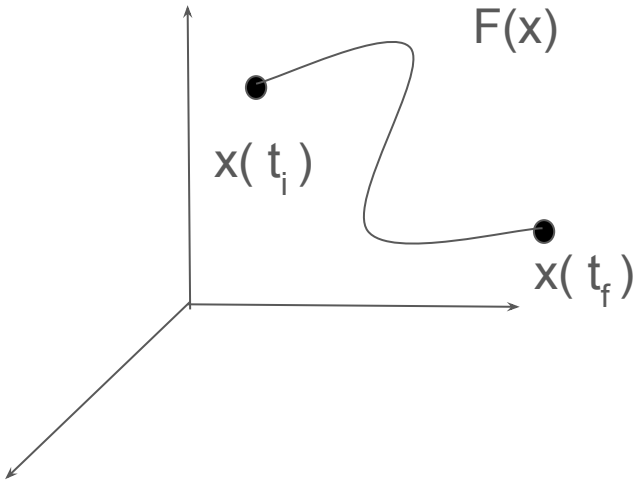
Molecular Dynamics: Basics

Tutor(s): Chiara Cignarella / Christoph Dähn / Edrick Solis

Content

- Simulation of particles under F(x)
- Interatomic potentials
- Formal properties of the dynamics
- Velocity Verlet method

Simulation of particles under F(x)



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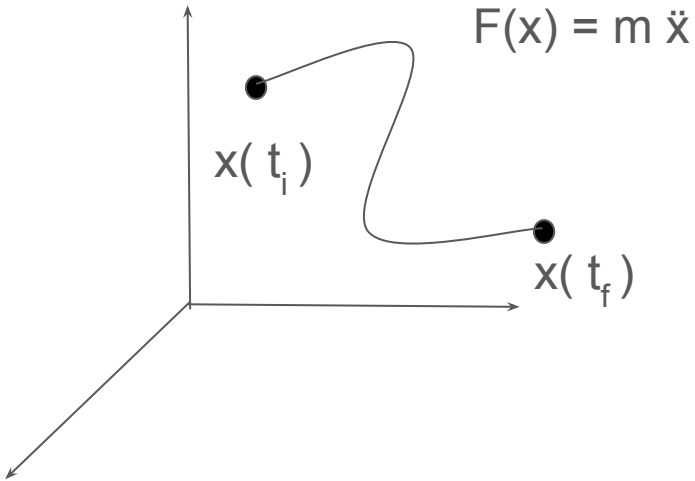
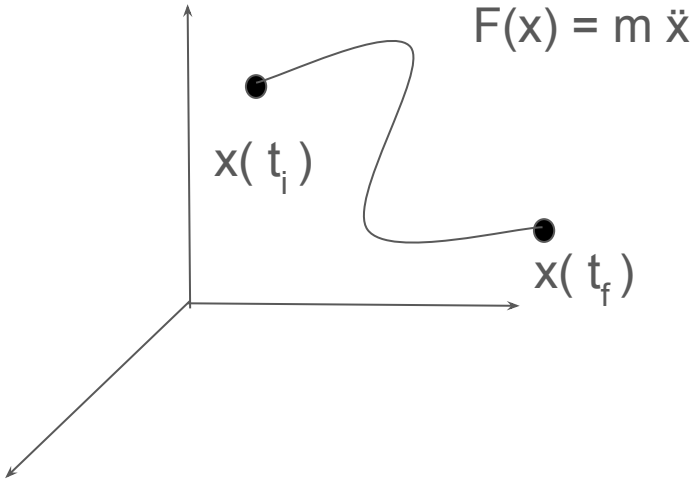


Simulation of particles under F(x)

Second order ODE

$F(x) = m\ddot{x}$



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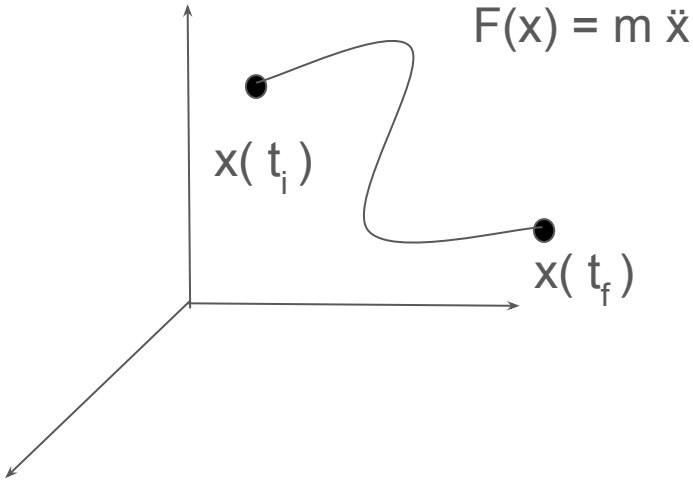
- Reduction of order



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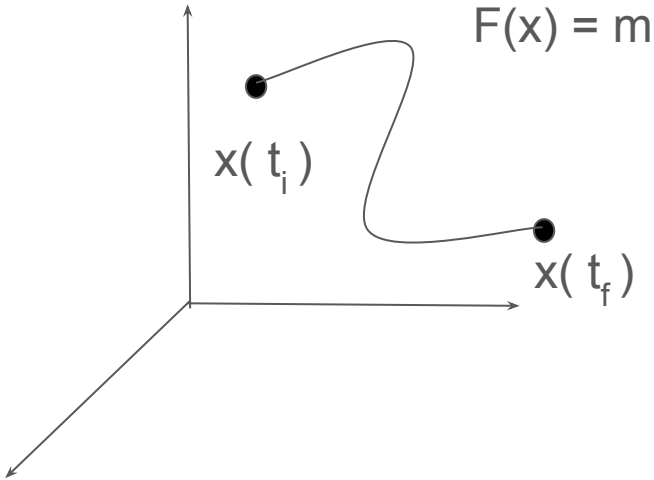

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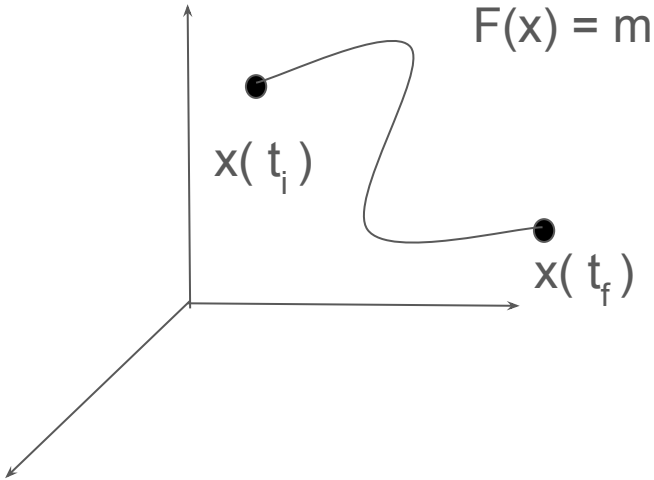

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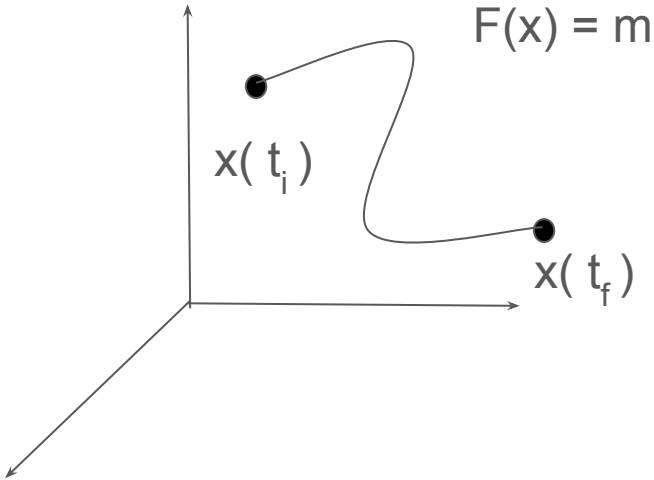

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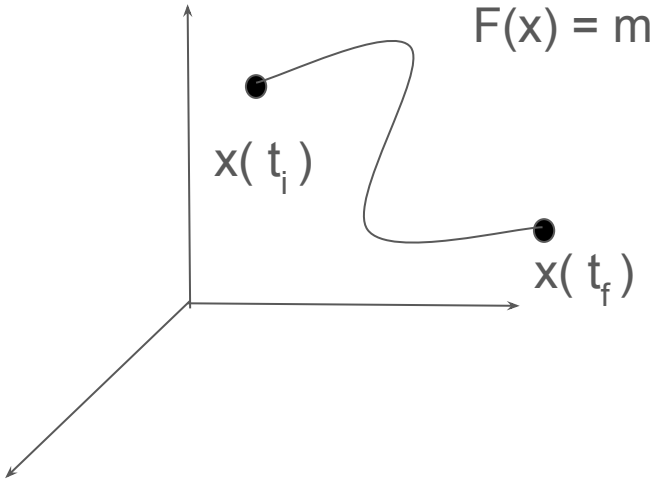

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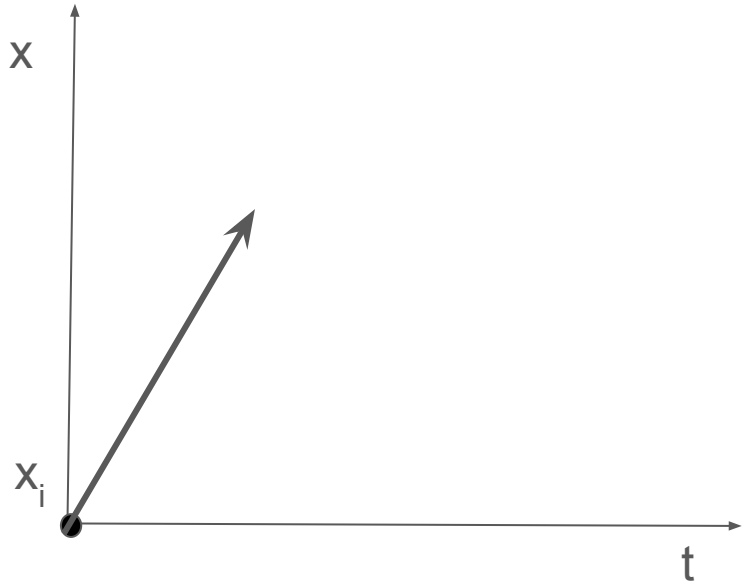

