Molecular Dynamics: *Basics*

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Our Itinerary

- Why molecular dynamics?
- Resources and codes
- Classical mechanics and the connection to kinetic theory
- Forces
- Initial conditions and boundary conditions
- Integrators
- Thermostats
- Analysis

Next lecture: details and examples specific to high energy density physics.

Molecular Dynamics: What Is It?

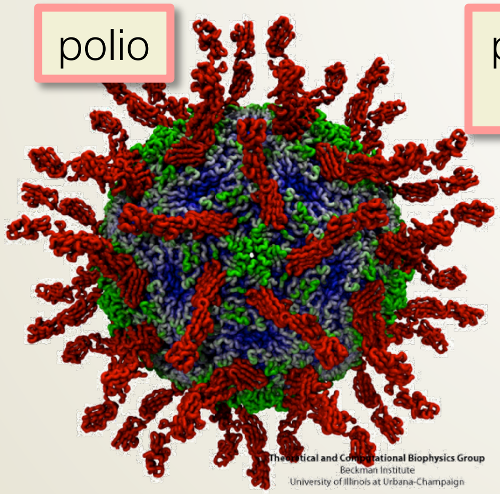
1) Molecular dynamics (MD) is a simulation method; that is, a computational method for solving hard, non-linear problems.

2) MD simulates particles to yield an understanding of how many-body interactions determine *time-dependent* material properties.

3) Particles are treated as discrete objects and forces are computed to high precision ("exactly").

4) Typically, MD is implemented as an atomistic method. The particles are electrons or ions.

polio



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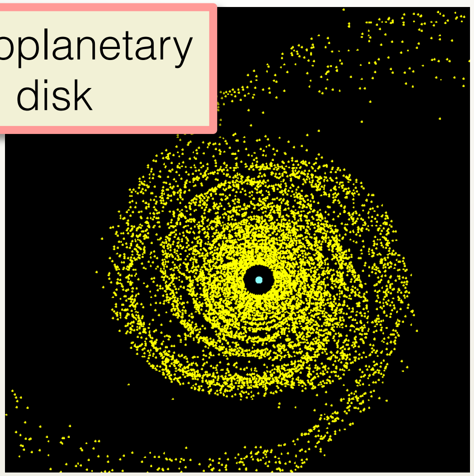
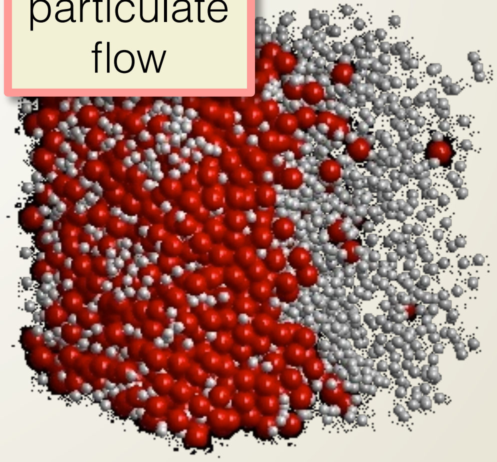
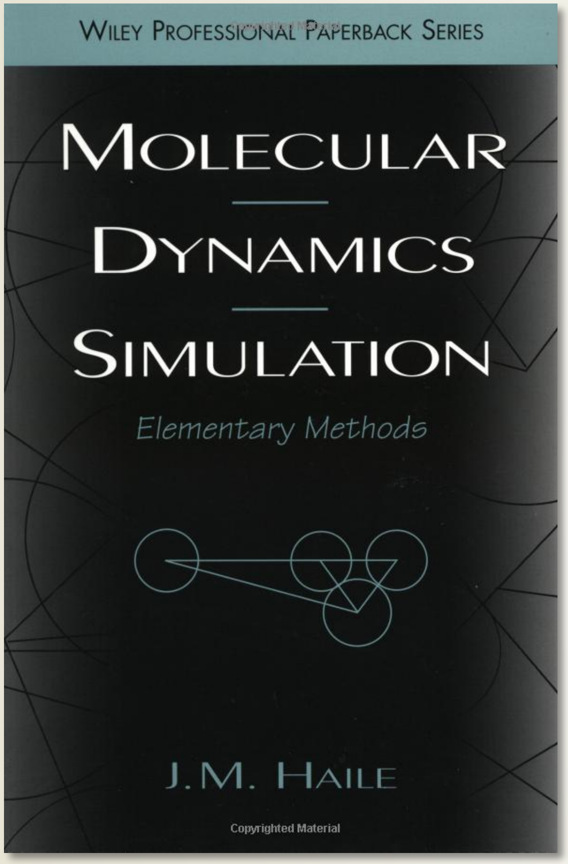
protoplanetary disk



particulate flow



Where To Look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MOLECULAR DYNAMICS SIMULATION

Elementary Methods

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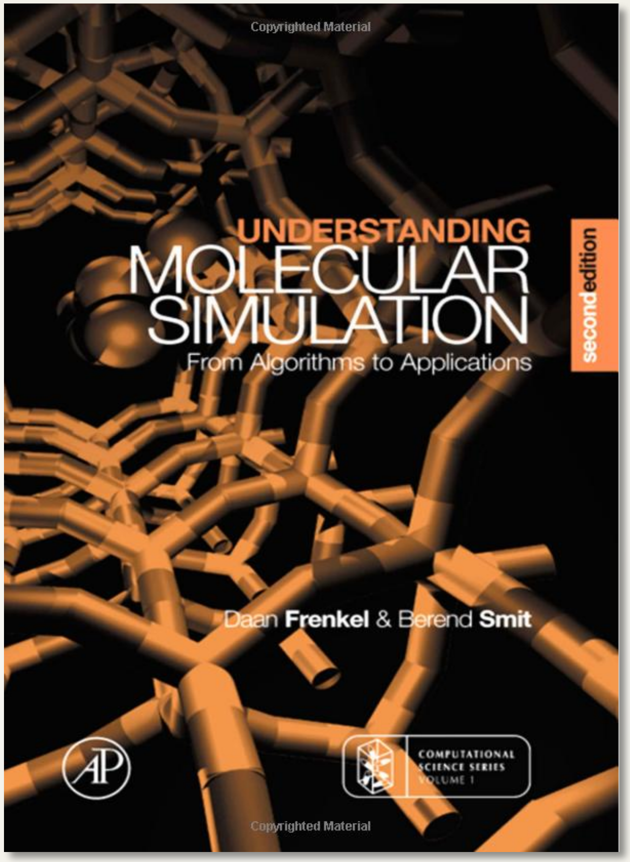

UNDERSTANDING MOLECULAR SIMULATION

From Algorithms to Applications

second edition

Daan Frenkel & Berend Smit

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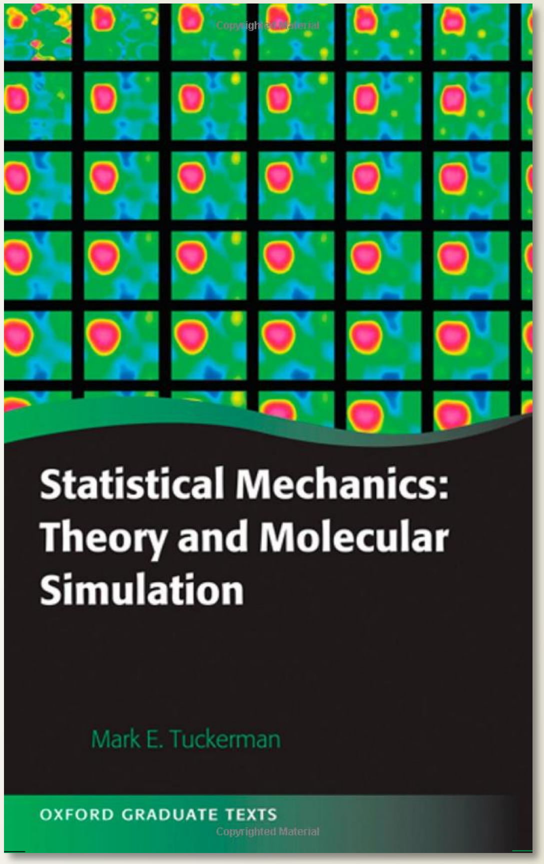
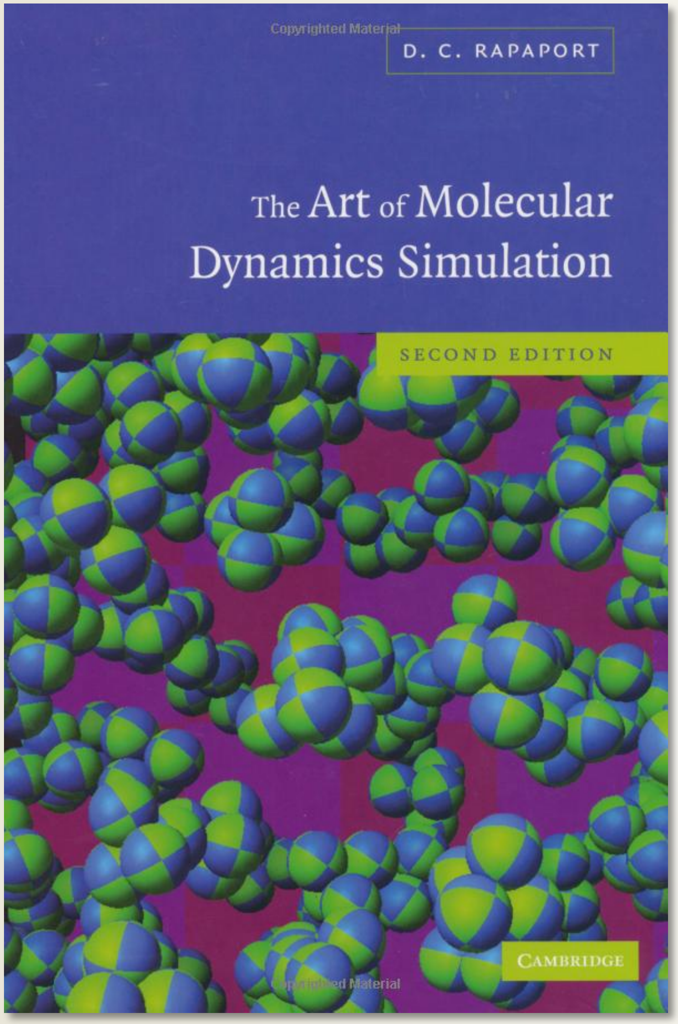

