Microscopic Theory I: Brownian Motion

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1 Fundamentals

- Recall that we described the motion of a large, massive particle in a fluid of small, rapidly moving solvent particles in terms of the stochastic Langevin equation

$$\dot{\mathbf{P}}(t) = -\gamma \mathbf{P}(t) + \xi(t),$$

  where γ was the *friction* the "Brownian" particle exeriences in the the fluid and $\xi(t)$ is the time-dependent stochastic force exerted by collisions of the solvent with the Brownian particle.

- Can we understand this equation starting from first principles? What are its limits of validity?

Consider a system composed of a large, spherical Brownian particle of mass M with position $\mathbf{R}$ and momentum $\mathbf{P}$ immersed in a fluid of N spherical, light particles of mass m with positions $\mathbf{r}^{(N)}$ and momenta $\mathbf{p}^{(N)}$.

- The general Hamiltonian of the system is assumed to be of the form:

$$\begin{aligned} H &= \frac{\mathbf{P}\cdot\mathbf{P}}{2M} + \frac{\mathbf{p}^{(N)}\cdot\mathbf{p}^{(N)}}{2m} + V(\mathbf{r}^{(N)}) + \phi(\mathbf{r}^{(N)},\mathbf{R}) \\ \phi(\mathbf{r}^{(N)},\mathbf{R}) &= \sum_{j=1}^{N} \phi(|\mathbf{R}-\mathbf{r}_j|) \qquad V(\mathbf{r}^{(N)}) = \sum_{i<j} V(|\mathbf{r}_{ij}|). \end{aligned}$$

- From this Hamiltonian, the equations of motion are

$$\begin{aligned} \dot{\mathbf{P}} &= -\nabla_{\mathbf{R}}\phi = \mathbf{F} \qquad \dot{\mathbf{p}}_j = -\nabla_{\mathbf{r}_j}(V+\phi) \\ \dot{\mathbf{R}} &= \frac{\mathbf{P}}{M} \qquad \dot{\mathbf{r}}_j = \frac{\mathbf{p}_j}{m}. \end{aligned}$$

- The Liouvillian for this system is

$$\mathcal{L} = \frac{\mathbf{P}}{M}\cdot\nabla_{\mathbf{R}} - \nabla_{\mathbf{R}}\phi\cdot\nabla_{\mathbf{P}} + \frac{\mathbf{p}^{(N)}}{m}\cdot\nabla_{\mathbf{r}^N} - \nabla_{\mathbf{r}^N}(V+\phi)\cdot\nabla_{\mathbf{p}^N}$$

- Physical conditions:
  1. $\epsilon^2 \equiv m/M << 1$.
  2. $|\mathbf{P}/M| < |\mathbf{p}_j/m|$.
  3. $|\mathbf{P}| > |\mathbf{p}_j|$.

  - Note that condition 2 implies that $|\mathbf{P}| < \epsilon^{-2}|\mathbf{p}_j|$ so that $\epsilon^{-2} > |\mathbf{P}|/|\mathbf{p}_j|$.

$$\langle \mathbf{P}_x^2 \rangle = MkT = \epsilon^{-2}(mkT) = \epsilon^{-2}\langle \mathbf{p}_{jx}^2 \rangle \sim \epsilon^{-2} m e^0$$

    where $e^0 = 3/2kT \sim E_b/N$ is the average energy per particle of the bath.

  - Combining the above analysis with condition 3, we have the limits of the momentum ratio is:

$$\epsilon^{-2} > |\mathbf{P}|/|\mathbf{p}_j| > \epsilon^0.$$

- Because of the great difference in the masses of the Brownian and fluid particles, the velocity of the Brownian particle is small compared to that of the fluid particles. On the other hand, its momentum is typically large due to its large mass.

- We will use ϵ as a perturbation parameter since it is the ratio of the masses of the Brownian and fluid particles that determines the *separation of time scale* between motion of the Brownian particle and motion of the fluid (or *bath*) particles.

- To make this explicit, we *define* the scaled momentum $\mathbf{P}^* = \epsilon \mathbf{P}$, so that $\epsilon^{-1} > |\mathbf{P}^*|/|\mathbf{p}_j|$ or $|\mathbf{P}^*|/|\mathbf{p}_j| \sim \epsilon^0$.

