

# NANOSTRUCTURES AND NANOMATERIALS

Prof. Nirat Ray

[MLL740]

# LECTURE 1 (04/01/2023)

{ Technically, 03/01/2024  
was the first class, but  
only course policy was  
discussed in it }

## 1] Scaling Laws

### Miniaturization

(we want to see how

the diff. laws  
of physics

change with reduction  
in size )

① eg: In the case of  
weightlifting

+ relevant parameters  $\rightarrow$  i.e. which  
are:

strength      weights  
 $(W = mg)$

$$\text{Strength} \propto D^2$$

this tells us how  
strength scales  
(it scales with  $D^2$ )

$\rightarrow$  i.e. which  
determine whether  
weight can be  
lifted  
successfully

$\rightarrow$  we need to  
know how this  
scales with  $D$

$\rightarrow$  We know  $g$  is a constant  
but  $m \propto D^3$

$$\Rightarrow \text{Then: weight } \propto D^3$$

$$\frac{\text{Strength}}{\text{weight}} \propto \frac{1}{D}$$

If we check this  
for the case of

a fly      an elephant  
 $(\sim 1 \text{ mm})$        $(\sim 1 \text{ m})$

$\Rightarrow$  This helps give an idea  
why a fly can fly  
but elephants

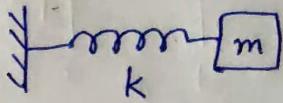
(Similarly, in  
weightlifting, performance  
is measured by % body weight lifted)

cannot jump

② For gravity acting on body:

$$F_g \propto D^3$$

③ For a spring:

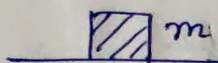


$$\text{K.E. of spring} \propto D^2$$

$$\text{P.E. of spring} \propto D^2$$

④ Frictional force

at ordinary scales



$$f_f = \mu mg \propto D^3$$

But at nanoscales

+

The ordinary friction

breaks down

+

instead, friction and adhesion forces combine

$$\text{called "Stick-slip"} \propto D^2$$

⑤ Wear

at ordinary scales

$$\text{Wear} \propto D$$

at nanoscales

this does not hold

instead we observe  
that nanomaterials  
are highly wear resistant

2]

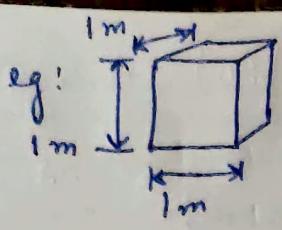
Scaling Laws

+ we generally observe that

velocity dependent force

scale as:

$$F \propto (D^2)^{1/3}$$



eg:  
(1 engine)

Taking  $F \propto D^2$

→ 1000 engines that  
occupy same  
volume as the  
1 original engine

Considering Power output  
is proportional to  $D^2$

Since  $P = Fv$  and  $v$  is constant

The power density  
for a single  
engine is

$$\frac{P}{V} \propto \frac{1}{D}$$

this is  
volume of object  
(not entire  
volume)

3] For Electrostatic fields

↑  
the scaling is  
given by:

$$E \propto \frac{1}{D}$$

## LECTURE 2 (08/01/2024)

4] Some key points that  
we need to know

↑  
from Quantum Mechanics

① Wave-particle duality

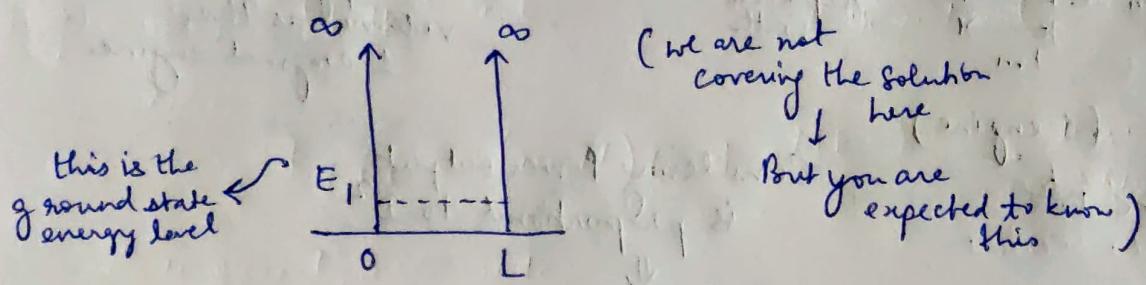
② Uncertainty principle

$$\Delta x \cdot \Delta p \sim h$$

$$\Delta E \cdot \Delta t \sim h \quad (\text{here, } E \text{ is energy})$$

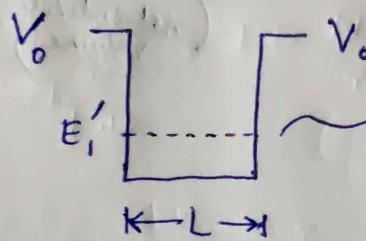
③ Schrödinger's equation

For a particle in a box:



Here,  $E_n = \frac{n^2 h^2}{8mL^2}$ ,  $n = 1, 2, 3, 4, \dots$   
we obtain quantized solution from Schrödinger's eq:  
\* (to be memorized)

For the case of a finite potential well:



\* Here,  $E'_1$  will be smaller than  $E_1$ , (i.e. the previous case ground state)  
Since here there will be a solution to the wave function outside the box as well  
so some energy will exist outside

NOTE: Making nanomaterials

often involves the concept of

\* Confinement

and thus is similar to the "particle in a box" situation

5] Nanomaterials can be classified as

↓  
2D (e.g.: Nanofilms)    1D (e.g.: nanowires)    0D (e.g.: Quantum Dots)

## 6] Thermodynamics

Extensive  
(i.e. depends on the size of system)  
eg:  $m$ ,  $G$ ,  $S$ , etc.

Intensive  
eg:  $\beta$ ,  $T$ , etc.

