Lecture 6-7: Space Charge Layers

Solid State Ionics

Fall 2022

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Things we will discuss in this lecture

Space charge layers:

- What is the physical picture and assumptions of the space charge layer theory?
- What are the difference between the Gouy-Chapman and Mott-Schottky cases?
- How to model the distribution of ionic/electronic defects in the space charge layers?
- What are the effects of space charge layers on the conductivity of bulk (poly-crystalline)materials?

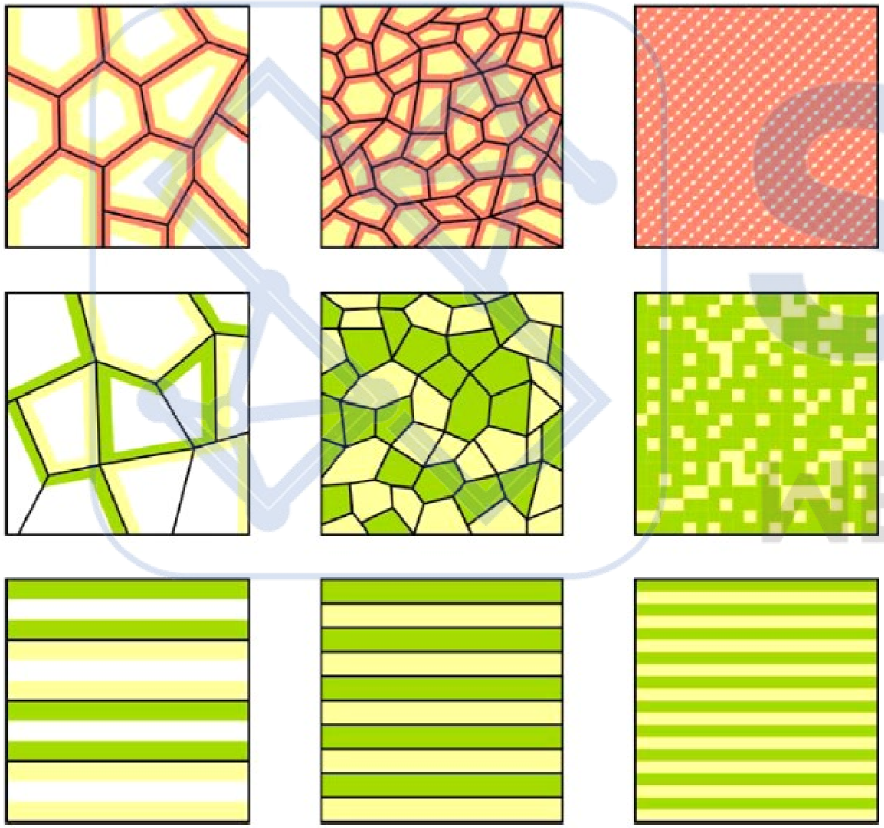
Goal of this lecture: you should be able to answer the questions above by the end of this lecture :)

Categories of defects with different dimensions

- Defects in crystalline solids
  - 0-D: point defects
    - Vacancy
    - Substitution
    - Interstitial
    - Anti-site
  - 1-D: dislocations
    - Edge dislocations
    - Screw dislocations
  - 2-D defects
    - Surfaces
    - Interfaces
    - Grain boundaries

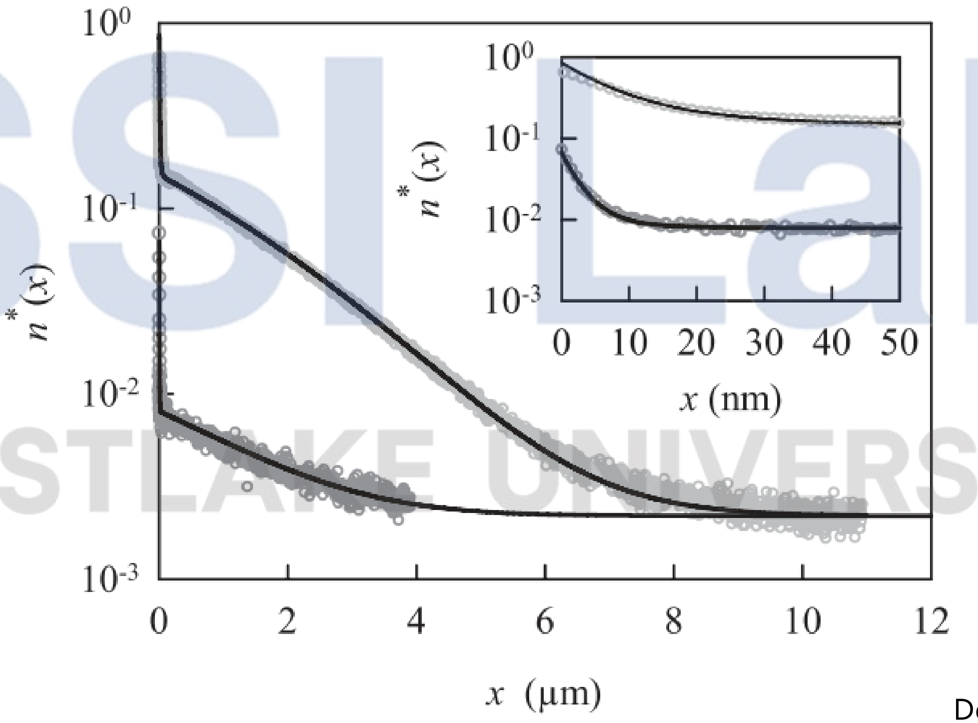
Grain boundaries, surfaces and interfaces

Increase # of interfaces

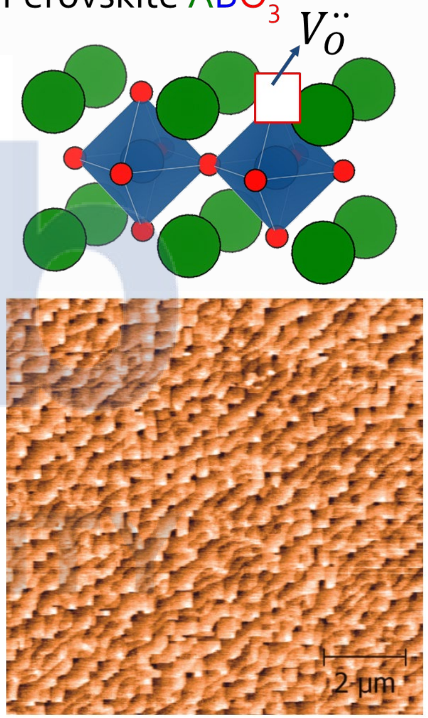


J. Maier, ***Chem. Mater.*** 2014

$SrTiO_{3-\delta}$ (STO) surfaces



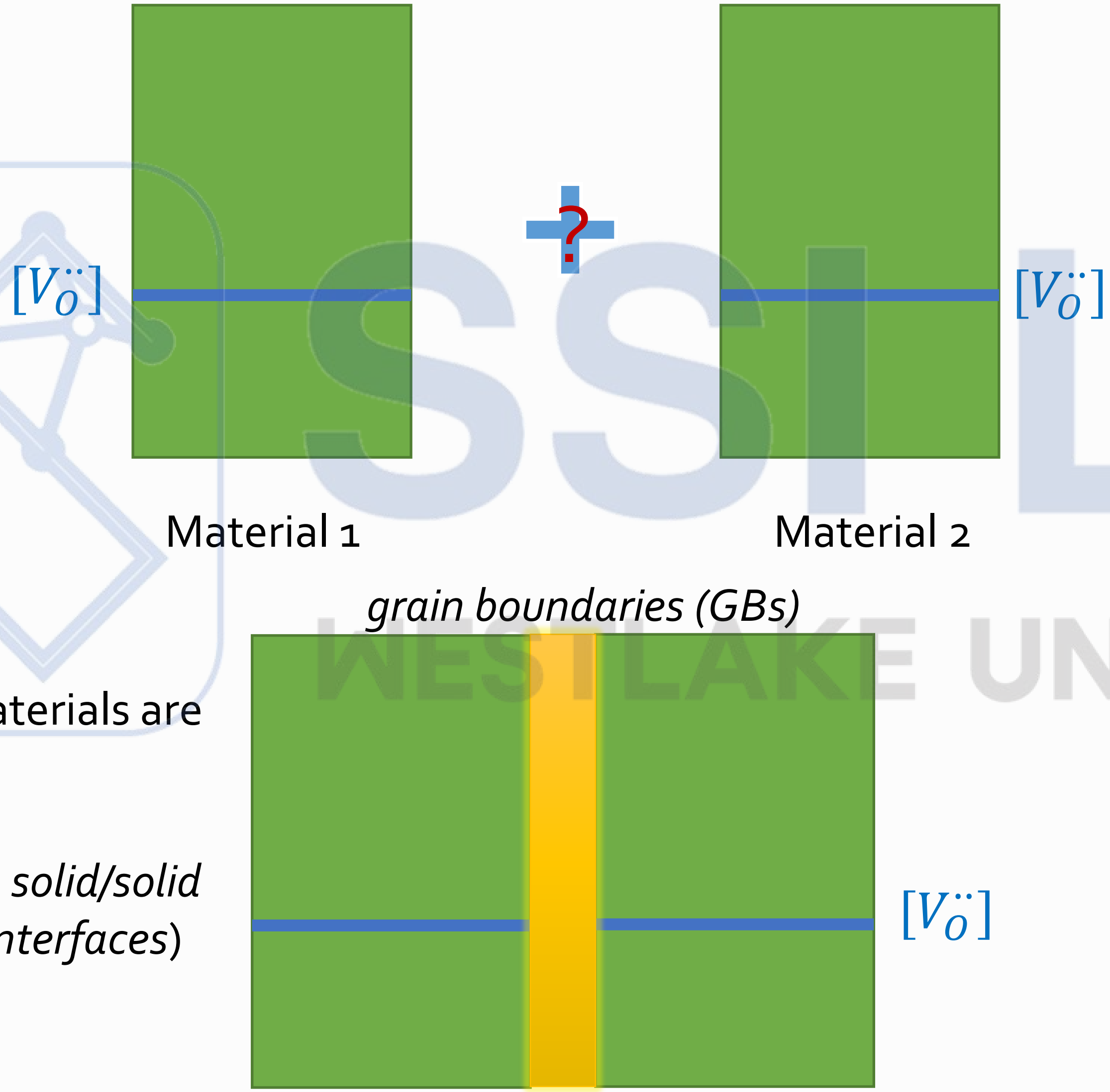
Perovskite ABO_3



De Souza *et al.*, ***Phys. Rev. B***, 2014

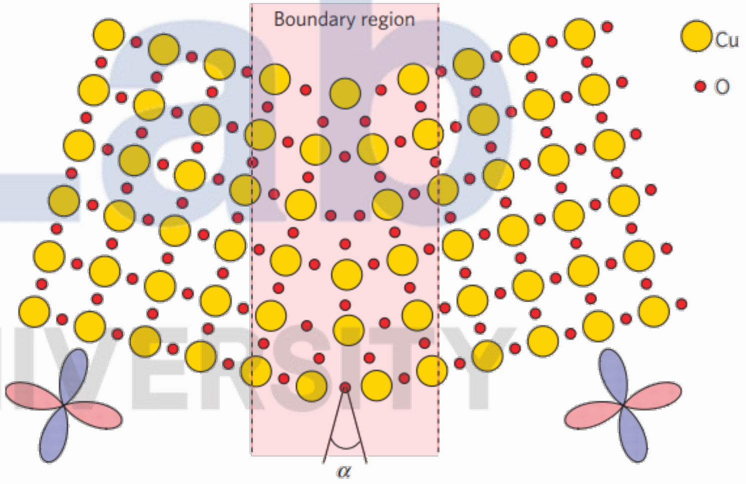
$D^*_{O^{2-}}$ became much lower at the near surface region due to the formation of a space charge layer

What happens when two materials are put together?