- Note that in terms of the small parameter,

$$\begin{aligned}
\dot{\mathbf{P}^*} &= \epsilon \mathbf{F} \qquad \dot{\mathbf{R}} = \epsilon \frac{\mathbf{P}^*}{m} \\
\mathcal{L} &= \epsilon \frac{\mathbf{P}^*}{m} \cdot \nabla_{\mathbf{R}} - \epsilon \nabla_{\mathbf{R}} \phi \cdot \nabla_{\mathbf{P}^*} + \frac{\mathbf{p}^{(N)}}{m} \cdot \nabla_{\mathbf{r}^N} - \nabla_{\mathbf{r}^N}(V + \phi) \cdot \nabla_{\mathbf{p}^N} \\
&= \epsilon \mathcal{L}_1 + \mathcal{L}_0,
\end{aligned}$$

  where the Liouvillian $\mathcal{L}_0$ for the bath corresponds to a Liouvillian for the fluid particles interacting in the presence of a *fixed* Brownian particle at position $\mathbf{R}$. The Hamiltonian for this bath subs-system is $H_0 = \mathbf{p}^{(N)} \cdot \mathbf{p}^{(N)}/2m + V + \phi$.

  - Given that changes in the Brownian particle position and momentum are proportional to ϵ , if the bath moves on relative time scale τ_b, the Brownian particle evolves on system time scale $\tau_s \sim \epsilon^{-1}\tau_b$.
  - From these definitions, it follows that $\mathcal{L}_0 H_0 = 0$.

- Basic idea: we look at evolution of the system on time-scales $\tau_s \gg \tau_b$, and so we want to represent the effect of the rapid collisions of the bath particles with the Brownian particle as time-averaged forces plus fluctuations from this time average. We will replace the time average by an **ensemble average over a** *conditional* **distribution** corresponding to an equilibrium bath in the presence of the fixed Brownian particle.

- The conditional distribution for the bath system is

$$\tilde{\rho}(\mathbf{x}^{(N)}; \mathbf{R}) = \frac{e^{-\beta H_0}}{\int d\mathbf{x}^{(N)}\, e^{-\beta H_0}},$$

  where $(\mathbf{x}^{(N)})$ are the phase space coordinates of the bath.

  - Note that since $\phi(\mathbf{r}^{(N)}, \mathbf{R}) = \sum_i \phi(\mathbf{r}_i - \mathbf{R}) = \sum_i \phi(y_i)$, where $y_i = |\mathbf{r}_i - \mathbf{R}|$, it follows that the normalization of the conditional distribution is independent of $\mathbf{R}$ since

$$\int d\mathbf{r}^{(N)}\, e^{-\sum_{i<j} \beta V(r_{ij})} e^{-\sum_i \beta\phi(\mathbf{r}_i - \mathbf{R})} = \int d\mathbf{y}^{(N)}\, e^{-\sum_{i<j} \beta V(y_i - y_j)} e^{-\sum_i \beta\phi(y_i)} = \text{constant}.$$

Note that $\tilde{\rho}$ is properly normalized so that $\int d\mathbf{x}^{(N)} \tilde{\rho}(\mathbf{x}^{(N)}, \mathbf{R}) = 1$.

2 Projection Operator Method

- In order to extract the bath-averaged quantitities explicitly, we define a *projection operator* $\mathcal{P}$ that acts on an arbitrary dynamical variable $B(\mathbf{x}^{(N)}, \mathbf{R}, \mathbf{P})$ as:

$$\mathcal{P}B = \int d\mathbf{x}^{(N)} \tilde{\rho}(\mathbf{x}^{(N)}; \mathbf{R}) B = \langle B \rangle_b \, .$$

  - A projection operator has the property: $\mathcal{P}^2 = \mathcal{P}$, which can be explicitly verified for the above definition since

$$\begin{aligned} \mathcal{P}^2 B &= \int d\mathbf{x}'^{(N)}\, \tilde{\rho}(\mathbf{x}'^{(N)}; \mathbf{R}') \int d\mathbf{x}^{(N)}\, \tilde{\rho}(\mathbf{x}^{(N)}; \mathbf{R}) B(\mathbf{x}^{(N)}; \mathbf{R}, \mathbf{P}) \\ &= \int d\mathbf{x}^{(N)}\, \tilde{\rho}(\mathbf{x}^{(N)}; \mathbf{R}) B(\mathbf{x}^{(N)}; \mathbf{R}, \mathbf{P}) = \mathcal{P}B. \end{aligned}$$

  - We can define a related projection operator $\mathcal{Q} = 1 - \mathcal{P}$ that is orthogonal to $\mathcal{P}$ in the sense that:

$$\mathcal{P}\mathcal{Q} = \mathcal{P}(1 - \mathcal{P}) = \mathcal{P} - \mathcal{P} = 0.$$

  - Note that $\mathcal{Q}^2 = \mathcal{Q}$ as well.
  - If we view $\mathcal{P}$ as an operator that averages out the bath dependency of a dynamical variable, then $\mathcal{Q}$ essentially looks at the effect of bath fluctuations on a dynamical variable.
  - If B is a function *only* of the Brownian coordinates $(\mathbf{R}, \mathbf{P})$, then $\mathcal{Q}B = 0$.
  - If we consider that the only really slow behavior on time scale τ_s arises from motion of the Brownian particle, then $\mathcal{Q}B$ removes any slow motion from B since it corresponds to $B - \langle B \rangle_b$.

