega) &= \frac{1}{\pi}\int_0^\infty dt \cos\omega t \int_{-\infty}^{+\infty} \chi''(\omega') \sin\omega' t \, d\omega' \\ &= \frac{1}{\pi}\lim_{L\to\infty}\int_{-\infty}^{+\infty} d\omega' \chi''(\omega') \int_0^L \cos\omega t \sin\omega' t \, dt \end{aligned} \tag{8.26}$$

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

$$\chi'(\omega)=\frac{1}{\pi}\lim_{L\to\infty}\mathrm{P}\int_{-\infty}^{+\infty}d\omega'\chi''(\omega)\tfrac{1}{2}\left[\frac{-\cos(\omega'+\omega)L+1}{\omega'+\omega}-\frac{\cos(\omega'-\omega)L+1}{\omega'-\omega}\right] \tag{8.27}$$

If we choose to evaluate the limit $L\to\infty$, 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 instead average over a single cycle: $L=2\pi/(\omega'-\omega)$ to obtain eq. (8.24). 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 $t_{initial}=0$ on the first integral evaluated above.

Example: Classical Response Function and Susceptibility

We can model 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:

$$\ddot{x} + \gamma\,\dot{x} + \omega_0^2\,x = F(t) \tag{8.28}$$

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

$$F(t) = F_0\,cos\,\omega t = \frac{qE_0}{m} cos\,\omega t\,. \tag{8.29}$$

Then, equation (8.28) has the solution

$$x(t) = \frac{qE_0}{m} \frac{1}{\left(\left(\omega_0^2 - \omega^2\right)^2 + 4\gamma^2\omega^2\right)^{1/2}} \sin\left(\omega t + \delta\right) \tag{8.30}$$

with
$$\tan\delta = \frac{\omega_0^2 - \omega^2}{2\gamma\omega}\,. \tag{8.31}$$

This shows that the driven oscillator has an oscillation period that is dictated by the driving frequency ω, and whose amplitude and phase shift relative to the driving field is dictated by the detuning ($\omega - \omega_0$). If we cycle average to obtain the average absorbed power from the field, the absorption spectrum is

$$\begin{aligned} P_{avg}(\omega) &= \left\langle F(t)\cdot\dot{x}(t)\right\rangle \\ &= \frac{\gamma\omega^2 F_0^2}{m} \frac{1}{\left[\left(\omega_0^2 - \omega^2\right)^2 + 4\gamma^2\omega^2\right]^{1/2}}\,. \end{aligned} \tag{8.32}$$

A response function approach would be to find the solution to

$$x(t) = \int_0^\infty d\tau\, R(\tau)\, f(t-\tau)\,, \tag{8.33}$$

which we can obtain by solving eq. (8.28) using an impulsive driving force. If $F(t) = F_0\delta(t - t_0)$, then $x(t) = F_0\ R(t)$, and we obtain

$$R(\tau) = \frac{1}{m\Omega} exp\left(-\frac{\gamma}{2}\tau\right) sin\,\Omega\tau \tag{8.34}$$

The reduced frequency is defined as

$$\Omega = \sqrt{\omega_0^2 - \gamma^2/4}\,. \tag{8.35}$$

From this we obtain the susceptibility

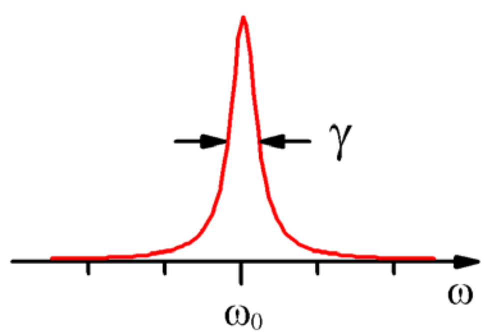
$$\chi(\omega) = \frac{1}{m\left(\omega_0^2 - \omega^2 - i\gamma\omega\right)}\,. \tag{8.36}$$

As we will see, the absorption of light by the oscillator is related to

$$\chi''(\omega) = \frac{2\gamma\omega}{m\left[\left(\omega_0^2 - \omega^2\right)^2 + \gamma^2\omega^2\right]}\,. \tag{8.37}$$

