

14.3: Gaussian-Stochastic Model for Spectral Diffusion

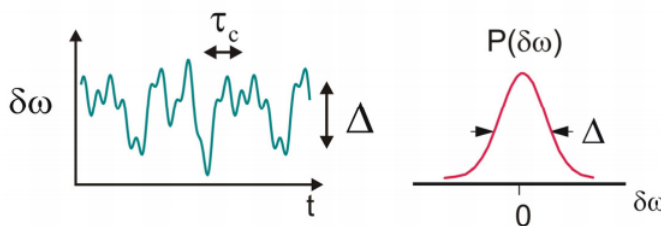
We will begin with a *classical* description of how random fluctuations in frequency influence the absorption lineshape, by calculating the dipole correlation function for the resonant transition. This is a Gaussian stochastic model for fluctuations, meaning that we will describe the time-dependence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

$$\omega(t) = \langle \omega \rangle + \delta\omega(t) \quad (14.3.1)$$

$$\langle \delta\omega(t) \rangle = 0 \quad (14.3.2)$$

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

$$\Delta = \sqrt{\langle \omega^2 \rangle - \langle \omega \rangle^2} = \sqrt{\langle \delta\omega^2 \rangle} \quad (14.3.3)$$



In many figures the width of the Gaussian distribution is labeled with the standard deviation (here Δ). This is meant to symbolize that Δ 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 2.35Δ .

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

$$C_{\delta\omega\delta\omega}(t) = \langle \delta\omega(t)\delta\omega(0) \rangle \quad (14.3.4)$$

Furthermore, we will describe the time scale of the random fluctuations through a correlation time τ_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 ω . Qualitatively, it is possible to write an equation of motion for μ 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 a unperturbed state, we expect that x will oscillate at a frequency ω , but with perturbations, it will vary through the distribution of available frequencies. One function that has this behavior is

$$x(t) = x_0 e^{-i\omega(t)t} \quad (14.3.5)$$

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

$$\frac{\partial \mu}{\partial t} = -i\omega(t)\mu(t) \quad (14.3.6)$$

Although it is a classical equation, note the similarity to the quantum Heisenberg equation for the dipole operator:

$$\partial \mu / \partial t = iH(t)\mu/\hbar + h.c. \quad (14.3.7)$$

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 Equation 14.3.6 is

$$\mu(t) = \mu(0) \exp \left[-i \int_0^t d\tau \omega(\tau) \right] \quad (14.3.8)$$

Substituting this expression and Equation 14.3.1 into the dipole correlation function gives or

$$C_{\mu\mu}(t) = |\mu|^2 e^{-i\langle \omega \rangle t} F(t) \quad (14.3.9)$$

where

$$F(t) = \left\langle \exp \left[-i \int_0^t d\tau \delta\omega(\tau) \right] \right\rangle \quad (14.3.10)$$

The dephasing function ($F(t)$) 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 below for details).

$$F(t) = \exp \left[-i \int_0^t d\tau' \langle \delta\omega(\tau') \rangle + \frac{i^2}{2!} \int_0^t d\tau' \int_0^t d\tau'' \{ \langle \delta\omega(\tau') \delta\omega(\tau'') \rangle - \langle \delta\omega(\tau') \rangle \langle \delta\omega(\tau'') \rangle \} \right] \quad (14.3.11)$$

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

$$F(t) = \exp \left[-\frac{1}{2} \int_0^t d\tau' \int_0^t d\tau'' \langle \delta\omega(\tau' - \tau'') \delta\omega(0) \rangle \right] \quad (14.3.12)$$

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 ($\tau = \tau' - \tau''$):

$$F(t) = \exp \left[-\int_0^t d\tau (t - \tau) \langle \delta\omega(\tau) \delta\omega(0) \rangle \right] \quad (14.3.13)$$

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 τ_c and takes on an exponential form

$$C_{\delta\omega\delta\omega}(t) = \Delta^2 \exp[-t/\tau_c] \quad (14.3.14)$$

Then Equation 14.3.13 gives

$$F(t) = \exp \left[-\Delta^2 \tau_c^2 (\exp(-t/\tau_c) + t/\tau_c - 1) \right] \quad (14.3.15)$$

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

$$g(t) = \Delta^2 \tau_c^2 (\exp(-t/\tau_c) + t/\tau_c - 1) \quad (14.3.16)$$

to interpret this lineshape function, let's look at its limiting forms.

