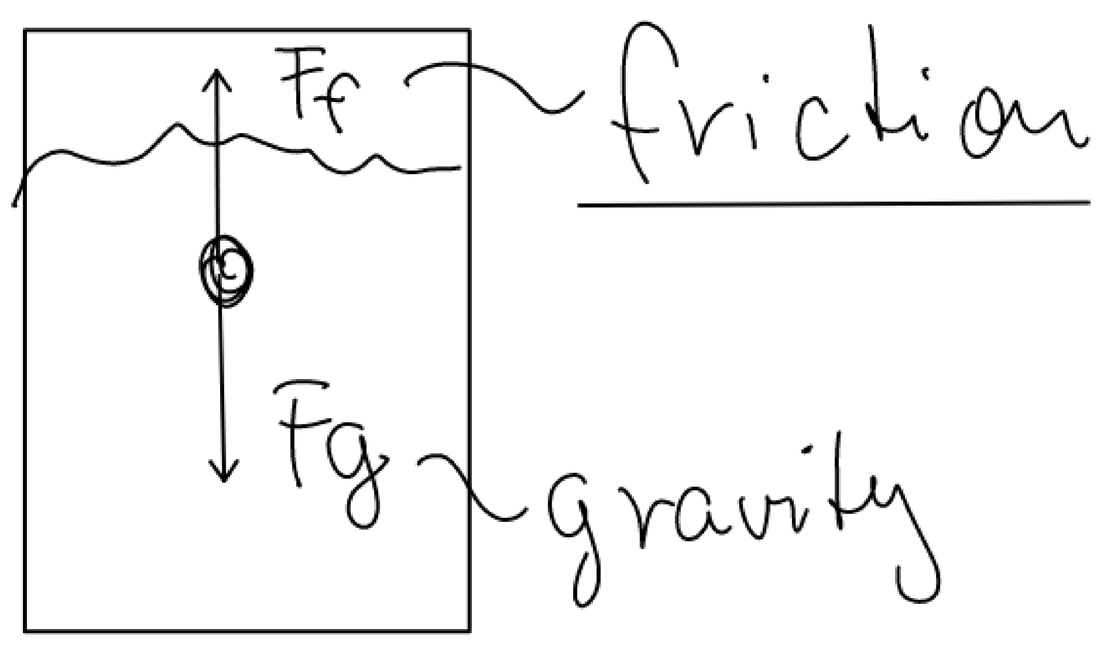
11. Langevin and Brownian dynamics

We can already simulate particle motion in fluid



$$m \cdot \ddot{y} = - g \cdot m + F_f$$

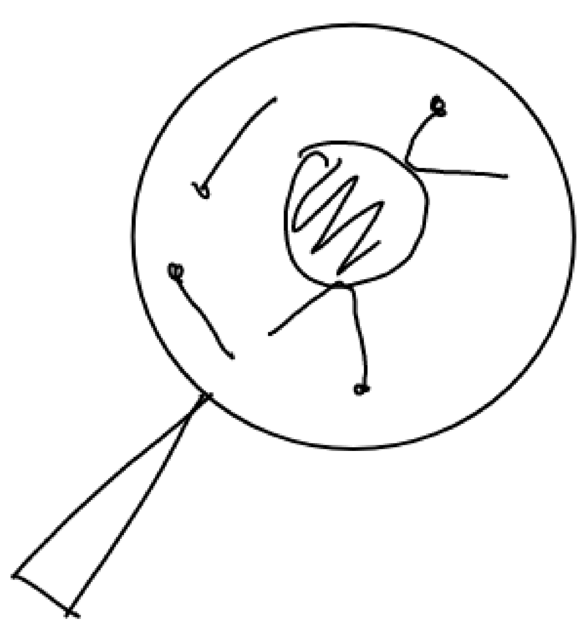
$$F_f \overset{?}{=} \Gamma \cdot \dot{\vec{y}}$$

