(Classical) Molecular Dynamics for Dummies

Computational Techniques for Molecular Modeling 2020-2021

CdF - 02/2021

Bibliography

will be extend as course continues

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- Allen, Tildesley, *Computer Simulation of Liquids,* (Clarendon Press, 1989)
- Leimkuhlerm, Reich, *Simulating Hamiltonian Dynamics* (Cambridge University Press, 2004)
- Israelachvili, *Intermolecular and Surface Forces*, (Academic Press, 2011)
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Interactions Among Molecules

Molecular dynamics: numerical, step-by-step, solution of the classical equations of motion

$$m_i \ddot{r}_i = f_i \text{ or, equivalently} \begin{cases} \dot{r}_i = \dfrac{p_i}{m_i} \\ \dot{p}_i = f_i \end{cases}$$

the **forces** f_i are assumed to be gradients of a potential energy U, $f_i = -\nabla_i U$

r_i are the **coordinates** of the $i-$th atom

Non-bonded Interactions Molecules

The non-bonded potential U_{nb} can be split as

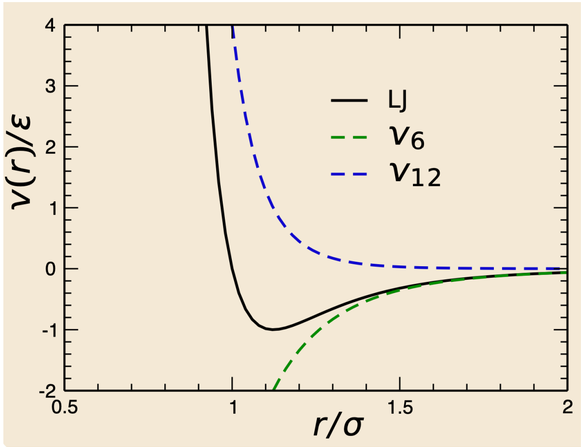
$$U_{nb}(r) = \sum_i u(r_i) + \sum_{i,j>i} v(r_i, r_j) + \dots$$

- The **external potential** u is often neglected for bulk systems
- Pair-wise interactions v
- **Higher order interactions** usually neglected

There is an extensive literature on how these potentials are computed (e.g. Israelachvili 20013)

Lennard-Jones Potential

- Sometimes even simplest models provide interesting insight into physics
- The **Lennard-Jones** potential is very often used



$$v^{LJ}(r_i, r_j) = 4\varepsilon \left(\left(\frac{\sigma}{|r_i - r_j|} \right)^{12} - \left(\frac{\sigma}{|r_i - r_j|} \right)^{6} \right)$$

- σ diameter, ε potential barrier height
- models empirically dipole-dipole and dipole-induced dipole interactions

Electrostatics

- Electrically charged ions interact via Coulomb potential (long range)

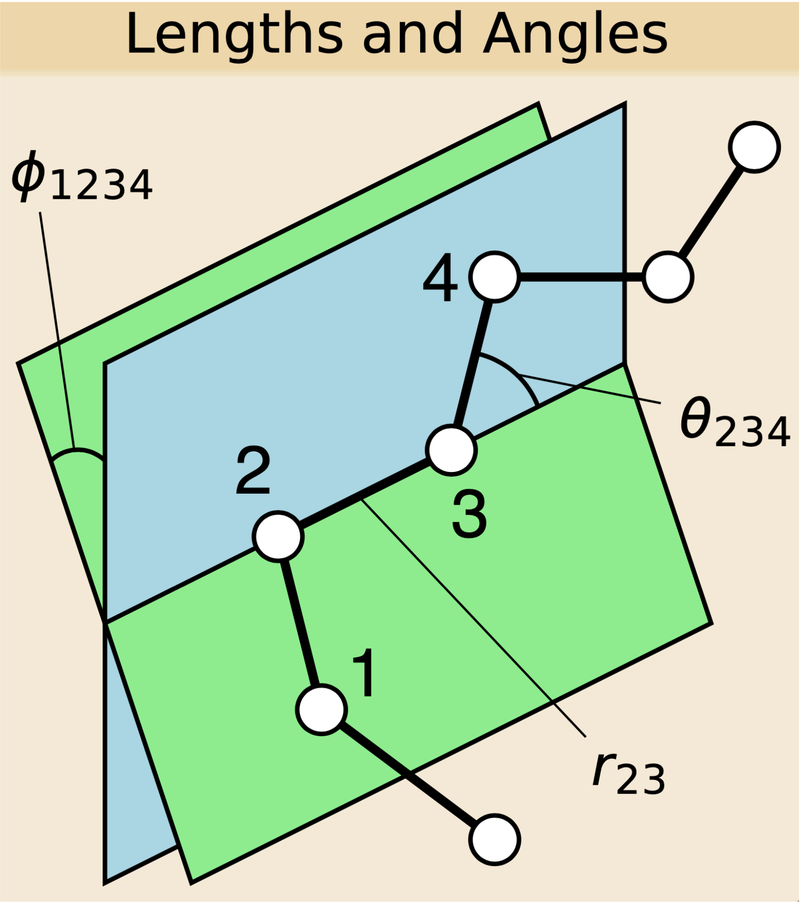
$$v^{qq}(r_i, r_j) = \frac{q_i q_j}{4\pi\ \varepsilon_0\ |r_i - r_j|}$$

- $q_i,\ q_j$ charges, ε_0 permittivity of free space
- correctly handling long range interactions in MD algorithms is a complex task
- dipole and multipole interactions

Atoms and Molecules

- For molecular systems, we simply build the molecules out of Lennard-Jones site-site potentials, or similar
- Typically, a single-molecule quantum-chemical calculation may be used to estimate the electron density throughout the molecule
- This may then be modelled by a distribution of partial charges
- or more accurately by a distribution of electrostatic multipoles

Bonding Interactions



- For molecules we must also consider the intramolecular bonding interactions. Consider this geometry of an alkyl chain (just showing the carbons).
- interatomic distance r_{23}
- bend angle θ_{234}
- torsion angle Φ_{1234}

Example

$$U_{int} = \frac{1}{2}\sum k_{ij}^{r}(\,|\,r_i - r_j\,| - r_0)^2 +$$

$$+\frac{1}{2}\sum k_{ijk}^{\theta}(\theta_{ijk} - \theta_0)^2 +$$

$$+\frac{1}{2}\sum\sum_{m} k_{ijkl}^{\Phi,m}\left[1 + \cos(m\Phi_{ijkl} - \gamma_m)\right]$$

Bond Stretching

$$\frac{1}{2}\sum k_{ij}^{r}(\,|\,r_i - r_j\,|\, - r_0)^2$$

- Distance between atoms
- Harmonic oscillator with specified equilibrium separation
- Trivial to compute forces
- High vibration frequencies
  - C-H bond implies about 10fs period
  - Explicit simulation would require time steps in the order of fs

