Brownian and Langevin Dynamics

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1 Brownian Dynamics

1.1 Theory

Brownian dynamics describes the motion of a particle interacting with much smaller and lighter solvent particles. Physically the system particle is subjected to many collisions with the surrounding fluid particles, this cause the fast relaxation of momentum (and velocity) distribution. This is why we call this limit overdamped langevin dynamics.

This theory is appliable when the timescale of the phenomen of interest is much bigger than the momentum relaxation time (see the analytical formula for $v(t)$). This regime is called diffusion regime.

Ballistic regime The faster timescale are referred usually as ballistic regime when beads just move in straight lines. The msd in ballistic regime is not diffusive (linearly scale with t) but it scale quadratically with t.

$r^2(t) \approx v^2t^2$ follows newton motion, at such small timescale brownian motion is (approximately) time-reversal invariant.

Diffusive regime : While when we consider larger timescales we approach the diffusion regime in which $r^2(t) \approx Dt$ suggesting an irreversible and energy dissipating process.

We loose information on the velocities of the brownian particle (the bigger one). Formally, the previous step velocity at the beginning of the the interval is dissipated further and does not contribute to the end one as well as to the positional random walk.

Equations Consider N brownian particles moving under the action of a conservative potential Φ describing inter-particle interactions or with an external field (gravity). The brownian particles are immersed in an uniform and isotropic solvent and their interactions with it is described by the friction coefficient γ. The forces acting on the particles are three:

- potential induced or external forces F_i
- friction forces

- random forces

Now the idea is to derive an equation describing the particle positions from the langevin momentum equation. The momentum Langevin equation for the particle i will be:

$$m_i \ddot{r}_i = F_i - \gamma v_i + \sqrt{2D}\eta$$

where $\langle \eta \rangle = 0$ and $\langle \eta(t)\eta(t') \rangle = \delta(t - t')$

We assume that the relaxation timescale for positions and momenta are well separated.

Then the idea is to expand in taylor expansion, integrating in time (by parts) and get an expression for the velocity:

see derivation in [2] or [3]

you'll end up with:

$$\dot{x} = -\frac{1}{\gamma}\nabla U(x) + \mathbf{R}(t)$$

1.2 Analytic solution of overdamped equation

Starting from continuous Langevin equation witth no interactions ($F = 0$)

$$m\frac{dv}{dt} = -\gamma v + \Gamma\eta(t)$$

we can handwavy take the limit of $m \to 0$ and rewrite as:

$$0 = -\gamma v + \Gamma\eta(t) \Rightarrow \gamma v(t) = \Gamma\eta(t).$$

Formally, you can write analytical solution for this equation:

$$v(t) = v(t')e^{-\frac{\gamma(t-t')}{m}} + \frac{1}{m}\int_{t'}^{t} d\tau e^{-\frac{\gamma(t-\tau)}{m}}\Gamma\eta(\tau)$$

1.3 Brownian motion for spherical particles

One of the most common procedure to simulate the **translational** brownian motion of spherical particles is the algorithm by Ermak and McCammon [2].

It is different if we are interested in the **rotational** degrees of motion. We'll need an additional brownian equation for the rotational motion. Approaching this problem leads to some degeneracy due to the integraion of

Euler angles and the paper from Ilie [4] solve this issue using an integration scheme for the orientation involving the quaternions. I think is still first order in δt.

Another work from [1] deal with that problem.

1.4 LAMMPS implementation of BD

We consider only the fix brownian/sphere.

it is not like fix langevin that adds force and torques terms but it rewrite and integrate the equation of motion.

Let's assume spherical particles, so friction tensor is diagonal:

$$d\mathbf{r} = \frac{1}{\gamma_t}\mathbf{F}dt + \sqrt{\frac{2K_BT}{\gamma_t}}d\mathbf{W}_t = \frac{D}{K_BT}\mathbf{F}dt + \sqrt{2D}\; d\mathbf{W}_t$$

Reminder: $d\mathbf{W}_t$ has units of $\sqrt{s}$

Given that $< d\mathbf{W}_t^2 >= dt$ I can rewrite it in terms of **unit** gaussian noise $\mu(t)\; d\mathbf{W}_t = \sqrt{dt} * \eta(t)$

In theory, the diffusion coefficient is given by $D_t = \frac{K_BT}{\gamma_t} = \frac{T}{\gamma_t}$ and rotational by $D_t = \frac{K_BT}{\gamma_r} = \frac{T}{\gamma_r}$.

1.5 General Numerical implementation of BD

Brownian dynamics algorithm use first order differential equation to propagate only positions in time.