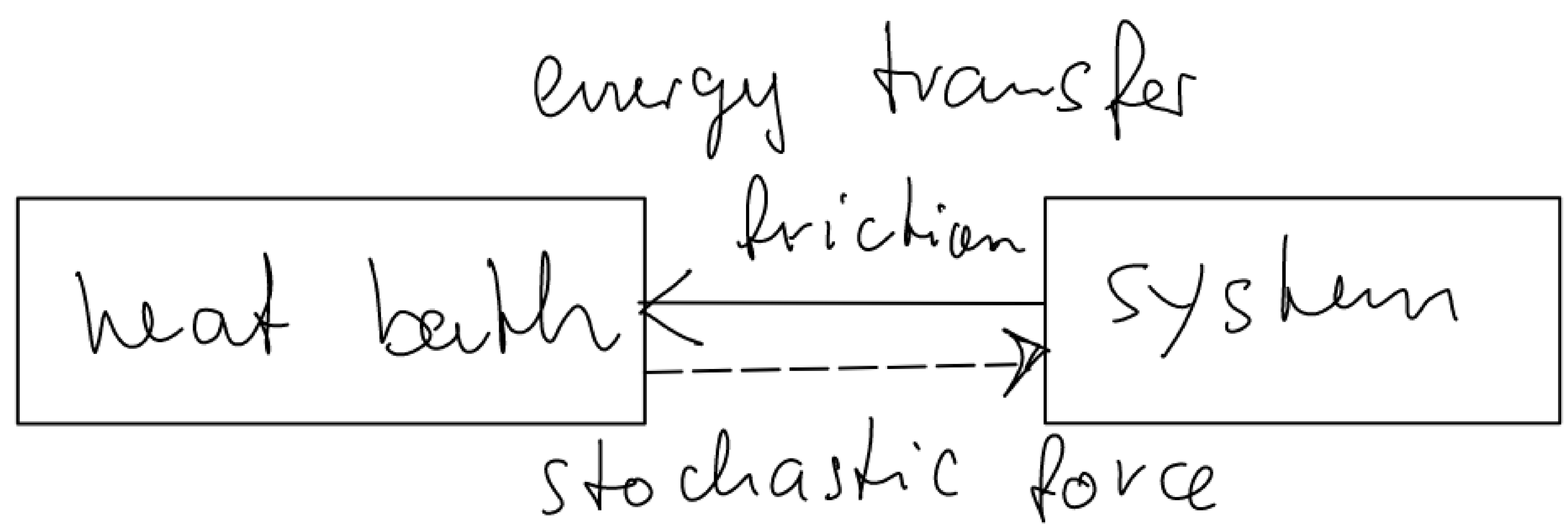
friction / coefficient

energy is not conserved, only in vacuum with

$$m \ddot{\vec{r}} = - \vec{\nabla} V(\vec{r})$$

<u>Question</u>: Where is the energy going ?
Into the fluid (= heat bath) ?





11.1. Langevin equation

$$\boxed{m \ddot{\vec{r}} = - \Gamma \dot{\vec{r}} - \vec{\nabla} U(\vec{r}) + \vec{\xi}(t)} \quad (1)$$

stochastic force

<u>Question</u>: How to model $\vec{\xi}(t)$

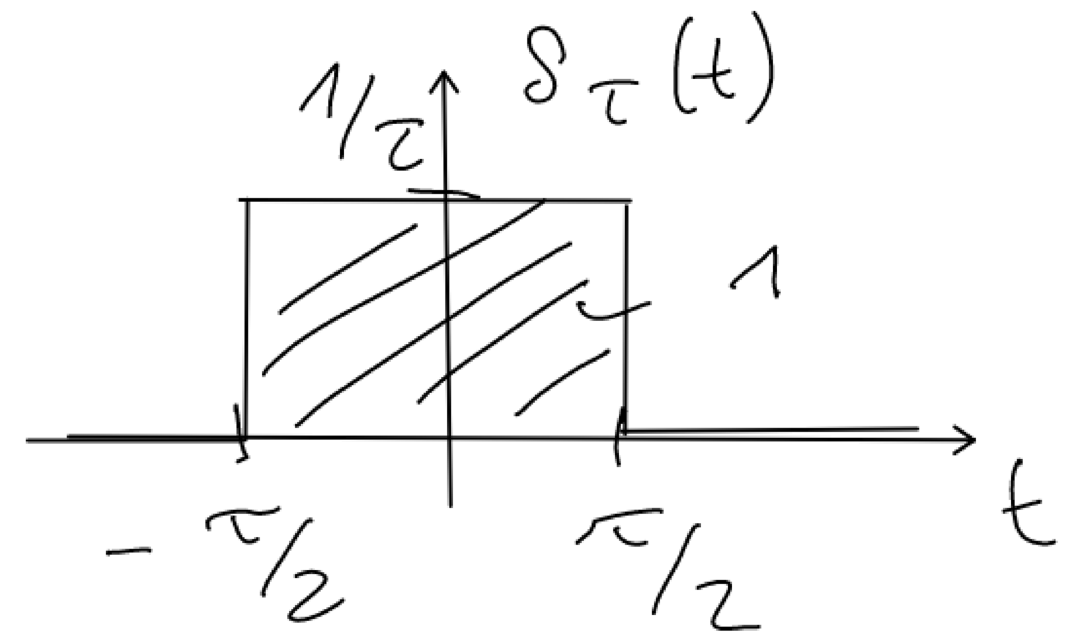
- remember 1^{st} and 2^{nd} law of thermodynamics
  - closed system energy is preserved
  - only net energy transfer to heat bath

$$\longrightarrow \boxed{\langle \underbrace{\vec{\xi}(t)}_{X} \rangle = 0 = \int d\underbrace{\vec{\xi}(t)}_{X} \, p[\underbrace{\vec{\xi}(t)}_{X}] \, \underbrace{\vec{\xi}(t)}_{X}}$$

