Campinas Advanced School of Thermodynamics
Workshop on Molecular Simulations
Session 1 – Basic MD

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All materials available on MaginnGroup GitHub site

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Maginn Group

Set up conda environments

- Follow the instructions provided earlier.
- Activate LAMMPS environment

> conda activate lammps-tutorial

- Make sure Ovito is installed

History of “models”

- *It seems to me that the test of “Do we or not understand a particular subject in physics?” is “Can we make a mechanical model of it?”*

  -W. Thomson (Lord Kelvin)
  “Baltimore Lectures on Molecular Dynamics and the Wave Theory of Light”, 1904.

Essence of molecular simulation

- Predict the macroscopic properties of many-body systems

- Described by wave function $\psi(q,t)$
  - **q** is position of nuclei and electrons at time *t*.
  - Solving wave equation gives expectation value of any mechanical property
  - Rigorous, but difficult to do for large systems

Subject of electronic structure theory.
Simplification: treat system *classically*.

- State of system given by generalized coordinates $\mathbf{q}^N$ and generalized momenta $\mathbf{p}^N$.

- Born-Oppenheimer approximation: neglect position of electrons and focus only on nuclei

  Uncertainty principle: we cannot know both $\mathbf{q}^N$ and $\mathbf{p}^N$ exactly. Let's ignore this!

Phase space

State vector or *system point* defined as

$$\mathbf{x}^N \equiv (\mathbf{q}^N, \mathbf{p}^N) = (\mathbf{q}_1, \mathbf{q}_2, \ldots, \mathbf{q}_N; \mathbf{p}_1, \mathbf{p}_2, \ldots, \mathbf{p}_N)$$

6-N dimensional set from which $\mathbf{x}^N$ takes a value is called the *phase space* of the system Γ

A point on Γ represents a *microstate* of the entire system.

If $\mathbf{x}^N$ is known at one time, it is *completely determined* for any other time (past and present) through the classical equations of motion.

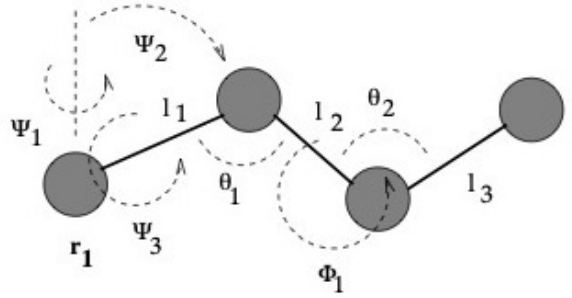
Phase space and state points

- "phase space" is the 6N generalized coordinates describing the state of a system: $\mathbf{x}^N(\mathbf{q}^N, \mathbf{p}^N)$
- Positions: $\mathbf{q}^N$
- Momenta $\mathbf{p}^N$

N atoms
Bold type = vector

- Several coordinate systems possible

Cartesian:
r(x,y,z)



"internal"

Classical energies, forces; equations of motion

$$H(\mathbf{q},\mathbf{p}) = K + \mathcal{V}$$ "Hamiltonian"

$$K = \sum_{i=1}^{N} \frac{m_i v_i^2}{2}$$ KE depends on atomic velocities

$$\mathcal{V} = \mathcal{V}(\mathbf{q})$$ PE depends on atomic positions

$$\mathbf{F} = -\nabla_{\mathbf{q}} \mathcal{V}$$ Force between pairs of atoms is conservative

Energy is conserved

dH/dt = 0 – a *microcanonical ensemble*

Newton's equations of motion

$$\frac{d\mathbf{p}}{dt} = m\frac{d\mathbf{v}}{dt} = m\ddot{\mathbf{r}} = m\mathbf{a}$$

$$m_i \ddot{r}_i = F_i$$ ← 3N 2nd order differential eqns.

$$\dot{r}_i = \frac{\dot{p}_i}{m_i}$$

$$\dot{p}_i = F_i$$ ← 6N 1st order differential equations

$$F_i \equiv -\nabla_{r_i} U$$

MD uses finite difference

- MD is a means of solving the following initial value problem: $\ddot{r}_i = \frac{F_i(r_1,...r_N)}{m_i}$
- Initial conditions: $r_i(0), \dot{r}_i(0)$
- Trajectories generated numerically using finite difference methods
- We will use LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator) lammps.org
- Classical particle simulator
  - Tremendous flexibility, very good documentation, and active user base
- We will start with some simple demonstrations and calculations to understand basics

Microstates, macrostates, and ensembles

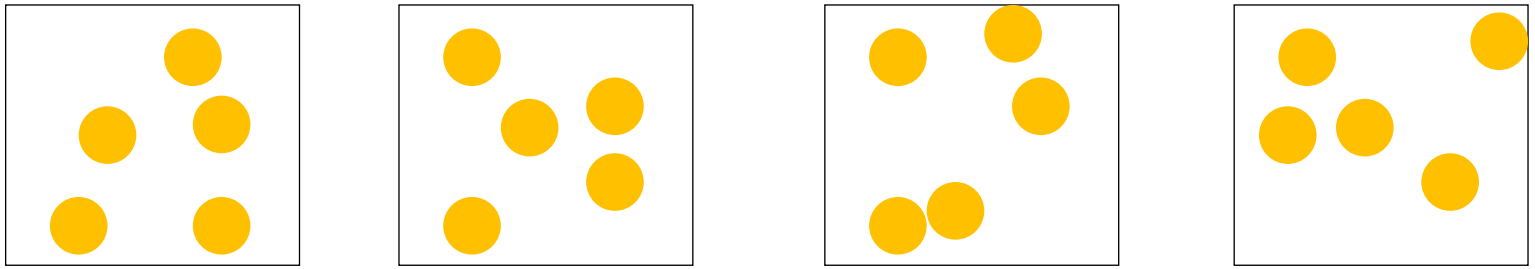
Systems with different *microstates* may exist at the same *thermodynamic state*.

Example: Many different sets of ($\mathbf{q}^N$,$\mathbf{p}^N$) can be at the same temperature and pressure.

A thermodynamic state is a *collection* of many different microstates.

- Identical in composition and at the same "macrostate"
- Gibbs called this collection an "ensemble"

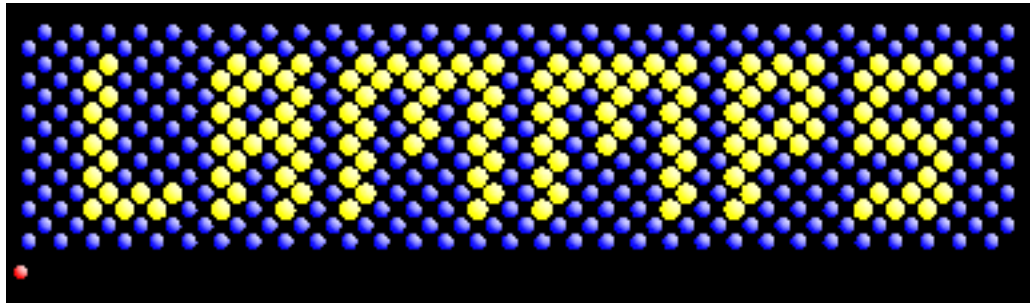
An ensemble is a collection of a large number of systems, each a replica of the thermodynamic state of the system, whose properties we are investigating



Example:
4 states having different (q,p) but same NVE

Time reversibility

Newtonian mechanics is time-reversible



$$H(\mathbf{x}^N) = H(\mathbf{p}^N, \mathbf{q}^N)$$

given $\mathbf{x}^N(t_1) \iff \mathbf{x}^N(t_2)$ **absolutely known**

Determinism

- Ever since Newton, deterministic, mechanical interpretation of Nature has dominated science.

- *Given for one instant an intelligence which could comprehend all the forces by which Nature is animated and the respective situation of the beings who compose it - an intelligence sufficiently vast to submit these data to analysis - it would embrace in the same formula the movements of the greatest bodies of the universe and those of the lightest atoms; for it, nothing would be uncertain and the future, as the past, would be present to its eyes.*

-- P. S. Laplace, “Philosophical Essay on Probabilities”, 1814

Averages in NVE ensemble

Consider an integrable function $f(\mathbf{x}^N)$ of state point $\mathbf{x}^N$ on a constant E-hypersurface. The phase average of $f(\mathbf{x}^N)$ is

$$\langle f \rangle_{NVE} = \frac{1}{\Sigma(E)} \int_\Gamma \delta(H(\mathbf{x}^N - E) f(\mathbf{x}^N) d\mathbf{x}^N$$

$$\langle f \rangle_{NVE} = \frac{\int_\Gamma \delta(H(\mathbf{x}^N - E) f(\mathbf{x}^N) d\mathbf{x}^N}{\int_\Gamma \delta(H(\mathbf{x}^N - E) d\mathbf{x}^N}$$

What we do with MC

Key: phase average taken by averaging over all state points on constant E hypersurface

Could also take a "time average" over a series of snapshots as system evolves *at equilibrium*