Bond Bending

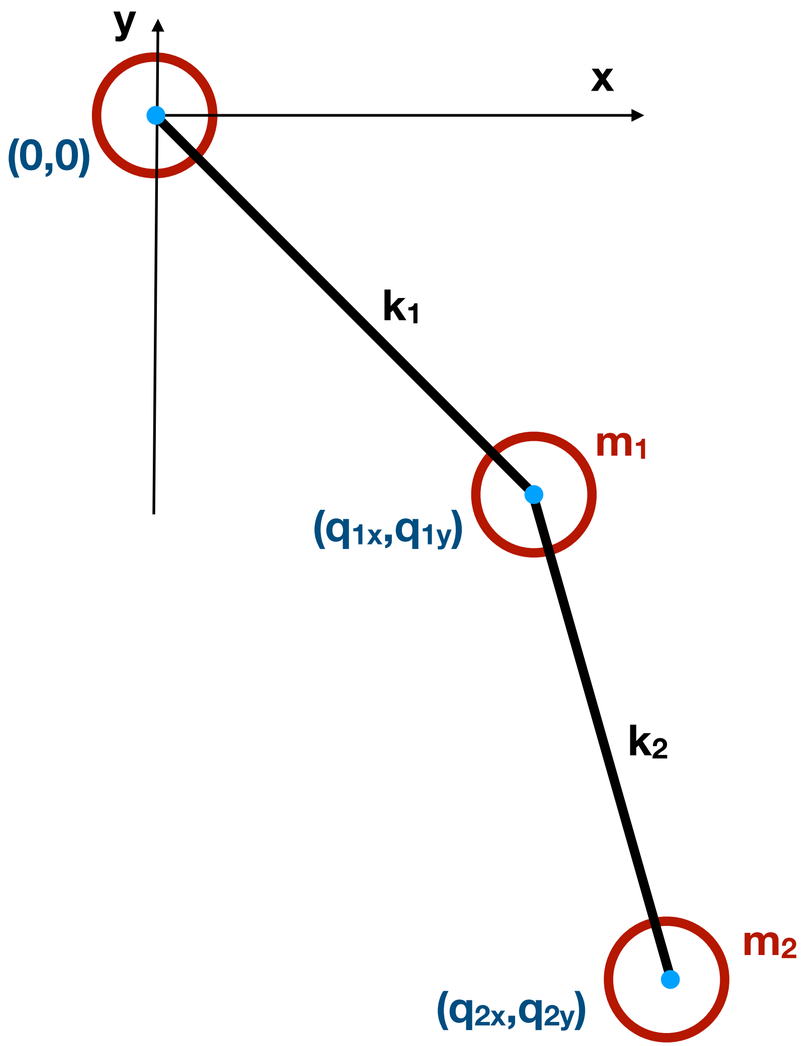
$$\frac{1}{2}\sum k^{\theta}_{ijk}(\theta_{ijk}-\theta_0)^2+\frac{1}{2}\sum_{m}\sum k^{\Phi,m}_{ijkl}\left[1+\cos(m\Phi_{ijkl}-\gamma_m)\right]$$

- Angles involve at least 2 bonds (3 atoms)
- Forces affect all involved atoms
- Computation involved but straightforward
- Timescales
  - in H_2O about 20 fs
  - Explicit simulation would require time steps in the order of fs

MD Algorithm

- Calculating forces is expensive, typically a pairwise sum over atoms, so we need to perform this as infrequently as possible.
  - Wish to make the timestep as large as possible
    - Hence, simulation algorithms tend to be low order (i.e. do not use high derivatives of r)
    - This allows the time step to be increased as much as possible without jeopardizing energy conservation.
- Cannot accurately follow true trajectory for very long simulation times.
  - trajectories diverge from each other exponentially
  - however long-term energy conservation is possible

Double Elastic Pendulum



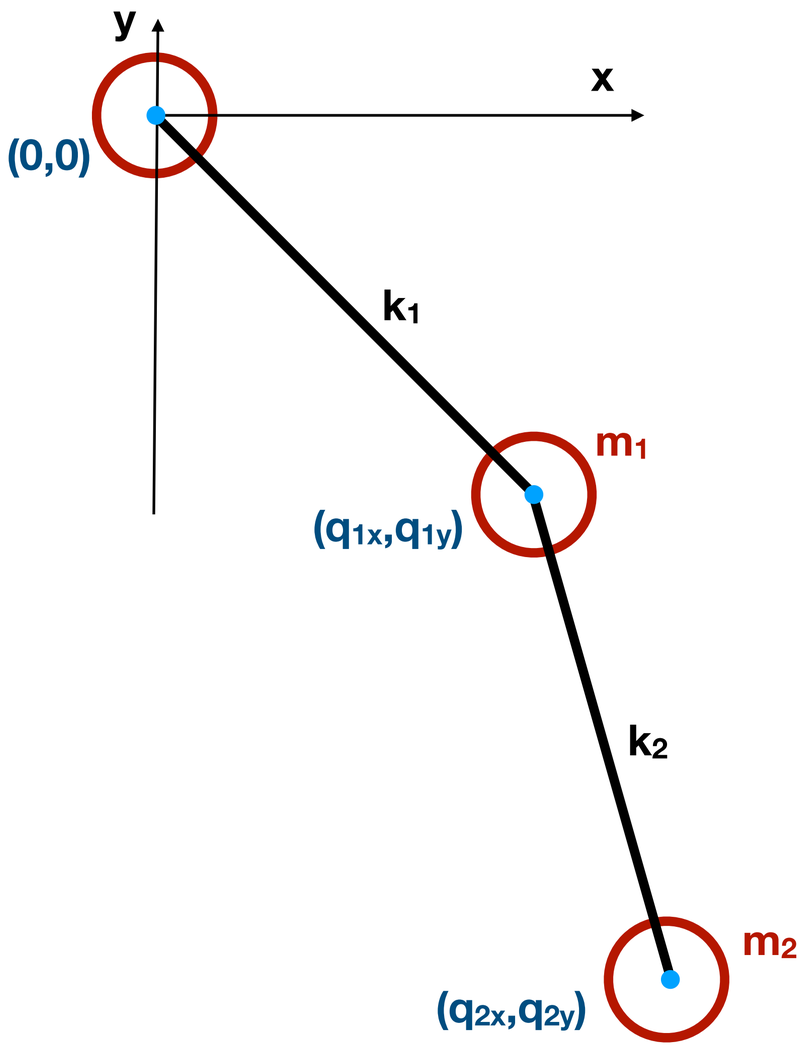
$$\mathbf{p}_i := m_i \dot{\mathbf{q}}_i$$

$$E = K(\mathbf{p}_1, \mathbf{p}_2) + T(\mathbf{q}_1, \mathbf{q}_2)$$

$$K(\mathbf{p}_1, \mathbf{p}_2) = \frac{\left|\mathbf{p}_1\right|^2}{2m_1} + \frac{\left|\mathbf{p}_2\right|^2}{2m_2}$$

$$T(\mathbf{q}_1, \mathbf{q}_2) = -m_1\mathbf{g}\cdot\mathbf{q}_1 - m_2\mathbf{g}\cdot\mathbf{q}_2 + \frac{k_1}{2}\left(\left|\mathbf{q}_1\right| - l_1\right)^2 + \frac{k_2}{2}\left(\left|\mathbf{q}_1 - \mathbf{q}_2\right| - l_2\right)^2$$