### Temperature

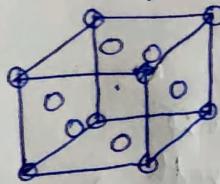
defined as the average energy:

$$k_B T \sim \frac{1}{2} m v_{\text{avg.}}^2$$

However, at nanoscales, the concept of temperature slightly breaks down

we observe that the temperature actually fluctuates by some  $\Delta T$

(FCC system)



Since there is no repetition here it has 14 atoms (NOT 8 atoms)

for a cubic system:

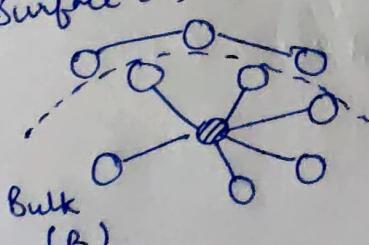
$$\frac{\Delta T}{T} = \sqrt{\frac{1}{NL^3}}$$

\* If  $\frac{\Delta T}{T} < 1\%$   
we say that classical thermodynamics is valid for the system!

## 7] In order to study "melting"

we need to be able to define it which will depend on bond energy

Surface (S)



The way we do this is through

Cohesive Energy per atom ( $E_0$ )

Let:  $N \rightarrow$  no. of atoms on surface  
 $n \rightarrow$  total no. of atoms

Thus, we have:

$$E_{\text{bulk}} = n E_0 \quad \rightarrow \text{this is for a Bulk material}$$

Now,

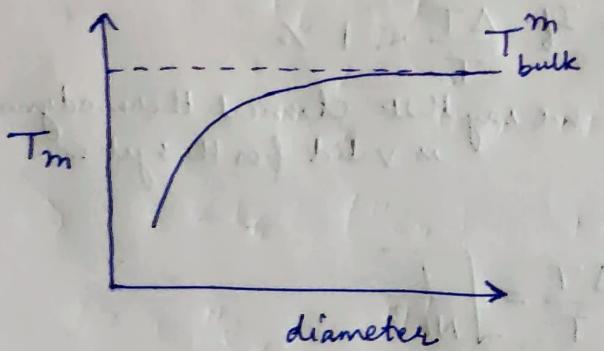
$$E_{\text{total}}^{\text{nano}} = (n-N) E_0 + \frac{N E_0}{2} \quad \rightarrow \text{this is for a Nanomaterial}$$

So in general we can write:

$$\boxed{\frac{E_{\text{nano}}}{E_{\text{bulk}}} = \left(1 - \frac{N}{2n}\right)}$$

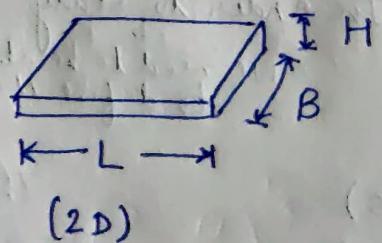
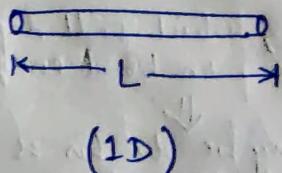
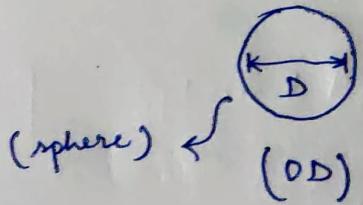
From this we  
get a relation for the  
melting point of bulk material  
vs nanomaterial

$$\boxed{\frac{T_m^{\text{nano}}}{T_m^{\text{bulk}}} = 1 - \frac{N}{2n}}$$



(i.e. melting point goes down with decreasing size)

### 8] Calculating $\frac{N}{n}$ ratio for different shapes:



taking atomic diameter  
as 'd'

Thus:

$$N = \frac{4\pi (\frac{D}{2})^2}{\pi (\frac{d}{2})^2} \quad \left. \begin{array}{l} \\ \end{array} \right\} \quad \frac{N}{n} = \frac{4D}{d} \Rightarrow \frac{T_{\text{nano}}^m}{T_{\text{bulk}}^m} = 1 - \frac{2D}{d}$$

$$n = \frac{\frac{4}{3}\pi (\frac{D}{2})^3}{\frac{4}{3}\pi (\frac{d}{2})^3}$$

Similarly, we get that:

For 1D:

$$\frac{N}{n} = \frac{8}{3} \frac{d}{L}$$

For 2D:

$$\frac{N}{n} = \frac{4}{3} \frac{d}{H}$$

9]

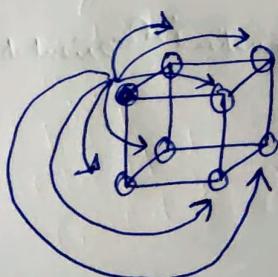
## Entropy

Configurational

given by:

$$S = k_B \ln W$$

(where  $W$  is the no. of different arrangements the system can have)



Can be swapped for all these locations

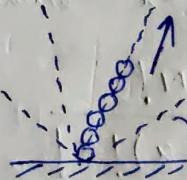
Conformal

this gives an idea of the orientation that is taken

generally during nucleation/growth phases

\* { configuration, on the other hand,

occurs after a crystal structure is already established }



these orientations could also have occurred

and this selection of orientation (conformation)

will influence further growth of crystals

e.g.



only this angular region is available

for this second line of particles to grow within

## LECTURE 3 (10/01/2024)

10]

### Entropy

Consider  $N$  no. of sites (on a large scale) where nucleation could take place { or lattice sites where nucleus can grow }

Nucleation initially starts at some  $x \ll N$  sites

Now, there are two terms that contribute to randomness

$N_{Cx}$  sites where it will grow spherically

(configurational entropy)

There will be some restrictions in directions where it cannot grow

i.e. Conformational entropy ( $\rightarrow$  orientation) (captured by: orientation)

