

## **13. FLUCTUATIONS IN SPECTROSCOPY**

Here we will describe how fluctuations are observed in experimental observables, as is common to experiments in molecular condensed phases. As our example, we will focus on absorption spectroscopy and how environmentally induced dephasing influences the absorption lineshape. Our approach will be to calculate a dipole correlation function for transition dipole interacting with a fluctuating environment, and show how the time scale and amplitude of fluctuations are encoded in the lineshape. Although the description here is for the case of a spectroscopic observable, the approach can be applied to any such problems in which the deterministic motions of an internal variable of a quantum system are influenced by a fluctuating environment.

We also aim to establish a connection between this problem and the Displaced Harmonic Oscillator model. Specifically, we will show that a frequency-domain representation of the coupling between a transition and a continuous distribution of harmonic modes is equivalent to a time-domain picture in which the transition energy gap fluctuates about an average frequency with a statistical time scale and amplitude given by the distribution of coupled modes. Thus an absorption spectrum is merely a spectral representation of the dynamics experienced by a experimentally probed transition.

### **13.1. Fluctuations and Randomness: Some Definitions**

“Fluctuations” is my word for the time-evolution of a randomly perturbed system at or near equilibrium. For chemical problems in the condensed phase we constantly come up against the problem of random fluctuations to dynamical variables as a result of their interactions with their environment. It is unreasonable to think that you will come up with an equation of motion for the internal deterministic variable, but we should be able to understand the behavior statistically and come up with equations of motion for probability distributions. Models of this form are commonly referred to as stochastic. A stochastic equation of motion is one which includes a random component to the time-development.

When we introduced correlation functions, we discussed the idea that a statistical description of a system is commonly formulated in terms of probability distribution functions  $P$ . Observables are commonly described by moments of this distribution, which are obtained by integrating over  $P$ , for instance

$$\begin{aligned}\langle x \rangle &= \int dx x P(x) \\ \langle x^2 \rangle &= \int dx x^2 P(x)\end{aligned}\tag{13.1}$$

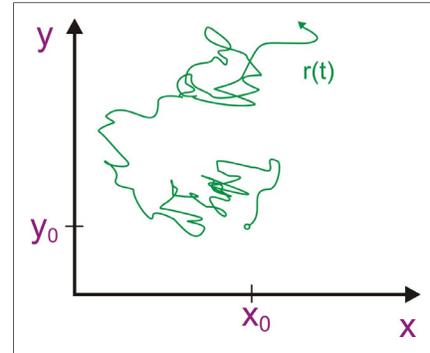
For time-dependent processes, we recognize that it is possible that the probability distribution carries a time-dependence.

$$\begin{aligned}\langle x(t) \rangle &= \int dx x(t) P(x, t) \\ \langle x^2(t) \rangle &= \int dx x^2(t) P(x, t)\end{aligned}\quad (13.2)$$

Correlation functions go a step further and depend on joint probability distributions  $P(t'', A; t', B)$  that give the probability of observing a value of  $A$  at time  $t''$  and a value of  $B$  at time  $t'$ :

$$\langle A(t'') B(t') \rangle = \int dA \int dB AB P(t'', A; t', B) \quad (13.3)$$

The statistical description of random fluctuations are described through these time-dependent probability distributions, and we need a stochastic equation of motion to describe their behavior. A common example of such a process is Brownian motion, the fluctuating position of a particle under the influence of a thermal environment. It is not practical to describe the absolute position of the particle, but we can formulate an equation of motion for the probability of finding the particle in time and space given that you know its initial position. Working from a random walk model, one can derive an equation of motion that takes the form of the well-known diffusion equation, here written in one dimension:



$$\frac{\partial P(x, t)}{\partial t} = \mathcal{D} \frac{\partial^2}{\partial x^2} P(x, t) \quad (13.4)$$

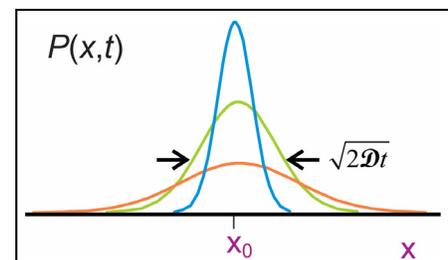
Here  $\mathcal{D}$  is the diffusion constant which sets the time scale and spatial extent of the random motion. [Note the similarity of this equation to the time-dependent Schrödinger equation for a free particle if  $\mathcal{D}$  is taken as imaginary]. Given the initial condition  $P(x, t_0) = \delta(x - x_0)$ , the solution is a conditional probability density

$$P(x, t; x_0, t_0) = \frac{1}{\sqrt{2\pi\mathcal{D}(t-t_0)}} \exp\left(-\frac{(x-x_0)^2}{4\mathcal{D}(t-t_0)}\right) \quad (13.5)$$

The probability distribution describes the statistics for fluctuations in the position of a particle averaged over many trajectories. Analyzing the moments of this probability density using eq. (13.2) we find that

$$\begin{aligned}\langle x(t) \rangle &= x_0 \\ \langle \delta x(t)^2 \rangle &= 2\mathcal{D}t\end{aligned}\quad (13.6)$$

where  $\delta x(t) = x(t) - x_0$ . So, the distribution maintains a Gaussian shape centered at  $x_0$ , and broadens with time as  $\sqrt{2\mathcal{D}t}$ .



Brownian motion is an example of a Gaussian-Markovian process. Here Gaussian refers to cases in which we describe the probability distribution for a variable  $P(x)$  as a Gaussian normal distribution. Here in one dimension:

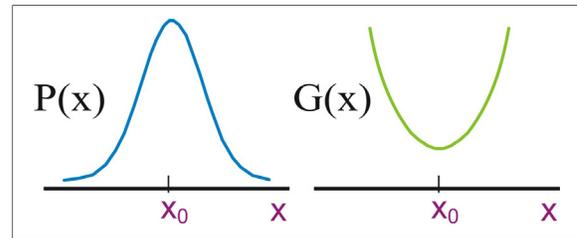
$$P(x) = A e^{-(x-x_0)^2/2\Delta^2}$$

$$\Delta^2 = \langle x^2 \rangle - \langle x \rangle^2 \quad (13.6)$$

The Gaussian distribution is important, because the central limit theorem states that the distribution of a continuous random variable with finite variance will follow the Gaussian distribution. Gaussian distributions also are completely defined in terms of their first and second moments, meaning that a time-dependent probability density  $P(x,t)$  is uniquely characterized by a mean value in the observable variable  $x$  and a correlation function that describes the fluctuations in  $x$ . Gaussian distributions for systems at thermal equilibrium are also important for the relationship between Gaussian distributions and parabolic free energy surfaces:

$$G(x) = -k_B T \ln P(x) \quad (13.7)$$

If the probability density is Gaussian along  $x$ , then the system's free energy projected onto this coordinate (often referred to as a potential of mean force) has a harmonic shape. Thus Gaussian statistics are effective for describing fluctuations about an equilibrium mean value  $x_0$ .



Markovian means that the time-dependent behavior of a system does not depend on its earlier history, statistically speaking. Naturally the state of any one molecule depends on its trajectory through phase space, however we are saying that from the perspective of an ensemble there is no memory of the state of the system at an earlier time. This can be stated in terms of joint probability functions as

$$P(x_2, t_2; x_1, t_1; x_0, t_0) = P(x_2, t_2; x_1, t_1) P(x_1, t_1; x_0, t_0) \quad (13.7)$$

or

$$P(t_2; t_1; t_0) = P(t_2; t_1) P(t_1; t_0)$$

The probability of observing a trajectory that takes you from state 1 at time 1 to state 2 at time 2 does not depend on where you were at time 0. Further, given the knowledge of the probability of executing changes during a single time interval, you can exactly describe  $P$  for any time interval. Markovian therefore refers to time-dependent processes on a time scale long compared to correlation time for the internal variable that you care about. For instance, the diffusion equation

only holds after the particle has experienced sufficient collisions with its surroundings that it has no memory of its earlier position and momentum:  $t > \tau_c$ .

### Readings

1. Nitzan, A., *Chemical Dynamics in Condensed Phases*. Oxford University Press: New York, 2006; Ch. 1.5 and Ch. 7.

## 13.2. Line-Broadening and Spectral diffusion

We will investigate how a fluctuating environment influences measurements of an experimentally observed internal variable. Specifically we focus on the spectroscopy of a chromophore, and how the chromophore's interactions with its environment influence its transition frequency and absorption lineshape. In the absence of interactions, the resonance frequency that we observe is  $\omega_{eg}$ . However, we have seen that interactions of this chromophore with its environment can shift this frequency. In condensed matter, time-dependent interactions with the surroundings can lead to time-dependent frequency shifts, known as spectral diffusion. How these dynamics influence the line width and lineshape of absorption features depends on the distribution of frequencies available to your system ( $\Delta$ ) and the time scale of sampling varying environments ( $\tau_c$ ). Consider the following cases of line broadening:

- 1) **Homogeneous.** Here, the absorption lineshape is *dynamically* broadened by rapid variations in the frequency or phase of dipoles. Rapid sampling of a distribution of frequencies acts to average the experimentally observed resonance frequency. The result is a “motionally narrowed” line width that is narrower than the distribution of frequencies available and proportional to the rate of fluctuation induced dephasing.
- 2) **Inhomogeneous.** In this limit, the lineshape reflects a *static* distribution of resonance frequencies, and the width of the line represents the distribution of frequencies,  $\Delta$ , which arise, from different structural environments available to the system.
- 3) **Spectral Diffusion.** More generally, every system lies between these limits. Given a distribution of configurations that the system can adopt, for instance an electronic chromophore in a liquid, an equilibrium system will be ergodic, and over a long enough time any molecule will sample all configurations available to it. Under these circumstances, we expect that every molecule will have a different “instantaneous frequency”  $\omega_i(t)$  which evolves in time as a result of its interactions with a dynamically evolving system. This process is known as spectral diffusion. The homogeneous and inhomogeneous limits can be described as limiting forms for the fluctuations of a frequency  $\omega_i(t)$  through a distribution of frequencies  $\Delta$ . If  $\omega_i(t)$  evolves rapidly relative to  $\Delta^{-1}$ , the system is homogeneously broadened. If  $\omega_i(t)$  evolves slowly the system is inhomogeneous. This behavior can be quantified through the transition frequency time-correlation function

$$C_{eg}(t) = \langle \omega_{eg}(t) \omega_{eg}(0) \rangle \quad (13.8)$$

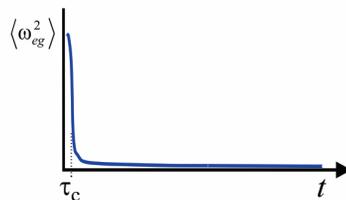
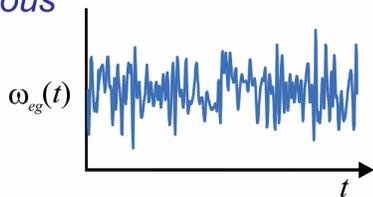
Our job will be to relate the transition frequency correlation function  $C_{eg}(t)$  with the dipole correlation function that determines the lineshape,  $C_{\mu\mu}(t)$ .

