$$W = N! \prod_i \frac{g_i^{N_i}}{N_i!}$$

note if $N_i = 0$ $\frac{g_i^{N_i}}{N_i!} = 1$

(Gr-234 gives another path to this result
— but all roads lead to Rome
— combinatorics always causes me self-doubt

Note there is NO pauli exclusion principle for distinct and classical particles

c) $W(\{N_i\})$ for identical Fermions

— This is easy because of symmetrization and the Pauli exclusion Principle

5-222

Recall the product state for N particles obeying Pauli exclusion principle from which a symmetrized state could be created, but we won't do one or the other for macroscopic N.

Pauli exclusion principle is first step to symmetrization $\chi_a(1)\chi_a(2)$. product state can't be symmetrized at all.

So is the $\chi(\ldots i \ldots j \ldots) = \pm\chi(\ldots j \ldots i \ldots)$ the origin of all symmetrized states?

$$\chi_{\text{product}} = \chi_1(1')\chi_2(2')\ldots\ldots\chi_N(N')$$

in symmetrized state — re-ordering of particles makes No New state

$$\chi_{\text{sym}} = \sum_P P\,\chi_{\text{pro}}$$

Thus

$$\frac{1}{N_1}\qquad\frac{2}{N_2}\qquad\qquad\frac{i}{N_i}$$

— No new states by interchange of particles between levels,

5-023

So N_i identical particles in level i

We have g_i ~~each~~ choices where to put the first one

$g_i - 1$ choices for the second one.

We are obeying Pauli exclusion principle

$\therefore$ $g_i(g_i-1)\ldots(g_i-(N_i-1))$

choices for the particles,

But this equals $W_i N_i!$ since there is no NeW state re-ordering the particles among themselves.

$$\therefore\ W_i = \frac{g_i(g_i-1)\ldots(g_i-(N_i-1))}{N_i!}$$

Weight for a single level i

$$= \frac{g_i!}{(g_i-N_i)!\,N_i!} = \binom{g_i}{N_i}$$

Binomial Coefficent

$$W = \prod_i W_i = \prod_i \binom{g_i}{N_i}$$

Note if $N_i = 0$ $\binom{g_i}{N_i} = 1$

5-624

d) $W(\{N_i\})$ for Identical Bosons

— like identical fermions, but no Pauli exclusion Principle —— which actually makes things tricky.

1	2	. . . .	i
N_1	N_2	. . .	N_i

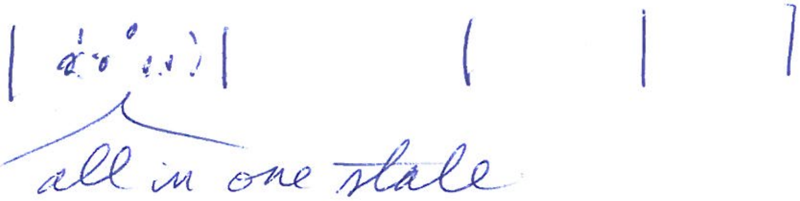
No new state for exchanging particles between energy levels.

So consider level i with its N_i particles.

Two cases are easy.

i) We put all particles into <u>1 state</u>

We g_i ways to do this



ii) We put only <u>one</u> <u>particle</u> into <u>each</u> <u>state.</u>

So just as for Fermions we have

$\binom{g_i}{N_i}$ ways to do this

$$\therefore \text{ So for } W_i = \underbrace{g_i}_{\substack{\text{all in}\\\text{one}\\\text{state}}} + \underbrace{\binom{g_i}{N_i}}_{\substack{\text{~~all in their~~}\\\text{one only}\\\text{in}\\\text{a state}}} + \underbrace{\dots}_{\text{The other possibilities}}$$

Cases (i) and (ii) collapse to one case if only 1 particle so only one term

Unless $N_i = 0$, $W_i = 1$

actually

$N_i = 1$, $W_i = g_i$

actually

$N_i = 2$, $W_i = g_i + \binom{g_i}{N_i}$

$= g_i + \binom{g_i}{2}$,

$$g_i + \binom{g_i}{2}$$
$$= g_i + \frac{g_i!}{(g_i-2)!\,2!}$$
$$= g_i!\left[\frac{1}{(g_i-1)!} + \frac{1}{(g-2)!\,2!}\right]$$
$$= g_i!\left[\frac{2 + g_i - 1}{(g-1)!\,2!}\right]$$
$$= ~~g_i!\,(g+1)!~~$$
$$= \frac{(g_i+1)!}{(g_i-1)!\,2!} = \binom{g_i+1}{2}$$