Thus  $\Rightarrow$

$$S = k_B \ln W$$

$N_{Cx}$   $\rightarrow$  orientation

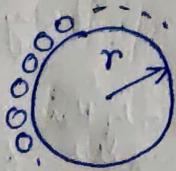
$$\Rightarrow S = k_B \ln (N_{Cx} \cdot \Omega_{\text{orientation}}) \equiv k_B \ln (\Omega_{\text{configurational}} \cdot \Omega_{\text{orientation}})$$

$$\text{Now, } N_{Cx} = \frac{N!}{(N-x)!x!}$$

\* NOTE:  $\Omega_{\text{orientation}}$  will be hard to calculate without assumptions

11]

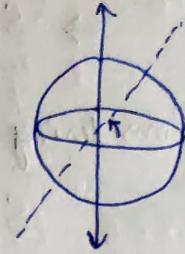
### Spherical Approximation



$$\frac{N}{x} = \frac{4}{3}\pi r^3 \Rightarrow r = \left(\frac{3}{4\pi} \frac{N}{x}\right)^{1/3}$$

$$\begin{aligned} \text{No. of orientations} &= 4\pi r^2 \times \text{No. of atoms} \\ &= (4\pi r^2) (2\pi r) \end{aligned}$$

↓      ↗ Total no. of orientations there can be



{ Symmetry breaking }

we can have this kind  
of growth for one direction  
but there are  $2\pi r$   
such directions

$$\Rightarrow \begin{aligned} \text{Total orientations} &= 8\pi^2 r^3 \\ &= 8\pi^2 \left( \frac{3}{4\pi} \frac{N}{x} \right) \\ &= 6\pi \frac{N}{x} \end{aligned}$$

↗ One nanocrystal can have these many orientations

Thus; for  $x$  sites :

$$\text{Total no. of orientations, } \Omega_{\text{orientations}} = \left( 6\pi \frac{N}{x} \right)^x$$

[2] We can now calculate entropy :

$$S = k_B \ln \left[ \left( \frac{N!}{x!(N-x)!} \right) \left( 6\pi \frac{N}{x} \right)^x \right]$$

Taking  $f = \frac{x}{N}$  :

$$S = k_B \left( x \ln \frac{6\pi}{f} \right) + k_B \left( N \ln N - N - x \ln x + x - (N-x) \ln(N-x) + N - x \right)$$

$$\Rightarrow S = k_B \left( x \ln \frac{6\pi}{f} \right) + k_B \left( -N \ln(N-x) + N \ln N + x \ln(N-x) - x \ln x \right)$$

$$\Rightarrow S = k_B \left( x \ln \frac{6\pi}{f} \right) + k_B N \left[ -\ln(1-f) - f \ln \left( \frac{f}{1-f} \right) \right]$$

$$\begin{aligned} &= k_B \left[ x \ln \frac{6\pi}{f} + N \left( -(1-f) \ln(1-f) \right) \right] - \underbrace{(f \ln f) N k_B}_{-k_B x \ln f} \\ &= k_B \left[ x \ln \left( \frac{1}{f^2} \right) - N (1-f) \ln(1-f) \right] \end{aligned}$$

ignoring  $\ln[(6\pi)^x]$  since it is v. small

$$\Rightarrow S = -k_B N [ (1-f) \ln(1-f) + 2f \ln f ]$$

Considering that  $f$  is very small ( $f \ll 1$ ):

$$S = -k_B N [ \cancel{(1-f) \ln(1-f)}^{\rightarrow -f} + 2f \ln f ]$$

Thus we get:

$$S = -N k_B [ 2f \ln f - f ]$$

or

$$\underbrace{N k_B (f - 2f \ln f)}$$

this is  
+ve in value

Hence  $\Rightarrow S > 0$

thus, it may be a  
dominating term

13] For a nanomaterialistic formulation,  $N$  is small

considering an arbitrary ("ball park") number,  
say  $N = 10000$

$S$  can get large relatively,  
about  $0.1 k_B$  at  $T_{room}$

Hence, as  $S \propto N$ , if we go to a very  
low size, this means that the  $T \Delta S$  term  
will start to dominate:

$$\text{i.e. } \Delta G = \Delta H - \underbrace{T \Delta S}_{\text{this will be a}}$$

dominating term (at nanoscales)

## LECTURE-4 (11/01/2024)

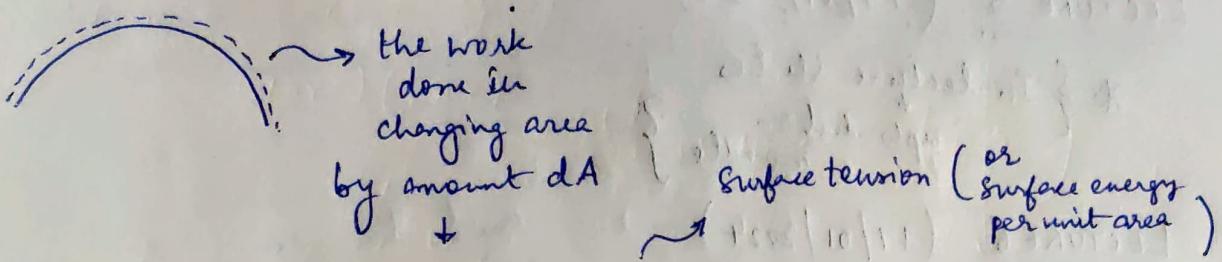
### Gibbs Free Energy

We will talk about

Gibbs-Thomson effect

- Surface effects
- melting temp.
- Vacancy conc. in nanomaterials
- Lattice parameter (\* open discussion you'll have to look it up on your own)

15]



$$\text{given by: } dW = \gamma dA$$

NOTE: We know,  $V = \frac{4}{3}\pi r^3$  }  $\Rightarrow dV = 4\pi r^2 dr$   
 $A = 4\pi r^2$  }  $dA = 8\pi r dr$

$$\therefore dA = 2 \frac{dV}{r}$$

NOTE: The Gibbs-Thomson effect tells us that

$$\text{with } r \downarrow \Rightarrow \Delta G \uparrow \text{ (or, } \Delta\mu \uparrow)$$