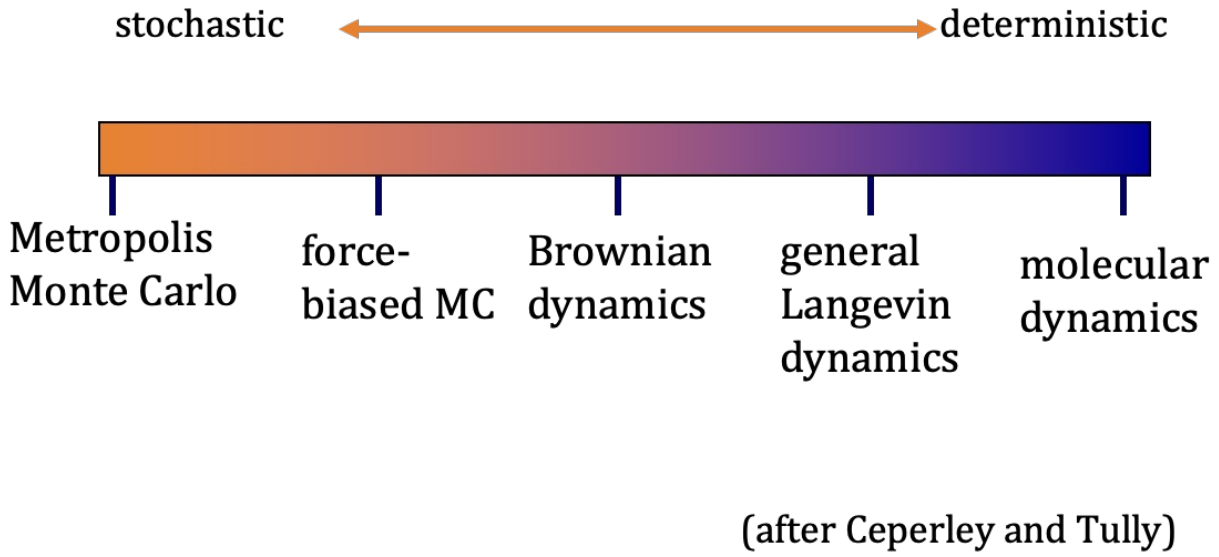
$$\langle f \rangle_t = \lim_{t\to\infty} \frac{1}{t} \int_{t_0}^{t_0+t} f(\mathbf{x}^N(t)) dt$$

What we do with MD

Steps of a molecular simulation

- A molecular simulation consists of three steps:
  1) construction of the molecular model
     > How are atoms connected and how do they interact?
  2) calculation of molecular trajectories
     > MC is stochastic
     > MD is deterministic
     > Many variants “in between”
  3) analysis of trajectories => properties

- A spectrum of methods

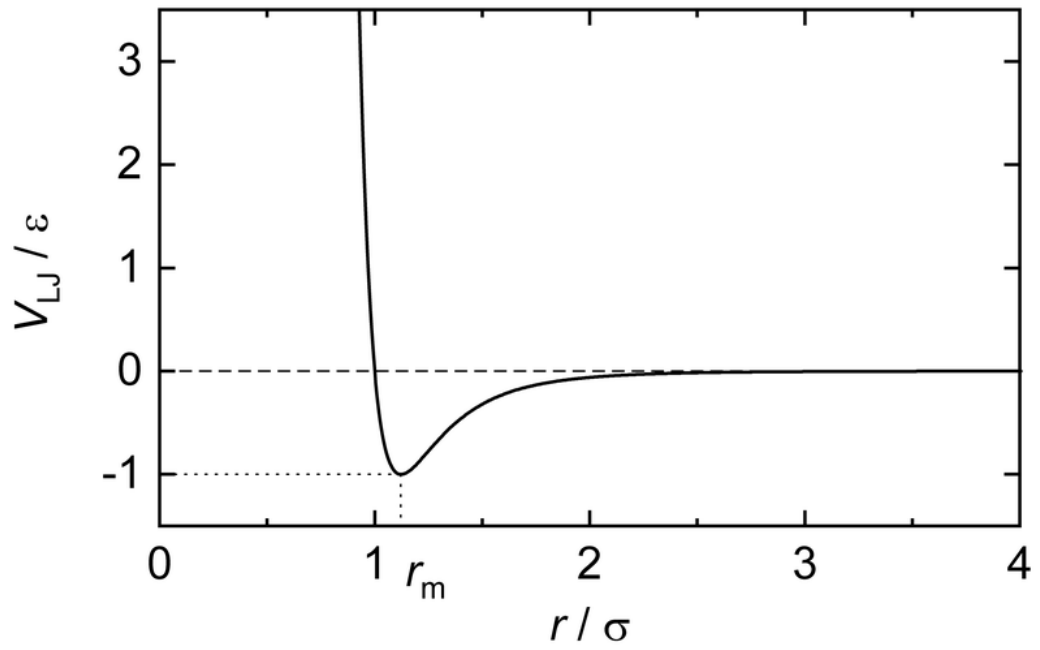


(after Ceperley and Tully)

Running a LAMMPS calculation

- Pass LAMMPS and input file - provides essential information
  - What kind of system
  - How long the run is
  - File names
  - Units
  - Many other things…
- Can provide the force field and molecule information
- A “data file” can also be used to provide force field and molecule information

Lennard-Jones 12-6 potential



$$\mathcal{V}(r_{ij}) = 4\epsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right]$$

LJ Units used by LAMMPS

- LAMMPS sets the fundamental quantities m, σ, ϵ, and the Boltzmann constant k_B=1.
- The masses, distances, energies are multiples of these fundamental values.
- Thus, you can use the mass, σ, and ϵ values for a specific material and convert the results from a unitless LJ simulation into physical quantities.
- Note that using these three properties as base, the unit of time must conform to the relation

•mass = $M^*=M/m$
•distance = $x^*=x/\sigma$
•time = $\tau^*=\tau\ \mathrm{sqrt}(\epsilon/m\sigma^2)$
•energy = $E^*=E/\epsilon$
•velocity = $v^*=v\ \tau/\sigma$
•force = $f^*=f\ \sigma/\epsilon$
•temperature = reduced LJ temperature, $T^*=T\ k_B\ /\ \epsilon$
•pressure = reduced LJ pressure, $P^* = P\ \sigma^3/\ \epsilon$

Example 1: Two LJ particles in an LJ sphere

Open example1.inp in your editor

You can call this anything you want. Suggestion is to develop a system so you can understand and organize results

```
# set name for this simulation
variable NAME index example1 # name style value
```

```
# set log file name. ${NAME} is the name you gave above.
# This will append "log" to it so have a logfile of the run.
log ${NAME}.log
```

 # comments can start a line or come after an entry

```
# configure and initialize system
units lj   # Lennard-Jones reduced units (not real)
atom_style atomic    # Simple atoms
boundary f f f # x y z (f = fixed boundary conditions)
```

"fixed" boundary will be a rigid LJ sphere

LJ units are dimensionless units for the LJ system

"real" units:
Length = A
Energy = kcal/mol
Time = fs

```
# Define the region of the simulation andx then create
# the simulation box
region MYBOX sphere 0 0 0 5 units box
create_box 1 MYBOX # number_of_atom_types region_ID
```

Creates the simulation "box" of diameter 5 LJ units and centered at 0,0,0

```
# Create the atoms and place them at a given position
create_atoms 1 single 0 2.0 0 units box # atom_type style
args
create_atoms 1 single 0 -2.0 0 units box # second
symmetric atom, non-ergodic
#create_atoms 1 single 0 -1.0 0 units box # second
asymmetric atom, ergodic
```

Place a single atom of type 1 at position 0,2,0

Place a second atom of the same type at position 0,-1,0.

Commented out: you could create more atoms at other positions for fun

```
mass 1 1.0 # atom_type mass
```

The mass of atoms of type 1 is 1.0 (LJ units)

```
# explicitly set atom velocities, use box units, do *not* zero total momentum
velocity all set 1 0 0 units box mom no # group_ID style args keyword value
```

Atoms need initial velocities. Give them all +1,0,0

```
# set forcefield parameters
pair_style lj/cut 2.5 # style args(=cutoff)
pair_coeff 1 1 1.0 1.0 2.5 # atom_i atom_j args(=epsilon,sigma,cutoff)
#pair_coeff 1 1 1.0 1.0 1.0 # repulsive only
```

Define the LJ potential

```
# create a spherical wall to contain the atom(s)
fix SPHERE all wall/region MYBOX lj126 1.0 1.0 2.5 # fix_ID group_ID style
args
#fix SPHERE all wall/region MYBOX lj126 1.0 1.0 1.0 # repulsive only
```

Make the sphere have an LJ potential (cutoff of 1.0 is a repulsive "Sutherland" potential

```
# include potential energy of wall fix in thermo 'pe' output
fix_modify SPHERE energy yes # fix_ID keyword value
```

Include energy between atoms and wall in PE LAMMPS calculates

```
# configure integrator
fix NVE all nve # fix_ID group_ID style
timestep 0.003 # The default timestep size is 0.005 for LJ units.
```

Tell LAMMPS how to integrate the EOM

```
# configure output of atom-specific trajectory data (e.g. coordinates)
dump DUMP all atom 50 ${NAME}.lammpstrj # dump_ID group_ID style interval file args
#dump_modify DUMP image yes # dump_ID keyword value
```

"dump" coordinates to trajectory file for analysis every 50 steps

```
# configure output of system property data
thermo_style custom step temp press pe ke etotal
thermo 1000 # output_interval
```

