G25.2651: Statistical Mechanics

Notes for Lecture 24

I. THE HARMONIC BATH HAMILTONIAN

In the theory of chemical reactions, it is often possible to isolate a small number or even a single degree of freedom in the system that can be used to characterize the reaction. This degree of freedom is coupled to other degrees of freedom (for example, reactions often take place in solution). Isomerization or dissociation of a diatomic molecule in solution is an excellent example of this type of system. The degree of freedom of paramount interest is the distance between the two atoms of the molecule – this is the degree of freedom whose detailed dynamics we would like to elucidate. The dynamics of the "bath" or environment to which is couples is less interesting, but still must be accounted for in some manner. A model that has maintained a certain level of both popularity and success is the so called "harmonic bath" model, in which the environment to which the special degree(s) of freedom couple is replaced by an effective set of harmonic oscillators. We will examine this model for the case of a single degree of freedom of interest, which we will designate q. For the case of the isomerizing or dissociating diatomic, q could be the coordinate $r - \langle r \rangle$, where r is the distance between the atoms. The particular definition of q ensures that $\langle q \rangle = 0$. The degree of freedom q is assumed to couple to the bath linearly, giving a Hamiltonian of the form

$$ H = \frac{p^2}{2m} + \phi(q) + \sum_\alpha \left[\frac{p_\alpha^2}{2m_\alpha} + \frac{1}{2} m_\alpha \omega_\alpha^2 \left(x_\alpha + \frac{g_\alpha}{m_\alpha \omega_\alpha^2} q \right)^2 \right] $$

where the index α runs over all the bath degrees of freedom, ω_α are the harmonic bath frequencies, m_α are the harmonic bath masses, and g_α are the coupling constants between the bath and the coordinate q. p is a momentum conjugate to q, and m is the mass associated with this degree of freedom (e.g., the reduced mass μ in the case of a diatomic). The coordinate q is assumed to be subject to a potential $\phi(q)$ as well (e.g., an internal bond potential). The form of the coupling between the system (q) and the bath (x_α) is known as *bilinear*.

Below, using a completely classical treatment of this Hamiltonian, we will derive an equation for the detailed dynamics of q alone. This equation is known as the generalized Langevin equation (GLE).

II. DERIVATION OF THE GLE

The GLE can be derived from the harmonic bath Hamiltonian by simply solving Hamilton's equations of motion, which take the form

$$ \dot{q} = \frac{p}{m} $$

$$ \dot{p} = -\frac{\partial \phi}{\partial q} - \sum_\alpha g_\alpha x_\alpha - \sum_\alpha \frac{g_\alpha^2}{m_\alpha \omega_\alpha^2} q $$

$$ \dot{x}_\alpha = \frac{p_\alpha}{m_\alpha} $$

$$ \dot{p}_\alpha = -m_\alpha \omega_\alpha^2 x_\alpha - g_\alpha q $$

This set of equations can also be written as second order differential equation:

$$ m\ddot{q} = -\frac{\partial \phi}{\partial q} - \sum_\alpha g_\alpha x_\alpha - \sum_\alpha \frac{g_\alpha^2}{m_\alpha \omega_\alpha^2} q $$

$$ m_\alpha \ddot{x}_\alpha = -m_\alpha \omega_\alpha^2 x_\alpha - g_\alpha q $$

In order to derive an equation for q, we solve explicitly for the dynamics of the bath variables and then substitute into the equation for q. The equation for x_α is a second order inhomogeneous differential equation, which can be solved by Laplace transforms. We simply take the Laplace transform of both sides. Denote the Laplace transforms of q and x_α as

$$\tilde{q}(s) = \int_0^\infty dt \, e^{-st} q(t)$$

$$\tilde{x}_\alpha = \int_0^\infty dt \, e^{-st} x_\alpha(t)$$

and recognizing that

$$\int_0^\infty dt \, e^{-st} \ddot{x}_\alpha(t) = s^2 \tilde{x}_\alpha(s) - s x_\alpha(0) - \dot{x}_\alpha(0)$$

