

Thu 14 Mar

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Plan

Mixing entropy

Therm. cycles

Otto cycle ~ petrol engine

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Useful trick:  $\Delta S_{\text{mix}} = S_c - S_0 = \frac{\partial}{\partial T} (T \log Z_c - T \log Z_0)$   
 $= \frac{\partial}{\partial T} (T \log \left( \frac{Z_{oc}}{Z_0} \right))$

$$\frac{Z_c}{Z_0} = \frac{\frac{1}{(N!)^2} \left( \frac{2V}{\lambda_{th}^3} \right)^{2N}}{\left[ \frac{1}{N!} \left( \frac{V}{\lambda_{th}^3} \right)^N \right]^2} = 2^{2N} \quad (T\text{-indep.})$$

$$\Delta S_{\text{mix}} = 2N \log 2$$

↳ same as fully dist'able

Less info but same relative increase upon mixing

$$S_F = (S_F - S_c) + S_c = \frac{\partial}{\partial T} (T \log \frac{Z_F}{Z_c}) + S_c$$

Gibbs approx. of  $N$  particles on each side

$r$  red on left  $\rightarrow N-r$  blue

$N-r$  red &  $r$  blue on right

$$Z_F = \sum_{r=0}^N Z_r = \sum_r \left[ \frac{1}{r!} \left( \frac{V}{\lambda_{th}^3} \right)^r \frac{1}{(N-r)!} \left( \frac{V}{\lambda_{th}^3} \right)^{N-r} \right]^2$$

$$Z_F = \left(\frac{V}{\lambda_{th}^3}\right)^{2N} \sum_v \frac{1}{(v!)^2 (2N-v)!^2} = \left(\frac{V}{\lambda_{th}^3}\right)^{2N} \frac{1}{(N!)^2} \sum_v \binom{2N}{v}^2$$

$$Z_F = \frac{1}{(N!)^2} \left(\frac{V}{\lambda_{th}^3}\right)^{2N} \binom{2N}{N}$$

$$\frac{Z_F}{Z_C} = \frac{1}{2^{2N}} \binom{2N}{N} \rightarrow S_F = S_C + \log\left(\frac{(2N)!}{(N!)^2}\right) - 2N \log 2$$

$$N \gg 1: S_F \approx S_C + 2N \log 2N - 2N - 2(N \log N - N) - 2N \log 2$$

$$= S_C$$

$$S_F \approx S_C > S_0 \quad \text{consistent w/second law } \checkmark$$

Next correction:  $\log(N!) \approx N \log N - N + \log(\sqrt{2\pi N})$

$$\frac{1}{2} \log(2\pi(2N)) - 2\left(\frac{1}{2} \log(2\pi N)\right) = \log\left(\frac{\sqrt{4\pi N}}{2\pi N}\right) \neq$$

$$= -\log(\sqrt{\pi N}) < 0$$

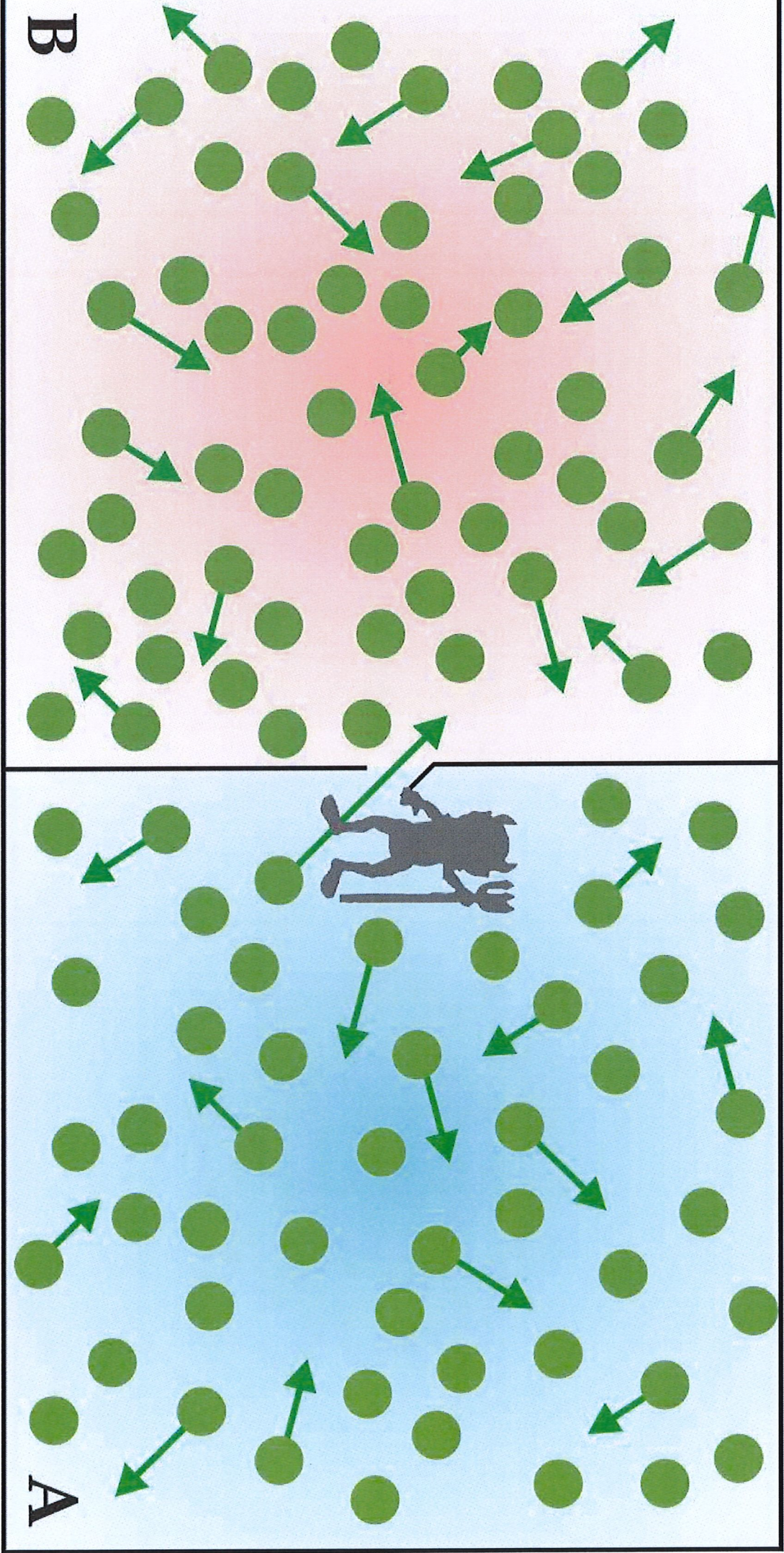
$$\rightarrow S_F \approx S_C - \log(\sqrt{\pi N}) < S_C$$

