The free electron gas assumes a flat potential bottom for the potential well of the solid and only deals with the delocalized ~~potential~~ eigenstates.

$V_\infty = 0$
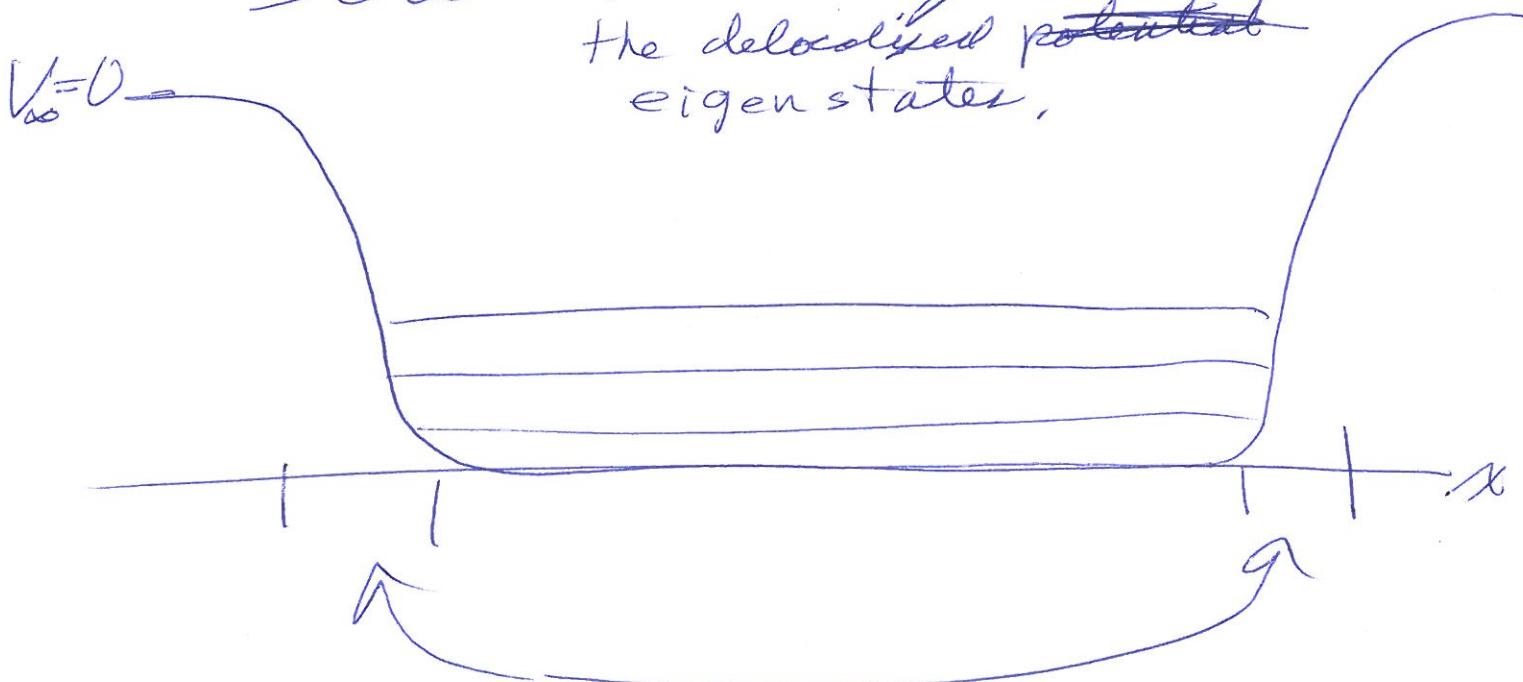
the sides of the well are steep.

— how narrow are the boundaries?

— Probably varies from a few Angstroms to hundreds of

nanometers for
a <u>solid</u> that is considered
uniform on the inside.

This flatness of inner part
of the well
(on average for periodic
potential case)
allows us to treat
the <u>boundary conditions</u>
of the potential very
approximately and still
get bulk properties accurately.
<u>Since</u> surfaces are often complex,
this is a very good thing.

Which
is unlike
many
physical
systems
where the
BCs
set
everything;
e.g.,
Many
electricity
&
magnetism
cases.

4) Boundary Conditions

for Free electron Gas model

There are two favored choices

a) Infinite-square well BCs.
   (ISW BCs)

b) Periodic BCs.

And these are for samples of solid material that could be irregular in shape and of any size

e.g.,

(as long as big enough to be macroscopic or mesoscopic)
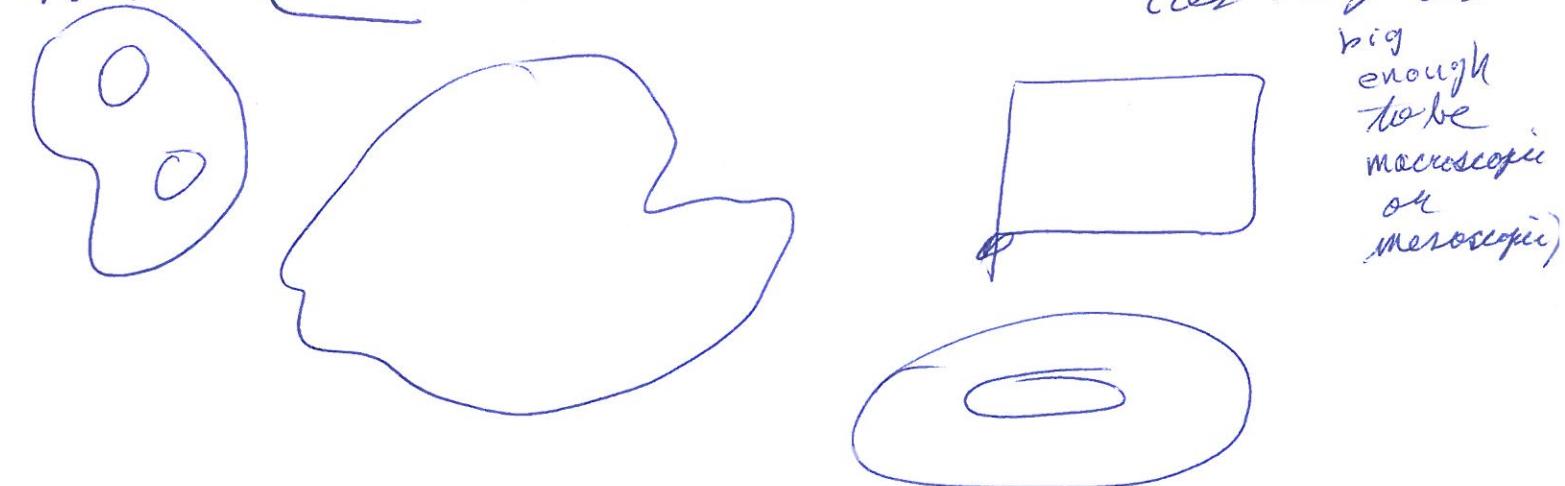
We have to show
or, at least, make
plausible that our idealized
BCs will give
realistic results.

a) Let's first consider
One dimension of
a rectangular box solid
sample

with ISW BC

$V = \infty$

$V = \infty$

x

ℓ
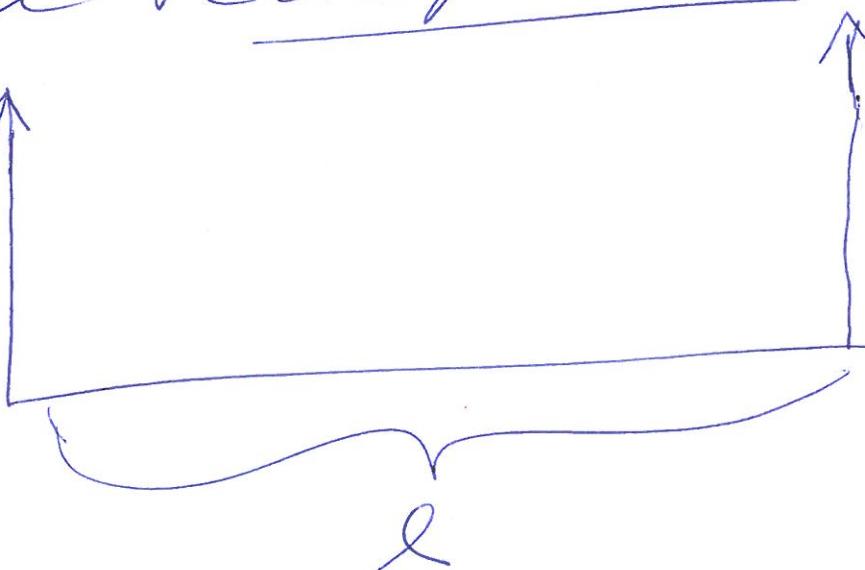
How can we get away with
these BCs?

