

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} + V\psi = \cancel{E}\psi = i\hbar \frac{\partial \psi}{\partial t}$$

V accounts for the field energy of some system that exerts a force on the particle. And the "tension"

~~We generally just,~~

between kinetic energy and potential energy causes the time evolution (or stationarity of particle)

But in fact if the system exerts a potential (force) on the particle, the particle exerts ~~force~~ back a reaction force

4-482

- we've just idealized  
the ~~back~~ reaction force  
a negligible usually

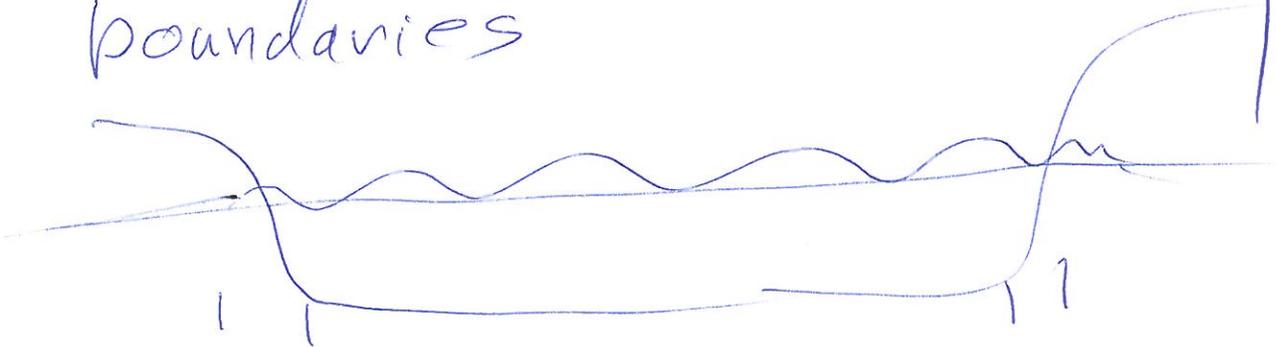
Not of course for  
hydrogenic atom  
where we considered  
two interacting particles  
explicitly

~~What~~ →

Where is the force / and  
reaction force?

At those well disregarded  
boundaries

Heaven  
knows  
where the  
force  
comes  
from  
in the  
periodic  
BC  
case.

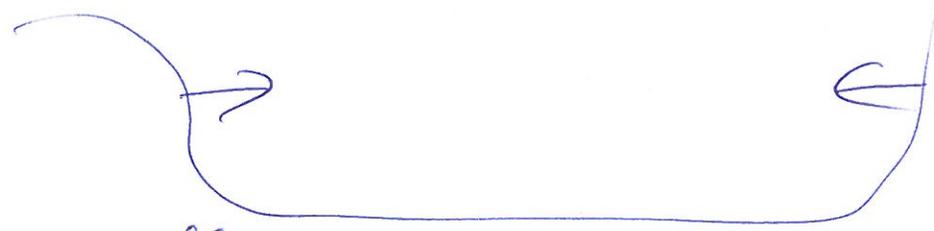


Recall we've approximated the electrons as non-interacting

At boundaries the collective force of ions ~~and the~~ combined with electron ~~at~~ Coulomb force we've sort of hidden act to confine the non-interacting electrons by a steep potential wall.

we've split this off from ~~the~~ "electrons" we've considered

The stationary states all change. The pressure comes from the electron in the occupied stationary states.



- wall presses in.
- NON-interacting electron
  - ↳ i.e., their kinetic energy pushes out.

5-584)

This is the emergent macroscopic ~~after~~ situation.

(the correspondance principle is being used)

So we can use macroscopic thermodynamics here.

~~(the by the correspondance)~~

Pressure

Recall

Changes of internal energy must come from Heat flow  $dQ = TdS$  or macroscopic work  $dW = -PdV$

$$dE_{\text{internal}} = TdS - PdV$$

total internal energy of sample      temperature      differential of entropy.

Say we keep  $T=0$  and/or consider adiabatic (isentropic) changes  $dS=0$

Then

$$dE_{\text{internal}} = -PdV \quad \boxed{5-585}$$

For our free electron gas all internal energy is the sum of the microscopic kinetic energy

$$E_{\text{internal}} = \underbrace{\epsilon V}_{\substack{\text{our energy} \\ \text{per unit volume}}} \quad \left\{ \begin{array}{l} \text{volume} \end{array} \right.$$

$$\therefore d(\epsilon V) = -PdV$$

$$P = - \frac{d(\epsilon V)}{dV}$$

$$= -V \frac{d\epsilon}{dV} \quad \cancel{\epsilon}$$

$$= -V \frac{d\epsilon}{dn_e} \frac{dn_e}{dV} - \epsilon$$

We're hypothesizing the microscopic pressure must arise from the microscopic sum of KE which we've identified as our free electron KE. Seems OK

5-586

$n_e = \frac{N}{V}$  is electron density.

