

# Time-Dependent Statistical Mechanics

## 11. Absorption spectroscopy

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Many absorption spectroscopy experiments can be regarded as situations in which a system is subject to an additional term in its Hamiltonian that represents interaction of an external field with the system. For example, one of the main ways in which electromagnetic radiation interacts with matter is through a term in the Hamiltonian that is of the form  $-\mathbf{E}(t) \cdot \boldsymbol{\mu}$ , where  $\boldsymbol{\mu}$  is the electric dipole moment of the system.<sup>1</sup> Another electromagnetic interaction is  $-\mathbf{H}(t) \cdot \boldsymbol{\mu}_m$ , where  $\boldsymbol{\mu}_m$  is the magnetic dipole moment.<sup>2</sup>

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In these experiments, the applied field is often (but not always) oscillatory in time and the quantity that is measured is, in one way or another, related to the rate at which the system absorbs energy from the field as a function of the frequency of the field. Here we want to use linear response theory to calculate the rate of energy absorption, so that we can relate it to microscopic quantities. We shall use classical statistical mechanics, which may provide an interesting contrast to the much more familiar quantum approach to electromagnetic absorption. You have studied the quantum approach primarily for dilute gases of isolated molecules. Using the classical theory, we can provide a unified but qualitative discussion of both gases and liquids.

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<sup>1</sup>This is merely a schematic discussion. In actual situations, the variation of the electric field with position must be taken into account.

<sup>2</sup>An example of a spectroscopy that is not of this form is sound absorption.

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**Many spectroscopy experiments have these characteristics:**

1. A system in equilibrium is subject to a weak external field that adds an additional term to its Hamiltonian.
2. The external field is oscillatory in time, with a frequency  $\omega$  that can be controlled.
3. The quantity measured is related to the rate at which the system absorbs energy from the external field.

**Example.** A liquid or gas subject to an external electric field  $\mathbf{E}(t)$

The additional term in the H is  $-\mathbf{E}(t) \cdot \boldsymbol{\mu}$

$\boldsymbol{\mu}$  = electric dipole moment of system = a dynamical variable of the system

Measure either of the following as a function of frequency  $\omega$ :

- a. the relative intensity of transmitted and incident fields (as in ir or visible spectroscopy)
- b. the electrical work dissipated in the external circuit that generates the field (as in microwave spectroscopy)

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# 1 Linear response theory of energy absorption

**Linear response theory of absorption of energy from an external field.** Suppose we have a system with a Hamiltonian of the form

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

with the field oscillatory with a specific frequency

$$g(t) = g_0 \cos(\omega t + \phi)$$

What is the rate at which the field does work on the system? What is the rate at which the system absorbs energy from the field?

There is some ambiguity in how to answer this question.

The ambiguity arises because it is not clear whether  $H_0$  or  $H$  should be regarded as the energy of the system.

Which of the following two formulas correctly gives the average energy of the ensemble at time  $t$ ?

$$E(t) = \langle H(t) \rangle_{ne,t} = \int d\Gamma P(\Gamma, t) H(\Gamma, t)$$

or

$$E(t) = \langle H_0 \rangle_{ne,t} = \int d\Gamma P(\Gamma, t) H_0(\Gamma)$$

where the subscript indicates that the average is to be calculated over the nonequilibrium ensemble at the time specified.

There is one unambiguously correct way of answering the question.

When there is no field acting on the system, the energy of the system is clearly equal to  $H_0$ .

Suppose the field is initially off (at time  $-T$ ), then we turn it on (with it oscillating in time), and then we turn it off (time  $T$ ).

The net total energy absorbed is

$$\langle H_0 \rangle_{ne,T} - \langle H_0 \rangle_{ne,-T} = \int_{-T}^T dt \frac{d}{dt} \langle H_0 \rangle_{ne,t}$$

The rate of absorption then is

$$\frac{1}{2T} \int_{-T}^T dt \frac{d}{dt} \langle H_0 \rangle_{ne,t}$$

However, since the field is off at  $-T$  and at  $T$ , it is equally correct to calculate

$$\langle H(T) \rangle_{ne,T} - \langle H(-T) \rangle_{ne,-T}$$

The rate of absorption then is

$$\frac{1}{2T} \int_{-T}^T dt \frac{d}{dt} \langle H(t) \rangle_{ne,t}$$

Calculation of this involves a detailed treatment of the initial transient as the field is turned on, the steady state energy absorption while the field is on, and then the final transient as the field is turned off.

A detailed calculation shows that

1. the two transients last for times that are finite and independent of  $T$ . Thus they ultimately make no contribution.
2. between the two transients, the calculation is the same as if the field had always been on.

Thus we can calculate the rate of energy absorption in the following way:

1. we assume that the system is in a steady state under the influence of an oscillatory field
2. we calculate the average, over one cycle of the field, of the quantity

$$\frac{d}{dt}\langle H \rangle_{ne,t} = \frac{d}{dt} \int d\Gamma P(\Gamma, t) H(\Gamma, t) = \frac{d}{dt} \langle H_0 - g(t)B \rangle_{ne,t}$$

But we can write this as

$$\langle \dot{H}_0 - g(t)\dot{B} - \dot{g}(t)B \rangle_{ne,t} = \langle \dot{H}_0 - g(t)\dot{B} \rangle_{ne,t} - \dot{g}(t)\langle B \rangle_{ne,t}$$

At every time,  $t$ , the first term on the right is zero.

This is because the Hamiltonian  $H$  is  $H_0 - g(t)B$ , and the dynamical motion is generated by that Hamiltonian. Dynamical motion conserves the value of the Hamiltonian that generates it.

(The proof is almost identical to the proof of the conservation of energy for a Hamiltonian that is independent of time.)

The net result is: The rate at which energy is absorbed by the system is equal to the average, over one cycle, of the quantity

$$-\dot{g}(t)\langle B \rangle_{ne,t}$$

We are working in the linear response regime, and notice that the variable we need to observe and average is the same as the variable in the time dependent part of the Hamiltonian. Therefore,  $\chi_{BB}$  is involved.

The response of  $\langle B \rangle_{ne,t}$  to an external oscillatory field that couples to  $g$  is given by

$$\langle B \rangle_{ne,t} = g_0 [\cos(\omega t + \phi) \chi'_{BB}(\omega) + \sin(\omega t + \phi) \chi''_{BB}(\omega)]$$

The quantity we want to average, over one cycle, is

$$- (-g_0 \omega \sin(\omega t + \phi)) g_0 (\cos(\omega t + \phi) \chi'_{BB}(\omega) + \sin(\omega t + \phi) \chi''_{BB}(\omega))$$

But  $\sin(\omega t + \phi) \cos(\omega t + \phi) = (1/2) \sin(2(\omega t + \phi))$  is oscillatory and gives zero when averaged over a cycle. On the other hand,  $\sin^2(\omega t + \phi)$  averaged over a cycle gives  $1/2$ . Thus we get that the rate of absorption of energy by the system is

$$R(\omega) = \frac{g_0^2}{2} \omega \chi''_{BB}(\omega)$$

This is also the rate at which mechanical energy in the external field is dissipated into internal energy of the system.

Note that it is only the out-of-phase component of the response (i.e. the component that is out of phase with the applied field) that contributes to the dissipation.