Consider 3 potential well shapes

a) finite square well

b) SHO potential up to the $V=0$ level

c) irregular

$V=0$

V_{min}

$2\Delta\ell$ $2\Delta\ell$ $2\Delta\ell$

} infinite square like state

} SHO-like states

irregular but with quantized states.
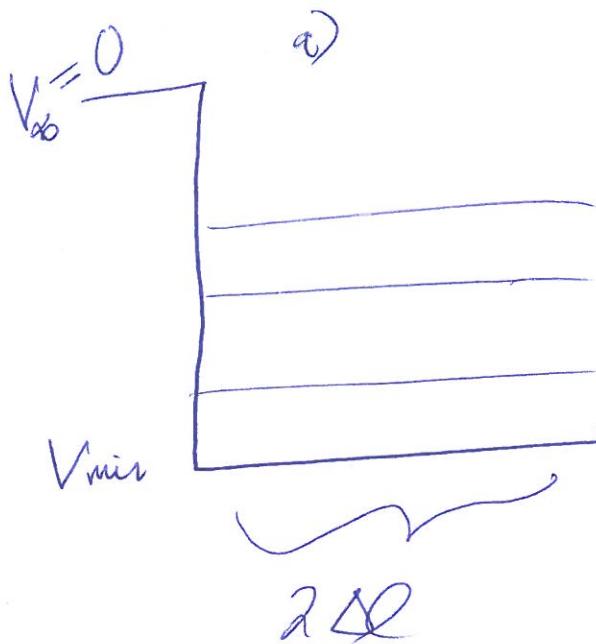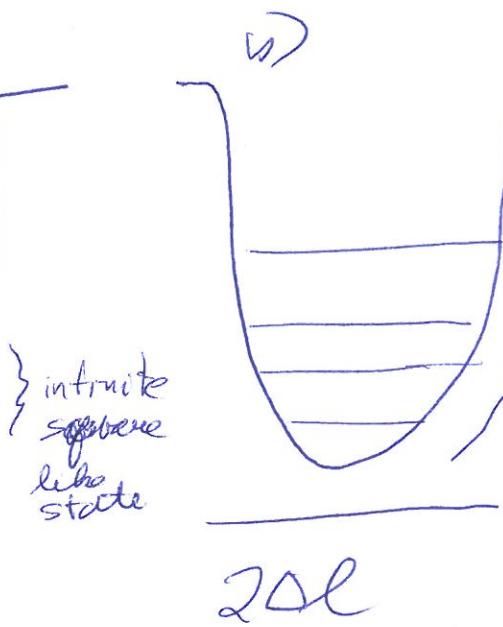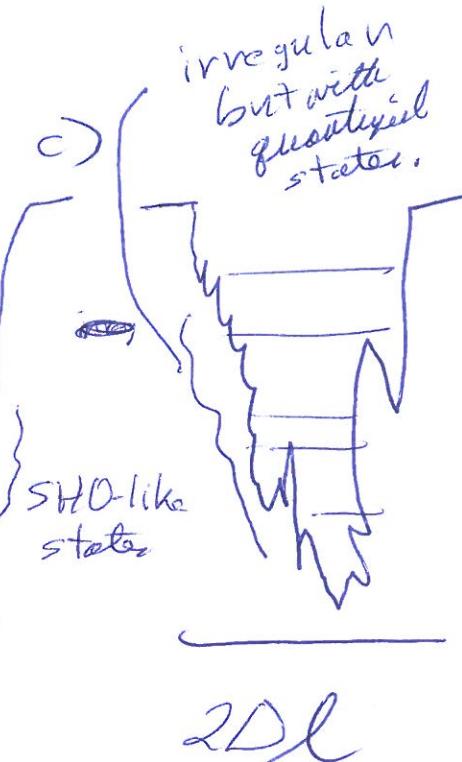
— all wells have characteristic ~~with~~ width 𝕖 $2\Delta\ell$ and the same V_{min}. Now imagine inserting a flat region just at the V_{min} point of length ℓ.

$V_{ab} = 0$

$\Delta \ell \quad \ell \quad \Delta 9$ $\qquad$ $\Delta \ell \quad \ell \quad \Delta \ell$ $\qquad$ $\Delta \ell \quad \ell \quad \Delta \ell$
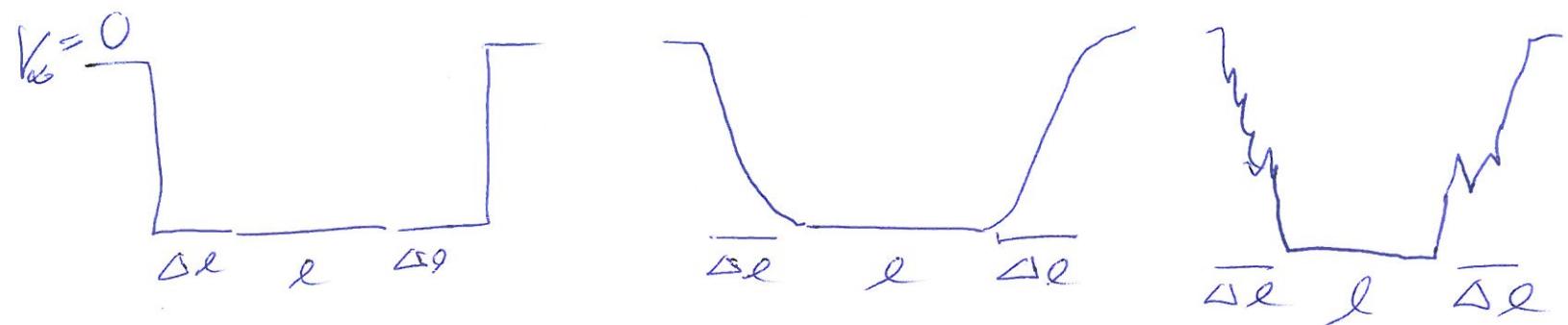
The finite square well
stays a finite square well
but is broader.

— The other two wells are
now kind of mixed.
Partially what they were
before and partially
finite — square wells.

As ℓ increases the other
wells become more finite square
well like.

When $\ell >> \Delta \ell$, it is

plausible, but not conclusive, in my mind, that that cases (b) & (c) approach (a) and as $l \to \infty$, they approach being exactly like (a).

So this is a reasonable plausible argument for using finite square well BCs for rectangular boxes no matter what the actual boundaries are like

If We now say the boundary potential walls are very big, we can approximate $V_{wall} = +\infty$.

and so arrive
at ISW BC
as good approximations
for rectangular boxes.

Now one can shape
a solid into a rectangular
Box
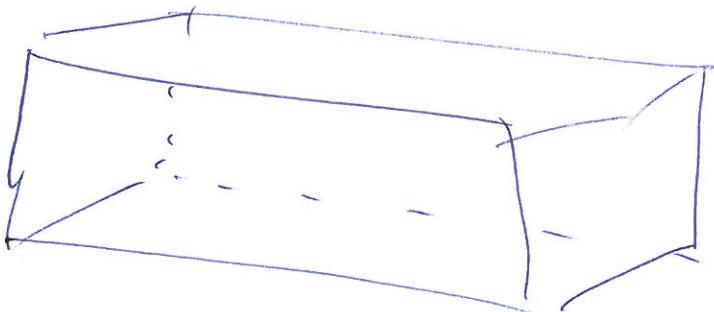
to high
accuracy.
But most samples are
NOT rectangular boxes.
— They come in all
shapes and sizes.

One can prove
that shape does not
matter to the main
results (density
of states per unit volume
per unit energy) in the
asymptotic limit of large
~~tot~~ ~~vol~~ samples
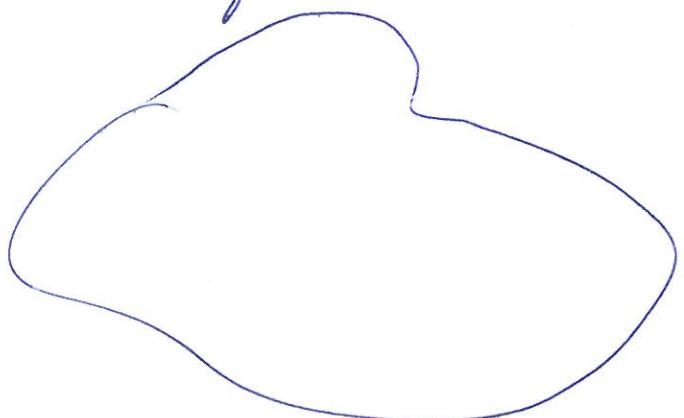
The ~~proof is sort of~~

etc.
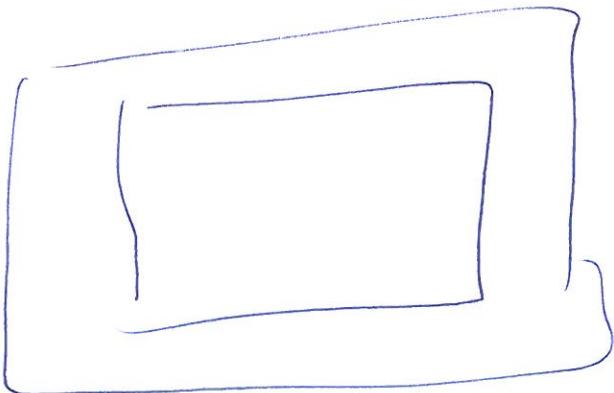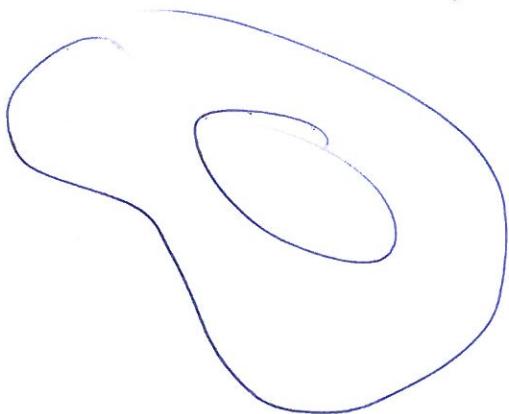
The proof is sort of a <u>tiling</u> of space proof. But we'll defer it until later when it will be more concrete. So it's fine to do ~~stuff~~ derivations for rectangular boxes.

b) <u>Periodic BCs</u>

~~An alternative view~~

Here you demand that

$$\gamma(a)^{(n)} = \gamma^{(n)}(b)$$

where (n) stands
for all orders of derivatives
and a & b are
boundary points.
An alternative view is that
the dimension is finite,
but unbounded
and we demand
single-valuedness
for the wave function.
Actually this is _not_
impossible for 1-d and
2-d curved spaces embedded
in a 3-d ~~world~~
Euclidean world.

