

7. OBSERVING FLUCTUATIONS IN SPECTROSCOPY¹

Here we will address how fluctuations are observed in spectroscopy and how dephasing influences the absorption lineshape. Our approach will be to calculate a dipole correlation function for a 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 object under an external potential are modulated by a random force.

We also aim to establish a connection between this picture 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 coupled modes.

7.1. FLUCTUATIONS AND RANDOMNESS: SOME DEFINITIONS²

“Fluctuations” is my word for the time-evolution of a randomly modulated system at or near equilibrium. You are observing an internal variable to a system under the influence of thermal agitation of the surroundings. Such processes are also commonly referred to as stochastic. A stochastic equation of motion is one in which there is both a deterministic and a random component to the time-development.

Randomness is a characteristic of all physical systems to a certain degree, even if the equations of motion that govern them are totally deterministic. This is because we generally have imperfect knowledge about all of the degrees of freedom for the system. This is the case when we look at a subset of particles which are under the influence of others that we have imperfect knowledge of. The result is that we may observe random fluctuations in our observables. This is always the case in condensed phase problems. It's unreasonable to think that you will come up with an equation of motion for the internal determinate variable, but we should be able to understand the behavior statistically and come up with equations of motion for probability distributions

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 a variable obtained by integrating over P , for instance

$$\begin{aligned}\langle x \rangle &= \int dx x P(x) \\ \langle x^2 \rangle &= \int dx x^2 P(x)\end{aligned}\quad (7.1)$$

For time-dependent processes, we use a time-dependent probability distribution

$$\begin{aligned}\langle x(t) \rangle &= \int dx x(t) P(x, t) \\ \langle x^2(t) \rangle &= \int dx x^2(t) P(x, t)\end{aligned}\quad (7.2)$$

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' :

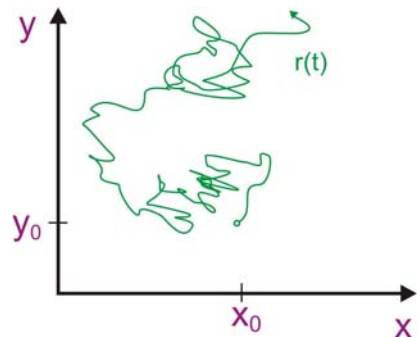
$$\langle A(t'') B(t') \rangle = \int dA \int dB AB P(t'', A; t', B). \quad (7.3)$$

Random fluctuations are also described through a time-dependent probability distribution, for which we need an equation of motion. A common example of such a process is Brownian motion, the fluctuating position of a particle under the influence of a thermal environment. It's 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. This probability density obeys the well known diffusion equation, here written in one dimension:

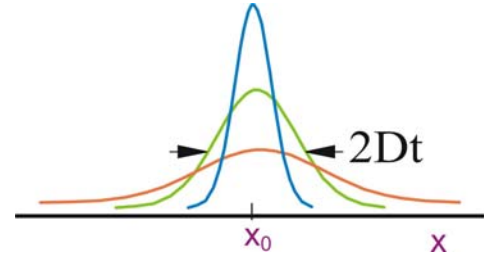
$$\frac{\partial P(x, t)}{\partial t} = D \frac{\partial^2}{\partial x^2} P(x, t) \quad (7.4)$$

Here 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 D is taken as imaginary. Given the initial condition $P(x, t_0) = \delta(x - x_0)$, the solution is a conditional probability density

$$P(x, t | x_0, t_0) = \frac{1}{\sqrt{2\pi Dt}} \exp\left(-\frac{(x - x_0)^2}{4Dt}\right) \quad (7.5)$$



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 in eq. (7.2) we find that



$$\begin{aligned}\langle x \rangle &= 0 \\ \langle x^2 \rangle &= 2Dt\end{aligned}\quad (7.6)$$

So, the distribution maintains a Gaussian shape centered at x_0 , and broadening with time as $2Dt$.

