14.6: Mori-Zwanzig Theory- A more general derivation of the GLE

A derivation of the GLE valid for a general bath can be worked out. The details of the derivation are given in the book by Berne and Pecora called *Dynamic Light Scattering*. The system coordinate q and its conjugate momentum p are introduced as a column vector:

$$\mathbf{A} = \begin{pmatrix} q \\ p \end{pmatrix}$$

and, in addition, one introduces statistical *projection operators* P and Q that project onto subspaces in phase space parallel and orthogonal to A. These operators take the form

$$P = \langle \ldots \mathbf{A}^{\mathrm{T}} \rangle \langle \mathbf{A}\mathbf{A}^{\mathrm{T}} \rangle^{-1}$$

$$Q = I - P$$

These operators are Hermitian and satisfy the property of idempotency:

$$P^2 = P$$

$$Q^2 = Q$$

Also, note that

$$P\mathbf{A} = \mathbf{A}$$

$$Q\mathbf{A} = 0$$

The time evolution of $\mathbf{A}$ is given by application of the classical propagator:

$$\mathbf{A}(t) = e^{iLt}\mathbf{A}(0)$$

Note that the evolution of $\mathbf{A}$ is unitary, i.e., it preserves the norm of $\mathbf{A}$:

$$|\mathbf{A}(t)|^2 = |\mathbf{A}(0)|^2$$

Differentiating both sides of the time evolution equation for $\mathbf{A}$ gives:

$$\frac{dA}{dt} = e^{iLt} iL\mathbf{A}(0)$$

Then, an identity operator is inserted in the above expression in the form $I = P + Q$:

$$\frac{dA}{dt} = e^{iLt}(P+Q)iL\mathbf{A}(0) = e^{iLt}PiL\mathbf{A}(0) + e^{iLt}QiL\mathbf{A}(0)$$

The first term in this expression defines a frequency matrix acting on $\mathbf{A}$:

$e^{iLt}PiL\mathbf{A}(0)$	$=$	$e^{iLt}\langle iL\mathbf{A}\mathbf{A}^{\mathrm{T}} \rangle \langle \mathbf{A}\mathbf{A}^{\mathrm{T}} \rangle^{-1}\mathbf{A}$
	$=$	$\langle iL\mathbf{A}\mathbf{A}^{\mathrm{T}} \rangle \langle \mathbf{A}\mathbf{A}^{\mathrm{T}} \rangle^{-1} e^{iLt}\mathbf{A}$
	$=$	$\langle iL\mathbf{A}\mathbf{A}^{\mathrm{T}} \rangle \langle \mathbf{A}\mathbf{A}^{\mathrm{T}} \rangle^{-1}\mathbf{A}(t)$
	$\equiv$	$i\mathbf{\Omega}\mathbf{A}(t)$

where

$$\mathbf{\Omega} = \langle L\mathbf{A}\mathbf{A}^{\mathrm{T}} \rangle \langle \mathbf{A}\mathbf{A}^{\mathrm{T}} \rangle^{-1}$$

In order to evaluate the second term, another identity operator is inserted directly into the propagator:

$$e^{iLt} = e^{i(P+Q)Lt}$$

Consider the difference between the two propagators:

$$e^{iLt} - e^{iQLt}$$

If this difference is Laplace transformed, it becomes

$$(s - iL)^{-1} - (s - iQL)^{-1}$$

which can be simplified via the general operator identity:

$$\mathrm{A}^{-1} - \mathrm{B}^{-1} = \mathrm{A}^{-1}(\mathrm{B} - \mathrm{A})\mathrm{B}^{-1}$$

Letting

$$A = (s - iL)$$

$$B = (s - iQL)$$

we have

$(s - iL)^{-1} - (s - iQL)^{-1}$	$=$	$(s - iL)^{-1}(s - iQL - s + iL)(s - iQL)^{-1}$
	$=$	$(s - iL)^{-1} iPL(s - iQL)^{-1}$

or

$$(s - iL)^{-1} = (s - iQL)^{-1} + (s - iL)^{-1}(s - iQL - s + iL)(s - iQL)^{-1}$$

Now, inverse Laplace transforming both sides gives

$$e^{iLt} = e^{iQLt} + \int_0^t d\tau\, e^{iL(t-\tau)}\, iPLe^{iQL\tau}$$

Thus, multiplying fromthe right by $QiL\mathbf{A}$ gives

$$e^{iLt}QiL\mathbf{A} = e^{iQLt}QiL\mathbf{A} + \int_0^t d\tau\, e^{iL(t-\tau)}\, iPLe^{iQL\tau}QiL\mathbf{A}$$

Define a vector

$$\mathbf{F}(t) = e^{iQLt}QiL\mathbf{A}(0)$$

so that

$$e^{iLt}QiL\mathbf{A} = \mathbf{F}(t) + \int_0^t d\tau\, \langle iL\mathbf{F}(\tau)\mathbf{A}^T\rangle\langle\mathbf{A}\mathbf{A}^{\mathrm{T}}\rangle^{-1}\mathbf{A}(t-\tau)$$

