Molecular Dynamics

Basics (4.1, 4.2, 4.3)

Liouville formulation (4.3.3)

Multiple timesteps (15.3)

Molecular Dynamics

- Theory:

$$\mathbf{F} = m\frac{d^2\mathbf{r}}{dt^2}$$

- Compute the forces on the particles
- Solve the equations of motion
- Sample after some timesteps

Algorithm 3 (A Simple Molecular Dynamics Program)

`program md`	simple MD program
`call init`	initialization
`t=0`	
`do while (t.lt.tmax)`	MD loop
`   call force(f,en)`	determine the forces
`   call integrate(f,en)`	integrate equations of motion
`   t=t+delt`	
`   call sample`	sample averages
`enddo`	
`stop`	
`end`	

Comment to this algorithm:

1. *Subroutines* `init`, `force`, `integrate`, *and* `sample` *will be described in Algorithms 4, 5, and 6, respectively. Subroutine* `sample` *is used to calculate averages like pressure or temperature.*

Algorithm 4 (Initialization of a Molecular Dynamics Program)

`subroutine init`	initialization of MD program
`sumv=0`	
`sumv2=0`	
`do i=1,npart`	
`  x(i)=lattice_pos(i)`	place the particles on a lattice
`  v(i)=(ranf()-0.5)`	give random velocities
`  sumv=sumv+v(i)`	velocity center of mass
`  sumv2=sumv2+v(i)**2`	kinetic energy
`enddo`	
`sumv=sumv/npart`	velocity center of mass
`sumv2=sumv2/npart`	mean-squared velocity
`fs=sqrt(3*temp/sumv2)`	scale factor of the velocities
`do i=1,npart`	set desired kinetic energy and set
`  v(i)=(v(i)-sumv)*fs`	velocity center of mass to zero
`  xm(i)=x(i)-v(i)*dt`	position previous time step
`enddo`	
`return`	
`end`	

Algorithm 5 (Calculation of the Forces)

`subroutine force(f,en)`	determine the force and energy
`en=0`	
`do i=1,npart`	
`   f(i)=0`	set forces to zero
`enddo`	
`do i=1,npart-1`	
`  do j=i+1,npart`	loop over all pairs
`     xr=x(i)-x(j)`	
`     xr=xr-box*nint(xr/box)`	periodic boundary conditions
`     r2=xr**2`	
`     if (r2.lt.rc2) then`	test cutoff
`       r2i=1/r2`	
`       r6i=r2i**3`	
`       ff=48*r2i*r6i*(r6i-0.5)`	Lennard-Jones potential
`       f(i)=f(i)+ff*xr`	update force
`       f(j)=f(j)-ff*xr`	
`       en=en+4*r6i*(r6i-1)-ecut`	update energy
`     endif`	
`  enddo`	
`enddo`	
`return`	
`end`	

