

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.

$$\dot{x} = v$$

$$\dot{v} = -\frac{1}{m} \frac{\partial U}{\partial x}$$



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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).



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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.



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Hamiltonian systems

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



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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.



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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.



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Verlet leapfrog integrator

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

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

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

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



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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.



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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.



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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 subtract 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.



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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.



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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.



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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.

$$\dot{v} = -\frac{1}{m} \frac{\partial U}{\partial x} - \xi v$$



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Langevin dynamics

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

$$\dot{v} = -\frac{1}{m} \frac{\partial U}{\partial x} - \xi v + R(t)$$



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Estimating pressure

- Think ideal gas plus continuum mechanics.

$$P = \sum (mv^2 + \vec{F} \cdot \vec{r}) / 3V$$

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



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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.



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Berendsen's method

- Simple first-order method.
- Goal is $\dot{P} = (P - P_0) / \tau$
- At each step, rescale volume by
$$1 + \beta_T h (P - P_0) / \tau$$
- Requires knowledge of compressibility.
- Controls pressure, not desired ensemble.



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Nose-Hoover barostats

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

$$\begin{aligned}\dot{x} &= v + \dot{\epsilon}x & \dot{V} &= 3V\dot{\epsilon} \\ \dot{v} &= -\frac{1}{m} \frac{\partial U}{\partial x} - \dot{\epsilon}v & \ddot{\epsilon} &= (3V/W)(P - P_0)\end{aligned}$$



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Langevin piston method

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

$$\ddot{\epsilon} = (3V/W)(P - P_0) - \gamma\dot{\epsilon} + R(t)$$



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