Thu 16 Mar

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

$$Z_c = \left(\frac{1}{N!}\right)^2 \left(\frac{2V}{\lambda_{th}^3}\right)^{2N} \qquad \frac{Z_{oc}}{Z_0} = \frac{\left(\frac{1}{N!}\right)^2 \left(\frac{2V}{\cancel{\lambda_{th}^3}}\right)^{2N}}{\left(\cancel{\frac{1}{N!}} \left(\frac{V}{\cancel{\lambda_{th}^3}}\right)^N\right)^2} = 2^{2N}$$

$$S_{mix} = \log \frac{Z_c}{Z_0} + \underbrace{T \frac{\partial}{\partial T} \log \frac{Z_c}{Z_0}}_{0} = 2N \log 2$$

same as fully dist'able

Less info but same relative increase from mixing

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

Z_F assuming N particles on each side

Left ν red $\rightarrow$ $N-\nu$ blue

$\rightarrow$ $N-\nu$ red & ν blue on right

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

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

$$\frac{1}{(N!)^2}\binom{N}{\nu}^2$$

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

$$\frac{Z_F}{Z_c} = \frac{1}{2^{2N}}\binom{2N}{N} \rightarrow \underline{S_F} = S_c + \log\cancel{\binom{2N}{N}} - 2\cancel{N\log 2} \approx S_c$$

$\underline{N \gg 1}$ Stirling: $\log\left(\frac{(2N)!}{N!\,N!}\right) \approx 2N\log 2\cancel{N} - \cancel{2N} - 2\left(\cancel{N\log N} - \cancel{N}\right) = 2N\log 2$

$$S_F \approx S_c > S_0 \qquad \text{second law ✓}$$

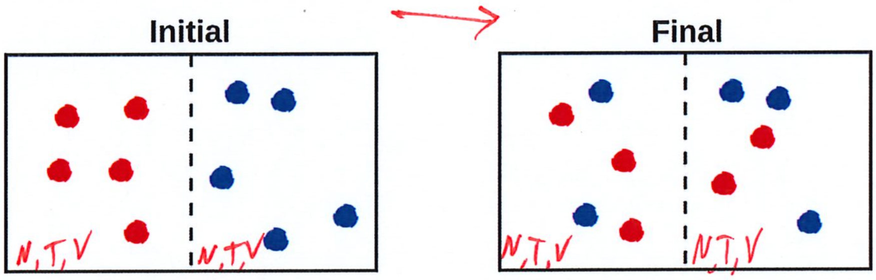
(Aside: $S_F = S_c - \log(\sqrt{\pi N}) < S_c$ — resolve by sum over particle #

MATH327: Statistical Physics, Spring 2023

Tutorial activity — Mixing entropy

Let's consider a slight variation to the particle exchange thought experiment we worked through in class. We again begin with two canonical ideal gases, initially separated by a wall, each with N particles in volume V at temperature T. *All* $2N$ particles have identical physical properties, *except* that those initially in the left compartment (the "reds") are distinguishable from those in right compartment (the "blues") by their colour. Call this initial system Ω_0. We have already computed its entropy $S_0 = 2S_I(N,V) = 5N + 2N \log\left(\frac{V}{N\lambda_{\text{th}}^3}\right)$, where $\lambda_{\text{th}} = \sqrt{2\pi\hbar^2/(mT)}$.

We then carry out the procedure of removing the wall, waiting for a while, and then re-inserting the wall to re-separate the two systems. Call the combined system Ω_C with entropy S_C. As discussed in class, it's safe to assume that N particles end up in each of the two re-separated systems. However, red and blue particles can now appear on either side of the wall. Call this final system Ω_F with entropy S_F. The initial and final systems are illustrated by the figure below.