For the case of weak damping $\gamma << \omega_0$, eq. (8.36) is commonly written as a Lorentzian lineshape by using the near-resonance approximation $\omega^2 - \omega_0^2 = (\omega + \omega_0)(\omega - \omega_0) \approx 2\omega(\omega - \omega_0)$

$$\chi(\omega) \approx \frac{1}{2m\omega_0}\frac{1}{\omega - \omega_0 + i\gamma/2}\,. \tag{8.38}$$



Nonlinear Response Functions

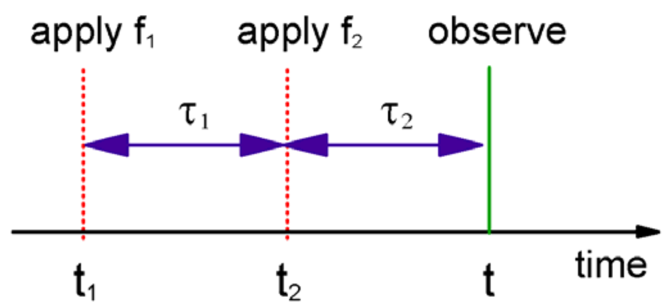
If the system does not respond in a manner linearly proportional to the applied potential but still perturbative, we can include nonlinear terms, i.e. higher expansion orders of $\overline{A(t)}$ in eq. (8.3).

Let's look at second order:

$$\delta\overline{A(t)}^{(2)} = \int dt_1 \int dt_2\; R^{(2)}(t;t_1,t_2)\; f_1(t_1)\; f_2(t_2) \tag{8.39}$$

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



$$R^{(2)}(t;t_1,t_2) \Rightarrow R^{(2)} \cdot \Theta(t-t_2)\cdot\Theta(t_2-t_1) \tag{8.40}$$

which leads to

$$\delta\overline{A(t)}^{(2)} = \int_{-\infty}^{t} dt_2 \int_{-\infty}^{t_2} dt_1 R^{(2)}(t;t_1,t_2)\; f_1(t_1)\; f_2(t_2) \tag{8.41}$$

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

$$\begin{aligned} \tau_1 &= t_2 - t_1 \\ \tau_2 &= t - t_2 \end{aligned} \tag{8.42}$$

Then we have

$$\delta\overline{A(t)}^{(2)} = \int_0^{\infty} d\tau_1 \int_0^{\infty} d\tau_2\; R^{(2)}(\tau_1,\tau_2)\; f_1(t-\tau_1-\tau_2)\; f_2(t-\tau_2) \tag{8.43}$$

8.2. 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

$$H(t) = H_0 - f(t)\hat{A} \quad = \quad H_0 + V(t) \tag{8.44}$$

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 non-equilibrium response $\overline{A(t)}$, which we will get by ensemble averaging the expectation value of $\hat{A}$. Remember the expectation value for a pure state in the interaction picture is

$$\begin{aligned} \langle A(t) \rangle &= \langle \psi_I(t) | A_I(t) | \psi_I(t) \rangle \\ &= \langle \psi_0 | U_I^\dagger A_I U_I | \psi_0 \rangle \end{aligned} . \tag{8.45}$$

The interaction picture Hamiltonian for eq. (8.44) is

$$\begin{aligned} V_I(t) &= U_0^\dagger(t) V(t) U_0(t) \\ &= -f(t) A_I(t) \end{aligned} \tag{8.46}$$

To calculate an ensemble average of the state of the system after applying the external potential, we recognize that the non-equilibrium state of the system characterized by described by $|\psi_I(t)\rangle$ is in fact related to the initial equilibrium state of the system $|\psi_0\rangle$, as seen in eq. (8.45). So the non-equilibrium expectation value $\overline{A(t)}$ is in fact obtained by an equilibrium average over the expectation value of $U_I^\dagger A_I U_I$:

$$\overline{A(t)} = \sum_n p_n \langle n | U_I^\dagger A_I U_I | n \rangle . \tag{8.47}$$

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

$$U_I(t, t_0) = 1 + \frac{i}{\hbar} \int_{t_0}^{t} dt' \; f(t') A_I(t') \tag{8.48}$$