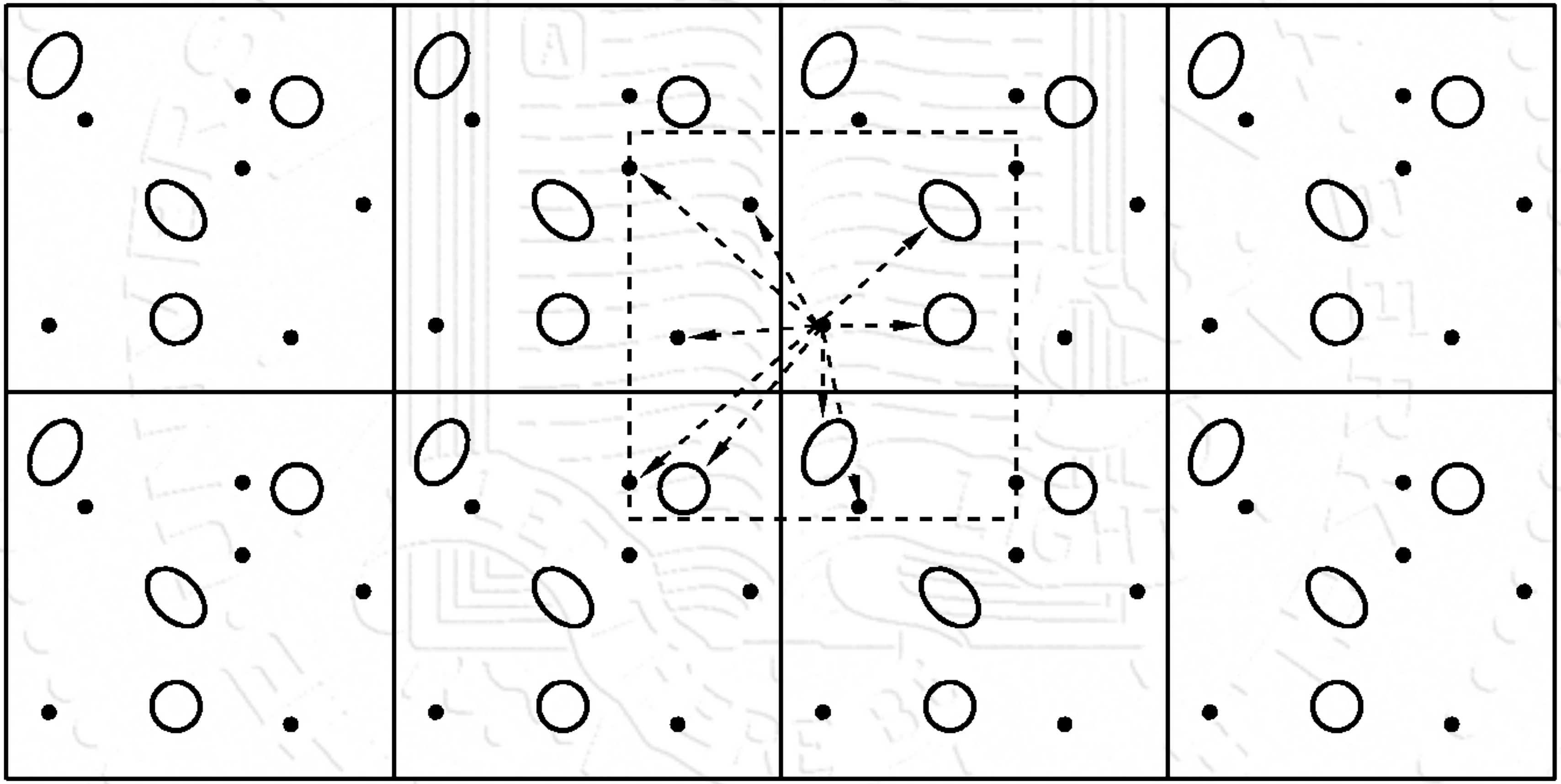
Algorithm 6 (Integrating the Equations of Motion)

```
subroutine integrate(f,en)          integrate equations of motion
sumv=0
sumv2=0
do i=1,npart                        MD loop
    xx=2*x(i)-xm(i)+delt**2*f(i)    Verlet algorithm (4.2.3)
    vi=(xx-xm(i))/(2*delt)          velocity (4.2.4)
    sumv=sumv+vi                    velocity center of mass
    sumv2=sumv2+vi**2               total kinetic energy
    xm(i)=x(i)                      update positions previous time
    x(i)=xx                         update positions current time
enddo
temp=sumv2/(3*npart)                instantaneous temperature
etot=(en+0.5*sumv2)/npart           total energy per particle
return
end
```

Molecular Dynamics

- Initialization
  - Total momentum should be zero (no external forces)
  - Temperature rescaling to desired temperature
  - Particles start on a lattice
- Force calculations
  - Periodic boundary conditions
  - Order NxN algorithm,
  - Order N: neighbor lists, linked cell
  - Truncation and shift of the potential
- Integrating the equations of motion
  - Velocity Verlet
  - Kinetic energy

