Molecular Dynamics

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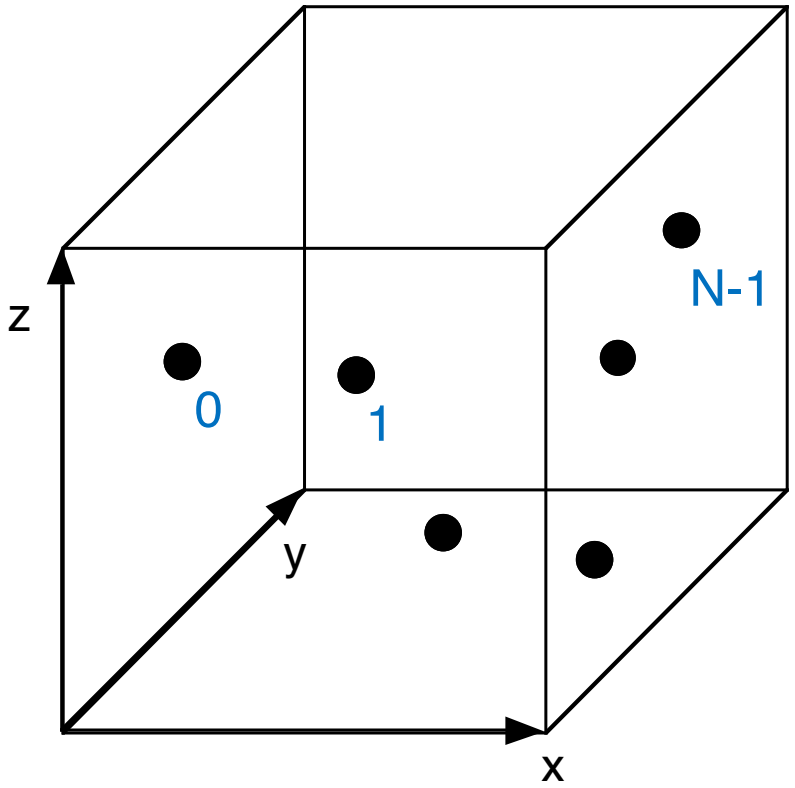
Goals:

1. **Math: ordinary differential equations**
2. **Practical MD simulation**

System: A Set of Point Atoms

Math symbol $\{\vec{r}_i = (x_i, y_i, z_i) \mid x_i, y_i, z_i \in \Re, i = 0, \ldots, N-1\}$

See lecture on Molecular dynamics basics



In program `md.c`:

Variable

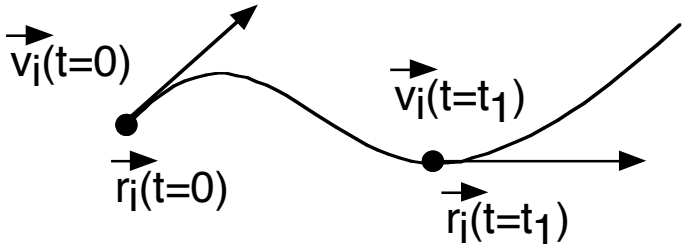
`int nAtom`: N, Number of atoms.

`NMAX`: Maximum number of atoms.

`double r[NMAX][3]`: `r[i][0|1|2]` = $x_i|y_i|z_i$.

Trajectory

- **Trace of atom positions**



$$t \in \Re \mapsto \vec{r}_i(t) \in \Re^3$$

Mapping

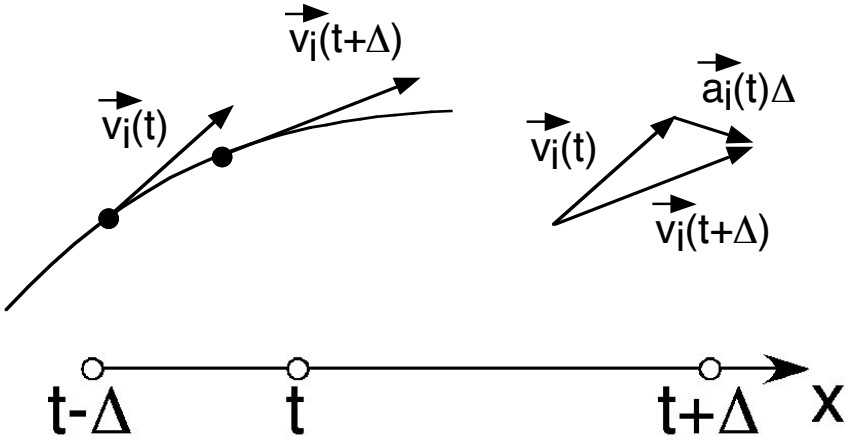
- **Velocity** $\vec{v}_i(t) = \dot{\vec{r}}_i(t) = \dfrac{d\vec{r}_i}{dt} \equiv \lim_{\Delta \to 0} \dfrac{\vec{r}_i(t+\Delta) - \vec{r}_i(t)}{\Delta}$ 2-point difference

`double rv[NMAX][3]: rv[i][0|1|2]` $= v_{ix}|v_{iy}|v_{iz}$

- **Acceleration** $\vec{a}_i(t) = \ddot{\vec{r}}_i(t) = \dfrac{d^2\vec{r}_i}{dt^2} = \dfrac{d\vec{v}_i}{dt} \equiv \lim_{\Delta \to 0} \dfrac{\vec{v}_i(t+\Delta) - \vec{v}_i(t)}{\Delta}$

`double ra[NMAX][3]: ra[i][0|1|2]` $= a_{ix}|a_{iy}|a_{iz}$

It's vector arithmetic



$$\vec{a}_i(t) = \lim_{\Delta \to 0} \frac{\vec{v}_i(t+\Delta/2) - \vec{v}_i(t-\Delta/2)}{\Delta}$$

$$= \lim_{\Delta \to 0} \frac{\dfrac{\vec{r}_i(t+\Delta) - \vec{r}_i(t)}{\Delta} - \dfrac{\vec{r}_i(t) - \vec{r}_i(t-\Delta)}{\Delta}}{\Delta}$$

$$= \lim_{\Delta \to 0} \frac{\vec{r}_i(t+\Delta) - 2\vec{r}_i(t) + \vec{r}_i(t-\Delta)}{\Delta^2}$$

3-point difference

Newton's Equation of Motion

Trajectory is determined by Newton's 2nd law:

mass $\longrightarrow m\ddot{\vec{r}}_i(t) = \vec{F}_i(t) \longleftarrow$ force

- **Initial value problem:** Given initial particle positions & velocities $\left\{\left(\vec{r}_i(0), \vec{v}_i(0)\right) | i = 0, \ldots, N-1\right\}$, obtain those at later times $\left\{\left(\vec{r}_i(t), \vec{v}_i(t)\right) | i = 0, \ldots, N-1; t > 0\right\}$ by numerically integrating Newton's equation of motion

- **Force from potential energy:** $\vec{F}_k = -\frac{\partial}{\partial \vec{r}_k} V\left(\vec{r}^N\right) = -\left(\frac{\partial V}{\partial x_k}, \frac{\partial V}{\partial y_k}, \frac{\partial V}{\partial z_k}\right)$

  where the partial derivative is

$$\frac{\partial V}{\partial x_k} = \lim_{h \to 0} \frac{V(x_0, y_0, z_0, \ldots, x_k + h, y_k, z_k, \ldots x_{N-1}, y_{N-1}, z_{N-1}) - V(x_0, y_0, z_0, \ldots, x_k, y_k, z_k, \ldots x_{N-1}, y_{N-1}, z_{N-1})}{h}$$

- **Pair potential:** $V\left(\vec{r}^N\right) = \sum_{i<j} u(r_{ij}) = \sum_{i=0}^{N-2} \sum_{j=i+1}^{N-1} u(|\vec{r}_{ij}|)$

  "for all pairs of atoms"

$$\vec{r}_{ij} = \vec{r}_i - \vec{r}_j$$

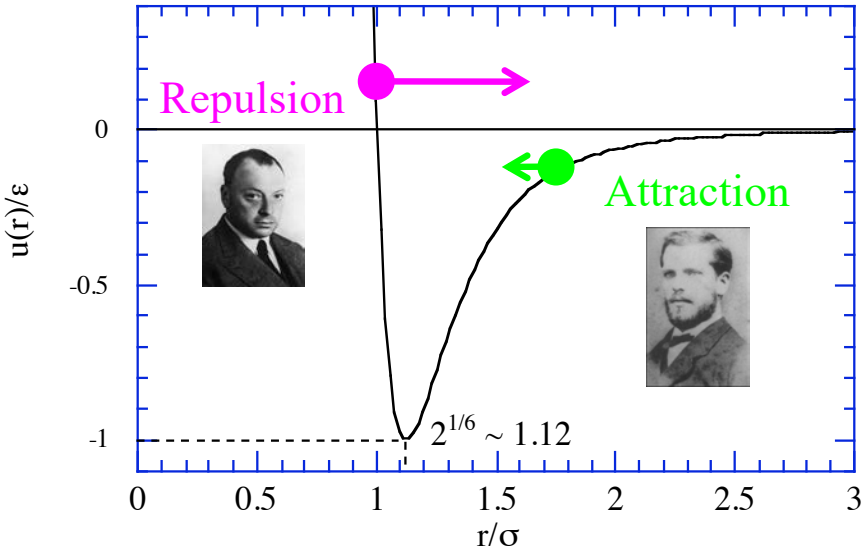
$i \backslash j$	0	1	2	3
0		X	X	X
1			X	X
2				X
3				

Lennard-Jones Potential

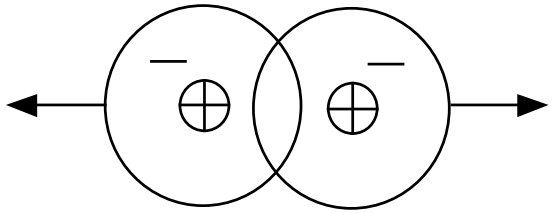
$$V\left(\vec{r}^{\,N}\right) = \sum_{i<j} u(r_{ij}) = \sum_{i=0}^{N-2} \sum_{j=i+1}^{N-1} u(|\vec{r}_{ij}|)$$

where $\vec{r}_{ij} = \vec{r}_i - \vec{r}_j$ and

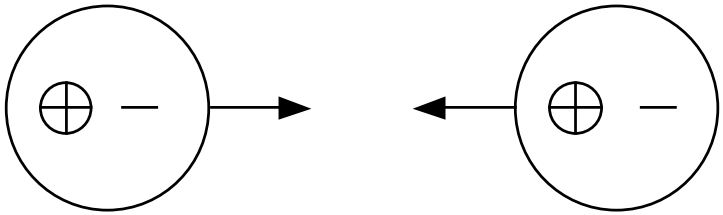
$$u(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$



Short-range repulsion by Pauli exclusion between electrons



Long-range attraction by polarization



Johanes D. van der Waals
Nobel Physics Prize (1910)

Wolfgang Pauli
Nobel Physics
Prize (1945)

John E. Lennard-Jones
PPS **43**, 461 (1931)

Normalization

For Argon atoms:

- $m = 6.6 \times 10^{-23}$ gram
- $\varepsilon = 1.66 \times 10^{-14}$ erg (erg = gram•cm^2/second^2)
- $\sigma = 3.4 \times 10^{-8}$ cm

Define length, energy & time units as

$$\begin{cases} \vec{r}_i = \vec{r}_i' \sigma = 3.4 \times 10^{-8} [\text{cm}] \times \vec{r}_i' \\ V = V' \varepsilon = 1.66 \times 10^{-14} [\text{erg}] \times V' \\ t = \sigma \sqrt{m/\varepsilon} t' = 2.2 \times 10^{-12} [\text{sec}] \times t' \end{cases}$$

The equation of motion in these units:

$$\frac{d^2 \vec{r}_i}{dt^2} = -\frac{\partial V}{\partial \vec{r}_i} = \vec{a}_i$$

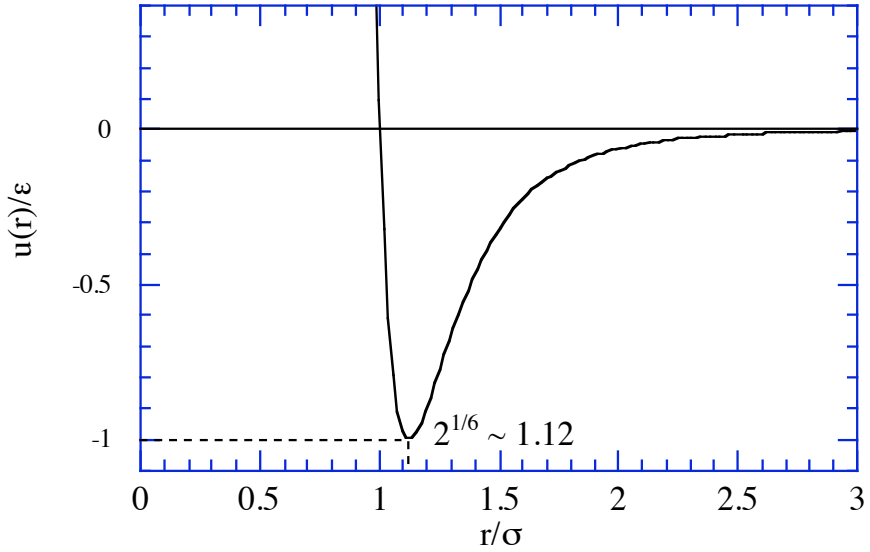
$$V(\vec{r}^N) = \sum_{i<j} u(r_{ij})$$

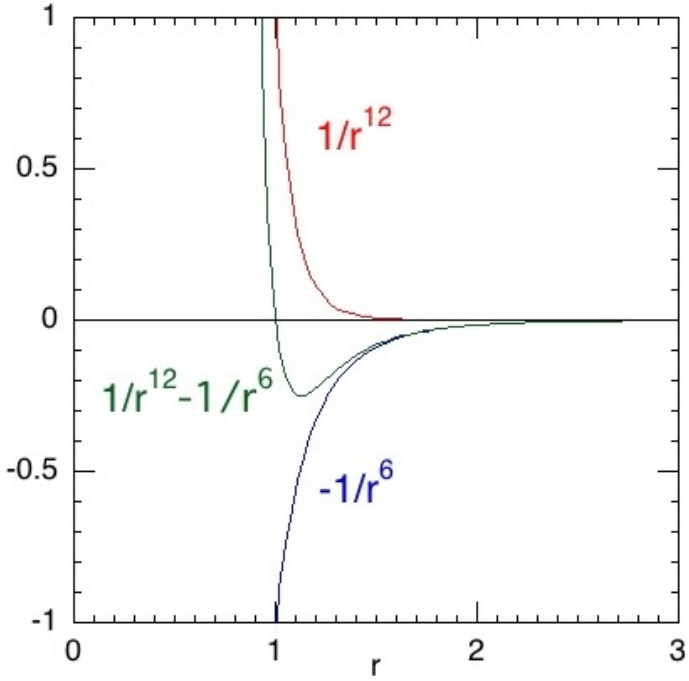
$$u(r) = 4\left(\frac{1}{r^{12}} - \frac{1}{r^6}\right)$$

1.66×10^{-14} erg
$= 3.97 \times 10^{-25}$ kcal
$= 7.35 \times 10^{-28}$ Big Mac

540 kcal

Repulsion *vs.* Attraction





$$u(r) = 4\left(\frac{1}{r^{12}} - \frac{1}{r^{6}}\right)$$

$$\frac{du}{dr} = 4\left(-\frac{12}{r^{13}} + \frac{6}{r^{7}}\right) = -\frac{48}{r^{7}}\left(\frac{1}{r^{6}} - \frac{1}{2}\right)$$

r	0	...	$2^{1/6}$	...	∞
du/dr		−	0	+	
u	∞	↘	−1	↗	0

Father of Molecular Dynamics

PHYSICAL REVIEW VOLUME 136, NUMBER 2A 19 OCTOBER 1964

Correlations in the Motion of Atoms in Liquid Argon*

A. RAHMAN
Argonne National Laboratory, Argonne, Illinois
(Received 6 May 1964)

A system of 864 particles interacting with a Lennard-Jones potential and obeying classical equations of motion has been studied on a digital computer (CDC 3600) to simulate molecular dynamics in liquid argon at 94.4°K and a density of 1.374 g cm^{-3}.