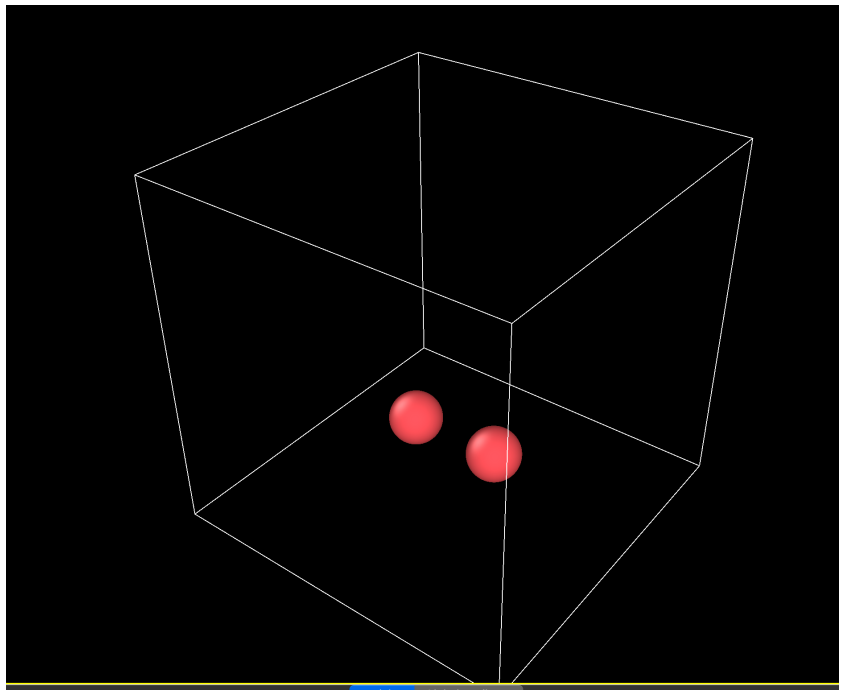
What properties do you want written out every 1000 steps

```
# run simulation
run 100000 # number_of_steps
write_restart ${NAME}.restart.*
```

Ignore other stuff for now…

Tell LAMMPS to run MD for 100000 steps and then write a restart file that can be used to run another simulation from the end of the first one

Example 1 output

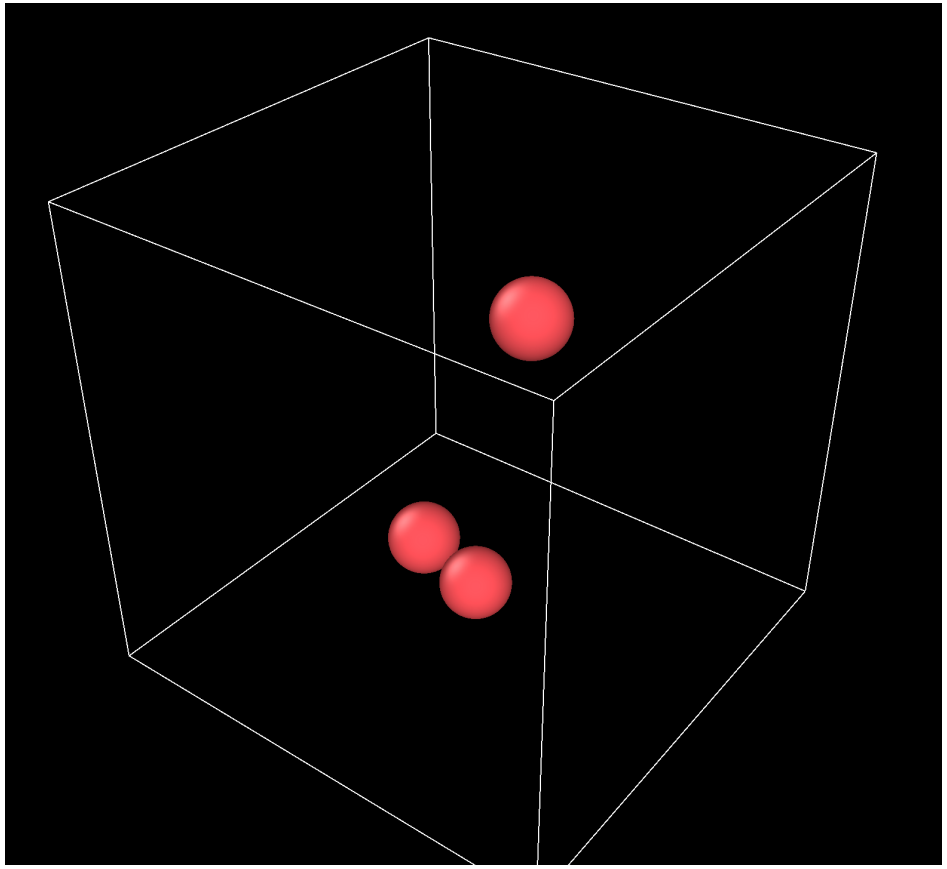


Log file has properties

Step	Temp	Press	PotEng	KinEng	TotEng
0	0.66666667	0.00066666667	0	0.5	0.5
1000	1.9276018	0.0019276018	0	1.4457013	1.4457013
2000	0.66997905	0.00066997905	0	0.50248429	0.50248429
3000	0.72222642	0.00072222642	0	0.54166981	0.54166981
4000	0.69498405	0.00069498405	0	0.52123804	0.52123804
5000	0.75054381	0.00075054381	0	0.56290786	0.56290786
6000	0.74614754	0.00074614754	0	0.55961065	0.55961065
7000	0.7478995	0.0007478995	0	0.56092462	0.56092462
8000	0.86172315	0.00077235532	-0.022603356	0.64629237	0.62368901
9000	1.1769	0.0011769	0	0.88267501	0.88267501
10000	1.8976579	0.0018976579	0	1.4232434	1.4232434
11000	1.4491928	0.003827198	-0.41223311	1.0868946	0.67466147
12000	1.1983254	0.0011983254	0	0.89874403	0.89874403
13000	0.91551879	0.00091551879	0	0.6866391	0.6866391
14000	1.7583265	0.00078678268	-0.4136154	1.3187448	0.90512944
15000	1.2961229	0.0012961229	0	0.97209217	0.97209217

- Why is energy not conserved?
- System is not “ergodic” as molecules do not explore all available space.
- Add the third atom to the box and re-run. What happens?

3 atoms - ergodic



Step	Temp	Press	PotEng	KinEng	TotEng
0	0.5	0.009	0	0.5	0.5
1000	0.83477215	0.0015143069	−0.02617744	0.83477215	0.80859471
2000	1.1149492	0.0022298985	0	1.1149492	1.1149492
3000	1.1561885	0.002312377	0	1.1561885	1.1561885
4000	0.75993387	0.0012081026	−0.054380556	0.75993387	0.70555331
5000	1.3042038	0.0016449011	−0.21512011	1.3042038	1.0890837
6000	0.82754341	0.0016550868	0	0.82754341	0.82754341
7000	1.0369676	0.0011097658	−0.21546579	1.0369676	0.82150178
8000	0.77669148	0.0013916085	−0.027556777	0.77669148	0.7491347
9000	0.52073028	0.00095543258	−0.014417638	0.52073028	0.50631264
10000	0.60680212	0.0011767117	−0.0061776457	0.60680212	0.60062447
11000	0.83508363	0.001319143	−0.06086272	0.83508363	0.77422091
12000	0.71825183	0.0013513439	−0.014351174	0.71825183	0.70390065
13000	0.70277162	0.0014055432	0	0.70277162	0.70277162

System is ergodic, but energy is still not conserved.

Integrating EOM – Verlet Algorithm

- Many “flavors” of this (good) algorithm

$$r(t+\Delta t) = 2r(t) - r(t-\Delta t) + \Delta t^2 a(t)$$

- Where did this come from, and where did the velocities go???
- Taylor series about r(t)

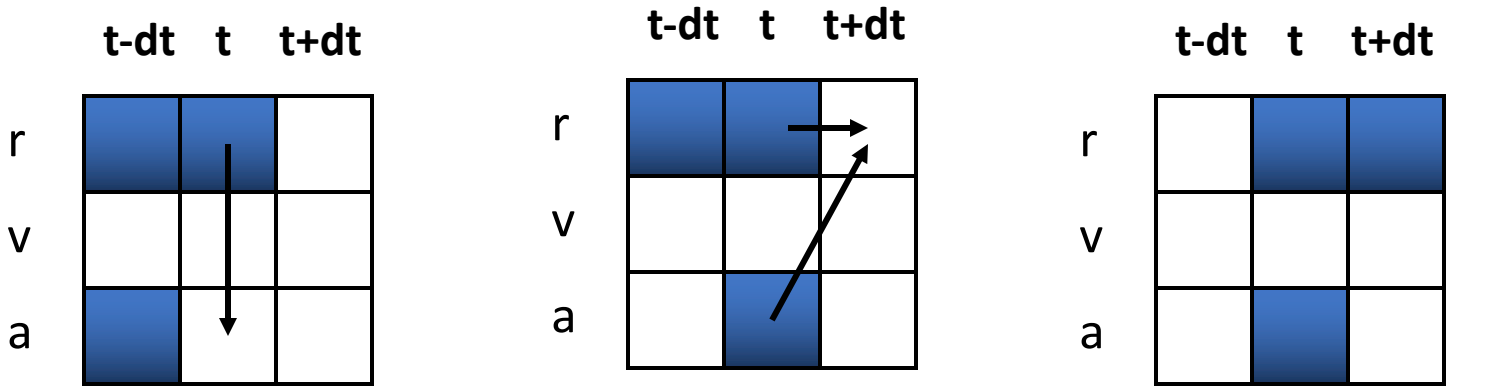
$$r(t+\Delta t) = r(t) + v(t)\Delta t + \frac{1}{2}\Delta t^2 a(t) + \frac{1}{6}\Delta t^3 b(t)$$

$$r(t-\Delta t) = r(t) - v(t)\Delta t + \frac{1}{2}\Delta t^2 a(t) - \frac{1}{6}\Delta t^3 b(t)$$

add two eqns to get Verlet algorithm

Verlet Algorithm

- A graphical representation



get a using r(t)

use a to advance to r(t+dt)

arrive at r(t+dt)

Verlet Algorithm

- No explicit velocities…problem?
- Yes! Need them to compute temperature
- Estimate from

$$v(t) = \frac{r(t+\Delta t) - r(t-\Delta t)}{2\Delta t}$$

- Positive aspects of Verlet algorithm
- accurate to dt^4
- time reversible
- good energy conservation
- one-step procedure (no predict-correct)
- very easy to code

Verlet Algorithm

- Drawbacks of Verlet algorithm
  - handling velocities is a bit awkward
  - more important: can lead to *numerical instabilities*

$$r(t+\Delta t) = \left[2r(t) - r(t-\Delta t)\right] + \Delta t^2 a(t)$$

relatively large number

very small number *squared*

rule of thumb: all numbers in an operation should be of the same order of magnitude.

