III) The Langevin equation : physical aspects

Goal : embark into the study of stochastic processes, ie with notion of time, on the example of Brownian motion. Discuss φ meaning of Langevin eq, fluctuation ⇔ dissipation. Framework includes large gamut applications in φ, χ, biology, engineering, finance ...

1°) Colloids and Brownian motion

The discovery of the erratic and never ending motion of small objects, such as pollen grains of ~ 1 μm, in water, is credited to **Robert Brown**, a botanist (1827).
Yet, a similar observation had been made by **Jan Ingenhausz** (1785), who described the irregular motion of coal dust on the surface of alcohol.
Brown noted that same phenomenon happens with small minerals → important observation, rules out "vitalism" (a "vital" force that would be specific to living bodies).
All objects (passive) of the same size feature similar motion. Objects have to be big enough to be visible under Brown's microscope, but not too big, to be moved by thermal agitation. Take a sphere of radius σ : constraint

$$(\rho g \sigma^3)\,\sigma < kT \qquad \text{where } g \text{ is gravity and } \rho \text{ mass density}$$

Assuming $\rho \simeq 10^3\ \mathrm{kg\,m^{-3}}$: $\sigma < \left(\frac{kT}{\rho g}\right)^{1/4} \rightarrow \left(\frac{10^{-20}}{10^3 \cdot 10}\right)^{1/4} = 10^{-6}\ \mathrm{m}$

→ defines the colloidal range : 10^{-9} or $10^{-8}\ \mathrm{m} < \sigma < 10^{-6}\ \mathrm{m}$

Colloids are the typical objects studied in soft matter

At time of Brown : molecules/atoms had not been proven to exist.
The idea that the erratic motion of colloids was due to collisions with the suspending fluid (water) gained ground in XIX th century

1888 : Georges Gouy made the best observations on Brownian motion

- motion very irregular, trajectory does not seem to have a tangent
- the smaller the "particles", the lively their motion
- motion most active in less viscous fluids
- " at high temperature
- " never stops

1905 (Einstein's annus mirabilis) comes the first clear explanation, quantitative, by Einstein). He also wrote 2 famous papers that same year: special relativity ; thermoelectric effect (→ Nobel prize, 1921). The paper on Brownian motion had, arguably, the most impact.

1926 : Jean Perrin gets Nobel prize for exp on sedimentation equilibrium that confirm Einstein's predictions ⇒ definitely proves the existence of molecules.

Yet 1900 : Louis Bachelier's doctoral thesis "Théorie de la spéculation", that contains the fundamental laws of Brownian motion. The pioneering nature of this work took decades to be recognized (by Kolmogorov, who told Lévy, who had blackballed Bachelier for a position in Dijon, in 1926!)
Bachelier, applying mathematics to finance, was not considered a true mathematician.

2) The Langevin approach

In early approaches (Einstein, Schmoluchowski), the inertia of colloids was not accounted for (overdamped description). Paul Langevin proposed a more complete treatment.
For simplicity, we treat pb in 1D, and denote $x(t)$ the position for center of mass

$$v = \frac{dx}{dt} \quad ; \quad m\frac{dv}{dt} = F_{ext} + \mathcal{F} \quad ;$$ a single colloid considered

$\mathcal{F}$ due to interactions with suspending fluid, hopelessly complicated, but

- the fluid is at equilibrium at temp T, which should thermalize the colloid at long times
- $\mathcal{F}$ fluctuates on a time scale $\tau_c \sim$ collision time, succession of molecular impacts ; τ_c very small, say 10^{-15} s
- Averaged over a time window $\gg \tau_c$, but $\ll$ time for motion (see below), $\mathcal{F}$ is expected to yield Stoke's law, eg $-6\pi\eta\sigma v$ for a sphere of radius σ in a solvent of viscosity η (dynamic viscosity)

Given the last 2 remarks, Langevin proposes a simplification of Newton's equations, phenomenological, a "stochastization" in the form:

$$m\frac{dv}{dt} = -\gamma m v + F_{ext} + R(t)$$

where γ (or $m\gamma$) is a friction coefficient and $R(t)$ a random force, independent from v
↳ Langevin force

