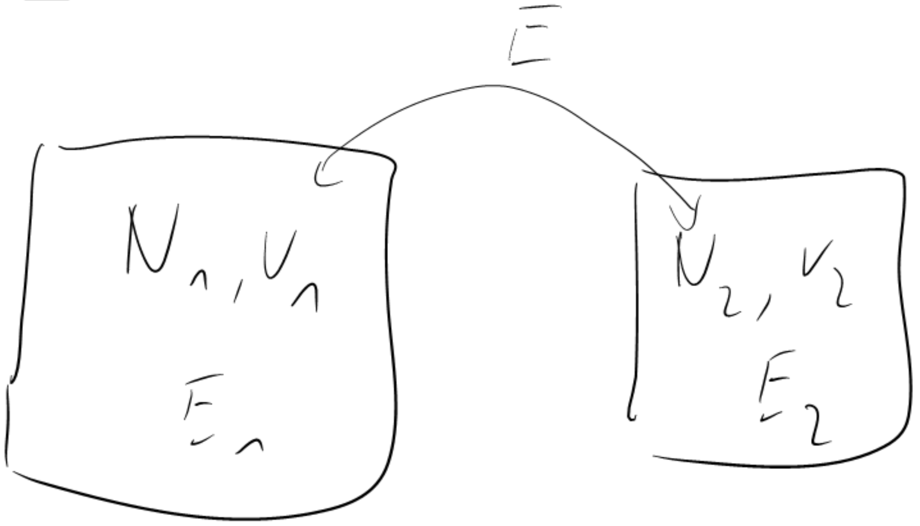
Temperature



N_1, N_2 fixed

V_1, V_2 fixed

$E_1 + E_2 = E$

$E_1 \geq 0 \quad , E_2 \geq 0$

$$\boxed{\Omega_{tot}(E) = \frac{1}{\Delta E} \int_0^E dE_1 \; \Omega_1(E_1) \, \Omega_2(E - E_1)}$$

PROOF

$$\Omega_1(E_1) = \frac{\Delta E}{N_1!}\,\frac{1}{(2\pi\hbar)^{3N_1}} \int d\Gamma_1 \, \delta\left[H_1(\Gamma_1) - E_1\right] =$$

$$= \frac{1}{2\pi}\,\frac{\Delta E}{N_1!}\,\frac{1}{(2\pi\hbar)^{3N_1}} \int_{-\infty}^{\infty} dq_1 \int d\Gamma_1 \exp\left[i q_1 (H_1 - E_1) \right]$$

$= E - E_1$

$$\Omega_2(E_2) = \frac{1}{2\pi}\,\frac{\Delta E}{N_2!}\,\frac{1}{(2\pi\hbar)^{3N_2}} \int dq_2 \int d\Gamma_2 \exp\left(i q_2 (H_2 - E + E_1) \right)$$

$$\frac{1}{\Delta E} \int_{-\infty}^{+\infty} dE_1 \, \Omega_1(E_1) \, \Omega_2(E - E_1) =$$

$$= \frac{1}{(2\pi)^2} \frac{\Delta E}{N_1!\, N_2!} \frac{1}{(2\pi\hbar)^{3(N_1+N_2)}} \int d\Gamma_1 \int d\Gamma_2 \int dq_1 \int dq_2$$

$$\exp\left[i\left(q_1 H_1 + q_2 (H_2 - E)\right)\right] \underbrace{\int dE_1 \exp\left[i(q_2 - q_1)E_1\right]}_{2\pi\,\delta(q_2 - q_1)} =$$

$$= \frac{1}{2\pi} \frac{\Delta E}{N_1!\, N_2!} \frac{1}{(2\pi\hbar)^{3(N_1+N_2)}} \int d\Gamma_1 \int d\Gamma_2 \underbrace{\int dq_1 \exp\left[iq_1 (H_1 + H_2 - E)\right]}_{= 2\pi\,\delta(H_1 + H_2 - E)}$$

