

$$\text{So } U = \sum_{i=1}^{\infty} \tilde{g}_i e^{-E_i/kT}$$

diverges to infinity!

What have we done wrong?

~~Really interactions between perturbations lower the ionization~~

This is NOT just hydrogen.

All atoms in highly excited states are hydrogenic.



So all atoms suffer a divergence of ~~atom~~ our partition function.

Resolution.

5-672)

i) Really interparticle perturbations lower ionization energy and there are only a finite number of excited states.

So divergence obviated.

(Mihalas - III, 112)

Calculating accurate partition functions is very important in modeling the interior of stars in particular where local Thermodynamic equilibrium ~~is to~~ (LTE) is to be expected.

~~Jan 07~~

5-673

LTE means atomic occupation numbers are set by thermodynamic equilibrium ($T, P, abundances$) even though the radiation field is NOT.

— In stellar atmospheres LTE is sometimes ~~valid~~ valid and often not.

ii) Formal solution
when there are an infinite number of energy levels

Recall
$$N_i = \text{Int} (g_i e^{-E_i/kT})$$

is actually a better approximation for the occupation numbers

5-674

when N_i becomes small.

Now if

$$N = \sum_{i=1}^{\infty} \cancel{g_i} g_i e^{\alpha - E_i/kT}$$

if $E_i \rightarrow E_{\infty}$ finite,

then the sum diverges,

unless $\alpha \rightarrow 0$ in just the right way

But

$$N = \sum_{i=1}^{\infty} \text{Int}(g_i e^{\alpha - E_i/kT})$$

In this case

α can be made
small enough

that for high enough E_i

$$\text{Int}(g_i e^{\alpha - E_i/kT}) = 0.$$

So divergence is formally
precluded.

5-674

This result probably has no practical use, but it's nice to know the divergence of the partition function is formally a result of an approximation \rightarrow an approximation which in all practical cases that I know of is valid.

Example 2 of Maxwell-Boltzmann

Distribution

- Classical gas / Distinct Particle gas

Let's assume that At finite Temperature

the energy density of states

that we got in considering the free electron gas

5-676

is valid for
distinct particles

~~But~~

we don't have the
Pauli exclusion principle
but we've got a distribution
function now for the
occupation of single particle
states.

From p. 5-593 for 3-d

$$\rho_E = \frac{g}{(2\pi)^3} 4\pi \left(\frac{km}{h^2}\right)^{3/2} \frac{1}{2} E^{1/2}$$

density
of
energy
states
per E
per
volume

but this was for electrons

But we say m is mass of
whatever gas atoms
we consider.

→ But it doesn't matter to distribution

directly.

5-677

This Mass ~~does~~ gets absorbed into normalization.

What of g ?

$g = 2$ for electrons.

What does g even mean for complex composite particles?

Vaguely I think we treat the internal ~~states~~ of energy states separately — in fact that's what we were doing in Example 1.

— We don't need to worry if the atoms are bosons or fermions since we make the assumption of occupation of a spatial state is on average

6-678

much less than 1,

and the particles wave packets don't overlap

~~So the Pauli antisymmetrization~~
So some "generalization" of Pauli exclusion principle is irrelevant.

magically since our derivation of the density of states assumed they

Practically g just vanishes into normalization, and so we never worry about it

were totally non local.

$$\rho_E dE \Rightarrow g_i / V$$

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

$$n = \sum_i \frac{g_i e^{-E_i/kT}}{V}$$

particle density

$$= \int C e^{-E/kT} E^{3/2} dE$$

normalization constant.