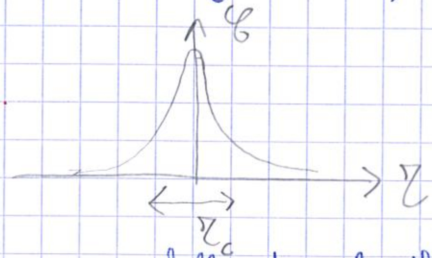
Because we cannot characterize exactly the state of the system, we resort to a **statistical description**, based on ensemble averages : we average over **different histories** of the colloid's motion, for given initial conditions, but each time in a different environment (hence with a ≠t realization of the Langevin force). Properties

→ $\boxed{\langle R(t) \rangle = 0}$, collisions at random over all directions. With $F_{ext} = 0$, this condition is needed for having $\langle v \rangle \xrightarrow{t\to\infty} 0$. Indeed

$$\left\langle \frac{dv}{dt} \right\rangle = \frac{d\langle v\rangle}{dt} = -\gamma\langle v\rangle + \langle R\rangle \; ; \quad \langle v\rangle \to 0 \Rightarrow \langle R\rangle = 0$$

→ The fluid is at equilibrium : one time averages do not depend on t, and $\langle R(t)\, R(t')\rangle$ only depends on $t - t'$

→ The correlation function $\boxed{\mathcal{C}(\tau) = \langle R(t)\, R(t+\tau)\rangle}$ quickly decays with $|\tau|$, on a scale $\sim \tau_c$. Besides, stationnarity $\Rightarrow \mathcal{C}(\tau) = \mathcal{C}(-\tau)$.



Also, $\langle A(t)\, B(t+\tau)\rangle$ defines a scalar product

$$\Rightarrow |\mathcal{C}(\tau)| \leqslant \sqrt{\langle R^2(t)\rangle \langle R^2(t+\tau)\rangle} = \mathcal{C}(0)$$

→ Because we shall not resolve the time scale τ_c, we take $\mathcal{C}(\tau) \propto \delta(\tau)$ where the coef of proportionnality stems from $\boxed{\int_{-\infty}^{+\infty} \langle R(t) R(t+\tau)\rangle d\tau \equiv 2\Gamma m^2}$ (definition of noise amplitude Γ).

Finally, the Langevin eq° reads :

$$m\,\dot{v} = -\gamma m\, v(t) + F_{ext}(x,t) + R(t) \; ; \quad \langle R(t) R(t+\tau)\rangle = 2\Gamma m^2 \delta(\tau)$$

The order of magnitude of $\mathcal{C}(0)$ is $\Gamma m^2/\tau_c$; keep in mind that τ_c is never strictly 0.

3°) Diffusion, relaxation, ~~and~~ response (and statistics)

a) Evolution of velocity

Force-free case : $F_{ext} = 0$. The equa° is linear, can be integrated by "variation of constant"

$$v(t) = A(t)\, e^{-\gamma t} \; ; \quad m\,\dot{A}\, e^{-\gamma t} = R(t)$$

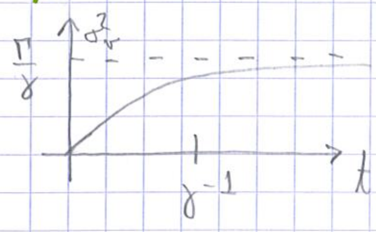
At $t = 0$, $v = v_0$ (initial condition) $\Rightarrow A(t) = v_0 + \int_0^t e^{+\gamma t'} R(t')/m \; dt'$

$$v(t) = v_0\, e^{-\gamma t} + \frac{1}{m}\int_0^t e^{-\gamma(t-t')} R(t')\, dt'$$

$$\Rightarrow \langle v(t)\rangle = v_0\, e^{-\gamma t} \qquad \text{characteristic time } \gamma^{-1}.$$

For the variance $\sigma_v^2 = \langle v^2\rangle - \langle v\rangle^2 = \left\langle \left(v - v_0 e^{-\gamma t}\right)^2 \right\rangle$

$$\sigma_v^2 = \frac{1}{m^2}\int_0^t dt' \int_0^t dt'' \, e^{-\gamma(t-t')} e^{-\gamma(t-t'')} \langle R(t')R(t'')\rangle$$
$$= 2\Gamma \int_0^t dt' \, e^{-2\gamma(t-t')}$$
$$\boxed{\sigma_v^2 = \frac{\Gamma}{\gamma}\left(1 - e^{-2\gamma t}\right)}$$