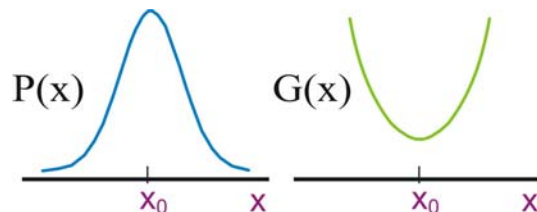
Brownian motion is an example of a Gaussian-Markovian process. Here Gaussian refers to cases in which we describe the probability distribution for a variable $P(x)$ as a Gaussian normal distribution. Here in one dimension:

$$\begin{aligned}P(x) &= A e^{-(x-x_0)^2/2\Delta^2} \\ \Delta^2 &= \langle x^2 \rangle - \langle x \rangle^2\end{aligned}\quad (7.7)$$

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:

$$G(x) = -kT \ln P(x)\quad (7.8)$$

If the probability density is Gaussian along x , then the system's free energy projected along 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, given the knowledge of the state of the system at time t_1 , you can exactly describe P for a later time t_2 . That is, the system has no memory of the behavior at an earlier time t_0 .

$$\begin{aligned} P(x, t_2; x, t_1; x, t_0) &= P(x, t_2; x, t_1)P(x, t_1; x, t_0) \\ P(t_2; t_1; t_0) &= P(t_2; t_1)P(t_1; t_0) \end{aligned} \quad (7.9)$$

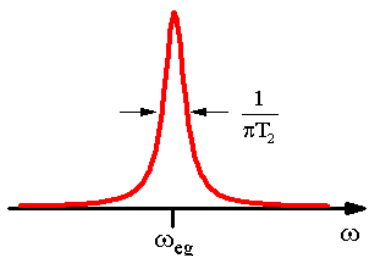
Markovian therefore refers to a timescale long compared to correlation time for the internal variable that you care about. For instance, the diffusion equation only holds after the particle has experienced sufficient collisions with its surroundings that it has no memory of its earlier position and momentum: $t > \tau_c$.

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7.2. FLUCTUATIONS IN SPECTROSCOPY: SPECTRAL DIFFUSION

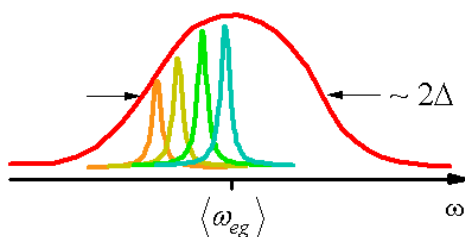
To begin our discussion about how fluctuations manifest themselves in spectroscopy, let's discuss their influence on the transition energy gap ω_{eg} for the absorption lineshape. Consider the two limiting cases of line broadening:

Homogeneous:



Here, the absorption lineshape is *dynamically* broadened by rapid variations in the amplitude, phase, or orientation of dipoles. Pure dephasing, lifetime, and rotation all contribute to an exponential decay time T_2 . For our current discussion, let's only concentrate on pure-dephasing T_2^* from rapid fluctuations in ω_{eg} .

Inhomogeneous:

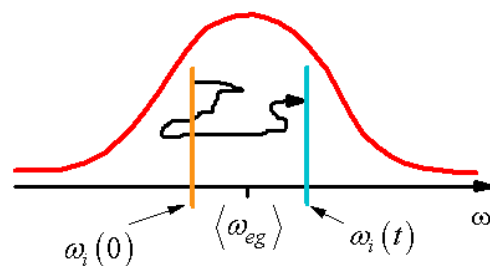


In this limit, the lineshape reflects a *static* distribution of resonance frequencies, and the width of the line represents the distribution of frequencies, which arise, for instance, from different structural environments.

Spectral Diffusion

More generally, every system lies between these limits. Imagine every molecule having a different "instantaneous frequency" $\omega_i(t)$ which evolves in time. 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 Δ .

