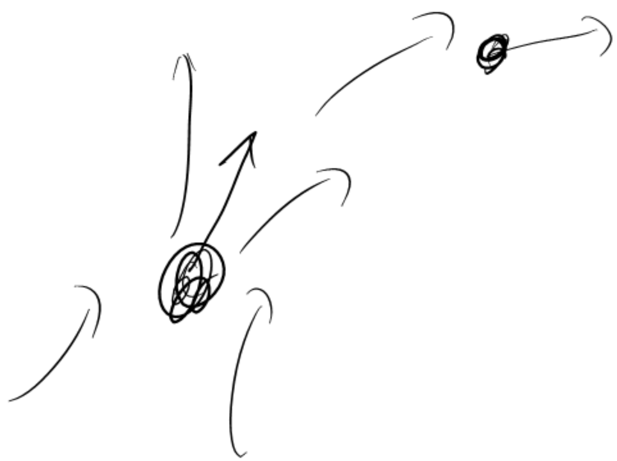
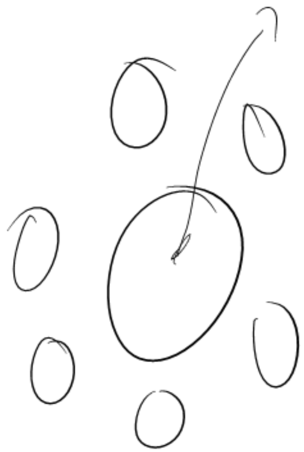
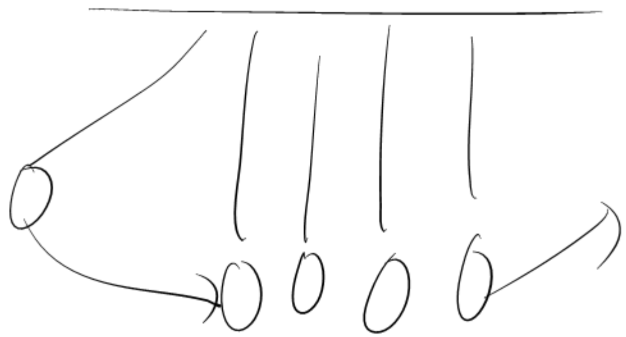






$$\frac{\partial}{\partial t}\vec{u} = \nu \nabla^2 \vec{u}$$

$$[\nu] = \frac{m^2}{s}$$

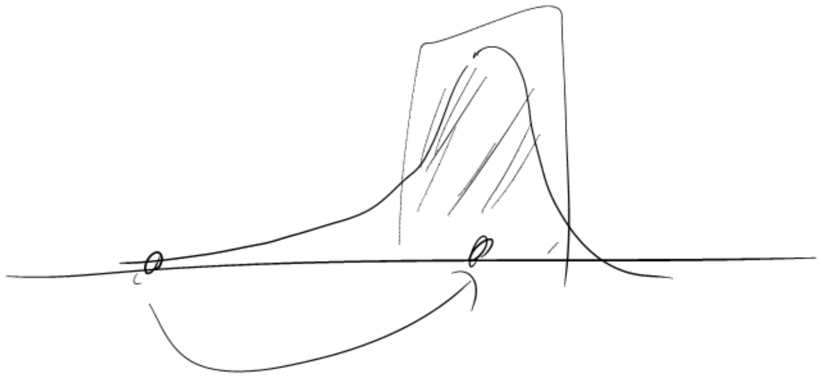
$$\frac{\partial}{\partial t}\rho = D \vec{\nabla}^2 \rho$$

$$[D] = \frac{m^2}{s}$$

$$Sc = \frac{\nu}{D} \gg 1 \quad \text{Schmidt \#}$$

$$\tau_D \sim \frac{\ell^2}{D}$$

$$\tau_\nu \sim \frac{\ell^2}{\nu}$$



$$x' = x + \gamma F + \sqrt{2T\gamma}\,\rho \qquad x \to x'$$

$$x = x' + \gamma F' + \sqrt{2T\gamma}\,\rho' \qquad x' \to x$$

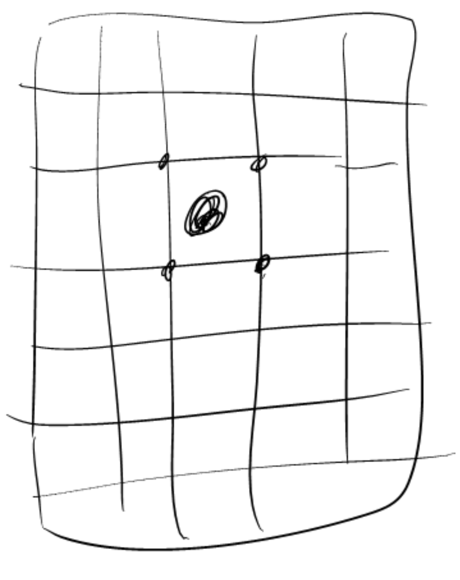
$$\rho' = (x - x' - \gamma F')\frac{1}{\sqrt{2T\gamma}}$$