The simplest integration scheme is a modified first order (in Δt) Euler scheme called Euler-Maruyama:

$$x(t+\Delta t) = x(t) + \frac{1}{\gamma_t}F(t)\Delta t + \sqrt{\frac{2K_BT}{\gamma_t}}\sqrt{\Delta t}\;\eta(t)$$

where $\eta(t)$ is a Gaussian or Uniform random number generator. see [?] for correctness of uniform distribution

There is higher order integration scheme allowing large time step being used. You evaluate more times the functions (like runge-kutta 4 evaluates 4 times the functions ? check pls)

Which are the timestep recommendation or limits of validity

- One condition for using BD is that the conservative forces vary only slightly over the course of the timestep. This introduce another time scale in addition to the τ_{BD}.
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2 Langevin Dynamics

2.1 From continuous to discrete Langevin equation

Starting from continuous Langevin euqation:

$$\frac{dv}{dt} = -\gamma v + \Gamma\eta(t)$$

with $\langle\eta(t)\rangle = 0$ and $\langle\eta(t)\eta(t')\rangle = \delta(t-t')$

To perform discretization $t \to n\tau$, $v(t) \to v_n$, $\eta(t) \to \eta_n$, $\frac{dv}{dt} \to \frac{v_{n+1}-v_n}{\tau}$ and $\delta(t-t') \to \frac{1}{\tau}\delta_{ij}$. Following $\langle\eta_n\rangle = 0$ and $\langle\eta_i\eta_j\rangle = \frac{1}{\tau}\delta_{ij}$

Note: The τ at denominator of the delta is important because of dimension: dirac delta is dimensionfull while Kronecker delta is dimensionless.

$$\frac{v_{n+1}-v_n}{\tau} = -\gamma v_n + \Gamma\sqrt{\frac{1}{\tau}}_n \eta_n$$

$$v_{n+1} = v_n - \gamma v_n\tau + \Gamma\tau\sqrt{\frac{1}{\tau}}\eta_n$$

$$v_{n+1} = v_n - \gamma v_n\tau + \Gamma\sqrt{\tau}\eta_n$$

Note: In the discretized version the $\sqrt{\tau}$ dependence of the random noise term emerge clearly.

2.2 General Numerical implementation of LD

One main difference is that solving the underdamped Langevin equation is a second order PDE while Brownian motion is a first order PDE. Try to understand what would be the speed up between the two cases ?

2.3 LAMMPS implementation of LD

LAMMPS uses a very simple integration scheme. It is the Velocity-Verlet algorithm where the force on a particle includes the friction drag term and the noise term. Since it is just a first order algorithm in terms of the random noise, it can not be used for large friction case.

2.4 Details of LE in MD

In molecular simulations, we want to compute statistical averages (i.e. ensemble averages) of observables MD uses the Ergodic hypothesis:

$$\langle A \rangle_{trajectory} = \langle A \rangle_{ensemble}$$

Accurate trajectories are not important Instead, the correct physical ensemble should be described throughout the simulation: - Conservation of energy, linear and angular momentum - Time-reversibility - (In fact: conservation of phase space)

Integrators that do this are "long-time stable" (or "symplectic")

with LD integrators you loose some of the sympletic integrators

Nice side-effect: LD thermalizes the system (simulates constant temperature, NVT ensemble) l Locality of the random force destroys hydrodynamic interactions

2.5 Reminder on fix langevin

2.5.1 random force term

From the fix langevin page of lammps documentation you will find the following:

$$F = F_c + F_f + F_r$$

$$F_f = -\frac{m}{\text{damp}} v$$

$$F_r \propto \sqrt{\frac{k_B T m}{dt \text{ damp}}}$$

The dt in denominator under the square root should not be a problem or a mistery is the same term found above in the discretization of the langevin equation. The F_r random force term will be integrated in time multiplying the term for dt, recovering the $t^{1/2}$ dependence.

Note: what change my diffusion coefficient is not only the damp parameter, but the coupling damp $\cdot$ dt. it makes no sense to compare simulations with different timestep! On the other hand with certain value of damp you should use a smaller timestep respect to the case with smaller damp parameter. Also, F_r depends on coupling but the friction temr F_f depends from damp only. So it would not be correct to compare simulations with same coupling!

Note: in this case dt is unitless, it is referred to the fraction of time units τ defined in lammps. damp instead has the dimension of a time. In this way the above formulas are consistent.

2.5.2 rotational friction coefficient

For a sphere of radius r and assuming no slip boundary conditions(speed fluid at the boundary is zero) with the fluid.

$$\gamma_r = \frac{4}{3}\gamma_t r^2$$

We can verify that using Stokes-Einstein-Debye relation for translational friction coefficient:

$$\gamma_t = 6\pi\mu r$$

for rotating instead we have

$$\gamma_t = 8\pi\mu r^3$$

2.5.3 rotational friction coefficient in LAMMPS

In lammps formalism,a scale factor of $\frac{10}{3}$ will be applied to the F_f damping term and $\sqrt{\frac{10}{3}}$ to the random force term F_r. see discussion on `https://matsci.org/t/error-in-fix-langevin/16327/3`

The factor is not $\frac{4}{3}$ because it express in terms of inertia of a sphere $I = \frac{2}{5}mR^2$.