- $t=0$: $\sigma_v^2 = 0$ since $v = v_0$ is certain. For $t>0$, fluctuations appear under influence of $R(t)$
- $t \ll \gamma^{-1}$: $\sigma_v^2 \sim 2\Gamma t$. Diffusion in velocity space, with coef of diff Γ. On those time scales, friction is inoperant and we have $m\dot{v} \simeq R(t) \to$ continuous version of random walk seen in previous chapter (with identification $v \Rightarrow x$, position of the walker).
- $t \gg \gamma^{-1}$: friction acts; the r.w analogy would be with a walker feeling a force $-\gamma x$, ie attached with a spring to the origin (a walker with braces/suspenders). Hence, its m.s.d saturates; here $\sigma_v^2 \to \Gamma/\gamma$, a constant.

Besides, the colloid should thermalize at long times, hence we expect
$m\langle v^2\rangle = kT$ for $t \to \infty$. Since $\langle v\rangle \to 0$, we get

$\frac{m}{kT} = \frac{\gamma}{\Gamma}$ $\quad \Gamma = \frac{\gamma kT}{m}$; $\langle R(t)R(t+\tau)\rangle = 2\gamma m kT\,\delta(\tau)$

↳ Fluctuations ↳ Dissipation

This is a fluctuation-dissipation relation. It stems from fact that collisions with the solvent are responsible for both fluctuations, and dissipation, that thus have a common origin.

3c) b) Evolution of the position

For $t=0$, we take $x = x_0$, $v = v_0$ (fixed).

$$x(t) = x_0 + v_0\frac{1}{\gamma}\left(1-e^{-\gamma t}\right) + \frac{1}{m}\int_0^t dt' \int_0^{t'} dt'' \, R(t'')\, e^{-\gamma(t'-t'')} \qquad (*)$$

$$\Rightarrow \langle x(t)\rangle = x_0 + v_0\frac{1}{\gamma}\left(1-e^{-\gamma t}\right)$$, varies from x_0 to $x_0 + v_0/\gamma$

Formula can also be used to compute $\sigma_x^2 = \langle x^2(t)\rangle - \langle x(t)\rangle^2$

A trick is to calculate $\frac{d}{dt}\sigma_x^2 = 2\left\langle (x(t)-\langle x\rangle)(v(t)-\langle v\rangle)\right\rangle$.

Another trick is to simplify $(*)$ by Integration by Parts.

$$\varphi(t) \equiv \int_0^t dt_1 \, R(t_1)\, e^{\gamma t_1}$$

$$x - \langle x\rangle = \frac{1}{m}\int_0^t dt' \, e^{-\gamma t'}\varphi(t') = \frac{1}{m}\left[-\frac{e^{-\gamma t'}}{\gamma}\varphi(t')\right]_0^t + \frac{1}{m}\int_0^t \frac{e^{-\gamma t'}}{\gamma}\varphi'(t')$$

$$x(t)-\langle x(t)\rangle = \frac{1}{m\gamma} e^{-\gamma t}\int_0^t dt' R(t') e^{\gamma t'} + \frac{1}{m}\int_0^t \frac{e^{-\gamma t'}}{\gamma} R(t') e^{\gamma t'}$$

$$x(t)-\langle x(t)\rangle = \frac{1}{m\gamma}\int_0^t \left[1-e^{-\gamma(t-t')}\right] R(t')\,dt'$$

Then, $\langle (x-\langle x\rangle)^2\rangle = \frac{1}{m^2\gamma^2}\int_0^t dt'\int_0^t dt''\left[1-e^{-\gamma(t-t')}\right]\left[1-e^{-\gamma(t-t'')}\right]\langle R(t')R(t'')\rangle$

$$= \frac{1}{m^2\gamma^2}\, 2m^2\Gamma \int_0^t dt' \underbrace{\left[1-\exp(-\gamma(t-t'))\right]^2}_{1-2e^{-\gamma(t-t')}+e^{-2\gamma(t-t')}}$$

$$\langle (x-\langle x\rangle)^2\rangle = 2\frac{\Gamma}{\gamma^2}\left[t-\frac{2}{\gamma}(1-e^{-\gamma t})+\frac{1}{2\gamma}\left(1-e^{-2\gamma t}\right)\right] \equiv \sigma_x^2$$