**Time-dependence  
of individual molecules**  
Dipole moment,  $\mu(t)$   
Instantaneous frequency,  $\omega(t)$

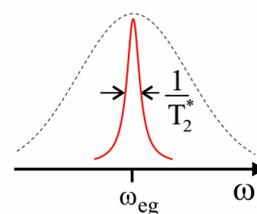
**Frequency Correlations**  
 $C_{eg}(t) = \langle \omega_{eg}(t) \omega_{eg}(0) \rangle$

**Absorption Spectrum**  
 $\mathcal{F} \langle \mu(t) \mu(0) \rangle$

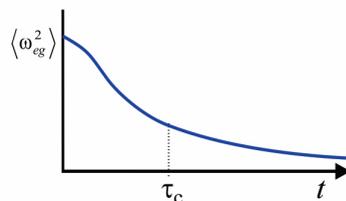
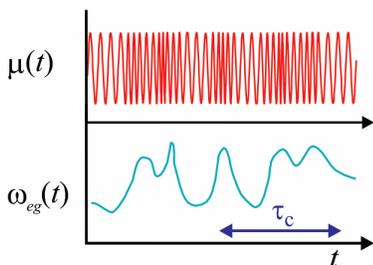
*Homogeneous*



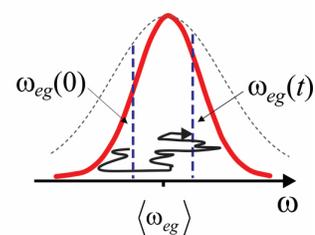
*"Motentially Narrowed"*



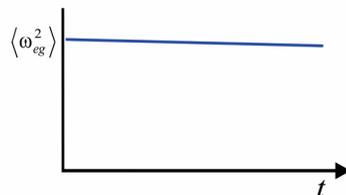
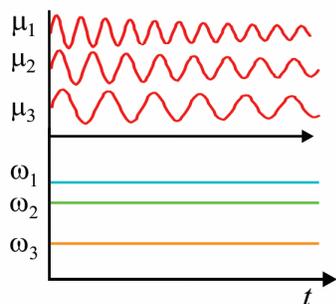
*Fluctuating  
frequency*



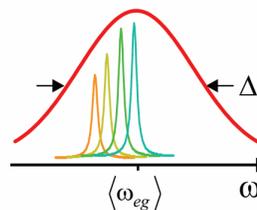
*"Spectral Diffusion"*



*Inhomogeneous*

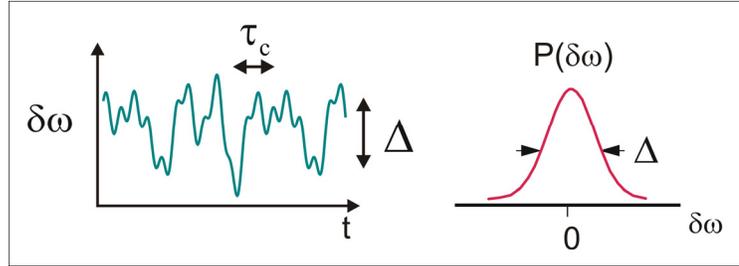


*Static Distribution*



### 13.3. Gaussian-Stochastic Model for Spectral Diffusion

We will begin with a *classical* description of how random fluctuations in frequency influence the absorption lineshape, by calculating the dipole correlation function for the resonant transition. This is a Gaussian stochastic model for fluctuations, meaning that we will describe the time-dependence of the transition energy as *random* fluctuations about an average value through a Gaussian distribution.



$$\omega(t) = \langle \omega \rangle + \delta\omega(t) \quad (13.9)$$

$$\langle \delta\omega(t) \rangle = 0 \quad (13.10)$$

The fluctuations in  $\omega$  allow the system to explore a Gaussian distribution of transitions frequencies characterized by a variance:<sup>1</sup>

$$\Delta = \sqrt{\langle \omega^2 \rangle - \langle \omega \rangle^2} = \sqrt{\langle \delta\omega^2 \rangle} \quad (13.11)$$

The time scales for the frequency shifts will be described in terms of a frequency correlation function

$$C_{\delta\omega\delta\omega}(t) = \langle \delta\omega(t) \delta\omega(0) \rangle \quad (13.12)$$

Furthermore, we will describe the time scale of the random fluctuations through a correlation time  $\tau_c$ .

The absorption lineshape is described with a dipole time-correlation function. Let's treat the dipole moment as an internal variable to the system, whose value depends on that of  $\omega$ . Qualitatively, it is possible to write an equation of motion for  $\mu$  by associating the dipole moment with the displacement of a bound particle ( $x$ ) times its charge, and using our intuition regarding how the system behaves. For an unperturbed state, we expect that  $x$  will oscillate at a frequency  $\omega$ , but with perturbations, it will vary through the distribution of available frequencies. One function that has this behavior is

$$x(t) = x_0 e^{-i\omega(t)t} \quad (13.13)$$

If we differentiate this equation with respect to time and multiply by charge we have

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<sup>1</sup> In many figures the width of the Gaussian distribution is labeled with the standard deviation (here  $\Delta$ ). This is meant to symbolize that  $\Delta$  is the parameter that determines the width, and not that it is the line width. For Gaussian distributions, the full line width at half maximum amplitude (FWHM) is  $2.35\Delta$ .

$$\frac{\partial \mu}{\partial t} = -i\omega(t)\mu(t) \quad (13.14)$$

Although it is a classical equation, note the similarity to the quantum Heisenberg equation for the dipole operator:  $\partial \mu / \partial t = iH(t)\mu / \hbar + h.c.$  The correspondence of  $\omega(t)$  with  $H(t) / \hbar$  offers some insight into how the quantum version of this problem will look.

The solution to eq. (13.14) is

$$\mu(t) = \mu(0) \exp \left[ -i \int_0^t d\tau \omega(\tau) \right] \quad (13.15)$$

Substituting this expression and eq. (13.9) into the dipole correlation function gives

$$\text{or} \quad C_{\mu\mu}(t) = |\mu|^2 e^{-i\langle \omega \rangle t} F(t) \quad (13.16)$$

$$\text{where} \quad F(t) = \left\langle \exp \left[ -i \int_0^t d\tau \delta\omega(\tau) \right] \right\rangle \quad (13.17)$$

The dephasing function here is obtained by performing an equilibrium average of the exponential argument over fluctuating trajectories. For ergodic systems, this is equivalent to averaging long enough over a single trajectory.

The dephasing function is a bit complicated to work with as written. However, for the case of Gaussian statistics for the fluctuations, it is possible to simplify  $F(t)$  by expanding it as a *cumulant expansion of averages* (see Appendix)

$$F(t) = \exp \left[ -i \int_0^t d\tau' \langle \delta\omega(\tau') \rangle + \frac{i^2}{2!} \int_0^t d\tau' \int_0^t d\tau'' \left\{ \langle \delta\omega(\tau') \delta\omega(\tau'') \rangle - \langle \delta\omega(\tau') \rangle \langle \delta\omega(\tau'') \rangle \right\} \right] \quad (13.18)$$

In this expression, the first term is zero, since  $\langle \delta\omega \rangle = 0$ . Only the second term survives for a system with Gaussian statistics. Now recognizing that we have a stationary system, we have

$$F(t) = \exp \left[ -\frac{1}{2} \int_0^t d\tau' \int_0^t d\tau'' \langle \delta\omega(\tau' - \tau'') \delta\omega(0) \rangle \right] \quad (13.19)$$

We have rewritten the dephasing function in terms of a correlation function that describes the fluctuating energy gap. Note that this is a classical exception, so there is no time-ordering to the exponential.  $F(t)$  can be rewritten through a change of variables ( $\tau = \tau' - \tau''$ ):

$$F(t) = \exp \left[ -\int_0^t d\tau (t - \tau) \langle \delta\omega(\tau) \delta\omega(0) \rangle \right] \quad (13.20)$$

So the Gaussian stochastic model allows the influence of the frequency fluctuations on the lineshape to be described by  $C_{\delta\omega\delta\omega}(t)$  a frequency correlation function that follows Gaussian statistics. Note, we are now dealing with two different correlation functions  $C_{\delta\omega\delta\omega}$  and  $C_{\mu\mu}$ . The frequency correlation function encodes the dynamics that result from molecules interacting with

the surroundings, whereas the dipole correlation function describes how the system interacts with a light field and thereby the absorption spectrum.

Now, we will calculate the lineshape assuming that  $C_{\delta\omega\delta\omega}$  decays with a correlation time  $\tau_c$  and takes on an exponential form

$$C_{\delta\omega\delta\omega}(t) = \Delta^2 \exp[-t / \tau_c] \quad (13.21)$$

Then eq. (13.20) gives

$$F(t) = \exp\left[-\Delta^2 \tau_c^2 \left(\exp(-t / \tau_c) + t / \tau_c - 1\right)\right] \quad (13.22)$$

which is in the form we have seen earlier  $F(t) = \exp(-g(t))$

$$g(t) = \Delta^2 \tau_c^2 \left(\exp(-t / \tau_c) + t / \tau_c - 1\right) \quad (13.23)$$

To interpret this lineshape function, let's look at its limiting forms:

- 1) **Long correlation times** ( $t \ll \tau_c$ ). This corresponds to the inhomogeneous case where  $C_{\delta\omega\delta\omega}(t) = \Delta^2$ , a constant. For  $t \ll \tau_c$  we can perform a short time expansion of exponential

$$e^{-t/\tau_c} \approx 1 - \frac{t}{\tau_c} + \frac{t^2}{2\tau_c^2} + \dots \quad (13.24)$$

and from eq. (13.23) we obtain

$$g(t) = \Delta^2 t^2 / 2 \quad (13.25)$$

At short times, the dipole correlation function will have a Gaussian decay with a rate given by  $\Delta^2$ :  $F(t) = \exp(-\Delta^2 t^2 / 2)$ . This has the proper behavior for a classical correlation function, i.e., even in time  $C_{\mu\mu}(t) = C_{\mu\mu}(-t)$ .

In this limit, the absorption lineshape is:

$$\begin{aligned} \sigma(\omega) &= |\mu|^2 \int_{-\infty}^{+\infty} dt e^{i\omega t} e^{-i\langle\omega\rangle t - g(t)} \\ &= |\mu|^2 \int_{-\infty}^{+\infty} dt e^{i(\omega - \langle\omega\rangle)t} e^{-\Delta^2 t^2 / 2} \\ &= \sqrt{\frac{2\pi}{\Delta^2}} |\mu|^2 \exp\left(-\frac{(\omega - \langle\omega\rangle)^2}{2\Delta^2}\right) \end{aligned} \quad (13.26)$$

We obtain a Gaussian inhomogeneous lineshape centered at the mean frequency with a width dictated by the frequency distribution.

