Integrating the Equations of Motion

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Newton's second law

- MD is just solving an initial value problem.
  - Initial velocities are random.
  - Science is in the dynamics, not the end point.

$$x' = v$$

$$v' = -1/m \, dU/dx$$

Numerical integration

- Given x(0), v(0), find x(t), v(t).
- Many advanced general methods for solving this type of differential equation problem:
  - High order approximations
  - Predictor corrector methods
  - Adaptive timesteps
- None of these are used in practice (for MD).

Biomolecular simulations

- Large number of degrees of freedom.
- Most oscillations on order of 10 fs.
- Evaluating forces is very expensive.
- Exact solution is not meaningful.
- Chaotic dependence on small perturbation.
- Long-time properties of great interest.

Hamiltonian systems

- Certain properties are of great importance:
  - Conservation of energy (the Hamiltonian).
  - Conservation of volume in phase space.
- Ideal integrator preserves these quantities.

Time reversibility

- Newtonian equations are reversible:
  - Set v to -v and the system runs backwards.
- Useful property in an integrator.
- Eliminates adaptive timestepping.
- Floating point arithmetic is not reversible, so an implementation will only be approximately reversible over a short time.

Symplectic integrators

- A symplectic transformation:
  - Determinant of Hessian is one.
  - Conserves volume in phase space.
- A symplectic integrator:
  - Uses symplectic transformation at each step.
  - Exactly integrates a “nearby” Hamiltonian.
  - Conserves energy over a long period, provided there are no resonances present.

Verlet leapfrog integrator

- Elegant, efficient, symplectic.
- Single fixed timestep h (usually 1 fs).

$$v_{1/2} = v_0 + h \cdot F(x_0) / 2m$$

$$x_1 = x_0 + h \cdot v_{1/2}$$

$$v_1 = v_{1/2} + h \cdot F(x_1) / 2m$$

Multiple timestepping

- Some parts of the force field are:
  - Expensive to calculate,
  - Slowly changing.
- Ideally these terms can be calculated less frequently than more rapid terms such as bonds and angle vibrations.
- There are limits imposed by resonance.

R-respa integrator

- Decompose F into fast and slow parts.
- Apply fast forces every timestep.
- Apply slow forces only every k steps, but with k times the impulse.
- Known as an impulse method or reference system propagator algorithm.

Rigid bonds

- Timestep can be increased to 2 fs by fixing the fastest bonds - those involving H atoms.
- SHAKE/Rattle algorithm:
  - Updates along vector from previous step.
  - Scale by 1/m to conserve momentum.
  - Iterate until convergence.

Estimating temperature

- Equipartition theorem gives kT/2 per DOF.
- Kinetic energy estimates T = 2E/3Nk.
- Need to subract DOF for:
  - Fixed atoms
  - Rigid bonds
  - Zero linear momentum
  - Zero angular momentum

Controlling temperature

- NVE ensemble:
  - Equilibrate at target temperature first.
- NVT ensemble:
  - Couple to heat bath to maintain temperature.
  - Ensure proper energy fluctuations.
- Minor difference in simulation results.

Periodic rescaling

- Calculate average temperature.
- Rescale velocities to match target.
- Minor change to dynamics, simple method.
- However, if done too frequently:
  - Drives kinetic energy to slowest DOF.
  - Results in “flying ice cube” behavior.
- May keep hot side hot, cold side cold.

Periodic reassignment

- Periodically reinitialize velocities.
- Drastically discontinuities in dynamics.
- Ensures entire system is equilibrated.
- Samples from canonical ensemble.
- Useful for simulated annealing.
- Limits sampling if done too frequently.

Nose-Hoover Thermostats

- Add variable "friction" to dynamics.
- Berendsen: friction proportional to T_0-T.
- Nose-Hoover: control friction "velocity"
  - Reversible system of equations.
  - Extra state variable to keep track of.

$$v' = -1/m\ dU/dx - \xi v$$

Langevin dynamics

- Constant friction with random noise.
- Atomic rather than global control.
- No extra state variables required.
- Samples from canonical ensemble.

$$v' = -1/m\ dU/dx - \xi v + R(t)$$

Estimating pressure

- Think ideal gas plus continuum mechanics.

$$P = \sum (m\ v\ v + F\ r) / 3V$$

- Sum may be over atoms or molecules.
- Atomic pressure fluctuates wildly.
- Molecular pressure inefficient to calculate.
- Compromise based on hydrogen groups.

Controlling pressure

- Basic (and wrong) equation is PV=NkT.
- Control P by varying V:
  - Rescale periodic cell.
  - Rescale atomic coordinates for atomic virial.
  - Rescale group coordinates for group virial.
- Pressure oscillates rapidly for small system, macroscopic observable is the time average.

Berendsen's method

- Simple first-order method.
- Goal is $P' = (P - P_0)/\tau$
- At each step, rescale volume by

$$1 + B_T h\,(P - P_0)/\tau$$

- Requires knowledge of compressibility.
- Controls pressure, not desired ensemble.

Nose-Hoover barostats

- Use ln V as a dynamic variable.
- Couple acceleration of ln V to pressure.
- Only parameter is timescale of fluctuation.

$$x' = v + \varepsilon' x \qquad V' = 3V\varepsilon'$$

$$v' = -1/m\ dU/dx - \varepsilon' v$$

$$\varepsilon'' = (3V/W)(P - P_0)$$

Langevin piston method

- Nose-Hoover can exhibit ringing.
- Apply Langevin dynamics to ln V.
- Adds parameter for damping timescale.

$$\varepsilon'' = (3V/W)(P-P_0) - \gamma\,\varepsilon' + R(t)$$