$t \ll \gamma^{-1}$: $\sigma_x^2 \propto t^3$, means $\langle x^2\rangle \sim \langle x\rangle^2 \sim t^2$.

Ballistic regime at short times; friction did not yet act

$t \gg \gamma^{-1}$ $\sigma_x^2 \sim 2\Gamma t/\gamma^2$ and $\langle x\rangle \to cst$

$\Rightarrow \langle x^2\rangle \sim 2Dt$ with $D = \Gamma/\gamma^2 = \frac{kT}{m\gamma}$; Stokes-Einstein

Phenomenon of normal diffusion.

3°) c) The overdamped regime (limit of large friction).

For colloids of μm size, the time scale for motion (change in x) is much larger than γ^{-1}, the time scale for velocity relaxation. We are in a limit "of large friction", which can equivalently be viewed as a limit of $m\to 0$, or $t\to\infty$. Then, the inertial term drops out in Langevin equation, that becomes

$$m\dot{v} = -\gamma m v + R(t) + F_{ext} \quad ; \quad v(t) \simeq \frac{1}{m\gamma}\left[R(t)+F_{ext}\right]$$

$$\Rightarrow \frac{dx}{dt} = \frac{1}{m\gamma}\left[F_{ext}(x(t)) + R(t)\right]$$

Indeed, go back to Stokes' law: $\frac{1}{\gamma} = \frac{m}{6\pi\eta\sigma}$; for given η and σ, take $m\to 0$, then $\gamma\to\infty$, and time scale $\frac{1}{\gamma}\to 0$. Same thing increasing viscosity: $\eta\to\infty$

Besides, we shall see below that velocity fluctuations relax on a time scale γ^{-1}. Then, for $\gamma^{-1}\to 0$, we stop resolving that time scale and thus $\langle v(t)v(0)\rangle \propto \delta(t) \propto \langle R(t)R(0)\rangle$

this is compatible with $v(t)\propto R(t)$ (take $F_{ext}=0$).

A final equivalent way of seeing that at long time, inertia does not matter, is to take Fourier Transform: $\underbrace{i\omega m\,\hat{v}(\omega)}_{\omega\to 0\ \to\ 0} = -m\gamma\hat{v}(\omega) + \hat{R}(\omega)$ $(F_{ext}=0)$

The overdamped eq is what Einstein and Schmoluchowski considered

$$\dot{x} = \frac{1}{m\gamma} R(t)$$ → defines the Wiener process $x(t)$

Readily integrated : $x(t) = x_0 + \int_0^t R(t')\,dt'/m$; take $x_0 = 0$.

$$\Rightarrow \langle x^2 \rangle = \frac{1}{m^2\gamma^2} \int_0^t dt' \int_0^t dt'' \langle R(t')R(t'') \rangle = \frac{2\Gamma}{\gamma^2} t = 2Dt$$

We recover diffusion, without the early ballistic regime (occuring on a short time scale γ^{-1}), not resolved here.

<u>Rk 1</u> Compute correlata $\langle x(t) x(t') \rangle = 2D \min(t, t')$

<u>Rk 2</u> The overdamped equad in a harmonic potential reads : $m\gamma\dot{x} = -m\omega_0^2 x + R(t)$ which is formally the same as our (underdamped, ie with inertia included) original Langevin eq : $m\dot{v} = -\gamma m v + R(t)$.