Maybe the wave packets for the particles are actually in a superposition of states strongly centered on the non-local states but the packets are local

We assume the density of states per energy per volume is a constant for any volume or even unconstrained space. (5-679)

There must be some reasoning behind these inconsistent assumptions, but it is unspeakable.

$$n = C \int_0^{\infty} e^{-E/kT} E^{1/2} dE$$

$E^{1/2}$ differs from p. 5-66d since there we assumed

$$n = C(kT)^{3/2} \int_0^{\infty} e^{-x} x^{1/2} dx \quad \left\{ \begin{array}{l} \mathcal{G}_i \rightarrow C dE \\ \text{Art - 453} \end{array} \right.$$

$$= C(kT)^{3/2} \left(\frac{1}{2}\right)!$$

5-680)

$$n = C (kT)^{3/2} \left(\frac{1}{2}\right) \left(-\frac{1}{2}\right)! \frac{m}{\sqrt{\pi}}$$

(Ans - 453)

$$\text{So } C = \frac{n}{\frac{\sqrt{\pi}}{2} (kT)^{3/2}}$$

$$\text{So } dn = n \frac{dE}{E}$$

where

$$\frac{dE}{E} = \frac{1}{\frac{\sqrt{\pi}}{2} (kT)^{3/2}} e^{-E/kT} E^{1/2}$$

This is Maxwell distribution
for an ideal gas

(Mihalas-10)

in the energy representation

~~Usually~~ Often one sees it
in the speed representation

~~EDP~~

$$f_E dE = f_v dv$$

$$f_v = f_E \frac{dE}{dv} \quad \text{where } E = \frac{1}{2}mv^2$$

$$= \frac{1}{\sqrt{\frac{\pi}{2}} (kT)^{3/2}} e^{-E/kT} E^{1/2} m v dv$$

$$= \left(\frac{m}{kT}\right)^{3/2} \frac{1}{\sqrt{\frac{\pi}{2}}} \frac{1}{\sqrt{2}} e^{-\frac{mv^2}{2kT}} v^2 dv$$

$$= \left(\frac{m}{kT}\right)^{3/2} \sqrt{\frac{2}{\pi}} e^{-\frac{mv^2}{2kT}} v^2 dv$$

or

$$= \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-\frac{mv^2}{2kT}} 4\pi v^2 dv$$

(Mihala's-110)

$$E_{ave} = \frac{\int_0^{\infty} E e^{-E/kT} E^{1/2} dE}{\int_0^{\infty} e^{-E/kT} E^{1/2} dE}$$

$$= kT \frac{\left(\frac{3}{2}\right)!}{\left(\frac{1}{2}\right)!} = \frac{3}{2} kT$$

(Arf-453)

5-682

$\mathcal{E} = \frac{E}{V} = nkT$ is the energy per unit volume.

$$p = - \left(\frac{\partial E_{int}}{\partial V} \right)_{S, N} = - \left(\frac{\partial (E/V)}{\partial V} \right)_{S, N} = V \left(\frac{\partial \mathcal{E}}{\partial V} \right)_{S, N} - \mathcal{E}$$

but we'd need

E as a function

~~$$E = E(S, V, N)$$~~

to get this derivative

and we have $E = E(T, V, N)$

$$p = -V \left(\frac{\partial E}{\partial V} \right)_{S, N} \left(\frac{-N}{V^2} \right) - E$$

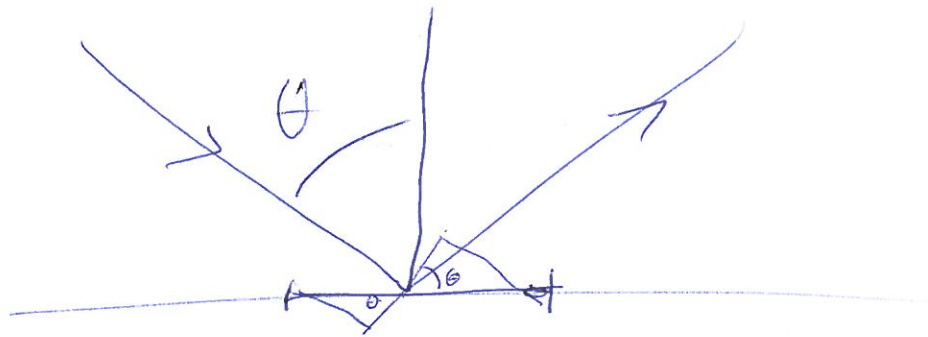
$$p = n \left(\frac{\partial E}{\partial n} \right)_{S, N} - E$$

Now $\left(\frac{\partial E}{\partial n} \right)_{S, N} = \left(\frac{\partial E}{\partial T} \right)_{S, 1}$

We could do it by going back and finding entropy and being careful about partial derivatives.