Statistical Mechanics: Theory and Molecular Simulation

Mark E. Tuckerman

OXFORD GRADUATE TEXTS

More: Where To Look



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The Art of Molecular Dynamics Simulation

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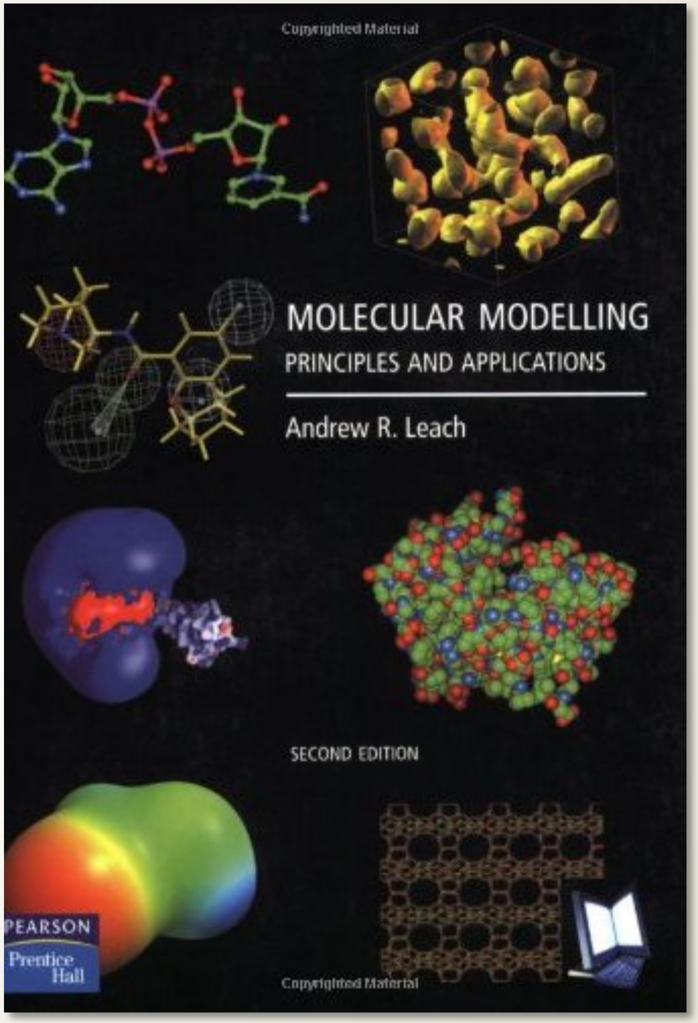

MOLECULAR MODELLING

PRINCIPLES AND APPLICATIONS

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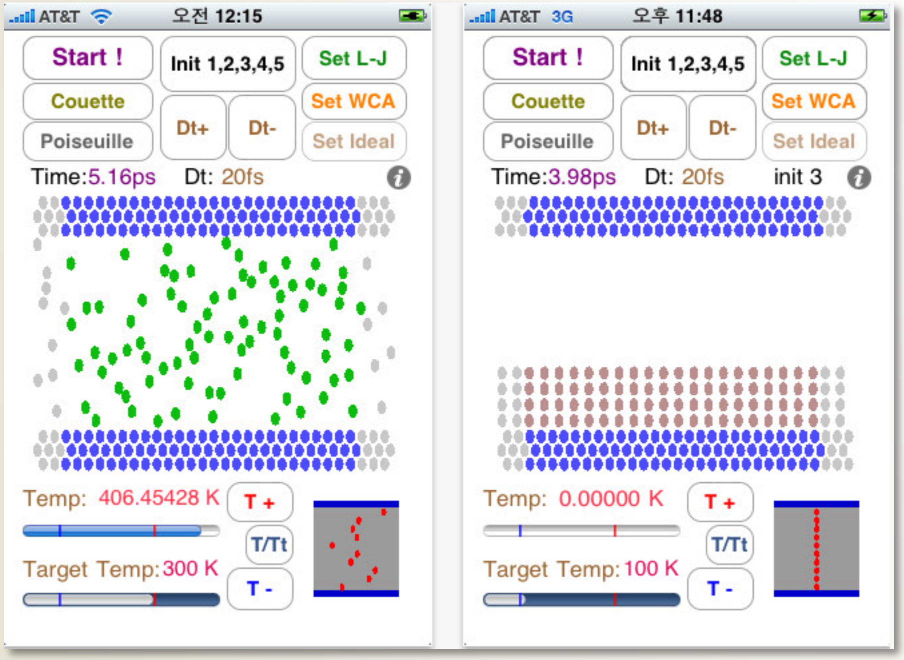
Of Course…The Internet

http://en.wikipedia.org/wiki/Molecular_dynamics

Free apps:



Time:5.16ps Dt: 20fs

Temp: 406.45428 K

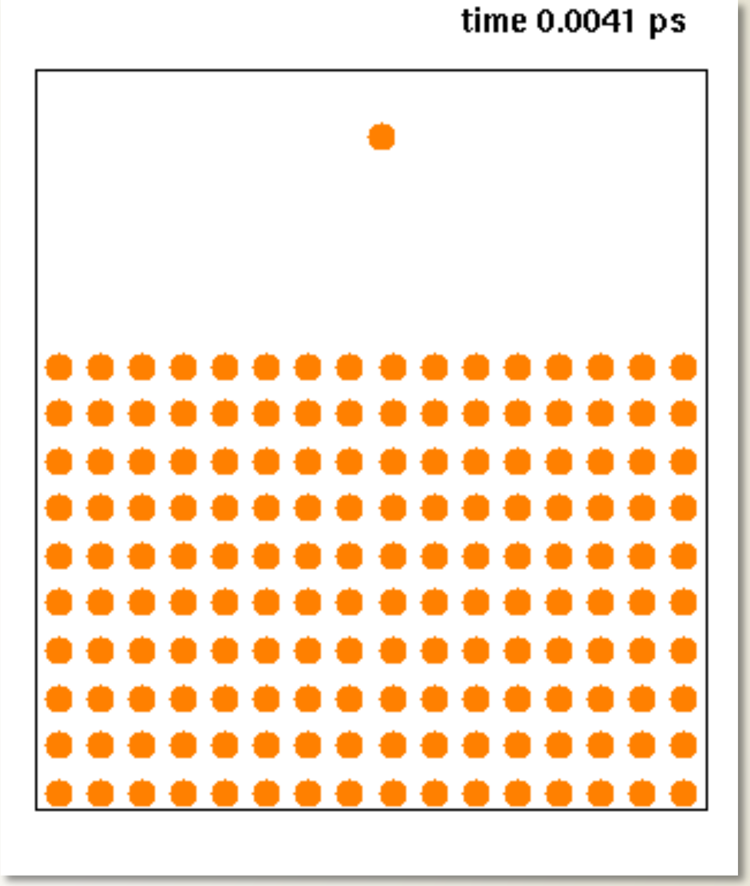
Target Temp: 300 K

Time:3.98ps Dt: 20fs init 3

Temp: 0.00000 K

Target Temp: 100 K

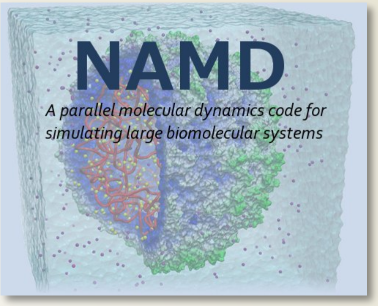
i2DMD



Molecular dynamics computer simulation of the deposition of a single copper atom with a kinetic energy of 1 eV on a copper surface. Technical details: cross section of two atom layers in the middle of a larger (10x10x10 unit cells) 3D simulation cell. Simulation made with Sabochick-Lam embedded-atom method potential, Berendsen temperature control used only at the outer boundaries to scale temperature down to 0 K. Initial temperature 0 K (cell prerelaxed to allow for surface relaxation inwards). This kind of processes occur in reality during physical vapour deposition.

Examples of MD Codes

1. NAMD (Not (just) Another Molecular Dynamics (code))
    - ✓ Free
    - ✓ Structural biology
    - ✓ http://www.ks.uiuc.edu/Research/namd/
2. Gromacs (GROningen MAchine for Chemical Simulation)
    - ✓ GNU GPL
    - ✓ Structural biology/polymers
    - ✓ http://www.gromacs.org/
3. VASP (Vienna Ab initio Simulation Package)
    - ✓ DFT-MD
    - ✓ Not public domain; must obtain license
    - ✓ http://www.vasp.at/
4. LAMMPS
5. AMBER (Assisted Model Building with Energy Refinement)
6. Etc.