Simulation of first order ODE

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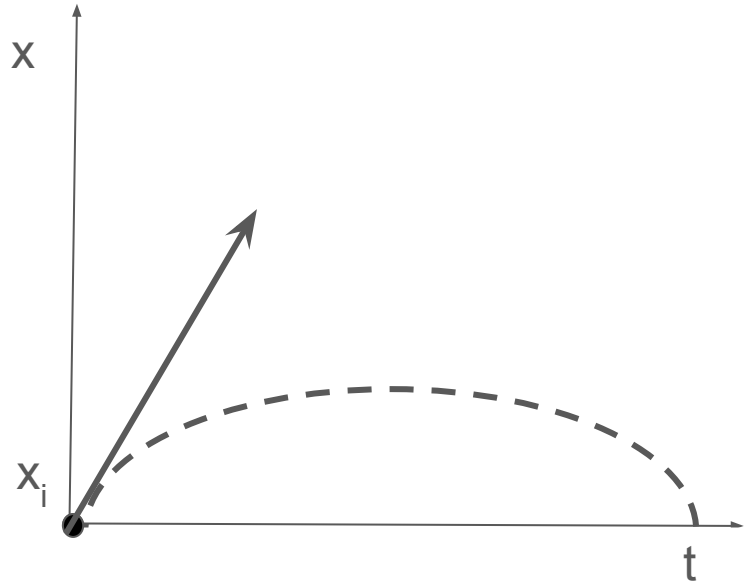

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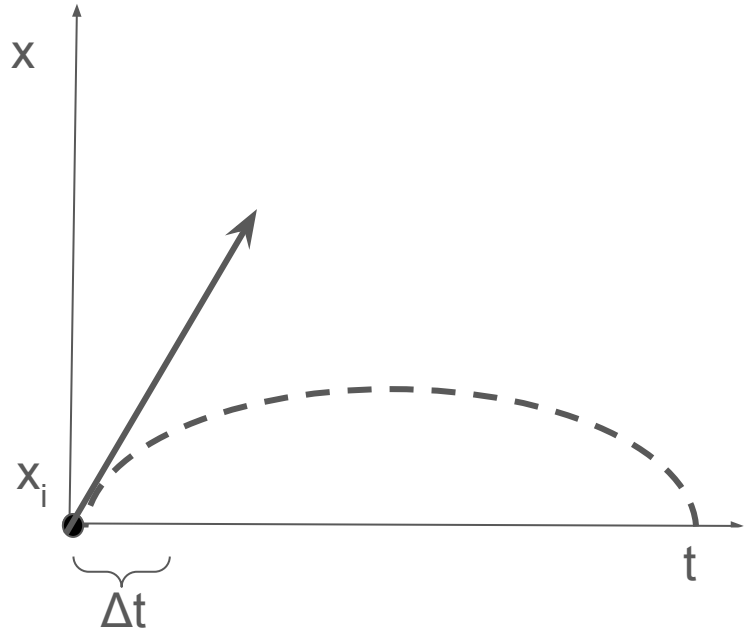
- Choose Δt



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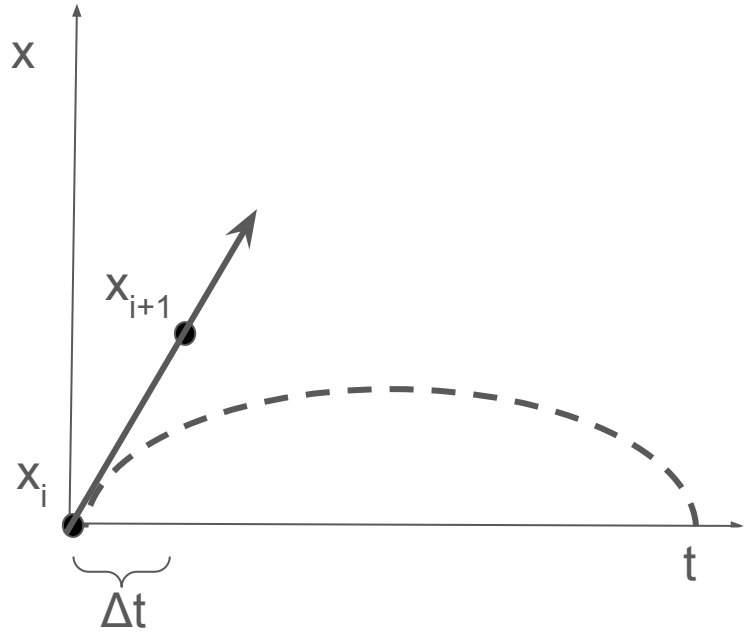

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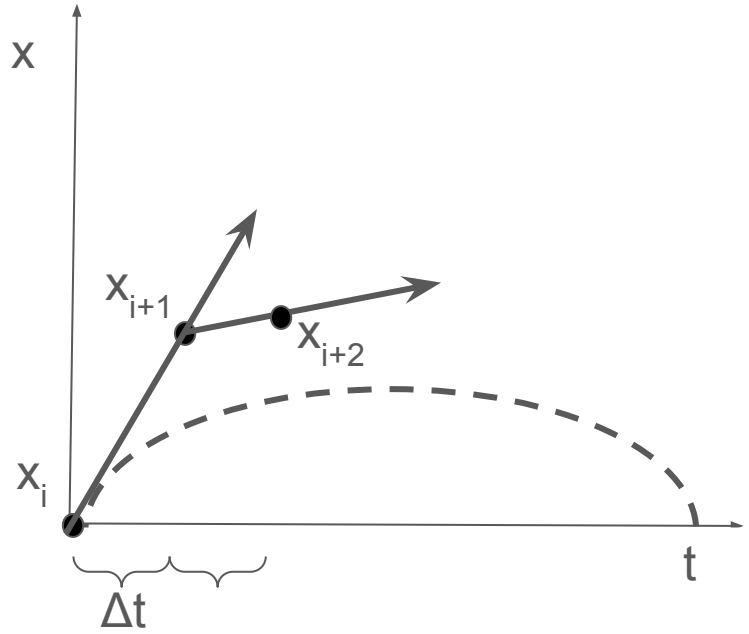

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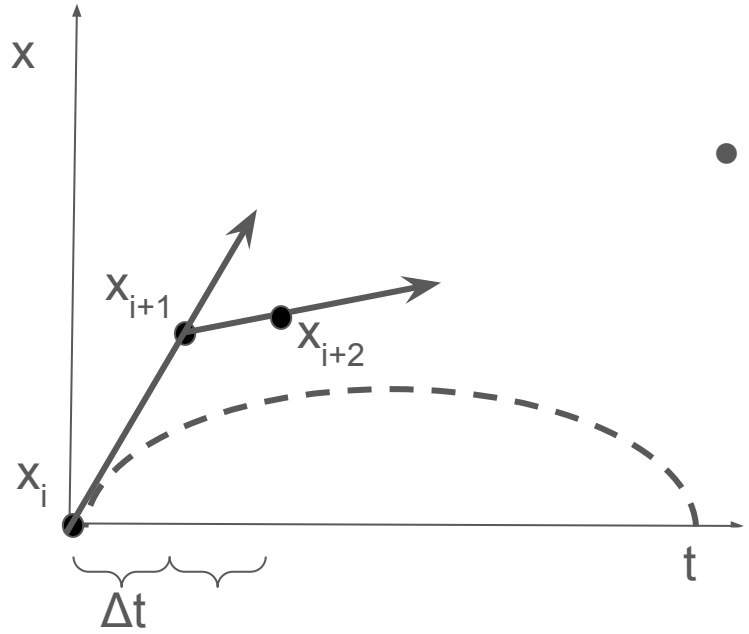

- Choose Δt

- For a given initial condition

$$x_{n+1} = x_n + \Delta t\, v(x_n)$$

Simulation of first order ODE

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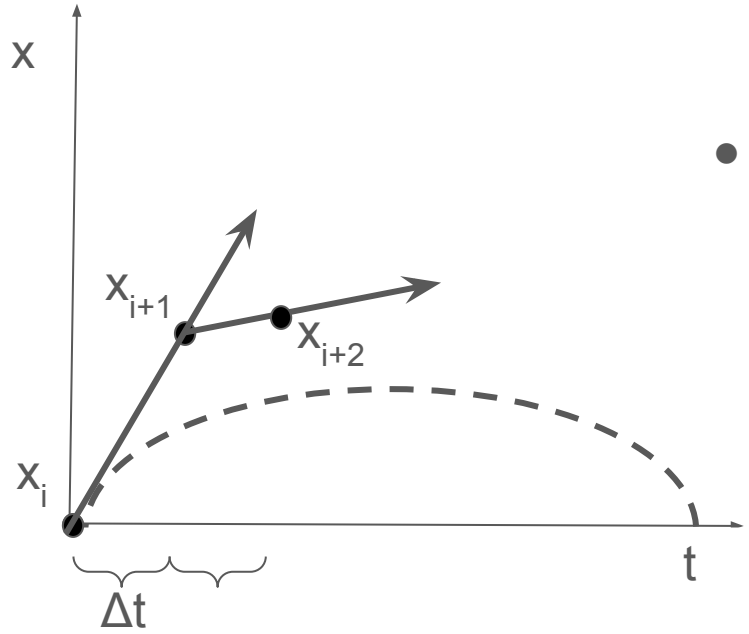

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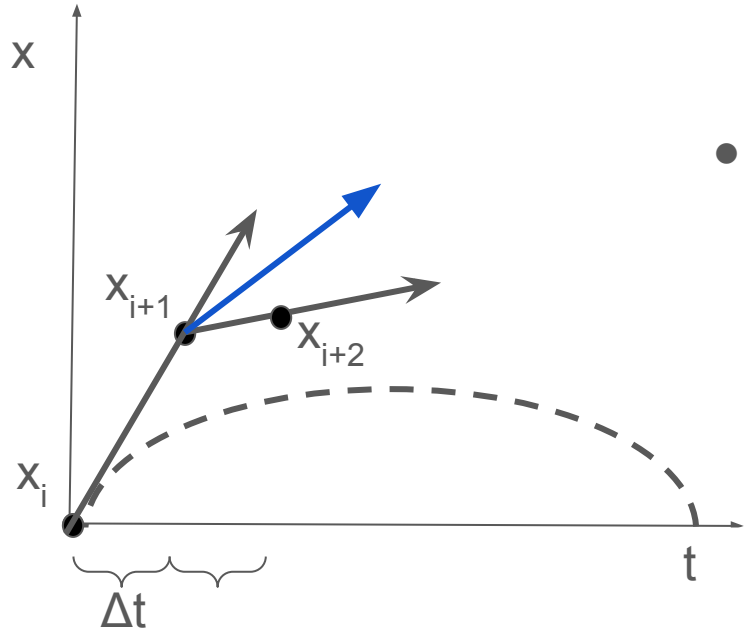