But it is easier to use kinetics and classical particle approximation

5-683



$$P = \int_0^{\infty} 2\pi \int_0^{\pi/2} 2pN \cos^2\theta \frac{N}{4\pi} f_E dE \sin\theta d\theta dE$$

$$P = 2 \int_0^{\infty} u^2 du \int_0^{\infty} E n f_E dE$$

$$\left. \begin{aligned} \frac{4\pi pN}{4\pi} \\ = 2E \end{aligned} \right\}$$

$$P = \frac{2}{3} E = nkT$$

$\therefore P = nkT$ the ideal gas law

$$PV = NkT = \mathcal{M}RT$$

5-684

where M is the number
of moles

$$Nk = \frac{N}{A_{AVO}} A_{AVO}k$$
$$= MR$$

h) Fermions

$$W = \prod_i \binom{g_i}{N_i} \quad \text{see p. 5-629}$$

$$\ln W = \sum_i \ln g_i! - \sum_i \ln (g_i - N_i)! - \sum_i \ln N_i!$$

~~$\sum_i \ln g_i!$~~
 ~~$\sum_i \ln N_i!$~~

5-686

But $\text{Int}(z_a)$

is consistent with

integer A_i ~~as the~~

~~true~~

and ~~prevents~~

the constraint $N_i \geq 0$

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

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

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

$$+ \alpha ~~N_j~~ + \beta ~~N_j~~ \epsilon_j$$

$$0 = \ln(g_j - N_j + 1) - \ln N_j + \alpha + \beta \epsilon_j$$

$$+ \alpha N_j + \beta N_j \epsilon_j$$

$$0 = \ln\left(\frac{g_j - N_j + 1}{N_j}\right) + \alpha + \beta \epsilon_j$$

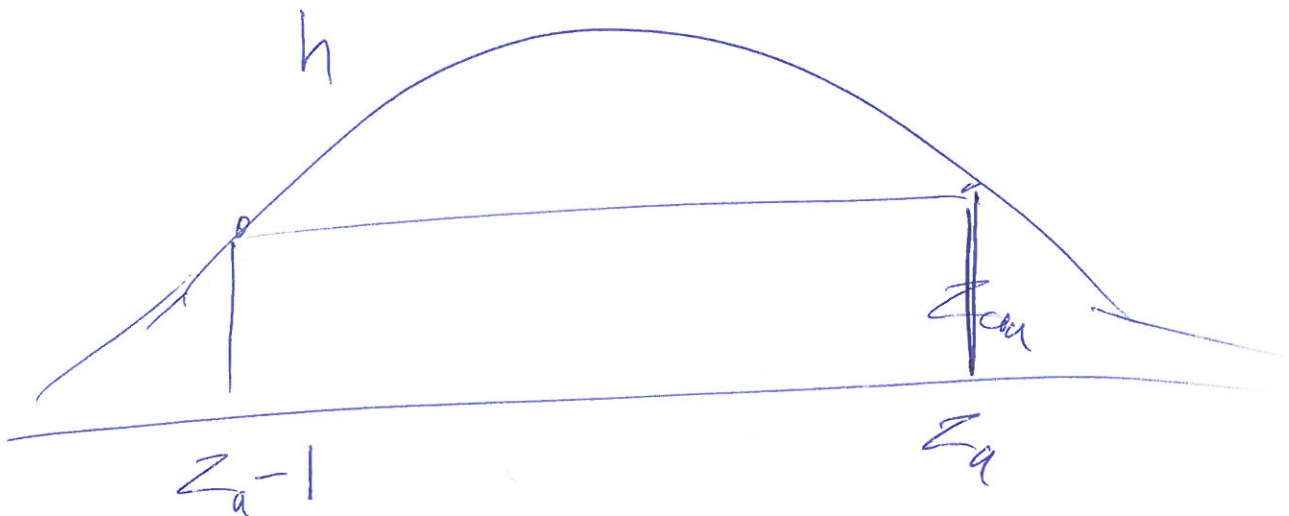
In this case there is a slight difference from the Stirling Approx. This I think the Stirling Approx leads to a slight smaller result for N_i