Aneesur Rahman—Father of molecular dynamics

Argonne physicist Aneesur Rahman, known worldwide as the "father of molecular dynamics," pioneered the application of computer science to physical systems.

In 1960, Rahman successfully modeled the behavior of a cluster of 864 argon atoms on a computer that could perform only 150,000 calculations per second.

While Argonne's new IBM Blue Gene ® /P supercomputer runs nearly 3 million times faster than Rahman's CDC 3600, today's scientists still base the code for their models on Rahman's algorithms.

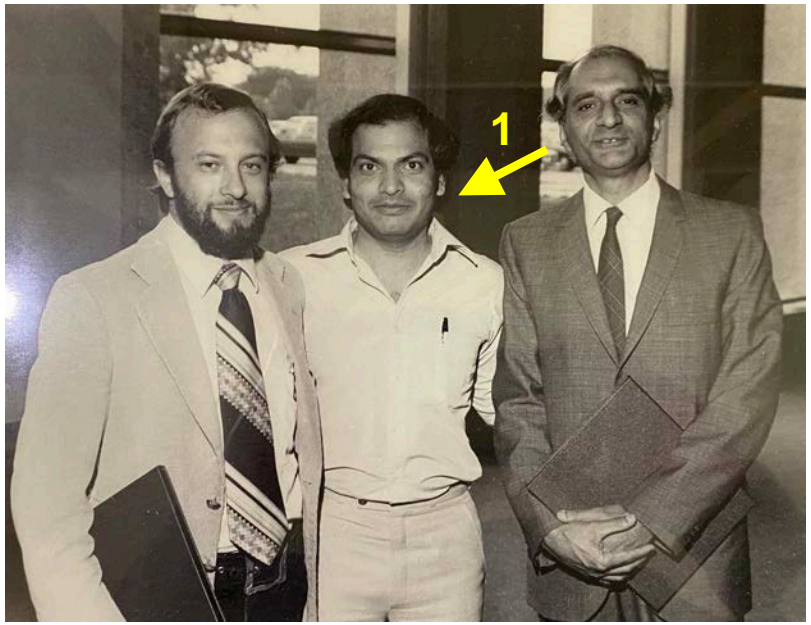
Since 1993, the American Physical Society has annually awarded the Aneesur Rahman Prize for outstanding achievement in computational physics research.

Anees Rahman (1927-1987)

See the Nobel lecture by Michael Levitt

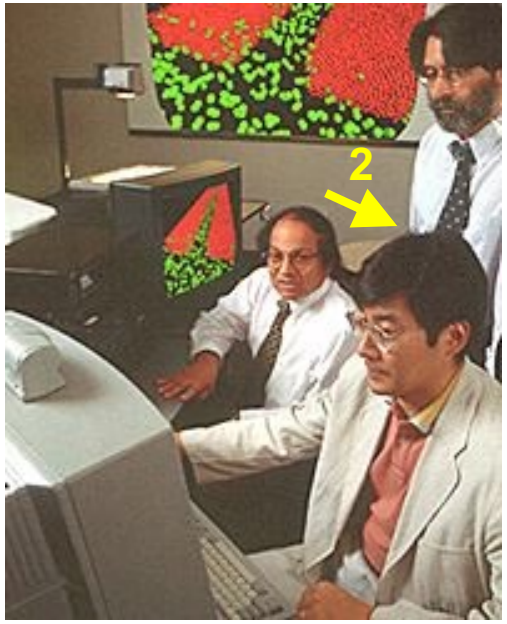
Your Rahman Number?

Anees Rahman ('67)



Anees Rahman & Priya Vashishta
at Argonne National Lab ('81)

https://aiichironakano.github.io/phys516/Battimelli-ComputerMeetsPhysics-Springer20.pdf, pp. 58 & 128



Priya Vashishta,
Rajiv Kalia
and AN ('02)

Your Rahman number is 3

Molecular Dynamics Equations

Given initial atomic positions & velocities $\{(\vec{r}_i(0), \vec{v}_i(0)) | i = 0, \ldots, N-1\}$,

obtain those at later times $\{(\vec{r}_i(t), \vec{v}_i(t)) | i = 0, \ldots, N-1; t > 0\}$

by integrating the ordinary differential equation,

$$\ddot{\vec{r}}_k(t) = \vec{a}_k(t) = -\frac{\partial}{\partial \vec{r}_k} \sum_{i<j} u(r_{ij}) = \sum_{i<j} \vec{r}_{ij}(t) \left(-\frac{1}{r}\frac{du}{dr}\right)_{r=r_{ij}(t)} (\delta_{ik} - \delta_{jk})$$

$$\vec{r}_{ij} = \vec{r}_i - \vec{r}_j$$

$$\delta_{ij} = \begin{cases} 1 & i = j \\ 0 & i \neq j \end{cases}$$

where $$-\frac{1}{r}\frac{du}{dr} = \frac{48}{r^2}\left(\frac{1}{r^{12}} - \frac{1}{2r^6}\right)$$

(for the Lennard-Jones potential in a dimensionless unit)

Force calculation algorithm—$O(N^2)$:

for $i = 0$ to N-1, $\vec{a}_i = 0$

for $i = 0$ to N-2

for $j = i$+1 to N-1

compute $\vec{\alpha} = \vec{r}_{ij}\left(-\frac{1}{r}\frac{du}{dr}\right)_{r=|\vec{r}_{ij}|}$

$\vec{a}_i += \vec{\alpha}$

$\vec{a}_j -= \vec{\alpha}$

```
for (n=0; n<nAtom; n++)
   for (k=0; k<3; k++) ra[n][k] = 0.0;
for (j1=0; j1<nAtom-1; j1++) {
   for (j2=j1+1; j2<nAtom; j2++) {
      for (rr=0.0, k=0; k<3; k++) {
         dr[k] = r[j1][k] - r[j2][k];
         dr[k] = dr[k] - SignR(RegionH[k],dr[k]-RegionH[k])
                       - SignR(RegionH[k],dr[k]+RegionH[k]);
         rr = rr + dr[k]*dr[k];
      }
      if (rr < rrCut) {
         ri2 = 1.0/rr; ri6 = ri2*ri2*ri2; r1 = sqrt(rr);
         fcVal = 48.0*ri2*ri6*(ri6-0.5) + Duc/r1;
         for (k=0; k<3; k++) {
            f = fcVal*dr[k];
            ra[j1][k] = ra[j1][k] + f;
            ra[j2][k] = ra[j2][k] - f;
         }
      }
   }
}
```

in computeAccel() in md.c

Analytic Formula for Forces

$$\vec{a}_k = -\frac{\partial}{\partial \vec{r}_k}\sum_{i<j} u(r_{ij}) = -\sum_{i<j}\frac{\partial r_{ij}}{\partial \vec{r}_k}\frac{du}{dr_{ij}}$$

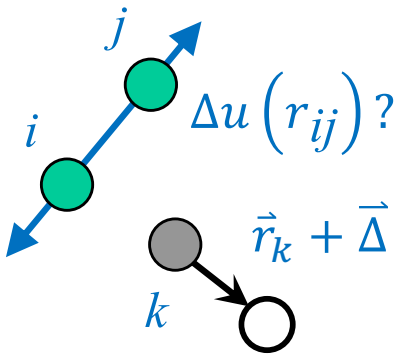
Chain rule

$$\frac{\partial r_{ij}}{\partial \vec{r}_k} = \left(\frac{\partial}{\partial x_k}, \frac{\partial}{\partial y_k}, \frac{\partial}{\partial z_k}\right)\sqrt{(x_i - x_j)^2 + (y_i - y_j)^2 + (z_i - z_j)^2}$$

$$= \frac{(2(x_i - x_j), 2(y_i - y_j), 2(z_i - z_j))}{2\sqrt{(x_i - x_j)^2 + (y_i - y_j)^2 + (z_i - z_j)^2}}\left(\delta_{ik} - \delta_{jk}\right)$$

$$= \frac{\vec{r}_{ij}}{r_{ij}}\left(\delta_{ik} - \delta_{jk}\right)$$

$$\left(\because \frac{d}{dx}[f(x)]^{1/2} = \frac{1}{2}[f(x)]^{-1/2}\frac{df}{dx}\right)$$



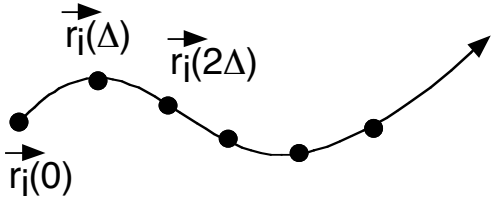
$$\frac{du}{dr} = 4\frac{d}{dr}\left(\frac{1}{r^{12}} + \frac{1}{r^6}\right) = 4\left(-\frac{12}{r^{13}} + \frac{6}{r^7}\right) = -\frac{48}{r}\left(\frac{1}{r^{12}} - \frac{1}{2r^6}\right)$$

$$\left(\because \frac{d}{dr}r^{-n} = -nr^{-n-1}\right)$$

Time Discretization

- **Snapshots with time interval Δ:** `double DeltaT`

$$\left(\vec{r}_i(0),\vec{v}_i(0)\right)\mapsto\left(\vec{r}_i(\Delta),\vec{v}_i(\Delta)\right)\mapsto\left(\vec{r}_i(2\Delta),\vec{v}_i(2\Delta)\right)\mapsto\cdots$$



- **Question: How to predict the next state,** $\left(\vec{r}_i(t+\Delta),\vec{v}_i(t+\Delta)\right)$**, from the current state,** $\left(\vec{r}_i(t),\vec{v}_i(t)\right)$**?**

- **Solution: Taylor expansion**

$$f(x_0+h)=\sum_{n=0}^{\infty}\frac{h^n}{n!}\frac{d^n f}{dx^n}\bigg|_{x=x_0}=f(x_0)+h\frac{df}{dx}\bigg|_{x=x_0}+\frac{h^2}{2}\frac{d^2 f}{dx^2}\bigg|_{x=x_0}+\frac{h^3}{3!}\frac{d^3 f}{dx^3}\bigg|_{x=x_0}+\cdots$$

See the note on Taylor's expansion

Verlet Discretization

Position:

$$\vec{r}_i(t+\Delta) = \vec{r}_i(t) + \vec{v}_i(t)\Delta + \frac{1}{2}\vec{a}_i(t)\Delta^2 + \frac{1}{6}\dddot{\vec{r}}_i(t)\Delta^3 + O(\Delta^4)$$

$$+ \quad \vec{r}_i(t-\Delta) = \vec{r}_i(t) - \vec{v}_i(t)\Delta + \frac{1}{2}\vec{a}_i(t)\Delta^2 - \frac{1}{6}\dddot{\vec{r}}_i(t)\Delta^3 + O(\Delta^4)$$

$$\vec{r}_i(t+\Delta) + \vec{r}_i(t-\Delta) = 2\vec{r}_i(t) + \vec{a}_i(t)\Delta^2 + O(\Delta^4)$$

$$\therefore \vec{r}_i(t+\Delta) = 2\vec{r}_i(t) - \vec{r}_i(t-\Delta) + \vec{a}_i(t)\Delta^2 + O(\Delta^4)$$

Velocity:

$$\vec{r}_i(t+\Delta) = \vec{r}_i(t) + \vec{v}_i(t)\Delta + \frac{1}{2}\vec{a}_i(t)\Delta^2 + \frac{1}{6}\dddot{\vec{r}}_i(t)\Delta^3 + O(\Delta^4)$$

$$- \quad \vec{r}_i(t-\Delta) = \vec{r}_i(t) - \vec{v}_i(t)\Delta + \frac{1}{2}\vec{a}_i(t)\Delta^2 - \frac{1}{6}\dddot{\vec{r}}_i(t)\Delta^3 + O(\Delta^4)$$

$$\vec{r}_i(t+\Delta) - \vec{r}_i(t-\Delta) = 2\vec{v}_i(t)\Delta + O(\Delta^3)$$

$$\therefore \vec{v}_i(t) = \frac{\vec{r}_i(t+\Delta) - \vec{r}_i(t-\Delta)}{2\Delta} + O(\Delta^2)$$

Verlet Algorithm

Verlet discretization:

$$\begin{cases} \vec{r}_i(t+\Delta) = 2\vec{r}_i(t) - \vec{r}_i(t-\Delta) + \vec{a}_i(t)\Delta^2 + O(\Delta^4) \\ \vec{v}_i(t) = \dfrac{\vec{r}_i(t+\Delta) - \vec{r}_i(t-\Delta)}{2\Delta} + O(\Delta^2) \end{cases}$$

Loup Verlet (1931-2019)

Verlet algorithm:

Given $\vec{r}_i(t-\Delta)$ & $\vec{r}_i(t)$,

1. Compute $\vec{a}_i(t)$ as a function of $\{\vec{r}_i(t)\}$
2. $\vec{r}_i(t+\Delta) \leftarrow 2\vec{r}_i(t) - \vec{r}_i(t-\Delta) + \vec{a}_i(t)\Delta^2$
3. $\vec{v}_i(t) \leftarrow \left[\vec{r}_i(t+\Delta) - \vec{r}_i(t-\Delta)\right]/(2\Delta)$

Out In

$\{\vec{a}_i\} \leftarrow \text{computeAccel}(\{\vec{r}_i\})$

```
for (n=0; n<nAtom; n++)
    for (k=0; k<3; k++) ra[n][k] = 0.0;
for (j1=0; j1<nAtom-1; j1++) {
    for (j2=j1+1; j2<nAtom; j2++) {
        for (rr=0.0, k=0; k<3; k++) {
            dr[k] = r[j1][k] - r[j2][k];
            dr[k] = dr[k] - SignR(RegionH[k],dr[k]-RegionH[k])
                          - SignR(RegionH[k],dr[k]+RegionH[k]);
            rr = rr + dr[k]*dr[k];
        }
        if (rr < rrCut) {
            ri2 = 1.0/rr; ri6 = ri2*ri2*ri2; r1 = sqrt(rr);
            fcVal = 48.0*ri2*ri6*(ri6-0.5) + Duc/r1;
            for (k=0; k<3; k++) {
                f = fcVal*dr[k];
                ra[j1][k] = ra[j1][k] + f;
                ra[j2][k] = ra[j2][k] - f;
            }
        }
    }
}
```

In

Out

Drawback: Positions & velocities are not simultaneously updated for the same time step

Loup Verlet, *Phys. Rev.* **159**, 98 ('67)

https://aiichironakano.github.io/phys516/Battimelli-ComputerMeetsPhysics-Springer20.pdf, p. 69

Velocity Verlet Algorithm

Theorem: **The following algebraic equation gives the same sequence of states, $(\vec{r}_i(n\Delta), \vec{v}_i(n\Delta))$, as that obtained by the Verlet discretization (see lecture note p. 7 for a proof and the velocity error).**

$$\begin{cases} \vec{r}_i(t+\Delta) = \vec{r}_i(t) + \vec{v}_i(t)\Delta + \frac{1}{2}\vec{a}_i(t)\Delta^2 + O(\Delta^4) \\ \vec{v}_i(t+\Delta) = \vec{v}_i(t) + \frac{\vec{a}_i(t) + \vec{a}_i(t+\Delta)}{2}\Delta + O(\Delta^3) \end{cases}$$

Velocity Verlet algorithm:

Given $(\vec{r}_i(t), \vec{v}_i(t))$,

1. Compute $\vec{a}_i(t)$ as a function of $\{\vec{r}_i(t)\}$ → $\{\vec{a}_i(t)\} \leftarrow \text{computeAccel}(\{\vec{r}_i(t)\})$
2. $\vec{v}_i(t+\frac{\Delta}{2}) \leftarrow \vec{v}_i(t) + \frac{\Delta}{2}\vec{a}_i(t)$
3. $\vec{r}_i(t+\Delta) \leftarrow \vec{r}_i(t) + \vec{v}_i(t+\frac{\Delta}{2})\Delta$
4. Compute $\vec{a}_i(t+\Delta)$ as a function of $\{\vec{r}_i(t+\Delta)\}$
5. $\vec{v}_i(t+\Delta) \leftarrow \vec{v}_i(t+\frac{\Delta}{2}) + \frac{\Delta}{2}\vec{a}_i(t+\Delta)$

$\{\vec{a}_i(t+\Delta)\} \leftarrow \text{computeAccel}(\{\vec{r}_i(t+\Delta)\})$

$$\vec{v}_i(t) + \frac{\vec{a}_i(t) + \vec{a}_i(t+\Delta)}{2}\Delta = \overbrace{\vec{v}_i(t) + \frac{\vec{a}_i(t)}{2}\Delta}^{\equiv \vec{v}_i\left(t+\frac{\Delta}{2}\right)} + \frac{\vec{a}_i(t+\Delta)}{2}\Delta$$

$$r_i(t+\Delta) = r_i(t) + \overbrace{\left(\vec{v}_i(t) + \frac{\vec{a}_i(t)}{2}\Delta\right)}^{\vec{v}_i\left(t+\frac{\Delta}{2}\right)}\Delta$$

Velocity Verlet Algorithm for `StepLimit` Steps

Initialize $(\vec{r}_i, \vec{v}_i)$ for all i

Compute $\vec{a}_i$ for all i as a function of $\{\vec{r}_i\}$ **function `computeAccel()`**

for `stepCount` = 1 to `StepLimit`

do the following **function `singleStep()`**

$\vec{v}_i \leftarrow \vec{v}_i + \vec{a}_i \Delta / 2$ for all i

$\vec{r}_i \leftarrow \vec{r}_i + \vec{v}_i \Delta$ for all i

Compute $\vec{a}_i$ for all i as a function of $\{\vec{r}_i\}$ **function `computeAccel()`**

$\vec{v}_i \leftarrow \vec{v}_i + \vec{a}_i \Delta / 2$ for all i

endfor

`stepLimit+1` calls to function `computeAccel()`

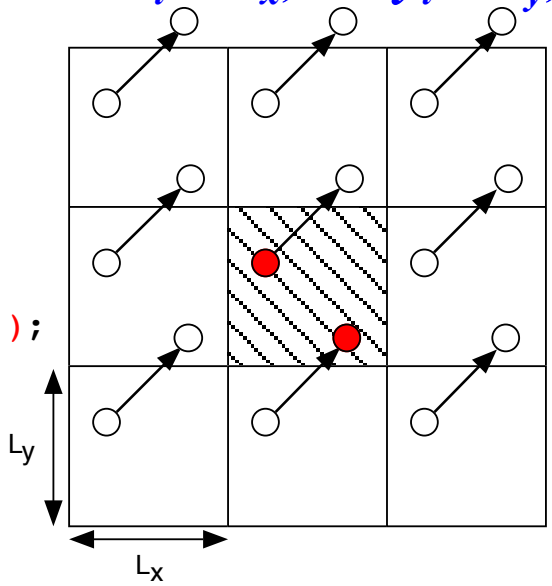
```
computeAccel();
for (stepCount=1; stepCount<=StepLimit; stepCount++) {
  singleStep(); // computeAccel() called once here
  if (stepCount%StepAvg == 0) evalProps();
}
```

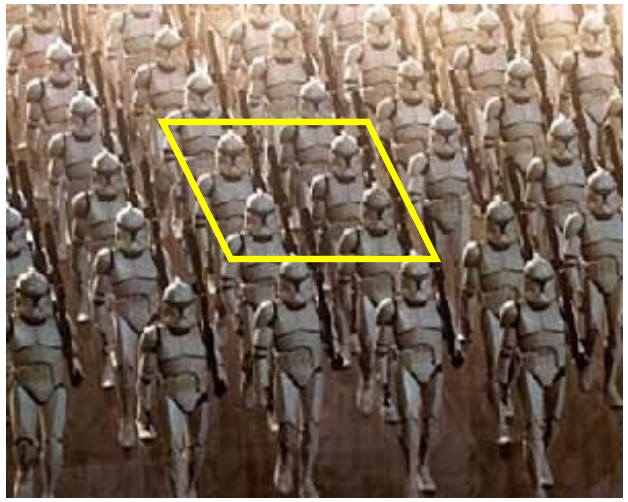
in main() in md.c

Periodic Boundary Conditions

- Replicate a simulation box of size $L_x \times L_y \times L_z$ to form an infinite lattice to simulate bulk materials
- Keep only the central image: $0 \le x_i < L_x$, $0 \le y_i < L_y$, $0 \le z_i < L_z$

```
void applyBoundaryCond() {
 int n,k;
 for (n=0; n<nAtom; n++)
  for (k=0; k<3; k++)
   r[n][k] = r[n][k]
   -SignR(RegionH[k],r[n][k])
   -SignR(RegionH[k],r[n][k]-Region[k]);
}
```





- Folding back atoms

$$\begin{cases} x_i \leftarrow x_i - \mathrm{SignR}\left(\frac{L_x}{2}, x_i\right) - \mathrm{SignR}\left(\frac{L_x}{2}, x_i - L_x\right) \\ y_i \leftarrow y_i - \mathrm{SignR}\left(\frac{L_y}{2}, y_i\right) - \mathrm{SignR}\left(\frac{L_y}{2}, y_i - L_y\right) \\ z_i \leftarrow z_i - \mathrm{SignR}\left(\frac{L_z}{2}, z_i\right) - \mathrm{SignR}\left(\frac{L_z}{2}, z_i - L_z\right) \end{cases}$$

$$\mathrm{SignR}\left(\frac{L_x}{2}, x_i\right) = \begin{cases} \frac{L_x}{2} & x_i > 0 \\ -\frac{L_x}{2} & x_i \le 0 \end{cases}$$

`double Region[3]`: (L_x, L_y, L_z) **`double RegionH[3]`**: $(L_x/2, L_y/2, L_z/2)$

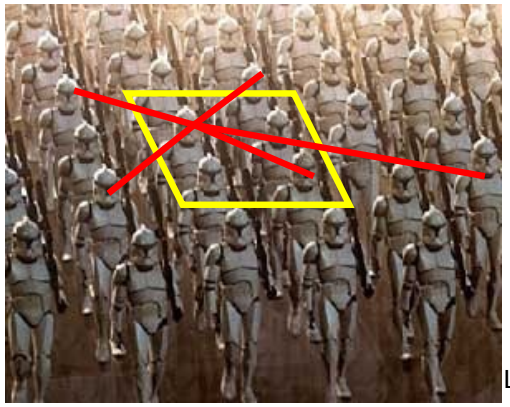
Minimum Image Convention

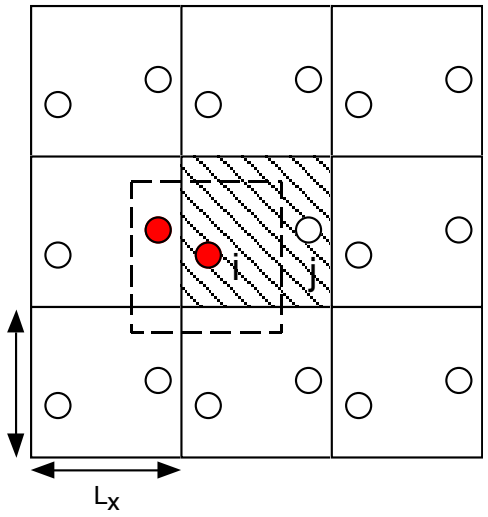
- Compute the interaction of an atom with only the nearest image
- Exact if the range of interaction, $r_c < \min(L_x, L_y, L_z)/2$
- Pick the other atoms only in the box centered around each atom

$$\vec{r}_{ij} \equiv \vec{r}_i - \vec{r}_j = (x_{ij}, y_{ij}, z_{ij})$$

$$\begin{cases} -\frac{L_x}{2} \le x_{ij} < \frac{L_x}{2} \\ -\frac{L_y}{2} \le y_{ij} < \frac{L_y}{2} \\ -\frac{L_z}{2} \le z_{ij} < \frac{L_z}{2} \end{cases}$$

$$\begin{cases} x_{ij} \leftarrow x_{ij} - \mathrm{SignR}\left(\frac{L_x}{2}, x_{ij} + \frac{L_x}{2}\right) - \mathrm{SignR}\left(\frac{L_x}{2}, x_{ij} - \frac{L_x}{2}\right) \\ y_{ij} \leftarrow y_{ij} - \mathrm{SignR}\left(\frac{L_y}{2}, y_{ij} + \frac{L_y}{2}\right) - \mathrm{SignR}\left(\frac{L_x}{2}, y_{ij} - \frac{L_x}{2}\right) \\ z_{ij} \leftarrow z_{ij} - \mathrm{SignR}\left(\frac{L_z}{2}, z_{ij} + \frac{L_z}{2}\right) - \mathrm{SignR}\left(\frac{L_z}{2}, z_{ij} - \frac{L_z}{2}\right) \end{cases}$$






```
for (j1=0; j1<nAtom-1; j1++) {
   for (j2=j1+1; j2<nAtom; j2++) {
      for (rr=0.0, k=0; k<3; k++) {
         dr[k] = r[j1][k] - r[j2][k];
         dr[k] = dr[k] - SignR(RegionH[k],dr[k]-RegionH[k])
                       - SignR(RegionH[k],dr[k]+RegionH[k]);
         rr = rr + dr[k]*dr[k];
      }
      if (rr < rrCut) {
         ri2 = 1.0/rr; ri6 = ri2*ri2*ri2; r1 = sqrt(rr);
         fcVal = 48.0*ri2*ri6*(ri6-0.5) + Duc/r1;
         for (k=0; k<3; k++) {
            f = fcVal*dr[k];
            ra[j1][k] = ra[j1][k] + f;
            ra[j2][k] = ra[j2][k] - f;
         }
      }
   }
}
```

in computeAccel() in md.c

Shifted Potential

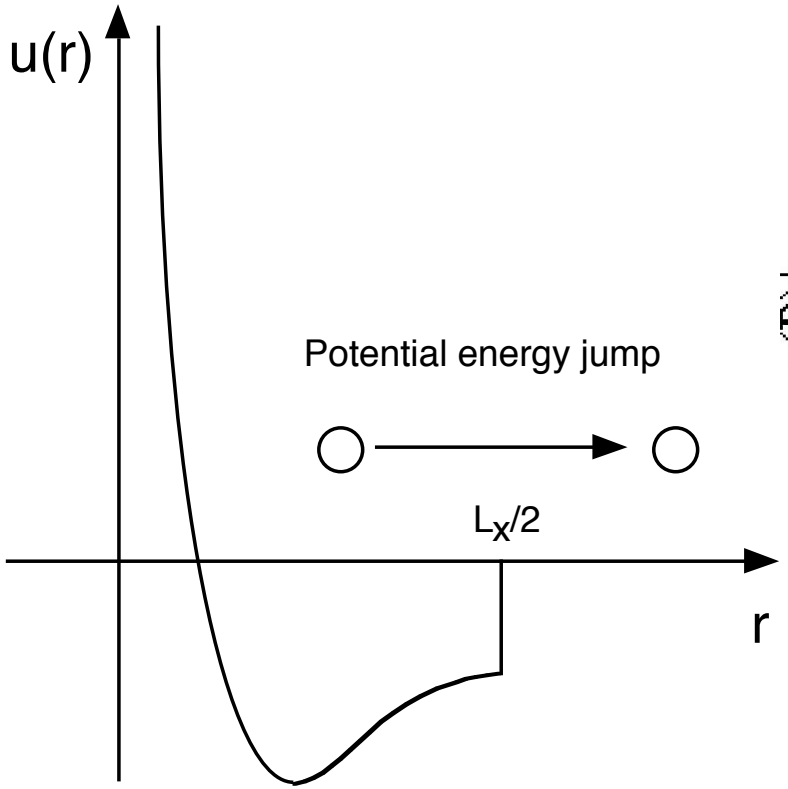
- Truncate the interaction $u(r)$ at a cut-off radius $r_c < \min(L_x, L_y, L_z)/2$ to make the minimal image convention exact
- Shift the potential to make $u(r)$ & du/dr continuous at $r = r_c$

