Molecular Dynamics Simulation

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An introduction to soft-particle Molecular Dynamics (MD) simulation. This file is also a working MD simulator. A companion file introMDpbc.m is also available with fewer comments.

- [MDIntro.pdf] pdf version.
- [MDIntro.php] html version.

Theory I: Solving Newtons Laws for collection of particles

A Molecular Dynamics (MD) simulation is a computer simulation of Newton's Laws for a collection of N particles. The n-th particle at initial position $\vec{x}_n(0)$ with velocity $\vec{v}_n(0)$ moves according to Newton's Law:

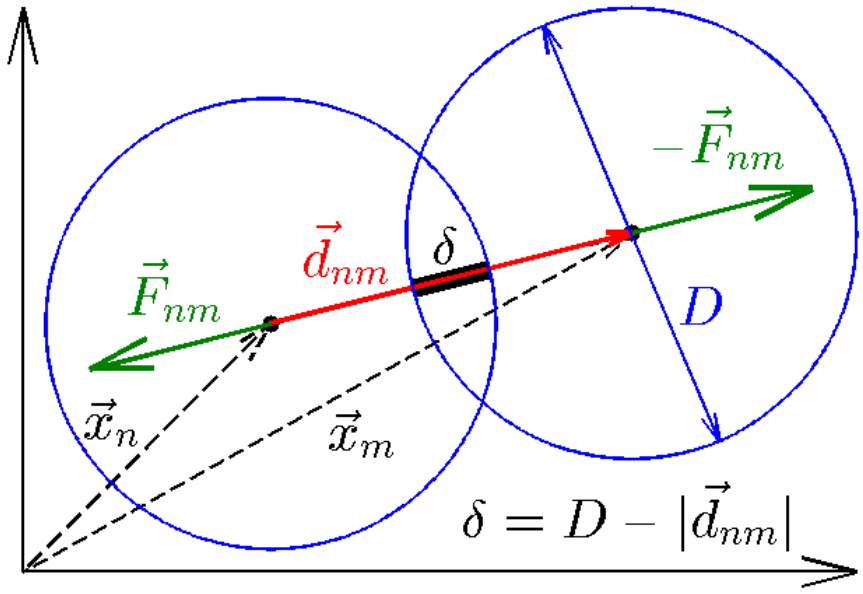
$$M_n \frac{d^2}{dt^2}\vec{x}_n(t) = \vec{F}_n(t) = \sum_{m=1}^{N} \vec{F}_{nm}(t) + \vec{F}_n^e(t), \qquad [1]$$

where M_n is the mass of particle n, $\vec{F}_n(t)$ is the force on particle n, $\vec{F}_{nm}(t)$ is the force on particle n from particle m, and $\vec{F}_n^e(t)$ is the sum of all external forces. For this introduction, we assume that the force is obtained from a scalar potential $\Phi(\vec{x}_n)$ such that

$$\vec{F}_{nm} = -\frac{\partial}{\partial \vec{x}_n}\Phi(\vec{x}_m, \vec{x}_n). \qquad [2]$$

Figure 1: Diagram defining particle-particle interaction variables.

```
MDfigures(1);
```



We will further assume the particles are disks with a simple harmonic potential:

$$\Phi(\vec{x}_m, \vec{x}_n) = \Phi(|\vec{x}_m - \vec{x}_n|) = \Phi(d_{nm}) = \frac{1}{2}K(D - d_{nm})^2 = \frac{1}{2}K\delta^2, \qquad [3a]$$

where

$$\vec{d}_{nm} = \vec{x}_m - \vec{x}_n \qquad [3b]$$

is the vector pointing from the center of particle n to the center of particle m and

$$d_{nm} = |\vec{d}_{nm}|; \qquad [3c]$$

K is a material constant that determines how hard the material is, D is the particle diameter, and

$$\delta = D - |\vec{d}_{nm}| \qquad [3d]$$

is the particle overlap. (See Figure 1.) Differentiating the potential, the force

