CE 530 Molecular Simulation

Lecture 23

Symmetric MD Integrators

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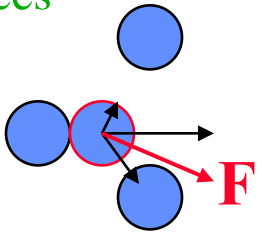
Molecular Dynamics Integration

- Equations of motion in cartesian coordinates

$$\boxed{\begin{aligned} \frac{d\mathbf{r}_j}{dt} &= \frac{\mathbf{p}_j}{m} \\ \frac{d\mathbf{p}_j}{dt} &= \mathbf{F}_j \end{aligned}}$$

$$\left.\begin{aligned} \mathbf{r} &= (r_x, r_y) \\ \mathbf{p} &= (p_x, p_y) \end{aligned}\right\}$$ 2-dimensional space (for example)

$$\mathbf{F}_j = \sum_{\substack{i=1 \\ i \neq j}}^{N} \mathbf{F}_{ij}$$ pairwise additive forces



- Previously, we examined basic MD integrators
  - *Verlet family*

    Verlet; Leap-frog; Velocity Verlet
  - *Popular because of their simplicity and effectiveness*
- Today we will consider
  - *Symmetry features that make the Verlet methods work so well*
  - *Multiple-timestep extensions of the Verlet algorithms*

Integration Algorithms

- Features of a good integrator
  - *minimal need to compute forces (a very expensive calculation)*
  - *good stability for large time steps*
  - *good accuracy*
  - *conserves energy and momentum*

    noise less important than drift
- The true (continuum) equations of motions display certain symmetries
  - *time-reversible*
  - *area-preserving (symplectic)*
- Good integrators can be constructed by paying attention to these features

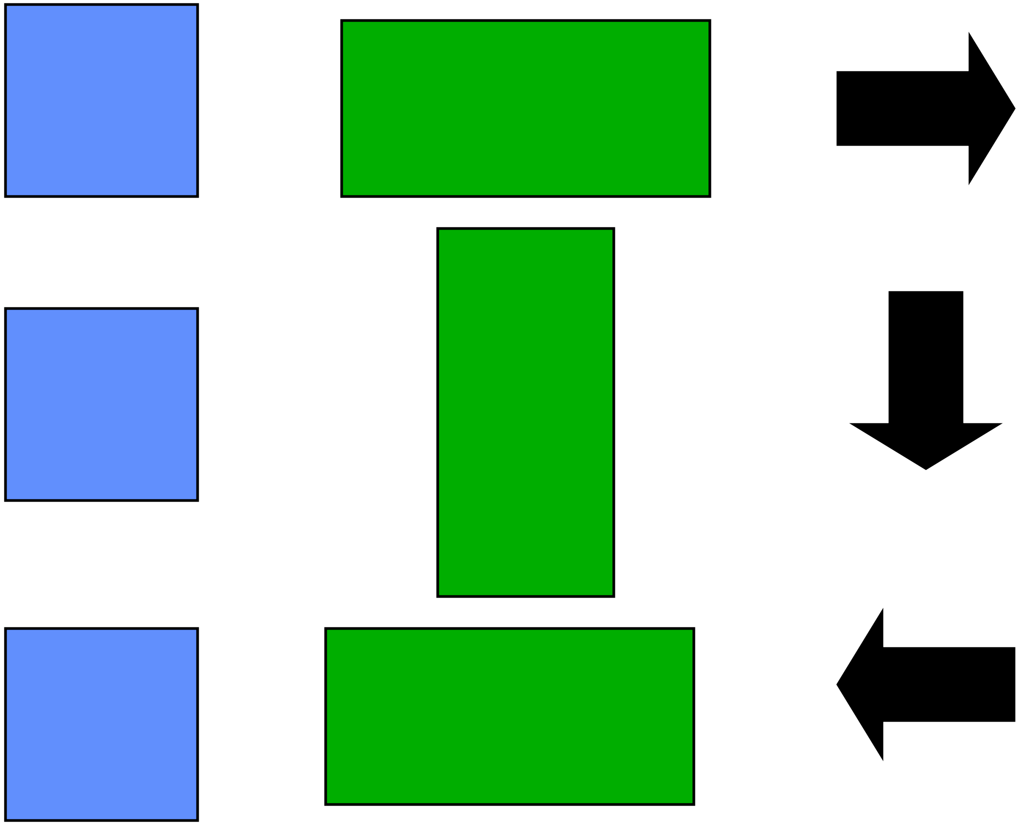
Symmetry

- An object displays symmetry if some transformation leaves it (or something about it) unaltered