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

$$e^{-t/\tau_c} \approx 1 - \frac{t}{\tau_c} + \frac{t^2}{2\tau_c^2} + \dots \quad (14.3.17)$$

and from Equation 14.3.16 we obtain

$$g(t) = \Delta^2 t^2 / 2 \quad (14.3.18)$$

At short times, the dipole correlation function will have a Gaussian decay with a rate given by Δ^2 :

$$F(t) = \exp(-\Delta^2 t^2 / 2) \quad (14.3.19)$$

This has the proper behavior for a classical correlation function, i.e., even in time

$$C_{\mu\mu}(t) = C_{\mu\mu}(-t). \quad (14.3.20)$$

In this limit, the absorption lineshape is:

$$\sigma(\omega) = |\mu|^2 \int_{-\infty}^{+\infty} dt e^{i\omega t} e^{-i(\omega - \langle\omega\rangle)t - g(t)} \quad (14.3.21)$$

$$= |\mu|^2 \int_{-\infty}^{+\infty} dt e^{i(\omega - \langle\omega\rangle)t} e^{-\Delta^2 t^2 / 2} \quad (14.3.22)$$

$$= \sqrt{\frac{2\pi}{\Delta^2}} |\mu|^2 \exp\left(-\frac{(\omega - \langle\omega\rangle)^2}{2\Delta^2}\right) \quad (14.3.23)$$

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

Short Correlation Times ($t \gg \tau_c$)

This corresponds to the homogeneous limit in which you can approximate

$$C_{\delta\omega\delta\omega}(t) = \Delta^2 \delta(t). \quad (14.3.24)$$

For $t \gg \tau_c$ we set $e^{-t/\tau_c} \approx 0$, $t/\tau_c \gg 1$, and Equation 14.3.16 gives

$$g(t) = -\Delta^2 \tau_c t \quad (14.3.25)$$

If we define the constant

$$\Delta^2 \tau_c \equiv \Gamma \quad (14.3.26)$$

we see that the dephasing function has an exponential decay:

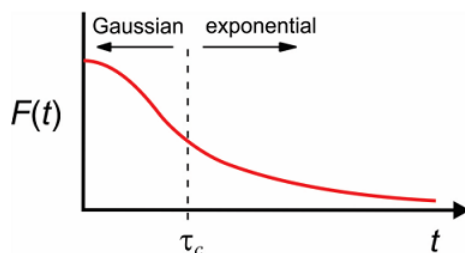
$$F(t) = \exp[-\Gamma t] \quad (14.3.27)$$

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

$$\begin{aligned} \sigma(\omega) &= |\mu|^2 \int_{-\infty}^{+\infty} dt e^{i(\omega - \langle\omega\rangle)t} e^{-\Gamma t} \\ \text{Re } \sigma(\omega) &= |\mu|^2 \frac{\Gamma}{(\omega - \langle\omega\rangle)^2 + \Gamma^2} \end{aligned} \quad (14.3.28)$$

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.

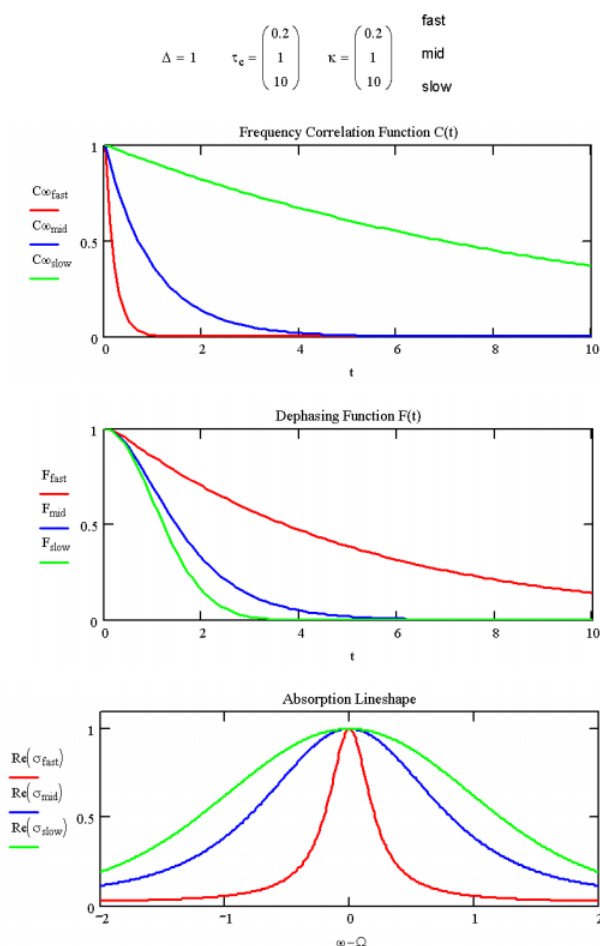
More generally, the envelope of the dipole correlation function will look Gaussian at short times and exponential at long times.