Here,  $dG = \gamma dA = \frac{2\gamma}{r} dV \Rightarrow$  Now,  $\Delta\mu = \frac{\partial G}{\partial n} = \frac{2\gamma}{r} \frac{dV}{dn} \Rightarrow \Delta\mu = \frac{2\gamma}{r} \Omega$

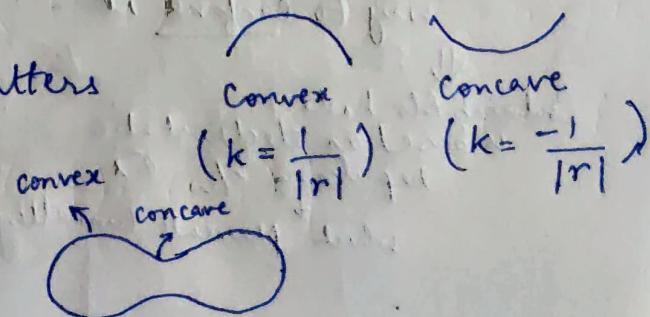
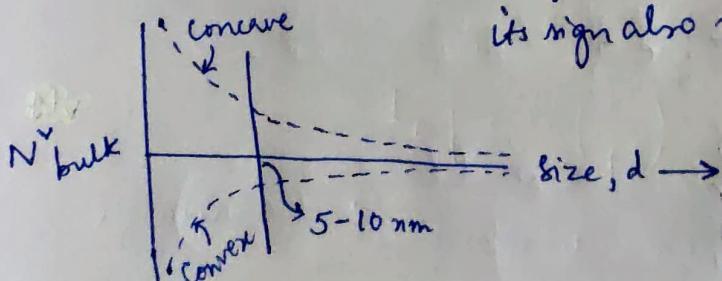
16] We can write:

$$\Delta G_{\text{particle}}^v = \Delta G_{\text{bulk}}^v + \frac{\gamma \Omega}{r} \quad (\Delta\mu = \mu_c - \mu_\infty)$$

\* { NOTE:  $N_{\text{bulk}}^v \sim N_0 e^{-\frac{\Delta G_{\text{bulk}}^v}{k_B T}}$  flat surface  
 $N_{\text{particle}}^v \sim N_0 e^{-\frac{\Delta G_{\text{bulk}}^v}{k_B T}} e^{-\frac{\Omega r}{r k_B T}}$  from a Taylor expansion  
 $\Rightarrow N_{\text{particle}}^v = N_{\text{bulk}} \left[ 1 - \frac{\Omega r}{r k_B T} \right]$  }

Here, dependence on radius of curvature also exists

its sign also matters



## LECTURE 5 (15/01/2024)

\* { In lecture slides  
uploaded on moodle }

## LECTURE 6 (17/01/2024)

\* { Slides uploaded }

## LECTURE 7 (24/01/2024)

### 17] Electrical Properties

The electrical properties

of 0D, 1D and 2D  
materials

are very different

#### NOTE:

There are different phenomena  
involved in each case

0D

Coulombic  
blockade

1D

involves  
diffusive  
or  
ballistic  
transport

2D

uses  
Quantum Hall  
effect

{ For a quantum dot  
to exist

we require that  
even without any  
bias voltage

the  $e^-$  in the dot should NOT  
tunnel out from the barriers

thus we need some  
way to confine it

Coulomb Blockade

is based on electrostatic  
repulsion b/w  $e^-$ 's

which prevents tunnelling }

NOTE: We see that these all structures deviate from \* Ohm's law

+  
and we will see ahead  
why this is so

+  
We shall also understand  
the idea of  
Density of states

+  
and how it  
changes with  
dimension & structure

18 ]

OD (Zero Dimensional)  $\rightarrow$  eg: Quantum Dot

+  
they are of  
very very small size and surface

+  
made from  
small piece of material  $\begin{cases} \text{can be metallic} \\ \text{OR} \\ \text{semiconducting} \end{cases}$

Quantum Dot



$r$  or  $d \sim \lambda$   
(radius) (diameter)

$\downarrow$  this is the  
\* de Broglie wavelength  
of the electron

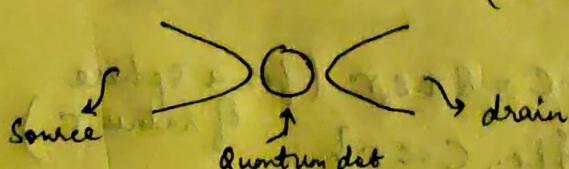
(5-10 nm)

source

drain

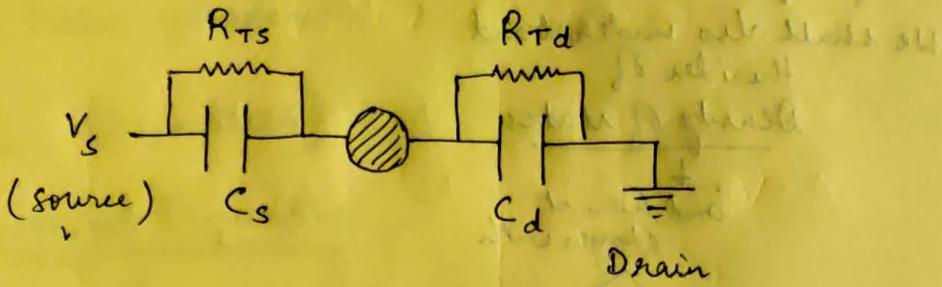
(which are  
essentially electrodes)

19] We can consider placing  
a quantum dot b/w two contacts  
(Quantum dot)



These contacts  
are not perfect  
↓

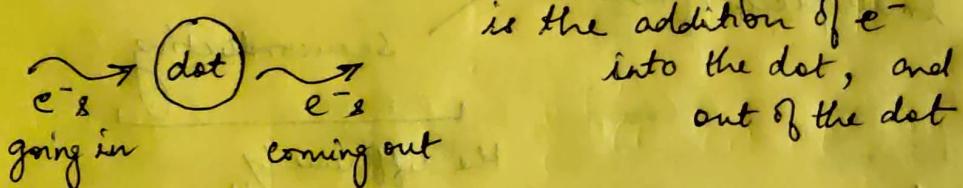
thus they have some  
capacitive effect \*