Consider rings &
spherical shells

ring   spherical
              shell.
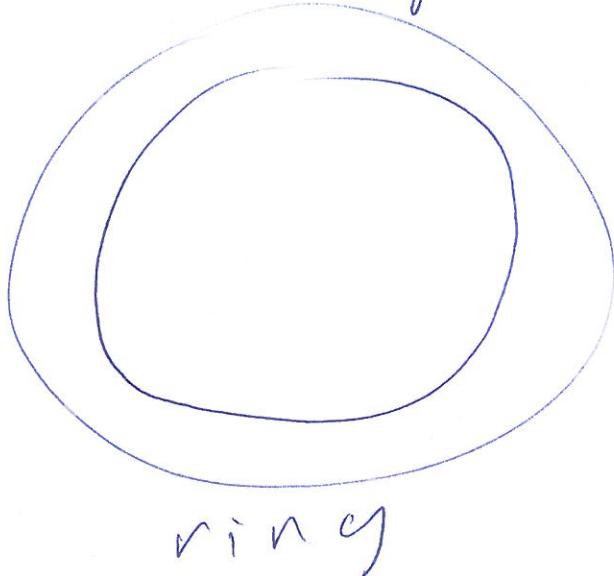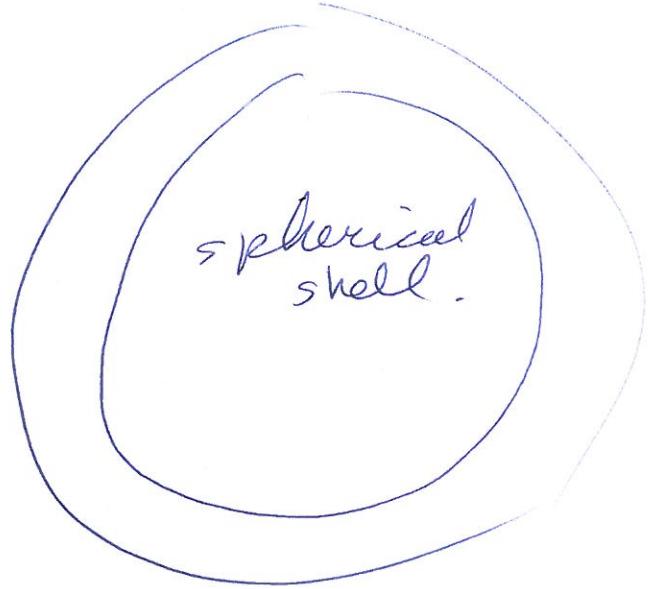
— if their thinkness is small,
the curvature is small
at any point.

Weirder curved dimensions
can exist too
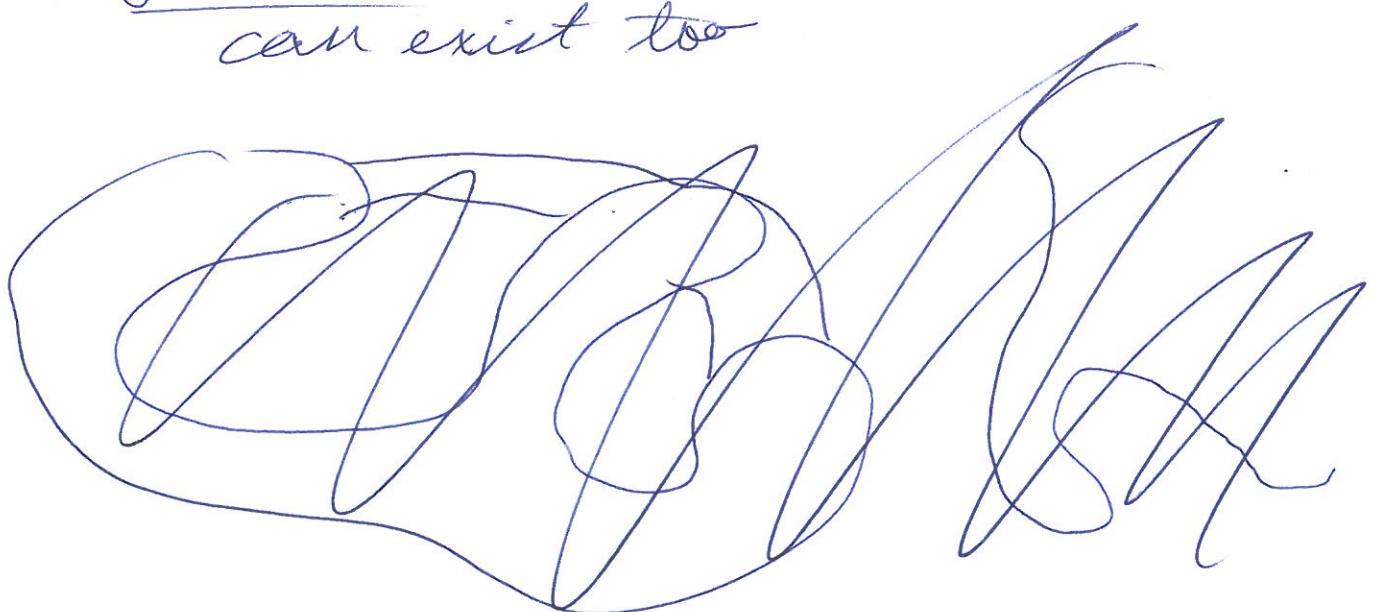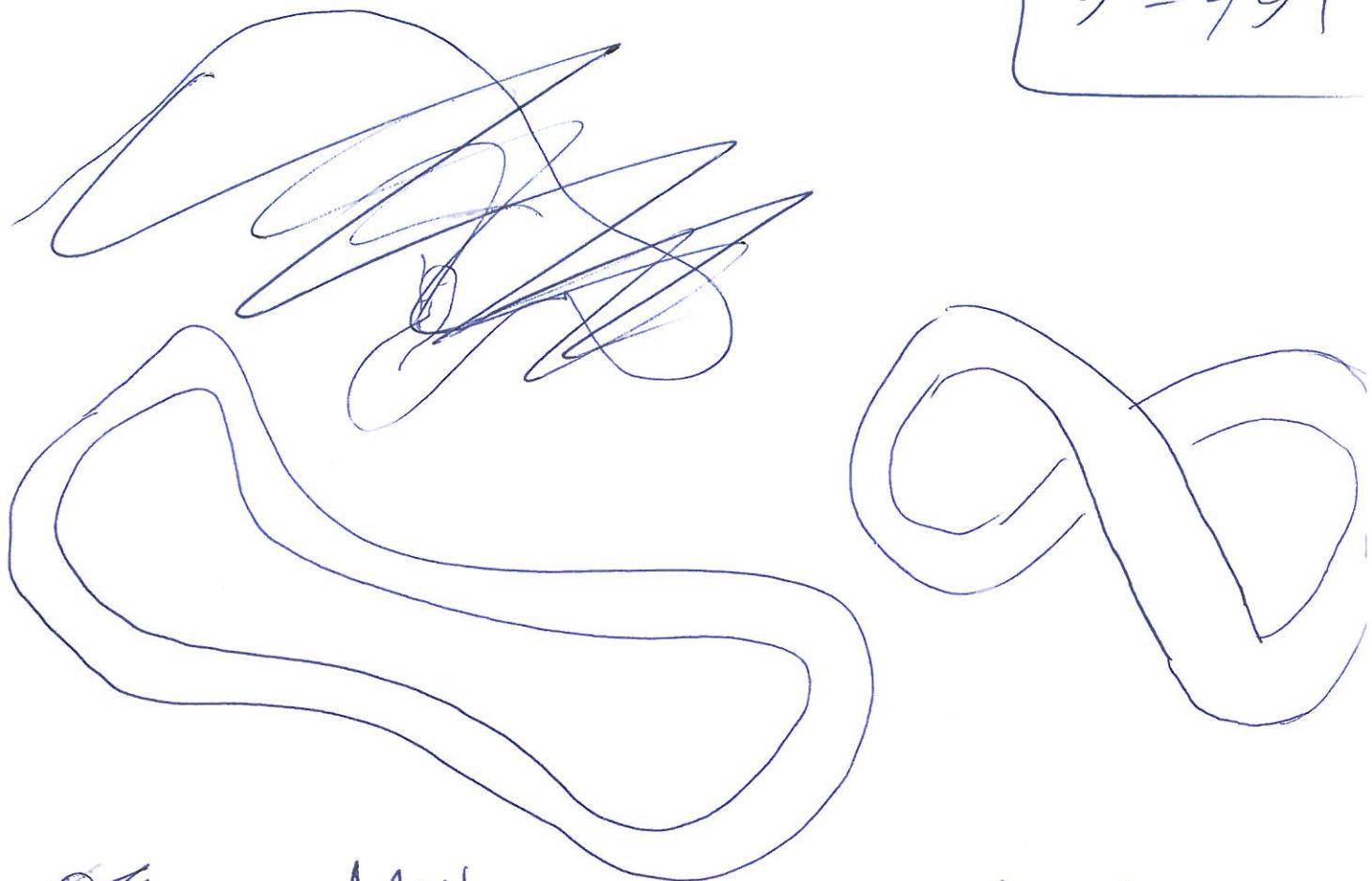
or a Möbius strip which
defies MY artistic
ability, but can
be made from a strip of paper.