Original shape

90º rotation

Horizontal reflection



Time Symmetry

- Path traced by a mechanical system is unchanged upon reversal of momenta or time
  - *e.g., motion in a constant gravitational field*

$$x(t) = x_0 + v_0 t + \tfrac{1}{2} g t^2$$

$$v(t) = v_0 + gt$$

- Another view
  - *Substitution*

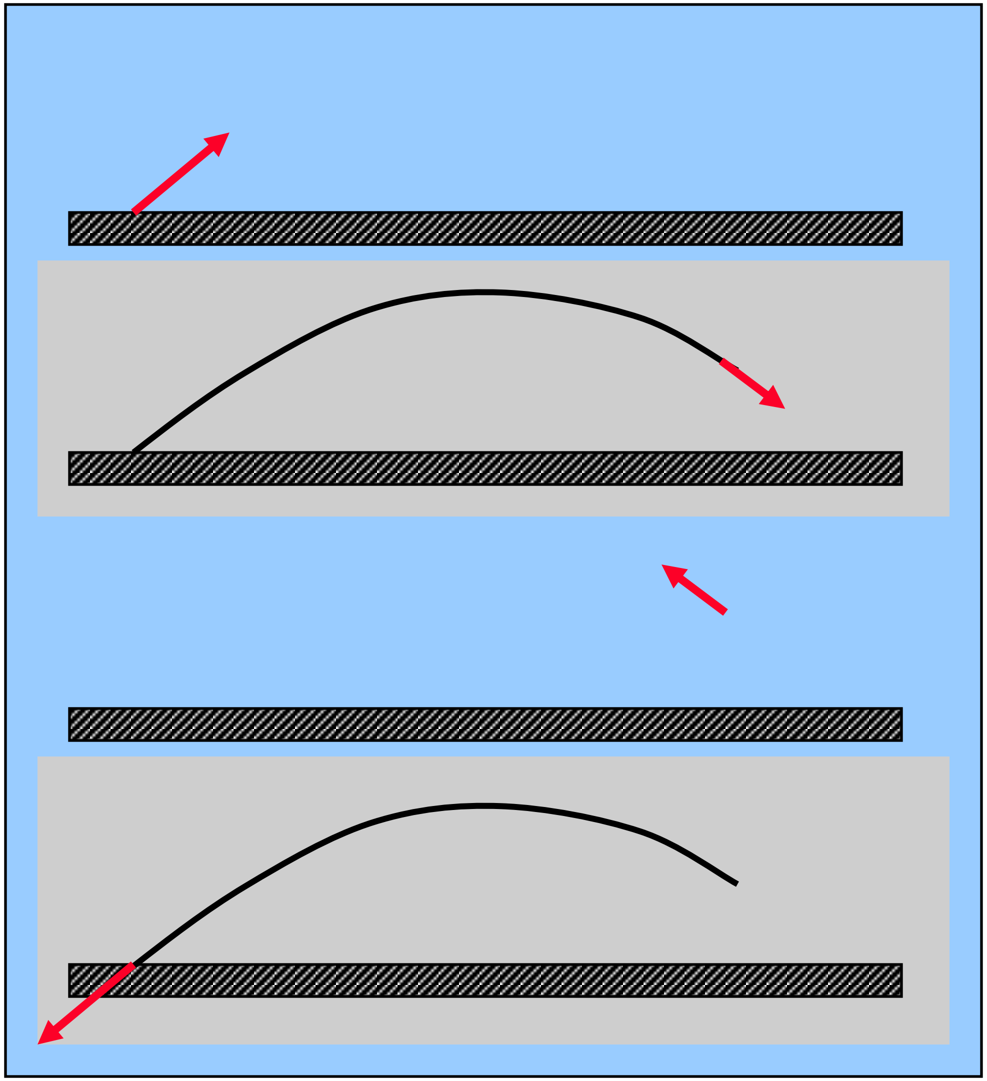
$$p \to -p$$

$$t \to -t$$

leaves equations of motion unchanged

$$\frac{d\mathbf{r}_j}{dt} = \frac{\mathbf{p}_j}{m}$$

$$\frac{d\mathbf{p}_j}{dt} = \mathbf{F}_j$$



An Irreversible Integrator

- Forward Euler
  - *well known to be quite bad*

$$\mathbf{r}(t+\delta t) = \mathbf{r}(t) + \mathbf{p}(t)\delta t + \tfrac{1}{2}\mathbf{F}(t)\delta t^2 \quad \text{unit mass}$$
$$\mathbf{p}(t+\delta t) = \mathbf{p}(t) + \mathbf{F}(t)\delta t$$

