We found for ideal gas $H = \sum p_i^2/2m$ that

$$N(E) = V^N (2\pi m)^{3N/2} E^{3N/2 - 1} / \Gamma(3N/2)$$

is total number of states of energy E. A key feature of this was rapid growth with E

What do I mean. Suppose you increase energy of system of 10^{23} particles by 1 part in a trillion. How many more states are accessible

$$[1 + 10^{-12}]^{10^{23}} = [1 + 10^{-12}]^{10^{12} \cdot 10^{11}}$$

$$= e^{10^{11}} \quad \text{a lot!}$$

We will come back to this again in a few minutes. First though, N(E) is a less familiar concept. Can we compute something a bit more familiar?

NB However one should get familiar with N(E) it is a central quantity in condensed matter physics $\Gamma \sim |\langle f | V | i \rangle|^2 N(E)$

$$\left[1 + \frac{x}{n}\right]^n = e^x \quad \text{for } n \text{ large}$$

momentum distribution function

~~REPRE~~ prob any particle has momentum p

$\rho(p) = \langle \sum \delta(p_i - p) \rangle$

Any ideas what to expect? $\rho(p)$

"Canonical", get answer before doing calculation

$$= \frac{1}{\int d\Gamma\, \delta(E-H)} \sum_i \int d\Gamma\, \delta(E-H)\, \delta(p_i - p)$$

total # of cases

cases satisfying desired condition

$\langle A(x) \rangle$
$= \int p(x) A(x)\, dx$

$\frac{\delta(E-H)}{\int d\Gamma\, \delta(E-H)}$

$\boxed{\text{Just do } \delta(p_1 - p)!}$

$$= \frac{N V^N}{N(E)} \int dp_1 \ldots dp_N\, \delta(p_1 - p)\, \delta\left[E - \frac{1}{2m}(p_1^2 + p_2^2 \cdots p_N^2)\right]$$

p_1^2

$$= 4\pi \frac{N V^N}{N(E)} p^2 \int dp_2 \ldots dp_N\, \delta\left[E - \frac{p^2}{2m} - \left(\frac{p_2^2}{2m} + \ldots \frac{p_N^2}{2m}\right)\right]$$

careful!

Same integral as for $N(E)$ except $N-1$ particles and energy $E \to E - p^2/2m$

$N(E) = V^N \frac{(2\pi m)^{\frac{3N}{2}} E^{\frac{3N}{2}-1}}{\Gamma(\frac{3N}{2})}$

$$= \frac{N\, \Gamma(\frac{3N}{2})}{\Gamma(\frac{3}{2}(N-1))} \frac{4\pi p^2}{(2\pi m)^{3/2}} \frac{1}{E^{3/2}} \left(1 - \frac{p^2}{2mE}\right)^{\frac{3}{2}(N-1)}$$

Use $\Gamma(z+1) = z\,\Gamma(z)$

$$\lim_{n \to \infty} \left(1 - \frac{x}{n}\right)^n = e^{-x} \qquad \epsilon \equiv \frac{E}{N}$$

$$N(p) = N \frac{4\pi p^2}{\left[2\pi m \frac{2}{3}\epsilon\right]^{3/2}} e^{-\frac{p^2}{2m} \frac{1}{2/3\,\epsilon}}$$

Looks sort of familiar. We expect to find

2-2A

$$N(p) = \underbrace{\frac{N\,\Gamma(3N/2)}{\Gamma(3N/2 - 3/2)}}\;\underbrace{\frac{4\pi p^2}{(2\pi m)^{3/2}}\,\frac{1}{E^{3/2}}}\;\Big(1 - \underbrace{\frac{p^2}{2mE}}\Big)^{3/2\,(N-1)}$$

$$= N\left(\frac{3N}{2}\right)^{3/2}\;\frac{4\pi p^2}{\left(2\pi m\,\frac{2}{3}\epsilon\right)^{3/2}\left(\frac{3}{2}\right)^{3/2} N^{3/2}}\left(1 - \frac{p^2}{\frac{3N}{2}\,2m\frac{2\epsilon}{3}}\right)^{3/2\,N}$$

$$\Gamma(z+1) = z\,\Gamma(z)$$

$$\epsilon = E/N$$

$$= N\,\frac{4\pi p^2}{\left(2\pi m\,{}^2\!/_3\,\epsilon\right)^{3/2}}\;e^{-p^2/2m\;1/(2/3\,\epsilon)}$$