<u>But</u> Periodic BCs for for 3-d
Euclidean world are impossible.
(I think)

In any case, periodic
BCs for solids

means we map opposite ends of a rectangular box into each other

particle leaves this end

re-enters this end
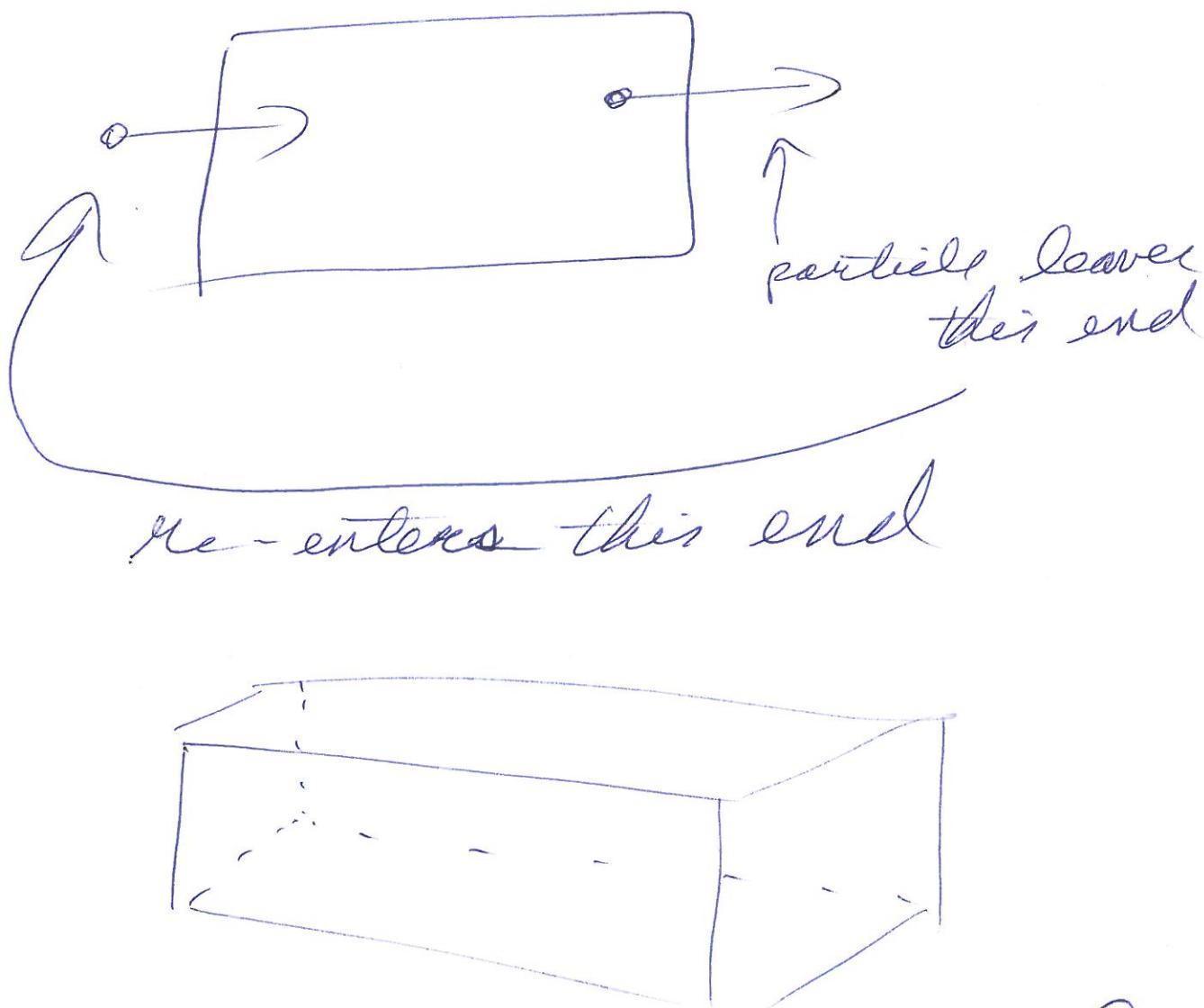
We demand this magical condition on opposite faces of a rectangular box.

Why is this ~~thing~~
hypothesis a good idea
as a basis for a
theory of solids.

a) It leads to the
same density of states
(per unit volume per energy)
as ISW BCs.
— if it didn't do this it
would be wrong.

b) It gives a complete set
(i.e, basis) of single-particle
eigenstates ~~this~~ just as
ISW BCs would do.
They aren't exactly the
actual physical basis,

as a complete ~~this~~ set
any real physical state
can be expanded in them

~~that~~

c) The ~~periodic~~ BC set
are <u>traveling waves</u>
while the ISW BC set
are <u>standing waves</u>

Traveling waves are more useful
for studying transport
phenomena.

And they are analytically
easier to manipulate.

d) If the magic periodic BC
hypothesis were true,
~~the~~ then periodic BCs

would be exactly right.

This idealization seems real ~~enough~~ enough.

Not an over-idealization that leads to false results.

e) Apparently Periodic Potentials are much more easily treated by periodic BCs and since they are **NOT** an over-idealization this is a good procedure.

f) At least in some dimension one can have periodic BC.
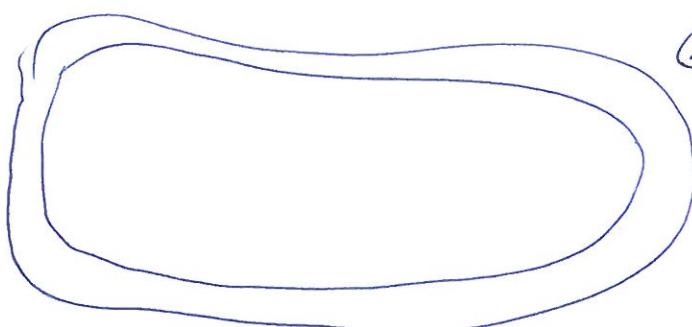
— A loop sample.

— So here the periodic BC states are

actual physical
alternatives to { *Which occurs really might depend on delicate ~~bou~~ surface effects..?*
IWS BC ~~states~~

g) The periodic BC ~~essentiates~~
~~are really~~ system
has no boundaries really.

So it's neutral
about boundaries

While IWS BC make
specific assumptions about
boundaries which are
only crude approximations
and so may be no better
than periodic BCs in modeling
actual samples.

Maybe there is an argument that shows periodic BCs must give the true limiting behavior of large samples. But I don't know it.

h) <u>Periodic BC</u> apply to any shape sample in the large-sample asymptotic limit just like ISW BCs

This is proven by the same argument.

5) <u>Solving</u> ~~For~~ <u>Rectangular Box Sample with</u> <u>ISW and Periodic BCs</u> <u>in Free Electron gas Model</u>

We will do both cases

in parallel to show similarities and differences clearly. Where the steps are the same, we write the parallel arguments.

When we get to important results the two BC cases merge — which they must do if periodic BCs are to be correct.

a) **Separation of Time - Independent Sch. Equ. for N electrons**

~~N well~~

We will consider the important limit of a macroscopic sample

where N is huge.

$$N = z \; \frac{M_{sample}}{A \; M_{amu}}$$

— Mass of sample

- Number of free electrons per atom.
  — usually 1 or 2 for metal I think
  $z = 1$ for Copper
  (Gr - 223)

- atomic mass of atom

- atomic mass unit (AMU)

$$N = z \; \frac{M_{sample}}{A \cdot 1g} \; \frac{1g}{M_{amu}}$$

$\mathcal{M}$
— number of moles in sample

$A_{AVO} = 6.022 \times 10^{23}$
Avogadro's number

At present, we have

two unit mass definitions

— i) The macroscopic
kilogram defined
by a cylinder kept
in Paris
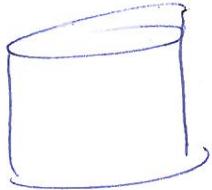
— but it's a destructable,
losable, ~~artifa~~ changeable,
artifact
and people hope to phase
it out

— ii) The AMU $\equiv \frac{1}{12}$ of mass
of C^{12}
atom.

Some time soon people
hope to make the AMU
the only ~~mass~~ unit mass
definition; and then

give A_{AVO} an exact value by definition

$$\therefore \quad 1\,kg \equiv 10^3 \cdot A_{AVO} \cdot m_{amu}$$

Any macroscopic or even mesoscopic sample contains a huge number of electrons N.

So actually formulating a full wave function is impossible, and one has to calculate results statistically.

But one starts by separating the ~~wave function~~ Sch. equ.

$$H\Psi = E\Psi$$

We've assumed non-interacting particles and $V = 0$ inside box.

$$\therefore \quad \Psi = \prod_i \Psi_i$$

product wave function separated into single-particle wave functions each particle dimension

$$H = \sum_i H_i$$

single particle dimension Hamiltonians — all identical, in fact,

Substituting into the initial equation gives

$$\sum_i \frac{H_i \Psi_i}{\Psi_i} = E$$

Take derivative with respect
to x_{ij} the coordinate
of ith particle.

x_j

the coordinate of one
particle dimension.

$$\frac{\partial E}{\partial x_j} = 0 = \frac{\partial}{\partial x_j}\left(\frac{H_j \, \chi_j}{\chi_j}\right)$$

And this one
is implicitly
zero

$\bigg\}$ all other
terms
are explicitly
zero

$\therefore \quad H_j \, \chi_j = E_j \, \chi_j$

E_j is the constant
of separation.

