Time-Dependent Statistical Mechanics
8. Introduction to Linear Response Theory

© Hans C. Andersen

October 8, 2009

1 Introduction

Many experiments involve starting with an equilibrium system and then subjecting it to some forces, like electromagnetic or gravitational forces, and observing the response to the forces. All absorption spectroscopy experiments are of this type.

Lecture 4 10/1/09 continued

Also, some experimentally measured quantities can be calculated theoretically by considering what happens to a system when it is subjected to specific types of external forces.

In most (but not all) cases of interest, the external force is weak and we are interested in measuring or calculating the response of the system in a regime in which the response is linear in the force. For example, in visible light spectroscopy, most experiments involve absorption of energy from a weak field. If the field is too large, we get nonlinear optical effects, which is not what is of concern here.

There are many other situations in which some time dependent quantity (like the properties of a system) are affected by some external time dependent variable (like the amplitude of an external force) and we are interested in the linear relationship between the two. E.g.

- When concentration of a solute is inhomogeneous, the flux $\mathbf{j}$ at time t is linear in ∇c, the gradient in the concentration at the same time t.

- For a Newtonian fluid, the stress tensor at time t is linear in the gradient of the velocity, $\nabla \mathbf{v}$ at time t.
- For a viscoelastic fluid, the stress tensor at time t is linear in the gradient of the velocity at present and previous times.
- In a complicated but linear electrical circuit that acts as a filter, the voltage at the output at time t is linear in the input voltage at earlier times t.

There is a common language used for various linear response situations, and that language is also used in analyzing spectroscopic experiments. Here we want to discuss that language in a very general way and then apply it to the understanding of spectroscopic experiments.

2 The general linear response situation

Suppose we have some sort of system or apparatus that produces an output signal $S(t)$ that is a function of time. Suppose that when then system is left alone, the signal is simply $S(t) = 0$.

Suppose, however, that we can feed in a signal or force, that is a function of time $F(t)$. For example, there could be a knob on the side of the apparatus, and we can twist the knob as time progresses and make the knob read anything we like at each time. Or, there could be an input jack on the apparatus that allows us to feed in a time dependent input signal $F(t)$.

If we feed in no input, then $S(t) = 0$ for all t. But if we feed in a nonzero input, then $S(t)$ will deviate from zero. We are interested in the response of S to F.

Let's assume that the response has the following characteristics:

- It is causal. S responds only after F has been made nonzero. If $F(t) = 0$ for $t < t_1$, then $S(t) = 0$ for $t \leq t_1$.
- It is linear.
  - If the input $F(t)$ leads to the response $S(t)$, then the input $\lambda F(t)$ leads to the response $\lambda S(t)$.

- If the input $F(t) = f_1(t)$ leads to the response $S(t) = s_1(t)$ and the input $F(t) = f_2(t)$ leads to the response $S(t) = s_2(t)$, then the input $F(t) = f_1(t)+f_2(t)$ leads to the response $S(t) = s_1(t)+s_2(t)$.

- It is stationary. The absolute value of the time makes no difference to the response. I.e. if the input $F(t) = f(t)$ leads to the response $S(t) = s(t)$, then the input $F(t) = f(t - t_1)$ leads to the response $S(t) = s(t - t_1)$. If we delay the input in time, then the response is delayed by the same amount, with no change in the overall signal.

The principles of causality, linearity, and stationarity are physical principles that any particular system might or might not be consistent with. But there is a large class of systems which are consistent with all these principles. Such systems have a number of features in common, and we want to develop the language used to describe them.

We now ask the following question: What is the most general relationship between $S(t)$ and $F(t)$ that is linear, causal, and stationary? Here is the answer:

$$S(t) = \int_{-\infty}^{t} dt'\, \chi(t - t')F(t')$$

where $\chi(\tau)$ is some function of time. χ is called a response function. This can also be written as

$$S(t) = \int_{-\infty}^{\infty} dt'\, \chi(t - t')F(t)$$

where $\chi(\tau) = 0$ for $\tau < 0$.

First let's check that it satisfies all the conditions.