5-626

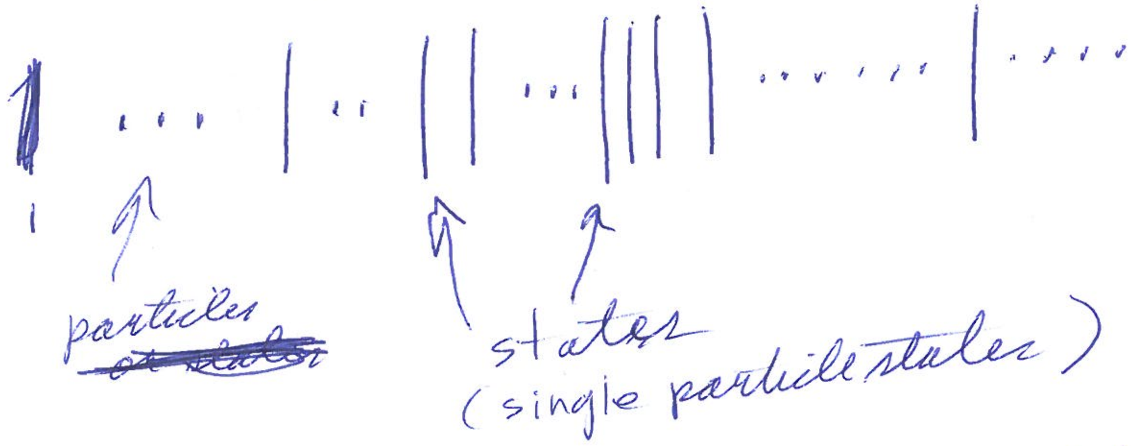
we are flummoxed.

This is where someone had to stay up nights (as my mother used to say) to find the general rule.

To think up an isomorphic problem.

Imagine putting down state 1

Now put down states or particles in any order



There are $(g_i - 1 + N_i)!$ ways of putting down the particles or states.

5-627

The particle is considered to be in the nearest state to the left.

$$W_i (g_i - 1)! N_i! = (g_i - 1 + N_i)!$$

w

re-orderings among particles create No new overall state for level.

There really only is 1 order for $g_i - 1$ states

We select one order

~~$W_i = \binom{g_i - 1 + N_i}{N_i}$~~ ~~Binomial coefficient again.~~

~~1~~

~~for $N_i = 0$~~

$$W_i = \frac{(g_i - 1 + N_i)!}{\overbrace{(g_i - 1)}^{(g_i - 1 + N_i) - N_i}!\; N_i!}$$

$$\therefore\; W_i = \binom{g_i - 1 + N_i}{N_i} \Bigg\}$$ Binomial coefficient again.

$$\begin{cases} 1 & \text{for } N_i = 0 \\ \binom{g_i}{1} = g_i & \text{for } N_i = 1 \\ \binom{g_i + 1}{2} = \cancel{\frac{(g_i+1)!}{(g_i-1)!\,2!}} & N_i = 2 \end{cases}$$

see p. 5-625

~~Note $g_i + \binom{g_i}{2}$~~ [illegible] ~~$\frac{g_i!}{(g_i-2)!\,2!}$~~

So all special known cases handled correctly.

$$W = \prod_i W_i$$

$$= \prod_i \binom{g_i - 1 + N_i}{N_i}$$

e) Summary of $W(\{N_i\})$

$$W = N! \prod_i \frac{g_i^{N_i}}{N_i!}$$ for classical and/or distinct particles

$$W = \prod_i \binom{g_i}{N_i}$$ for identical fermions

$$W = \prod_i \binom{g_i - 1 + N_i}{N_i}$$ for identical Bosons.

They all look pretty different, ~~but~~ In some limits, they lead ~~to similar~~ to the same result. In others to very different results.

5-630)

f) Finding Most Probable Configuration

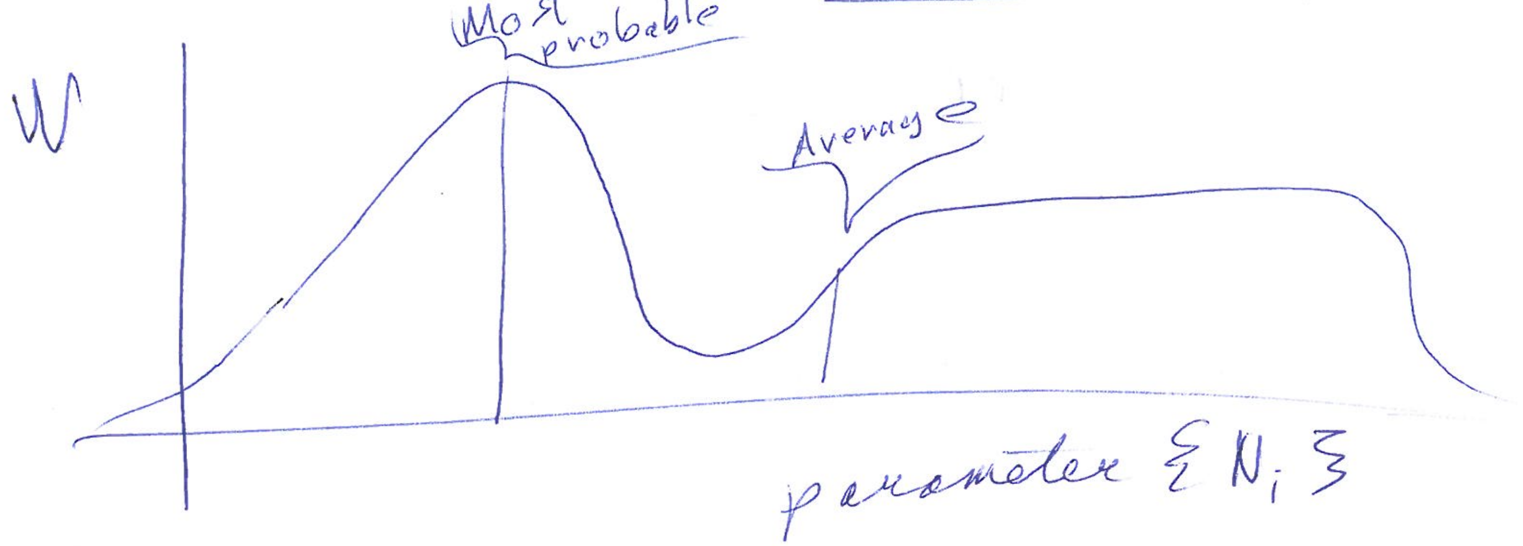
- Recall the fundamental axiom. $W(\{N_i\})$ is ~~the time~~ proportional to the probability of finding the system in configuration $\{N_i\}$.