**The relationship to correlation functions.** We showed earlier that the response function is related to the correlation function of fluctuations of the dynamical variables. We want to apply that result to the present situation. In particular, we showed that

$$\chi_{BB}(t) = -\frac{1}{k_B T} \Theta(t) \dot{C}_{\delta B \delta B}(t)$$

We need  $\hat{\chi}''_{BB}(\omega)$ . There is such a close relationship between this and  $C_{\delta B \delta B}(t)$ , that you might think there is a relationship between  $\hat{\chi}''_{BB}(\omega)$  and  $\hat{C}_{BB}(\omega)$ ,

and there is. The procedure of getting this is straightforward.

$$\begin{aligned}
\hat{\chi}_{BB}''(\omega) &= \int_{-\infty}^{\infty} dt \chi_{BB}(t) \sin \omega t \\
&= -\frac{1}{k_B T} \int_{-\infty}^{\infty} dt \Theta(t) \dot{C}_{\delta B \delta B}(t) \sin \omega t \\
&= -\frac{1}{k_B T} \int_0^{\infty} dt \dot{C}_{\delta B \delta B}(t) \sin \omega t \\
&= -\frac{1}{k_B T} \int_0^{\infty} dt \frac{dC_{\delta B \delta B}(t)}{dt} \sin \omega t \\
&= -\frac{1}{k_B T} \left( C_{\delta B \delta B}(t) \sin \omega t \Big|_0^{\infty} - \omega \int_0^{\infty} dt C_{\delta B \delta B}(t) \cos \omega t \right) \\
&= \frac{\omega}{k_B T} \int_0^{\infty} dt C_{\delta B \delta B}(t) \cos \omega t \\
&= \frac{\omega}{2k_B T} \int_0^{\infty} dt C_{\delta B \delta B}(t) (e^{i\omega t} + e^{-i\omega t}) \\
&= \frac{\omega}{2k_B T} \int_{-\infty}^{\infty} dt C_{\delta B \delta B}(t) e^{i\omega t} \\
&= \frac{\omega}{2k_B T} \hat{C}_{\delta B \delta B}(\omega)
\end{aligned}$$

In getting the sixth equality, note that the boundary terms each vanish but for different reasons. At  $t = 0$ , the sine term is zero. At  $t = \infty$ , the correlation function is zero. In getting the eighth equality, we used the fact that the correlation function is an even function of time.

Thus we have that

$$R(\omega) = \frac{g_0^2}{4k_B T} \omega^2 \hat{C}_{\delta B \delta B}(\omega) = \frac{g_0^2}{4k_B T} \omega^2 \int_{-\infty}^{\infty} dt C_{\delta B \delta B}(t) e^{i\omega t}$$

This is one statement of a set of ideas that go by the name of the ‘*fluctuation-dissipation theorem*’. It relates the dissipation of energy from the applied field into the system to the correlation function of fluctuations of the system in the absence of the field.

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### The relationship to correlation functions

We want

$$\hat{\chi}_{BB}''(\omega) = \int_{-\infty}^{\infty} dt \chi_{BB}(t) \sin \omega t$$

From linear response theory for classical systems we know

$$\chi_{BB}(t) = -\frac{1}{k_B T} \Theta(t) \dot{C}_{\delta B \delta B}(t)$$

So we can relate  $\hat{\chi}_{BB}''(\omega)$  to  $C_{\delta B \delta B}(t)$ .

$$\begin{aligned} \hat{\chi}_{BB}''(\omega) &= \int_{-\infty}^{\infty} dt \chi_{BB}(t) \sin \omega t \\ &= -\frac{1}{k_B T} \int_{-\infty}^{\infty} dt \Theta(t) \dot{C}_{\delta B \delta B}(t) \sin \omega t \\ &= -\frac{1}{k_B T} \int_0^{\infty} dt \dot{C}_{\delta B \delta B}(t) \sin \omega t \\ &= -\frac{1}{k_B T} \int_0^{\infty} dt \frac{dC_{\delta B \delta B}(t)}{dt} \sin \omega t \\ &= -\frac{1}{k_B T} \left( C_{\delta B \delta B}(t) \sin \omega t \Big|_0^{\infty} - \omega \int_0^{\infty} dt C_{\delta B \delta B}(t) \cos \omega t \right) \\ &= \frac{\omega}{k_B T} \int_0^{\infty} dt C_{\delta B \delta B}(t) \cos \omega t \\ &= \frac{\omega}{2k_B T} \int_0^{\infty} dt C_{\delta B \delta B}(t) (e^{i\omega t} + e^{-i\omega t}) \\ &= \frac{\omega}{2k_B T} \int_{-\infty}^{\infty} dt C_{\delta B \delta B}(t) e^{i\omega t} \\ &= \frac{\omega}{2k_B T} \hat{C}_{\delta B \delta B}(\omega) \end{aligned}$$

In getting the sixth equality, note that the boundary terms each vanish but for different reasons. At  $t = 0$ , the sine term is zero. At  $t = \infty$ , the correlation function is zero. In getting the eighth equality, we used the fact that the correlation function is an even function of time.

### Final result for the rate of energy absorption

$$R(\omega) = \frac{g_0^2}{4k_B T} \omega^2 \hat{C}_{\delta B \delta B}(\omega) = \frac{g_0^2}{4k_B T} \omega^2 \int_{-\infty}^{\infty} dt C_{\delta B \delta B}(t) e^{i\omega t}$$

This is one statement of a set of ideas that go by the name of the

*‘fluctuation-dissipation theorem’*

It relates the dissipation of energy from the applied field into the system to the correlation function of fluctuations of the system in the absence of the field.

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Comments.

- Note the presence of the additional two powers of  $\omega$ . In order for the field to do any work on the system, the field must be changing with time and the system must be changing with time. Therefore, the mere fact that  $\hat{C}(\omega)$  is nonzero does not necessarily mean that the field can dissipate energy at that frequency, especially for very low frequency.
- Note the two powers of  $g_0$ . The leading term in the dissipation is quadratic in the applied field. This is because the applied field is linear in  $g_0$  and the response to the field is linear in  $g_0$ , and the dissipation is accomplished by the work of the field against the response that it generates in the system. The field does no work against the existing average of  $B$  in the system.
- Many spectroscopic experiments are direct or indirect measurements of  $R(\omega)$ . Thus, they in effect measure the Fourier transform of the autocorrelation function of  $\delta B$ .
- From the Second Law of Thermodynamics, we expect that  $R(\omega) \geq 0$  for all  $\omega$ . If this is to be true, then this suggests that the correlation function  $C_{\delta B \delta B}(t)$  must be such that its Fourier transform is positive semidefinite at all frequencies. This is a pretty strong statement, but it is possible to show that under very general circumstances it is correct.