2) **Short correlation times** ( $t \gg \tau_c$ ). This corresponds to the homogeneous limit in which you can approximate  $C_{\delta\omega\delta\omega}(t) = \Delta^2 \delta(t)$ . For  $t \gg \tau_c$  we set  $e^{-t/\tau_c} \approx 0$ ,  $t/\tau_c \gg 1$  and eq. (13.23) gives

$$g(t) = -\Delta^2 \tau_c t \quad (13.27)$$

If we define the constant

$$\Delta^2 \tau_c \equiv \Gamma \quad (13.28)$$

we see that the dephasing function has an exponential decay:

$$F(t) = \exp[-\Gamma t] \quad (13.29)$$

The lineshape for short correlation times (or fast fluctuations) takes on a Lorentzian shape

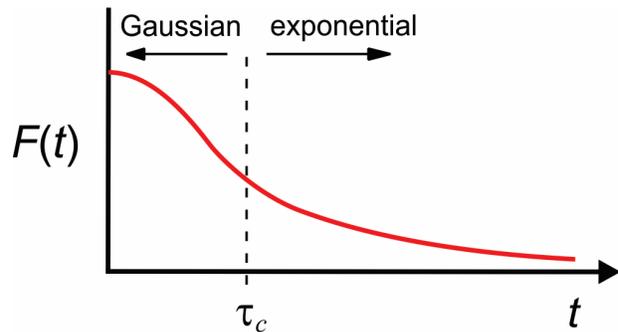
$$\begin{aligned} \sigma(\omega) &= |\mu|^2 \int_{-\infty}^{+\infty} dt e^{i(\omega - \langle\omega\rangle)t} e^{-\Gamma t} \\ \text{Re } \sigma(\omega) &= |\mu|^2 \frac{\Gamma}{(\omega - \langle\omega\rangle)^2 + \Gamma^2} \end{aligned} \quad (13.30)$$

This represents the homogeneous limit. Even with a broad distribution of accessible frequencies, if the system explores all of these frequencies on a time scale fast compared to the inverse of the distribution ( $\Delta \tau_c > 1$ ), then the resonance will be “motionally narrowed” into a Lorentzian line.

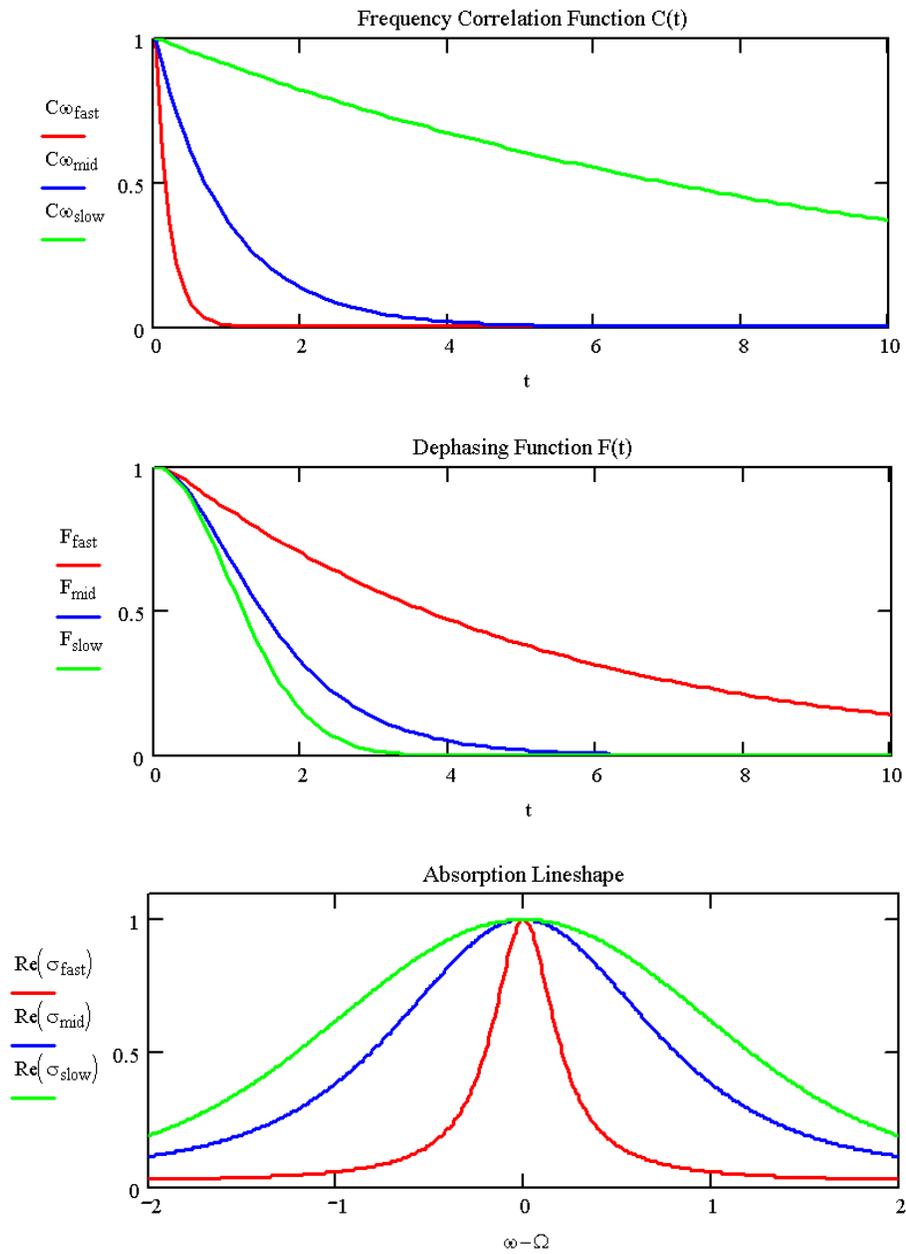
More generally, the envelope of the dipole correlation function will look Gaussian at short times and exponential at long times. The correlation time is the separation between these regimes. The behavior for varying time scales of the dynamics ( $\tau_c$ ) are best characterized with respect to the distribution of accessible frequencies ( $\Delta$ ). So we can define a factor

$$\kappa = \Delta \cdot \tau_c \quad (13.31)$$

$\kappa \ll 1$  is the fast modulation limit and  $\kappa \gg 1$  is the slow modulation limit. Let's look at how  $C_{\delta\omega\delta\omega}$ ,  $F(t)$ , and  $\sigma_{abs}(\omega)$  change as a function of  $\kappa$ .



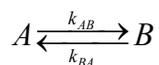
$$\Delta = 1 \quad \tau_{\mathbf{c}} = \begin{pmatrix} 0.2 \\ 1 \\ 10 \end{pmatrix} \quad \kappa = \begin{pmatrix} 0.2 \\ 1 \\ 10 \end{pmatrix} \quad \begin{array}{l} \text{fast} \\ \text{mid} \\ \text{slow} \end{array}$$



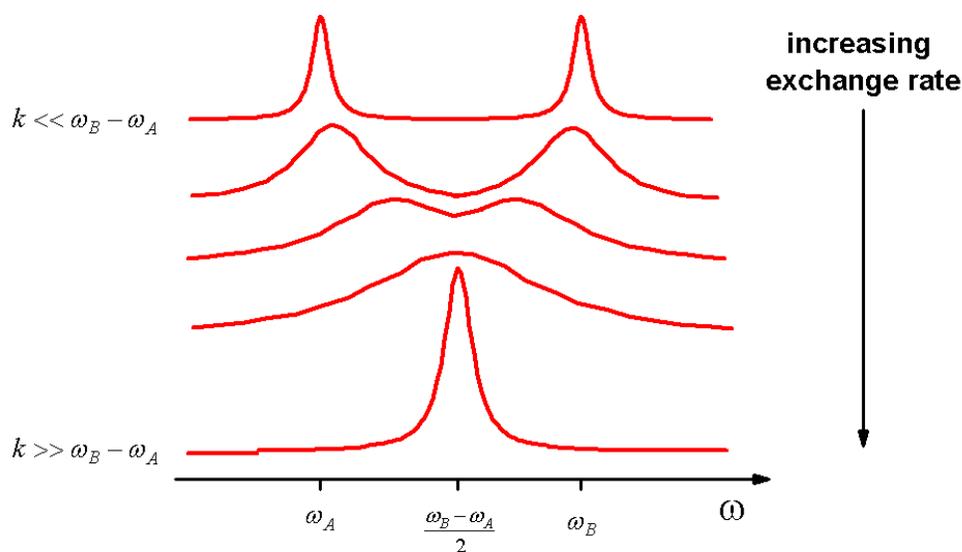
We see that for a fixed distribution of frequencies  $\Delta$  the effect of increasing the time scale of fluctuations through this distribution (decreasing  $\tau_{\mathbf{c}}$ ) is to gradually narrow the observed lineshape

from a Gaussian distribution of static frequencies with width (FWHM) of  $2.35 \cdot \Delta$  to a motionally narrowed Lorentzian lineshape with width (FWHM) of  $\Delta^2 \tau_c / \pi = \Delta \cdot \kappa / \pi$ .

This is analogous to the motional narrowing effect first described in the case of temperature dependent NMR spectra of two exchanging species. Assume we have two resonances at  $\omega_A$  and  $\omega_B$  associated with two chemical species that are exchanging at a rate  $k_{AB}$



If the rate of exchange is slow relative to the frequency splitting,  $k_{AB} \ll \omega_A - \omega_B$ , then we expect two resonances, each with a linewidth dictated by the molecular relaxation processes ( $T_2$ ) and transfer rate of each species. On the other hand, when the rate of exchange between the two species becomes faster than the energy splitting, then the two resonances narrow together to form one resonance at the mean frequency.<sup>2</sup>



<sup>2</sup> Anderson, P. W. A mathematical model for the narrowing of spectral lines by exchange or motion. *J. Phys. Soc. Japan* **9**, 316 (1954).; Kubo, R. in *Fluctuation, Relaxation, and Resonance in Magnetic Systems* (ed. Ter Haar, D.) (Oliver and Boyd, London, 1962).

## Appendix: The Cumulant Expansion

For a statistical description of the random variable  $x$ , we wish to characterize the moments of  $x$ :  $\langle x \rangle, \langle x^2 \rangle, \dots$ . Then the average of an exponential of  $x$  can be expressed as an expansion in moments

$$\langle e^{ikx} \rangle = \sum_{n=0}^{\infty} \frac{(ik)^n}{n!} \langle x^n \rangle \quad (13.31)$$

An alternate way of expressing this expansion is in terms of cumulants  $c_n(x)$

$$\langle e^{ikx} \rangle = \exp \left( \sum_{n=1}^{\infty} \frac{(ik)^n}{n!} c_n(x) \right) \quad (13.32)$$

where the first few cumulants are:

$$c_1(x) = \langle x \rangle \quad \text{mean} \quad (13.33)$$

$$c_2(x) = \langle x^2 \rangle - \langle x \rangle^2 \quad \text{variance} \quad (13.34)$$

$$c_3(x) = \langle x^3 \rangle - 3\langle x \rangle \langle x^2 \rangle + 2\langle x \rangle^3 \quad \text{skewness} \quad (13.35)$$

An expansion in cumulants converges much more rapidly than an expansion in moments, particularly when you consider that  $x$  may be a time-dependent variable. Particularly useful is the observation that all cumulants with  $n > 2$  vanish for a system that obeys Gaussian statistics.