Verlet “Leap Frog”

- Verlet “Leap Frog” an improvement over standard Verlet

1. $$r(t+\Delta t) = r(t) + \Delta t v\left(t + \frac{1}{2}\Delta t\right)$$

2. $$v\left(t + \frac{1}{2}\Delta t\right) = v\left(t - \frac{1}{2}\Delta t\right) + \Delta t a(t)$$

Default in Gromacs

Verlet “Leap Frog”

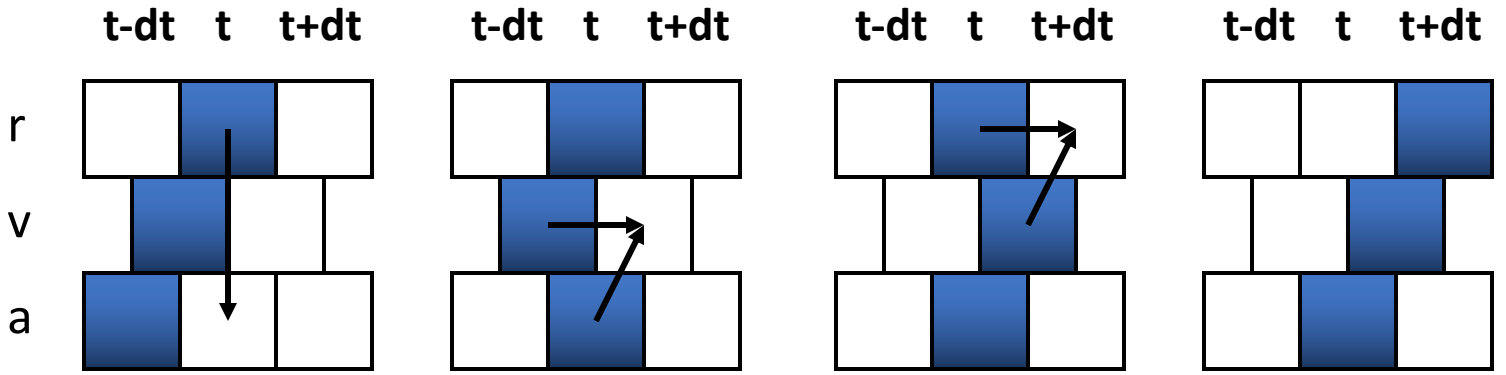
- Implementation
  - Apply 2nd equation to allow v to “leap over” r by 1/2 time step.
  - Compute current velocities

$$v(t) = \frac{1}{2}\left[v\left(t + \frac{1}{2}\Delta t \right) + v\left(t - \frac{1}{2}\Delta t \right) \right]$$

- Use $v\left(t + \frac{1}{2}\Delta t \right)$ to allow r to “catch up”

Verlet “Leap Frog”

- Graphical representation



use r(t) to get a(t)

“leap over” r(t) to get v(t+1/2dt)

use these to get r(t+dt)

Velocity Verlet algorithm

- Leap frog formally equivalent to Verlet
- Does not have instability problem
- Velocities still handled in clumsy manner
- Perhaps the "best" algorithm: "Velocity Verlet" (*J. Chem. Phys.*, **76**, *637* (1982))

$$r(t+\Delta t) = r(t) + \Delta t v(t) + \frac{1}{2}\Delta t^2 a(t)$$

$$v(t+\Delta t) = v(t) + \frac{1}{2}\Delta t\left[a(t) + a(t+\Delta t)\right]$$

Velocity Verlet

- Implementation

1 $$r(t+\Delta t) = r(t) + \Delta t v(t) + \frac{1}{2}\Delta t^2 a(t)$$

2 $$v(t+1/2\Delta t) = v(t) + \frac{1}{2}\Delta t\left[a(t)\right]$$

3 $$a(t+\Delta t) = -\frac{\nabla U\left[r(t+\Delta t)\right]}{m}$$

4 $$v(t+\Delta t) = v\left(t+\frac{1}{2}\Delta t\right) + \frac{1}{2}\Delta t\left[a(t+\Delta t)\right]$$

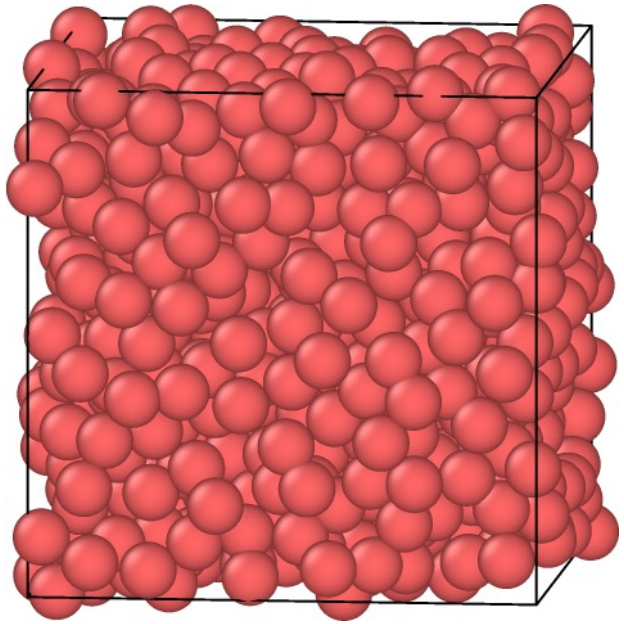
LAMMPS

run_style style args

•style = *verlet* or *verlet/split* or *respa* or *respa/omp*

"verlet" = velocity Verlet

Creating LJ molecules with LAMMPS



```
lattice fcc 0.70 # style scale(=reduced_density)
#lattice fcc 0.8442 # style scale(=reduced_density)


# Region in LJ units: 0 6.0 0 6.0 0 6.0 864 molecules
region MYBOX block 0 6.0 0 6.0 0 6.0
create_box 1 MYBOX # number_of_atom_types region_ID


create_atoms 1 box # atom_type style args
```

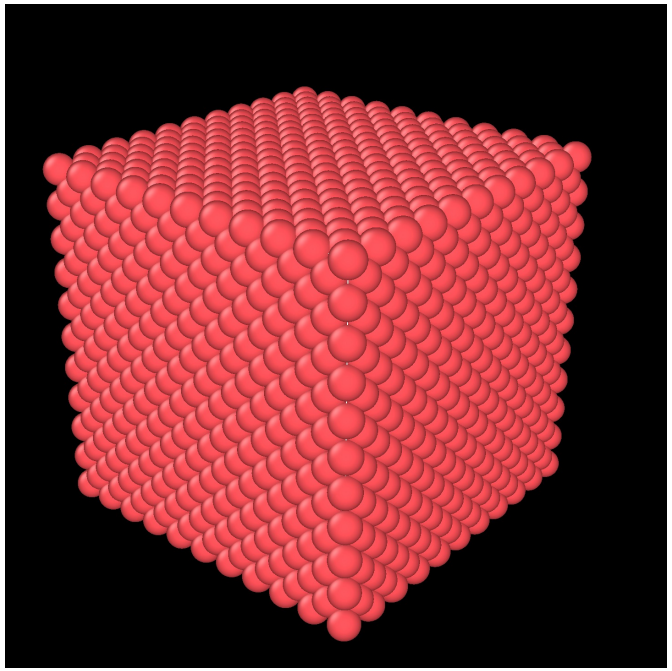
Reduced LJ density N/V* = 0.7

N=864 molecules

L* = 10.73

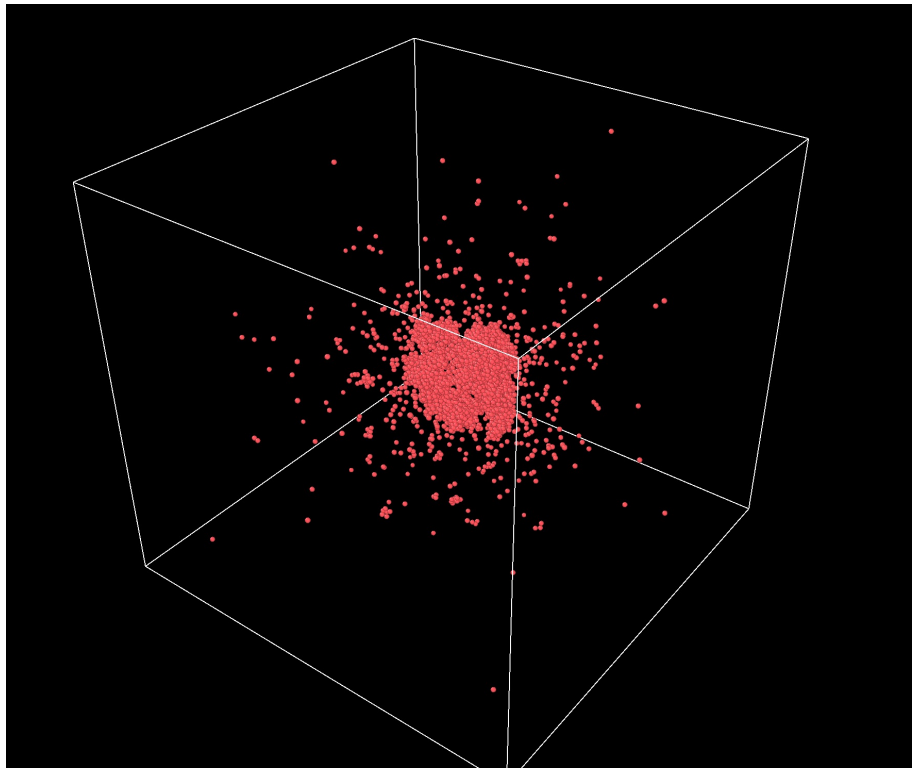
Property	Conversion
density	$\rho^* = \rho\sigma^3$
temperature	$T^* = k_B T/\epsilon$
energy	$E^* = E/\epsilon$
pressure	$P^* = P\sigma^3/\epsilon$
time	$t^* = (\epsilon/m\sigma^3)^{1/2} t$