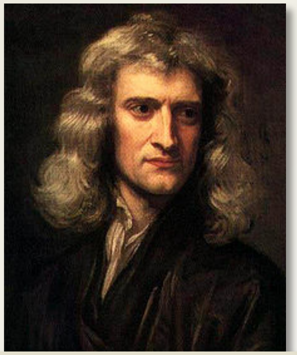


GROMACS FAST. FLEXIBLE. FREE.

VASP b-initio ackage imulation ienna

LAMMPS

Building an MD Code Starting From Newton


Sir Isaac Newton

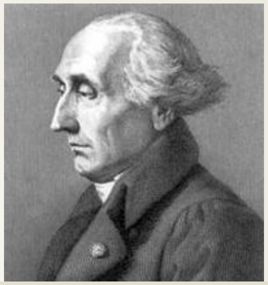
$$\begin{aligned} F &= ma \\ &= m\ddot{x}(t) \end{aligned}$$

1. Figure out what your forces are.
   - ✓ This can be quite simple or require complex calculations.
2. Identify the initial conditions and boundary conditions.
   - ✓ Thermal equilibrium or non-equilibrium? Periodic?
3. Integrate Newton's Second Law to obtain trajectories.
   - ✓ Identify optimal numerical scheme for your problem.
4. Process data to generate observables.
   - ✓ Pre-compute during run or post-process. Visualization.

Reformulate: Hamiltonians and Lagrangians

Classical mechanics can be reformulated in a number of ways, each of which reveals something interesting and useful.

William Rowan Hamilton



Joseph-Louis Lagrange

$$
\begin{aligned}
H &= \sum_{i=1}^{N} \frac{p_i^2}{2m_i} + U(q) \\
\frac{dp_i}{dt} &= -\frac{\partial H}{\partial q_i} \\
\frac{dq_i}{dt} &= \frac{\partial H}{\partial p_i}
\end{aligned}
$$

$$
\begin{aligned}
S &= \int_{t_1}^{t_2} dt\, L(t) \\
L &= T - U \\
\delta S &= 0 \\
\frac{d}{dt}\frac{\partial L}{\partial \dot{q}_i} &= \frac{\partial L}{\partial q_i}
\end{aligned}
$$

MD and Kinetic Theory: The Connection

Question: What is the probability of finding a particle at phase space position (x,p)?

$$F(x,p,t) = \sum_{i=1}^{N} \delta(x - x_i(t))\delta(p - p_i(t))$$

We can find an equation of motion for this probability, since we know the equations of motion for the positions and momenta (Hamilton Equations).

***Note**: Given the initial conditions for the phase-space coordinates and the Hamilton Equations, this is exact and just a definition.*

$$\frac{\partial F(x,p,t)}{\partial t} + \frac{p}{m} \cdot \frac{\partial F(x,p,t)}{\partial x} + \mathcal{F}(x,t) \cdot \frac{\partial F(x,p,t)}{\partial p} = 0$$

This is an exact equation that is very difficult to solve. *Take ensemble average of this equation.*

$$f(x,p,t) = \langle F(x,p,t) \rangle$$

$$\frac{\partial f(x,p,t)}{\partial t} + \frac{p}{m} \cdot \frac{\partial f(x,p,t)}{\partial x} + \underbrace{\left\langle \mathcal{F}(x,t) \cdot \frac{\partial F(x,p,t)}{\partial p} \right\rangle} = 0$$

Requires: $f(x,p,x',p',t)$

BBGKY hierarchy…

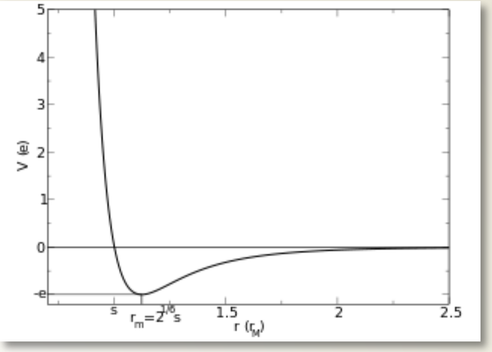
- Kinetic theory deals with how to truncate this hierarchy: "collision integrals".
- Kinetic theory is therefore approximate.
- Kinetic theory involves solving partial differential equations (PDEs).

Choice of Forces is Highly Problem Dependent

- Most MD is performed with *pair* potentials.
    - Lennard-Jones
    - Morse
    - Double Yukawa
    - Harmonic
    - Dipole
    - Embedded atom
- There are many types of forces/potentials.
    - Ionic bond
    - Hydrogen bond
    - Coulomb attraction/repulsion
    - Covalent bond
- Non-pair potentials are often required.

$$V_{ijk} = E_0 \left[\frac{1 + 3\cos\gamma_i \cos\gamma_j \cos\gamma_k}{(r_{ij} r_{jk} r_{ik})^3} \right]$$

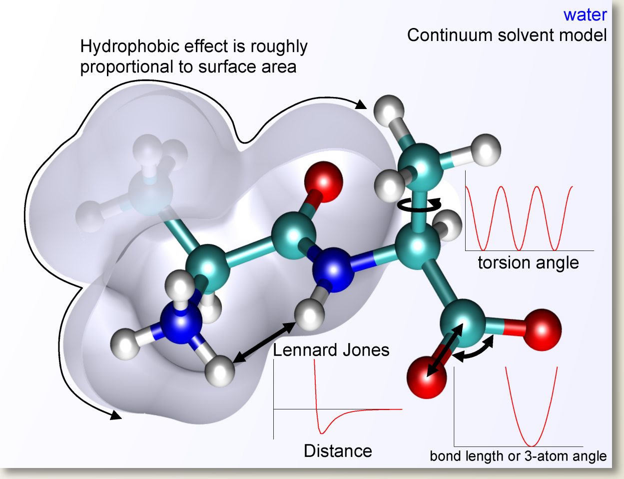
- Often referred to as “force fields” (e.g., AMBER).
- *I will say a lot more about this in the second lecture*.



$$V(r^N) = \sum_{\text{bonds}} \frac{1}{2} k_b (l - l_0)^2 + \sum_{\text{angles}} \frac{1}{2} k_a (\theta - \theta_0)^2$$

$$+ \sum_{j=1}^{N-1} \sum_{i=j+1}^{N} \left\{ \epsilon_{i,j} \left[\left(\frac{r_{0ij}}{r_{ij}} \right)^{12} - 2 \left(\frac{r_{0ij}}{r_{ij}} \right)^{6} \right] + \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} \right\}$$

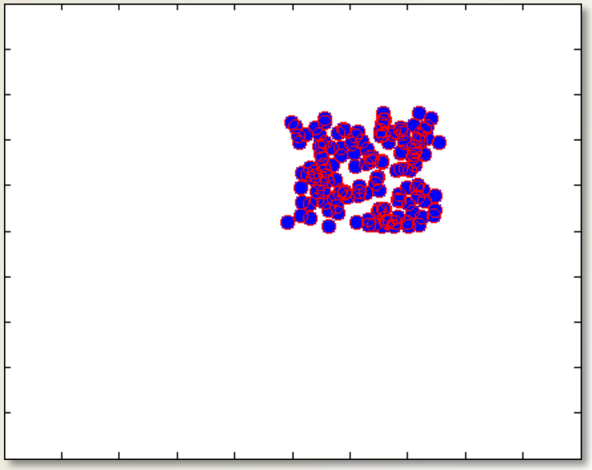
http://en.wikipedia.org/wiki/AMBER



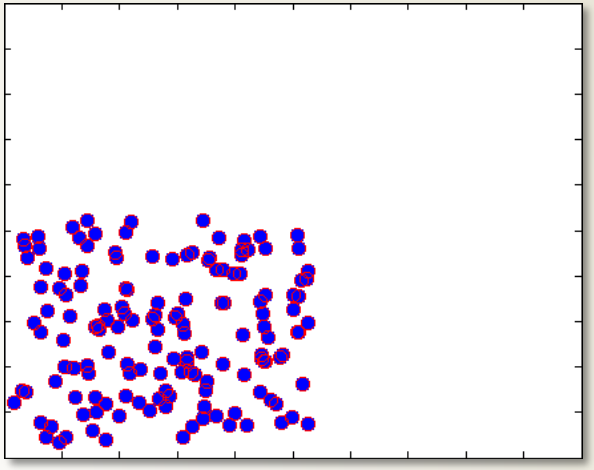
http://en.wikipedia.org/wiki/File:MM_PEF.png

Initial Conditions and Boundary Conditions

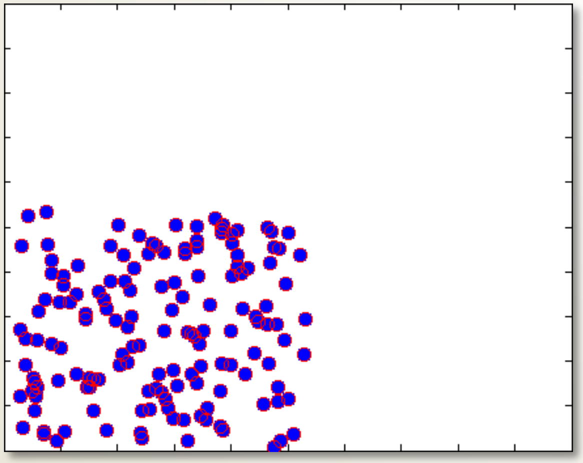
Obviously, this is highly problem dependent.