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$$R(\omega) = \frac{g_0^2}{4k_B T} \omega^2 \hat{C}_{\delta B \delta B}(\omega) = \frac{g_0^2}{4k_B T} \omega^2 \int_{-\infty}^{\infty} dt C_{\delta B \delta B}(t) e^{i\omega t}$$

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2. Note the two powers of  $g_0$ . The applied field is linear in  $g_0$ , and the response to the field is linear in  $g_0$ . The dissipation is accomplished by the work of the field against the response that it generates in the system. The field does no work against the preexisting equilibrium average of  $B$  in the system.
3. Many spectroscopic experiments are direct or indirect measurements of  $R(\omega)$ . Thus, they in effect measure the Fourier transform of the autocorrelation function of  $\delta B$ .
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**Theorem.** Let  $A(\Gamma)$  be a real dynamical variable and let  $\langle \dots \rangle$  denote the average over an equilibrium ensemble. Then  $\langle A(t)A(t') \rangle$  is stationary, i.e. it is a function of  $t - t'$ , not the two times individually. Suppose that  $\langle A \rangle = 0$  and  $\langle A(t)A(t') \rangle \rightarrow 0$  as  $t - t' \rightarrow \infty$ . Then  $\hat{C}_{AA}(\omega) \geq 0$  for all  $\omega$ .

**Proof.** Consider, for any one system in the ensemble, the following quantity.

$$\int_{-T}^T dt e^{i\omega t} A(t)$$

Then

$$\frac{1}{2T} \left| \int_{-T}^T dt e^{i\omega t} A(t) \right|^2 \geq 0$$

Take the ensemble average of both sides.

$$\frac{1}{2T} \left\langle \left| \int_{-T}^T dt e^{i\omega t} A(t) \right|^2 \right\rangle \geq 0$$

$$\frac{1}{2T} \left\langle \int_{-T}^T dt_1 \int_{-T}^T dt_2 e^{i\omega(t_1-t_2)} A(t_1)A(t_2) \right\rangle \geq 0$$

$$\frac{1}{2T} \int_{-T}^T dt_1 \int_{-T}^T dt_2 e^{i\omega(t_1-t_2)} \langle A(t_1)A(t_2) \rangle \geq 0$$

$$\frac{1}{2T} \int_{-T}^T dt_1 \int_{-T}^T dt_2 e^{i\omega(t_1-t_2)} C_{AA}(t_1 - t_2) \geq 0$$

We have seen integrals like this in our discussion of Brownian motion. Let's consider the way it behaves in the limit  $T \rightarrow \infty$ . It must be true that

$$\lim_{T \rightarrow \infty} \frac{1}{2T} \int_{-T}^T dt_1 \int_{-T}^T dt_2 e^{i\omega(t_1-t_2)} C_{AA}(t_1 - t_2) \geq 0$$

For large  $T$ , we convert the  $t_2$  integration into an integration over  $t_1 - t_2$ . We can eliminate the limits on that integration because the correlation function is zero for large time argument. We get a factor of  $\hat{C}_{AA}(\omega)$ , which comes outside the integral. The remaining  $t_1$  integration gives  $2T$  which cancels the  $1/2T$ . We get

$$\hat{C}_{AA}(\omega) \geq 0$$

Q.E.D.

## 2 Classical theory of the absorption of electromagnetic radiation

### 2.1 Application of the fluctuation-dissipation theorem

Now let's consider the case that the external field is an electromagnetic field. Such a field consists of a combination of an electric field  $\mathbf{E}(t)$  and a magnetic field  $\mathbf{H}(t)$ . The former interacts with electric dipole moments of the system and the latter interacts with magnetic dipoles. (Each field can also interact with quadrupoles, but this interaction is usually weaker.) Whenever the electric interaction is nonzero because of the presence of electric dipole moments, it is usually the dominant interaction.

Let's restrict attention to radiation that is in the visible region of the spectrum and to lower frequencies (ir, far ir, microwave). (Higher frequency radiation usually interacts with degrees of freedom that are intrinsically quantum mechanical at ordinary temperatures, so the classical theory would not be accurate. It is problematic to use the classical theory even in the visible region, but let's do it anyway because we will learn something.

In this range of frequencies the wavelength of the radiation is much longer than microscopic lengths. It is of the order of thousands of Angstroms or longer. Thus, in the vicinity of any one molecule or group of molecules, the electric field is independent of position (but it does depend on time). A useful way of thinking about a physical system is to carve it up into regions whose size is large compared with one molecule but still small compared with a wavelength. Then regard each region as the 'system' to which we apply statistical mechanics. Each such system has a Hamiltonian of the form

$$H = H_0(\Gamma) - \mathbf{E}(t) \cdot \boldsymbol{\mu}(\Gamma)$$

where  $\boldsymbol{\mu}$  is the electric dipole moment of the system (i.e. of the small region under consideration). We are evaluating the field at the center of the region, and the position is not indicated, but the same field applies to the entire region.

Let's simplify the discussion a little by assuming that the electric field is polarized in one direction, say the  $x$  direction. Then we have

$$H = H_0(\Gamma) - E_x(t)\mu_x(\Gamma)$$

In a typical (cw) absorption experiment, the electric field varies sinusoidally with time. We observe the absorption of energy by the system in various ways depending on the type of spectroscopy.

- For visible light and infrared radiation, we usually monitor the diminution of the intensity of the radiation as it passes through the sample.
- For microwave radiation, we usually monitor the power drained from the electrical circuit that generates the radiation.

Let's suppose that we have figured out how to relate the quantity actually measured to  $R(\omega)$ , the rate at which the region absorbs energy from the field, as a function of frequency.

Then the fluctuation-dissipation theorem says that  $R(\omega)$  is closely related to the correlation function of the dipole moment of the region.

$$R(\omega) \propto \omega^2 \hat{C}_{\delta\mu_x \delta\mu_x}(\omega)$$

For most samples of interest, the average dipole moment is zero so we have

$$R(\omega) \propto \omega^2 \hat{C}_{\mu_x \mu_x}(\omega)$$

Here  $\mu_x$  is a function of  $\Gamma$ , i.e. of all the coordinates and momenta needed to specify the mechanical state of one of the regions.

In order to use this result, we need to know how  $\mu_x$  depends on  $\Gamma$ . The answer depends on the specific type of system involved. Let's discuss some specific examples.

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The external field is an electromagnetic field.

It is a combination of an electric field  $\mathbf{E}(t)$  and a magnetic field  $\mathbf{H}(t)$ .

$\mathbf{E}(t)$  interacts with the electric dipole moment of the system.

$\mathbf{H}(t)$  interacts with the magnetic dipole moment.

Each field can also interact with quadrupoles, but this interaction is usually weaker.

Whenever the electric interaction is nonzero, it is usually the dominant interaction.

Let's restrict attention to

- the electric interaction
- radiation that is in the visible region of the spectrum and lower frequencies (ir, far ir, microwave).

In this range of frequencies the wavelength is of the order of thousands of Angstroms or longer.

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where  $\boldsymbol{\mu}$  is the electric dipole moment of the system (i.e. of the small region under consideration). We are evaluating the field at the center of the region, and the position is not indicated, but the same field applies to the entire region.

Restrict attention to the case that the electric field is polarized in one direction, say the  $x$  direction.

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For most samples of interest, the average dipole moment is zero so we have

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In order to use this result, we need to know how  $\mu_x$  depends on  $\Gamma$ . The answer depends on the specific type of system involved. Let's discuss some specific examples.