Defining

5-685

$$h = \ln W + \cancel{\alpha(N - \sum_i N_i)} + \cancel{\beta(Y)}$$
$$+ \alpha(\sum_i N_i - N) + \beta(\sum_i N_i E_i - E)$$
$$= \sum_i \ln g_i! - \sum_i \ln (g_i - N_i)! - \sum_i \ln N_i!$$
$$+ \alpha(\sum_i N_i - N) + \beta(\sum_i N_i E_i - E)$$

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



we know h maximizes
between these points and
best guess is $z_a - \frac{1}{2}$ again.

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

$$= - \left(\ln(g_j - N_j)! - \ln(g_j - (N_j - 1))! \right) - \left(\ln N_j! - \ln(N_j - 1)! \right) + \alpha + \beta E_j$$

$$0 = +\ln(g_j - N_j + 1) - \ln N_j + \alpha + \beta E_j$$

$$\frac{N_j}{g_j - N_j + 1} = e^{\alpha + \beta E_j} = e$$

$$N_j = e(g_j - N_j + 1)$$

$$N_j(1 + e) = e(g_j + 1)$$

$$N_j = \frac{g_j + 1}{e^{-1} + 1}$$

$$\therefore N_j = \frac{g_j + 1}{e^{-(\alpha + \beta E_j)} + 1}$$

Reverting to index i

4-688

$$N_i = \text{Int} \left[\frac{g_i + 1}{e^{-(\alpha + \beta E_i)} + 1} \right] \quad \left. \begin{array}{l} \text{reverting} \\ \text{to} \\ \text{index } i \end{array} \right\}$$

our best guess at the maximizing N_i

What does the Stirling's approximation give?

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

$$\frac{\partial h}{\partial N_j} = 0 = \ln(g_j - N_j) + 1 + 1 - (\ln N_j + 1 + 1) + \alpha + \beta E_j$$

$$0 = \ln \left(\frac{g_j - N_j}{N_j} \right) + \alpha + \beta E_j$$

$$\therefore N_i = \frac{g_i}{e^{-(\alpha + \beta E_i)} + 1} \quad \left. \begin{array}{l} \text{reverting} \\ \text{to } i \text{ index} \end{array} \right\}$$

For the distinct particle [5 - 689]
 case the Stirling Approximation
 led to ^{distinct} overestimate.

~~In this on under~~
 In this case is there a distinct
 underestimate?

$$\frac{g+1}{D} > \frac{g}{D} \stackrel{?}{\geq} \frac{g+1}{D} - 1$$

upper bound on maximizing value
lower bound on maximizing value

clear

$$g \stackrel{?}{\geq} g+1-D$$

$$D \stackrel{?}{\geq} 1$$

yes this is always true.

So No.

The Stirling Approximation does Not
 lead to an overestimate nor
 an underestimate in this case.

5-690

But the difference approach
is still a better approximation,
~~it~~ since it is better for
small N_i .

$$\text{So } N_i = \text{Int} \left[\frac{g_i + 1}{e^{-(\alpha + \beta E_i)} + 1} \right]$$

but the Int - function is
analytically intractable
and ~~$g_i + 1$~~ the +1
is a nuisance and analytically
intractable and tricky to treat
in the continuum limit.
and negligible when $g_i \gg 1$.

