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
en=0                                    and energy
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
```

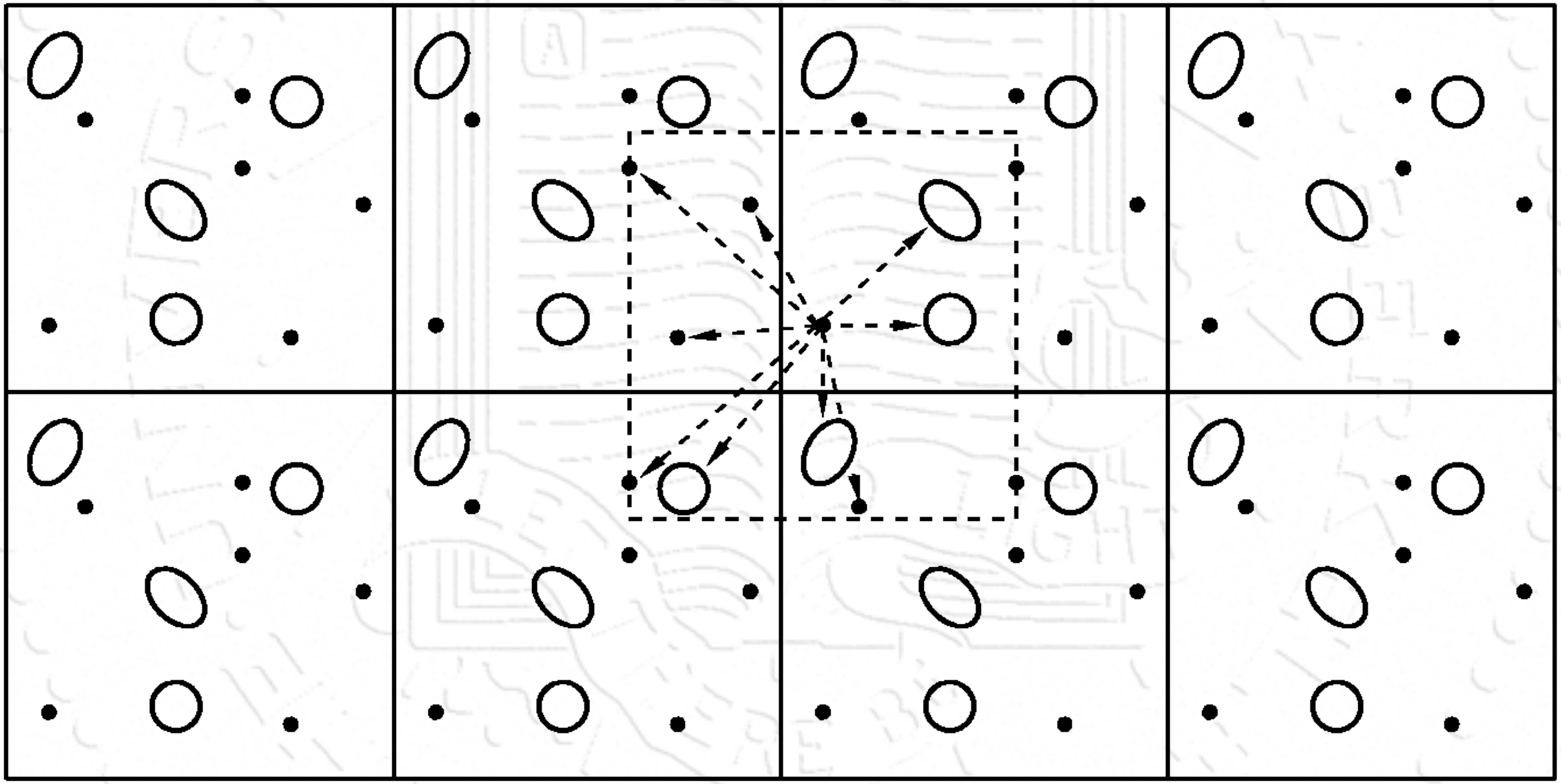
Algorithm 6 (Integrating the Equations of Motion)

`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

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

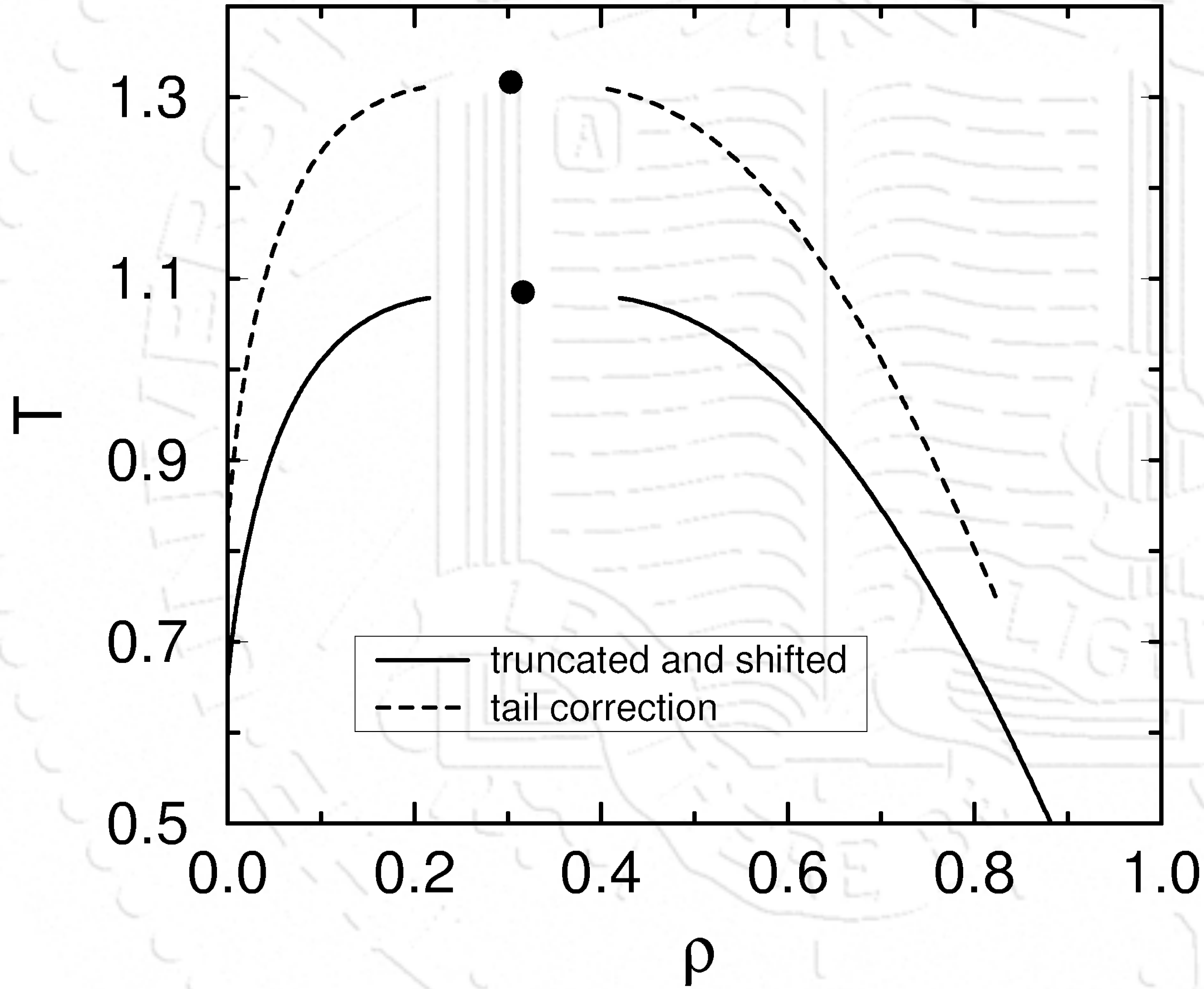
- The truncated Lennard-Jones potential

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

- The truncated and shifted Lennard-Jones potential

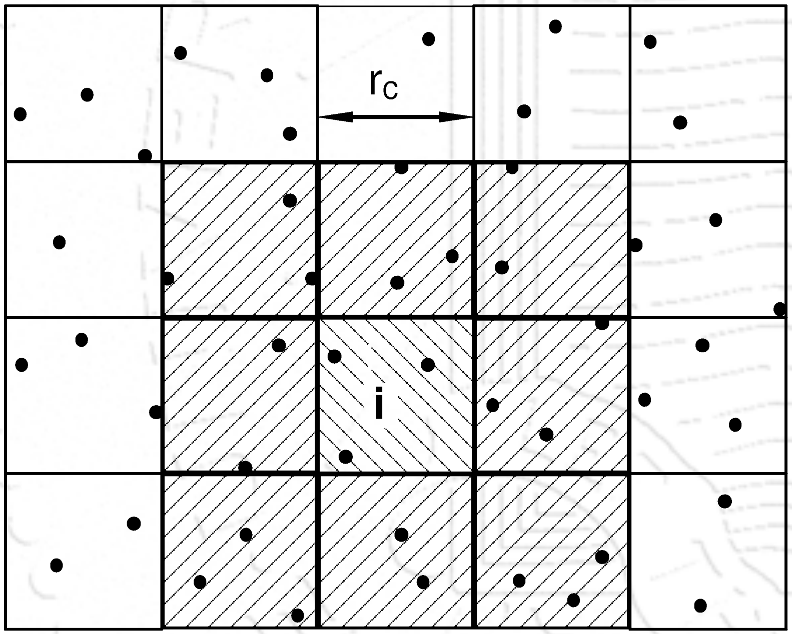
$$u(r) = \begin{cases} u^{LJ}(r) - u^{LJ}(r_c) & r \le r_c \\ 0 & r > r_c \end{cases}$$

Phase diagrams of Lennard Jones fluids

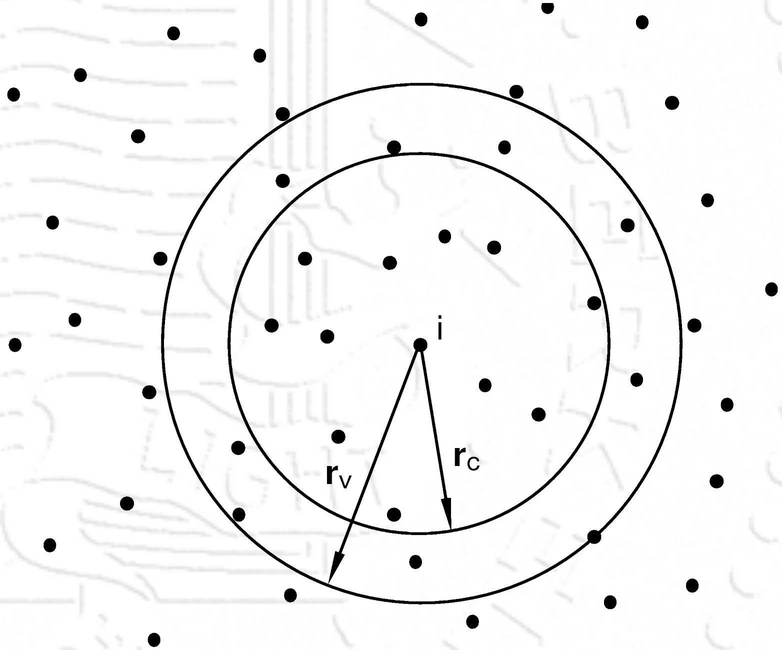


Saving cpu time

Cell list



Verlet-list



Equations of motion

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

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

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

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

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

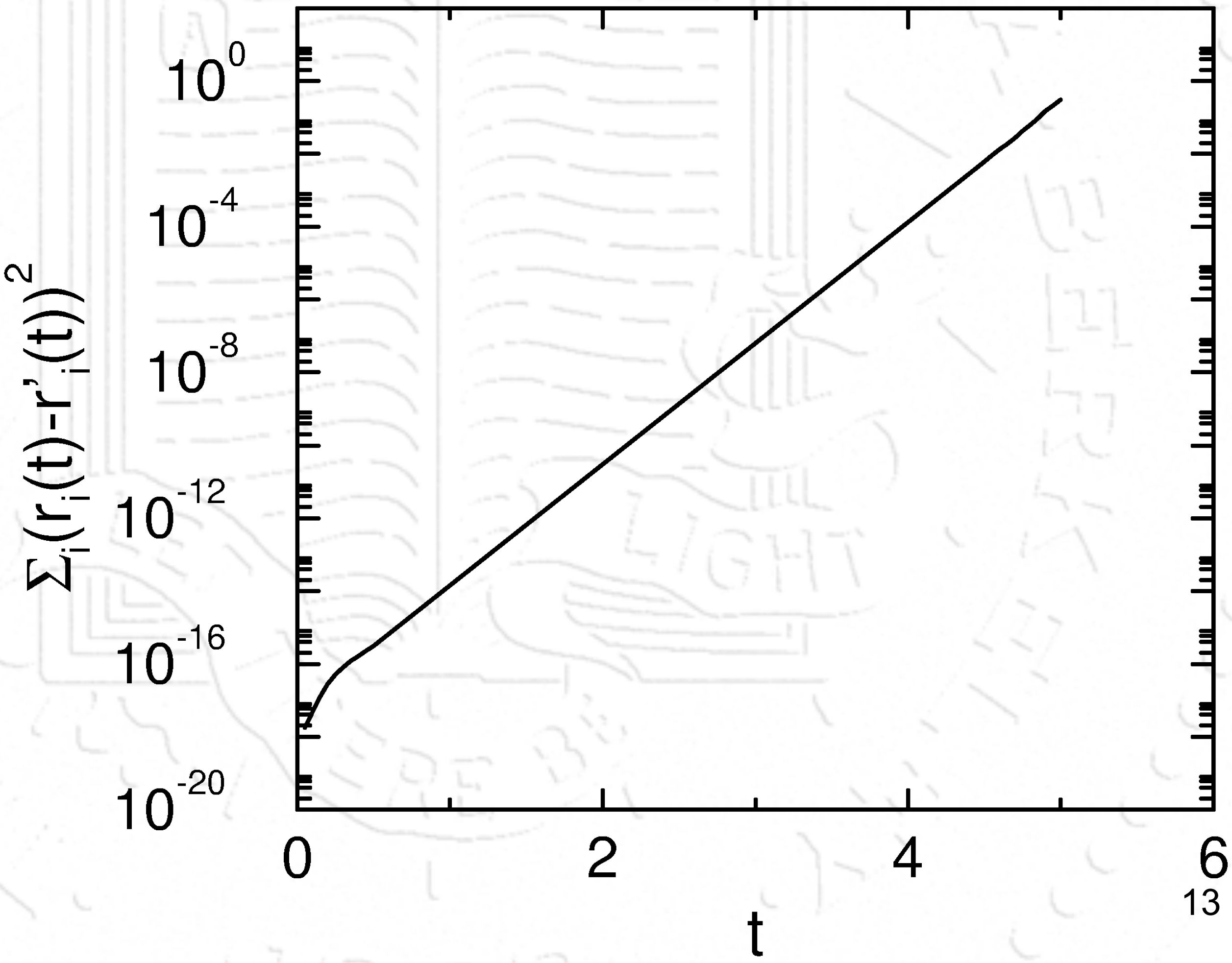
$$\mathbf{v}(t+\Delta t) \approx \mathbf{v}(t) + \frac{\Delta t}{2m}\left[\mathbf{f}(t+\Delta t) + \mathbf{f}(t)\right]$$

