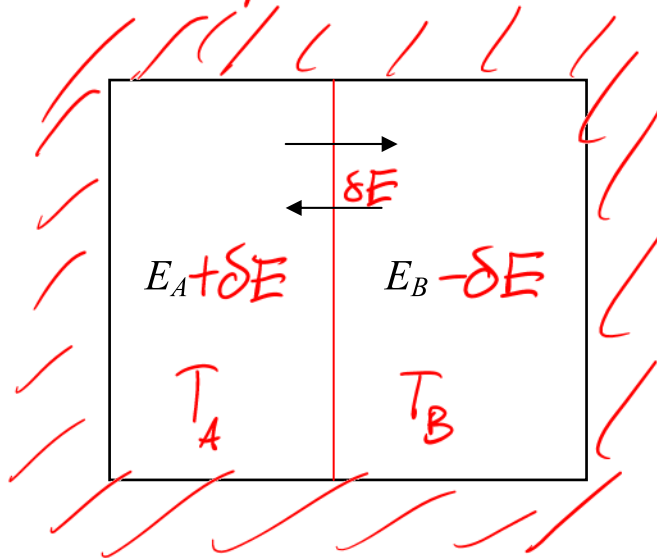


## Chapter 2.6: Microcanonical Irreversibility

Equilibrium is "most probable" state

Consider the change of entropy under energy exchange

How likely is heat exchange, What is probability to find  $E_A, E_B$



$$S = k_B \ln \Omega(E_A, E_B) = k_B \ln \Omega_A(E_A) \Omega_B(E_B)$$

$$\delta S = k_B \delta (\ln \Omega_A + \ln \Omega_B)$$

$$= k_B \frac{\partial \ln \Omega_A}{\partial E_A} \delta E - \frac{\partial \ln \Omega_B}{\partial E_B} \delta E + \mathcal{O}(\delta E^2)$$

$$= k_B (\beta_A - \beta_B) \delta E + \mathcal{O}(\delta E^2)$$

$$k_B \beta = \frac{1}{T}$$

Entropy increase

$$\delta S = \left( \frac{1}{T_A} - \frac{1}{T_B} \right) \delta E + \mathcal{O}(\delta E^2)$$

Number of states increases if  $T_A < T_B$  and  $\delta E > 0$

$$S = k_B \ln \Omega$$

$$\Omega = e^{S/k_B}$$

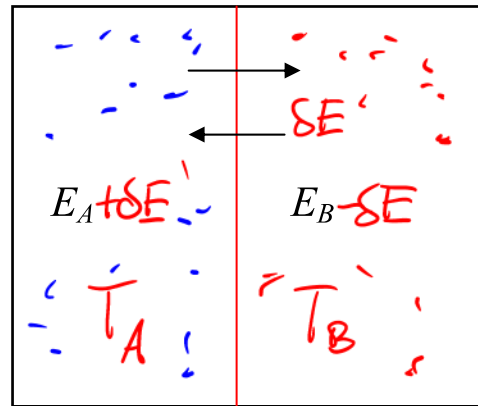
$$\Omega(E_A + \delta E, E_B - \delta E) = e^{\frac{S + \delta S}{k_B}} = \underbrace{\Omega(E_A, E_B)}_{\Omega_{\text{before}}} e^{\frac{\delta S}{k_B}}$$

$$\frac{\Omega_{\text{after}}}{\Omega_{\text{before}}} = e^{\frac{\delta S}{k_B}} = e^{\frac{1}{k_B} \left( \frac{1}{T_A} - \frac{1}{T_B} \right) \delta E} = e^{(\beta_A - \beta_B) \delta E}$$

exponentially more likely to transfer heat from  $T_A < T_B$   
 $\rightarrow$  2nd law of thermodyn.

