Statistical Thermodynamics

Fundamentals of Entropy

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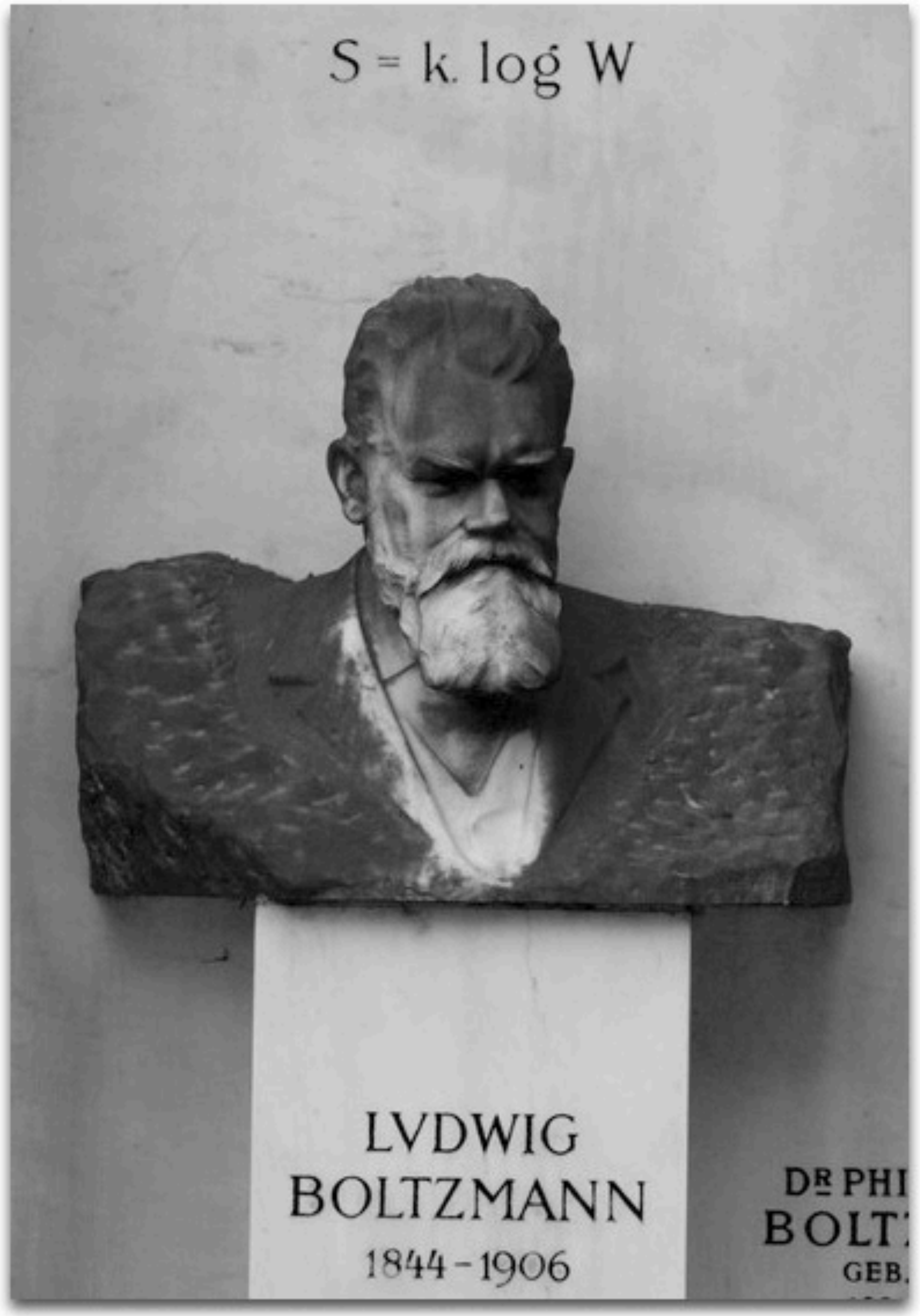
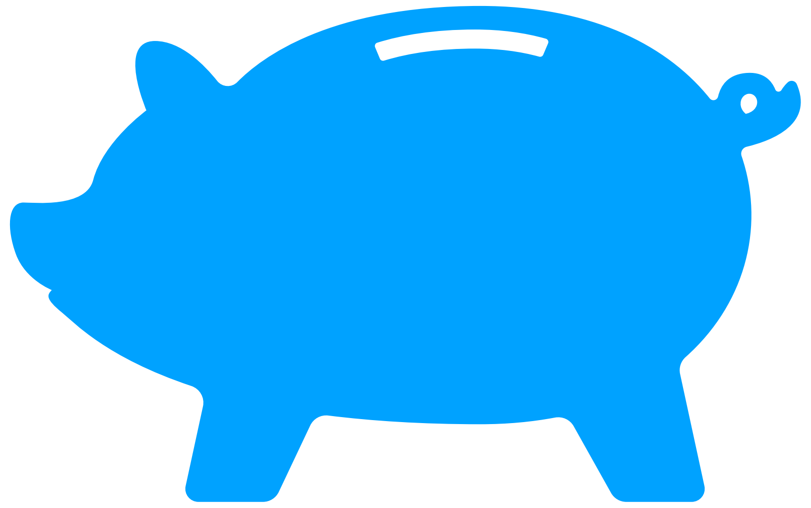
Entropy