Periodic boundary conditions



Lennard Jones potentials

- The Lennard-Jones potential

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

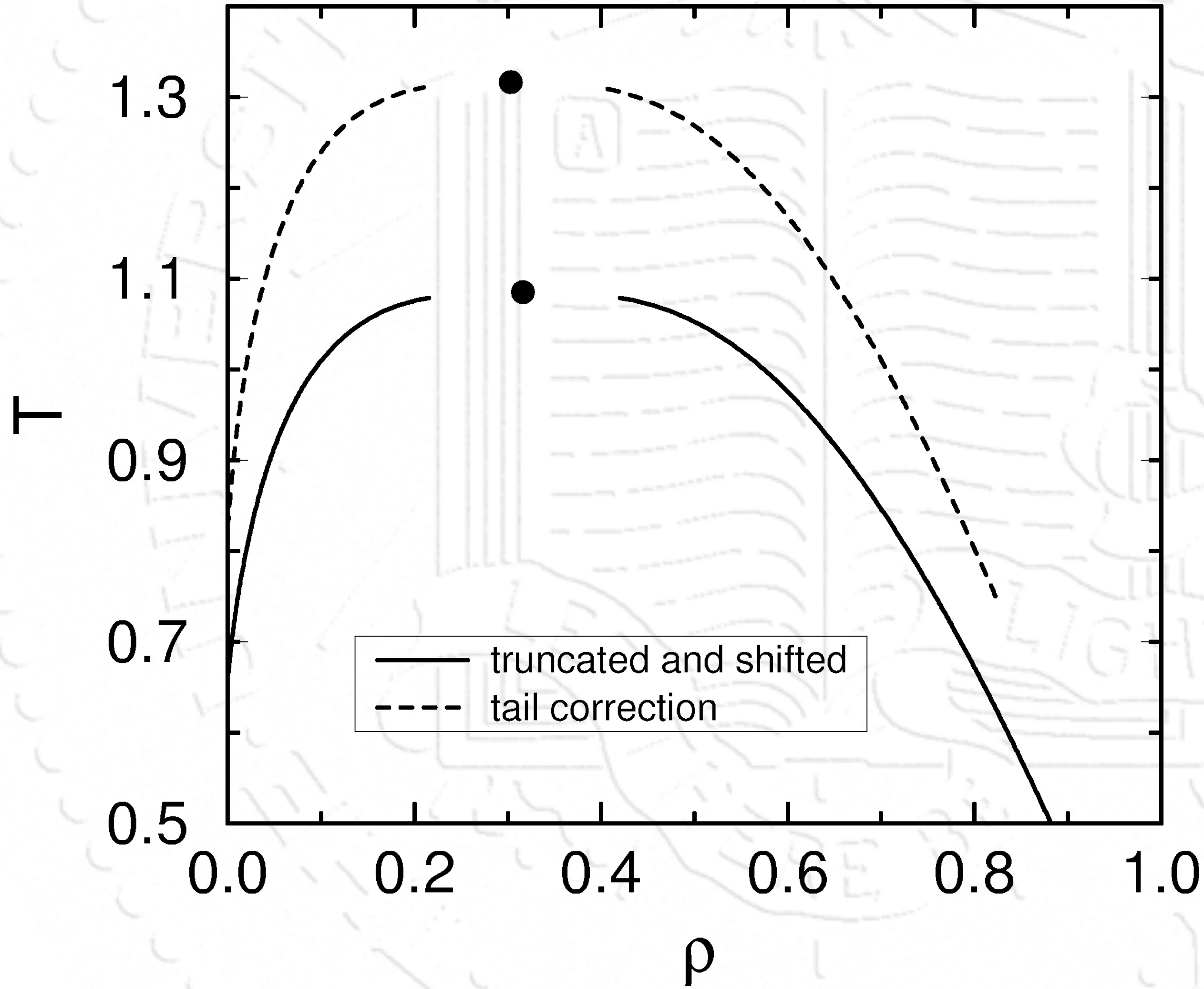
- The truncated Lennard-Jones potential

$$u(r) = \begin{cases} u^{LJ}(r) & r \le r_c \\ 0 & r > r_c \end{cases}$$

- The truncated and shifted Lennard-Jones potential

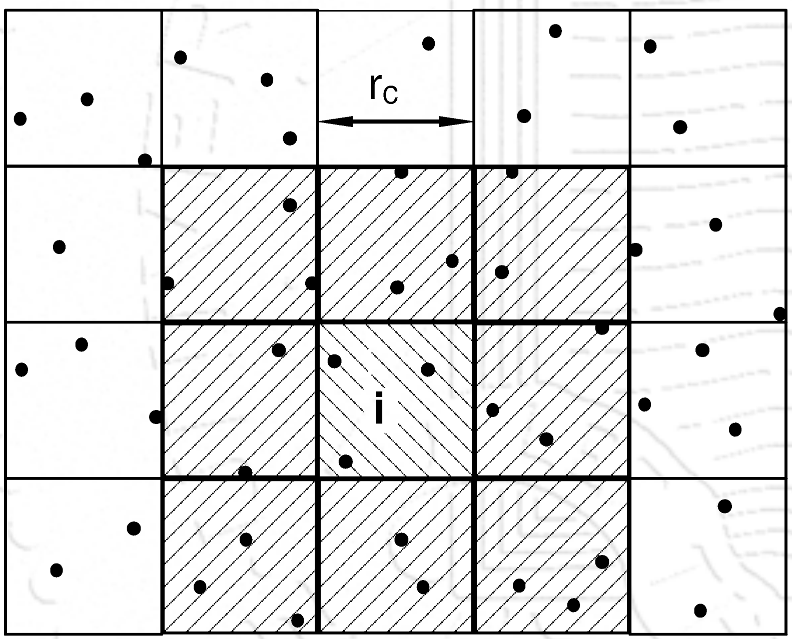
$$u(r) = \begin{cases} u^{LJ}(r) - u^{LJ}(r_c) & r \le r_c \\ 0 & r > r_c \end{cases}$$

