Stirling's Formula

In lecture we used the saddle point approx to discuss the relation between the Helmholtz free energy in the canonical vs. the microcanonical ensemble. The saddle pt approx is also how one derives Stirling's approx for \( n! \).

Consider the integral

\[
I = \int_0^\infty x^n e^{-x} \, dx
\]

Integrate by parts

\[
I = -x^n e^{-x} \bigg|_0^\infty + \int_0^\infty n x^{n-1} e^{-x} \, dx
\]

boundary term vanishes at its limits so

\[
I = \int_0^\infty n x^{n-1} e^{-x} \, dx
\]

Integrate by parts again

\[
I = \int_0^\infty n(n-1) x^{n-2} e^{-x} \, dx
\]

and so on to get

\[
I = \int_0^\infty n(n-1)(n-2) \cdots (1) e^{-x} = n!
\]
Now evaluate $I$ at saddle point approx.

Define $U(x) = -x + n \ln x$

$$I = \int_0^\infty dx \ e^{-U(x)}$$

Expand $U(x)$ about its minimum:

$$U'(x) = -1 + \frac{n}{x} \quad \Rightarrow \quad x = n \quad \text{is the maximum}$$

$$U''(x) = -\frac{n}{x^2} \quad \Rightarrow \quad U''(n) = -\frac{1}{n}$$

$$U'''(x) = -\frac{2n}{x^3} \quad U'''(n) = 2/n^2$$

$$U^{iv}(x) = -\frac{6n}{x^4} \quad U^{iv}(n) = -6/n^3$$

For $\delta x = x - n$,

$$U(x) \approx -n + n \ln n - \frac{\delta x^2}{2n} + \frac{1}{6} \frac{\delta x^3}{n^2} - \frac{1}{24} \frac{6 \delta x^4}{n^3} + \cdots$$

$$= -n + n \ln n - \frac{\delta x^2}{2n} + \frac{\delta x^3}{3n^2} - \frac{\delta x^4}{4n^3} + \cdots$$

$$I = \int_0^\infty dx \ e^{-n + n \ln n - \delta x^2/2n} e^{-\delta x^2/2n} \ e^{\frac{\delta x^3}{3n^2} - \delta x^4/4n^3}$$

Expand for small $\delta x$

$$= \int_{-\infty}^\infty d\delta x \ e^{-n + n \ln n - \delta x^2/2n} \left[ 1 + \frac{\delta x^3}{3n^2} - \frac{\delta x^4}{4n^3} + o(\delta x^6) \right]$$

$$= e^{-n + n \ln n} \int_{-\infty}^\infty d\delta x \ e^{-\delta x^2/2n} \left[ 1 + \frac{\delta x^3}{3n^2} - \frac{\delta x^4}{4n^3} + \cdots \right]$$

$$= e^{-n + n \ln n} \sqrt{2\pi n} \left[ 1 + \frac{\langle \delta x^3 \rangle}{3n^2} - \frac{\langle \delta x^4 \rangle}{4n^3} + \cdots \right]$$
Now $\langle f x^3 \rangle = 0$, $\langle f x^4 \rangle \approx n^2$, so

$$I = n^! = e^{-n + \ln n} \sqrt{\frac{2\pi}{n}} \left[ 1 + O\left(\frac{1}{n}\right) \right]$$

$$\ln n^! = n \ln n - n + \frac{1}{2} \ln n + \frac{1}{2} \ln 2\pi + \ln(1 + O\left(\frac{1}{n}\right))$$

$$= n \ln n - n + \frac{1}{2} \ln n + \frac{1}{2} \ln 2\pi + o\left(\frac{1}{n}\right)$$

these are the leading terms

these are next order corrections
Comparison of entropy in microcanonical and canonical ensembles

Micro canonical

\[ S_{\text{micro}} = k_B \ln \Omega \quad \text{where} \quad \Omega = \left[ \frac{\sqrt{\frac{\nu^3}{h^3}} (2\pi m E)^{3/2}}{(3N-1)!} \right]^N \frac{1}{N!} \frac{\Delta}{E} \]

\[ S_{\text{micro}} = N k_B \left[ \frac{\nu^3}{h^3} (2\pi m E)^{3/2} \right] - N \ln \left( \frac{3N-1}{\frac{3N}{2}} \right) - \ln N! + \ln \frac{\Delta}{E} \]

