14.7: Example- Vibrational dephasing and energy relaxation

Recall that the Fourier transform of a time correlation function can be related to some kind of frequency spectrum. For example, the Fourier transform of the velocity autocorrelation function of a particular degree of freedom q of interest

$$v = \dot{q}$$

where $I(\omega)$, gives the relevant frequencies contributing to the dynamics of q, but does not give amplitudes. This "frequency" spectrum $I(\omega) = \int_0^\infty dt\, e^{i\omega t} C_{\text{vv}}(t)$ is simply given by

$$C_{vv}(t)$$

That is, we take the Laplace transform of $s = -i\omega$ using T_2. Since $s = -i\omega$ carries information about the relevant frequencies of the system, the decay of $s = -i\omega$ in time is a measure of how strongly coupled the motion of q is to the rest of the bath, i.e., how much of an overlap there is between the relevant frequencies of the bath and those of q. The more of an overlap there is, the more mixing there will be between the system and the bath, and hence, the more rapidly the motion of the system will become vibrationally "out of phase" or decorrelated with itself. Thus, the decay time of $s = -i\omega$, which is denoted $C_{\varepsilon\varepsilon} = \frac{\langle \varepsilon(0)\varepsilon(t)\rangle}{\langle \varepsilon^2 \rangle}$ is called the *vibrational dephasing time*.

Another measure of the strength of the coupling between the system and the bath is the time required for the system to dissipate energy into the bath when it is excited away from equilibrium. This time can be obtained by studying the decay of the energy autocorrelation function:

$$\varepsilon(t)$$

where $\varepsilon(t) = \frac{1}{2}m\dot{q}^2 + \phi(q) - kT$ is defined to be

$$T_1$$

The decay time of this correlation function is denoted $\phi(q) = \frac{1}{2}m\omega^2 q^2$.

The question then becomes: what are these characteristic decay times and how are they related? To answer this, we will take a phenomenological approach. We will assume the validity of the GLE for q:

$$m\ddot{q} = -\frac{\partial \phi}{\partial q} - \int_0^t d\tau\, \dot{q}(\tau)\zeta(t-\tau) + R(t)$$

and use it to calculate $\phi(q) = \frac{1}{2}m\omega^2 q^2$ and $C_{\varepsilon\varepsilon} = \frac{\langle \varepsilon(0)\varepsilon(t)\rangle}{\langle \varepsilon^2 \rangle}$.

Suppose the potential $\phi(q)$ is harmonic and takes the form

$$\ddot{q} = -\omega^2 q - \int_0^t d\tau\, \dot{q}(t-\tau)\gamma(\tau) + f(t)$$

Substituting into the GLE and dividing through by m gives

$$\gamma(t) = \frac{\zeta(t)}{m} \qquad f(t) = \frac{R(t)}{m}$$

where

$$\dot{q}(0)$$

An equation of motion for $s = -i\omega$ can be obtained directly by multiplying both sides of the GLE by $\langle \dot{q}(0)\ddot{q}(t)\rangle = -\omega^2\langle \dot{q}(0)q(t)\rangle - \int_0^t d\tau\langle \dot{q}(0)\dot{q}(t-\tau)\rangle\gamma(\tau) + \langle \dot{q}(0)f(t)\rangle$ and averaging over a canonical ensemble:

$$\langle \dot{q}(0)f(t)\rangle = \frac{1}{m}\langle \dot{q}(0)R(t)\rangle = 0$$

Recall that

$$\langle \dot{q}(0)\ddot{q}(t)\rangle = \frac{d}{dt}\langle \dot{q}(0)\dot{q}(t)\rangle = \frac{dC_{\text{vv}}}{dt}$$

and note that

$$\int_0^t d\tau \, \langle \dot{q}(0)\dot{q}(\tau) \rangle = \langle \dot{q}(0)q(t) \rangle - \langle \dot{q}(0)q(0) \rangle = \langle \dot{q}(0)q(t) \rangle$$