- Based on our study of stochastic systems and the Langevin equation, we need to define some rapidly-varying force to account for the "random" collisions of bath with the Brownian particle. We therefore *define* the stochastic force $\mathbf{K}(t)$ to be:

$$\mathbf{K}(t) \;=\; e^{(1-\mathcal{P})\mathcal{L}t}(1 - \mathcal{P})\mathcal{L}P^* = e^{\mathcal{Q}\mathcal{L}t}\mathcal{Q}\dot{\mathbf{P}}^*.$$

  - Note that the stochastic force obeys the equation:

$$\dot{\mathbf{K}}(t) \;=\; \mathcal{Q}\mathcal{L}\,\mathbf{K}(t) = \mathcal{L}\mathbf{K}(t) - \langle \mathcal{L}\mathbf{K}(t) \rangle_b \, .$$

  - Interpretation: the stochastic force $\mathbf{K}(t)$ has no slow behavior at all since it is governed by an effective Liouvillian operator $\mathcal{Q}\mathcal{L}$ that has no projection along the slow variables. In other words, although the Liouville operator does depend on the Brownian coordinates, $\mathcal{Q}\mathcal{L}$ effectively gives the contibution of the time derivative due to fluctuations in the bath away from their average contribution.

- The expectation is that $\mathbf{K}(t)$ varies on time scale τ_b.
- Properties:
  1. $\langle \mathbf{K}(t)\rangle_b = \mathcal{P}\mathbf{K}(t) = 0$ since $\mathcal{Q}\mathbf{K}(t) = \mathbf{K}(t)$ and hence $\mathcal{P}\mathbf{K}(t) = \mathcal{P}\mathcal{Q}\mathbf{K}(t) = 0$.
  2. $\langle \mathbf{K}(t)B(\mathbf{R},\mathbf{P})\rangle_b = \langle \mathbf{K}(t)\rangle_b B(\mathbf{R},\mathbf{P}) = 0$.
  3. $\langle \mathbf{K}(t)\mathbf{K}(0)\rangle_b \to \langle \mathbf{K}(t)\rangle_b \langle \mathbf{K}(0)\rangle_b = 0$ for $t > \tau_b$, where τ_b is the time scale of the bath over which motions of the bath become uncorrelated.

- The *generalized Langevin equation* can be derived by noting that:

$$\dot{\mathbf{P}}^*(t) \;=\; e^{\mathcal{L}t}\dot{\mathbf{P}}^*(0) = e^{\mathcal{L}t}(\mathcal{P}+\mathcal{Q})\dot{\mathbf{P}}^*(0) = e^{\mathcal{L}t}\mathcal{P}\dot{\mathbf{P}}^*(0) + e^{\mathcal{L}t}\mathcal{Q}\dot{\mathbf{P}}^*(0).$$

  - Note that the last term is almost the stochastic force, except that we have the time "propagator" $\exp\{\mathcal{L}t\}$ instead of the effective, "fast" propagator $\exp\{\mathcal{Q}\mathcal{L}t\} = \exp\{(1-\mathcal{P})\mathcal{L}t\}$ which gives rise to the "projected dynamics". What is the relation between them?

- Key operator identity: Consider the exponential of two operators (or non-commuting matrices) A and B;

$$f(t) = e^{(A+B)t} \;=\; e^{At}g(t).$$

  - $f(0) = g(0) = 1$ and we must have

$$\begin{aligned}
g(t) &= e^{-At}e^{(A+B)t} \quad \text{hence} \\
\dot{g}(t) &= e^{-At}(-A)e^{(A+B)t} + e^{-At}(A+B)e^{(A+B)t} = e^{-At}Be^{(A+B)t} \\
g(t)-1 &= \int_0^t d\tau\, \dot{g}(\tau) = \int_0^t d\tau\, e^{-A\tau}Be^{(A+B)\tau} \qquad \text{and hence} \\
e^{(A+B)t} &= e^{At}g(t) = e^{At} + \int_0^t d\tau\, e^{A(t-\tau)}Be^{(A+B)\tau}
\end{aligned}$$