~~$\frac{dE}{dn_e}$~~

$$\frac{dn_e}{dV} = -\frac{N}{V^2} = -\frac{n_e}{V}$$

$$-V \frac{dE}{dn_e} \frac{dn_e}{dV} = n_e \frac{dE}{dn_e}$$

From p. 5-579

$$P = n_e \frac{dE}{dn_e} - E$$

$$= \frac{h^2}{2m} \left( \frac{(2\pi)^d d}{2f} \right)^{2/d} \frac{d/2}{d/2+1} \left[ \left(1 + \frac{2}{d}\right) - 1 \right]$$

$$\times \left( \frac{\rho}{M_e M_{amu}} \right)^{1+2/d}$$

$$= \frac{h^2}{2m} \left( \frac{(2\pi)^d d}{2f} \right)^{2/d} \frac{1}{d/2+1} \left( \frac{\rho}{M_e M_{amu}} \right)^{1+2/d}$$

For 3-d

$$P = \frac{h^2}{2m} (3\pi^2)^{2/3} \frac{2}{5} \left( \frac{\rho}{M_e M_{amu}} \right)^{5/3}$$

which is the equation of state (EOS) (5-587)  
of  $T=0$  free electron gas.

(Very important in modeling white dwarf stars)

$$P \propto \rho^{5/3} \text{ with no } T \text{ dependence}$$

Recall the ideal gas law

$$PV = NkT$$

$$P = nkT \text{ where } n = N/V$$

$$P \propto \rho T$$

is the number of particles

If  $T=0$  no pressure

The free electron gas  
(AKA Fermi gas  
or degenerate gas)

5-588

has pressure at zero T.

This holds up White dwarfs and neutron stars (with neutrons instead of electrons) as they cool off forever (or until their nucleons decay)

Actually one needs to account for relativistic and temperature effects.

I used to know a lot about degenerate stars in the days when I was blowing up Type Ia supernova models.

The degenerate pressure is stiffer than an ideal gas since it goes as higher power of density ( $^{5/3}$  rather than 1).

Recall from p. 5-586 for  $d=3$

$$\begin{aligned}
 P &= \frac{h^2}{2m} (3\pi^2)^{2/3} \frac{2}{5} \left( \frac{\rho}{\mu_e m_{\text{atom}}} \right)^{5/3} \\
 &= 1.0035 \dots \times 10^{13} \frac{\text{dyne}}{\text{cm}^2} \left( \frac{\rho}{\mu_e} \right)^{5/3} \\
 &= 1.0035 \dots \times 10^{12} \text{ Pa} \left( \frac{\rho}{\mu_e} \right)^{5/3} \\
 &\cong 10^7 \text{ atm} \left( \frac{\rho}{\mu_e} \right)^{5/3}
 \end{aligned}$$

} P still in CGS i.e.,  $\text{g}/\text{cm}^3$

$$\rho_{\text{copper}} = 3.819 \times 10^{10} \frac{\text{dyne}}{\text{cm}^2}$$

$$= 3.819 \times 10^{10} \frac{\text{Pa}}{10}$$

$$\approx 4 \times 10^5 \text{ atm}$$

(Gr-198  
Ans-14  
agree)

These are huge pressures

— why aren't metals explosive?

Well the confining potential balances ~~and~~ the degeneracy pressure very stably.

— Recall Earth atmosphere pressure is close to zero for solids

→ Put them in vacuum and they expand only a little bit.

5-590

# Bulk modulus

- Can we calculate this?

$$B \equiv -V \frac{dP}{dV}$$

a quantity with units of pressure

So Bulk modulus is a

$$\frac{dV}{V} = - \frac{dP}{B}$$

Bulk modulus is minus one over

characteristic pressure for changing density or volume by a factor of 1/2

~~It measures the relative change in volume with a change in pressure per unit pressure~~

But  $\rho = \frac{M}{V}$ ,  $V = \frac{M}{\rho}$

$$dV = (-M/\rho^2) d\rho$$

$$dV = -\frac{V}{\rho} d\rho$$

$$\frac{dV}{V} = -\frac{d\rho}{\rho}$$

$$\frac{d\rho}{\rho} = \frac{dP}{B}$$

So Bulk modulus is also one over the relative change in density per unit pressure.

Say B was constant  $\ln(P/P_0) = \frac{P-P_0}{B}$

$P = P_0 e^{\frac{P-P_0}{B}}$   
So B is an e-folding pressure.

$$B = \rho \frac{dP}{d\rho}$$

$$= \frac{\hbar^2}{2m} (3T^2)^{2/3} \frac{2}{3} \left(\frac{\rho}{\rho_0 m_{\text{atom}}}\right)^{5/3}$$

for 3-d

(from p. 5-586)

$$= \frac{5}{3} P$$

~~Copper~~

$$= 1.672 \dots \times 10^{12} \frac{\text{dyne}}{\text{cm}^2} \left(\frac{\rho}{\rho_0}\right)^{5/3}$$

$$= 1.672 \dots \times 10^{11} \text{ Pa} \left(\frac{\rho}{\rho_0}\right)^{5/3}$$

$$\approx 1.7 \times 10^6 \text{ atm} \left(\frac{\rho}{\rho_0}\right)^{5/3}$$

} still in cgs

$$B_{\text{Copper}} = 6.36 \dots \times 10^{11} \frac{\text{dyne}}{\text{cm}^2}$$

$$= 6.36 \dots \times 10^{10} \text{ Pa}$$

$$= 6 \times 10^5 \text{ atm}$$

(Gr-223  
Ans-141)  
agrees.