Now all particles are identical,

So we only need to consider one particle's single-particle energy eigenstate.

— and it's dimension are the same except for dimension length of box

$$\Big\} \, l_2 = l_3$$

$$l_x = l_1$$

$$l_y = l_2$$
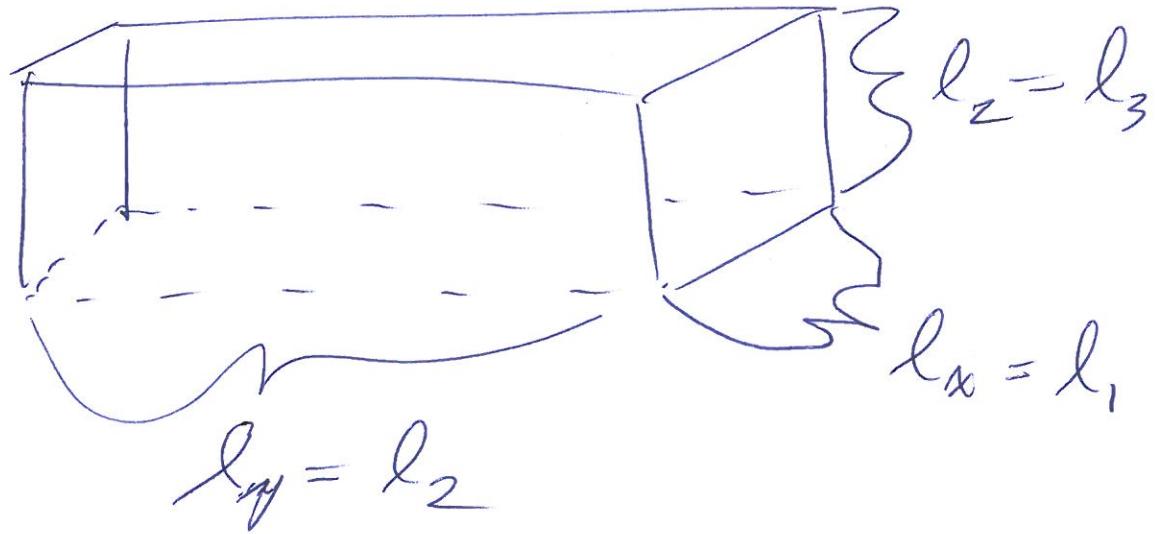
So we can just consider the general case for the ith dimension

$$H_i \, \chi = E_i \, \chi$$

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \chi}{\partial x_i^2} = E_i \, \chi$$

$$\frac{\partial^2 \psi}{\partial x^2} = -\frac{2mE}{\hbar^2}\psi$$

If $E < 0$,

$$\kappa = \sqrt{-\frac{2mE}{\hbar^2}}$$

and we have $\psi = Ae^{\kappa x_i} + Be^{-\kappa x_i}$ which can't satisfy the BCs.

If $E = 0$, $\psi = A + Bx$

Can for periodic BCs — their difference is unimportant in the large N limit.

Can't satisfy BCs

If $E > 0$ (or $E \geq 0$ for periodic BCs)

$$k = \sqrt{\frac{2mE}{\hbar^2}}$$

Just as for infinite-square well (6v-32)

$$\psi = \sqrt{\frac{2}{\ell_i}} \sin(k_i x_i)$$

$$k_i \ell_i = \pi n_i$$

$$n_i = 1, 2, 3, \ldots$$

other integer values do not give physically distinct (or expansion distinct solution)

i the imaginary unit, not i the index

$$\psi = \frac{1}{\sqrt{\ell_i}} e^{ik_i x_i}$$

$$k_i \ell_i = 2\pi n_i$$

$$n_i = 0, \pm 1, \pm 2, \ldots$$

k_i is wave number

$$k_i \lambda_i = 2\pi$$

$$k_i = \frac{2\pi}{\lambda_i} \quad \text{or} \quad \lambda_i = \frac{2\pi}{k_i}$$

Ψ gives standing waves

$$\Psi(x_i, t) = \sqrt{\frac{2}{l_i}} \, \text{sin}(k_i x_i) e^{-E_i t/\hbar}$$
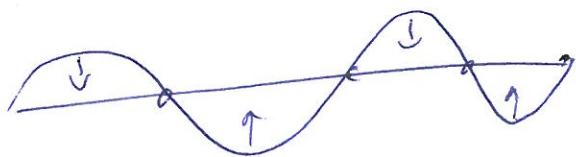
The loops just go up & down.

~~Nodes~~

— Nodes, in particular, are fixed.

Ψ gives traveling waves

$$\Psi(x_i, t) = \frac{1}{\sqrt{l_i}} e^{i(k_i x_i - w_i t)}$$

$$w_i = E_i/\hbar$$
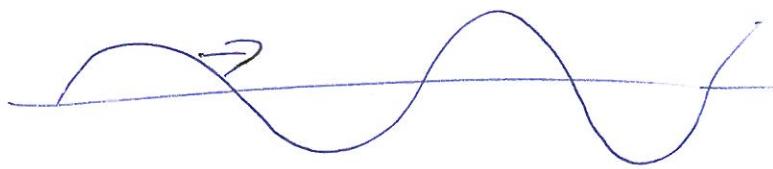
— either real or imaginary parts.

$$k_i x_i - w_i t$$

$$= k_i \left(x_i - \frac{w_i}{k_i} t \right)$$

$\dfrac{w_i}{k_i}$ is the phase velocity.

— the velocity at which the waves travel.

Periodic BC's are consistent since the waves slide out one end of box and back in the other

Probability density for a particle

$$P = \frac{2}{\ell_i} \sin^2(k_i x_i)$$

— let's average over one wavelength

$$\frac{1}{\lambda_i} \int_0^{\lambda_i} \sin^2(k_i x_i)\, dx_i$$

$$= \frac{1}{2\pi} \int_0^{2\pi} \sin^2 y \, dy$$

$$= \frac{1}{2\pi} \int_0^{2\pi} \frac{1}{2}(1 - \cos 2y)\, dy$$

$$= \frac{1}{2}$$

$$\boxed{\begin{array}{l} \cos 2y = \cos^2 y \\ \qquad - \sin^2 y \\ \quad = 1 - 2\sin^2 y \\ \sin^2 y = \frac{1}{2}(1 - \cos 2y) \end{array}}$$

$$\therefore P = \frac{1}{\ell_i} \text{ averaged}$$

over a wavelength

$$P = |\Psi_i| = \frac{1}{\ell_i}$$

a constant.
and the same
for all k_i actually.

— ~~these probab~~

So the probability densities are
distinct, but not when averaged
over a wavelength.

Considering the real electron density will depend on the total symmetrized wave function, the difference is not significant for macroscopic properties.

Which is way beyond our calculation range — and in reality is modified by electron-electron repulsion and the periodic potential anyway.

In both ISW & Periodic BC cases, the single-particle eigenstates can be located in <u>k-space</u>.

<u>k-space</u> is the wave number space.

It's <u>not</u> space space.

For the free electron gas everything in simple in k-space. Not so with periodic potentials. (In k-space, ~~nobo~~ no one can hear you scream — as the old saying goes)

ISW BCs
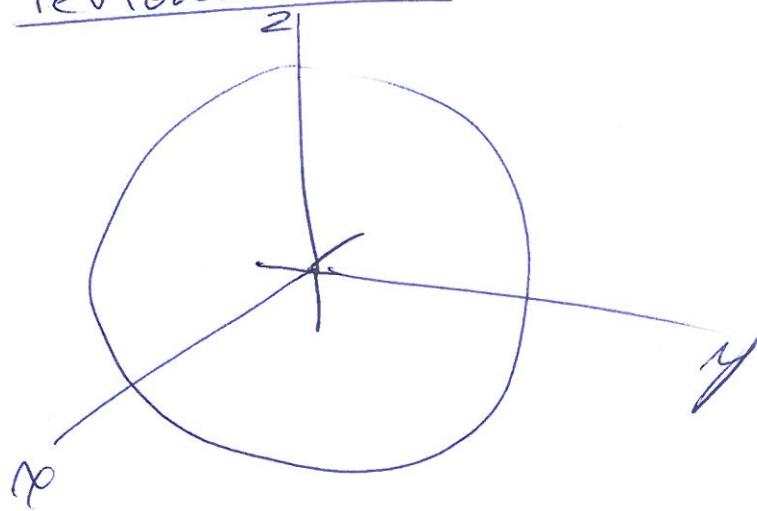
The allowed states are only on

$\frac{1}{2}$ of line for d=1

1 quadrant for d=2

1 octant for d=3

Periodic BCs

The allowed states ~~ones in~~

a line for d=1

a ~~circle~~ plane for d=2

all space for d=3

It's rather hard to
draw the *locations* in 3-d.
So in 2-d
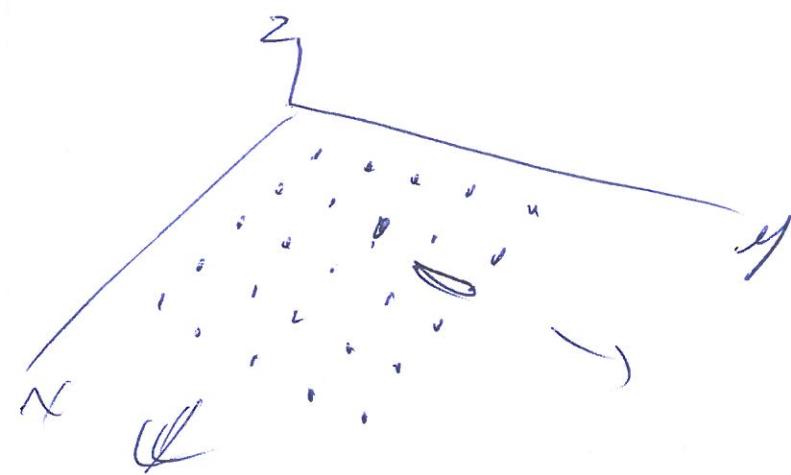
$$k = (k_1, k_2, k_3)$$