The first task is to compute the mixing entropy $S_{\text{mix}} = S_C - S_0$. Since the combined system Ω_C has two (distinguishable) sets of N (indistinguishable) particles, its partition function is

$$Z_C = \frac{1}{N!}\frac{1}{N!} Z_1^{2N} = \frac{1}{N!}\frac{1}{N!}\left(\frac{2V}{\lambda_{\text{th}}^3}\right)^{2N},$$

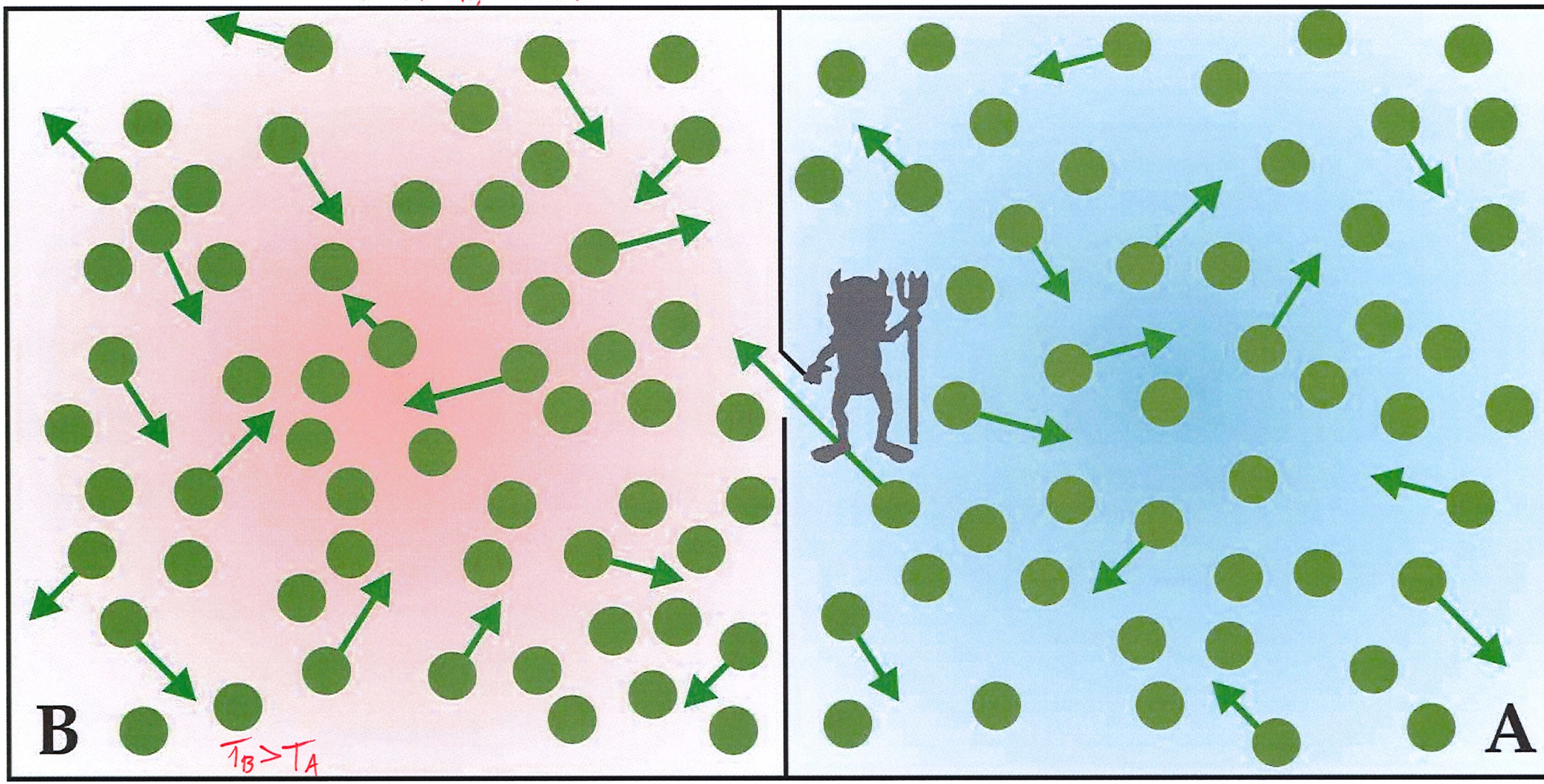
where $Z_1 = 2V/\lambda_{\text{th}}^3$ is the single-particle partition function. It may be useful to relate the difference of entropies to a ratio of partition functions.