### Comment

- The correlation function of interest is an autocorrelation function.
- Therefore it is symmetric under change of the sign of time.

$$C(t) = C(-t)$$

- Therefore its Fourier transform is equal to its cosine transform.

$$\int_{-\infty}^{\infty} dt C(t) e^{-i\omega t} = \int_{-\infty}^{\infty} dt C(t) \cos \omega t$$

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## 2.2 A gas or liquid of rigid molecules with electric dipoles

### 2.2.1 The correlation function for the experiment

Suppose the material is a gas or liquid of rigid molecules with permanent electric dipole moments. The molecules might be linear or nonlinear. Let's

assume that there is only one species of molecule. Let's also assume that the total dipole moment of a collection of molecules is of the following simple form:

$$\mu(\Gamma) = \mu \sum_{i=1}^N \hat{\mathbf{u}}_i$$

where  $\mathbf{u}_i$  is a unit vector along the direction of the dipole moment of the  $i$ th linear molecule. Then the  $x$  component of this is

$$\mu_x(\Gamma) = \mu \sum_{i=1}^N \hat{u}_{ix}$$

Then the correlation function of interest is

$$C_{\mu_x \mu_x}(t) = \langle \mu_x(t) \mu_x(0) \rangle = \mu^2 \sum_{i,j=1}^N \langle \hat{u}_{ix}(t) \hat{u}_{jx}(0) \rangle$$

Let's discuss two immediate consequences of this formula, some of which are familiar to you but others of which may not be.

- If  $\mu$  were zero, there would be no absorption.
- The correlations to which the absorption experiment are sensitive are of two types:
  - correlations of the orientation of a molecule at time 0 with the orientation of the *same* molecule at time  $t$ ;
  - correlations of the orientation of a molecule at time 0 with the orientation of a *different* molecule at time  $t$ .

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**Gas or liquid of rigid molecules with permanent electric dipole moments.** The molecules might be linear or nonlinear.

Consider a one component system.

Assume that the total dipole moment of a collection of molecules is of the simple form:

$$\mu(\Gamma) = \mu \sum_{i=1}^N \hat{\mathbf{u}}_i$$

where  $\mathbf{u}_i$  is a unit vector along the direction of the dipole moment of the  $i$ th linear molecule.

The  $x$  component is

$$\mu_x(\Gamma) = \mu \sum_{i=1}^N \hat{u}_{ix}$$

The correlation function of interest is

$$C_{\mu_x \mu_x}(t) = \langle \mu_x(t) \mu_x(0) \rangle = \mu^2 \sum_{i,j=1}^N \langle \hat{u}_{ix}(t) \hat{u}_{jx}(0) \rangle$$

Two immediate consequences:

- If  $\mu$  were zero, there would be no absorption.
- The correlations to which the absorption experiment are sensitive are of two types:
  - correlations of the orientation of a molecule at time 0 with the orientation of the *same* molecule at time  $t$ ;
  - correlations of the orientation of a molecule at time 0 with the orientation of a *different* molecule at time  $t$ .

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### 2.2.2 Self and collective correlations

The latter point is especially important, especially since it is likely that many of you have not come across this idea before. It turns out that many different spectroscopic experiments measure correlations between properties of the same molecule and between properties of two different molecules, whereas many others measure correlations between properties of the *same* molecule *only*. Correlations of properties of the same molecule at two times are often called self correlations. Correlations of properties of two different molecules are often called collective correlations. Whenever you develop the theory of what any type of measurement is actually measuring, it is important to note whether it measures self correlations only or whether it also measures

collective correlations. The absorption of electromagnetic radiation by the electric dipole mechanism in general measures both self and collective correlations.

We can separately consider the two different types of correlations.

$$C_{\mu_x\mu_x}(t) = N\mu^2\langle\hat{u}_{1x}(t)\hat{u}_{1x}(0)\rangle + N(N-1)\mu^2\langle\hat{u}_{1x}(t)\hat{u}_{2x}(0)\rangle$$

Let's consider two different situations.

- A dilute gas. In a dilute gas, the molecules are far apart from one another most of the time and hence they do not interact most of the time. To lowest order in the density, there are in fact no correlations among different molecules, so

$$\langle\hat{u}_{1x}(t)\hat{u}_{2x}(0)\rangle \approx 0$$

We get

$$C_{\mu_x\mu_x}(t) = N\mu^2\langle\hat{u}_{1x}(t)\hat{u}_{1x}(0)\rangle$$

Only the self correlations are important for a dilute gas.

- A dense liquid. Let's estimate the magnitude of the two terms for a dense liquid. Let's start by considering  $t = 0$ . Then

$$\langle\hat{u}_{1x}(0)\hat{u}_{1x}(0)\rangle = \langle(\hat{u}_{1x}(0))^2\rangle = 1/3$$

since  $\mathbf{u}_1 \cdot \mathbf{u}_1 = 1$  and the averages for each of the three directions are equal. So the first term is equal to

$$N\mu^2/3$$

where  $N$  is the number of molecules in the region under consideration. The other average is

$$\langle\hat{u}_{1x}(0)\hat{u}_{2x}(0)\rangle$$

What do we expect the magnitude of this to be? We might expect that molecules are correlated with one another only when they are close together, say within a certain distance  $\Delta$  of one another. Here  $\Delta$  might be of the order of the length of the molecule. Even when they are that close, they are not necessarily perfectly aligned. Let's suppose that when they are close together, the value of  $\hat{u}_{1x}\hat{u}_{2x}$  is about

$c$ , on the average. (We expect  $c$  to be smaller than  $1/3$ , perhaps it is much smaller than this.) The region of interest contains  $N$  molecules, and if the density is  $n$ , then the volume of the region must be such that  $N/V = n$  or  $V = N/n$ . Thus an estimate of  $\langle \hat{u}_{1x}(0)\hat{u}_{2x}(0) \rangle$  is approximately  $c(\Delta^3/V) = c(n\Delta^3/N)$ , i.e. it is  $c$  multiplied by a factor that takes into account that the two molecules spend only part of their time close enough together to be correlated with one another. Thus the second term in the correlation function has a magnitude, at time 0, of about

$$N(N-1)\mu^2 c(n\Delta^3/N) \approx N\mu^2 cn\Delta^3$$

The ratio of the second term to the first term is

$$\frac{N\mu^2 cn\Delta^3}{N\mu^2/3} = \left(\frac{c}{3}\right) n\Delta^3$$

The first factor is less than 1, but the second factor represents approximately the number of neighbors of a molecule that have their orientation aligned with the molecule.

The net conclusion is that there is no reason to think that we can neglect the collective correlations in the case of a dense liquid. At  $t = 0$ , the zero time values of the two contributions to the correlation function might in fact be similar in magnitude.

It is hard, in general, to know what to expect about the time dependence. Some simple models of molecular motion predict that the collective correlations decay to zero somewhat more rapidly than the self correlations, but in general there is no reason to think that they decay so quickly that they give no contribution to the Fourier transform of the correlation function at the frequencies of interest. Moreover, other simple models predict that the two types of correlations decay in a very similar way.

*slide*

**Self and collective correlations.** Many different spectroscopic experiments measure correlations

- between properties of the same molecule *and* between properties of molecules

whereas many others measure correlations

- between properties of the *same* molecule *only*.

Correlations of properties of the same molecule at two times are often called *self correlations*. (The word *incoherent* is used in some contexts.)

Correlations of properties of two different molecules are often called *collective correlations*. (The word *coherent* is used in some contexts.)