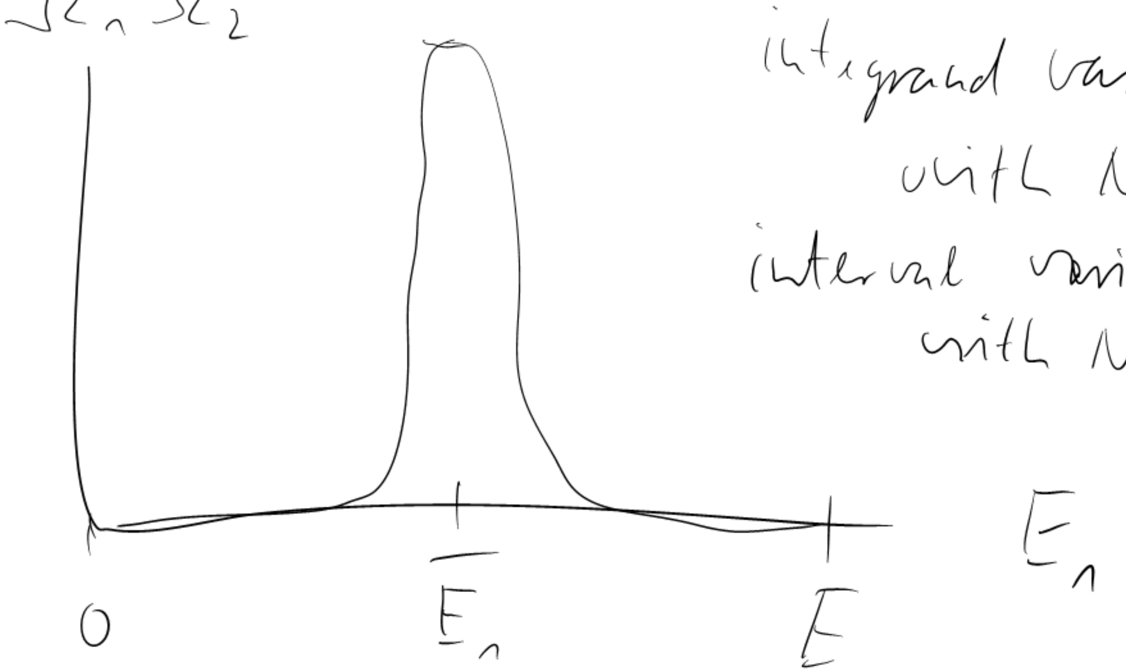
$$= \frac{\Delta E}{N_1!\, N_2!} \frac{1}{(2\pi\hbar)^{3(N_1+N_2)}} \int d\Gamma_1 \int d\Gamma_2\, \delta(H_1 + H_2 - E) = \Omega_{tot}(E) \checkmark$$

$$\Omega_{tot}(E) = \frac{1}{\Delta E} \int_0^E dE_1\, \Omega_1(E_1)\, \Omega_2(E - E_1)$$

$$S_{tot}(E) = \ln \Omega_{tot}(E) \quad \text{vs.} \quad S_1(E_1) = \ln \Omega_1(E_1)$$

$$S_2(E_2) = \ln \Omega_2(E_2)$$

Idea:



integrand varies exponent. with N

interval varies only linearly with N

appr.

$$\text{integral} = \underbrace{\text{term } 1}_{\hookrightarrow\ \text{exp. in } N} \times \underbrace{\text{term } 2}_{\hookrightarrow\ \text{lin. in } N}$$