Run Example 2



- fcc lattice: Common initial starting configuration (get high density)
- System needs to “melt” to get liquid
- Must assign random velocities to start

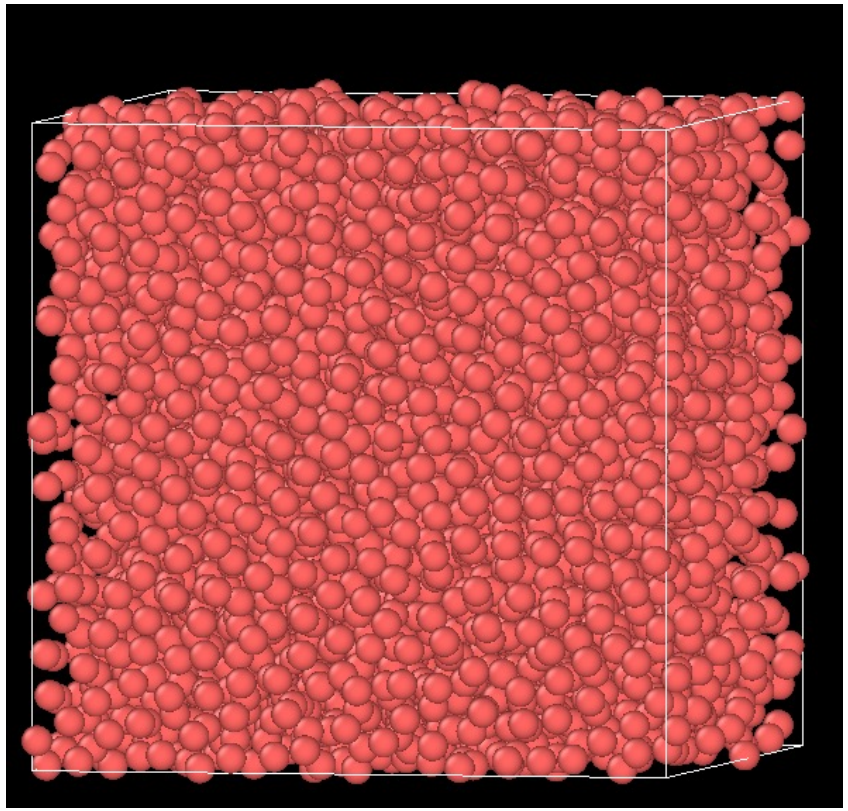
What happened?



- Atoms start at a state point that wants to be a liquid
- As atoms melt, they are exposed to a vacuum
- “Droplet” vaporizes
- V and E not constant – not microcanonical ensemble

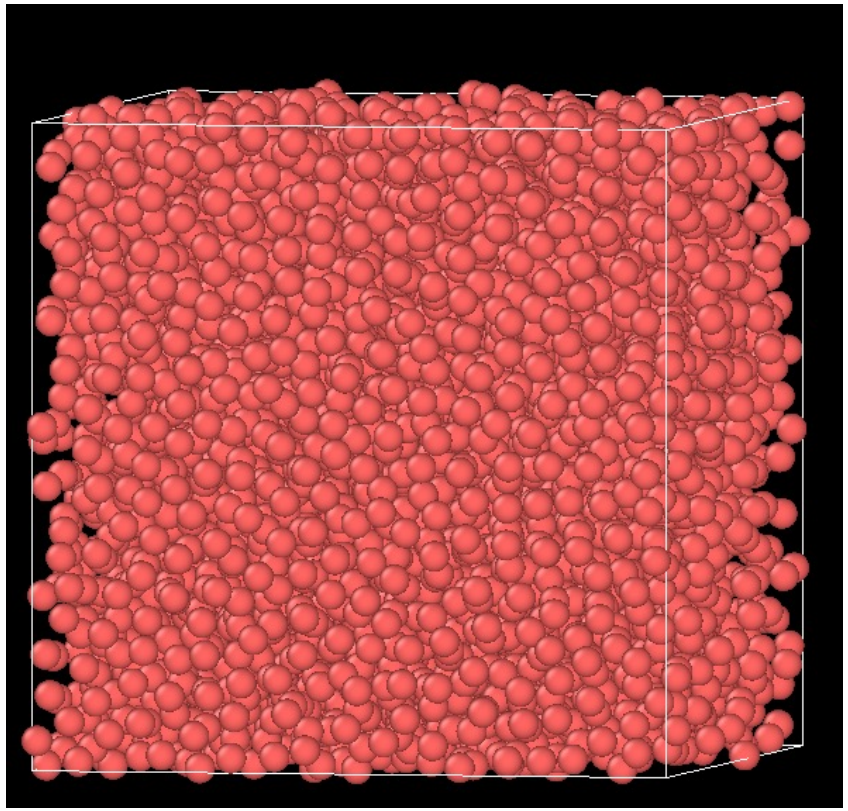
Step	Temp	Press	PotEng	KinEng	TotEng
0	3	−3.4845053	−6.0761475	4.4990283	−1.5771192
50	1.7748417	5.3570512	−4.243752	2.6616876	−1.5820644
100	1.731976	3.4268938	−4.1649181	2.5974029	−1.5675152
150	1.6790648	2.1594135	−4.0673572	2.5180534	−1.5493038
200	1.6041826	1.2516878	−3.9366626	2.4057542	−1.5309084
250	1.5091256	0.76269251	−3.7770188	2.2631995	−1.5138192
300	1.4432827	0.34099098	−3.6624767	2.1644565	−1.4980202
350	1.3603465	0.1378712	−3.5230795	2.0400792	−1.4830004
400	1.270896	0.030005588	−3.3755461	1.9059324	−1.4696137
450	1.1910348	−0.039600614	−3.2434006	1.7861664	−1.4572342
500	1.1328023	−0.090115967	−3.145119	1.6988366	−1.4462824
550	1.0687906	−0.098623743	−3.0400953	1.6028397	−1.4372555
600	1.0239435	−0.11814921	−2.9647217	1.5355836	−1.429138
650	0.97483568	−0.10659398	−2.8838015	1.4619378	−1.4218638
700	0.94299048	−0.094648988	−2.8297054	1.4141803	−1.4155252
750	0.91212726	−0.072597343	−2.7784189	1.3678955	−1.4105234
800	0.89796418	−0.063266876	−2.7533238	1.3466554	−1.4066684
850	0.88730808	−0.062104992	−2.7337885	1.3306747	−1.4031138
900	0.86641968	−0.044796873	−2.6992878	1.2993489	−1.3999389
950	0.86587028	−0.047253967	−2.6958261	1.298525	−1.3973011
1000	0.84943225	−0.0278741	−2.6692931	1.2738732	−1.3954199

Add a boundary to box



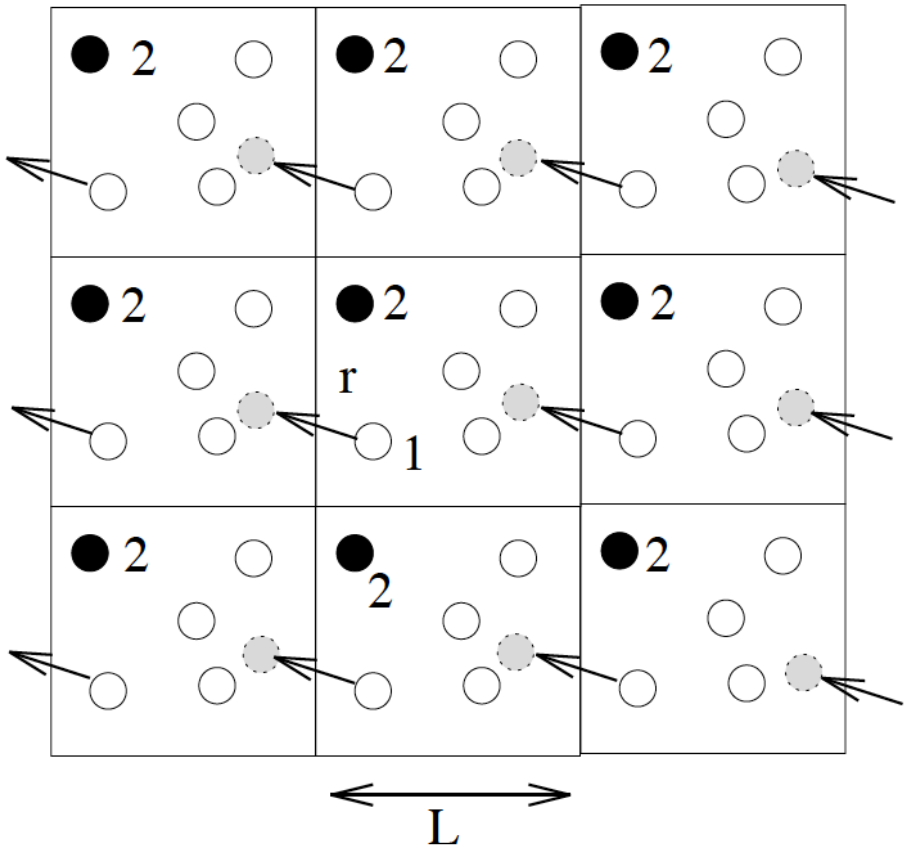
- To keep molecules inside the box, we could add a reflecting boundary or “walls”
- Keep simulation at NVE
- Do you see any problems with this?