- Causality. The fact that $\chi(\tau) = 0$ for $\tau < 0$ guarantees causailty.
- Linearity. It is straightforward to demonstate linearity.
- Stationarity. This is also easy to verify.

Thus it satisfies all the conditions.

Now we need to verify that it is the most general function that satisfies these conditions.

Suppose we consider the special case of an input that is a delta function in time at the origin of time. So suppose $F(t) = \delta(t)$. There will be some response $S(t)$. Let us define $\chi(t)$ to be the response to the input function $\delta(t)$. From the definition and the causality of the system, $\chi(t) = 0$ for $t < 0$.

Now suppose that $F(t) = \delta(t - t')$, where t' is some particular time. Because of stationarity, the response will have to be $\chi(t - t')$.

Next suppose that $F(t) = \lambda\delta(t - t')$. Because of stationarity, the response will have to be $\lambda\chi(t - t')$.

Now suppose that we have an arbitrary signal $F(t)$. Let us write this as

$$F(t) = \int_{-\infty}^{\infty} dt'\, F(t')\delta(t - t')$$

The input then is a superposition of δ functions at various times. The amplitude of the delta function at $t = t'$ is $F(t')$. Then, because of linearity, the response must be a linear combination of the responses to the individual delta functions.

$$S(t) = \int_{\infty}^{\infty} dt_1\, F(t_1)\chi(t - t_1)$$

This establishes that this is the most general form.

Thus, if a response system is linear, causal, and stationary, then knowing the response of the system to a δ function signal applied at any one time is enough to construct the response function, and with this it is possible to predict the response of the system to any other input.

(slide)

A linear response situation

- We have some sort of box that produces an output signal $S(t)$.
- We can feed in an input signal $F(t)$.
- The S we get out depends on the F we put in. If the input signal is zero for all t, then $S(t) = 0$ for all t, but if the input signal is nonzero, then $S(t)$ will deviate from zero.

We are interested in the response of S to F.

Let's assume that the response has the following characteristics:

The response is *deterministic*, *causal*, *linear*, and *stationary*.

- *deterministic*

  the response is determined by the input

- *causal*

  S responds only after F has been made nonzero.

  If $F(t) = 0$ for $t < t_1$, then $S(t) = 0$ for $t \le t_1$.

- *linear*

  If

  $$F(t) = f_1(t) \quad \text{leads to} \quad S(t) = s_1(t)$$

  then

  $$F(t) = \lambda f_1(t) \quad \text{leads to} \quad S(t) = \lambda s_1(t)$$

  If

  $$F(t) = f_1(t) \quad \text{leads to} \quad S(t) = s_1(t)$$

  and

  $$F(t) = f_2(t) \quad \text{leads to} \quad S(t) = s_2(t)$$

  then

  $$F(t) = f_1(t) + f_2(t) \quad \text{leads to} \quad S(t) = s_1(t) + s_2(t)$$

- *stationary*

  If
  $$F(t) = f_1(t) \quad \text{leads to} \quad S(t) = s_1(t)$$
  then
  $$F(t) = f_1(t - t_1) \quad \text{leads to} \quad S(t) = s_1(t - t_1)$$

What is the most general relationship between $S(t)$ and $F(t)$ that is deterministic, linear, causal, and stationary?

Here is the answer:
$$S(t) = \int_{-\infty}^{t} dt'\, \chi(t - t')F(t')$$
where $\chi(\tau)$ is some function of time. χ is called a response function. This can also be written as
$$S(t) = \int_{-\infty}^{\infty} dt'\, \chi(t - t')F(t')$$
where $\chi(\tau) = 0$ for $\tau < 0$.

$$S(t) = \int_{-\infty}^{t} dt'\, \chi(t - t')F(t')$$

First let's check that it satisfies all the conditions.

- Deterministic. OK.
- Causal. The fact that $\chi(\tau) = 0$ for $\tau < 0$ guarantees causality.
- Linearity. It is straightforward to demonstate linearity.
- Stationarity. This is also easy to verify.

Thus it satisfies all the conditions.

Now we need to verify that it is the *most* general form that satisfies these conditions.