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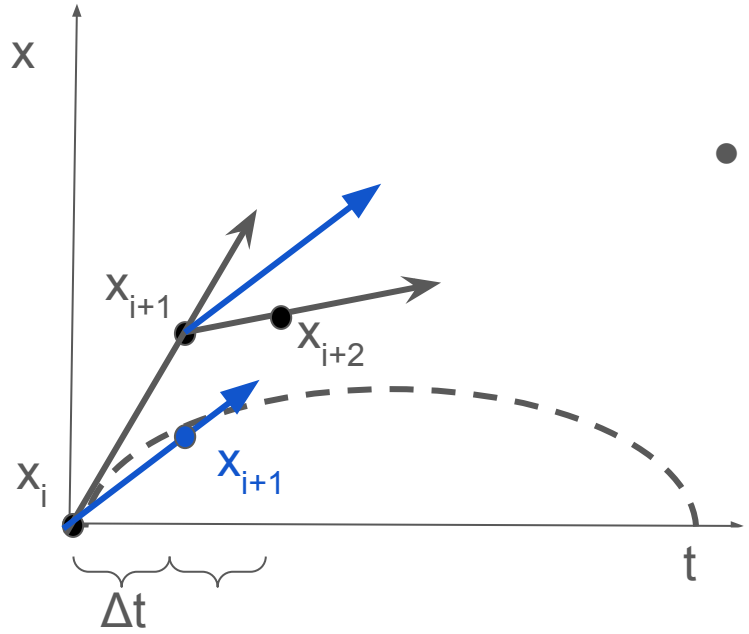

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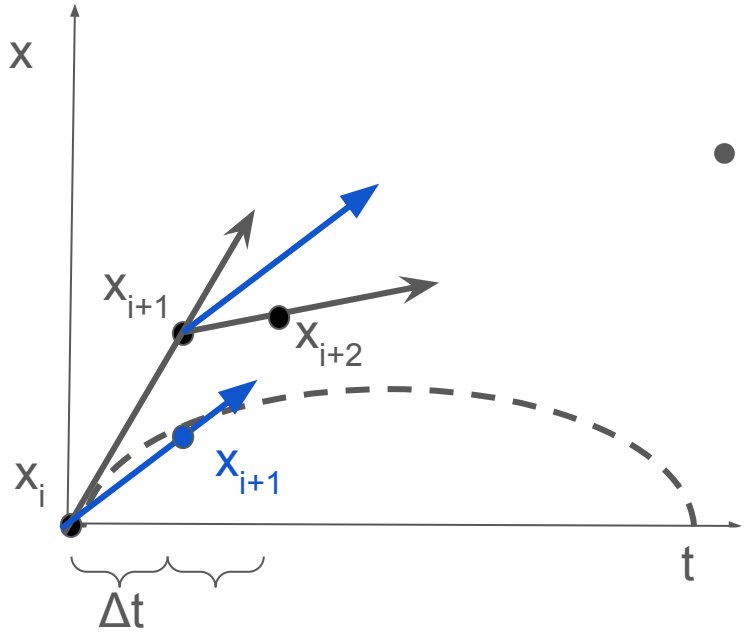


- Choose Δt
- For a given initial condition

$$x_{n+1} = x_n + \Delta t\, v(x_n)$$

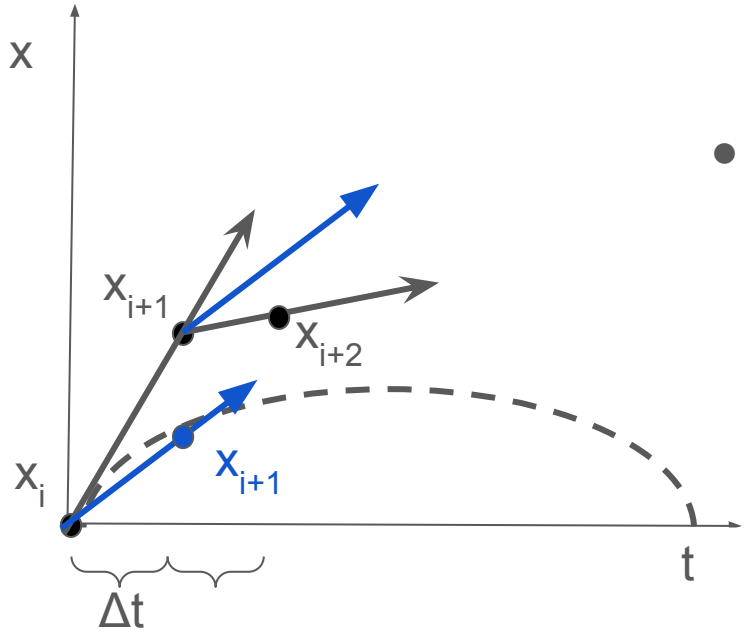
↑

Euler method

$$x_{n+1} = x_n + \Delta t\,(v(x_n) + v(x_n + \Delta t\, v(x_n))/2$$

Simulation of first order ODE

$$\dot{x}(t) = v(x)$$



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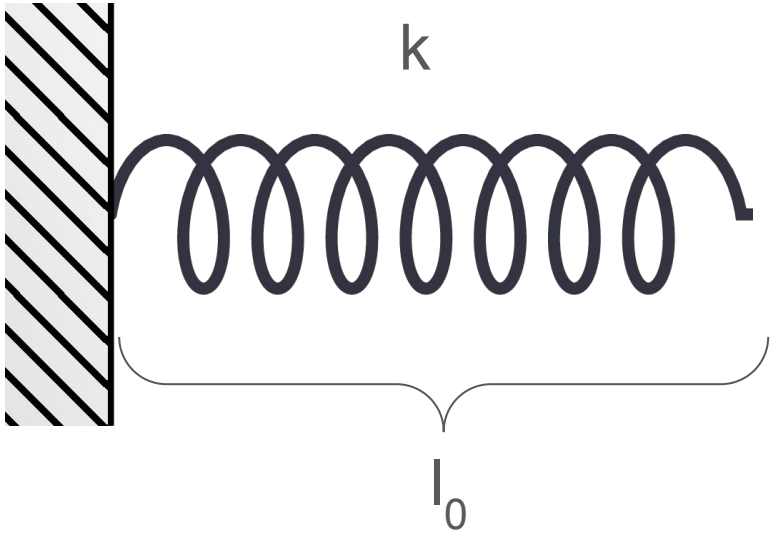
Heun method

Exercise: Harmonic Oscillator

distance from equilibrium

$$F(x) = - k\, x$$



source python_source/venvs/asesma_general/bin/activate

Exercise: Harmonic Oscillator

$$\dot{x}(t) = v(x)$$

$$m\,\dot{v}(x) = F(x)$$

$$x_{n+1} = x_n + \Delta t\, v(x_n)$$

Euler method

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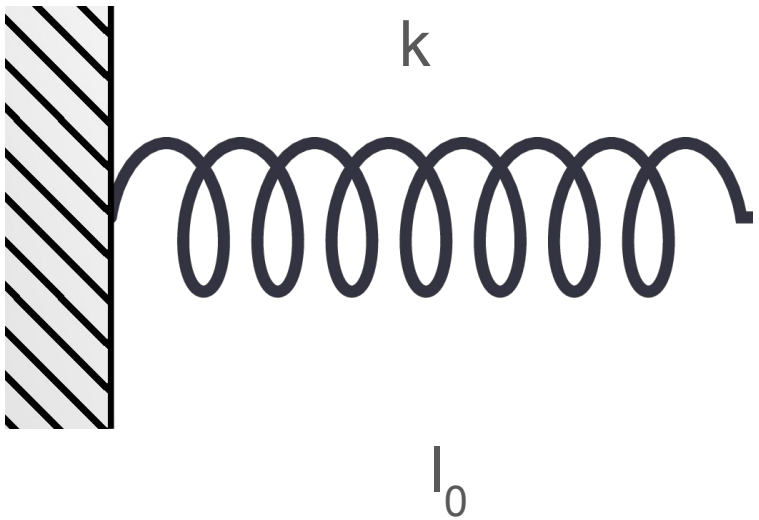

Solution

```
def harmonic_force(l0, k, x):
    return - k * ( x - l0)
```

```
for i in range(N - 1):  # Loop over timesteps
    x[i+1] = x[i] + dt*v[i]
    v[i+1] = v[i] + dt*harmonic_force(l0, k, x[i])/m
```

Interatomic Forces

- Assumptions:
  a. Pair-wise interaction
  b. Depend on the distance between particles

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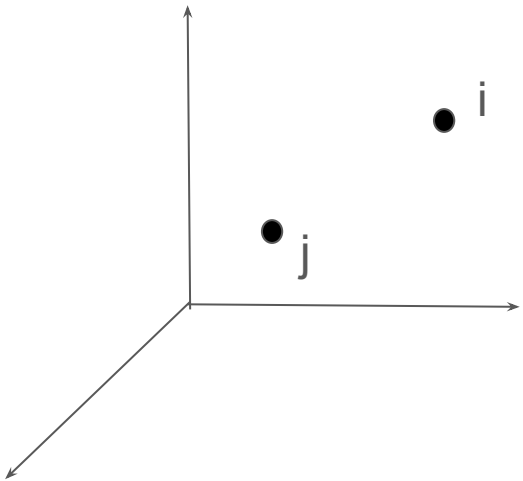

Interatomic Forces

- Assumptions: $F_{ij}(r_{ij})$
  a. Pair-wise interaction
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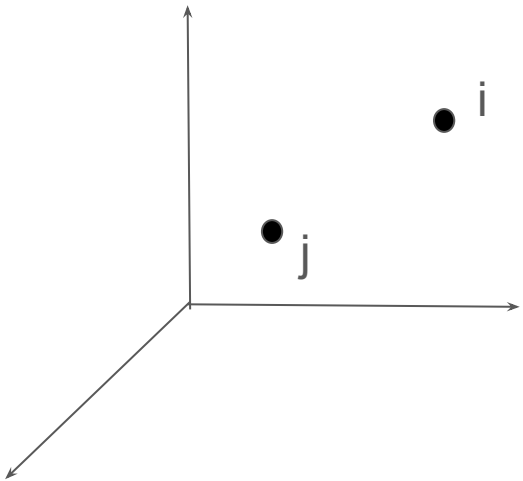

