The Brownian Oscillator Model

Analyze limiting behavior for the general expression.
References are to equation numbers in: S.Mukamel, *Principles of Nonlinear Spectroscopy* (Oxford, 1995).

Imaginary part of correlation function, eq. 8.67b   h is defined as h/2π

$$C''(t) = \frac{-h}{2\cdot m}\cdot\frac{1}{\zeta}\cdot\exp\left(\frac{-\gamma\cdot t}{2}\right)\cdot\sin(\zeta\cdot t) \qquad \zeta = \sqrt{\omega^2 - \frac{\gamma^2}{4}} \qquad (1)$$

$$C''(t) = \frac{-h}{\left(m\cdot\sqrt{4\cdot\omega^2-\gamma^2}\right)}\cdot\exp\left(\frac{-1}{2}\cdot\gamma\cdot t\right)\cdot\sin\left(\frac{1}{2}\cdot\sqrt{4\cdot\omega^2-\gamma^2}\cdot t\right) \qquad (2)$$

Overdamped Oscillator ($\omega \ll \gamma$)

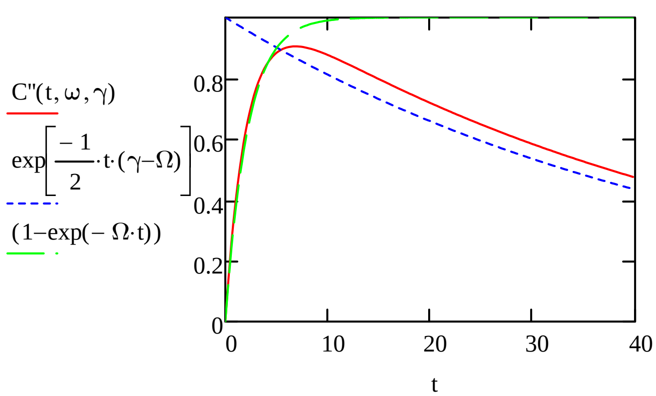
$$C''(t) = \frac{-h}{\left(m\cdot\sqrt{-4\cdot\omega^2+\gamma^2}\right)}\cdot\exp\left(\frac{-1}{2}\cdot\gamma\cdot t\right)\cdot\sinh\left(\frac{1}{2}\cdot\sqrt{-4\cdot\omega^2+\gamma^2}\cdot t\right) \qquad (3)$$

define $\Omega = \sqrt{-4\cdot\omega^2+\gamma^2}$ (4)

$$C''(t) = \frac{-h}{m\cdot\Omega}\cdot\exp\left(\frac{-1}{2}\cdot\gamma\cdot t\right)\cdot\sinh\left(\frac{1}{2}\cdot\Omega\cdot t\right) = \frac{-h}{2\cdot m\cdot\Omega}\cdot\exp\left(\frac{-1}{2}\cdot\gamma\cdot t\right)\cdot\left(\exp\left(\frac{1}{2}\cdot\Omega\cdot t\right) - \exp\left(-\frac{1}{2}\cdot\Omega\cdot t\right)\right)$$

$$C''(t) = \frac{-1}{2}\cdot\frac{h}{m\cdot\Omega}\cdot(1-\exp(-\Omega\cdot t))\cdot\exp\left[\frac{-1}{2}\cdot t\cdot(\gamma-\Omega)\right] \qquad (5)$$

$\omega := 0.1 \qquad \gamma := 0.5 \qquad\qquad t := 0, 0.2 .. 39.8$



$\Omega = 0.458$

$\gamma - \Omega = 0.042$

Overdamped Oscillator (ω<<γ)

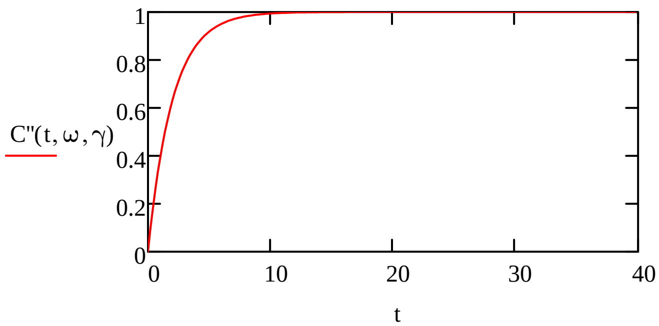
for ω=0:

$$C''(t) = \frac{-h}{(m \cdot \gamma)} \cdot \exp\left(\frac{-1}{2} \cdot \gamma \cdot t\right) \cdot \sinh\left(\frac{1}{2} \cdot \gamma \cdot t\right)$$

$$C''(t) = \frac{-1}{2} \cdot h \cdot \frac{1 - \exp(-\gamma \cdot t)}{m \cdot \gamma} \qquad (6)$$

(....this seems to have the wrong limiting behavior...?)