- Examine time reversibility
  - *Assume we have progressed forward in time an increment δt; positions and momenta are now* $\mathbf{r}_f(t), \mathbf{p}_f(t)$

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$$\mathbf{p}(t+\delta t)=\mathbf{p}(t)+\mathbf{F}(t)\delta t$$

- Examine time reversibility
  - *Assume we have progressed forward in time an increment δt; positions and momenta are now* $\mathbf{r}_f(t),\mathbf{p}_f(t)$
  - *Reverse time, and step back to original condition*

$$\mathbf{r}_r(t_o+\delta t-\delta t)=\mathbf{r}_f(t_o+\delta t)+\mathbf{p}_f(t_o+\delta t)(-\delta t)+\tfrac{1}{2}\mathbf{F}(t_o+\delta t)(-\delta t)^2$$

$$\mathbf{p}_r(t_o+\delta t-\delta t)=\mathbf{p}_f(t_o+\delta t)+\mathbf{F}(t_o+\delta t)(-\delta t)$$

An Irreversible Integrator

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- *well known to be quite bad*

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$$\mathbf{p}(t+\delta t)=\mathbf{p}(t)+\mathbf{F}(t)\delta t$$

Examine time reversibility

- *Assume we have progressed forward in time an increment δt; positions and momenta are now* $\mathbf{r}_f(t),\mathbf{p}_f(t)$
- *Reverse time, and step back to original condition*

$$\mathbf{r}_r(t_o+\delta t-\delta t)=\mathbf{r}_f(t_o+\delta t)+\mathbf{p}_f(t_o+\delta t)(-\delta t)+\tfrac{1}{2}\mathbf{F}(t_o+\delta t)(-\delta t)^2$$

$$\mathbf{p}_r(t_o+\delta t-\delta t)=\mathbf{p}_f(t_o+\delta t)+\mathbf{F}(t_o+\delta t)(-\delta t)$$

- *Insert from above for* $\mathbf{r}_f(t_o+\delta t),\mathbf{p}_f(t_o+\delta t)$

$$\mathbf{r}_r(t_o)=\left[\mathbf{r}_f(t_o)+\mathbf{p}(t_o)\delta t+\tfrac{1}{2}\mathbf{F}(t_o)\delta t^2\right]+\left[\mathbf{p}(t_o)+\mathbf{F}(t_o)\delta t\right](-\delta t)+\tfrac{1}{2}\mathbf{F}(t_o+\delta t)(-\delta t)^2$$

$$\mathbf{p}_r(t_o)=\left[\mathbf{p}_f(t_o)+\mathbf{F}(t_o)\delta t\right]+\mathbf{F}(t_o+\delta t)(-\delta t)$$

An Irreversible Integrator

Forward Euler

- *well known to be quite bad*

$$\mathbf{r}(t+\delta t)=\mathbf{r}(t)+\mathbf{p}(t)\delta t+\tfrac{1}{2}\mathbf{F}(t)\delta t^2 \qquad \text{unit mass}$$

$$\mathbf{p}(t+\delta t)=\mathbf{p}(t)+\mathbf{F}(t)\delta t$$

Examine time reversibility

- *Assume we have progressed forward in time an increment δt; positions and momenta are now* $\mathbf{r}_f(t),\mathbf{p}_f(t)$
- *Reverse time, and step back to original condition*

$$\mathbf{r}_r(t_o+\delta t-\delta t)=\mathbf{r}_f(t_o+\delta t)+\mathbf{p}_f(t_o+\delta t)(-\delta t)+\tfrac{1}{2}\mathbf{F}(t_o+\delta t)(-\delta t)^2$$

$$\mathbf{p}_r(t_o+\delta t-\delta t)=\mathbf{p}_f(t_o+\delta t)+\mathbf{F}(t_o+\delta t)(-\delta t)$$

- *Insert from above for* $\mathbf{r}_f(t_o+\delta t),\mathbf{p}_f(t_o+\delta t)$; *Cancel*

$$\mathbf{r}_r(t_o)=\left[\mathbf{r}_f(t_o)+\cancel{\mathbf{p}(t_o)}\delta t+\cancel{\tfrac{1}{2}}\mathbf{F}(t_o)\delta t^2\right]+\left[\cancel{\mathbf{p}(t_o)}+\tfrac{1}{2}\mathbf{F}(t_o)\delta t\right](-\delta t)+\tfrac{1}{2}\mathbf{F}(t_o+\delta t)(-\delta t)^2$$

$$\mathbf{p}_r(t_o)=\left[\mathbf{p}_f(t_o)+\mathbf{F}(t_o)\delta t\right]+\mathbf{F}(t_o+\delta t)(-\delta t)$$