$$\vec{F}_{nm} = -K\delta\hat{d}_{nm}. \qquad [3e]$$

The direction of the force is opposite to the unit vector $\hat{d}_{nm}$ pointing from particle n to m, which pushes the particles apart. From Newton's third law the force on particle m from n is

$$\vec{F}_{mn} = -\vec{F}_{nm}. \qquad [3f]$$

In this introduction we use a contact force, which only acts when the particles are in contact. That is, the force is zero if

$$\delta <= 0. \qquad [3g]$$

Simple Molecular Dynamics Simulation

introMDpbc.m contains the same code without the explanation:

Experimental Parameters (particle)

Here we define all of the particle parameters needed to determine the forces between particle pairs:

```
N=80;  % number of particles
D=2;   % diameter of particles
K=100; % force vector n<-m Fnm=-K*(D/|dnm|-1)*dnm, where vect dnm=Xm-Xn
M=3;   % mass of particles
```

Experimental Parameters (space-domain)

This simulation uses a periodic domain. In a periodic domain there are copies or images of each particle separated by L_x and L_y such that for each particle a positions (x, y) there are also particles at

$$(x + kL_x, y + lL_y),$$

for all integers k and l. In the main simulation box $k = 0$ and $l = 0$. For this simulation we need the distance between all particle pairs, but since we have a short range potential [3g] we only need the nearest image distance. This calculation is done below in the main loop.

Here we define parameters needed to determine the space-domain for the particles in a periodic box of size `Lx` by `Ly`.

```
Lx=10*D;  % size of box
Ly=10*D;
```

Experimental Parameters (initial conditions)

We choose random velocities with the property that the total kinetic energy: `M/2*sum(vx.^2+vy.^2)=KEset`.

```
KEset=5;  % initial total Kinetic Energy (KE)
```

Experimental Parameters (time-domain)

The time-domain is from 0 to TT.

```
TT=1;    % total simulation time (short for demo).
```

Display Parameters

This section controls the simulation plotting animation

```
demo=true;       % true for this demo
plotit=false;    % plot ? off for this demo
Nplotskip=50;    % number of time steps to skip before plotting
```

Theory II: Numeric integration of Newton's laws Part I

To solve [1] we first rewrite it as two first-order equations:

$$\begin{aligned} \frac{d}{dt}\vec{x}_n(t) &= \vec{v}_n(t). \\ \frac{d}{dt}\vec{v}_n(t) &= \vec{F}_n(t)/M_n. \end{aligned} \qquad [4]$$

When solving [4] numerically, time is broken up into discrete steps of size Δt (i.e., $t = k\Delta t$, where k is an integer). If Δt is small we can approximate [4] with:

$$\begin{aligned} \left[\vec{x}_n\left((k+1)\Delta t\right) - \vec{x}_n(k\Delta t)\right]/\Delta t &\simeq \vec{v}_n(k\Delta t). \\ \left[\vec{v}_n\left((k+1)\Delta t\right) - \vec{v}_n(k\Delta t)\right]/\Delta t &\simeq \vec{F}_n(t)/M_n. \end{aligned} \qquad [5]$$

Solving for the later times $(k+1)\Delta t$ in terms of earlier times $k\Delta t$:

$$\begin{aligned} \vec{x}_n^{(k+1)} \equiv \vec{x}_n\left((k+1)\Delta t\right) &\simeq \vec{x}_n^{(k)} + \vec{v}_n^{(k)}\Delta t \\ \vec{v}_n^{(k+1)} \equiv \vec{v}_n\left((k+1)\Delta t\right) &\simeq \vec{v}_n^{(k)} + \vec{F}_n^{(k)}/M_n\Delta t \end{aligned} \qquad [6]$$

