

$$P(q_1, \dots, q_{3N}, p_1, \dots, p_{3N}) = \text{[scribbled out]}$$

a particular cell

$$P = \sum \frac{1}{\Omega}$$

states w/ desired value of observable

$$P(q_1, \dots, q_{3N}, p_1, \dots, p_{3N}) = \begin{cases} \frac{1}{\Omega} & \text{if } E < E_{q_1, \dots, p_{3N}} < E + \Delta E \\ 0 & \text{otherwise} \end{cases}$$

To calculate probability of obtaining a certain value for our observable we just count the # of states w/ a given value of our observable & divide by  $\Omega$

Coarse graining: equivalently, if we wanted to speak about values of volumes ~~of the system~~ so that we can use integrals we speak of the probability density

value

$$P(q_1, \dots, q_{3N}, p_1, \dots, p_{3N}) = \begin{cases} \frac{1}{\Omega h^{3N}} & \text{if } E < E_{q_1, \dots, p_{3N}} < E + \Delta E \\ 0 & \text{otherwise} \end{cases}$$

technically for coarse graining we should use a  $dpdq \gg h$  but it will not end up making a difference in our calculations

$\Delta E$  gives us some width to the distribution

$P = \int_{\text{states w/ desired value of observable}} \frac{1}{\Omega h^{3N}} dq_1, \dots, dq_{3N} dp_1, \dots, dp_{3N}$  or using  $\delta$  function

so that we can integrate over all states

$$P(q_1, \dots, q_{3N}, p_1, \dots, p_{3N}) = \frac{\Delta E}{\Omega h^{3N}} \int \delta(H(q_1, \dots, q_{3N}, p_1, \dots, p_{3N}) - E)$$

QM description

$$P = \int_{\text{all states}} \frac{\Delta E}{\Omega h^{3N}} \int \delta(H(q_1, \dots, q_{3N}, p_1, \dots, p_{3N}) - E)$$

Say system is in a pure quantum state  $|\psi\rangle$  w/ classical probability  $P_\psi$

We define a density operator

$$\hat{\rho} \equiv \sum_{\psi} P_{\psi} |\psi\rangle \langle \psi| \quad \text{where } P_{\psi} \geq 0 \text{ and } \sum_{\psi} P_{\psi} = 1$$

$|\psi\rangle$  could be a designation of spins on a lattice  
 $|++---++-\rangle$   
 or quantum #'s for many particles in a box  
 $|n_1, n_2, n_3, \dots, n_f\rangle$

Probability of finding system in state  $|a\rangle$  is  $\langle a | \hat{\rho} | a \rangle$

for basis  $|n_1, \dots, n_f\rangle$

takes into account wave nature of system and allows for interference

$$P(n_1, \dots, n_f) = \langle n_1, \dots, n_f | \hat{\rho} | n_1, \dots, n_f \rangle = \sum_{\psi} P_{\psi} |\langle n_1, \dots, n_f | \psi \rangle|^2$$

Classical probability to be in state  $\psi$       quantum prob to measure  $|n_1, \dots, n_f\rangle$  in quantum state  $|\psi\rangle$

The basic postulate of Stat Mech (microcanonical ensemble) is that

$$\langle n_1, \dots, n_f | \hat{\rho} | m_1, \dots, m_f \rangle = \begin{cases} \frac{1}{\Omega} \delta_{n_1, m_1} \dots \delta_{n_f, m_f} & \text{if } E < E_{n_1, \dots, n_f} < E + \Delta E \\ 0 & \text{otherwise} \end{cases}$$

i.e. No off diagonal terms & ~~equal~~ states are equally probable if they are consistent w/ the energy requirement

as we did before, we can define  $\hat{\rho} = \frac{1}{\Omega} \delta(\hat{H} - E) \Delta E$  & sum over all states w/ obvious energy

Aside: In order for ergodicity to hold, there must be small residual interactions (off diagonal terms) that do not significantly affect  $E_{n_1, \dots, n_f}$

All probabilities depend on  $\Omega$  for some energy  $E$ .