we obtain the following equation for $\tilde{x}_\alpha(s)$:

$$(s^2 + \omega_\alpha^2) \tilde{x}_\alpha(s) = s x_\alpha(0) + \dot{x}_\alpha(0) - \frac{g_\alpha}{m_\alpha} \tilde{q}(s)$$

or

$$\tilde{x}_\alpha(s) = \frac{s}{s^2 + \omega_\alpha^2} x_\alpha(0) + \frac{1}{s^2 + \omega_\alpha^2} \dot{x}_\alpha(0) - \frac{g_\alpha}{m_\alpha} \frac{\tilde{q}(s)}{s^2 + \omega_\alpha^2}$$

$x_\alpha(t)$ can be obtained by inverse Laplace transformation, which is equivalent to a contour integral in the complex s-plane around a contour that encloses all the poles of the integrand. This contour is known as the *Bromwich* contour. To see how this works, consider the first term in the above expression. The inverse Laplace transform is

$$\frac{1}{2\pi i} \oint ds \, \frac{s e^{st}}{s^2 + \omega_\alpha^2} = \frac{1}{2\pi i} \oint ds \, \frac{s e^{st}}{(s + i\omega_\alpha)(s - i\omega_\alpha)}$$

The integrand has two poles on the imaginary s-axis at $\pm i\omega_\alpha$. Integration over the contour that encloses these poles picks up both residues from these poles. Since the poles are simple poles, then, from the residue theorem:

$$\frac{1}{2\pi i} \oint ds \, \frac{s e^{st}}{(s + i\omega_\alpha)(s - i\omega_\alpha)} = \frac{1}{2\pi i} \left[2\pi i \left(\frac{i\omega_\alpha e^{i\omega_\alpha t}}{2i\omega_\alpha} + \frac{-i\omega_\alpha e^{-i\omega_\alpha t}}{-2i\omega_\alpha} \right) \right] = \cos \omega_\alpha t$$

By the same method, the second term will give $(\sin \omega_\alpha t)/\omega_\alpha$. The last term is the inverse Laplace transform of a product of $\tilde{q}(s)$ and $1/(s^2 + \omega_\alpha^2)$. From the convolution theorem of Laplace transforms, the Laplace transform of a convolution gives the product of Laplace transforms:

$$\int_0^\infty dt \, e^{-st} \int_0^t d\tau \, f(\tau) g(t - \tau) = \tilde{f}(s) \tilde{g}(s)$$

Thus, the last term will be the convolution of $q(t)$ with $(\sin \omega_\alpha t)/\omega_\alpha$. Putting these results together, gives, as the solution for $x_\alpha(t)$:

$$x_\alpha(t) = x_\alpha(0) \cos \omega_\alpha t + \frac{\dot{x}_\alpha(0)}{\omega_\alpha} \sin \omega_\alpha t - \frac{g_\alpha}{m_\alpha \omega_\alpha} \int_0^t d\tau \, q(\tau) \sin \omega_\alpha (t - \tau)$$

The convolution term can be expressed in terms of $\dot{q}$ rather than q by integrating it by parts:

$$\frac{g_\alpha}{m_\alpha \omega_\alpha} \int_0^t d\tau \, q(\tau) \sin \omega_\alpha (t - \tau) = \frac{g_\alpha}{m_\alpha \omega_\alpha^2} [q(t) - q(0) \cos \omega_\alpha t] - \frac{g_\alpha}{m_\alpha \omega_\alpha^2} \int_0^t d\tau \, \dot{q}(\tau) \cos \omega_\alpha (t - \tau)$$