- So we seek the most probable configuration $\rightarrow$ the maximum of $W(\{N_i\})$

Now a priori nothing tells us that the most probable configuration will be anything like the average configuration or that average configuration

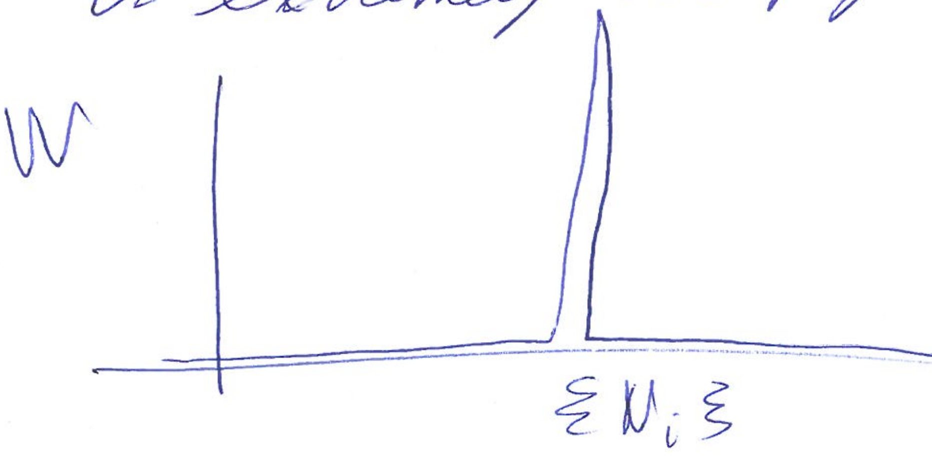
is a useful concept 5 631
~~at all~~ for defining the macroscopic state.

Schematic Plot of W



The distribution could be so ~~pro~~ broad the system could often be in any configuration.

But, in fact, analysis beyond our scope shows that for large numbers, the distribution is extremely sharply peaked



5-632

So the most probable configuration is nearly the average configuration and gives the macroscopic thermodynamic parameters of equilibrium state to super high accuracy.

How do we find the maximum of $W(\{N_i\})$ as a function of the set of parameters $\{N_i\}$?

A key first point, the set $\{N_i\}$ are NOT independent. They are subject to two constraints

$$N = \sum_i N_i \quad , \quad E = \sum_i E_i N_i$$

Finding stationary points subject to constraints.

This looks like a job for Lagrange (undetermined) multipliers

Actually there is another constraint $N_i \geq 0$ ~~for~~ all i. But ~~this~~ can't be imposed since an inequality

Lagrange Multipliers

— the quick proof.

$f(\{x_i\})$ → a function of the set of coordinates $\{x_i\}$)

Now consider a path ~~through~~ the space $\underset{\sim}{x} = \underset{\sim}{x}(t)$

where t is a path parameter.

as t advances the vector $\underset{\sim}{x}(t)$ traces out the path.

5-634

$$f(\{x_i\}) = f(\underset{\sim}{x}(t))$$

$$\frac{df}{dt} = \frac{\partial f}{\partial x_i}\frac{\partial x_i}{\partial t}$$

With
Einstein
summation
on the
repeated
index.

Now if $\frac{df}{dt} = 0$ for some point for every possible path thru it, then any or all of $\frac{dx_i}{dt} \neq 0$ there.