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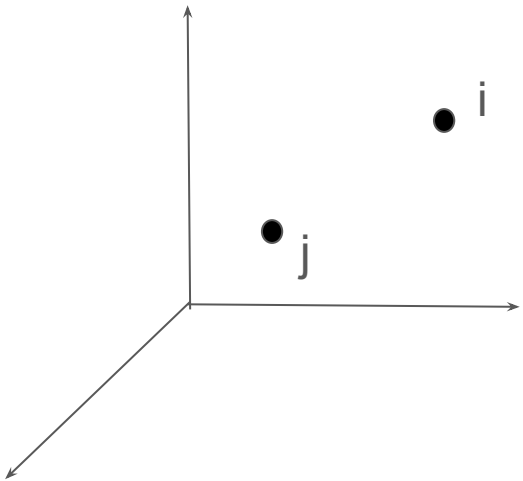
$$F_{ij}(r_{ij})$$

$$r_i - r_j$$



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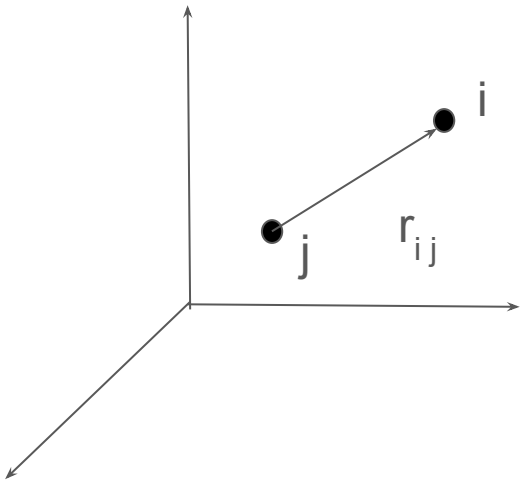

Interatomic Forces

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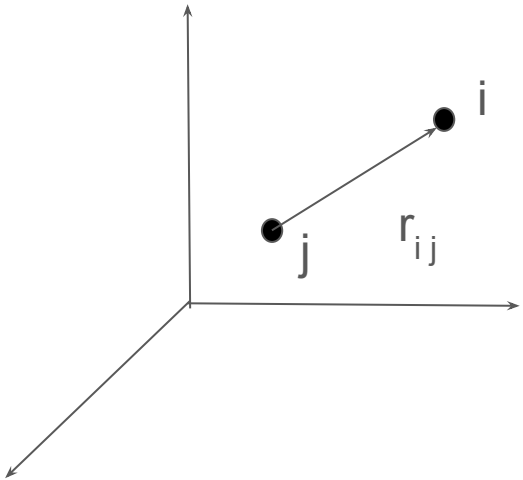
$$F_{ij}(r_{ij}) = f_{ij}(|r_{ij}|)\,\hat{r}_{ij}$$

$$r_i - r_j$$



Interatomic Forces

- Assumptions:
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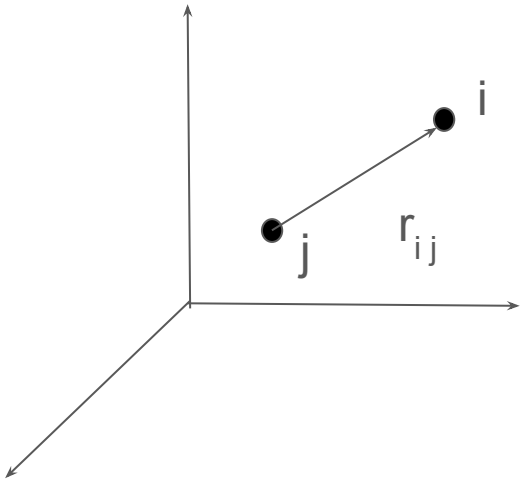
$$F_{ij}(r_{ij}) = f_{ij}(|r_{ij}|)\,\hat{r}_{ij}$$

$r_{ij} = r_i - r_j$

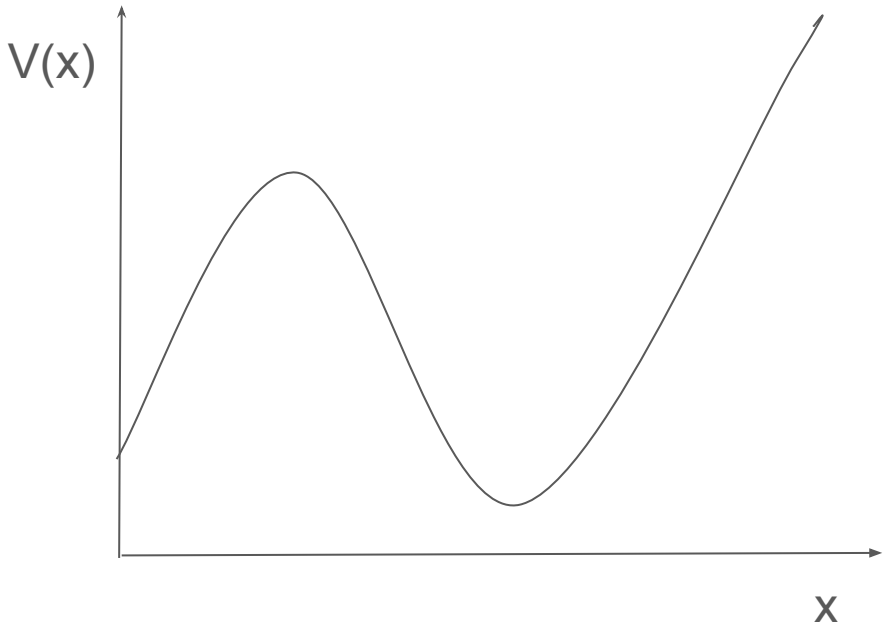


$f_{ij} > 0$ repulsive

$f_{ij} < 0$ attractive

Potential Energy

$F(x) = - d V(x) / dx$



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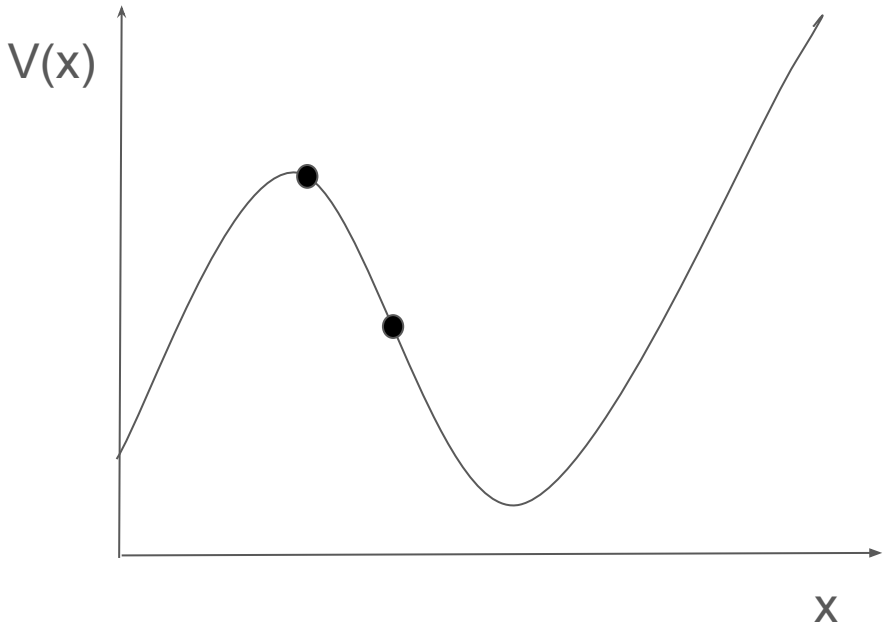

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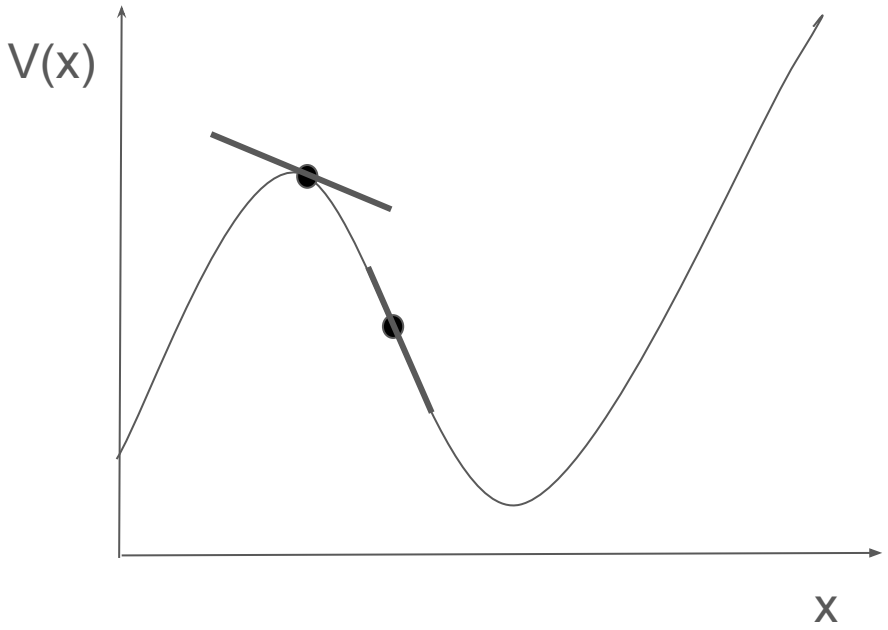

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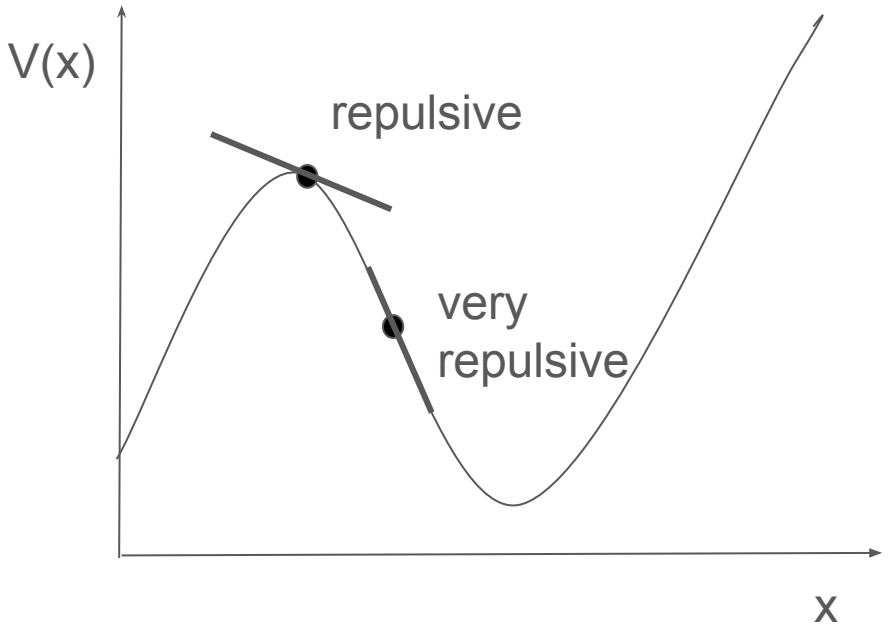