What happens when two materials are put together?

(e.g., grain boundaries (GBs), solid/solid heterostructure, solid/liquid interfaces)



Graser *et al.*, ***Nat. Phys.***, 2010

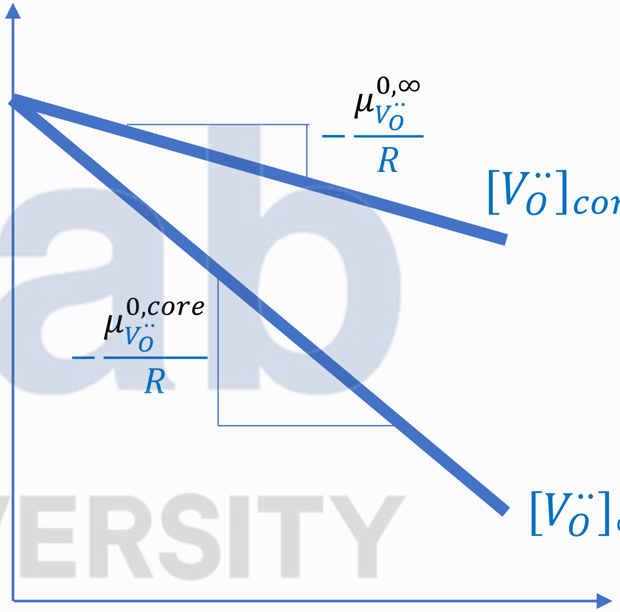
What happens when two materials are put together?

Normally defect formation energy is lower at GBs due to more open space.

$$\mu_{V_O^{\cdot\cdot}} = \mu^0_{V_O^{\cdot\cdot}} + RT\ln[V_O^{\cdot\cdot}]$$

$$\frac{[V_O^{\cdot\cdot}]_{core}}{[V_O^{\cdot\cdot}]_{\infty}} = \exp\left(-\frac{\mu^{0,core}_{V_O^{\cdot\cdot}} - \mu^{0,\infty}_{V_O^{\cdot\cdot}}}{RT}\right)$$

core = grain boundary
∞ = bulk



1. At equilibrium, the chemical potential of defects must be the same inside the core and in the bulk (here we ignore the charge for the moment)
2. A lower standard chemical potential ($\mu^0_{V_O^{\cdot\cdot}}$) means higher $[V_O^{\cdot\cdot}]$.

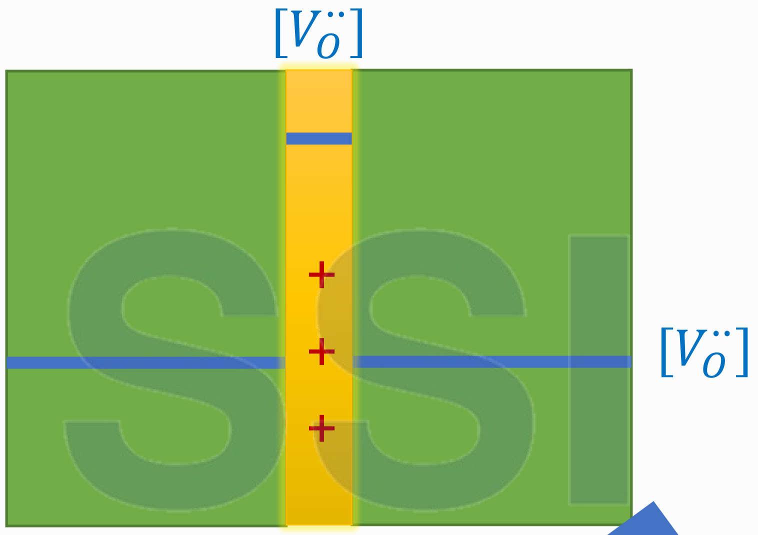
Now we also need to consider the extra charge

The treatment in the last slide ignored the fact that oxygen vacancies are positively charged.

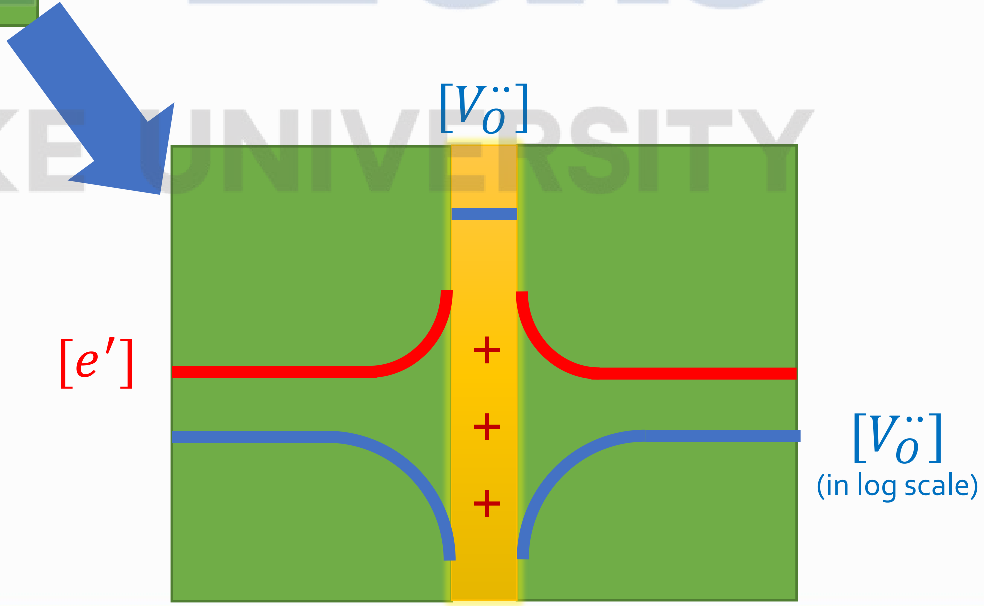
Instead, we should use electrochemical potential rather than chemical potential

Electrochemical potential

$$\tilde{\mu}_{V_O^{\cdot\cdot}} = \mu_{V_O^{\cdot\cdot}} + 2F\phi$$



Question: How to give a quantitative description on the change of defect concentrations?

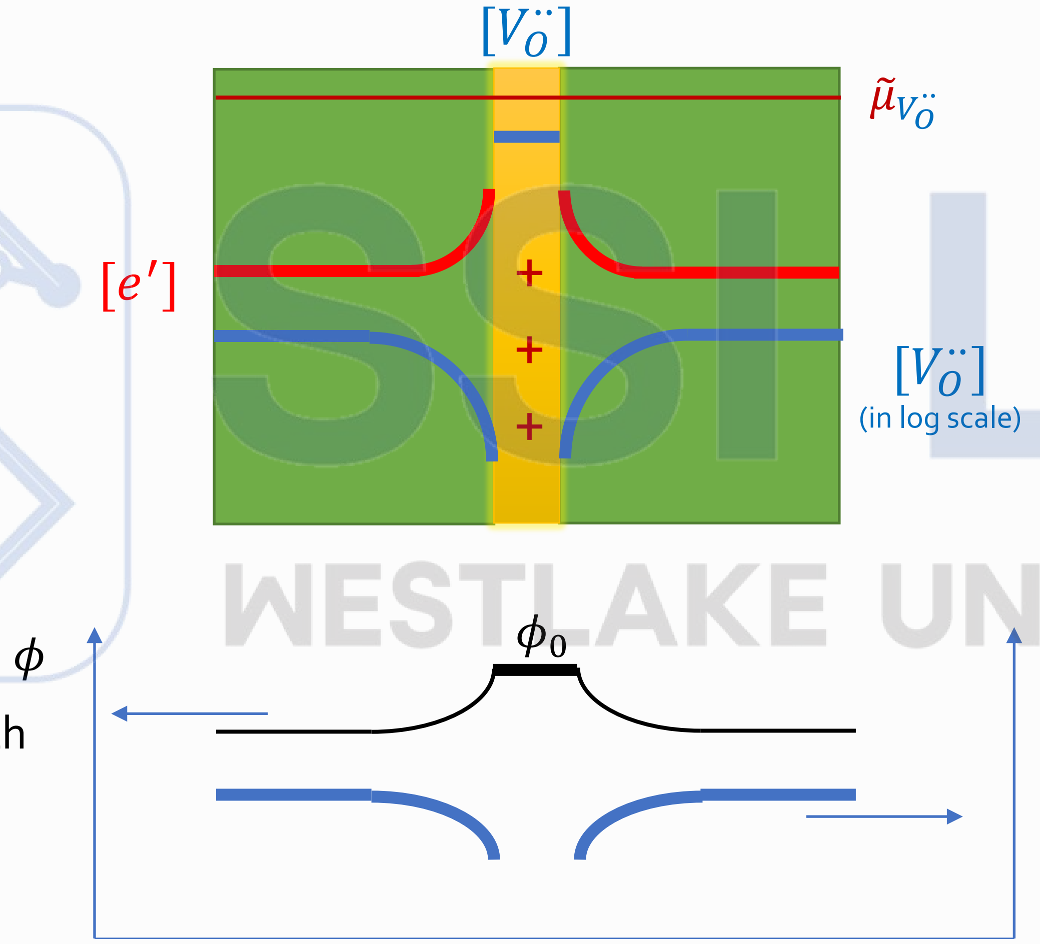


The existence of extra charge will change the distribution of all *charged* point defects, including ionic defects and electronic defects (electrons/holes).

How to solve for the defect concentration profile at equilibrium?