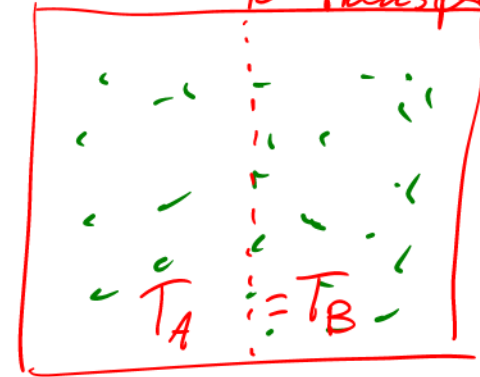
Probability  
of change

**Summary:** All microstates with the same total energy are equally probable, but overwhelmingly many are observed in equilibrium.



time  $\rightarrow$

exponentially likely/unlikely to transfer heat



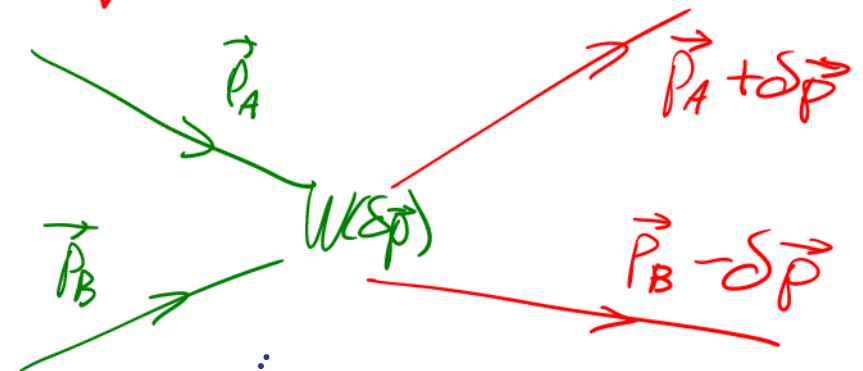
Arrow of time is "more likely"

## Boltzmann H-Theorem (1872)

assume time-reversible laws with  
 with uncorrelated scattering events

derive that  $S(t)$  increases in time  
 not a "general" proof

scattering probability



**Criticism:**

Loschmidt Paradox (1876)

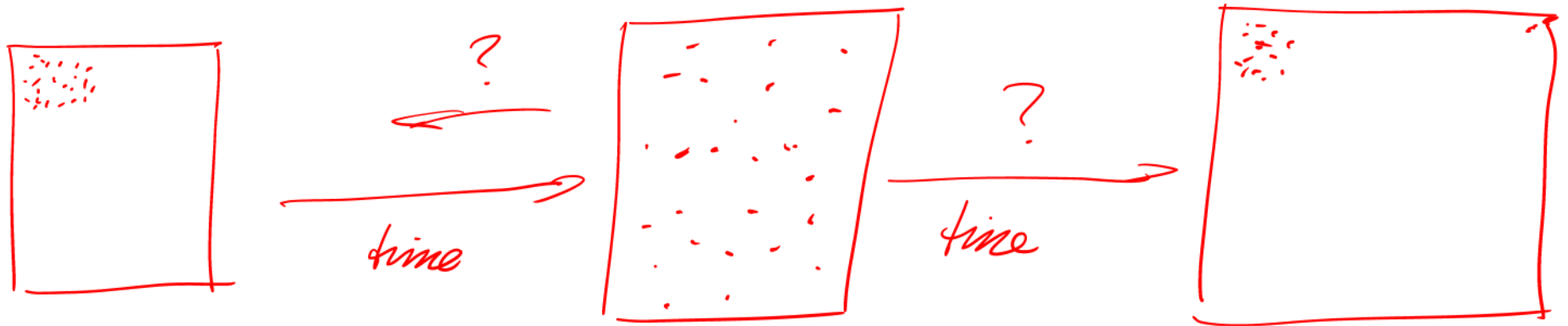
If microscopic laws are time reversible, entropy will decrease if initial state is taken with all velocities reversed.

*start with "later state" equally likely if  $\vec{p}_j \rightarrow -\vec{p}_j$*

Poincare (1890) and Zermelo (1896)

