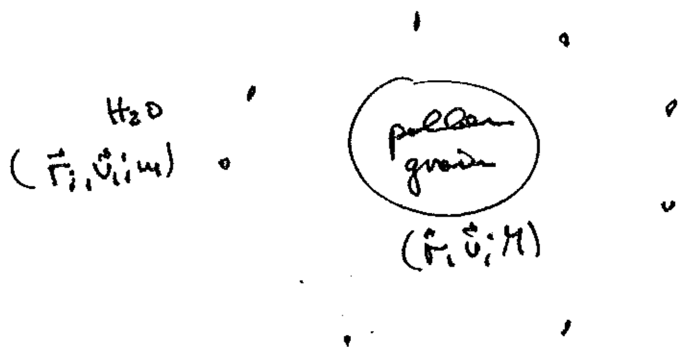
# Stochastic dynamics: Brownian Motion

**Paradigm:** Brownian Motion 1827

Einstein 1905

Perrin: Nobel prize 1926




Newtonian eq. of motion

$$M \dot{\vec{v}} = \sum_i \vec{F}_i(\{\vec{r}_i\})$$

$$m \dot{\vec{v}}_i = \sum_{j \neq i} \vec{F}_{ij} + \vec{F}_{pollen}$$

Formal solution: $\vec{r}_i(t, \{\vec{r}(t)\}; \{\vec{r}^0, \vec{v}^0\}_i)$

$\vec{v}_i(t, \{\vec{r}(t)\}; \{\vec{r}^0, \vec{v}^0\}_i)$.

→ insert into eom for pollen grain
(c.f. Schwabl 10.3)

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Different approach: determine average effect of all forces on the pollen grain

friction: $-\gamma \vec{v}$ + average effect of dissipating forces


e.o.m. $\boxed{M \dot{\vec{v}} = -\gamma \vec{v} + \vec{f}(t)}$

stochastic force

Properties of $\vec{f}$:

- $\langle f(t) \rangle = 0$
- $f$ is normally distributed (central limit thm)
- $f(t)$ and $f(t+\tau)$ are statistically indep. even for very small $\tau$

estimate $\tau \sim \frac{\text{radius pollen grain}}{\text{mean mol. velocity}}$

idealization

$$\boxed{\begin{aligned} &\langle f(t)\rangle = 0 \\ &\langle f(t)\, f(t')\rangle = g(t-t') = \lambda \cdot \delta(t-t') . \end{aligned}}$$

white noise

strength of fluct. relation to $\gamma$?

## Einstein relation

Langevin equation: (Ld)

$$\boxed{M\dot{v} = -\gamma v + f(t)}$$

Solution: $v(t) = v_0 e^{-\frac{\gamma}{M}t} + \frac{1}{M} e^{-\frac{\gamma}{M}t} \int_0^t d\tau\, e^{+\frac{\gamma}{M}\tau} f(\tau)$.

mean: $\langle v(t)\rangle = v_0 e^{-\frac{\gamma}{M}t}$

Now consider $\langle v^2(t)\rangle$: interesting because $\frac{M}{2}\langle v^2(t)\rangle$ is the kinetic energy

$$\langle v^2(t)\rangle = v_0^2 e^{-\frac{2\gamma}{M}t} + \frac{1}{M^2} e^{-\frac{2\gamma}{M}t} \int_0^t d\tau_1 \int_0^t d\tau_2\, e^{+\frac{\gamma}{M}(\tau_1+\tau_2)} \underbrace{\langle f(\tau_1) f(\tau_2)\rangle}_{=\lambda\, \delta(\tau_1-\tau_2)} .$$

$$= v_0^2 e^{-\frac{2\gamma}{M}t} + \frac{\lambda}{2M\gamma}\left(1 - e^{-2\frac{\gamma}{M}t}\right)$$

for $t \gg \left(\frac{\gamma}{M}\right)^{-1}$ $\quad \frac{\lambda}{2M\gamma} = \langle v^2\rangle_{th}$

relax. time $\tau = \left(\frac{\gamma}{M}\right)^{-1}$

$$\Rightarrow \quad \frac{1}{2} M \langle v^2\rangle_{th} \left( = \frac{\lambda}{4M\tau}\right) = \frac{\lambda}{4\gamma}$$

equipartition theor.!

$$\frac{1}{2} M \langle v(t)^2\rangle = \frac{1}{2} kT$$

$$\Rightarrow \quad \boxed{\lambda \left(= 2\tfrac{1}{\tau} M kT\right) = 2\gamma kT}$$

Einstein relation

fluctuation ($\lambda$) – dissipation ($\gamma$) relation.

