Stochastic Dynamics Simulations

Heuristic Consideration:

Augment Newton's equation with friction and stochastic force:

$$m_i \frac{d^2\vec{r}_i}{dt^2} = \vec{F}_i - \gamma m_i \dot{\vec{r}}_i + \vec{\eta}_i^{\,\text{random}}$$

Motivation: Brownian motion; consider (a) big particle (a colloid) in a fluid: there may be an external force and interactions ($\vec{F}_i$) but there is friction from the solvent $(+m_i\gamma\vec{v}_i)$ and stochastic collisions with the solvent ($\vec{\eta}_i$).

Suppose we only consider one particle (Brownian motion) and no external force

$$m\frac{d\vec{v}_i}{dt} = -m\gamma\vec{v}_i + \vec{\eta}_i$$

$$\frac{d\vec{r}}{dt} = \vec{v}$$

Assumption for the random force: Gaussian White Noise

$$\text{"}\langle \eta_\alpha(t)\,\eta_\beta(t')\rangle = \sqrt{2m\gamma k_B T}\;\delta_{\alpha\beta}\,\delta(t-t')\text{"}$$

$$\langle \eta_\alpha(t)\rangle = 0$$

Sometimes one calls this a Langevin equation. It is also the Ornstein-Uhlenbeck process (the $\vec{v}$-part)

Is this a MD equation + some extra terms?

NO !

Let us derive such equations from the basis of our Markov-chain Monte Carlo simulations, the master equation.

$$\frac{\partial}{\partial t} p(x,t) = \int dx'\, w(x|x')\, p(x',t) - \int dx'\, w(x'|x)\, p(x,t)$$

rewrite: i) $w(x|x') = w(x-r; r)$ with $r := x - x'$)

$\equiv$ probability to jump a distance r from $x-r$ to x.

ii) assume small jumps.

$$\exists\ \delta > 0 \quad \text{with} \quad w(x-r;r) \approx 0 \ ; \ |r| > \delta$$

iii) $\left.\begin{matrix} w(x-r;r) \\ p(x,t) \end{matrix}\right\}$ are slowly varying in first argument

$$\exists\ \delta' > 0 \qquad \left.\begin{matrix} w(x-r;r) \approx w(x;r) \\ p(x+r,t) \approx p(x,t) \end{matrix}\right\} \text{for } |r| < \delta'$$

(iv) $p(x,t)$ and $w(x;r)$ are infinitely differentiable

$$\Rightarrow \frac{\partial}{\partial t} p(x,t) = \int w(x-r;r)\, p(x-r,t)\, dr - p(x,t) \int dr\, w(x;-r)$$

perform a Taylor expansion in first argument $x-r$ around $r=0$

$$\Rightarrow \frac{\partial}{\partial t} p(x,t) = p(x,t) \int dr\, w(x;r) - p(x,t) \int dr\, w(x;-r)$$

$$- \int r \frac{\partial}{\partial x} \left[w(x;r)\, p(x,t) \right]_{r=0} dr + \frac{1}{2} \int r^2 \frac{\partial^2}{\partial x^2} w(x;r)\, p(x,t)\, dr$$

$$\pm \ldots$$

$$\Rightarrow \frac{\partial}{\partial t} p(x,t) = \sum_{n=1}^{\infty} \frac{(-1)^n}{n!} \frac{\partial^n}{\partial x^n} \left[a_n\, p(x,t) \right]$$

with $a_n = \int_{-\infty}^{\infty} r^n\, w(x;r)\, dr$ $\Big\}$ Kramers-Moyal expansion of master equation

For some processes this expansion stops exactly in second order: <u>diffusion processes</u>

$$\frac{\partial}{\partial t} p(x,t) = -\frac{\partial}{\partial x} \left[a_1(x)\, p(x,t) \right] + \frac{1}{2} \frac{\partial^2}{\partial x^2} \left[a_2(x)\, p(x,t) \right]$$

Fokker-Planck equation

Equation for the probability of observable x at time t. Let us suppose that x is position and we start at $x=0$ at time $t=0$:

$$p(x,0) = \delta(x)$$

Then one can derive using the F.P.-equation

$$\langle x(\Delta t)\rangle = \langle a_1(x(0))\rangle \Delta t + o(\Delta t)$$
$$\langle x^2(\Delta t)\rangle = \langle a_2(x(0))\rangle \Delta t + o(\Delta t)$$

The same result one would obtain from a Langevin equation of the form

$$\frac{dx}{dt} = v(x(t)) + b(x(t))\,\eta(t)$$

with $v(x) = a_1(x)$
$b^2(x) = a_2(x)$

Note: Langevin and Brownian dynamics simulations generate particle trajectories for a probability distribution that obeys a Fokker-Planck equation

Newton $\leftrightarrow$ Liouville
Langevin $\leftrightarrow$ Fokker_Planck

Let us consider the simplest case, Brownian motion as treated by Einstein.

$$\dot{x}(t) = \eta(t) \rightarrow x(t) = \int_{t_0}^{t} \eta(t')\,dt'$$

$x(t_0) = 0$; η = Gaussian white noise

equivalent Fokker-Planck equation

$$\frac{\partial}{\partial t} p(x,t) = \frac{1}{2}\frac{\partial^2}{\partial x^2} p(x,t) \quad ; \quad p(x,t_0) = \delta(x)$$

The solution of this partial differential equation is

$$p(x,t) = \frac{1}{\sqrt{2\pi(t+t_0)}} \exp\left\{-\frac{x^2}{2(t+t_0)}\right\}$$

[Propagator of the diffusion equation]