Phase diagrams of Lennard Jones fluids

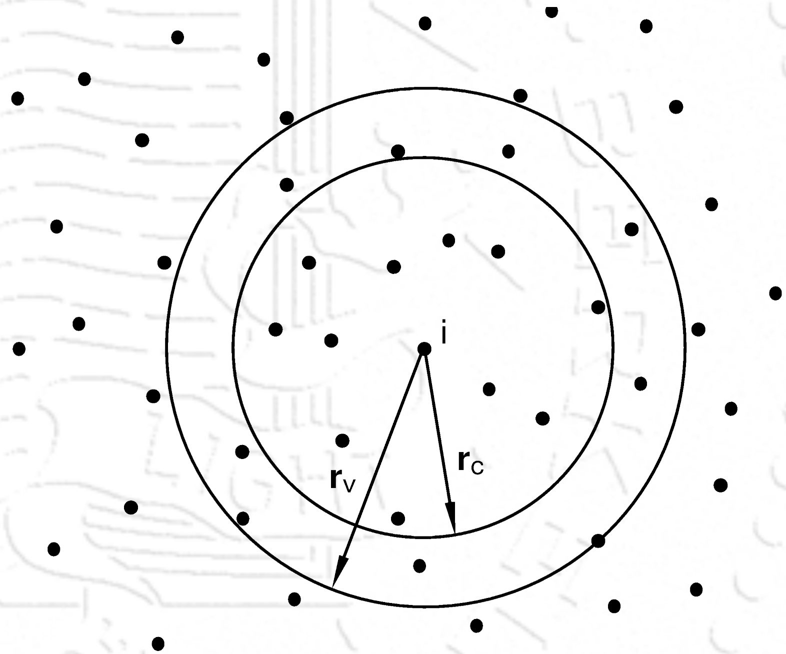


Saving cpu time

Cell list



Verlet-list



Equations of motion

$$\mathbf{r}(t+\Delta t)=\mathbf{r}(t)+\mathbf{v}(t)\Delta t+\frac{\Delta t^2}{2m}\mathbf{f}(t)+\frac{\Delta t^3}{3!}\dddot{\mathbf{r}}(t)+\mathrm{O}(\Delta t^4)$$

$$\mathbf{r}(t-\Delta t)=\mathbf{r}(t)-\mathbf{v}(t)\Delta t+\frac{\Delta t^2}{2m}\mathbf{f}(t)-\frac{\Delta t^3}{3!}\dddot{\mathbf{r}}(t)+\mathrm{O}(\Delta t^4)$$

$$\mathbf{r}(t+\Delta t)+\mathbf{r}(t-\Delta t)=2\mathbf{r}(t)+\frac{\Delta t^2}{m}\mathbf{f}(t)+\mathrm{O}(\Delta t^4)$$

Verlet algorithm

$$\mathbf{r}(t+\Delta t)\approx 2\mathbf{r}(t)-\mathbf{r}(t-\Delta t)+\frac{\Delta t^2}{m}\mathbf{f}(t)$$

Velocity Verlet algorithm

$$\mathbf{r}(t+\Delta t)\approx\mathbf{r}(t)+\mathbf{v}(t)\Delta t+\frac{\Delta t^2}{2m}\mathbf{f}(t)$$

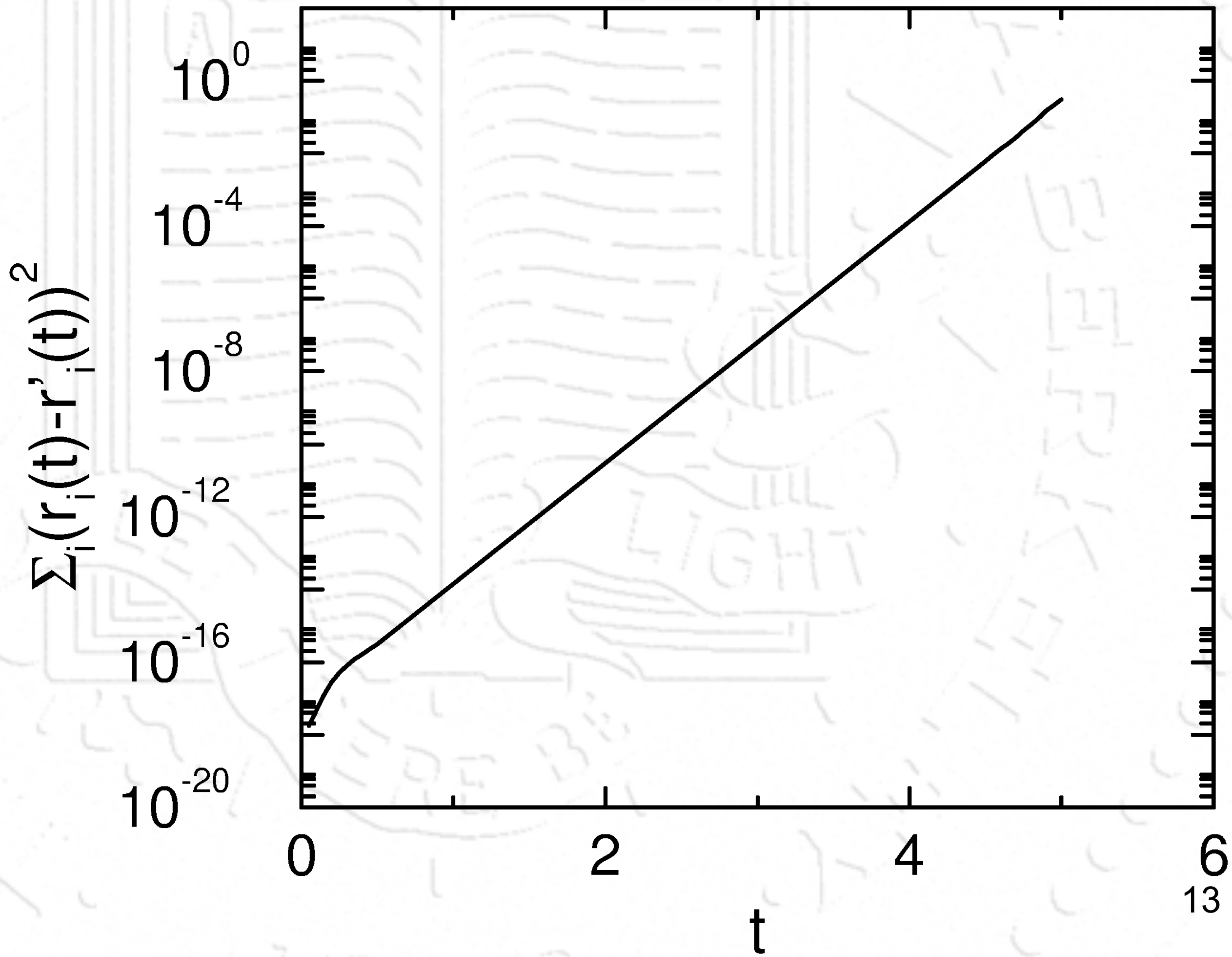
$$\mathbf{v}(t+\Delta t)\approx\mathbf{v}(t)+\frac{\Delta t}{2m}\left[\mathbf{f}(t+\Delta t)+\mathbf{f}(t)\right]$$