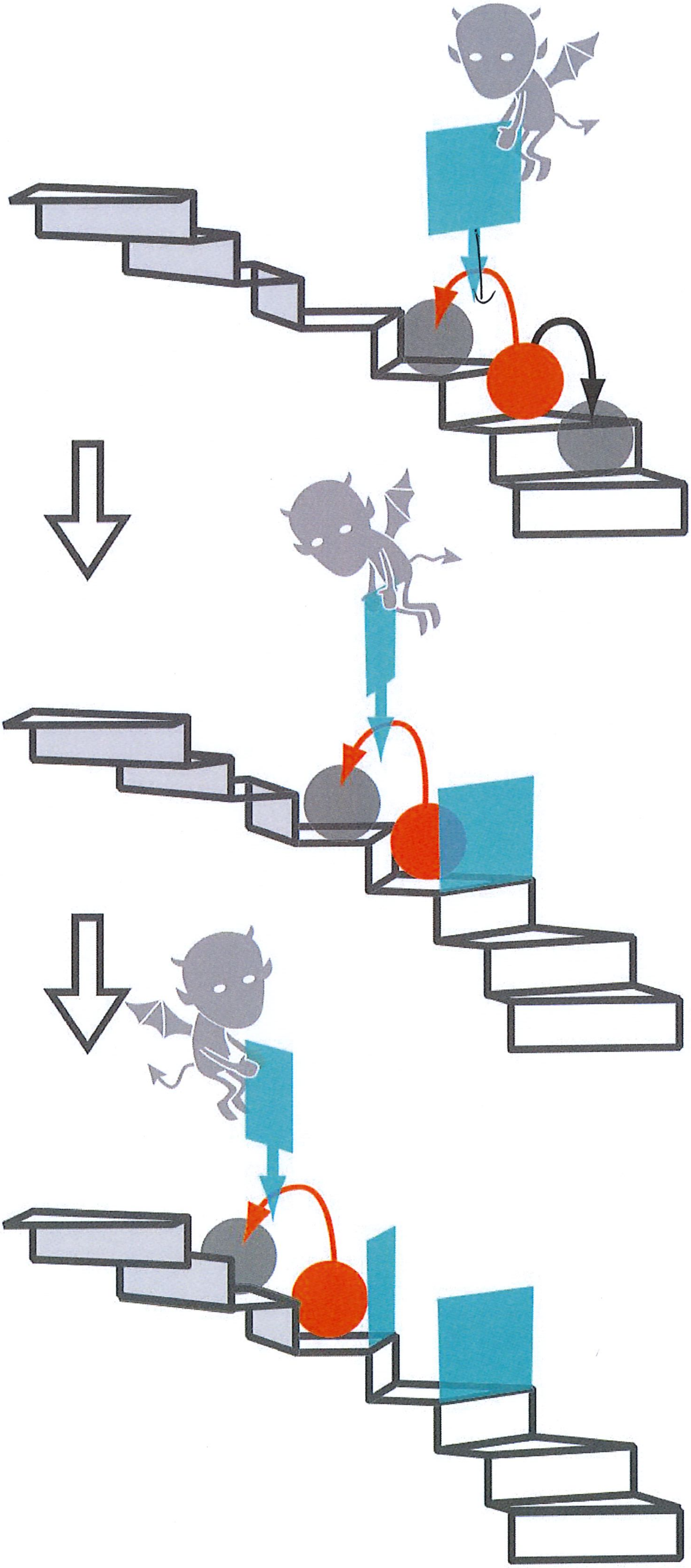
The second task is to compute the final entropy S_F, to see whether $S_F \geq S_C$ as demanded by the second law of thermodynamics. We can break this up into two steps. The first of these is to compute the partition function Z_F of the two re-separated systems (each with N particles), summing over all ways of dividing the red and blue particles between them. The following special case of the Zhu–Vandermonde identity may be useful for this step:

$$\sum_{k=0}^{N} \binom{N}{k}^2 = \binom{2N}{N}.$$

Finally, use your result for Z_F to determine the final entropy S_F. It may be useful to apply Stirling's formula and neglect $\mathcal{O}(\log N)$ contributions.