<u>Rk 3</u> The overdamped regime hides subtelties with equal time correlations such as

$$\langle x(t) R(t) \rangle = \frac{1}{m\gamma} \int_0^t \langle R(t) R(t') \rangle dt'$$, ill defined with the $\delta(t-t')$

We can come back to τ_c small but finite, to find $\langle x(t) R(t) \rangle \simeq \frac{1}{m\gamma} m^2\Gamma = m\Gamma/\gamma$

When inertia is accounted for, problem disappears : the position cannot follow instantaneously the force. From the $x(t)$ above :

$$\langle x(t) R(t) \rangle = \frac{1}{m\gamma} \int_0^t \underbrace{[1 - e^{-\gamma(t-t')}]}_{\gamma|t-t'|} \langle R(t')R(t) \rangle dt' \quad , \quad |t-t'| \text{ of } \mathcal{O}(\tau_c)$$

$$\simeq \frac{1}{m\gamma} \int_0^t \gamma|t-t'|\, \mathcal{C}(t-t')$$

$$\sim \frac{1}{m\gamma} \gamma \tau_c \Gamma m^2$$

$$\sim m\Gamma\tau_c \ll m\Gamma/\gamma$$

3°) d) <u>Mobility and Einstein relation</u>

In overdamped regime : $v = \frac{1}{m\gamma}[F_{ext} + R]$; $\mu = \frac{1}{m\gamma}$ is the <u>mobility</u>

Given Stokes-Einstein relation

$$D = \frac{kT}{m\gamma}$$, we have $\boxed{D = \mu kT}$ (another) Einstein relation

This another aspect of deep connection between fluctuations and dissipation

<u>Historic note</u> : Einstein used another reasoning. Considering colloids in an external potential U_{ext}) at equilibrium in a solvent, at temp. T. Let $n(\vec{r})$ denote the colloid density (assumed small, so that colloids do not interact ⇒ ideal gas view).

At equilibrium, the diffusive current (Fick's law) should balance the drift current due to the external force applied :

$$\vec{j} = \vec{0} = -D\vec{\nabla} n + \mu \vec{F}_{ext}\, n \Rightarrow -D\vec{\nabla}\log n - \mu\vec{\nabla}U_{ext} = \vec{0}$$

$$\Rightarrow n(\vec{r}) = n_0 \exp\left[-\frac{\mu}{D} U_{ext}(\vec{r})\right]$$

This should coincide with Boltzmann weigt $\exp\left[-\frac{1}{kT}U_{ext}\right] \Rightarrow \frac{\mu}{D} = \frac{1}{kT}$

Note that the flux balance can be written

$$-\frac{1}{n}\vec{\nabla}(nkT) + \vec{F}_{ext} = \vec{0}$$

; hydrostatic balance, pressure $= nkT$ (osmotic pressure)

3°) e) Velocity statistics

We did not make any assumption on the statistics of $R(t)$ (which pdf ?)

For $\tau_c \ll \gamma^{-1}$, this is not necessary to find the v-statistics (and also the x-statistics).

For $t \gg \tau_c$, we slice the time interval into bins Δt : $\tau_c \ll \Delta t \ll \gamma^{-1}$

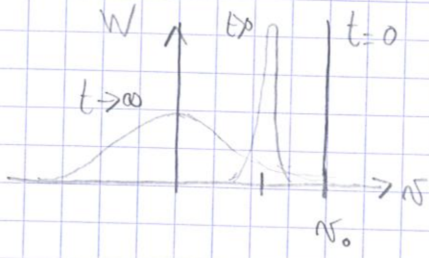
$$v(t) = v_0 e^{-\gamma t} + \frac{1}{m}\int_0^t R(t')\, e^{-\gamma(t-t')}\, dt'$$

$$= v_0 e^{-\gamma t} + m^{-1} e^{-\gamma t} \sum_{j=0}^{N} e^{j\Delta t\gamma} \underbrace{\int_{j\Delta t}^{(j+1)\Delta t} R(t')\, dt'}_{\equiv \mathcal{B}(\Delta t)}$$

this is the sum of a large number of random variables

↳ Central limit theorem $\Rightarrow v(t)$ is gaussian. We know $\langle v(t)\rangle$ and σ_v^2, so we know the velocity pdf.

$$W(v,t) = \frac{\sqrt{m}}{\sqrt{2\pi kT(1-e^{-2\gamma t})}} \exp\left[-\frac{m(v - v_0 e^{-\gamma t})^2}{2kT(1-e^{-2\gamma t})}\right] \equiv W(v,t|v_0)$$



Same reasoning possible for $W(x,t|x_0,v_0)$ also gaussian.