$$k = (k_1, k_2, k_3)$$
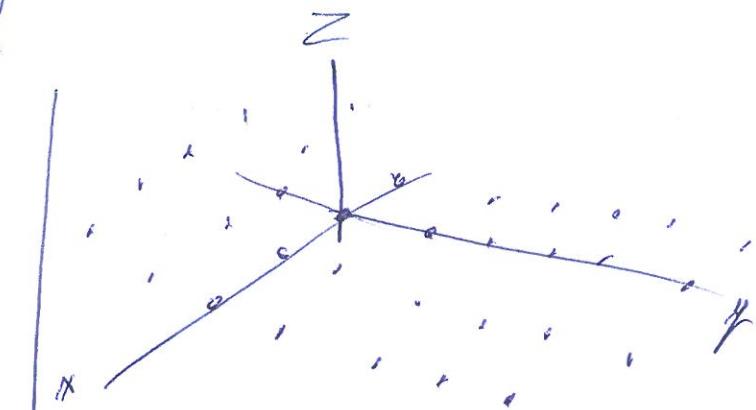
a wave vector locates
each state.

In a given direction

$$\Delta k = \frac{\pi}{l_i}$$

↖ distance between states

In a given direction

$$\Delta k = \frac{2\pi}{l_i}$$

↖ distance between states.

Each state has its own cell

$$V_k = \frac{\pi^d}{\prod_i l_i}$$

$$= \frac{\pi^d}{V}$$

Each state has its own cell

$$V_k = \frac{(2\pi)^d}{\prod_i l_i}$$

$$= \frac{(2\pi)^d}{V}$$

V is the volume of the system in space-space.
$V =$ a length for $d=1$, an area for $d=2$ and a volume for $d=3$.

$$P_k = \frac{V}{\pi^d}$$

$$P_k = \frac{V}{(2\pi)^d}$$

density of states in k-space for a system of volume V.

$$\frac{P_k}{V} = \frac{1}{\pi^d}$$

$$\frac{P_k}{V} = \frac{1}{(2\pi)^d}$$

Note c_k/N is
a constant in both cases.
— This leads ultimately
to the result that the
the density of states per
unit k (k magnitude to
be precise) per space volume
is independent of space volume.

→ So number of states per k
scales linearly with space volume.

At first this seems odd.
The states are ~~the~~
delocalized throughout
the volume.
If they'd been, localized
in a bit of volume, it
would have seemed natural.

Here's a concrete illustration
of why number of states per k scales
with volume.
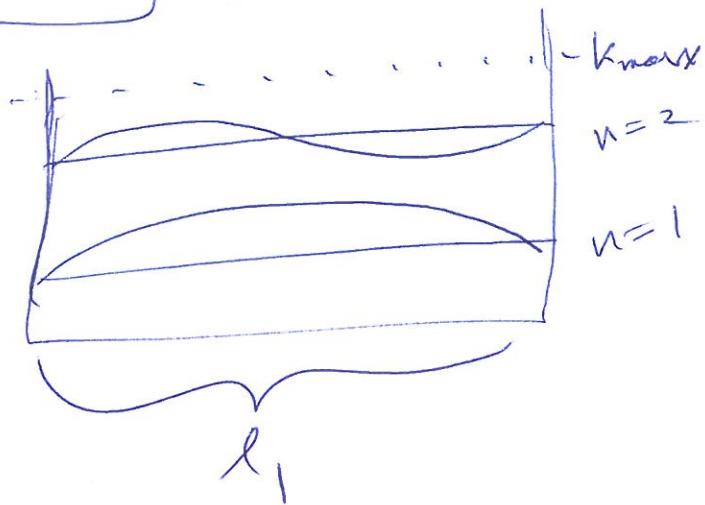
5-562c) 1-d case
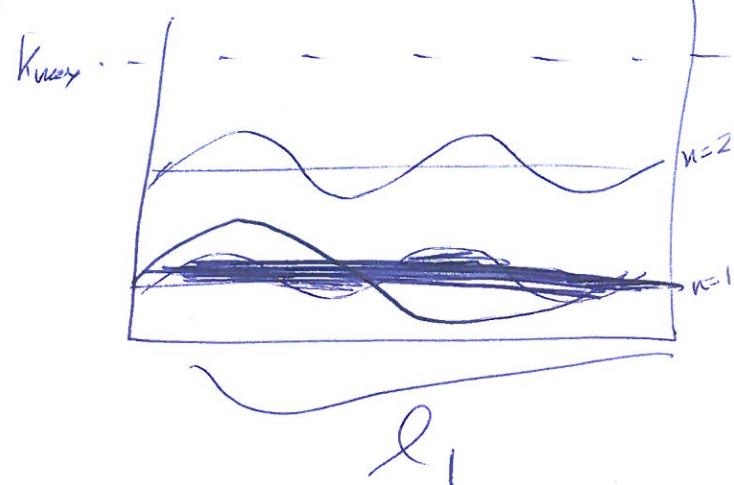
Now double l_1
$l_2 = 2l_1$

1-d case

$l_2 = 2l_1$

old states

New states that have apeared.
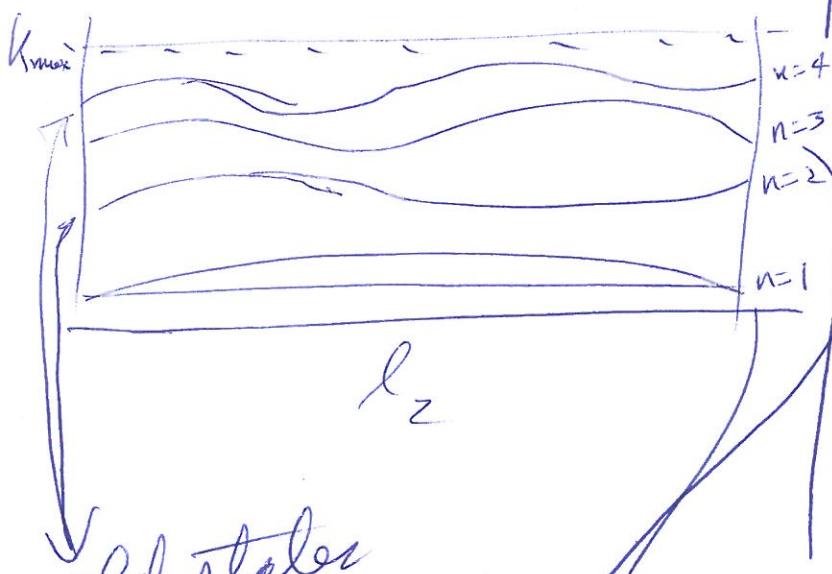
old states

new states. That have appeared.

— As one imagined stetching l_1 to l_2, the two old states would decline to be the two lowest states and two states from above kmax would have declined into the kmax region.

By the way phase space
is defined as

k-space tensor space space.

The size of the cells in phase space
is

$$\Delta T = \pi^d \qquad \bigg| \qquad \Delta T = (2\pi)^d$$

Recall the Heisenberg uncertainty
principle $\quad \sigma_{x_i} \sigma_{P_i} \geq \dfrac{\hbar}{2}$ or $\sigma_{x_i} \sigma_{u_i} \geq \dfrac{1}{2}$

$$(Gr-III)$$

For a multi-d state

$$\prod_i \sigma_{x_i} \sigma_{k_i} \geq \left(\frac{1}{2}\right)^d .$$

{ But
there
are
subtleties,

Read
on .

On the _face of it_, the k-space
cell indicate the states are
NOT minimum uncertainty states.

Note k for the ISW BCs are _not_
exactly the free particle k of the
uncertainty principle.