We obtain the cumulants above by expanding eq. (13.31) and (13.32), and comparing terms in powers of  $x$ . We start by postulating that, instead of expanding the exponential directly, we can instead expand the exponential argument in powers of an operator or variable  $H$

$$F = \exp[c] = 1 + c + \frac{1}{2}c^2 + \dots \quad (13.36)$$

$$c = c_1 H + \frac{1}{2}c_2 H^2 + \dots \quad (13.37)$$

Inserting eq. (13.37) into eq. (13.36) and collecting terms in orders of  $H$  gives

$$\begin{aligned} F &= 1 + \left( c_1 H + \frac{1}{2}c_2 H^2 + \dots \right) + \frac{1}{2} \left( c_1 H + \frac{1}{2}c_2 H^2 + \dots \right)^2 + \dots \\ &= 1 + (c_1)H + \frac{1}{2}(c_2 + c_1^2)H^2 + \dots \end{aligned} \quad (13.38)$$

Now comparing this with the expansion of the exponential

$$\begin{aligned} F &= \exp[fH] \\ &= 1 + f_1 H + \frac{1}{2}f_2 H^2 + \dots \end{aligned} \quad (13.39)$$

allows one to see that

$$\begin{aligned}c_1 &= f_1 \\c_2 &= f_2 - f_1^2\end{aligned}\tag{13.40}$$

The cumulant expansion can also be applied to time-correlations. Applying this to the time-ordered exponential operator we obtain:

$$\begin{aligned}F(t) &= \left\langle \exp_+ \left[ -i \int_0^t dt \omega(t) \right] \right\rangle \\ &\approx \exp \left[ c_1(t) + c_2(t) \right]\end{aligned}\tag{13.41}$$

$$c_1 = -i \int_0^t d\tau \langle \omega(\tau) \rangle\tag{13.42}$$

$$\begin{aligned}c_2 &= -\int_0^t d\tau_2 \int_0^{\tau_2} d\tau_1 \left\{ \langle \omega(\tau_2) \omega(\tau_1) \rangle - \langle \omega(\tau_2) \rangle \langle \omega(\tau_1) \rangle \right\} \\ &= -\int_0^t d\tau_2 \int_0^{\tau_2} d\tau_1 \langle \delta\omega(\tau_2) \delta\omega(\tau_1) \rangle\end{aligned}\tag{13.43}$$

For Gaussian statistics, all higher cumulants vanish.

## Readings

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## 13.4. The Energy Gap Hamiltonian

### Introduction

In describing fluctuations in a quantum mechanical system, we describe how an experimental observable is influenced by its interactions with a thermally agitated environment. For this, we work with the specific example of an electronic absorption spectrum and return to the Displaced Harmonic Oscillator model. We previously described this model in terms of the eigenstates of the material Hamiltonian  $H_0$ , and interpreted the dipole correlation function and resulting lineshape in terms of the overlap between two wave packets evolving on the ground and excited surfaces  $|E\rangle$  and  $|G\rangle$ .

$$C_{\mu\mu}(t) = |\mu_{eg}|^2 e^{-i(E_e - E_g)t/\hbar} \langle \varphi_g(t) | \varphi_e(t) \rangle \quad (13.43)$$

It is worth noting a similarity between the DHO Hamiltonian, and a general form for the interaction of an electronic two-level “system” with a harmonic oscillator “bath” whose degrees of freedom are dark to the observation, but which influence the behavior of the system.

Expressed in a slightly different physical picture, we can also conceive of this process as nuclear motions that act to modulate the electronic energy gap  $\omega_{eg}$ . We can imagine rewriting the same Hamiltonian in a form with a new physical picture that describes the electronic energy gap’s dependence on  $q$ , i.e., its variation relative to  $\omega_{eg}$ . If we define an Energy Gap Hamiltonian:

$$H_{eg} = H_e - H_g \quad (13.43)$$

we can rewrite the DHO Hamiltonian

$$H_0 = |e\rangle E_e \langle e| + |g\rangle E_g \langle g| + H_e + H_g \quad (13.44)$$

as an electronic transition linearly coupled to a harmonic oscillator:

$$H_0 = |e\rangle E_e \langle e| + |g\rangle E_g \langle g| + H_{eg} + 2H_g \quad (13.44)$$

Noting that

$$H_g = \frac{p^2}{2m} + \frac{1}{2} m \omega_0^2 q^2 \quad (13.44)$$

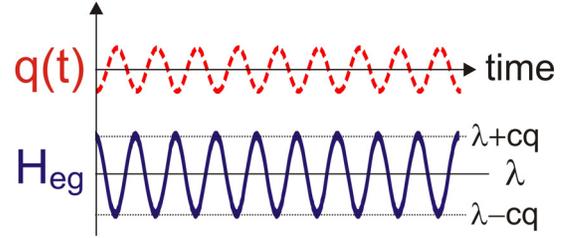
we can write this as a system-bath Hamiltonian:

$$H_0 = H_S + H_B + H_{SB} \quad (13.44)$$

where  $H_{SB}$  describes the interaction of the electronic system ( $H_S$ ) with the vibrational bath ( $H_B$ ). Here  $H_S = |e\rangle E_e \langle e| + |g\rangle E_g \langle g|$ ,  $H_B = 2H_g$  and

$$\begin{aligned}
H_{SB} = H_{eg} &= \frac{1}{2} m \omega_0^2 (q - d)^2 - \frac{1}{2} m \omega_0^2 q^2 \\
&= -m \omega_0^2 d q + \frac{1}{2} m \omega_0^2 d^2 \\
&= -c q + \lambda
\end{aligned} \tag{13.44}$$

The Energy Gap Hamiltonian describes a linear coupling between the electronic transition and a harmonic oscillator. The strength of the coupling is  $c$  and the Hamiltonian has a constant energy offset value given by the reorganization energy. Any motion in the bath coordinate  $q$  introduces a proportional change in the electronic energy gap.



In an alternate form, the Energy Gap Hamiltonian can also be written to incorporate the reorganization energy into the system:

$$\begin{aligned}
H_0 &= H'_S + H'_B + H'_{SB} \\
H'_S &= |e\rangle (E_e + \lambda) \langle e| + |g\rangle E_g \langle g| \\
H'_B &= \frac{p^2}{2m} + \frac{1}{2} m \omega_0^2 q^2 \\
H'_{SB} &= -m \omega_0^2 d q
\end{aligned} \tag{13.44}$$

This formulation describes fluctuations about the average value of the energy gap  $\hbar \omega_{eg} + \lambda$ , however, the observables calculated are the same.

From the picture of a modulated energy gap one can begin to see how random fluctuations can be treated by coupling to a harmonic bath. If each oscillator modulates the energy gap at a given frequency, and the phase between oscillators is random as a result of their independence, then time-domain fluctuations and dephasing can be cast in terms of a Fourier spectrum of couplings to oscillators with continuously varying frequency.

## Energy Gap Hamiltonian

Now let's work through the description of electronic spectroscopy with the Energy Gap Hamiltonian more carefully. Working from eqs. (13.43) and (13.44) we express the energy gap Hamiltonian through reduced coordinates for the momentum, coordinate, and displacement of the oscillator

$$\underline{p} = \hat{p}(2\hbar\omega_0 m)^{-1/2} \quad (13.45)$$

$$\underline{q} = \hat{q}(m\omega_0/2\hbar)^{1/2} \quad (13.46)$$

$$\underline{d} = d(m\omega_0/2\hbar)^{1/2} \quad (13.47)$$

$$H_e = \hbar\omega_0 \left( \underline{p}^2 + (\underline{q} - \underline{d})^2 \right) \quad (13.48)$$

$$H_g = \hbar\omega_0 \left( \underline{p}^2 + \underline{q}^2 \right)$$

From eq. (13.43) we have

$$\begin{aligned} H_{eg} &= -2\hbar\omega_0 \underline{d} \underline{q} + \hbar\omega_0 \underline{d}^2 \\ &= -m\omega_0^2 d \underline{q} + \lambda \end{aligned} \quad (13.49)$$

The energy gap Hamiltonian describes a linear coupling of the electronic system to the coordinate  $q$ . The slope of  $H_{eg}$  versus  $q$  is the coupling strength, and the average value of  $H_{eg}$  in the ground state,  $H_{eg}(q=0)$ , is offset by the reorganization energy  $\lambda$ . We note that the average value of the energy gap Hamiltonian is  $\langle H_{eg} \rangle = \lambda$ .

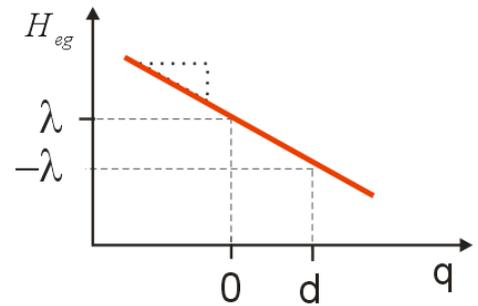
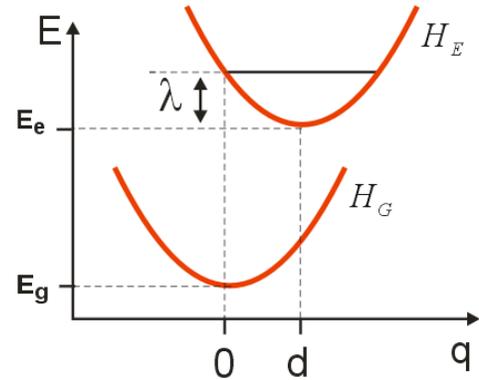
To obtain the absorption lineshape from the dipole correlation function

$$C_{\mu\mu}(t) = |\mu_{eg}|^2 e^{-i\omega_{eg}t} F(t) \quad (13.50)$$

we must evaluate the dephasing function.

$$F(t) = \left\langle e^{iH_g t} e^{-iH_e t} \right\rangle = \left\langle U_g^\dagger U_e \right\rangle \quad (13.51)$$

We want to rewrite the dephasing function in terms of the time dependence to the energy gap  $H_{eg}$ ; that is, if  $F(t) = \langle U_{eg} \rangle$ , then what is  $U_{eg}$ ? This involves a unitary transformation of the dynamics to a new frame of reference. The transformation from the DHO Hamiltonian to the EG Hamiltonian is similar to our derivation of the interaction picture.



### Transformation of time-propagators

If we have a time dependent quantity of the form

$$e^{iH_A t} A e^{-iH_B t} \quad (13.52)$$

we can also express the dynamics through the difference Hamiltonian  $H_{BA} = H_B - H_A$

$$A e^{-i(H_B - H_A)t} = A e^{-iH_{BA}t} \quad (13.53)$$

using a commonly performed unitary transformation. If we write

$$H_B = H_A + H_{BA} \quad (13.54)$$

we can use the same procedure for partitioning the dynamics in the interaction picture to write

$$e^{-iH_B t} = e^{-iH_A t} \exp_+ \left[ -\frac{i}{\hbar} \int_0^t d\tau H_{BA}(\tau) \right] \quad (13.55)$$

where

$$H_{BA}(\tau) = e^{iH_A \tau} H_{BA} e^{-iH_A \tau} \quad (13.56)$$

Then, we can also write:

$$e^{iH_A t} e^{-iH_B t} = \exp_+ \left[ -\frac{i}{\hbar} \int_0^t d\tau H_{BA}(\tau) \right] \quad (13.57)$$

Noting the mapping to the interaction picture

$$H_e = H_g + H_{eg} \quad \Leftrightarrow \quad H = H_0 + V \quad (13.58)$$

we see that we can represent the time dependence of the electronic energy gap  $H_{eg}$  using

$$e^{-iH_e t/\hbar} = e^{-iH_g t/\hbar} \exp_+ \left[ \frac{-i}{\hbar} \int_0^t d\tau H_{eg}(\tau) \right] \quad (13.59)$$

$$U_e = U_g U_{eg}$$

where

$$H_{eg}(t) = e^{iH_g t/\hbar} H_{eg} e^{-iH_g t/\hbar} \quad (13.60)$$

$$= U_g^\dagger H_{eg} U_g$$

Remembering the equivalence between the harmonic mode  $H_g$  and the bath mode(s)  $H_B$  indicates that the time dependence of the EG Hamiltonian reflects how the electronic energy gap is modulated as a result of the interactions with the bath. That is  $U_g \Leftrightarrow U_B$ .