$$\Rightarrow \ln(\text{integral}) = \ln(\text{term } 1) + \ln(\text{term } 2)$$

$$\sim \ln e^{N} \qquad \ln N$$

$$\sim N \qquad \ln N \longrightarrow \text{NEGLECT}$$

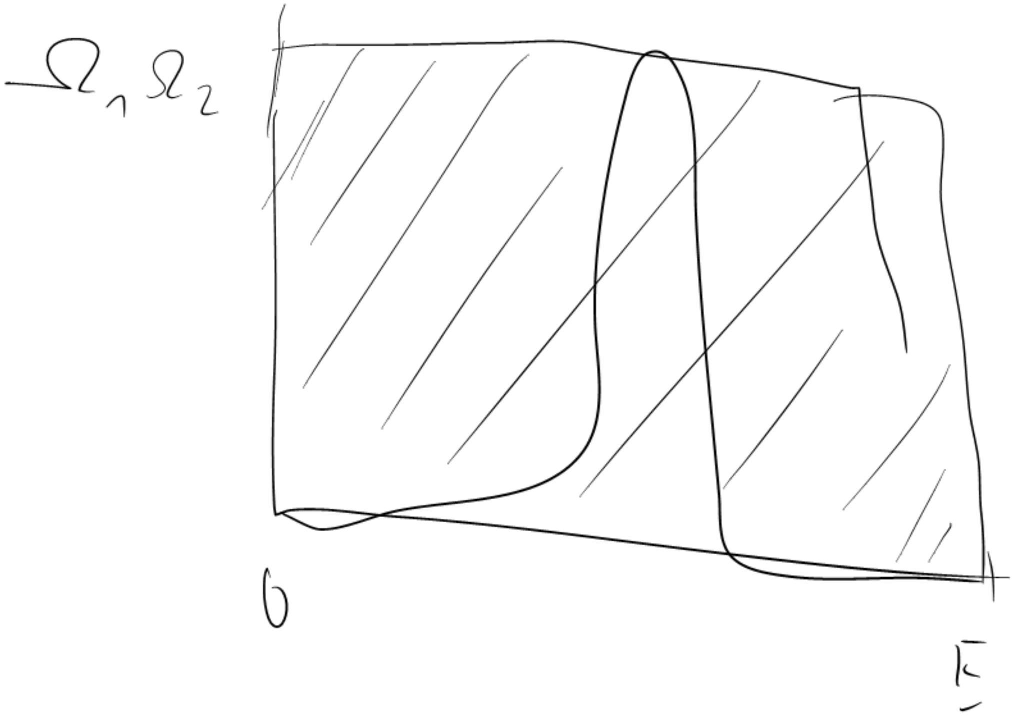
$\rightsquigarrow$ important technique in Stat Phys:

replace an integral by the maximum value of the integrand

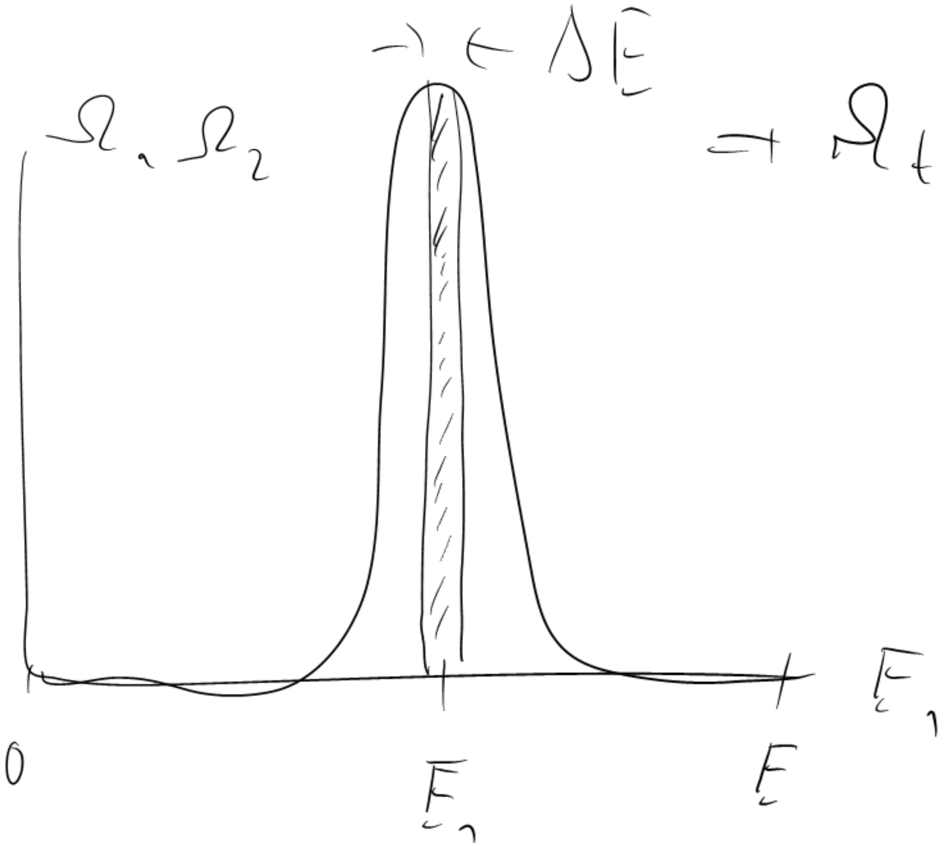
More precisely: $\bar{E}_1$ is given by

$$\Omega_1(\bar{E}_1)\,\Omega_2(E-\bar{E}_1) = \max_{E_1} \Omega_1(E_1)\,\Omega_2(E-E_1)$$