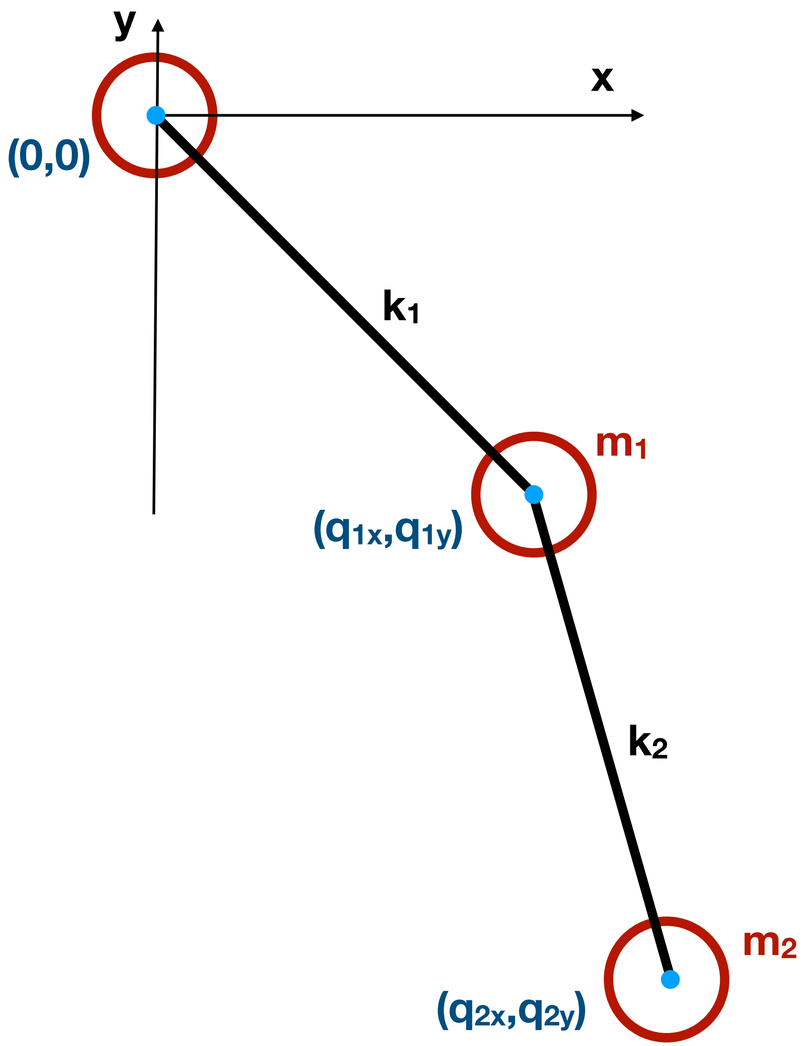
Double Elastic Pendulum



$$\dot{\mathbf{q}}_i = \frac{\partial\, K}{\partial\, \mathbf{p}_i}$$

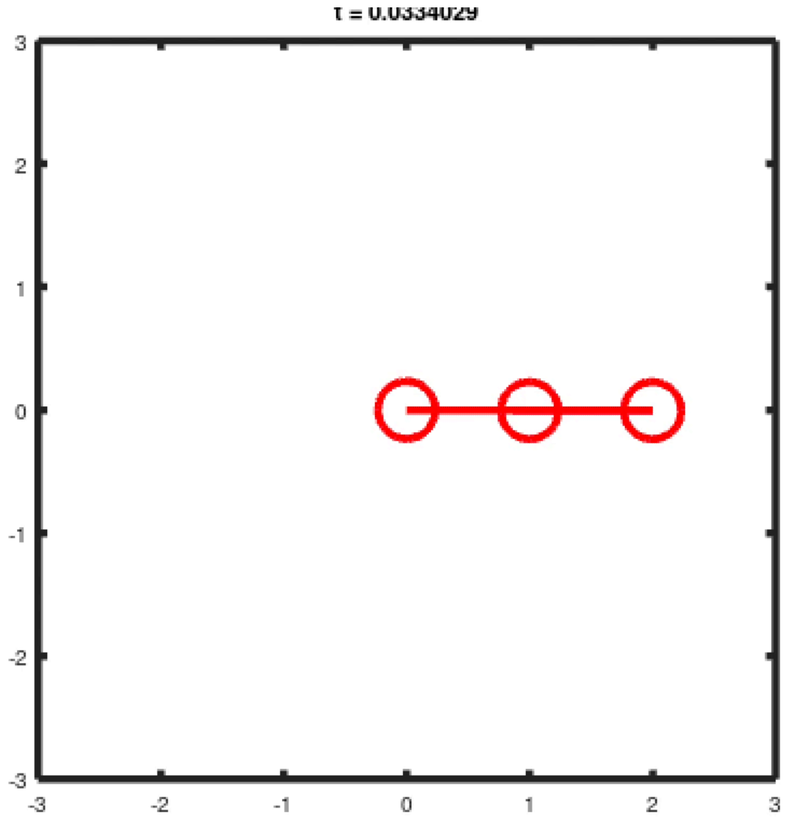
$$\dot{\mathbf{p}}_i = -\frac{\partial\, T}{\partial\, \mathbf{q}_i}$$