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

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

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

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

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

Solution

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

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

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

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

$$f(t) = \exp(\mathrm{i}L_r t) f(0)$$
$$= \exp\left(\dot{\mathbf{r}}(0)t\frac{\partial}{\partial \mathbf{r}}\right) f(0)$$
$$= \sum_{n=0}^{\infty}\frac{(\dot{\mathbf{r}}(0)t)^n}{n!}\frac{\partial^n}{\partial \mathbf{r}^n} f(0)$$
$$= f\left(\mathbf{p}^N(0), (\mathbf{r}(0)+\dot{\mathbf{r}}(0)t)^N\right)$$

Shift of coordinates

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

$$f(t) = \exp(\mathrm{i}L_p t) f(0)$$
$$= \exp\left(\dot{\mathbf{p}}(0)t\frac{\partial}{\partial \mathbf{p}}\right) f(0)$$
$$= \sum_{n=0}^{\infty}\frac{(\dot{\mathbf{p}}(0)t)^n}{n!}\frac{\partial^n}{\partial \mathbf{p}^n} f(0)$$
$$= f\left((\mathbf{p}(0)+\dot{\mathbf{p}}(0)t)^N, \mathbf{r}^N(0)\right)$$

Shift of momenta

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

$$iL \equiv iL_r + iL_p = \dot{\mathbf{r}}\frac{\partial}{\partial \mathbf{r}} + \dot{\mathbf{p}}\frac{\partial}{\partial \mathbf{p}}$$

Let us look at them separately

$$f(t) = \exp(iL_r t) f(0)$$

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

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

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

Shift of coordinates

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

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

Taylor expansion

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

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

Shift of momenta

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

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

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

$$\begin{aligned} f\left(\mathbf{p}^N(t),\mathbf{r}^N(t)\right) &= e^{(\mathrm{i}Lt)} f\left(\mathbf{p}^N(0),\mathbf{r}^N(0)\right) \\ &= e^{\left(\mathrm{i}L_r t + \mathrm{i}L_p t\right)} f\left(\mathbf{p}^N(0),\mathbf{r}^N(0)\right) \\ &\neq e^{\left(\mathrm{i}L_r t\right)} e^{\left(\mathrm{i}L_p t\right)} f\left(\mathbf{p}^N(0),\mathbf{r}^N(0)\right) \end{aligned}$$

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