$$\Omega_{tot}(E) \le \Omega_1(\bar{E}_1)\,\Omega_2(E-\bar{E}_1)\,\frac{E}{\Delta E}$$



on the other hand:



$$\Rightarrow \Omega_{tot}(E) \geq \Omega_1(\bar{E}_1)\,\Omega_2(E-\bar{E}_1)\frac{\Delta E}{\Delta E}$$

$$= \Omega_1(\bar{E}_1)\,\Omega_2(E-\bar{E}_1)$$

together:

$$\underbrace{\Omega_1(\bar{E}_1)\,\Omega_2(E-\bar{E}_1) \leq \Omega_{tot}(E) \leq \Omega_1(\bar{E}_1)\,\Omega_2(E-\bar{E}_1)\frac{E}{\Delta E}}_{\ln\ \Rightarrow}$$

$$\underbrace{S_1(\bar{E}_1)}_{\propto N_1} + \underbrace{S_2(E-\bar{E}_1)}_{\propto N_2} \leq \underbrace{S_{tot}(E)}_{\propto N_1+N_2} \leq \underbrace{S_1(\bar{E}_1)}_{\propto N_1} + \underbrace{S_2(E-\bar{E}_1)}_{\propto N_2} + \underbrace{\ln\frac{E}{\Delta E}}_{\propto \ln(N_1+N_2)}$$

in the thermodynamic limit:

$$\boxed{S_{tot} = S_1 + S_2}$$

Determine $\bar{E}_1$:

$$0 = \frac{\partial}{\partial E_1}\left[S_1(E_1) + S_2(E-E_1)\right] = \frac{\partial S_1(E_1)}{\partial E_1} - \frac{\partial S_2(E_2)}{\partial E_2}\Bigg|_{E_2 = E-E_1}$$

Definition: $\beta = \frac{1}{T} = \frac{\partial S}{\partial E}$ T Temperature!

Two systems in thermal contact in equilibrium must have the same temperature!

If $E_1 \neq \bar{E}_1$ before contact: Then relaxation into equilibrium

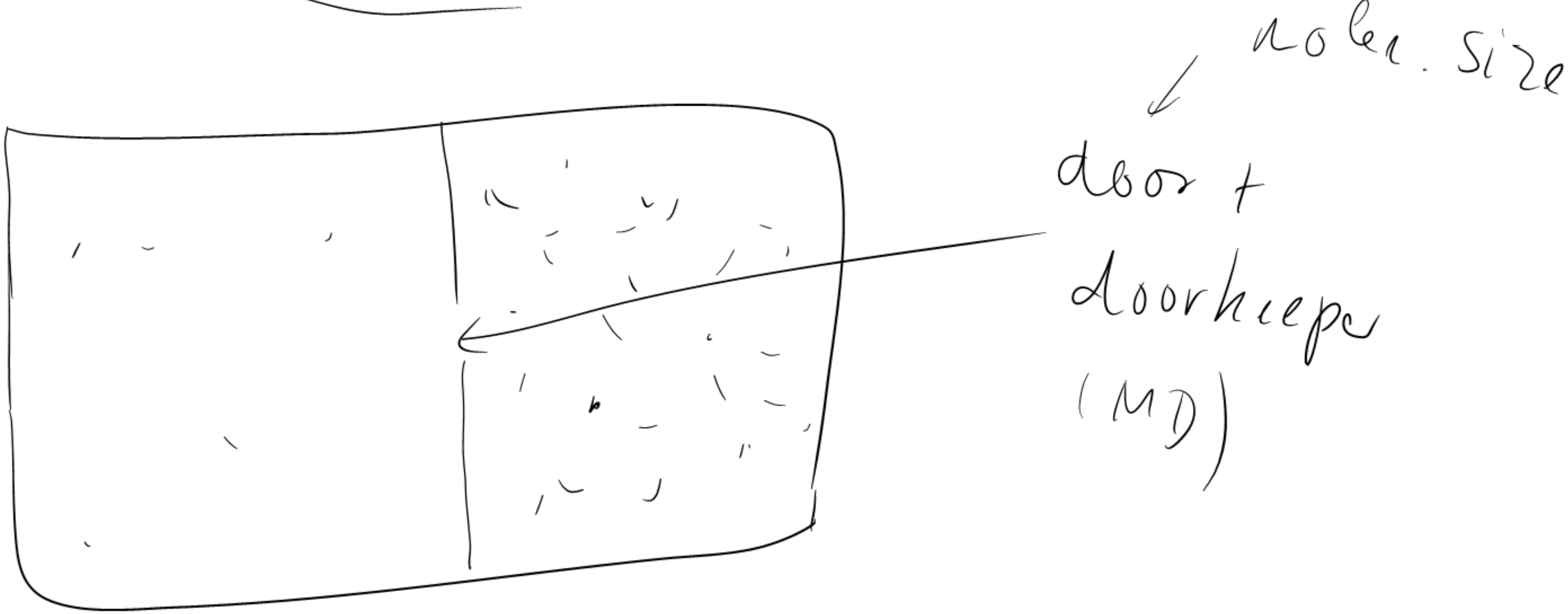
Before: $S_{\text{before}} = S_1(E_1) + S_2(E - E_1)$