Suppose we have some $S(t)$ that responds to $F(t)$ in a way that is deterministic, causal, linear, and stationary. We want to see if we can find its χ and verify that the response must be of the form above.

Consider the special case:

$$F(t) = \delta(t)$$

There will be some response $S(t)$.

Define $\chi(t)$ to be the $S(t)$ that occurs when $F(t) = \delta(t)$.

From the definition and the causality of the system, $\chi(t) = 0$ for $t < 0$.

Consider the special case:

$$F(t) = \delta(t - t')$$

where t' is some particular time. Because of stationarity, the response will have to be

$$S(t) = \chi(t - t')$$

Consider the special case:

$$F(t) = \lambda\delta(t - t')$$

Because of stationarity, the response will have to be

$$S = \lambda\chi(t - t')$$

Now consider an arbitrary input signal $F(t)$: Write this as

$$F(t) = \int_{-\infty}^{\infty} dt' \, F(t')\delta(t - t')$$

Any input function can be regarded as a linear combination of delta function.

Because of linearity, the response must be the sum of the responses to each of the delta functions.

$$S(t) = \int_{\infty}^{\infty} dt_1 \, F(t_1)\chi(t - t_1)$$

This establishes that this is the most general form.

Thus, if a response system is deterministic, linear, causal, and stationary, then knowing the response of the system to a δ function signal applied at $t = 0$ is enough to construct the response function, and with this formula it is possible to predict the response of the system to any other input.

(end of slide)

3 Various behaviors of response functions

The behavior of the response is governed by the response function χ. An infinite variety of responses is consistent with the basic principles of linearity, causality, and stationarity. Let's discuss a few simple possibilities.

3.1 Instantaneous response with no memory

Suppose $\chi(t) = a\delta(t)$. That is, the response exists only while the force is being applied. We get

$$S(t) = \int_{-\infty}^{\infty} a\delta(t - t_1)F(t_1) = aF(t)$$

The signal is simply proportional to the input *at the same time.*

3.2 Delayed response with no oscillation

Suppose $\chi(t)$ is a function that is rises from zero then falls quickly to zero. Then $S(t)$ is related the behavior of F at times just slightly before t. We say that $S(t)$ has some memory of the previous values of $F(t)$.

3.3 Delayed response with oscillation

Suppose $\chi(t)$ oscillates with time and decays to zero. This is the behavior of a tuning fork when it is struck lightly. It is also the behavior of a molecular vibration.

(slide)

Qualitative discussion of various types of response functions

- Instantaneous response with no memory.

$$\chi(t) = a\delta(t)$$

$$S(t) = \int_{-\infty}^{\infty} a\delta(t - t_1)F(t_1) = aF(t)$$

- Delayed response with no oscillation
- Delayed response with oscillation.

(end of slide)

3.4 Behavior of response functions at long time

In many cases of interest, $\chi(t) \to 0$ as $t \to \infty$. When the input is turned off, the system might give a transient response, but the signal eventually returns to its value of 0, which is what it was before an signal was applied. This behavior is associated with a certain type of stability of the system that is responding.

Alternative behaviors are usually a sign of some sort of instability or at least metastability. For example, suppose at long times $\chi(t) \propto \cos \alpha t$. Then after being hit by a delta function input, the system will emit an oscillator signal for all times. Some minor perturbation has caused a long time change in the behavior of the system. No system in thermodynamic equilibrium would behave this way.

As another example, suppose at long times $\chi(t) \to a$, a constant not equal to zero. Then a small input can cause the system to emit a nonzero signal for all times. A thermodynamic equilibrium system could behave this way only under certain special circumstances.

We are usually interested in stable situations in which $\chi(t) \to 0$ for $t \to \infty$.

(slide)

Long time behavior of response functions

Typical case we are interested in:

$$\chi(t) \to 0 \quad \text{as} \quad t \to \infty$$

This is the typical behavior of stable equilibrium systems.

Other possibilities:

- $\chi(t) \to \infty$ as $t \to \infty$.

  Indicative of some sort of instability. E.g. positive feedback in a sound system.