Here  $R_{TS}$ ,  $R_{Td}$ ,  $C_{Ts}$  and  $C_{Td}$   
will all be different

## 20] Charging Energy

The idea of passing current  
through this dimension (i.e. zero dimensional  
quantum dot)



is the addition of  $e^-$   
into the dot, and  
out of the dot

let's say the  $e^-$   
cannot come out of the dot

Now, if we try to add  
another  $e^-$

This would require ↓ energy (extra energy)

This energy is  
called the

\* Charging energy

For a sphere of  
capacitance  $C$ ,  
we get:

$$E_C = \frac{e^2}{2C}$$

, where  $C = 8\pi\epsilon_0 r$  (for a sphere  
{i.e.,  $C \propto r$ } of radius  $r$ )

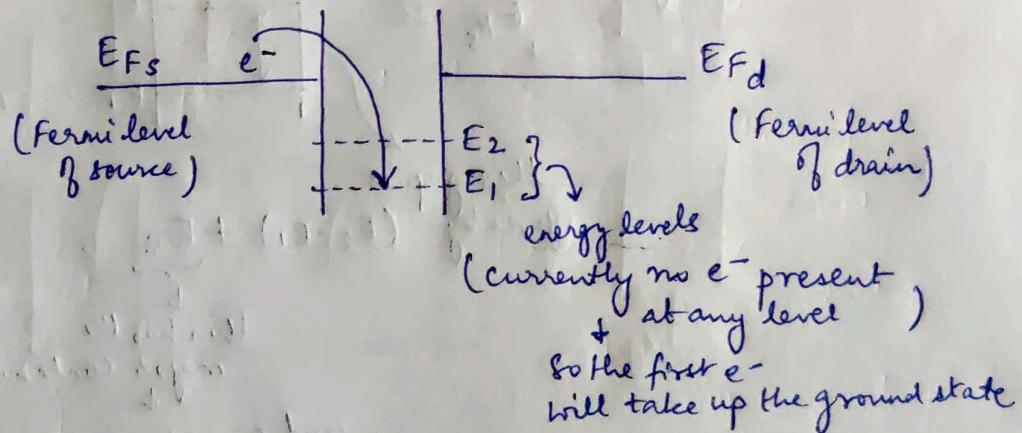
Since  $C \propto r$ ,  
this means that

as the size gets smaller  
the capacitance will  
also get smaller

and thus, the energy  
reqd. will get huge for a  
very small size

{ in such a case,  
 $C$  would be in units of  
the order of  $10^{-18}$   $\rightarrow$  i.e.  
atto farads }

21] Considering the case of  
no  $e^-$  in the capacitor (i.e. the dot)  
↓  
i.e. the first  $e^-$   
is now going to enter in it



Now for the case of  
the next incoming  $e^-$

it is supposed to sit in  $E_2$

But extra energy  $E_c$  (charging energy)  
is also required

→ and this cannot  
be neglected, since  
it will be a high value

i.e. ↓

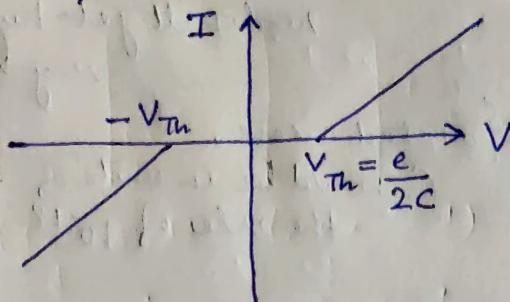
$E_c \gg E_2 - E_1$  and  $E_c \gg k_B T$   
(for a very small dot)

{ NOTE: This effect  
occurs in bulk also,  
but is just not very  
apparent }

\* NOTE: Here, the Thvenin voltage  $V_{Th}$   
(i.e. open circuit voltage)

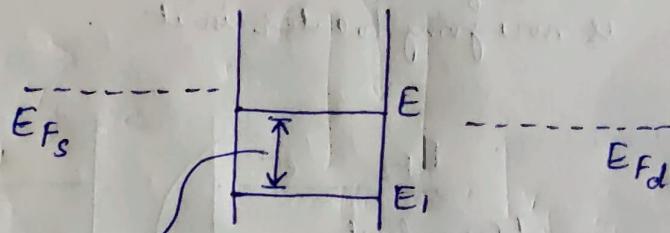
$$\text{is given by: } V_{Th} = \frac{E_c}{e} = \frac{1}{e} \left( \frac{e^2}{2C} \right) = \frac{e}{2C}$$

Thus, we can see that  
the I-V plot looks as follows:



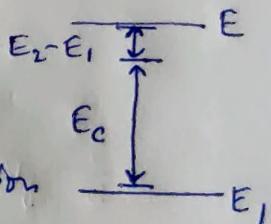
22] Now, since we know  
 $E_c \gg E_2 - E_1$

we get:



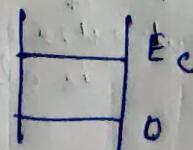
this gap is  
given by  $(E_2 - E_1) + E_c$

this has the  
major contribution



and so we may even  
thus consider the gap  
as given by

NOTE: If we take  $E_1 = 0$  as reference,  
then we can just write  
 $E_c$  instead of  $E$   $\Rightarrow$