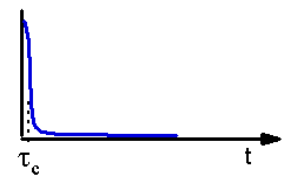
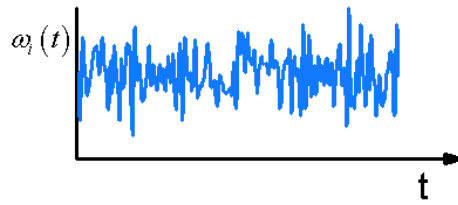
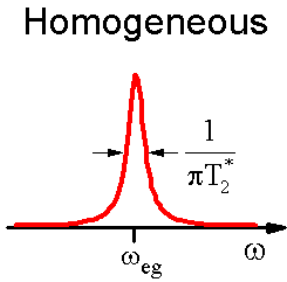
If $\omega_i(t)$ evolves rapidly relative to Δ^{-1} , the system is homogeneously broadened. If $\omega_i(t)$ evolves slowly the system is inhomogeneous. This behavior can be quantified through the transition frequency time-correlation function $C_{eg}(t) = \langle \omega_{eg}(t) \omega_{eg}(0) \rangle$. Our job will be to relate the behavior of $C_{eg}(t)$ with the correlation function that determined the lineshape, $C_{\mu\mu}(t)$.



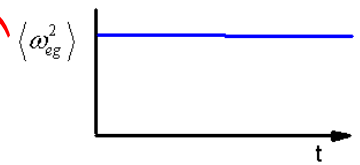
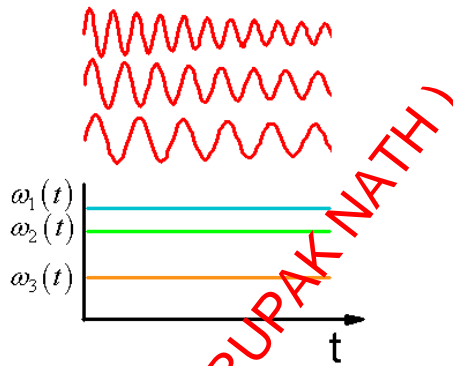
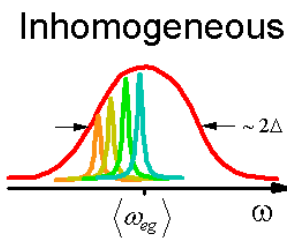
Time-domain behavior

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

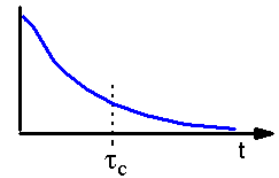
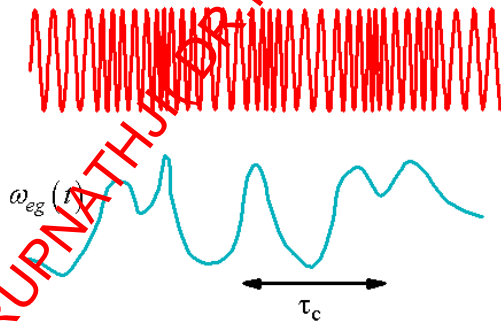
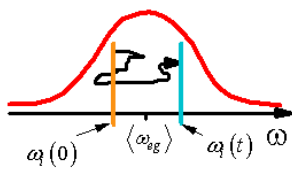
“Motionally narrowed”



Static distribution



Time-varying freq.

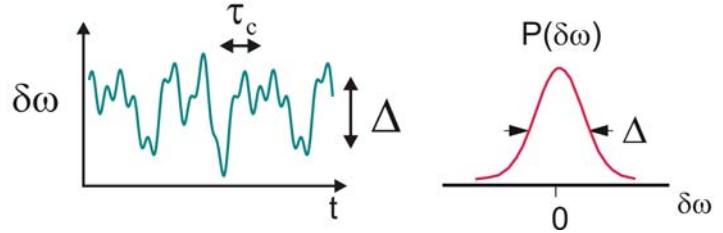


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7.3. GAUSSIAN-STOCHASTIC MODEL FOR SPECTRAL DIFFUSION

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 with a Gaussian statistics.



$$\omega(t) = \langle \omega \rangle + \delta\omega(t) \quad (7.10)$$

$$\langle \delta\omega(t) \rangle = 0 \quad (7.11)$$

The fluctuations in ω allow the system to explore a Gaussian distribution of transition frequencies characterized by a variance:

$$\Delta = \langle \delta\omega^2 \rangle^{1/2}. \quad (7.12)$$

Furthermore, we will describe the time scale of the random fluctuations through a correlation time:

$$\tau_c = \frac{1}{\Delta^2} \int_0^\infty dt \langle \delta\omega(t) \delta\omega(0) \rangle. \quad (7.13)$$