But the actual Copper bulk modulus is

~~1.31~~

$$= 134 \times 10^{10} \text{ Pa}$$

5-592

So our free electron  
gas result is  
off by a factor ~~of  $\frac{1}{2}$~~   
of  $\sim \frac{1}{2}$ .

Not so bad  
considering we aren't  
treating the actual  
attractive and repulsive forces.

My guess is that one  
can say the ions cancel  
the ~~electron~~ free electron  
charge still,

but they resist being  
compressed together.

So squeezing requires both  
increasing electron  $\nabla E$

Adds } and the positive PE of ion-ion  
repulsion.  
on extra resistance,  
pressure and so increases  
the Bulk Modulus.

# Summary of Free electron gas model Results for $T=0$

5-593

$$d\mathcal{N} = \frac{g}{(2\pi)^d} f k^{d-1} dk \quad \left\{ \begin{array}{l} d=1, 2, 3 \\ f = \begin{cases} 1, & d=1 \\ 2\pi, & d=2 \\ 4\pi, & d=3 \end{cases} \end{array} \right.$$

(p. 5-570)

$$E = \frac{\hbar^2 k^2}{2m}$$

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

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

} p. 5-570

$$d\mathcal{N} = \frac{g}{(2\pi)^d} f \left(\frac{2m}{\hbar^2}\right)^{d/2} \frac{1}{2} E^{d/2-1} dE$$

} p. 5-571

Not it is volume independent.  
It is also shape independent.  
But that takes another proof.  
See p. 5-597

~~density~~ density of states per unit volume per unit energy  
— usually the density of states that one means (there are many density of states)

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

p. 5-572

5-574

$$n_e = \frac{N}{V} = \rho \sum_i \frac{x_i Z_i}{A_i M_{amu}} = \frac{\rho}{M_e M_{amu}}$$

$$\frac{1}{M_e} = \sum_i \frac{x_i Z_i}{A_i} \quad (\text{p. 5-573})$$

$M_e$  is mean number  
of nucleons per free electron

Fermi energy

$$E_F = \left( \frac{\hbar^2}{2m} \right) \left( \frac{(2\pi)^d}{g f} \right)^{2/d} \left( \frac{\rho}{M_e M_{amu}} \right)^{2/d} \quad \left\{ \begin{array}{l} \text{see} \\ \text{p. 5-574} \end{array} \right.$$

$$= \frac{\hbar^2}{2m} (3\pi^2)^{2/3} \left( \frac{\rho}{M_e M_{amu}} \right)^{2/3}$$

for  $d=3$

$$= 4.166... \times 10^{-11} \text{ ergs} \left( \frac{\rho}{M_e} \right)^{2/3}$$

$$= 26.00 \text{ eV} \times \left( \frac{\rho}{M_e} \right)^{2/3}$$

Fermi Temperature

$$T_F = \frac{1}{k} \frac{\hbar^2}{2m} (3\pi^2)^{2/3} \left( \frac{\rho}{M_e M_{amu}} \right)^{2/3} \quad \text{for 3-d}$$

$$= 3.0176... \times 10^5 \text{ K} \left( \frac{\rho}{M_e} \right)^{2/3} \quad \left\{ \begin{array}{l} \text{p. 5-576} \end{array} \right.$$

$$\bar{E}_{\text{mean}} = \frac{d}{d+2} E_F$$

$$\bar{E}_{\text{mean}} = \frac{3}{5} E_F \text{ for } 3\text{-d}$$

(5-594)

p. 5-578

free electron gas KE at  $T=0$

~~$$E = \frac{\hbar^2}{2m} \left( \frac{(2\pi)^d d}{9f} \right)^{1+2/d} \left( \frac{\rho}{\mu_e m_{\text{amu}}} \right)^{1+2/d}$$~~

for  $d=3$

~~$$E = \frac{\hbar^2}{2m}$$~~

$$E = \frac{\hbar^2}{2m} \left( \frac{(2\pi)^d d}{9f} \right)^{3/2} \frac{d/2}{d/2+1} \left( \frac{\rho}{\mu_e m_{\text{amu}}} \right)^{1+2/d}$$

free electron gas KE per unit volume

$$E = \frac{\hbar^2}{2m} \frac{3}{5} (3\pi^2)^{2/3} \left( \frac{\rho}{\mu_e m_{\text{amu}}} \right)^{5/3} \quad (5-579)$$

for 3-d

5-596

~~$$P = -V dE$$~~

$$P = n_e \frac{dE}{dn_e} - E$$

p. 5-586

$$= \frac{\hbar^2}{2m} \left( \frac{(2\pi)^d}{g_f} \right)^{2/d} \frac{1}{d/2+1} \left( \frac{\rho}{m_e m_{amu}} \right)^{1+2/d}$$

for 3-d

$$P = \frac{\hbar^2}{2m} (3\pi^2)^{2/3} \frac{2}{5} \left( \frac{\rho}{m_e m_{amu}} \right)^{5/3}$$