$$\therefore \frac{\partial f}{\partial x_i} = 0$$

for all x_i

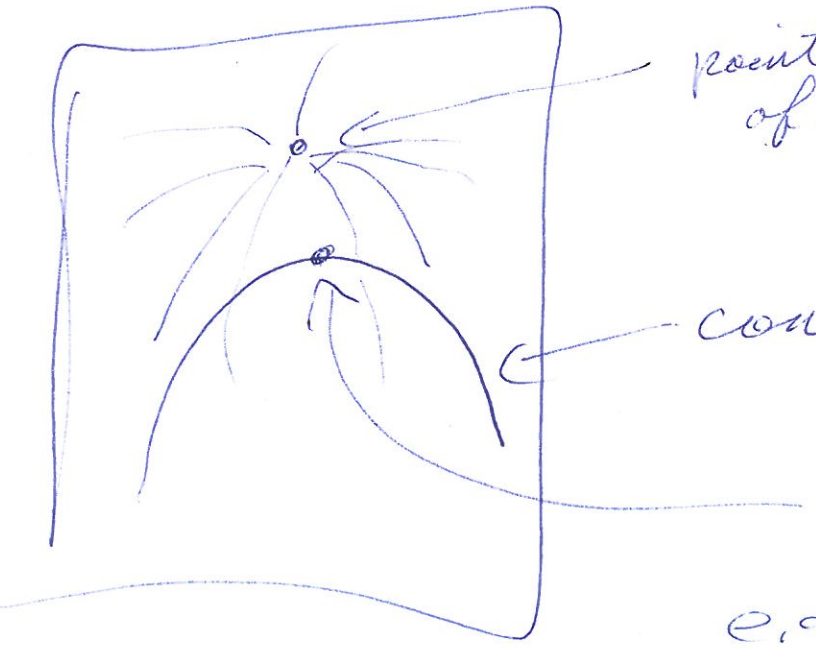
for an
unconstrained
stationary
path.

stationary for all paths thru it.

If you have I dimensions, you have I $\frac{\partial f}{\partial x_i} = 0$ equations and can solve for I x_i values.

But now say you ~~only~~ wanted the stationary point of f constrained to certain surfaces in the space.

Example



point of unconstrained stationary point

constraint surface

constrained stationary point, e.g., lowest point on the surface of constraint.

To be general say we had J constraints of form

$$g_j(\underset{\sim}{x}) = 0$$

The trick is to form a new function $h(\underset{\sim}{x})$

$$h(\underset{\sim}{x}) = f(\underset{\sim}{x}) + \underbrace{\lambda_j \, g_j(\underset{\sim}{x})}_{\text{Eistien sum over J constraints.}}$$

The λ_j are the unknown Lagrange multipliers.

There are J of them.

The $g_j(\underset{\sim}{x})$ are Not set to zero in this function.

The unconstrained stationary point of $h(\underset{\sim}{x})$ is found from the I

$$\frac{\partial h}{\partial x_i} = \frac{\partial f}{\partial x_i} + \lambda_j \frac{\partial g}{\partial x_j} = 0$$

equations.

~~There or~~
But there are I + J unknowns
since there are the J λ_js.

So now demand

$g_j(x_i) = 0$ for all J constraints too.

Now we have I + J unknowns and I + J equations.

Say the stationary point $\underset{\sim}{x}_{st}$.

Any path thru $\underset{\sim}{x}_{st}$ gives stationary $h(x)$,
including paths consistent with $g_j(\underset{\sim}{x}) = 0$ for all constraints.

But on such paths

$$h(\underset{\sim}{x}) = f(\underset{\sim}{x}).$$

So $f(\underset{\sim}{x})$ is stationary at $\underset{\sim}{x}_{st}$ for all paths consistent with the constraints

The Lagrange multipliers usually turn out to have some important meaning in physical applications

ergo $\underset{\sim}{x}_{st}$ is the constrained stationary point of $f(x)$.

9) Finding Most Probable Configuration for Distinct Particles

(or classical identical particles)

Recall the weight of configuration $\{N_i\}$ is $W = N! \prod_i \frac{g_i^{N_i}}{N_i!}$ (see p. 5-621)

5-639

Rather than find the maximum of W, it turns out to be better to better to find the max of ln W

$$\ln W = \ln N! + \sum_i N_i \ln g_i - \sum_i \ln N_i!$$

We'll use Lagrange multipliers to build in the imposed constraints

$$N = \sum_i N_i \text{ and } E = \sum_i N_i E_i$$

are constants

By using the Lagrange multipliers, we are making a continuum approximation and thinking of N_i as continuous variables.

G-640) Note bad for large numbers,
Maybe even small numbers depending on the case.

$$h \equiv \ln W + \alpha\left(\sum_i N_i - N\right) + \beta\left(\sum_i N_i E_i - E\right)$$

opposite choice of sign from Gr-236 to be consistent with Pointon

— Recall there is another constraint $N_i \geq 0$ for all i.
But this constraint can't be built into the max-finding procedure —— We hope for the best that $N_i < 0$ don't turn up to maximizing

$$h = \ln N! - \sum_i \ln N_i! + \alpha\left(\sum_i N_i - N\right) + \beta\left(\sum_i N_i E_i - E\right)$$

$$+ \sum_i N_i \ln g_i$$

5-641

The first + last terms are the only one that varies between the three cases (distinct particles, identical fermions, identical bosons)

But the first is just a constant.

The usual way to find a derivative of $\ln z!$ is to use the Stirling series to 2nd order (AKA Stirling's approximation).

The Stirling's series to 7th order is

$$\ln z! = z\ln z - z + \tfrac{1}{2}\ln z + \tfrac{1}{2}\ln(2\pi) + \frac{1}{12z} - \frac{1}{360z^3} + \frac{1}{1260z^5} - \dots$$

(Arf-464)

$$\simeq z\ln z - z \text{ to 2nd order.}$$

5-642

Stirling's series is an asymptotic series.