The reasons for preferring this form will be made clear shortly. The bath variables can now be seen to evolve according to

$$x_\alpha(t) = x_\alpha(0) \cos \omega_\alpha t + \frac{\dot{x}_\alpha(0)}{\omega_\alpha} \sin \omega_\alpha t + \frac{g_\alpha}{m_\alpha \omega_\alpha^2} \int_0^t d\tau \, \dot{q}(\tau) \cos \omega_\alpha (t - \tau) - \frac{g_\alpha}{m_\alpha \omega_\alpha^2} [q(t) - q(0) \cos \omega_\alpha t]$$

Substituting this into the equation of motion for q, we find

$$m\ddot{q} = -\frac{\partial \phi}{\partial q} - \sum_\alpha g_\alpha \left[x_\alpha(0) \cos \omega_\alpha t + \frac{p_\alpha(0)}{m_\alpha \omega_\alpha} \sin \omega_\alpha t + \frac{g_\alpha}{m_\alpha \omega_\alpha^2} q(0) \cos \omega_\alpha t \right] - \sum_\alpha \frac{g_\alpha^2}{m_\alpha \omega_\alpha^2} \int_0^t d\tau \, \dot{q}(\tau) \cos \omega_\alpha (t - \tau) + \sum_\alpha \frac{g_\alpha^2}{m_\alpha \omega_\alpha^2} q(t) - \sum_\alpha$$

We now introduce the following notation for the sums over bath modes appearing in this equation:

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1. Define a dynamic *friction kernel*

$$\zeta(t) = \sum_\alpha \frac{g_\alpha}{m_\alpha \omega_\alpha^2} \cos \omega_\alpha t$$

2. Define a *random force*

$$R(t) = -\sum_\alpha g_\alpha \left[\left(x_\alpha(0) + \frac{g_\alpha}{m_\alpha \omega_\alpha^2} q(0) \right) \cos \omega_\alpha t + \frac{p_\alpha(0)}{m_\alpha \omega_\alpha} \sin \omega_\alpha t \right]$$

Using these definitions, the equation of motion for q reads

$$m\ddot{q} = -\frac{\partial \phi}{\partial q} - \int_0^t d\tau \, \dot{q}(\tau) \zeta(t - \tau) + R(t) \tag{1}$$

Eq. (1) is known as the *generalized Langevin equation*. Note that it takes the form of a one-dimensional particle subject to a potential $\phi(q)$, driven by a forcing function $R(t)$ and with a nonlocal (in time) damping term $-\int_0^t d\tau \, \dot{q}(\tau)\zeta(t-\tau)$, which depends, in general, on the entire history of the evolution of q. The GLE is often taken as a phenomenological equation of motion for a coordinate q coupled to a general bath. In this spirit, it is worth taking a moment to discuss the physical meaning of the terms appearing in the equation.

III. PROPERTIES OF THE GLE

Below we discuss the physical meaning of the terms appearing the GLE

A. The random force term

Within the context of a harmonic bath, the term "random force" is something of a misnomer, since $R(t)$ is completely deterministic and not random at all!!! We will return to this point momentarily, however, let us examine particular features of $R(t)$ from its explicit expression from the harmonic bath dynamics. Note, first of all, that it does not depend on the dynamics of the system coordinate q (except for the appearance of $q(0)$). In this sense, it is independent or "orthogonal" to q within a phase space picture. From the explicit form of $R(t)$, it is straightforward to see that the correlation function

$$\langle \dot{q}(0) R(t) \rangle = 0$$

i.e., the correlation function of the system velocity $\dot{q}$ with the random force is 0. This can be seen by substituting in the expression for $R(t)$ and integrating over initial conditions with a canonical distribution weighting. For certain potentials $\phi(q)$ that are even in q (such as a harmonic oscillator), one can also show that

