Molecular dynamics is the numerical integration of Hamilton / Newton's equations for a large number of interacting particles.

Several things are necessary:

(1) Specify the force field or interaction potential $\mathcal{U}(r_1, \ldots, r_N)$ ← usually empirical
→ chemistry, physics (quantum)

(2) Specify the ensemble in which the calculation is to be performed. Purely Hamiltonian MD is in the microcanonical or NVE ensemble.

(3) Specify the (periodic) boundary conditions

(4) Numerical algorithm

Force field

$$\mathcal{U} = \mathcal{U}_{ext} + \underbrace{\sum_{i<j} u(r_i, r_j)}_{\text{pairwise interactions}} + \underbrace{\sum_{i,j,k} u(r_i, r_j, r_k)}_{\text{triplets}}$$

Interactions are classified according to some common features:

(1) Bonded interactions are chemical bonds between specified particles that remain close forever due to the presence of a strong bond.

$$\mathcal{U}_{bonded} = \sum_{bonds} K_r (r - r_{eq})^2 + \sum_{angles} K_\theta (\theta - \theta_{eq})^2$$

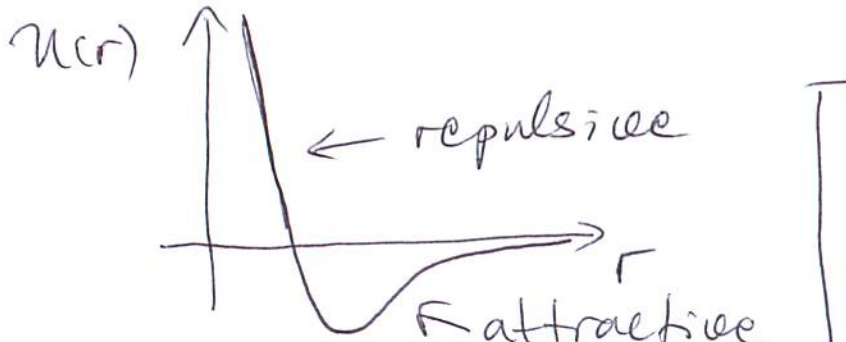
+ hydrogen bonds etc.

(2) Non-bonded interactions:

a) **Short-ranged** or near-neighbor interactions

[requires data structures and algorithms such as linked-list cells (LLCs) or near-neighbor lists (NNLs), see review of AED particle methods by A. Donev]

$$U_{LJ} = \sum_{i,j} \frac{A_{ij}}{r_{ij}^{12}} - \frac{B_{ij}}{r_{ij}^{6}}$$ ← Lennard Jones



b) **Long-ranged** (slower than r^{-d} decay) notably **electrostatic**

$$U_E = \sum_{i,j} \frac{q_i q_j}{r_{ij}}$$ ← Requires FAST SUMMATION algorithms (FFTs, FMMs)

Temperal integraters for MD are a tricky subject. Naively using standard ODE methods such as RK45 is not a good idea.

A good integrator would:

1) Minimize force-field calculations per time step
2) Conserve energy with no systematic drifts over long periods
3) Maximize time step while remaining stable
4) Reproduce the correct physics (???)
   → This is a chaotic system so no pathwise convergence

One of the crucial properties of Hamiltonian dynamics is the Incompressibility of phase flow (Liouville's theorem).

Another way to state this is that the flow map $z(t) = z \longrightarrow z' = z(t+\Delta t)$ has unit Jacobian, i.e., it preserves volume in phase space:

really oriented area

$$\left| \frac{\partial z'}{\partial z} \right| = \left| \frac{\partial (q', p')}{\partial (q, p)} \right| = 1$$

where $J = \frac{\partial z'}{\partial z}$ is the Jacobian matrix of the flow map.