It's accuracy improves as $z \to \infty$.

At small z, it can be badly in error.

(coincidentally $\ln z! \cong z \ln z - z$ is exactly right for $z = 0$ in a limit sense

$$\ln 0! = 0$$

$$\lim_{z \to 0} (z \ln z - z) = \lim_{z \to 0} \left(\frac{\ln z}{1/z} \right)$$

$$= \lim_{z \to 0} \left(\frac{1/z}{-1/z^2} \right) = 0 \quad)$$

But it's really the derivative $\frac{\partial \ln z!}{\partial z}$, we need.

5-643

$$\frac{d(\ln z!)_{2nd}}{dz} = \frac{d}{dz}(z\ln z - z)$$

$$= \ln z + z/z - 1$$

$$= \ln z$$

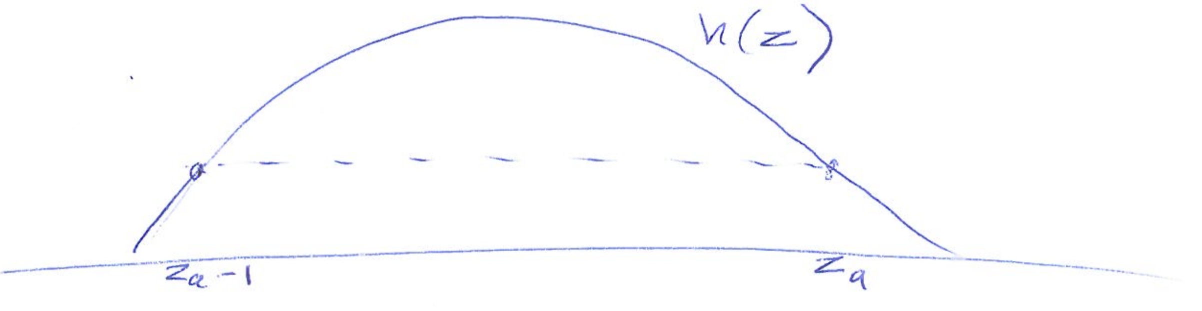
- which is pretty accurate for $z \gtrsim 2$

- so-so for $z = 1$

- rotten for $z = 0$
It gives $-\infty$, but the real value is $\sim -1/2$.

I think a better idea is to find z_a such that

$$h(z_a) - h(z_a - 1) = 0$$



5-644

Unless $h(z)$ is pathological,

$$Z_{max} \in [Z_a, Z_a - 1]$$

A best ~~guess~~ estimate at

$$Z_{max} \cong Z_a - 1/2$$

<u>But</u> remember in our case the real numbers are integers and we want to build in the constraint $N_i \geq 0$.

∴ I suggest best estimate

$$Z_{max} \cong \underbrace{\mathrm{Int}}(Z_a)$$

a function that truncates to an integer — z_a does turn out to be positive always.

5-645

$0 = h(N_j) - h(N_j - 1)$ where N_j is one the set $\{N_i\}$

$= 0 - (\ln N_j! - \ln (N_j - 1)!)$

$+ \alpha (N_j - (N_j - 1))$

$+ \beta (N_j E_j - (N_j - 1) E_j)$

$+ N_j \ln g_j - (N_j - 1) \ln g_j$

$= -\ln N_j + \alpha + \beta E_j + \ln g_j$

This is exactly what using Stirling's approximation would give

$$\frac{\partial h}{\partial N_j} = 0 \cancel{+} \ln N_j + \alpha + \beta E_j + \ln g_j$$

In either case, we get

$$N_i = g_i e^{\alpha + \beta E_i}$$

converting back to subscript i

~~for the maximizer~~

but from the difference approach we know

$$N_i = \text{Int}(g_i e^{\alpha + \beta E_i})$$

is a better approximation to Maximizing N_i (see p. 5-644)

However, the Int function is analytically intractable and as long as $N_i \lesssim$ a few are of negligible importance to the overall system, it is best to drop the int and use

$$N_i = g_i e^{\alpha + \beta E_i}$$

as our approximate

(~~but~~ maximizing N_i function.

We note it turns out to be very accurate in most context — negligible error — but there might be cases where the ln ~~!~~ form might be better — if N turned out be rather small.

One case turns up in an example.

What are α and β?

Well α gives the normalization

$$N = \sum_i g_i e^{\alpha + \beta E_i}$$

$$e^{\alpha} = \frac{N}{\sum_i g_i e^{\beta E_i}}$$

It turns out to be more than that

It turns out that $\alpha = \frac{\mu}{kT}$ where

μ is the chemical potential (Pointon-154)

5-648)

All of our education tells use $\beta = -\frac{1}{kT}$.

But can we prove that?

Yes and it is educational to do so.

First since in many cases the energy levels go ~~up~~ infinity in number, $\beta < 0$ at least in those cases.

Second We ~~identify~~ define

$$S \equiv k \ln W$$

Macroscopic entropy which ~~must be classical~~ should turn out correspond to ~~be~~ classical entropy.