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

$$\begin{aligned} A(t) &= U_I^\dagger\, A_I\, U_I \\ &= \left\{1-\frac{i}{\hbar}\int_{t_0}^{t} dt'\ f(t')\, A_I(t')\right\}\ A_I(t)\ \left\{1+\frac{i}{\hbar}\int_{t_0}^{t} dt'\ f(t')\, A_I(t')\right\} \end{aligned} \tag{8.49}$$

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

$$\begin{aligned} A(t) &\cong A_I(t) + \frac{i}{\hbar}\int_{t_0}^{t} dt'\ f(t')\left\{A_I(t)\,A_I(t') - A_I(t')\,A_I(t)\right\} \\ &= A_I(t) + \frac{i}{\hbar}\int_{t_0}^{t} dt'\ f(t')\left[A_I(t), A_I(t')\right] \end{aligned} \tag{8.50}$$

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

$$A(t) = A_I(t) + \frac{i}{\hbar}\int_0^{\infty} d\tau\, f(t-\tau)\left[A_I(\tau), A_I(0)\right] \tag{8.51}$$

We can now calculate the expectation value of A by performing the ensemble-average described in eq. (8.47). Noting that the force is applied equally to each member of ensemble, we have

$$\overline{A(t)} = \langle A\rangle + \frac{i}{\hbar}\int_0^{\infty} d\tau\, f(t-\tau)\left\langle\left[A_I(\tau), A_I(0)\right]\right\rangle \tag{8.52}$$

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

$$\langle A(t)\rangle = \sum_n p_n \langle n|A_I|n\rangle = \langle A\rangle \tag{8.53}$$

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

$$\left\langle\left[A_I(\tau), A_I(0)\right]\right\rangle = \sum_n p_n \left\langle n\left|\left[A_I(\tau), A_I(0)\right]\right|n\right\rangle . \tag{8.54}$$

Comparing eq. (8.52) with the expression for the linear response function, we find that the quantum linear response function is

$$R(\tau) = -\frac{i}{\hbar}\left\langle\left[A_I(\tau), A_I(0)\right]\right\rangle \qquad \tau \geq 0$$
$$= 0 \qquad \tau < 0 \tag{8.55}$$

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

$$R(\tau) = -\frac{i}{\hbar}\Theta(\tau)\left\langle\left[A_I(\tau), A_I(0)\right]\right\rangle \tag{8.56}$$

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 $C''(\tau)$

$$\begin{aligned} R(\tau) &= -\frac{i}{\hbar}\Theta(\tau)\left\{\left\langle A_I(\tau)A_I(0)\right\rangle - \left\langle A_I(0)A_I(\tau)\right\rangle\right\} \\ &= -\frac{i}{\hbar}\Theta(\tau)\left(C_{AA}(\tau) - C^*_{AA}(\tau)\right) \quad . \\ &= \frac{2}{\hbar}\Theta(\tau)C''(\tau) \end{aligned} \tag{8.57}$$

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

$$C(t) = \sum_{n,m} p_n \left|A_{mn}\right|^2 e^{-i\omega_{mn}t} \tag{8.58}$$

then

$$R(t) = \frac{2}{\hbar}\Theta(t)\sum_{n,m} p_n \left|A_{mn}\right|^2 \sin\omega_{mn}t \tag{8.59}$$

$R(\tau)$ 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.

8.3. THE RESPONSE FUNCTION AND ENERGY ABSORPTION

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

$$H = H_0 - f(t)A \quad = \quad H_0 - \mu \cdot E(t) \tag{8.60}$$

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

$$\dot{E} = \frac{\partial \bar{H}}{\partial t} = -\frac{\partial f}{\partial t}\overline{A(t)} \tag{8.61}$$

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

$$\begin{aligned} \dot{E} &= \frac{1}{T}\int_0^T dt \left[-\frac{\partial f}{\partial t}\overline{A(t)} \right] \\ &= \frac{1}{T}\int_0^T dt \frac{\partial f(t)}{\partial t}\left[\langle A \rangle + \int_0^\infty d\tau \, R(\tau) \, f(t-\tau) \right] \end{aligned} \tag{8.62}$$