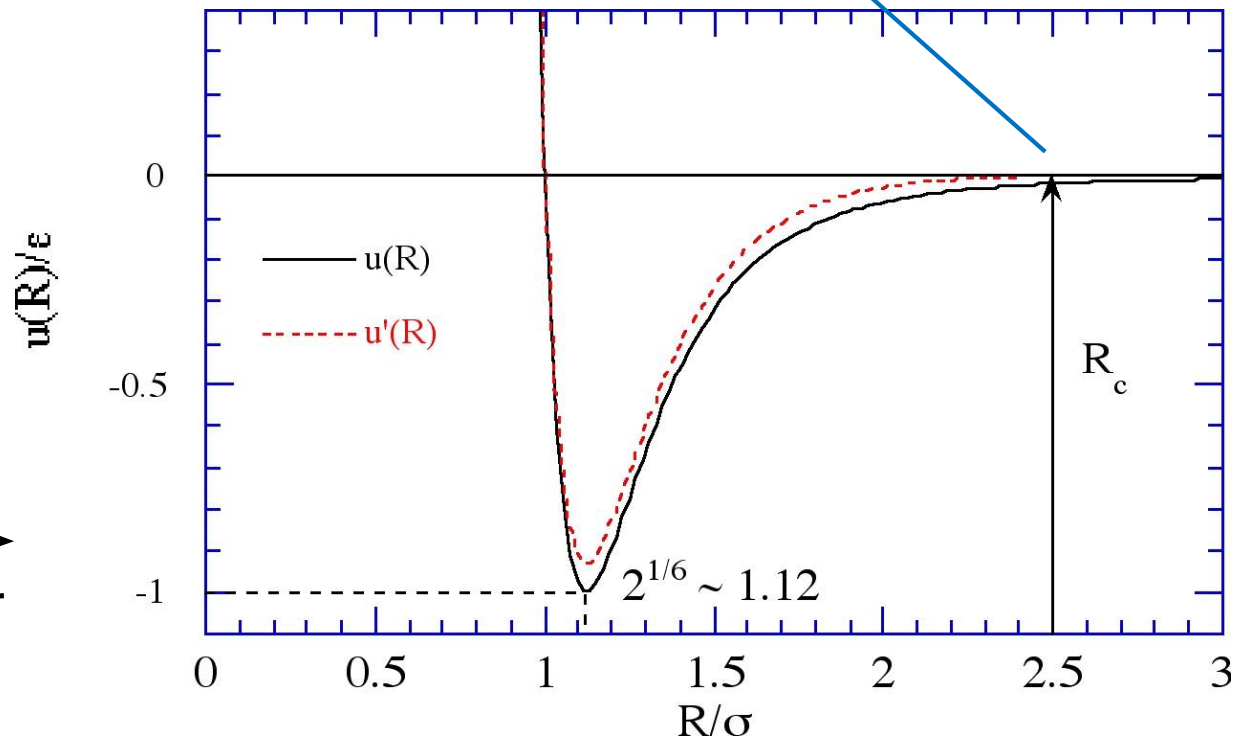
$$u'(r) = \begin{cases} u(r) - u(r_c) - (r - r_c)\left.\dfrac{du}{dr}\right|_{r=r_c} & r < r_c \\ 0 & r \geq r_c \end{cases}$$

$$u'(r) = u(r) - u(r_c) \xrightarrow{r \to r_c} 0$$

$$\frac{du'}{dr} = \frac{du}{dr} - \left.\frac{du}{dr}\right|_{r=r_c} \xrightarrow{r \to r_c} 0$$

- We take $r_c = 2.5\sigma$ for the Lennard-Jones potential





Energy & Temperature

- **Energy**

$$E = K + V = \sum_{i=0}^{N-1} \frac{m}{2} |\dot{\vec{r}}_i|^2 + \sum_{i<j} u(r_{ij})$$

total, kinetic & potential energies

- **Temperature, *T***

$$\frac{3Nk_BT}{2} = \sum_{i=0}^{N-1} \frac{m}{2} |\dot{\vec{r}}_i|^2$$

where $k_B = 1.38062 \times 10^{-16}$ erg/K—Boltzmann constant

- **In the Lennard-Jones unit,**

$$\frac{T}{\varepsilon / k_B} = \frac{1}{3N} \sum_{i=0}^{N-1} \left| \dot{\vec{r}}_i' \right|^2$$

where $\varepsilon/k_B \sim 120$ K

```
double kinEnergy;     /* Kinetic energy */
double potEnergy;     /* Potential energy */
double totEnergy;     /* Total energy */
double temperature;
```

Energy Conservation

- **The total energy, *E*, does not change in time, if Newton's equation is exactly integrated**

$$\dot{E} = \dot{K} + \dot{V}$$

Chain rule!

$$= \sum_{i=0}^{N-1} \frac{m}{2} \frac{d}{dt}\left(\dot{x}_i^2 + \dot{y}_i^2 + \dot{z}_i^2\right) + \sum_{i=0}^{N-1}\left(\frac{dx_i}{dt}\frac{\partial V}{\partial x_i} + \frac{dy_i}{dt}\frac{\partial V}{\partial y_i} + \frac{dz_i}{dt}\frac{\partial V}{\partial z_i}\right)$$

$$= \sum_{i=0}^{N-1} \frac{m}{2} 2\left(\dot{x}_i\ddot{x}_i + \dot{y}_i\ddot{y}_i + \dot{z}_i\ddot{z}_i\right) + \sum_{i=0}^{N-1}\left(\dot{x}_i\frac{\partial V}{\partial x_i} + \dot{y}_i\frac{\partial V}{\partial y_i} + \dot{z}_i\frac{\partial V}{\partial z_i}\right)$$

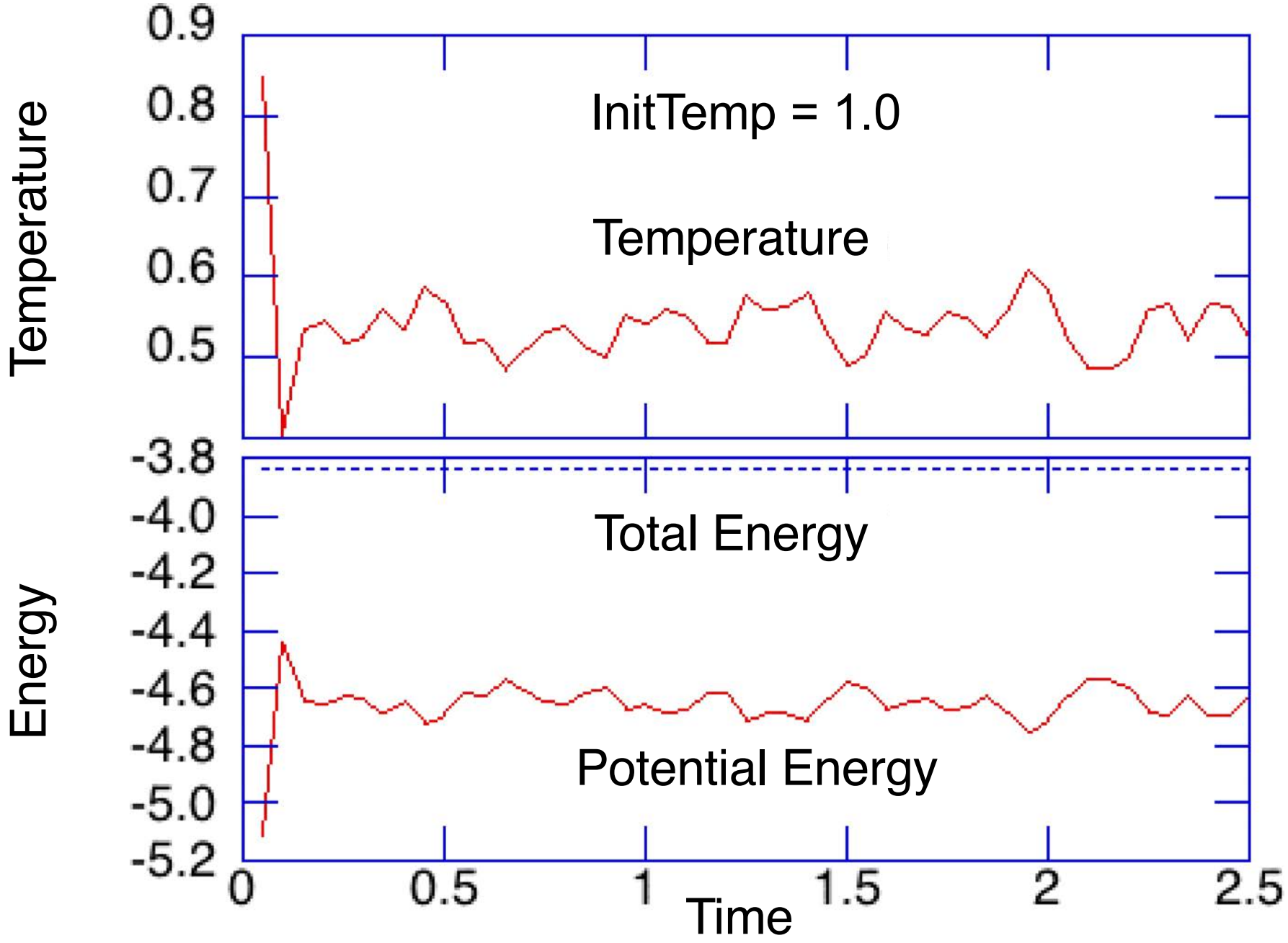
$$= \sum_{i=0}^{N-1} m\dot{\vec{r}}_i \bullet \ddot{\vec{r}}_i + \sum_{i=0}^{N-1} \dot{\vec{r}}_i \bullet \frac{\partial V}{\partial \vec{r}_i}$$

$$= \sum_{i=0}^{N-1} \dot{\vec{r}}_i \bullet \underbrace{\left(m\ddot{\vec{r}}_i - \vec{F}_i\right)}$$

$$= 0$$

0 from Netwton's equation

Standard Output from md.c



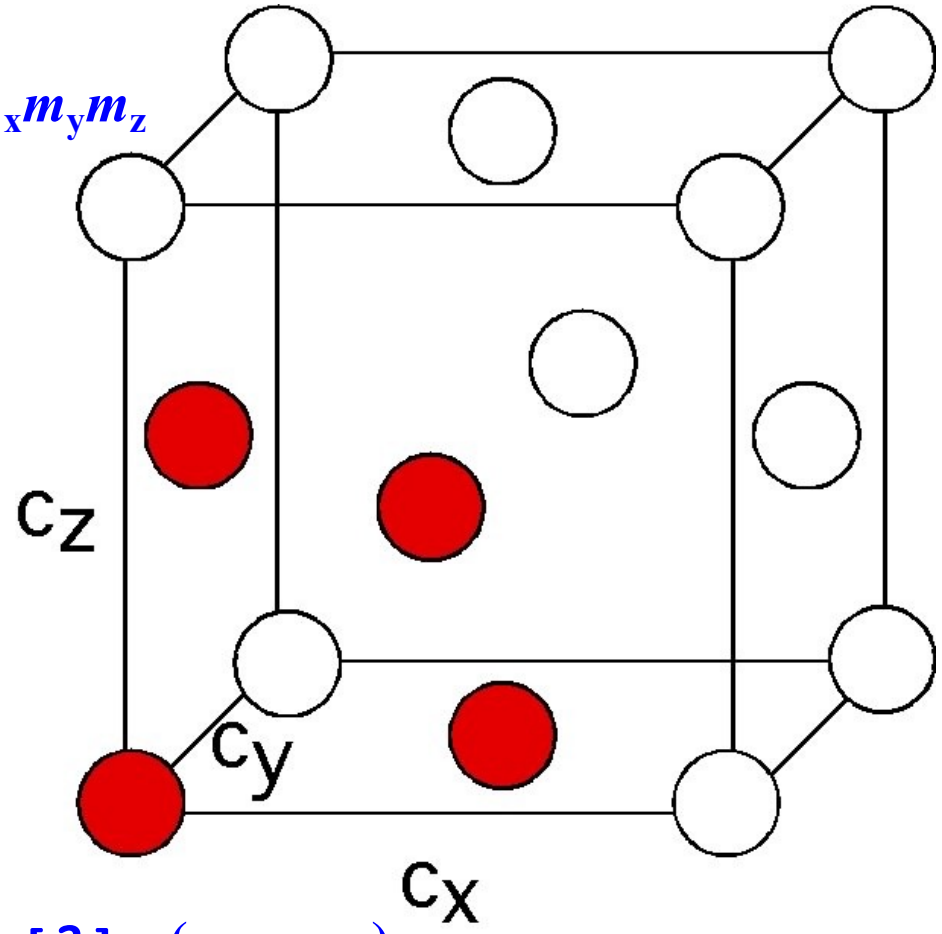
Initial Condition: Atomic Positions

- Face centered cubic (FCC) lattice
- 4 atoms per unit cell of size $c_x = c_y = c_z = c$, at positions (in unit of c)

  (0,0,0), (0,1/2,1/2), (1/2,0,1/2), (1/2,1/2,0) double origAtom[4][3]

  repeated $m_x \times m_y \times m_z$ times
- Total number of atoms $N = 4m_xm_ym_z$
- Density $\rho = 4/c^3$ or $c = (4/\rho)^{1/3}$

`double Density`



See USC X-crystallography database

`double gap[3]`: (c_x, c_y, c_z)

`int InitUcell[3]`: (m_x, m_y, m_z)

Initial Condition: Atomic Velocities

- **Random velocities of magnitude v_0, where**

$$\frac{v_0^2}{3} = T_{\text{init}} \quad \Rightarrow \quad v_0 = \sqrt{3T_{\text{init}}} \qquad \frac{m|\vec{v}|^2}{2} = \frac{3k_{\text{B}}T}{2}$$

`double InitTemp`: Initial temperature

- **For each atom, generate random velocity,**

$$\vec{v}_i = v_0(\xi_0, \xi_1, \xi_2) = v_0\,\vec{\xi}$$

where $\vec{\xi}$ is a randomly oriented vector of unit length

(Algorithm)