Boltzmann's constant which gives S the right units of energy/kelvin and helps complete correspondence to classical entropy.

(5 - 649

Why is this a good definition

i) Maximum classical entropy is thermodynamic equilibrium state.

↳ the state an isolated system reaches eventually.

Maximum S is the most probable configuration, and so after initial conditions effects die out, we expect the system to correspond to the most probable configuration which we can identify with classical equilibrium.

ii) If we had two systems with config. $\{N_i\}_1$ and $\{N_i\}_2$, then they have corresponding distinct states W_1 & W_2 (or weights)

∴ The joint system has weight

$$W = W_1 W_2$$

The W's are multiplicative, but S are additive $S = S_1 + S_2$ like classical entropy.

Conclusion S is the ~~correspond~~ ~~anal~~ (analog correspond) to classical entropy.

Now look back at our h function on p. 5-640

$$h \equiv \ln W + \alpha\left(\sum_i N_i - N\right) + \beta\left(\sum_i E_i N_i - E\right)$$

It has an unconstrained stationary point ~~minimum af~~for $N_i = g_i e^{\alpha + \beta E_i}$ which give the constrained ~~Max~~ maximum of ln W.

So any path $\{N_i(t)\}$ thru that stationary point gives $\frac{dh}{dt} = 0$

Not just ones consistent with the constraints.

$$N_{\text{unconstrained}} - N = \sum_i N_i - N$$

$$E_{\text{unconstrained}} - E = \sum_i N_i E - E$$

$$\frac{d N_{\text{unconstrained}}}{dt} = \frac{d}{dt}\left(N_{\text{unc}} - N\right)$$

(5-65)

and

$$\frac{dE_{unc}}{dt} = \frac{d(E_{unc} - E)}{dt}$$

$$\therefore 0 = \frac{dh}{dt} = \frac{d\ln W}{dt} + \alpha\frac{dN_{un}}{dt} + \beta\frac{dE_{un}}{dt}$$

or in differential form at the equilibrium point
with ~~only a~~ the path parameter
left implicit as thermo/statmech
looks like

$$0 = dh = d\ln W + \alpha\, dN_{un} + \beta\, dE_{un}$$

let's drop
the "unconstrained"
subscript.

$$\therefore dE = -\frac{1}{\beta}d\ln W - \frac{\alpha}{\beta}dN$$

We've already identified $S = k\ln W$
as the correspondant to
classical entropy

E corresponds to classical
internal energy.

N is the same as the classical number of particles.

The classical 1st law of thermodynamics is

(MiK)

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

the chemical potential

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

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

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

In our development, we held volume fixed since we held the eigen-energies fixed. All QM solutions ~~should~~ show the eigen-energies depend on volume.

∴ The corresponding classical 1st law for our case is

$$dE = T\,dS + \mu\,dN$$

or result

$$dE = -\frac{1}{k\beta}\,dS - \frac{\alpha}{\beta}\,dN$$

$$\therefore\ T = -\frac{1}{k\beta}$$

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

$\Big\}$ $\beta < 0$ as we thought.

$$\mu = -\frac{\alpha}{\beta} = kT\alpha$$

$$\alpha = \frac{\mu}{kT}$$ (Pointon 154)

So we find by reasonable identifications that

$$S = k\ln W, \quad \beta = -\frac{1}{kT}, \quad \alpha = \frac{\mu}{kT}$$

5-654)

Actually these last 3 results did NOT depend on the distinct particle case — as one can observe

The so these result also apply to the Fermion and boson cases too.

They didn't depend on the nature of W or the specific formula for the N_i at equilibrium $N_i = g_i e^{\alpha_i + \beta E_i}$

5-65

Why is this a good definition?

Maximum classical entropy is thermodynamic equilibrium entropy.

Maximum S is the most probable configuration and so ~~which~~ we can identify it with classical thermo. equil.

If we had two systems with configurations $\{N_i\}_1$ and $\{N_i\}_2$, ~~then~~ number of corresponding distinct states is W_1 and W_2

∴ The joint system has weight

$$W = W_1 W_2$$

So W's are multiplicative, but

$$S = S_1 + S_2$$

is additive like classical entropy.

5-656

Omit — a tedious proof of what was just proven

Third From classical thermo

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

(MiK)

internal energy

temperature

pressure

chemical potential.

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

subscripts mean hold N, V constant.

This S is actually thermo. equil. S not any S. Something which I recall is obscured in Thermo books

We use this as our definition of temperature.

