14.5: Correspondence of Harmonic Bath and Stochastic Equations of Motion

So, why does the mathematical model for coupling of a system to a harmonic bath give the same results as the classical stochastic equations of motion for fluctuations? Why does coupling to a continuum of bath states have the same physical manifestation as perturbation by random fluctuations? The answer is that in both cases, we really have imperfect knowledge of the behavior of all the particles present. Observing a small subset of particles will have dynamics with a random character. These dynamics can be quantified through a correlation function or a spectral density for the time-scales of motion of the bath. In this section, we will demonstrate a more formal relationship that illustrates the equivalence of these pictures.

To take our discussion further, let's again consider the electronic absorption spectrum from a classical perspective. It's quite common to think that the electronic transition of interest is coupled to a particular nuclear coordinate Q which we will call a local coordinate. This local coordinate could be an intramolecular normal vibrational mode, an intermolecular rattling in a solvent shell, a lattice vibration, or another motion that influences the electronic transition. The idea is that we take the observed electronic transition to be linearly dependent on one or more local coordinates. Therefore describing Q allows us to describe the spectroscopy. However, since this local mode has further degrees of freedom that it may be interacting with, we are extracting a particular coordinate out or a continuum of other motions, the local mode will appear to feel a fluctuating environment—a friction.

Classically, we describe fluctuations in Q as Brownian motion, typically through a Langevin equation. In the simplest sense, this is an equation that restates Newton's equation of motion $F = ma$ for a fluctuating force acting on a particle with position Q. For the case that this particle is confined in a harmonic potential,

$$m\ddot{Q}(t) + m\omega_0^2 Q^2 + m\gamma\dot{Q} = f_R(t) \tag{14.5.1}$$

Here the terms on the left side represent a damped harmonic oscillator. The first term is the force due to acceleration of the particle of mass $m\ (F_{acc} = ma)$. The second term is the restoring force of the potential, $F_{res} = -\partial V/\partial Q = m\omega_0^2$. The third term allows friction to damp the motion of the coordinate at a rate γ. The motion of Q is under the influence of $f_R(t)$, a random fluctuating force exerted on Q by its surroundings.

Under steady-state conditions, it stands to reason that the random force acting on Q is the origin of the damping. The environment acts on Q with stochastic perturbations that add and remove kinetic energy, which ultimately leads to dissipation of any excess energy. Therefore, the Langevin equation is modelled as a Gaussian stationary process. We take $f_R(t)$ to have a timeaveraged value of zero,

$$\langle f_R(t)\rangle = 0 \tag{14.5.2}$$

and obey the classical fluctuation-dissipation theorem:

$$\gamma = \frac{1}{2mk_BT}\int_{-\infty}^{\infty}\langle f_R(t) f_R(0)\rangle \tag{14.5.3}$$

This shows explicitly how the damping is related to the correlation time for the random force. We will pay particular attention to the Markovian case

$$\langle f_R(t) f_R(0)\rangle = 2m\gamma k_B T\delta(t) \tag{14.5.4}$$

which indicate that the fluctuations immediately lose all correlation on the time scale of the evolution of Q. The Langevin equation can be used to describe the correlation function for the time dependence of Q. For the Markovian case, Equation 14.5.1 leads to

$$C_{QQ}(t) = \frac{k_BT}{m\omega_0^2}\left(\cos\zeta t + \frac{\gamma}{2\zeta}\sin\zeta t\right)e^{-\gamma t/2} \tag{14.5.5}$$

where the reduced frequency $\zeta = \sqrt{\omega_0^2 - \gamma^2/4}$. The frequency domain expression, obtained by Fourier transformation, is

$$\tilde{C}_{QQ}(\omega) = \frac{\gamma kT}{m\pi}\frac{1}{\left(\omega_0^2 - \omega^2\right)^2 + \omega^2\gamma^2} \tag{14.5.6}$$

Remembering that the absorption lineshape was determined by the quantum mechanical energy gap correlation function $\langle q(t)q(0)\rangle$, one can imagine an analogous classical description of the spectroscopy of a molecule that experiences interactions with a fluctuating environment. In essence this is what we did when discussing the Gaussian stochastic model of the lineshape. A more general description of the position of a particle subject to a fluctuating force is the Generalized Langevin Equation. The GLE accounts for the possibility that the damping may be time-dependent and carry memory of earlier configurations of the system:

$$m\ddot{Q}(t)+m\omega_0^2 Q^2+m\int_0^t d\tau\gamma(t-\tau)\dot{Q}(\tau)=f(t) \tag{14.5.7}$$

The memory kernel, $\gamma(t-\tau)$, is a correlation function that describes the time-scales over which the fluctuating force retains memory of its previous state. The force due to friction on Q depends on the history of the system through τ, the time preceding t, and the relaxation of $\gamma(t-\tau)$. The classical fluctuation-dissipation relationship relates the magnitude of the fluctuating forces on the system coordinate to the damping

$$\langle f_R(t) f_R(\tau)\rangle=2mk_BT\gamma(t-\tau) \tag{14.5.8}$$

As expected, for the case that $\gamma(t-\tau)=\gamma\delta(t-\tau)$, the GLE reduces to the Markovian case, Equation 14.5.1.