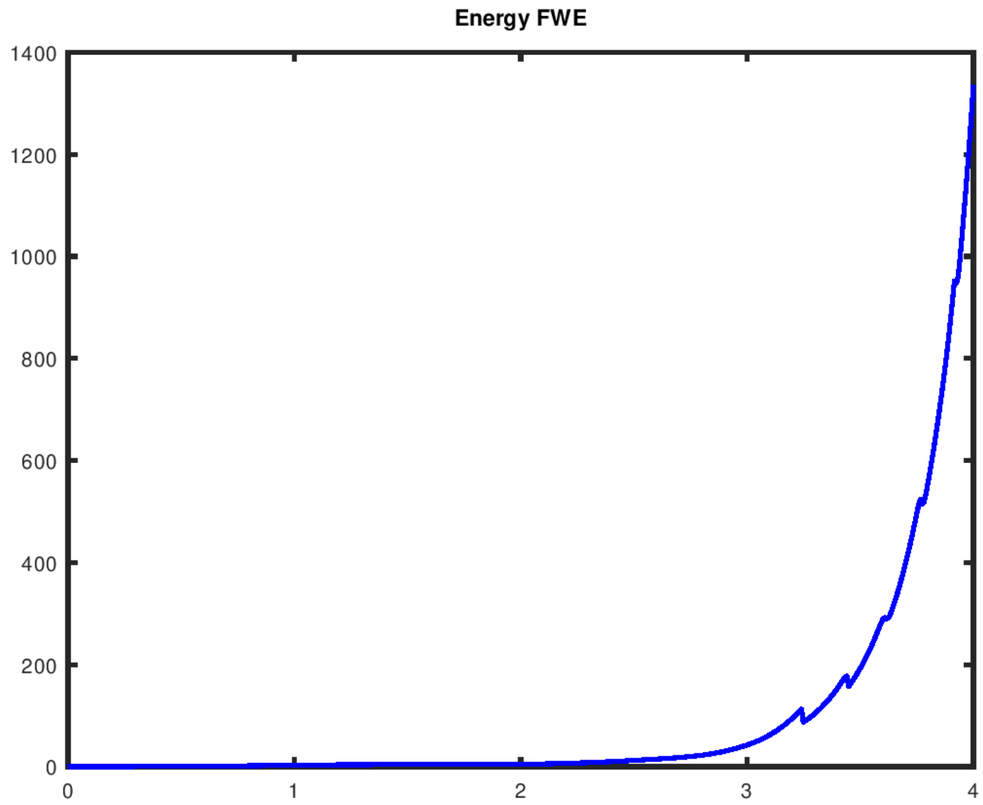
Double Elastic Pendulum



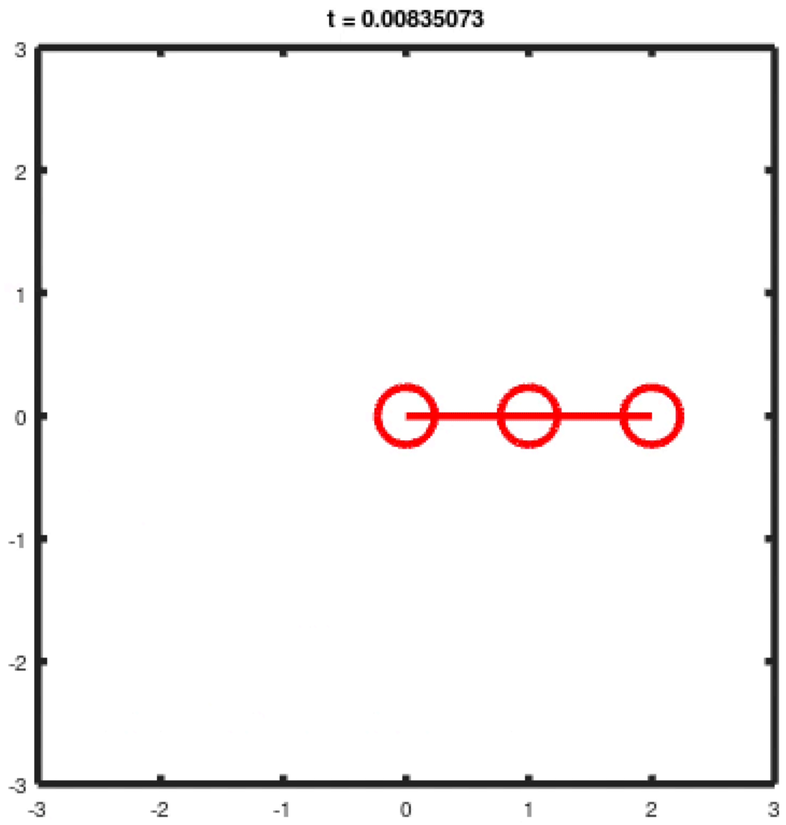

```
m1    = 1;
m2    = .2;
k1    = 100;
k2    = 100;
l1    = 1;
l2    = 1;
gx    = 0;
gy    = -9.81;
```