An Irreversible Integrator

Forward Euler

- *well known to be quite bad*

$$\mathbf{r}(t+\delta t)=\mathbf{r}(t)+\mathbf{p}(t)\delta t+\tfrac{1}{2}\mathbf{F}(t)\delta t^2$$ unit mass

$$\mathbf{p}(t+\delta t)=\mathbf{p}(t)+\mathbf{F}(t)\delta t$$

Examine time reversibility

- *Assume we have progressed forward in time an increment δt; positions and momenta are now* $\mathbf{r}_f(t),\mathbf{p}_f(t)$
- *Reverse time, and step back to original condition*

$$\mathbf{r}_r(t_o+\delta t-\delta t)=\mathbf{r}_f(t_o+\delta t)+\mathbf{p}_f(t_o+\delta t)(-\delta t)+\tfrac{1}{2}\mathbf{F}(t_o+\delta t)(-\delta t)^2$$

$$\mathbf{p}_r(t_o+\delta t-\delta t)=\mathbf{p}_f(t_o+\delta t)+\mathbf{F}(t_o+\delta t)(-\delta t)$$

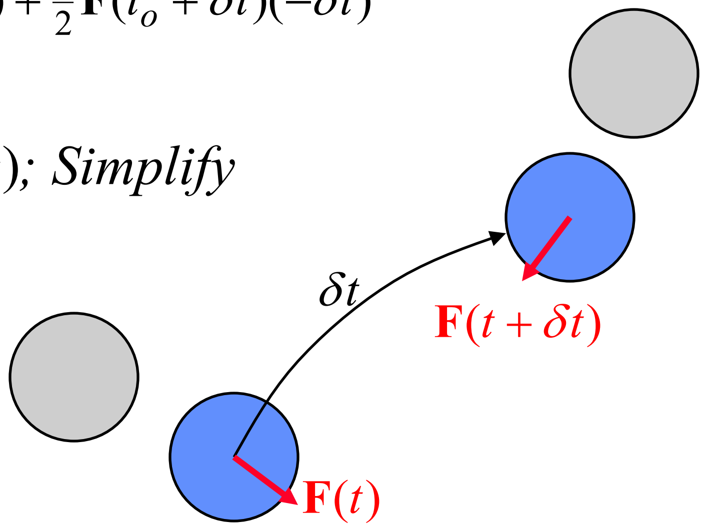
- *Insert from above for* $\mathbf{r}_f(t_o+\delta t),\mathbf{p}_f(t_o+\delta t)$*; Simplify*

$$\boxed{\begin{aligned}\mathbf{r}_r(t_o)&=\mathbf{r}_f(t_o)+\tfrac{1}{2}\left[\mathbf{F}(t_o+\delta t)-\mathbf{F}(t_o)\right]\delta t^2\\ \mathbf{p}_r(t_o)&=\mathbf{p}_f(t_o)-\left[\mathbf{F}(t_o+\delta t)-\mathbf{F}(t_o)\right]\delta t\end{aligned}}$$

- *Equal only in limit of zero time step*

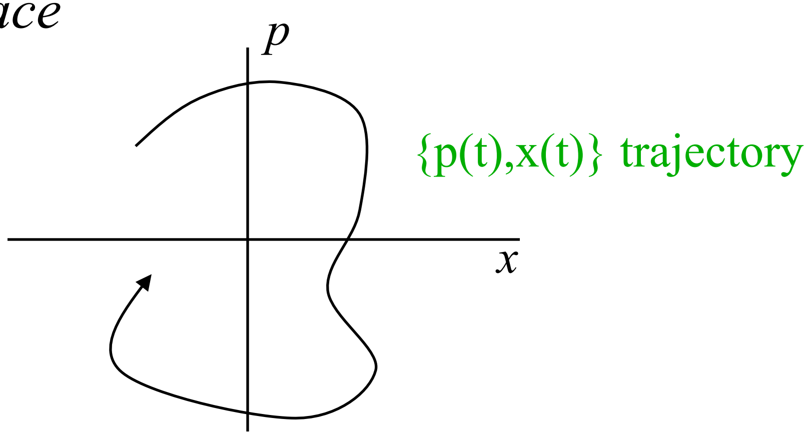
Inequality indicates lack of time reversibility

Verlet integrators *are* time reversible



Symplectic Symmetry 1.