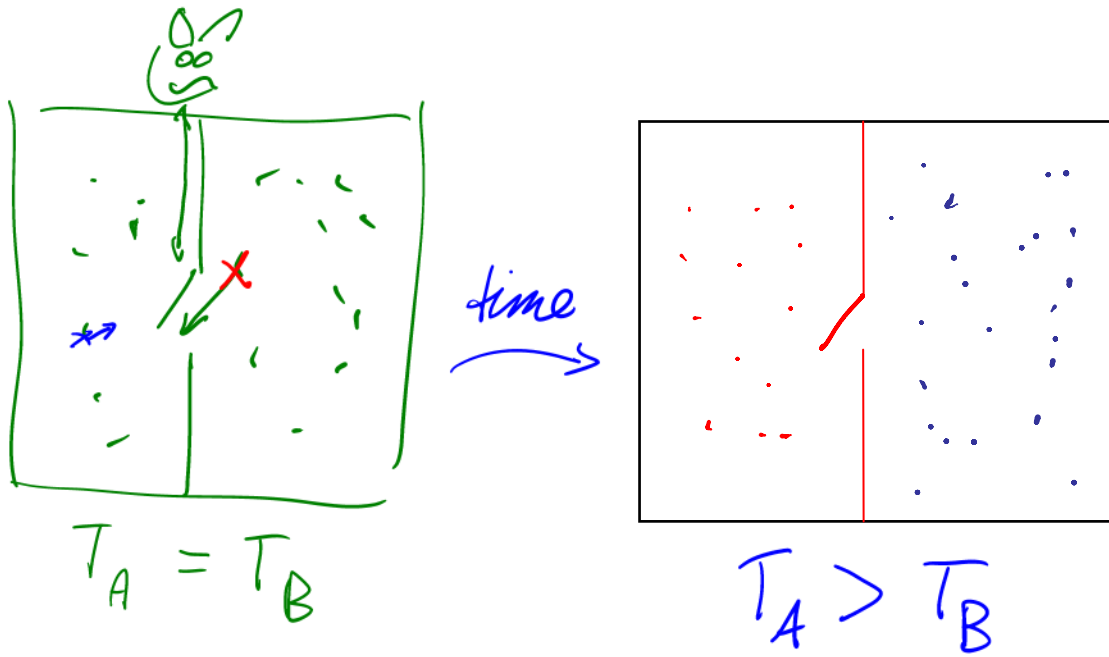
Recurrence theorem

In certain dynamical systems the time evolved state will return arbitrarily close to the initial state in finite time.

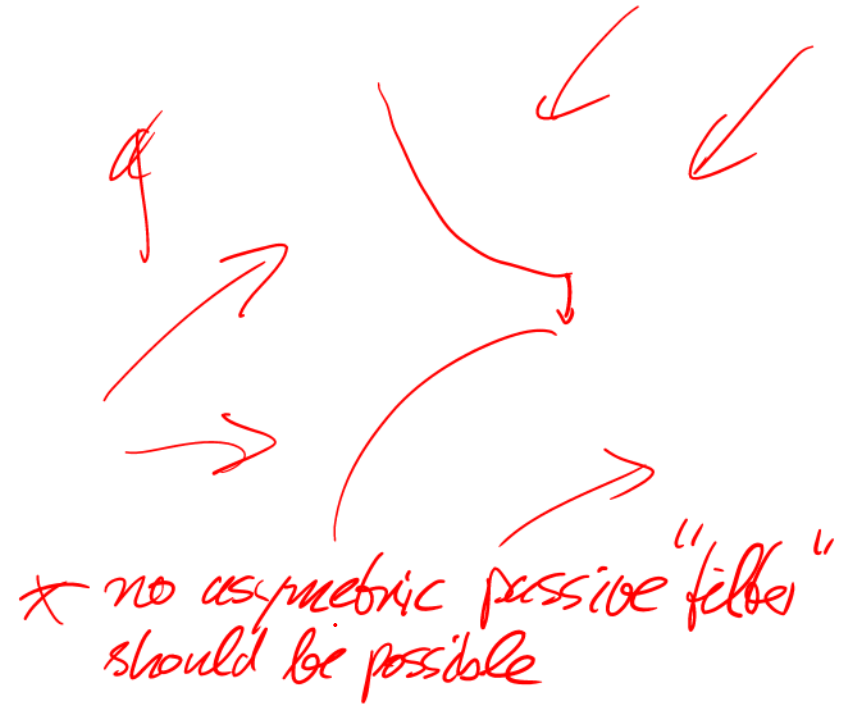


$$|\Gamma_{\text{initial}} - \Gamma_{\text{final}}| < \underline{\delta\Gamma} \quad t(\delta\Gamma)$$

Maxwell's Demon (1867)



open if cold particle from left  
or hot from right  
closed otherwise



\* no asymmetric passive "filter" should be possible

Maxwell Demon requires negative entropy to work

- measure momenta of particle
  - information increase
  - entropy decrease
- blocking?