2nd Order Langevin Integrators

Stochastic Dynamics

friction coefficient   const.

$$\frac{d}{dt}\vec{r}_i = \frac{1}{m_i}\vec{p}_i \qquad \frac{d}{dt}\vec{p}_i = \vec{F}_i - \Gamma_i\left[\frac{1}{m_i}\vec{p}_i - \vec{u}_i\right] + \vec{f}_i$$



$$\langle f_{i\alpha} \rangle = 0$$

$$\langle f_{i\alpha}(t)\, f_{j\beta}(t') \rangle = 2T\Gamma_i\, \delta_{ij}\, \delta_{\alpha\beta}\, \delta(t-t')$$

FPE: $\partial_t P = \mathcal{L} P \qquad \mathcal{L} = \mathcal{L}_1 + \mathcal{L}_2 + \mathcal{L}_3 + \mathcal{L}_4$

$$\mathcal{L}_1 = -\sum_i \frac{\partial}{\partial \vec{r}_i} \cdot \frac{\vec{p}_i}{m_i} \qquad \mathcal{L}_2 = -\sum_i \frac{\partial}{\partial \vec{p}_i} \cdot \vec{F}_i$$

$$\mathcal{L}_3 = \sum_i \Gamma_i \frac{\partial}{\partial \vec{p}_i} \cdot \left[\frac{1}{m_i} \vec{p}_i - \vec{u}_i \right], \quad \mathcal{L}_4 = T \sum_i \Gamma_i \frac{\partial^2}{\partial \vec{p}_i^{\,2}}$$

formal solution: $P(\{\vec{r}_i\}, \{\vec{p}_i\}, h \mid \{\vec{r}_i^{\,0}\}, \{\vec{p}_i^{\,0}\}, 0)$

$$= \underline{\underline{\exp\{[\mathcal{L}_1 + \mathcal{L}_2 + \mathcal{L}_3 + \mathcal{L}_4] h\}}} \; \delta(\vec{r}_i - \vec{r}_i^{\,0}) \, \delta(\vec{p}_i - \vec{p}_i^{\,0})$$

Trotter decomposition:

$$\exp\left[(L_1+L_2+L_3+L_4)h\right] = \underbrace{e^{L_1 h/2}\, e^{(L_2+L_3+L_4)h}\, e^{L_1 h/2}}_{} + O(h^3)$$

- update positions by $h/2$: $\vec{r}_i(t+\frac{h}{2}) = \vec{r}_i(t) + \frac{h}{2}\frac{\vec{p}_i(t)}{m_i}$
- update momenta by h $\rightarrow$ see later $\rightarrow \vec{p}_i(t+h)$
- update positions by $h/2$: $\vec{r}_i(t+h) = \vec{r}_i(t+\frac{h}{2}) + \frac{h}{2}\frac{\vec{p}_i(t+h)}{m_i}$

mom. update: integrate mom. eq. for FIXED $\vec{F}_i$ (and $\vec{u}_i$)

$$\underbrace{\frac{d}{dt}\vec{p}_i}_{} = \underbrace{\vec{F}_i}_{\text{const.}} - \Gamma_i \underbrace{\left(\frac{\vec{p}_i}{m_i} - \underbrace{\vec{u}_i}_{\text{Const.}} \right)}_{} + \underbrace{\vec{f}_i}_{}$$

can be solved EXACTLY

$$\vec{\phi}_i = \vec{F}_i + \Gamma_i \vec{u}_i$$

$$\left(\frac{d}{dt} + \frac{\Gamma_i}{m_i} \right) \vec{p}_i = \underbrace{\vec{\phi}_i + \vec{f}_i}_{\text{inhomogeneity}}$$

solution is Gaussian → calc. 1st moment

2nd "