- $\chi(t) \to a$ as $t \to \infty$.

  A small temporary input signal can cause the system to have a nonzero output for all times in the future. Sometimes indicates some sort of instability. Sometimes it is a minor quirk of the system.

(end of slide)

End of Lecture 4 10/1/09

4 Examples of responses

Lecture 5 10/6/09

Response to a general $F(t)$. Suppose we have a linear response system with a response function χ. The general response is

$$S(t) = \int_{-\infty}^{\infty} dt'\, \chi(t-t')F(t') = \int_{-\infty}^{\infty} dt'\, \chi(t')F(t-t')$$

(The two forms of the integral are equal.)

Recall that $\chi(t) = 0$ for $t < 0$, which is a consequence of causality.

We want to consider four special cases.

Response to a delta function input Suppose $F(t) = a\delta(t - t_1)$. Then we get

$$S(t) = \int_{-\infty}^{\infty} dt'\, \chi(t-t')F(t') = \int_{-\infty}^{\infty} dt'\, \chi(t-t')a\delta(t'-t_1) = a\chi(t-t_1)$$

$$S(t) = a\chi(t-t_1)$$

The signal turns on after t reaches t_1.

Special case: $F(t) = \delta(t)$. Then

$$S(t) = \chi(t)$$

Thus $\chi(t)$ is the response to a delta function input at $t = 0$.

Response to an oscillatory input with a single frequency. Suppose

$$F(t) = a\cos(\omega t + \phi)$$

Then

$$\begin{aligned}
S(t) &= \int_{-\infty}^{\infty} dt'\,\chi(t')F(t-t') \\
&= \int_{-\infty}^{\infty} dt'\,\chi(t')a\cos(\omega(t-t')+\phi) \\
&= \int_{-\infty}^{\infty} dt'\,\chi(t')a\cos(\omega t+\phi-\omega t') \\
&= \int_{-\infty}^{\infty} dt'\,\chi(t')a\left(\cos(\omega t+\phi)\cos\omega t' + \sin(\omega t+\phi)\sin\omega t\right) \\
&= a\left(\cos(\omega t+\phi)\int_{-\infty}^{\infty} dt'\,\chi(t')\cos\omega t' + \sin(\omega t+\phi)\int_{-\infty}^{\infty} dt'\,\chi(t')\sin\omega t\right)
\end{aligned}$$

In getting the fourth equality, we used the following trigonometric identity.

$$\cos(A-B) = \cos A\cos B + \sin A\sin B$$

Let us *define*

$$\begin{aligned}
\chi'(\omega) &= \int_{-\infty}^{\infty} dt'\,\chi(t')\cos\omega t' \\
\chi''(\omega) &= \int_{-\infty}^{\infty} dt'\,\chi(t')\sin\omega t
\end{aligned}$$

(Recall that $\chi(t) = 0$ for $t < 0$.) Then we get

$$S(t) = a\left[\cos(\omega t+\phi)\chi'(\omega) + \sin(\omega t+\phi)\chi''(\omega)\right]$$

The first term is in phase with the input.

Its amplitude is proportional to $\chi'(\omega)$, which is the cosine Fourier transform of the response function t.

The second term is $\pi/2$ out of phase with the input.

It is proportional to the sine Fourier transform of $\chi(t)$.

These two Fourier transforms of the response function play an important role in situations in which the input is oscillatory, which corresponds to the situation in many spectroscopic experiments.

This separation of the response into the in-phase and out-of-phase components is usually very important from a physical point of view.

In particular, χ'' is usually associated with the dissipation of energy.

Response to a constant input. Suppose $F(t) = a$, a constant input. This is a special case of oscillatory input with $\omega = 0$. Then

$$S(t) = \int_{-\infty}^{\infty} dt'\,\chi(t')F(t-t') = a\int_{-\infty}^{\infty} dt'\,\chi(t') = a\chi'(0)$$

Then the signal is steady and proportional to the input. The coefficient of proportionality is the cosine transform of the response function, evaluated at zero frequency.