Q: How does  $\Omega$  change as  $E$  increases?

$$\Omega(E) = \underbrace{W(E)}_{\text{density of states}} \Delta E$$

$$W(E) = \frac{d\Phi(E)}{dE}$$

$W(E) \equiv$  density of states

$\Phi(E) \equiv$  # of states w/ energy  $< E$

$\Delta E$  is large compared to spacing between energy levels but sufficiently small compared to ~~macroscopic~~ microscopic energy  $E$

for a system with 1 degree of freedom

$$\Phi_1 \sim E^\alpha \quad \text{where } \alpha \text{ is of order unity}$$

Ex: S.H.O.  $E = \hbar\omega(n + \frac{1}{2}) \quad n=0,1,2, \dots \quad \alpha=1$

P.I.B  $E = \frac{\hbar^2}{2m} \left(\frac{\pi n}{L}\right)^2 \quad n=0,1,2, \dots \quad \alpha=1/2$

for system with  $f$  degrees of freedom

$$\Phi \sim E^{\alpha f} \quad \text{where } E = \frac{E}{f} \quad \text{all states get an equal share of the energy}$$

$E = f E_i \quad \Phi_i \sim E_i^{\alpha}$   
 $dE = f dE_i$

$$\Omega(E) = \frac{d\Phi}{dE} \Delta E = \frac{d\Phi_i^f}{dE} \Delta E = f \Phi_i^{f-1} \frac{d\Phi_i}{dE_i} \Delta E = \Phi_i^{f-1} \frac{d\Phi_i}{dE_i} \Delta E$$

$$\ln[\Omega(E)] = (f-1) \ln \Phi_i + \ln\left(\frac{d\Phi_i}{dE_i} \Delta E\right)$$

$$\frac{d\Phi_j}{dE} = \alpha E^{\alpha-1} \text{ of order unity}$$

$\int dE$  is some multiple of  $E$  but it is certainly ~~greater~~ smaller than ~~f~~ since  $fE = E$  &  $\int dE \ll E$

$$\therefore \ln[\Omega(E)] \equiv f \ln \Phi_1$$

or

$$\Omega(E) \approx \Phi_1^f \propto E^{f\alpha}$$

$\Omega$  increases very quickly as a function of energy!

Lets do an Example: particle in a box

QM  
how many states are there with

$$\sum_j \frac{n_j^2 \pi^2 \hbar^2}{2mL^2} = E_{n_1, \dots, n_f} < E?$$

$$\sum n_j^2 < \frac{2mEL^2}{\pi^2 \hbar^2}$$

$$\Phi(E) = \frac{1}{2^f} \mathcal{V}_f \left( \sqrt{\frac{2mEL^2}{\pi^2 \hbar^2}} \right)$$

Count only positive  $n_j$

$\mathcal{V}_f(R) \equiv$  Volume of sphere with radius  $R$  in  $f$  dimensions

Classical

$$\Phi(E) = \frac{1}{h^f} \int dq_1 \dots dq_f dp_1 \dots dp_f$$

$0 < q_i < L$  integrated over  $q_i$ 's gives  $L^f$

$$\sum_j \frac{p_j^2}{2m} < E$$

$$\Phi(E) = \frac{1}{h^f} L^f \mathcal{V}_f(\sqrt{2mE})$$

In both cases this problem reduces to calculating the volume of a sphere in  $f$  dimensions

Math Aside:  $\Gamma$  functions

$$\Gamma(n) \equiv \int_0^\infty e^{-x} x^{n-1} dx = -\int_0^\infty x^{n-1} d(e^{-x}) = -x^{n-1} e^{-x} \Big|_0^\infty + (n-1) \int_0^\infty x^{n-2} e^{-x} dx$$

$$\Gamma(n) = (n-1) \Gamma(n-1) \quad \text{or} \quad \Gamma(n) = (n-1)! \quad \Gamma(1) = 0! = 1$$

$$\Gamma\left(\frac{1}{2}\right) = \int_0^\infty e^{-x} x^{1/2} dx = 2 \int_0^\infty e^{-y^2} dy = \sqrt{\pi}$$

$$\Gamma\left(m + \frac{1}{2}\right) = \left(m - \frac{1}{2}\right)! = \frac{(2m-1)(2m-3)\dots 3 \cdot 1}{2^m} \pi^{1/2} \quad \left. \begin{array}{l} \frac{1}{2}! = \Gamma\left(\frac{3}{2}\right) = \frac{\sqrt{\pi}}{2} \\ \frac{3}{2}! = \Gamma\left(\frac{5}{2}\right) = \frac{3}{4} \sqrt{\pi} \text{ etc.} \end{array} \right\}$$