Equation [6] discovered by L. Euler is called the Euler Method and could be used to integrate the system to get the new positions $\vec{x}_n^{(k+1)}$ and velocities $\vec{v}_n^{(k+1)}$ from the old positions $\vec{x}_n^{(k)}$, velocities $\vec{v}_n^{(k)}$, and forces $\vec{F}_n^{(k)}(\vec{x}_n^{(k)})$, which only depends on $\vec{x}_n^{(k)}$. However [6] is not recommended. If we use [6] the energy of the system will grow without bounds as seen in Figure 2. To make a useful integration scheme we can change the order of integration. If we calculate $\vec{v}_n^{(k+1)}$ first we can use it to calculate $\vec{x}_n^{(k+1)}$. These equation are an enhanced version of Euler's method called the Semi-implicit Euler Method:

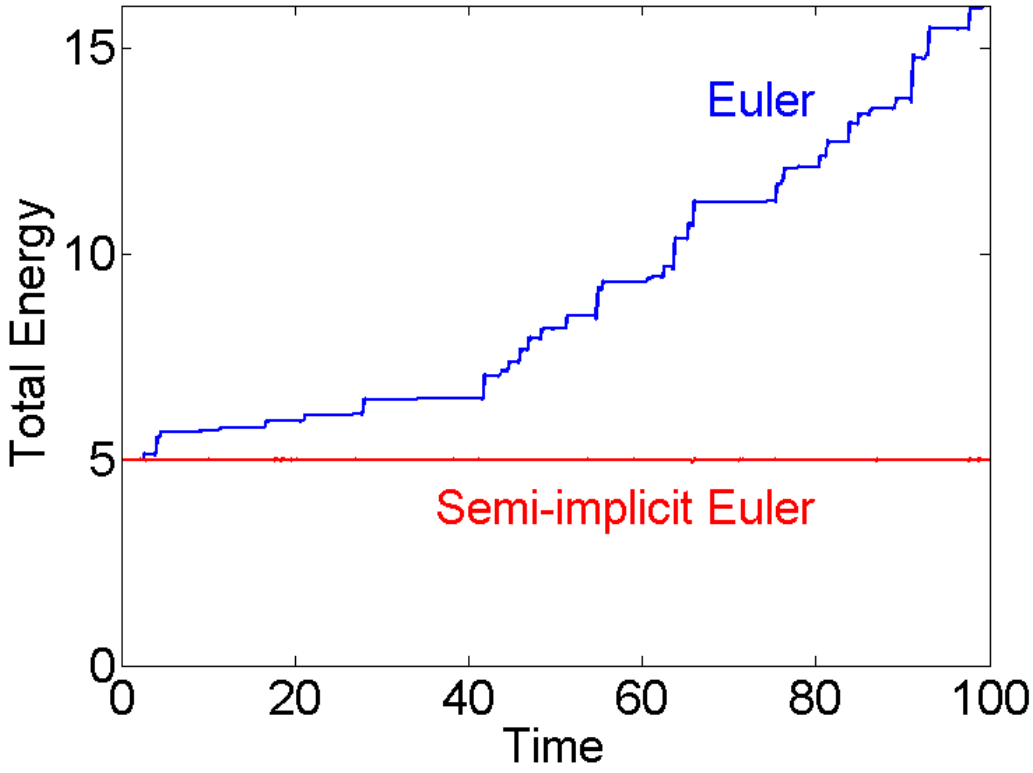
$$\begin{aligned} \vec{v}_n^{(k+1)} &\simeq \vec{v}_n^{(k)} + \vec{F}_n^{(k)}/M_n\Delta t. \\ \vec{x}_n^{(k+1)} &\simeq \vec{x}_n^{(k)} + \vec{v}_n^{(k+1)}\Delta t. \end{aligned} \qquad [7]$$

Figure 2 compares an Euler simulation from eulerMDpbc.m with an semi-implicit Euler simulation from eEulerMDpbc.m. The semi-implicit Euler method is the simplest example of a general method called Symplectic Integration, which is designed to conserve energy.

Figure 2: Euler vs. Semi-implicit Euler Integration.