For later use, we derive here the relation between \( T \) ad \( E \) in the microcanonical ensemble

\[ \frac{1}{T} = \left( \frac{\partial S_{\text{micro}}}{\partial E} \right)_N \frac{1}{N} = k_B \frac{2}{\partial E} \int \frac{N \ln E^{3/2}}{E} - \ln E \right] = \left( \frac{3N}{2} - 1 \right) k_B \frac{1}{E} \]

So \( E = \left( \frac{3N}{2} - 1 \right) k_B T \) \( \text{(compare to } \langle E \rangle = \frac{3}{2} N k_B T \text{ in canonical)} \)

Canonical - from factorization \( Q_N = \frac{1}{N}, Q_1 ^N \) we had

\[ A = -k_B T \ln Q_N = -k_B T \left[ N \ln \left( \frac{\nu^3}{h^3} (2\pi m k_B T)^{3/2} \right) - \ln N! \right] \]

\[ S = -\left( \frac{\partial A}{\partial T} \right)_N = k_B \left[ N \ln \left( \frac{\nu^3}{h^3} (2\pi m k_B T)^{3/2} \right) - \ln N! \right] \]

\[ + \frac{k_B T}{\frac{3}{2} N} \frac{1}{T} \]

\[ = k_B \left[ \frac{3}{2} N + N \ln \left( \frac{\nu^3}{h^3} (2\pi m k_B T)^{3/2} \right) - \ln N! \right] \]

To compare \( S_{\text{micro}} \) to \( S \) we have to change \( E \) in \( S_{\text{micro}} \) to \( T \) or change \( T \) in \( S \) to \( E \). We do the latter, using the relation between \( E \) ad \( T \) of the microcanonical ensemble while \( E \) is fixed and does not fluctuate. \( \Rightarrow k_B T = \frac{E}{\left( \frac{3}{2} N - 1 \right)} \)
\[
\frac{S}{k_B} = \frac{3}{2} N + N \ln \left[ \frac{\frac{V}{h^3} \left( \frac{2\pi m E}{(2\pi)^2 - 1} \right)}{\frac{2\pi}{2} - 1} \right] - \ln N!
\]

\[
= \frac{3}{2} N + N \ln \left[ \frac{\frac{V}{h^3} (2\pi m E)^{3/2}}{\frac{2\pi}{2} - 1} \right] - \ln N! - \frac{3}{2} N \ln \left( \frac{2\pi}{2} - 1 \right)
\]

\[
\frac{\Delta S}{k_B} = \frac{S - S_{\text{micro}}}{k_B} = \frac{3}{2} N - \frac{3}{2} N \ln \left( \frac{3N}{2} - 1 \right) + \ln \left( \frac{3N}{2} - 1 \right)! - \ln \frac{A}{E}
\]

\[
\text{Use Stirling's approx}
\]

\[
\frac{\Delta S}{k_B} = \frac{3}{2} N - \frac{3}{2} N \ln \left( \frac{3N}{2} - 1 \right) + \left( \frac{3N}{2} - 1 \right) \ln \left( \frac{3N}{2} - 1 \right) - \left( \frac{3N}{2} - 1 \right)
\]

\[
+ \frac{1}{2} \ln \left( \frac{2\pi}{2} - 1 \right) + \frac{1}{2} \ln 2\pi + O \left( \frac{1}{N} \right) - \ln \frac{A}{E}
\]

\[
\frac{\Delta S}{k_B} = 1 - \frac{1}{2} \ln \left( \frac{3N}{2} - 1 \right) + \frac{1}{2} \ln 2\pi + O \left( \frac{1}{N} \right) - \ln \frac{A}{E}
\]

