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 micro canonical ensemble. The saddle pt approx is also how one derives Stirling's approx for $n!$

Consider the integral

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

integrate by parts

$$I = -x^n e^{-x} \Big]_0^\infty + \int_0^\infty n x^{n-1} e^{-x} dx$$

boundary term vanishes at its limits so

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

integrate by parts again

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

and so on to get

$$I = \int_0^\infty dx\, n(n-1)(n-2)\cdots(1)\, e^{-x} = n!$$

Now evaluate I in saddle pt approx.

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

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

expand $U(x)$ about its maximum

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

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

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

$$U''''(x) = \frac{-6n}{x^4} \qquad U''''(\bar{x}) = -6/n^3$$

For $\delta x = x - \bar{x}$,

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

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

$$I = \int_0^\infty dx \; e^{-n+n\ln n} \, e^{-\delta x^2/2n} \, \underbrace{e^{\frac{\delta x^3}{3n^2} - \frac{\delta x^4}{4n^3}}}_{\text{expand for small } \delta x}$$

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

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

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

Now $\langle \delta x^3 \rangle = 0$, $\langle \delta x^4 \rangle \sim n^2$, so

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

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

$$= \underbrace{n\ln n - n}_{\text{these are the leading terms}} + \underbrace{\tfrac{1}{2}\ln n + \tfrac{1}{2}\ln 2\pi}_{\text{these are next order corrections}} + O\left(\tfrac{1}{n}\right)$$

Comparison of entropy $\overbrace{\text{in}}^{\text{of ideal gas}}$ microcanonical and canonical ensembles

microcanonical

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

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

For later use, we derive here the relation between T and E in the microcanonical ensemble

$$\frac{1}{T} = \left(\frac{\partial S_{micro}}{\partial E}\right)_{V,N} = k_B \frac{\partial}{\partial E}\left[N \ln E^{3/2} - \ln E\right] = \left(\frac{3N}{2}-1\right) k_B \frac{1}{E}$$

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

canonical - from factorization $Q_N = \frac{1}{N!} Q_1^N$ we had

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

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

$$+ k_B T \, \frac{3}{2} N \frac{1}{T}$$

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

To compare S_{micro} to S we have to change E in S_{micro} to T or change T in S to E. We do the latter, using the relation between E and T of the microcanonical ensemble where E is fixed and does not fluctuate. $\Rightarrow k_B T = \frac{E}{(\frac{3}{2}N-1)}$

⑤

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

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

$$\frac{\Delta S}{k_B} = \frac{S - S_{micro}}{k_B} = \frac{3}{2}N - \frac{3}{2}N\ln\left(\frac{3N}{2}-1\right) + \underbrace{\ln\left(\frac{3N}{2}-1\right)!}_{\text{use Stirling's approx}} - \ln\frac{\Delta}{E}$$

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

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

leading term goes like $\ln N$, so

$$\frac{\Delta S}{S} \sim \frac{\ln N}{N} \to 0 \quad \text{as } N \to \infty$$

To compare with above result we can also use the general relation we derived between A in the canonical ensemble and A_{micro} in the micro canonical ensemble (this relation was derived using the saddle point approx). We had

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

where C_V in the above came from

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

So C_V in the above is C_V as computed in the micro canonical ensemble

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

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

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

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

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

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

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

which is just what we got before!

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

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

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

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

Call this minimizing E, $\bar{E}$

Now in canonical ensemble, the prob distribution for E is

$$P(E) = \frac{\frac{\Omega}{\Delta}(E)\, e^{-\beta E}}{\int \frac{dE}{\Delta}\, \Omega(E)\, e^{-\beta E}} = \frac{e^{-(E - TS(E))/k_B T}}{\text{constant}}$$

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

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

For the ideal gas we have

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

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

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