23] There are three  
possible cases now

Case 1

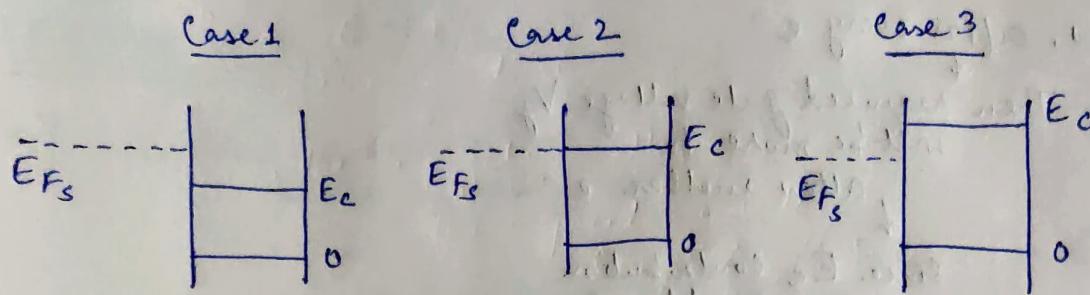
Case 2

Case 3

$E_{F_s} > E$

$E_{F_s} = E$

$E_{F_s} < E$



If we are in a case 1 situation ↓

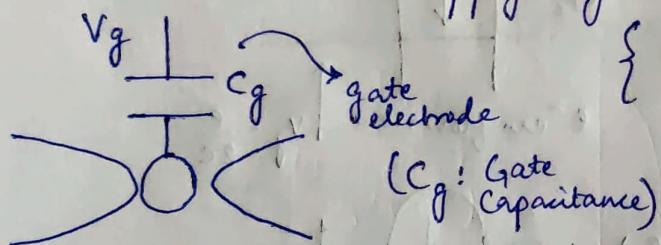
then  $e^-$  will be able to flow from source to the dot

But in case 3

energy level is too high  
and thus flow won't happen

\* Thus, in order to allow flow from source to dot, we need to apply a gate voltage  $V_g$

This kind of system is called a single-electron Transistor

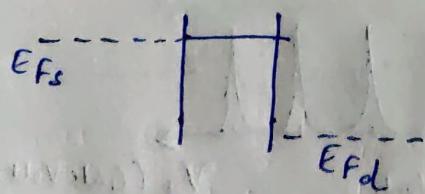


{ The electric field created causes the energy levels to shift downwards thus allowing flow from source to dot }

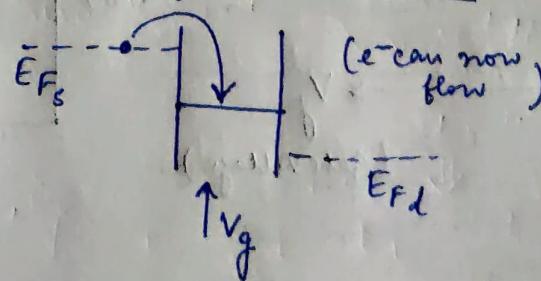
{ \* NOTE: Since  $e^-$  can exist in the dot only in certain quantized energy levels }

thus the gate voltage  $V_g$  will have an effect only at those discrete values }

Without  $V_g$

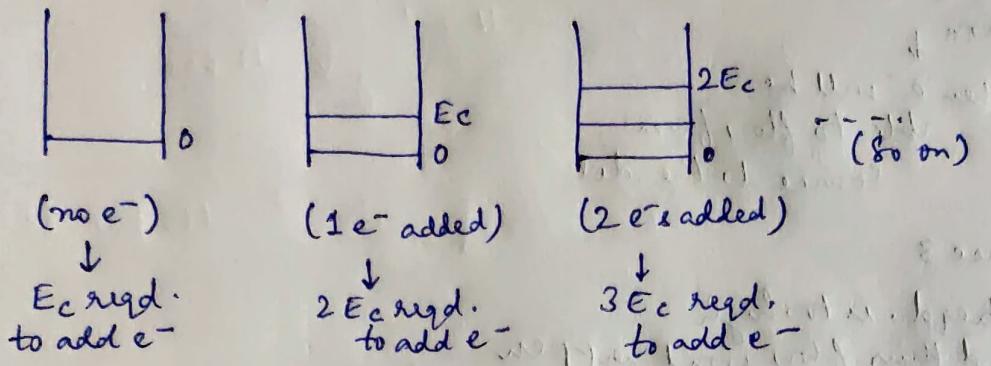


$$\text{By using } V_g = \frac{E_c}{e} = \frac{e}{2C} :$$

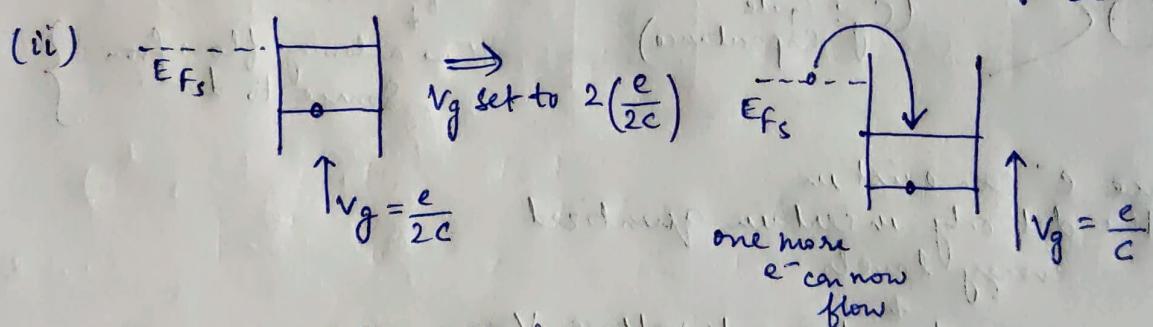
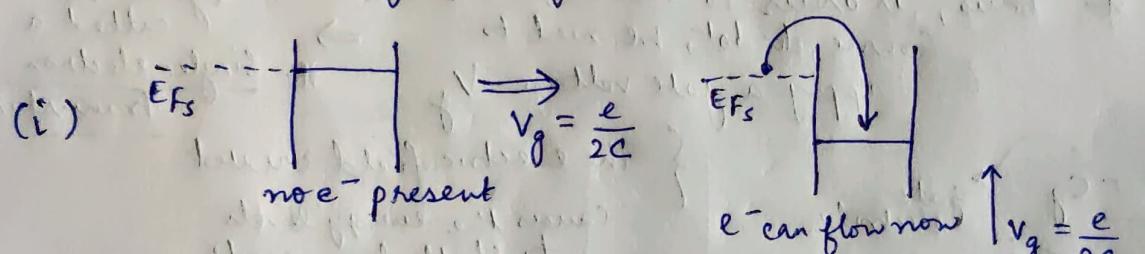