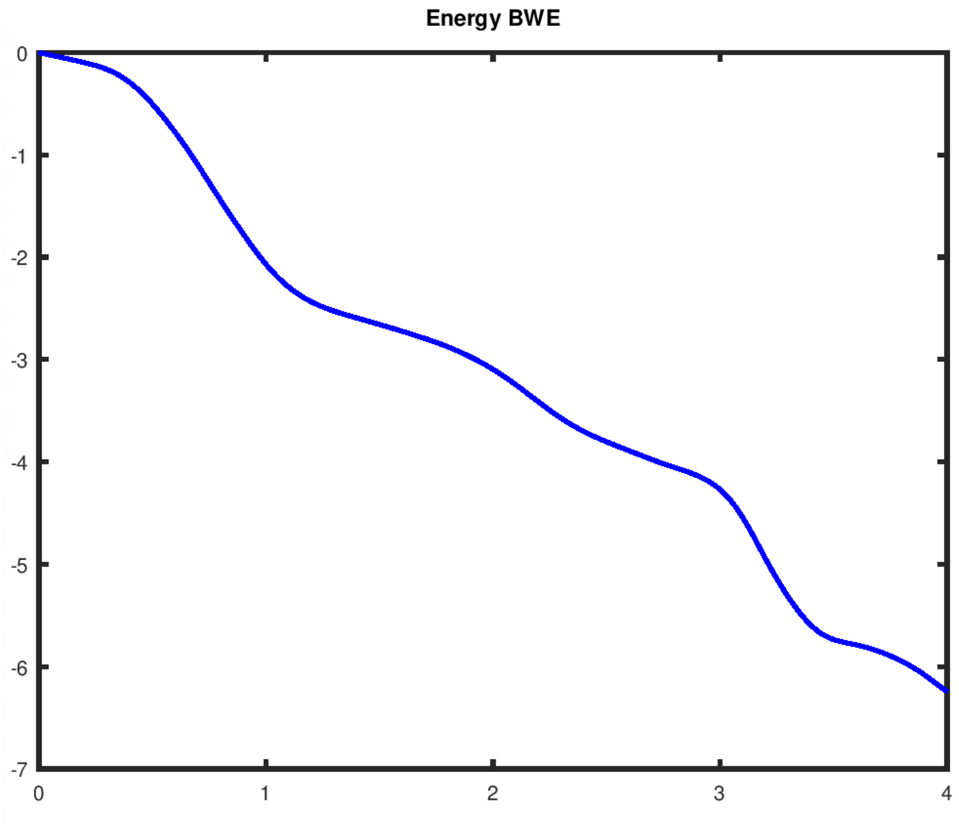
Forward Euler



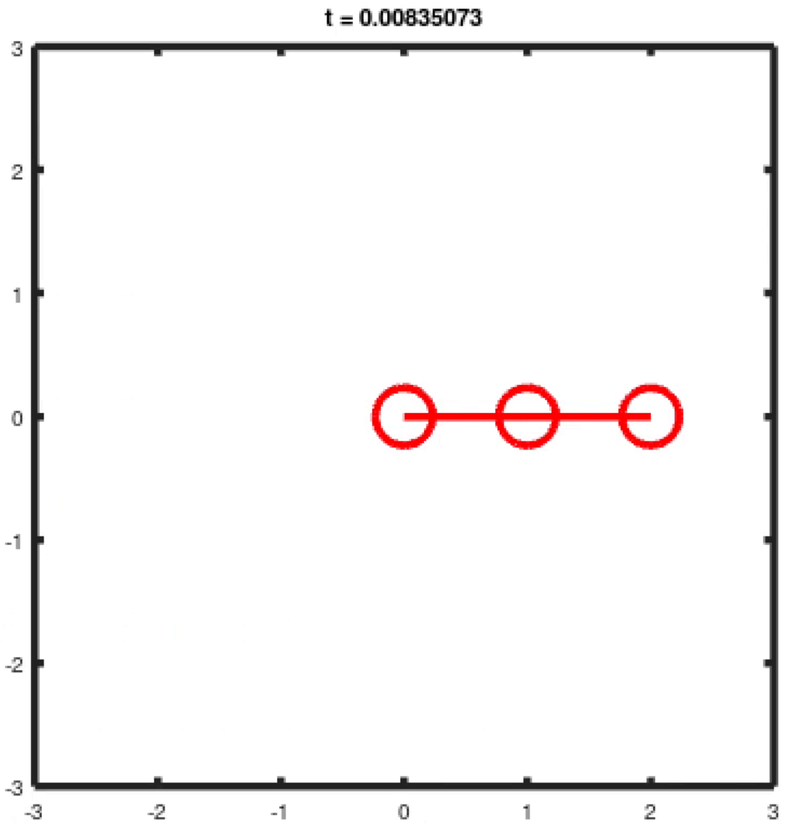


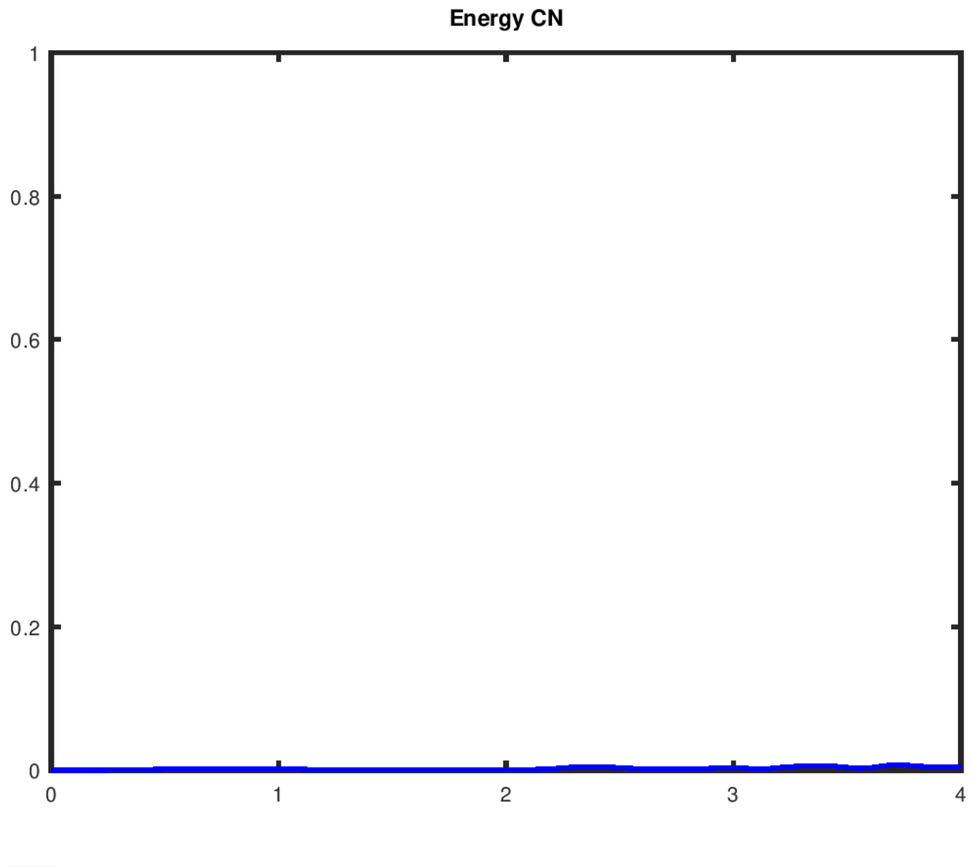
Backward Euler



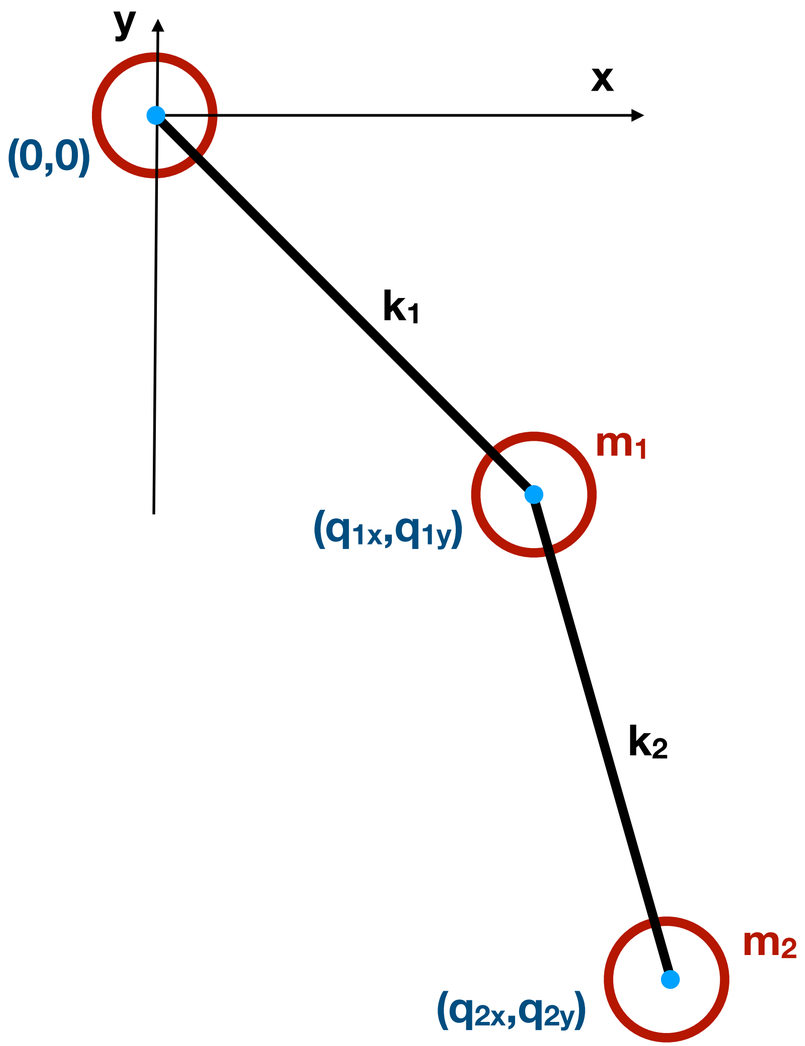


Trapezoidal Rule





Double Elastic Pendulum with Friction



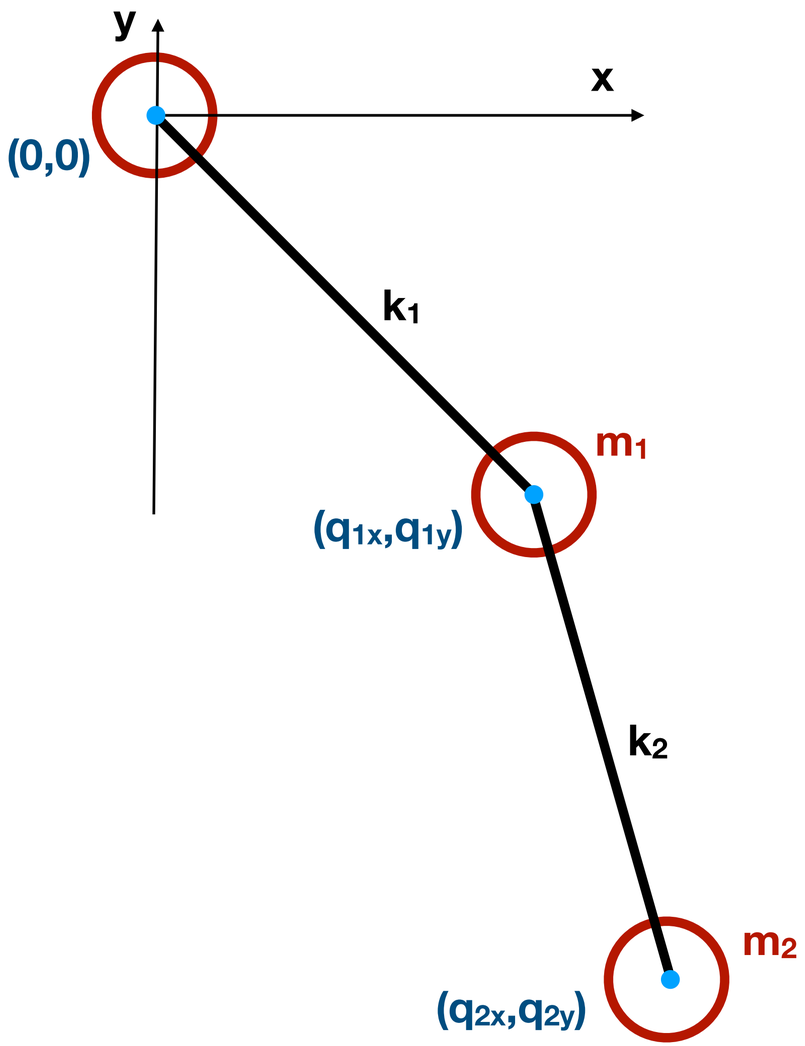
$$\mathbf{p}_i := m_i \dot{\mathbf{q}}_i$$

$$E = K(\mathbf{p}_1, \mathbf{p}_2) + T(\mathbf{q}_1, \mathbf{q}_2) + \theta S$$

$$K(\mathbf{p}_1, \mathbf{p}_2) = \frac{\left|\mathbf{p}_1\right|^2}{2m_1} + \frac{\left|\mathbf{p}_2\right|^2}{2m_2}$$