Equation (13.59) immediately implies that

$$F(t) = \left\langle e^{iH_g t/\hbar} e^{-iH_e t/\hbar} \right\rangle = \left\langle \exp_+ \left[ \frac{-i}{\hbar} \int_0^t d\tau H_{eg}(\tau) \right] \right\rangle \quad (13.61)$$

Now the quantum dephasing function is in the same form as we saw in our earlier classical derivation. Using the second-order cumulant expansion allows the dephasing function to be written as

$$F(t) = \exp \left[ \frac{-i}{\hbar} \int_0^t d\tau \langle H_{eg}(\tau) \rangle + \left( \frac{-i}{\hbar} \right)^2 \int_0^t d\tau_2 \int_0^{\tau_2} d\tau_1 \langle H_{eg}(\tau_2) H_{eg}(\tau_1) \rangle - \langle H_{eg}(\tau_2) \rangle \langle H_{eg}(\tau_1) \rangle \right] \quad (13.62)$$

Note that the cumulant expansion is here written as a time-ordered expansion. The first exponential term depends on the mean value of  $H_{eg}$

$$\langle H_{eg} \rangle = \hbar \omega_0 d^2 = \lambda \quad (13.63)$$

This is a result of how we defined  $H_{eg}$ . Alternatively, the EG Hamiltonian could have been defined relative to the energy gap at  $Q=0$ :  $H_{eg} = H_e - H_g + \lambda$ . In this case the leading term in (13.62) would be zero, and the mean energy gap that describes the high frequency (system) oscillation in the dipole correlation function is  $\omega_{eg} + \lambda$ .

The second exponential term in (13.62) is a correlation function that describes the time dependence of the energy gap

$$\begin{aligned} & \langle H_{eg}(\tau_2) H_{eg}(\tau_1) \rangle - \langle H_{eg}(\tau_2) \rangle \langle H_{eg}(\tau_1) \rangle \\ &= \langle \delta H_{eg}(\tau_2) \delta H_{eg}(\tau_1) \rangle \end{aligned} \quad (13.64)$$

where

$$\begin{aligned} \delta H_{eg} &= H_{eg} - \langle H_{eg} \rangle \\ &= -m\omega_0^2 d q \end{aligned} \quad (13.65)$$

Defining the time-dependent energy gap transition frequency in terms of the EG Hamiltonian as

$$\delta \hat{\omega}_{eg} \equiv \frac{\delta H_{eg}}{\hbar} \quad (13.66)$$

we can write the energy gap correlation function

$$C_{eg}(\tau_2, \tau_1) = \langle \delta \hat{\omega}_{eg}(\tau_2 - \tau_1) \delta \hat{\omega}_{eg}(0) \rangle \quad (13.67)$$

It follows that

$$F(t) = e^{-i\lambda t/\hbar} e^{-g(t)} \quad (13.68)$$

$$g(t) = \int_0^t d\tau_2 \int_0^{\tau_2} d\tau_1 C_{eg}(\tau_2, \tau_1) \quad (13.69)$$

and the dipole correlation function can be expressed as

$$C_{\mu\mu}(t) = |\mu_{eg}|^2 e^{-i(E_e - E_g + \lambda)t/\hbar} e^{-g(t)} \quad (13.70)$$

This is the correlation function expression that determines the absorption lineshape for a time-dependent energy gap. It is a general expression at this point, for all forms of the energy gap correlation function. The only approximation made for the bath is the second cumulant expansion.

Now, let's look specifically at the case where the bath we are coupled to is a single harmonic mode. The energy gap correlation function is evaluated from

$$\begin{aligned} C_{eg}(t) &= \sum_n p_n \langle n | \delta\hat{\omega}_{eg}(t) \delta\hat{\omega}_{eg}(0) | n \rangle \\ &= \frac{1}{\hbar^2} \sum_n p_n \langle n | e^{iH_g t/\hbar} \delta H_{eg} e^{-iH_g t/\hbar} \delta H_{eg} | n \rangle \end{aligned} \quad (13.71)$$

Noting that the bath oscillator correlation function

$$C_{qq}(t) = \langle q(t)q(0) \rangle = \frac{\hbar}{2m\omega_0} \left[ (\bar{n} + 1) e^{-i\omega_0 t} + \bar{n} e^{i\omega_0 t} \right] \quad (13.72)$$

we find

$$C_{eg}(t) = \omega_0^2 D \left[ (\bar{n} + 1) e^{-i\omega_0 t} + \bar{n} e^{i\omega_0 t} \right] \quad (13.73)$$

Here, as before,  $D = d^2(m\omega_0/2\hbar)$ ,  $\bar{n}$  is the thermally averaged occupation number for the oscillator

$$\bar{n} = \sum_n p_n \langle n | a^\dagger a | n \rangle = (e^{\beta\hbar\omega_0} - 1)^{-1} \quad (13.74)$$

and  $\beta = 1/k_B T$ . Note that the energy gap correlation function is a complex function. We can separate the real and imaginary parts of  $C_{eg}$  as

$$C_{eg}(t) = C'_{eg} + iC''_{eg} \quad (13.75)$$

$$C'_{eg}(t) = \omega_0^2 D \coth(\beta\hbar\omega_0/2) \cos(\omega_0 t)$$

$$C''_{eg}(t) = \omega_0^2 D \sin(\omega_0 t) \quad (13.76)$$

where we have made use of the relation

$$2\bar{n}(\omega) + 1 = \coth(\beta\hbar\omega/2) \quad (13.77)$$

and  $\coth(x) = (e^x + e^{-x}) / (e^x - e^{-x})$ . We see that the imaginary part of the energy gap correlation function is temperature independent. The real part has the same amplitude at  $T=0$ , and rises with temperature. We can analyze the high and low temperature limits of this expression from

$$\lim_{x \rightarrow \infty} \coth(x) = 1$$

$$\lim_{x \rightarrow 0} \coth(x) \approx \frac{1}{x} \quad (13.78)$$

Looking at the low temperature limit,  $\coth(\beta\hbar\omega_0/2) \rightarrow 1$  and  $\bar{n} \rightarrow 0$ , we see that eq. (13.82) reduces to eq. (13.84). In the high temperature limit,  $kT \gg \hbar\omega_0$ ,  $\coth(\hbar\omega_0/2kT) \rightarrow 2kT/\hbar\omega_0$ , and we recover the expected classical result. The magnitude of the real component dominates the imaginary part  $|C_{eg}'| \gg |C_{eg}''|$ , and the energy gap correlation function  $C_{eg}(t)$  becomes real and even in time.

Similarly, we can evaluate (13.69), the lineshape function

$$g(t) = -D \left[ (\bar{n} + 1)(e^{-i\omega_0 t} - 1) + \bar{n}(e^{i\omega_0 t} - 1) \right] - iD\omega_0 t \quad (13.79)$$

The leading term in eq. (13.79) gives us a vibrational progression, the second term leads to hot bands, and the final term is the reorganization energy ( $-iD\omega_0 t = -i\lambda t / \hbar$ ). The lineshape function can be written in terms of its real and imaginary parts

$$g(t) = g' + ig'' \quad (13.80)$$

$$g'(t) = D \coth(\beta\hbar\omega_0/2)(1 - \cos \omega_0 t)$$

$$g''(t) = D(\sin \omega_0 t - \omega_0 t) \quad (13.81)$$

Because these enter into the dipole correlation function as exponential arguments, the imaginary part of  $g(t)$  will reflect the bath-induced energy shift of the electronic transition gap and vibronic structure, and the real part will reflect damping, and therefore the broadening of the lineshape. Similarly to  $C_{eg}(t)$ , in the high temperature limit  $g' \gg g''$ .

Now, using eq. (13.68), we see that the dephasing function is given by

$$F(t) = \exp \left[ D \left( (\bar{n} + 1)(e^{-i\omega_0 t} - 1) + \bar{n}(e^{i\omega_0 t} - 1) \right) \right]. \quad (13.82)$$

$$= \exp \left[ D \left( \coth \left( \frac{\beta\hbar\omega}{2} \right) (1 - \cos \omega t) + i \sin \omega t \right) \right] \quad (13.83)$$

Let's confirm that we get the same result as with our original DHO model, when we take the low temperature limit. Setting  $\bar{n} \rightarrow 0$  in (13.83), we have our original result

$$F_{kT=0}(t) = \exp \left[ D \left( e^{-i\omega_0 t} - 1 \right) \right] \quad (13.84)$$

In the high temperature limit  $g' \gg g''$ , and from eq. (13.78) we obtain

$$\begin{aligned}
F(t) &= \exp \left[ \frac{2DkT}{\hbar\omega_0} \cos(\omega_0 t) \right] \\
&= \sum_{j=0}^{\infty} \frac{1}{j!} \left( \frac{2DkT}{\hbar\omega_0} \right)^j \cos^j(\omega_0 t)
\end{aligned} \tag{13.85}$$

which leads to an absorption spectrum which is a series of sidebands equally spaced on either side of  $\omega_{eg}$ .

### Spectral representation of energy gap correlation function

Since time- and frequency-domain representations are complementary, and one form may be preferable over another, it is possible to express the frequency correlation function in terms of its spectrum. For a complex spectrum of vibrational motions composed of many modes, representing the nuclear motions in terms of a spectrum rather than a beat pattern is often easier. It turns out that calculation are often easier performed in the frequency domain.

To start we define a Fourier transform pair that relates the time and frequency domain representations:

$$\tilde{C}_{eg}(\omega) = \int_{-\infty}^{+\infty} e^{i\omega t} C_{eg}(t) dt \tag{13.86}$$

$$C_{eg}(t) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} e^{-i\omega t} \tilde{C}_{eg}(\omega) d\omega \tag{13.87}$$

Since the energy gap correlation function has the property  $C_{eg}(-t) = C_{eg}^*(t)$ , it also follows from (13.86) that the energy gap correlation *spectrum* is entirely real:

$$\tilde{C}_{eg}(\omega) = 2 \operatorname{Re} \int_0^{\infty} e^{i\omega t} C_{eg}(t) dt \tag{13.88}$$

or

$$\tilde{C}_{eg}(\omega) = \tilde{C}'_{eg}(\omega) + \tilde{C}''_{eg}(\omega) \tag{13.89}$$

Here  $\tilde{C}'_{eg}(\omega)$  and  $\tilde{C}''_{eg}(\omega)$  are the Fourier transforms of the real and imaginary components of  $C_{eg}(t)$ , respectively.  $\tilde{C}'_{eg}(\omega)$  and  $\tilde{C}''_{eg}(\omega)$  are even and odd in frequency. Thus while  $\tilde{C}_{eg}(\omega)$  is entirely real valued, it is asymmetric about  $\omega=0$ .