Let's treat the dipole moment as a classical internal variable to the system, whose time dependence arises from a linear relationship to the frequency fluctuations $\omega(t)$

$$\frac{\partial \mu}{\partial t} = -i\omega(t)\mu \quad (7.14)$$

Although it is a classical equation, note the similarity to the quantum Heisenberg equation for the dipole operator: $\partial\mu/\partial t = i[H(t)\mu - \mu H(t)]/\hbar$. This offers some insight into how the quantum version of this problem will look. The solution to eq. (7.14) is

$$\mu(t) = \mu(0) \exp\left[-i \int_0^t d\tau \omega(\tau)\right] \quad (7.15)$$

Substituting eq. (7.10) we have

$$\mu(t) = \mu(0) \exp\left[-i \langle \omega \rangle t - i \int_0^t d\tau \delta\omega(\tau)\right]. \quad (7.16)$$

Now to evaluate the dipole correlation function we have to perform an average over an equilibrium system.

$$C_{\mu\mu}(t) = \langle \mu(t) \mu(0) \rangle = \left\langle |\mu(0)|^2 \exp \left[-i \langle \omega \rangle t - i \int_0^t d\tau \delta\omega(\tau) \right] \right\rangle \quad (7.17)$$

or making the Condon approximation

$$C_{\mu\mu}(t) = |\mu|^2 e^{-i \langle \omega \rangle t} F(t) \quad (7.18)$$

where

$$F(t) = \left\langle \exp \left[-i \int_0^t d\tau \delta\omega(\tau) \right] \right\rangle. \quad (7.19)$$

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 of a 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)

$$F(t) = \exp \left[-i \int_0^t d\tau' \langle \delta\omega(\tau') \rangle + \frac{i^2}{2} \int_0^t d\tau' \int_0^t d\tau'' \langle \delta\omega(\tau') \delta\omega(\tau'') \rangle + \dots \right] \quad (7.20)$$

In this expression the first term is zero, and only the second term survives for a system with Gaussian statistics. We have re-written the dephasing function in terms of a correlation function that describes the fluctuating energy gap. Note that this is a classical description, so there is no time-ordering to the exponential. Now recognizing that we have a stationary system, we have

$$F(t) = \exp \left[-\frac{1}{2} \int_0^t d\tau' \int_0^t d\tau'' \langle \delta\omega(\tau' - \tau'') \delta\omega(0) \rangle \right] \quad (7.21)$$

$F(t)$ can be rewritten through a change of variables ($\tau = \tau' - \tau''$):

$$F(t) = \exp \left[-\int_0^t d\tau (t - \tau) \langle \delta\omega(\tau) \delta\omega(0) \rangle \right] \quad (7.22)$$

So the Gaussian stochastic model allows the influence of the frequency fluctuations on the lineshape to be described by a frequency correlation function that follows Gaussian statistics.

$$C_{\delta\omega\delta\omega}(t) = \langle \delta\omega(t) \delta\omega(0) \rangle \quad (7.23)$$

Note we are now dealing with two different correlation functions $C_{\delta\omega\delta\omega}$ and $C_{\mu\mu}$.

Now, we will calculate the lineshape assuming that $C_{\delta\omega\delta\omega}$ takes on an exponential form

$$C_{\delta\omega\delta\omega}(t) = \Delta^2 \exp[-t/\tau_c] \quad (7.24)$$

Then eq. (7.22) gives

$$F(t) = \exp\left[-\Delta^2 \tau_c^2 \left(\exp(-t/\tau_c) + t/\tau_c - 1\right)\right]. \quad (7.25)$$

Or given $F(t) = \exp(-g(t))$

$$g(t) = \Delta^2 \tau_c^2 \left(\exp(-t/\tau_c) + t/\tau_c - 1\right) \quad (7.26)$$

Let's look at the limiting forms of $g(t)$:

- 1) **Long correlation times** (or short t): $t \ll \tau_c$. 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

$$e^{-t/\tau_c} \approx 1 - t/\tau_c + \frac{t^2}{2\tau_c^2} + \dots \quad (7.27)$$

and from eq. (7.26) we obtain

$$g(t) = \Delta^2 t^2 / 2 \quad (7.28)$$

At short times, our dipole correlation function will have a Gaussian decay with a rate given by Δ^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:

$$\begin{aligned} \sigma(\omega) &= |\mu|^2 \int_{-\infty}^{+\infty} dt e^{i\omega t} e^{-i(\omega)\langle\omega\rangle t - g(t)} \\ &= |\mu|^2 \int_{-\infty}^{+\infty} dt e^{i(\omega - \langle\omega\rangle)t} e^{-\Delta^2 t^2 / 2} \\ &= \sqrt{\pi} |\mu|^2 \exp\left(-\frac{(\omega - \langle\omega\rangle)^2}{2\Delta^2}\right) \end{aligned} \quad (7.29)$$

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

- 2) **Very 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. (7.26) gives

$$g(t) = -\Delta^2 \tau_c t \quad (7.30)$$

If we define the constant

$$\Delta^2 \tau_c \equiv \Gamma = \frac{1}{T_2} \quad (7.31)$$

we see that the dephasing function has an exponential decay!

$$F(t) = \exp[-t/T_2] \quad (7.32)$$

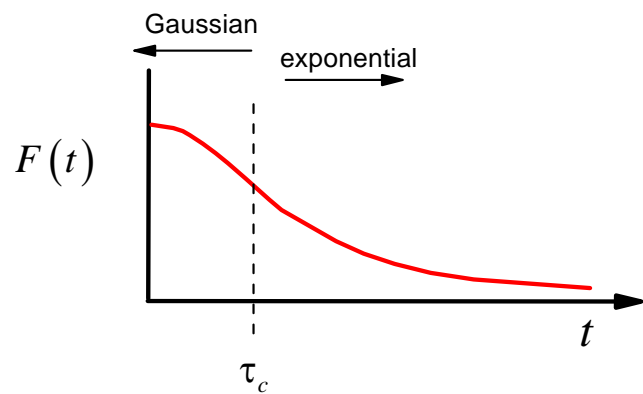
The lineshape for very short correlation times (or very fast fluctuations) takes on a Lorentzian shape

$$\begin{aligned} \sigma(\omega) &= |\mu|^2 \int_{-\infty}^{+\infty} dt e^{i(\omega - \langle\omega\rangle)t} e^{-t/T_2} \\ \text{Re } \sigma(\omega) &\propto \frac{1}{(\omega - \langle\omega\rangle)^2 + \frac{1}{T_2^2}} \end{aligned} \quad (7.33)$$

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.

General Behavior

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 (τ_c) are best characterized with respect to the distribution of accessible frequencies (Δ). So