$$T(\mathbf{q}_1, \mathbf{q}_2) = -m_1\mathbf{g}\cdot\mathbf{q}_1 - m_2\mathbf{g}\cdot\mathbf{q}_2 + \frac{k_1}{2}\left(\left|\mathbf{q}_1\right| - l_1\right)^2 + \frac{k_2}{2}\left(\left|\mathbf{q}_1 - \mathbf{q}_2\right| - l_2\right)^2$$

Double Elastic Pendulum

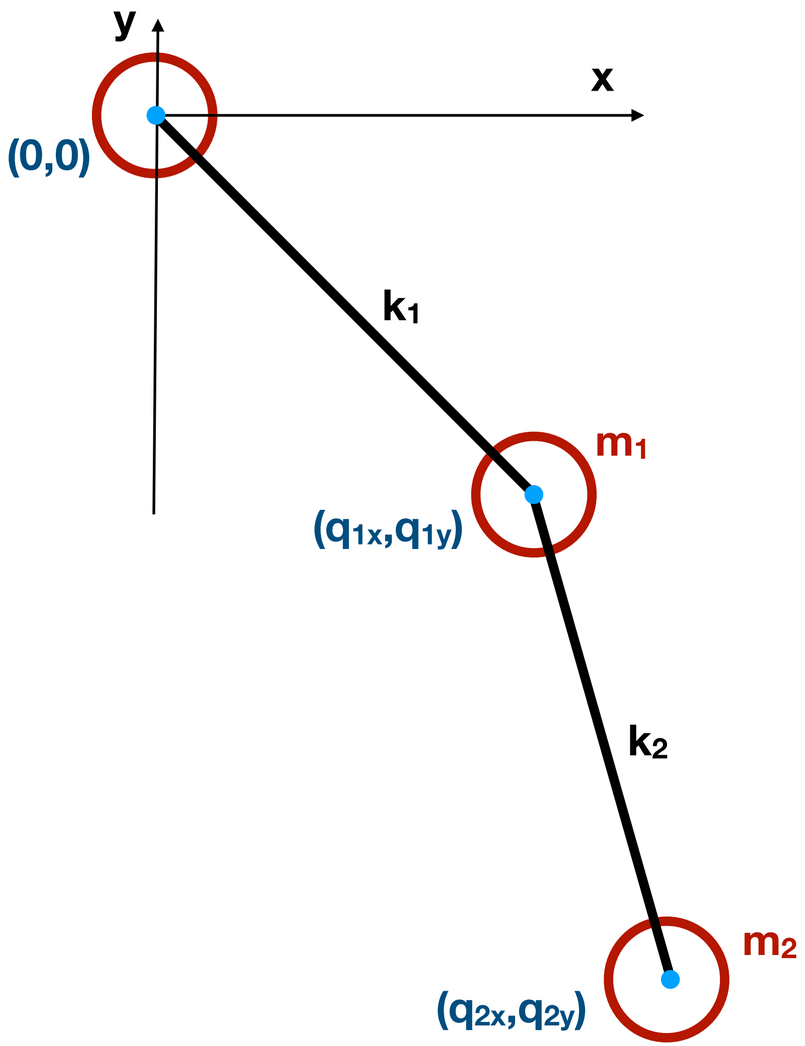


$$\dot{\mathbf{q}}_i = \frac{\partial K}{\partial \mathbf{p}_i}$$

$$\dot{\mathbf{p}}_i = -\frac{\partial T}{\partial \mathbf{q}_i} - \frac{\lambda}{m_i}\mathbf{p}_i$$