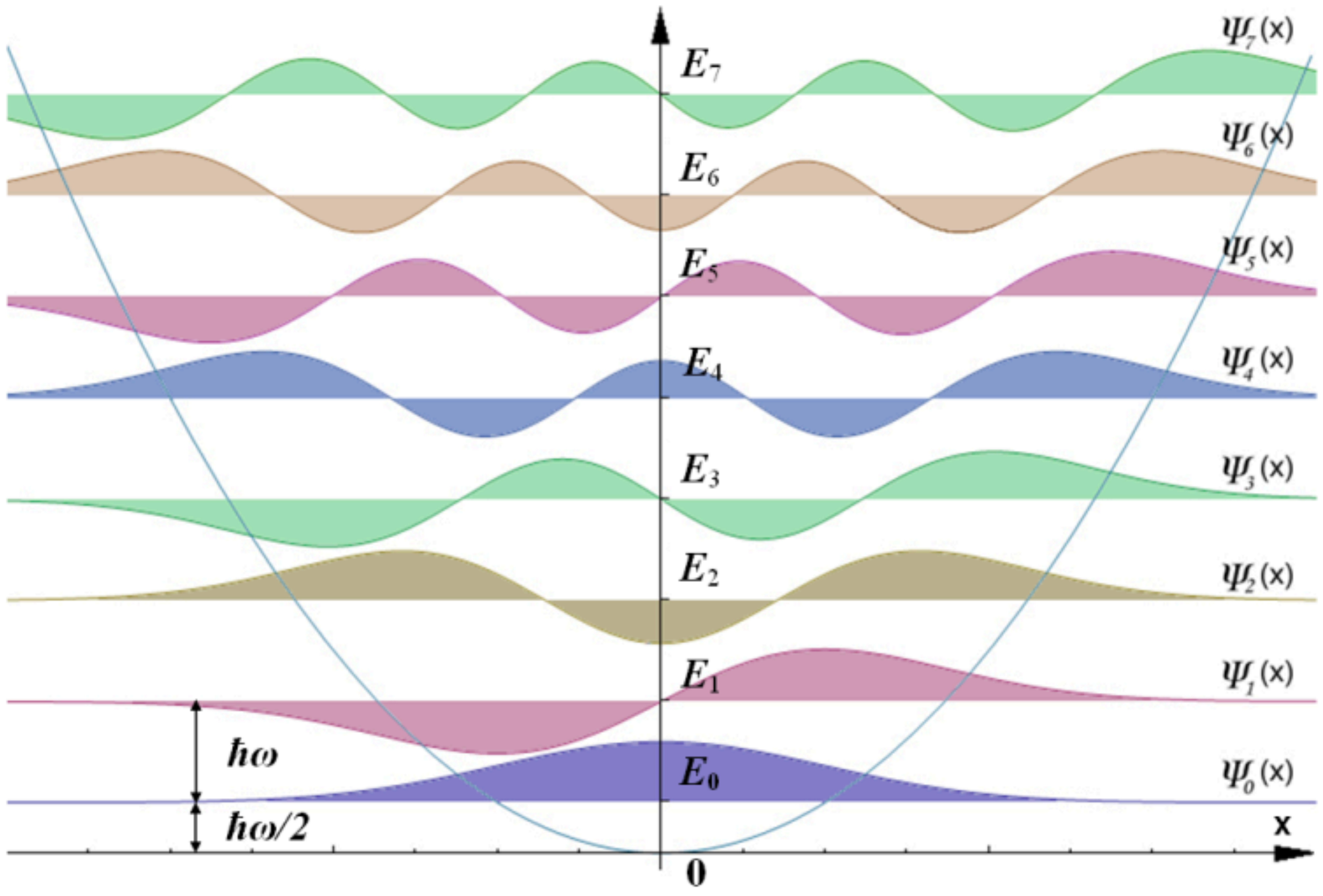
$$S = k_B \log W$$

Entropy



Macrostates	Microstates	W
HH	HH	1
HT	HT, TH	2
TT	TT	1