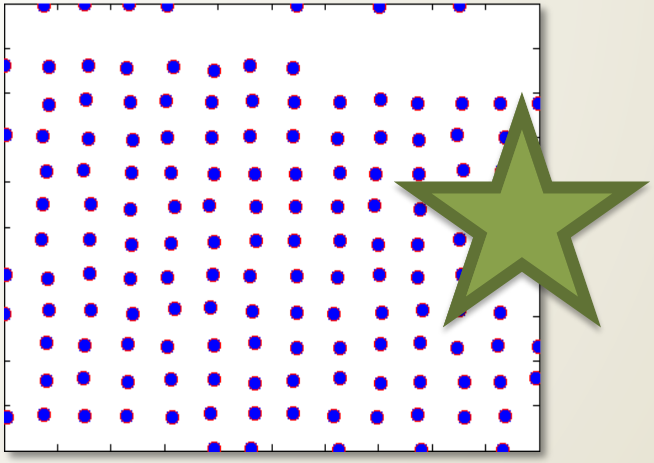
random velocities, clustered positions, reflecting boundary conditions



directed velocities, clustered positions, open boundary conditions



directed velocities, clustered positions, periodic boundary conditions



random velocities, almost random positions, periodic boundary conditions

Basics of ODE Integration

$$\frac{dy(t)}{dt} = f(y(t), t)$$

$$\frac{dy(t)}{dt} \approx \frac{f_{n+1} - f_n}{\Delta t}$$

forward Euler (explicit)

$$\begin{aligned} \frac{y_{n+1} - y_n}{\Delta t} &= f_n \\ y_{n+1} &= y_n + \Delta t f_n \end{aligned}$$

backward Euler (implicit)

$$\begin{aligned} \frac{y_{n+1} - y_n}{\Delta t} &= f_{n+1} \\ y_{n+1} &= y_n + \Delta t f_{n+1} \end{aligned}$$

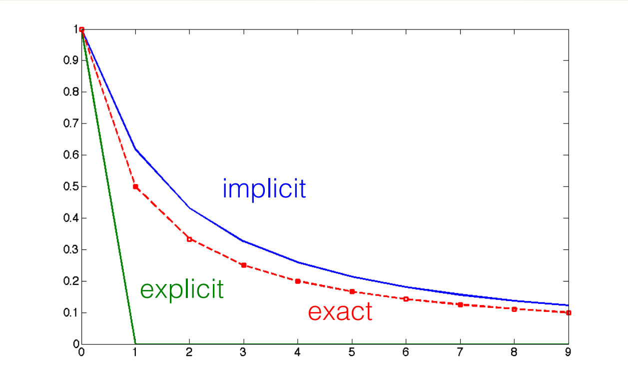
$$\begin{aligned} \frac{dy}{dt} &= -ay^2 \\ y^e_{n+1} &= y^e_n - a\Delta t (y^e_n)^2 \\ y^i_{n+1} &= y^i_n - a\Delta t \left(y^i_{n+1}\right)^2 \\ y^i_{n+1} &= \frac{\sqrt{1 + 4a\Delta t y^i_n} - 1}{2a\Delta t} \end{aligned}$$

Numerical Results

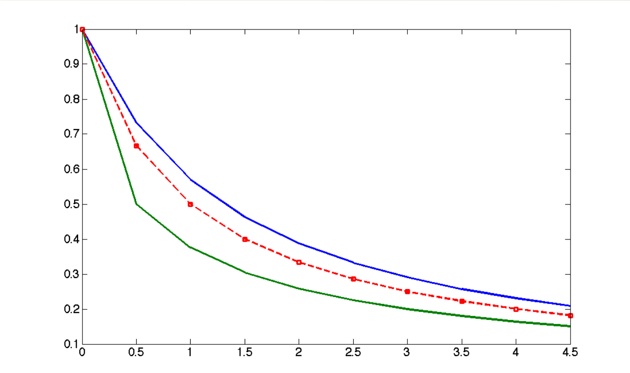
$$\begin{aligned} a &= 1 \\ N_{steps} &= 10 \end{aligned}$$

Exact solution:

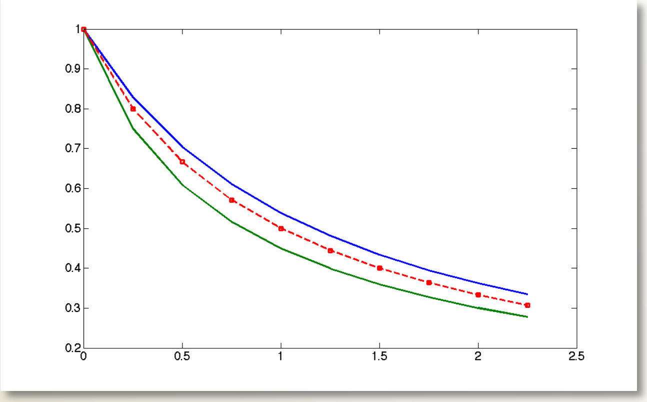
$$y(t) = \frac{y(0)}{1 + aty(0)}$$



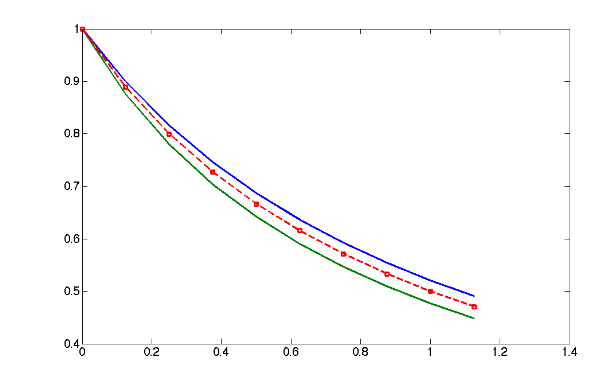
$$\Delta t = 1$$



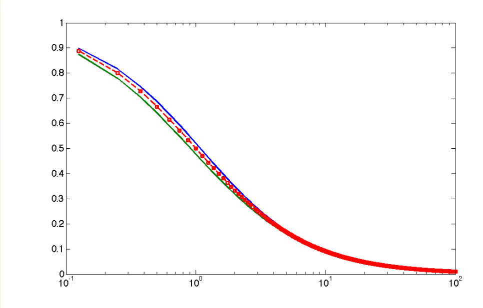
$$\Delta t = 0.5$$



$$\Delta t = 0.25$$



$$\Delta t = 0.125$$



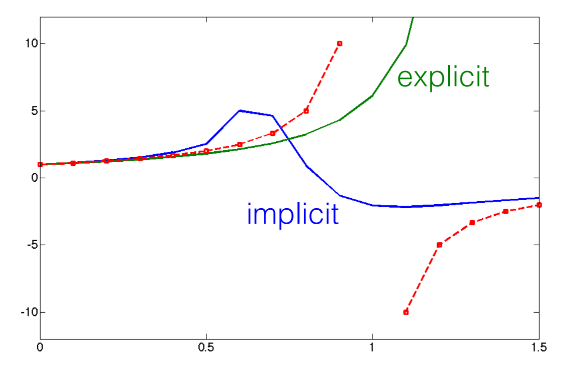
$$\Delta t = 0.125$$

$$N_{steps} = 1000$$

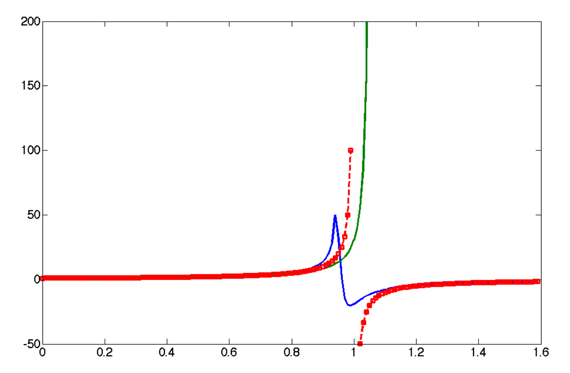
Another Numerical Example: Small Change

$$y(t) = \frac{y(0)}{1 + aty(0)}$$

$$a = -1$$



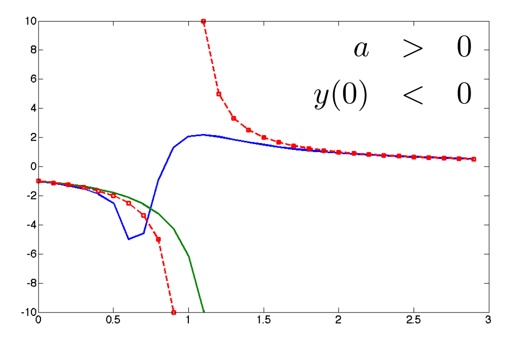
$$\Delta t = 0.1$$



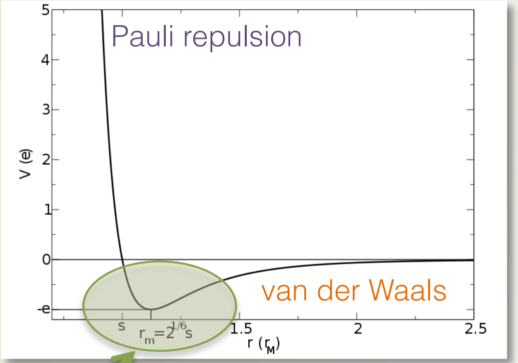
$$\Delta t = 0.01$$

Some initial conclusions:

- Have a good test case, preferably analytic, to compare with.
- Implicit solvers often “better”, but always much slower.
- Choose a test case with properties similar to your system.
- There are a wide variety of algorithms; optimize for your problem.
- Understand your initial conditions.
- In MD, implicit solvers are almost never used.
- Remember the universe that you live in.