- Applying this identity with $A = \mathcal{L}$ and $B = -\mathcal{P}\mathcal{L}$, we can write:

$$e^{\mathcal{Q}\mathcal{L}t} \;=\; e^{(1-\mathcal{P})\mathcal{L}t} = e^{\mathcal{L}t} - \int_0^t d\tau\, e^{\mathcal{L}t}\mathcal{P}\mathcal{L}e^{\mathcal{Q}\mathcal{L}\tau}.$$

- Using this in the equation of motion for the scaled momentum $\mathbf{P}^*$ gives:

$$\begin{aligned}
\dot{\mathbf{P}}^*(t) &= e^{\mathcal{L}t}\mathcal{P}\dot{\mathbf{P}}^*(0) + \left(e^{\mathcal{Q}\mathcal{L}t} + \int_0^t d\tau\, e^{\mathcal{L}t}\mathcal{P}\mathcal{L}e^{\mathcal{Q}\mathcal{L}\tau}\right)\mathcal{Q}\dot{\mathbf{P}}^*(0) \\
&= e^{\mathcal{L}t}\left\langle \dot{\mathbf{P}}^*(0)\right\rangle_b + \int_0^t d\tau\, e^{\mathcal{L}t}\mathcal{P}\mathcal{L}\mathbf{K}(\tau) + \mathbf{K}(t).
\end{aligned}$$

- Consider the first term on the right hand side:

$$\left\langle \dot{\mathbf{P}}^*(0)\right\rangle_b \;=\; -\epsilon\left\langle \nabla_{\mathbf{R}}\phi\right\rangle_b = \epsilon\frac{\int d\mathbf{x}^{(N)}\,(-\nabla_{\mathbf{R}}\phi)\,e^{-\beta H_0}}{\int d\mathbf{x}^{(N)}\,e^{-\beta H_0}} = \frac{\epsilon}{\beta}\frac{\nabla_{\mathbf{R}}\left(\int d\mathbf{x}^{(N)}\,e^{-\beta H_0}\right)}{\int d\mathbf{x}^{(N)}\,e^{-\beta H_0}} = 0$$

  since the normalization factor is independent of $\mathbf{R}$!

- Now consider the term $\mathcal{PL}\mathbf{K}(\tau) = \langle \mathcal{L}\mathbf{K}(\tau)\rangle_b$. Since $\mathcal{L} = \mathcal{L}_0 + \epsilon\mathcal{L}_1$ and $\mathcal{L}_0\tilde{\rho} = 0$, we have

$$\begin{aligned}\mathcal{PL}\mathbf{K}(\tau) &= \epsilon\,\langle \mathcal{L}_1\mathbf{K}(\tau)\rangle_b = \epsilon\left\langle \left(\frac{\mathbf{P}^*}{m}\cdot\nabla_{\mathbf{R}} - \nabla_{\mathbf{R}}\cdot\nabla_{\mathbf{P}^*}\right)\mathbf{K}(\tau)\right\rangle_b \\ &= \epsilon\left(\frac{\mathbf{P}^*}{m}\cdot\langle\nabla_{\mathbf{R}}\mathbf{K}(\tau)\rangle_b - \nabla_{\mathbf{P}^*}\cdot\langle\nabla_{\mathbf{R}}\phi\mathbf{K}(\tau)\rangle_b\right).\end{aligned}$$

  - Looking at $\langle\nabla_{\mathbf{R}}\mathbf{K}(\tau)\rangle_b$, we can write

$$\begin{aligned}\langle\nabla_{\mathbf{R}}\mathbf{K}(\tau)\rangle_b &= \int d\mathbf{x}^{(N)}\,\tilde{\rho}(\mathbf{x}^{(N)};\mathbf{R})\nabla_{\mathbf{R}}\mathbf{K}(\tau) = \nabla_{\mathbf{R}}\,\langle\mathbf{K}(\tau)\rangle_b - \int d\mathbf{x}^{(N)}\,\left(\nabla_{\mathbf{R}}\tilde{\rho}\right)\mathbf{K}(\tau) \\ &= \beta\int d\mathbf{x}^{(N)}\,\nabla_{\mathbf{R}}\phi\tilde{\rho}\,\mathbf{K}(\tau) = \beta\,\langle\nabla_{\mathbf{R}}\phi\,\mathbf{K}(\tau)\rangle_b\end{aligned}$$

    since $\nabla_{\mathbf{R}}\tilde{\rho} = -\beta\nabla_{\mathbf{R}}\phi\tilde{\rho}$. Thus we conclude

$$\mathcal{PL}\mathbf{K}(\tau) = \epsilon\left(\frac{\beta\mathbf{P}^*}{m} - \nabla_{\mathbf{P}^*}\right)\cdot\langle\nabla_{\mathbf{R}}\phi\,\mathbf{K}(\tau)\rangle_b\,.$$