③

# Mean ~~squared~~ squared displacement

[Init] Random walk.

$$\boxed{\begin{aligned} \langle \vec{r}(t) \rangle &= \vec{0} \\ \text{but} \quad \langle \vec{r}^{\,2} \rangle &= \alpha t \end{aligned}}$$

N-th step: $\vec{r}_N$

$$\vec{r}_{N+1} = \vec{r}_N + L\vec{u}$$ — (random) unit vector for next step

$$\vec{r}_{N+1}^{\,2} = \vec{r}_N^{\,2} + L^2 + \underbrace{2L\,\vec{u}\,\vec{r}_N}_{\to 0 \text{ after averaging}}$$

$$\Rightarrow \langle r_{N+1}^2 \rangle = \langle \vec{r}_N^{\,2} \rangle + L^2$$

$$\Rightarrow \langle \vec{r}_N^{\,2} \rangle = N L^2 . \quad \propto t.$$

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[Schwabl]:

$$\langle x^2(t) \rangle = \int_0^t dt_1 \int_0^t dt_2 \quad \langle v(t_1)\, v(t_2) \rangle$$

↑ velocity correlation function

$$\left[ \begin{array}{l} \text{because} \\ x(t) = \underbrace{x(0)}_{\to 0 \text{ wlog}} + \int_0^t dt'\, v(t'). \end{array} \right.$$

$$\langle v(t_1) v(t_2) \rangle = v_0^2\, e^{-\gamma/M (t_1+t_2)} + \frac{1}{M^2}\, e^{-\frac{\gamma}{M}(t_1+t_2)} \underbrace{\int_0^{t_1} d\tau_1 \int_0^{t_2} d\tau_2\, e^{\frac{\gamma}{M}(\tau_1+\tau_2)}\, \lambda\, \delta(\tau_1-\tau_2)}_{⊛}$$

$$\left[ ⊛ = \int_0^{\min(t_1 t_2)} d\tau \quad e^{2\frac{\gamma}{M}\tau} = \frac{M}{2\gamma}\left( e^{\frac{2\gamma}{M}\min(t_1 t_2)} - 1 \right) \right]$$

$$\ldots = \frac{\lambda}{2\gamma M}\, e^{-\frac{\gamma}{M}|t_1 - t_2|} + \left(v_0^2 - \frac{\lambda}{2\gamma M}\right) e^{-\frac{\gamma}{M}(t_1+t_2)}$$

$$\left[ t_1 + t_2 - 2\min(t_1 t_2) = |t_1 - t_2| \right]$$

$$\langle x^2(t)\rangle \underset{t \gg \frac{\gamma}{M}}{\leadsto} \int_0^t dt_1 \int_0^t dt_2 \; \frac{\lambda}{2\gamma M} \, e^{-\frac{\gamma}{M}|t_1-t_2|}$$

Aside $$I = \int_0^t dt_1 \int_0^t dt_2 \, f(t_1-t_2) = \int_0^t du \; (t-u)\,[f(u)+f(-u)].$$

<u>Proof:</u> $t_1$ int.

$$I = \int_0^t dt_2 \left[F(t-t_2) - F(-t_2)\right]$$

$$= \int_0^t du \left[F(u) - F(-u)\right]$$

subst.: $u = t - t_2$

$$\underset{\text{int. by parts}}{=} t\,(F(t) - F(-t)) - \int_0^t du \; u \; (f(u) - f(-u))$$

$$= \int_0^t du \; (t-u)\,(f(u)+f(-u))$$

$$\langle x^2(t)\rangle \leadsto \frac{\lambda}{2\gamma M} \cdot \underset{|\ldots|}{2} \cdot \int_0^t du \; (t-u)\, e^{-\frac{\gamma}{M}u}$$

$$\underset{t \gg \frac{\gamma}{M}}{\leadsto} \frac{\lambda}{\gamma M}\frac{M}{\gamma}\, t$$ grows linearly with $t$

$$\boxed{\langle x^2(t)\rangle \leadsto 2Dt}$$

where $\boxed{D = \frac{\lambda}{2\gamma^2} = \frac{kT}{\gamma}}$ <u>diffusion constant</u>

Einstein relation.

