This suggests a connection between F + Z

$Z \sim -F$

- In an isolated system:

  $S = k \ln \Omega$ tends to <u>increase</u>

- Exchange energy @ const T, V, N

  S <u>can</u> decrease

  F tends to <u>decrease</u>

  $Z = \langle \Omega \rangle$ tends to increase

Guess: $F \sim -\ln Z$?

$[F] = \text{Eng}$

$[\ln Z] = -$

Try:

$$F = -kT \ln Z$$

$$S = k \ln \Omega \longrightarrow F = -kT \ln Z$$

Proof:

$$F \equiv U - TS$$

$$dF = dU - TdS - SdT$$

$$= TdS - PdV + \mu dN - TdS - SdT$$

$$dF = -SdT - PdV + \mu dN$$

$$\left(\frac{\partial F}{\partial T}\right)_{V,N} = -S$$

$$\frac{F-U}{T} = -S$$

$$\boxed{\left(\frac{\partial F}{\partial T}\right)_{V,N} = \frac{F-U}{T}}$$

Show that this holds when

$$F = -kT \ln Z$$

$$\frac{\partial F}{\partial T} = \frac{\partial}{\partial T}\left(-kT \ln Z\right) = -k \ln Z - kT \frac{\partial}{\partial T} \ln Z$$

$$\frac{\partial}{\partial T} \ln Z = ?$$

$$Z = \sum_{\vec{s}} e^{-\frac{E(\vec{s})}{kT}} = \sum_{\vec{s}} e^{-\beta E(\vec{s})}$$

$$\frac{\partial}{\partial T} = \frac{\partial \beta}{\partial T} \frac{\partial}{\partial \beta}$$

$$\frac{\partial}{\partial T} \ln Z = \frac{\partial \beta}{\partial T} \frac{\partial}{\partial \beta} \ln Z$$

$$= -\frac{\partial}{\partial T}\left(\frac{1}{kT}\right) U$$

$$\frac{\partial}{\partial T} \ln Z = \frac{U}{kT^2}$$

so:

$$\frac{\partial F}{\partial T} = -k \ln Z - kT \frac{\partial}{\partial T} \ln Z$$

$$= -k \ln Z - kT\left(\frac{U}{kT^2}\right)$$

$$\frac{\partial}{\partial T}\left(-kT \ln Z\right) = -k \ln Z - \frac{U}{T}$$

$$= \frac{-kT \ln Z - U}{T}$$

$$\frac{\partial F}{\partial T} = \frac{F - U}{T}$$ so: $F = -kT \ln Z$

Once we have F, we have everything we need

Exercise: Show how to calculate

S, P, + μ from F

$$F = U - TS$$

$$dF = dU - TdS - SdT$$

$$= TdS - PdV + \mu dN - TdS - SdT$$

$$dF = -SdT - PdV + \mu dN$$

$$dF = \left(\frac{\partial F}{\partial T}\right)_{V,N} dT + \left(\frac{\partial F}{\partial V}\right)_{T,N} dV + \left(\frac{\partial F}{\partial N}\right)_{T,V} dN$$

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N}$$

$$P = -\left(\frac{\partial F}{\partial V}\right)_{T,N}$$

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{V,N}$$

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V}$$

Einstein solid:

$$Z_1 = \frac{1}{2\sinh\left(\frac{1}{2}\beta\hbar\omega\right)}$$

$$Z_N = \frac{1}{2^N} \frac{1}{\sinh^N\left(\frac{1}{2}\beta\hbar\omega\right)}$$

$$F = -kT \ln Z$$

$$F = -kT \ln\left[\frac{1}{2^N} \frac{1}{\sinh^N\left(\frac{1}{2}\beta\hbar\omega\right)}\right]$$

$$F = -kTN \ln\left[\frac{1}{2} \frac{1}{\sinh\left(\frac{1}{2}\beta\hbar\omega\right)}\right]$$