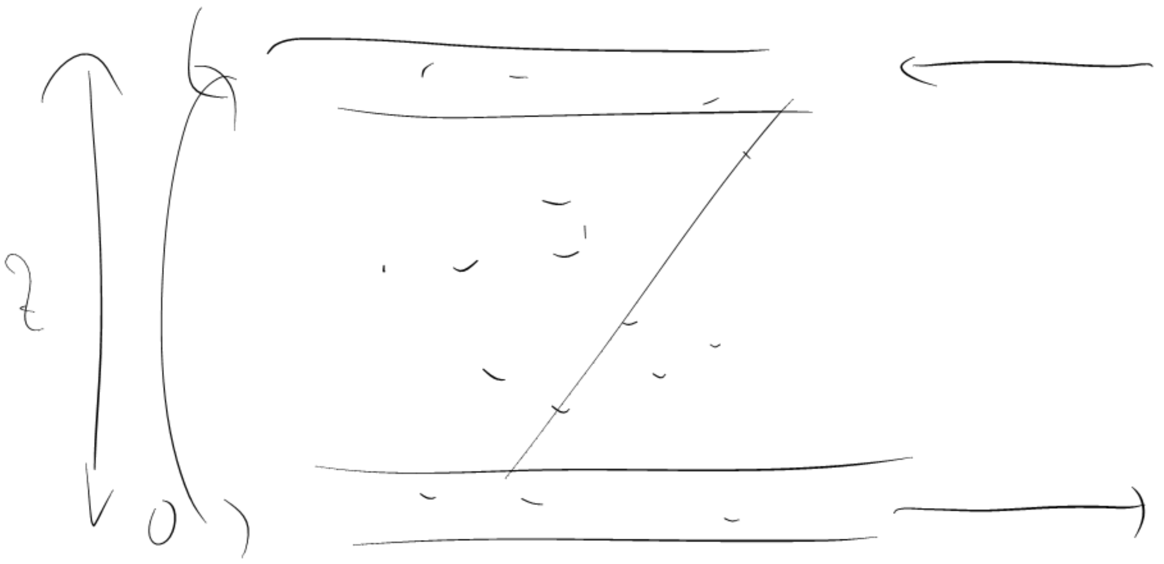
After: $S_{\text{after}} = S_1(\bar{E}_1) + S_2(E - \bar{E}_1) \geq S_{\text{before}}$

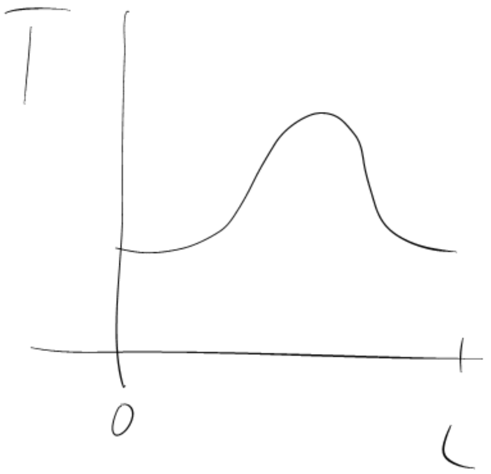
$$\boxed{\Delta S \geq 0}$$ (2nd law of thermodynamics)

This is true more generally: In an isolated system only such state changes are possible that either increase the entropy or leave it constant.

