IP326. Lecture 19. Thursday, March 7, 2019

● The generalized Langevin equation applied to a large mass in a fluid of smaller masses

Consider a system consisting of a single large particle (say, a colloid) of mass M in a bath of N solvent particles of mass m, with $M >> m$. The position and momentum of the colloid are taken to be $\mathbf{r}_0$ and $\mathbf{p}_0$, respectively, while the position and momentum of the ith solvent molecule are similarly taken to be $\mathbf{r}_i$ and $\mathbf{p}_i$. If only pairwise interactions are assumed to occur between the particles, the Hamiltonian H of the system is given by

$$H = \underbrace{\frac{1}{2m}\sum_{i=1}^{N}\mathbf{p}_i^2 + \frac{1}{2}\sum_{i=1}^{N}\sum_{j\neq i}^{N}V(|\mathbf{r}_i-\mathbf{r}_j|)}_{H_B} + \underbrace{\frac{\mathbf{p}_0^2}{2M} + \sum_{j=1}^{N}V(|\mathbf{r}_0-\mathbf{r}_j|)}_{H_0} \tag{1}$$

The corresponding Liouvillian iL can therefore be expressed as $iL = iL_B + iL_0$, where

$$\begin{aligned} iL_B &= \sum_{i=1}^{N}\left(\frac{\partial H_B}{\partial \mathbf{p}_i}\cdot\frac{\partial}{\partial \mathbf{r}_i} - \frac{\partial H_B}{\partial \mathbf{r}_i}\cdot\frac{\partial}{\partial \mathbf{p}_i}\right) \\ &= \sum_{i=1}^{N}\left(\frac{\mathbf{p}_i}{m}\cdot\nabla_{\mathbf{r}_i} - \frac{1}{2}\nabla_{\mathbf{r}_i}\left\{\sum_{j\neq i}^{N}V(|\mathbf{r}_i-\mathbf{r}_j|) + \sum_{k\neq i}^{N}V(|\mathbf{r}_k-\mathbf{r}_i|)\right\}\cdot\nabla_{\mathbf{p}_i}\right) \\ &= \sum_{i=1}^{N}\left(\frac{\mathbf{p}_i}{m}\cdot\nabla_{\mathbf{r}_i} + \mathbf{F}_i\cdot\nabla_{\mathbf{p}_i}\right) \end{aligned} \tag{2}$$

and

$$iL_0 = \frac{\mathbf{p}_0}{M}\cdot\nabla_{\mathbf{r}_0} + \mathbf{F}_0\cdot\nabla_{\mathbf{p}_0} \tag{3}$$

where $\mathbf{F}_0$ and $\mathbf{F}_i$ are the forces acting on the colloid and the ith solvent molecule, respectively. The bath Liouvillian depends on the phase space variables of *only* the solvent particles, while iL_0 depends on both the phase variables of the colloid as well as the coordinates of the solvent (through the intermolecular force term.)

Let's assume that we're interested in knowing only how the colloid evolves in time, irrespective of what happens to all the other solvent molecules in the medium. What we need to do, then, is extract that part of the dynamics of those other molecules that are relevant to the dynamics of the colloid. We can do this by introducing a projector P, defined as

$$P = | p_{0\alpha} \rangle \langle p_{0\alpha} | p_{0\alpha} \rangle^{-1} \langle p_{0\alpha} | \tag{4}$$

that projects an arbitrary dynamical variable onto the αth component of the colloid's momentum, and then applying *P* to the Liouville equation for $| p_{0\alpha}(t) \rangle$, which is

$$\frac{\partial | p_{0\alpha}(t) \rangle}{\partial t} = iL | p_{0\alpha}(t) \rangle \tag{5}$$

From our previous results, we know that we then end up with the following GLE

$$\frac{\partial | p_{0\alpha}(t) \rangle}{\partial t} = i\Omega | p_{0\alpha}(t) \rangle - \int_0^t dt' K(t-t') | p_{0\alpha}(t') \rangle + | f_\alpha(t) \rangle, \tag{6}$$

where $\Omega = \langle p_{0\alpha} | p_{0\alpha} \rangle^{-1} \langle p_{0\alpha} | L p_{0\alpha} \rangle$, $f_\alpha(t)$ is the generalized random force (the use of lower case for this variable is to distinguish it from the symbols for the forces acting on colloid and solvent, which are in upper case), defined as

$$| f_\alpha(t) \rangle = e^{QiLt} QiL | p_{0\alpha} \rangle \tag{7}$$

and $K(t)$ is the memory function, defined as $\langle p_{0\alpha} | p_{0\alpha} \rangle^{-1} \langle f_\alpha | f_\alpha(t) \rangle$.

