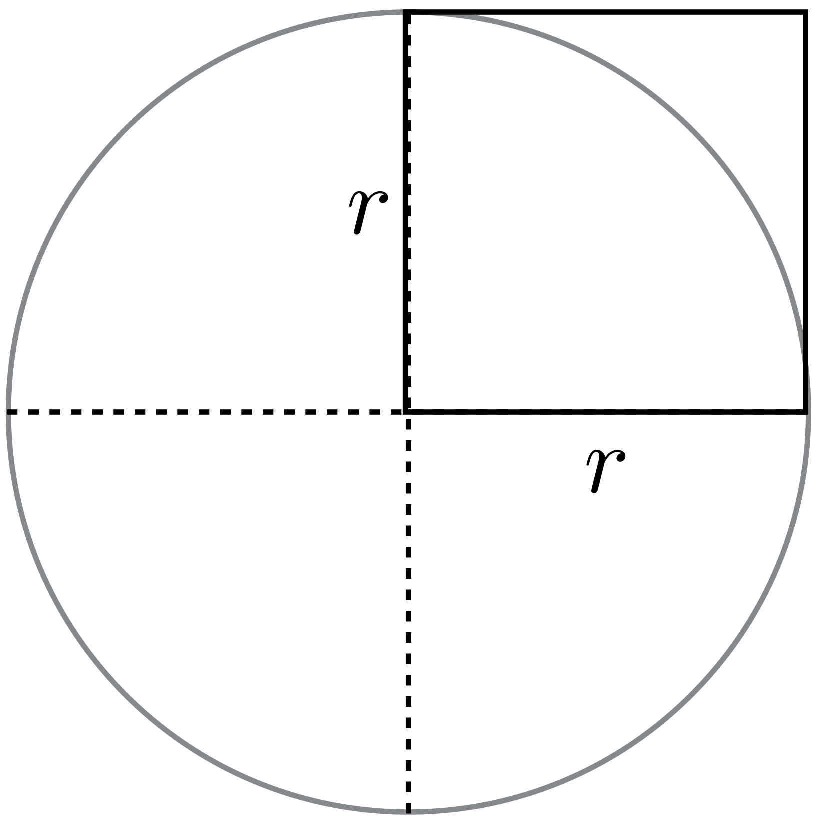
Computational Sciences Projektseminar

Lennard-Jones interaction

Repetition: approximate π via Metropolis MC



$$\pi_{\text{sampled}} = \frac{4}{N}\sum_{n=0}^{N-1}\chi(x_n, y_n)$$

$$\mathbb{A}(x,y) = \begin{cases} 1, & (x,y) \in [0,1]^2 \\ 0, & else \end{cases}$$

$$\begin{aligned} (x_{\text{trial}}, y_{\text{trial}}) &= (x_{n-1}, y_{n-1}) + (\delta x, \delta y) \\ (x_n, y_n) &= \begin{cases} (x_{\text{trial}}, y_{\text{trial}}), & \mathbb{A}(x_{\text{trial}}, y_{\text{trial}}) = 1 \\ (x_{n-1}, y_{n-1}), & \text{else} \end{cases} \end{aligned}$$

Repetition: approximate π via Metropolis MC

```python
def metropolis_update(xy, step):
    xy_trial = xy + 2.0 * step * (
        np.random.rand(*xy.shape) - 0.5)
    if np.all(xy_trial <= 1.0) and np.all(xy_trial >= 0.0):
        return xy_trial
    return xy

def metropolis(xy_init, size, step):
    xy = [np.array(xy_init)]
    for i in range(size):
        xy.append(metropolis_update(xy[-1], step))
    return np.asarray(xy[1:])

def chi(xy):
    return (np.linalg.norm(xy, axis=1) <= 1.0)
```

Detailed balance

$$\pi(x)\,p(y|x) = \pi(y)\,p(x|y)$$

$$\begin{aligned}
\int_\Omega \mathrm{d}x\,\pi(x)\,p(y|x) &= \int_\Omega \mathrm{d}x\,\pi(y)\,p(x|y) \\
&= \pi(y)\int_\Omega \mathrm{d}x\,p(x|y) \\
&= \pi(y)
\end{aligned}$$