24] Now, after every  $e^-$

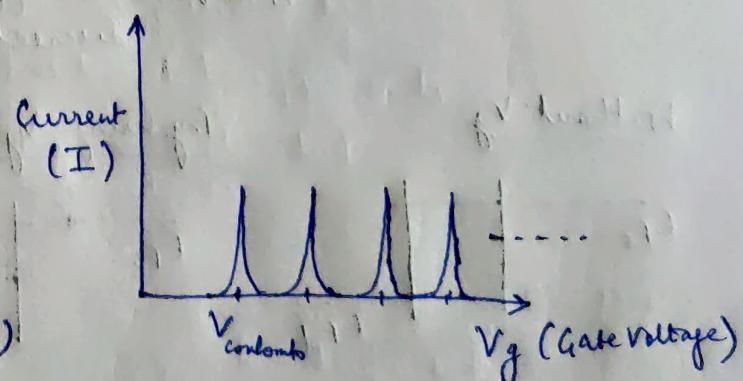
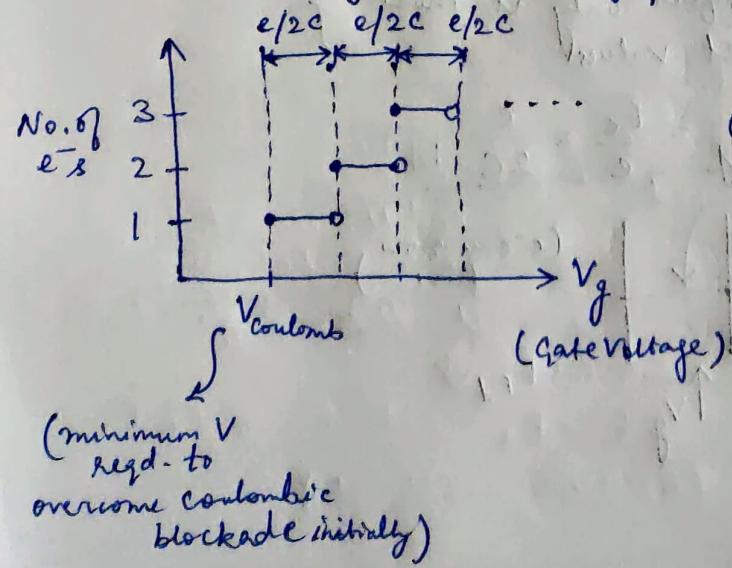
Then required gate voltage  $V_g$   
will be more to  
allow another  $e^-$   
since  $E_c$  contribution  
of each adds up



Effect of gate voltage can be seen as :



Thus, we get the following plots:

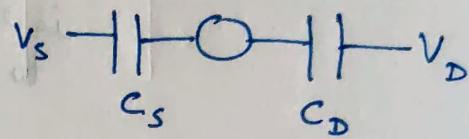


## LECTURE 8

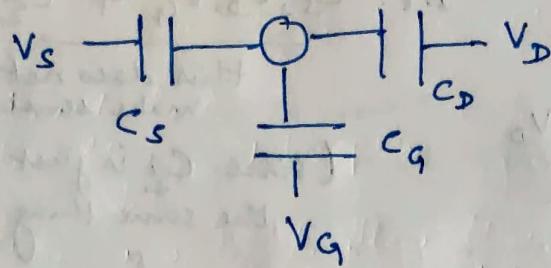
(25/01/2024)

25] Earlier we saw a case where  $V_D$  was grounded

↑  
instead we could also just take a general  $V_D$ :



Along with the gate, we get the following:



Now, the conditions to observe a Coulomb Blockade are:

①  $E_c \gg k_B T$  } i.e. small capacitance effect  
and,  $E_c \gg E_2 - E_1$

② Resistance effect

↓  
this can come from the Uncertainty principle

$$\Delta E \cdot \Delta t \sim h$$

↓ ↓

$$\text{here: } \Delta E \sim E_c \quad \Delta t \sim R C$$

→ this resistance occurs in the system

\* This can be called the quantum of resistance

By solving from the above eq<sup>n</sup>:

$$R \sim \frac{h}{e^2} \sim 28 \text{ k}\Omega$$

↓  
this is the overall resistance

the should be there  
↑ (b/w  $V_s$  and the dot)

in order for Coulomb Blockade to occur

NOTE: We don't know exactly the source of this resistance directly

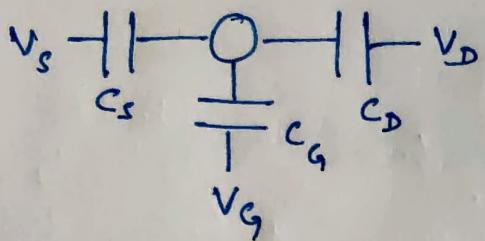
26] Thinking of three separate capacitances  
 $\downarrow (C_S, C_D \text{ and } C_G)$   
 is equivalent to thinking of a single  $C_{\Sigma}$   
 (capacitance of the sphere)