- interactions are fast and independent

$$\langle \xi^i(t) \xi^j(t) \rangle = \lambda \delta^{ij} \delta_\tau(t-t')$$

We will use limit $\tau \to 0$
$\hat{=}$ force instantly changes values, no memory



- $\xi(t)$ is a total force from multiple collisions

$\longrightarrow$ Gauss distributed by <u>central limit theorem</u>

$$\boxed{P[\xi(t)] = \mathcal{N} \exp\left(-\int_{-\infty}^{\infty} dt \frac{1}{2\lambda} \vec{\xi}^{\,2}(t)\right)}$$

Free Particle, $U(\vec{r}) = 0$

$$m \dot{\vec{v}} = -\Gamma \vec{v} + \vec{\xi}(t) \quad \text{with} \quad \vec{v} = \dot{\vec{r}}$$

$$\dot{\vec{v}} = -\gamma \vec{v} + \vec{\eta}(t) = \frac{d\vec{v}}{dt} \qquad \gamma = \Gamma/m, \quad \vec{\eta}(t) = \vec{\xi}(t)/m$$

inhomogeneous linear ODE

ansatz: $\vec{v}(t) = \vec{v}_0(t) \cdot f(t)$

homogeneous part $\vec{v}_0(t) = C_1 e^{-\gamma \cdot t}$

$$\dot{\vec{v}}(t) = \dot{\vec{v}}_0(t) \cdot f(t) + \vec{v}_0(t) \cdot \dot{f}(t) = -\gamma \vec{v}_0(t) f(t) + \vec{\eta}(t)$$

$$\vec{v}_0(t) \dot{f}(t) = \big(\underbrace{-\gamma \vec{v}_0(t) - \dot{\vec{v}}_0(t)}_{=0}\big) f(t) + \vec{\eta}(t)$$

$$\int df = \int dt\, \vec{\eta}(t) / \vec{v}_0(t)$$

$$\rightsquigarrow v(t) = e^{-\gamma t}\left(\vec{v}(0) + \int_0^t dt'\, e^{\gamma t'} \vec{\eta}(t')\right)$$

- average speed

$$\boxed{\langle v(t) \rangle = e^{-\gamma t} \vec{v}(0)} \qquad \text{because } \langle \vec{\eta}(t) \rangle = 0$$

∘ correlation between $\vec{v}(t_1)$ and $\vec{v}(t_2)$

$$\langle \vec{v}(t_1)\vec{v}(t_2)\rangle = \langle \vec{v}(t_1)\rangle\langle \vec{v}(t_2)\rangle - \frac{D\lambda}{m^2}\frac{1}{2\gamma}\left(e^{-\gamma|t_1+t_2|} - e^{-\gamma|t_1-t_2|}\right)$$

$$D = \sum_i \delta^{ii}$$

for $t_1 = t_2 \gg \gamma^{-1}$ (stationary state)

$$\boxed{\langle \vec{v}^2(t)\rangle = \frac{D\lambda}{m^2}\frac{1}{2\gamma}}$$

from statistical physics we know

$$\frac{1}{2}m\langle \vec{v}^2\rangle = D\frac{k_B \cdot T}{2}$$ Boltzmann constant

or $$\boxed{\lambda = 2k_B T m\gamma = 2k_B T \Gamma}$$

fluctuation-dissipation theorem friction

Same for position $$\boxed{\langle (\vec{r}(t)-\vec{r}(0))^2\rangle = \frac{D\lambda}{m^2}\frac{1}{\gamma^2}t \quad t \gg \gamma^{-1}}$$

diffusion

In limit $m \to 0$ we get $$\boxed{\Gamma\dot{\vec{r}} = -\vec{\nabla}u(\vec{r}) + \vec{\xi}(t)}$$

Brownian dynamics

11.2 Simulation

two possible routes to do simulation:

a) 1. get different realizations $\vec{\xi}_k(t)$ with PRNG from last lecture

2. for each solve ODE (1)

3. compute average for observables $\langle O(\vec{r},\vec{v})\rangle$ over realizations

b) for time independent systems, <u>ergodicity</u> allows 1 long simulation and time average

$$\langle O(\vec{r},\vec{v})\rangle = \frac{\Delta t}{T}\sum_{n=1}^{T/\Delta t} O\left(\vec{r}(n\Delta t),\vec{v}(n\Delta t)\right)$$

For time independent systems combinations of a) and b) are possible.

Implementation

<u>Euler method</u> is usually sufficient

$$\vec{r}_{n+1} = \vec{r}_n + \vec{v}_n \Delta t$$

$$m\vec{v}_{n+1} = m\vec{v}_n + \vec{F}_n \Delta t - \Gamma \vec{v}_n \Delta t - \underbrace{\vec{\xi}_n \Delta t}_{\vec{R}_n}$$

force from potential $U(\vec{r})$

$\vec{R}_n$ Gauss distributed with $\langle \vec{R}_n \rangle = 0$ and

$\langle R_n^2 \rangle = 2 k_B T \, \Gamma \cdot \Delta t$.