Because $\mathbf{F}(t)$ is completely orthogonal to $\mathbf{A}(t)$, it is straightforward to show that

$$Q\mathbf{F}(t) = \mathbf{F}(t)$$

Then,

$\langle iL\mathbf{F}(\tau)\mathbf{A}^{\mathrm{T}}\rangle\langle\mathbf{A}\mathbf{A}^{\mathrm{T}}\rangle^{-1}\mathbf{A}$	$=$	$\langle iLQ\mathbf{F}(\tau)\mathbf{A}^{\mathrm{T}}\rangle\langle\mathbf{A}\mathbf{A}^{\mathrm{T}}\rangle^{-1}\mathbf{A}$
	$=$	$-\langle Q\mathbf{F}(\tau)(iL\mathbf{A})^{\mathrm{T}}\rangle\langle\mathbf{A}\mathbf{A}^{\mathrm{T}}\rangle^{-1}\mathbf{A}$
	$=$	$-\langle Q^2\mathbf{F}(\tau)(iL\mathbf{A})^{\mathrm{T}}\rangle\langle\mathbf{A}\mathbf{A}^{\mathrm{T}}\rangle^{-1}\mathbf{A}$

	$=$	$-\langle Q\mathbf{F}(\tau)(QiL\mathbf{A})^{\mathrm{T}}\rangle\langle\mathbf{A}\mathbf{A}^{\mathrm{T}}\rangle^{-1}\mathbf{A}$
	$=$	$-\langle\mathbf{F}(\tau)\mathbf{F}^{\mathrm{T}}(0)\rangle\langle\mathbf{A}\mathbf{A}^{\mathrm{T}}\rangle^{-1}\mathbf{A}$

Thus,

$$e^{iLt}QiL\mathbf{A}=\mathbf{F}(t)-\int_0^t d\tau\ \langle\mathbf{F}(\tau)\mathbf{F}^T(0)\rangle\langle\mathbf{A}\mathbf{A}^{\mathrm{T}}\rangle^{-1}\mathbf{A}(t-\tau)$$

Finally, we define a memory kernel matrix:

$$\mathbf{K}(t)=\langle\mathbf{F}(\tau)\mathbf{F}^{\mathrm{T}}(0)\rangle\langle\mathbf{A}\mathbf{A}^{\mathrm{T}}\rangle^{-1}$$

Then, combining all results, we find, for $\frac{dbfA}{dt}$:

$$\frac{d\mathbf{A}}{dt}=i\mathbf{\Omega}(t)\mathbf{A}-\int_0^t d\tau\ \mathbf{K}(\tau)\mathbf{A}(t-\tau)+\mathbf{F}(t)$$

which equivalent to a generalized Langevin equation for a particle subject to a harmonic potential, but coupled to a general bath. For most systems, the quantities appearing in this form of the generalized Langevin equation are

$i\mathbf{\Omega}$	$=$	$\mathbf{K}(t)$
$\mathbf{F}(t)$	$=$	$\mathbf{K}(t)$
$\begin{pmatrix}0\\R(t)\end{pmatrix}$	$=$	$\phi(q)=\frac{m\omega^2q^2}{2}$

It is easy to derive these expressions for the case of the harmonic bath Hamiltonian when

$$\langle R(0)R(t)\rangle=\langle R(0)e^{iLt}R(0)\rangle=kT\zeta(t)$$

For the case of a harmonic bath Hamiltonian, we had shown that the friction kernel was related to the random force by the fluctuation dissipation theorem:

$$exp(iQLt)$$

For a general bath, the relation is not as simple, owing to the fact that $\mathbf{F}(t)$ is evolved using a modified propagator $\langle R(0)e^{iQLt}R(0)\rangle=kT\zeta(t)$. Thus, the more general form of the fluctuation dissipation theorem is

$$\langle R(0)e^{iQLt}R(0)\rangle\approx\langle R(0)e^{iL_{\text{cons}}t}R(0)\rangle$$

so that the dynamics of $R(t)$ is prescribed by the propagator $\langle R(0)e^{iQLt}R(0)\rangle=kT\zeta(t)$. This more general relation illustrates the difficulty of defining a friction kernel for a general bath. However, for the special case of a stiff harmonic diatomic molecule interacting with a bath for which all the modes are soft compared to the frequency of the diatomic, a very useful approximation results. One can show that

$$iL_{cons}$$

where $C_{vv}(t)=\frac{\langle\dot{q}(0)\dot{q}(t)\rangle}{\langle\dot{q}^2\rangle}$ is the Liouville operator for a system in which the diatomic is held rigidly fixed at some particular bond length (i.e., a constrained dynamics). Since the friction kernel is not sensitive to the details of the internal potential of the diatomic, this approximation can also be used for diatomics with stiff, *anharmonic* potentials. This approximation is referred to as the *rigid bond approximation* (see Berne, *et al*, *J. Chem. Phys.* **93**, 5084 (1990)).

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