The correlation time is the separation between these regimes. The behavior for varying time scales of the dynamics (τ_c) are best characterized with respect to the distribution of accessible frequencies (Δ). So we can define a factor

$$\kappa = \Delta \cdot \tau_c \quad (14.3.29)$$

$\kappa \ll 1$ 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 .



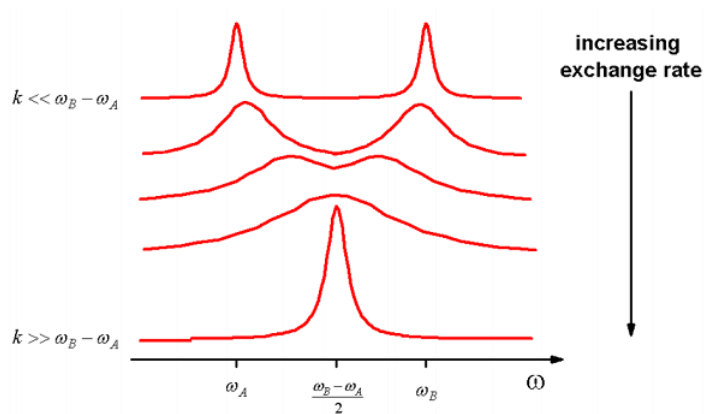
We see that for a fixed distribution of frequencies Δ the effect of increasing the time scale of fluctuations through this distribution (decreasing τ_c) is to gradually narrow the observed lineshape from a Gaussian distribution of static frequencies with width (FWHM) of 2.35Δ to a motionally narrowed Lorentzian lineshape with width (FWHM) of

$$\Delta^2 \tau_c / \pi = \Delta \cdot \kappa / \pi. \quad (14.3.30)$$

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.



Appendix: The Cumulant Expansion

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

$$\underbrace{\langle e^{ikx} \rangle = \sum_{n=0}^{\infty} \frac{(ik)^n}{n!} \langle x^n \rangle}_{\text{expansion in moments}} \quad (14.3.32)$$

An alternate way of expressing this expansion is in terms of cumulants

$$\underbrace{\langle e^{ikx} \rangle = \exp \left(\sum_{n=1}^{\infty} \frac{(ik)^n}{n!} c_n(x) \right)}_{\text{expansion in cumulants}} \quad (14.3.33)$$

where the first few cumulants are:

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

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

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

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 Equation 14.3.29 and 14.3.33 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

$$F = \exp[c] = 1 + c + \frac{1}{2}c^2 + \dots \quad (14.3.34)$$

$$c = c_1 H + \frac{1}{2}c_2 H^2 + \dots \quad (14.3.35)$$

Inserting Equation 14.3.35 into Equation 14.3.34 and collecting terms in orders of H gives

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

Now comparing this with the expansion of the exponential operator (of H)

$$F = \exp[fH] \quad (14.3.36)$$

$$= 1 + f_1 H + \frac{1}{2} f_2 H^2 + \dots \quad (14.3.37)$$

allows one to see that

$$\begin{aligned} c_1 &= f_1 \\ c_2 &= f_2 - f_1^2 \end{aligned} \quad (14.3.38)$$

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

$$F(t) = \left\langle \exp_+ \left[-i \int_0^t dt \omega(t) \right] \right\rangle \quad (14.3.39)$$

$$\approx \exp[c_1(t) + c_2(t)] \quad (14.3.40)$$

$$\begin{aligned} c_1 &= -i \int_0^t d\tau \langle \omega(\tau) \rangle \\ c_2 &= - \int_0^t d\tau_2 \int_0^{\tau_2} d\tau_1 \{ \langle \omega(\tau_2) \omega(\tau_1) \rangle - \langle \omega(\tau_2) \rangle \langle \omega(\tau_1) \rangle \} \\ &= - \int_0^t d\tau_2 \int_0^{\tau_2} d\tau_1 \langle \delta\omega(\tau_2) \delta\omega(\tau_1) \rangle \end{aligned}$$

For Gaussian statistics, all higher cumulants vanish.

Readings

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