At equilibrium, the electrochemical potential is flat everywhere

$$\tilde{\mu}_{V_O^{\cdot\cdot}} = \mu_{V_O^{\cdot\cdot}} + 2F\phi$$



$$\mu_{V_O^{\cdot\cdot}} = \mu^0_{V_O^{\cdot\cdot}} + \mathrm{RTln}[V_O^{\cdot\cdot}]$$

Connecting electric potential ϕ with defect (charge) concentration

Poisson's equation

$$\frac{d^2\phi}{dx^2} = -\frac{\rho}{\varepsilon}$$

ρ: charge density; ε: permittivity

How to solve for concentration profile in the space charge region

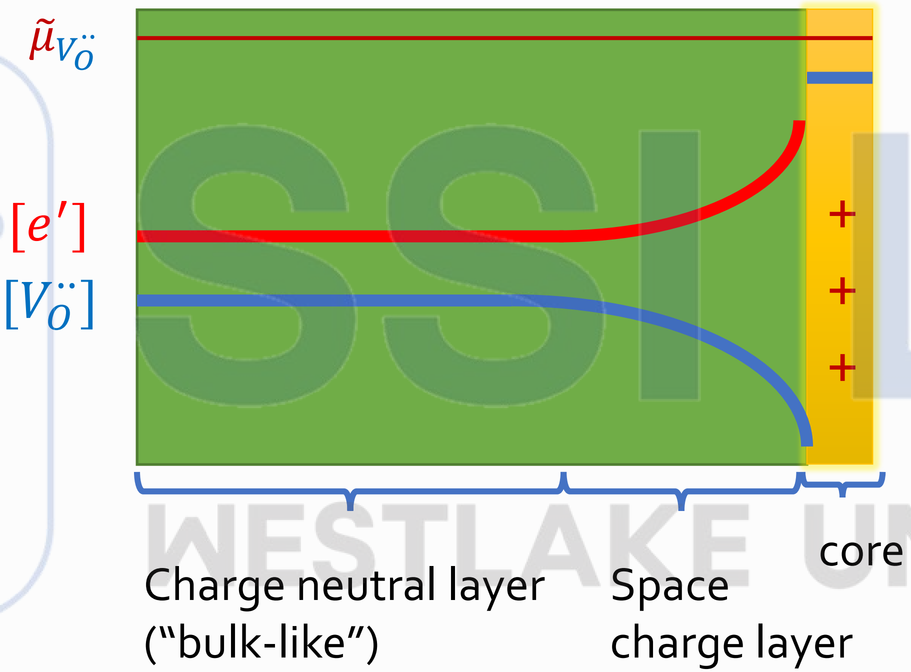
At equilibrium, the electrochemical potential is flat everywhere

$$\tilde{\mu}_{V_O^{\cdot\cdot}} = \mu^0_{V_O^{\cdot\cdot}} + \mathrm{RT}\ln[V_O^{\cdot\cdot}] + 2F\phi$$

i.e., $\dfrac{\partial \tilde{\mu}_{V_O^{\cdot\cdot}}}{\partial x} = 0$

$$\frac{\partial(\mu^0_{V_O^{\cdot\cdot}} + \mathrm{RT}\ln[V_O^{\cdot\cdot}] + 2F\phi)}{\partial x} = 0$$

$$RT\frac{\partial \ln[V_O^{\cdot\cdot}]}{\partial x} = -2F\frac{\partial \phi}{\partial x}$$

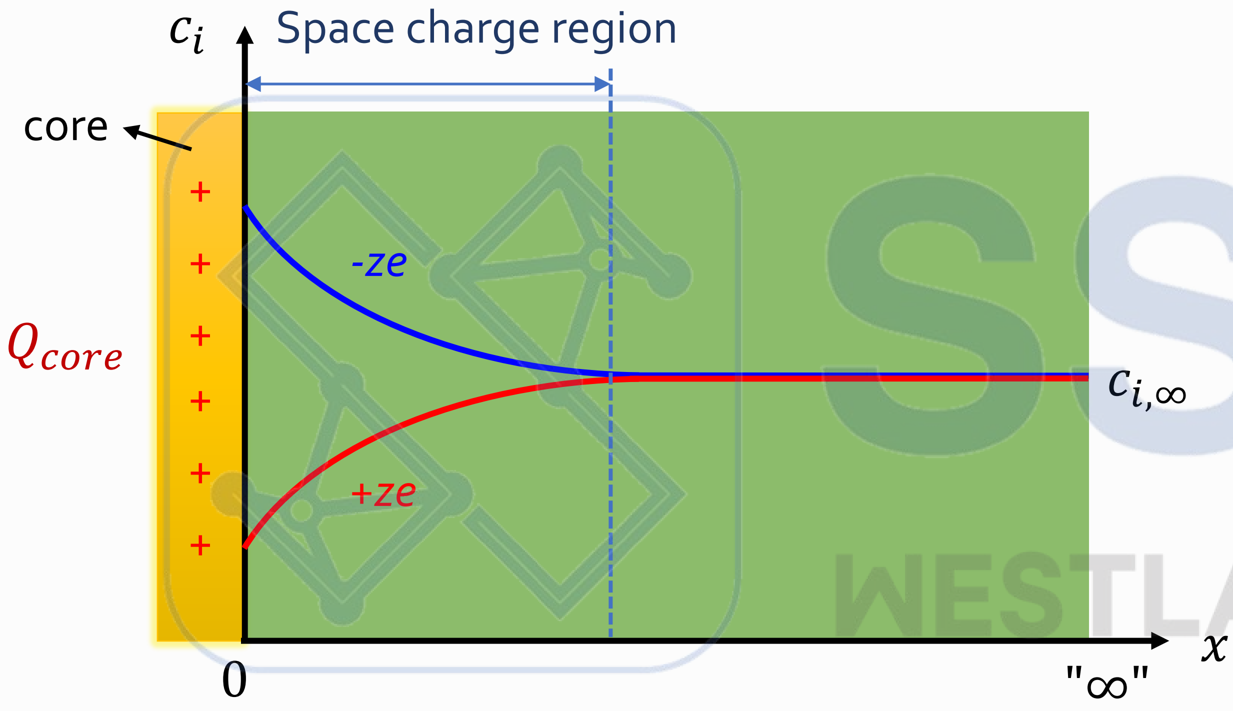


Defect concentration inside the space charge layer goes back to bulk value *exponentially*.

Therefore, we have:

$$[V_O^{\cdot\cdot}] = [V_O^{\cdot\cdot}]_\infty \exp\left(-\frac{2F(\phi - \phi_\infty)}{RT}\right)$$

Gouy-Chapman case: how to set up the problem?



Surface/Interface
Grain Boundary (GB) → Bulk

Gouy-Chapman case → all defects are mobile

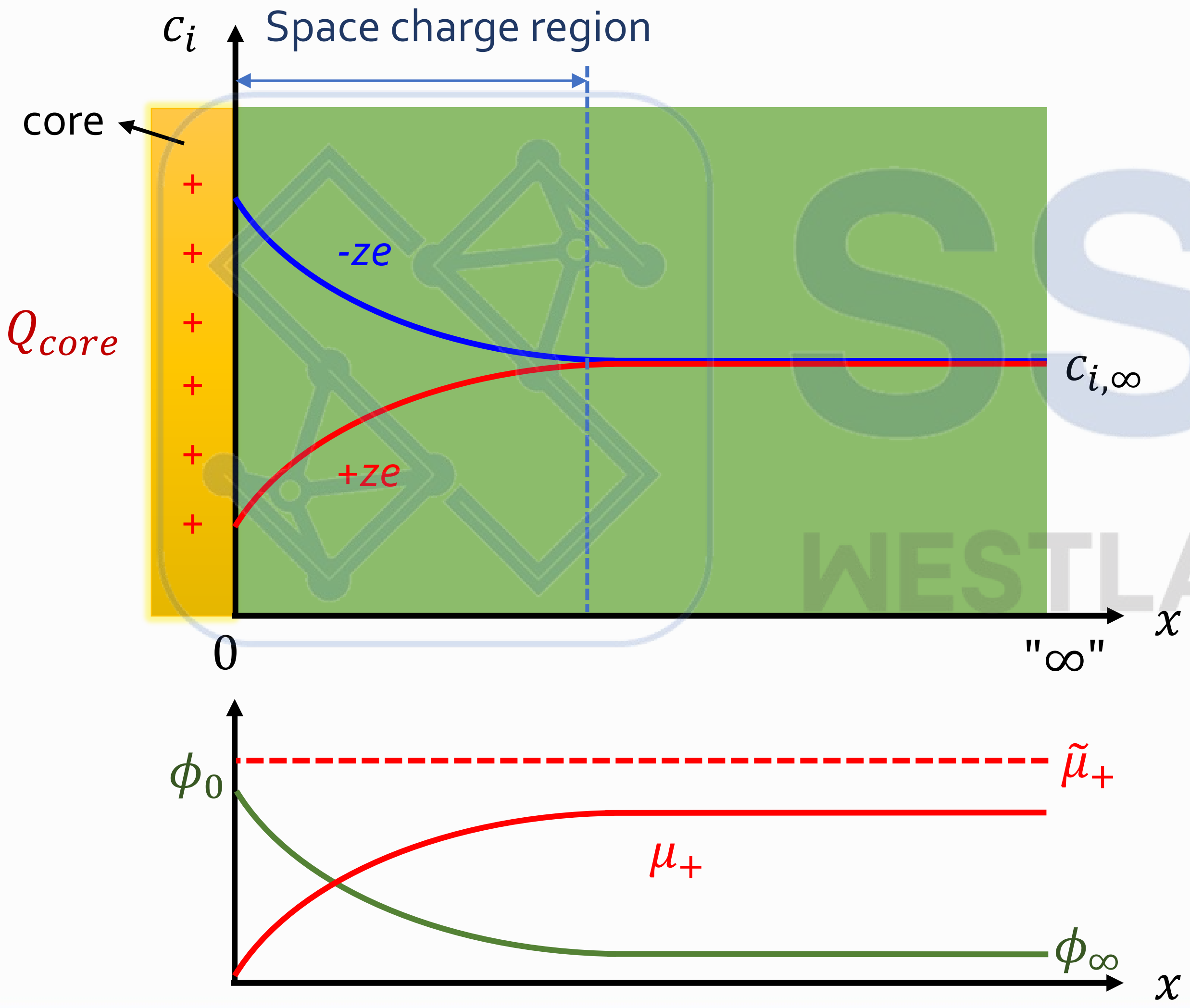
We assume a positively charged core with
$+Q_{core}$ *charge.*
(ignore the details of the space charge core)

Assume that there are only two types of mobile defects, with positive and negative charge of +ze/-ze