## Why diffusion?

Continuity eq. for particle density:

$$\dot{n}(x) + \vec{\nabla}\vec{j}(x) = 0$$

with current density

$$\vec{j}(x) = -D\,\vec{\nabla} n(x)$$

$$\Rightarrow \boxed{\dot{n}(x) = D\,\vec{\nabla}^2 n(x)} \qquad \text{diffusion eq.}$$

in 1d: solution (or spherically sym. solution in $d > 1$)

$$n(x,t) = \frac{N}{\sqrt{4\pi D t}}\, e^{-\frac{x^2}{4Dt}}.$$

- diffusive motion of $N$ particles
- at $t=0$ centered at $x=0$ $\quad n(x,0) = N\,\delta(x)$.
- $\int n(x,t)\,dx = N$
- $\int x\, n(x,t)\,dx = 0 \Rightarrow \langle r(t)\rangle = 0$
- $\int x^2\, n(x,t)\,dx = (2Dt)\,N \quad \Rightarrow \langle r^2(t)\rangle = 2Dt$

$\Rightarrow$ mean squared displacement grows

$\sim 2Dt$

Generalization

Brownian motion in an external force field

$$K(x) = -\frac{\partial V}{\partial x}$$

Langevin equation:

$$\boxed{M\ddot{x} = -\gamma\dot{x} + K(x) + f(t)}$$

Special case: strong damping $\gamma\dot{x} \gg M\ddot{x}$

$$\Rightarrow \quad \dot{x} = -\Gamma\frac{\partial V}{\partial x} + \xi(t)$$

$\Gamma = \frac{1}{\gamma}$

$\xi(t) = \frac{f(t)}{\gamma}$.

$\Rightarrow \langle \xi(t) \rangle = 0$

$\langle \xi(t)\xi(t') \rangle = 2\Gamma kT\,\delta(t-t')$

Over-damped HO: PS 4.

Calculate the response function

$$\chi(t,t') = \frac{\delta\langle x(t)\rangle}{\delta h(t')}.$$

for $\dot{x} = -\Gamma x + h(t) + \xi(t)$.

## Outlook: Fokker – Planck equation

$\rho(\xi, t) = \langle \delta(\xi - v(t)) \rangle$

probability density for the particle to have velocity $\xi$ at time $t$.

For a Langevin eq. $M\dot{v} = -\gamma + f(t)$

$$\boxed{\frac{\partial}{\partial t}\rho(v,t) = \frac{\gamma}{M}\frac{\partial}{\partial v} v\rho(v,t) + \frac{\gamma}{M}\frac{kT}{M}\frac{\partial^2}{\partial v^2}\rho(v,t)}$$

Fokker – Planck equation.

1st term: drift

2nd term: diffusion

~~$\partial_t \rho = D \frac{\partial^2}{\partial v^2}$~~

Stationary solution:

$\rho(v,t) \propto e^{-\frac{Mv^2}{2kT}}$ Maxwell distribution.

even more: for $t \to \infty$

$\rho(v,t)$ converges towards the Maxwell distribution

$\Rightarrow$ Maxwell distribution is the only equilibrium distribution of the FP eq.

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Equivalently for the overdamped case:

$\dot{x} = -\Gamma \frac{\partial U}{\partial x} + r(t)$ $\qquad k(x) = -\frac{\partial U}{\partial x}$

Define probability density $\rho(\xi,t) = \langle \delta(\xi - x(t)) \rangle$

$$\Rightarrow \boxed{\partial_t \rho(\xi,t) = \underbrace{-\frac{\partial}{\partial \xi}\left(\Gamma \rho(\xi,t) k(\xi)\right)}_{\text{drift}} + \underbrace{\Gamma kT \frac{\partial^2}{\partial \xi^2}\rho(\xi,t)}_{\text{diffusion}}}$$

Smoluchowski equation.

Stationary solution: $\rho(x,t) \propto e^{-V(x)/kT}$

Similarly for the general Langevin eq: $M\ddot{x} = -\gamma\dot{x} + k(x) + f(t)$.