To demonstrate that the classical dynamics of the particle described under the GLE is related to the quantum mechanical dynamics for a particle interacting with a harmonic bath, we will outline the derivation of a quantum mechanical analog of the classical GLE. To do this we will derive an expression for the time-evolution of the system under the influence of the harmonic bath. We work with a Hamiltonian with a linear coupling between the system and the bath

$$H_{HB}=H_S(P,Q)+H_B\left(p_\alpha,q_\alpha\right)+H_{SB}(Q,q) \tag{14.5.9}$$

We take the system to be a particle of mass M, described through variables P and Q, whereas m_α, p_α, and q_α are bath variables. For the present case, we will take the system to be a quantum harmonic oscillator,

$$H_s=\frac{P^2}{2M}+\frac{1}{2}M\Omega^2 Q^2 \tag{14.5.10}$$

and the Hamiltonian for the bath and its interaction with the system is written as

$$H_B+H_{SB}=\sum_\alpha\left(\frac{p_\alpha^2}{2m_\alpha}+\frac{m_\alpha\omega_\alpha^2}{2}\left(q_\alpha-\frac{c_\alpha}{m_\alpha\omega_\alpha^2}Q\right)^2\right) \tag{14.5.11}$$

This expression explicitly shows that each of the bath oscillators is displaced with respect to the system by an amount dependent on their mutual coupling. In analogy to our work with the Displaced Harmonic Oscillator, if we define a displacement operator

$$\hat{D}=\exp\left(-\frac{i}{\hbar}\sum_\alpha\hat{p}_\alpha\xi_\alpha\right) \tag{14.5.12}$$

where

$$\xi_\alpha=\frac{c_\alpha}{m_\alpha\omega_\alpha^2}Q \tag{14.5.13}$$

then

$$H_B+H_{SB}=\hat{D}^\dagger H_B\hat{D} \tag{14.5.14}$$

Equation 14.5.11is merely a different representation of our earlier harmonic bath model. To see this we write Equation 14.5.11as

$$H_B+H_{SB}=\sum_\alpha\hbar\omega_\alpha\left(p_\alpha^2+\left(q_\alpha-c_\alpha Q\right)^2\right) \tag{14.5.15}$$

where the coordinates and momenta are written in reduced form

$$\begin{aligned}\underline{Q}&=Q\sqrt{m\omega_0/2\hbar}\\ q_\alpha&=q_\alpha\sqrt{m_\alpha\omega_\alpha/2\hbar}\\ p_\alpha&=p_\alpha/\sqrt{2\hbar m_\alpha\omega_\alpha}\end{aligned} \tag{14.5.16}$$

Also, the reduced coupling is of the system to the α^{th} oscillator is

$$\mathcal{C}_\alpha=c_\alpha/\omega_\alpha\sqrt{m_\alpha\omega_\alpha m\omega_0} \tag{14.5.17}$$

Expanding Equation 14.5.15and collecting terms, we find that we can separate terms as in the harmonic bath model

$$H_B = \sum_\alpha \hbar\omega_\alpha \left(p_\alpha^2 + q_\alpha^2\right) \tag{14.5.18}$$

$$H_{SB} = -2\sum_\alpha \hbar\omega_\alpha d_\alpha q_\alpha + \lambda_B \tag{14.5.19}$$

The reorganization energy due to the bath oscillators is

$$\lambda_B = \sum_\alpha \hbar\omega_\alpha d_\alpha^2 \tag{14.5.20}$$

and the unit less bath oscillator displacement is

$$d_\alpha = \underset{Q}{\approx} \mathcal{C}_\alpha \tag{14.5.21}$$

For our current work we regroup the total Hamiltonian (Equation 14.5.9) as

$$H_{HB} = \left[\frac{P^2}{2M} + \frac{1}{2}M\overline{\Omega}^2 Q^2\right] + \sum_\alpha \hbar\omega_\alpha \left(p_\alpha^2 + q_\alpha^2\right) - 2\sum_\alpha \hbar\omega_\alpha c_\alpha Q q_\alpha \tag{14.5.22}$$

where the renormalized frequency is

$$\overline{\Omega}^2 = \Omega^2 + \Omega\sum_\alpha \omega_\alpha c_\alpha^2 \tag{14.5.23}$$

To demonstrate the equivalence of the dynamics under this Hamiltonian and the GLE, we can derive an equation of motion for the system coordinate Q. We approach this by first expressing these variables in terms of ladder operators

$$\hat{P} = i\left(\hat{a}^\dagger - \hat{a}\right) \quad \hat{p}_\alpha = i\left(\hat{b}_\alpha^\dagger - \hat{b}_\alpha\right) \tag{14.5.24}$$

$$\hat{Q} = \left(\hat{a}^\dagger + \hat{a}\right) \quad \hat{q}_\alpha = \left(\hat{b}_\alpha^\dagger + \hat{b}_\alpha\right) \tag{14.5.25}$$