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

$$f(t) = E_0 \cos \omega t = \tfrac{1}{2}\left[E_0 e^{-i\omega t} + E_0^* e^{i\omega t} \right], \tag{8.63}$$

which leads to the following for the second term in (8.62):

$$\frac{1}{2}\int_0^\infty d\tau \, R(\tau)\left[E_0 \, e^{-i\omega(t-\tau)} + E_0^* \, e^{i\omega(t-\tau)} \right] \; = \; \frac{1}{2}\left[E_0 \, e^{-i\omega t}\chi(\omega) + E_0^* \, e^{i\omega t} \, \chi(-\omega) \right] \tag{8.64}$$

By differentiating (8.63), and using it with (8.64) in eq. (8.62), we have

$$\dot{E} = -\frac{1}{T}\langle A \rangle \left[f(T) - f(0) \right] - \frac{1}{4T}\int_0^T dt \left[-i\omega E_0 e^{-i\omega t} + i\omega E_0^* e^{i\omega t} \right]\left[E_0 e^{-i\omega t}\chi(\omega) + E_0^* e^{i\omega t}\chi(-\omega) \right] \tag{8.65}$$

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 $\int_0^T dt \, e^{-i\omega t} \, e^{-i\omega t} = 0$.

So, the rate of energy absorption from the field is

$$\begin{aligned}\dot{E} &= \frac{i}{4}\omega\left|E_0\right|^2\left[\chi(-\omega)-\chi(\omega)\right] \\ &= \frac{\omega}{2}\left|E_0\right|^2\chi''(\omega)\end{aligned} \tag{8.66}$$

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, $I = c\left|E_0\right|^2/8\pi$, the absorption coefficient is

$$\alpha(\omega) = \frac{\dot{E}}{I} = \frac{4\pi\omega}{c}\chi''(\omega). \tag{8.67}$$

Now, let's show that this is consistent with the expression we found earlier

$$\alpha(\omega) = \frac{4\pi^2}{\hbar c}\omega\left(1-e^{-\beta\hbar\omega}\right)\int_{-\infty}^{\infty} dt\, e^{i\omega t}\, C_{\mu\mu}(t). \tag{8.68}$$

Starting with the imaginary part of the susceptibility

$$\begin{aligned}\chi''(\omega) &= \frac{1}{2i}\left(\chi(\omega)-\chi(-\omega)\right) \\ &= \frac{1}{2\hbar}\left\{\int_0^\infty dt\, e^{i\omega t}\left[C_{AA}(t)-C_{AA}(-t)\right]-\int_0^\infty dt\, e^{-i\omega t}\left[C_{AA}(t)-C_{AA}(-t)\right]\right\} \\ &= \frac{1}{2\hbar}\left\{\int_0^\infty dt\, e^{i\omega t}\left[C_{AA}(t)-C_{AA}(-t)\right]-\int_{-\infty}^0 dt'\, e^{i\omega t'}\left[C_{AA}(t')-C_{AA}(-t')\right]\right\} \\ &= \frac{1}{2\hbar}\left(\tilde{C}_{AA}(\omega)-\tilde{C}_{AA}(-\omega)\right)\end{aligned} \tag{8.69}$$

We have also established that the correlation functions obey the detailed balance condition:

$$\tilde{C}_{AA}(-\omega) = e^{-\beta\hbar\omega}\tilde{C}_{AA}(\omega) = \tilde{C}^*_{AA}(\omega) \tag{8.70}$$

This relationship reflects the fact that upward and downward transition rates between states separated by ω are related by the population difference. This allows us to write:

$$\tilde{C}_{AA}(\omega) \pm \tilde{C}_{AA}(-\omega) = \left(1 \pm e^{-\beta\hbar\omega}\right)\tilde{C}_{AA}(\omega) \tag{8.71}$$