← dimension / momentum

$$\int_0^\infty N(p)\,dp = N\,\frac{4\pi}{\left(2\pi m\,\frac{2}{3}\epsilon\right)^{3/2}}\int_0^\infty p^2\, e^{-p^2/2m\frac{2}{3}\epsilon}\,dp$$

$$\int_0^\infty e^{-ax^2}\,dx = \frac{1}{2}\sqrt{\frac{\pi}{a}}$$

$$\int_0^\infty x\, e^{-ax^2}\,dx = \frac{1}{2}\,\frac{\sqrt{\pi}}{2a^{3/2}}$$

$$\int_0^\infty x^2\, e^{2x^2}\,dx = \frac{1}{2}\,\frac{\sqrt{\pi}}{2a^{5/2}}\,\frac{3}{2}$$

$$= N\,\frac{4\pi}{\left(2\pi m\,{}^2\!/_3\,\epsilon\right)^{3/2}}\,\frac{3\sqrt{\pi}}{8}\left(2m\,\tfrac{2}{3}\epsilon\right)^{5/2}$$

$$= \frac{N}{\cancel{\pi}}\,\frac{\cancel{3}}{\cancel{2}}\,2m\,\cancel{\tfrac{2}{3}}\,\cancel{\pi}\,\epsilon$$

$$= N\,2m\epsilon.$$

$$N(p) \sim p^2 e^{-\frac{p^2}{2m}\frac{1}{k_BT}}$$

so we would be okay as long as $\frac{2}{3}\epsilon = k_BT$

which in fact is okay $\epsilon = \frac{3}{2}k_BT$.

Let us now consider putting 2 systems into contact so they can exchange energy

$\boxed{1 \mid 2}$ $\qquad H = H_1 + H_2$

$$N(E) = \int d\Gamma\, \delta(H_1 + H_2 - E)$$

1/ ~~total~~ # of states with total Energy E

simple logic in microcanon

probability system 1 has energy E_1

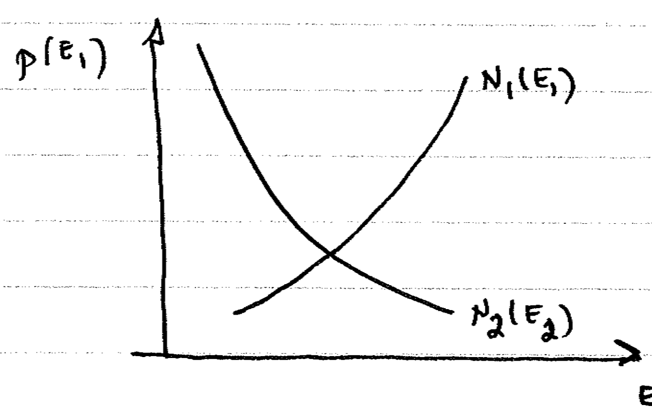
$$p(E_1) = \frac{1}{N(E)} \int d\Gamma_2\, \delta(H_2 - (E - E_1))$$

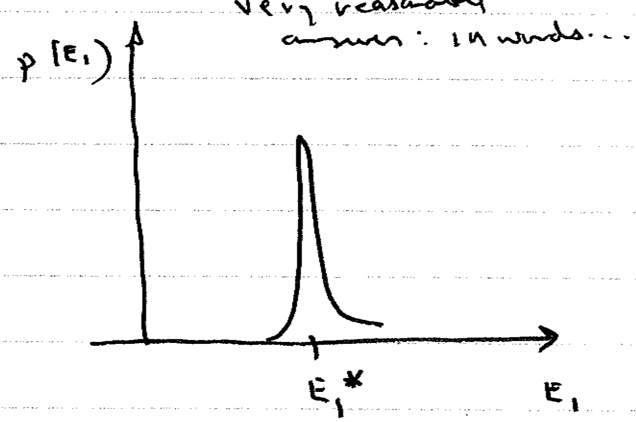
← System 2 must have $E_2 = E - E_1$

$$= \frac{1}{N(E)} \int d\Gamma_1\, d\Gamma_2\, \delta(H_1 - E_1)\, \delta(H_1 + H_2 - E)$$

$$= \frac{1}{N(E)} N_1(E_1) N_2(E_2) \qquad E_2 = E - E_1$$

very reasonable answer: in words...