The following code is used to produce figure 2. External files eulerMDpbc.m and eEulerMDpbc.m are used.

```
KE=5;                                  % initial Kinetic Energy
Ts=100;                                % total simulation time
[Ek Ep]=eulerMDpbc(10,KE,Ts,false);  % 10 particle--Euler integration
eTe=Ek+Ep;                             % save total energy for Euler;
[Ek Ep]=eEulerMDpbc(10,KE,Ts,false); % 10 particle--Semi-implicit Euler
eTse=Ek+Ep;                            % save total energy for semi-implicit Euler
Nt=length(Ek);                         % number of time steps
t=(0:Nt-1)/Nt*Ts;                      % simulation time
fs=25;
plot(t,eTe,t,eTse,'r','linewidth',2);  % plot total energy
axis([0 Ts 0 inf]);
set(gca,'fontsize',fs);
xlabel('Time');
ylabel('Total Energy');
text(80,eTe(fix(90/Ts*Nt)),'Euler',...
  'color','b','fontsize',fs,'horizontal','right');
text(80,.9*KE,'Semi-implicit Euler',...
  'color','r','fontsize',fs,...
  'horizontal','right','vertical','top');
```



Theory II: Numeric integration of Newton's laws Part II

It is clear that energy conservation is poor using the (blue) Euler method. In principle Equation [7] could be used for simple MD simulations. However, both methods are only accurate to first order in Δt, and this limits the usefulness of the semi-implicit Euler method.

In this introduction we use a Symplectic Integrator with errors proportional to $(\Delta t)^2$ and good energy conservation due to L. Verlet called Velocity Verlet integration. The main drawback of the semi-implicit Euler method the error is proportional to Δt. Since we used `dt=0.01`, we can expect errors of order 1% (see Figure 3). Sometimes that is not sufficient. One option is to decrease `dt`, but the drawback is that the simulation time is increase proportionally. So with `dt=0.01/100=0.0001` semi-implicit Euler would give error of order 0.01% the simulation time would increase by a factor of 100. To overcome this deficiency Verlet devised a different integration scheme based on a second order approximation to [4] as follows:

$$\vec{x}_n^{(k+1)} \simeq \vec{x}_n^{(k)} + \vec{v}_n^{(k)}\Delta t + \tfrac{1}{2}\vec{a}_n^{(k-1)}(\Delta t)^2. \quad [8]$$

$$\vec{a}_n^{(k)} = \frac{1}{M_n}\sum_{m=1}^{N}\vec{F}_{nm}(|\vec{x}_m^{(k+1)} - \vec{x}_n^{(k+1)}|) \quad [9]$$

$$\vec{v}_n^{(k+1)} \simeq \vec{v}_n^{(k)} + \tfrac{1}{2}(\vec{a}_n^{(k)} + \vec{a}_n^{(k-1)})\Delta t. \quad [10]$$

Figure 3: Velocity Verlet vs. Semi-implicit Euler Integration.

The following code is used to produce figure 3. External files verletMDpbc.m and eEulerMDpbc.m are used.

```
KE=5;                                   % initial Kinetic Energy
Ts=100;                                 % total simulation time
[Ek Ep]=verletMDpbc(10,KE,Ts,false);  % 10 particle--Verlet integration
eTv=Ek+Ep;                              % save total energy for Verlet;
Nt=length(Ek);                          % number of time steps
t=(0:Nt-1)/Nt*Ts;                       % simulation time
fs=25;
plot(t,eTv,t,eTse,'r','linewidth',2); % plot total energy
hold on;
plot(t,[0*t+1.01*KE;0*t+.99*KE],'r--','linewidth',2);  % 1% error
plot([73 85],[1.014 1]*KE,'linewidth',2);
hold off;
axis([0 Ts 5*(1+[-.02 .0201])]);
set(gca,'fontsize',fs);
xlabel('Time');
ylabel('Total Energy');
text(50,1.014*KE,'Velocity Verlet',...
  'color','b','fontsize',fs,'horizontal','center');
text(50,.988*KE,'Semi-implicit Euler \pm 1%',...
  'color','r','fontsize',fs,...
  'horizontal','center','vertical','top');
```