Volumes of spheres in  $n$  dimensions

$$V_n(R) = C_n R^n \quad \text{trick is to determine } C_n$$

$$dV_n \equiv S_n(R) dR = n C_n R^{n-1} dR$$

where  $S_n(R)$  is the surface area of the sphere

recall  $\int_{-\infty}^{\infty} \exp(-x^2) dx = \pi^{1/2}$

$$\pi^{n/2} = \int_{x_1=-\infty}^{\infty} \dots \int_{x_n=-\infty}^{\infty} \exp\left[-\sum_{i=1}^n x_i^2\right] dx_1 dx_2 \dots dx_n$$

go to polar coords

$$\pi^{n/2} = \int_0^{\infty} \exp(-R^2) n C_n R^{n-1} dR$$

$$\pi^{n/2} = n C_n \int_0^{\infty} \exp(-R^2) R^{n-1} dR = n C_n \frac{1}{2} \Gamma\left(\frac{n}{2}\right) = \left(\frac{n}{2}\right)! C_n$$

$$C_n = \frac{\pi^{n/2}}{\left(\frac{n}{2}\right)!} \quad \checkmark$$

$$V_n(R) = \frac{\pi^{n/2}}{\left(\frac{n}{2}\right)!} R^n$$

$$S_n(R) = \frac{2\pi^{n/2}}{\left(\frac{n}{2}-1\right)!} R^{n-1}$$

try this for dimensions we are familiar with 1, 2, 3

$$V_3(R) = \frac{\pi^{3/2} R^3}{\frac{3}{4} \pi^{1/2}} = \frac{4}{3} \pi R^3$$

$$S_3 = \frac{2\pi^{3/2} R^2}{\left(\frac{1}{2}\right)!} = \frac{2\pi^{3/2} R^2}{\Gamma\left(\frac{3}{2}\right)} = 4\pi R^2$$

$$V_2(R) = \frac{\pi R^2}{1!}$$

$$S_2 = 2\pi R$$

$$V_1(R) = 2R$$

$$S_1 = 2$$

↑  
# of end points

Back to our Counting of states

QM

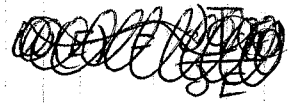
$$\Phi(E) = \frac{1}{2^f} \sqrt[2^f]{\frac{2mL^2 E}{\pi^2 \hbar^2}}$$

$$= \frac{1}{2^f} \pi^{f/2} \left( \frac{2mL^2 E}{\pi^2 \hbar^2} \right)^{f/2}$$

Use Stirling's formula  
 $n! = \sqrt{2\pi n} n^n e^{-n}$  (A.6)

$$\Phi(E) = \left( \frac{4mL^2 \pi E e}{\hbar^2 f} \right)^{f/2} \frac{1}{\sqrt{\pi f}}$$

negligible since  $\frac{f-1}{2} \approx \frac{f}{2}$



Classical

$$\Phi(E) = L^{-f} L^f \sqrt[2^f]{\frac{2mE^f}{\hbar^2}}$$

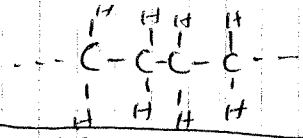
$$= \frac{L^{-f} L^f \pi^{f/2} (2mEe)^{f/2}}{\left(\frac{f}{2}\right)^{f/2}}$$

$$\approx \left( \frac{4mL^2 \pi E e}{\hbar^2 f} \right)^{f/2}$$

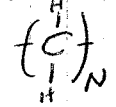
Indeed  $\Phi \sim \left(\frac{E}{f}\right)^{f/2}$   
 and  $\Omega(E) \propto E^{f/2}$

So our <sup>previous</sup> argument holds

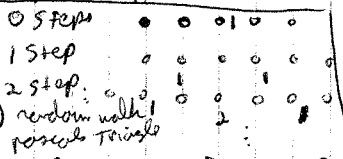
Other ~~examples~~ examples of Counting states:



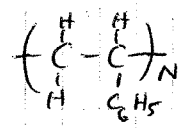
poly ethylene



Polymers  
 film, bottles, cups, electrical insulators



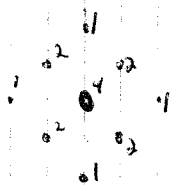
Poly styrene



Coffee cups, rockers

Polymers in 2D are like random walkers in 2-D taking steps "a"

Pascal's Pyramid



give out handout showing a 2 step walk & a 4 step walk

$$\langle r^2 \rangle_2 = \frac{4}{16} \times 0^2 + 4 \times \frac{2}{16} \times (\sqrt{2})^2 + 4 \times \frac{1}{16} \times 2^2 = 2$$

$$\langle r^2 \rangle_4 = \frac{36 \times 0^2 + 4 \times 24 \times (\sqrt{2})^2 + 4 \times 16 \times 2^2 + 4 \times 6 \times (\sqrt{8})^2 + 8 \times 4 \times (\sqrt{10})^2 + 4 \times 4^2}{256} = 4$$

in the limit of large #'s

$$P(\vec{r}) = \frac{1}{\pi N a^2} e^{-r^2 / Na^2}$$

$\sqrt{\Delta r^2} \equiv$  radius of gyration of the polymer

We've now looked at single particles & systems of many particles  
 Next lets discuss Interactions Between Macroscopic Systems

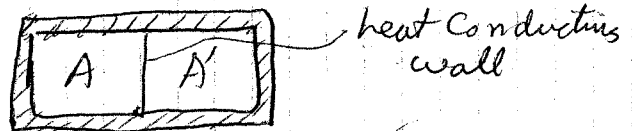
Two systems A & A'

Total energy of combined system  $A_{tot}$  stays constant

From  
macroscopic  
point of  
view

Energy can be transferred in two ways: heat  $Q$ , work  $W$

Let's first discuss heat



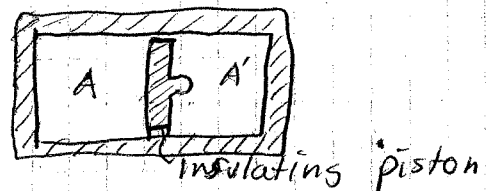
$Q \equiv \Delta \bar{E}$  the change of the mean energy of system A is the heat  $Q$  absorbed

$\Delta \bar{E} + \Delta \bar{E}' = 0$  Conservation of energy

$Q + Q' = 0$  or  $Q = -Q'$

heat gained by one system equals heat lost by other system

Work only (no heat) thermally isolated

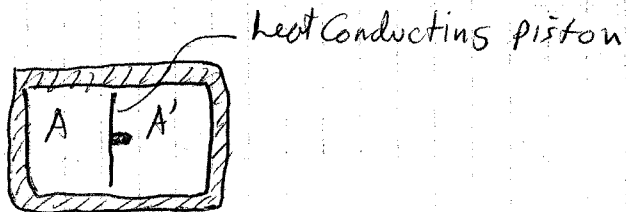


$W \equiv \Delta \bar{E}$  work done by the system

$W + W' = 0$  or  $W = -W'$  Conservation of energy

work done by one system must equal to the work done on other system

Heat + work



$\Delta \bar{E} \equiv Q - W$

$Q = \Delta \bar{E} + W$

See small changes in energy

$dQ = dE + dW$  path dependent

$dQ$  infinitesimal amount of heat absorbed

$dW$  infinitesimal amount of work done by system

# Exact vs. Inexact differentials

Math Aside

$$F = F(x, y)$$

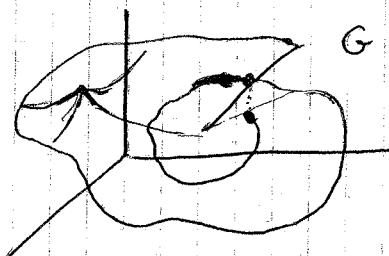
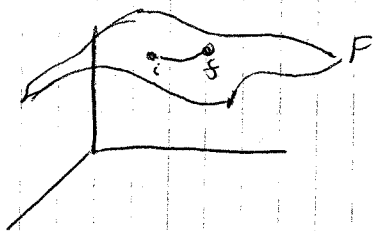
$$dF = \underbrace{A(x, y)}_{\frac{\partial F}{\partial x}} dx + \underbrace{B(x, y)}_{\frac{\partial F}{\partial y}} dy$$

$$\Delta F = F_f - F_i = \int_i^f dF = \int_i^f (A dx + B dy)$$

path dependent portions cancel out

Not all infinitesimal quantities that can be written as sums of derivatives in  $x$  &  $y$  are exact differentials