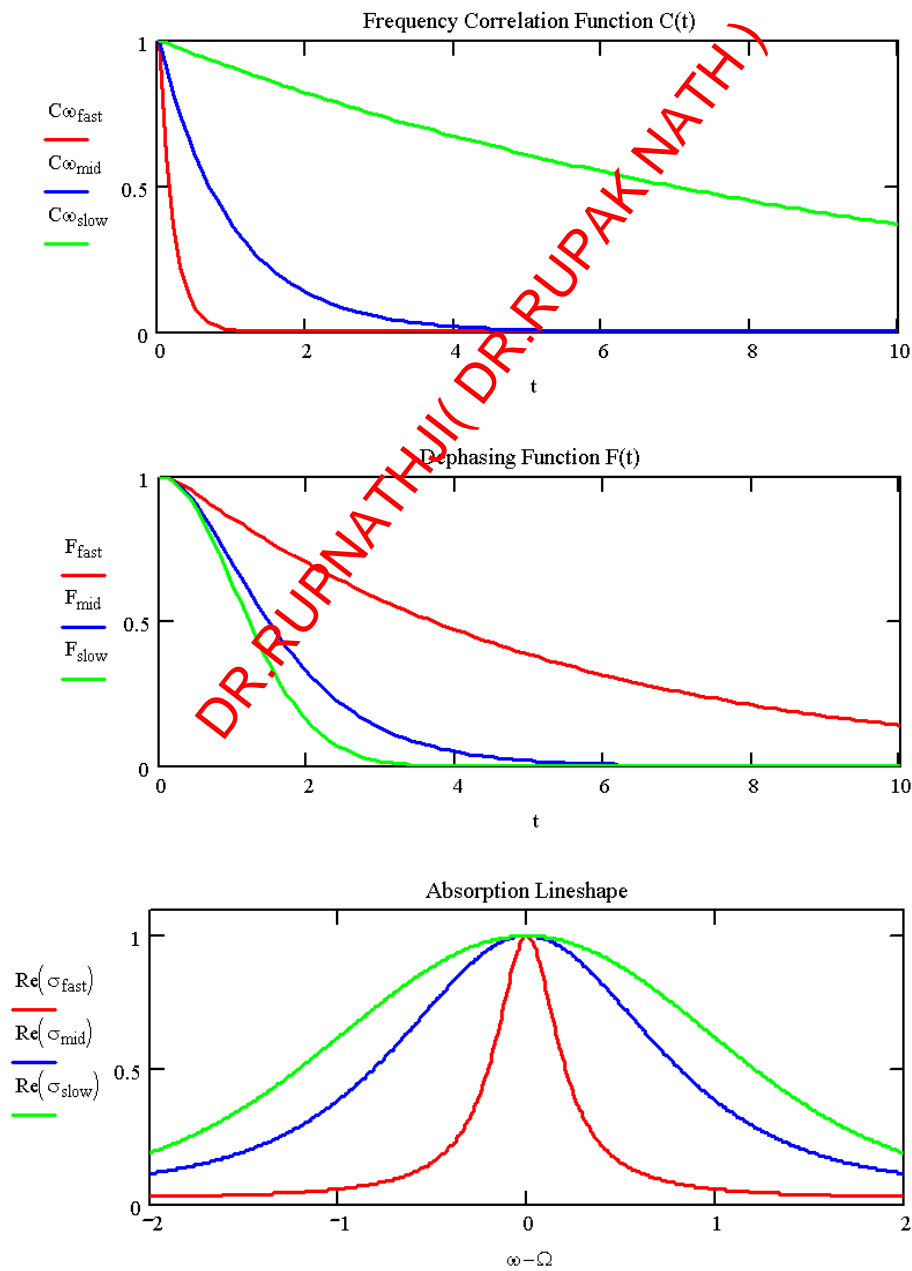
we can define a factor

$$\kappa = \Delta \cdot \tau_c \quad (7.34)$$

$\kappa \ll 1$ is the fast modulation limit and $\kappa \gg 1$ is the slow modulation limit. Let's look at how

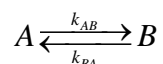
$C_{\delta\omega\delta\omega}$, $F(t)$, and $\sigma_{abs}(\omega)$ change as a function of κ .