Internal energy E is $E = \sum_i E_i g_i e^{\alpha + \beta E_i}$

N is $N = \sum_i g_i e^{\alpha + \beta E_i}$

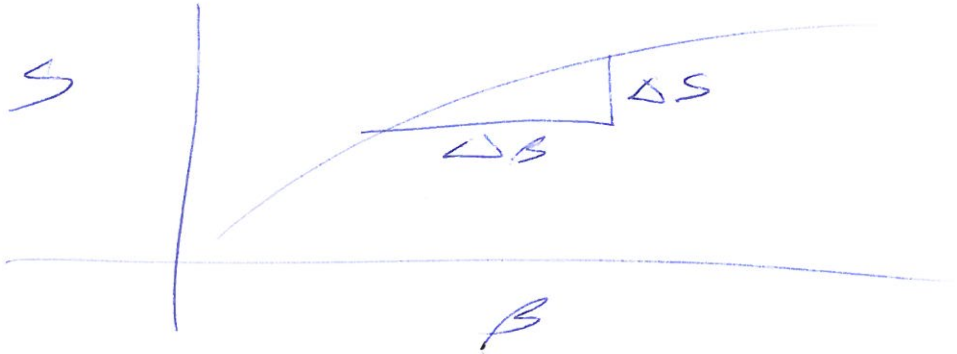
$S = k(\ln W)_{\text{equilibrium}}$ $\Big\{$ we must evaluate with the $N_i = g_i e^{\alpha + \beta E_i}$

5-657

Now how do we get an expression for T?

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

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



If all other variables are constant, one gets the ~~r~~eciprocal relation

How do we hold V constant?
We just keep the E_i constant.
All QM tells us the eigen-energies change with volume.

We must also hold N constant as β varies

$$\left(\frac{\partial N}{\partial \beta}\right)_{V,N} = \sum_i \left[\left(\frac{\partial \alpha}{\partial \beta}\right)_{N,V} + E_i\right] N_i = 0$$

$$\left(\frac{\partial N_i}{\partial \beta}\right)_{N,V} = \frac{\partial}{\partial \beta}\left(g_i e^{\alpha + \beta E_i}\right) = \left[\left(\frac{\partial \alpha}{\partial \beta}\right)_{N,V} + E_i\right] N_i$$

for equilibrium N_i

we will need this result.

E is no longer fixed.

We are seeing how it varies.

$$\left(\frac{\partial E}{\partial \beta}\right)_{NV} = \sum_i \frac{\partial (N_i E_i)}{\partial \beta}$$

$$= \sum_i E_i \left(\left(\frac{\partial \alpha}{\partial \beta}\right)_{N,V} + E_i\right) N_i$$

$$\left(\frac{\partial S}{\partial \beta}\right)_{N,V} = k\left[\left(\frac{\partial}{\partial \beta}\right)_{N,V}\right]\left[\ln N! - \sum_i \ln N_i! + \sum_i N_i \ln g_i\right]$$

all at equilibrium values

$$= k\left[0 - \sum_i \frac{\partial \ln N_i!}{\partial \beta} + \sum_i \frac{\partial N_i}{\partial \beta} \ln g_i\right]$$

Here we will just use the Stirling approx.

$$\left(\frac{\partial}{\partial\beta}\right)_{N,V}\left[\ln N_i!\right]$$

$$\triangleq \frac{\partial}{\partial\beta}\left[N_i\ln N_i - N_i\right]$$

$$= \frac{\partial}{\partial N_i}\left[N_i\ln N_i - N_i\right]\left(\frac{\partial N_i}{\partial\beta}\right)_{N,V}$$

$$= \left(\ln N_i\right)\left(\left(\frac{\partial\alpha}{\partial\beta}\right)_{N,V} + E_i\right)N_i$$

$$\therefore \left(\frac{\partial S}{\partial\beta}\right)_{N,V} = k\left[\sum_i\left[\left(\frac{\partial\alpha}{\partial\beta}\right)_{N,V} + E_i\right]N_i\underbrace{\left(-\ln N_i + \ln g_i\right)}_{\underbrace{-\ln g_i - (\alpha+\beta E_i) + \ln g_i}_{-(\alpha+\beta E_i)}}\right]$$

$$= -k\beta\sum_i E_i\left[\left(\frac{\partial\alpha}{\partial\beta}\right)_{N,V} + E_i\right]N_i$$

$$- k\alpha\underbrace{\sum_i\left[\left(\frac{\partial\alpha}{\partial\beta}\right)_{N,V} + E_i\right]N_i}$$

~~sums to~~

is zero by p. 5-652

$$= -k\beta\left(\frac{\partial E}{\partial\beta}\right)_{N,V}$$

t5-660

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

$$= \left(\frac{\partial E}{\partial \beta}\right)_{N,V} \Big/ \left(\frac{\partial S}{\partial \beta}\right)_{N,V}$$

$$= -\frac{1}{k\beta}$$

$$\beta = -\frac{1}{kT}$$ as expected.

We've related β to classical temperature.

$\therefore\ N_i = g_i e^{\alpha - E_i/kT}$ which is a pretty familiar result.

$f = \frac{N_i}{N}$ is called the Maxwell-Boltzmann distribution

What is temperature?

5-66

Well classically it is in the first instance a measure of thermodynamic equilibrium state of a system,

One measures it by using a volume or pressure thermometer

or by running a Carnot cycle between systems.

One notes if two equilibrium systems have the same temperature this way, then if they are put into thermal contact that nothing happens — the two systems stay just as they were.

One can prove this must be so from the 1st and 2nd laws of thermodynamics.

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Say system 1 has S_1 and T_1 and system 2 has S_2 and T_2 and we put the systems in ~~thermal contact.~~ ~~we can let them~~

in thermal contact → heat can be exchanged.

