

Thu 13 Mar

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Plan

Mixing entropy

Maxwell's demon

Therm. cycles

otto cycle ~ petrol engine

Useful trick:  $\Delta S_{\text{mix}} = S_c - S_o$

$$= \frac{\partial}{\partial T} (T \log Z_c - T \log Z_o)$$

$$= \frac{\partial}{\partial T} \left( T \log \frac{Z_c}{Z_o} \right)$$

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

$$\Delta S_{\text{mix}} = \log \left( \frac{Z_c}{Z_o} \right) = 2N \log 2 > 0 \quad \checkmark$$

same as fully dist'able!

Less info but same relative increase upon mixing

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

Gibbs approx. of  $N$  particle on each side

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

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

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

$$\frac{Z_F}{Z_C} = \frac{1}{2^{2N}} \binom{2N}{N}$$

$$S_F \approx S_C + \log \left( \frac{(2N)!}{(N!)^2} \right) - 2N \log 2$$

$$\begin{aligned}
N \gg 1: \quad S_F &\approx S_C + 2N \log(2N) - 2N - 2(N \log N - N) - 2N \log 2 \\
&= S_C
\end{aligned}$$

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

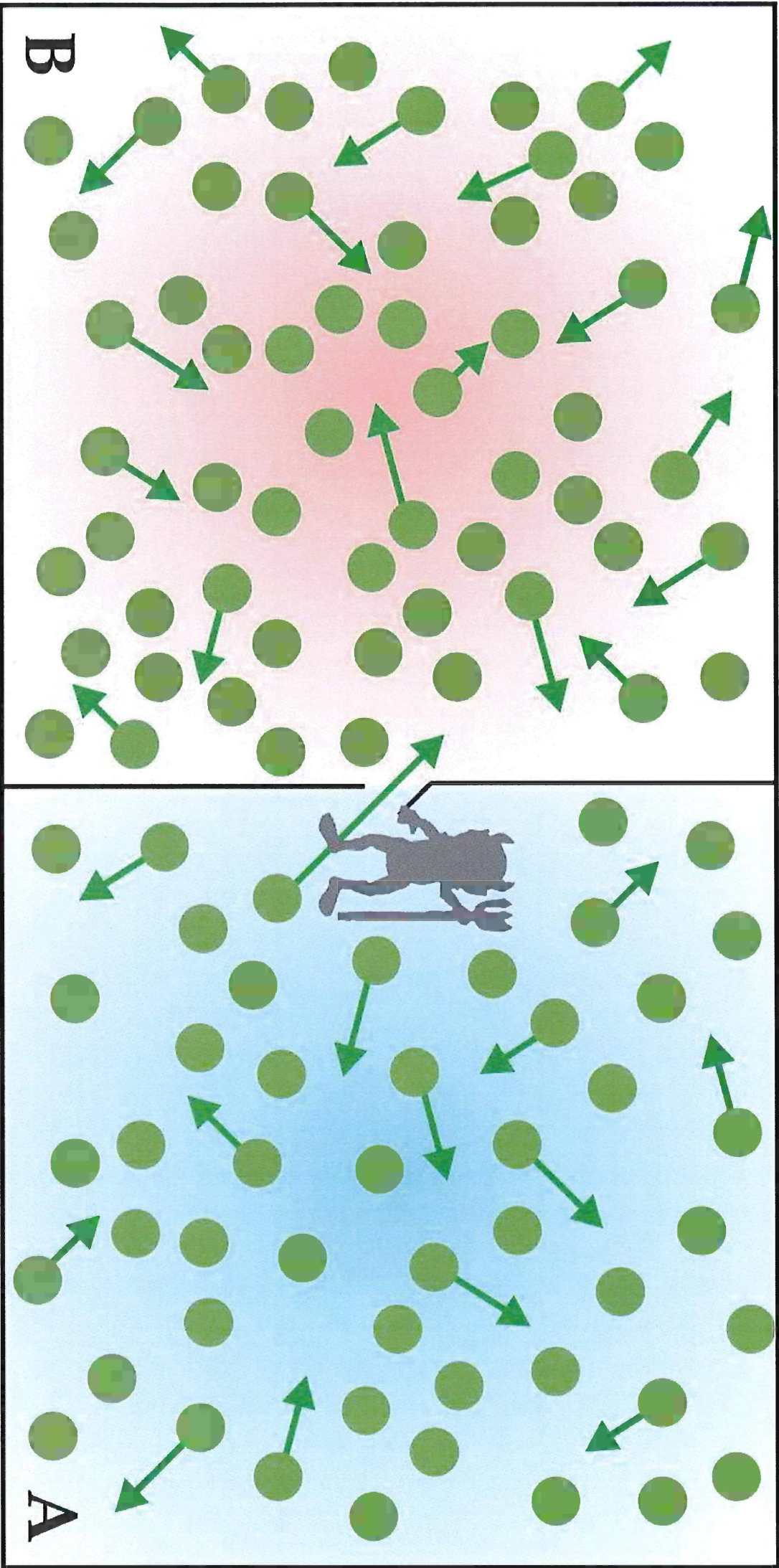
$$\begin{aligned}
\text{Next terms: } &\frac{1}{2} \log(2\pi \cdot 2N) - 2 \cdot \frac{1}{2} \log(2\pi N) \\
&= \log \left( \frac{\sqrt{4\pi N}}{2\pi N} \right) = -\log(\sqrt{\pi N}) < 0
\end{aligned}$$