$$\propto \rho^{5/3}$$

a fermion

$T=0$  free electron gas result in the non-relativistic limit

$$= 1.0035 \times 10^{12} \text{ Pa} \left( \frac{\rho}{m_e} \right)^{5/3} \quad \left. \begin{array}{l} \text{p. 5-588} \\ P \text{ in CGS units.} \end{array} \right\}$$

$$B = -V \frac{dP}{dV} = \rho \frac{dP}{d\rho}$$

$$= \frac{5}{3} P$$

p. 5-591

$$B = \frac{\hbar^2}{2m} (3\pi^2)^{2/3} \frac{2}{3} \left( \frac{\rho}{M_e m_{\text{atom}}} \right)^{1/3}$$

$$= 1.672 \times 10^{11} \text{ Pa} \left( \frac{\rho}{M_e} \right)^{1/3}$$

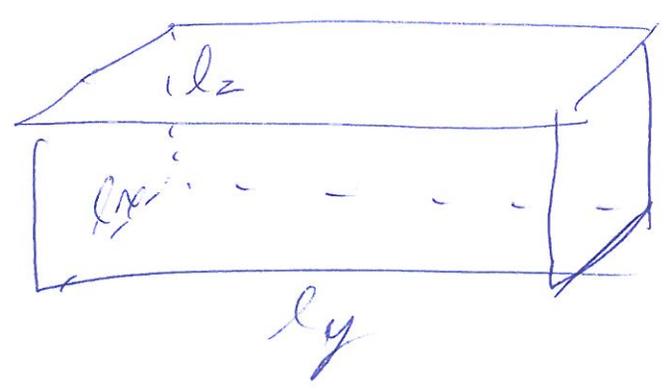
5-597

p. 5-591  
with  
P in  
CGS  
units

## 6) Any Shape

### Solid for Free Electron Gas ~~Result~~ Formalism

We solved our free electron gas model assuming a rectangular box for both ISW & periodic BCs



~~Because this~~  
The box could have any dimensions  $l_x, l_y, l_z$ , one could argue that

5-598

this could only be true  
if the results in  
the large asymptotic  
limit ~~should be~~

and our large  $N$  results  
(asymptotic results  
for large)

were independent of  
 $l_x, l_y, l_z$  individually

and of their volume  ~~$V = l_x l_y l_z$~~

Thus it is  
plausible that our  
results are shape independent.

In particular, that the  
density of states is volume independent  
is also shape independent.

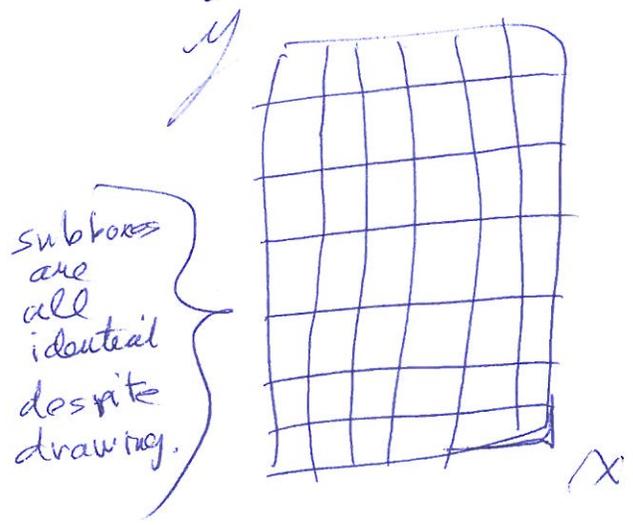
$$V = \prod_{i=1}^d l_i \quad \text{for all } d=1, 2, 3 \text{ cases.}$$

The 1-d case is simple.

It's always a rectangular box.  
So we have to concern ourselves  
with 2-d and 3-d.

The 2-d case actually suffices to explain shape independence

Consider a 2-rectangular box of ~~not~~ space space volume  $V$



Each subbox is  $\frac{1}{2}$  ~~( $\lambda$ )~~ wavelength in the  $x$  and  $y$  direction for some  $k$ -state defined by  $(k_x, k_y)$

- the  $\frac{1}{2}$  is for  $\text{I S W BCs}$
- the  $1$  is for periodic BC.

for  $\text{I S W}$   $k_i l_i = n_i \pi$ ,  $n_i = 1, 2, \dots$

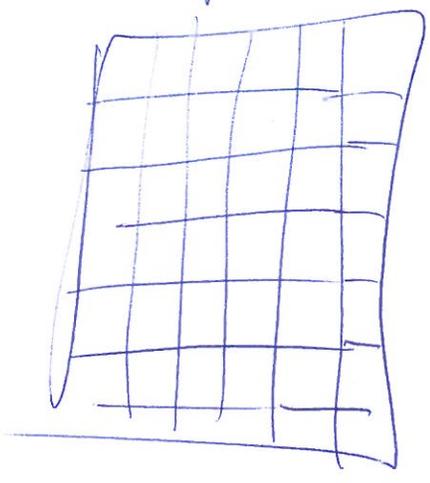
for periodic  $k_i l_i = 2\pi n_i$ ,  $n_i = 0, \pm 1, \pm 2, \dots$