4°) Dynamics of velocity fluctuations at equilibrium

From Langevin :

$$\frac{d}{dt}\langle v(t)v(t')\rangle = -\gamma\langle v(t)v(t')\rangle + \frac{1}{m}\overbrace{\langle R(t)v(t')\rangle}^{0 \text{ for } t>t'}$$

$$= -\gamma\langle v(t)v(t')\rangle \quad \text{for } t>t'$$

$$\Rightarrow \langle v(t)v(t')\rangle = A(t')\, e^{-\gamma t} \quad \text{for } t>t'$$

From this, knowing $\langle v^2(t)\rangle$ is sufficient to infer $A(t)$ and thus $\langle v(t)v(t')\rangle$. The calculation has to be completed, symmetrizing $t \leftrightarrow t'$, to have expression valid for both $t \le t'$ and $t \ge t'$. This calculation works for a fixed v_0 at $t=0$, or also when averaging over v_0, with Maxwellian distribution, as necessary at equilibrium. Here, we restrict to equilibrium, thus time translationally invariant, for which $\langle v(t)\, v(t')\rangle \equiv \mathcal{C}_v(t-t') = \mathcal{C}_v(t'-t)$. (parity)

At equilibrium: $\langle v^2\rangle = kT/m$ (equipartition)

$$\Rightarrow A(t) = \frac{kT}{m} e^{\gamma t}$$

$$\Rightarrow \langle v(t)\, v(t')\rangle = \frac{kT}{m} e^{-\gamma(t-t')} \quad \text{for } t > t'$$

From parity: $$\langle v(t)\, v(t')\rangle = \frac{kT}{m} e^{-\gamma|t-t'|}$$

NB There are here 2 layers of averaging; let us denote them differently.

$\langle\ \rangle$ is for a given initial condition (v_0), averaging over possible trajectories

$\langle\langle\ \rangle\rangle$ has, in addition, an average over v_0 with weight $\sqrt{\frac{m}{2\pi kT}}\, e^{-mv_0^2/2kT}$.

We found
$$\begin{cases} \frac{d}{dt}\langle\langle v(t)\, v(t')\rangle\rangle = -\gamma \langle\langle v(t)\, v(t')\rangle\rangle, & t > t' \\ \frac{d}{dt}\langle v(t)\rangle = -\gamma\langle v(t)\rangle \end{cases}$$

Same differential equation : same solution. This connection is deep, it has first been formulated by Lars Onsager, as the regression hypothesis

It asserts that a spontaneous fluctuation at equilibrium, and a non equilibrium perturbation, follow same law (same time dependence). This is another fluctuation-dissipation relation. Useful in practice to relate a friction computed at equilibrium, to a non equilibrium situation. This is why all transport coef. (viscosity, thermal conductivity etc) can be expressed from equilibrium fluctuations alone.

Obtaining new fluctuation-dissipation relations

$$\int_{-\infty}^{+\infty} \langle v(0)\, v(t)\rangle\, dt = \frac{2kT}{\gamma m} = 2D \; ; \qquad D = \int_0^{\infty} \langle v(0)\, v(t)\rangle\, dt$$

This is a Green-Kubo relation ; first derived by Geoffrey Taylor (1921) in the context of turbulence. It is very general, as can be seen below:

$$\frac{d}{dt}\langle (x(t)-x_0)^2\rangle = 2\langle (x(t)-x_0)\, v(t)\rangle = 2\int_0^t \langle v(t')\, v(t)\rangle\, dt'$$
$$= 2\int_0^t \langle v(0)\, v(\tau)\rangle\, d\tau \qquad \tau = t - t'$$

If the limit $t \to \infty$ of this integral exists, it yields D

5°) Conclusion

a) Back to the separation of time scales

We have singled out 2 time scales, τ_c (correlation time of the Langevin force, the "noise") and γ^{-1}, for the velocity relaxation. Langevin model requires $\gamma^{-1} \gg \tau_c$.