$\chi = \begin{cases} \sqrt{\frac{2}{x_i}} \, nw \, k_i \text{ in well} \\ 0 \quad \text{out of well} \end{cases} = \begin{cases} \sqrt{\frac{2}{x_i}} \, \dfrac{e^{ik x_i} - e^{-ik x_i}}{2i} \\ 0 \end{cases}$ { Not an expansion
in all free particle
k-states because
of $\chi = 0$ region.

$$k_{op}^n = \frac{1}{i}\frac{\partial}{\partial x}$$

$$\langle k^n \rangle = \sqrt{\frac{2}{\ell}} \int_0^\ell \sin kx \, k_{op}^n \sin kx \, dx$$

$$= \left(\frac{2}{\ell}\right)\int_0^\ell \frac{k^n}{i} \sin kx \, \sin kx \, dx$$

$$= k^n \left(\frac{2}{k\ell}\right)\int_0^\ell \sin^n kx \, dx$$

$$= \frac{2}{k\ell}\int_0^{k\ell}$$

$$= \left(\frac{2}{\ell}\right)$$

$$= \frac{2}{k\ell}\int_0^{k\ell} \sin \frac{?}{i}$$

$$= \frac{k\ell}{\ell}\int_0^{k\ell}$$

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

$$= \frac{2}{k\ell} k^n \int_0^{k\ell} \sin y \left(\frac{1}{i}\frac{\partial}{\partial y}\right)^n \sin y \, dy$$

$$= \begin{cases} 0 & \text{for } n \text{ odd since those are NOT pure real} \end{cases}$$

$$\frac{2}{n\pi} k^n \int_0^{n\pi} \sin^2 y \, dy$$

$$k_{op}^n = \frac{1}{i}\frac{\partial}{\partial x}$$

$$\langle k^n \rangle = \frac{1}{\ell}\int_0^\ell k^n \, dx$$

$$= \frac{k^n}{\ell}\ell$$

$$\sigma_k = \sqrt{k^2 - k^2}$$

$$= 0$$

But $\sigma_x \sim \ell$, and so have we broken the uncertainty principle?

After a lot of thought **No.**

The derivation of the uncertainty principle relies

$x_{op} x$ being a vector in the Hilbert space. (Gr-110)

But $x_{op} x = x \, x$ which doesn't obey periodic BCs and so is NOT in the Hilbert space.

$$= \begin{cases} 0 & \text{for } n \text{ odd} \\ \dfrac{2}{n\pi} k^n \dfrac{n\pi}{2} \end{cases}$$

$$= \begin{cases} k^n & n \text{ even} \\ 0 & n \text{ odd} \end{cases}$$

$$\sigma_u = \sqrt{k^2 - 0^2}$$

$$= |k| = k \text{ , } k \text{ are all positive anyway}$$

$$\langle x^n \rangle = \frac{2}{\ell} \int_0^\ell x^n \sin^2 kx \, dx$$

$$= \frac{2}{k\ell} \frac{1}{k^n} \int_0^{k\ell} y^n \sin^2 y \, dy$$

$$= \frac{1}{k^n} \frac{2}{n\pi} \int_0^{n\pi} y^n \sin^2 y \, dy$$

$$= \frac{1}{k^n} \frac{2}{n\pi} \int_0^{n\pi} y^n \frac{1}{2}(1 - \cos 2y) \, dy$$

$$\simeq \frac{1}{k^n} \frac{2}{n\pi} \frac{y^{n+1}}{(n+1)} \frac{1}{2} + 0$$

wiggles average to zero approximate

$$= \frac{1}{k^n} \frac{(n\pi)^{n}}{(n+1)}$$

$$\langle x^n \rangle = \frac{\ell^n}{(n\pi)^n} \frac{(n\pi)^n}{n+1}$$

$$= \frac{\ell^n}{n+1}$$

One could still evaluate $\langle x^n \rangle$, but it's understood the uncertainty principle doesn't hold, and so it's fine for

$$\sigma_x \sigma_k = 0$$

since $\sigma_k = 0$

We have an exact value for k and limited range for x.

$$\Delta \Gamma = \left(\frac{2\pi}{V}\right)^d > 0$$

and so this consistent uncertainty contraints.

(c) $\langle x \rangle = \dfrac{l}{2}$

which must be exactly correct really.

$$\langle x^2 \rangle = \dfrac{l^2}{3}$$

$$\sigma_x \overset{\sim}{=} \sqrt{\dfrac{l^2}{3} - \dfrac{l^2}{4}}$$

$$\overset{\sim}{=} \sqrt{\dfrac{l^2}{12}} = \dfrac{l}{2\sqrt{3}}$$

$$\therefore \sigma_x \sigma_k = \dfrac{l}{2\sqrt{3}} \cdot k$$

$$= \dfrac{n\pi}{2\sqrt{3}}$$

$$\geq \dfrac{\pi}{2\sqrt{3}} \qquad n=1 \\ \text{cor}$$

$$\approx \dfrac{3}{2\sqrt{3}} = \dfrac{\sqrt{3}}{2}$$

$$= .85 > \dfrac{1}{2}$$

So even $n=1$ is NOT a minimum uncertainty state.

required by uncertainty principle

they state all

What a fascinating discovery

Since N is a _macroscopic_ _number_, we can't form the symmetrized or product states really.

But we can deal _statistically_.

In this section on _free electron_ _gas_ _model_ we'll just consider the $T = 0$ state which is the _ground state_.

statistically speaking

The _product_ state would be formed by filling all the lowest energy _single-particle_ states out to a _Maximum k_ in k-space.

Consistent with Pauli-exclusion principle.

(Including a state beyond this would be clearly higher energy).

This ~~k max~~ maximum k is K_F the Fermi wave number.

We make the continuum approximation (seems plausible and someone in a detailed study has shown it in the correct large asymptotic limit) and <u>integrate</u>

k-space

we don't worry about including edges — negligible.

Asymptotic ~~density~~ number of states in a shell of dk

$$dN' = \frac{g}{2^d} \rho_k \, f_k \, dk$$

k-space.

$$dN' = g \rho_k \, f_k \, dk$$

$$f_k = \begin{cases} 1 & d=1 \\ 2\pi k & d=2 \\ 4\pi k^2 & d=3 \end{cases}$$

$$g = 2$$
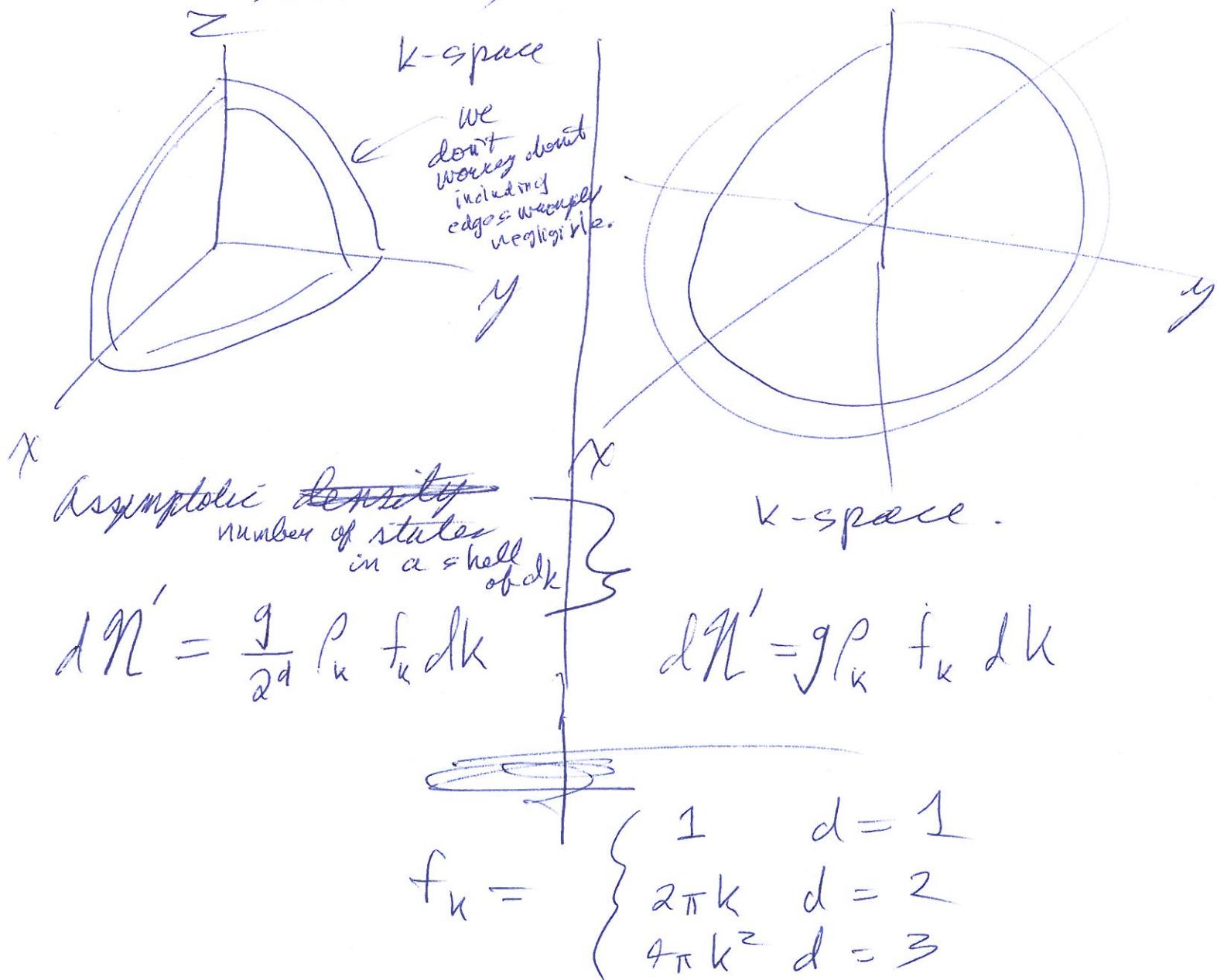
for the spin state degeneracy of electrons.