Need a smooth (contake derivatives) & single valued



double valued or kinked  
cannot write derivatives or exact differentials

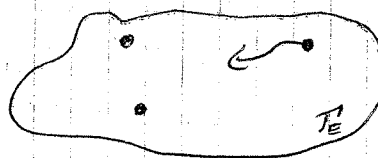
All our thermodynamic energies will be exact differentials  
our variables  $dtq, dtw$  may be inexact but their sum will be exact

• think object in a gravitational field

## From a microscopic point of view

isolated systems are in a sense constrained

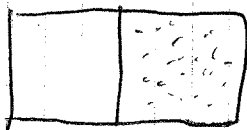
$$\Omega = \Omega(\underbrace{y_1, \dots, y_n}_{\text{constraints}})$$



Once you remove the constraints the system immediately has access to a huge amount of phase space that it can explore

value of the  
the macroscopic variables/observables associated w/ the new phase space are the equilibrium values  
new

ex! Gas in a room



Constraint: all molecules are on ~~left~~ <sup>right</sup> half of the room  
Once we lift the constraint what is the probability that the molecules all stay on the right side of the room

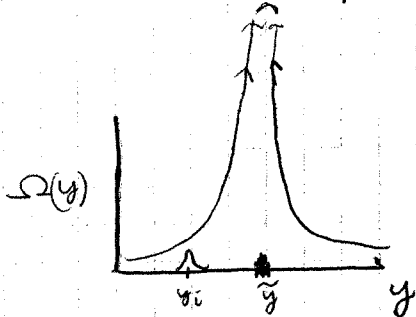
$$P_i = \frac{\Omega_i}{\Omega_f} \leftarrow \begin{array}{l} \text{\# of states on right side} \\ \text{\# of states for full room} \end{array}$$

~~Regardless~~ Regardless of how we split up the phase space  
 the molecules can explore twice as many states in the full  
 room. ~~the molecules can explore twice as many states in the full~~  
 Note: it does not matter what we  
 choose for volume of a state  $\Delta \Omega$

$P_i = \left(\frac{1}{\Omega}\right)^N$  for large  $N$  this is a very small #

Other examples:

thermal equilibrium  
 pressure equilibration



If some constraints of an isolated system are removed, the parameters of the system readjust so that

$\Omega(y_1, \dots, y_n)$  approaches a maximum

$\Omega_f \geq \Omega_i$

- if  $\Omega_f = \Omega_i$  process is reversible
- if  $\Omega_f > \Omega_i$  process is irreversible - we would need to do work to get system back into initial state.

~~is~~ is we consider  $\Omega$  for system + machine it increases during this process

Why does ~~it~~ a stretched rubber band recoil once you let go?

Time Scales

Every system has a relaxation time Silly puts demo

Deborah #, Panta Rei - everything flows

$\tau \ll \tau_{exp}$  System equilibrates very quickly

$\tau \gg \tau_{exp}$  treat system as though constraints are there (this works some of the time) slow constraint

$\tau \sim \tau_{exp}$  hard, sheared colloidal particles

Kivelson's paper on glasses



# Partial derivatives & indep variables

$$z = z(x, y) \quad \text{Exact differential}$$

$$dz = \left. \frac{\partial z}{\partial x} \right|_y dx + \left. \frac{\partial z}{\partial y} \right|_x dy \quad (1)$$

$$dx = \left. \frac{\partial x}{\partial y} \right|_z dy + \left. \frac{\partial x}{\partial z} \right|_y dz$$

to evaluate  $\left. \frac{\partial x}{\partial y} \right|_z$  set  $dz=0$

$$0 = \left. \frac{\partial z}{\partial x} \right|_y dx + \left. \frac{\partial z}{\partial y} \right|_x dy$$

$$\left. \frac{\partial x}{\partial y} \right|_z = - \frac{\left. \frac{\partial z}{\partial y} \right|_x}{\left. \frac{\partial z}{\partial x} \right|_y} \quad (2)$$