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

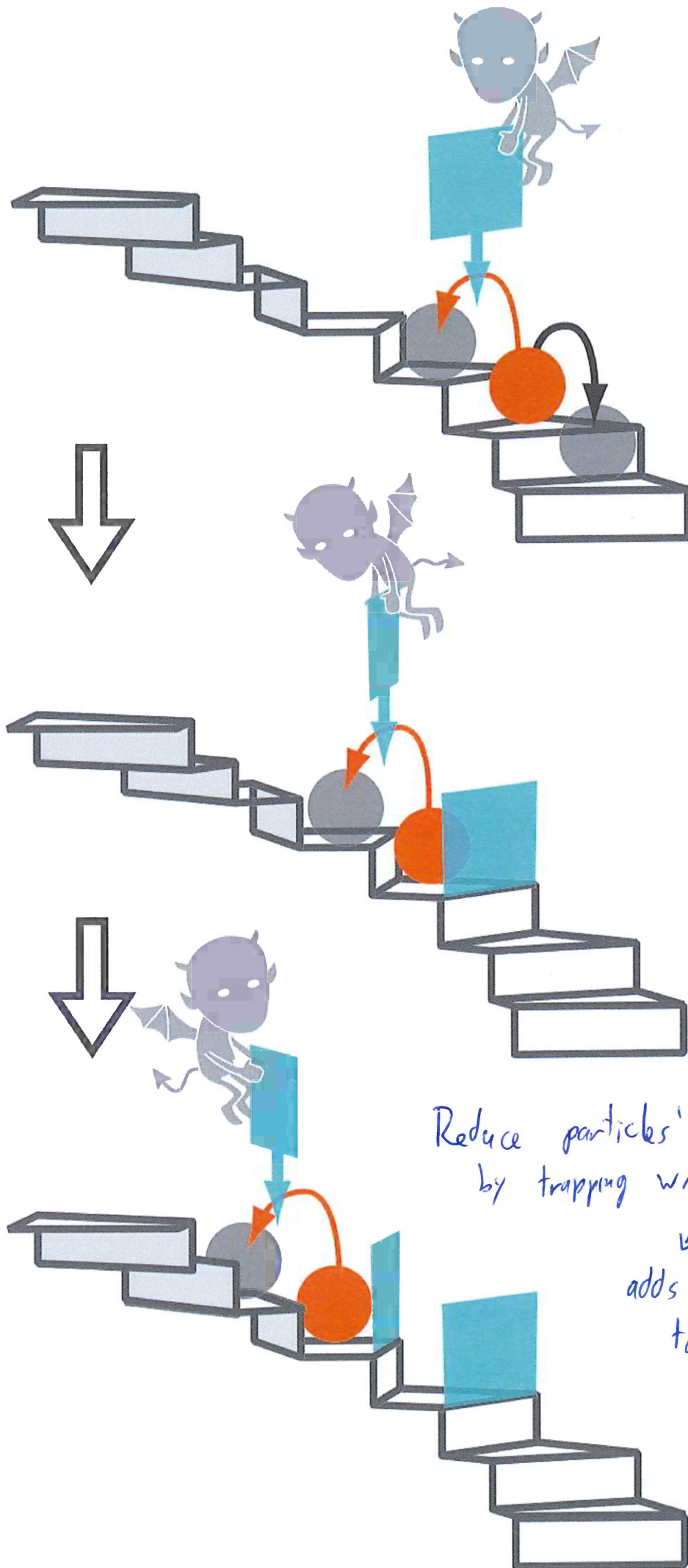
Solution: Go beyond Gibbs approx, ( $N \pm k$ )  
to see second law obeyed

Maxwell's demon (1867) ~~an~~ - experimentally tested (2010)