(I prefer to keep g as a an explicit variable. I don't like losing track of quantities in a mess of constants

$$\frac{P_n}{2^d} = \frac{V}{2^d \pi d}$$

$$= \frac{V}{(2\pi)^d}$$

$$C_k = \frac{V}{(2\pi)^d}$$

Both quantities are the same. From this point on, there is NO difference between IBW and periodic BCs

$$dn = \frac{dn'}{V} = \frac{g}{(2\pi)^d} f_k \, dk$$

See Gr-222
with $d = 3$
$f_k = 4\pi k^2$
$g = 2$

Note that is
volume independent
This is remarkable
since the states
are delocalized
They are spread over
the whole of a sample

density of states
per unit k
per unit volume
of space space.

A beautiful simple formula.

Even memorable.

Alas, it has to ruined by
messy constants and ~~physics~~
quantities connecting to the
real world.

$$E = \frac{\hbar^2 k^2}{2m} \quad \text{is the single}$$
particle
state
energy.

$$k = \left(\frac{2m}{\hbar^2}\right)^{\frac{1}{2}} E^{\frac{1}{2}}$$

$$dk = \left(\frac{2m}{\hbar^2}\right)^{\frac{1}{2}} \frac{1}{2} E^{-\frac{1}{2}} dE$$

So $d\eta = \dfrac{q}{(2\pi)^d} f \left(\dfrac{2m}{\hbar^2}\right)^{\frac{d}{2}} \dfrac{1}{2} E^{\frac{d}{2}-1} \Bigg| \dfrac{\text{[5-57]}}{dE}$

$$f = \begin{cases} 1 & d = 1 \\ 2\pi & d = 2 \\ 4\pi & d = 3 \end{cases}$$

We now integrate out to $E_F = \dfrac{\hbar^2 k_F^2}{2m}$.

E_F is the <u>Fermi Energy</u>

The high single-particle state energy of the $T = 0$ state.

$\underset{\sim}{k}_F$ the k-space vector

traces out a sphere (assuming periodic BCs).

This sphere is the <u>Fermi surface</u>

It's a surface in k-space.

For free electron gas, it's very simple: Just a sphere.

But for periodic potentials the ~~Be~~ Fermi surface can be very complex — oddly shaped, gaps — a work ~~of~~ of abstract art.

We divided by volume (see p. 5-570)

$$n_e = \frac{N}{V} = \int_0^{E_F} d\eta = \frac{gf}{2(2\pi)^d}\left(\frac{2m}{\hbar^2}\right)^{d/2}\frac{E_F^{d/2}}{d/2}$$

$$= \frac{gf}{(2\pi)^d d}\left(\frac{2m}{\hbar^2}\right)^{d/2} E_F^{d/2}$$

Assuming our sample has

$$T = 0 \quad \text{or} \quad T \text{ very}$$

small, we can solve for E_F for real materials (insofar as the free electron gees model applies.) Actual metals at room temperatures are __cold__ (T very small) as we'll see.

$$n_e = \frac{N}{V} = \rho \sum_i \frac{X_i Z_i}{A_i \, m_{amu}}$$

For a homogeneous mix. (like in White dwarf stars.

mass density

— for d=1, 2, 3 to keep being general.

X_i mass fraction of element i

Z_i valence electrons per atom (see p. 5-489)

A_i atomic mass ~~density~~

m_{amu} the AMU

$$\overline{\mu_e} = \sum_i \frac{X_i Z_i}{A_i}$$

μ_e is ~~the mean free electron~~ ~~just a~~ mean number of nucleons per free electron.

— a strange sort of mean but useful.

$$\frac{N}{V} = \frac{\rho}{\mu_e \, m_{amu}}$$

$$E_F = \left(\frac{\hbar^2}{2m}\right)\left(\frac{(2\pi)^d d}{g f}\right)^{2/d} \frac{1}{(\mu_e \, m_{am})^{2/d}} \rho^{2/d}$$

$k_F = \sqrt{\frac{2m}{\hbar^2} E_F}$ if one needs it.

So in 3-d (which is the most important case)

$$E_F \propto \rho^{2/3}$$

— Fermi energy increases with density.

3-d case $\Bigg\{$ $E_F = \frac{\hbar^2}{2m}(3\pi^2)^{2/3} \frac{1}{m_{am}^{2/3}} \frac{\rho^{2/3}}{\mu_e^{2/3}}$

$$= 4.166_{...} \times 10^{-11} \; \overline{\text{ergs}} \times \frac{\rho^{2/3}}{\mu_e^{2/3}} \Bigg\}$$ $\begin{array}{l}\rho \\ \text{in} \\ \text{CGS} \\ \text{or} \\ g/cm^3\end{array}$

$$= 26.00_{...} \text{ eV} \times \frac{\rho^{2/3}}{\mu_e^{2/3}}$$

For example for Copper $\mu_e = \frac{A}{3} = \frac{63.\overline{5}46}{1}$ $\Big\{$ $\underbrace{}_{\text{standard atomic mass}}$ Wik and Gr-223 for $3=1$

$\rho = 8.94 \; g/cm^3$
(Room T and P)

$$E_{F_{copper}} = 7.034... \ eV$$

which agrees
with Gr-223
(answer ~140)

Now as it turns out,
the distribution of electrons
with temperature ~~~~~
(Fermi-Dirac statistics)
depends on

$$\wedge \quad \frac{E - E_F}{KT} \qquad (see \ Gr-241)$$

and free electron gas is
cold if

$$\frac{\Delta E}{KT} \gg 1$$

$$\frac{\Delta E}{KT} = \frac{E_F}{KT} \gg 1$$

$$= \frac{T_F}{T} \gg 1$$

where $T_F = \dfrac{E_F}{k}$ is the Fermi Temperature

$$= \frac{1}{k} \frac{\hbar^2}{2m} \left(3\pi^2\right)^{2/3} \frac{1}{M_{aver}^{2/3}} \frac{\rho^{2/3}}{\mu_e^{2/3}}$$

in 3-d

$$= 301761.7...K \frac{\rho^{2/3}}{\mu_e^{2/3}}$$

for Copper
$T_F = 81626\ K$

(Gr-223,
Ans-141)
agrees

For ~~most~~ metals at room temperature $T \ll T_F$ and they are in fact cold with most electrons in the lowest

energy single-particle states.

It's only a few excited electrons that give the electrical and thermal conduction properties.

A few other interesting quantities can be calculated for the $T = 0$ free electron gas.

E_{mean} the mean single particle energy

E the energy per unit volume

P the pressure of the electron gas.

5-578

E_{mean}

$$\mathcal{E} = \int_0^{E_F} E \, dn = \frac{g}{2(2\pi)^d} f \left(\frac{2m}{\hbar^2}\right)^{\frac{d}{2}} \int_0^{E_F} E^{d/2} \, dE$$

$$= \frac{g f}{2(2\pi)^d} \left(\frac{2m}{\hbar^2}\right)^{d/2} \frac{E_F^{d/2+1}}{d/2+1}$$

$$= \sqrt{\frac{\hbar^2}{2m}} \frac{g f}{2(2\pi)^d} \frac{1}{d/2+1} \frac{(2\pi)^d}{g f} \quad \text{(see 5-574)}$$

$$E_{mean} = \frac{\mathcal{E}}{N/V} = \frac{d}{2(d/2+1)} E_F$$

$$= \begin{cases} \dfrac{d}{d+2} E_F \\[3mm] \dfrac{1}{2} E_F \quad \text{for } 1\text{-}d \\[3mm] \dfrac{2}{3} E_F \quad \text{for } 3\text{-}d \\[3mm] \dfrac{3}{5} E_F \quad \text{for } 3\text{-}d \text{ a well known} \\ \qquad\qquad\qquad\qquad \text{result.} \end{cases}$$

$$\mathcal{E} = \frac{\hbar^2}{2m} \; \frac{gf}{2(2\pi)^d} \left(\frac{(2\pi)^d d}{gf} \right)^{1+\frac{2}{d}} \frac{1}{d/2+1} \; \frac{\rho^{1+\frac{2}{d}}}{(\mu_e m_{am})^{1+\frac{2}{d}}}$$

units
of
energy
per
unit
Volume

units
of energy
per length squared

units of
$(\ell^{-d})^{1+\frac{2}{d}}$

$$= L^{-d+2}$$

correct.

$$\mathcal{E} = \begin{cases} \dfrac{\hbar^2}{2m} \dfrac{1}{2} \left(\dfrac{(2\pi)^d}{gf} \right)^{\frac{2}{d}} d^{1+\frac{2}{d}} \dfrac{1}{d/2+1} \left(\dfrac{\rho}{\mu_e m_{am}} \right)^{1+\frac{2}{d}} \\[4mm] = \dfrac{\hbar^2}{2m} \left(\dfrac{(2\pi)^d d}{gf} \right)^{\frac{2}{d}} \dfrac{d/2}{d/2+1} \left(\dfrac{\rho}{\mu_e m_{am}} \right)^{1+\frac{2}{d}} \end{cases}$$

which is about as
simple as I can make
it in general.

$$\mathcal{E} = \frac{\hbar^2}{2M} \frac{3}{5} \cdot \left(\pi^2 \cdot 3 \right)^{2/3} \left(\frac{1}{\mu_c \, M_{avv}} \right)^{5/3}$$

for
$d=3$

$$\mathcal{E} \propto \rho^{5/3}$$ which is a famous result for a free electron gas.

Now what of __pressure__?

Where does pressure come from anyway in a quantum system?

~~When one A~~

Well there is still the 3rd law sort of.

Say we specified a 1 - particle system in a well of potential V.