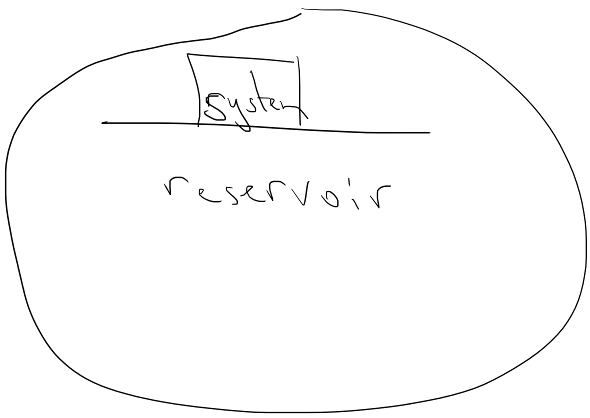
$S = k \ln \Omega$



r, E_r

$$P_r = \frac{e^{-\beta E_r}}{Z} \Leftarrow$$

$$\beta = \frac{1}{kT}$$

$$\sum n_r = N, \quad \frac{1}{N} \sum_r E_r n_r = U$$

$$U = \sum_r E_r P_r = \frac{\sum_r E_r e^{-\beta E_r}}{\sum_r e^{-\beta E_r}}$$

$$U = \left(-\frac{\partial}{\partial \beta} \sum_r e^{-\beta E_r} \right) \frac{1}{\sum_r e^{-\beta E_r}}$$

$\Downarrow$

$$\boxed{U = -\frac{\partial}{\partial \beta} \ln Q_N} \qquad U(\beta, V, N) \overset{T}{?}$$

$$Q_N = \sum_r e^{-\beta E_r} \; : \text{partition function}$$

$$\underline{Z} \quad \text{(sum over states)}$$

$$dU = T dS - P dV + \mu dN$$

$$d(\underbrace{U - TS}_{A}) = -S dT - P dV + \mu dN$$

$$dA = -S\,dT - P\,dV + \mu\,dN$$

$$U = A + TS = A + T\left(-\frac{\partial A}{\partial T}\right)_{V,N}$$

$$U = A - T\frac{\partial A}{\partial T}$$

$$U = -T^2\frac{\partial}{\partial T}\left(\frac{A}{T}\right)_{V,N}$$

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

$$U = \frac{\partial}{\partial\beta}\left(-\ln Q_N\right)_{V,N}$$

$$\beta = \frac{1}{kT}$$

$$-\ln Q_N = \frac{A}{kT} \Rightarrow \boxed{A = -kT\ln Q_N}$$

$$\boxed{dA = -S\,dT - P\,dV + \mu\,dN}$$

$$\boxed{Q_N = \sum_r e^{-\beta E_r}}$$

<u>For a classical system:</u>

$$Q_N = \frac{1}{N!}\int\frac{d^{3N}p\,d^{3N}q}{(2\pi\hbar)^{3N}}\,e^{-\beta H(p,q)}$$

Classical Ideal Gas

$$H = \sum_i \frac{p_i^2}{2m}$$

$$Q_N = \frac{1}{N!}\int \frac{d^{3N}p\, d^{3N}q}{(2\pi\hbar)^{3N}} e^{-\beta \sum_i \frac{p_i^2}{2m}}$$

$$= \frac{1}{N!}\int \frac{d^{3N}p\, d^{3N}q}{(2\pi\hbar)^{3N}} \prod_{i=} e^{-\frac{\beta p_i^2}{2m}}$$

$$= \frac{1}{N!}\underbrace{\left(\int \frac{d^3p\, d^3q}{(2\pi\hbar)^3} e^{-\frac{\beta p^2}{2m}}\right)^N}_{Q_1}$$

$$\boxed{Q_N = \frac{1}{N!} Q_1^N} \qquad H = \sum_i H_i$$

$$Q_1 = \int \frac{d^3p\, d^3q}{(2\pi\hbar)^3} e^{-\frac{\beta p^2}{2m}} = \frac{V}{(2\pi\hbar)^3}\left(\frac{\pi}{\frac{\beta}{2m}}\right)^{3/2}$$

$$Q_1 = V\left(\frac{2m\pi}{\beta\, 2\cdot 4\pi^2 \hbar^2}\right)^{3/2} = V\left(\frac{m}{2\pi\beta\hbar^2}\right)^{3/2}$$

$$Q_N = \frac{Q_1^N}{N!} \Rightarrow A \simeq -kT N \ln Q_1 + kTN\ln N$$

$$A = -kTN \ln V\left(\frac{mkT}{2\pi\hbar^2}\right)^{3/2} + NkT\ln N$$

$$P = -\left(\frac{\partial A}{\partial V}\right)_{N,T} = -\frac{\partial}{\partial V}\left[-NkT\ln V + \dots\right] = \frac{NkT}{V}$$

