Wed 11 Mar

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Plan

Mixing entropy

Maxwell's demon

Otto cycle ~ petrol engine

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

$$= \frac{\partial}{\partial T}\left(T \log \frac{Z_c}{Z_0}\right)$$

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

$$\Delta S_{mix} = \log\left(\frac{Z_c}{Z_0}\right) = 2N \log 2 > 0 \quad \checkmark$$

same as fully dist'able!

Less info but same relative increase upon mixing

Final entropy

Gibbs approx of N particles on each side

$\nu = 0, 1, \ldots N$ red on left $\to$ $N-\nu$ blue

$N-\nu$ red and ν blue on right

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

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

$$= \left(\frac{V}{\lambda_{th}^3}\right)^{2N} \sum_\nu \frac{1}{(\nu!)^2 [(N-\nu)!]^2}$$

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

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

$$\frac{Z_F}{Z_c} = \frac{1}{2^{2N}} \binom{2N}{N} \longrightarrow S_F \approx S_c + \log\left(\frac{(2N)!}{(N!)^2}\right) - \log 2^{2N}$$

$N \gg 1$ $\quad S_F \approx S_c + 2N \log(2N) - \cancel{2N} - 2(N \log N - \cancel{N}) - 2N \log 2$

$$= S_c$$

S_0 $\quad S_F \approx S_c > S_0$ $\quad$ consistent with second law ✓

Next terms: $\quad \log\left(\sqrt{2\pi \, 2N}\right) - 2\log\left(\sqrt{2\pi N}\right) = \log\left(\frac{2\sqrt{\pi N}}{2\pi N}\right)$

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

$$S_F = S_c - \log\left(\sqrt{\pi N}\right) < S_c \quad \text{X}$$

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

Maxwell's demon (1867)

Suppose demon/device can sort hot vs. cold
Get back to $S_0 < S_c$ (or increase T difference)
Violate second law

Conceptual argument: Demon's actions add more entropy to universe

Experimentally tested, including Toyabe et. al, 2010

<u>Otto cycle</u> - idealized petrol engine

Gas is mixture of air and vaporized petrol

Compress (adiabatically) to high pressure and ignite ~ hot reservoir

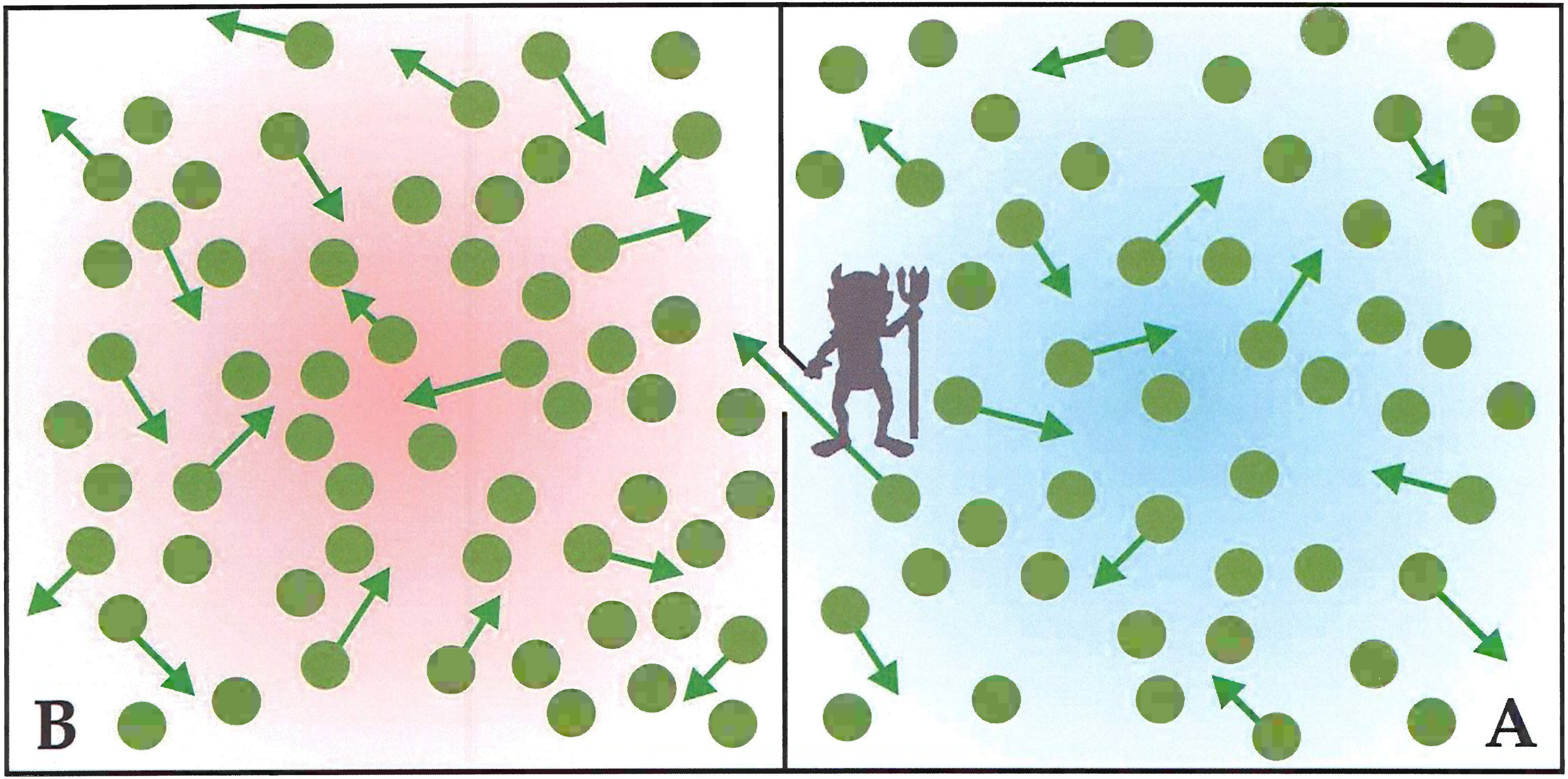
After (adiabatic) power, swap exhaust with fresh gas ~ cold res.