Lyaponov instability

$$\left(\mathbf{r}^N(0),\mathbf{p}^N(0)\right)$$

$$\left(\mathbf{r}^N(0),\mathbf{p}_1(0),\cdots,\mathbf{p}_j(0)+\varepsilon,\mathbf{p}_i(0)-\varepsilon\cdots,\mathbf{p}_N(0)\right)$$

$\varepsilon=10^{-10}$



Liouville formulation

$$f\left(\mathbf{p}^N, \mathbf{r}^N\right)$$

Depends implicitly on t

$$\dot{f} = \dot{\mathbf{r}} \frac{\partial f}{\partial \mathbf{r}} + \dot{\mathbf{p}} \frac{\partial f}{\partial \mathbf{p}}$$

$$\mathrm{i}L \equiv \dot{\mathbf{r}} \frac{\partial}{\partial \mathbf{r}} + \dot{\mathbf{p}} \frac{\partial}{\partial \mathbf{p}}$$

$$\frac{\mathrm{d}f}{\mathrm{d}t} = \mathrm{i}Lf$$

Beware: this solution is equally useless as the differential equation!

Solution

$$f(t) = \exp(\mathrm{i}Lt) f(0)$$

$$\mathrm{i}L \equiv \mathrm{i}L_r + \mathrm{i}L_p = \dot{\mathbf{r}}\frac{\partial}{\partial \mathbf{r}} + \dot{\mathbf{p}}\frac{\partial}{\partial \mathbf{p}}$$

Let us look at them separately

$$f(t) = \exp\left(\mathrm{i}L_r t\right) f(0)$$

$$= \exp\left(\dot{\mathbf{r}}(0)t\frac{\partial}{\partial \mathbf{r}} \right) f(0)$$

$$= \sum_{n=0}^{\infty} \frac{\left(\dot{\mathbf{r}}(0)t\right)^n}{n!}\frac{\partial^n}{\partial \mathbf{r}^n} f(0)$$

$$= f\left(\mathbf{p}^N(0), \left(\mathbf{r}(0) + \dot{\mathbf{r}}(0)t\right)^N\right)$$

Shift of coordinates

$$\mathbf{r}(0) \to \mathbf{r}(0) + \dot{\mathbf{r}}(0)t$$

Taylor expansion

$$= \exp\left(\dot{\mathbf{p}}(0)t\frac{\partial}{\partial \mathbf{p}} \right) f(0)$$

$$= \sum_{n=0}^{\infty} \frac{\left(\dot{\mathbf{p}}(0)t\right)^n}{n!}\frac{\partial^n}{\partial \mathbf{p}^n} f(0)$$

$$= f\left(\left(\mathbf{p}(0) + \dot{\mathbf{p}}(0)t\right)^N, \mathbf{r}^N(0)\right)$$

Shift of momenta

$$\mathbf{p}(0) \to \mathbf{p}(0) + \dot{\mathbf{p}}(0)t$$

$$\mathrm{i}L_r \Rightarrow \mathbf{r}(0) \rightarrow \mathbf{r}(0) + \dot{\mathbf{r}}(0)t$$

$$\mathrm{i}L_p \Rightarrow \mathbf{p}(0) \rightarrow \mathbf{p}(0) + \dot{\mathbf{p}}(0)t$$

We have *noncommuting* operators!