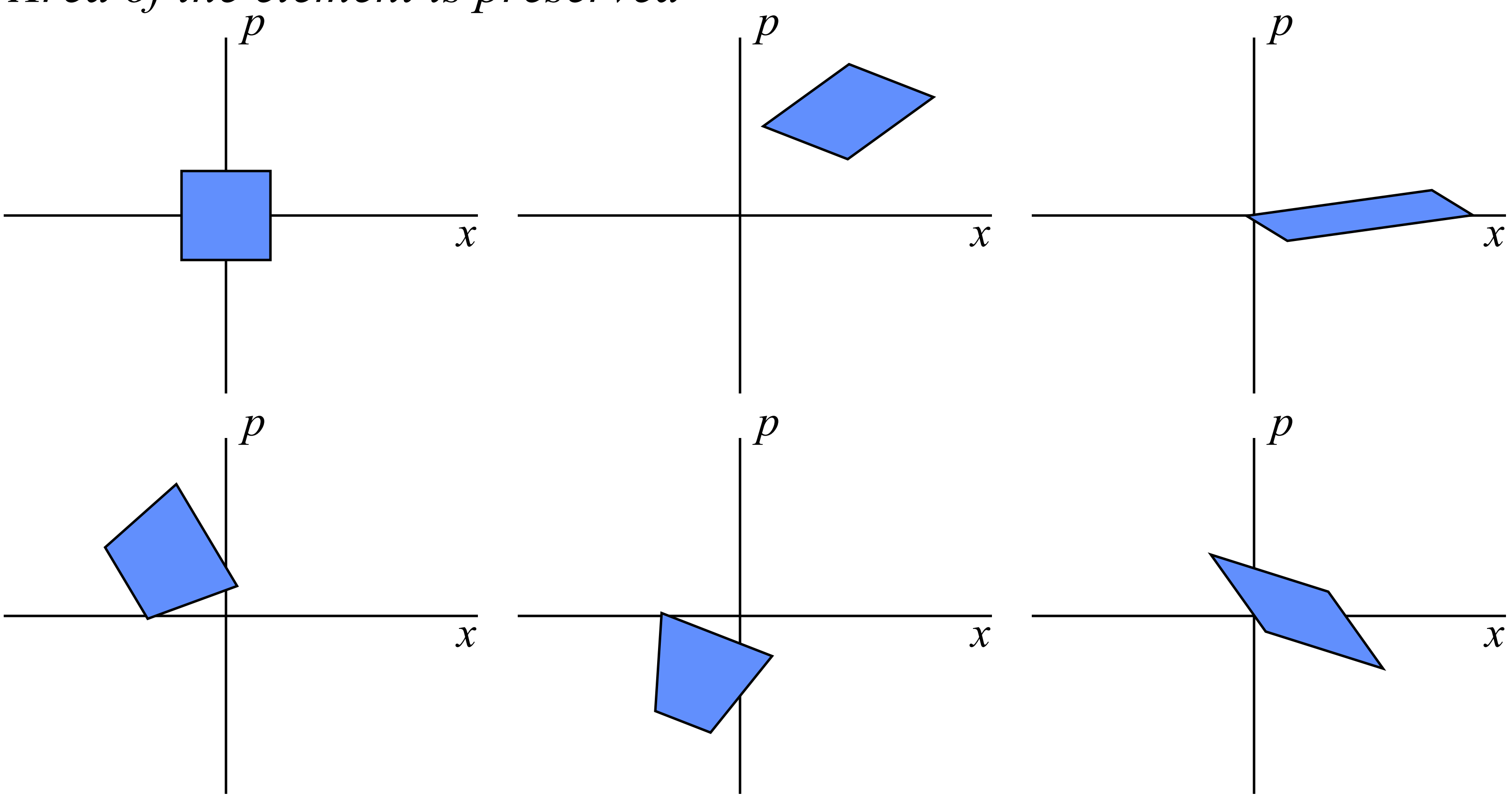
- Consider motion of a single particle in 1D
  - *Described using a 2D phase space* (x,p)
  - *Hamiltonian* $H(p,x) = \frac{1}{2} p^2 + V(x)$ unit mass
  - *Equations of motion* $\boxed{\dfrac{dx}{dt} = +\dfrac{\partial H}{\partial p} = p}$ $\boxed{\dfrac{dp}{dt} = -\dfrac{\partial H}{\partial x} = F(x)}$
  - *Phase space*



  - *Forthcoming result are easily generalized to higher dimensional phase space, but hard to visualize*

Symplectic Symmetry 2.