In the bulk ("∞") of the solid, *electro-neutrality* applies, we have:

$$c_-(\infty) = c_+(\infty) = c_{i,\infty}$$

Gouy-Chapman case: concentration/potential profile



In the space charge region, the ***electrochemical potential*** of each defects determines the equilibrium:

$$\tilde{\mu}_+(x) = \mu_+(x) + ze\phi(x)$$

$$\tilde{\mu}_-(x) = \mu_-(x) - ze\phi(x)$$

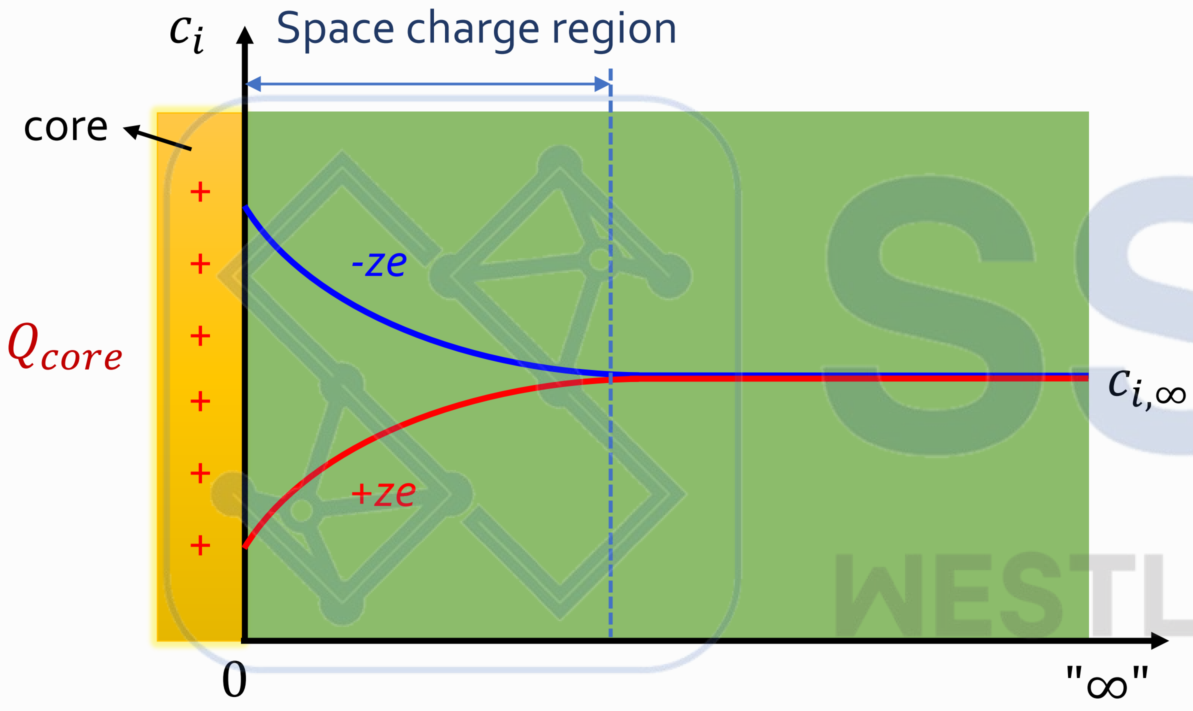
$$\mu_+(x) = \mu_+^0 + k_B T \ln c_+(x)$$

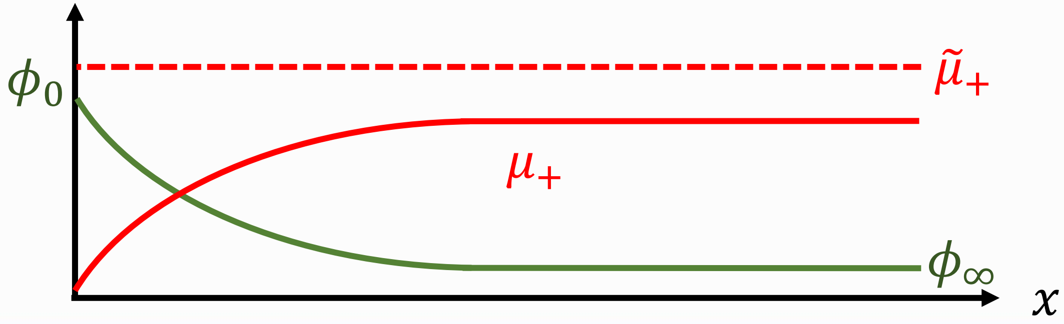
$$c_+(0) = c_+(\infty)\exp(-\frac{ze(\phi_0 - \phi_\infty)}{k_B T})$$

We can set $\phi_\infty = 0$ (reference point), then

$$\frac{c_+(x)}{c_{i,\infty}} = \exp(-\frac{ze\phi(x)}{k_B T})$$

Gouy-Chapman case: concentration/potential profile





$$c_+(x) = c_{i,\infty}\exp\left(-\frac{ze\phi(x)}{k_BT}\right)$$

$$c_-(x) = c_{i,\infty}\exp\left(+\frac{ze\phi(x)}{k_BT}\right)$$

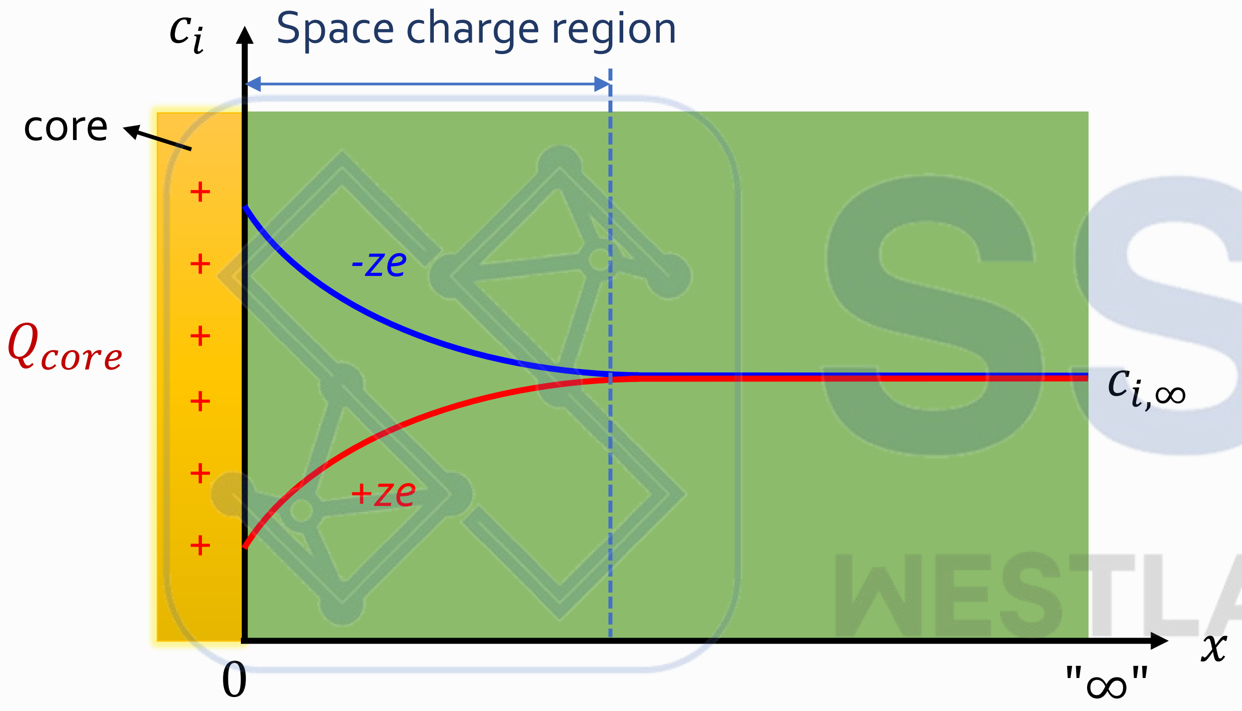
At $x = 0$:

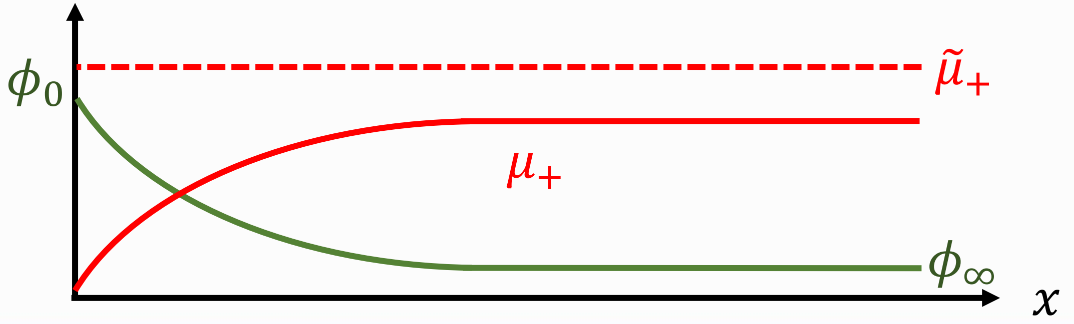
$$\rho(0) = zec_+(0) - zec_-(0) = 2zec_{i,\infty}\sinh\left(-\frac{ze\phi_0}{k_BT}\right)$$

If $ze\phi_0 \ll k_BT$, we can linearize the equation:

$$\rho(0) = -2zec_{i,\infty}\frac{ze\phi_0}{k_BT} \rightarrow \rho(x) = -2zec_{i,\infty}\frac{ze\phi(x)}{k_BT}$$

Gouy-Chapman case: concentration/potential profile





$$\rho(x) = -2zec_{i,\infty}\frac{ze\phi(x)}{k_BT}$$

Apply Poisson's equation:

$$\frac{d^2\phi}{dx^2} = -\frac{\rho(x)}{\varepsilon_0\varepsilon_r} = \frac{2z^2e^2c_{i,\infty}}{\varepsilon_0\varepsilon_r k_BT}\phi(x)$$

We define ***Debye length*** λ_D as:

$$\lambda_D = \sqrt{\frac{\varepsilon_0\varepsilon_r k_BT}{2z_i^2 c_{i,\infty}e^2}}$$

Then we have:

$$\frac{d^2\phi}{dx^2} = \frac{\phi(x)}{\lambda_D{}^2} \rightarrow \phi(x) = \phi_0\exp(-x/\lambda_D)$$

(We set $\phi_\infty = 0$)

Debye length: how wide is the space charge region?

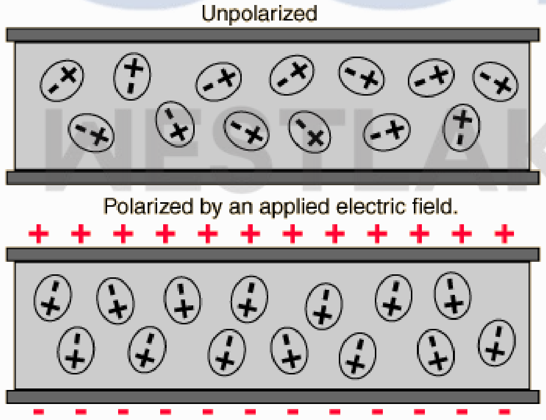
In Gouy-Chapman case, ***Debye length*** λ_D is defined as:

$$\lambda_D = \sqrt{\frac{\varepsilon_0 \varepsilon_r k_B T}{2 z_i^2 c_{i,\infty} e^2}}$$

For z_i^2 = 1, ε_r = 10, T = 300 K:

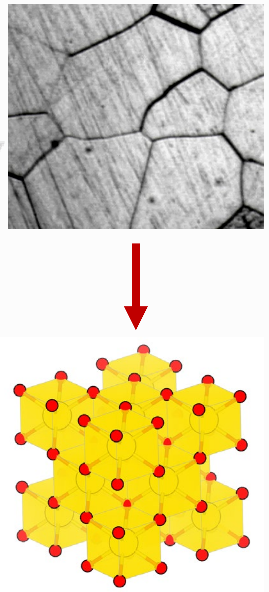
Note: 1. $\varepsilon_0 \varepsilon_r$: dielectric constant (permittivity) strongly affects space charge width

2. $c_{i,\infty}$: charge carrier concentration in the bulk. A higher charge carrier concentration will ***screen*** the core charges more effectively.



http://hyperphysics.phy-astr.gsu.edu/hbase/electric/dielec.html#c1

$c_{i,\infty}$	λ_D
10^{18} cm^{-3} (~1 mM)	~100 nm
10^{20} cm^{-3} (~0.1 mol/L)	~10 nm
10^{22} cm^{-3} (~10 mol/L)	~1 nm



From continuum-level modeling to atomistic scale

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Discrete modeling of ionic space charge zones in solids†

Chuanlian Xiao, Chia-Chin Chen‡ and Joachim Maier*

The discrete model of space charge zones in solids reveals and remedies a variety of problems with the classic continuous Gouy–Chapman solution that occur for pronounced space charge potentials. Besides inherent problems of internal consistency, it is essentially the extremely steep profile close to the interface which makes this continuum approach questionable. Not only is quasi-1D discrete modeling a sensible approach for large space charge effects, it can also favorably be combined with the continuum description. A particularly useful application is the explicit implementation of crystallographic details and non-idealities close to the interface. This enables us to consider elastic, structural or saturation effects as well as permittivity variations in a simple but realistic way. We address details of the charge carrier profiles, but also overall properties such as space charge capacitance and space charge resistance. In the latter case the difference in the total charge (at identical concentration) is of importance, in the first case it is the inherent difference in the centroid of charge (at identical total charge) that is remarkable. The model is equally applicable for ionic charge carriers and small polarons.