1. ζ_i = 2*rand()/RAND_MAX − 1 (i = 0, 1) so that $-1 \le \zeta_i < 1$
2. $s^2 = \zeta_0^2 + \zeta_1^2$
3. if $s^2 < 1$, accept $(\xi_0, \xi_1, \xi_2) = (2\sqrt{1-s^2}\zeta_0, 2\sqrt{1-s^2}\zeta_1, 1-2s^2)$
4. else reject & go to 1

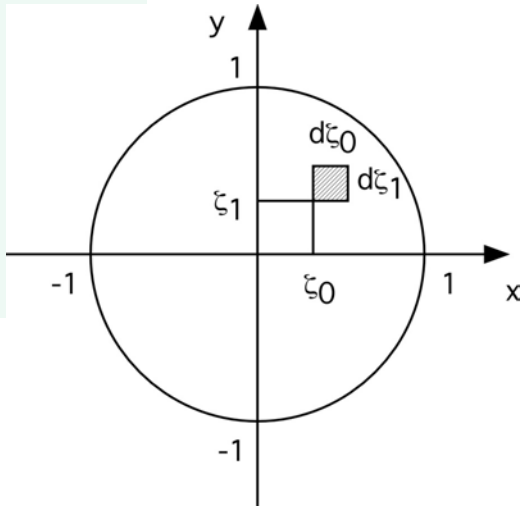
***cf.* Box-Muller algorithm**

$$\rho(v_{x|y|z}) = \sqrt{\frac{m}{2\pi k_{\text{B}}T}}\exp\left(-\frac{mv_{x|y|z}^2}{2k_{\text{B}}T}\right)$$

Random Point in a Unit Circle

(Algorithm)

1. $\zeta_i = 2*\texttt{rand()/RAND\_MAX} - 1$ $(i = 0, 1)$ so that $-1 \le \zeta_i < 1$
2. $s^2 = \zeta_0^2 + \zeta_1^2$
3. if $s^2 < 1$, accept $\vec{\zeta} = (\zeta_0, \zeta_1)$
4. else reject & go to 1



- **Probability density**

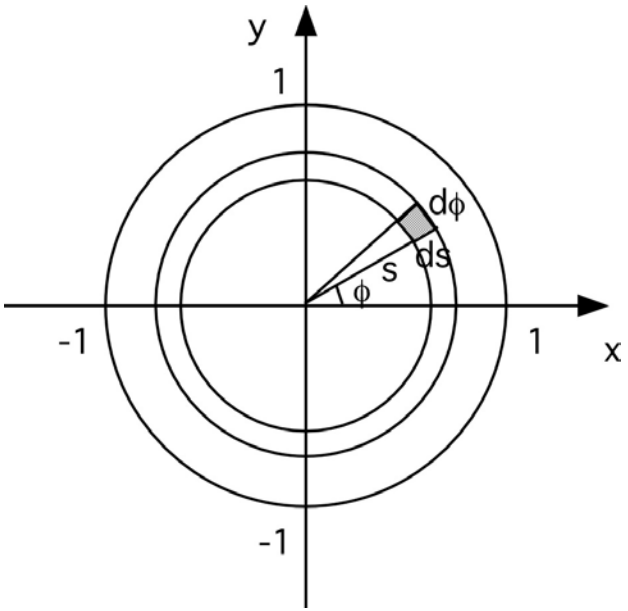
  Probability to find a point in the shaded area
  = (# of points in the shaded area)/(total # of generated points)
  = $P(\zeta_0, \zeta_1)\mathrm{d}\zeta_0\mathrm{d}\zeta_1$
  = ($\mathrm{d}\zeta_0\mathrm{d}\zeta_1$ ~ shaded area)/($\pi \cdot 1^2$ ~ area of unit circle)
  $\therefore P(\zeta_0, \zeta_1) = 1/\pi$

- **Probability density in polar coordinate**

  $(\zeta_0, \zeta_1) = (s\cos\phi, s\sin\phi) \quad 0 \le s < 1; 0 \le \phi < 2\pi$

  $P(s,\phi)dsd\phi = \dfrac{ds \cdot sd\phi}{\pi \cdot 1^2}$ if uniform

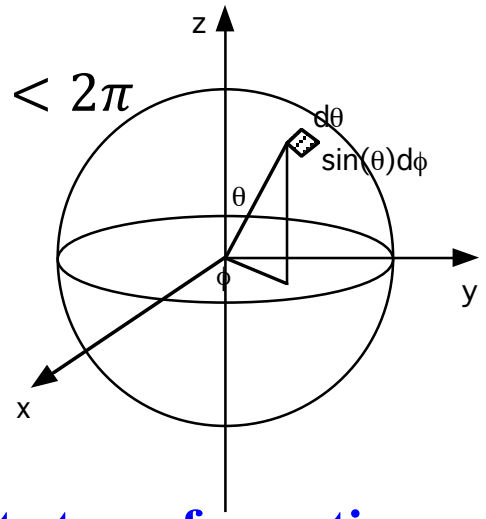
  $\therefore P(s,\phi) = \dfrac{s}{\pi}$



Random Point on a Unit Sphere

- **Spherical coordinate**

$$(\xi_0, \xi_1, \xi_2) = (\sin\theta\cos\varphi, \sin\theta\sin\varphi, \cos\theta) \quad 0 \le \theta < \pi, 0 \le \varphi < 2\pi$$



- **Probability density (if uniform)**

$$P(\theta,\varphi)d\theta d\varphi = \frac{d\theta \bullet \sin\theta d\varphi}{4\pi \bullet 1^2}$$

$$\therefore P(\theta,\varphi) = \frac{\sin\theta}{4\pi}$$

- **Equivalence to uniform distribution in a circle by coordinate transformation:**

$$s \equiv \sin\frac{\theta}{2} \quad \because 0 \le \theta < \pi \Leftrightarrow 0 \le \frac{\theta}{2} < \frac{\pi}{2} \Leftrightarrow 0 \le s \equiv \sin\frac{\theta}{2} < 1$$

$$\frac{sdsd\varphi}{\pi} = \frac{\sin\frac{\theta}{2}\frac{ds}{d\theta}d\theta d\varphi}{\pi} = \frac{\sin\frac{\theta}{2}\left(\frac{1}{2}\cos\frac{\theta}{2}\right)d\theta d\varphi}{\pi} = \frac{2\sin\frac{\theta}{2}\cos\frac{\theta}{2}d\theta d\varphi}{4\pi} = \frac{\sin\theta d\theta d\varphi}{4\pi}$$

P(s,φ) **P(θ,φ)**

$$\begin{cases} \xi_0 = \sin\theta\cos\varphi = 2\sin\frac{\theta}{2}\cos\frac{\theta}{2}\cos\varphi = 2s\sqrt{1-s^2}\frac{\zeta_0}{s} = 2\sqrt{1-s^2}\zeta_0 \\ \xi_1 = \sin\theta\sin\varphi = 2\sin\frac{\theta}{2}\cos\frac{\theta}{2}\sin\varphi = 2s\sqrt{1-s^2}\frac{\zeta_1}{s} = 2\sqrt{1-s^2}\zeta_1 \\ \xi_2 = \cos\theta = 1 - 2\sin^2\frac{\theta}{2} = 1 - 2s^2 \end{cases}$$

Liouville's Theorem

- **Phase-space trajectory as a mapping**

$$(x, p)_{t} \rightarrow (x', p')_{t+\Delta}$$

- **Phase-space volume conservation: Jacobian of the mapping (areal enlargement factor) = 1**

$$\frac{\partial(x', p')}{\partial(x, p)} = 1$$

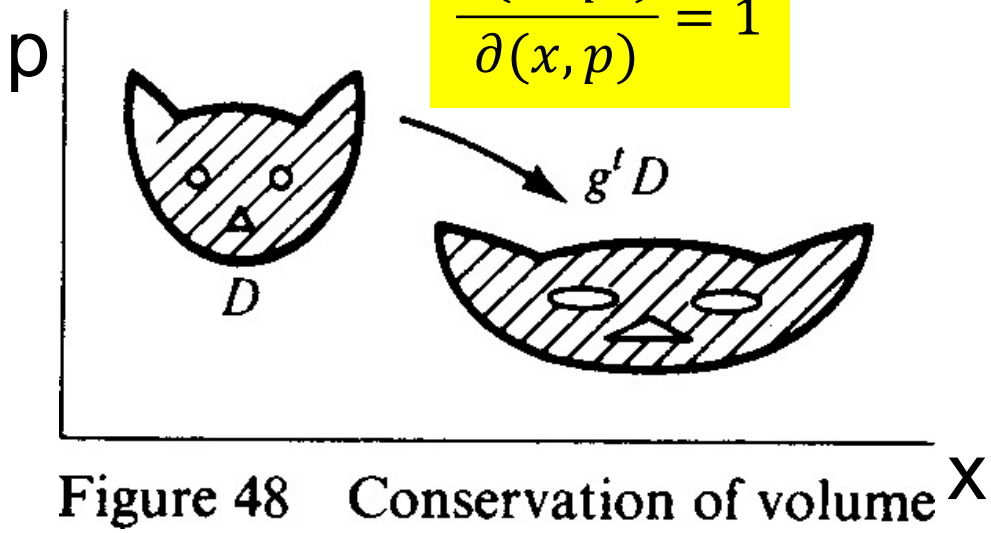
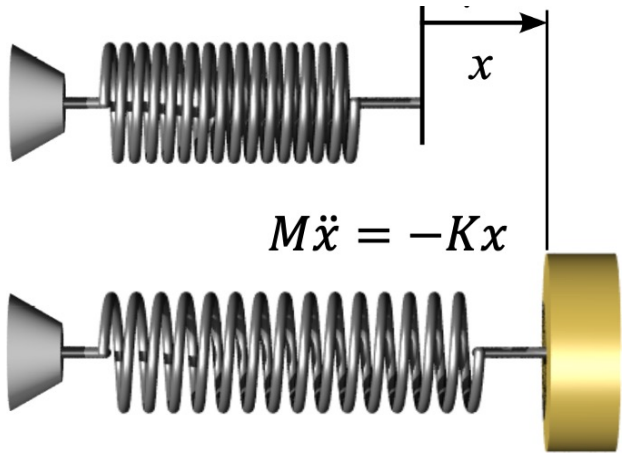
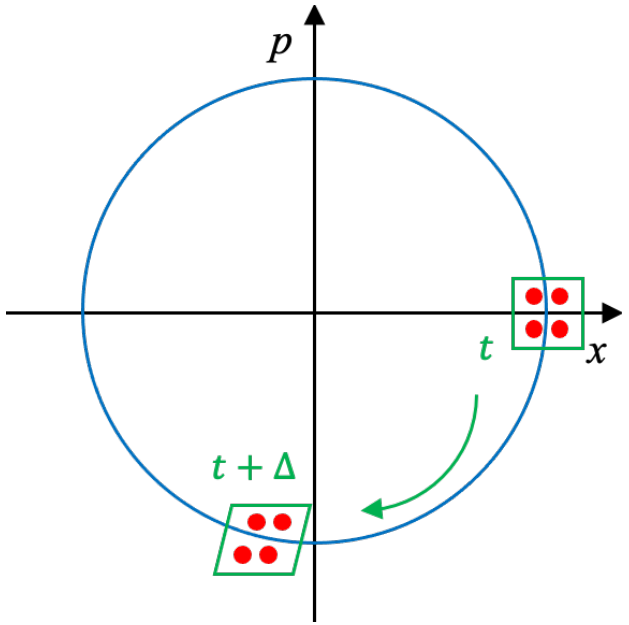


Figure 48 Conservation of volume

V. I. Arnold, *Mathematical Methods of Classical Mechanics, 2nd Ed.* (Springer, '89)





- **The cat is a phase-space volume occupied by an ensemble of phase-space points, each representing a specific instance of the initial condition (see `anim_spring.c`)**

Velocity Verlet Algorithm in 1D

$$\begin{cases} x' \leftarrow x + p\Delta + \dfrac{1}{2}a(x)\Delta^2 \equiv x'(x,p) \\ p' \leftarrow p + \dfrac{a(x) + a\left(x + p\Delta + \frac{1}{2}a(x)\Delta^2\right)}{2}\Delta \equiv p'(x,p) \end{cases}$$

Bottom-line: Velocity Verlet algorithm "exactly" satisfies Liouville's theorem

Prove phase-space volume conservation: $\dfrac{\partial(x',p')}{\partial(x,p)} = 1$

What phase-space volume conservation means? It's ensemble!