Leading term goes like \( \ln N \), so

\[
\frac{\Delta S}{S} \sim \frac{\ln N}{N} \to 0 \text{ as } N \to \infty
\]
To compare with above result we can also use the general relation we derived between $A$ in the canonical ensemble and $A_{\text{micro}}$ in the microcanonical ensemble (the relation was derived using the saddle point approx.). We had

$$A - A_{\text{micro}} = -k_B T \frac{1}{2} \ln \left[ \frac{2\pi k_B}{\Delta^2} \right]$$

where $C_V$ in the above came from

$$\frac{\partial^2 S_{\text{micro}}}{\partial E^2} = \frac{\partial}{\partial E} \left( \frac{1}{T} \right) - \frac{1}{T^2} \frac{\partial T}{\partial E} = \frac{-1}{T^2} \frac{1}{T} = -\frac{1}{T^2}$$

So $C_V$ in the above is $C_V$ as computed in the microcanonical ensemble

$$\Rightarrow C_V = \frac{\partial E}{\partial T} = \frac{3}{2} \left( \frac{\partial N}{\partial T} \right) = \frac{3}{2} \left( \frac{3N-1}{2} \right) k_B$$

where we used the relation between $E$ and $T$ of the microcanonical ensemble.

$$\Delta S = -\left( \frac{\partial \Delta A}{\partial T} \right)_{N,N} = +k_B \frac{1}{2} \ln \left[ \frac{2\pi k_B T^2 C_V}{\Delta^2} \right]$$

$$+ k_B \frac{T}{2} - \frac{1}{T}$$

$$\frac{\Delta S}{k_B} = +\frac{1}{2} \ln \left[ \frac{2\pi k_B T^2 C_V}{\Delta^2} \right] + 1$$

use $k_B T^2 C_V = k_B \frac{2}{2} \left( \frac{3N-1}{2} \right) = \frac{E^2}{\left( \frac{3N}{2} - 1 \right)^2}$

$$= \frac{E^2}{\left( \frac{3N}{2} - 1 \right)}$$
\[
\frac{\Delta S}{k_B} = 1 + \frac{1}{2} \ln 2\pi + \frac{1}{2} \ln \left[ \frac{E^2}{\Delta^2} \frac{1}{2} \left( \frac{3N}{2} - 1 \right) \right] \\
= 1 + \frac{1}{2} \ln 2\pi - \ln \frac{\Delta}{E} - \frac{1}{2} \ln \left( \frac{3N}{2} - 1 \right)
\]
which is just what we got before!

Note the relation between \(E\) and \(T\) in the microcanonical ensemble, \(\frac{1}{T} = \frac{\partial S_{\text{micro}}}{\partial E}\), can also be viewed as the \(E\) that maximizes the expression below for fixed \(T\):

\[
-A_{\text{micro}} = \max_E \left[ S(E) - \frac{E}{T} \right]
\]

(above is by our alternate formulation of the Legendre transform, or equivalently the \(E\) that minimizes

\[
A_{\text{micro}} = \min_E \left[ E - TS(E) \right] \quad \text{for fixed } T
\]

Call this minimizing \(E^*\).

Now in canonical ensemble, the probability distribution for \(E\) is

\[
\rho(E) = \frac{\mathcal{Z}(E) e^{-\beta E}}{\int \mathcal{Z}(E) e^{-\beta E} \, dE} \quad \text{constant}
\]

The \(E\) that minimizes \(E - TS(E)\) also maximizes \(\rho(E)\). \(\Rightarrow\) The relation between \(E\) and \(T\) in the microcanonical ensemble gives the most probable \(E\) of the canonical ensemble (i.e. the \(E\) that
maximizes the prob distribution $P(E)$

The relation between $E$ and $T$ in the canonical ensemble gives the average value of $E$.

For the ideal gas we have

$$\langle E \rangle = \frac{3}{2} N k_B T$$ average energy

$$\bar{E} = (\frac{3N}{2} - 1) k_B T$$ most probable energy

The difference $\frac{\langle E \rangle - \bar{E}}{\langle E \rangle} = \frac{2}{3N} \xrightarrow{N \to \infty} 0$