$\therefore N_i = \frac{g_i}{e^{-(\alpha + \beta E_i)} + 1}$ is the
preferred
form.

~~$N_i = \text{Int} \left[\frac{g_i + 1}{e^{-(\alpha + \beta E_i)} + 1} \right]$~~

5-692

where $g = 2$.

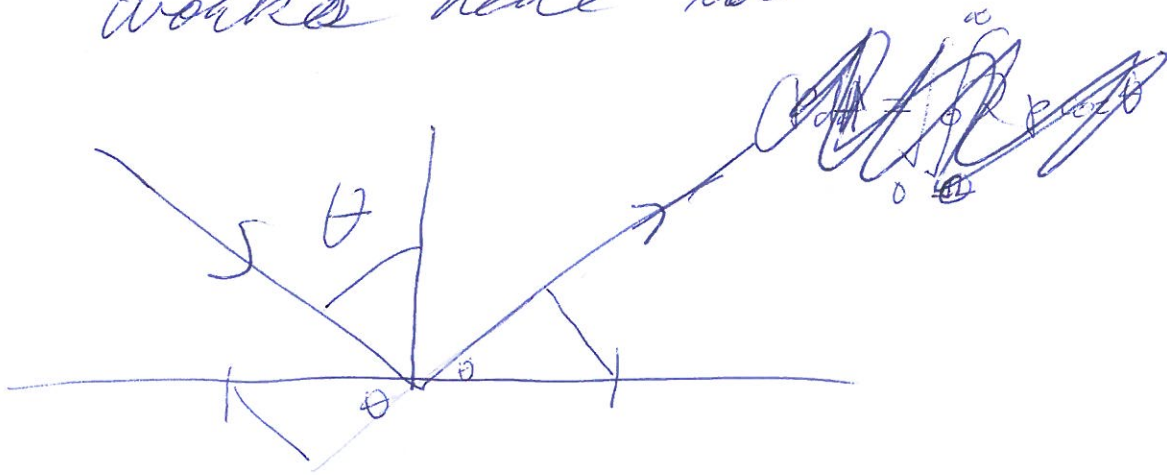
We can now calculate free electron gas quantities for finite temperature.

$$n_e = \int_0^{\infty} f P_E dE$$

$$E = \int_0^{\infty} f E P_E dE$$

$$P = \frac{2}{3} E, \quad E_F = E/n_e$$

The ~~semi~~-classical kinetic proof of this works here too



$$P dA = \int_0^{\infty} \int_0^{\pi} 2 P \cos \theta \cdot N \frac{f P_E}{4\pi} dE \cos \theta dA d\Omega$$

$$\mu = \cos \theta$$

We already know

5-691

From p. ~~563~~ ~~563~~

v. 5-653

that $\alpha = \frac{\mu}{kT}$ and $\beta = \frac{1}{kT}$

$$N_i = \frac{g_i}{e^{(\epsilon_i - \mu)/kT} + 1}$$

$$f = \frac{1}{e^{(\epsilon - \mu)/kT} + 1}$$

If $e^{(\epsilon - \mu)/kT} \rightarrow \infty$
 $f_{FD} \rightarrow f_{MB}$,
but we already know about that limit.

is the Fermi-Dirac distribution.

which is a suitable form when one goes to the continuum limit for the density of states.

For a 3-d, free electron gas

$$\rho_{\epsilon} = \frac{g}{(2\pi)^3} 4\pi \left(\frac{2m}{\hbar^2}\right)^{3/2} \frac{1}{2} \epsilon^{1/2} d\epsilon$$
$$= \frac{g}{(2\pi)^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} \epsilon^{1/2} d\epsilon \quad (\text{see p. 5-563})$$

is the density of states (per energy per volume)

Where $p v = 2E$

$$P = 2 \int_0^1 n^2 dn \quad E$$

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

Why does this ~~seem~~ classical kinetic argument work.

Well ~~remember~~ in each dE range you have the right amount of energy and the right amount of momentum for the quantum ~~etc~~ calculation.