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

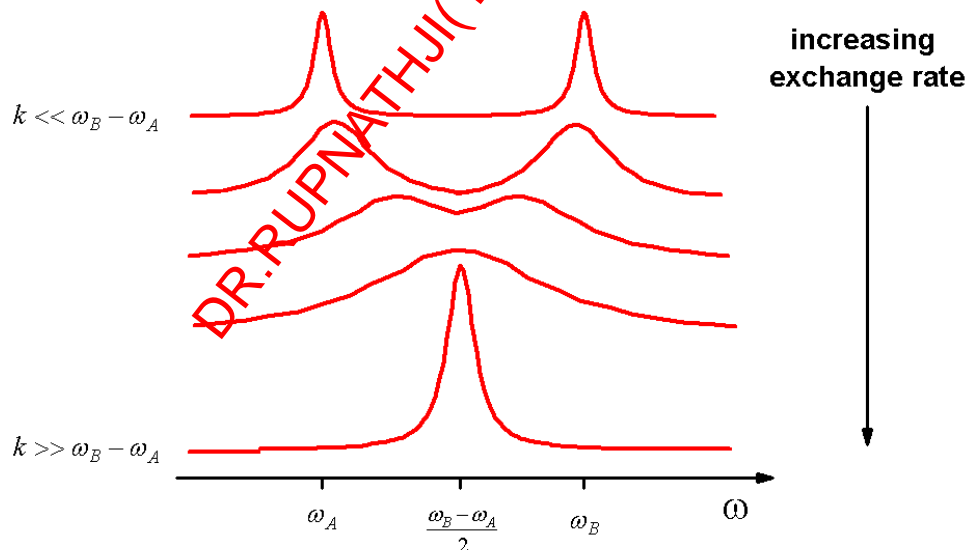


We see that for a fixed distribution of frequencies Δ the effect of increasing the time scale of fluctuations through this distribution (decreasing τ_c) is to gradually narrow the observed lineshape from a Gaussian distribution of static frequencies with width (FWHM) of $2.35 \cdot \Delta$ to a motionally 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 ω_A and ω_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.³



³ 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).

7.4. 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 in x can be expressed as an expansion in moments

$$\langle e^{ikx} \rangle = \sum_{n=0}^{\infty} \frac{(ik)^n}{n!} \langle x^n \rangle \quad (7.35)$$

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

$$\langle e^{ikx} \rangle = \exp \left(\sum_{n=1}^{\infty} \frac{(ik)^n}{n!} c_n(x) \right), \quad (7.36)$$

where the first few cumulants are:

$$c_1(x) = \langle x \rangle \quad \text{mean} \quad (7.37)$$

$$c_2(x) = \langle x^2 \rangle - \langle x \rangle^2 \quad \text{variance} \quad (7.38)$$

$$c_3(x) = \langle x^3 \rangle - 3\langle x \rangle \langle x^2 \rangle + 2\langle x \rangle^3 \quad \text{skewness} \quad (7.39)$$

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. For a system that obeys Gaussian statistics, all cumulants with $n > 2$ vanish!

We obtain the cumulants above by comparing terms in powers of x in eq. (7.35) and (7.36). 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

$$F = \exp[c] = 1 + c + \frac{1}{2}c^2 + \dots \quad (7.40)$$

$$c = c_1 H + \frac{1}{2}c_2 H^2 + \dots \quad (7.41)$$

Inserting eq. (7.41) into eq. (7.40) and collecting terms in orders of H gives

$$\begin{aligned} F &= 1 + \left(c_1 H + \frac{1}{2}c_2 H^2 + \dots \right) + \frac{1}{2} \left(c_1 H + \frac{1}{2}c_2 H^2 + \dots \right)^2 + \dots \\ &= 1 + (c_1)H + \frac{1}{2}(c_2 + c_1^2)H^2 + \dots \end{aligned} \quad (7.42)$$

Now comparing this with the expansion of the exponential

$$\begin{aligned} F &= \exp[fH] \\ &= 1 + f_1 H + \frac{1}{2}f_2 H^2 + \dots \end{aligned} \quad (7.43)$$

allows one to see that

$$\begin{aligned}
 c_1 &= f_1 \\
 c_2 &= f_2 - f_1^2
 \end{aligned}
 \tag{7.44}$$

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

$$\begin{aligned}
 F(t) &= \left\langle \exp_+ \left[-i \int_0^t dt \omega(t) \right] \right\rangle \\
 &\approx \exp [c_1(t) + c_2(t)]
 \end{aligned}
 \tag{7.45}$$

$$c_1 = -i \int_0^t d\tau \langle \omega(\tau) \rangle
 \tag{7.46}$$

$$\begin{aligned}
 c_2 &= -i \int_0^t d\tau_2 \int_0^{\tau_2} d\tau_1 \langle \omega(\tau_2) \omega(\tau_1) \rangle - \langle \omega(\tau_2) \rangle \langle \omega(\tau_1) \rangle \\
 &= -i \int_0^t d\tau_2 \int_0^{\tau_2} d\tau_1 \langle \delta\omega(\tau_2) \delta\omega(\tau_1) \rangle
 \end{aligned}
 \tag{7.47}$$

For Gaussian statistics, all higher cumulants vanish.

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