Note that  $\frac{dx}{dy} \rightarrow \left. \frac{\partial x}{\partial y} \right|_z$  since  $z = \text{const}$

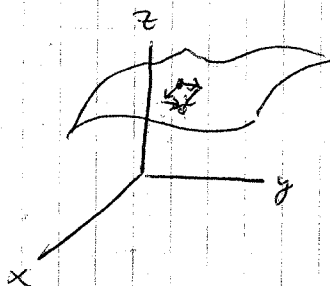
Note also

$$\left. \frac{\partial x}{\partial y} \right|_z = \frac{1}{\left. \frac{\partial y}{\partial x} \right|_z}$$

$$\therefore \left. \frac{\partial z}{\partial x} \right|_y \left. \frac{\partial x}{\partial y} \right|_z \left. \frac{\partial y}{\partial z} \right|_x = -1 \quad (2)$$

$$\frac{\partial^2 z}{\partial x \partial y} = \frac{\partial^2 z}{\partial y \partial x} \quad (3)$$

Comes from path independence

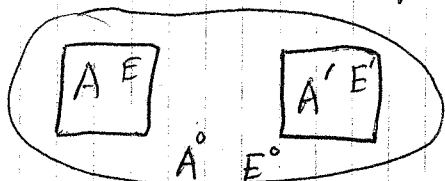


Curvature is well defined

## Back to $\Omega$ & Counting States

recall  $\Omega$  is a very rapidly increasing function of  $E$   
 $\Omega \sim E^{90}$

Let's take two systems & put them in contact

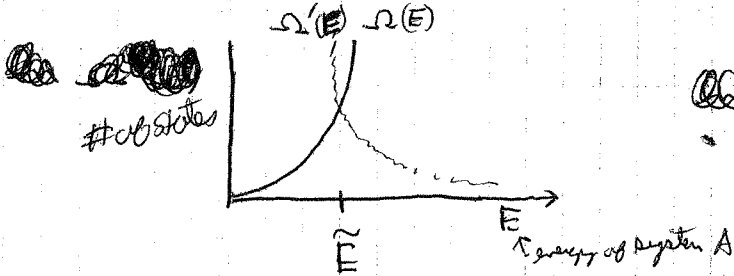


If we put them in contact these systems will exchange energies & the # of states for each system will change

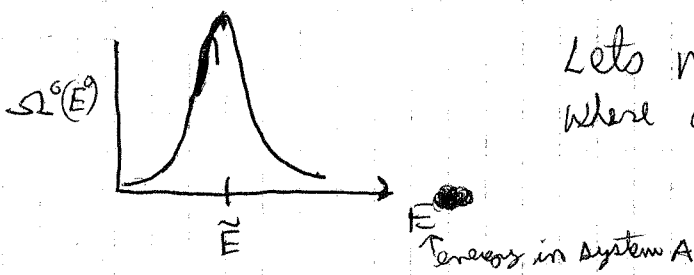
$$\underbrace{\Omega^{\circ}(E^{\circ})}_{A^{\circ}} = \underbrace{\Omega(E)}_A \underbrace{\Omega'(E^{\circ}-E)}_{A'}$$

Where does  $\Omega^{\circ}$  peak?

~~the probability of finding the system in state  $E$  is  $\frac{\Omega(E)}{\Omega(E) + \Omega(E^0 - E)}$~~



~~$\Omega(E) + \Omega(E^0 - E)$~~   
 " ~ " equilibrium



Lets modify our question  
 where does  $\frac{d \ln \Omega^0}{dE} = 0$

$$\frac{d \ln \Omega^0(E^0)}{dE} = \frac{d \ln \Omega(E)}{dE} + \frac{d \ln \Omega'(E^0 - E)}{dE}$$

$$E' = E^0 - E$$

$$dE' = -dE$$

$$= \frac{d \ln \Omega(E)}{dE} + \frac{d \ln \Omega'(E')}{dE'} (-1)$$

if  $\frac{d \ln \Omega^0(E^0)}{dE} = 0$  Equil

$$\left. \frac{d \ln \Omega(E)}{dE} \right|_{E=\tilde{E}} = \left. \frac{d \ln \Omega'(E')}{dE'} \right|_{E'=\tilde{E}'}$$

$\beta(\tilde{E}) = \beta'(E')$  ← this is what temperature does!