Great Choice For MD: Pendulum Equation



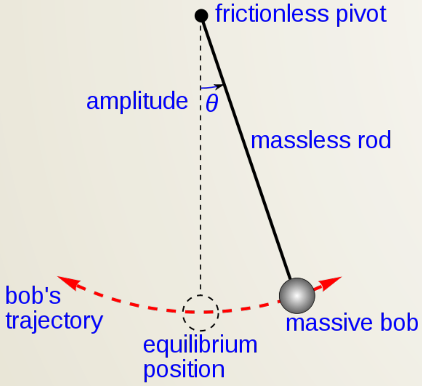
anharmonic oscillator

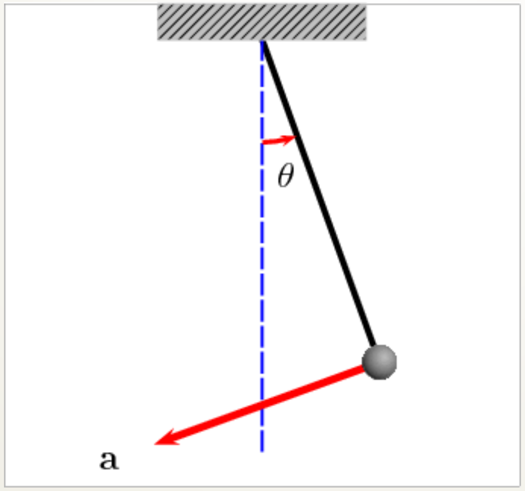
$$V_{LJ}(r) = 4\epsilon\left(\frac{\sigma^{12}}{r^{12}} - \frac{\sigma^6}{r^6}\right)$$

Lennard-Jones 6-12

$$V_{Buck}(r) = A\exp\left(-Br\right) - \frac{C}{r^6}$$

Buckingham





A “generic” equation is then:

$$\frac{d^2y}{dt^2} + \omega^2\sin(y) = 0$$

$$\frac{d^2y}{dt^2} + \omega^2 y \approx 0$$

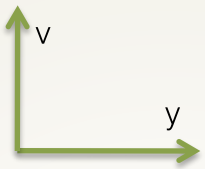
- Arises from Newton’s Laws.
- Is non-linear; mimics real systems.
- Approximate solution (SHO) well known.
- Displays rich behavior.

http://en.wikipedia.org/wiki/Pendulum

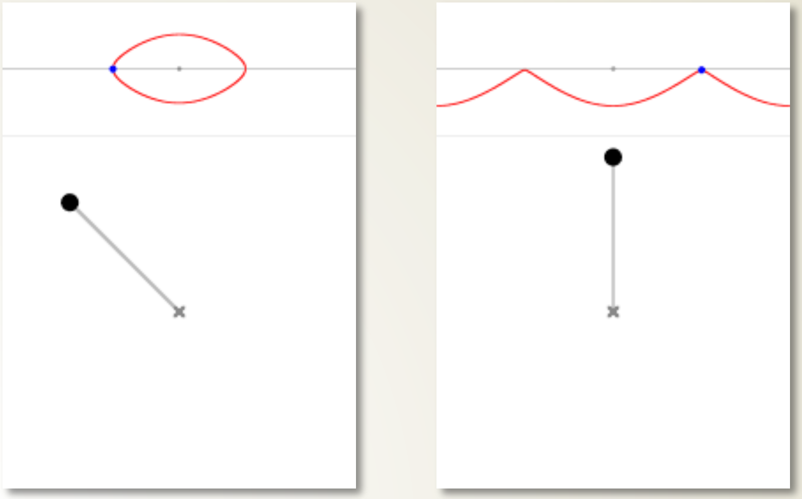
Dynamics in Phase Space

- We would like to try out our first-order integrators.
- Position and velocity natural variables.

$$
\begin{aligned}
\frac{dy}{dt} &= v \\
\frac{dv}{dt} &= -\omega^2 \sin(y)
\end{aligned}
$$



http://en.wikipedia.org/wiki/Pendulum_(mathematics)

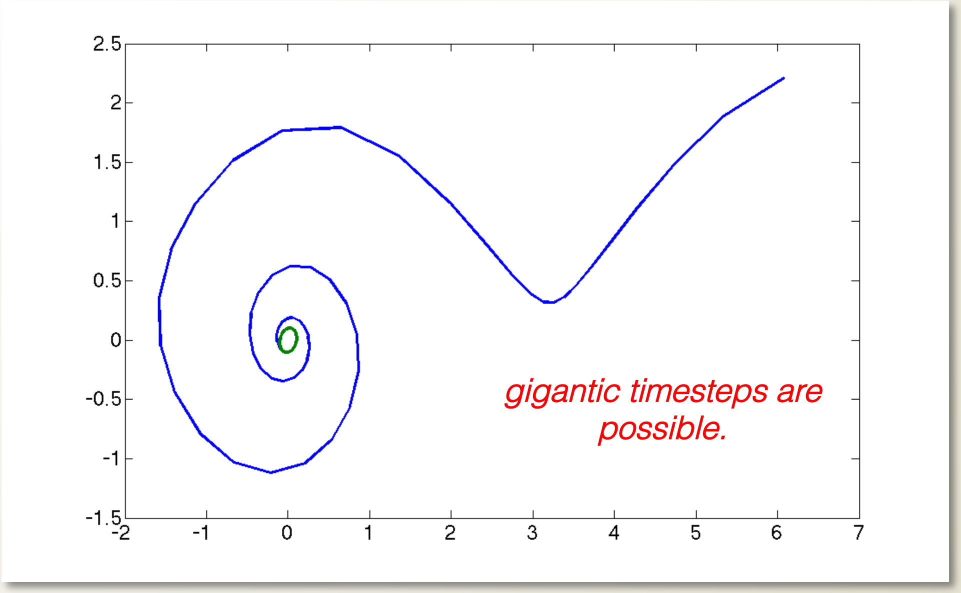


Forward Euler:

$$
\begin{aligned}
y_{n+1} &= y_n + \Delta t v_n \\
v_{n+1} &= v_n - \omega^2 \Delta t \sin(y_n)
\end{aligned}
$$

Minor change (semi-implicit):

$$
\begin{aligned}
v_{n+1} &= v_n - \omega^2 \Delta t \sin(y_n) \\
y_{n+1} &= y_n + \Delta t v_{n+1}
\end{aligned}
$$



gigantic timesteps are possible.

Remember, both are first-order.

Semi-implicit is completely stable.

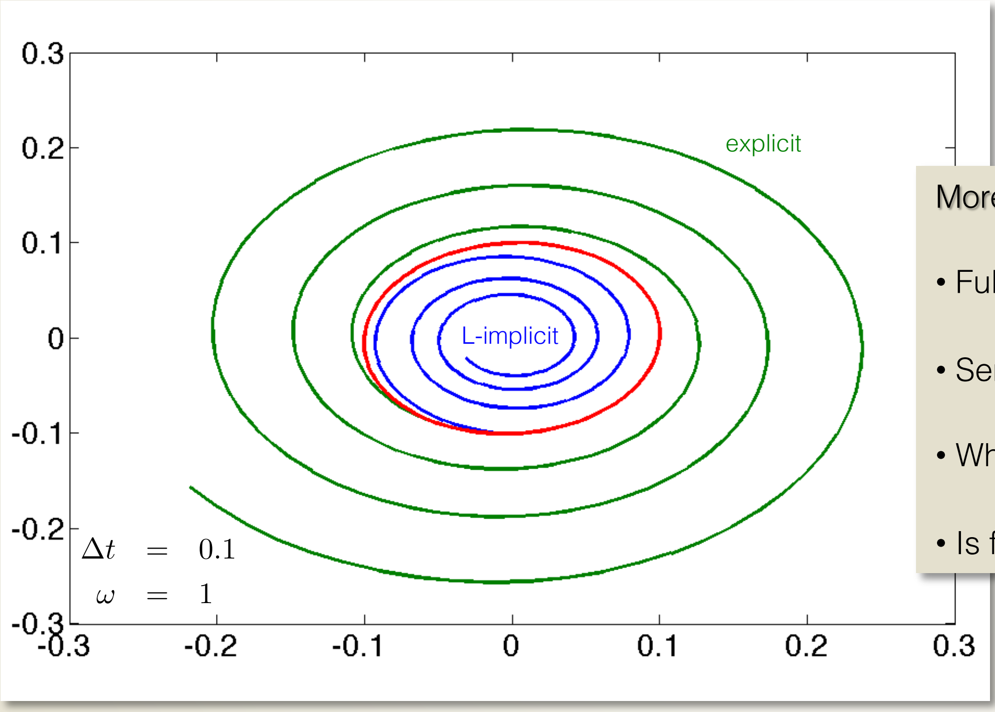
What About Fully Implicit?

Lazy man's implicit: linearize and invert.

$$\begin{aligned} y_{n+1} &= y_n + \Delta t v_{n+1} \\ v_{n+1} &= v_n - \omega^2 \Delta t \sin(y_{n+1}) \\ \sin(y_{n+1}) &\approx \sin(y_n) + (y_{n+1} - y_n)\cos(y_n) \end{aligned}$$

Mea culpa:

- I was too lazy.