- Consider motion of a differential element through phase space
  - *Shape of element is distorted by motion*
  - *Area of the element is preserved*



- This is a manifestation of the symplectic symmetry of the equations of motion

Classical Harmonic Oscillator

- Exactly solvable example $H(p,x)=\frac{1}{2}p^2+\frac{1}{2}x^2$

$$\frac{dx}{dt}=+p \qquad x(0)=x_0$$

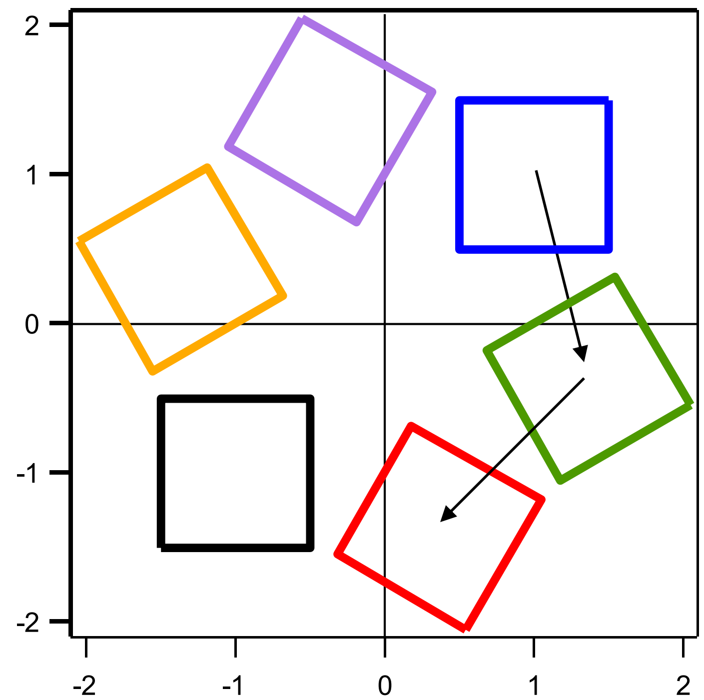
$$\frac{dp}{dt}=-x \qquad p(0)=p_0$$

- Solution

$$x=+x_0\cos t+p_0\sin t$$

$$p=-x_0\sin t+p_0\cos t$$

$$H(t)=\frac{1}{2}p_0^2+\frac{1}{2}x_0^2=\text{constant}$$



Liouville Formulation 1.

- Operator-based view of mechanics
- Very useful for deriving symplectic, time-reversible integration schemes
- Consider an arbitrary function of phase-space coordinates
  - *and thereby a function of time*

    $$f\left(x(t), p(t)\right)$$

  - *time derivative is* $\dot{f} = \dot{x}\frac{\partial f}{\partial x} + \dot{p}\frac{\partial f}{\partial p}$
- Define the Liouville operator

  $$iL \equiv \dot{x}\frac{\partial}{\partial x} + \dot{p}\frac{\partial}{\partial p}$$

- So

  $$\dot{f} = iLf$$

Liouville Formulation 2.

- Operator form

$$\frac{\partial f}{\partial t} = iLf$$

- This has the solution

$$f(t) = e^{iLt} f(0)$$

  - *in principle this gives f at any time t*
  - *in practice it is not directly useful*

- Let f be the phase-space vector $f \equiv \mathbf{\Gamma}(t) = \left(x(t), p(t)\right)^T$
  - *then the solution gives the trajectory through phase space*

- Harmonic oscillator

$$\begin{pmatrix} x \\ p \end{pmatrix} = \begin{pmatrix} \cos t & \sin t \\ -\sin t & \cos t \end{pmatrix} \begin{pmatrix} x_o \\ p_o \end{pmatrix}$$

$$\Rightarrow \quad e^{iLt} = \begin{pmatrix} \cos t & \sin t \\ -\sin t & \cos t \end{pmatrix}$$

Separation of Liouville Operator 1.

- Position and momentum parts

$$iL \equiv \dot{x}\frac{\partial}{\partial x} + \dot{p}\frac{\partial}{\partial p}$$
$$\equiv iL_x + iL_p$$

- Propagator of either part can be solved analytically by itself

$$iL_x = \dot{x}\frac{\partial}{\partial x}\begin{pmatrix} x \\ p \end{pmatrix} = \begin{pmatrix} \dot{x} \\ 0 \end{pmatrix} \quad \begin{pmatrix} x(t) \\ p(t) \end{pmatrix} = \begin{pmatrix} x_0 + p_0 t \\ p_0 \end{pmatrix} \qquad e^{iL_x t} = \begin{pmatrix} 1 & t \\ 0 & 1 \end{pmatrix}$$

$$iL_p = \dot{p}\frac{\partial}{\partial p}\begin{pmatrix} x \\ p \end{pmatrix} = \begin{pmatrix} 0 \\ \dot{p} \end{pmatrix} \quad \begin{pmatrix} x(t) \\ p(t) \end{pmatrix} = \begin{pmatrix} x_0 \\ p_0 + \dot{p}_0 t \end{pmatrix}$$

Separation of Liouville Operator 2.

