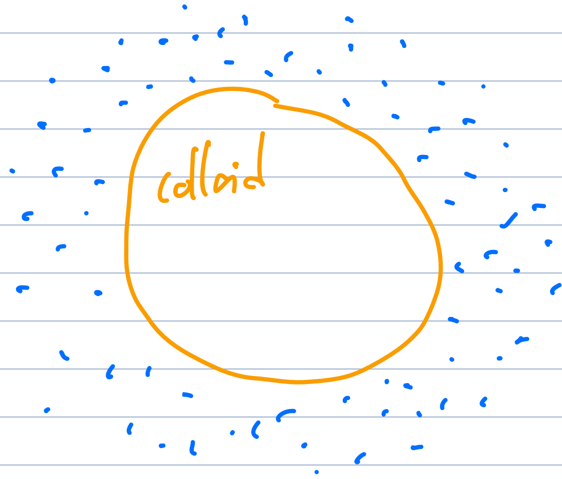
Chap I: The Langevin Equation



Take $H = \frac{p^2}{2M} + V(x) + \sum_i \frac{p_i}{2} + \frac{\omega_i^2}{2}(q_i - x)^2$

Integrating out the dynamics of $\{q_i, p_i\}$, we find a closed evolution for x & p:

$$\Leftrightarrow M\dot{x} = p \quad \& \quad \dot{p} = -V'(x) - \int_0^t ds \, \frac{p(s)}{M} K(t-s) + \xi(t) \quad (*)$$

where $K(u) = \sum_{i=1}^{N} \omega_i^2 \cos(\omega_i u)$ is the friction "kernel"

and $\xi(u) = \sum_i \left[\omega_i p_i(0) \sin(\omega_i t) + \omega_i^2 (q_i(0) - x(0)) \cos(\omega_i t) \right]$ represent the fluctuating part of the force exerted by the fluid on the colloid.

In principle, $(*)$ is a deterministic equation: $p(t)$ & $x(t)$ are entirely determined by $p(0)$, $x(0)$, $\{q_i(0), p_i(0)\}$. In practice $\{q_i(0), p_i(0)\}$ are both impossible to measure and widely fluctuating from experiments to experiments $\Rightarrow$ while $K(u)$ is always the same $\xi(t)$ fluctuates widely.

2.1.2) Fluctuation and friction

The fluctuations

If we assume that, at $t=0$, the fluid is equilibrated, then we can characterize the fluctuations of $\zeta(t)$.

For concision, we write $q_i(0) \equiv q_i^0$ & $p_i(0) \equiv p_i^0$, and assume

$$P(\{q_i^0, p_i^0\}) = \frac{1}{Z} \exp\left[-\beta \sum_i \frac{(p_i^0)^2}{2} + \frac{\omega_i^2}{2}(q_i^0 - x)^2\right] = \prod_i P_p(p_i^0) \times P_q(q_i^0)$$

$\Rightarrow$ independent Gaussian random variables (RV).

* $\zeta(t)$ is thus a linear combination of Gaussian RV $\Rightarrow$ it is also a Gaussian RV.

The characteristic function of a Gaussian is a Gaussian

Let z be a GRV; $p(z) = \frac{1}{\sqrt{2\pi\sigma^2}} \exp\left[-\frac{(z-\bar{z})^2}{2\sigma^2}\right]$

$$\langle e^{i\lambda z}\rangle = \frac{1}{\sqrt{2\pi\sigma^2}} \int_{-\infty}^{+\infty} dz\, e^{i\lambda z - \frac{(z-\bar{z})^2}{2\sigma^2}} = \frac{1}{\sqrt{2\pi\sigma^2}} \sqrt{2\pi\sigma^2}\, e^{i\lambda\bar{z}}\, e^{-\frac{\lambda^2}{2}\sigma^2}$$

$$= e^{i\lambda\bar{z} - \frac{\lambda^2}{2}\sigma^2}$$

Conversely, if $\langle e^{i\lambda z}\rangle = e^{i\lambda\bar{z} - \frac{\lambda^2}{2}\sigma^2}$, the inversion theorem tells us that z is a GRV.