$$\langle q(0) R(t) \rangle = 0$$

Thus, $R(t)$ is completely uncorrelated from both q and $\dot{q}$, which is a property we might expect from a truly random process. In fact, $R(t)$ is determined by the detailed dynamics of the bath. However, we are not particularly interested or able to follow these detailed dynamics for a large number of bath degrees of freedom. Thus, we could just as well model $R(t)$ by a completely random process (satisfying certain desirable features that are characteristic of a more general bath), and, in fact, this is often done. One could, for example, postulate that $R(t)$ act over a maximum time $t_{\max}$ at discrete points in time $k\Delta t$, giving $N = t_{\max}/\Delta t$ values of $R_k = R(k\Delta t)$, and assume that R_k takes the form of a *gaussian random process*:

$$R_k = \sum_{j=1}^N \left[a_j e^{2\pi i j k / N} + b_j e^{-2\pi i j k / N} \right]$$

where the coefficients $\{a_j\}$ and $\{b_j\}$ are chosen at random from a gaussian distribution function. This might be expected to be suitable for a bath of high density, where strong collisions between the system and a bath particle are essentially nonexistent, but where the system only sees feels the relatively "soft" fluctuations of the less mobile bath. For a low density bath, one might try modeling $R(t)$ as a Poisson process of very strong collisions.

Whatever model is chosen for $R(t)$, if it is a truly random process that can only act at discrete points in time, then the GLE takes the form of a stochastic (based on random numbers) integro-differential equation. There is a whole body of mathematics devoted to the properties of such equations, where heavy use of an *Itô calculus* is made.

B. The dynamic friction kernel

The convolution integral term

$$\int_0^t d\tau \ \dot{q}(\tau)\zeta(t-\tau)$$

is called the *memory integral* because it depends, in general, on the entire history of the evolution of q. Physically it expresses the fact that the bath requires a finite time to respond to any fluctuation in the motion of the system (q). This, in turn, affects how the bath acts back on the system. Thus, the force that the bath exerts on the system presently depends on what the system coordinate q did in the past. However, we have seen previously the regression of fluctuations (their decay to 0) over time. Thus, we expect that what the system did very far in the past will no longer the force it feels presently, i.e., that the lower limit of the memory integral (which is rigorously 0) could be replaced by $t - t_{\text{mem}}$, where t_{mem} is the maximum time over which memory of what the system coordinate did in the past is important. This can be interpreted as a indicating a certain decay time for the friction kernel $\zeta(t)$. In fact, $\zeta(t)$ often does decay to 0 in a relatively short time. Often this decay takes the form of a rapid initial decay followed by a slow final decay, as shown in the figure below:

Consider the extreme case that the bath is capable of responding infinitely quickly to changes in the system coordinate q. This would be the case, for example, if there were a large mass disparity between the system and the bath ($m >> m_\alpha$). Then, the bath retains *no* memory of what the system did in the past, and we could take $\zeta(t)$ to be a δ-function in time:

$$\zeta(t) = 2\zeta_0 \delta(t)$$

Then

$$\int_0^t d\tau \ \dot{q}(\tau)\zeta(t-\tau) = \int_0^t d\tau \ \dot{q}(t-\tau)\zeta(\tau) = 2\zeta_0 \int_0^t d\tau \ \delta(\tau)\dot{q}(t-\tau) = \zeta_0\dot{q}(t)$$

and the GLE becomes

$$m\ddot{q} = -\frac{\partial\phi}{\partial q} - \zeta_0\dot{q} + R(t)$$

This simpler equation of motion is known as the *Langevin* equation and it is clearly a special case of the more generalized equation of motion. It is often invoked to describe brownian motion where clearly such a mass disparity is present. The constant ζ_0 is known as the static friction and is given by

$$\zeta_0 = \int_0^\infty dt \ \zeta(t)$$

In fact, this is a general relation for determining the static friction constant.