$\beta \equiv \frac{1}{kT}$  where  $T \equiv$  temperature so  $T=T'$  at equilibrium

$S = k \ln \Omega$   $S$  is the entropy so that

$S + S' = \text{maximum at equilibrium}$  (lets why we used  $\ln \Omega$ )

If we start w/ systems out of equilibrium we are not at the most likely  $\Omega(E^0)$

$S_{total} = S_1 + S_2$  so if we bring two systems together

$S_{1i} + S_{2i} \leq S_{1f} + S_{2f}$  or

$\Delta S + \Delta S' \geq 0$  entropy always increases

$Q \equiv \bar{E}_f - \bar{E}_i$   $Q' \equiv \bar{E}'_f - \bar{E}'_i$   $Q + Q' = 0$

discussing  
 all this must have been very exciting

most famous eq in stat mech on Boltzmann's grave

by conservation of Energy

2 cases: 1) initial energies are such that  $\beta_i = \beta_i'$  or  $\bar{E}_i = \bar{E}$   
 $\bar{E}_i' = \bar{E}'$

Stat is already maximized

2)  $\beta_i \neq \beta_i'$  then  $\bar{E}_i \neq \bar{E}$  then systems are in a very  
 $\bar{E}_i' \neq \bar{E}'$

improbable non equilibrium situation

as time progresses Stat is maximized &  $\beta_s = \beta_s'$  &  $\bar{E}_s = \bar{E}$   
 $\bar{E}_s' = \bar{E}'$

If we allow volume to change  $\Omega = \Omega(E, V)$   $E' = E^0 - E$   
 $V' = V^0 - V$

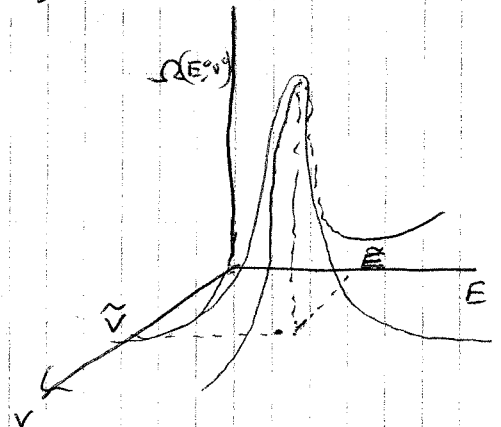
$$\Omega^0(E^0, V^0) = \Omega(E, V) \Omega'(E', V')$$

$$\ln \Omega^0 = \ln \Omega + \ln \Omega'$$

$$d \ln(\Omega^0) = \frac{d \ln \Omega}{dE} dE + \frac{d \ln \Omega'}{dV} dV$$

$$= \left( \frac{d \ln \Omega}{dE} + \frac{d \ln \Omega'}{dE} \right) dE + \left( \frac{d \ln \Omega}{dV} + \frac{d \ln \Omega'}{dV} \right) dV$$

$$= (\beta - \beta') dE + \left( \underbrace{\frac{d \ln \Omega}{dV}}_{\beta \bar{p}} - \underbrace{\frac{d \ln \Omega'}{dV'}}_{\beta' \bar{p}'} \right) dV$$



$$d \ln \Omega^0 = d(\ln \Omega + \ln \Omega')$$

$$d \ln \Omega = \frac{d \ln \Omega}{dE} dE + \frac{d \ln \Omega}{dV} dV = \beta dE + \beta \bar{p} dV$$

$$d \ln \Omega' = \frac{d \ln \Omega'}{dE'} dE' + \frac{d \ln \Omega'}{dV'} dV' = -\beta' dE - \beta' \bar{p}' dV$$

For equilibrium  $d \ln \Omega^0 = 0$

$$\beta = \beta'$$

$$\bar{p} = \bar{p}'$$