Metropolis Monte Carlo

$$
\begin{aligned}
x_{\text{trial}} &= x_{n-1} + \delta x \\
x_n &= \begin{cases} x_{\text{trial}}, & p < \mathbb{A}(x_{\text{trial}} | x_{n-1}) \\ x_{n-1}, & \text{else} \end{cases}
\end{aligned}
$$

$$
\begin{aligned}
\mathbb{A}(y|x) &= \min\left\{1, \frac{\pi(y)}{\pi(x)}\right\} \\
&= \min\left\{1, \frac{e^{-\beta\Phi(y)}}{e^{-\beta\Phi(x)}}\right\} \\
&= \min\left\{1, e^{\beta(\Phi(x)-\Phi(y))}\right\}
\end{aligned}
$$

Potential energy

- **interaction potential: particle with particle**
  example: electrostatics, gravity

- **external potential: particle with environment**
  example: harmonic trap, infinite wall

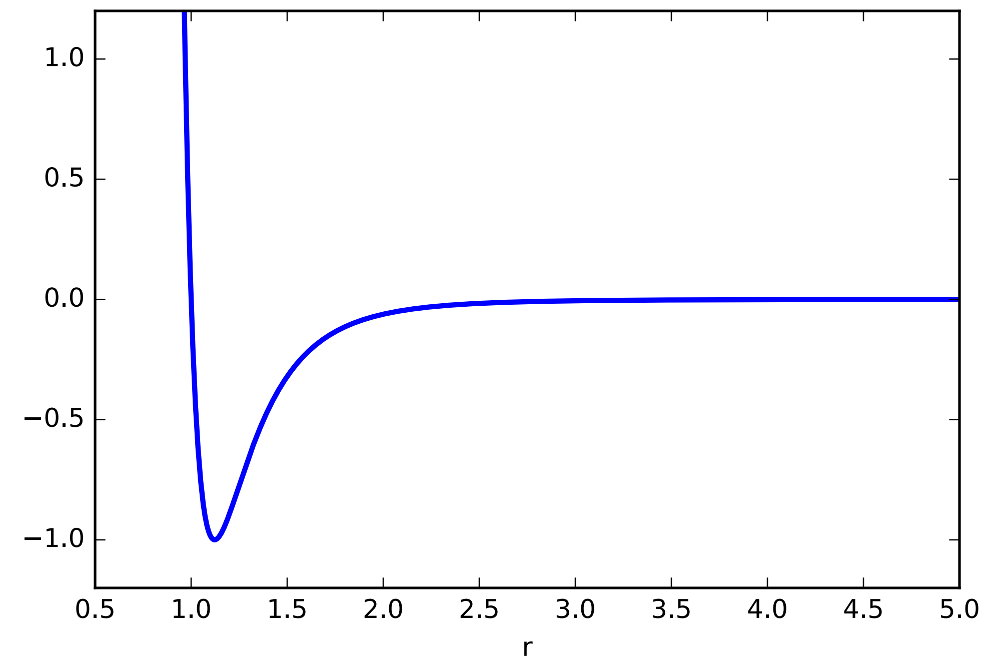
$$\Phi(x_1, \ldots, x_n) = \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} \Phi_{\text{int}}(x_i, x_j) + \sum_{k=1}^{n} \Phi_{\text{ext}}(x_k)$$

Interaction potential: Lennard-Jones

$$r = \|x_i - x_j\|_2$$

$$\Phi_{\mathrm{LJ}}(r) = 4\epsilon\left(\frac{\sigma^{12}}{r^{12}} - \frac{\sigma^6}{r^6}\right)$$

- **Pauli repulsion and van der Waals attraction**
- **very short-ranged**
- **easy to truncate**



External potential: infinite wall

$$\Phi_{\mathrm{IW}}(x) = \begin{cases} 0, & 0 \leq x \leq b \\ \infty, & \text{else} \end{cases}$$

- **restriction to predefined area**

Exercise: Lennard-Jones dimer in three dimensions

- implement the Lennard-Jones interaction
- implement an infinite wall
- implement a Metropolis MC procedure
- sample 10^5 steps at $\beta=10$ inside a cube with edge length b=5
- plot the distribution of particle—particle distances

Homework: Lennard-Jones tetramer (➡jupyter notebook)

- extend your dimer solution to n particles
- sample 10^5 steps at $\beta=1$ and $\beta=10$ inside a cube with edge length b=5
- plot the particle—particle distance distributions for each particle pair
- explain your observations for $\beta=1$ and $\beta=10$