2.5.4 details on the implementation in lammps

In lammps langevin equation are implemented modifying the forces and the torques:

$$F = -\frac{m}{damp} + \sqrt{\frac{24mK_BT}{\text{damp } dt}}\eta$$

$$T = -\frac{10}{3}\frac{I}{damp}\omega + \sqrt{\frac{80IK_BT}{\text{damp } dt}}\eta = -\frac{4}{3}\frac{mr^2}{damp}\omega + \sqrt{\frac{32mr^2K_BT}{\text{damp } dt}}\eta$$

i still not understand why there is 24 and 80 as factor (?) see `https://matsci.org/t/brownian-dynamics-in-lammps/13739`. the factors should come from the uniform random number generator, see [3] or [5].

2.5.5 bound on time scales

I would like to have clear which are the upper and lower bounds for langevin integrator in lammps and why it breaks when I use a lammps damp parameter too high (10)

also minimum/maximum timestep

However, the algorithm LAMMPS use to integrate Langevin dynamics equation is Velocity-Verlet. This is not suitable for high friction(overdamped) simulation.

2.6 Timescales between LD or BD

To decide whether to use LD or BD in the simulation, one need to compare relevant timescales. Consider a free particle governed by the Langevin equation:

$$m\ddot{x} = -\nabla U(x) - \gamma\dot{x} + \mathbf{R}(t)$$

Solving for the velocity autocorrelation function leads to,

$$< v(0)v(t) >= \frac{K_B T}{m} e^{-t/\tau_m}$$

.

This shows that the relaxation time for momentum is $\tau_m = \frac{m}{\gamma}$. γ is the drag coefficient. $[\gamma] = \frac{[\text{kg}]}{[\text{s}]}$.

There is another timescale called Brownian timescale at which the particle diffuses about its own size. Starting from diffusion relation:

$$x^2 = Dt = \frac{kT}{\gamma}$$

and substituting for $x = \sigma$ you get $\tau_{BD} = \sigma^2 \frac{\gamma}{K_B T}$ where σ is the size of the particle.

If $\tau_{BD} \gg \tau_m$ and if you are not interested at the dynamics on the timescale τ_m, then one can use BD since the momentum can be safely integrated out. However, if these two timescales are comparable or $\tau_{BD} < \tau_m$, then only LD can be used because the momentum cannot be neglected in this case.

To make the proble more complicated, there are more than just these two timescales in most of simulation cases, such as the relaxation time of bond vibration, etc... Fortunately, practically, comparing these two timescales is good enough for many cases.

Estimated values: we can check if we are in the overdamped case:

Viscosity for water: $\mu = 1 \times 10^{-3} kgm^{-1}s^{-1}$

$\gamma = 6\pi\mu\sigma = 6\pi 10^{-3} 1.4 \times 10^{-}9 = 2.63 \times 10^{-11} kg/s$

$\tau_m = \frac{m}{\gamma} = \frac{3.63 \times 10^{-24}}{2.63 \times 10^{-11}} = 1.38 \times 10^{-13} s$

$\tau_{BD} = \frac{\sigma^2 \gamma}{KT} = \frac{(1.4 \times 10^{-9})^2 \, 2.63 \times 10^{-11}}{410 \times 10^{-23}} = 1.25 \times 10^{-8} s$

In principle yes, we should use Brownian dynamics and not Langevin because we are observing timescale 5 orders of magnitude bigger than the momentum relaxation scale.

3 Numerical integrators

- verlet type for MD
- Euler for general ode first order
- definition of implicit/explicit method, their stability
-

References

[1] Steven Delong, Florencio Balboa Usabiaga, and Aleksandar Donev. Brownian dynamics of confined rigid bodies. 143(14):144107.

[2] Donald L. Ermak and J. A. McCammon. Brownian dynamics with hydrodynamic interactions. 69(4):1352–1360.

[3] given-i=BURKHARD family=DÜNWEG, given=BURKHARD and given-i=WOLFGANG family=PAUL, given=WOLFGANG. BROWNIAN DYNAMICS SIMULATIONS WITHOUT GAUSSIAN RANDOM NUMBERS.

[4] Ioana M. Ilie, Wim J. Briels, and Wouter K. Den Otter. An elementary singularity-free Rotational Brownian Dynamics algorithm for anisotropic particles. 142(11):114103.

[5] T. Schneider and E. Stoll. Molecular-dynamics study of a three-dimensional one-component model for distortive phase transitions. 17(3):1302–1322.