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N}$$

Without further ado: the ideal gas

Non-interacting, indistinguishable

Find Z_1, then $Z_N = \frac{1}{N!} Z_1^N$

$$Z_1 = \sum_{\vec{s}} e^{-\frac{E(\vec{s})}{kT}}$$

$\vec{s}$ specified by $\vec{r}$ + $\vec{p}$

$$\vec{s} = \langle x, y, z, p_x, p_y, p_z \rangle$$

$$Z_1 = \sum_{\substack{x,y,z \\ p_x,p_y,p_z}} e^{-\frac{(p_x^2+p_y^2+p_z^2)}{2m} \frac{1}{kT}}$$

In general, $x\,y\,z$, $p_x\,p_y\,p_z$ are continuous

(they can take on any value)

$$\sum \longrightarrow \int$$

How to convert a sum to an integral

$$\int_{x_0}^{x_1} f(x)\,dx = \lim_{\substack{\Delta x \to 0 \\ n \to \infty}} \sum_{i=0}^{n} f(x_0 + i\Delta x)\cdot \Delta x$$

I have: $\sum_{i}^{n} f(x_0 + i\Delta x)$

$\times$ + $\div$ by Δx

$$\sum f(x) = \frac{1}{\Delta x}\sum f(x)\Delta x \rightarrow \frac{1}{\Delta x}\int f(x)\,dx$$

$$\sum_{\substack{x,y,z \\ p_x,p_y,p_z}} e^{-\frac{(p_x^2+p_y^2+p_z^2)}{2m}\frac{1}{kT}} \longrightarrow$$

$$\frac{\int e^{-\frac{(p_x^2+p_y^2+p_z^2)}{2mkT}} dx\,dy\,dz\,dp_x\,dp_y\,dp_z}{\underbrace{\Delta x\,\Delta y\,\Delta z\,\Delta p_x\,\Delta p_y\,\Delta p_x}}$$

$$\Delta x \Delta p_x \cdot \Delta y \Delta p_y \cdot \Delta z \Delta p_z$$

$$\geq$$

$$\frac{\hbar}{2} \qquad \frac{\hbar}{2} \qquad \frac{\hbar}{2}$$

$$Z_1 = \frac{1}{\left(\frac{\hbar}{2}\right)^3} \int e^{-\left(\frac{p_x^2+p_y^2+p_z^2}{2mkT}\right)} dx\,dy\,dz\,dp_x\,dp_x\,dp_z$$

$$\frac{1}{\hbar^3}$$

Now let's look at the integral

$$\int e^{-\left(\frac{p_x^2+p_y^2+p_z^2}{2mkT}\right)} dx\,dy\,dz\,dp_x\,dp_y\,dp_z$$

$$= \int dx \int dy \int dz \int e^{\frac{-(p_x^2+p_y^2+p_z^2)}{2mkT}} dp_x\,dp_y\,dp_z$$

$$L \cdot L \cdot L$$

$$= L^3 = V$$

$$\int e^{-\left(\frac{p_x^2+p_y^2+p_z^2}{2mkT}\right)} dx\,dy\,dz\,dp_x\,dp_y\,dp_z$$

$$= V \int e^{-(\quad)} dp_x\,dp_y\,dp_z$$

Now, what is

$$\int e^{\frac{-(p_x^2+p_y^2+p_z^2)}{2mkT}} dp_x\,dp_y\,dp_z$$

p_x, p_y, p_z are independent

$$\int e^{\frac{-(p_x^2+p_y^2+p_z^2)}{2mkT}} dp_x dp_y dp_z$$

$$= \int e^{\frac{-p_x^2}{2mkT}} e^{\frac{-p_y^2}{2mkT}} e^{\frac{-p_z^2}{2mkT}} dp_x dp_y dp_z$$

$$= \underbrace{\int_{-\infty}^{\infty} e^{\frac{-p_x^2}{2mkT}} dp_x}_{} \underbrace{\int_{-\infty}^{\infty} e^{\frac{-p_y^2}{2mkT}} dp_y}_{} \underbrace{\int e^{\frac{-p_z^2}{2mkT}} dp_z}_{}$$