A linear combination of GRVs is a GRV

Let $p(g_i) = \frac{1}{\sqrt{2\pi\sigma_i^2}} e^{-\frac{1}{2}\frac{(g_i - g_i^0)^2}{\sigma_i^2}}$ and $x = \sum_i \alpha_i g_i$

$$\langle e^{i\lambda x}\rangle = \langle e^{i\lambda \sum_i \alpha_i q_i}\rangle = \prod_i \langle e^{i\alpha_i \lambda q_i}\rangle$$

$$= \prod_i e^{i\alpha_i\lambda q_i^0 - \frac{\alpha_i^2\lambda^2}{2}\sigma_i^2} = e^{i\lambda \underbrace{\sum \alpha_i q_i^0}_{\bar{x}} - \frac{\lambda^2}{2}\underbrace{\sum_i \alpha_i^2\sigma_i^2}_{\bar{\sigma}^2}}$$

$$\Rightarrow p(x) = \frac{1}{\sqrt{2\pi\bar{\sigma}^2}}\, e^{-\frac{(x-\bar{x})^2}{2\bar{\sigma}^2}}$$

Comment: a Gaussian distribution like $p(x)$ is entirely characterized by its two first cumulants $\langle x\rangle$ and $\langle x^2\rangle_c = \langle x^2\rangle - \langle x\rangle^2$.

For each value of t, $\xi(t)$ is a GRV but $\xi(t)$ and $\xi(t')$ are not independent.

$\Rightarrow$ characterized by $\langle \xi(t)\rangle$ and $\langle \xi(t)\,\xi(t')\rangle_c$.

Using that $P(q_i^0) \propto e^{-\beta\frac{\omega_i^2}{2}(x-q_i^0)^2}$ & $P(p_i^0) \propto e^{-\beta\frac{p_i^{0\,2}}{2}}$, we can now proceed

$$\langle \xi(t)\rangle = \sum_j \omega_j \sin(\omega_j t)\underbrace{\langle p_j^0\rangle}_{=0} + \omega_j^2\cos(\omega_j t)\underbrace{\langle q_j^0 - x\rangle}_{=0} = 0$$

$$\langle \xi(t)\xi(t')\rangle_c = \langle \xi(t)\xi(t')\rangle$$

$$= \left\langle \sum_j\left[\omega_j\sin(\omega_j t)p_j^0 + \omega_j^2\cos(\omega_j t)(q_j^0 - x)\right]\sum_k\left[\omega_k\sin(\omega_k t')p_k^0 + \omega_k^2\cos(\omega_k t')(q_k^0 - x)\right]\right\rangle$$

$\Rightarrow$ Three types of terms $\langle p_j^0\ p_k^0\rangle = kT\,\delta_{jk}$

$$\langle (q_j^0 - x)\ (q_k^0 - x)\rangle = \frac{kT}{\omega_j^2}\delta_{jk}$$

$$\langle p_\alpha^0\ (q_\beta^0 - x)\rangle = \langle p_\alpha^0\rangle\langle q_\beta^0 - x\rangle = 0$$

$$\langle \xi(t)\xi(t')\rangle = \sum_j \omega_j^2\, kT\sin(\omega_j t)\sin(\omega_j t') + \omega_j^2\, kT\cos(\omega_j t)\cos(\omega_j t')$$

$$= kT\sum_j \omega_j^2\cos\left[\omega_j(t-t')\right]$$

$$\boxed{\langle \xi(t)\,\xi(t')\rangle = kT\,K(t-t')}$$

This relation is called the Fluctuation Dissipation Theorem. It shows how, for the dynamics induced by an equilibrated bath, friction and fluctuation are related to each other by the temperature of the fluid.

Non-Markovian dynamics: $\dot p(t)$ depends on $p(s)$ a earlier times $s \leq t$.
The system has a memory, stored in the degrees of freedom of the fluid. Dynamics like (**) which are not entirely determined at t by the values of the degrees of freedom considered at time t are called non-Markovian.
On the contrary, (1-4) were Markovian for the full set of d.o.f $\{x, p, \{q_i, p_i\}\}$.
Eliminating $\{q_i, p_i\}$ is nice, but it comes at a price $\Rightarrow$ the memory kernel $K(u)$.