also

$$\langle \dot{q}(0)q(t) \rangle = \int_0^t d\tau \, C_{vv}(\tau)$$

Thus,

$$\frac{d}{dt}C_{vv}(t)$$

Combining these results gives an equation for $s = -i\omega$

$-\int_0^t d\tau \, \left(\omega^2 + \gamma(t-\tau) \right) C_{vv}(\tau)$	$=$	$-\int_0^t d\tau \, K(t-\tau)C_{vv}(\tau)$
$-\int_0^t d\tau \, \left(\omega^2 + \gamma(t-\tau) \right) C_{vv}(\tau)$	$=$	$K(t)$

which is known as the *memory function equation* and the kernel $s\tilde{C}_{vv}(s) - C_{vv}(0) = -\tilde{C}_{vv}(s)\tilde{K}(s)$ is known as the memory function or memory kernel. This type of integro-differential equation is called a *Volterra* equation and it can be solved by Laplace transforms.

Taking the Laplace transform of both sides gives

$$C_{vv}(0) = 1$$

However, it is clear that $\tilde{K}(s) = \frac{\omega^2}{s} + \tilde{\gamma}(s)$ and also

$$s\tilde{C}_{vv}(s) - 1$$

Thus, it follows that

$\left(\frac{\omega^2}{s} + \tilde{\gamma}(s) \right) \tilde{C}_{vv}(s)$	$=$	$\tilde{C}_{vv}(s)$
$\frac{s}{s^2 + s\tilde{\gamma}(s) + \omega^2}$	$=$	$s^2 + s\tilde{\gamma}(s) + \omega^2 = 0$

In order to perform the inverse Laplace transform, we need the poles of the integrand, which will be determined by the solutions of

$$\tilde{\gamma}(s)$$

which we could solve directly if we knew the explicit form of ω.

However, if $\tilde{\gamma}(0)$ is sufficiently larger than $s = s_0 + s_1 + s_2 + \cdots$, then it is possible to develop a perturbation solution to this equation. Let us assume the solutions for s can be written as $(s_0 + s_1 + s_2 + \cdots)^2 + (s_0 + s_1 + s_2 + \cdots)\tilde{\gamma}(s_0 + s_1 + s_2 + \cdots) + \omega^2 = 0$

Substituting in this ansatz gives

$$\tilde{\gamma}$$

Since we are assuming $s_0^2 + \omega^2 = 0$ is small, then to lowest order, we have

$$s_0 = \pm i\omega$$

so that $2s_0 s_1 + s_0\tilde{\gamma}(s_0) = 0$. The first order equation then becomes

$$s_1 = -\frac{\tilde{\gamma}(s_0)}{2} = -\frac{\tilde{\gamma}(\pm i\omega)}{2}$$

or

$$\tilde{\gamma}(\pm i\omega)$$

Note, however, that

$\int_0^\infty \; dt \; \gamma(t)e^{\pm i\omega t}$	=	$\int_0^\infty \; dt \; [\gamma(t)\cos\omega t \pm i\gamma(t)\sin\omega t]$
	=	$\gamma'(\omega) \pm i\gamma''(\omega)$
	=	$s \approx \pm i\,(\omega + \gamma''(\omega)) - \frac{\gamma'(\omega)}{2} \equiv \pm i\Omega - \frac{\gamma'(\omega)}{2}$

Thus, stopping the first order result, the poles of the integrand occur at

$$s_+$$

Define

$i\Omega - \frac{\gamma'(\omega)}{2}$	=	$s-$
$-i\Omega - \frac{\gamma'(\omega)}{2}$	=	$\tilde{C}_{vv}(s) \approx \frac{s}{(s-s_+)(s-s_-)}$

Then

$$C_{\mathrm{vv}}(t) = \frac{1}{2\pi i}\oint \frac{s e^{st}\; ds}{(s-s_+)(s-s_-)}$$

and $s = -i\omega$ is then given by the contour integral

$$C_{\mathrm{vv}}(t) = \frac{s_+ e^{s_+ t}}{(s_+ - s_-)} + \frac{s_- e^{s_- t}}{(s_- - s_+)}$$