$$e^{A+B} \neq e^{A}e^{B}$$

Trotter identity

$$e^{A+B} = \lim_{P\rightarrow\infty}\left(e^{A/2P}e^{B/P}e^{A/2P}\right)^{P}$$

$$e^{A+B} \approx \left(e^{A/2P}e^{B/P}e^{A/2P}\right)^{P}$$

$$\frac{A}{P} = \frac{\mathrm{i}L_p t}{P} \qquad \frac{B}{P} = \frac{\mathrm{i}L_r t}{P} \qquad \Delta t = \frac{t}{P}$$

$$f\left(\mathbf{p}^{N}(t),\mathbf{r}^{N}(t)\right) = \left(e \;\; e \;\; e\right) f\left(\mathbf{p}^{N}(0),\mathbf{r}^{N}(0)\right)$$

$$\mathrm{i}L_r \Delta t \Rightarrow \mathbf{r} \rightarrow \mathbf{r} + \dot{\mathbf{r}}\Delta t$$

$$\mathrm{i}L_p \Delta t \Rightarrow \mathbf{p} \rightarrow \mathbf{p} + \dot{\mathbf{p}}\Delta t$$

$$\left(e^{\left(\mathrm{i}L_p \Delta t/2\right)} e^{\left(\mathrm{i}L_r \Delta t\right)} e^{\left(\mathrm{i}L_p \Delta t/2\right)} \right)^P$$

$$e^{\left(\mathrm{i}L_p \Delta t/2\right)} f\left(\mathbf{p}^N(0), \mathbf{r}^N(0)\right) = f\left(\left[\mathbf{p}(0) + \frac{\Delta t}{2}\dot{\mathbf{p}}(0) \right]^N, \mathbf{r}^N(0) \right)$$

Velocity Verlet!

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

$$\mathbf{v}(t+\Delta t) = \mathbf{v}(t) + \frac{\Delta t}{2m}\left[\mathbf{F}(t) + \mathbf{F}(t+\Delta t)\right]$$

$$\mathbf{p}(0) \rightarrow \mathbf{p}(0) + \frac{\Delta t}{2}\left[\dot{\mathbf{p}}(0) + \dot{\mathbf{p}}(\Delta t)\right]$$

$$\mathbf{r}(0) \rightarrow \mathbf{r}(0) + \Delta t\dot{\mathbf{r}}(\Delta t/2) = \mathbf{r}(0) + \Delta t\dot{\mathbf{r}}(0) + \frac{\Delta t^2}{2m}\mathbf{F}(0)$$

Velocity Verlet:

$$e^{\left(\mathrm{i}L_p \Delta t/2\right)} e^{\left(\mathrm{i}L_r \Delta t\right)} e^{\left(\mathrm{i}L_p \Delta t/2\right)}$$

```
Call force(fx)
Do while (t<tmax)
```

$$e^{\left(\mathrm{i}L_p \Delta t/2\right)} : \mathbf{v}\left(t+\frac{\Delta t}{2}\right) \to \mathbf{v}(t) + \frac{\Delta t}{2m}\mathbf{f}(t)$$

```
vx=vx+delt*fx/2
```

$$e^{\left(\mathrm{i}L_r \Delta t\right)} : \mathbf{r}(t+\Delta t) \to \mathbf{r}(t) + \Delta t \mathbf{v}(t+\Delta t/2)$$

```
x=x+delt*vx
Call force(fx)
```

$$e^{\left(\mathrm{i}L_p \Delta t/2\right)} : \mathbf{v}(t+\Delta t) \to \mathbf{v}(t+\Delta t/2) + \frac{\Delta t}{2m}\mathbf{f}(t+\Delta t)$$

```
vx=vx+delt*fx/2
```

```
enddo
```

Liouville Formulation

Velocity Verlet algorithm:

$$\mathbf{p}(t+\Delta t) = \mathbf{p}(t) + \frac{\Delta t}{2}\left[\dot{\mathbf{p}}(t) + \dot{\mathbf{p}}(t+\Delta t)\right]$$

$$\mathbf{r}(t+\Delta t) = \mathbf{r}(t) + \Delta t\,\dot{\mathbf{r}}(t) + \frac{\Delta t^2}{2m}\mathbf{F}(t)$$

Three subsequent coordinate transformations in either **r** or **p** of which the *Jacobian* is one: *Area preserving*

$$\mathbf{p}(t+\Delta t/2) = \mathbf{p}(t) + \frac{\Delta t}{2}\mathbf{F}(\mathbf{r})$$

$$\mathbf{r}(t) = \mathbf{r}(t)$$

$$J_1 = \det\begin{vmatrix} 1 & \frac{\Delta t}{2}\frac{\partial \mathbf{F}(\mathbf{r})}{\partial \mathbf{r}} \\ 0 & 1 \end{vmatrix} = 1$$

$$\mathbf{p}(t+\Delta t/2) = \mathbf{p}(t+\Delta t/2)$$

$$\mathbf{r}(t+\Delta t) = \mathbf{r}(t) + \frac{\Delta t}{m}\mathbf{p}(t+\Delta t/2)$$

$$J_2 = \det\begin{vmatrix} 1 & 0 \\ \Delta t/m & 1 \end{vmatrix} = 1$$

$$\mathbf{p}(t+\Delta t) = \mathbf{p}(t+\Delta t/2) + \frac{\Delta t}{2}\mathbf{F}(\mathbf{r}(t))$$