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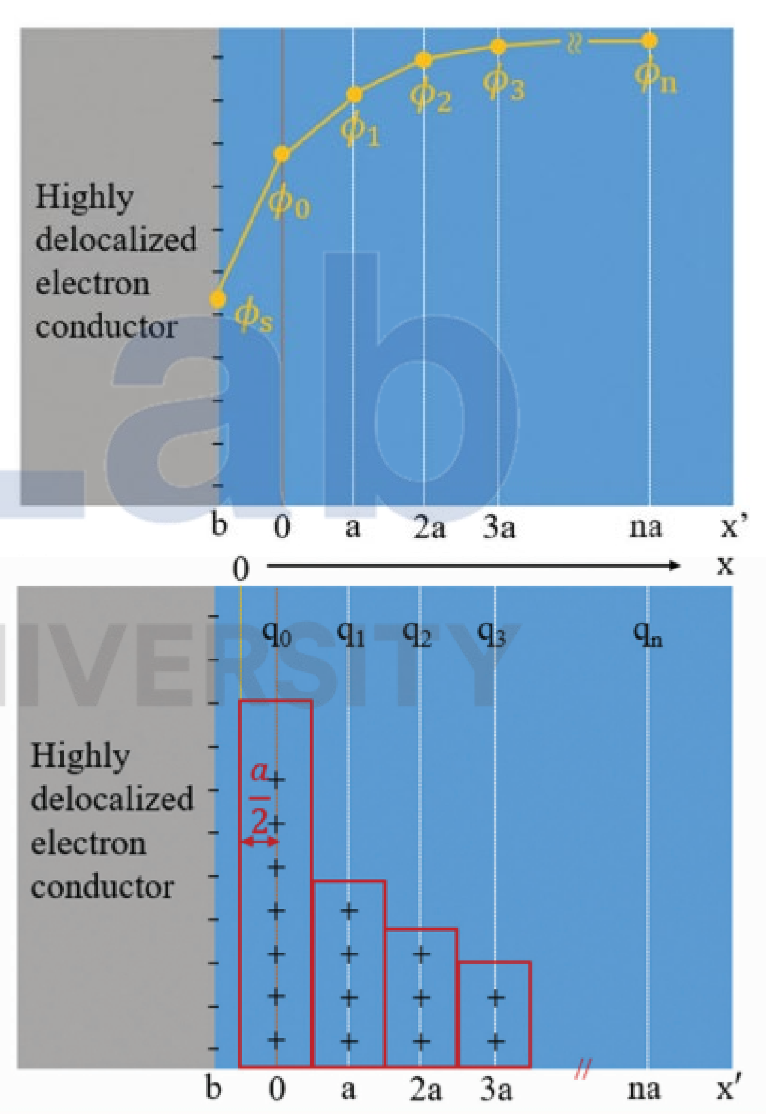
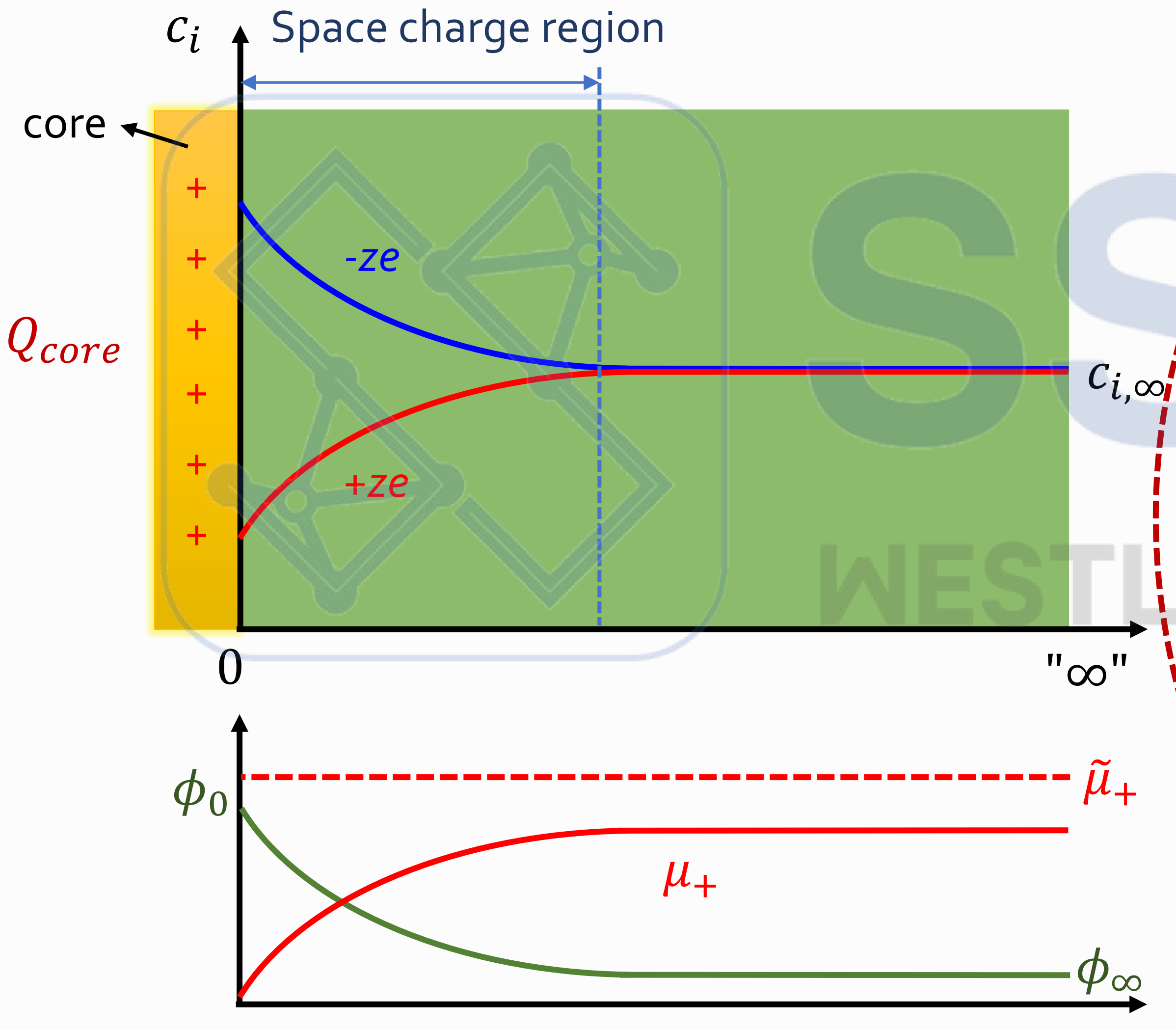


Continuous → Discrete as the λ_D shrinks

Gouy-Chapman case: concentration/potential profile



Electrostatic potential

$$\phi(x) = \phi_0 \exp(-x/\lambda_D)$$

Concentrations

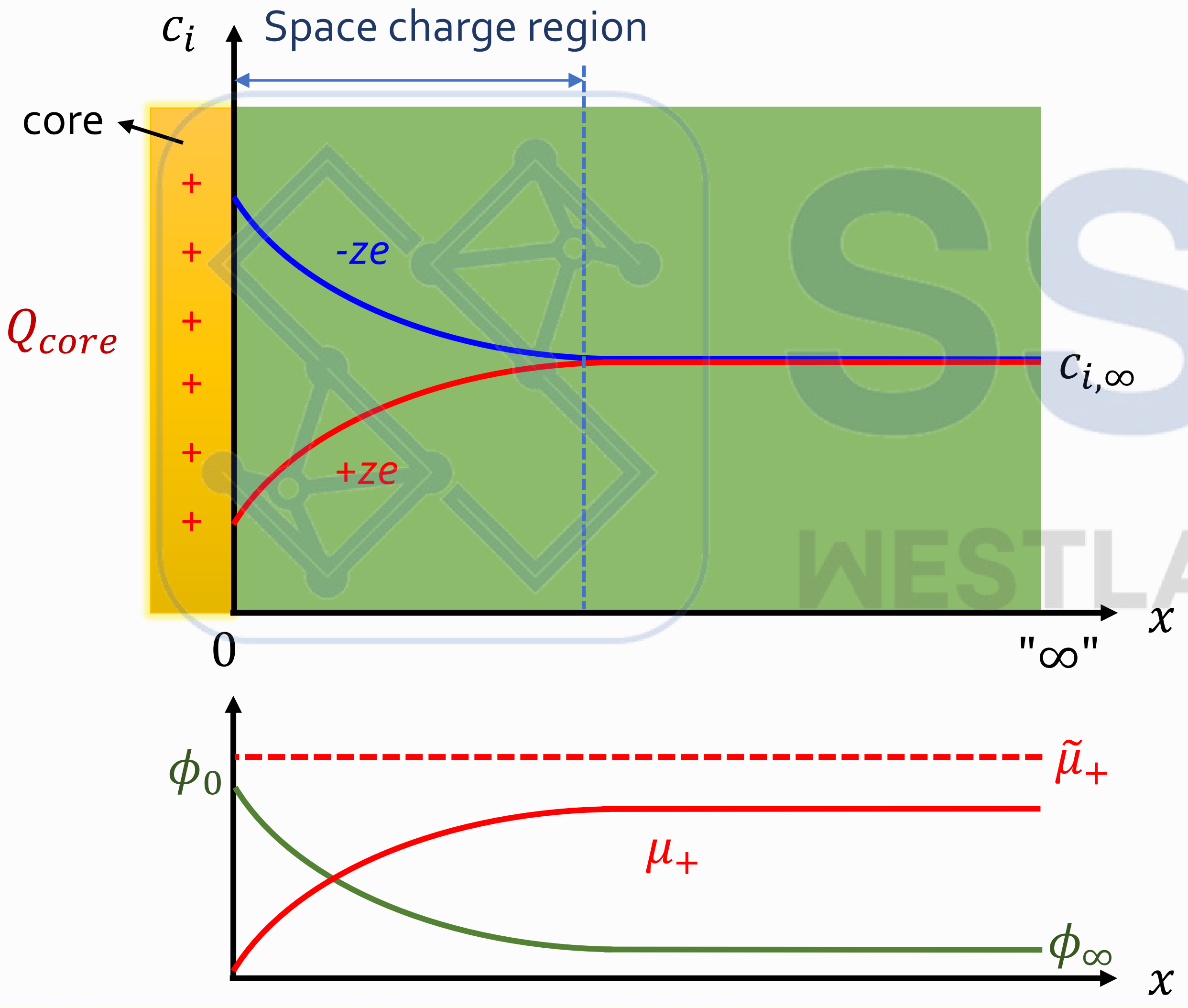
$$c_+(x) \approx c_{i,\infty}\left(1 - \frac{ze\phi(x)}{k_B T}\right) = c_{i,\infty}\left(1 - \frac{ze\phi_0 \exp(-x/\lambda_D)}{k_B T}\right)$$

$$c_-(x) \approx c_{i,\infty} \exp\left(+\frac{ze\phi(x)}{k_B T}\right) = c_{i,\infty}\left(1 + \frac{ze\phi_0 \exp(-x/\lambda_D)}{k_B T}\right)$$