Taking the residue at each pole, we find

$$C_{\mathrm{vv}}(t) = e^{-\gamma'(\omega)t/2}\left[\cos\Omega t - \frac{\gamma'(\omega)}{2\Omega}\sin\Omega t\right]$$

which can be simplified to give

$$\Omega$$

Thus, we see that the GLE predicts $s = -i\omega$ oscillates with a frequency $\frac{1}{T_2} = \frac{\gamma'(\omega)}{2} = \frac{\zeta'(\omega)}{2m}$ and decays exponentially. From the exponential decay, we can directly read off the time $C_{\epsilon\epsilon} = \frac{\langle\epsilon(0)\epsilon(t)\rangle}{\langle\epsilon^2\rangle}$:

$$2m$$

That is, the value of the real part of the Fourier (Laplace) transform of the friction kernel evaluated at the renormalized frequency divided by $C_{\mathrm{qq}}(t) = \langle q(0)q(t)\rangle$ gives the vibrational dephasing time! By a similar scheme, one can easily show that the position autocorrelation function $C_{\mathrm{qq}}(t) = e^{-\gamma'(\omega)t/2}\left[\cos\Omega t + \frac{\gamma'(\omega)}{2\Omega}\sin\Omega t\right]$ decays with the same dephasing time. It's explicit form is

$$C_{\varepsilon\varepsilon}(t)$$

The energy autocorrelation function $C_{\mathrm{qq}}(t)$ can be expressed in terms of the more primitive correlation functions $C_{\varepsilon\varepsilon}(t) = \frac{1}{2}C_{\mathrm{vv}}^2(t) + \frac{1}{2}C_{qq}^2(t) + \frac{1}{\omega^2}\dot{C}_{qq}^2(t)$ and $s = -i\omega$. It is a straightforward, although extremely tedious, matter to show that the relation, valid for the harmonic potential of mean force, is

$$C_{\varepsilon\varepsilon}(t) = e^{-\gamma'(\omega)t} \times (\text{oscillatory functions of } t)$$

Substituting in the expressions for $c_{\varepsilon\varepsilon}(t) = \frac{1}{2}C_{vv}^2(t) + \frac{1}{2}C_{qq}^2(t) + \frac{1}{\omega^2}C_{qq}^2(t)$ and $s = -i\omega \; C_{\mathrm{vv}}(t)$ gives

$$\frac{1}{T_1} = \gamma'(\omega) = \frac{\zeta'(\omega)}{m}$$

so that the decay time $\phi(q) = \frac{1}{2}m\omega^2 q^2$ can be seen to be

$$\frac{1}{T_2} = \frac{1}{2T_1}$$

and therefore, the relation between $\phi(q) = \frac{1}{2}m\omega^2 q^2$ and $C_{\varepsilon\varepsilon} = \frac{\langle \varepsilon(0)\varepsilon(t)\rangle}{\langle \varepsilon^2 \rangle}$ can be seen immediately to be

$$\omega$$

The incredible fact is that this result is also true quantum mechanically. That is, by doing a simple, purely classical treatment of the problem, we obtained a result that turns out to be the correct *quantum mechanical* result!

Just how big are these times? If ω is very large compared to any typical frequency relevant to the bath, then the friction kernel evaluated at this frequency will be extremely small, giving rise to a long decay time. This result is expect, since, if $\tilde{\gamma}(0)$ is large compared to the bath, there are very few ways in which the system can dissipate energy into the bath. The situation changes dramatically, however, if a small amount of anharmonicity is added to the potential of mean force. The figure below illustrates the point for a harmonic diatomic molecule interacting with a Lennard-Jones bath. The top figure shows the velocity autocorrelation function for an oscillator whose frequency is approximately 3 times the characteristic frequency of the bath, while the bottom one shows the velocity autocorrelation function for the case that the frequency disparity is a factor of 6.
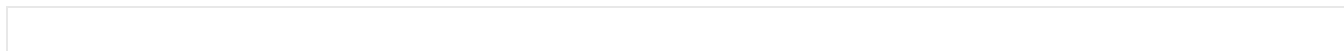
Figure 1:

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