Response to a steady input that is abruptly turned off. Suppose $F(t)$ has the following behavior

$$\begin{aligned} F(t) &= a \quad \text{for } t < 0 \\ &= 0 \quad \text{for } t > 0 \end{aligned}$$

Then

$$S(t) = a\int_{-\infty}^{\infty} dt'\,\chi(t')F(t-t')$$

For $t < 0$, since we have not turned off the field, the result must be the same as the previous case.

$$S(t) = a\chi'(0) \quad \text{for } t < 0$$

Let's consider $t > 0$.

$$S(t) = a\int_{t}^{\infty} dt'\,\chi(t')$$

The behavior of $S(t)$ for $t \geq 0$, describes how the signal relaxes to zero when the input is turned off.

Let's define the *relaxation function* $R(t)$ as the response, for positive times, when a steady input of unit amplitude is turned off at $t = 0$. Then

$$R(t) = \int_{t}^{\infty} dt'\chi(t')$$

Then

$$\dot{R}(t) = -\chi(t)$$
$$\chi(t) = -\dot{R}(t)$$

Summary of various responses

Delta function input. $F(t) = a\delta(t)$.

$$S(t) = a\chi(t)$$

Single frequency input. $F(t) = a\cos(\omega t + \phi)$.

$$S(t) = a\left[\cos(\omega t + \phi)\chi'(\omega) + \sin(\omega t + \phi)\chi''(\omega)\right]$$

Constant input. $F(t) = a$.

$$S(t) = a\chi'(0)$$

Constant input for negative times, abruptly shut off at $t = 0$.

$$\begin{aligned} F(t) &= a \quad \text{for } t < 0 \\ &= 0 \quad \text{for } t > 0 \end{aligned}$$

$$\begin{aligned} S(t) &= a\chi'(0) && \text{for } t < 0 \\ &= aR(t) = \int_t^\infty dt'\chi(t') && \text{for } t > 0 \end{aligned}$$

Comment. So far we have been talking about general linear response.

We have assumed something about the phenomenology of the response (i.e. about the phenomena: we send in a signal - we get out a signal).

The response is linear, causal, stationary. We typically also have assumed that the system is stable, which means that the output signal goes to zero for long times when the input signal is turned off.

We have not assumed anything about the underlying system other than these characteristics of the response. We could be talking about:

- an electrical circuit
- a detector of some sort
- a tuning fork
- a mole of molecules whose molecular motion is well described in terms of classical mechanics
- a mole of molecules whose molecular motion is well described in terms of quantum mechanics
- a mole of particles whose molecular motion is well described by Brownian motion theory

For almost all such systems, if you send in a weak enough signal, the response will be linear.

Recall:

$\chi'(\omega)$ is the cosine Fourier transform of $\chi(t)$.

$\chi''(\omega)$ is the sine Fourier transform of $\chi(t)$.

$R(t)$ is a definite integral of $\chi(t)$.

Consequence:

Since all responses are determined by a single response function $\chi(t)$, this means that almost any two responses are related.

1. (obvious) $\chi(t)$ for all t determines $\chi'(\omega)$ and $\chi''(\omega)$ for all ω.

   The response to a pulse determines the in-phase and out-of-phase response to a single frequency input for any frequency.

2. (obvious) $\chi'(\omega)$ and $\chi''(\omega)$ for all ω determines $\chi(t)$ for all t.

   The in-phase and out-of-phase response to a single frequency input for all frequencies determines $\chi(t)$ for all t.

3. (less obvious) $\chi'(\omega)$ for all ω determines $\chi(t)$ for all t.
4. (less obvious) $\chi'(\omega)$ for all ω determines $\chi''(\omega)$ for all ω.

For item 3, note that for a general function of t, knowing the cosine Fourier transform for all frequencies is not enough to reconstruct the function by taking the inverse Fourier transform. But if you know that the function is zero for $t < 0$, then the cosine Fourier transform is in fact enough.

More examples:

1. The response to a steady input is related to $\chi'(0)$, the zero frequency cosine transform of $\chi(t)$.

2. The response to a delta function input is the negative of the derivative of the relaxation function for positive times.

Lecture 5 10/6/09 continued in N9