The damping

Let us denote by $g(\omega)d\omega$ the number of oscillators with $\omega_i \in [\omega, \omega+d\omega]$.

$$K(u) = \sum_j \omega_j^2 \cos(\omega_j u) \simeq \int_0^\infty g(\omega)\,\omega^2 \cos(\omega u)\,d\omega$$

$g(\omega)$ is a property of the "fluid", which determines its memory kernel $K(u)$.

Let us choose $g(\omega) = \frac{2\gamma}{\pi\omega^2}$

then $K(t) = \frac{2\gamma}{\pi}\int_0^{\infty} \cos\omega t \, d\omega = \frac{\gamma}{\pi}\int_0^{\infty} d\omega \left(e^{i\omega t} + e^{-i\omega t}\right) = \frac{\gamma}{\pi}\int_{-\infty}^{+\infty} e^{i\omega t} d\omega$

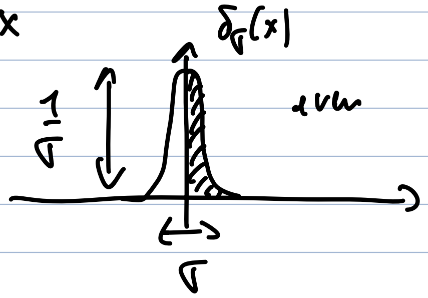
Since $\hat{\delta}(\omega) = \int_{-\infty}^{+\infty} \delta(t) e^{-i\omega t} dt = 1$; then $\delta(t) = \frac{1}{2\pi}\int_{-\infty}^{+\infty} d\omega \, e^{i\omega t}\hat{\delta}(\omega)$

$= \frac{1}{2\pi}\int_{-\infty}^{+\infty} d\omega \, e^{i\omega t}$

$\Rightarrow \boxed{K(t) = 2\gamma\,\delta(t)}$

Damping $\quad -\int_0^t \frac{p(s)}{M} 2\gamma\,\delta(t-s) = ?$

$\int_{-x}^{x} ds\, f(s)\,\delta(s) = f(0)$ $\qquad$ Then $\int_0^{x} ds\, f(s)\,\delta(s) = ?$



$\delta(x) = \lim_{\sigma\to 0} \delta_\sigma(x)$

$\int_0^{x} ds\, f(s)\,\delta(s) = \frac{1}{2}\int_{-x}^{x} ds\, f(s)\,\delta(s) = \frac{f(0)}{2}$

$\Rightarrow -\int_0^t \frac{p(s)}{M} 2\gamma\,\delta(t-s) = -\frac{\gamma}{M} p(t)$

The full dynamics then read

$$\boxed{\dot{q} = p \quad ; \quad \dot{p} = -\frac{\gamma}{M} p - V'(x) + \xi(t)} \qquad (***)$$

where $\xi(t)$ is then a Gaussian white noise:

$$\boxed{\begin{aligned} &\langle \xi(t) \rangle = 0 \\ &\langle \xi(t)\,\xi(t') \rangle = 2\gamma k T\,\delta(t-t') \end{aligned}}$$

$k(t-t') = \delta(t-t') \Rightarrow$ white noise $(\hat{k}(\omega) = 1)$

$k(t-t') \neq \delta(t-t') \Rightarrow$ colored noise

(***) is the celebrated Langevin equation (1908)

Comment: $k(t)$ is a property of the fluid. Some fluid have memory, and are called "visco elastic", others do not and are typically called Newtonian fluid.

Comment:

Note that $\xi(t)$ with $\langle \xi \rangle = 0$ & $\langle \xi(t)\, \xi(t') \rangle = 2\gamma k T \delta(t-t')$

and $\sqrt{2\gamma k T}\, \eta(t)$ with $\langle \eta \rangle = 0$ & $\langle \eta(t) \eta(t') \rangle = \delta(t-t')$

are two GRV with the same average and covariance $\Rightarrow$ these processes are identical. One thus often write the Langevin equation as $\dot{q} = p$; $\dot{p} = -\gamma p - V'(x) + \sqrt{2\gamma k T}\, \eta$.

We will often silently switch from one notation to the other.