Maxwell, 1867





Maxwell's demon

Conceptual argument: Demon's activities add net entropy to universe

Second law ✓

Practically checked in real experiments

Toyabe et al. 2010 – lasers to trap particles

adds entropy through lasers ✓

Otto cycle

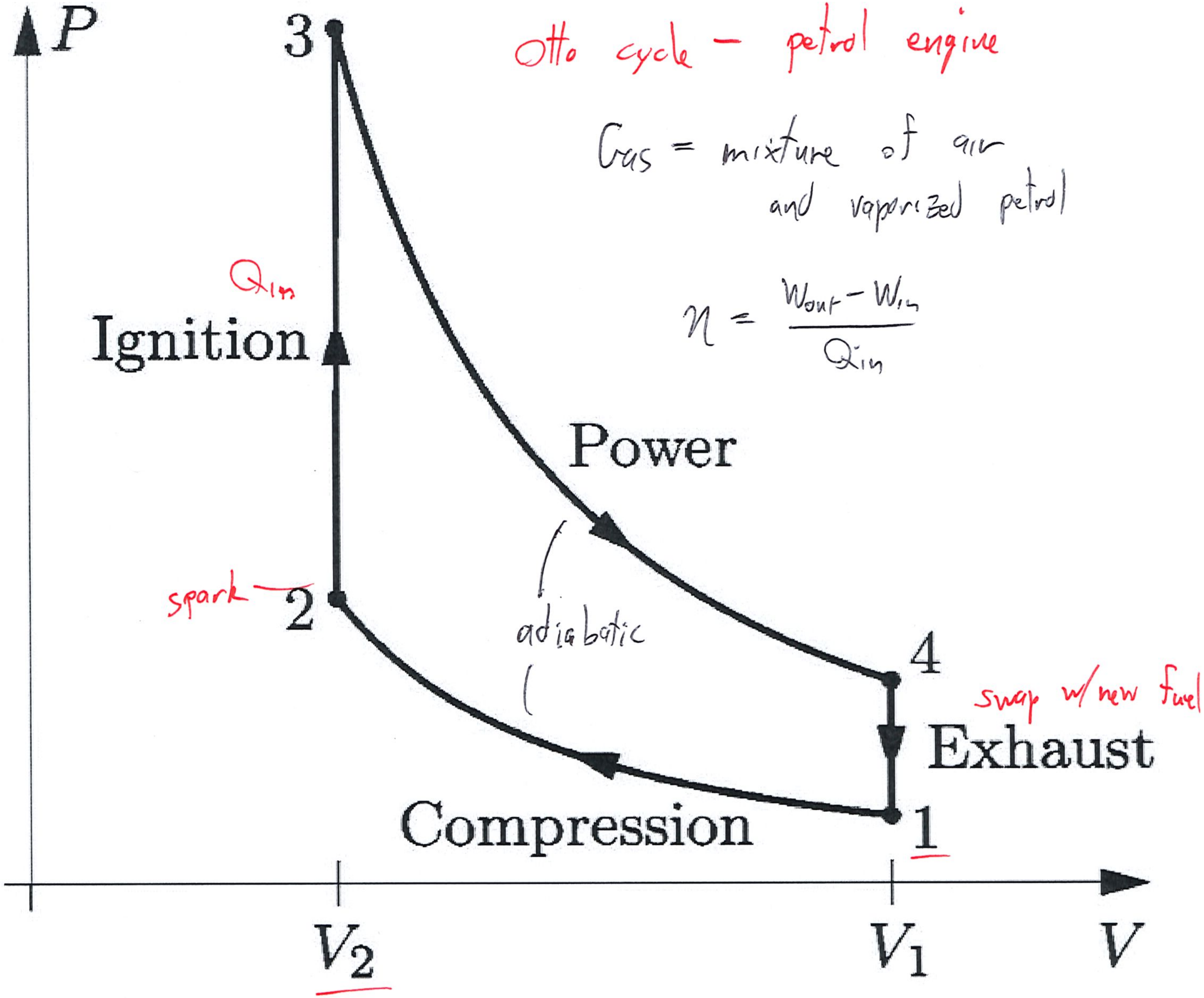
What is the efficiency η?