$$\dot{s} = \frac{\lambda}{\theta\, m_i^2} \left|\mathbf{p}_i\right|^2$$

Double Elastic Pendulum

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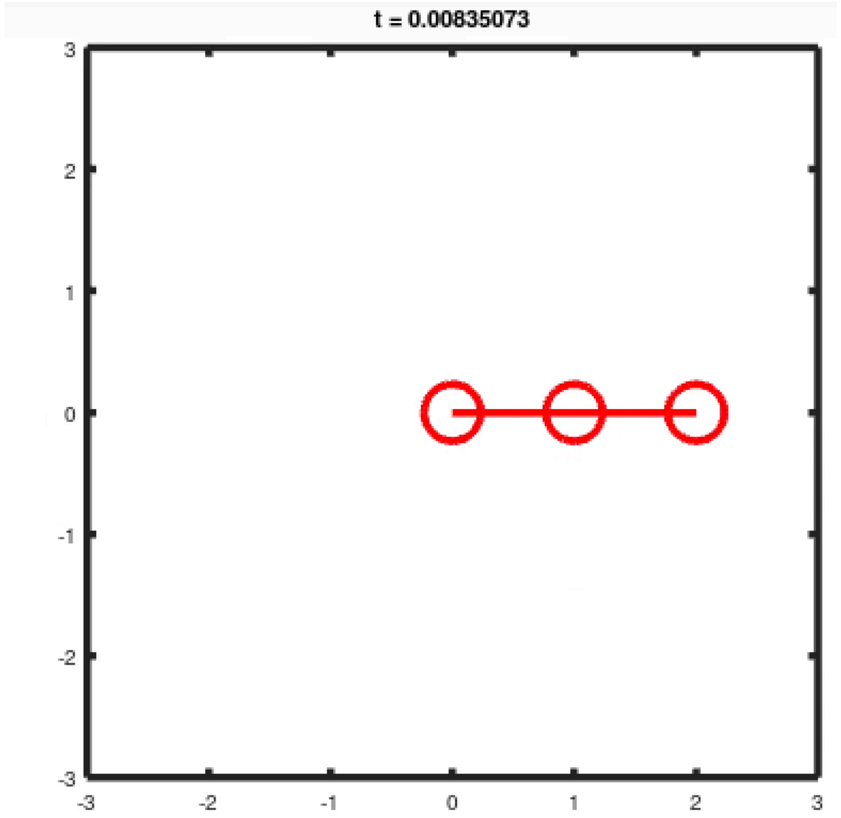
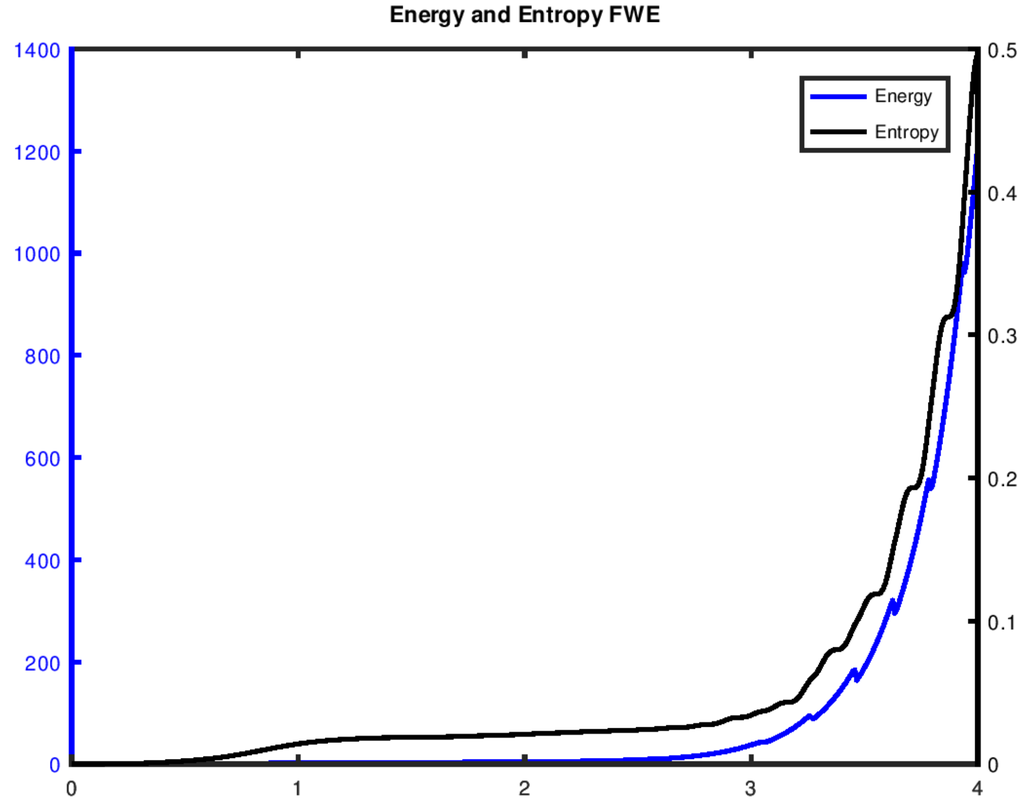
m2   = .2;
k1   = 100;
k2   = 100;
l1   = 1;
l2   = 1;
gx   = 0;
gy   = -9.81;
fr   = .1;
th   = 300;
```

Forward Euler





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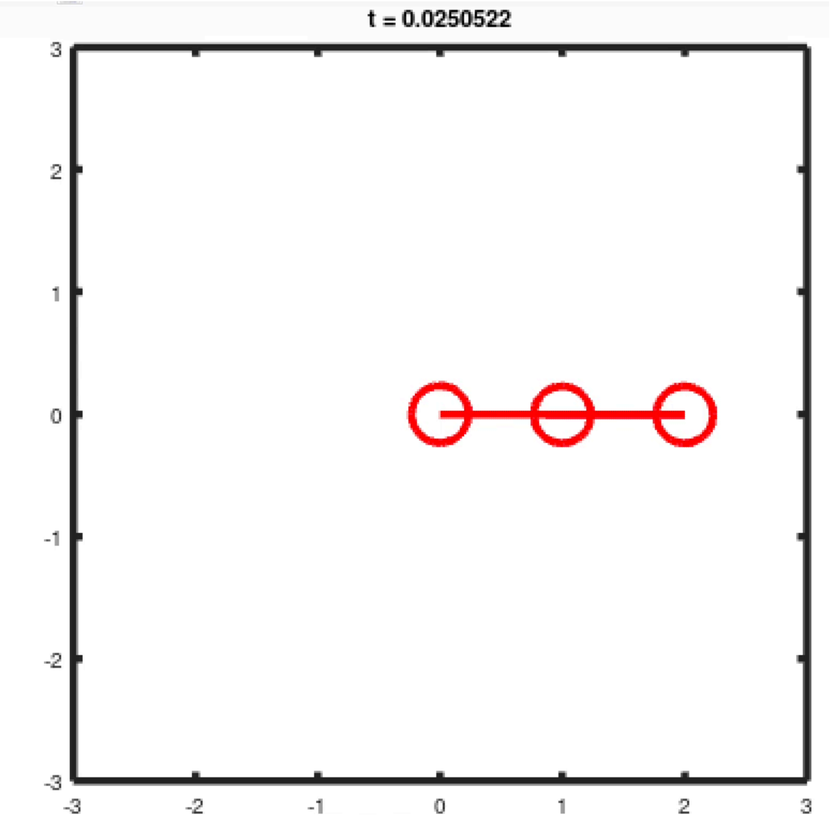

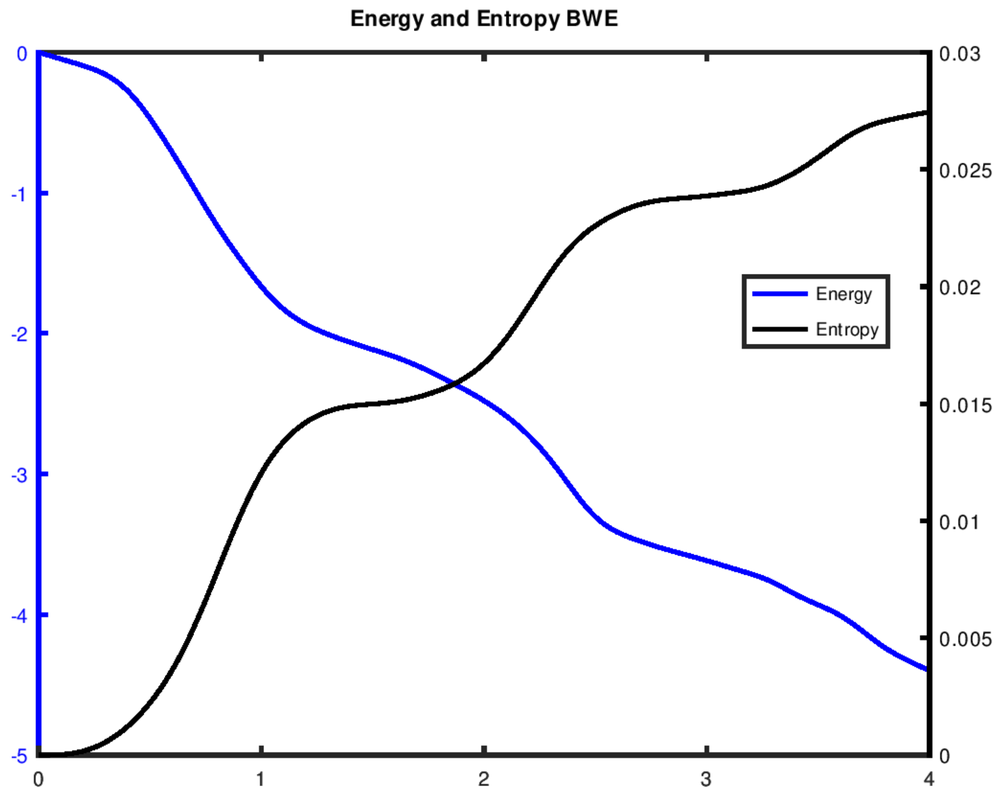

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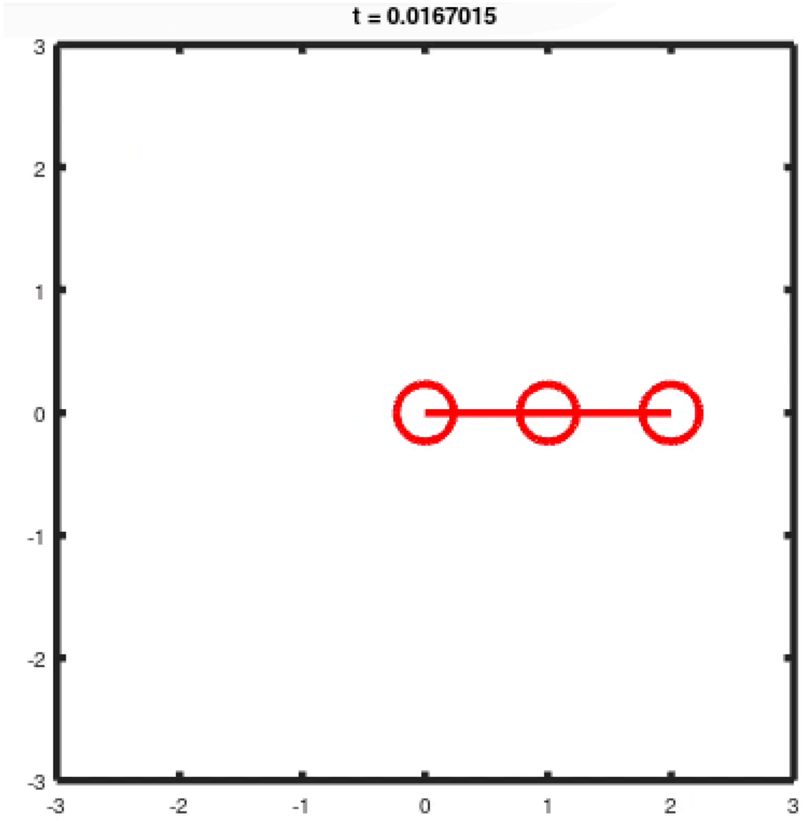

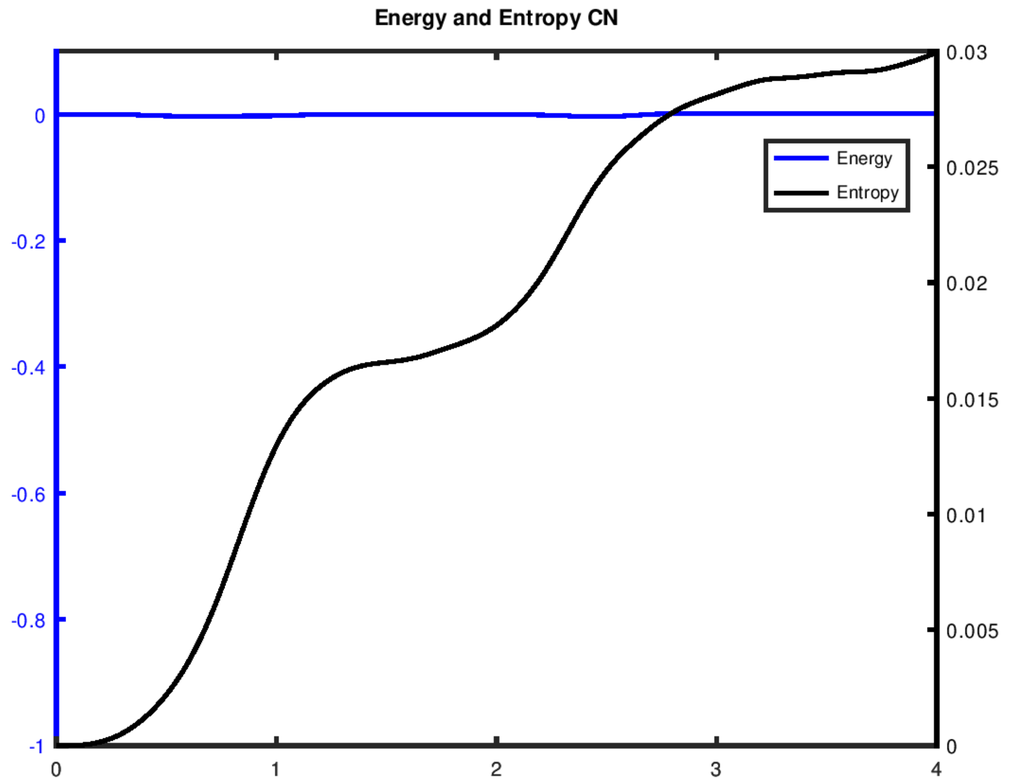

Symplectic (Geometric) Integrators

- Methods especially tailored for simulating Hamiltonian systems
- Very popular in MD is the Velocity-Verlet algorithm

$$p_{n+1/2} = p_n + h/2\, f_n$$

$$r_{n+1} = r_n + h\, p_{n+1/2}/m$$

$$p_{n+1} = p_{n+1/2} + h/2\, f_{n+1}$$

- Explicit, 1-step, 2-stage method
- h time step

Verlet Algorithm

- Important features of the Verlet algorithm are:
  - it is exactly time reversible
  - it is symplectic
  - it is 2nd order in time, permitting long timesteps
  - it requires just one force evaluation per step
  - it is easy to program

Verlet Algorithm

- The trajectories generated by the above scheme are approximate, and will not conserve the true energy H.
- Nonetheless, they do exactly conserve a “pseudo-hamiltonian” or “shadow hamiltonian” $H^{\ddagger}$
- H and $H^{\ddagger}$ differ from each other by a small amount, $H^{\ddagger} = H + O(\Delta t2)$.
- This means that the system will remain on a hypersurface in phase space which is “close” to the true constant-energy hypersurface.
- Such a stability property is extremely useful in MD, since we wish to sample constant-energy states.