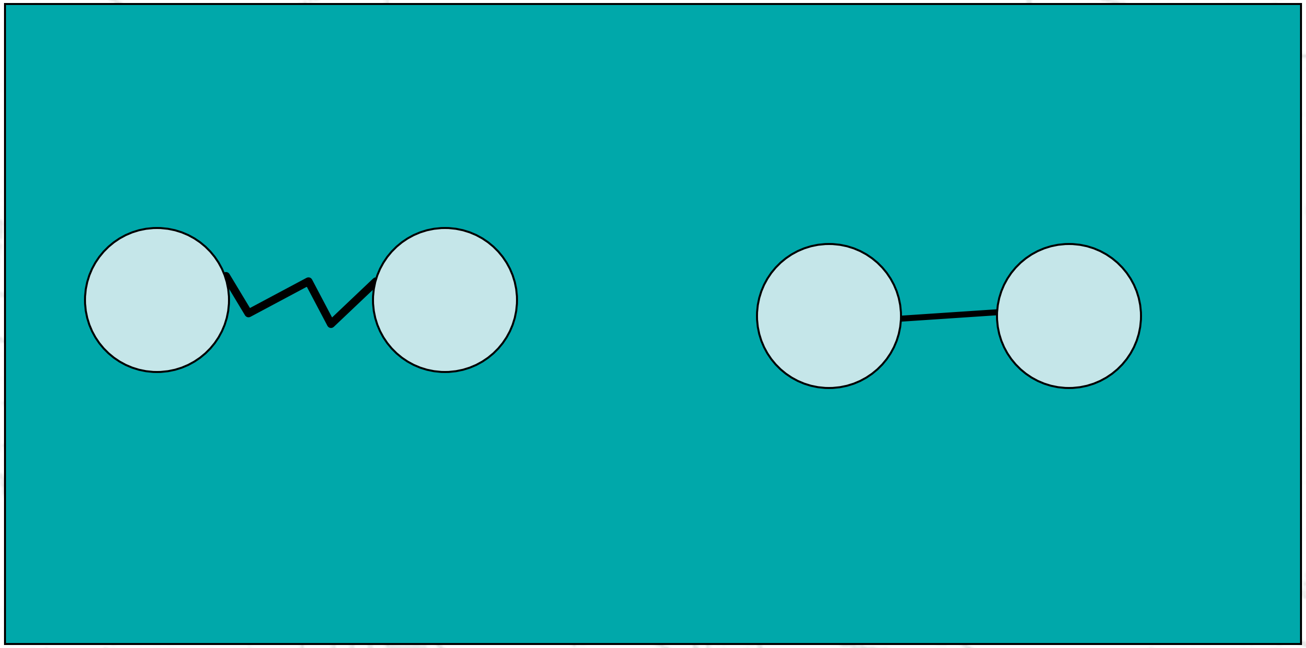
$$\mathbf{r}(t) = \mathbf{r}(t)$$

$$J_3 = \det\begin{vmatrix} 1 & \frac{\Delta t}{2}\frac{\partial \mathbf{F}(\mathbf{r})}{\partial \mathbf{r}} \\ 0 & 1 \end{vmatrix} = 1$$

Other Trotter decompositions are possible!

Multiple time steps

- What to use for stiff potentials:



  – Fixed bond-length: constraints (Shake)
  – Very small time step

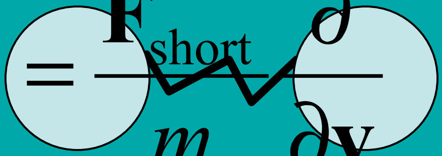
Multiple Time steps

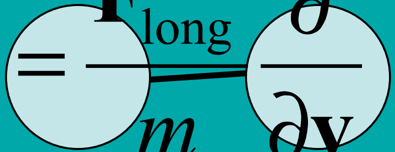
$$\mathbf{F} = \mathbf{F}_{\text{short}} + \mathbf{F}_{\text{long}}$$

$$\mathrm{i}L \equiv \mathrm{i}L_r + \mathrm{i}L_p = \mathbf{v}\frac{\partial}{\partial \mathbf{r}} + \frac{\mathbf{F}}{m}\frac{\partial}{\partial \mathbf{v}}$$

$$\mathrm{i}L_p = \mathrm{i}L_{\text{short}} + \mathrm{i}L_{\text{long}}$$

$$\mathrm{i}L_{\text{short}} = \frac{\mathbf{F}_{\text{short}}}{m}\frac{\partial}{\partial \mathbf{v}} \qquad \mathrm{i}L_{\text{long}} = \frac{\mathbf{F}_{\text{long}}}{m}\frac{\partial}{\partial \mathbf{v}}$$





Trotter expansion:

$$e^{\mathrm{i}\left(L_{\text{long}} + L_{\text{short}} + L_r\right)\Delta t} \approx e^{\mathrm{i}L_{\text{long}}\Delta t/2} e^{\mathrm{i}\left(L_{\text{short}} + L_r\right)\Delta t} e^{\mathrm{i}L_{\text{long}}\Delta t/2}$$