Interatomic potential

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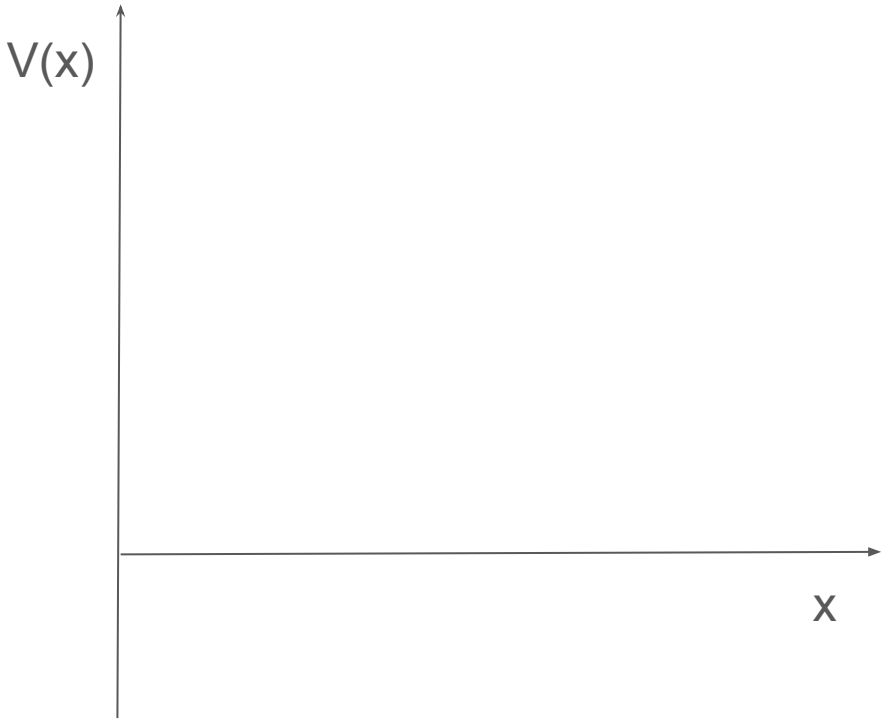
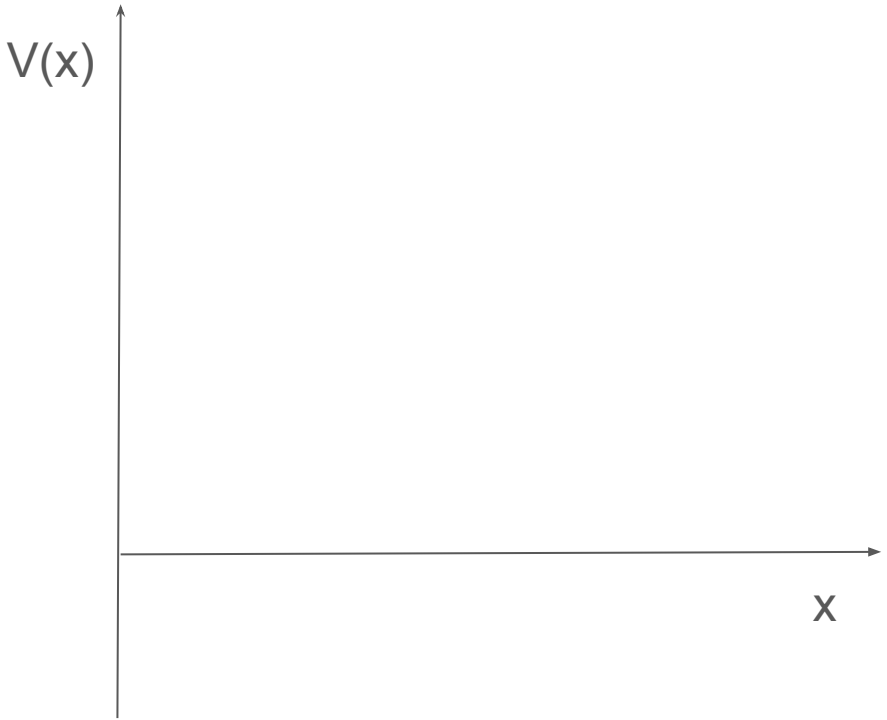


Interatomic potential

- $F(x) = - d V(x) / dx$

- Long distance



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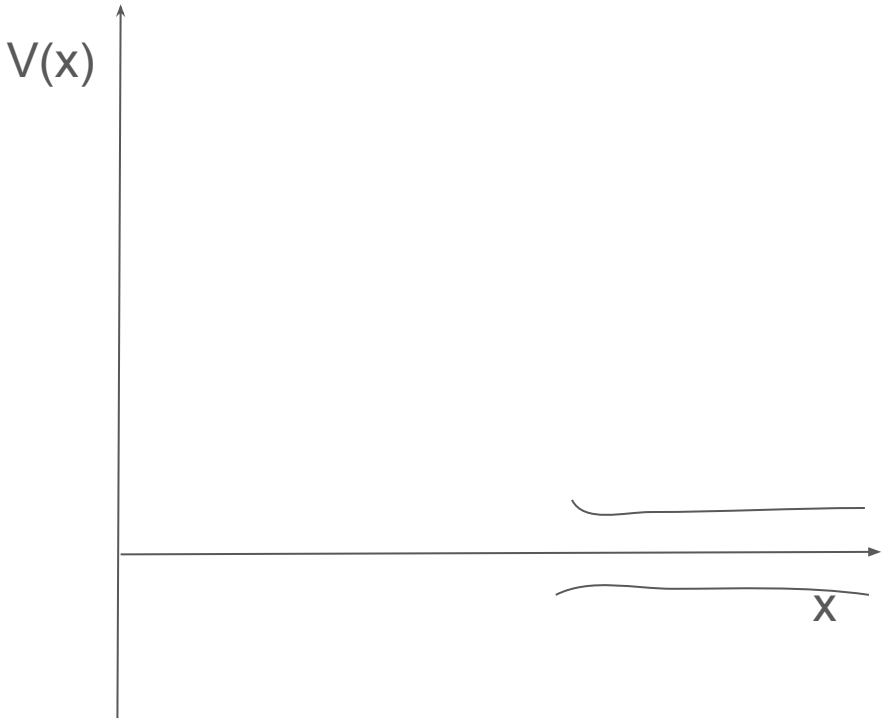
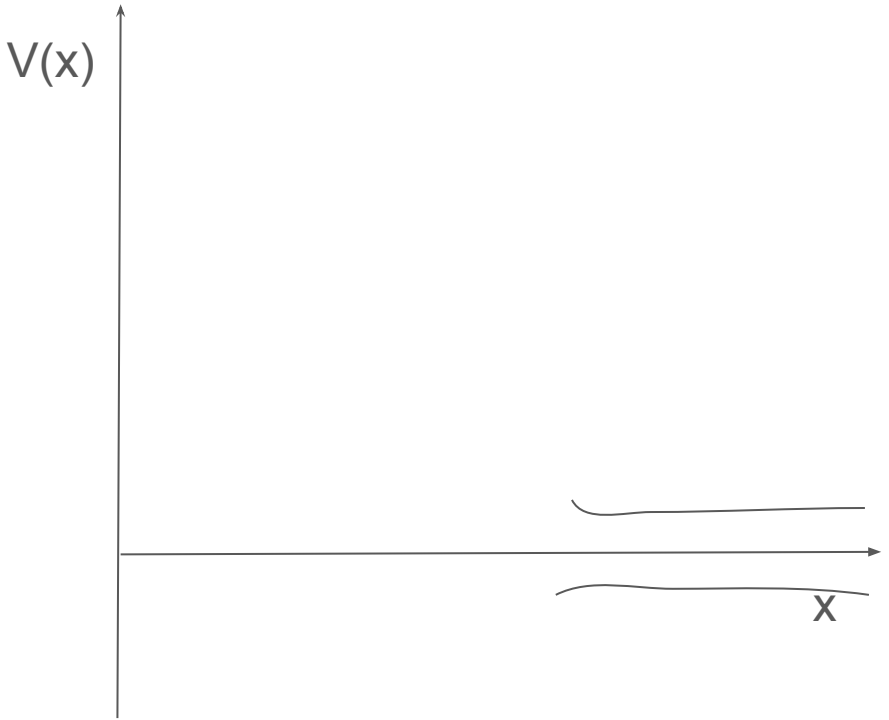