Since $iL | p_{0\alpha} \rangle = | \dot{p}_{0\alpha} \rangle$, the frequency, $\Omega \propto \langle p_{0\alpha} | \dot{p}_{0\alpha} \rangle$, is identically 0 by symmetry. Using the same symmetry property, the generalized random force $| f_\alpha(t) \rangle$ in Eq. (7) can be rewritten as

$$\begin{aligned} | f_\alpha(t) \rangle &= e^{QiLt} Q | \dot{p}_{0\alpha} \rangle \\ &= e^{QiLt} (1 - | p_{0\alpha} \rangle \langle p_{0\alpha} | p_{0\alpha} \rangle^{-1} \langle p_{0\alpha} |) | \dot{p}_{0\alpha} \rangle \\ &= e^{QiLt} | \dot{p}_{0\alpha} \rangle = e^{QiLt} | F_{0\alpha} \rangle \end{aligned} \tag{8}$$

where $| F_{0\alpha} \rangle$ is the force on the colloid along α.

So far the treatment has been exact; we haven't yet exploited the fact that $M >> m$. To do so, let's recognize that if the system is at the temperature *T*, the momenta of the bath particles are of the order of $\sqrt{m k_B T}$ (because the thermal energy available to the particles is on the order of $k_B T$, and by equipartition $p^2 / 2m \sim k_B T$), while the momentum of the colloid is, for similar reasons, of the order of $\sqrt{Mk_BT}$. These considerations suggest that we introduce a new colloid momentum P_0 defined as

$$\mathbf{P}_0 = \sqrt{\frac{m}{M}}\mathbf{p}_0 \equiv \lambda \mathbf{p}_0 \tag{9}$$

which in turn suggests that we relabel the coordinates $\mathbf{r}_0$ as $\mathbf{R}_0$ for consistency of notation. In terms of these new variables, the colloid Liouvillian becomes

$$\begin{aligned} iL_0 &= \frac{\mathbf{P}_0}{M\sqrt{m/M}} \cdot \nabla_{\mathbf{R}_0} + \mathbf{F}_0 \cdot \sqrt{\frac{m}{M}} \nabla_{\mathbf{P}_0} \\ &= \sqrt{\frac{m}{M}}\left(\frac{\mathbf{P}_0}{m} \cdot \nabla_{\mathbf{R}_0} + \mathbf{F}_0 \cdot \nabla_{\mathbf{P}_0}\right) = \lambda\left(\frac{\mathbf{P}_0}{m} \cdot \nabla_{\mathbf{R}_0} + \mathbf{F}_0 \cdot \nabla_{\mathbf{P}_0}\right) \end{aligned} \tag{10}$$

The bath Liouvillian remains the same. What we've accomplished by the above change of variable is to establish explicitly that iL_0 is of order λ relative to iL_B; this will make it possible to introduce simplifying approximations later.

Returning to the expression for the random force in Eq. (8), we can make use of the identity

$$e^{-(M+N)t} = e^{-Mt} - \int_0^t dt' e^{-M(t-t')} N e^{-(M+N)t'} \tag{11}$$

with *M* and *N* chosen to be $-QiL$ and $-PiL$, respectively, to rewrite the term $e^{QiLt}\left|F_{0\alpha}\right\rangle$ as

$$e^{QiLt}\left|F_{0\alpha}\right\rangle = e^{iLt}\left|F_{0\alpha}\right\rangle - \int_0^t dt' e^{QiL(t-t')} PiLe^{iLt'}\left|F_{0\alpha}\right\rangle \tag{12}$$

The second term on the RHS of Eq. (12) can be simplified as follows:

$$\begin{aligned} \int_0^t dt' e^{QiL(t-t')} PiLe^{iLt'}\left|F_{0\alpha}\right\rangle &= \int_0^t dt' e^{QiL(t-t')}\left|p_{0\alpha}\right\rangle\left\langle p_{0\alpha} \mid p_{0\alpha}\right\rangle^{-1}\left\langle p_{0\alpha}\right| iLe^{iLt'}F_{0\alpha}\left.\right\rangle \\ &= -\int_0^t dt' e^{QiL(t-t')}\left|p_{0\alpha}\right\rangle\left\langle p_{0\alpha} \mid p_{0\alpha}\right\rangle^{-1}\left\langle iLp_{0\alpha}\right| e^{iLt'}F_{0\alpha}\left.\right\rangle \end{aligned} \tag{13}$$

Recall that $iL = iL_B + iL_0$, and that iL_B acts only on the phase space variables of the bath molecules, so the term $\langle iLp_{0\alpha}|$ in the integrand of Eq. (13) reduces to $\langle iL_0 p_{0\alpha}|$. But from what we've shown in Eq. (10), this is a term of order λ, and can therefore be neglected in comparison to the leading term in Eq. (12), which now becomes

$$e^{QiLt}|F_{0\alpha}\rangle \approx e^{iLt}|F_{0\alpha}\rangle \tag{14}$$

This result can be simplified even further by replacing iL by $iL = iL_B + iL_0$, using the identity in Eq. (11) again, but this time substituting $-iL_B$ for M and $-iL_0$ for N, and then noting that the contribution from the resulting convolution integral is again of order λ, and is therefore negligible in comparison to the leading term. So we finally have

$$|f_\alpha(t)\rangle = e^{QiLt}|F_{0\alpha}\rangle \approx e^{iL_B t}|F_{0\alpha}\rangle \tag{15}$$