With these definitions in hand, we can write the spectrum of the energy gap correlation function for coupling to a single harmonic mode spectrum (eq. (13.71)):

$$\tilde{C}_{eg}(\omega_\alpha) = \omega_\alpha^2 D(\omega_\alpha) \left[ (\bar{n}_\alpha + 1) \delta(\omega - \omega_\alpha) + \bar{n}_\alpha \delta(\omega + \omega_\alpha) \right] \tag{13.90}$$

This is a spectrum that characterizes how bath vibrational modes of a certain frequency and thermal occupation act to modify the observed energy of the system. The first and second terms in (13.90) describe upward and downward energy shifts of the system, respectively. Coupling to a vibration typically leads to an upshift of the energy gap transition energy since energy must be put into the system and bath. However, as with hot bands, when there is thermal energy available in the bath, it also allows for down-shifts in the energy gap. The net balance of upward and downward shifts averaged over the bath follows the detailed balance expression

$$\tilde{C}(-\omega) = e^{-\beta\hbar\omega} \tilde{C}(\omega) \quad (13.91)$$

The balance of rates tends toward equal with increasing temperature. Fourier transforms of eqs. (13.76) gives two other representations of the energy gap spectrum

$$\tilde{C}'_{eg}(\omega_\alpha) = \omega_\alpha^2 D(\omega_\alpha) \coth(\beta\hbar\omega_\alpha/2) [\delta(\omega - \omega_\alpha) + \delta(\omega + \omega_\alpha)] \quad (13.92)$$

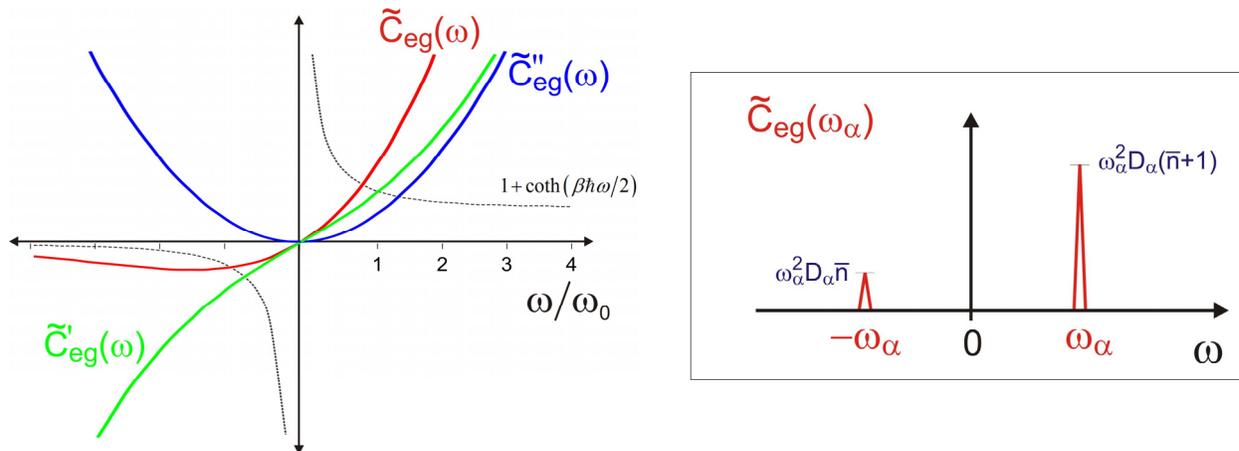
$$\tilde{C}''_{eg}(\omega_\alpha) = \omega_\alpha^2 D(\omega_\alpha) [\delta(\omega - \omega_\alpha) + \delta(\omega + \omega_\alpha)] \quad (13.93)$$

The representations in eqs. (13.90), (13.92), and (13.93) are not independent, but can be related to one another through

$$\tilde{C}'_{eg}(\omega_\alpha) = \coth(\beta\hbar\omega_\alpha/2) \tilde{C}''_{eg}(\omega_\alpha) \quad (13.94)$$

$$\tilde{C}_{eg}(\omega_\alpha) = (1 + \coth(\beta\hbar\omega_\alpha/2)) \tilde{C}''_{eg}(\omega_\alpha) \quad (13.95)$$

That is, given either the real or imaginary part of the energy gap correlation spectrum, we can predict the other part. As we will see, this relationship is one manifestation of the fluctuation-dissipation theorem that we address later. Due to its independence on temperature, the spectral density  $\tilde{C}''_{eg}(\omega_\alpha)$  is the commonly used representation.



Also from eqs. (13.69) and (13.87) we obtain the lineshape function as

$$\begin{aligned}
 g(t) &= \int_{-\infty}^{+\infty} d\omega \frac{1}{2\pi} \frac{\tilde{C}_{eg}(\omega)}{\omega^2} [\exp(-i\omega t) + i\omega t - 1] \\
 &= \int_0^{\infty} d\omega \frac{\tilde{C}_{eg}''(\omega)}{\pi\omega^2} \left[ \coth\left(\frac{\beta\hbar\omega}{2}\right) (1 - \cos \omega t) + i(\sin \omega t - \omega t) \right].
 \end{aligned} \tag{13.96}$$

The first expression relates  $g(t)$  to the complex energy gap correlation function, whereas the second separates the real and the imaginary parts and relates them to the imaginary part of the energy gap correlation function.

### Coupling to a Harmonic Bath

More generally for condensed phase problems, the system coordinates that we observe in an experiment will interact with a continuum of nuclear motions that may reflect molecular vibrations, phonons, or intermolecular interactions. We describe this continuum as continuous distribution of harmonic oscillators of varying mode frequency and coupling strength. The Energy Gap Hamiltonian is readily generalized to the case of a continuous distribution of motions if we statistically characterize the density of states and the strength of interaction between the system and this bath. This method is also referred to as the Spin-Boson Model used for treating a two-level spin- $\frac{1}{2}$  system interacting with a quantum harmonic bath.

Following our earlier discussion of the DHO model, the generalization of the EG Hamiltonian to the multimode case is

$$H_0 = \hbar\omega_{eg} + H_{eg} + H_B \tag{13.97}$$

$$H_B = \sum_{\alpha} \hbar\omega_{\alpha} (p_{\alpha}^2 + q_{\alpha}^2) \tag{13.98}$$

$$H_{eg} = \sum_{\alpha} 2\hbar\omega_{\alpha} d_{\alpha} q_{\alpha} + \lambda \tag{13.99}$$

$$\lambda = \sum_{\alpha} \hbar\omega_{\alpha} d_{\alpha}^2 \tag{13.100}$$

Note that the time-dependence to  $H_{eg}$  results from the interaction with the bath:

$$H_{eg}(t) = e^{iH_B t/\hbar} H_{eg} e^{-iH_B t/\hbar} \tag{13.101}$$

Also, since the harmonic modes are normal to one another, the dephasing function and lineshape function are obtained from

$$F(t) = \prod_{\alpha} F_{\alpha}(t) \quad g(t) = \sum_{\alpha} g_{\alpha}(t) \tag{13.102}$$

For a continuum, we assume that the number of modes are so numerous as to be continuous, and that the sums in the equations above can be replaced by integrals over a continuous distribution of states characterized by a density of states  $W(\omega)$ . Also the interaction with modes of a particular frequency are equal so that we can simply average over a frequency dependent coupling constant  $D(\omega) = \underline{d}^2(\omega)$ . For instance, eq. (13.102) becomes

$$g(t) = \int d\omega_\alpha W(\omega_\alpha) g(t, \omega_\alpha) \quad (13.103)$$

Coupling to a continuum leads to dephasing resulting from interaction to a continuum of modes of varying frequency. This will be characterized by damping of the energy gap frequency correlation function  $C_{eg}(t)$

$$C_{eg}(t) = \int d\omega_\alpha C_{eg}(\omega_\alpha, t) W(\omega_\alpha). \quad (13.104)$$

Here  $C_{eg}(\omega_\alpha, t) = \langle \delta\omega_{eg}(\omega_\alpha, t) \delta\omega_{eg}(\omega_\alpha, 0) \rangle$  refers to the energy gap frequency correlation function for a single harmonic mode given in eq. (13.71).

While eq. (13.104) expresses the modulation of the energy gap in the time domain, we can alternatively express the continuous distribution of coupled bath modes in the frequency domain:

$$\tilde{C}_{eg}(\omega) = \int d\omega_\alpha W(\omega_\alpha) \tilde{C}_{eg}(\omega_\alpha). \quad (13.105)$$

An integral of a single harmonic mode spectrum over a continuous density of states provides a coupling weighted density of states that reflects the action spectrum for the system-bath interaction. We evaluate this with the single harmonic mode spectrum, eq. (13.90). We see that the spectrum of the correlation function for positive frequencies is related to the product of the density of states and the frequency dependent coupling

$$\tilde{C}_{eg}(\omega) = \omega^2 D(\omega) W(\omega) (\bar{n} + 1) \quad (\omega > 0) \quad (13.106)$$

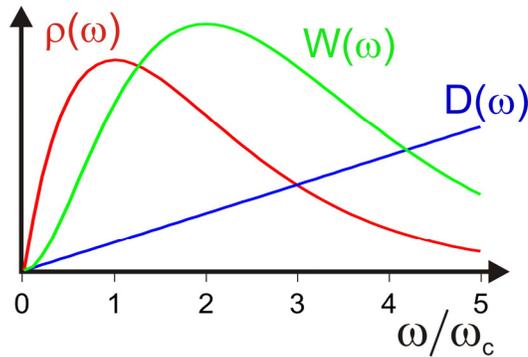
$$\tilde{C}_{eg}(\omega) = \omega^2 D(\omega) W(\omega) \bar{n} \quad (\omega < 0) \quad (13.107)$$

This is an action spectrum that reflects the coupling weighted density of states of the bath that contributes to the spectrum.

In practice, the unusually symmetry of  $\tilde{C}_{eg}(\omega)$  and its growth as  $\omega^2$  make it difficult to work with. Therefore we choose to express the frequency domain representation of the coupling-weighted density of states in eq. (13.106) as a *spectral density*, defined as

$$\begin{aligned}
\rho(\omega) &\equiv \frac{\tilde{C}_{eg}''(\omega)}{\pi\omega^2} \\
&= \frac{1}{\pi} \int d\omega_\alpha W(\omega_\alpha) D(\omega_\alpha) \delta(\omega - \omega_\alpha) \\
&= \frac{1}{\pi} W(\omega) D(\omega)
\end{aligned} \tag{13.108}$$

This expression is real and defined only for positive frequencies. Note  $\tilde{C}_{eg}''(\omega)$  is an odd function in  $\omega$ , and therefore  $\rho(\omega)$  is also.



Example of spectral density using an ohmic density of states,  $W(\omega) = \omega \exp[-\omega/\omega_c]$  and a linearly varying frequency dependent coupling.

The reorganization energy can be obtained from the first moment of the spectral density

$$\lambda = \hbar \int_0^\infty d\omega \omega \rho(\omega) \tag{13.109}$$

Furthermore, from eqs. (13.69) and (13.105) we obtain the lineshape function in two forms

$$\begin{aligned}
g(t) &= \int_{-\infty}^{+\infty} d\omega \frac{1}{2\pi} \frac{\tilde{C}_{eg}(\omega)}{\omega^2} [\exp(-i\omega t) + i\omega t - 1] \\
&= -\frac{i\lambda t}{\hbar} + \int_0^\infty d\omega \rho(\omega) \left[ \coth\left(\frac{\beta\hbar\omega}{2}\right) (1 - \cos \omega t) + i \sin \omega t \right]
\end{aligned} \tag{13.110}$$

In this expression the temperature dependence implies that in the high temperature limit, the real part of  $g(t)$  will dominate, as expected for a classical system. This is a perfectly general expression for the lineshape function in terms of an arbitrary spectral distribution describing the time scale and amplitude of energy gap fluctuations. Given a spectral density  $\rho(\omega)$ , you can calculate various spectroscopic observables and other time-dependent processes in a fluctuating environment.