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

Otto cycle – petrol engine

Gas = mixture of air and vaporized petrol

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

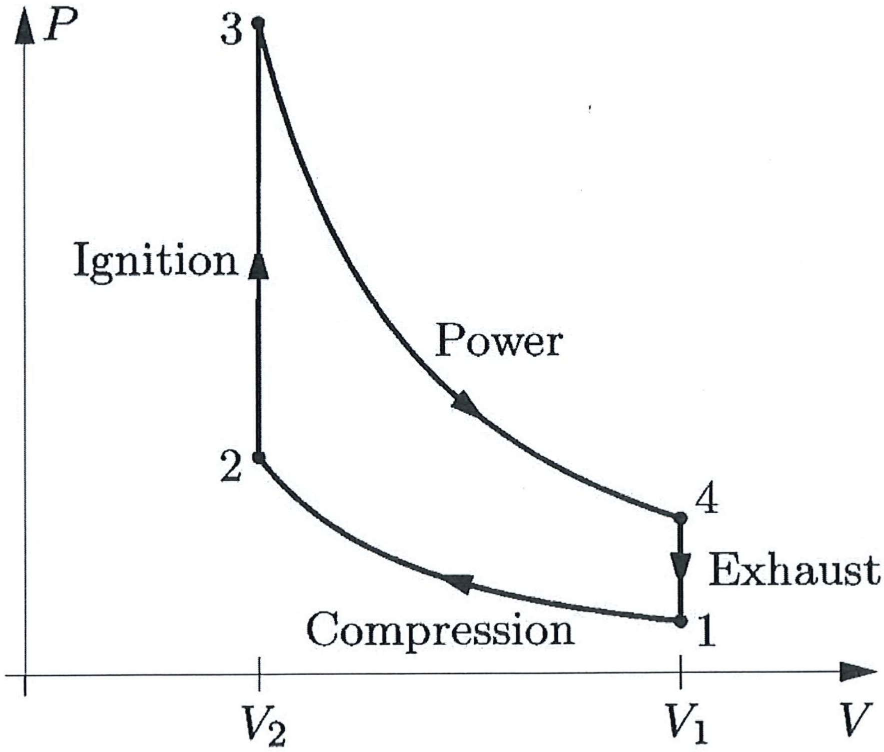


MATH327: Statistical Physics, Spring 2023

Tutorial activity — Otto cycle

The figure below shows the 'Otto cycle' that describes an idealized petrol engine.

- Fast (adiabatic) compression increases the pressure of the gas (a mixture of air and vaporized petrol), until a spark ignites it.
- This ignition introduces lots of heat almost instantaneously, while the volume is fixed at V_2. Even though the gas itself is burning, we can interpret this heat as coming from energy exchange with a hot thermal reservoir.
- The gas then does work by adiabatically expanding back to volume $V_1 > V_2$.
- Finally, heat is expelled at fixed volume V_1 by swapping the hot exhaust for an equal amount of cooler, fresh gas ready to be burned.



The efficiency η of the Otto cycle depends on the **compression ratio**

$$r \equiv \frac{V_1}{V_2} > 1.$$

What is this efficiency? How does it compare to the efficiency of the Carnot cycle? How should V_1 and V_2 be chosen to maximize the efficiency?