and recall  $\lambda_i = \frac{2\pi}{k_i}$

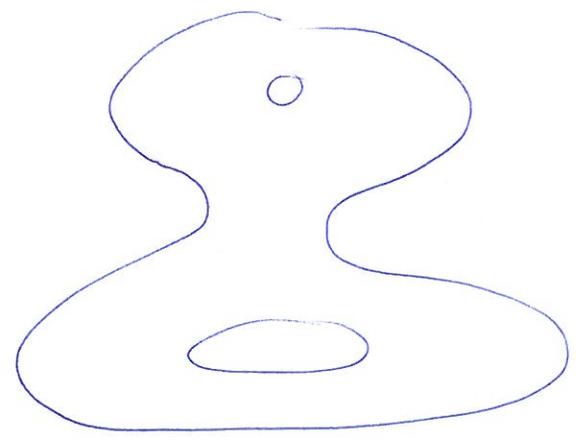
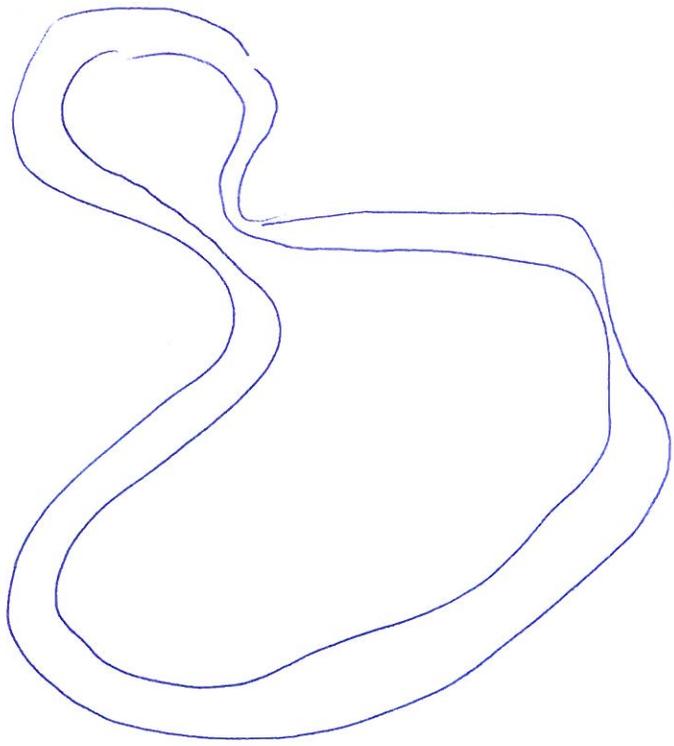
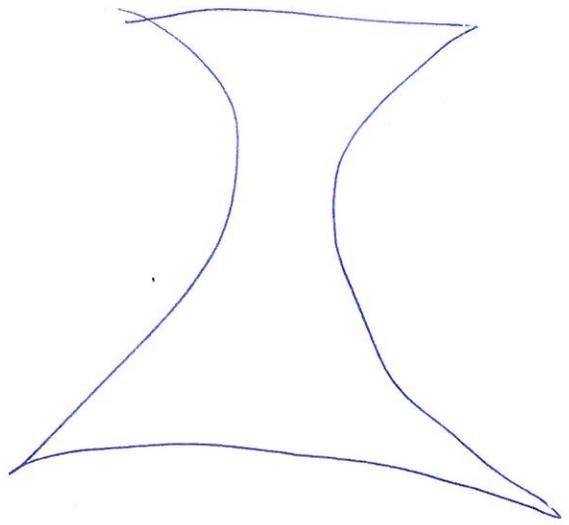
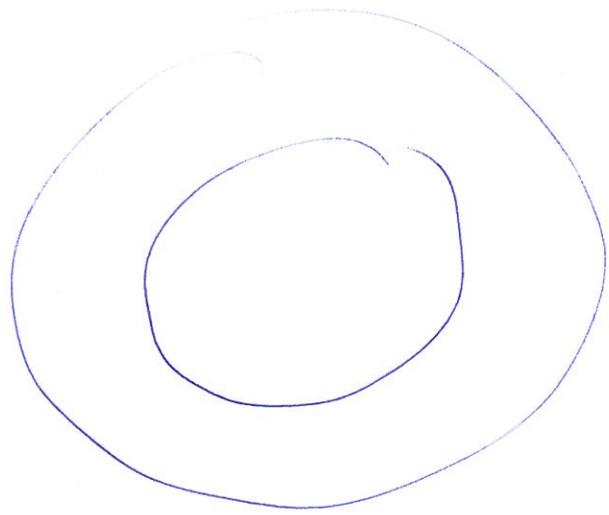
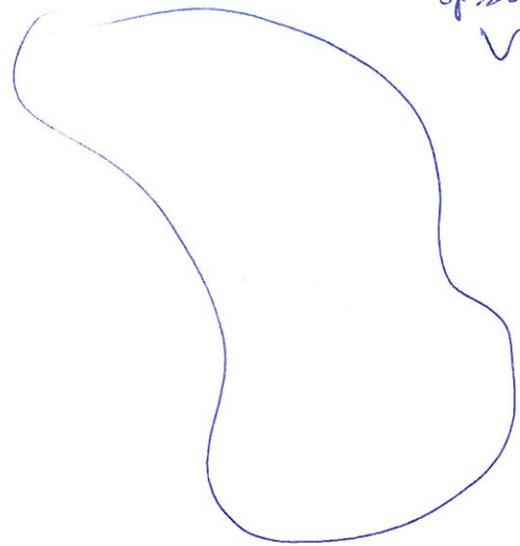
Now consider a general 2-d shape of the same volume