Charge

$$\rho(x) = -\frac{2z^2e^2\phi_0 c_{i,\infty}}{k_B T}\exp(-x/\lambda_D)$$

Gouy-Chapman case: concentration/potential profile



Electrostatic potential: $\phi(x)$

Concentrations:

$$c_+(x) = c_{i,\infty}\exp\left(-\frac{ze\phi(x)}{k_BT}\right)$$

$$c_-(x) = c_{i,\infty}\exp\left(+\frac{ze\phi(x)}{k_BT}\right)$$

Charge:

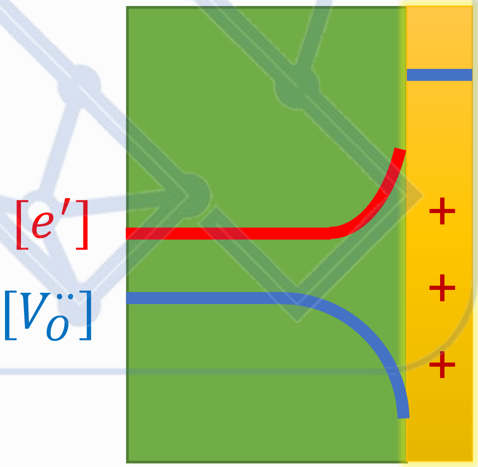
$$\rho(x) = 2zec_{i,\infty}\sinh\left(-\frac{ze\phi(x)}{k_BT}\right)$$

If $ze\phi_0 \sim k_BT$, then we cannot linearize the equations, the solution becomes more complicated.

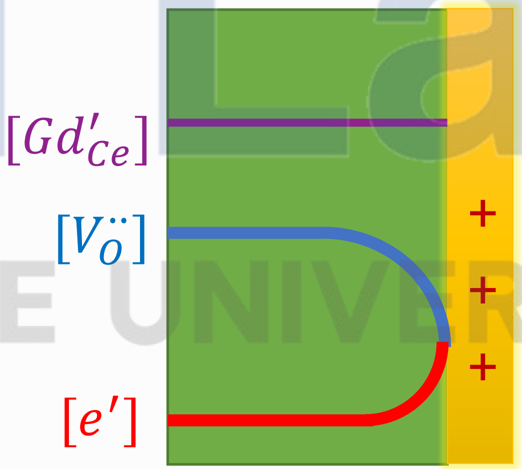
See ***pg.*** 546-550 in Bard & Faulkner *Electrochemical Methods* or ***pg.*** 223-225 in Maier, *Phys. Chem. Of Ionic Materials*.

The complication introduced by immobile dopants

Gouy-Chapman case
(All defects are mobile)

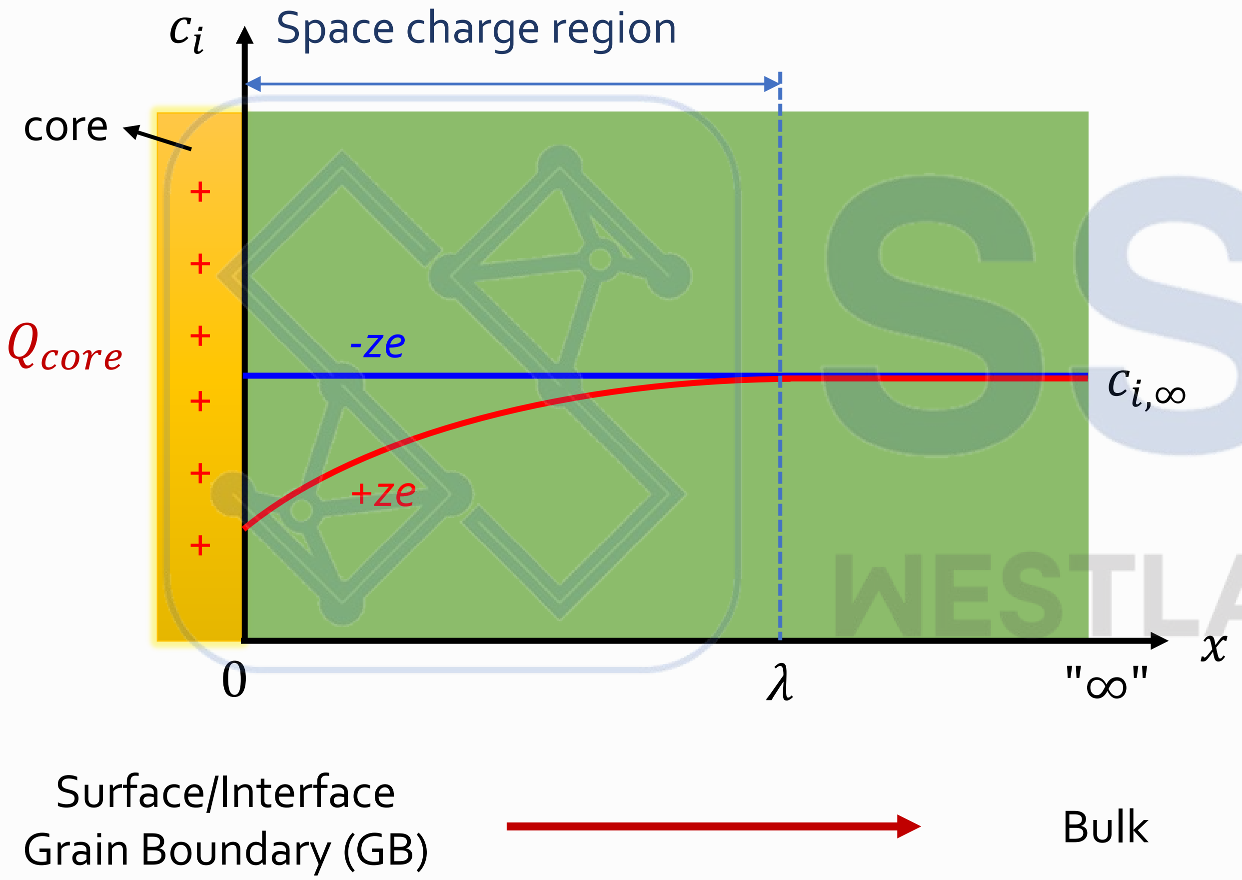


Mott-Schottky case
(Majority dopants are frozen (*immobile*))



Note: We are going to discuss how to solve for the concentration and potential profiles of these two cases in this lecture.

Mott-Schottky case: how to set up the problem?



Intuitively, the space charge region becomes ***thicker*** in Mott-Schottky case due to ***insufficient screening***

Mott-Schottky case → one of the majority charge carrier defects (usually dopants) are immobile (frozen)

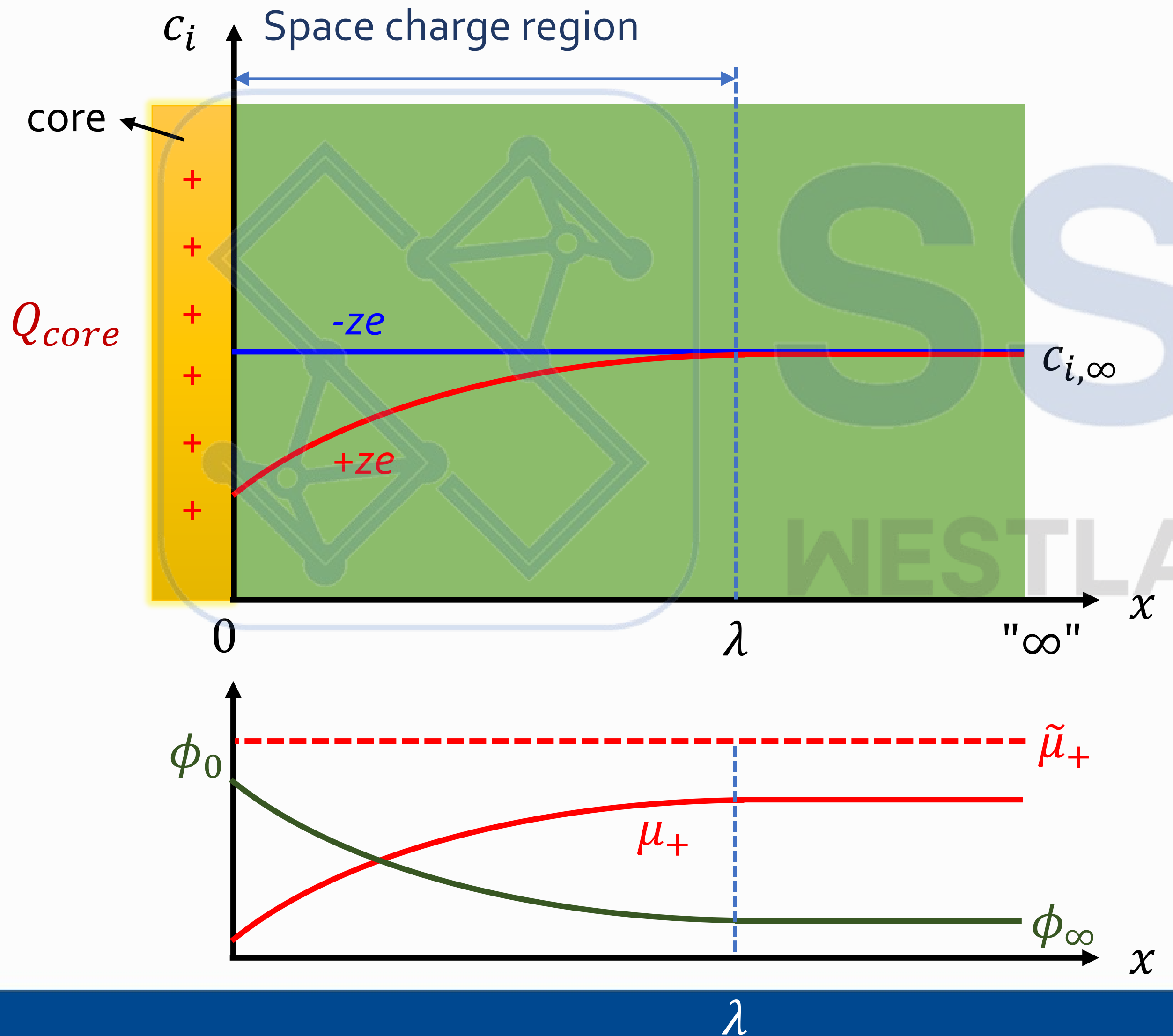
Assume the negatively charged (*-ze*) defects are immobile, while the positively charged defects are mobile (*+ze*)

Ex. 1 in p-n junctions, the dopants at "depletion layer" are frozen, while electrons/holes are mobile.
Ex. 2 in (Sm,Ce)$O_{2-\delta}$ Sm'_{Ce} are immobile while $V_O^{\cdot\cdot}$ are mobile at intermediate temperature.

