Thu 9 Mar

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Plan

Computer project

Entropy bounds

Stirling's formula

Mixing entropy

$$\frac{d}{da}\left(\int_0^\infty e^{-ax}\, dx = a^{-1} \right)$$

$$\int_0^\infty -x e^{-ax}\, dx = -a^{-2}$$

$$\vdots$$

$$\frac{d^N}{da^N} : \int_0^\infty (-x)^N e^{-ax}\, dx = (-1)^N \underline{N!}\, a^{-(N+1)}$$

$$\downarrow 1$$

$$\int_0^\infty x^N e^{-x}\, dx = N!$$

↳ gaussian

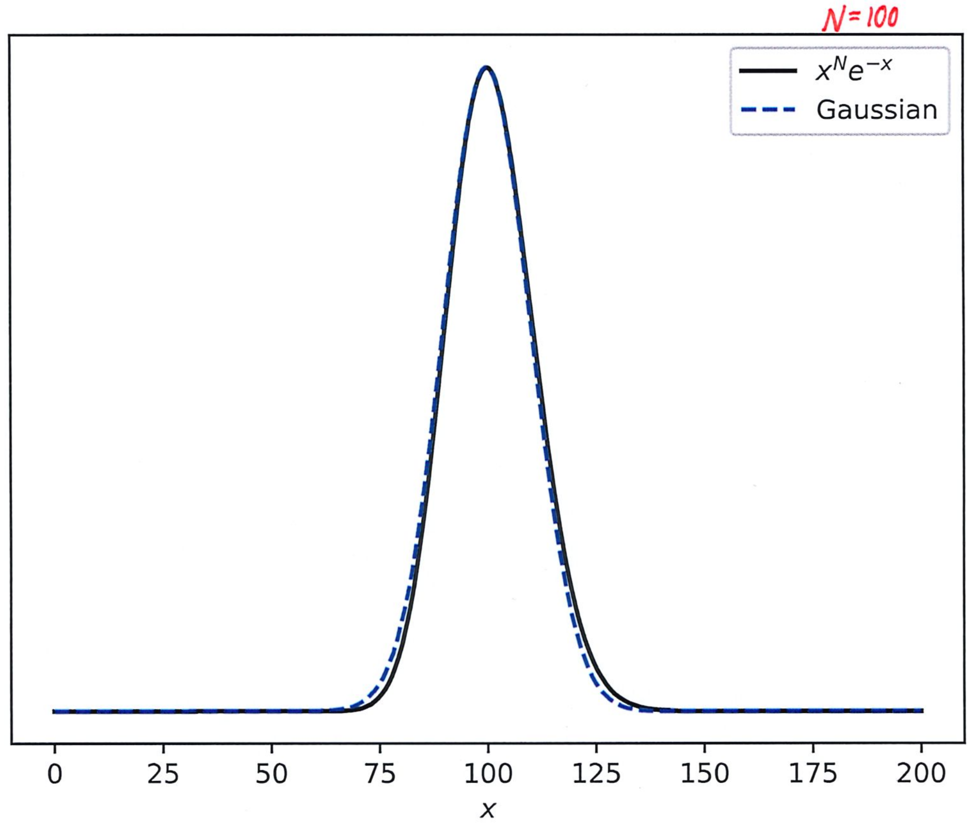
$$N! = \int_{-N}^{\infty} dy\ \exp\left[N \log N - N - \frac{y^2}{2N} + \mathcal{O}\left(\frac{y^3}{N^3}\right)\right]$$

$$= N^N e^{-N} \int_{-N}^{\infty} dy\ e^{-y^2/2N + \mathcal{O}(y^3/N^3)}$$

$$\hookrightarrow -\infty$$

$$= \sqrt{2\pi N}\ N^N e^{-N}$$

$$\log(N!) = N \log N - N + \frac{1}{2}\log(2\pi N)$$



N=100
$x^N e^{-x}$
Gaussian
0
25
50
75
100
125
150
175
200
x

$$(N+1)! = (N+1)\, N!$$

$$\sqrt{2\pi(N+1)}\left(\frac{N+1}{e}\right)^{N+1}\left(1+\frac{A}{N+1}+\frac{B}{(N+1)^2}+O\left(\frac{1}{(N+1)^3}\right)\right)$$

$$= (N+1)\sqrt{2\pi N}\left(\frac{N}{e}\right)^{N}\left(1+\frac{A}{N}+\frac{B}{N^2}+O\left(\frac{1}{N^3}\right)\right)$$