5-600

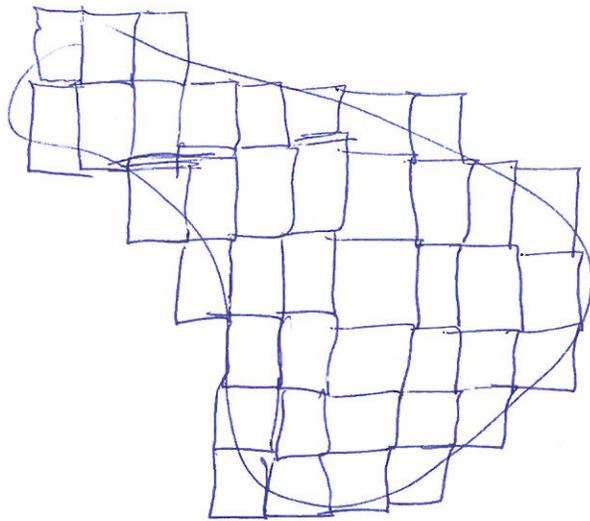
rectangular  
Box of volume  $V$



Other shapes all  
of same  
volume



We can take the subboxes 5-601  
from the rectangular box <sup>general</sup>  
and tile them over a ~~another~~ <sup>arbitrary</sup> shape.



We conserve  
number  
of  
subboxes

The tiling is NOT perfect.

Some bits of ~~arbitrary~~ <sup>the</sup> general shape are uncovered,  
and some bits of empty space  
are covered.

But the tiling of general shape  
approximates the general shape  
and the  $(k_x, k_y)$  state is an  
eigenstate of the tiled general shape.

5-602)

Now as  $k_x$  and  $k_y$  get bigger and bigger,  $\lambda_x$  and  $\lambda_y$  get smaller and smaller. The subboxes get smaller and smaller and we are able to make the tiled general shape approach the general shape more and more closely.

In the asymptotically large  $k_x$  &  $k_y$  <sup>limit</sup> ~~approx~~, the tiled general shape approaches the general shape arbitrarily closely.

So a large  $k_x$  &  $k_y$  state of the rectangular box approaches

being an  $k_x$  &  $k_y$  state of the general state. 5-603

The approach becomes arbitrarily close as  $k_x$  &  $k_y$  are made arbitrarily large.

Now small  $k_x$  or  $k_y$  states are NOT good approximations to states of the arbitrary shape. But for macroscopic (number of electrons), the large  $k_x$  and  $k_y$  states dominate both because they are more numerous & have more energy.

5-607)

Recall  $d\mathcal{R} = \frac{g}{(2\pi)^d} \int k^{d-1} dk$  (see p. 5-573)

$\rho_{kV}$  ~~density~~ number of  $k$ -states per ~~unit~~ unit  $k$  per volume (of a rectangular box)

$$k = \sqrt{k_x^2 + k_y^2}$$

So as  $k_x$  &  $k_y \rightarrow$  large

$$\rho_{kV} \implies \frac{g}{(2\pi)^d} \int k^{d-1} \rightarrow \text{large}$$

for  $d \geq 2$

So large  $k_x, k_y$  dominate number of  $k$ -states.

Also  $\epsilon = \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2}{2m} (k_x^2 + k_y^2)$   
energy of a ~~state~~  $k$ -state.

So we can expect large  $k_x$  &  $k_y$  states to dominate the behavior for ~~For~~ a rectangular box and general shape.

The same argument can be made in  $d=3$

where it is even stronger

since  $\rho_{kV} = \frac{g}{(2\pi)^d} k^{d-1}$

grows faster with  $k$  for larger  $d$ .

(i.e., faster for  $d=3$  than for  $d=2$ )

Two points to ponder

- a) Can a general shape have more states than a rectangular box of the same volume.
  - i.e., higher density of states

5-600

Well I think NOT.

Well I know not  
or all of  
solid  
state  
physics  
would  
disappear.

But  
what is  
the  
argument  
?

~~If you had a good  
tiling with~~

$$k_i l_{ij} = n_{ij} \pi$$

~~for some  
straight path  
across  
direction,~~

~~then you'd also  
get a good tiling for~~

$$k_{ij} l_{ij} = (n_{ij} \pm 1) \pi$$

I'm not sure I've got a  
good argument.

~~First we~~ But the old college try,

First the general shape of volume  $V$   
must have quantized states.

Second say you started with  
a rectangular box that

5-607

The tiling argument  
is reasonably convincing  
that the general shape  
in the large  $k_x$  &  $k_y$  limit  
has at least the density  
of states of rectangular box  
of the same volume.

Could it have a higher density  
of states?