In the bulk ("∞") of the solid, *electro-neutrality* ***still*** applies, we have:

$$c_-(\infty) = c_+(\infty) = c_{i,\infty}$$

Mott-Schottky case: concentration/potential profile



Since $-ze$ defects are immobile:

$$c_-(x) = c_{i,\infty} \quad (const.)$$

In the space charge region, the screening (negative) charge is mainly provided by the $-ze$ defects, therefore:

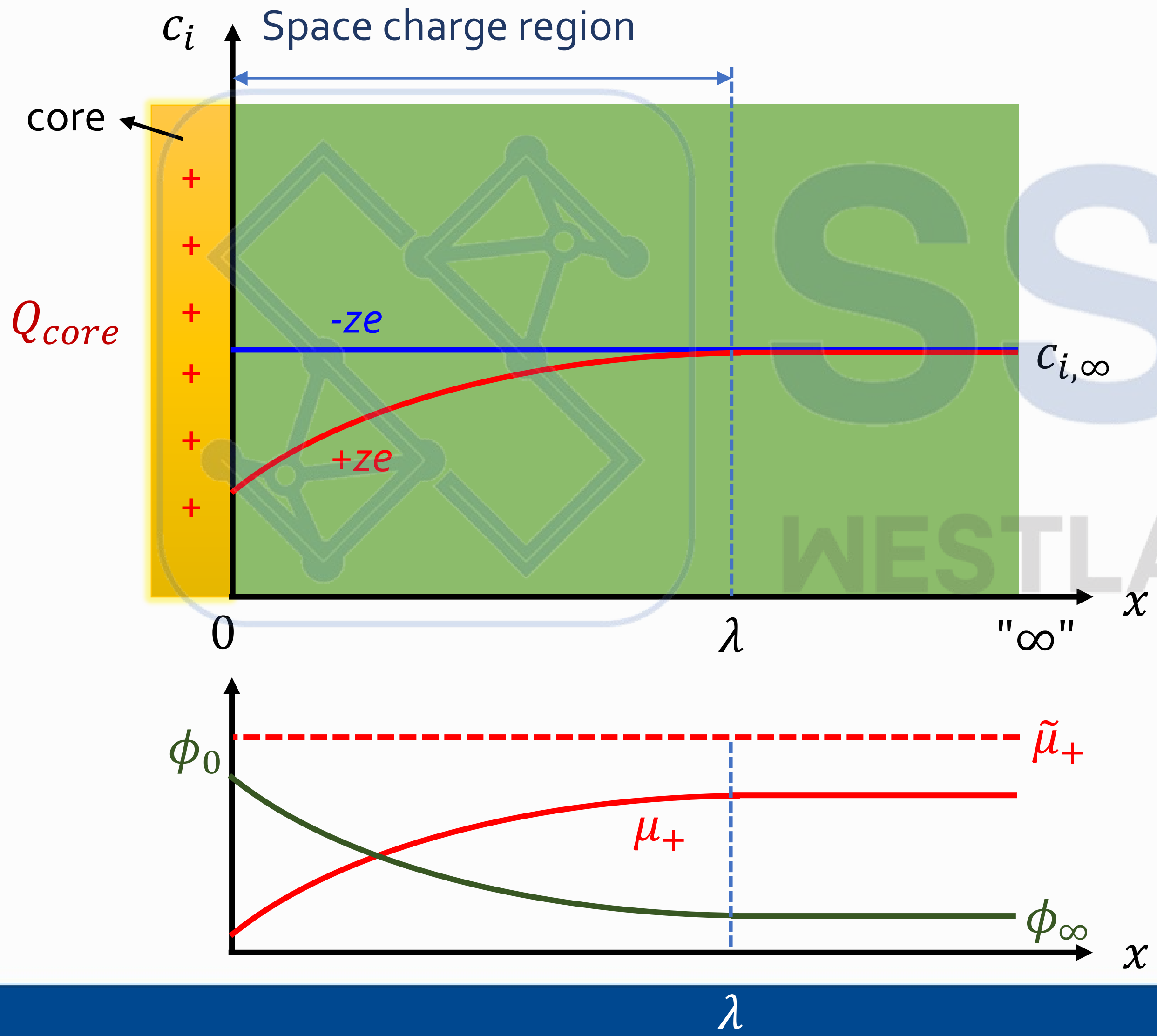
$$\rho(x) \approx -zec_-(x) = -zec_{i,\infty}$$

Apply Poisson's *eqn.*:

$$\frac{d^2\phi}{dx^2} = -\frac{\rho(x)}{\varepsilon_0\varepsilon_r} = \frac{zec_{i,\infty}}{\varepsilon_0\varepsilon_r}$$

const.

Mott-Schottky case: concentration/potential profile



Poisson's *eqn.*

$$\frac{d^2\phi}{dx^2} = -\frac{\rho(x)}{\varepsilon_0\varepsilon_r} = \frac{zec_{i,\infty}}{\varepsilon_0\varepsilon_r}$$

We need to integrate ***twice*** to get the potential profile.

Boundary conditions are:

$$\phi(0) = \phi_0 \;\&\; \phi(\lambda) = \phi_\infty = 0$$

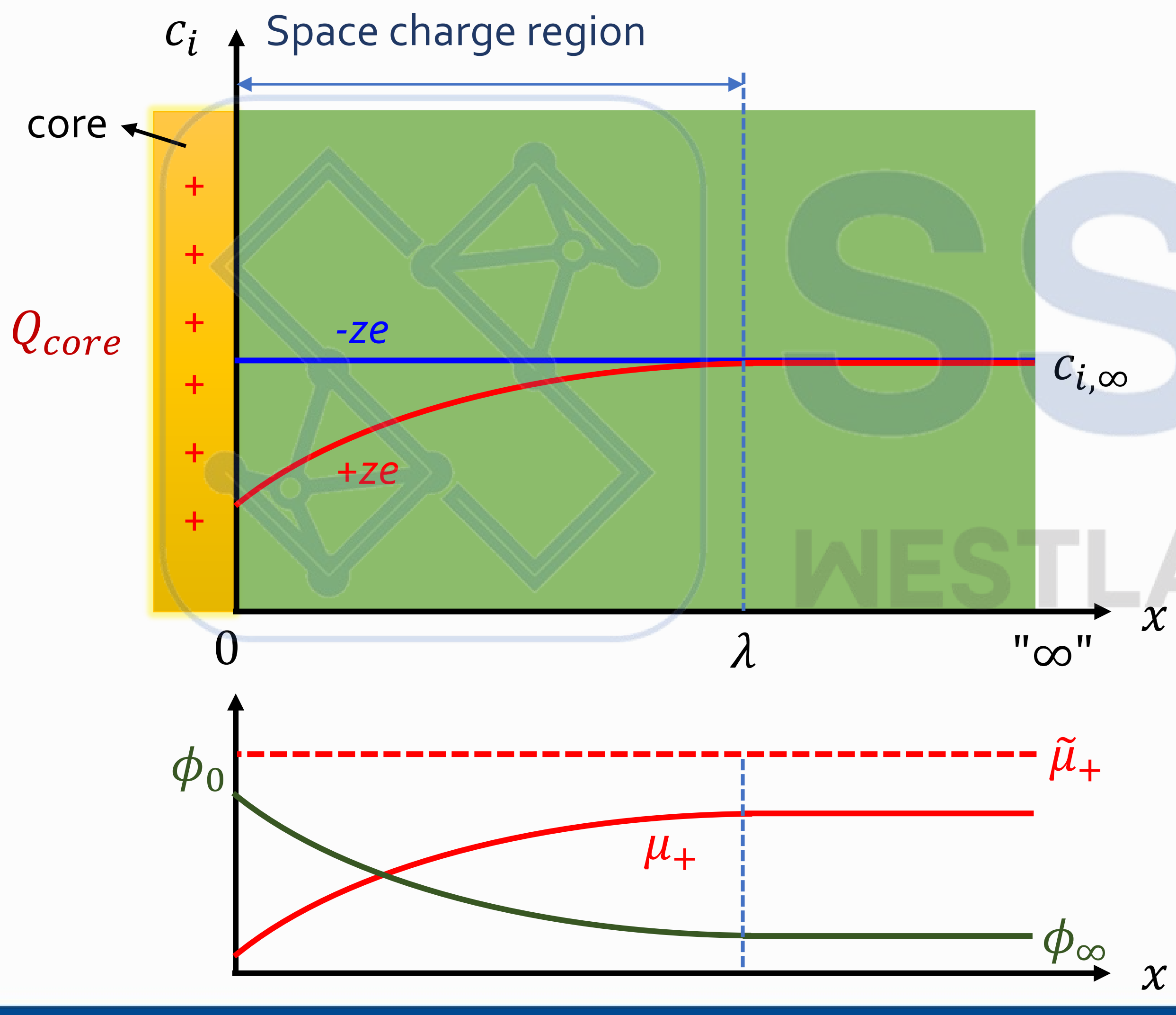
$$\phi'(\lambda) = 0$$

$$\phi'(x) = \frac{zec_{i,\infty}}{\varepsilon_0\varepsilon_r}(x-\lambda)$$

$$\phi\,(x) = \frac{zec_{i,\infty}}{2\varepsilon_0\varepsilon_r}(x-\lambda)^2$$

$$\lambda = \sqrt{\frac{2\varepsilon_0\varepsilon_r\phi_0}{zec_{i,\infty}}}$$

Mott-Schottky case: how to set up the problem?



$$\phi(x) = \frac{zec_{i,\infty}}{2\varepsilon_0\varepsilon_r}(x-\lambda)^2, \lambda = \sqrt{\frac{2\varepsilon_0\varepsilon_r\phi_0}{zec_{i,\infty}}}$$