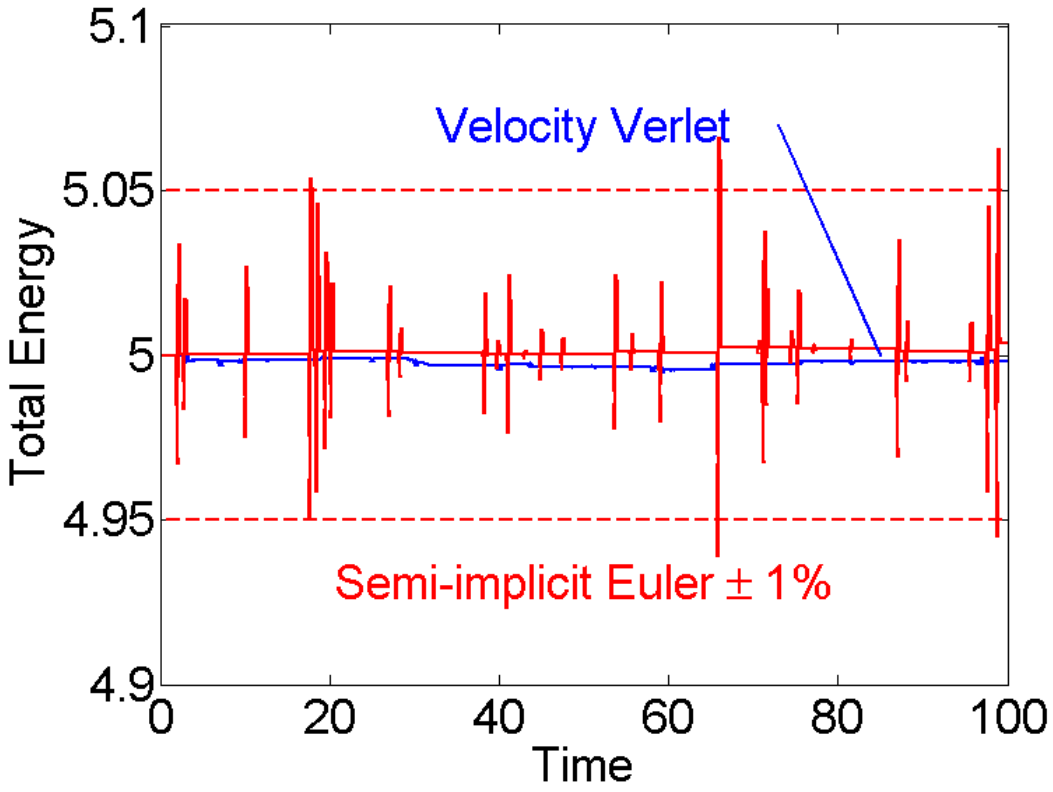


Figure 3: Velocity Verlet vs. Semi-implicit Euler Integration (caption).

Figure 3 shows the total energy over time for a 10 particle system using the Semi-implicit Euler integration method from [7] (red) and Velocity Verlet from [8-10] (blue). Red dashed lines show a range of $\pm 1\%$. The error for the Velocity Verlet is ≈ 100 times smaller.

Simulation Parameters

Regardless of the integration method Δt (`dt` in code) must be determined. Here we use a fixed time step `dt=0.01` $\simeq \sqrt{M/K}/20$. The total number of time steps `Nt` is determined from the total simulation time `TT`.

```
dt=1e-2;       % integration time step
Nt=fix(TT/dt); % number of time steps
```

Initial Conditions (Positions)