→ Gaussian distribution of $\vec{p}_i(t)$ "

$$\Rightarrow \tilde{\vec{p}}_i(h) = \underbrace{d_i(h)\,\vec{p}_i(0) + q_i(h)\,\vec{\phi}_i}_{\equiv \langle \vec{p}_i(h) \rangle} + \sigma_i(h)\,\tilde{\vec{\rho}}_i$$

<u>with</u> $$d_i(h) = \exp\left(-\frac{\Gamma_i}{m_i} h\right)$$

$$q_i(h) = \frac{m_i}{\Gamma_i}\left\{1 - \exp\left(-\frac{\Gamma_i}{m_i} h\right)\right\}$$

$$\sigma_i(h) = \left\{m_i T \left[1 - \exp\left(-2\frac{\Gamma_i}{m_i} h\right)\right]\right\}^{1/2}$$

<u>$\tilde{\rho}_i$: Gaussian RN</u>, $\langle \rho_{i\alpha} \rangle = 0$, $\langle \rho_{i\alpha} \rho_{j\beta} \rangle = \delta_{ij}\,\delta_{\alpha\beta}$

→ method as a whole is 2nd order accurate!

$$G_i(h) \propto h^{1/2}$$

$$\left\langle \left[\rho_i(h) - \langle \rho_i(h) \rangle\right]^n \right\rangle \propto h^{n/2}$$

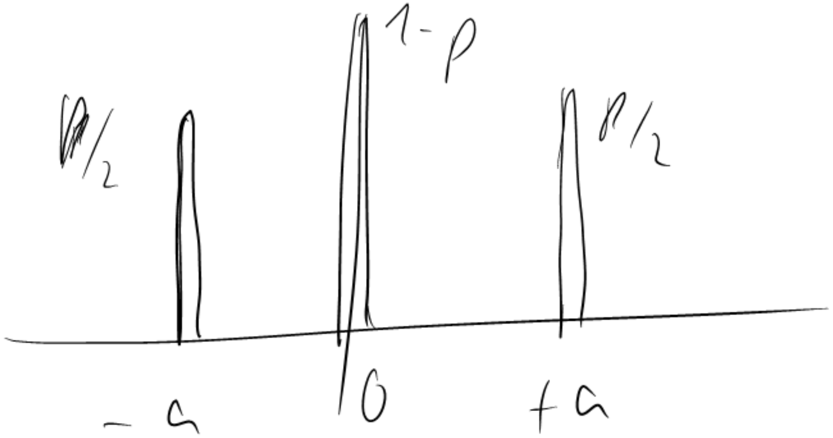
$\Rightarrow$ accurate sampling only up to h^2

$n = 4$

$\Rightarrow$ need RN with: $\langle \rho \rangle = 0$, $\langle \rho^3 \rangle = 0$,

$\langle \rho^{2n+1} \rangle = 0$, $\langle \rho^2 \rangle = 1$, $\langle \rho^4 \rangle = 3$

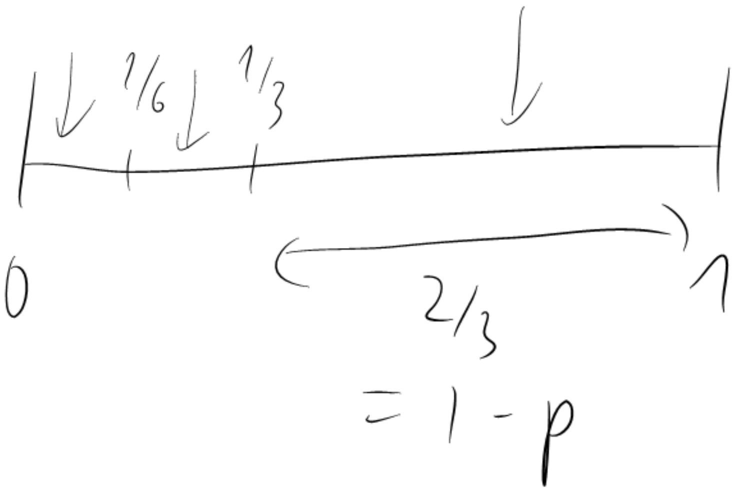
3-delta



$$P(x) = (1-p)\,\delta(x) + \frac{p}{2}\,\delta(x-a) + \frac{p}{2}\,\delta(x+a)$$

$$\langle \rho^n \rangle = \int_{-\infty}^{\infty} dx\; x^n\, P(x)$$

$$\left.\begin{aligned} p a^2 &= 1 \\ p a^4 &= 3 \end{aligned}\right\} \quad \begin{aligned} a &= \sqrt{3} \\ p &= 1/3 \end{aligned}$$



Test: yarn5 generator (S. Mertens)

10^9 RN $\rightarrow$ 127 sec. CPU

+ Box-Muller $\rightarrow$ 287 sec. "

10^9 RN + triple δ $\rightarrow$ 134 sec. CPU

What about DPD?