{ However, we DO NOT mean to consider both together at the same time

$$\downarrow \text{i.e. } C_S, C_D, C_G + C_{\Sigma}$$

this does not make sense

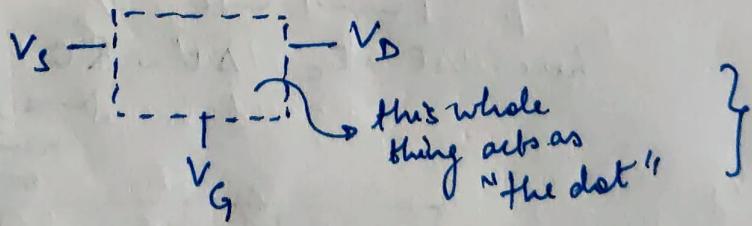
(since  $C_{\Sigma}$  is just capturing the same thing as  $C_S, C_D \text{ & } C_G$  separately)



Here, when we say the charging energy :  $E_c = \frac{q^2}{2C_{\Sigma}}$

$$\text{and } C_{\Sigma} = C_S + C_D + C_G$$

\* NOTE: { The reason for this is that practically we can't distinguish b/w  $C_S, C_D$  and  $C_G$  ! }



27] Let's say we have an initial charge  $Q_0$   $\leftarrow$   $V_s - \frac{1}{C_S} - \frac{1}{C_D} - V_d$  for this case  
 and then  $N_i$  electrons are removed (here,  $C_{\Sigma} = C_S + C_D$ )

$$\therefore \Rightarrow \Delta E_c = \frac{(Q_0 - N_i q)^2}{2C_{\Sigma}} - \frac{Q_0^2}{2C_{\Sigma}} = \frac{N_i^2 q^2}{2C_{\Sigma}} - \frac{Q_0 N_i q}{C_{\Sigma}}$$

Here, initially we had:

$$Q_0 = C_{\Sigma} V \quad (\text{where } V \text{ was the potential diff. b/w source and drain})$$

So we can write:

$$\Delta E_c = \frac{N_i q^2}{2 C_{\Sigma}} - N_i q V$$

From here, if we solve for the case of  $\Delta E_c = 0$ , we get:

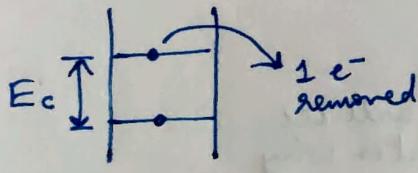
$$V = \frac{N_i q}{2 C_{\Sigma}}$$

This means that to remove 1  $e^-$  from the system, if we apply a voltage

$$V = \frac{q}{2 C_{\Sigma}} \quad \begin{matrix} \downarrow \\ \text{of} \end{matrix} \quad \begin{matrix} \text{this is the} \\ \text{threshold} \\ \text{voltage } (V_{Th}) \end{matrix}$$

then there will be NO energy change in the system  
(i.e.  $\Delta E_c = 0$ )

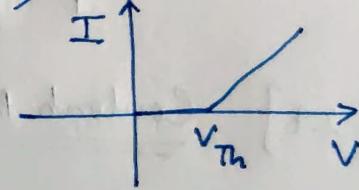
{ What will happen is :



$$V = \frac{q}{2 C_{\Sigma}} \text{ applied}$$

$\Rightarrow$   
the remaining  
 $e^-$ s below

charge energy level such that  $\rightarrow$  overall  $\Delta E_c = 0$



28] Now we will try to take into account the modifications  
regd.  $\downarrow$

for the case of  
a Gate

$$\text{We had: } \Delta E_c = \frac{N_i q^2}{2 C_{\Sigma}} - N_i q V$$

$$\text{For the case of a gate, we know: } V = \frac{C_G}{C_{\Sigma}} V_G$$

this will allow us to solve in terms of  
gate voltage

From here we can see:

$$\begin{aligned} & (\Delta E_c)_{N_i+1} - (\Delta E_c)_{N_i} \\ = & \frac{(N_i+1)^2 q^2}{2 C_\Sigma} - (N_i+1) q \frac{C_G}{C_\Sigma} V_G - \frac{N_i^2 q^2}{2 C_\Sigma} + N_i q \frac{C_G}{C_\Sigma} V_G \end{aligned}$$

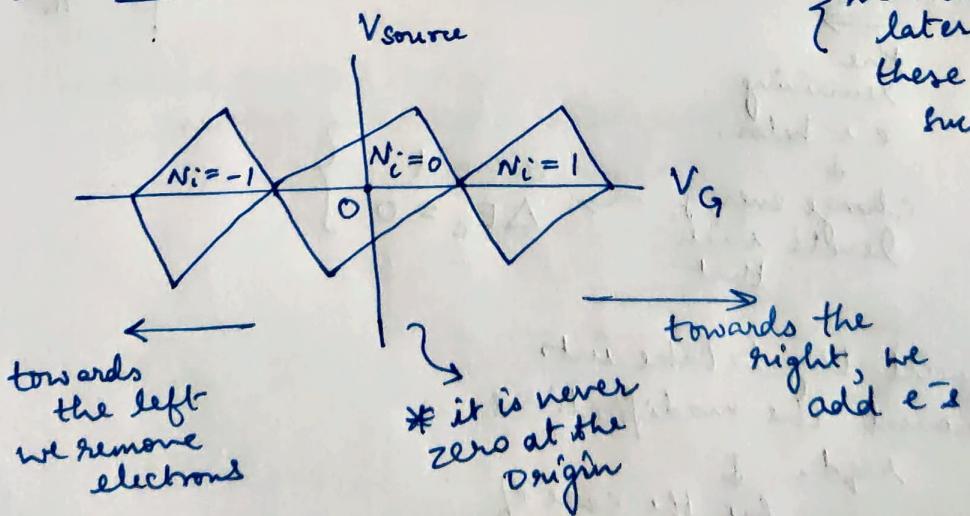
We can see from this, the value of  $V_G$  where change in charge of energy is zero:

$$V_G = \frac{q}{C_G} \left( N_i + \frac{1}{2} \right)$$

NOTE: It is possible to have a case where an upper state is occupied and lower is unoccupied (though, it's unlikely)



## 29] Coulomb Blockade Diamonds



{ we will see later why these plots have such shape }

[ \* NOTE: These are NOT squares (which is why we call the coulomb blockade "diamonds") ]