constant N

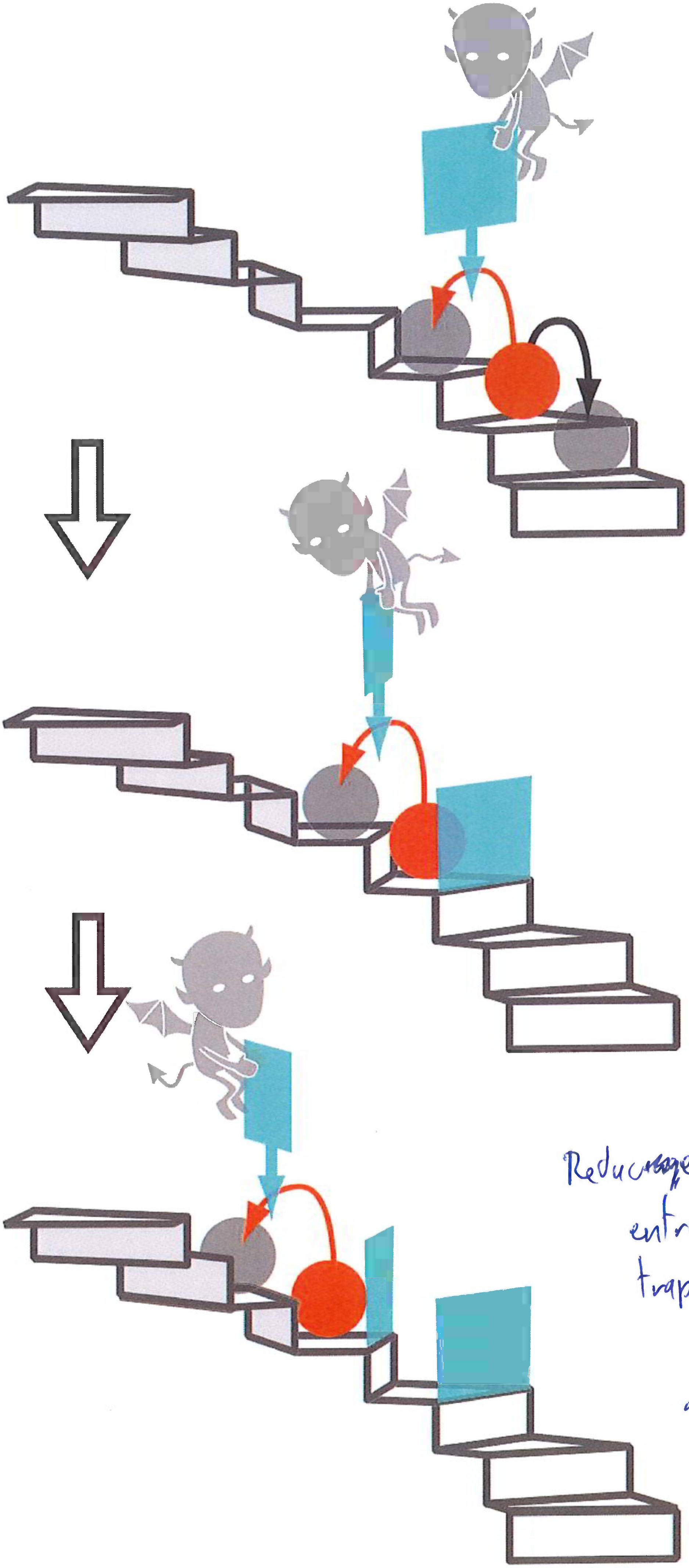
Efficiency $\eta = \frac{W_{out} - W_{in}}{\eta}$ depends on compression ratio $r = \frac{V_1}{V_2} > 1$