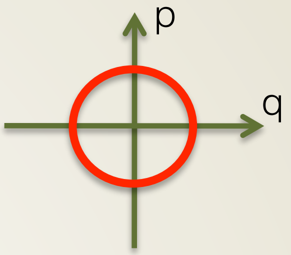


More conclusions, and some questions:

- Fully implicit solution yields qualitatively the same result.
- Semi-implicit is better! *Implicit is not the Holy Grail.*
- What gives?
- Is first-order enough?

Energy Drift Analysis

Consider the Simple Harmonic Oscillator (SHO):



$$H = p^2 + q^2$$

Forward Euler:

$$H = \left(p_0^2 + q_0^2\right)\left(1 + 4\Delta t^2\right)$$

Backward Euler:

$$H = \frac{\left(p_0^2 + q_0^2\right)}{\left(1 + 4\Delta t^2\right)}$$

Semi-implicit Euler:

$$H = \left(p_0^2 + q_0^2\right) + 4\Delta t^2\left(p_0^2 - q_0^2\right)$$

How Does One Construct Second-Order Methods?

Consider the Taylor expansion:

$$\begin{array}{lrcl} & r(t+\Delta t) & = & r(t) + v(t)\Delta t + \frac{1}{2}a(t)\Delta t^2 + \frac{1}{6}b(t)\Delta t^3 + \cdots \\ + & r(t-\Delta t) & = & r(t) - v(t)\Delta t + \frac{1}{2}a(t)\Delta t^2 - \frac{1}{6}b(t)\Delta t^3 + \cdots \\ \hline = & r(t+\Delta t) & = & 2r(t) - r(t-\Delta t) + a(t)\Delta t^2 + \mathcal{O}(\Delta t^4) \end{array}$$

This is the celebrated Verlet algorithm.

Usually, we also want the velocities:

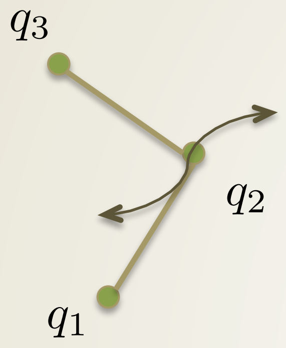
$$v(t+\Delta t) = v(t) + \frac{a(t+\Delta t) + a(t-\Delta t)}{2}\Delta t + \mathcal{O}(\Delta t^2)$$

This is the most popular integrator: good accuracy and time reversible.

$$\begin{aligned} v(t+\Delta t/2) &= v(t) + \frac{a(t)}{2}\Delta t \\ r(t+\Delta t) &= r(t) + \left[v(t+\Delta t/2)\right]\Delta t \\ v(t+\Delta t) &= v(t+\Delta t/2) + \frac{a(t+\Delta t)}{2}\Delta t \end{aligned}$$

Variational Integrators: Connection to Lagrange

We know that mechanics in our universe obeys the action principle – use it!



Which path makes the action stationary?

$$\begin{aligned}
\frac{d}{dt}\frac{\partial L}{\partial \dot q} &= \frac{\partial L}{\partial q} \\
\left.\frac{\partial L}{\partial \dot q}\right|_{t+\Delta t} - \left.\frac{\partial L}{\partial \dot q}\right|_{t} &= -\Delta t \frac{\partial V}{\partial q_2} \\
m\left(q_3 - q_2\right) - m\left(q_2 - q_1\right) &= -\Delta t^2 \frac{\partial V}{\partial q_2} \\
q_3 &= 2q_2 - q_1 - \frac{\Delta t^2}{m}\frac{\partial V}{\partial q_2}
\end{aligned}$$

One can also use the action directly.

There is something very special about Verlet.

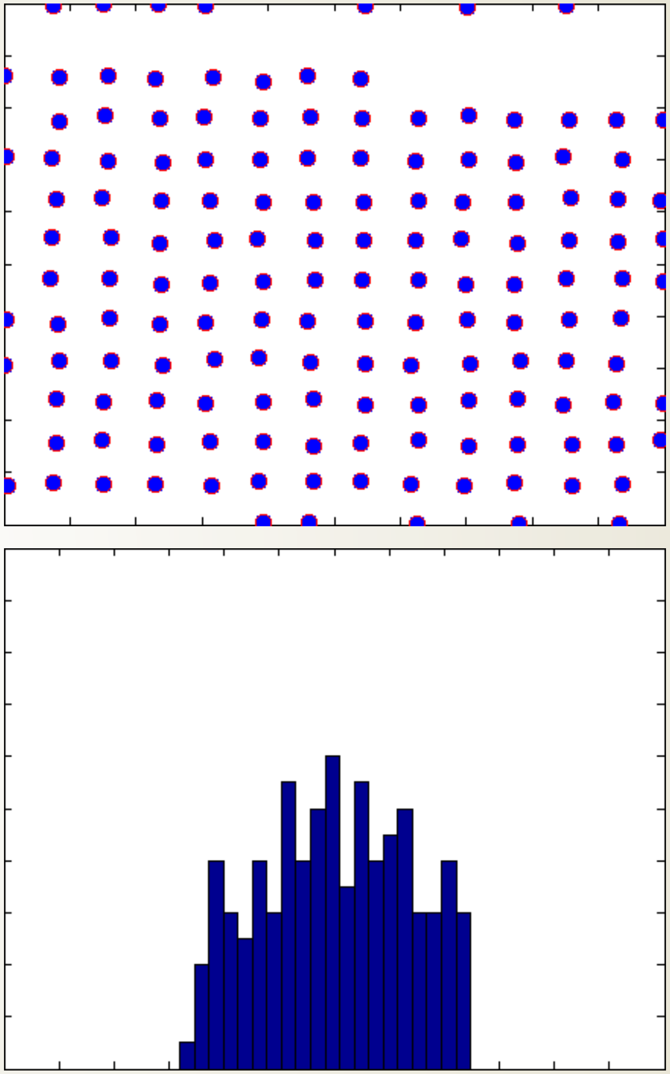
$$\begin{aligned}
S &= \int_{t_1}^{t_3} dt\, L(t) \\
&\approx \Delta t \left[\frac{1}{2}L_1 + L_2 + \frac{1}{2}L_3\right] \\
&\approx \Delta t \left[\frac{m}{4}\left(\frac{q_2(t) - q_1(t)}{\Delta t}\right)^2 - \frac{1}{2}V(q_1(t))\cdots\right] \\
\frac{\partial S}{\partial q_2} &= 0
\end{aligned}$$

Minimum Image Convention and Neighbor Lists

Now that we have forces, tricks are needed.

1. Need to ensure that particles are not too close.
2. Need to sum forces accounting for boundary conditions.

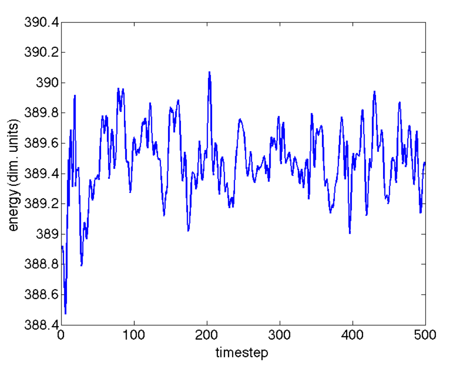
Better would be to use nearest neighbor lists. *More in next lecture.*

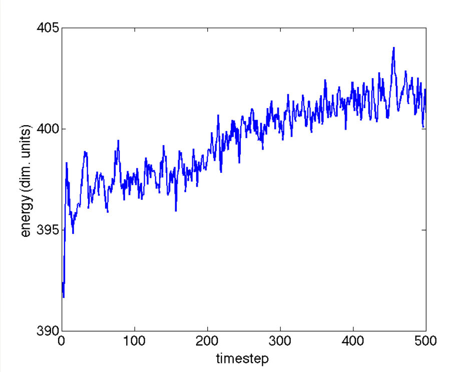


Repulsive Yukawa interaction: $u(r) = \frac{A}{r}\exp(-Br)$

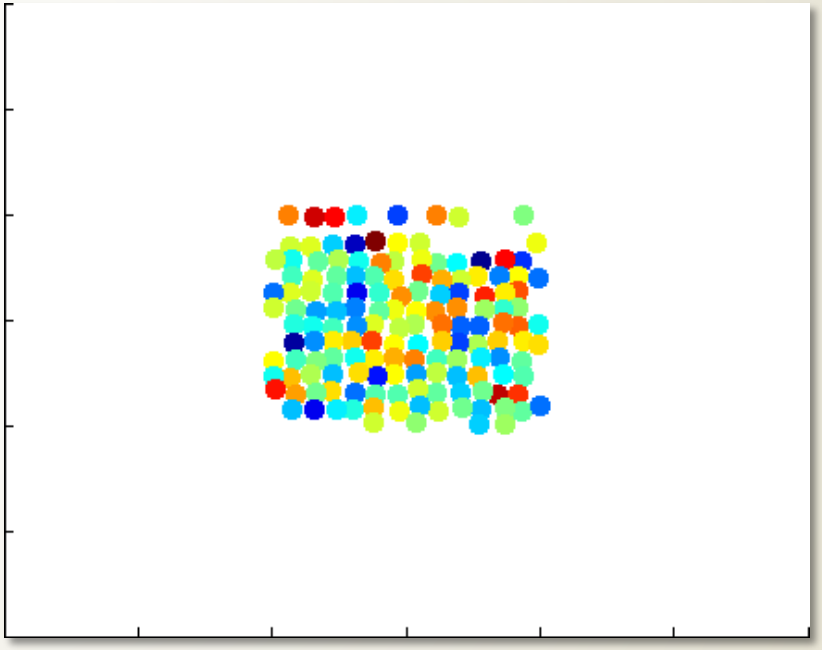
Is The Code Working?