Compare an algorithm variant, Euler:

$$\begin{cases} x' \leftarrow x + p\Delta + \dfrac{1}{2}a(x)\Delta^2 \\ p' \leftarrow p + a(x)\Delta \end{cases}$$

$$\rightarrow \frac{\partial(x',p')}{\partial(x,p)} \neq 1$$

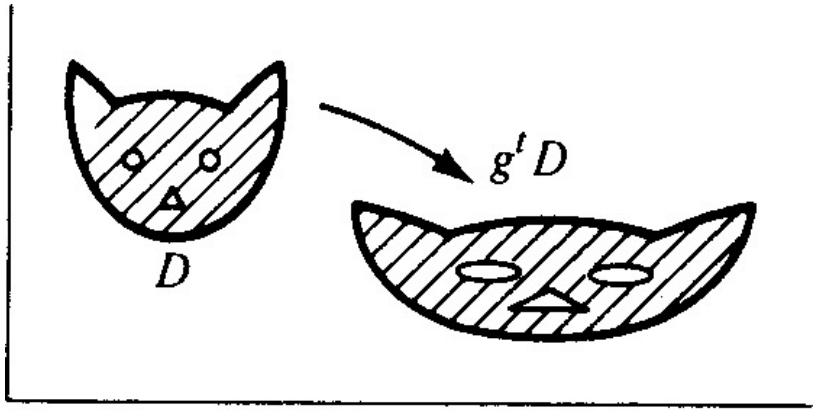


Figure 48 Conservation of volume

Algorithm Variants

(Velocity Verlet Algorithm)

Given a configuration, $\{\vec{r}_i(t), \vec{v}_i(t) \mid i = 1, \ldots, N_{\text{atom}}\}$

1. (Compute the acceleration, $\vec{a}_i(t)$)
2. $\vec{v}_i(t + \Delta/2) \leftarrow \vec{v}_i(t) + \vec{a}_i(t)\Delta/2$
3. $\vec{r}_i(t + \Delta) \leftarrow \vec{r}_i(t) + \vec{v}_i(t + \Delta/2)\Delta$
4. Compute the updated acceleration, $\vec{a}_i(t + \Delta)$
5. $\vec{v}_i(t + \Delta) \leftarrow \vec{v}_i(t + \Delta/2) + \vec{a}_i(t + \Delta)\Delta/2$

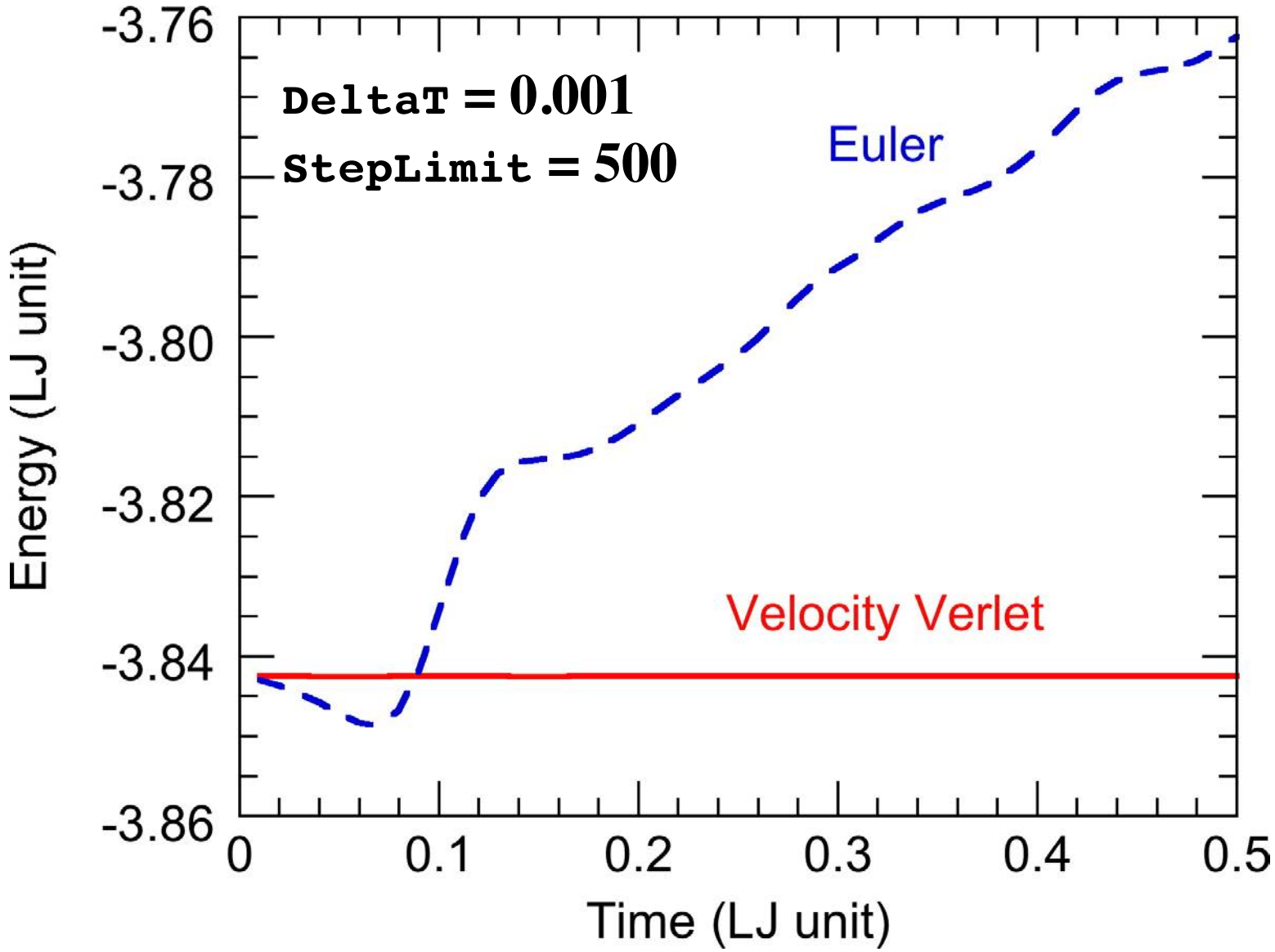
(Explicit Euler Algorithm) **Only modify SingleStep()!**

Given a configuration, $\{\vec{r}_i(t), \vec{v}_i(t) \mid i = 1, \ldots, N_{\text{atom}}\}$

1. Compute the acceleration, $\vec{a}_i(t)$
2. Update the positions, $\vec{r}_i(t + \Delta) \leftarrow \vec{r}_i(t) + \vec{v}_i(t)\Delta\left[+\vec{a}_i(t)\Delta^2/2\right]$
3. Update the velocities, $\vec{v}_i(t + \Delta) \leftarrow \vec{v}_i(t) + \vec{a}_i(t)\Delta$

Algorithm Variants

Energy conservation: Velocity-Verlet *vs.* explicit-Euler algorithms



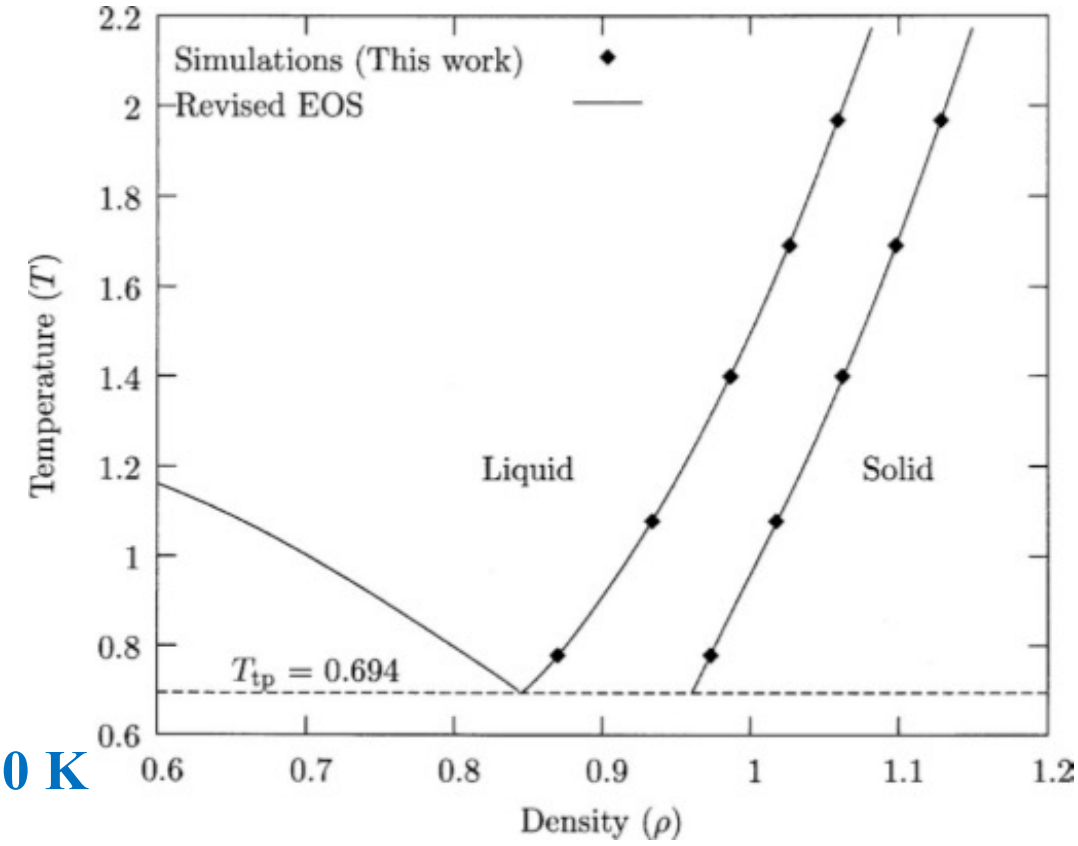
MD Input Parameters

```
3 3 3     InitUcell[3]
0.8       Density
1.0       InitTemp
0.001     DeltaT
500       StepLimit
10        StepAvg
```

in 0.0254 Å^{-3} for Ar

in 120 K

in 2.2 ps



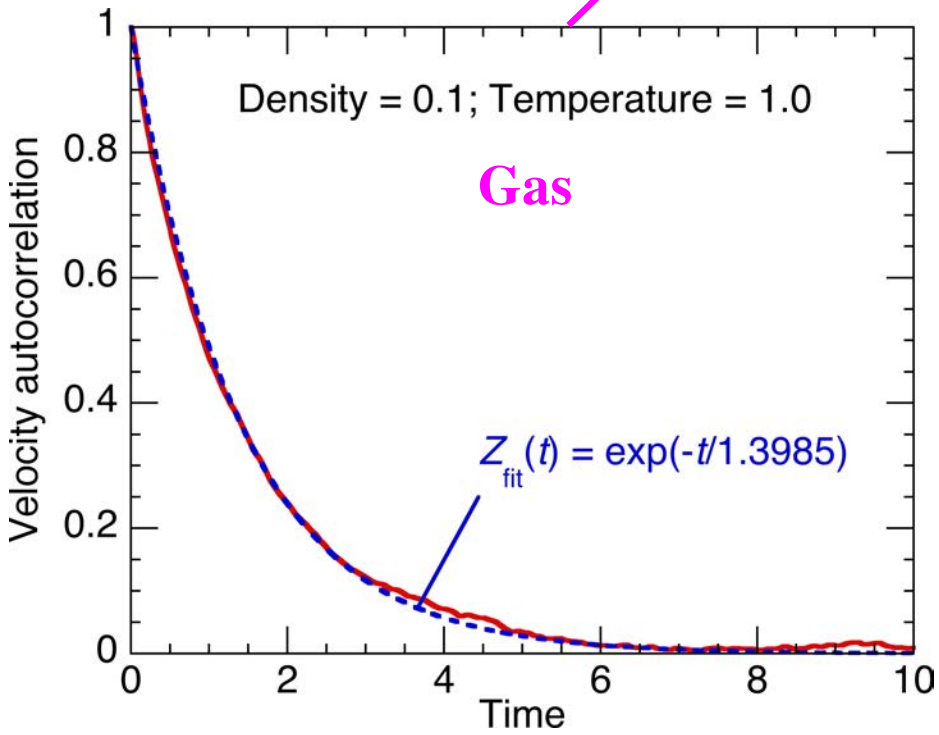
Velocity Autocorrelation

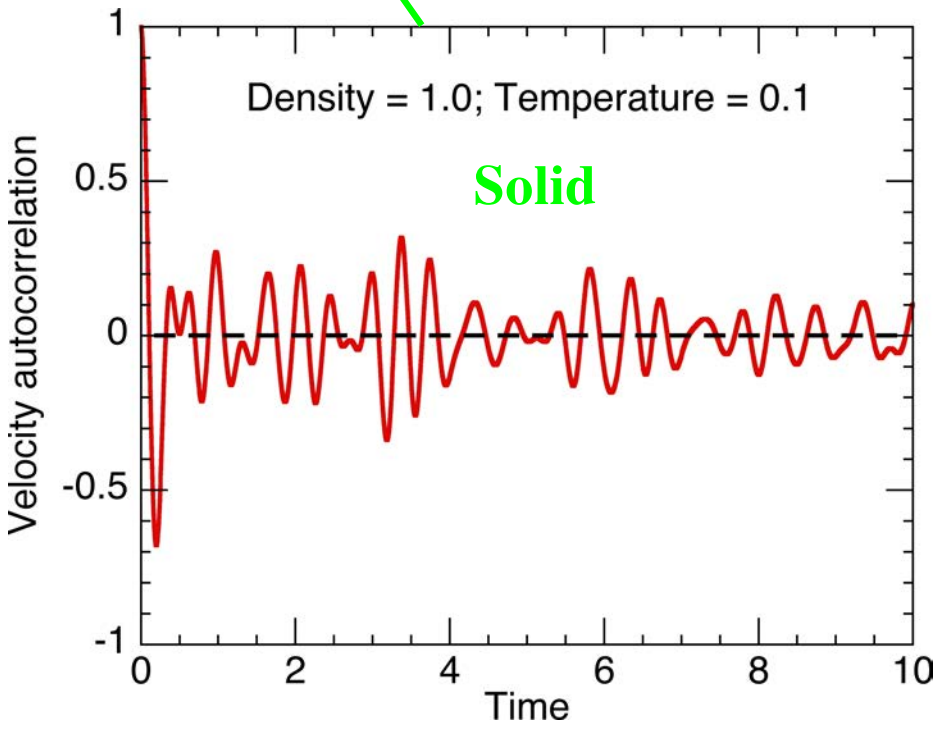
$$Z(t) = \frac{\langle \vec{v}_i(t+t_0) \bullet \vec{v}_i(t_0) \rangle}{\langle \vec{v}_i(t_0) \bullet \vec{v}_i(t_0) \rangle}$$

$$= \frac{\sum_{t_0} \quad \sum_{i=0}^{N-1} \vec{v}_i(t+t_0) \bullet \vec{v}_i(t_0)}{\sum_{t_0} \quad \sum_{i=0}^{N-1} \vec{v}_i(t_0) \bullet \vec{v}_i(t_0)}$$

```
3  3  3
0.1 | 1.0
1.0 | 0.1
0.005
2000
1000
```

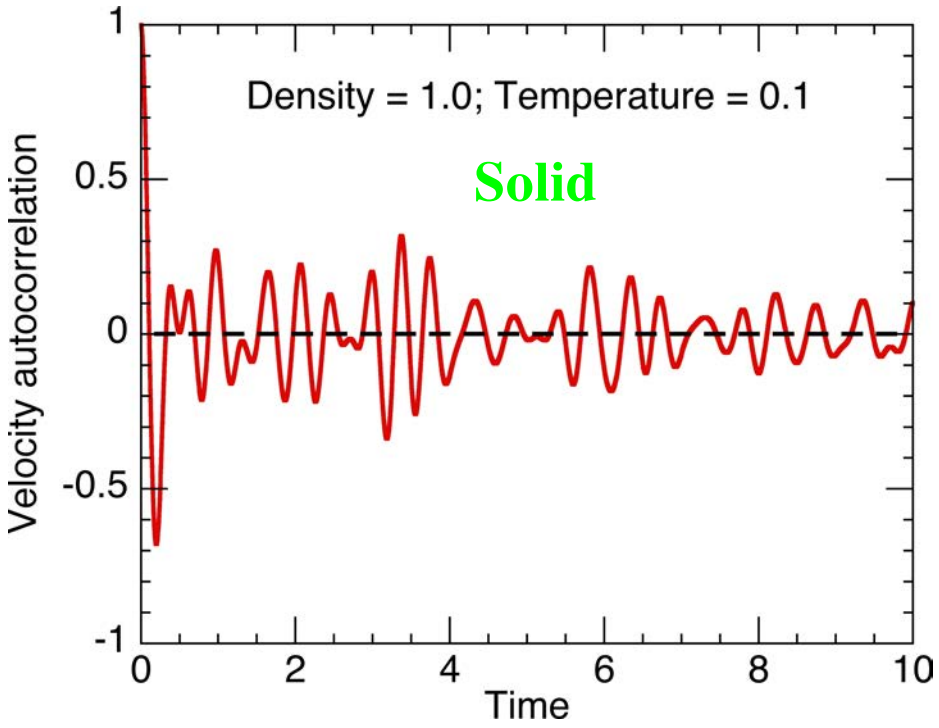
InitUcell[3]
Density
InitTemp
DeltaT
StepLimit
StepAvg