This means that the random force can be interpreted as the intermolecular force exerted on the colloid by all the solvent molecules when the colloid is essentially stationary (stationary because $\lambda << 1$, so $M >> 1$.) Under this interpretation, $|f_\alpha(t)\rangle$ can be regarded as a "fast" variable (in relation to the colloid, which is sluggish) that loses its correlation with its initial value very quickly. In other words, the memory function $K(t)$ in the GLE for the colloid momentum can be assumed to decay to 0 extremely fast. That being the case, the GLE itself (cf. Eq. (6)), after setting Ω to 0, can be rewritten as

$$\begin{aligned}\frac{\partial|p_{0\alpha}(t)\rangle}{\partial t} &= -\int_0^t dxK(x)|p_{0\alpha}(t-x)\rangle + |f_\alpha(t)\rangle \\ &\approx -\int_0^t dxK(x)\big(|p_{0\alpha}(t)\rangle - x|\dot{p}_{0\alpha}(t) + \cdots\rangle\big) + |f_\alpha(t)\rangle \\ &\approx -\int_0^\infty dxK(x)|p_{0\alpha}(t)\rangle + |f_\alpha(t)\rangle\end{aligned} \tag{16}$$

Defining a parameter ζ as $\zeta \equiv \int_0^\infty dtK(t)$, we see that the evolution equation for $|p_{0\alpha}(t)\rangle$ finally takes the form (after dropping the bra-ket notation for now)

$$\frac{\partial p_{0\alpha}(t)}{\partial t} = -\zeta p_{0\alpha}(t) + f_\alpha(t) \tag{17}$$

or the form,

$$\frac{\partial \mathbf{p}_0(t)}{\partial t} = -\zeta \mathbf{p}_0(t) + \mathbf{f}(t) \tag{18}$$

since we've assumed – implicitly – that the system is isotropic, and that no direction is privileged. Equation (18) is the Langevin equation, and ζ is referred to as the friction coefficient. The Langevin equation is one of the simplest models of Brownian motion, the kind of random motion that a particle like the colloid in our example would execute in a fluid of many more lighter particles.

● The fluctuation-dissipation relation

We can get a better handle on the meaning of the parameter ζ that appears in the Langevin equation by deriving an expression for the mean kinetic energy of the colloid, which we know from the equipartition theorem should be $k_B T/2$ per quadratic degree of freedom. We'll use Eq. (17) for the purpose, first rewriting it in terms of the velocity (omitting the subscript α for convenience)

$$m\frac{\partial v(t)}{\partial t} = -\zeta v(t) + f(t) \tag{19}$$

To solve this equation, we need to know what to do about the random force *f*. We've shown that it acts effectively like a random variable (always being uncorrelated with the initial value of *v*), and that its correlations die off very rapidly. This suggests that it probably wouldn't be unreasonable to assume that it has these two properties:

$$\langle f(t) \rangle = 0 \tag{20a}$$

$$\langle f(t) f(t') \rangle = 2C\delta(t-t') \tag{20b}$$

The first is a statement that the force is 0 on average and the second is a statement that the force at one instant of time is completely uncorrelated with the force at any other time. The coefficient *C* is an unknown (adjustable) parameter that is a measure of how strong the force is.

We can now proceed to solve Eq. (19); the solution is

$$v(t) = v(0)e^{-\zeta t/m} + \frac{1}{m}\int_0^t dt' e^{-\zeta(t-t')/m} f(t') \tag{21}$$

When this result is squared, and then averaged over the distribution of initial velocities, we end up with

$$\left\langle v(t)^2 \right\rangle = \left\langle v(0)^2 \right\rangle e^{-2\zeta t/m} + \frac{2C}{m^2}\int_0^t dt_1 \int_0^t dt_2 e^{-\zeta(t-t_1)/m} e^{-\zeta(t-t_2)/m}\delta(t_1 - t_2) \tag{22}$$

In deriving this expression, we've made use of the fact that $\left\langle v(0) f(t) \right\rangle = 0$. After carrying out the integrations in (22), we find that

$$\left\langle v(t)^2 \right\rangle = \left\langle v(0)^2 \right\rangle e^{-2\zeta t/m} + \frac{C}{m\zeta}\left(1 - e^{-2\zeta t/m}\right) \tag{23}$$

which at long times, when the system has settled into a time-independent stationary state, reduces to

$$\left\langle v(\infty)^2 \right\rangle = \frac{C}{m\zeta}$$

In this limit, the mean kinetic energy of the particle is $C/2\zeta$, and so from the equipartition theorem,

$$C = \zeta k_B T$$

The time correlation function of the random force is therefore given by

$$\left\langle f(t) f(t') \right\rangle = 2\zeta k_B T \delta(t - t') \tag{24}$$

which is sometimes referred to as the fluctuation-dissipation theorem. The word dissipation appears here by virtue of the fact that in Eq. (19), if there had been no random force term, the velocity of the particle would eventually have decayed to 0, which would have required the particle to dissipate all its energy to the surroundings, essentially because of friction, which can be ascribed to the parameter ζ (hence its name – friction coefficient.) The presence of the random force f in Eq. (19) ensures that the particle actually remains forever in motion, the energy it dissipates frictionally being constantly replenished by *f*.