The other extreme is a very sluggish bath that responds slowly to changes in the system coordinate. In this case, we may take $\zeta(t)$ to be a constant $\zeta \equiv \zeta(0)$, at least, for times short compared to the response time of the bath. Then, the memory integral becomes

$$\int_0^t d\tau \ \dot{q}(\tau)\zeta(t-\tau) \approx \zeta(q(t) - q(0))$$

and the GLE becomes

$$m\ddot{q} = -\frac{\partial}{\partial q}\left(\phi(q) + \frac{1}{2}\zeta(q - q_0)^2\right) + R(t)$$

where the friction term now manifests itself as an extra harmonic term added to the potential. Such a term has the effect of trapping the system in certain regions of configuration space, an effect known as *dynamic caging*. An example of this is a dilute mixture of small, light particles in a bath of heavy, large particles. The light particles can get trapped in regions of space where many bath particles are in a sort of spatial "cage." Only the rare fluctuations in the bath that open up larger holes in configuration space allow the light particles to escape the cage, occasionally, after which, they often get trapped again in a new cage for a similar time interval.

C. Relation between the dynamic friction kernel and the random force

From the definitions of $R(t)$ and $\zeta(t)$, it is straightforward to show that there is a relation between them of the form

$$\langle R(0)R(t)\rangle = kT\zeta(t)$$

This relation is known as the *second fluctuation dissipation theorem*. The fact that it involves a simple autocorrelation function of the random force is particular to the harmonic bath model. We will see later that a more general form of this relation exists, valid for a general bath. This relation must be kept in mind when introducing models for $R(t)$ and $\zeta(t)$. In effect, it acts as a constraint on the possible ways in which one can model the random force and friction kernel.

IV. 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 $\mathbf{A}$. These operators take the form

$$P = \langle ...\mathbf{A}^{\mathrm{T}}\rangle\langle\mathbf{A}\mathbf{A}^{\mathrm{T}}\rangle^{-1}$$
$$Q = I - P$$

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 $\mathbf{A}$:

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

$$= \langle iL\mathbf{AA}^{\mathrm{T}}\rangle\langle \mathbf{AA}^{\mathrm{T}}\rangle^{-1}e^{iLt}\mathbf{A}$$

$$= \langle iL\mathbf{AA}^{\mathrm{T}}\rangle\langle \mathbf{AA}^{\mathrm{T}}\rangle^{-1}\mathbf{A}(t)$$

$$\equiv i\mathbf{\Omega A}(t)$$

where

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

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

$$\mathrm{A} = (s - iL)$$
$$\mathrm{B} = (s - iQL)$$

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

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

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,

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

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 $d\mathbf{A}/dt$:

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

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

$$i\mathbf{\Omega} = \begin{pmatrix} 0 & 1/m \\ -m\omega^2 & 0 \end{pmatrix}$$

$$\mathbf{K}(t) = \begin{pmatrix} 0 & 0 \\ 0 & \zeta(t)/m \end{pmatrix}$$

$$\mathbf{F}(t) = \begin{pmatrix} 0 \\ R(t) \end{pmatrix}$$

It is easy to derive these expressions for the case of the harmonic bath Hamiltonian when $\phi(q) = m\omega^2 q^2/2$.

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:

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

For a general bath, the relation is not as simple, owing to the fact that $\mathbf{F}(t)$ is evolved using a modified propagator $\exp(iQLt)$. Thus, the more general form of the fluctuation dissipation theorem is

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

so that the dynamics of $R(t)$ is prescribed by the propagator $\exp(iQLt)$. 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

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

where iL_{cons} 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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V. 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

$$C_{\text{vv}}(t) = \frac{\langle \dot{q}(0)\dot{q}(t)\rangle}{\langle \dot{q}^2\rangle}$$

where $v = \dot{q}$, gives the relevant frequencies contributing to the dynamics of q, but does not give amplitudes. This "frequency" spectrum $I(\omega)$ is simply given by

$$I(\omega) = \int_0^\infty dt \ e^{i\omega t} C_{\text{vv}}(t)$$

That is, we take the Laplace transform of $C_{\text{vv}}(t)$ using $s = -i\omega$. Since $C_{\text{vv}}(t)$ carries information about the relevant frequencies of the system, the decay of $C_{\text{vv}}(t)$ 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 $C_{\text{vv}}(t)$, which is denoted T_2 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:

$$C_{\varepsilon\varepsilon} = \frac{\langle \varepsilon(0)\varepsilon(t)\rangle}{\langle \varepsilon^2\rangle}$$

where $\varepsilon(t)$ is defined to be

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

The decay time of this correlation function is denoted T_1.