The absorption of electromagnetic radiation by the electric dipole mechanism in general measures both self and collective correlations.

$$C_{\mu_x\mu_x}(t) = N\mu^2\langle\hat{u}_{1x}(t)\hat{u}_{1x}(0)\rangle + N(N-1)\mu^2\langle\hat{u}_{1x}(t)\hat{u}_{2x}(0)\rangle$$

**A dilute gas.** The molecules are far apart from one another most of the time and hence they do not interact most of the time.

To lowest order in the density, there are in fact no correlations among different molecules, so

$$\langle\hat{u}_{1x}(t)\hat{u}_{2x}(0)\rangle \approx 0$$

We get

$$C_{\mu_x\mu_x}(t) = N\mu^2\langle\hat{u}_{1x}(t)\hat{u}_{1x}(0)\rangle$$

Only the self correlations are important for a dilute gas.

$$C_{\mu_x\mu_x}(t) = N\mu^2\langle\hat{u}_{1x}(t)\hat{u}_{1x}(0)\rangle + N(N-1)\mu^2\langle\hat{u}_{1x}(t)\hat{u}_{2x}(0)\rangle$$

**A dense liquid.** Let's estimate the magnitudes of the two terms for a dense liquid.

Consider  $t = 0$ .

The first average is

$$\langle\hat{u}_{1x}(0)\hat{u}_{1x}(0)\rangle = \langle(\hat{u}_{1x}(0))^2\rangle = 1/3$$

since  $\mathbf{u}_1 \cdot \mathbf{u}_1 = 1$  and the averages for each of the three directions are equal. The first term is equal to

$$N\mu^2/3$$

where  $N$  is the number of molecules in the region under observation.

The second average is  $\langle \hat{u}_{1x}(0)\hat{u}_{2x}(0) \rangle$ .

We expect

- molecules are correlated with one another only when they are close together, say within a certain distance  $\Delta$  of one another. Here  $\Delta$  might be of the order of the length of the molecule.
- even when they are that close, they are not necessarily perfectly aligned.

Suppose that when they are close together, the value of  $\hat{u}_{1x}\hat{u}_{2x}$  is about  $c$ , on the average. (We expect  $c$  to be smaller than  $1/3$ , perhaps it is much smaller than this.)

Hence

$$\langle \hat{u}_{1x}(0)\hat{u}_{2x}(0) \rangle \approx c\Delta^3/V$$

where  $\Delta^3/V$  is the probability that molecule 2 is in a volume  $\Delta^3$  about molecule 1.

The second term is approximately  $N(N-1)\mu^2c\Delta^3/V \approx N\mu^2c\Delta^3n$ ,

where  $n = N/V$  is the density.

The ratio of the second term to the first term is

$$\frac{N\mu^2c\Delta^3n}{N\mu^2/3} = \left(\frac{c}{3}\right)n\Delta^3$$

The first factor is less than 1, but the second factor represents approximately the number of neighbors of a molecule that have their orientation aligned with the molecule.

There is no reason to think that we can neglect the collective correlations in the case of a dense liquid.

At  $t = 0$ , the zero time values of the two contributions to the correlation function might in fact be similar in magnitude.

Little is known about the relative time dependence of the two terms.

*end of slide*

### 2.2.3 Qualitative discussion of the correlation function

Let's now discuss qualitatively what the correlation function looks like. For the sake of simplicity, we shall assume that the collective correlations are either negligible or that they decay with the same time dependence as the self correlations.

Since the classical rotational motion of a rigid nonlinear molecule is actually quite complicated to describe, let's restrict attention to a linear molecule. The dipole moment of the molecule is along the axis of the molecule. (Much of our discussion will also be applicable to a nonlinear molecules with an axis of rotational symmetry, such that the dipole moment is along the symmetry axis.)

**Dilute gas of linear molecules in the absence of collisions.** A linear molecule rotates so that its axis and its dipole moment are perpendicular to its fixed angular momentum. Any one molecule will have

$$\mu_x(t) = \mu f(\hat{\mathbf{J}}) \cos(\omega' t + \phi)$$

where:

- $\mu$  is the magnitude of the dipole moment of a molecule
- $\omega'$  is the magnitude of the rotational frequency of the molecule
- $\phi$  is the phase angle for the rotation of the molecule
- $\hat{\mathbf{J}}$  is a unit vector in the direction of the angular momentum
- $f(\hat{\mathbf{J}})$  is some function of  $\hat{\mathbf{J}}$ .

Thus

$$\begin{aligned} \mu_x(t)\mu_x(0) &= (\mu f(\hat{\mathbf{J}}))^2 \cos(\omega' t + \phi) \cos \phi \\ &= \frac{1}{2} (\mu f(\hat{\mathbf{J}}))^2 (\cos \omega' t + \cos(\omega' t + 2\phi)) \end{aligned}$$

This is an oscillatory function of time and it depends on what the  $\omega'$  and  $\phi$  happen to be. But no matter what the values are, it is positive at  $t = 0$ . If  $\omega'$  is large, it oscillates rapidly. If  $\omega'$  is small, it oscillates slowly. The

correlation function, in the absence of collisions, is an average of this over all relevant, thermally possible, values of  $\omega'$ ,  $\hat{\mathbf{J}}$ ,  $\phi$ .

$$\begin{aligned} & \langle \mu_x(t) \mu_x(0) \rangle \\ &= \int_0^\infty d\omega' \int d\hat{\mathbf{J}} \int_0^{2\pi} d\phi P(\omega', \hat{\mathbf{J}}, \phi) \frac{1}{2} (\mu f(\hat{\mathbf{J}}))^2 (\cos \omega' t + \cos(\omega' t + 2\phi)) \end{aligned}$$

where  $P$  is the probability distribution of  $\omega'$ ,  $\hat{\mathbf{J}}$ ,  $\phi$ .

But the probability distribution does not depend on the value of  $\phi$ .

$$P(\omega', \hat{\mathbf{J}}, \phi) = \frac{1}{2\pi} P(\omega', \hat{\mathbf{J}})$$

where  $P(\omega', \hat{\mathbf{J}})$  is the probability distribution of  $\omega'$ ,  $\hat{\mathbf{J}}$ . All phase angles are equally likely. So the angle integration makes the second term zero.

$$\begin{aligned} \langle \mu_x(t) \mu_x(0) \rangle &= \int_0^\infty d\omega' \cos(\omega' t) \int d\hat{\mathbf{J}} P(\omega', \hat{\mathbf{J}}) \frac{1}{2} (\mu f(\hat{\mathbf{J}}))^2 \\ &= \int_0^\infty d\omega' \cos(\omega' t) P(\omega') \end{aligned}$$

where

$$P(\omega') = \int d\hat{\mathbf{J}} P(\omega', \hat{\mathbf{J}}) \frac{1}{2} (\mu f(\hat{\mathbf{J}}))^2$$

Then

$$C_{\mu_x \mu_x}(t) = N \langle \mu_x(t) \mu_x(0) \rangle$$

**Side discussion - doing a certain type of integral by inspection.**

Consider

$$f(t) = \int_{-\infty}^{\infty} d\omega \cos(\omega t) F(\omega)$$

where  $F(\omega)$  is reasonably smooth and  $F(\omega) \geq 0$ .

Properties of the integral:

$$f(0) = \int_a^b d\omega F(\omega) \geq 0$$

$$|f(t)| = \left| \int_a^b d\omega \cos(\omega t) F(\omega) \right| = \int_a^b d\omega |\cos(\omega t)| F(\omega) \leq \int_a^b d\omega F(\omega) = f(0)$$

$f(t)$  is an even function of  $t$ .