Introduce: $\delta t = \Delta t / n$

$$e^{\mathrm{i}\left(L_{\text{long}} + L_{\text{short}} + L_r\right)\Delta t} \approx e^{\mathrm{i}L_{\text{long}}\Delta t/2}\left[e^{\mathrm{i}L_{\text{short}}\delta t/2} e^{\mathrm{i}L_r \delta t} e^{\mathrm{i}L_{\text{short}}\delta t/2}\right]^{\mathrm{n}} e^{\mathrm{i}L_{\text{long}}\Delta t/2}$$

$$e^{i\left(L_{\text{long}}+L_{\text{short}}+L_r\right)\Delta t} \approx e^{iL_{\text{long}}\,\Delta t/2}\left[e^{iL_{\text{short}}\,\delta t/2}e^{iL_r\delta t}e^{iL_{\text{short}}\,\delta t/2}\right]^{n}e^{iL_{\text{long}}\,\Delta t/2}$$

$$iL_{\text{long}}\,\Delta t/2 \Rightarrow v \rightarrow v + F_{\text{long}}\,\Delta t/2m$$

$$iL_{\text{short}}\,\delta t/2 \Rightarrow v \rightarrow v + F_{\text{short}}\,\delta t/2m$$

$$iL_r\delta t \Rightarrow r \rightarrow r + v\delta t$$

First

$$e^{iL_{\text{long}}\,\Delta t/2} f\left[r(0),v(0)\right] = f\left[r(0),v(0)+F_{\text{long}}(0)\Delta t/2m\right]$$

Now n times:

$$\left[e^{iL_{\text{short}}\,\delta t/2}e^{iL_r\delta t}e^{iL_{\text{short}}\,\delta t/2}\right]^{n} f\left[r(0),v(0)+F_{\text{long}}(0)\Delta t/2m\right]$$

$$e^{\left(iL_{p\text{Long}}\Delta t/2\right)} : \mathbf{v}\left(t+\frac{\Delta t}{2}\right) \rightarrow \mathbf{v}(t) + \frac{\Delta t}{2m}\mathbf{f}_{\text{long}}(t)$$

```
Call force(fx_l
vx=vx+delt*fx_l
Do ddt=1,n
```

$$e^{\left(iL_{p\text{Short}}\delta t/2\right)} : \mathbf{v}\left(t+\right.$$

```
    vx=vx+ddelt*fx_short/2
```

$$e^{\left(iL_r\delta t\right)} : \mathbf{r}(t+\delta t) \rightarrow \mathbf{r}(t) + \delta t\mathbf{v}(t+\Delta t/2+\delta t/2)$$

```
    x=x+ddelt*
    Call force
```

$$e^{\left(iL_{p\text{Short}}\delta t/2\right)} : \mathbf{v}\left(t+\right.$$

```
    vx=vx+ddel
enddo
```

$$\mathrm{e}^{iL_{\text{long}}\Delta t/2}\left[\mathrm{e}^{iL_{\text{short}}\delta t/2}\mathrm{e}^{iL_r\delta t}\mathrm{e}^{iL_{\text{short}}\delta t/2}\right]^{\mathrm{n}}\mathrm{e}^{iL_{\text{long}}\Delta t/2}$$

$$iL_{\text{long}}\ \Delta t/2 \Rightarrow v \rightarrow v + F_{\text{long}}\ \Delta t/2m$$

$$iL_{\text{short}}\ \delta t/2 \Rightarrow v \rightarrow v + F_{\text{short}}\ \delta t/2m$$

$$iL_r\delta t \Rightarrow r \rightarrow r + v\delta t$$

$$\mathrm{e}^{iL_{\text{long}}\Delta t/2}\left[\mathrm{e}^{iL_{\text{short}}\delta t/2}\mathrm{e}^{iL_r\delta t}\mathrm{e}^{iL_{\text{short}}\delta t/2}\right]^{\mathrm{n}}\mathrm{e}^{iL_{\text{long}}\Delta t/2}$$

$$iL_{\text{long}}\ \Delta t/2 \Rightarrow v \rightarrow v + F_{\text{long}}\ \Delta t/2m$$

$$iL_{\text{short}}\ \delta t/2 \Rightarrow v \rightarrow v + F_{\text{short}}\ \delta t/2m$$

$$iL_r\delta t \Rightarrow r \rightarrow r + v\delta t$$

Algorithm 29 (Multiple Time Step)

`subroutine`	Multiple time step, `f_long` is the long-range part and `f_short` the short-range part of the force
`+     multi(f_long,f_short)`	
`vx=vx+0.5*delt*f_long`	velocity Verlet with time step Δt
`do it=1,n`	loop for the small time step
`   vx=vx+0.5*(delt/n)*f_short`	velocity Verlet with timestep $\Delta t/n$
`   x=x+(delt/n)2*vx`	
`   call force_short(f_short)`	short-range forces
`   vx=vx+0.5*(delt/n)*f_short`	
`enddo`	
`call force_all(f_long,f_short)`	all forces
`vx=vx+0.5*delt*f_long`	
`return`	
`end`	