Assuming $\tau_c \simeq 10^{-15}$ s, and Stokes friction $m\gamma = 6\pi\eta\sigma$:

$$\gamma^{-1} \propto \frac{\rho\sigma^3}{6\pi\eta\sigma} \simeq \frac{\rho\sigma^2}{10\eta} \gg \tau_c \Rightarrow \sigma \gg \left(\frac{10\eta\tau_c}{\rho}\right)^{1/2}$$

Putting numbers: $\sigma \gg \left(\frac{10 \cdot 10^{-3}\, 10^{-15}}{10^3}\right)^{1/2} = 10^{-10}$ m ; this is fully verified in the colloidal regime. For $\sigma = 1\ \mu m$, we get

$$\gamma^{-1} \simeq \frac{10^3\ 10^{-12}}{10 \cdot 10^{-3}} = 10^{-7}\ s \gg \tau_c$$

For these colloids, let us estimate D

$$D = \frac{kT}{m\gamma} \sim \frac{kT}{10\eta\sigma} \sim \frac{10^{-20}}{10 \cdot 10^{-3}\, 10^{-6}} \sim 10^{-12}\ m^2/s$$

From D and σ, we form the third important time scale in the problem: the charact time for displacement, i.e. the time needed for diffusing over a length $\sigma \Rightarrow t^*$

$$D t^* \equiv \sigma^2$$

For $\sigma = 10^{-6}$ m, $D = 10^{-12}\ m^2/s$: $1s \simeq$ $t^* \gg \gamma^{-1} \gg \tau_c$

The overdamped regime corresponds to $t^* \gg \gamma^{-1}$. For σ, this means

$$\sigma^2/D \gg \frac{\rho\sigma^2}{10\eta} \Leftrightarrow \sigma^2\frac{10\eta\sigma}{kT} \gg \frac{\rho\sigma^2}{10\eta} \quad \text{ie} \quad \sigma \gg \sqrt{\frac{\rho\, kT}{(10\eta)^2}}$$

10^{-13} m

The colloidal range ($10^{-9} < \sigma < 10^{-6}$ m) is strongly overdamped.

Note that Stokes-Einstein relation for D also provides a reasonable estimation for molecules of size $\sim 10^{-9}$ m. Indeed, $D \propto 1/\sigma \Rightarrow 10^{-9}\ m^2/s$, not bad ↳ in water. For comparison, with a N_2 gas at room T and P: $D \simeq 10^{-5}\ m^2/s$

b) Generality of the approach

In higher dimensions: we can work component by component from

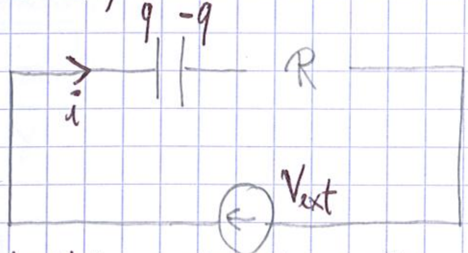
$$m\dot{\vec{v}} = -\gamma m\vec{v} + \vec{F}_{ext} + \vec{R}(t)$$

One often takes $\langle R_\alpha(t) R_\beta(t')\rangle = 2m^2\Gamma\,\delta(t-t')\,\delta_{\alpha\beta}$ → Cartesian coordinates

In d-dimensions $\langle \vec{x}^2(t)\rangle \sim 2dDt$, large t

$$D = \int_0^\infty \langle v_x(0)\, v_x(t')\rangle dt' = \frac{1}{d}\int_0^\infty \langle \vec{v}(0)\,\vec{v}(t')\rangle dt'$$

Framework goes well beyond soft matter: relevant when "noise" is important.
Take R-C circuit (do not confuse the resistance $\mathcal{R}$ with Langevin force, here denoted $U(t)$):



Macroscopic equation: $V_{ext} = \frac{\langle q \rangle}{C} + \mathcal{R}\langle \dot{q} \rangle$

But dissipation $\Rightarrow$ fluctuation of microscopic $\dot{q}$'s

$\Rightarrow \mathcal{R}\dot{q} = -\frac{q}{C} + V_{ext} + U(t)$

$\langle U(t) \rangle = 0$

$\langle U(t) U(t+\tau) \rangle = 2\Gamma \delta(\tau)$

So, there should be a fluctuating voltage across $\mathcal{R}$. We can here also find its amplitude Γ: we could use $q(t) = q_0 e^{-t/RC} + \int_0^t \frac{1}{R} U(t') e^{-(t-t')/RC} dt'$ and invoke equilibrium relation $\left\langle \frac{q^2}{2C} \right\rangle = \frac{1}{2} kT$.