The function has its maximum value at  $t = 0$ .

Its magnitude for  $t \neq 0$  is less than its value at  $t = 0$ .

As  $t \rightarrow \pm\infty$ ,  $f(t)$  goes to zero because of extensive cancellation due to the oscillation of the cosine factor.

*Important special case:* Suppose  $F(\omega)$  is large primarily for  $|\omega| \leq \Delta\omega$ .

Then  $f(t) \approx f(0)$  for  $|t| \ll 1/\Delta\omega$ .

$|f(t)|$  is significantly less than  $f(0)$  for  $(\Delta\omega)t = \pi$ .

Consider the time dependence of this function.

- It is an even function of time  $t$ . (This is expected for autocorrelation functions.)
- It is clearly at its largest for  $t = 0$ .
- As time increases from zero, there is cancellation among the contributions of different values of  $\omega'$ .

**Back to the linear molecules.** What is the range of frequencies  $\Delta\omega_r$  that are relevant for the molecular rotation at any given temperature?

I.e. for what range of  $\omega'$  is  $P(\omega') \neq 0$ ?

Estimate:

- the lowest frequency is about zero
- the highest is such that  $I\omega^2/2$ , where  $I$  is the moment of inertia, is about  $k_B T$ .

Thus,  $\Delta\omega_r \approx (2kT/I)^{1/2}$ .

The average is likely to be a function that decays to zero monotonically because of the dephasing of the various components with different  $\omega'$ . But the time for the decay of the function will be of the order of the reciprocal of  $\Delta\omega_r$ .

The correlation function will then have a maximum at  $t = 0$  and will fall off to zero for times larger than about  $1/\Delta\omega_r$ .

We need the Fourier transform of the correlation function to get the spectrum.

**Side discussion: doing a second type of integral by inspection** We want

$$\hat{f}(\omega) = \int_{-\infty}^{\infty} dt \cos \omega t f(t)$$

where  $f(t)$  is an even function of  $t$  and is large primarily for  $|t| < \Delta t$ .

$\hat{f}(\omega)$  is large primarily for  $|\omega| < \pi/\Delta t$ .

**Back to linear molecules.** The Fourier transform of the correlation function then

- has its maximum at or near  $\omega = 0$
- falls off to zero for frequencies much larger than about  $\Delta\omega_r$ .

To get  $R(\omega)$ , we multiply by  $\omega^2$ . The result will

- be zero at zero frequency
- then rise to a maximum at about  $\Delta\omega_r$ .
- then fall off.

This is the classical prediction for the rotational absorption spectrum of a linear molecule (or of a molecule with an axis of rotational symmetry) in the absence of collisions. There is a broad featureless peak, whose width is of the order of the frequency of its maximum. This prediction has much in common with the quantum mechanical prediction, provided the spacing of rotational lines is much smaller than  $\Delta\omega_r$ , which is the condition that many rotational eigenstates are thermally populated.

The value of  $1/\Delta\omega_r$  corresponds to the time it takes for the most rapidly rotating molecules to rotate by about  $\pi$ .

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**Dilute gas in the presence of collisions.** The effect of collisions will be to interrupt the free rotation of the molecule. A collision has several effects.

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- It changes the direction of the angular momentum. This affects the amplitude of the oscillation of the dipole moment along any particular coordinate axis.
- It changes the magnitude of the angular momentum, thus changing the frequency with which the rotation takes place. This leads the dipole moment to become uncorrelated with its value at zero time.
- It changes the phase of the rotation. This also leads the dipole moment to become uncorrelated with its value at zero time.

The net effect of these is to make the correlation function decay slightly more quickly. But the correlation function already decays very quickly. For a dilute gas, the time between collisions is much longer than the time it takes a molecule to rotate. Thus, collisions will not have much effect on the lineshape for absorption.<sup>3</sup>

**Rotational Brownian motion.** A much more drastic effect on the spectrum occurs when the density is increased enough so that the material becomes a liquid. In this case, free rotation of an isolated molecule is not a good first approximation. A molecule can be trapped in a particular orientation, with only minor freedom to rotate, for long periods of time. This type of motion is often described as rotational Brownian motion, something that we shall discuss later in the course. The net result is that the molecule's orientation remains roughly parallel to its original orientation for long periods of time. The dipole moment correlation function decays *much more slowly* than in a gas phase. Hence the Fourier transform moves to lower frequencies. In general this means that the absorption moves from the microwave region to lower frequencies.

*slide*

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<sup>3</sup>Note that this is the classical result. Quantum mechanically, the absorption spectrum is a set of sharp rotational lines. Collisions will broaden these lines so that they will tend to merge together, but this will not have much effect on the overall envelope of the bunch of lines. It is this envelope that corresponds to the classical prediction.

**Rotational Brownian motion.** Consider a dense liquid.

Free rotation of an isolated molecule is not a good first approximation.

A molecule can be trapped in a particular orientation, with only minor freedom to rotate, for long periods of time.

This type of motion is often described as rotational Brownian motion, something that we shall discuss later in the course.

The net result is that the molecule's orientation remains roughly parallel to its original orientation for long periods of time.

The dipole moment correlation function decays *much more slowly* than in a gas phase.

Hence the Fourier transform moves to lower frequencies.

In general this means that the absorption moves from the microwave region to lower frequencies.

*end of slide*

### 2.3 A gas or liquid of vibrating molecules

In the previous discussion, we assumed that each molecule had a dipole moment that was constant in a molecule fixed frame of reference, but whose laboratory components varied with time as the molecule rotates.

In addition, there can be a part of the dipole moment of a molecule that varies as the molecule vibrates.

As before, let's restrict our attention to molecules that are linear. Much of what we say will also be applicable to molecules that have an axis of rotational symmetry or that have less symmetry.

The vibration-induced part of the dipole moment might be along the symmetry axis of the molecule or it might be perpendicular to the symmetry axis.

Let's consider the special case that the vibration-induced part is along the symmetry axis of the molecule.

Then the dipole moment of a molecule is of the form

$$\hat{\mathbf{u}}_i (\mu_0 + \mu_1 \xi_i)$$

where  $\xi$  is the amplitude of the vibrational normal mode of interest.  $\mu_0$  is the dipole moment for the nonvibrating molecules, and  $\mu_1$  is the derivative of the dipole moment with regard to the normal coordinate.

The total  $x$  component of the dipole moment of a collection of molecules in a region then is

$$\mu_x(\Gamma) = \sum_{i=1}^N \hat{u}_{ix} (\mu_0 + \mu_1 \xi_i)$$

The correlation function that we need is

$$\langle \mu_x(t) \mu_x(0) \rangle$$

When the previous expression is substituted into this one, we get a variety of types of terms. They can be categorized in two ways:

- according to the two molecules involved:
  - self correlations
  - collective correlations
- according to the degrees of freedom involved
  - terms involving no vibrational coordinates
  - terms involving a vibrational coordinate at one time
  - terms involving vibrational coordinates at both times.

Here we do not want to go through a complete analysis of all the terms. Let's just make a few comments.

- The terms with no vibrational coordinates are exactly of the type we have already considered. These in general give rise to absorption in the microwave region or at lower frequencies. These contributions are in general not negligible (if  $\mu_0 \neq 0$ ). They include both self and collective correlations, except for gases, in which the collective correlations are small or negligible.