This process is called : WIENER process

- $x(t)$ is continuous

$$\text{Prob}\left[\,|x(t+\Delta t) - x(t)| > k\right] = \int_k^\infty dx \, \underbrace{\frac{2}{\sqrt{2\pi\Delta t}}\, e^{-\frac{x^2}{2\Delta t}}}_{\text{approximates } \delta(x)}$$

$$\Rightarrow \lim_{\Delta t \to 0} \text{Prob}\left[\,|x(t+\Delta t) - x(t)| > k\right] = 0 \quad \forall k$$

BUT

- $x(t)$ is nowhere differentiable

$$\text{Prob}\left[\,\left|\frac{x(t+\Delta t) - x(t)}{\Delta t}\right| > k\right] = \int_{k\Delta t}^\infty dx \, \frac{2}{\sqrt{2\pi\Delta t}}\, e^{-\frac{x^2}{2\Delta t}}$$

$$\lim_{\Delta t \to 0} \text{Prob}\left[\,\left|\frac{x(t+\Delta t) - x(t)}{\Delta t}\right| > k\right] = 1 \quad \forall k$$

$$\Rightarrow \boxed{dx(t) = dW(t) \neq \eta(t)\, dt}$$

Itô stochastic differential equation

$$dx(t) = a(x(t),t)\, dt + b(x(t),t)\, dW(t)$$

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

$$\langle dW(t)\, dW(t') \rangle = \begin{cases} 0 & t \neq t' \\ dt & t = t' \end{cases}$$

$$\text{"} dW(t) = O(dt^{\frac{1}{2}}) \text{"}$$

↳ all numerical algorithms for a SDE are therefore expansions in $(\Delta t)^{\frac{1}{2}}$ and not Δt as for ordinary diff. equations.

In our problems we will typically encounter SDEs of the form

$$dx = a(x,t)\, dt + \sigma\, dW$$

a: Drift coefficient; σ: $\sqrt{\text{Diffusion coefficient}}$

A second order integration algorithm for this equation is generated by the Heun algorithm (2nd order Runge-Kutta)

$$x(t+\Delta t) = x(t) + \frac{1}{2}\Delta t\left[a(x(0),0) + a(\xi(\Delta t), \Delta t)\right] + \sigma\, \Delta W(\Delta t) + O(\Delta t^3)$$

with intermediate Euler steps

$$\xi(\Delta t) = x(t) + a(x(0),0)\,\Delta t + \sigma\, \Delta W(\Delta t)$$

Let us now consider this integrator for the N-particle system obeying the following equation of motion

$$\left.\begin{aligned} d\vec{r}_i &= \vec{v}_i\, dt \\ m_i\, d\vec{v}_i &= (\vec{F}_i - m_i \gamma \vec{v}_i)\, dt + \sigma\, d\vec{W}_i(t) \end{aligned}\right\} \text{ the Langevin equations we discussed earlier}$$

$$\vec{r}_i(t+\Delta t) = \vec{r}_i(t) + \vec{v}_i(t)\,\Delta t\left(1 - \frac{1}{2}\gamma\Delta t\right) + \frac{1}{2}\Delta t^2\, \vec{F}_i(\{\vec{r}_i(t)\}) + \frac{1}{2}\sigma\,\Delta t\,\Delta W_i(\Delta t)$$

$$m_i \vec{v}_i(t+\Delta t) = m_i \vec{v}_i(t) + \frac{1}{2}\Delta t(1-\gamma\Delta t)\,\vec{F}_i(\{\vec{r}_i(t)\}) + \frac{1}{2}\Delta t\,\vec{F}_i(\{\vec{r}_i(t+\Delta t)\})$$
$$- \gamma\Delta t\left(1 - \frac{1}{2}\gamma\Delta t\right) m_i \vec{v}_i(t) + \sigma\left(1 - \frac{1}{2}\gamma\Delta t\right)\Delta W_i(\Delta t)$$

<u>remarks</u>: i) $\Delta W_i(\Delta t)$ is a Gaussian distributed random number zero mean and variance Δt. In fact <u>any</u> distribution which agrees with the Gaussian in the <u>first four moments</u> suffices.

example: $$\Delta W(\Delta t) = \begin{cases} -\sqrt{3\Delta t} & r < \frac{1}{6} \\ 0 & \frac{1}{6} \le r < \frac{5}{6} \\ \sqrt{3\Delta t} & \frac{5}{6} \le r \end{cases}$$

$r \in U[0,1]$

R. Dünweg, W. Paul, Int. J. Mod. Phys. C 2, 817 (1991)

(ii) we actually calculate $\vec{F}_i(\{\vec{r}_i(t+\Delta t)\})$

instead of $\vec{F}_i(\{\vec{r}_i^{EULER}(t+\Delta t)\})$

This does not change the order of treatment of the deterministic force and we only need one force calculation per integration step.

(iii) for $\gamma = 0$ $\sigma = 0$ one obtains

$$\vec{r}_i(t+\Delta t) = \vec{r}_i(t) + \vec{v}_i(t)\Delta t + \frac{1}{2}\Delta t^2 \vec{F}_i(\{\vec{r}_i(t)\})$$

$$m_i\vec{v}_i(t+\Delta t) = m_i\vec{v}_i(t) + \frac{1}{2}\Delta t\left\{\vec{F}_i(\{\vec{r}_i(t)\}) + \vec{F}_i(\{\vec{r}_i(t+\Delta t)\})\right\}$$

i.e. the velocity Verlet integrator.

Literature: W. Paul, J. Baschnagel, „Stochastic Processes: From Physics to Finance", Springer, Berlin 1999

P.E. Kloeden, E. Platen, „Numerical Solution of Stochastic Differential Equations", Springer, Heidelberg, 1995

(iv) When I do not consider that the numerical solution and algorithms for a SDE are different from the algorithms used for MD I obtain a very complicated integrator with the accuracy of the simple Euler algorithm