$$f\left(\mathbf{p}^N(t),\mathbf{r}^N(t)\right) = \left(e^{\left(\mathrm{i}L_p \Delta t/2\right)} e^{\left(\mathrm{i}L_r \Delta t\right)} e^{\left(\mathrm{i}L_p \Delta t/2\right)}\right)^P f\left(\mathbf{p}^N(0),\mathbf{r}^N(0)\right)$$

$$iL_r \Rightarrow \mathbf{r}(0) \rightarrow \mathbf{r}(0) + \dot{\mathbf{r}}(0)t$$

$$iL_p \Rightarrow \mathbf{p}(0) \rightarrow \mathbf{p}(0) + \dot{\mathbf{p}}(0)t$$

We have *noncommuting* operators!

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

Trotter identity

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

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

$$\frac{A}{P} = \frac{iL_p t}{P} \qquad \frac{B}{P} = \frac{iL_r t}{P} \qquad \Delta t = \frac{t}{P}$$

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

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

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

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

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

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

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

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

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

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

$$\left(e^{\left(iL_p\Delta t/2\right)}e^{\left(iL_r\Delta t\right)}e^{\left(iL_p\Delta t/2\right)}\right)^P$$

$$iL_r\Delta t \Rightarrow \mathbf{r}\to\mathbf{r}+\dot{\mathbf{r}}\Delta t$$

$$iL_p\Delta t \Rightarrow \mathbf{p}\to\mathbf{p}+\dot{\mathbf{p}}\Delta t$$

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

$$\ldots,\left[\mathbf{r}(0)+\Delta t\,\dot{\mathbf{r}}\left(\frac{\Delta t}{2}\right)\right]^N\Bigg)$$

$$\ldots\left(\frac{\Delta t}{2}\right)\Bigg]^N\Bigg)$$

Velocity Verlet!

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

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

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

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

Velocity Verlet:

$$e^{(iL_p\Delta t/2)} e^{(iL_r\Delta t)} e^{(iL_p\Delta t/2)}$$

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

$$e^{(iL_p\Delta t/2)} : \mathbf{v}\left(t+\frac{\Delta t}{2}\right) \rightarrow \mathbf{v}(t) + \frac{\Delta t}{2m}\mathbf{f}(t)$$

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

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

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

$$e^{(iL_p\Delta t/2)} : \mathbf{v}(t+\Delta t) \rightarrow \mathbf{v}(t+\Delta t/2) + \frac{\Delta t}{2m}\mathbf{f}(t+\Delta t)$$