- In many cases of interest, the amplitude of vibrational motion is small, so there is little interaction between the vibrational motion and the other degrees of freedom of a molecule. Moreover, the time scale for vibrational motion is much smaller than that for rotation. This means that the vibrational coordinate of a molecule is statistically independent of the other degrees of freedom of the system, which make lots of terms zero.

– Terms with one vibrational coordinate. E.g.

$$\langle \mu_0 \hat{u}_{1x}(t) \mu_1 \hat{u}_{1x}(0) \xi_1(0) \rangle \approx \mu_0 \mu_1 \langle \hat{u}_{1x}(t) \hat{u}_{1x}(0) \rangle \langle \xi_1(0) \rangle = 0$$

since  $\langle \xi_1(t) \rangle = 0$ .

– Terms with two vibrational coordinates on different molecules.

$$\langle \mu_1 \hat{u}_{1x}(t) \xi_1(t) \mu_1 \hat{u}_{2x}(0) \xi_2(0) \rangle \approx \mu_1^2 \langle \hat{u}_{1x}(t) \hat{u}_{2x}(0) \rangle \langle \xi_1(t) \rangle \langle \xi_2(0) \rangle = 0$$

- The only remaining terms are those that have two vibrational coordinates on the same molecule. These terms are

$$N \mu_1^2 \langle \hat{u}_{1x}(t) \xi_1(t) u_{1x}(0) \xi_1(0) \rangle \approx N \mu_1^2 \langle \hat{u}_{1x}(t) u_{1x}(0) \rangle \langle \xi_1(t) \xi_1(0) \rangle$$

These terms have a vibrational correlation function, which oscillates with the frequency of the vibration. This makes the Fourier transform large only for frequencies near the vibrational frequency, usually in the infrared. Thus, the high frequency (infrared, vibrational) part of the spectrum is determined only by self correlations, not collective correlations.

Let's consider the latter terms in a little more detail. The rotational correlation function that appears here is exactly the same as the self correlation function that is applicable to the pure rotational spectrum. Let's assume that the vibrational coordinate is perfectly harmonic and undamped. Then the vibrational correlation function is proportional to  $\cos \omega_1 t$ , where  $\omega_1$  is the vibrational frequency. But we can write

$$\cos \omega_1 t = (1/2)(e^{i\omega_1 t} + e^{-i\omega_1 t})$$

The Fourier transform of the correlation function then has peaks at  $\omega = \pm\omega_1$  with width of  $\Delta\omega_r$ . Multiplication by  $\omega^2$  changes the intensity but does not

affect the shape of the spectrum (unlike the case of a spectrum centered at  $\omega = 0$ ).

Vibrational relaxation can broaden the line somewhat. Moreover, vibration-rotation interaction can change the shape slightly. Going to a liquid will cause the rotational part of the correlation function to decay more slowly, which makes the line shape narrow considerably.

*slides*

### **A gas or liquid of vibrating molecules**

Previous discussion: we considered that each molecule had a dipole moment that was constant in a molecule fixed frame of reference, but whose laboratory components varied with time as the molecule rotates.

Now consider: In addition, there can be a part of the dipole moment of a molecule that varies as the molecule vibrates.

Restrict our attention to molecules that are linear.

The vibration-induced part of the dipole moment might be along the symmetry axis of the molecule or it might be perpendicular to the symmetry axis or it might be in some other direction.

Consider the special case that the vibration-induced part is along the symmetry axis of the molecule.

Then the dipole moment of a molecule is of the form

$$\hat{\mathbf{u}}_i (\mu_0 + \mu_1 \xi_i)$$

where

$\xi$  is the amplitude of the vibrational normal mode of interest.

$\mu_0$  is the dipole moment for the nonvibrating molecules,

$\mu_1$  is the derivative of the dipole moment with regard to the normal coordinate.

The total  $x$  component of the dipole moment of a collection of molecules in a region is

$$\mu_x(\Gamma) = \sum_{i=1}^N \hat{u}_{ix} (\mu_0 + \mu_1 \xi_i)$$

The correlation function that we need is

$$\langle \mu_x(t) \mu_x(0) \rangle$$

We get a variety of types of terms. They can be categorized in two ways:

- according to the two molecules involved:
  - self correlations
  - collective correlations
- according to the degrees of freedom involved
  - terms involving no vibrational coordinates
  - terms involving a vibrational coordinate at one time
  - terms involving vibrational coordinates at both times.

Just a few comments.

- The terms with no vibrational coordinates give rise to absorption in the microwave region or at lower frequencies.
- In many cases of interest, the amplitude of vibrational motion is small.

There is little interaction between the vibrational motion and the other degrees of freedom of a molecule.

The time scale for vibrational motion is much smaller than that for rotation.

The vibrational coordinate of a molecule is approximately statistically independent of the other degrees of freedom of the system, which make lots of terms zero.

- Terms with one vibrational coordinate. E.g.

$$\langle \mu_0 \hat{u}_{1x}(t) \mu_1 \hat{u}_{1x}(0) \xi_1(0) \rangle \approx \mu_0 \mu_1 \langle \hat{u}_{1x}(t) \hat{u}_{1x}(0) \rangle \langle \xi_1(0) \rangle = 0$$

since  $\langle \xi_1(t) \rangle = 0$ .

- Terms with two vibrational coordinates on different molecules.

$$\langle \mu_1 \hat{u}_{1x}(t) \xi_1(t) \mu_1 \hat{u}_{2x}(0) \xi_2(0) \rangle \approx \mu_1^2 \langle \hat{u}_{1x}(t) \hat{u}_{2x}(0) \rangle \langle \xi_1(t) \rangle \langle \xi_2(0) \rangle = 0$$

- The only remaining terms are those that have two vibrational coordinates on the same molecule. These terms are

$$N \mu_1^2 \langle \hat{u}_{1x}(t) \xi_1(t) u_{1x}(0) \xi_1(0) \rangle \approx N \mu_1^2 \langle \hat{u}_{1x}(t) u_{1x}(0) \rangle \langle \xi_1(t) \xi_1(0) \rangle$$

These terms

- have a vibrational correlation function, which oscillates with the frequency of the vibration.
- make the Fourier transform have intensity at higher frequencies, usually in the infrared.

Thus, the high frequency (infrared, vibrational) part of the spectrum is determined only by self correlations, not collective correlations.

**More examples of doing Fourier transforms by inspection.** Let  $f(t)$  be a function of time. Its Fourier transform is

$$\hat{f}(\omega) = \int_{-\infty}^{\infty} dt e^{i\omega t} f(t)$$

Let's suppose you know the shape of this function.

*Example 1.* Consider the function

$$g(t) \equiv e^{i\omega_0 t} f(t)$$

What is its Fourier transform?

$$\hat{g}(\omega) = \int_{-\infty}^{\infty} dt e^{i\omega t} e^{i\omega_0 t} f(t) = \int_{-\infty}^{\infty} dt e^{i(\omega+\omega_0)t} f(t) = \hat{f}(\omega + \omega_0)$$

This function has the same 'shape' as  $\hat{f}(\omega)$  but it is shifted to the left by an amount  $\omega_0$ .