- Putting this all together and using the fact that $\mathbf{K}(t) = e^{\mathcal{QL}t}\mathcal{Q}\dot{\mathbf{P}}^* = e^{\mathcal{QL}t}\mathbf{F}$, we arrive at an **EXACT** expression:

$$\dot{\mathbf{P}}^*(t) = \epsilon e^{\mathcal{QL}t}\mathbf{F} + \epsilon^2\int_0^t d\tau\,e^{\mathcal{L}(t-\tau)}\left(\nabla_{\mathbf{P}^*} - \frac{\beta\mathbf{P}^*}{m}\right)\cdot\left\langle\mathbf{F}\,e^{\mathcal{QL}\tau}\mathbf{F}\right\rangle_b.$$

  - Note that although the force on the Brownian particle $\mathbf{F}$ and the bath average are independent of $\mathbf{P}^*$, the term $\left\langle\mathbf{F}\,e^{\mathcal{QL}\tau}\mathbf{F}\right\rangle_b$ does depend on $\mathbf{P}^*$ through the projected propagator since $\mathcal{L}$ contains $\mathbf{P}^*$.
  - The effect of the full propagator $\exp\{\mathcal{L}(t-\tau)\}$ is to evolve the positions of the Brownian coordinates form time $t = 0$ to time $t - \tau$ for *all* quantities to the right of it.

3 Simplifications

- Using the small parameter ϵ, the exact expression for the time evolution of $\mathbf{P}^*$ can be simplified considerably.

- Recall that

$$\begin{aligned}\mathcal{L} &= \mathcal{L}_0 + \epsilon\mathcal{L}_1 \qquad \text{and since } \mathcal{P}\mathrm{L}_0 = 0 \\ \mathcal{QL} &= L_0 + \epsilon\mathcal{QL}_1 \qquad \text{and since by the operator identity} \\ e^{\mathcal{QL}\tau} &= e^{\mathcal{L}_0\tau} + \epsilon\int_0^\tau d\tau_1 e^{\mathcal{L}_0(\tau-\tau_1)}\mathcal{QL}_1 e^{\mathcal{QL}\tau_1} \qquad \text{we have} \\ \left\langle\mathbf{F}e^{\mathcal{QL}\tau}\mathbf{F}\right\rangle_b &= \left\langle\mathbf{F}e^{\mathcal{L}_0\tau}\mathbf{F}\right\rangle_b + \epsilon\int_0^\tau d\tau_1\,\left\langle\mathbf{F}e^{\mathcal{L}_0(\tau-\tau_1)}\mathcal{QL}_1 e^{\mathcal{L}_0\tau_1}\mathbf{F}\right\rangle_b \\ &\quad + \epsilon^2\int_0^\tau d\tau_1\int_0^{\tau_1} d\tau_2\,\left\langle\mathbf{F}e^{\mathcal{L}_0(\tau-\tau_1)}\mathcal{QL}_1 e^{\mathcal{L}_0(\tau_1-\tau_2)}\mathcal{QL}_1 e^{\mathcal{L}_0\tau_2}\mathbf{F}\right\rangle_b + \cdots\end{aligned}$$

- Consider the first term on the r.h.s:

$\left\langle\mathbf{F}e^{\mathcal{L}_0\tau}\mathbf{F}\right\rangle_b \to \langle\mathbf{F}\rangle_b\,\langle\mathbf{F}\rangle_b = 0$ for $\tau \geq \tau_b$ by isotropy assuming mixing (independence at long times).

  - Since $\mathcal{L}_0$ depends only on bath coordinates and parametrically on $\mathbf{R}$, it is independent of $\mathbf{P}^*$ and hence $\nabla_{\mathbf{P}^*} \left\langle \mathbf{F} e^{\mathcal{L}_0 \tau} \mathbf{F} \right\rangle_b = 0$.
  - We *define* $\mathbf{F}_b(\tau; \mathbf{R})) = \mathbf{e}^{\mathcal{L}_0 \tau} \mathbf{F}$ and note that since $\mathcal{L}_0 \tilde{\rho} = 0$, the first term is simply $\langle \mathbf{F}^x \mathbf{F}_b^x(\tau) \rangle_b \, \mathbf{I}$ by isotropy.