But say they can't exchange particles or do ~~work~~ macroscopic work on each other.

$$S = S_1 + S_2$$

$$dS = dS_1 + dS_2$$

If the joint state is in ~~thermodynamic equil~~ equilibrium $dS = 0$ for any path

S is a maximum.

$$0 = dS_1 + dS_2 = \frac{dE_1}{T_1} + \frac{dE_2}{T_2}$$

Since energy is conserved $dE_1 = -dE_2$ and so $T_1 = T_2$

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~~If the two systems have~~

Perhaps one needs a qualification
if $T_1 = T_2$ the systems
are in thermo. equ. as far
as heat flow is concerned.

If one allowse just pdV work

$$0 = dS = dS_1 + dS_2$$

$$= \frac{P_1 dV_1}{T_1} + \frac{P_2 dV_2}{T_2}$$

$$= \left(\frac{P_1}{T_1} - \frac{P_2}{T_2}\right) dV_1$$ since $dV_1 = -dV_2$

In this case if one wants no change
— neither net heat flow or pdV work
$T_1 = T_2$ and $P_1 = P_2$

If one allows particle exchange only

$$0 = dS = dS_1 + dS_2 = -\frac{\mu_1 dN_1}{T_1} - \frac{\mu_2 dN_2}{T_2}$$

$$= -\left(\frac{\mu_1}{T_1} - \frac{\mu_2}{T_2}\right) dN_1$$ since $dN_1 = -dN_2$

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If one wants no change
in this case

$$T_1 = T_2 \text{ and } \mu_1 = \mu_2$$

So for two systems, to stay unchange when all possible energy exchanges occur

$$T_1 = T_2 , \; P_1 = P_2 , \; \mu_1 = \mu_2$$

How does measurable temperature connect up to T in the 1st law?

Well the <u>Carnot cycle</u> T can be shown to be the first law T.
The ideal gas law T is the same as the Carnot T.

What is T in our stat.mech. case

$$N_i = g_i e^{\alpha - E_i/kT}$$

So it's a parameter that determines the distribution of particles in states.

~~[illegible]~~

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If $g = C\Delta E$ where C is a constant and ΔE is energy width between energy levels then

$$dN = C e^{\alpha - E/kT} dE$$

$$E_{ave} = \frac{\int_0^\infty E e^{-E/kT} dE}{\int_0^\infty e^{-E/kT} dE}$$

$$= kT \frac{\int_0^\infty x e^{-x} dx}{\int_0^\infty e^{-x} dx}$$

$$= kT \frac{1!}{0!} \quad (\text{Art}-453)$$

$$= kT.$$

In this case it is the average energy of a particle.

In general, one would expect kT to closely related to the average energy of particle.
for a MB system NOT a fermion system.

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But T is a parameter that tells how energy is distributed among energy levels,

Of course, temperature in a human sense is a measure of our ~~sense~~ feeling of hot and cold.

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

$\therefore$ The equilibrium N_i are given by

$$N_i = g_i e^{\alpha - E_i/kT}$$

and

$$f = \frac{N_i}{N} = \frac{g_i e^{-E_i/kT}}{\sum_i g_i e^{-E_i/kT}}$$

Note α cancels out

is called ~~the~~ the <u>Maxwell-Boltzmann distribution</u>

The quantity $U = \sum_i g_i e^{-E_i/kT}$

is called the partition function (Mihalas p. 111).

5-66~~g~~

Example of use of Maxwell-Boltzmann Distribution

- Consider atoms in gas.
- Consider their internal state of excitation
  - almost always a one-electron excitation.

The electron can be thought of as our particle that can be in various states of atomic excitation

Electrons are identical ~~bosons~~ fermions

But they are dynamically distinct here — their wave functions don't overlap and each one has its own set of ~~sta~~ stationary states.

Or one can think of atom as whole being in such states. Not counting the CM state.

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If n the atom or ion abundance — number density

$n_i = n f$ is the number density in state i

Note giv $f = \frac{g_i e^{-E_i/kT}}{\sum g_i e^{-E_i/kT}}$

the g_i is only the degeneracy of states in a single atom

— The total degeneracy is Ng_i ~~but the n's~~ where N is the total number of atoms, but N cancels out of the MB distribution.

The MB distribution gets a lot of use in astrophysical atmospheres which is my specialty.

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There is a paradox,

Consider hydrogen gas.

— Not counting the multiplet and other energy level splittings, each energy level has a degeneracy of $g = 2n^2$ where n is the principle quantum number

and $E_n = -\frac{1}{2} m c^2 \frac{\alpha^2}{n^2} \left(\frac{\mu}{m}\right)$ (6r-149)

Usually, one sets E_0 as the zero level so as to make the E_i positive — Mental clarity.

$E_{i=0} = 0$

$$E_i = E_n - E_{n=0}$$

$$= E_0 \left(1 - \frac{1}{n^2}\right)$$

The factor $e^{E_i/kT}$ cancels out the MB distribution

$n = 1, 2, 3, \ldots, \infty$ formally.

But $E_\infty = E_0$