Quantum Harmonic Oscillators



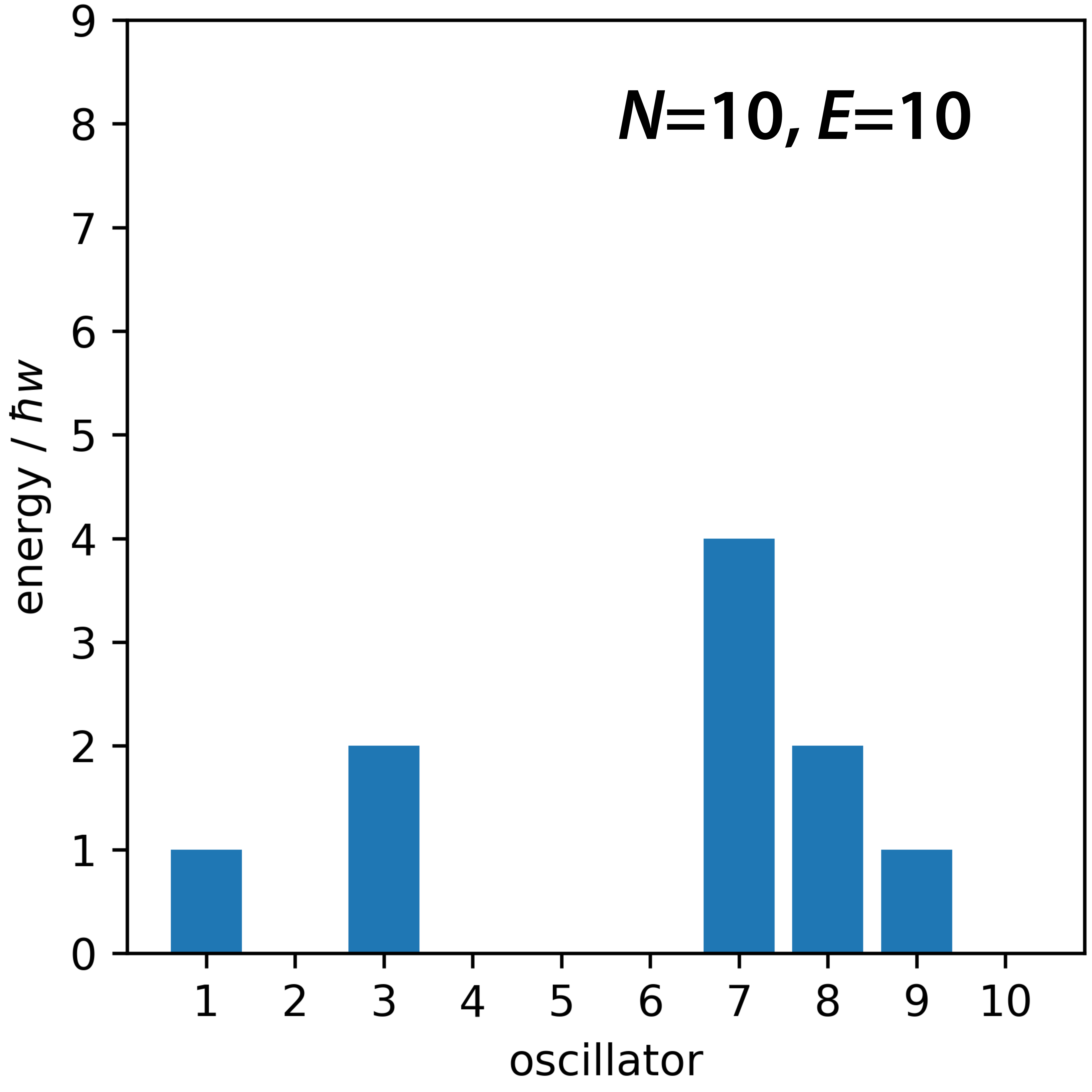
- a harmonic oscillator has equally spaced energy levels:

$$E_k = (k + \frac{1}{2})\hbar w$$

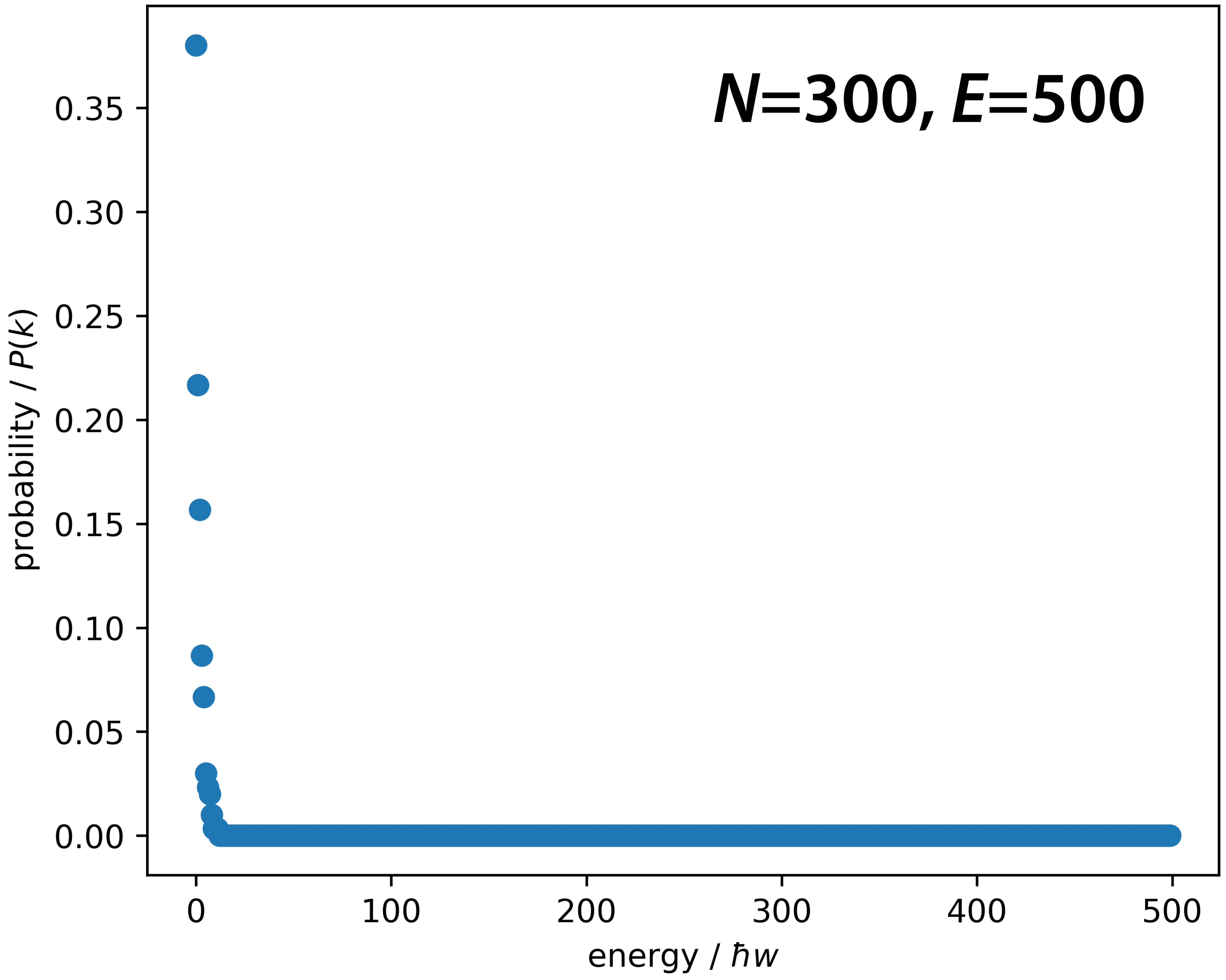
- A series of oscillators (*N*) can emit photons immediately absorbed by another oscillator.
- For an isolated system total energy is constant (*E*).