$\mathcal{L}_1$: position update

$\mathcal{L}_2$: momentum update, conservative forces

$\mathcal{L}_3$: dissipation (momentum relaxation)

$\mathcal{L}_4$: momentum diffusion

dissipation:

$$\frac{d}{dt}\vec{p}_i = -\sum_{j(\neq i)} \xi(r_{ij}) \left[\left(\frac{\vec{p}_i}{m_i} - \frac{\vec{p}_j}{m_j}\right)\cdot \hat{r}_{ij}\right] \hat{r}_{ij}$$

symbolic:

$$\frac{d}{dt}\vec{P} = \overleftrightarrow{A}\,\vec{P}$$

$3N \times 3N$

formal solution: $\vec{P}(h) = e^{\overleftrightarrow{A} h}\,\vec{P}(0)$

$$\cong \left(1 + \overleftrightarrow{A} h + \frac{1}{2}\overleftrightarrow{A}^2 h^2\right)\vec{P}(0)$$

$$\left.\begin{aligned}
\vec{P}_0 &= \vec{P}(0) \\
\vec{P}_1 &= \vec{A} h \vec{P}_0 \\
\vec{P}_2 &= \frac{1}{2} \vec{A} h \vec{P}_1
\end{aligned}\right\} \quad \vec{P}(h) = \vec{P}_0 + \vec{P}_1 + \vec{P}_2$$

$$\exp\left\{ \left[L_1 + L_2 + L_3 + L_4 \right] h \right\} \overset{\text{Trotter}}{\simeq}$$

$$\exp\left[L_1 \frac{h}{2} \right] \exp\left[(L_2 + L_4) \frac{h}{2} \right] \exp(L_3 h) \exp\left[(L_2 + L_4) \frac{h}{2} \right]$$

$$\exp(L_1 h/2) + O(h^3)$$

$$e^{(A+B)h} = e^{A/2} e^{Bh} e^{A/2} + O(h^3)$$

$$e^{A+B} = e^{B+A}$$

<u>BD</u>: $\frac{d}{dt}\vec{r}_i = \mu_i \vec{F}_i + \vec{f}_i \qquad \langle f_{i\alpha} \rangle = 0$

$$\langle f_{i\alpha}(t) f_{j\beta}(t') \rangle = 2\mu_i T \delta_{ij} \delta_{\alpha\beta} \delta(t-t')$$

$$\mathcal{L}_1 = -\sum_i \mu_i \frac{\partial}{\partial \vec{r}_i} \cdot \vec{F}_i$$

$$\mathcal{L}_2 = T \sum_i \mu_i \frac{\partial^2}{\partial \vec{r}_i^{\,2}}$$

$$\exp[(\mathcal{L}_1 + \mathcal{L}_2)h] \simeq \underbrace{e^{\mathcal{L}_2 h/2}}_{\text{diffusion}} e^{\mathcal{L}_1 h} \underbrace{e^{\mathcal{L}_2 h/2}}_{\text{diffusion}} + O(h^3)$$

L_n: $$\frac{d}{dt}\vec{r}_i = \mu_i \vec{F}_i \qquad \vec{F}_i(\{\vec{r}_i\})$$

$$\vec{r}_i(t+h) = \vec{r}_i(t) + \mu_i \int_t^{t+h} d\tau\, \vec{F}_i(\tau)$$

predictor-corrector:

$$\mu_i \int_t^{t+h} d\tau\, \vec{F}_i(\tau) \cong \mu_i \frac{h}{2}\left[\vec{F}_i(t) + \overbrace{\vec{F}_i(t+h)}^{\text{unknown}}\right] + O(h^3)$$

[trapezoidal rule]

$$\Delta\vec{r}_i = \mu_i \frac{h}{2}\left(\vec{F}_i(t) + \vec{F}_i(t+h)\right)$$

Start: $\Delta\vec{r}_i^{(0)} = \vec{F}_i(t)\, h\, \mu_i$

$$\Delta\vec{r}_i^{(n+1)} = \mu_i \frac{h}{2}\left[\vec{F}_i(\vec{r}_i) + \vec{F}_i(\vec{r}_i + \Delta\vec{r}_i^{(n)})\right]$$

iterate to convergence!