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 T_1 and T_2.

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

$$\phi(q) = \frac{1}{2}m\omega^2 q^2$$

Substituting into the GLE and dividing through by m gives

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

where

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

An equation of motion for $C_{\text{vv}}(t)$ can be obtained directly by multiplying both sides of the GLE by $\dot{q}(0)$ and averaging over a canonical ensemble:

$$\langle \dot{q}(0)\ddot{q}(t)\rangle = -\omega^2 \langle \dot{q}(0)q(t)\rangle - \int_0^t d\tau \ \langle \dot{q}(0)\dot{q}(t-\tau)\rangle\gamma(\tau) + \langle \dot{q}(0)f(t)\rangle$$

Recall that

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

and note that

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

also

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

Thus,

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

Combining these results gives an equation for $C_{vv}(t)$

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

$$\frac{d}{dt} C_{vv}(t) = - \int_0^t d\tau \, K(t-\tau) C_{vv}(\tau)$$

which is known as the *memory function equation* and the kernel $K(t)$ 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

$$s\tilde{C}_{vv}(s) - C_{vv}(0) = -\tilde{C}_{vv}(s)\tilde{K}(s)$$

However, it is clear that $C_{vv}(0) = 1$ and also

$$\tilde{K}(s) = \frac{\omega^2}{s} + \tilde{\gamma}(s)$$

Thus, it follows that

$$s\tilde{C}_{vv}(s) - 1 = \left(\frac{\omega^2}{s} + \tilde{\gamma}(s) \right) \tilde{C}_{vv}(s)$$

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

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

$$s^2 + s\tilde{\gamma}(s) + \omega^2 = 0$$

which we could solve directly if we knew the explicit form of $\tilde{\gamma}(s)$.

However, if ω is sufficiently larger than $\tilde{\gamma}(0)$, then it is possible to develop a perturbation solution to this equation. Let us assume the solutions for s can be written as

$$s = s_0 + s_1 + s_2 + \cdots$$

Substituting in this ansatz gives

$$(s_0 + s_1 + s_2 + \cdots)^2 + (s_0 + s_1 + s_2 + \cdots)\tilde{\gamma}(s_0 + s_1 + s_2 + \cdots) + \omega^2 = 0$$

Since we are assuming $\tilde{\gamma}$ is small, then to lowest order, we have

$$s_0^2 + \omega^2 = 0$$

so that $s_0 = \pm\imath\omega$. The first order equation then becomes

$$2s_0 s_1 + s_0 \tilde{\gamma}(s_0) = 0$$

or

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

Note, however, that

$$
\begin{aligned}
\tilde{\gamma}(\pm i\omega) &= \int_0^\infty dt \; \gamma(t) e^{\pm i\omega t} \\
&= \int_0^\infty dt \; [\gamma(t)\cos\omega t \pm i\gamma(t)\sin\omega t] \\
&\equiv \gamma'(\omega) \pm i\gamma''(\omega)
\end{aligned}
$$

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

$$s \approx \pm i \left(\omega + \gamma''(\omega)\right) - \frac{\gamma'(\omega)}{2} \equiv \pm i\Omega - \frac{\gamma'(\omega)}{2}$$

Define

$$s_+ = i\Omega - \frac{\gamma'(\omega)}{2}$$
$$s_- = -i\Omega - \frac{\gamma'(\omega)}{2}$$