$PV = NkT$

$\uparrow$ Boltzmann's constant

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

$$\langle P \rangle = \left\langle -\left(\frac{\partial E_r}{\partial V}\right)_N \right\rangle$$

E_r is independent of T!

$$\Rightarrow \quad = \frac{\sum_r \left(-\frac{\partial E_r}{\partial V}\right)_N e^{-\beta E_r}}{\sum_r e^{-\beta E_r}}$$

$$= -\frac{1}{Q_N}\left(\frac{-1}{\beta}\frac{\partial}{\partial V}\right)_{N,T} \underbrace{\left(\sum_r \cancel{E_r}\, e^{-\beta E_r}\right)}_{Q_N}$$

$$P = \left(-\frac{\partial}{\partial V}\right)_{N,T} \underbrace{\ln Q_N}_{-\left(\frac{A}{kT}\right)} \frac{1}{\beta}$$

$$P = \sum \left(-\frac{\partial E_r}{\partial V} \right) P_r$$

$$P\,dV = -\sum P_r \left(dE_r \right) = -d\langle E_r \rangle = -dU$$

$$\boxed{P\,dV = -dU}$$

$$\langle \ln P_r \rangle = \left\langle \ln \frac{e^{-\beta E_r}}{Q_N} \right\rangle$$

$$= -\beta \langle E_r \rangle - \langle \ln Q_N \rangle$$

$$= -\beta U - \ln Q_N$$

$$= -\frac{U}{kT} - \left(\frac{-A}{kT}\right)$$

$$= \left(\frac{A-U}{kT}\right) = \frac{U - TS - U}{kT} = -\frac{S}{k}$$

$$\boxed{S = -k \langle \ln P_r \rangle}$$ Shannon's entropy

$$\boxed{S = -k \sum_r (\ln P_r) P_r}$$

$$\lim_{x \to 0} x \ln x = 0$$

$$\Omega(E) \qquad P_r = \frac{1}{\Omega(E)}$$

$$S = -k \langle \ln P_r \rangle = +k \langle \ln \Omega(E) \rangle$$

$$S = k \ln \Omega(E)$$

Ex $S = -k \langle \ln P_r \rangle$

$$\sum P_r = 1, \quad \sum P_r E_r = U$$

$$\delta S = 0 \Rightarrow P_r \propto e^{-\beta E_r}$$

$$PV = NkT \qquad U = \frac{3}{2} NkT$$

$$Q_N = \sum_r e^{-\beta E_r}$$

$$\langle f \rangle = \int d\omega \, f(E) \, e^{-\beta E}$$

$$= \sum_r f(E) e^{-\beta E_r}$$

density of states

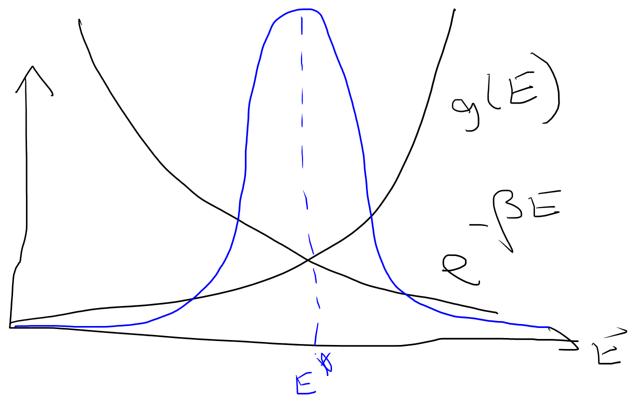
$$= \sum_E g(E) f(E) e^{-\beta E} \Rightarrow \int_0^\infty dE \, g_N(E) f(E) e^{-\beta E}$$