- Liouville components do not commute
  - *result differs depending on order in which they are applied*

$$\left(iL_x\right)\left(iL_p\right) \neq \left(iL_p\right)\left(iL_x\right)$$

- Otherwise we could write

$$e^{iLt} = e^{iL_x t + iL_p t} = e^{iL_x t} e^{iL_p t}$$

This is incorrect

- We could then apply each propagator in sequence to move the system ahead in time

$$e^{iLt}\mathbf{\Gamma} = \underbrace{e^{iL_x t}\underbrace{\left(e^{iL_p t}\mathbf{\Gamma}\right)}_{\text{Advance momentum}}}_{\text{Advance position}}$$

Trotter Expansion

- The following relation does hold

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

  - *for example, if P = 2*

$$e^{A+B} = \left(e^{A/4}e^{B/2}e^{A/4}\right)\left(e^{A/4}e^{B/2}e^{A/4}\right) \quad \text{…plus a correction}$$

$$= \left(e^{A/4}e^{B/2}e^{A/4}e^{A/4}e^{B/2}e^{A/4}\right)$$

$$= \left(e^{A/4}e^{B/2}e^{A/2}e^{B/2}e^{A/4}\right)$$

- We cannot work with infinite P
  - *but for large P*

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

Formulating an Integrator

- Using the large-P approximation

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

- To advance the system over the time interval T
  - *break Liouville operator into displacement parts* $iL_x + iL_p$
  - *write* $e^{iLT} = e^{iL_x T + iL_p T}$
  - *apply the Trotter expansion, and interpret T/P as a discretized time* δt

$$e^{iLT} = \left(e^{iL_p \delta t/2} e^{iL_x \delta t} e^{iL_p \delta t/2}\right)^P$$

  - *application of* $e^{iL_p \delta t/2} e^{iL_x \delta t} e^{iL_p \delta t/2}$ *P times advances the system (approximately) through T*
- An integrator formulated this way will be both time-reversible and symplectic

Examination of Integrator 1.

- Consider effect of one time step on positions and momenta

$$e^{iL_p\delta t/2}e^{iL_x\delta t}e^{iL_p\delta t/2}\begin{pmatrix} x \\ p \end{pmatrix}$$

- First apply $\exp(iL_p\delta t/2)$

$$e^{iL_p\delta t/2}\begin{pmatrix} x(0) \\ p(0) \end{pmatrix} = \begin{pmatrix} x(0) \\ p(0)+\dot{p}(0)\frac{\delta t}{2} \end{pmatrix}$$

- Then apply $\exp(iL_x\delta t)$

$$e^{iL_x\delta t}\begin{pmatrix} x(0) \\ p(0)+\dot{p}(0)\frac{\delta t}{2} \end{pmatrix} = \begin{pmatrix} x(0)+\dot{p}\left(\frac{\delta t}{2}\right)\delta t \\ p(0)+\dot{p}(0)\frac{\delta t}{2} \end{pmatrix}$$

- Finally apply $\exp(iL_p\delta t/2)$ again

$$e^{iL_p\delta t/2}\begin{pmatrix} x(0)+\dot{p}\left(\frac{\delta t}{2}\right)\delta t \\ p(0)+\dot{p}(0)\frac{\delta t}{2} \end{pmatrix} = \begin{pmatrix} x(0)+\dot{p}\left(\frac{\delta t}{2}\right)\delta t \\ p(0)+\dot{p}(0)\frac{\delta t}{2}+\dot{p}\left(\frac{\delta t}{2}\right)\frac{\delta t}{2} \end{pmatrix}$$

Examination of Integrator 2.