A Simple Simulation

```python
import numpy as np
import copy


def harmonic_oscillators(N, E, t):
    #initialise oscillators
    oscillators = np.zeros(N)
    oscillators[0] = E
    #print(oscillators)

    #loop over t steps
    for step in range(t):

        #take a trial move
        oscillators_trial = copy.deepcopy(oscillators)

        #randomly exchange energy
        A =  np.random.randint(0, high=N)
        B =  np.random.randint(0, high=N)
        oscillators_trial[A] = oscillators_trial[A]+1
        oscillators_trial[B] = oscillators_trial[B]-1

        #test if move is unphysical and reject
        if any(i < 0 for i in oscillators_trial):
            continue

        #accept move
        oscillators =  copy.deepcopy(oscillators_trial)

    return(oscillators)

num_oscillators = 10
total_energy = 10
eq_oscillators =
harmonic_oscillators(num_oscillators,total_energy,1000000)
```



Entropy of Quantum Harmonic Oscillators



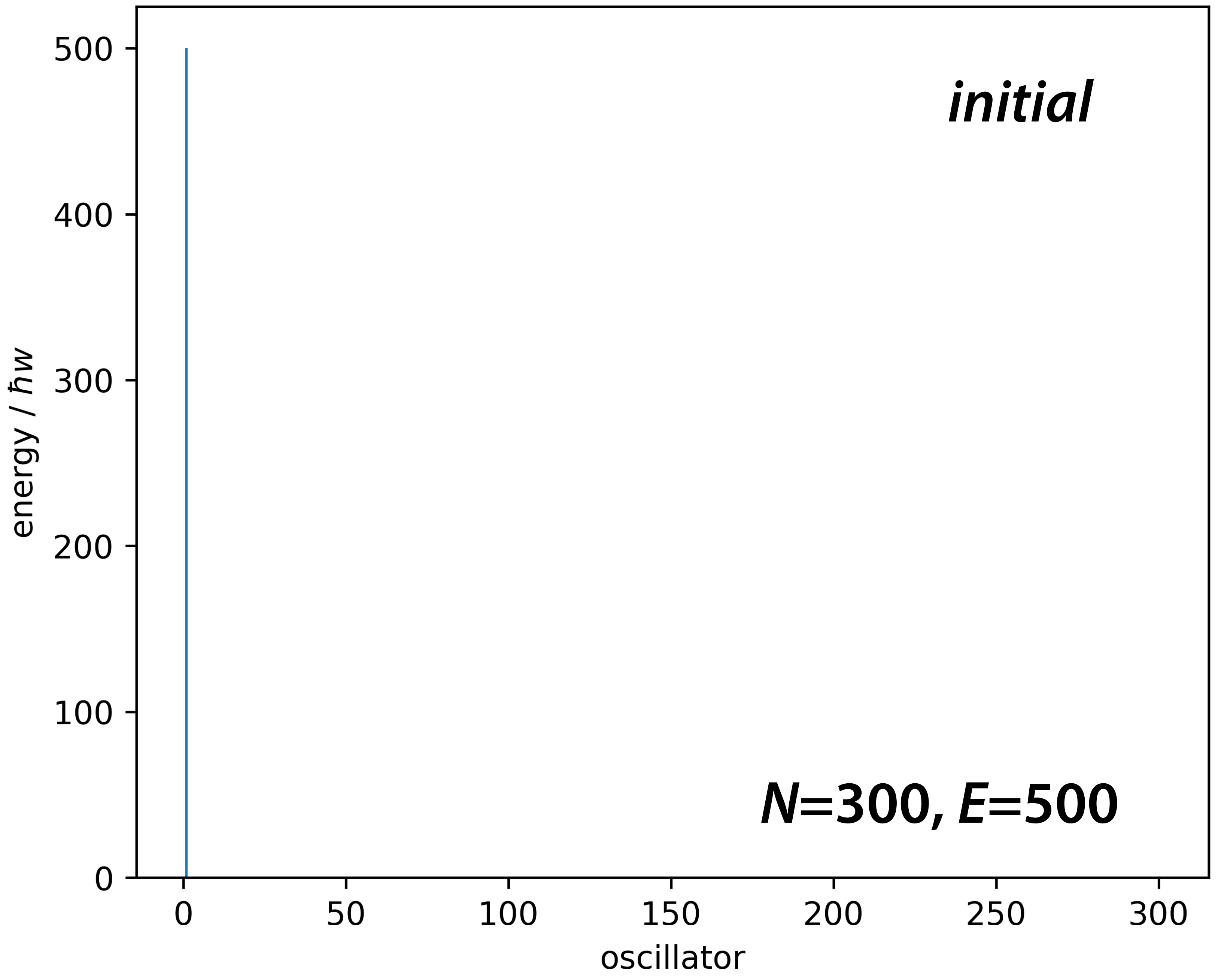
- Consider the probability, *P(k)*, of finding an oscillator with energy $k\,\hbar w$.
- We find the most probable state is the energy at k=0 (ground state).
- This actually follows the relationship:

$$P(k) = \frac{\exp(-\beta E_k)}{q}$$

Time Dependence

$$S = -Nk_B \sum_k P(k)\ln[P(k)]$$

- Consider the system in an initial starting configuration.
- For each time step one quanta of energy is transferred between random oscillators.
- How does entropy change over time?



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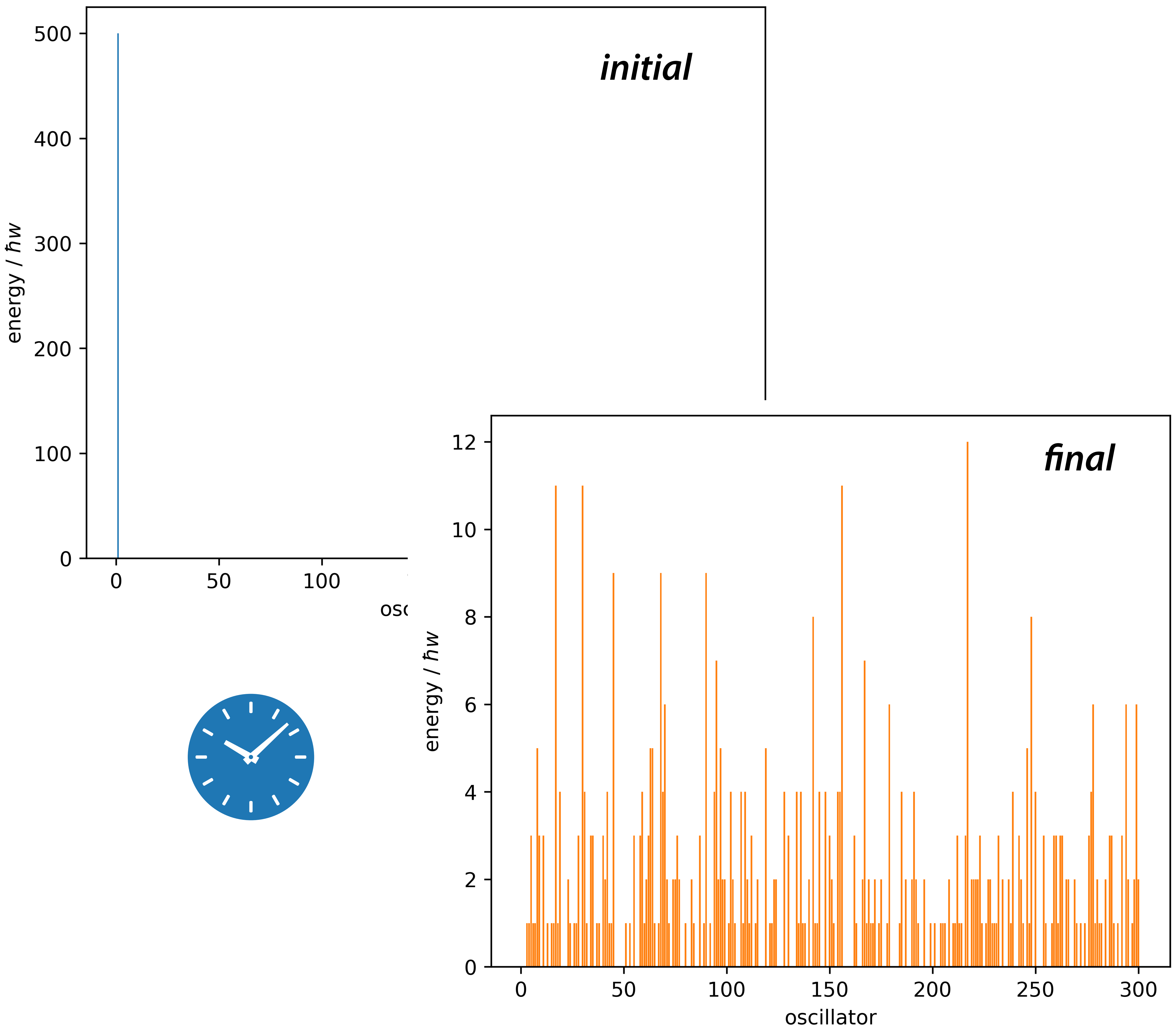