Maximize $p(E_1)$ or equivalently $\ln p(E_1)$

$$\ln p(E_1) = \ln N_1(E_1) + \ln N_2(E_2) - \ln N(E)$$

$$0 = \frac{\partial}{\partial E_1} \ln N_1(E_1) - \frac{\partial}{\partial E_2} \ln N_2(E_2)$$

$$\boxed{\frac{\partial}{\partial E_1} \ln N_1(E_1) = \frac{\partial}{\partial E_2} \ln N_2(E_2)}$$

We have discovered a quantity that must be the same for two systems in contact. We will define it to be the inverse temperature

How is [e]quilibrium approached!?

$$\boxed{1/k_B T \equiv \frac{\partial}{\partial E} \ln N(E)}$$

Reiterating $T_1 = T_2$ when systems in contact. Ideal gas

$$N(E) = c\, E^{3N/2}$$

$$\ln N(E) = \ln c + \frac{3N}{2} \ln E$$

$$1/k_B T = \frac{3N}{2E}$$

$$E = \frac{3}{2} N k_B T$$

Specific heat

$$C = \frac{dE}{dT} = \frac{3}{2} N k_B$$

Eqn of state ?? ← HW

So indeed

$$N(p) \sim p^2 e^{-p^2/2m \; 1/k_B T}$$

We will talk later at greater length about thermodynamics,
but for the moment remember that $dE = TdS - pdV$

so $\frac{1}{T} = \frac{\partial S}{\partial E}$ $\qquad 1/k_BT = \frac{\partial}{\partial E} \ln N(E)$

$$\rightarrow \quad \boxed{S = k_B \ln N(E)}$$

Perhaps this is familiar to you "entropy is the logarithm of number of states accessible to system"

~~May as well check out pressure~~

$\cancel{\partial^2 E}$ $\qquad \cancel{T = \partial E/\partial S \qquad p = -\partial E/\partial V}$

Before abandoning MCE for CE which is much easier to work with, let's do one more example.

N degrees of freedom S_i which can take on values ± 1

$$\mathcal{H} = -B \sum_i S_i \qquad N_\uparrow + N_\downarrow = N$$

$$E = -B(N_\uparrow - N_\downarrow) = -B(2N_\uparrow - N)$$

$$N(E) = \frac{N!}{N_\uparrow! \, N_\downarrow!}$$

$$\ln N(E) = N \ln N - N_\uparrow \ln N_\uparrow - N_\downarrow \ln N_\downarrow$$

$$1/k_BT = \frac{\partial}{\partial E} \ln N(E) = -\frac{\partial N_\uparrow}{\partial E}(1 + \ln N_\uparrow) - \frac{\partial N_\downarrow}{\partial E}(1 + \ln N_\downarrow)$$

We also know that

$$\frac{\partial N_\downarrow}{\partial E} = -\frac{\partial N_\uparrow}{\partial E} \qquad \text{since } N_\uparrow + N_\downarrow = N \text{ a constant}$$

$$\frac{\partial N_\uparrow}{\partial E} = -\frac{1}{2B}$$

$$\frac{1}{k_BT} = +\frac{1}{2B}(1 + \ln N_\uparrow) - \frac{1}{2B}(1 + \ln N_\downarrow)$$

$$\ln(N_\uparrow / N_\downarrow) = e^{2B/k_BT}$$

$$N_\uparrow / N_\downarrow = e^{2B/k_BT}$$

This should again be familiar since we have two possible choices of Energy $-B$ for $S_i = \uparrow = 1$ and $+B$ for $S_i = \downarrow = -1$ and the difference is then $2B$ so we learn relative #s of 2 possibilities