- One time step

$$e^{iL_p\delta t/2}e^{iL_x\delta t}e^{iL_p\delta t/2}\begin{pmatrix} x \\ p \end{pmatrix} = \begin{pmatrix} x(0)+\dot{p}\left(\frac{\delta t}{2}\right)\delta t \\ p(0)+\dot{p}(0)\frac{\delta t}{2}+\dot{p}\left(\frac{\delta t}{2}\right)\frac{\delta t}{2} \end{pmatrix}$$

- Examine effect on coordinate and momentum

$$p(0)\rightarrow p(0)+\frac{\delta t}{2}\left(F(0)+F\left(\frac{\delta t}{2}\right)\right)$$

$$x(0)\rightarrow x(0)+\frac{\delta t}{2}\dot{x}\left(\frac{\delta t}{2}\right)$$

$$=x(0)+\dot{x}(0)\delta t+\frac{1}{2}F(0)\left(\delta t\right)^2$$

- It's the Velocity Verlet integrator!
- Higher-order algorithms can be derived systematically by including higher orders in the Trotter factorization
  - *Not appealing because introduces derivatives of forces*

A Deep Truth

- Verlet integrator replaces the true Liouville propagator by an approximate one

$$e^{iL\delta t} \approx e^{iL_p\delta t/2} e^{iL_x\delta t} e^{iL_p\delta t/2}$$

- We can make these equal by saying the approximate propagator is obtained as the propagator of an approximate Liouville operator

$$e^{iL\delta t+\varepsilon} = e^{iL_{\text{pseudo}}t} = e^{iL_p\delta t/2} e^{iL_x\delta t} e^{iL_p\delta t/2}$$

- or

$$iL_{\text{pseudo}} = iL + \varepsilon / \delta t$$

- This corresponds to some unknown Hamiltonian
  - *and this Hamiltonian is conserved by the Verlet propagator*
  - *the Verlet algorithm will not likely give rise to drift in the true Hamiltonian, since this "shadow" Hamiltonian is conserved*

Other Decompositions

- Other choices for the decomposition of the Liouville operator can be worthwhile
- Some choices:
  - *Separation of short- and long-ranged forces*
  - *Separation of fast and slow time-scale motions*
- Approach involves defining a reference system that is solved more precisely (more frequently)
- Difference between real and reference is updated over a longer time scale
- RESPA
  - *(Reversible) REference System Propagator Algorithm*
  - *Uses numerical solution of reference*
- NAPA
  - *Numerical Analytical Propagator Algorithm*
  - *Uses a reference that can be solved analytically*

RESPA: Force Decomposition 1.

- Decompose force into short (F_s) and long (F_l) range contributions

$$F(x) = S(x)F(x) + \left[1 - S(x)\right]F(x)$$
$$\equiv F_s(x) + F_l(x)$$

  - *S(x) is a switching function that turns off the force at some distance*

- Liouville operator

$$iL = \dot{x}\frac{\partial}{\partial x} + F_s(x)\frac{\partial}{\partial p} + F_l(x)\frac{\partial}{\partial p}$$
$$= iL_s + F_l(x)\frac{\partial}{\partial p}$$

RESPA: Force Decomposition 2.

- Liouville operator

$$iL = iL_s + F_l(x)\frac{\partial}{\partial p}$$

- Trotter factorization of propagator

$$e^{iL\Delta t} \approx e^{\frac{\Delta t}{2}F_l(x)\frac{\partial}{\partial p}} \boxed{e^{iL_s\Delta t}} e^{\frac{\Delta t}{2}F_l(x)\frac{\partial}{\partial p}}$$

- Decompose term treating short-range forces

$$e^{iL_s\Delta t} \approx \left[e^{iL_{s,p}\frac{\delta t}{2}} \; e^{iL_{s,x}\delta t} \; e^{iL_{s,p}\frac{\delta t}{2}} \right]^n \qquad \delta t \equiv \frac{\Delta t}{n}$$

- Long-range forces are computed *n* times less frequently than short-range ones
  - *Long-range forces vary more slowly*
  - *They are more expensive to calculate, because more pairs*

RESPA: Force Decomposition 3.

Full RESPA propagator

$$e^{iL\Delta t} \approx e^{\frac{\Delta t}{2}F_l(x)\frac{\partial}{\partial p}} \left[e^{\frac{\delta t}{2}F_s(x)\frac{\partial}{\partial p}} \; e^{\delta t \dot{x}\frac{\partial}{\partial x}} \; e^{\frac{\delta t}{2}F_s(x)\frac{\partial}{\partial p}} \right]^n e^{\frac{\Delta t}{2}F_l(x)\frac{\partial}{\partial p}} \qquad \delta t \equiv \frac{\Delta t}{n}$$

Procedure

- *Repeat for n steps*

  update short-range force, evaluate new momenta

  evaluate new positions
- *Evaluate long-range forces, update momenta*
- *Repeat*

RESPA: Time-Scale Decomposition

- Many systems display disparate time scales of motion
  - *Massive particles interacting with light ones*
    - helium in argon
  - *Stiff and loose potentials*
    - intramolecular and intermolecular forces
- Approach works as before
  - *Integrate fast motions (degrees of freedom) using short time step*
  - *Integrate slow motions using long time step*