

Gaussian-stochastic model for the absorption lineshape

This worksheet plots the frequency correlation function $C_{\omega\omega}$, dephasing function F , and absorption lineshape σ . The parameters that determine the lineshape are the width of the frequency distribution Δ and the frequency correlation time τ_c . Defining $\kappa = \Delta\tau_c$, we will investigate the fast ($\kappa > 1$), intermediate ($\kappa = 1$) and slow ($\kappa < 1$) modulation cases.

First define variables. Range variables for the time and frequency axes : $ma := 2^{12}$ $i := 0..ma - 1$ $ii := 0..2^{13} - 1$

time grid: $t_i := i \cdot 0.1$

We will perform all calculations for a fixed value of Δ , and calculate for three correlation times: $z := 0, 1..2$

$$\Delta := 1 \quad \tau_{c_z} := \begin{array}{|c|} \hline 0.2 \\ \hline 1 \\ \hline 10 \\ \hline \end{array} \quad \kappa_z := \tau_{c_z} \cdot \Delta \quad \kappa = \begin{pmatrix} 0.2 \\ 1 \\ 10 \end{pmatrix}$$

Define the lineshape function and dephasing function:

$$g(t, \tau_c) := \left[\Delta^2 \cdot \tau_c^2 \cdot \left(\exp\left(\frac{-t}{\tau_c}\right) + \frac{t}{\tau_c} - 1 \right) \right] \quad F(t, \tau_c) := \exp(-g(t, \tau_c))$$

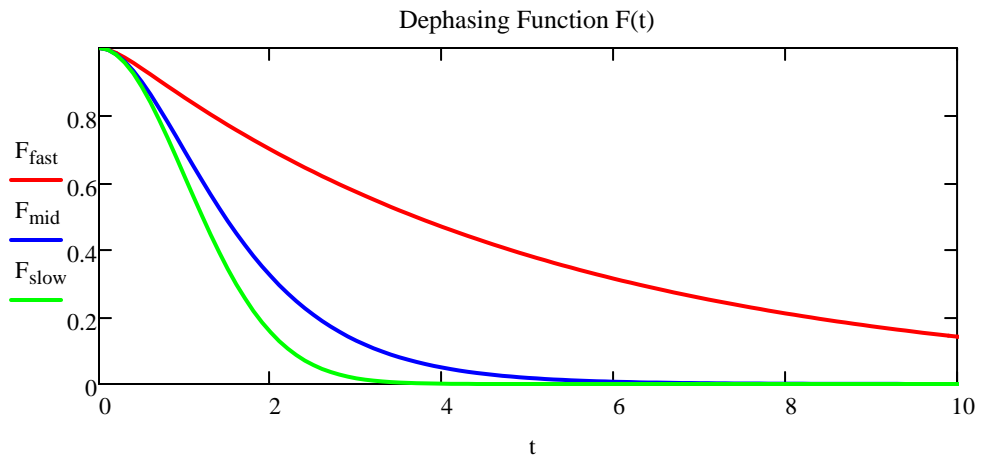
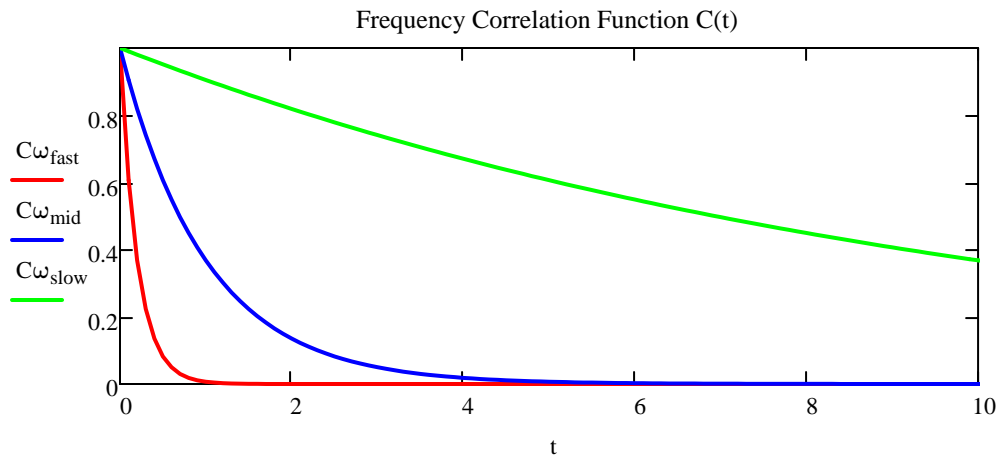
Evaluate the correlation function and lineshape function

$$C\omega_{fast_1} := \exp\left(\frac{-t_i}{\tau_{c_0}}\right) \quad C\omega_{slow_1} := \exp\left(\frac{-t_i}{\tau_{c_2}}\right) \quad C\omega_{mid_1} := \exp\left(\frac{-t_i}{\tau_{c_1}}\right)$$

$$F_{fast_{ii}} := 0 \quad F_{slow_{ii}} := 0 \quad F_{mid_{ii}} := 0$$

$$F_{fast_1} := F(t_i, \tau_{c_0}) \quad F_{slow_1} := F(t_i, \tau_{c_2}) \quad F_{mid_1} := F(t_i, \tau_{c_1})$$

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



Now Fourier transform the dipole correlation function $C_{\mu\mu}$ and use the real part to obtain the lineshape.

$$\begin{aligned}
 C_{\mu_{fast}_i} &:= F(t_i, \tau_{c_0}) & C_{\mu_{slow}_i} &:= F(t_i, \tau_{c_2}) & C_{\mu_{mid}_i} &:= F(t_i, \tau_{c_1}) \\
 S_{fast} &:= \text{cfft}(C_{\mu_{fast}}) & S_{slow} &:= \text{cfft}(C_{\mu_{slow}}) & S_{mid} &:= \text{cfft}(C_{\mu_{mid}})
 \end{aligned}$$

Some manipulations to wrap and normalize the Fourier transform:

$$\sigma_{fast} := \frac{\text{stack}(S_{fast}, S_{fast})}{\max(\text{Re}(S_{fast}))} \quad \sigma_{slow} := \frac{\text{stack}(S_{slow}, S_{slow})}{\max(\text{Re}(S_{slow}))} \quad \sigma_{mid} := \frac{\text{stack}(S_{mid}, S_{mid})}{\max(\text{Re}(S_{mid}))}$$

Determine the frequency axis for the Fourier transform

$$\text{freq} := \frac{1}{t_1 - t_0} \quad t_{max} := t_{ma-1} \quad \omega_{ii} := \frac{ii \cdot \text{freq}}{\pi \cdot t_{max}} \quad \underline{\underline{\Omega}} := \omega_{ma-1}$$