$\omega := 0.001 \quad \gamma := 0.5$



Undamped Oscillator (ω>>γ) (γ=0)

$$C''(t) = \frac{-1}{2} \cdot \frac{h}{m \cdot \omega} \cdot \sin(\omega \cdot t) \qquad (7)$$

Underdamped Oscillator (ω>>γ) (γ>0)

$$C''(t) = \frac{-1}{2} \cdot \frac{h}{m \cdot \omega} \cdot \exp\left(\frac{-1}{2} \cdot \gamma \cdot t\right) \cdot \sin(\omega \cdot t) \qquad (8)$$

Critically Damped Oscillator (2ω=γ)

$$C''(t) = \lim_{\zeta \to 0} \left(\frac{-h}{2 \cdot m} \cdot \frac{1}{\zeta} \cdot \exp\left(\frac{-\gamma \cdot t}{2}\right) \cdot \sin(\zeta \cdot t)\right)$$

$$C''(t) = \frac{-1}{2} \cdot \frac{h}{m} \cdot \exp\left(\frac{-1}{2} \cdot \gamma \cdot t\right) \cdot t \qquad (9)$$

Real part of correlation function (from eq.8.67c)

$$C'(t) = \frac{-h}{4\cdot m}\cdot\frac{1}{\zeta}\cdot\left(\coth\left(\frac{i\cdot\phi\cdot h\cdot\beta}{2}\right)\cdot\exp(-\phi\cdot t) - \coth\left(\frac{i\cdot\phi'\cdot h\cdot\beta}{2}\right)\cdot\exp(-\phi'\cdot t)\right) \qquad (10)$$

h is defined as h/2π $\quad \phi = \frac{\gamma}{2} + i\cdot\zeta \quad \phi' = \frac{\gamma}{2} - i\cdot\zeta \quad \zeta = \sqrt{\omega^2 - \frac{\gamma^2}{4}} \quad \phi\cdot\phi' = \omega^2$ (11)

$$C'(t) = \frac{-h}{4\cdot m}\cdot\frac{1}{\zeta}\cdot\left(\coth\left(\frac{i\cdot\phi\cdot h\cdot\beta}{2}\right)\cdot\exp(-i\cdot\zeta\cdot t) - \coth\left(\frac{i\cdot\phi'\cdot h\cdot\beta}{2}\right)\cdot\exp(i\cdot\zeta\cdot t)\right)\cdot\exp\left(-\frac{\gamma}{2}\cdot t\right) \qquad (12)$$

In the high temperature limit ($1/\beta$=0), coth(x)=1/x from the series expansion

$$C'(t) = \frac{1}{m\cdot\beta\cdot\omega^2\cdot\sqrt{-4\cdot\omega^2+\gamma^2}}\cdot(\exp(-\phi\cdot t)\cdot\phi' - \exp(-\phi'\cdot t)\cdot\phi)$$

$$C'(t) = \frac{1}{m\cdot\beta\cdot\omega^2\cdot 2i\cdot\zeta}\cdot(\exp(-i\cdot\zeta\cdot t)\cdot\phi' - \exp(i\cdot\zeta\cdot t)\cdot\phi)\cdot\exp\left(\frac{-\gamma\cdot t}{2}\right) \qquad (13)$$

Overdamped Oscillator ($\omega \ll \gamma$)

from (13) with $\phi=\gamma$ $\quad \phi'=0$ $\quad \zeta=i\gamma/2$

$$C'(t) = \frac{1}{m\cdot\beta\cdot\omega^2}\cdot\exp(-\gamma\cdot t) \qquad (14)$$

This is Mukamel's eq. 8.71b

Undamped Oscillator ($\omega \gg \gamma$) (γ=0) $\quad \phi = i\omega \quad \phi' = -i\omega \quad \zeta=\omega$

from (10) - not high temp limit - Mukamel's eq. 8.68

$$C'(t) = \frac{1}{2}\cdot\frac{h}{m\cdot\omega}\cdot\coth\left(\frac{1}{2}\cdot\omega\cdot h\cdot\beta\right)\cdot\cos(\omega\cdot t) \qquad (15)$$

from (13) (16)

$$C'(t) = \frac{-\cos(\omega\cdot t)}{m\cdot\beta\cdot\omega^2}$$

Underdamped Oscillator $(\omega >> \gamma)$ $(\gamma > 0)$

From (12) - not high T $\phi = i\omega$ $\phi' = -i\omega$ $\zeta = \omega$

$$C'(t) = \frac{1}{2}\cdot\frac{h}{m\cdot\omega}\cdot\coth\left(\frac{1}{2}\cdot\omega\cdot h\cdot\beta\right)\cdot\cos(\omega\cdot t)\cdot\exp\left(-\frac{\gamma}{2}\cdot t\right) \qquad (17)$$

From (13) $\phi = i\omega$ $\phi' = -i\omega$ $\zeta = \omega$

$$C'(t) = \frac{-\cos(\omega\cdot t)}{m\cdot\beta\cdot\omega^2}\cdot\exp\left(\frac{-\gamma\cdot t}{2}\right) \qquad (18)$$

Start with (13)

$$C'(t) = \frac{1}{m\cdot\beta\cdot\omega^2}\cdot\left[\frac{\exp(-i\cdot\zeta\cdot t)\cdot\left(\frac{\gamma}{2} - i\cdot\zeta\right) - \exp(i\cdot\zeta\cdot t)\cdot\left(\frac{\gamma}{2} + i\cdot\zeta\right)}{2i\cdot\zeta}\right]\cdot\exp\left(\frac{-\gamma\cdot t}{2}\right)$$

$\zeta = \omega$

$$C'(t) = \frac{-1}{2\cdot m\cdot\beta\cdot\omega^3}\cdot\exp\left(\frac{-1}{2}\cdot\gamma\cdot t\right)\cdot(2\cdot\cos(\omega\cdot t)\cdot\omega + \gamma\cdot\sin(\omega\cdot t)) \qquad (19)$$

(this is Mukamel's eq. 8.69)