Match coefficients of $\frac{1}{N^p}$ terms on both sides

$$\frac{A}{N+1} = \frac{A}{N}\left(\frac{1}{1+1/N}\right) = \frac{A}{N}\left(1-\frac{1}{N}+O\left(\frac{1}{N^2}\right)\right) = \frac{A}{N}-\frac{A}{N^2}+O\left(\frac{1}{N^3}\right)$$

$$\frac{1}{e}\left(1+\frac{1}{N}\right)^{N+1/2} = 1+\frac{1}{12N^2}+O\left(\frac{1}{N^3}\right)$$

$$\to \quad e = \lim_{N\to\infty}\left(1+\frac{1}{N}\right)^N$$

Match $O(1)$ terms: $1=1$

$O\left(\frac{1}{N}\right)$ $\quad A=A$

$O\left(\frac{1}{N^2}\right)$ $\quad \frac{1}{12}+B-A=B \quad \to \quad A=\frac{1}{12}$

$$B=\frac{A}{24}=\frac{1}{288}$$

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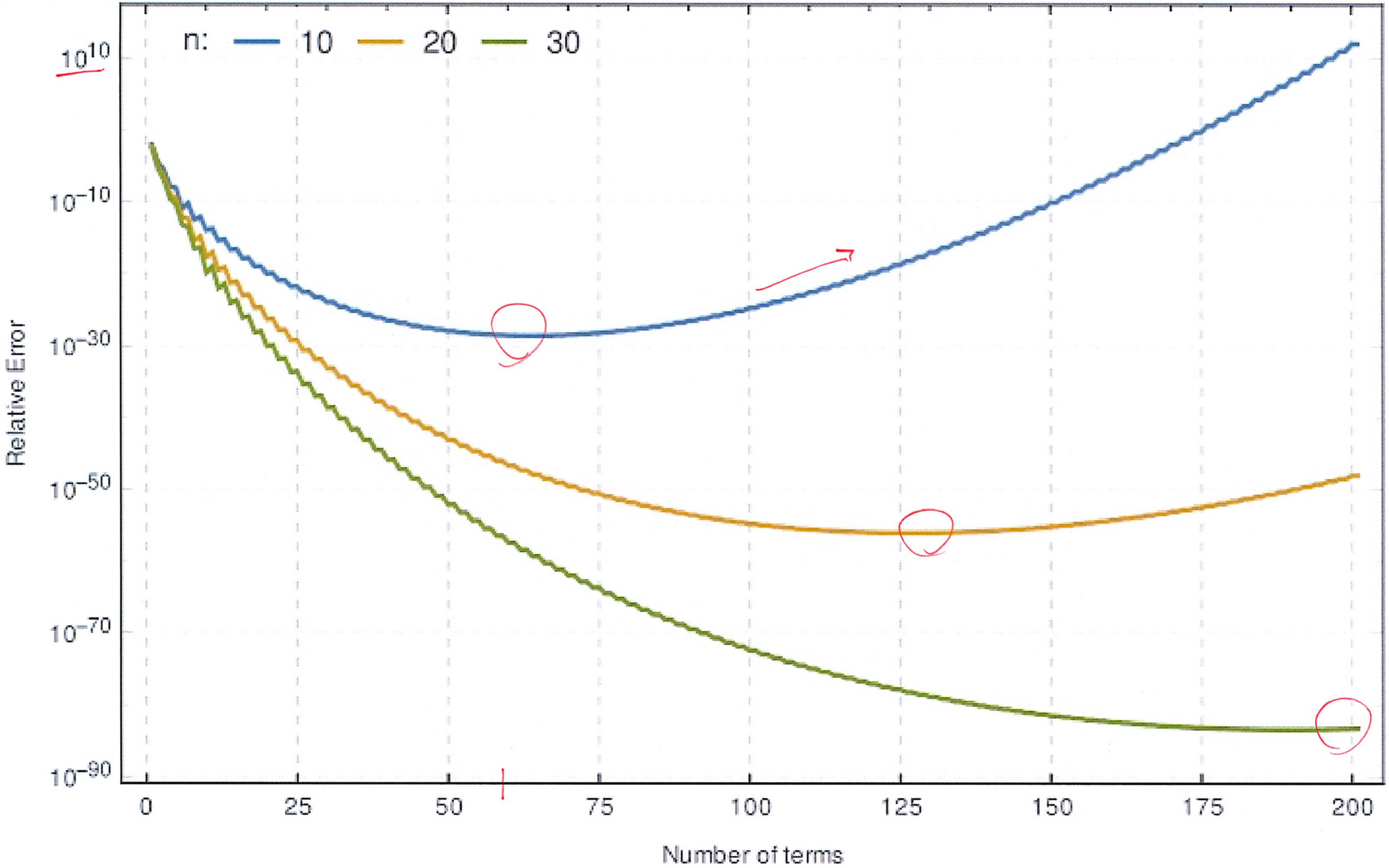
commons.wikimedia.org/wiki/File:Stirling_error_vs_number_of_terms.svg

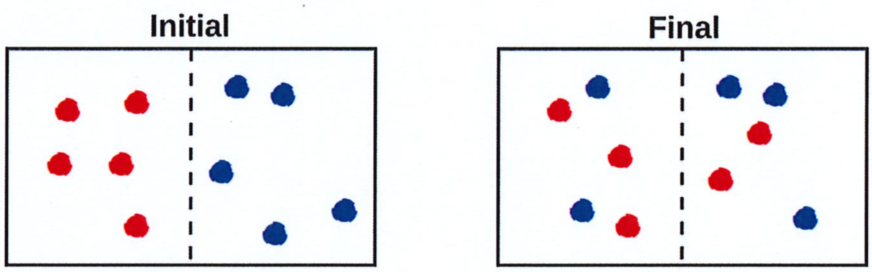


MATH327: Statistical Physics, Spring 2023

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.