Now, let's evaluate the behavior of the lineshape function and absorption lineshape for different forms of the spectral density. To keep things simple, we will consider the high temperature limit,  $k_B T \gg \hbar\omega$ . Here  $\coth(\beta\hbar\omega/2) \rightarrow 2/\beta\hbar\omega$  and we can neglect the imaginary part of the frequency correlation function and lineshape function. These examples are motivated by the spectral densities observed for random or noisy processes. Depending on the frequency

range and process of interest, noise tends to scale as  $\rho \sim \omega^{-n}$ , where  $n = 0, 1$  or  $2$ . This behavior is often described in terms of a spectral density of the form

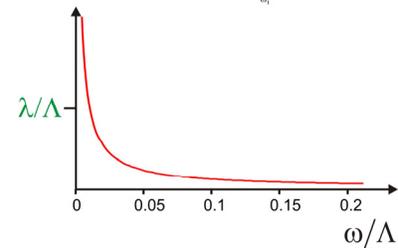
$$\rho(\omega) \propto \omega_c^{1-s} \omega^{s-2} e^{-\omega/\omega_c} \quad (13.111)$$

where  $\omega_c$  is a cut-off frequency, and the units are inverse frequency. These spectral densities have the desired property of being an odd function in  $\omega$ , and can be integrated to a finite value. The case  $s = 1$  is known as the Ohmic spectral density, whereas  $s > 1$  is super-ohmic and  $s < 1$  is sub-ohmic.

- 1) Let's first consider the example when  $\rho$  drops as  $1/\omega$  with frequency, which refers to the Ohmic spectral density with a high cut-off frequency. This is the spectral density that corresponds to an energy gap correlation function that decays infinitely fast:  $C_{eg}(t) \sim \delta(t)$ . To choose a definition consistent with eq. (13.109), we set

$$\rho(\omega) = \lambda / \Lambda \hbar \omega \quad (13.112)$$

where  $\Lambda$  is a finite high frequency integration limit that we enforce to keep  $\rho$  well behaved.  $\Lambda$  has units of frequency, it is equated with the inverse correlation time for the fast decay of  $C_{eg}(t)$ . Now we evaluate



$$\begin{aligned} g(t) &= \int_0^\infty d\omega \frac{2k_B T}{\Lambda \hbar \omega} \rho(\omega) (1 - \cos \omega t) - \frac{i\lambda t}{\hbar} \\ &= \int_0^\infty d\omega \frac{2\lambda k_B T}{\Lambda \hbar^2} \frac{(1 - \cos \omega t)}{\omega^2} - \frac{i\lambda t}{\hbar} \\ &= \lambda \frac{\pi k_B T}{\Lambda \hbar^2} t - \frac{i\lambda t}{\hbar} \end{aligned} \quad (13.113)$$

Then we obtain the dephasing function

$$F(t) = e^{-\Gamma t} \quad (13.114)$$

where we have defined the exponential damping constant as

$$\Gamma = \lambda \frac{\pi k_B T}{\Lambda \hbar^2} \quad (13.115)$$

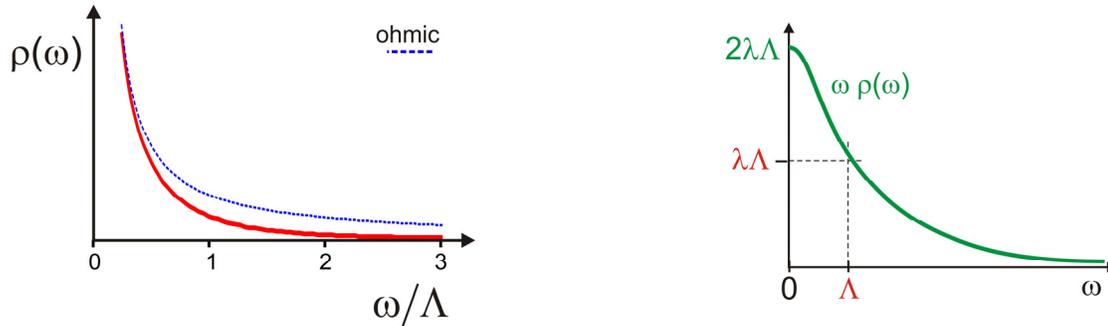
From this we obtain the absorption lineshape

$$\sigma_{abs} \propto \frac{|\mu_{eg}|^2}{(\omega - \omega_{eg}) + i\Gamma} \quad (13.116)$$

Thus, a spectral density that scales as  $1/\omega$  has a rapidly fluctuating bath and leads to a homogeneous Lorentzian lineshape with a half-width  $\Gamma$ .

- 2) Now take the case that we choose a Lorentzian spectral density centered at  $\omega = 0$ . To keep the proper odd function of  $\omega$  and definition of  $\lambda$  we write:

$$\rho(\omega) = \frac{\lambda}{\hbar\omega} \frac{\Lambda}{\omega^2 + \Lambda^2} \quad (13.117)$$



Note that for frequencies  $\omega \ll \Lambda$ , this has the ohmic form of eq. (13.112). This is a spectral density that corresponds to an energy gap correlation function that drops exponentially as  $C_{eg}(t) \sim \exp(-\Lambda t)$ . Here, in the high temperature (classical) limit  $kT \gg \hbar\Lambda$ , neglecting the imaginary part, we find

$$g(t) \approx \frac{\pi\lambda kT}{\hbar^2 \Lambda^2} [\exp(-\Lambda t) + \Lambda t - 1] \quad (13.118)$$

This expression looks familiar. If we equate

$$\Delta^2 = \lambda \frac{\pi kT}{\hbar^2} \quad (13.119)$$

and

$$\tau_c = \frac{1}{\Lambda} \quad (13.120)$$

we obtain the same lineshape function as the classical Gaussian-stochastic model:

$$g(t) = \Delta^2 \tau_c^2 [\exp(-t/\tau_c) + t/\tau_c - 1] \quad (13.121)$$

So, the interaction of an electronic transition with a harmonic bath leads to line broadening that is equivalent to random fluctuations of the energy gap. As we noted earlier, for the homogeneous limit, we find  $\Gamma = \Delta^2 \tau_c$ .

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### 13.5. Correspondence of Harmonic Bath and Stochastic Equations

So, why does the mathematical model for coupling of a system to a harmonic bath give the same results as the classical stochastic equations of motion for fluctuations? Why does coupling to a continuum of bath states have the same physical manifestation as perturbation by random fluctuations? The answer is that in both cases, we really have imperfect knowledge of the behavior of all the particles present. Observing a small subset of particles will have dynamics with a random character. These dynamics can be quantified through a correlation function or a spectral density for the time-scales of motion of the bath. In this section, we will demonstrate a more formal relationship that illustrates the equivalence of these pictures.

To take our discussion further, let's again consider the electronic absorption spectrum from a classical perspective. It's quite common to think that the electronic transition of interest is coupled to a particular nuclear coordinate  $Q$  which we will call a *local coordinate*. This local coordinate could be an intramolecular normal vibrational mode, an intermolecular rattling in a solvent shell, a lattice vibration, or another motion that influences the electronic transition. The idea is that we take the observed electronic transition to be linearly dependent on one or more local coordinates. Therefore describing  $Q$  allows us to describe the spectroscopy. However, since this local mode has further degrees of freedom that it may be interacting with, we are extracting a particular coordinate out of a continuum of other motions, the local mode will appear to feel a fluctuating environment—a friction.

Classically, we describe fluctuations in  $Q$  as Brownian motion, typically through a Langevin equation. In the simplest sense, this is an equation that restates Newton's equation of motion  $F=ma$  for a fluctuating force acting on a particle with position  $Q$ . For the case that this particle is confined in a harmonic potential,

$$m\ddot{Q}(t) + m\omega_0^2 Q^2 + m\gamma\dot{Q} = f_r(t) \quad (13.122)$$

Here the terms on the left side represent a damped harmonic oscillator. The first term is the force due to acceleration of the particle of mass  $m$  ( $F_{acc} = ma$ ). The second term is the restoring force of the potential,  $F_{res} = -\partial V/\partial Q = m\omega_0^2 Q$ . The third term allows friction to damp the motion of the coordinate at a rate  $\gamma$ . The motion of  $Q$  is under the influence of  $f_r(t)$ , a random fluctuating force exerted on  $Q$  by its surroundings.

Under steady-state conditions, it stands to reason that the random force acting on  $Q$  is the origin of the damping. The environment acts on  $Q$  with stochastic perturbations that add and remove kinetic energy, which ultimately leads to dissipation of any excess energy. Therefore, the Langevin equation is modelled as a Gaussian stationary process. We take  $f_r(t)$  to have a time-averaged value of zero,

$$\langle f_R(t) \rangle = 0 \quad (13.123)$$

and obey the classical fluctuation-dissipation theorem:

$$\gamma = \frac{1}{2mk_B T} \int_{-\infty}^{\infty} \langle f_R(t) f_R(0) \rangle \quad (13.124)$$

This shows explicitly how the damping is related to the correlation time for the random force. We will pay particular attention to the Markovian case

$$\langle f_R(t) f_R(0) \rangle = 2m\gamma k_B T \delta(t) \quad (13.125)$$

which indicate that the fluctuations immediately lose all correlation on the time scale of the evolution of  $Q$ .

The Langevin equation can be used to describe the correlation function for the time dependence of  $Q$ . For the Markovian case, eq. (13.122) leads to

$$C_{QQ}(t) = \frac{k_B T}{m\omega_0^2} \left( \cos \zeta t + \frac{\gamma}{2\zeta} \sin \zeta t \right) e^{-\gamma t/2} \quad (13.126)$$

where the reduced frequency  $\zeta = \sqrt{\omega_0^2 - \gamma^2/4}$ . The frequency domain expression, obtained by Fourier transformation, is

$$\tilde{C}_{QQ}(\omega) = \frac{\gamma k_B T}{m\pi} \frac{1}{(\omega_0^2 - \omega^2)^2 + \omega^2 \gamma^2} \quad (13.127)$$

Remembering that the absorption lineshape was determined by the quantum mechanical energy gap correlation function  $\langle \underline{q}(t) \underline{q}(0) \rangle$ , one can imagine an analogous classical description of the spectroscopy of a molecule that experiences interactions with a fluctuating environment. In essence this is what we did when discussing the Gaussian stochastic model of the lineshape.

A more general description of the position of a particle subject to a fluctuating force is the Generalized Langevin Equation. The GLE accounts for the possibility that the damping may be time-dependent and carry memory of earlier configurations of the system:<sup>1</sup>

$$m\ddot{Q}(t) + m\omega_0^2 Q^2 + m \int_0^t d\tau \gamma(t-\tau) \dot{Q}(\tau) = f(t) \quad (13.128)$$

The memory kernel,  $\gamma(t-\tau)$ , is a correlation function that describes the time-scales over which the fluctuating force retains memory of its previous state. The force due to friction on  $Q$  depends on the history of the system through  $\tau$ , the time preceding  $t$ , and the relaxation of  $\gamma(t-\tau)$ . The

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<sup>1</sup> Nitzan, A., *Chemical Dynamics in Condensed Phases*. Oxford University Press: New York, 2006.

classical fluctuation-dissipation relationship relates the magnitude of the fluctuating forces on the system coordinate to the damping

$$\langle f_R(t) f_R(\tau) \rangle = 2mk_B T \gamma(t-\tau) \quad (13.129)$$

As expected, for the case that  $\gamma(t-\tau) = \gamma\delta(t-\tau)$ , the GLE reduces to the Markovian case, eq. (13.122).