Add a boundary to box



- To keep molecules inside the box, we could add a reflecting boundary or “walls”
- Keep simulation at NVE
- Problem?
- Simulations are ~ 1000 molecules
- Huge fraction are on surface – not representative of “bulk” behavior

Periodic boundary conditions



- Surround central box with 26 identical images
- Only track molecules in central box, but energies calculated with image particles
- Rcut < ½ box

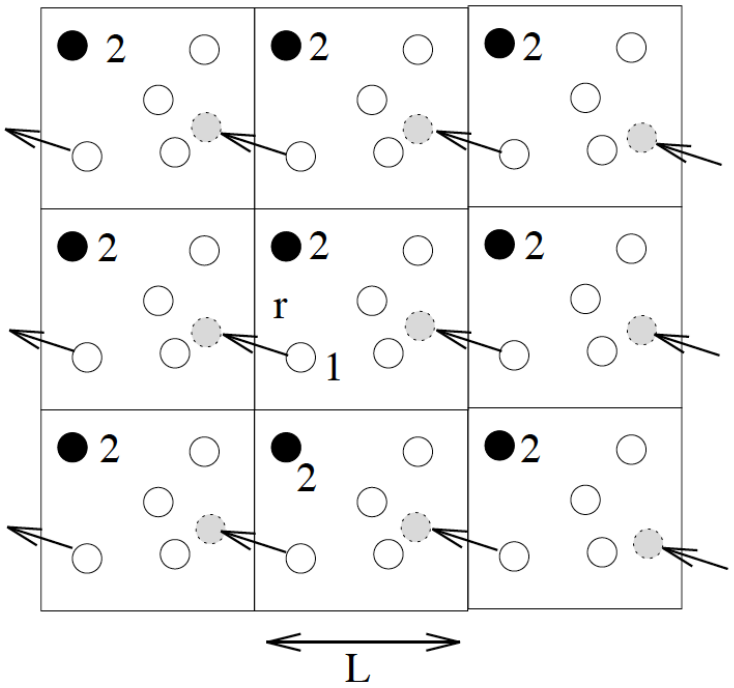
boundary p p p # x y z (p = periodic boundary conditions)
#boundary s s s # x y z (s = shrink wrapped boundary conditions)

Conserved quantities in NVE MD?

1. Hamiltonian (energy, H = U + K)

Conserved quantities in NVE MD?

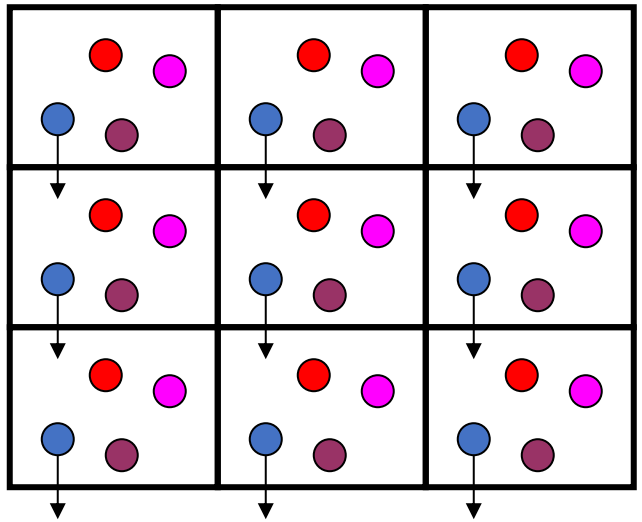
1. Hamiltonian (energy, H = U + K)
2. Linear momentum

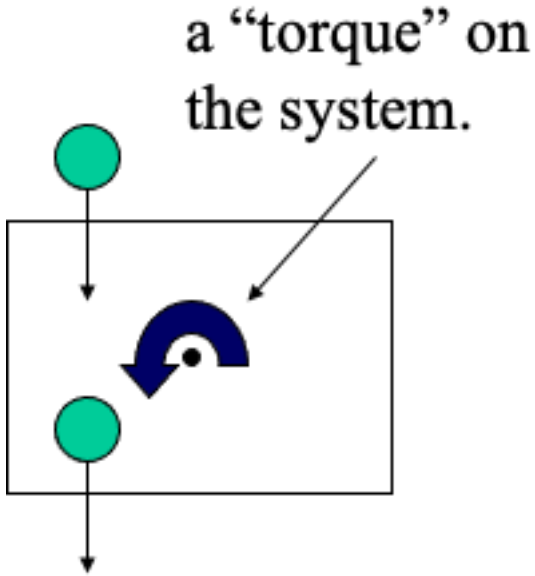


Conserved quantities in NVE MD?

1. Hamiltonian (energy, H = U + K)
2. Linear momentum
3. NOT angular momentum

4 constraints – need to account for when using the number of degrees of freedom (more on this later)





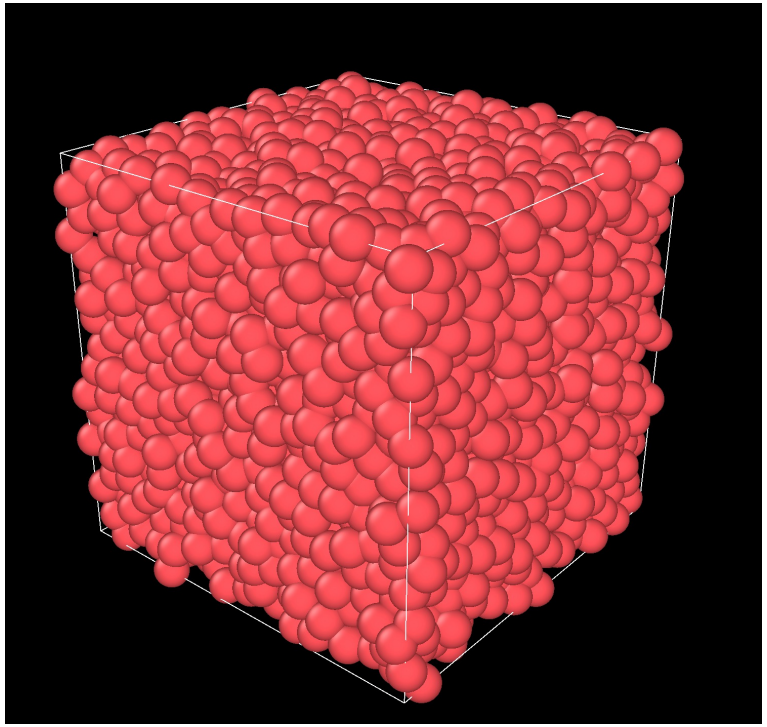
Run example 3

```
boundary p p p # x y z (p = periodic boundary conditions)
```

Implements PBC in all 3 dimensions

- What happens to NVE?
- Visualize the trajectory
  - What happens to molecules near the edges of the box?

Example 3 with PBC



Step	Temp	Press	PotEng	KinEng	TotEng
0	3	−3.7033504	−6.7733681	4.498875	−2.2744931
50	1.6762688	5.6211062	−4.7966884	2.5137746	−2.2829138
100	1.6751365	5.6745042	−4.7930126	2.5120766	−2.280936
150	1.6503181	5.8247966	−4.754385	2.4748583	−2.2795267
200	1.6439636	5.8864021	−4.7455259	2.4653289	−2.280197
250	1.6332109	5.9623581	−4.7284008	2.4492038	−2.2791969
300	1.6524852	5.8259333	−4.7570534	2.4781081	−2.2789453
350	1.6547879	5.8178479	−4.7606833	2.4815613	−2.279122
400	1.6290272	5.958913	−4.7225629	2.4429299	−2.279633
450	1.657992	5.762083	−4.7659903	2.4863663	−2.2796241
500	1.6440357	5.8575351	−4.7459147	2.4654371	−2.2804776
550	1.6348257	5.9405456	−4.7307789	2.4516255	−2.2791534
600	1.6406392	5.9643588	−4.7393391	2.4603436	−2.2789955
650	1.6450391	5.8591064	−4.7459475	2.4669417	−2.2790058
700	1.6544808	5.8686647	−4.7598262	2.4811007	−2.2787254
750	1.6355088	5.9352799	−4.7324059	2.4526499	−2.279756
800	1.6426811	5.9005846	−4.7431883	2.4634056	−2.2797827