Then

$$\tilde{C}_{vv}(s) \approx \frac{s}{(s - s_+)(s - s_-)}$$

and $C_{vv}(t)$ is then given by the contour integral

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

Taking the residue at each pole, we find

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

which can be simplified to give

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

Thus, we see that the GLE predicts $C_{vv}(t)$ oscillates with a frequency Ω and decays exponentially. From the exponential decay, we can directly read off the time T_2:

$$\frac{1}{T_2} = \frac{\gamma'(\omega)}{2} = \frac{\zeta'(\omega)}{2m}$$

That is, the value of the real part of the Fourier (Laplace) transform of the friction kernel evaluated at the renormalized frequency divided by $2m$ gives the vibrational dephasing time! By a similar scheme, one can easily show that the position autocorrelation function $C_{qq}(t) = \langle q(0)q(t)\rangle$ decays with the same dephasing time. It's explicit form is

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

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The energy autocorrelation function $C_{\varepsilon\varepsilon}(t)$ can be expressed in terms of the more primitive correlation functions $C_{qq}(t)$ and $C_{vv}(t)$. It is a straightforward, although extremely tedious, matter to show that the relation, valid for the harmonic potential of mean force, is

$$C_{\varepsilon\varepsilon}(t) = \frac{1}{2}C_{vv}^2(t) + \frac{1}{2}C_{qq}^2(t) + \frac{1}{\omega^2}\dot{C}_{qq}^2(t)$$