$$\frac{\partial p'}{\partial p}\frac{\partial q'}{\partial q} - \frac{\partial p'}{\partial q}\frac{\partial q'}{\partial p} = 1$$

which is written in matrix form as

$$\boxed{J^T L_0 J = L_0} = \begin{bmatrix} 0 & I \\ -I & 0 \end{bmatrix}$$

This ensures that Hamilton's equations are invariant, i.e., that the transformation $z \to z'$ is a canonical one

$$\dot{z}' = L_0 \frac{\partial H}{\partial z'} \quad \text{if} \quad \dot{z} = L_0 \frac{\partial H}{\partial z}$$

NOTE: $|J| = 1$ automatically

For numerical schemes, the discrete flow map is simply advancing the time from t to $t+\Delta t$, where Δt is the time-step. The condition

$$J^T L_0 J = L_0$$

characterizes symplectic integrators, which seem to have many favorable properties for long-time integration.

(See review article by Tony Ladd)

Consider "sequential-Euler" method

$$\begin{cases} q' = q + \frac{p}{m}\Delta t & \text{new position} \\ p' = p + F(q')\Delta t = p + F\left(q + \frac{p}{m}\Delta t\right)\Delta t \end{cases}$$

$$J = \begin{bmatrix} \frac{\partial q'}{\partial q} & \frac{\partial q'}{\partial p} \\ \frac{\partial p'}{\partial q} & \frac{\partial p'}{\partial p} \end{bmatrix} = \begin{bmatrix} 1 & \Delta t/m \\ \Delta t\, F'(q') & 1 + \frac{\Delta t^2}{m} F'(q') \end{bmatrix}$$

which does satisfy $J^T L_0 J = L_0$, so the method is symplectic. (but still only first-order in terms of local truncation error)

The midpoint (implicit) method:

$$\begin{cases} q' = q + \frac{\Delta t}{2m}(p + p') \\ p' = p + \frac{\Delta t}{2}\left[F(q) + F(q')\right] \end{cases}$$

try it!

is also symplectic, but expensive

To construct higher-order symplectic integraters that are explicit and simple, we can use operator-splitting.

Recall the Liouville operator

$$iL = \frac{\partial H}{\partial p}\cdot\frac{\partial}{\partial q} - \frac{\partial H}{\partial q}\cdot\frac{\partial}{\partial p} = -\frac{\partial H}{\partial z}\cdot L_0\,\frac{\partial}{\partial z}$$

The evolution law for any observeable

$$X = X(z)$$

is given by

$$\boxed{\dot{X} = iLX} \Rightarrow \boxed{X(t) = e^{iLt}\,X(0)}$$

where $e^{At} = \sum_{n=0}^{\infty} \frac{(At)^n}{n!}$ is the exponential of an operator

The classical or Liouville propagator

$$\exp(iLt)$$

contains the solution entirely, e.g. the probability density

$$\rho(t) = e^{-iLt} \cdot \rho(0)$$

If we split the dynamics into components

$$L = L_1 + L_2$$

then this decomposition corresponds to two propagators

$$e^{iL_1 t} \quad \text{and} \quad e^{iL_2 t}$$

If L_1 and L_2 commute, i.e., if

$$L_1 L_2 = L_2 L_1$$

then this means the two physical processes are independent and can be applied independently in <u>any</u> order,

$$e^{iLt} = e^{i(L_1+L_2)t} = e^{iL_1 t} e^{iL_2 t}$$

Making the approximation

$$e^{iLt} \approx e^{iL_1 t} e^{iL_2 t}$$

is a splitting algorithm, and corresponds to <u>sequential</u> application of two exact propagators, each of which only contains part of the physics.

In terms of the Jacobians

$$J = J_1 J_2 \quad \text{by chain rule}$$

$$\Rightarrow J^T L_0 J = J_2^T \underbrace{J_1^T L_0 J_1}_{L_0} J_2 = J_2^T L_0 J_2 = L_0$$

if J_1 and J_2 are symplectic.