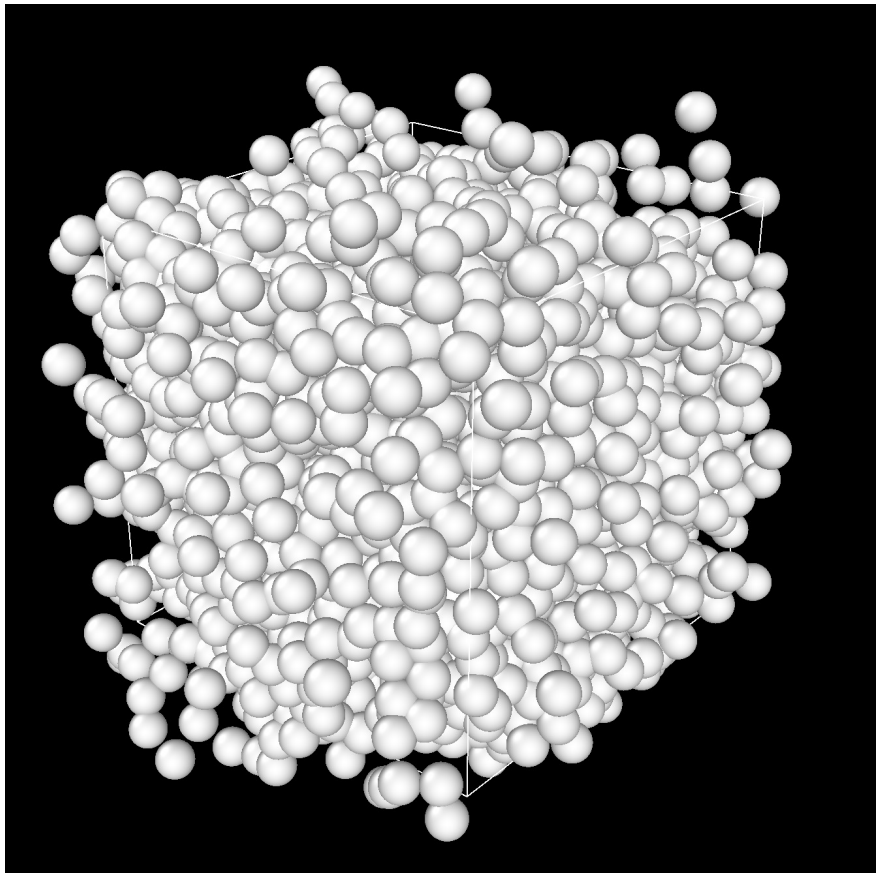
- Total energy constant (as is volume): NVE!
- Why does the potential energy go up?
- Why does the kinetic energy go down?

Run Example 4

```
# dump_ID group_ID style interval file args
dump DUMP all custom 50 ${NAME}.lammpstrj xu yu zu
```

- PBC is applied to all atoms but when we write the trajectory, we don't apply PBC to them
  - Useful when computing diffusivity
- Visualize trajectory
- Compare this and thermo properties with Example 3

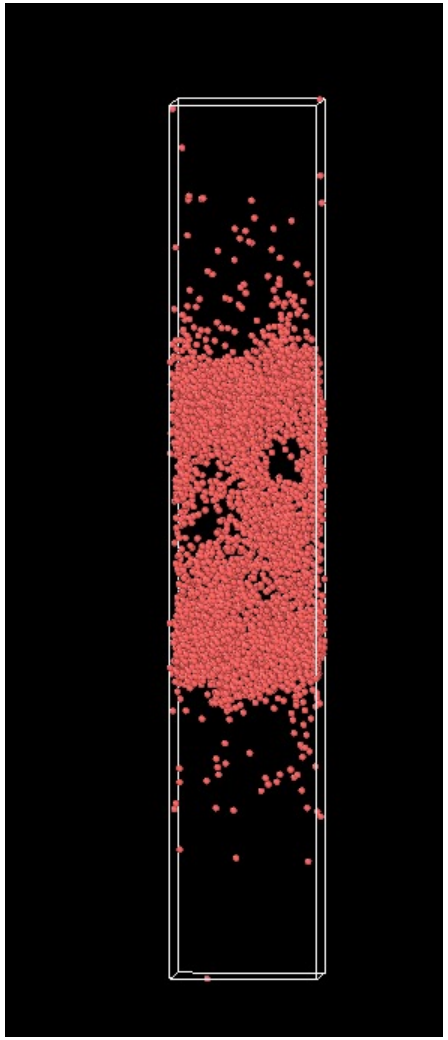
Example 4 – PBC and unwrapped coords



Step	Temp	Press	PotEng	KinEng	TotEng
0	3	−3.7033504	−6.7733681	4.498875	−2.2744931
50	1.6762688	5.6211062	−4.7966884	2.5137746	−2.2829138
100	1.6751365	5.6745042	−4.7930126	2.5120766	−2.280936
150	1.6503181	5.8247966	−4.754385	2.4748583	−2.2795267
200	1.6439636	5.8864021	−4.7455259	2.4653289	−2.280197
250	1.6332109	5.9623581	−4.7284008	2.4492038	−2.2791969
300	1.6524852	5.8259333	−4.7570534	2.4781081	−2.2789453
350	1.6547879	5.8178479	−4.7606833	2.4815613	−2.279122
400	1.6290272	5.958913	−4.7225629	2.4429299	−2.279633
450	1.657992	5.762083	−4.7659903	2.4863663	−2.2796241
500	1.6440357	5.8575351	−4.7459147	2.4654371	−2.2804776
550	1.6348257	5.9405456	−4.7307789	2.4516255	−2.2791534
600	1.6406392	5.9643588	−4.7393391	2.4603436	−2.2789955
650	1.6450391	5.8591064	−4.7459475	2.4669417	−2.2790058
700	1.6544808	5.8686647	−4.7598262	2.4811007	−2.2787254
750	1.6355088	5.9352799	−4.7324059	2.4526499	−2.279756
800	1.6426811	5.9005846	−4.7431883	2.4634056	−2.2797827

- **Exactly the same as Example 3!**
- **Atom coordinates are “unwrapped” and allow for diffusion determination**

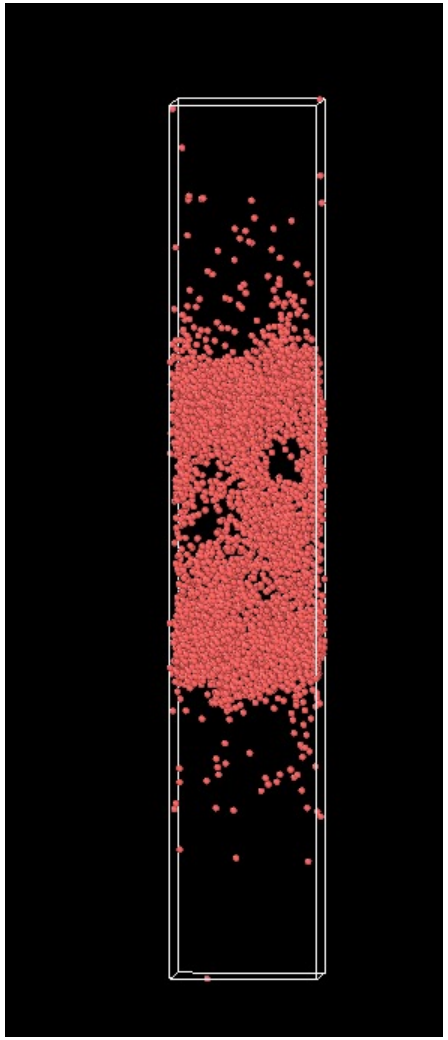
Apply PBC in 2 directions



Simulate a vacuum interface in Z; periodic liquid in X, Y

Edit example3.inp to run this simulation.

Apply PBC in 2 directions

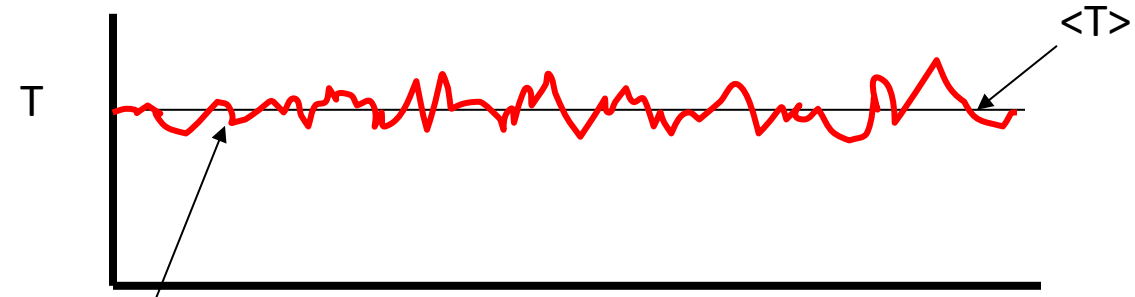


Simulate a vacuum interface in Z; periodic liquid in X, Y

```
boundary p p s # x y z (p in x, y s in z)
```

Problems With NVE MD

- Typical MD is in NVE ensemble.
- How do you compare with experiments at a given T?



Instantaneous temparature

$$T = \frac{1}{(3N - N_c)k_B} \sum_{i=1}^{N} \frac{|p_i|^2}{m_i}$$

Not always properly computed in codes!

Different ensembles

The NVE ensemble is the “natural” ensemble of molecular dynamics since the Newtonian equations of motion keep energy constant.

Simulate at NVE => compute what T, P are…

BUT, most experiments are at constant T and/or P. What to do?