So

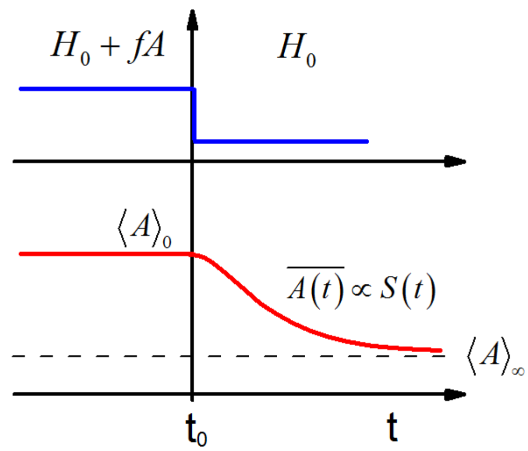
$$\begin{aligned}\chi''(\omega) &= \frac{1}{2\hbar}\left(1-e^{-\beta\hbar\omega}\right)C_{AA}(\omega) \\ &= \frac{1}{2\hbar}\left(1-e^{-\beta\hbar\omega}\right)\int_{-\infty}^{+\infty} e^{i\omega t}\left\langle A(t)A(0)\right\rangle dt\end{aligned} \tag{8.72}$$

Inserting into eq. (8.67), we have the result from earlier:

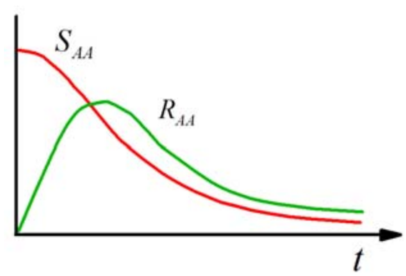
$$\alpha(\omega) = \frac{2\pi\omega}{\hbar c}\left(1-e^{-\beta\hbar\omega}\right)\int_{-\infty}^{+\infty} e^{i\omega t}\left\langle \mu(t)\mu(0)\right\rangle dt \tag{8.73}$$

So the absorption of energy from an external force, that is the time-evolution of a non-equilibrium system, is related to the imaginary part of χ. In turn, within the weak perturbations allowed by linear response, χ is related to the Fourier transform of the correlation function that describes the fluctuations and dynamics of the equilibrium system $C_{AA}(t)$. Relationships of this form that relate non-equilibrium dynamics of the system driven away or relaxing toward equilibrium to the fluctuations about the equilibrium state are known as fluctuation-dissipation relationships.

8.4. 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 non-equilibrium 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 form 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.

$$R(t) = \frac{1}{kT}\frac{d}{dt}S(t) \tag{8.74}$$

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:

$$\begin{aligned} S_{AA}(t) &= \tfrac{1}{2}\left\{\langle A_I(t)A_I(0)\rangle + \langle A_I(0)A_I(t)\rangle\right\} \\ &= \tfrac{1}{2}\left\{C_{AA}(t) + C_{AA}(-t)\right\} \\ &= C'_{AA}(t) \end{aligned} \tag{8.75}$$

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

$$S(\tau) \equiv \frac{1}{\hbar}\Theta(\tau)\left\langle\left[A_I(\tau), A_I(0)\right]\right\rangle_+ \tag{8.76}$$

From the eigenstate representation of the correlation function,

$$C(t) = \sum_{n,m} p_n \left|A_{mn}\right|^2 e^{-i\omega_{mn}t} \tag{8.77}$$

One can readily show that the real and imaginary parts are related by

$$\begin{aligned} \omega\frac{dC'}{dt} &= C'' \\ \omega\frac{dC''}{dt} &= C' \end{aligned} \tag{8.78}$$

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

$$S_{AA}(\omega) = \int_0^\infty dt\, S_{AA}(t) e^{i\omega t} \tag{8.79}$$

$$\begin{aligned} S_{AA}(\omega) &= \tfrac{1}{2}\left[C_{AA}(\omega) + C_{AA}(-\omega)\right] \\ &= \tfrac{1}{2}\left(1 + e^{-\beta\hbar\omega}\right)C_{AA}(\omega) \end{aligned} \tag{8.80}$$

Now, with the expression for the imaginary part of the susceptibility, eq. (8.72), we obtain the relationship

$$\chi''(\omega) = \frac{1}{\hbar}\tanh\left(\frac{\beta\hbar\omega}{2}\right)S_{AA}(\omega) \tag{8.81}$$

This is the formal expression for the fluctuation-dissipation theorem, proven in 1951 by Callen and Welton, for which they received the 1968 Chemistry Nobel Prize. It relates the absorption and dissipation of energy to the spontaneous fluctuations in the equilibrium state. It demonstrated an observation made many years earlier by Lars Onsager (1930): The relaxation of macroscopic non-equilibrium disturbance is governed by the same laws as the regression of spontaneous microscopic fluctuations in an equilibrium state.