For computing $\langle q^2 \rangle$, we can proceed as above for $\langle v^2 \rangle$ with $t \to \infty$.

$\Rightarrow \langle q^2 \rangle = C\,\Gamma/R$ (exercise) $= C\,kT$ from equipartition

$\Rightarrow \Gamma = \mathcal{R}\,kT$, does not depend on C!

$\Rightarrow \mathcal{R} = \frac{1}{2kT}\int_0^\infty \langle U(t) U(t+\tau) \rangle d\tau$: Nyquist theorem

T is a priori the temperature of the whole circuit at equilibrium, but it is in fact the temp of the resistance that matters. Note that we can recover $\Gamma = \mathcal{R}kT$ from dimensional argument: $\Gamma/\mathcal{R}^2$ plays the role of a diffusion coeff in q-space

$\Rightarrow \left[\frac{\Gamma}{\mathcal{R}^2}\right] = \frac{[q]^2}{\text{time scale}} = \frac{1}{RC} \times [q^2] = \frac{1}{RC} C\,kT$ (equipartition)

$\Rightarrow \Gamma \propto \mathcal{R}\,kT$

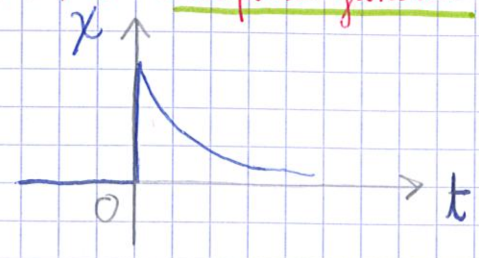
5°) c) The generalized Langevin approach

We have been inconsistent in our discussion of the case $\tau_c \neq 0$, since we focussed only on the consequences for fluctuations of $R(t)$. But fluctuation and dissipation are linked. The friction force is affected when $\tau_c \neq 0$. Indeed, sending initial condition to $-\infty$

$$v(t) = \int_{-\infty}^{t} \frac{1}{m} e^{-\gamma(t-t')} \left[R(t') + F_{ext}(t')\right] dt' \qquad \text{take } F_{ext} = 0$$

$$= \int_{-\infty}^{+\infty} \chi(t-t')\, R(t')\, dt'$$

$\chi(t)$ is the response function, here: $\chi(t) = \theta(t)\, e^{-\gamma t}/m$



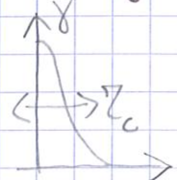
Linear filter with instantaneous response $\Rightarrow$ impossible

Friction, resulting from collisions cannot establish instantaneously. Should take at least a few τ_c

Hence, writing the friction force as $-m\gamma v$ is incorrect on short time scales, on order of τ_c (while fine if temporal resolution $\gg \tau_c$). It would be more reasonable to consider the generalized Langevin equation

$$m\frac{dv}{dt} = -m\int_{-\infty}^{t} \tilde{\gamma}(t-t')\,v(t')\,dt' + F_{ext}(x,t) + R(t)$$

where $\gamma = \int_0^\infty \tilde{\gamma}(\tau)\,d\tau$ and $\tilde{\gamma}(\tau) \propto \delta(\tau)$ only for $\tau_c \to 0$ (meaning: when we decide not to resolve the time scale τ_c, for instance if our apparatus of measure do not allow it). For the memory kernel $\tilde{\gamma}$ we expect



while $\gamma = \frac{1}{mkT}\int_0^\infty \langle R(t)R(t+\tau)\rangle d\tau$ remains true

we will show that here:

$$\tilde{\gamma}(\tau) = \frac{1}{mkT}\langle R(t)R(t+\tau)\rangle, \quad \tau \geq 0$$

this is a refined fluctuation-dissipation relation.