$$\sim e^{-\Delta E / k_B T}$$

Summarize ME

1) $P(\Gamma)$ = same for all Γ of energy E

   Formally $P(\Gamma) = \delta(E - H) / \int d\Gamma\, \delta(E - H)$

   just check if $H(\Gamma) = E$ — divide by total # of Γ satisfying this

2) $N(E) = \int d\Gamma\, \delta(E - H)$

3) $1/k_B T = \partial/\partial E \ln N(E)$ $\qquad T_1 = T_2$

4) $S = k_B \ln N(E)$

Ideal gas example, Spin 1/2 Example

Now relate to canonical ensemble

Imagine system 1 is in contact with some much larger system 2. Consider computing the average of some quantity depending on variables in 1.

$$\langle \hat{O}_1 \rangle = \frac{1}{N(E)} \int d\Gamma_1 \, d\Gamma_2 \; \hat{O}_1 \; \delta(H_1 + H_2 - E) \ldots$$

$$N(E) = \int d\Gamma_1 \, d\Gamma_2 \; \delta(H_1 + H_2 - E)$$

$$\langle \hat{O}_1 \rangle = \int d\Gamma_1 \; \hat{O}_1 \; \frac{\int d\Gamma_2 \; \delta(H_1 + H_2 - E)}{\int d\Gamma_1 \, d\Gamma_2 \; \delta(H_1 + H_2 - E)}$$

$p_1(\Gamma_1) \equiv$ factor associated with "integrating out" degrees of freedom of system 2

This factor $\sim N_2(E - H_1)$

$$\ln N_2(E - H_1) = \ln N_2(E) - H_1 \frac{\partial}{\partial E} \ln N_2(E) + \frac{1}{2} H_1^2 \frac{\partial^2}{\partial E^2} \ln N_2(E) \ldots$$

since $H_1 \ll E$ is small

$\frac{1}{k_B T}$ $\qquad T_2$

Compare terms: Ideal gas $N_2(E) \sim E^{3N/2}$

$$\frac{\partial}{\partial E} \ln N_2(E) = \frac{3N}{2E}$$

$$\frac{\partial^2}{\partial E^2} \ln N_2(E) \sim -\frac{3N}{2E^2}$$

so $$\ln N_2(E) - o\left(\frac{H_1}{E}\right) + o\left(\frac{H_1^2}{E^2}\right)$$

$$\ln N_2(E - H_1) = C - H_1/k_B T$$

$$N_2(E - H_1) = \tilde{c}\, e^{-H_1/k_B T} \qquad \therefore\ p(\Gamma_1) \propto e^{-H_1/k_B T}$$

$$\langle \hat{O}_1 \rangle = \frac{\int d\Gamma_1\, \hat{O}_1\, e^{-H_1/k_B T}}{\int d\Gamma_1\, e^{-H_1/k_B T}}$$

must be this to get
normalization correct
$Z(\beta)$ $\quad \beta = 1/k_B T$

Aside: Shannon argument.

"If you know nothing about probability distribution, make all probabilities equal subject to $\sum p_i = 1$"

["Maximum Entropy" method in numerical simulations]

"If you know a little make broadest prob. distrib. consistent with that knowledge"

[Again Maxent - know the moments ? and know $G(p\tau)$ from Monte carlo at some points]

Shannon's claim is maximize

$$\sum p_i \ln p_i \qquad \text{subject to } \sum p_i = 1 \qquad \sum p_i A_i = \langle A \rangle$$

accomplishes this

$$f = \sum p_i \ln p_i + \lambda_1 \left(\sum p_i - 1\right) + \lambda_2 \left(\sum p_i A_i - \langle A \rangle\right)$$

$$\frac{\partial}{\partial p_i} f = \ln p_i + 1 + \lambda_1 + \lambda_2 A_i = 0$$

$$p_i = e^{-\lambda_1 - 1} e^{-\lambda_2 A_i}$$

$$\sum p_i = 1 \longrightarrow p_i = \frac{e^{-\lambda_2 A_i}}{\sum e^{-\lambda_2 A_i}}$$

This is basically what our deriv of CE told us.