Integrals are identical

Solve one + cube

$$\int e^{\frac{-(p_x^2+p_y^2+p_z^2)}{2mkT}} dp_x dp_y dp_z = \left[\int_{-\infty}^{\infty} e^{\frac{-p^2}{2mkT}} dp\right]^3$$

$$x := \frac{p}{\sqrt{2mkT}} \qquad = \sqrt{2mkT} \int_{-\infty}^{\infty} e^{-x^2} dx$$

$$I = \int_{-\infty}^{\infty} e^{-x^2}\,dx$$

$$I^2 = \int_{-\infty}^{\infty} e^{-x^2}\,dx \int_{-\infty}^{\infty} e^{-y^2}\,dy$$

$$I^2 = \iint_{-\infty}^{\infty} e^{-x^2-y^2}\,dx\,dy$$

$$= \iint_{-\infty}^{\infty} e^{-(x^2+y^2)}\,dx\,dy$$

$$x^2 + y^2 \longrightarrow r^2$$

$$dx\,dy \longrightarrow r\,dr\,d\phi$$

$$I^2 = \int_0^{2\pi}\int_0^{\infty} r e^{-r^2}\,dr\,d\phi$$

$$= 2\pi \int_0^{\infty} r e^{-r^2}\,dr$$

$$s = -r^2 \qquad r = \sqrt{-s}$$

$$ds = -2r\,dr \qquad dr = -\frac{ds}{2r}$$

$$\int_0^\infty r e^{-r^2}\,dr \rightarrow \int_0^{-\infty} \sqrt{-s}\, e^{s} \left(\frac{-1}{2\sqrt{-s}}\right) ds$$

$$= -\int_0^{-\infty} \frac{1}{2} e^{s}\,ds = \frac{1}{2}\int_{-\infty}^{0} e^{s}\,ds$$

$$= \frac{1}{2}(1 - 0) = \frac{1}{2}$$

$$I^2 = (2\pi)\left(\frac{1}{2}\right) = \pi$$

$$I = \sqrt{\pi}$$

$$\int_{-\infty}^{\infty} e^{-x^2}\,dx = \sqrt{\pi}$$

$$\sqrt{2mkT} \int_{-\infty}^{\infty} e^{-x^2}\, dx = \sqrt{2\pi mkT}$$

$$Z_1 = \frac{V}{h^3} \left(2\pi mkT \right)^{3/2}$$

$$Z_1 = V \left(\frac{2\pi mkT}{h^2} \right)^{3/2}$$

$$Z_N = \frac{V^N \left(\frac{2\pi mkT}{h^2} \right)^{\frac{3N}{2}}}{N!}$$

What is $\frac{2\pi mkT}{h^2}$?

Dimensions: $\frac{M \cdot E}{E^2 \cdot T^2} = \frac{M}{E \cdot T^2} = \frac{M}{M \frac{L^2}{T^2} T^2} = \frac{1}{L^2}$

$\sqrt{\frac{h^2}{2\pi mkT}}$ is a length

Call it the thermal de Broglie wavelength

$$\lambda_T = \sqrt{\frac{h^2}{2\pi mkT}}$$

de Broglie wavelength

$$\lambda = \frac{h}{p}$$, wavelength of ψ (distance over which matter is wavelike)

For an ideal gas, $\frac{p^2}{2m} = E \longrightarrow p = \sqrt{2mE}$

$$\lambda = \frac{h}{\sqrt{2mE}}$$

$$U = NE = \frac{3}{2}NkT$$

$$E = \frac{3}{2}kT$$

$$\lambda = \frac{h}{\sqrt{3mkT}}$$

compare to: $\lambda_T = \sqrt{\frac{\hbar^2}{2\pi mkT}}$

Interpretation: λ_T is the average de Broglie wavelength

$$Z_N = \frac{1}{N!}\frac{V^N}{\lambda^{3N}}$$