- To analyze the second term, recall that

$$\mathcal{Q}\mathcal{L}_1 = \mathcal{Q} \left[\frac{\mathbf{P}^*}{m} \cdot \nabla_{\mathbf{R}} + \mathbf{F} \cdot \nabla_{\mathbf{P}^*} \right].$$

  - Since the average is over phase space coordinates and depends parametrically on $\mathbf{R}$, we can pull $\mathbf{P}^*$ and $\nabla_{\mathbf{P}^*}$ out of average.
  - Effect is to leave odd-ranked tensors

$$\left\langle \mathbf{F} e^{\mathcal{L}_0 (\tau - \tau_1)} \left(\nabla_{\mathbf{R}} \mathbf{F}_b(\tau_1) + \mathbf{F}_b(\tau_1) \beta \mathbf{F} \right) \right\rangle_b \qquad \text{and} \qquad \left\langle \mathbf{F} \mathbf{F}_b(\tau - \tau_1) \mathbf{F}_b(\tau) \right\rangle_b .$$

  - Since potentials depend only on scalar distances (spherical symmetry), all odd-ranked tensors must vanish.
  - Thus, $O(\epsilon)$ term is zero.

- Defining $\tilde{\mathcal{L}_1} = \mathcal{Q}\mathcal{L}_1$ and $T_0(\tau) = e^{\mathcal{L}_0 \tau}$, the next order term is

$$\int_0^\tau d\tau_1 \int_0^{\tau_1} d\tau_2 \left\langle \mathbf{F} T_0(\tau - \tau_1) \tilde{\mathcal{L}}_1 T_0(\tau_1 - \tau_2) \tilde{\mathcal{L}}_1 T_0(\tau_2) \mathbf{F} \right\rangle_b = \int_0^\tau d\tau_1 \int_0^{\tau_1} d\tau_2 T_2$$

  - To analyze this term, we assume the mixing property:

$$\langle A \left(T_0(t) B \right) \rangle_b = \langle \left(T_0(-t) A \right) B \rangle_b \to \langle A \rangle_b \langle B \rangle_b \qquad \text{for } t > \tau_b.$$

    - If $\tau_2 > \tau_b$ the correlation function factors into:

$$T_2 \to \left\langle \mathbf{F} T_0(\tau - \tau_1) \tilde{\mathcal{L}}_1 T_0(\tau_1 - \tau_2) \tilde{\mathcal{L}}_1 \right\rangle_b \langle \mathbf{F} \rangle_b = 0$$

    - If $\tau - \tau_1 > \tau_b$ the correlation function factors into:

$$T_2 \to \langle \mathbf{F} \rangle_b \left\langle \tilde{\mathcal{L}}_1 T_0(\tau_1 - \tau_2) \tilde{\mathcal{L}}_1 T_0(\tau_2) \mathbf{F} \right\rangle_b = 0$$

    - If $\tau_1 - \tau_2 > \tau_b$ the correlation function factors into:

$$\begin{aligned} T_2 &\to \left\langle \mathbf{F} T_0(\tau - \tau_1) \tilde{\mathcal{L}}_1 \right\rangle_b \left\langle \tilde{\mathcal{L}}_1 T_0(\tau_2) \mathbf{F} \right\rangle_b \\ &= \left\langle \mathbf{F} T_0(\tau - \tau_1) \tilde{\mathcal{L}}_1 \right\rangle_b \langle \mathcal{Q}\mathcal{L}_1 T_0(\tau_2) \mathbf{F} \rangle_b \\ &= \left\langle \mathbf{F} T_0(\tau - \tau_1) \tilde{\mathcal{L}}_1 \right\rangle_b \mathcal{P}\mathcal{Q}\mathcal{L}_1 T_0(\tau_2) \mathbf{F} = 0. \end{aligned}$$

  - These three conditions imply that T_2 vanishes except when τ, τ_1 and τ_2 are not too far apart (on the order of τ_b).
  - If we set $a_2 = \max\{T_2\}$ on the interval $\tau \in [0, \tau_b]$, then $|T_2| \leq \epsilon^2 \tau_b^2 a_2$.
  - Analysis of higher order terms proceeds similarly, and we find that (see Mazur and Oppenheim, Physica **50**, 1970, pp. 241 - 258),

$$|T_{2n}| \leq \epsilon^{2n} \tau_b^{2n} a_{2n}$$

  - Using this information, it can be shown that the time-integral converges so that $\int_0^\infty d\tau \, \langle \mathbf{F}\mathbf{F}^+(\tau)\rangle_b$ exists, where $\mathbf{F}^+(\tau) = e^{\mathcal{QL}\tau}\mathbf{F}$.

- We can conclude that to a good approximation,

$$\int_0^t d\tau \, \langle \mathbf{F}\mathbf{F}^+(\tau)\rangle_b = \int_0^t d\tau \, \langle \mathbf{F}\mathbf{F}_0(\tau)\rangle_b + O\left(\epsilon^2\right),$$

where $\mathbf{F}_0(\tau) = e^{\mathcal{L}_0\tau}\mathbf{F}$ denotes the time-dependent force of the bath in the presence of a fixed Brownian particle.