To demonstrate that the classical dynamics of the particle described under the GLE is related to the quantum mechanical dynamics for a particle interacting with a harmonic bath, we will outline the derivation of a quantum mechanical analog of the classical GLE. To do this we will derive an expression for the time-evolution of the system under the influence of the harmonic bath. We work with a Hamiltonian with a linear coupling between the system and the bath

$$H_{HB} = H_S(P, Q) + H_B(p_\alpha, q_\alpha) + H_{SB}(Q, q) \quad (13.130)$$

We take the system to be a particle of mass  $M$ , described through variables  $P$  and  $Q$ , whereas  $m_\alpha$ ,  $p_\alpha$  and  $q_\alpha$  are bath variables. For the present case, we will take the system to be a quantum harmonic oscillator,

$$H_s = \frac{P^2}{2M} + \frac{1}{2}M\Omega^2 Q^2 \quad (13.131)$$

and the Hamiltonian for the bath and its interaction with the system is written as<sup>2</sup>

$$H_B + H_{SB} = \sum_\alpha \left( \frac{p_\alpha^2}{2m_\alpha} + \frac{m_\alpha \omega_\alpha^2}{2} \left( q_\alpha - \frac{c_\alpha}{m_\alpha \omega_\alpha^2} Q \right)^2 \right) \quad (13.132)$$

This expression explicitly shows that each of the bath oscillators is displaced with respect to the system by an amount dependent on their mutual coupling. In analogy to our work with the Displaced Harmonic Oscillator, if we define a displacement operator<sup>3</sup>

$$\hat{D} = \exp \left( -\frac{i}{\hbar} \sum_\alpha \hat{p}_\alpha \xi_\alpha \right) \quad (13.133)$$

where

$$\xi_\alpha = \frac{c_\alpha}{m_\alpha \omega_\alpha^2} Q \quad (13.134)$$

then

$$H_B + H_{SB} = \hat{D}^\dagger H_B \hat{D} \quad (13.135)$$

<sup>2</sup> Nitzan, A., *Chemical Dynamics in Condensed Phases*. Oxford University Press: New York, 2006.; Mukamel, S., *Principles of Nonlinear Optical Spectroscopy*. Oxford University Press: New York, 1995.

<sup>3</sup> Caldeira, A. O.; Legget, A. J., *Ann. Phys* **1983**, *149*, 372-456.

Eqn. (13.132) is merely a different representation of our earlier harmonic bath model. To see this we write (13.132) as

$$H_B + H_{SB} = \sum_{\alpha} \hbar \omega_{\alpha} \left( \tilde{p}_{\alpha}^2 + (q_{\alpha} - \xi_{\alpha} \tilde{Q})^2 \right) \quad (13.136)$$

where the coordinates and momenta are written in reduced form

$$\begin{aligned} \tilde{Q} &= Q \sqrt{m \omega_0 / 2 \hbar} \\ \tilde{q}_{\alpha} &= q_{\alpha} \sqrt{m_{\alpha} \omega_{\alpha} / 2 \hbar} \\ \tilde{p}_{\alpha} &= p_{\alpha} / \sqrt{2 \hbar m_{\alpha} \omega_{\alpha}} \end{aligned} \quad (13.137)$$

Also, the reduced coupling is of the system to the  $\alpha^{\text{th}}$  oscillator is

$$\xi_{\alpha} = c_{\alpha} / \omega_{\alpha} \sqrt{m_{\alpha} \omega_{\alpha} m \omega_0} \quad (13.138)$$

Expanding (13.136) and collecting terms, we find that we can separate terms as in the harmonic bath model

$$H_B = \sum_{\alpha} \hbar \omega_{\alpha} \left( \tilde{p}_{\alpha}^2 + \tilde{q}_{\alpha}^2 \right) \quad (13.139)$$

$$H_{SB} = -2 \sum_{\alpha} \hbar \omega_{\alpha} \tilde{d}_{\alpha} \tilde{q}_{\alpha} + \lambda_B \quad (13.140)$$

The reorganization energy due to the bath oscillators is

$$\lambda_B = \sum_{\alpha} \hbar \omega_{\alpha} \tilde{d}_{\alpha}^2 \quad (13.141)$$

and the unitless bath oscillator displacement is

$$\tilde{d}_{\alpha} = \tilde{Q} \xi_{\alpha} \quad (13.142)$$

For our current work we regroup the total Hamiltonian (eq. (13.130)) as

$$H_{HB} = \left[ \frac{P^2}{2M} + \frac{1}{2} M \bar{\Omega}^2 Q^2 \right] + \sum_{\alpha} \hbar \omega_{\alpha} \left( \tilde{p}_{\alpha}^2 + \tilde{q}_{\alpha}^2 \right) - 2 \sum_{\alpha} \hbar \omega_{\alpha} \xi_{\alpha} \tilde{Q} \tilde{q}_{\alpha} \quad (13.143)$$

where the renormalized frequency is

$$\bar{\Omega}^2 = \Omega^2 + \Omega \sum_{\alpha} \omega_{\alpha} \xi_{\alpha}^2 \quad (13.144)$$

To demonstrate the equivalence of the dynamics under this Hamiltonian and the GLE, we can derive an equation of motion for the system coordinate  $Q$ . We approach this by first expressing these variables in terms of ladder operators

$$\hat{P} = i(\hat{a}^\dagger - \hat{a}) \quad \hat{p}_\alpha = i(\hat{b}_\alpha^\dagger - \hat{b}_\alpha) \quad (13.145)$$

$$\hat{Q} = (\hat{a}^\dagger + \hat{a}) \quad \hat{q}_\alpha = (\hat{b}_\alpha^\dagger + \hat{b}_\alpha) \quad (13.146)$$

Here  $\hat{a}, \hat{a}^\dagger$  are system operators,  $\hat{b}$  and  $\hat{b}^\dagger$  are bath operators. If the observed particle is taken to be bound in a harmonic potential, then the Hamiltonian in eq. (13.130) can be written as

$$H_{HB} = \hbar\bar{\Omega}\left(\hat{a}^\dagger\hat{a} + \frac{1}{2}\right) + \sum_\alpha \hbar\omega_\alpha\left(\hat{b}_\alpha^\dagger\hat{b}_\alpha + \frac{1}{2}\right) - (\hat{a}^\dagger + \hat{a})\sum_\alpha \hbar\omega_\alpha\mathcal{C}_\alpha\left(\hat{b}_\alpha^\dagger + \hat{b}_\alpha\right) \quad (13.147)$$

The equations of motion for the operators in eqs. (13.145) and (13.146) can be obtained from the Heisenberg equation of motion.

$$\dot{\hat{a}} = \frac{i}{\hbar}[H_{HB}, \hat{a}] \quad (13.148)$$

from which we find

$$\dot{\hat{a}} = -i\bar{\Omega}\hat{a} + i\sum_\alpha \omega_\alpha\mathcal{C}_\alpha\left(\hat{b}_\alpha^\dagger + \hat{b}_\alpha\right) \quad (13.149)$$

$$\dot{\hat{b}}_\alpha = -i\omega_\alpha\hat{b}_\alpha + i\omega_\alpha\mathcal{C}_\alpha(\hat{a}^\dagger + \hat{a}) \quad (13.150)$$

To derive an equation of motion for the system coordinate, we begin by solving for the time-evolution of the bath coordinates by directly integrating eq. (13.150),

$$\hat{b}_\alpha(t) = e^{-i\omega_\alpha t} \int_0^t e^{i\omega_\alpha t'} \left( i\omega_\alpha\mathcal{C}_\alpha(\hat{a}^\dagger + \hat{a}) \right) dt' + \hat{b}_\alpha(0)e^{-i\omega_\alpha t} \quad (13.151)$$

and insert the result into eq. (13.149). This leads to

$$\dot{\hat{a}} + i\bar{\Omega}\hat{a} - i\sum_\alpha \omega_\alpha\mathcal{C}_\alpha^2(\hat{a}^\dagger + \hat{a}) + i\int_0^t dt' \kappa(t-t')\left(\dot{\hat{a}}^\dagger(t') + \dot{\hat{a}}(t')\right) = iF(t) \quad (13.152)$$

where

$$\kappa(t) = \sum_\alpha \omega_\alpha\mathcal{C}_\alpha^2 \cos(\omega_\alpha t) \quad (13.153)$$

and

$$F(t) = \sum_\alpha \mathcal{C}_\alpha \left[ \hat{b}_\alpha(0) - \omega_\alpha\mathcal{C}_\alpha(\hat{a}^\dagger(0) + \hat{a}(0)) \right] e^{-i\omega_\alpha t} + h.c. \quad (13.154)$$

Now, recognizing that the time-derivative of the system variables is given by

$$\dot{\hat{P}} = i(\dot{\hat{a}}^\dagger - \dot{\hat{a}}) \quad (13.155)$$

$$\dot{\hat{Q}} = (\dot{\hat{a}}^\dagger + \dot{\hat{a}}) \quad (13.156)$$

and substituting eq. (13.152) into (13.155), we can write an equation of motion

$$\dot{\tilde{Q}}(t) + \left( \bar{\Omega} - 2 \sum_{\alpha} \frac{2c_{\alpha}^2}{\omega_{\alpha}} \right) \tilde{Q} + \int_0^t dt' 2\kappa(t-t') \dot{\tilde{Q}}(t') = F(t) + F^{\dagger}(t) \quad (13.157)$$

Equation (13.157) bears a striking resemblance to the classical GLE, eq. (13.128). In fact, if we define

$$\begin{aligned} \gamma(t) &= 2\bar{\Omega}\kappa(t) \\ &= \frac{1}{M} \sum_{\alpha} \frac{c_{\alpha}^2}{m_{\alpha}\omega_{\alpha}^2} \cos \omega_{\alpha}t \end{aligned} \quad (13.158)$$

$$\begin{aligned} f_R(t) &= \sqrt{2\hbar M \bar{\Omega}} [F(t) + F^{\dagger}(t)] \\ &= \sum_{\alpha} c_{\alpha} \left[ q_{\alpha}(0) \cos \omega_{\alpha}t + \frac{p_{\alpha}(0)}{m_{\alpha}\omega_{\alpha}} \sin \omega_{\alpha}t \right] \end{aligned} \quad (13.159)$$

then the resulting equation is isomorphic to the classical GLE

$$\dot{P}(t) + M\bar{\Omega}^2 Q(t) + M \int_0^t dt' \gamma(t-t') \dot{Q}(t') = f_R(t) \quad (13.160)$$

This demonstrates that the quantum harmonic bath acts a dissipative environment, whose friction on the system coordinate is given by eq. (13.158). What we have shown here is an outline of the proof, but detailed discussion of these relationships can be found elsewhere.<sup>4</sup>

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<sup>4</sup> Weiss, U. *Quantum Dissipative Systems*. 3rd ed.; World Scientific: Hackensack, N.J., 2008; Leggett, A. J.; Chakravarty, S.; Dorsey, A. T.; Fisher, M. P. A.; Garg, A.; Zwerger, W. Dynamics of the dissipative two-state system. *Reviews of Modern Physics* **1987**, 59 (1), 1-85; Yan, Y.; Xu, R. Quantum Mechanics of Dissipative Systems. *Annual Review of Physical Chemistry* **2005**, 56 (1), 187-219.

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