Express in terms of T_1, T_2, T_3, T_4

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

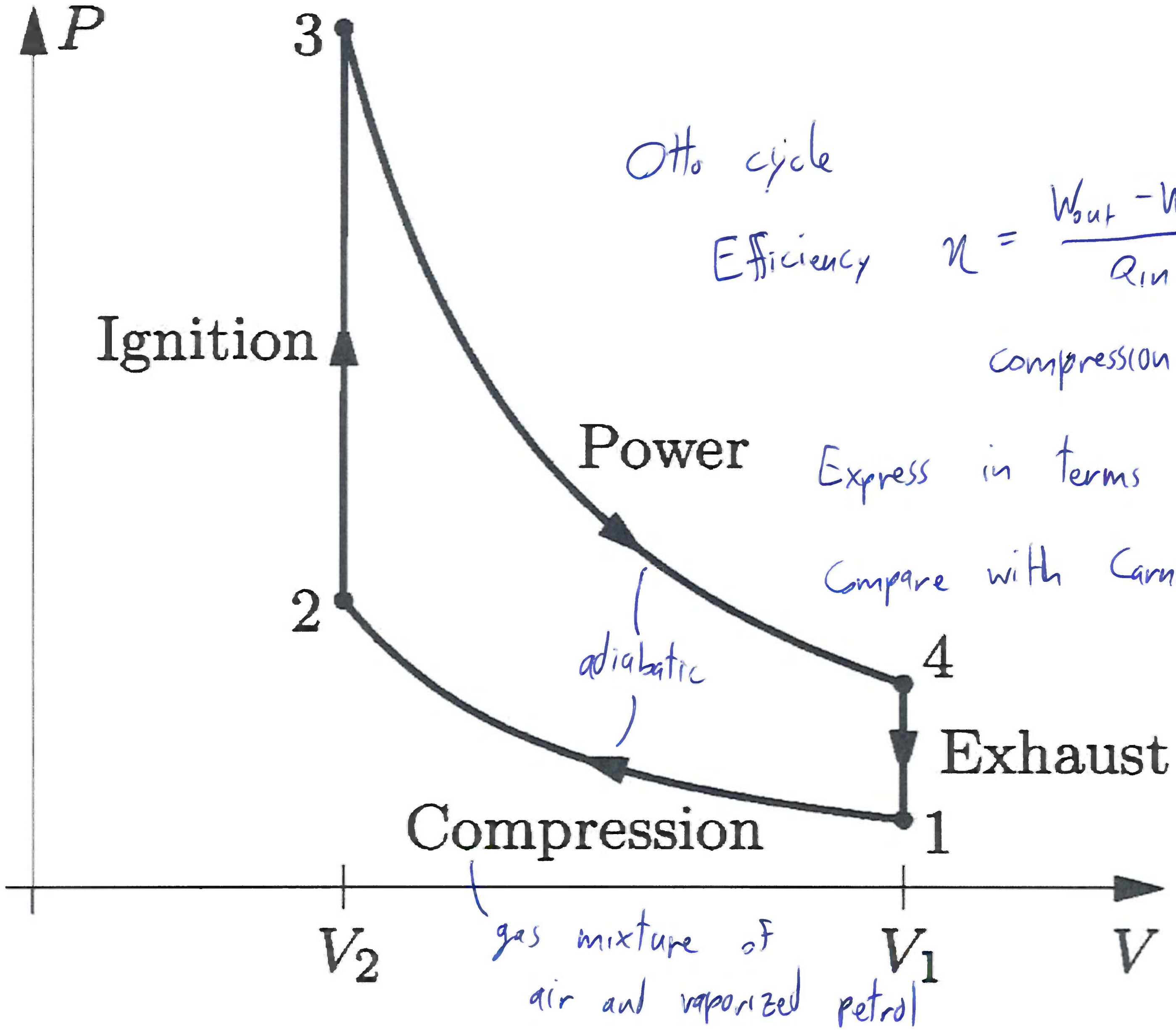


$T_B > T_A$



Reduce particle's entropy by trapping with laser

add entropy to universe



Otto cycle

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

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

Express in terms T_1, T_2, T_3, T_4

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