Canonical (NVT) ensemble

$$Q(NVT) = \frac{1}{\Lambda^{3N} N!} \int d\mathbf{q}^N \exp\left[-\beta U(q^N)\right]$$

Isothermal-isobaric (NPT) ensemble

$$Q(NPT) = \frac{1}{V_0} \int dV \exp[-\beta PV] Q(NVT)$$

Simulating in these ensembles requires new equations of motion; “thermostat” for NVT; “thermostat” and “barostat” for NPT

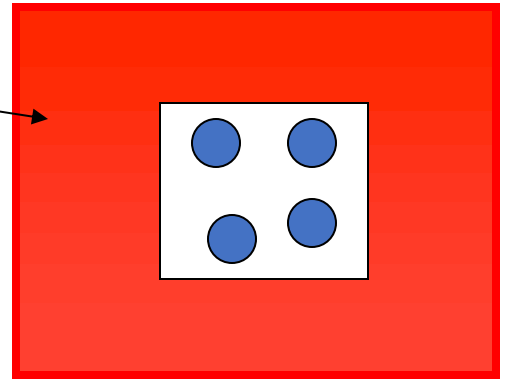
MD in Other Ensembles

- It is desirable to *set* T at start
- Perform MD in canonical (NVT) ensemble
- Can we use classical equations of motion to do this?
- No!
- A (very) crude approach: rescale v_i at each time step so

$$T = \frac{1}{\left(3N - N_c\right)k_B} \sum_{i=1}^{N} \frac{\left| p_i \right|^2}{m_i} = T_{set}$$

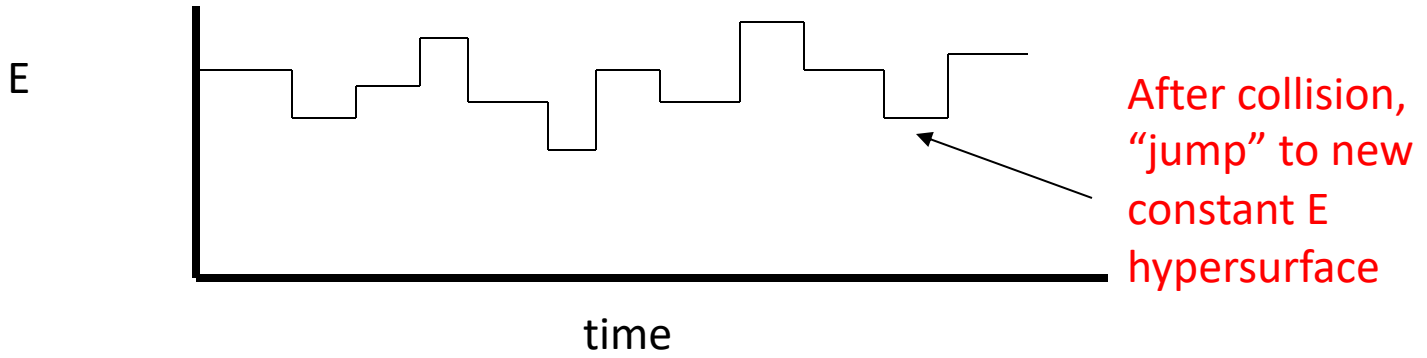
NVT MD

- Thermal reservoir at setpoint T
- At some frequency, allow a particle to "collide" with a heat bath particle.
- Reassign particle velocity from Maxwell-Boltzmann distribution at T.



NVT MD

- Phase space trajectory looks like this



- Over time, all constant E hypersurfaces sampled about T_{set}
- $\langle T \rangle \sim T_{set}$

NVT MD

- “Bath particle collision” method does yield averages consistent with canonical ensemble
- Dynamic properties may be altered however!
- This is a “zeroth order” method.
- See: H. C. Anderson, “Molecular Dynamics at Constant Pressure and/or Temperature”, *J. Chem. Phys*., **72**, 2384 (1980).

Extended Systems

- A more sophisticated approach: “extended system” methods.
- Idea: simulate an extra degree of freedom representative of a thermal reservoir.
- Coordinate has “velocity” (rate of change)
- Coordinate has “mass” (inertia)
- Common method: Nosé-Hoover

  S. Nosé, “A Molecular Dynamics Method for Simulations in the Canonical Ensemble”, *Mol. Phys.*, **53**, 255 (1984).

  W. G. Hoover, “Canonical Dynamics: Equilibrium Phase-Space Distributions”, *Phys. Rev. A*, **31**, 1695 (1985).

Extended Systems

- The Nosé-Hoover “thermostat” appears naturally in the equations of motion
- A “thermal inertia” term governs rate of heat transfer and thus KE fluctuations.
- A “time constant” of ~ 1ps typically used (~1000 dt)
- Extended system methods generalized to maintain P in NPH MD
  - see *J. Chem. Phys*., **72**, 2384 (1980).

LAMMPS *fix nvt* command

LAMMPS implements “fixes” that are any operation that is applied to the system during time stepping or minimization.

```
fix ID group-ID style_name keyword value ...
style_name = nvt or npt or nph
```

fix 1 all nve # microcanonical for all atoms

fix 3 all nvt temp 300.0 300.0 10.0 # canonical for all atoms
Start 300; stop 300; damping constant 10.0

Tdamp = temperature damping parameter (time units)

NVT simulations

- In LAMMPS, fix NVT command performs time integration on Nosé-Hoover style non-Hamiltonian equations of motion.

- The desired temperature at each timestep is a ramped value during the run from *Tstart* to *Tstop*.

- *Tdamp* is in time units and determines how rapidly the temperature is relaxed.
  - A value of 10.0 means to relax the temperature in a timespan of (roughly) 10 time units

Tdamp

From user documentation

- A Nosé-Hoover thermostat will not work well for arbitrary values of *Tdamp*.
- If *Tdamp* is too small, the temperature can fluctuate wildly; if it is too large, the temperature will take a very long time to equilibrate.
- A good choice for many models is a *Tdamp* of around 100 timesteps. Note that this is NOT the same as 100 time units.
- A simple way to ensure this, is via using an immediate variable expression accessing the thermo property 'dt', which is the length of the time step. Example:

```
fix 1 all nvt temp 300.0 300.0 $(100.0*dt)
```

Run Example 5: NVT

```
fix TEMP all nvt temp 1.7 1.7 0.3 # T1 T2 Tdamp
```

Step	Density	Temp	Press	PotEng	KinEng	TotEng
0	0.8442	3	-4.4654851	-7.2253807	4.498875	-2.7265057
5	0.8442	2.9479538	-4.0538529	-7.156045	4.4208252	-2.7352198
10	0.8442	2.7447312	-2.6017674	-6.8726962	4.1160675	-2.7566287
15	0.8442	2.2781444	0.33586859	-6.2053195	3.4163624	-2.7889572
20	0.8442	1.6831137	3.8926871	-5.3358811	2.5240394	-2.8118417
25	0.8442	1.4624299	5.387245	-5.0195891	2.1930964	-2.8264927
30	0.8442	1.5510769	5.0876634	-5.161707	2.3260336	-2.8356733
35	0.8442	1.6448668	4.6122982	-5.3070914	2.4666834	-2.840408
40	0.8442	1.6626398	4.4833398	-5.3367398	2.4933363	-2.8434036
45	0.8442	1.6446739	4.5495101	-5.3120582	2.466394	-2.8456641
50	0.8442	1.6294816	4.6214826	-5.2910339	2.4436113	-2.8474226
…						
950	0.8442	1.7036442	5.4694596	-5.1337292	2.5548274	-2.5789017
955	0.8442	1.7143303	5.4107694	-5.1507754	2.5708526	-2.5799228
960	0.8442	1.7223772	5.3660442	-5.1640457	2.5829199	-2.5811259
965	0.8442	1.7114629	5.4179554	-5.1482196	2.5665526	-2.581667
970	0.8442	1.7022124	5.4606582	-5.1359445	2.5526803	-2.5832642
975	0.8442	1.7034176	5.4516946	-5.1390778	2.5544876	-2.5845902
980	0.8442	1.7009249	5.4585891	-5.1366219	2.5507495	-2.5858723
985	0.8442	1.6969487	5.4686266	-5.131996	2.5447867	-2.5872092
990	0.8442	1.6991331	5.4419508	-5.1367317	2.5480624	-2.5886693
995	0.8442	1.7078689	5.3786159	-5.1514502	2.5611628	-2.5902874
1000	0.8442	1.724012	5.2839742	-5.1771125	2.5853715	-2.591741

T slowly approaches setpoint

KE goes down

Total energy is NOT conserved

What is the actual temperature?

$$T_{inst} = \frac{1}{(3N - N_c)k_B} \sum_{i=1} N \frac{|p_i|^2}{m_i}$$

Instantaneous temperature

$T = T_{set}$

We should obtain $\langle T_{inst} \rangle = T_{set}$

- We should not take averages over parts of the trajectory that have not yet reached the desired statepoint
- “Equilibration” phase is thrown away
- “Production” phase is recorded.
- Use “restart” feature to start from the end of an equilibrated trajectory

Run Example 6 – restart from end of Example 5

If you are unhappy with how well equilibrated Example 5 is, re-run it for a longer time.

Examine the KE, PE, E, T, and P

Example 7 – Play with different options

Other ways to run NVT
Play with potential cutoff method, etc.

NPT simulations

LAMMPS uses an extended system Nosé-Hoover style

```
fix TEMP all npt temp 1.7 1.7 0.3 iso 5.0 5.0 1000.0 #
```

iso values = Pstart Pstop Pdamp; scalar external pressure at start/end of run (pressure units); Pdamp = pressure damping parameter (time units)

- A Nosé-Hoover barostat will not work well for arbitrary values of *Pdamp*.
- If *Pdamp* is too small, the pressure and volume can fluctuate wildly; if it is too large, the pressure will take a very long time to equilibrate.
- A good choice for many models is a *Pdamp* of around 1000 timesteps.

Run Example 8

Run basic case and look at how T, E, P vary

Adjust the barostat (or thermostat) time constants and see what happens

```
# configure integrator and thermostats/barostats
fix TEMP all npt temp 1.7 1.7 0.3 iso 5.0 5.0 1000.0
timestep 0.003 # The default timestep size is 0.005 for LJ units.
```

Look at the T, P, and density.