  - This correlation function depends only on the time τ so that $\nabla_{\mathbf{P}^*} \langle \mathbf{F}\mathbf{F}_0(\tau)\rangle_b = 0$.

- Inserting this approximation into the exact expression, we arrive at

$$\dot{\mathbf{P}}^*(t) \quad = \quad \epsilon e^{\mathcal{QL}t}\mathbf{F} - \epsilon^2 \int_0^t d\tau \, \frac{\beta \mathbf{P}^*(t-\tau)}{m} \cdot \left\langle \mathbf{F}\, e^{\mathcal{QL}\tau}\mathbf{F}\right\rangle_b .$$

- Further simplifications are possible noting that the correlation function in the integral vanishes on time scales $t \sim \tau_b$, and that the momentum is essentially constant on the time scale τ_b since

$$\mathbf{P}^*(t-\tau) = \mathbf{P}^*(t) - \int_{t-\tau}^t d\tau_1 \dot{\mathbf{P}}^*(\tau_1) = \mathbf{P}^*(t) + O(\epsilon).$$

- Putting this all together, we arrive at our phenomenological equation for $t > \tau_b$, and to order ϵ^3,

$$\dot{\mathbf{P}}^*(t) = \epsilon \mathbf{K}(t) - \epsilon^2 \frac{\beta}{m} \int_0^\infty d\tau \, \langle \mathbf{F}^x(0)\mathbf{F}_0^x(\tau)\rangle_b \, \mathbf{P}^*(t) + O\left(\epsilon^3\right),$$

and hence the *friction* in the Langevin equation can be calulated by the time integral of the autocorrelation function of the force exerted by the fluid on the Brownian particle

$$\gamma = \frac{\beta\epsilon^2}{m} \int_0^\infty d\tau \, \langle \mathbf{F}^x(0)\mathbf{F}_0^x(\tau)\rangle_b = \frac{\beta}{M} \int_0^\infty d\tau \, \langle \mathbf{F}^x(0)\mathbf{F}_0^x(\tau)\rangle_b .$$

- Basic assumptions to get Langevin equation from exact expression:
  1. $\epsilon^2 \ll 1$.
  2. $\epsilon^{-2} > |\mathbf{P}|/|\mathbf{p}_j| > \epsilon^0$.
  3. The mixing property $\langle A(t)B\rangle_b \to \langle A\rangle_b \langle B\rangle_b$ for $t > \tau_b$.

- It turns out the third assumption is problematic since slow motions of the fluid (to be studied very soon) lead to long-lived correlations in the fluid and in fact are necessary to explain the relationship between the friction and the viscosity ν of the fluid $\gamma \sim \nu R$, where R is the radius of the Brownian particle.

4 The relation between projected and unprojected dynamics

Consider the *unprojected* correlation function $\langle \mathbf{F}\mathbf{F}(t)\rangle_b$. How does this differ from the correlation function in the expression for the friction in the previous section?

- One clear difference between the time integral of the unprojected versus projected correlation function is that

$$\int_0^\infty d\tau\ \langle \mathbf{F}\mathbf{F}(\tau)\rangle_b = \lim_{t\to\infty} \langle \mathbf{F}\mathbf{P}(t)\rangle_b - \langle \mathbf{F}\mathbf{P}\rangle_b = 0 \qquad \int_0^\infty d\tau\ \langle \mathbf{F}\mathbf{F}^+(\tau)\rangle_b = mkT\gamma.$$

- Once again, we can expand for small ϵ using our favorite operator identity:

$$\begin{aligned}\langle \mathbf{F}\mathbf{F}(t)\rangle_b &= \langle \mathbf{F}\mathbf{F}_0(t)\rangle_b + \epsilon \int_0^t d\tau\ \langle \mathbf{F}T_0(t-\tau_1)\mathcal{L}_1 T_0(\tau_1)\mathbf{F}\rangle_b \\ &+\epsilon^2 \int_0^t d\tau_1 \int_0^{\tau_1} d\tau_2\ \langle \mathbf{F}T_0(t-\tau_1)\mathcal{L}_1 T_0(\tau_1-\tau_2)\mathcal{L}_1 T_0(\tau_2)\mathbf{F}\rangle_b + \cdots\end{aligned}$$