Means: The system grabs as much phase space as it can, only restricted by boundary conditions or conservation laws. If I want to decrease the entropy (i.e. the phase space volume), I have to change the boundary conditions. But this cost, either energy, or INFORMATION (→ Maxwell demon)







F. M.-Plathe (1994 ± 3)
PRE / JCP

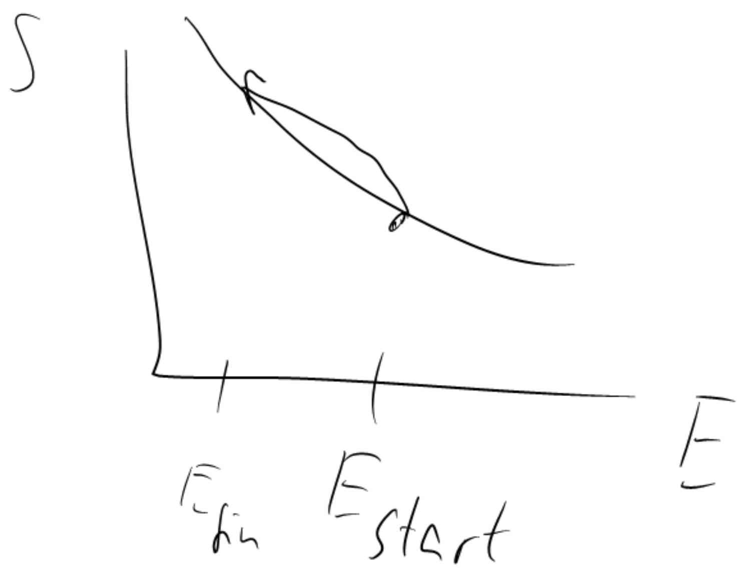
MD - MD

Maxwell demon

molecular dynamics

T is always positive. Proof: Assume $T < 0$ or $\beta < 0$

$$\rightarrow \frac{\partial S}{\partial E} < 0$$



$$\Downarrow$$

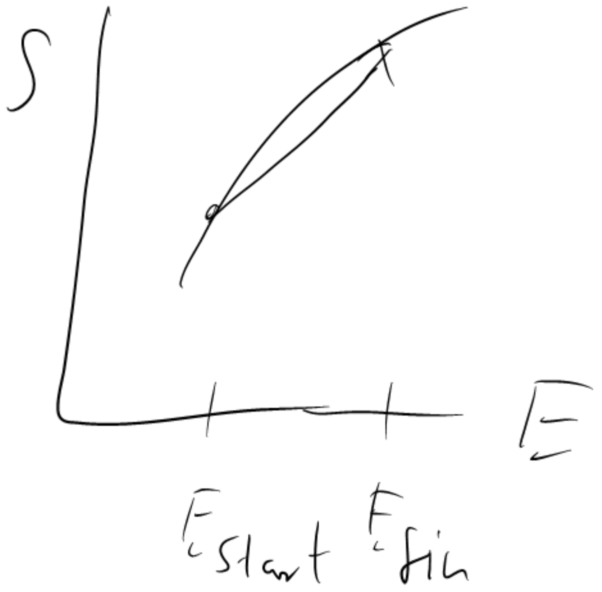
$$E_{fin} < E_{start}$$

System increases the entropy by releasing energy to the surroundings!

→ fundamentally instable situation

Conversely

$T > 0$



$E_{fin} > E_{start}$ will only happen if the additional energy is *available* from the outside world process of energy exchange between to systems.

(quasi-static)

$$\frac{dE_1}{dt} = -\frac{dE_2}{dt} > 0$$

(assume that E_1 increases, i.e. $E_1(\text{start}) < \bar{E}_1$)

$$0 < \frac{d}{dt} S_{tot} = \frac{d}{dt} S_1 + \frac{d}{dt} S_2 = \underbrace{\frac{\partial S_1}{\partial E_1}}_{\beta_1} \frac{d}{dt} E_1 + \underbrace{\frac{\partial S_2}{\partial E_2}}_{\beta_2} \frac{d}{dt} E_2$$