$g(E)$ = # of microstates having energy E

$g(E)\,dE$ = # of " " in the interval $(E, E+dE)$

$$\langle f \rangle = \sum_E \left(e^{-\beta E} g(E) \right) f(E)$$

$$P(E) = g(E) e^{-\beta E}$$



$$\left. \frac{\partial P(E)}{\partial E} \right|_{E=E^*} = 0$$

$$g'(E^*) e^{-\beta E^*} - \beta g(E^*) e^{-\beta E^*} = 0$$

$$\frac{g'(E^*)}{g(E^*)} = \beta$$

$$k \left. \frac{\partial (\ln g)}{\partial E} \right|_{E=E^*} = \frac{1}{T}$$

$$k \ln g = S(E)$$

$$\boxed{\left(\frac{\partial S}{\partial E}\right)\Bigg|_{E=E^*} = \frac{1}{T}}$$

$$\frac{\langle (E-U)^2 \rangle}{U^2} \propto \frac{1}{N} \quad \Rightarrow \quad \langle E \rangle \equiv U = E^*$$

$$\frac{\langle E^2 \rangle - U^2}{U^2}$$

$$\langle E^2 \rangle = \sum_r E_r^2 P_r$$

$$= \frac{1}{Q_N} \sum_r E_r^2 e^{-\beta E_r}$$

$$\langle E^2 \rangle = \frac{1}{Q_N} \frac{\partial^2}{\partial \beta^2} \underbrace{\sum_r e^{-\beta E_r}}_{Q_N}$$

$$= \frac{1}{Q_N} \left[\frac{\partial}{\partial \beta} Q_N \underbrace{\left(\frac{1}{Q_N} \frac{\partial}{\partial \beta} Q_N \right)}_{\frac{\partial}{\partial \beta}(\ln Q_N)} \right]$$

$$\langle E^2\rangle = \frac{1}{Q_N}\left[\left(\frac{\partial Q_N}{\partial\beta}\right)\frac{\partial}{\partial\beta}(\ln Q_N) + Q_N\frac{\partial^2}{\partial\beta^2}(\ln Q_N)\right]$$

$$= \underbrace{\left(\frac{\partial}{\partial\beta}\ln Q_N\right)^2}_{\langle E\rangle \equiv U} + \frac{\partial^2}{\partial\beta^2}\ln Q_N$$

$$\langle E^2\rangle - U^2 = \frac{\partial^2}{\partial\beta^2}\underbrace{(\ln Q_N)}_{-\beta A}$$

$$\langle E^2\rangle - U^2 = -\frac{\partial}{\partial\beta}\frac{\partial}{\partial\beta}(\beta A)$$

$U \propto N$ $\qquad U(T, N, V)$

$\langle E^2\rangle \propto N^2$ $\qquad U(T, \lambda N, \lambda V) = \lambda U(T, N, V)$

$\langle U^2\rangle \propto N^2$

$A = U - TS \propto N$ $\qquad \langle E^2\rangle - U^2 \propto N$

$$\Rightarrow \frac{\langle E^2\rangle - U^2}{U^2} \propto \frac{N}{N^2} = \frac{1}{N}$$

$$\boxed{\frac{\Delta E}{E} \propto \frac{1}{\sqrt{N}}}$$

$$Q_N(\beta) = \int_0^\infty dE\, g(E)\, e^{-\beta E}$$: Laplace transform of $g(E)$

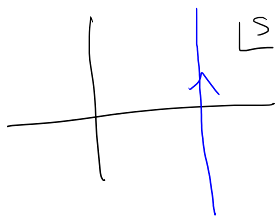
$$g(E) = \frac{1}{2\pi i}\int_{s'+i\infty}^{s'-i\infty} ds\, Q_N(s)\, e^{+sE}$$ s large enough

$$Q_1 = V\left(\frac{\cancel{2m\pi}\, m}{\beta 2\pi\hbar^2}\right)^{3/2}$$

$$Q_N = \frac{1}{N!} V^N \left(\frac{m}{\beta\, 2\pi\hbar^2}\right)^{\frac{3N}{2}}$$

$$g(E) = \frac{1}{2\pi i}\,\frac{V^N}{N!}\left(\frac{m}{2\pi\hbar^2}\right)^{\frac{3N}{2}}\int_{s'-i\infty}^{s'+i\infty} ds\, \frac{e^{+sE}}{s^{\frac{3N}{2}}}$$

$$\frac{1}{2\pi i}\int_{s'-i\infty}^{s'+i\infty} ds\, \frac{e^{+sx}}{s^n} = \frac{x^{n-1}}{(n-1)!}\begin{cases} 1 & x > 0 \\ 0 & x < 0\end{cases}$$



$$\Rightarrow\quad g(E) = \frac{V^N}{N!}\left(\frac{m}{2\pi\hbar^2}\right)^{\frac{3N}{2}} \frac{E^{\frac{3N}{2}-1}}{\left(\frac{3N}{2}-1\right)!}\,\Theta(E)$$