- Momentum should be conserved to machine precision, using Newton’s First Law.
- Energy conservation is then the most important metric available.
- Make plots and movies to check for egregious errors.





further 15% increase
in time step



Finite Temperature: Thermostats

Finite temperature simulations are quite common. There are several methods to handle this case.

1. **Do nothing**. Perform simulation at constant energy (microcanonical ensemble). Collisions will randomize any non-Maxwellian behavior in the initial conditions. For large particle numbers, this works quite well.

2. **Velocity scaling**. Every so often, examine the second moment of the velocity distribution. Scale all velocities so that the target second moment (desired temperature) is reached. This can be done gently by relaxing the distribution to the target over many time steps.

3. **Nose'-Hoover**. Solve a deterministic equation with extra degrees of freedom that are chosen to yield the canonical ensemble.

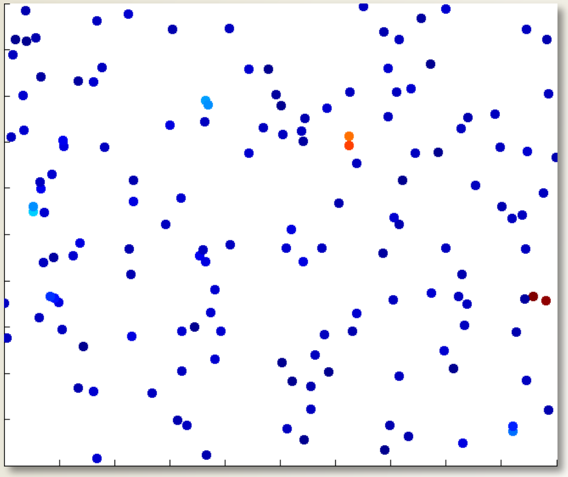
$$\mathcal{H}(P,R,p_s,s) = \sum_i \frac{\mathbf{p}_i^2}{2ms^2} + \frac{1}{2}\sum_{ij,i\neq j} U\left(\mathbf{r_i} - \mathbf{r_j}\right) + \frac{p_s^2}{2Q} + gkT\ln\left(s\right),$$

wikipedia.org/wiki/Nosé–Hoover_thermostat

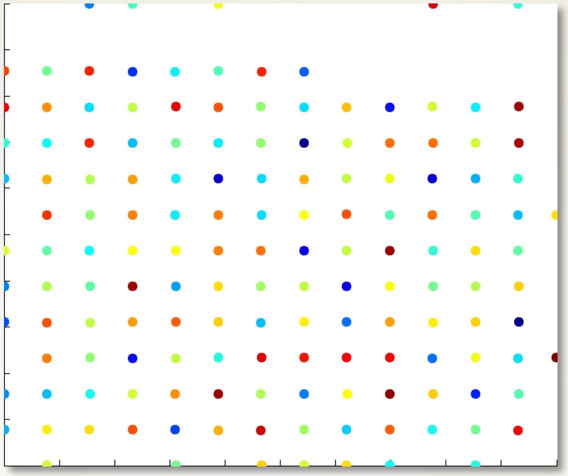
4. **Langevin**. Picture system as being in contact with a stochastic bath/reservoir. Modify equations of motion to account for system+bath coupling.

$$\boxed{\begin{aligned} m\dot{v} &= F - \gamma v + \xi(t) \\ \langle \xi(t)\xi(t')\rangle &= 2T\gamma\delta(t-t') \end{aligned}}$$

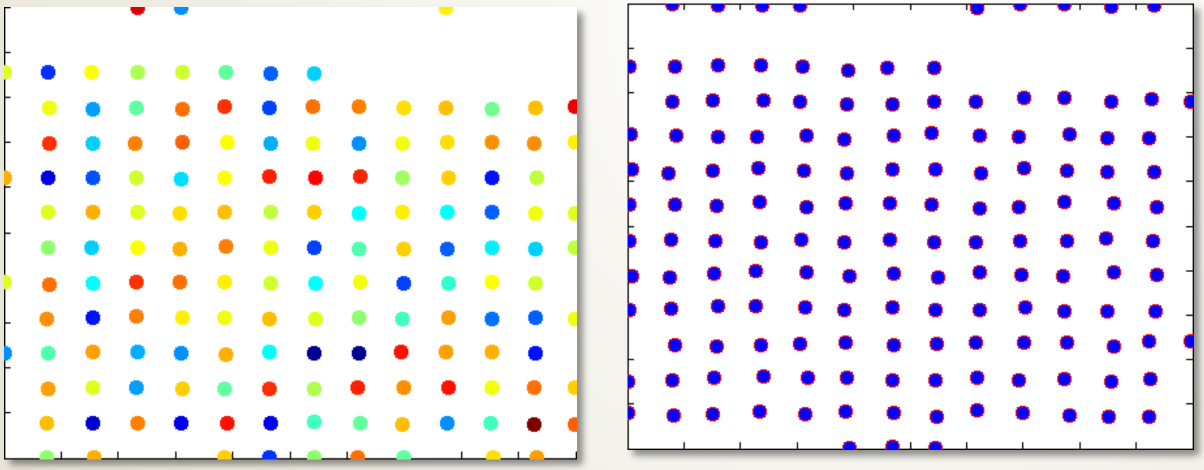
Initial Conditions and Equilibration



- random ICs



- ordered ICs



- 200 time steps
- Velocity set to zero between steps 80 and 120

Input

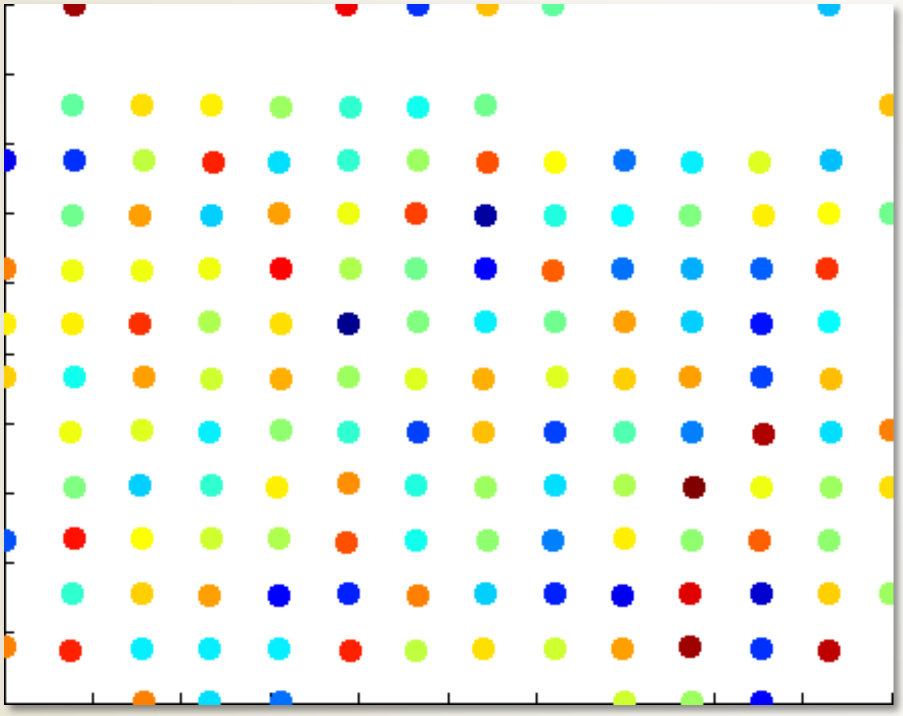
Initialize (x,p)