$$= \underbrace{\frac{dE_1}{dt}}_{>0} (\beta_1 - \beta_2)$$

$\Rightarrow \beta_1 > \beta_2$ or $T_1 < T_2$

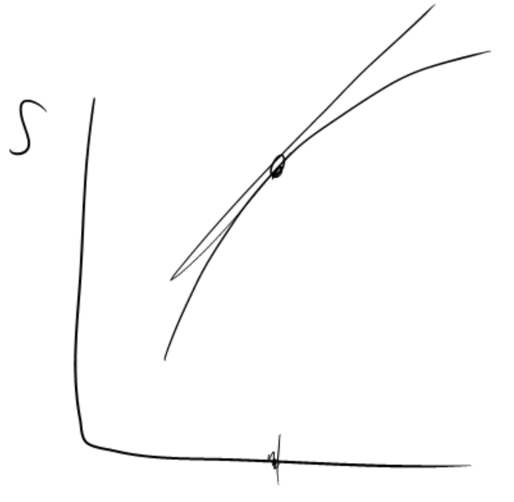
energy flows to the COLD body!

Assume: Body 1 & body 2 have the same physical properties (same material, same conditions)

$\Rightarrow S_1(E_1)$, $S_2(E_2)$ are the same functions

$e := \frac{E}{N}$ energy per particle $\quad s = \frac{S}{N}$ entropy per particle

$$\beta = \frac{\partial S}{\partial E} = \frac{\partial s}{\partial e}$$



$\boxed{\beta_1 = \beta_2} \Rightarrow$

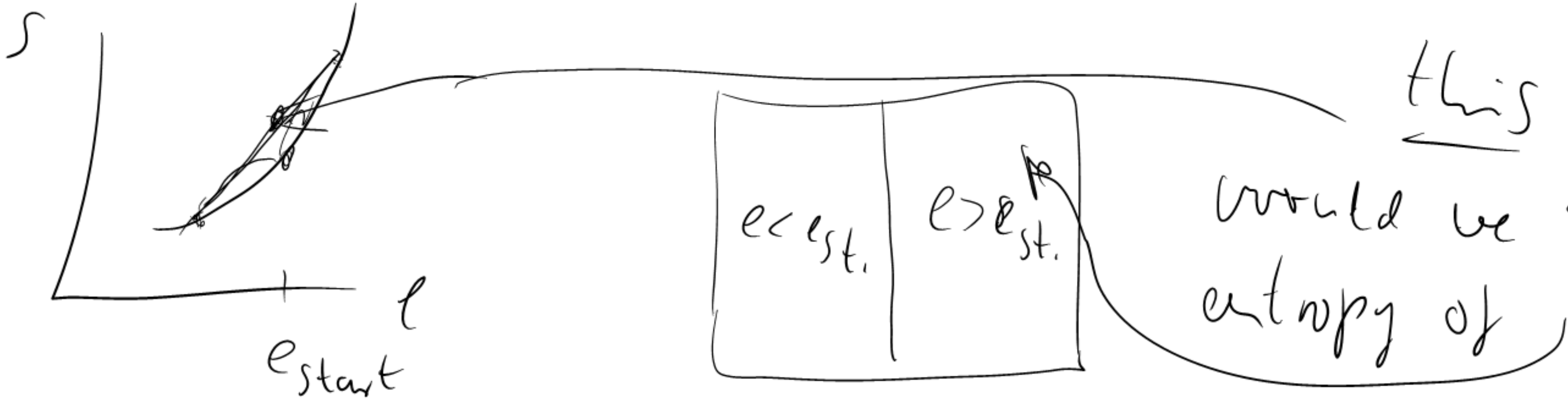
$\Rightarrow$ same slope

$\Rightarrow$ same e

$\Rightarrow$ energy is distributed onto the two bodies according to the respective particle numbers (or volumes)

Remark: $s(e)$ must be concave! **Proof:**

Assume $s(e)$ convex i.e. $\frac{\partial^2 s}{\partial e^2} > 0$



this would be the entropy of this state

i.e. System could increase its entropy by decaying into subsystems with different energy density! Instable! → Prohibited!

Back to the ideal gas

$$S(E) = \frac{3}{2} N \ln E + \text{terms independent of } E$$

$$\beta = \frac{\partial S}{\partial E} = \frac{3}{2} N \frac{1}{E} = \frac{1}{T} \Rightarrow \boxed{E = \frac{3}{2} NT}$$