*Example 2.* Consider the function

$$g(t) \equiv e^{-i\omega_0 t} f(t)$$

Its Fourier transform is

$$\hat{g}(\omega) = \hat{f}(\omega - \omega_0)$$

This function has the same 'shape' as  $\hat{f}(\omega)$  but it is shifted to the right by an amount  $\omega_0$ .

*Example 3.* Consider the function

$$g(t) \equiv f(t) \cos \omega_0 t = \frac{1}{2} (e^{i\omega_0 t} + e^{-i\omega_0 t})$$

Its Fourier transform is the average of the previous two.

$$\hat{g}(\omega) = \frac{1}{2} (\hat{f}(\omega + \omega_0) + \hat{f}(\omega - \omega_0))$$

It is as if half of the intensity of  $\hat{f}$  has been shifted to the left by an amount  $\omega_0$  and half the intensity has been shifted to the right by an amount  $\omega_0$ .

**Back to the vibrating linear molecules.** We were considering terms in the correlation function

$$\langle \mu_x(t) \mu_x(0) \rangle$$

of the form

$$N \mu_1^2 \langle \hat{u}_{1x}(t) u_{1x}(0) \rangle \langle \xi_1(t) \xi_1(0) \rangle$$

The rotational correlation function here is exactly the same as the *self* correlation function that determines the pure rotational spectrum. Its Fourier transform has

- a peak at  $\omega = 0$  and
- a width of about  $\Delta\omega_r$ .

Assume, as a first approximation, that the vibrational coordinate is perfectly harmonic and undamped.

$$\langle \xi_1(t) \xi_1(0) \rangle = \langle \xi_1^2 \rangle \cos \omega_1 t$$

where  $\omega_1$  is the vibrational frequency.

The terms of interest are

$$N \mu_1^2 \langle \hat{u}_{1x}(t) u_{1x}(0) \rangle \langle \xi_1(t) \xi_1(0) \rangle = N \mu_1^2 \langle \xi_1^2 \rangle \langle \hat{u}_{1x}(t) u_{1x}(0) \rangle \cos \omega_1 t$$

The Fourier transform of the correlation function then has peaks

- at  $\omega = \pm\omega_1$
- with width of  $\Delta\omega_r$ .

Multiplication by  $\omega^2$  to get the rate of energy absorption  $R(\omega)$  changes the intensity but does not affect the shape of the spectrum very much (unlike the case of a spectrum centered at  $\omega = 0$ ).

### **Additional effects**

- Vibrational relaxation can broaden the line somewhat.
- Vibration-rotation interaction can change the shape slightly.
- In a liquid will cause the rotational part of the correlation function to decay more slowly than in a gas, which makes the line narrower in a liquid, but it is still in the infrared.

### **More dramatic effects**

- Sometimes there are large changes in the frequency and width of vibrational lines in going from a gas to a liquid, e.g. OH vibrations in hydrogen bonding molecules. This is a signature of the fact that in the condensed phase the interactions between molecules are having a profound effect on the molecular vibrations.

*end of slides*

## **2.4 Collision-induced absorption**

In the previous discussion, the dipole moment was regarded as a property of individual molecules. The magnitude of the dipole moment depends on the vibration of the molecule, and the direction of the dipole moment depends on the orientation of the molecule. Molecular motions and interactions affect the spectrum only through their effect on the orientation and vibration coordinates of each molecule.

Thus you might expect that if you had a gas or liquid of atoms, e.g. argon or krypton, there should be no absorption of energy from electromagnetic radiation. In fact, as far as I know, a sample of pure argon or krypton has no appreciable absorption in the infrared region of the spectrum or at lower frequencies. Spherical atoms have no permanent dipole moment and no vibrational degrees of freedom.

Thus, it is somewhat surprising to hear that mixtures of two or more different atoms, e.g. neon-krypton mixtures, have low frequency absorptions. The physical origin of this absorption is the fact that collisions between atoms of

different types can give temporary dipole moments even though the individual atoms by themselves do not have dipole moments.

During the short duration of a collision between unlike atoms, the electronic structure of the pair is analogous to that of a heteronuclear diatomic. There is no reason why the distribution of electronic charge can't be shifted in such a way that the pair has a dipole moment. The dipole moment is presumably along the line of centers of the pair and it is a function of the distance between the pair. It goes to zero when the pair is separated by a large enough distance that fractional charge transfer is negligible.

Thus the dipole moment of a collection of molecules is of the form

$$\mu(\Gamma) = \sum_{i=1}^{N_A} \sum_{j=1}^{N_B} \hat{\mathbf{r}}_{iAjB} f(|\mathbf{r}_{iAjB}|)$$

where  $N_A$  and  $N_B$  are the number of atoms of each of the two types,  $\mathbf{r}_{iAjB}$  is the vector distance from the  $i$ th A atom to the  $j$ th B atom, and  $\hat{\mathbf{r}}_{iAjB}$  is a unit vector in the direction of  $\mathbf{r}_{iAjB}$ . During a collision,  $\mathbf{r}_{iAjB}$  changes in both magnitude and direction.

Thus for a typical collision, the time dependence of the induced dipole moment (in any particular direction) is likely to become nonzero and then fall to zero or become nonzero then change sign then become zero. Different collisions are presumably uncorrelated.

It is thus reasonable to expect that the correlation function is at it largest for  $t = 0$  and that it decays to zero in the time it takes for two interacting atoms to come apart. Let us call this  $\tau_c$ . Moreover, the value at  $t = 0$  is proportional to the  $Nn$ , where  $n = N/V$ , and thus the absorption per atom is proportional to the density. (This is different from the case for linear dipolar molecules, were for low density the absorption per molecule is independent of the density.) The Fourier transform of the correlation function will have a peak at  $\omega = 0$  and a half width of about  $1/\tau_c$ . Thus the absorption spectrum will be a broad peak with a location and a width of about  $1/\tau_c$ .

*slide*

### Collision induced absorption

Dilute gas of inert gas atoms.

Temporary dipole moments develop within pairs of colliding atoms if they are not of the same element.

The dipole moment of a collection of molecules is of the form

$$\mu(\Gamma) = \sum_{i=1}^{N_A} \sum_{j=1}^{N_B} \hat{\mathbf{r}}_{iAjB} f(|\mathbf{r}_{iAjB}|)$$

where

$N_A$  and  $N_B$  are the number of atoms of each of the two types,

$\mathbf{r}_{iAjB}$  is the vector distance from the  $i$ th A atom to the  $j$ th B atom, and

$\hat{\mathbf{r}}_{iAjB}$  is a unit vector in the direction of  $\mathbf{r}_{iAjB}$ .

$f(r)$  is nonzero only if the atoms are close together.

$$\mu(\Gamma) = \sum_{i=1}^{N_A} \sum_{j=1}^{N_B} \hat{\mathbf{r}}_{iAjB} f(|\mathbf{r}_{iAjB}|)$$

- The correlation function of this decays to zero on the time scale of the duration of a collision  $\tau_c$ .
- The Fourier transform of the correlation function will have a peak at  $\omega = 0$  and a half width of about  $1/\tau_c$ .
- The energy absorption spectrum will be a broad peak with a location and a width of about  $1/\tau_c$ , much like the case for the rotational spectrum of a dipolar molecule.

This mechanism for absorption is possible for molecular gases as well.

*end of slide*

Lecture  
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