Well all solid state physics  
would be wrong if it did.

But one would like a convincing  
theoretical argument.

And I don't know it.

5-608

But there are <sup>three</sup> ~~a couple~~ of points

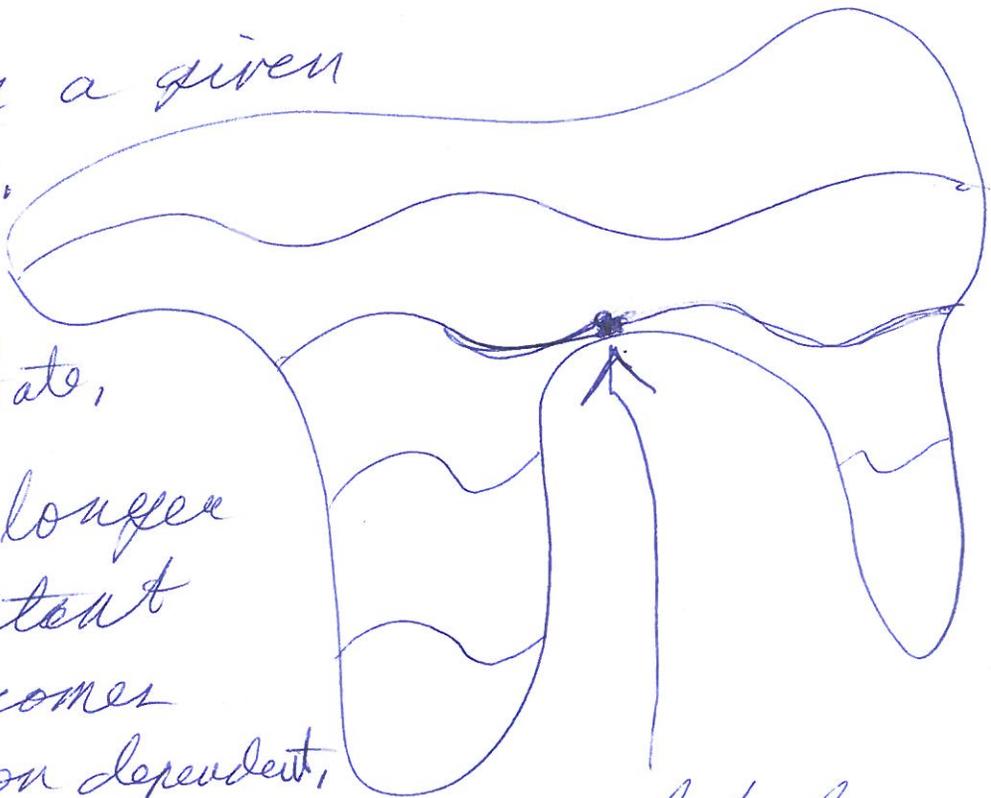
i) The general shape must have quantized stationary states

ii) For a given  $k$ -state,

Say an  $X$ -state,

$k_x$  is no longer a constant but becomes position dependent,

$k_x(y)$



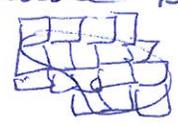
- what happens at this point?

- discontinuously the sharp infinite wall BC changes.

- argument breaks off inconclusively

iii) Maybe the tiling argument can be made better or run backwards.

- argument breaks off inconclusively



cover with squares of  $n \times n$  number?

$d_s$   $k_F$  large enough 5-609  
and  $\lambda_F = \frac{2\pi}{k_F}$

large enough in  
real cases for our  
large  $k$ -shape independence  
to be valid?

$\lambda_F \ll l$  characteristic  
of sample.

~~Q~~ Recall p. 5-570

$$d\mathcal{N} = \frac{g}{(2\pi)^d} k^{d-1} dk$$

$$\therefore n_e = \frac{N}{V} = \frac{g}{(2\pi)^d} \int_0^{k_F} k^{d-1} dk$$

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

$$\therefore k_F = \left( \frac{(2\pi)^d d}{g} n_e \right)^{1/d} n_e^{1/d}$$

5-600)

$$k_F = \left( \frac{(2\pi)^d d}{g f} \right)^{1/d} \left( \frac{\rho}{\mu_e M_{amu}} \right)^{1/d}$$

$$\lambda_F = \frac{2\pi}{k_F} = 2\pi \left( \frac{g f}{(2\pi)^d d} \right)^{1/d} \left( \frac{\mu_e M_{amu}}{\rho} \right)^{1/d}$$

For  $d=3$ ,  $\lambda_F = 2\pi \left( \frac{1}{3\pi^2} \right)^{1/3} \left( \frac{\mu_e M_{amu}}{\rho} \right)^{1/3}$

~~$= 3.663 \dots \left( \frac{\mu_e}{\rho} \right)^{1/3}$~~

$\lambda_{F \text{ copper}} = 7.04 \dots$

These seem small enough for the typing argument to hold on the face of it.

For 3-d,

5-611

$$\lambda_F = 2.409... \text{ \AA} \left(\frac{\mu_e}{\rho}\right)^{1/3}$$

$$\lambda_{F_{\text{copper}}} = 4.624... \text{ \AA}$$

To me on the face of it, these seem small enough for the tiling argument to be valid.