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

$$\chi''(\omega) \Rightarrow \frac{1}{2kT}\omega S_{AA}(\omega). \tag{8.82}$$

Appendix: Derivation of Step Response

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

$$H = \begin{cases} H_0 - fA & t < 0 \\ H_0 & t \geq 0 \end{cases} \tag{8.83}$$

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

$$\langle A \rangle_0 = \left\langle \frac{e^{-\beta(H_0 - fA)}}{Z_0} A \right\rangle \qquad Z_0 = \left\langle e^{-\beta(H_0 - fA)} \right\rangle \tag{8.84}$$

$$\langle A \rangle_\infty = \left\langle \frac{e^{-\beta H_0}}{Z_\infty} A \right\rangle \qquad Z_\infty = \left\langle e^{-\beta H_0} \right\rangle \tag{8.85}$$

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

$$e^{-\beta(H_0 - fA)} \approx e^{-\beta H_0}\left(1 + \beta fA\right) \tag{8.86}$$

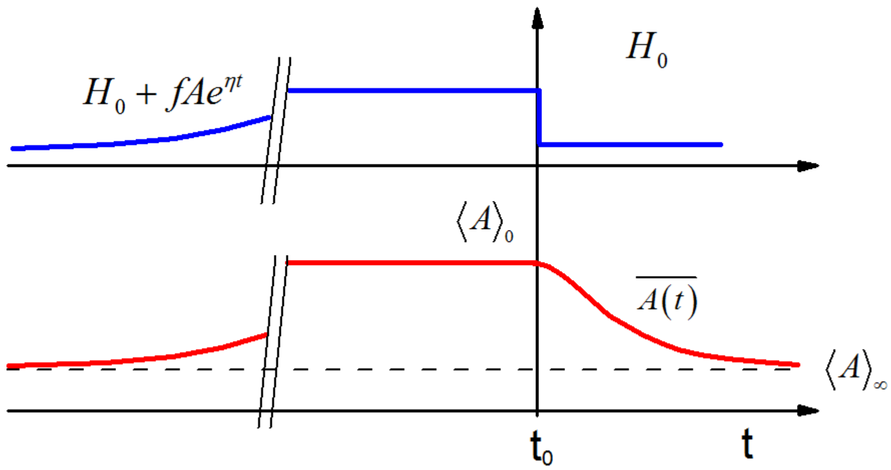
and $Z_0 \approx Z_\infty$, that

$$\delta A = \langle A \rangle_0 - \langle A \rangle_\infty \approx \beta f \left\langle A^2 \right\rangle, \tag{8.87}$$

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

$$\delta A(t) = \beta f \left\langle A(0) A(t) \right\rangle. \tag{8.88}$$

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



$$H = \begin{cases} H_0 + fAe^{\eta t} & t < 0 \\ H_0 & t \geq 0 \end{cases} \tag{8.89}$$

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

$$\overline{\delta A(t)} = \lim_{\eta \to 0} \int_{-\infty}^{0} dt' \Theta(t-t') R(t-t') e^{\eta t'} f \tag{8.90}$$

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

$$\begin{aligned} \overline{\delta A(t)} &= \lim_{\eta \to 0} \frac{f}{2\pi} \int_{-\infty}^{0} dt' \int_{-\infty}^{\infty} d\omega\, e^{(\eta - i\omega)t'} e^{i\omega t} \chi''(\omega) \\ &= \frac{f}{2\pi} \int_{-\infty}^{\infty} d\omega\, PP\left(\frac{1}{-i\omega}\right) \chi''(\omega) e^{i\omega t} \\ &= \frac{f}{2\pi i} \int_{-\infty}^{\infty} d\omega\, \chi'(\omega) e^{i\omega t} \\ &= f\, C'(t) \end{aligned} \tag{8.91}$$

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

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[i] Robert Zwanzig, *Nonequilibrium Statistical Mechanics* (Oxford Univ. Press, New York, 2001). Gene F. Mazenko, *Nonequilibrium Statistical Mechanics* (Wiley-VCH, Weinheim, 2006).