  - Same expression as that previously analyzed except that $\tilde{\mathcal{L}}_1 = \mathcal{Q}\mathcal{L}_1$ is replaced with $\mathcal{L}_1$ (i.e. no projection operator removing the slow time component).
  - As before, the odd orders of ϵ vanish by symmetry for isotropic systems.
  - First term is same as before.
  - Observe differences at order ϵ^2 since the correlation function doesn't vanish when $\tau_1 - \tau_2 > \tau_b$ but factors into:

$$\begin{aligned}\langle \mathbf{F}T_0(t-\tau_1)\mathcal{L}_1 T_0(\tau_1-\tau_2)\mathcal{L}_1 T_0(\tau_2)\mathbf{F}\rangle_b &\to \langle \mathbf{F}T_0(t-\tau_1)\mathcal{L}_1\rangle_b \langle \mathcal{L}_1 T_0(\tau_2)\mathbf{F}\rangle_b \\ &= \langle \mathbf{F}\mathbf{F}_0(t-\tau_1)\rangle_b \cdot \nabla_{\mathbf{P}^*}\frac{\mathbf{P}^*}{m} \cdot \langle \nabla_{\mathbf{R}}\mathbf{F}_0(t_2)\rangle_b \\ &= -\frac{\beta}{m}\langle \mathbf{F}\mathbf{F}_0(t-\tau_1)\rangle_b \cdot \nabla_{\mathbf{P}^*}\mathbf{P}^* \cdot \langle \mathbf{F}\mathbf{F}_0(\tau_2)\rangle_b \\ &= -\frac{\beta}{m}\mathbf{I}\,\alpha(t-\tau_1)\alpha(\tau_2),\end{aligned}$$

    where we have defined $\alpha(t) = \langle \mathbf{F}^x(0)\mathbf{F}_0^x(t)\rangle_b$.
  - In the long time limit, for $\tau_1 - \tau_2 > \tau_b$, the ϵ^2 term becomes the $s = 0$ value of the Laplace transform

$$-\frac{\beta\epsilon^2}{m}\mathbf{I}\int_0^t d\tau_1 \int_0^{\tau_1} d\tau_2\ \alpha(t-\tau_1)\alpha(\tau_2) \approx -\frac{\beta\epsilon^2}{m}\mathbf{I}\,\theta^2 \qquad \theta = \int_0^\infty d\tau\alpha(\tau).$$

  - Note that because there is no projection operator $\mathcal{Q}$, the long time limit of this term is non-zero.
  - Analogous treatment of the ϵ^4 term and higher show that there are long time, non-zero contributions when arguments $\tau_1 - \tau_2 > \tau_b$, $\tau_3 - \tau_4 > \tau_b$, etc..
  - The ϵ^4 term looks like (see Mazur and Oppenheim)

$$-\left(\frac{\beta}{m}\right)^2 \epsilon^4 \int_0^t d\tau_1\alpha(t-\tau_1)\int_0^{\tau_1} d\tau_2 \int_0^{\tau_2} d\tau_3\alpha(\tau_2-\tau_3)\int_0^{\tau_3} d\tau_4\alpha(\tau_4) \approx -\left(\frac{\beta}{m}\right)^2 \epsilon^4\theta^3 t$$

- Including all orders of ϵ gives, in the long time limit,

$$\begin{aligned}\langle \mathbf{F}\mathbf{F}(t)\rangle_b &= \langle \mathbf{F}\mathbf{F}_0(t)\rangle_b + \sum_{n=1}^{\infty}\left(\frac{-\beta\epsilon^2}{m}\right)^n \theta^{n+1}\frac{t^{n-1}}{(n-1)!} \\ &= \langle \mathbf{F}\mathbf{F}_0(t)\rangle_b - \frac{\beta\epsilon^2}{m}\theta^2\mathbf{I}e^{-\beta\epsilon^2\theta t/m}\end{aligned}$$

  - Note that the second term *cannot* be neglected at long times as it decays very slowly due to the ϵ^2 in the exponential.

- In the *weak coupling limit* where $s = \epsilon^2 t$ is fixed as $\epsilon \longrightarrow 0$ and $t \longrightarrow \infty$, we see that

$$\begin{aligned}\langle \mathbf{F}\mathbf{F}^+(t)\rangle_b &= \langle \mathbf{F}\mathbf{F}_0(t)\rangle_b \quad \text{whereas} \\ \langle \mathbf{F}\mathbf{F}(t)\rangle_b &= \langle \mathbf{F}\mathbf{F}_0(t)\rangle_b - \frac{\beta\epsilon^2\theta^2}{m}e^{-\beta\theta\epsilon^2 t/m}\end{aligned}$$

  - Note that since $\int_0^\infty dt\ \langle \mathbf{F}\mathbf{F}_0(t)\rangle_b = \theta$, we see explicity that $\int_0^\infty dt\ \langle \mathbf{F}\mathbf{F}(t)\rangle_b = 0$.
  - The effect of the $\mathcal{Q}$ propagator is to remove the slowly-decaying component of the force given by the second term on the r.h.s above.