Substituting in the expressions for $C_{qq}(t)$ and $C_{vv}(t)$ gives

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

so that the decay time T_1 can be seen to be

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

and therefore, the relation between T_1 and T_2 can be seen immediately to be

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

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 ω 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.
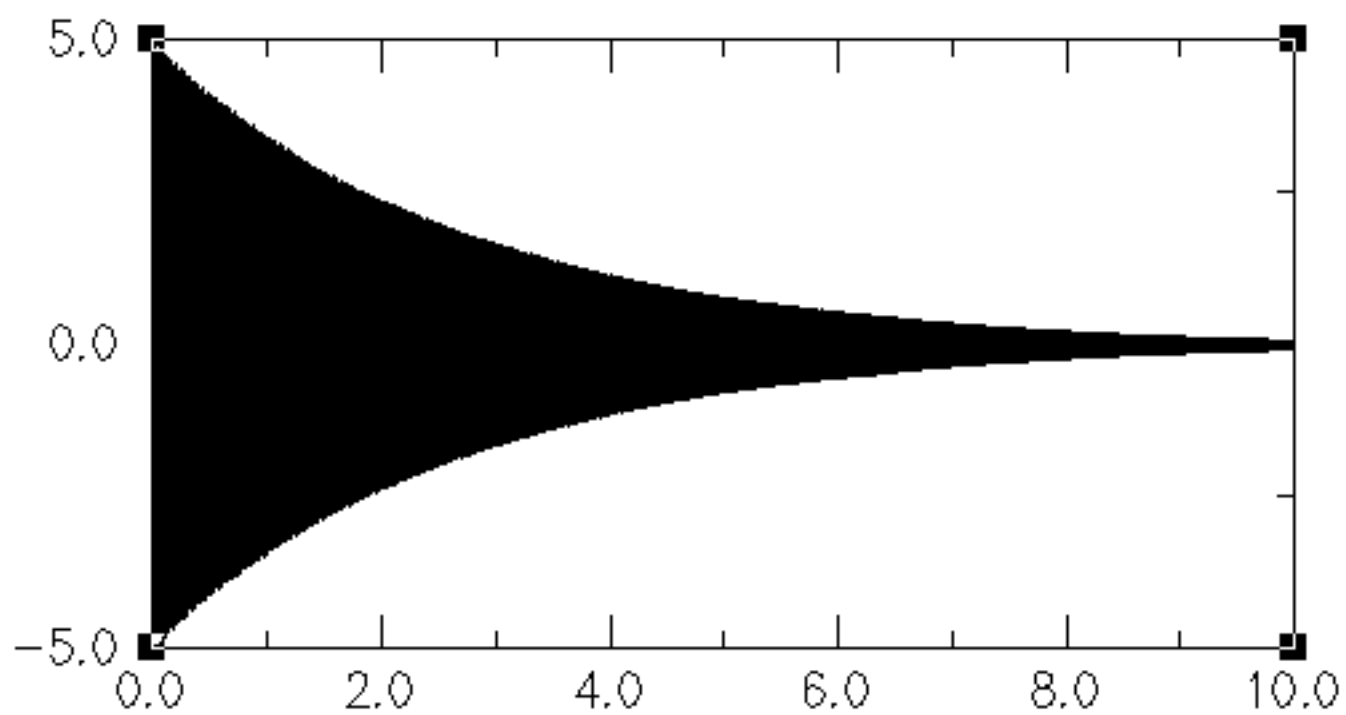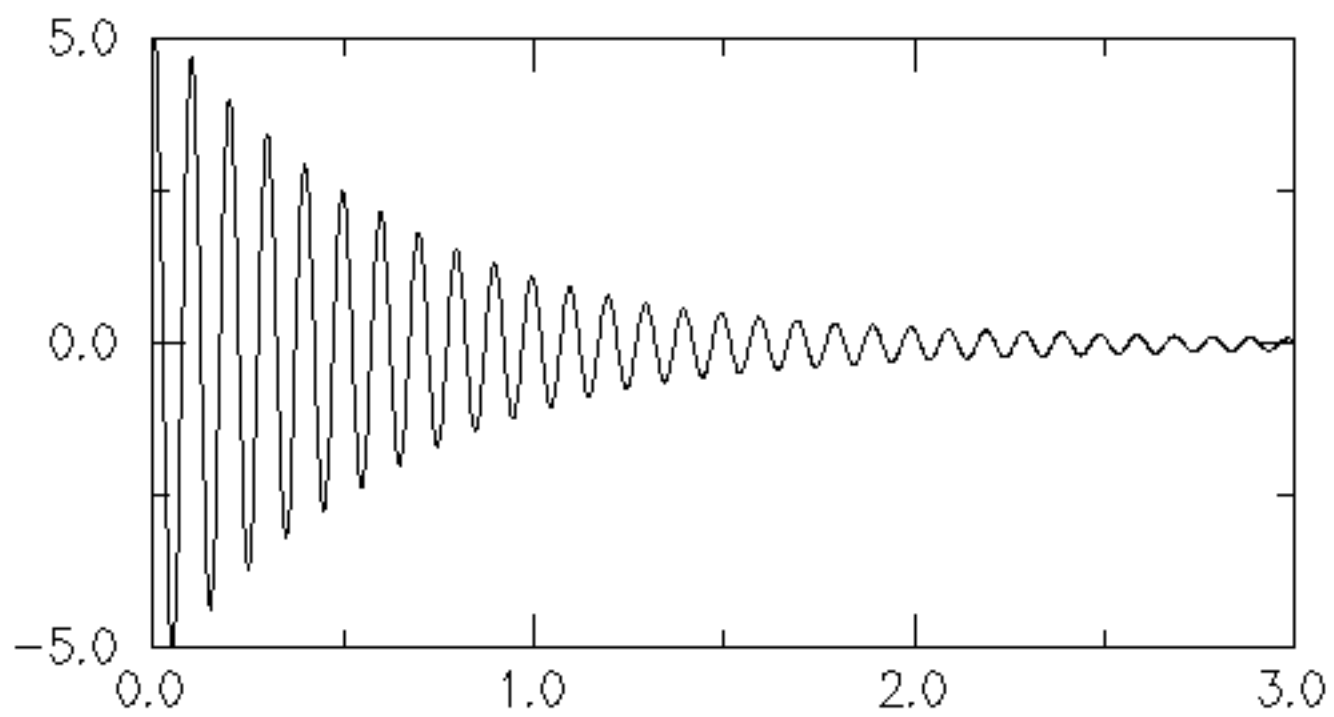
FIG. 1.