And, of course, experiment confirms ~~the rule~~ that volume and shape independence hold.

5-612

## 7) Statistical Mechanics

— a hodge podge treatment mixing classical and QM ideas.

— Results justify the mixed treatment.

( ) experiment shows the mixture is the right one to some degree of approximation.

a) Consider an arbitrary General Potential Well.

— the well has quantized states.

In fact, <sup>many</sup> ~~many~~ results 5-613  
~~do~~ turn out to be independent  
of quantization;

So there could be a  
continuum of states just  
as for free particles  
— which is one of the  
cases of interest.

You can imagine in those  
cases that we've just  
gone to the continuum limit.

Each state has its own  
single-particle energy

But many states are energy degenerate.

Let all states of energy  $E_i$   
constitute energy level  $i$

5-619

Note the term energy level is used in various ways, context must decide.

Let all states of the same energy constitute an energy level  $i$

The energy of the level  $i$  is  $E_i$

The degeneracy of level  $i$  is  $g_i$

Number of single-particle states in level

The number of ~~identical~~ particles in level  $i$  is  $N_i$

The total energy of the system is

$$E = \sum_i N_i E_i$$

and the total number of particles is

$$N = \sum_i N_i$$

For our developments, 5-615  
we assume  $E$  and  $N$   
are conserved. One can  
generalize to cases where  
they aren't, but that's  
beyond our scope.

A set of  $\{N_i\}$  consistent  
with conservation of particles  
is a configuration.

The number of distinct states  
that correspond to  
a configuration is  
the weight  $W$  of the  
configuration

$$W = W(\{N_i\})$$

5-616

The fundamental axiom  
of equilibrium <sup>statistical mechanics</sup> ~~thermodynamics~~

is that the probability  
of the system

being in a configuration  $\{N_i\}$   
is proportional to  $W(\{N_i\})$ .

this axiom or postulate oddly  
doesn't seem to have fixed name  
(but maybe I just don't know it).

Note "equilibrium statistical mechanics".

In non-equilibrium statistical mechanics  
the state of the system must be  
determined by solving rate equations  
e.g., for level  $i$

$$n_i \sum_j R_{ij} = \sum_j n_j R_{ji} \quad \left\{ \begin{array}{l} \text{assembly} \\ \text{time independence.} \end{array} \right.$$

Valid  
by  
all  
of  
history

This is  
a time  
average,  
Not an  
ensemble  
average  
But for  
an ensemble,

it  
will be  
an  
ensemble  
average too  
Ergodic  
hypothesis  
(Wik)

Not  
a wave  
function  
collapse  
probability

$n_i$  is the occupation number  
of state  $i$

5-617

$R_{ij}$  is the rate of transition  
from state  $i$  to state  $j$ .

— One has a large matrix  
equation to solve.

↳ which is frequently ~~not~~  
part of a self-consistent  
convergence problem since

$R_{ij}$  often depend on  $n_i$   
and other varying parameters

In equilibrium stat mech,  
we assume there are processes  
that causes transitions of  
particles between states  
and the system between  
configurations — but  
we never need to specify  
them other than that they exist.

4-618

The fundamental axiom  
obviates the need.

If there were no transitions  
a system could  
be put in an arbitrary  
configuration and it  
would just stay there

b) Determining  $W(\{N_i, \Xi\})$   
for Distinct or classical  
Identical Particles

— one has to count  
up the ~~configurations~~  
distinct states for  
configuration  $\{N_i, \Xi\}$ .

classical  
identical  
particles  
are  
distinct  
in the  
sense  
they can  
always  
be told apart  
somehow.

— There are several ways  
to ~~do~~ do it or think about it.

My Way

5-619

Put the energy levels in  
a mental line

$$\frac{N_1}{1} \quad \frac{N_2}{2} \quad \dots \quad \frac{N_i}{i}$$

There are  $N_1$  particles in level 1  
 $N_2$  in level 2  
 $N_i$  in level  $i$

The particles are lined up to,

$$N! = C \prod N_i!$$

number of  
ways of  
ordering particles  
on a line

distinct  
ways of  
slotting  
particles in to levels

ordering of  
particles in  
a level ~~is not~~  
is NOT  
counted here

5-620

$$C = \frac{N!}{\prod_i N_i!}$$

distinct ways of slotting particles in to levels to get configuration  $\{N_i\}$

But now consider the  $N_i$  particles in level  $i$ .

The degeneracy of the level  $i$  is  $g_i$

You have  $g_i$  choices for putting each particle into a state.

- Example states 1, 2, 3 and particles a and b
- $3^2 = 9$
- 1 a | 1 | 1
  - 1 a | 1 | 2
  - 1 a | 2 | 1
  - 1 a | 2 | 2
  - 1 b | 1 | 1
  - 1 b | 1 | 2
  - 1 b | 2 | 1
  - 1 b | 2 | 2

$g_i^{N_i}$  is the number

of distinct states for a level for a particular set of  $N_i$  distinct particles

For a given number of slot-ways there are  $\prod_i g_i^{N_i}$  distinct states

$W = C \prod_i g_i^{N_i}$

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