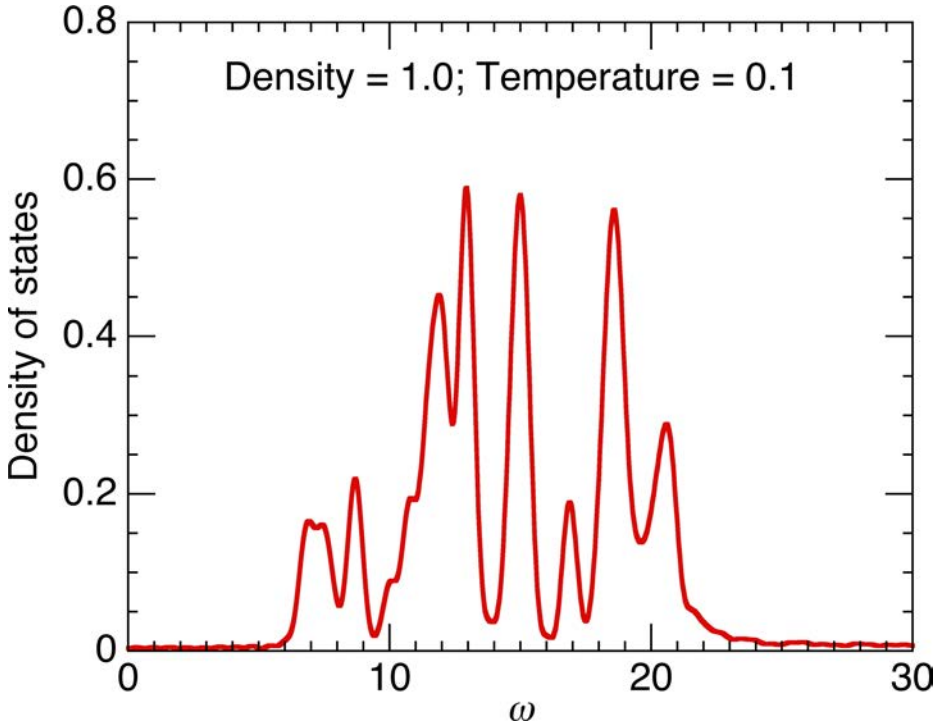


Phonon Density of States

$$\tilde{Z}(\omega) \equiv \int_{-\infty}^{\infty} dt\, Z(t) e^{i\omega t} = 2\int_{0}^{\infty} dt\, Z(t)\cos(\omega t)$$



Fourier transform

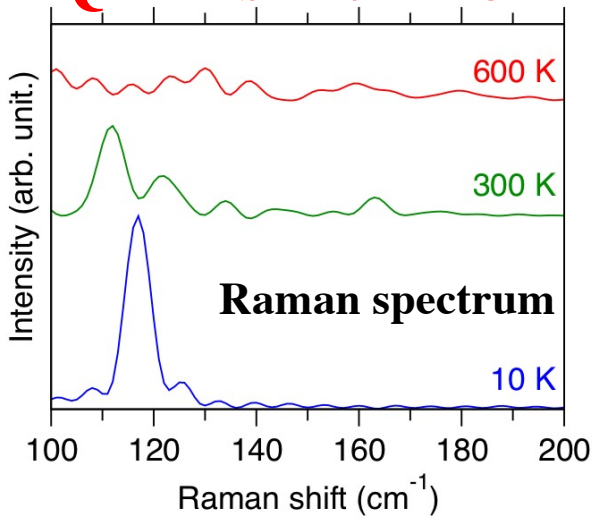


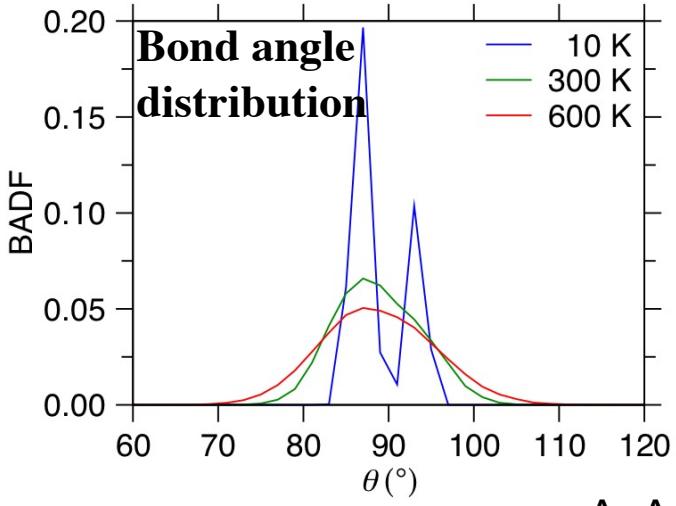
See lecture note on velocity autocorrelation function

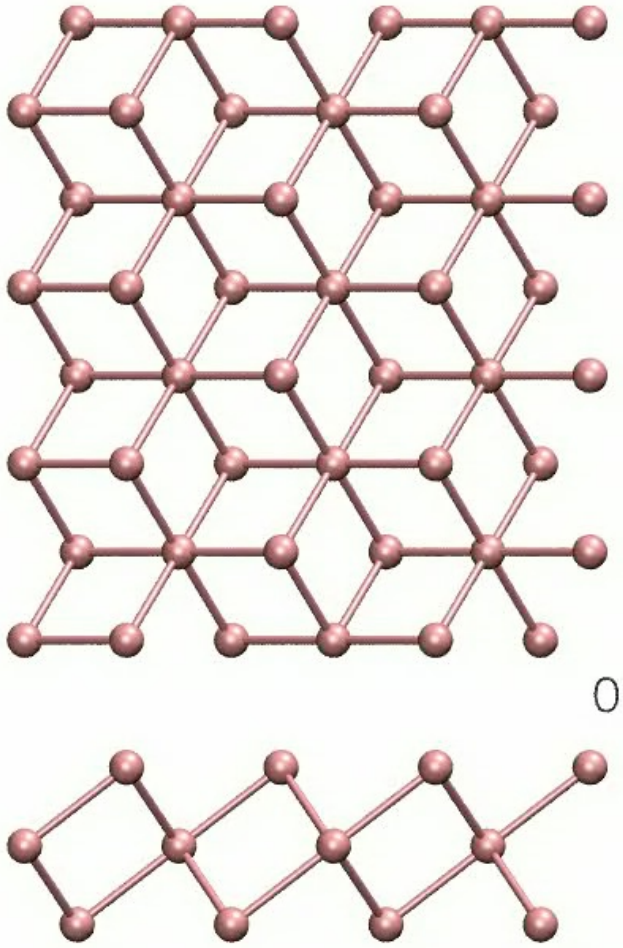
Example: Tellurene (Monolayer Tellurium)

- **Quantum MD simulations explain the observed temperature dependence of Raman spectra as progressive angular disorder at elevated temperatures**

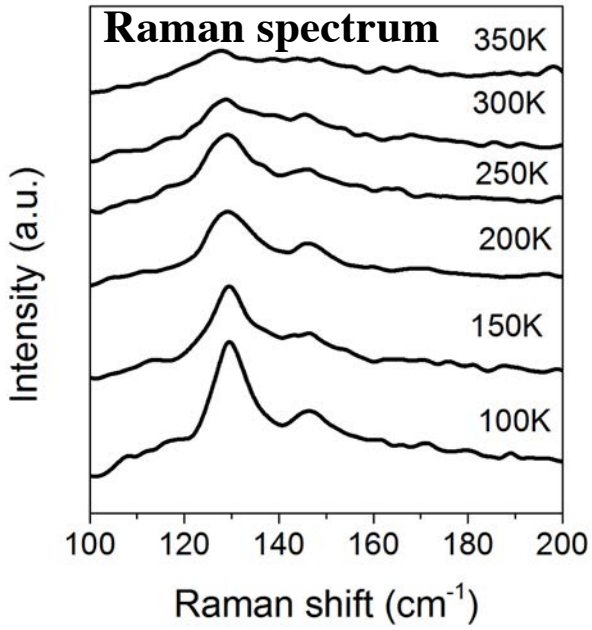
QMD simulation

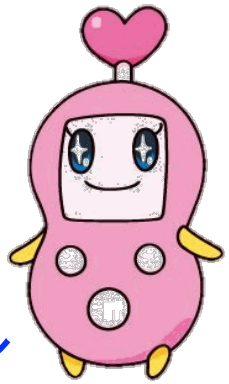






Experiment





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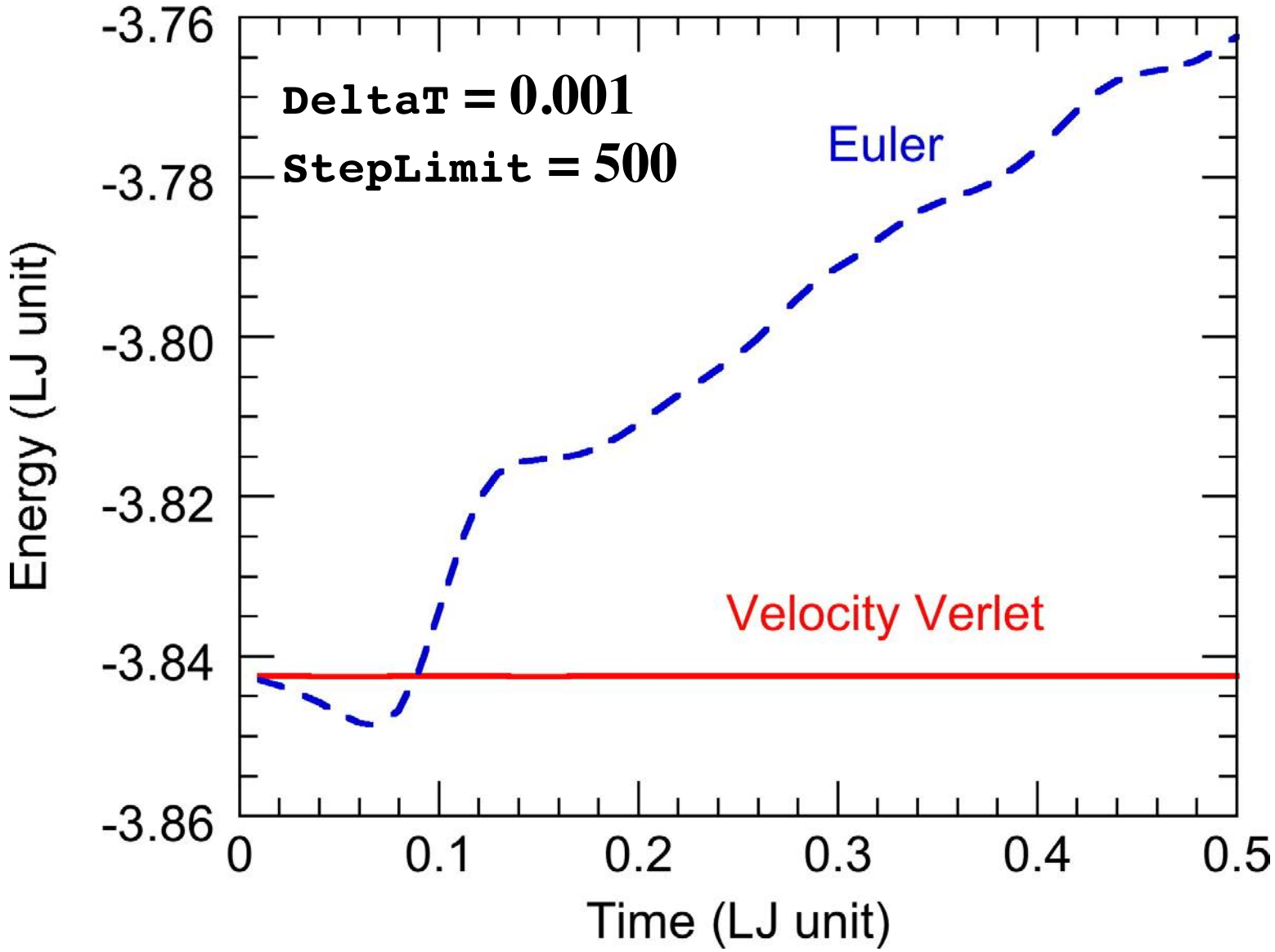
A. Apte *et al.*, *2D Mater.* **6**, 015013 ('19)