2.1.4) The large damping limit

Naively, one would think that a large damping coefficient γ implies a large dissipation and thus no motion.

The life of a Brownian particle is very different.

Large friction γ $\Rightarrow$ slow system $\Rightarrow$ evolves on large time scale

consider $t = \gamma \tau$ with $\tau \sim O(1)$

$$\underset{\text{large}}{\Downarrow} \quad \begin{cases} \to O(1) \\ \to \text{large} \end{cases}$$

dynamics

$$m \frac{d^2x}{dt^2} = \frac{m}{\gamma^2} \frac{d^2x}{d\tau^2} = -\frac{\gamma}{\gamma} \frac{dx}{d\tau} - V'(x) + \sqrt{2\gamma kT}\, \underbrace{\eta(\gamma\tau)}_{=?} \qquad (\Delta)$$

Note that $\langle \eta(t)\eta(t')\rangle = \delta(t-t') = \delta(\gamma(\tau-\tau')) = \frac{1}{\gamma}\delta(\tau-\tau')$

$$= \frac{1}{\gamma} \langle \tilde{\eta}(\tau) \underbrace{\tilde{\eta}(\tau')}_{\to \text{ unitary GWN}} \rangle$$

$\Rightarrow \eta(t=\gamma\tau) = \frac{1}{\sqrt{\gamma}} \tilde{\eta}(\tau)$

$$(\Delta) \Leftrightarrow \underbrace{\frac{m}{\gamma^2} \frac{d^2x}{d\tau^2}}_{\xrightarrow[\gamma\to\infty]{} 0} = -\frac{dx}{d\tau} - V'(x) + \sqrt{2kT}\, \tilde{\eta}(\tau)$$

overdamped Langevin equation

$$\boxed{\frac{dx}{d\tau} = -V'(x) + \sqrt{2kT}\, \tilde{\eta}(\tau)} \qquad (\Delta\Delta)$$

Speed = Sum of forces

Aristotelian physics ;-)

Thanks to the fluctuation dissipation relation, damping & noise scale the same way and both survive in the $\gamma \to \infty$ limit.

$\Rightarrow$ motion survives on time scale $t \sim \gamma$.

$\Rightarrow$ inertia is irrelevant (speed = Σ forces)

($\Delta\Delta$) is the love of theoretician (up to setting $k=1$) but it has weird units.

$$[\gamma] = \frac{M}{T} \Rightarrow \tau = \frac{t}{\gamma} \quad \text{measured in } s^2 \cdot kg^{-1} \dots$$

To compare with experiments, restore the real units:

$$\frac{dx}{dt} = -\frac{1}{\gamma} V'(x) + \sqrt{2 \frac{kT}{\gamma}}\, \eta(t)$$

Mobility: Apply a constant force $-V'(x) = F_0$

Then the average speed is $\langle v \rangle = \left\langle \frac{dx}{dt} \right\rangle = \frac{1}{\gamma} F_0$

The mobility μ is defined as $\mu = \frac{\langle v \rangle}{F_0} = \frac{1}{\gamma}$

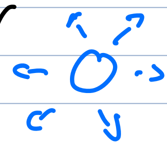
It measures the response of the particle to an external drive.

The overdamped Langevin equation then reads

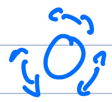
$$\boxed{\dot{x} = -\mu V'(x) + \sqrt{2\mu k T}\, \eta(t)}$$

Comment: μ is a property of the fluid that can be computed independently.

For water, one can use Stokes equation to show that,



for a sphere of radius R, $\gamma = 6\pi R \underbrace{\eta}_{\text{dynamic viscosity of water}}$

Rotational diffusion  $\gamma_R = 8\pi R^3 \eta$

As $R \to 0$ $\gamma_R \ll \gamma$ & it's easier to rotate than to move.

Summary:

Large object connected to many equilibrated fluid molecules

$\Downarrow$ "coarse-graining"
eliminate degrees of freedom

Dynamical equation for the object that is stochastic, depends on a small number of parameters ($kT, \gamma, \dots$) that can be measured independently.

The Langevin equation is the $PV = NkT$ of non-equilibrium statistical mechanics $\Rightarrow$ let's learn how to use it.