Conceptual argument: Demon's action add net entropy of universe



$T_B > T_A$



Reduce particles' entropy  
by trapping w/lasers

↓  
adds entropy  
to universe



Otto cycle - idealized petrol engine  
No slow isothermal stages

Gas is mixture of air and vaporized petrol

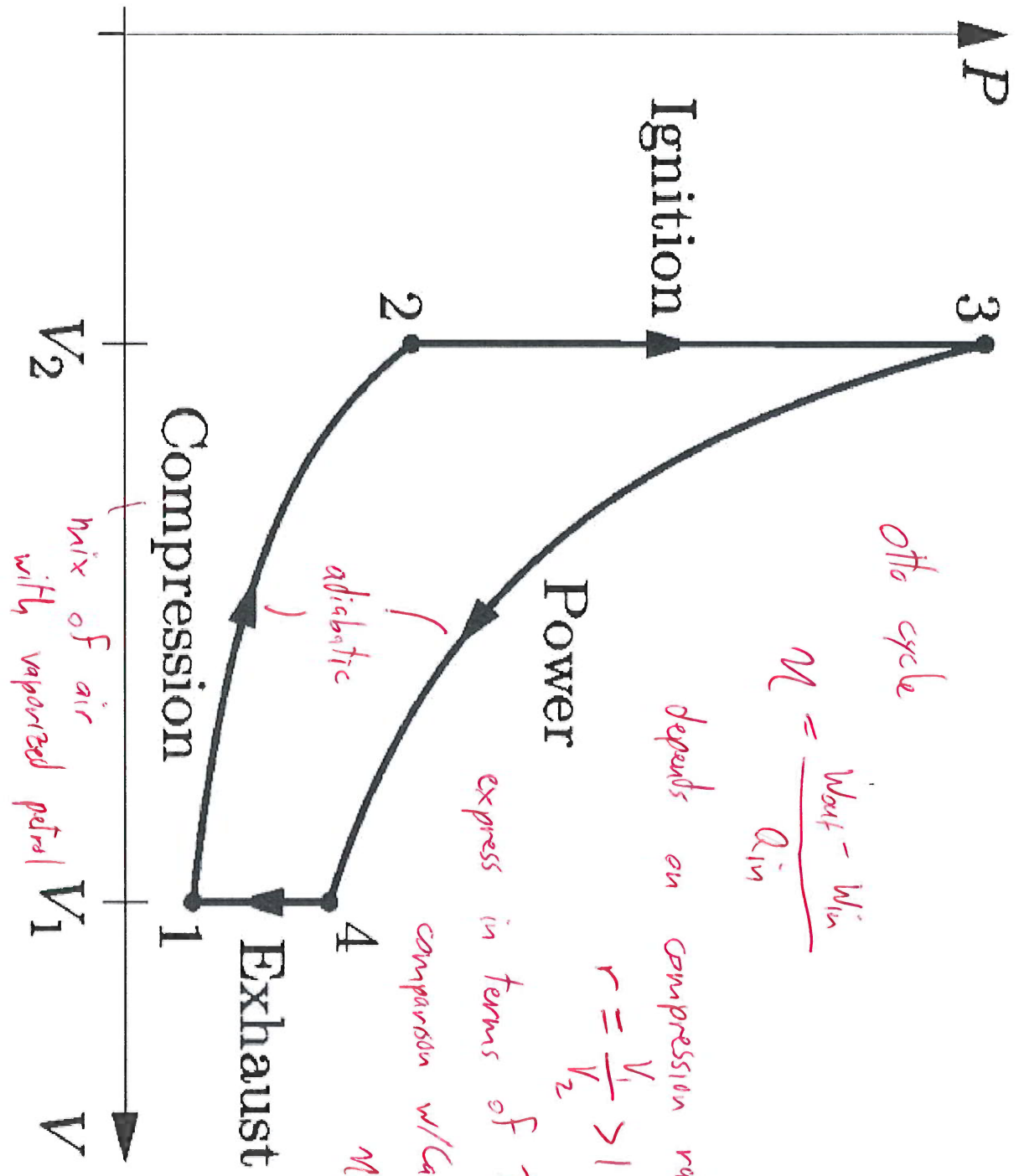
Compress to high pressure, ignite ~ hot reservoir

after power ~~apph~~ replace with fresh ~ cold reservoir

Efficiency  $\eta = \frac{W_{out} - W_{in}}{Q_{in}}$  depends on compression ratio  
 $r = \frac{V_1}{V_2} > 1$

Express in terms of  $T_1, T_2, T_3, T_4$ ,

compare with Carnot  $\eta_c = 1 - \frac{T_1}{T_3}$



Otto cycle

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

depends on compression ratio

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

express in terms of  $T_1, T_2, T_3, T_4$

comparison w/ Carnot

$$\eta_c = 1 - \frac{T_1}{T_3}$$