```
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*

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

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

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

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

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

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

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

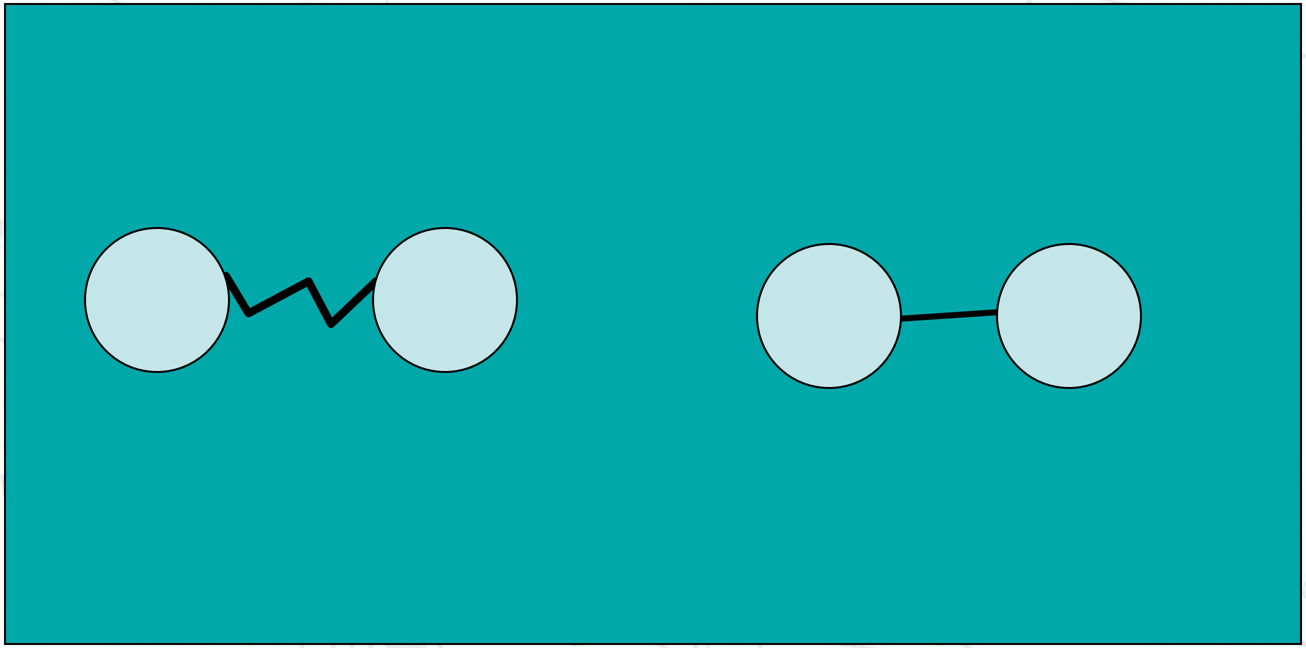
$$\mathbf{r}(t)=\mathbf{r}(t)$$

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

Other Trotter decompositions are possible!

Multiple time steps

- What to use for stiff potentials:



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

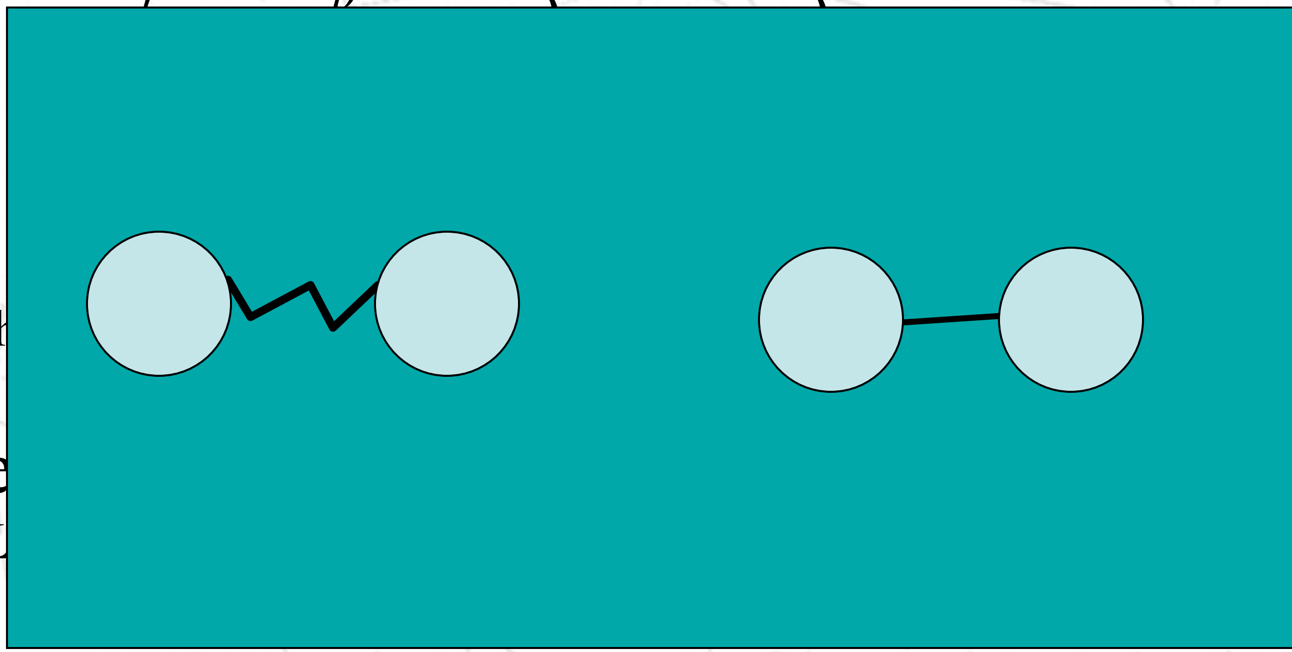
Multiple Time steps

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

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

$\mathrm{i}L_p$

$\mathrm{i}L_{\text{sh}}$



Trotte

$e^{\mathrm{i}(L}$ … $/2$

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

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

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:

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

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

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

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

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

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

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

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_long,f_short)
vx=vx+delt*fx_long/2
Do ddt=1,n
```

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

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

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

```
    x=x+ddelt*vx
    Call force_short(fx_short)
```

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

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

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

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

$$\mathrm{i}L_{\mathrm{long}}\,\Delta t/2\Rightarrow v\rightarrow v+F_{\mathrm{long}}\,\Delta t/2m$$

$$\mathrm{i}L_{\mathrm{short}}\,\delta t/2\Rightarrow v\rightarrow v+F_{\mathrm{short}}\,\delta t/2m$$

$$\mathrm{i}L_r\delta t\Rightarrow r\rightarrow r+v\delta t$$

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

$$e^{(\mathrm{i}L_{p\mathrm{Short}}\delta t/2)}:\mathbf{v}\left(t+\ldots\right.$$

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

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

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

$$e^{(\mathrm{i}L_{p\mathrm{Short}}\delta t/2)}:\mathbf{v}\left(t+\ldots\right.$$

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

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

$$\mathrm{i}L_{\mathrm{long}}\,\Delta t/2\Rightarrow v\rightarrow v+F_{\mathrm{long}}\,\Delta t/2m$$

$$\mathrm{i}L_{\mathrm{short}}\,\delta t/2\Rightarrow v\rightarrow v+F_{\mathrm{short}}\,\delta t/2m$$

$$\mathrm{i}L_r\delta t\Rightarrow r\rightarrow r+v\delta t$$

Algorithm 29 (Multiple Time Step)

```
      subroutine
     +    multi(f_long,f_short)

      vx=vx+0.5*delt*f_long
      do it=1,n
         vx=vx+0.5*(delt/n)*f_short
         x=x+(delt/n)2*vx
         call force_short(f_short)
         vx=vx+0.5*(delt/n)*f_short
      enddo
      call force_all(f_long,f_short)
      vx=vx+0.5*delt*f_long
      return
      end
```

`subroutine multi(f_long,f_short)`	Multiple time step, `f_long` is the long-range part and `f_short` the short-range part of the force
`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 $\Delta t/n$
`call force_short(f_short)`	short-range forces
`call force_all(f_long,f_short)`	all forces