Here $\hat{a}$, $\hat{a}^\dagger$ are system operators, $\hat{b}$ and $\hat{b}^\dagger$ are bath operators. If the observed particle is taken to be bound in a harmonic potential, then the Hamiltonian in Equation 14.5.9can be written as

$$H_{HB} = \hbar\overline{\Omega}\left(\hat{a}^\dagger\hat{a} + \frac{1}{2}\right) + \sum_\alpha \hbar\omega_\alpha\left(\hat{b}_\alpha^\dagger\hat{b}_\alpha + \frac{1}{2}\right) - \left(\hat{a}^\dagger + \hat{a}\right)\sum_\alpha \hbar\omega_\alpha c_\alpha\left(\hat{b}_\alpha^\dagger + \hat{b}_\alpha\right) \tag{14.5.26}$$

The equations of motion for the operators in Equations 14.5.24and 14.5.25can be obtained from the Heisenberg equation of motion.

$$\dot{\hat{a}} = \frac{i}{\hbar}[H_{HB}, \hat{a}] \tag{14.5.27}$$

from which we find

$$\dot{\hat{a}} = -i\overline{\Omega}\hat{a} + i\sum_\alpha \omega_\alpha c_\alpha\left(\hat{b}_\alpha^\dagger + \hat{b}_\alpha\right) \tag{14.5.28}$$

$$\dot{\hat{b}}_\alpha = -i\omega_\alpha\hat{b}_\alpha + i\omega_\alpha\mathcal{C}_\alpha\left(\hat{a}^\dagger + \hat{a}\right) \tag{14.5.29}$$

To derive an equation of motion for the system coordinate, we begin by solving for the time evolution of the bath coordinates by directly integrating Equation 14.5.29,

$$\hat{b}_\alpha(t) = e^{-i\omega_\alpha t}\int_0^t e^{i\omega_\alpha t'}\left(i\omega_\alpha\mathcal{C}_\alpha\left(\hat{a}^\dagger + \hat{a}\right)\right)dt' + \hat{b}_\alpha(0)e^{-i\omega_\alpha t} \tag{14.5.30}$$

and insert the result into Equation 14.5.28. This leads to

$$\dot{\hat{a}}+i\bar{\Omega}\hat{a}-i\sum_\alpha \omega_\alpha c_\alpha^2\left(\hat{a}^\dagger+\hat{a}\right)+i\int_0^t dt'\kappa\left(t-t'\right)\left(\dot{\hat{a}}^\dagger\left(t'\right)+\dot{\hat{a}}\left(t'\right)\right)=iF(t) \tag{14.5.31}$$

where

$$\kappa(t)=\sum_\alpha \omega_\alpha c_\alpha^2\cos(\omega_\alpha t) \tag{14.5.32}$$

and

$$F(t)=\sum_\alpha c_\alpha\left[\hat{b}_\alpha(0)-\omega_\alpha c_\alpha\left(\hat{a}^\dagger(0)+\hat{a}(0)\right)\right]e^{-i\omega_\alpha t}+h.c. \tag{14.5.33}$$

Now, recognizing that the time-derivative of the system variables is given by

$$\dot{\hat{P}}=i\left(\dot{\hat{a}}^\dagger-\dot{\hat{a}}\right) \tag{14.5.34}$$

$$\dot{\hat{Q}}\left(\dot{\hat{a}}^\dagger+\dot{\hat{a}}\right) \tag{14.5.35}$$

and substituting Equation 14.5.31into 14.5.34, we can write an equation of motion

$$\dot{P}(t)+\left(\bar{\Omega}-2\sum_\alpha\frac{2c_\alpha^2}{\omega_\alpha}\right)Q+\int_0^t dt'2\kappa\left(t-t'\right)\hat{Q}\left(t'\right)=F(t)+F^\dagger(t) \tag{14.5.36}$$

Equation 14.5.36bears a striking resemblance to the classical GLE, Equation 14.5.7. In fact, if we define

$$\gamma(t)=2\bar{\Omega}\kappa(t) \tag{14.5.37}$$

$$=\frac{1}{M}\sum_\alpha\frac{c_\alpha^2}{m_\alpha\omega_\alpha^2}\cos\omega_\alpha t \tag{14.5.38}$$

$$f_R(t)=\sqrt{2\hbar M\Omega}\left[F(t)+F^\dagger(t)\right] \tag{14.5.39}$$

$$=\sum_\alpha c_\alpha\left[q_\alpha(0)\cos\omega_\alpha t+\frac{p_\alpha(0)}{m_\alpha\omega_\alpha}\sin\omega_\alpha t\right] \tag{14.5.40}$$

then the resulting equation is isomorphic to the classical GLE

$$\dot{P}(t)+M\Omega^2Q(t)+M\int_0^t dt'\gamma\left(t-t'\right)\dot{Q}\left(t'\right)=f_R(t) \tag{14.5.41}$$

This demonstrates that the quantum harmonic bath acts a dissipative environment, whose friction on the system coordinate is given by Equation 14.5.38. What we have shown here is an outline of the proof, but detailed discussion of these relationships can be found elsewhere.

Readings

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