The classical $p v = m v^2 = 2 (\frac{1}{2} m v^2) = 2E$

5-694

gives the right connection
~~between~~ between ~~E~~ and
energy and momentum.

Hm

Will the correspondence principle
tell you the macroscopic
average behavior should agree
with classical.

— So we just assume microscopic
classical = "particles" and if we
~~can~~ only are interested
in the macroscopic average result
we should get right average.

Hm.

Discussion breaks of inconclusively

The $e^{(E - \mu)/kT} \rightarrow$ large is
just the Maxwell Boltzmann
case

1/10

Although not obvious

5-699

this is actually the high T

~~limit~~ low density limit (see p. 5-696 below)

The reason is, is that μ goes negative for high T.

In the low T limit $\mu \rightarrow E_F$.

At $T=0$, one can only add an electron at the top of the Fermi surface

$$\text{so } \mu dN = E_F dN$$

As $T \rightarrow 0$

$$\frac{1}{e^{(E-\mu)/kT} + 1} \rightarrow H(E_F - E)$$

Heaviside step function.

$$h(x) = \begin{cases} 1 & x > 0 \\ 0 & x < 0 \end{cases}$$

5-6%

One recovers the $T=0$ results, we got before for the free electron gas.

For MB limit

$$f = e^{(\mu - E)/kT}$$

$$n_e = \int_0^{\infty} e^{(\mu - E)/kT} \frac{g}{(2\pi)^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} E^{1/2} dE$$

(see p. 5-69)

$$= e^{\frac{\mu}{kT}} \frac{g}{(2\pi)^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} \int_0^{\infty} e^{-E/kT} E^{1/2} dE$$

$$(kT)^{3/2} \int_0^{\infty} e^{-x} x^{1/2} dx$$

$$n = e^{\frac{\mu}{kT}} \frac{g}{(2\pi)^2} \left(\frac{2m kT}{\hbar^2}\right)^{3/2} \frac{\sqrt{\pi}}{2} = \frac{\sqrt{\pi}}{2} \quad (\text{Art. 453})$$

$$= e^{\frac{\mu}{kT}} \frac{g}{\pi \hbar^2} \left(\frac{2m kT}{\pi \hbar^2}\right)^{3/2}$$

5-628

What of excited levels.

Usually for gas calculation purposes they can be ignored as ~~deposits~~ energy reservoirs, but not as energy controllers.

- I'm thinking of low ionization plasmas
- which are the gases I'm familiar with.

~~But note~~

Now note $g e^{-kT \ln g} / kT = 1$

and so g is often unimportant.

It cancels out of density

$$\mu = kT \ln \left[\frac{n}{\frac{g}{8} \left(\frac{2m kT}{\pi h^2} \right)^{3/2}} \right]$$

$$= kT \ln \left[\frac{n}{g \left(\frac{m kT}{2\pi h^2} \right)^{3/2}} \right]$$

For electrons, $g = 2$ ($G_v = 242$)

~~For atoms, $g = 1$.~~

~~But why?~~

For atoms?

Well g is an internal degeneracy.

Most atoms are in their ground state or very low-lying states.

So often g is the degeneracy of the ground ~~low~~ or near ground states states.

of states.

5-6)9

But if you add/subtract particles

$$dE = \mu dN$$

and μ itself and g are needed.

From $\mu = kT \ln \left[\frac{n}{g \left(\frac{m kT}{2\pi \hbar^2} \right)^{3/2}} \right],$

we see if $n/T^{3/2}$

is low enough

μ goes negative.

It may seem strange that adding particles to a sample can be decrease energy,

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

5-700

You are adding particles
at constant entropy.

— so decreasing energy
as you add particles
becomes necessary to
keeping entropy fixed.
↳ Maybe a tricky thing to do
in practice.

Degenerate gases where
the Fermi-Dirac distribution
holds have $\frac{\mu}{T^{3/2}} \gg 1$,

but the MB μ formula
does NOT apply then.