Composing symplectic integrators in any order thus gives a new symplectic integrator. The order matters, and the best second-order one is the Strang-type splitting:

$$e^{iL\Delta t} \approx e^{iL_1 \Delta t/2} e^{iL_2 \Delta t} e^{iL_1 \Delta t/2} + O(\Delta t^3)$$

Convergence of the numerical solution as $\Delta t \to 0$ is demonstrated via Trotter's theorem

$$e^{A+B} = \lim_{N\to\infty} \left(e^{A/N} e^{B/N} \right)^N$$

The best known splitting for Hamilton's equations is

$$iL_1 = \frac{\partial H}{\partial p} \cdot \frac{\partial}{\partial q} \leftarrow \text{Fixed momentum (streaming or free advection)}$$

$$iL_2 = -\frac{\partial H}{\partial q} \cdot \frac{\partial}{\partial p} \leftarrow \text{Fixed position and thus } \underline{\text{fixed Force}} \text{ momentum kick}$$

The approximation $e^{iL_1\Delta t/2}\, e^{iL_2\Delta t}\, e^{iL_1\Delta t/2}$ corresponds to the so-called (positional) Verlet algorithm: $v^n \equiv v(n\Delta t)$

$$\begin{cases} r^{n+1/2} = r^n + v^n \dfrac{\Delta t}{2} \\ v^{n+1} = v^n + \dfrac{\Delta t}{m} F(r^{n+1/2}) \leftarrow \text{single force calculation} \\ r^{n+1} = r^{n+1/2} + v^{n+1} \dfrac{\Delta t}{2} \end{cases}$$

$$\Rightarrow \begin{cases} r^{n+1} = r^n + v^n \Delta t + \dfrac{\Delta t^2}{2m} F\left(r^n + v^n \dfrac{\Delta t}{2}\right) \\ v^{n+1} = v^n + \dfrac{\Delta t}{m} F\left(r^n + v^n \dfrac{\Delta t}{2}\right) \end{cases}$$

the approximation $e^{iL_2\Delta t/2}\, e^{iL_1\Delta t}\, e^{iL_2\Delta t/2}$ corresponds to the velocity Verlet algorithm:

$$\begin{cases} v^{n+1/2} = v^n + \frac{\Delta t}{2m} F(r^n) \\ r^{n+1} = r^n + \Delta t \cdot v^{n+1/2} \\ v^{n+1} = v^{n+1/2} + \frac{\Delta t}{2m} F(r^{n+1}) \end{cases}$$

two force calculations BUT reuse NEXT STEP!

$$\Rightarrow \begin{cases} r^{n+1} = r^n + v^n \Delta t + \frac{\Delta t^2}{2m} F(r^n) \\ v^{n+1} = v^n + \frac{\Delta t}{2m}\left[F(r^n) + F(r^{n+1}) \right] \end{cases}$$

Observe however that these two (velocity and positional Verlet) are identical if observed after a long period:

$$e^{iL_1\Delta t/2}\, e^{iL_2\Delta t}\, e^{iL_1\Delta t/2}\, e^{iL_1\Delta t/2}\, e^{iL_2\Delta t}\, e^{iL_1\Delta t/2}$$

$$= \ldots e^{iL_2\Delta t}\, e^{iL_1\Delta t}\, e^{iL_2\Delta t} \ldots$$

So this is just "sequential":

$$\frac{r^{n+1} - 2r^n + r^{n-1}}{\Delta t^2} = \frac{F(r^n)}{m}$$

"classic" Stormer-Verlet algorithm

Example:

Integrating the motion of a Harmonic oscillator

$$H = \frac{m v^2}{2} + \frac{m \omega^2 q^2}{2}$$

For the Verlet algorithms, the Hamiltonian (energy) is not conserved exactly, but it can be shown that a shadow hamiltonian is conserved strictly:

$$H_{\Delta t} = \frac{p^2}{2m(\Delta t)} + \frac{m(\Delta t)\,\omega^2(\Delta t)\,q^2}{2}$$

e.g. $m(\Delta t) = m\left(1 - \omega \frac{\Delta t}{2}\right)$ for velocity Verlet