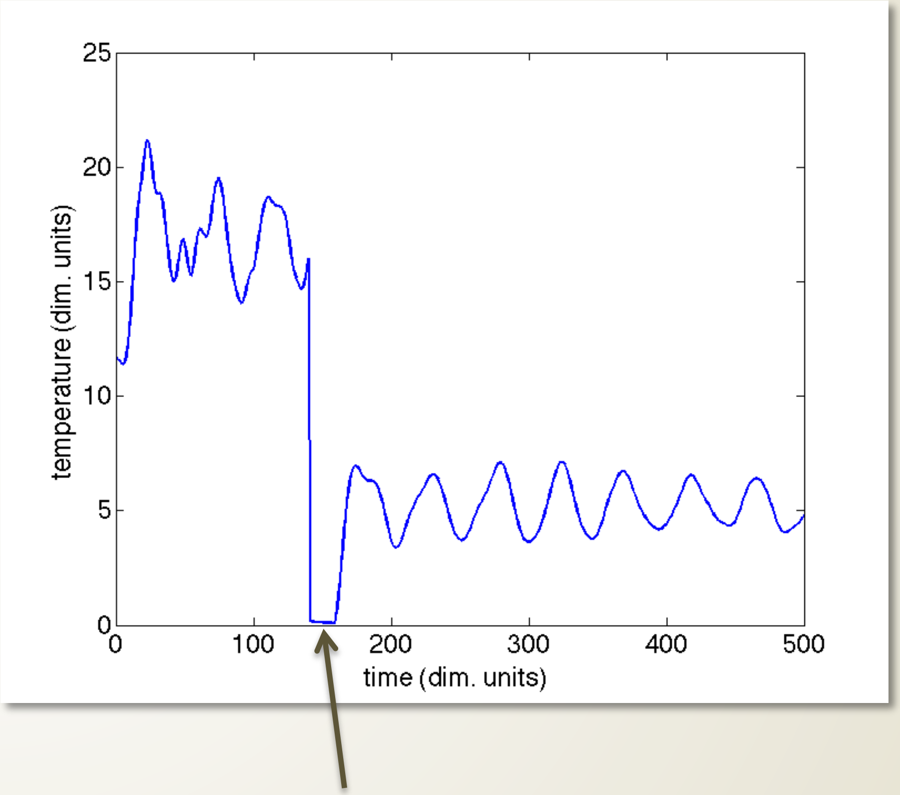
Equilibrate

Perform Run

Analyze Results

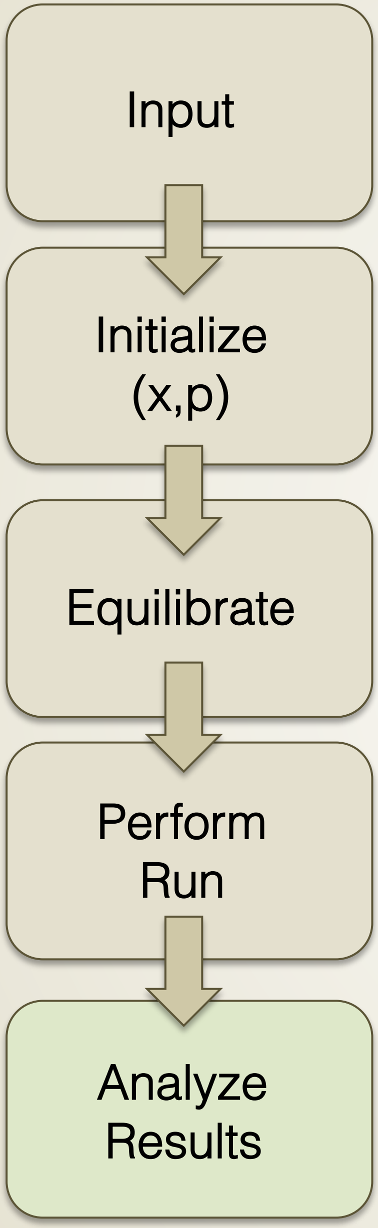
Achieving Target Temperature





equilibration too short

Run Completed: Now What?



Once again, it greatly depends upon the problem. But, there is one general principle:

You have all phase space information. Whatever you are interested in, you must be able to know how it is connected to the full phase space history.

Equilibrium

- energy
- pressure
- free energy
- phase diagrams

Transport

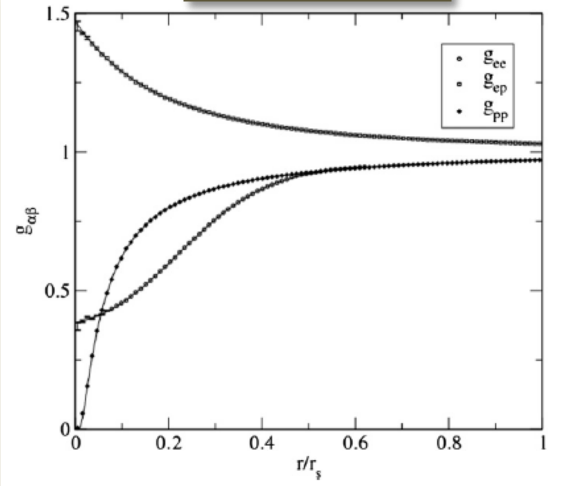
- diffusion
- viscosity
- conduction
- other time autocorrelation functions

Non-Equilibrium MD (NEMD)

- relaxation
- shocks
- external fields
- reactions

Specific Examples of Observables

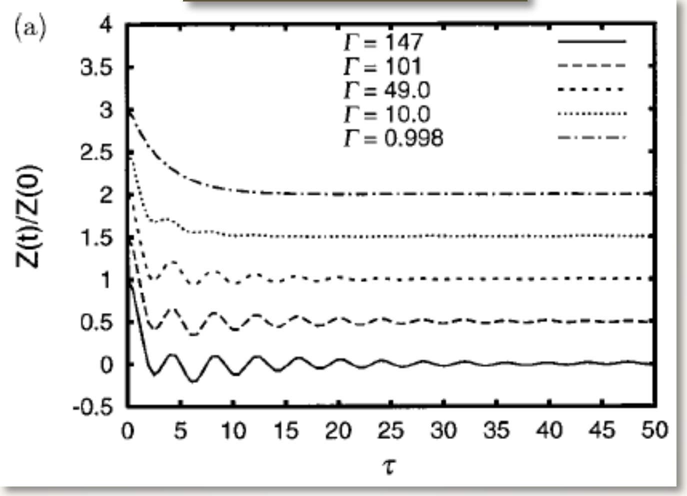
radial distribution functions



$$P = nT - \frac{1}{6}\sum_{i\neq j} n_i n_j \int d^3r\, \frac{\partial u_{ij}(r)}{\partial r} g_{ij}(r)$$

Graziani et al., HEDP 8, 105 (2012).

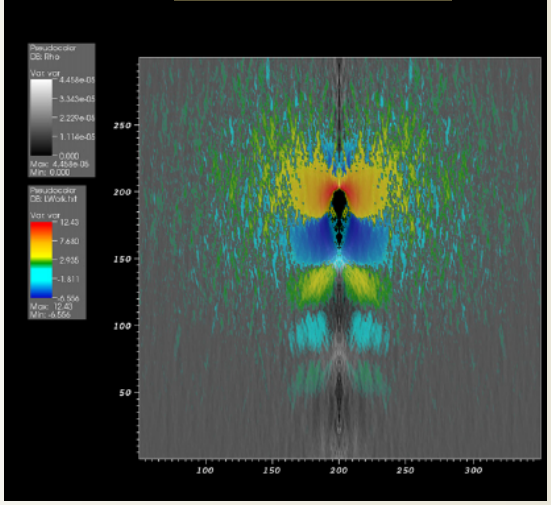
velocity autocorrelation functions



$$D = \frac{1}{3}\int_0^\infty dt\ \langle v(t)\cdot v(0)\rangle$$

Ohta & Hamaguchi, PoP 7, 4506 (2000).

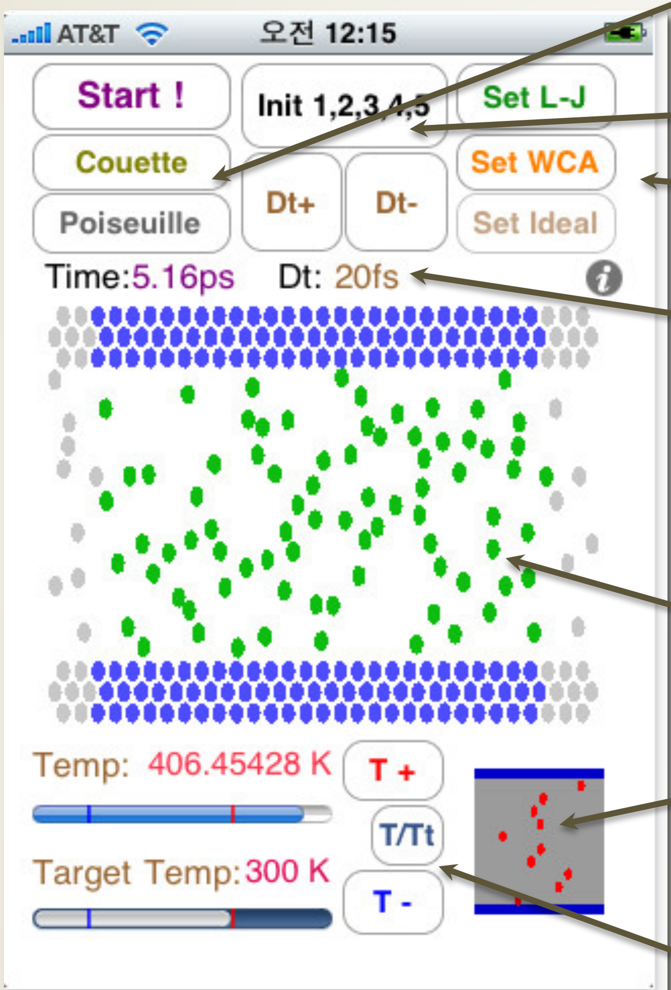
energy deposition in NEMD



$$dE/dx$$

Graziani et al., HEDP 8, 105 (2012).

Back To That App…



Time:5.16ps Dt: 20fs

Temp: 406.45428 K

Target Temp:300 K

Boundary conditions.

Initial conditions.

Forces/potentials.

Time step.

Observables.

Thermostat.

B. H. Kim, A. Beskok, and T. Cagin
Viscous heating in nanoscale shear driven liquid flows
Microfluidics and Nanofluidics **9**, 31 (2009)

Segue Into Second Lecture

- What you now know:
  1. What MD is and what MD is not.
  2. Some of the details of what goes into an MD code.
  3. The MD procedure from specifications to running to analysis.
- What you don't (hopefully) yet know:
  1. What are the physical HEDP regimes of interest for MD?
  2. What types of forces do we need to describe HED matter?
  3. Which algorithms need to be adapted to such plasmas?
  4. What are some of the outstanding interesting problem?