The particles need to be placed in the box with minimal overlap to avoid excess potential energy at the beginning of the simulation. For moderately dense systems a square grid can be used. The matlab command `ndgrid` creates D spaced points on a grid inside of the Lx by Ly box. `randperm` randomly chooses N positions from all `numel(x)` available locations. The final result is a pair of matlab vectors `x` and `y` each

with `size(x)=[1,N]` that represents $\vec{x}_n^{(k)}$ at each time $k\Delta t$. Here, for the initial conditions before the simulation starts $k = 0$. In the code k is represented in matlab as `nt`, the time step number.

```
[x y]=ndgrid(D/2:D:Lx-D/2,D/2:D:Ly-D/2); % place particles on grid
ii=randperm(numel(x),N);                 % N random position on grid
x=x(ii);                                 % set x-positions
y=y(ii);                                 % set y-positions
```

Initial Conditions (Velocities)

The velocities `vx` and `vy` each with `size(vx)=[1,N]` represent $\vec{v}_n^{(k)}$ at time $k\Delta t$. Here, for the initial conditions before the simulation starts $k = 0$. The velocities are chosen randomly from a normal distribution using [randn](). The mean velocity is removed to avoid center of mass drift. The variance of the distribution is set so that the total kinetic energy: `M/2*sum(vx.^2+vy.^2)=KEset`.

```
vx=randn(1,N)/3;  % normal (Maxwell) distribution of velocities
vy=randn(1,N)/3;

vx=vx-mean(vx);   % remove center of mass drift
vy=vy-mean(vy);

tmp=sqrt(2*KEset/M/sum((vx.^2+vy.^2)));  % set Kinetic energy
vx=vx*tmp;
vy=vy*tmp;
```

Initial Conditions (Accelerations)

The accelerations from the $k - 1$ previous time step is need for Verlet's second order integration scheme.

```
ax_old=0*x;       % need initial condition for velocity Verlet integration
ay_old=0*y;
```

Save variables

List of quantities to be saved at each time step.

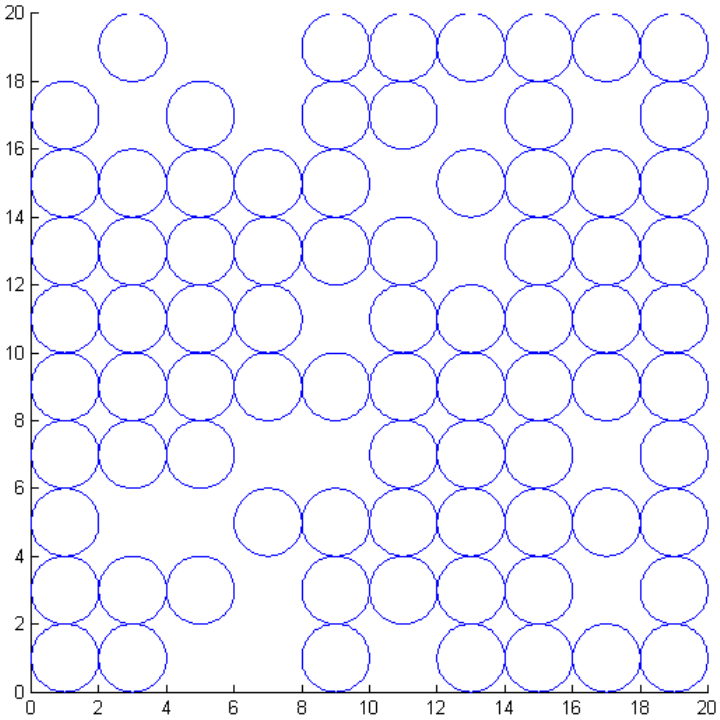
```
Ek=zeros(Nt,1);    % Kinetic Energy
Ep=zeros(Nt,1);    % particle-particle potential
xs=zeros(Nt,N);    % x-position
ys=zeros(Nt,N);    % y-position
vxs=zeros(Nt,N);   % x-velocity
vys=zeros(Nt,N);   % y-velocity
```

Figure 3: Setup Plotting

Here we use an external function plotNCirc.m to create an animation of the simulations progress. plotNCirc returns an array of handles `h` to a [rectangle]() object for each of the `N` particles. Matlab rectangles contain a curvature property with turns them into circles. The handles are used later to animate the particle positions. An example initial condition is shown here.