Solution: Go beyond Gibbs approx ( $N \pm h$ )  
to see second law obeyed

Maxwell's demon (1867) and 2010 experiment (below)

Therm. cycles - two "reservoirs", hot ( $T_H$ ) and cold ( $T_L$ )

otto cycle ~ petrol engine (below)

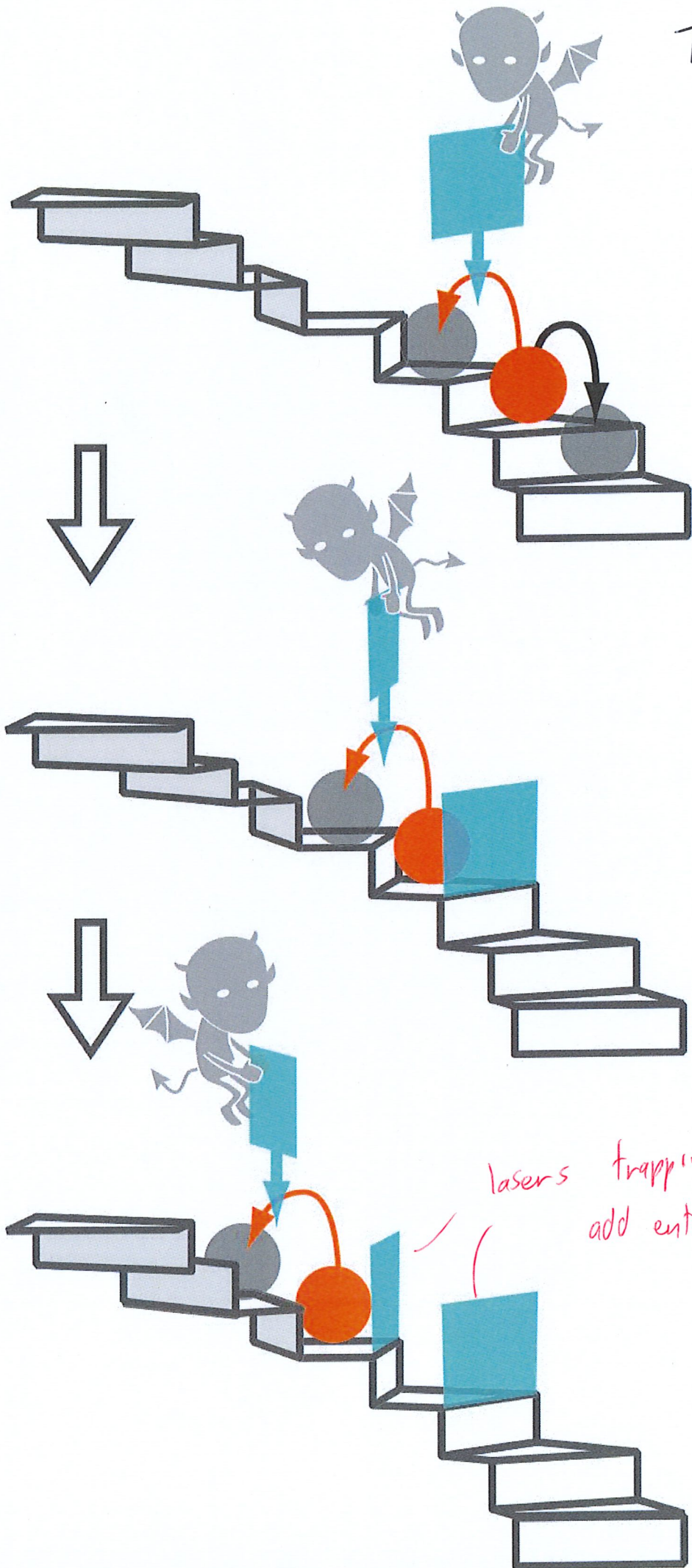


B

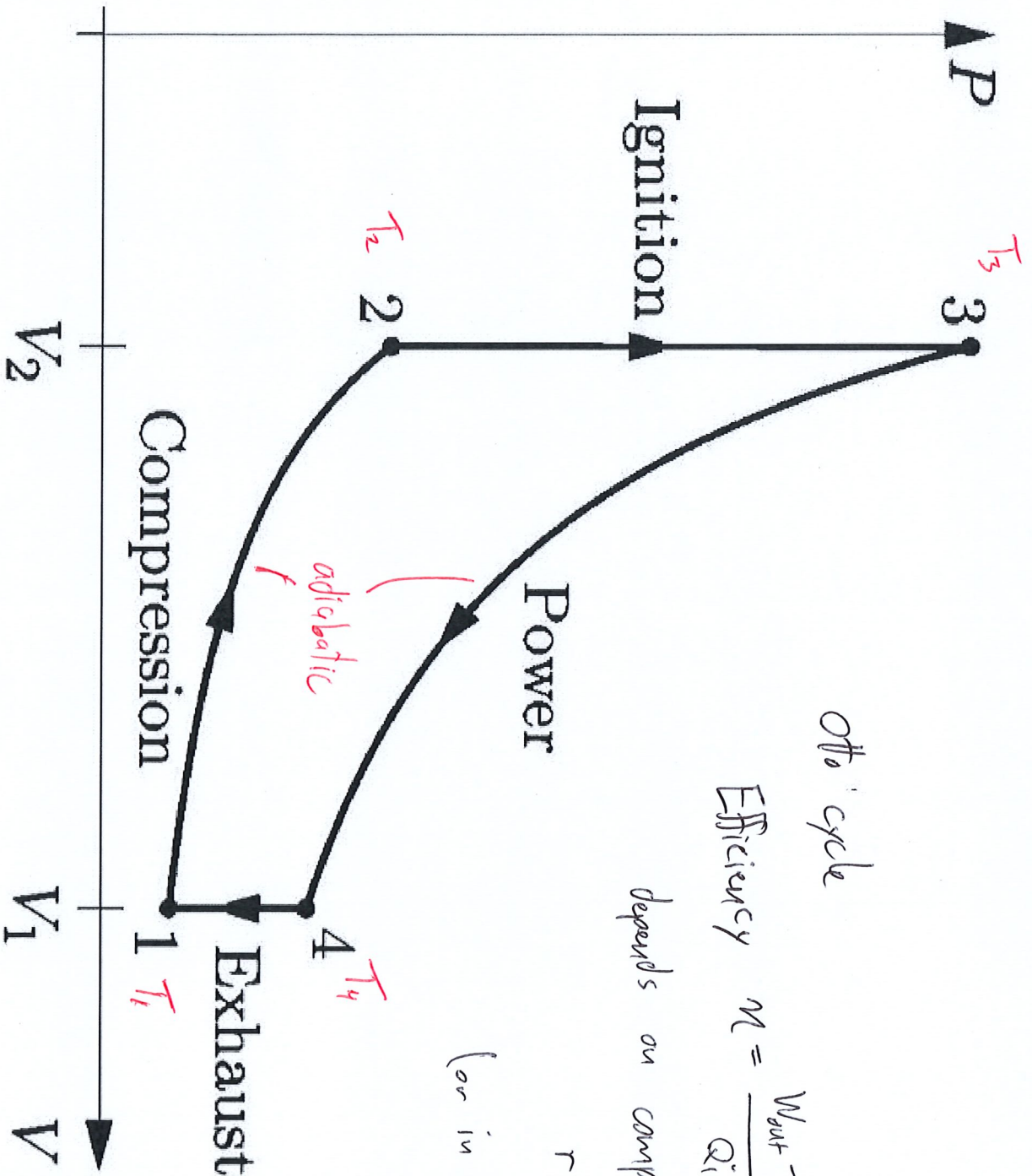
A

$T_B > T_A$

Toyabe et al.  
2010



lasers trapping particles  
add entropy to  
universe



Otto cycle

$$\text{Efficiency } \eta = \frac{W_{\text{out}} - W_{\text{in}}}{Q_{\text{in}}}$$

depends on compression ratio

$$r = \frac{V_1}{V_2} > 1$$

(or in terms of  $T_i$ )

Exhaust - swap w/ fresh