Interatomic potential

- $F(x) = - d V(x) / dx$
- Long distance
- Short distance



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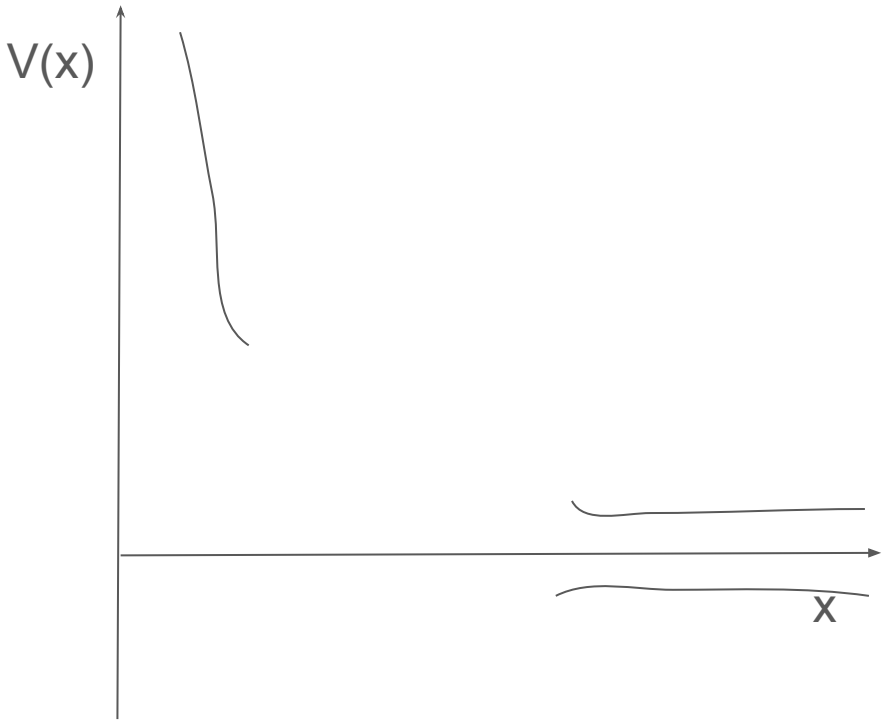
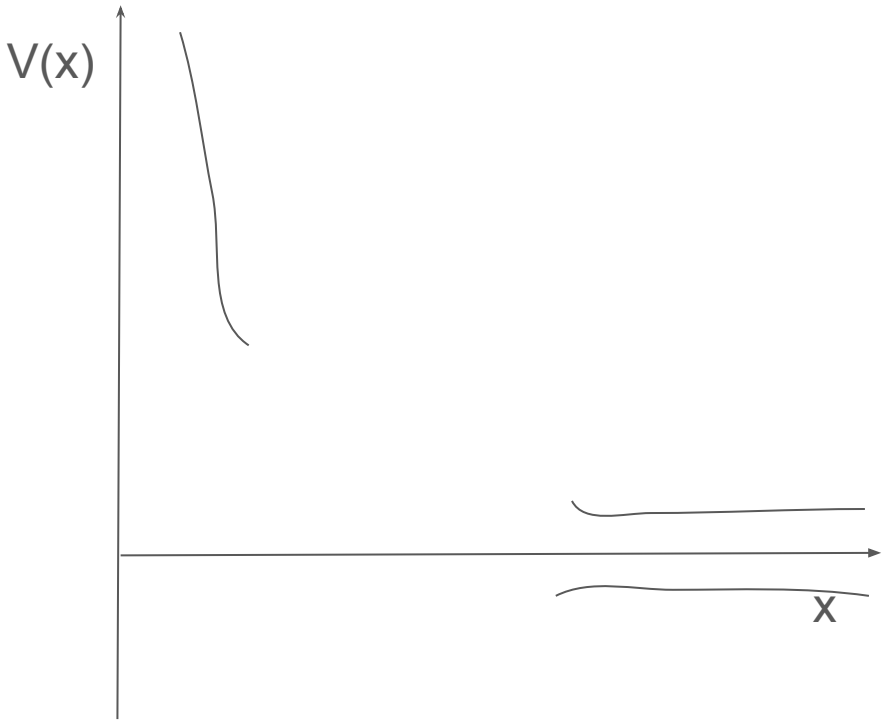


Interatomic potential

- $F(x) = - d V(x) / dx$
- Long distance
- Short distance
- In between



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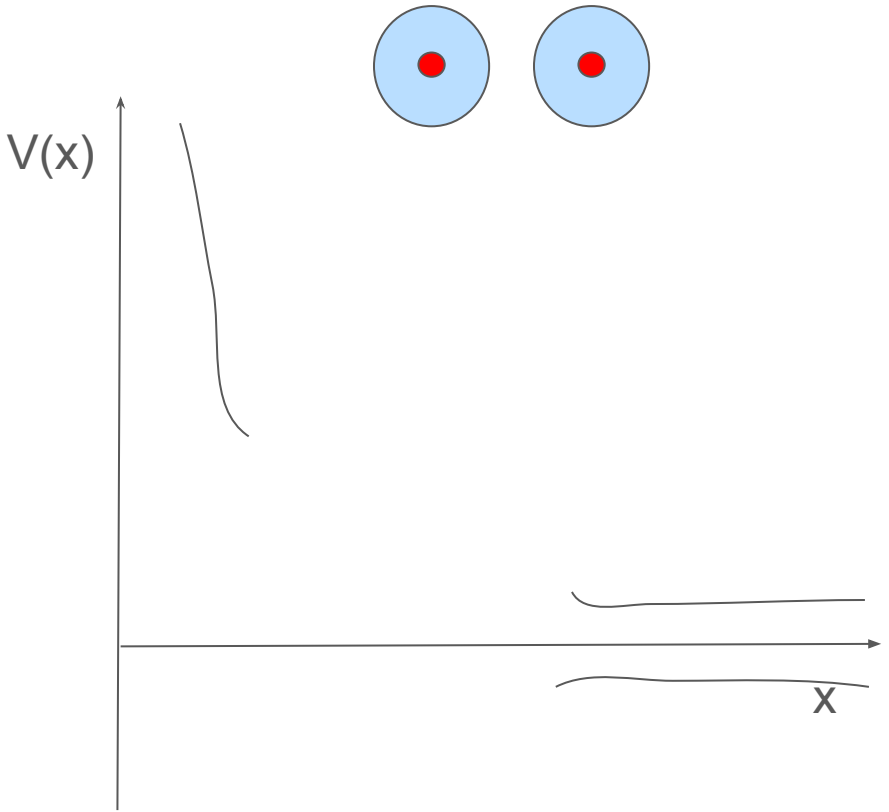

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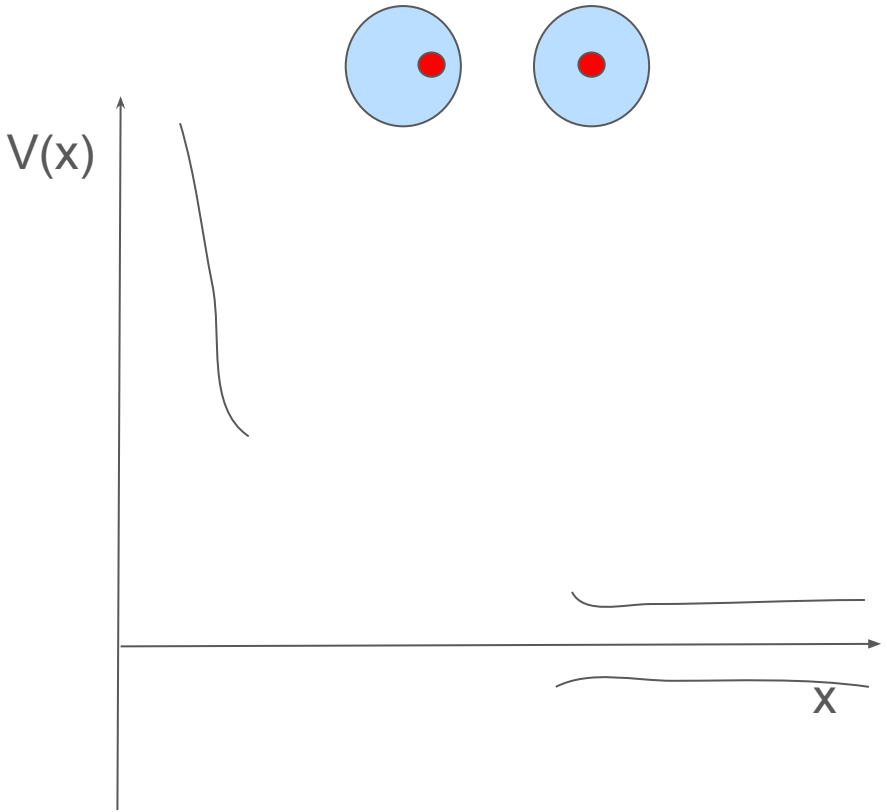

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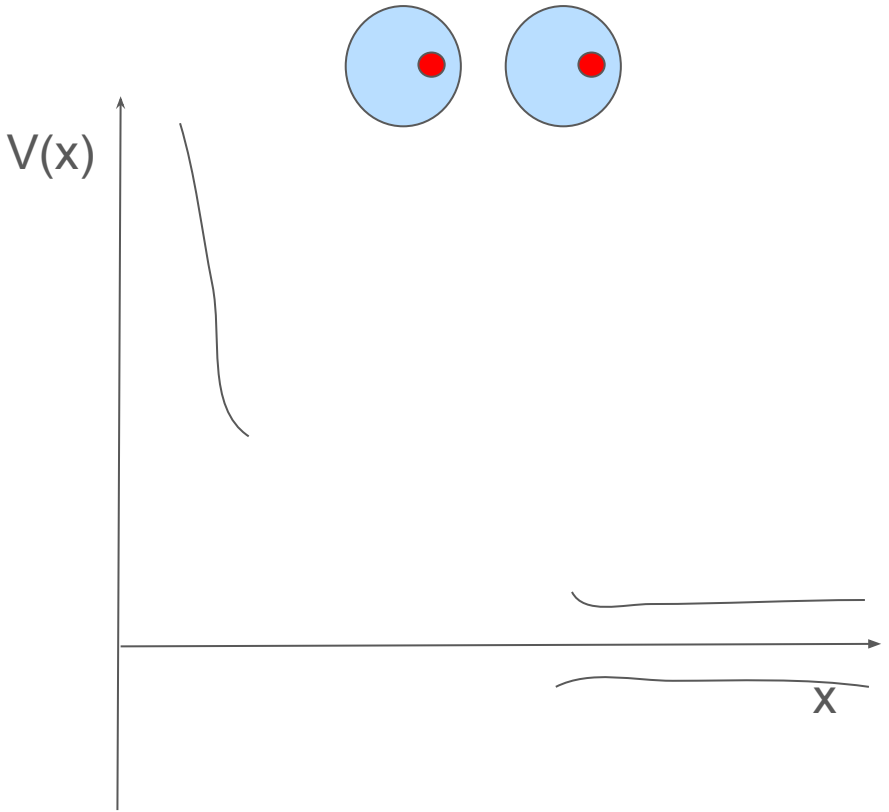
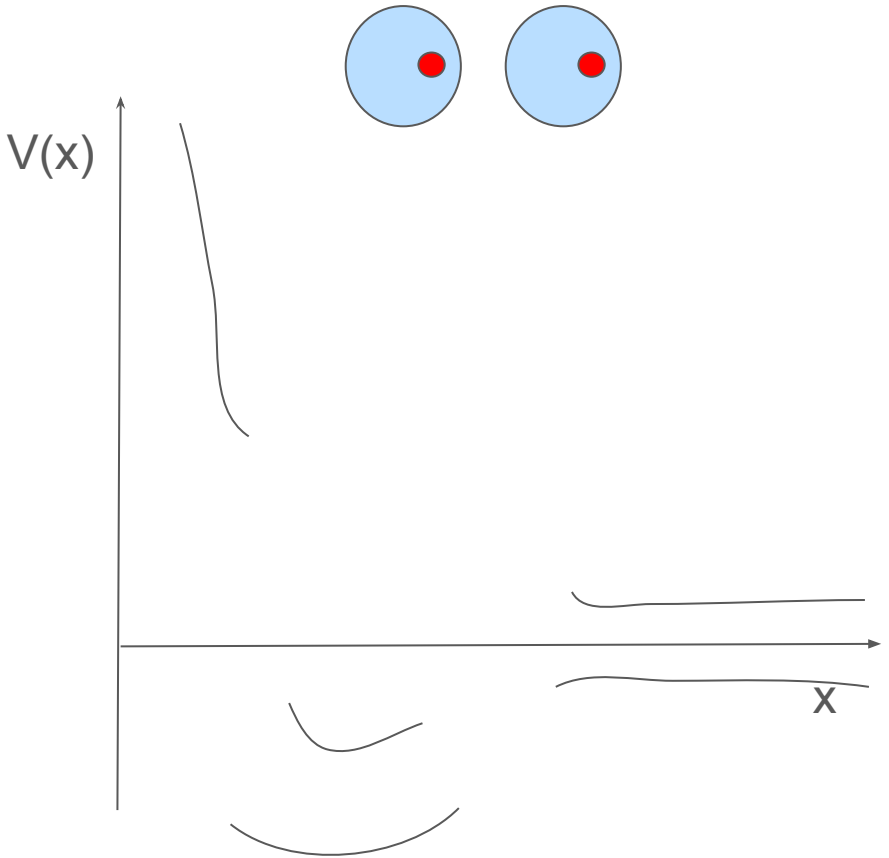
- In between