NB: periodic images of particles are not shown

```
if(plotit || demo)            % only if plotit true
  clf;                        % clear figure
  h=plotNCirc(x,y,D,'none');  % plot particles no color; store handle h
  axis('equal');              % square pixels
  axis([0 Lx 0 Ly]);          % piloting range
end
```



Main Loop

In the main loop the simulation steps through Nt time steps, advancing time, the particle positions, forces, and velocities. Comments refer back to sections and equations above.

```
for nt=1:Nt

  % plot particles
  if(plotit && rem(nt-1,Nplotskip+1)==0)  % nt-1 divides Nplotskip+1
    xp=mod(x,Lx);
    yp=mod(y,Ly);
    for np=1:N
      set(h(np),'Position',[xp(np)-.5*D yp(np)-.5*D D D]); % update handle
    end
    drawnow;
  end

  x=x+vx*dt+ax_old*dt^2/2;  % first step in Verlet integration eq.[8]
```

```
  y=y+vy*dt+ay_old*dt^2/2;

  % position dependent calculations
  xs(nt,:)=x;                          % save positions
  ys(nt,:)=y;

  % Force between particles eq. [9] and [3a-g]
  Fx=zeros(1,N);                       % zero forces
  Fy=zeros(1,N);

  for nn=1:N                         % check particle n
    for mm=nn+1:N                    % against particle m from n+1->N
      dy=y(mm)-y(nn);                % [3b] y-comp dnm vector from from n->m
      dy=dy-round(dy/Ly)*Ly;         % closest periodic image
      if(abs(dy)<D)                  % [3g] y-distance close enough?
        dx=x(mm)-x(nn);              % [3b] x-comp dnm vector from from n->m
        dx=dx-round(dx/Lx)*Lx;       % closest periodic image
        dnm=dx.^2+dy.^2;             % [3c] squared distance between n and m
        if(dnm<D^2)                  % [3g] overlapping?
          dnm=sqrt(dnm);             % [3c] distance
          F=-K*(D/dnm-1);            % [3d-e] force magnitude
          Fx(nn)=Fx(nn)+F.*dx;       % [9,3e] accumulate x force on n
          Fx(mm)=Fx(mm)-F.*dx;       % [9,3ef] x force on m (equal opposite)
          Fy(nn)=Fy(nn)+F.*dy;       % [9,3e] accumulate y force on n
          Fy(mm)=Fy(mm)-F.*dy;       % [9,3ef] y force on m (equal opposite)
          Ep(nt)=Ep(nt)+(D-dnm).^2;% [3a] particle-particle potential I
        end
      end
    end
  end
  Ep(nt)=K/2*Ep(nt);         % eq [3a] particle particle potential II

  ax=Fx./M;                  % eq [9] calc a from F=Ma
  ay=Fy./M;

  vx=vx+(ax_old+ax)*dt/2;    % eq [10] second step in Verlet integration
  vy=vy+(ay_old+ay)*dt/2;

  % velocity dependent calculations
  Ek(nt)=M*sum((vx.^2+vy.^2))/2; % Kinetic energy
  vxs(nt,:)=vx;                  % save velocities
  vys(nt,:)=vy;

  ax_old=ax;                 % need for eqs [8-10] save for next step
  ay_old=ay;
end
```

m-files

- MDIntro.zip All files in one zip file.
- MDIntro.m Introduction to Molecular dynamics (This File).
- MDIntro.pdf (pdf version).

- introMDpbc.m Version of this file without discussion.
- introMDwalls.m Version with walls instead of periodic boundaries.
- eulerMDpbc.m Function to demonstrate Euler Integration.
- eEulerMDpbc.m Function to demonstrate Semi-implicit Euler Integration.
- verletMDpbc.m Function to demonstrate Velocity Verlet Integration.
- MDfigures.m Create figures.
- plotNCirc.m Plot N circles and return handles.

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