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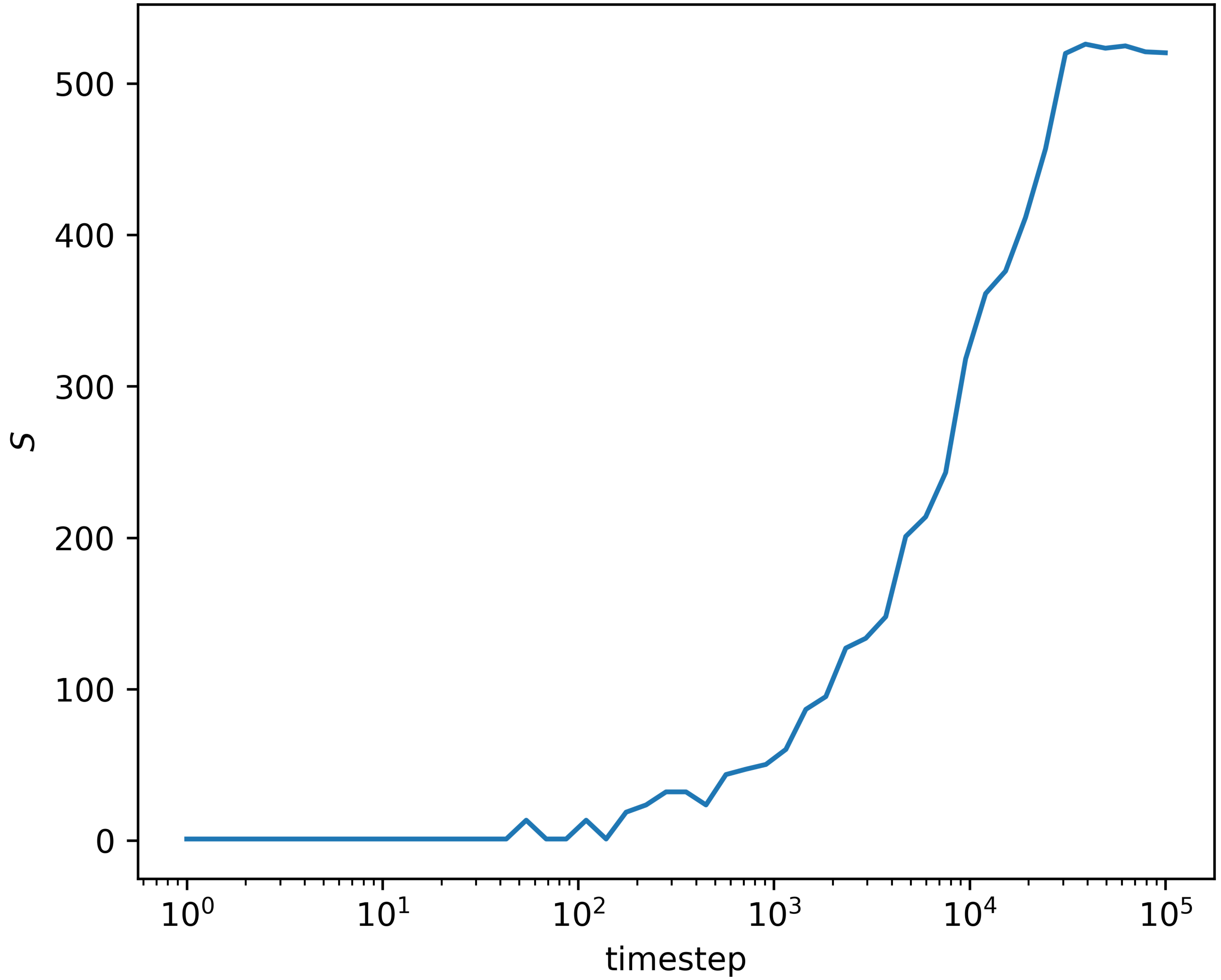

- Entropy increases over time!
- Demonstration of the second law of thermodynamics:

"total entropy of an isolated system can never decrease over time"