London dispersion



Interatomic potential

- $F(x) = - d V(x) / dx$
- Long distance
- Short distance
- In between



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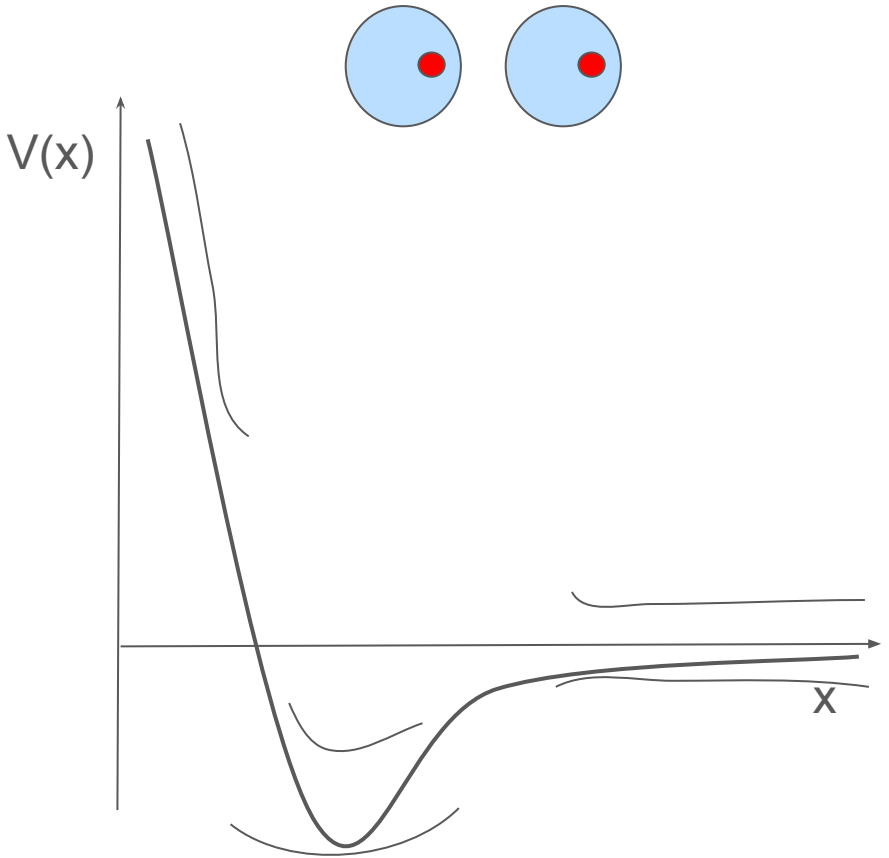

Exercise: Create your own interatomic potential

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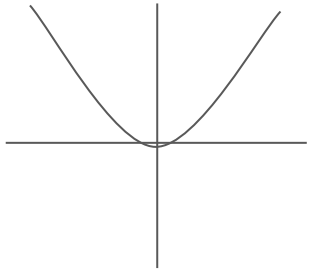

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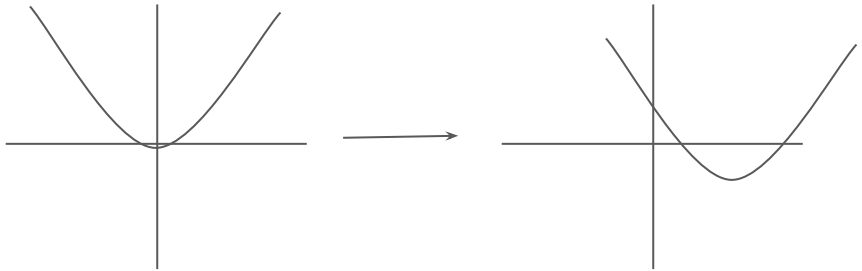

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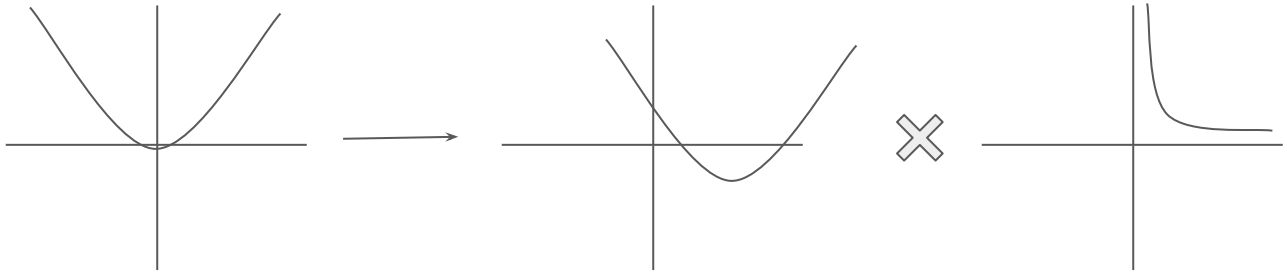
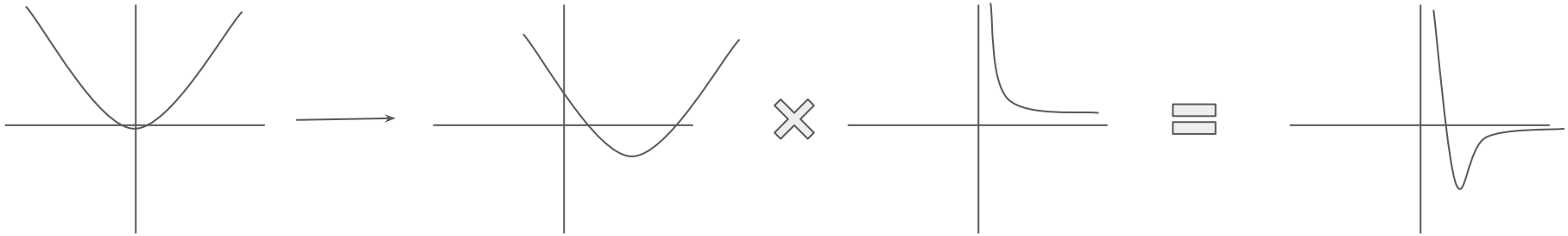
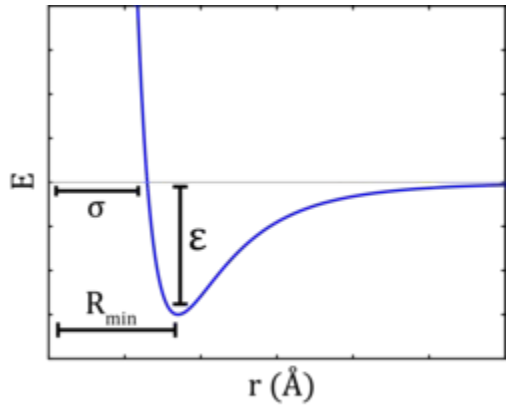


Exercise: Create your own interatomic potential



Lennard-Jones potential

$$\phi(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$



Potential Energy

- Definition

$$F(x) = - d V(x) / dx$$

- How do we obtain U(x) ?
  a. Model: Empirical Force field MD
     - Ex. Lennard-Jones potential
     - Codes: LAMMPS, CHARMM, etc.
  b. Derive it from quantum mechanics: Ab Initio MD or First principles MD
     - Ex. Born-Oppenheimer MD (BOMD), Car-Parrinello MD (CPMD)
     - Codes: CPMD, Quantum ESPRESSO, CP2K, etc.
  c. Machine-learned interatomic potentials

Formal properties of the dynamics

1. Time reversibility

Formal properties of the dynamics

1. Time reversibility

2. Conservation of energy

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1. Time reversibility

2. Conservation of energy

3. Conservation of phase space volume

Exercise

Does the Euler method have any of the ”formal properties” just mentioned?

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Does the Euler method have any of the ”formal properties” just mentioned?

```
for j, (x0, v0) in enumerate(zip(x0s, v0s)):
    for i in range(N - 1):    # Loop over timesteps
        xn = x0 + dt*v0 +(dt**2)*  harmonic_force(l0, k, x0)/(2*m)
        vn = v0 + dt* (harmonic_force(l0, k, x0)  + harmonic_force(l0, k, xn))/(2*m)
        x0 = xn
        v0 = vn
    xfs[j] = xn
    vfs[j] = vn
```

Velocity Verlet method

$$x(t+\Delta t) \approx x(t) + \Delta t\, v(t) + (\Delta t)^2\, a (t) / 2$$

$$v(t + \Delta t) \approx v(t) + \Delta t\, a(t) + (\Delta t)^2\, \ddot{v} (t) / 2$$

$$\ddot{v} (t) \approx (a(t + \Delta t) - a(t)) / \Delta t$$

$$v(t + \Delta t) \approx v(t) + \Delta t (a(t) + a(t +\Delta t))/ 2$$

Exercise

Does the Velocity Verlet method have any of the ”formal properties” just mentioned?

$$x(t+\Delta t) \approx x(t) + \Delta t\, v(t) + (\Delta t)^2\, a (t) / 2$$

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Exercise

Does the Velocity Verlet method have any of the ”formal properties” just mentioned?