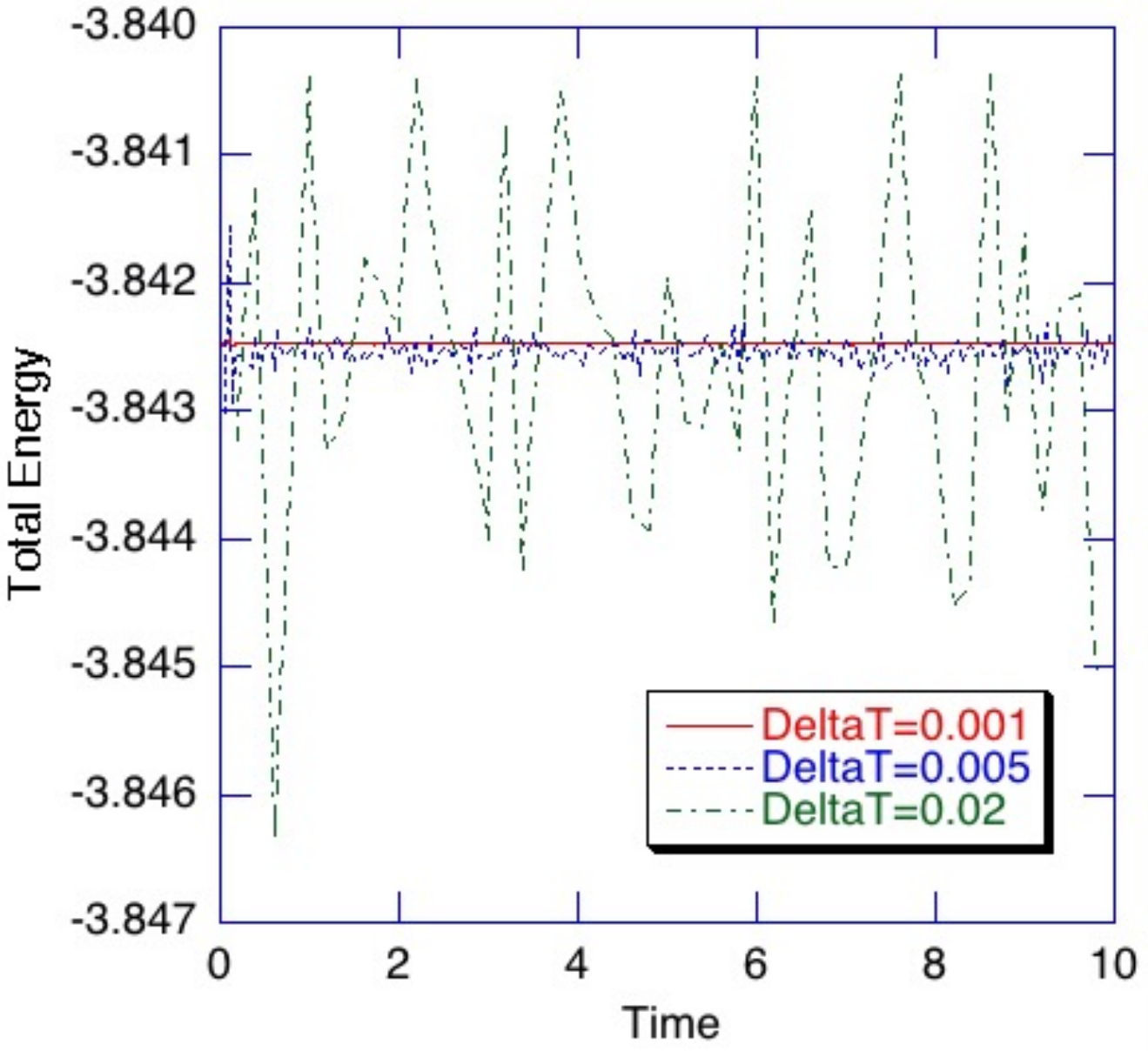
Energy Conservation Revisited

Energy conservation: Velocity-Verlet *vs.* explicit-Euler algorithms



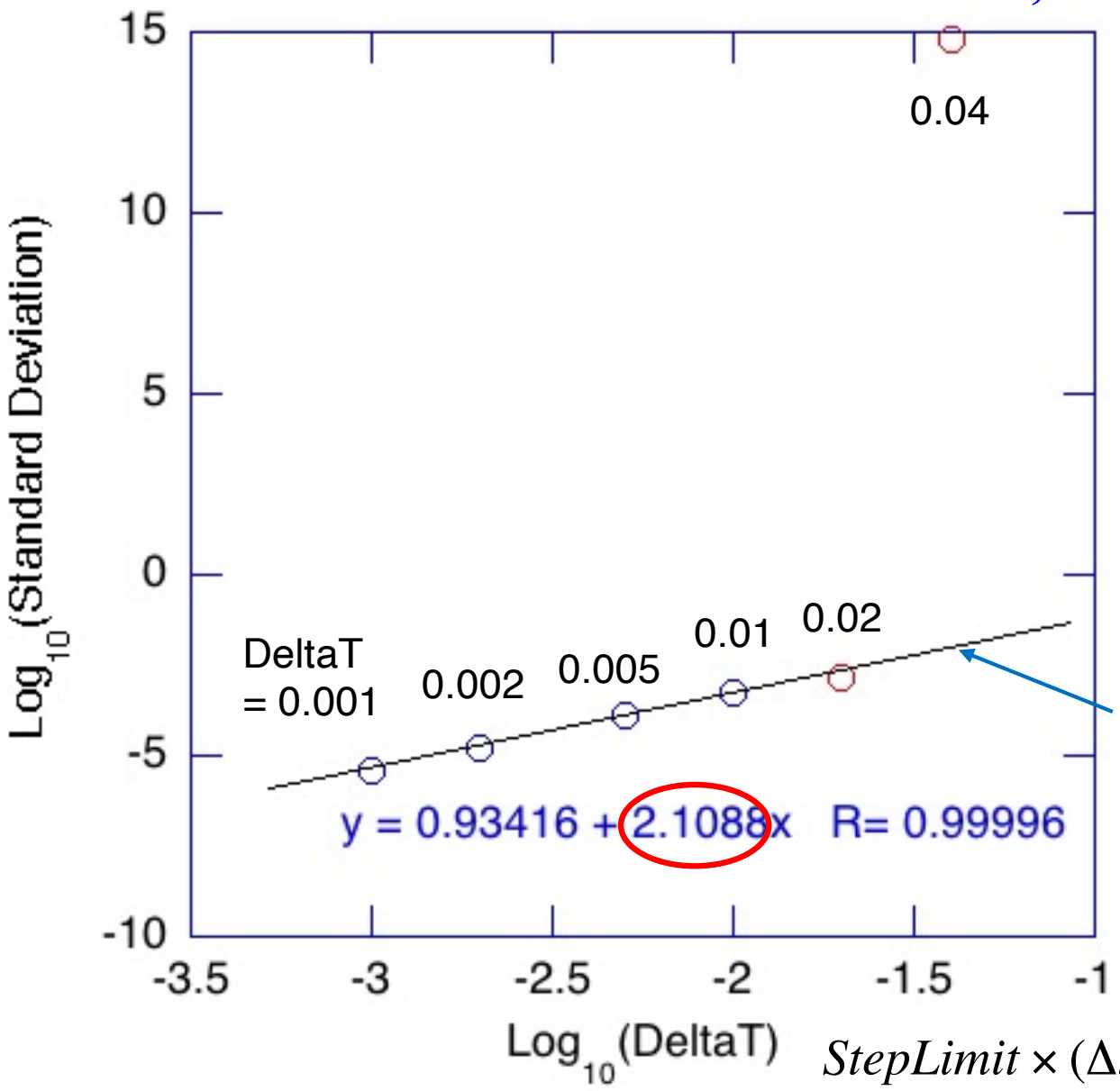
Energy Conservation

Effect of time-discretization unit, `DeltaT`



Error in Energy Conservation

Effect of time-discretization unit, `DeltaT`



Least square fit excluding the outliers

$$StepLimit \times (\Delta t)^3 = \frac{t}{\Delta t}(\Delta t)^3 = t(\Delta t)^2$$

Numerical Error in Energy Conservation

- **Trajectory error due to time discretization (p. 7 in the lecture note)**

$$\begin{cases} \vec{r}_i(t+\Delta) = \vec{r}_i(t) + \vec{v}_i(t)\Delta + \dfrac{1}{2}\vec{a}_i(t)\Delta^2 + O(\Delta^4) \\ \vec{v}_i(t+\Delta) = \vec{v}_i(t) + \dfrac{\vec{a}_i(t) + \vec{a}_i(t+\Delta)}{2}\Delta + O(\Delta^3) \end{cases}$$

***cf.* Trotter expansion**
Tuckerman *et al.*,
J. Chem. Phys. **97**, 1990 ('92)

- **For $t = n\Delta$**

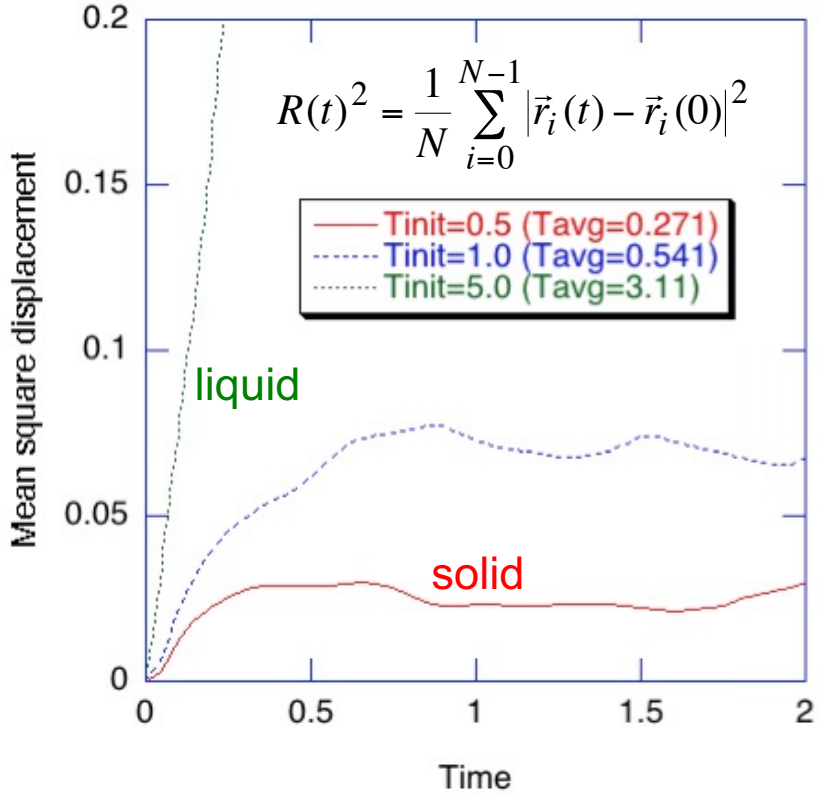
$$\begin{cases} \Delta\vec{r}_i = O\left(n\Delta^4 = \dfrac{t}{\Delta}\Delta^4 = t\Delta^3\right) = O(\Delta^3) \\ \Delta\vec{v}_i = O\left(n\Delta^3 = \dfrac{t}{\Delta}\Delta^3 = t\Delta^2\right) = O(\Delta^2) \end{cases}$$

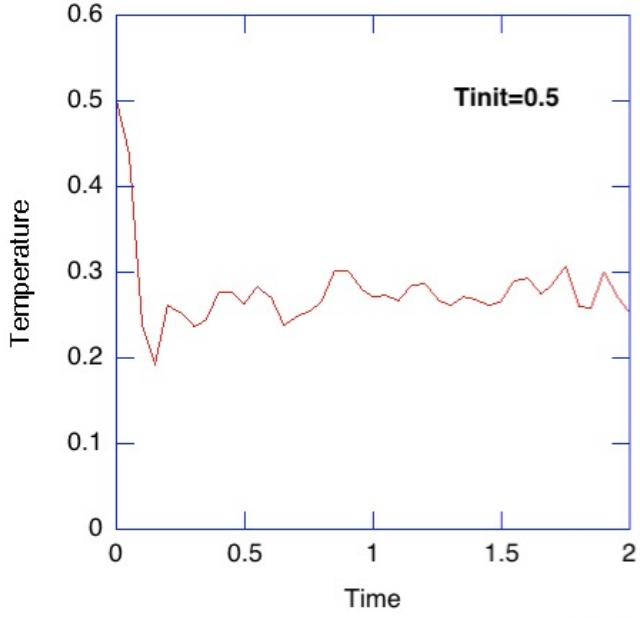
- **Energy error (see the note on error propagation)**

$$\left\langle (\Delta E)^2 \right\rangle = \left|\frac{\partial E}{\partial p}\right|^2 \underbrace{\left\langle (\Delta p)^2 \right\rangle}_{(O(\Delta^2))^2} + \left|\frac{\partial E}{\partial x}\right|^2 \underbrace{\left\langle (\Delta x)^2 \right\rangle}_{(O(\Delta^3))^2}$$

- **$O(\Delta^2)$ energy error due to time discretization!**

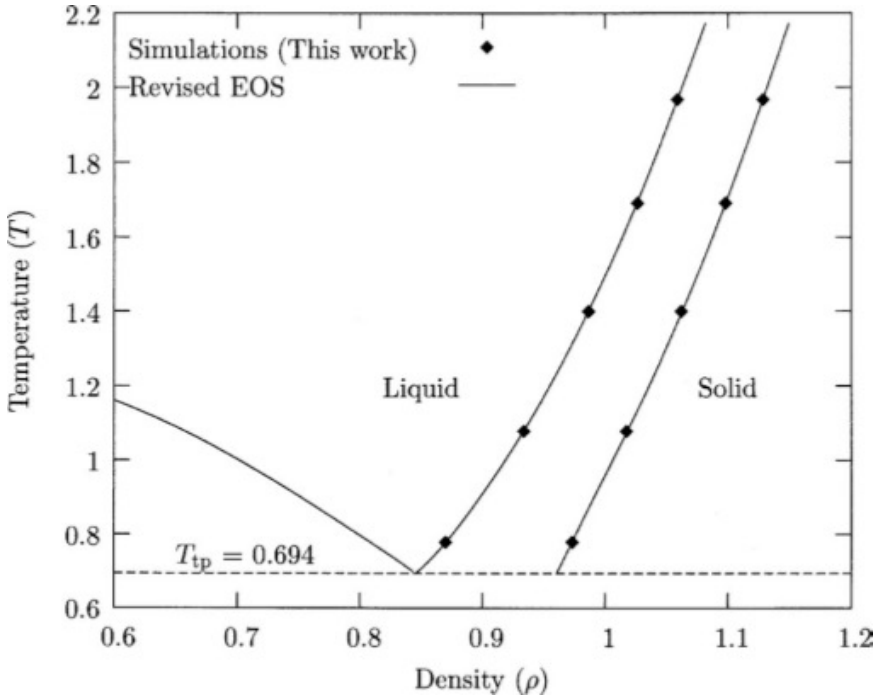
Mean Square Displacement






```
3 3 3
0.8
0.5|1.0|5.0
0.005
400
10
```

InitUcell[3]
Density
InitTemp
DeltaT
StepLimit
StepAvg



Where to Go from Here

- **MD simulation of materials**

  MASC 575: ***Basics of atomic simulation of materials***

  MASC 576: ***Molecular dynamics simulations of materials & processes***

- **MD simulation on massively parallel computers & visualization**

  CSCI 596: ***Scientific computing and visualization***

  https://aiichironakano.github.io/cs596.html

  CSCI 653: ***High performance computing and simulations***

  https://aiichironakano.github.io/cs653.html

- **Textbooks on advanced MD techniques**

  Understanding Molecular Simulation, 2nd Ed.**, D. Frenkel & B. Smit (Academic Press, '01)**

  Computer Simulation of Liquids, 2nd Ed.**, M. P. Allen & D. J. Tildesley (Oxford University Press, '17)**