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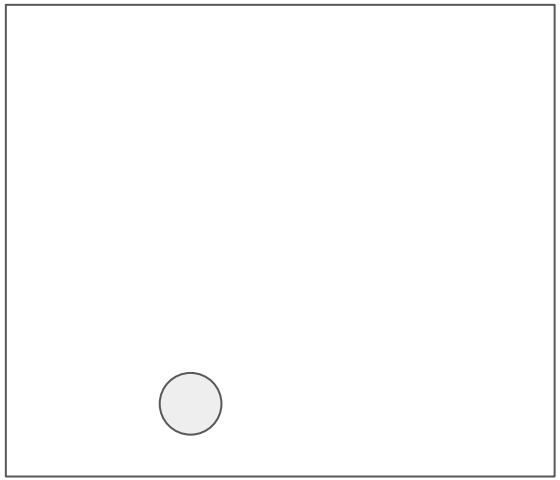
```
for i in range(N - 1):     # Loop over timesteps
    x[i+1] = x[i] + dt*v[i] +(dt**2)*  harmonic_force(l0, k, x[i])/(2*m)
    v[i+1] = v[i] + dt* (harmonic_force(l0, k, x[i])  + harmonic_force(l0, k, x[i+1]))/(2*m)
```

Last slide…

Last slide…



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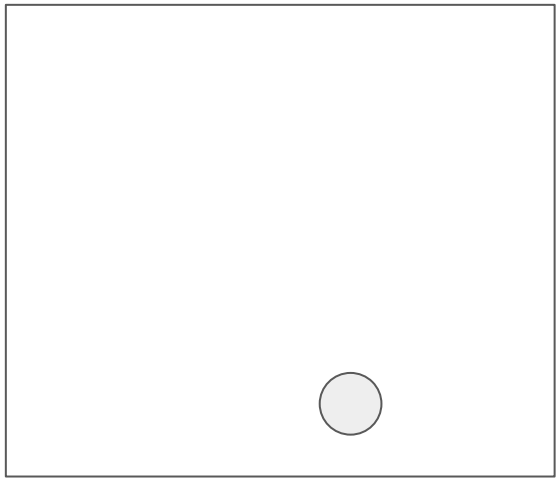
Last slide…



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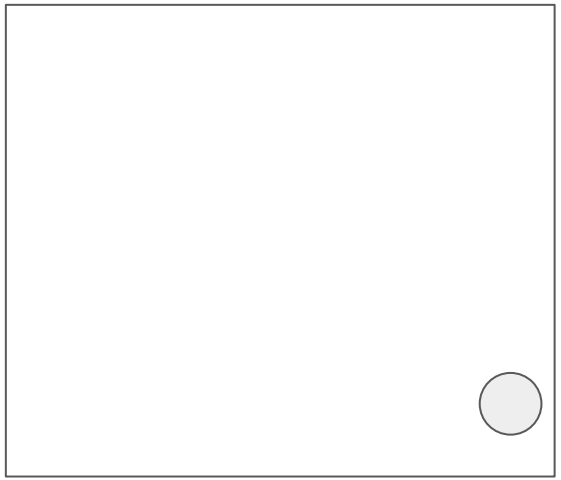

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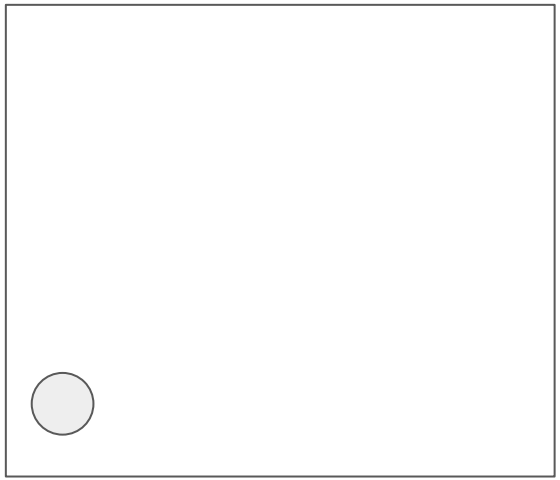
Last slide…



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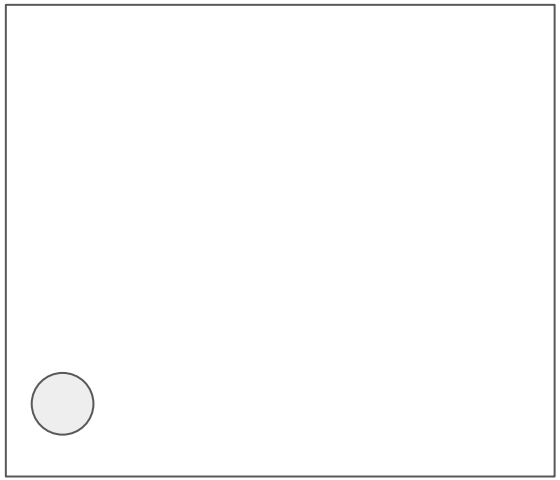

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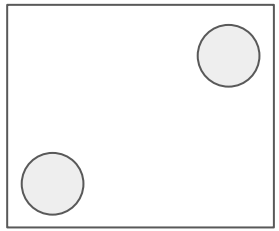
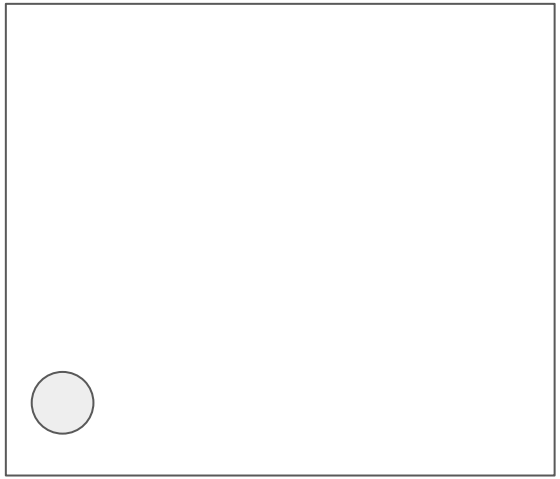


Minimum image convention

Last slide…



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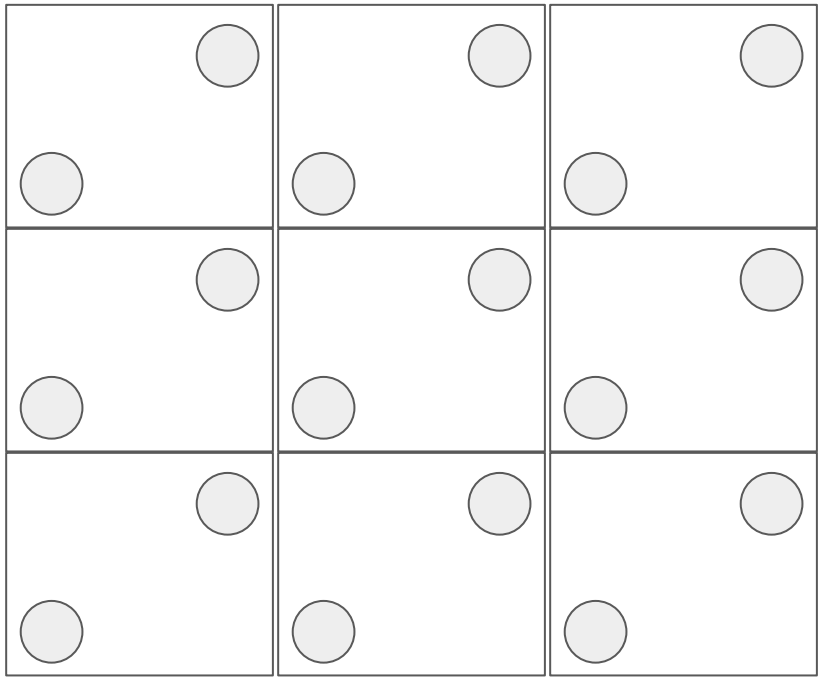

Minimum image convention

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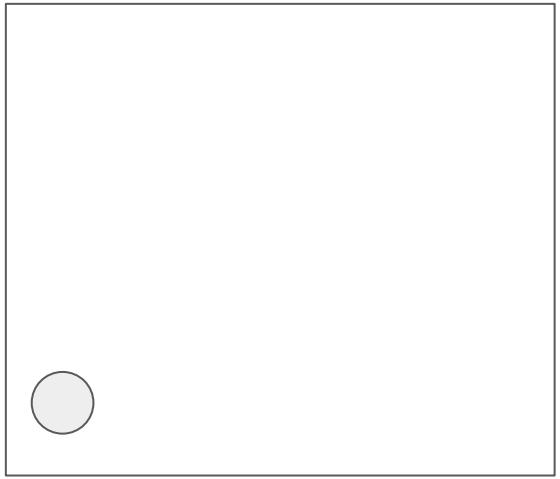

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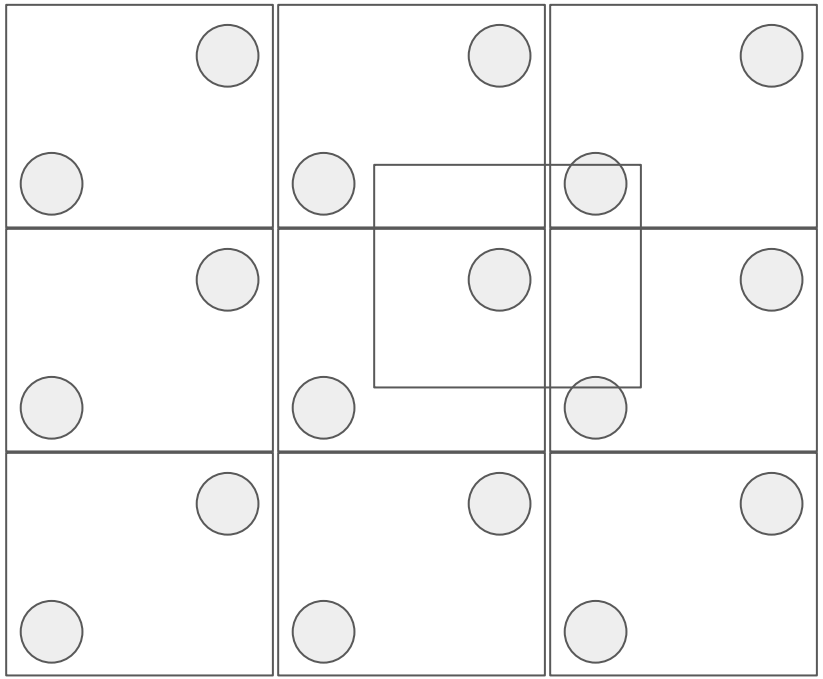

Minimum image convention

Thank you for your attention!