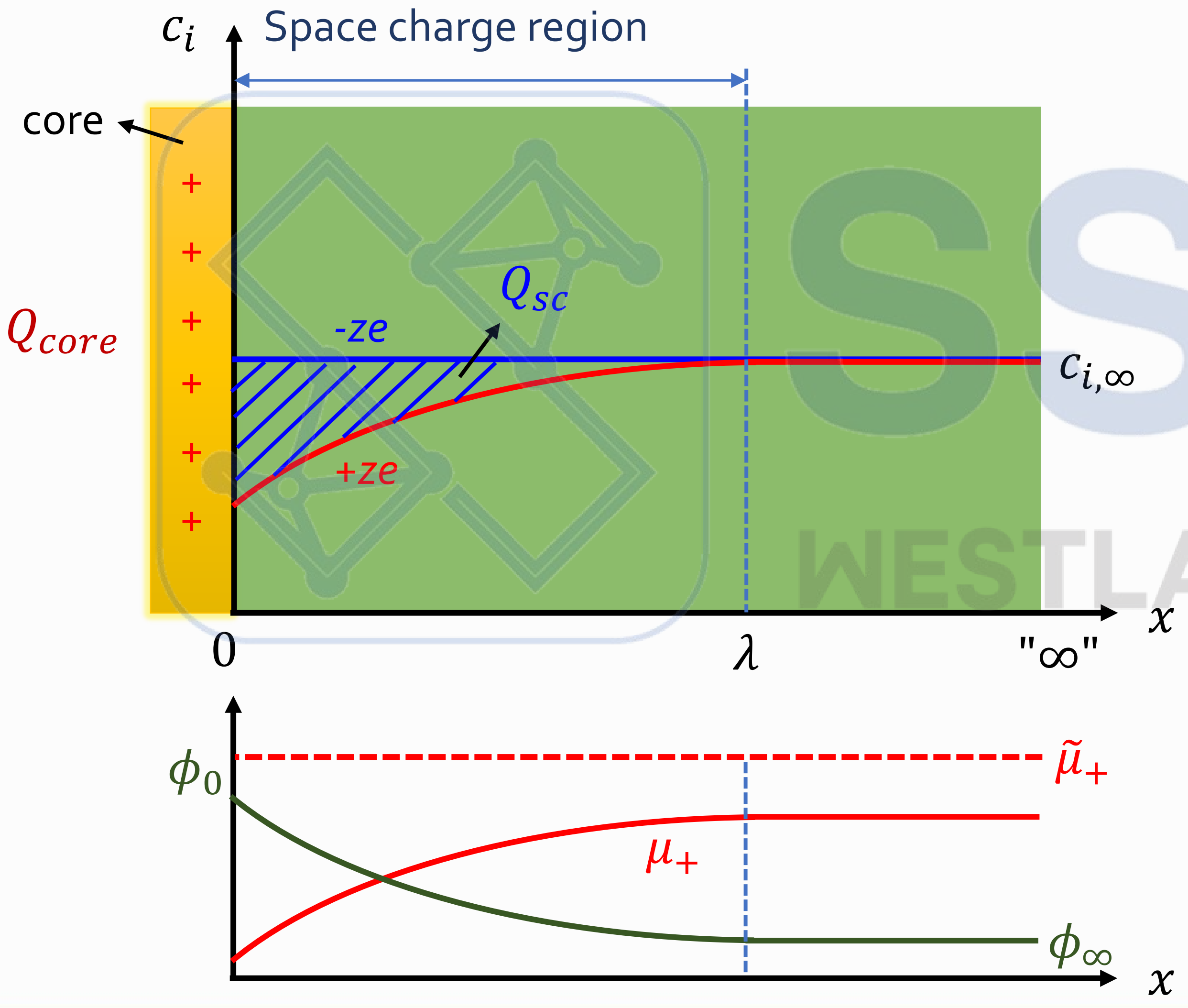
This solution only applies *within* the space charge region.

$$\phi(x) = \begin{cases} \phi_0(\frac{x}{\lambda}-1)^2 & 0 < x \le \lambda \\ 0 & x > \lambda \end{cases}$$

$$\lambda = \sqrt{\frac{2\varepsilon_0\varepsilon_r\phi_0}{zec_{i,\infty}}}$$

$$\frac{c_+(x)}{c_{i,\infty}} = \exp(-\frac{ze\phi_0}{k_BT}(\frac{x}{\lambda}-1)^2) \ (0 < x \le \lambda)$$

Mott-Schottky case: total charges in space charge region



If we think about the whole sample (***core*** + ***space charge region*** + ***bulk***), the charge neutrality condition should still apply.

Therefore, we have:

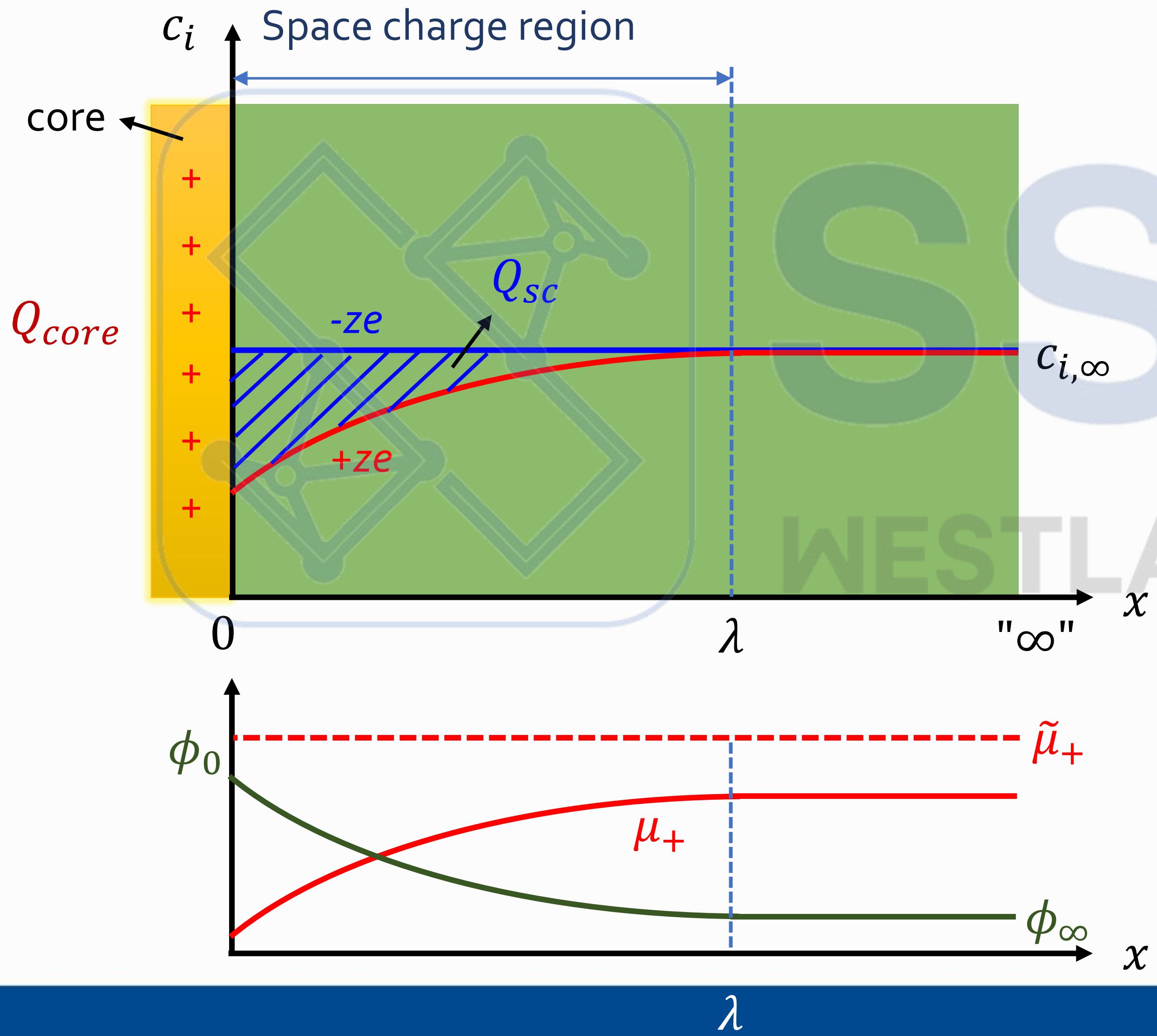
$$Q_{core} = -Q_{sc} \approx zec_{i,\infty}\lambda$$

In other words, if we know the core charge Q_{core}, then we can predict the width of the space charge region λ:

$$\lambda = \frac{Q_{core}}{zec_{i,\infty}}$$

We can further calculate ϕ_0 using: $\lambda = \sqrt{\dfrac{2\varepsilon_0\varepsilon_r\phi_0}{zec_{i,\infty}}}$

Mott-Schottky case: Gauss's Law



We can reach the same conclusion by applying 1-D Gauss's Law:

Electric field ← $E = \dfrac{Q_{enc}}{\varepsilon_0 \varepsilon_r}$ → *"enclosed charge"*

At position $x = 0$:

$$\phi(x) = \phi_0\left(\frac{x}{\lambda} - 1\right)^2$$

↓

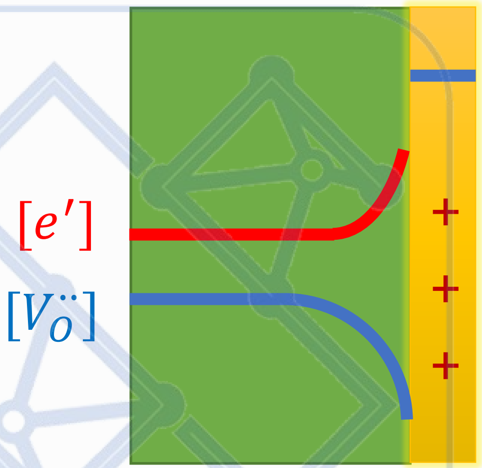
$$E(x) = -\frac{d\phi}{dx} = -\frac{2\phi_0}{\lambda}\left(\frac{x}{\lambda} - 1\right)$$

↓

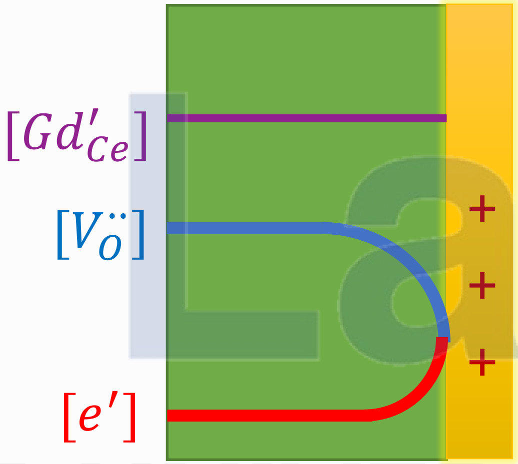
$$E(0) = \frac{2\phi_0}{\lambda} = \frac{Q_{core}}{\varepsilon_0 \varepsilon_r} \qquad \lambda = \sqrt{\frac{2\varepsilon_0 \varepsilon_r \phi_0}{zec_{i,\infty}}}$$

Compare Gouy-Chapman and Mott Schottky cases

Gouy-Chapman case
(All defects are mobile)



Mott-Schottky case
(Majority dopants are frozen (*immobile*))



Space charge layer (SCL) width

$$\lambda_D = \sqrt{\frac{\varepsilon_0 \varepsilon_r k_B T}{2 z_i^2 c_{i,\infty} e^2}}$$

$$\lambda = \sqrt{\frac{2\varepsilon_0 \varepsilon_r \phi_0}{z e c_{i,\infty}}}$$ or $$\lambda = \frac{Q_{core}}{z e c_{i,\infty}}$$

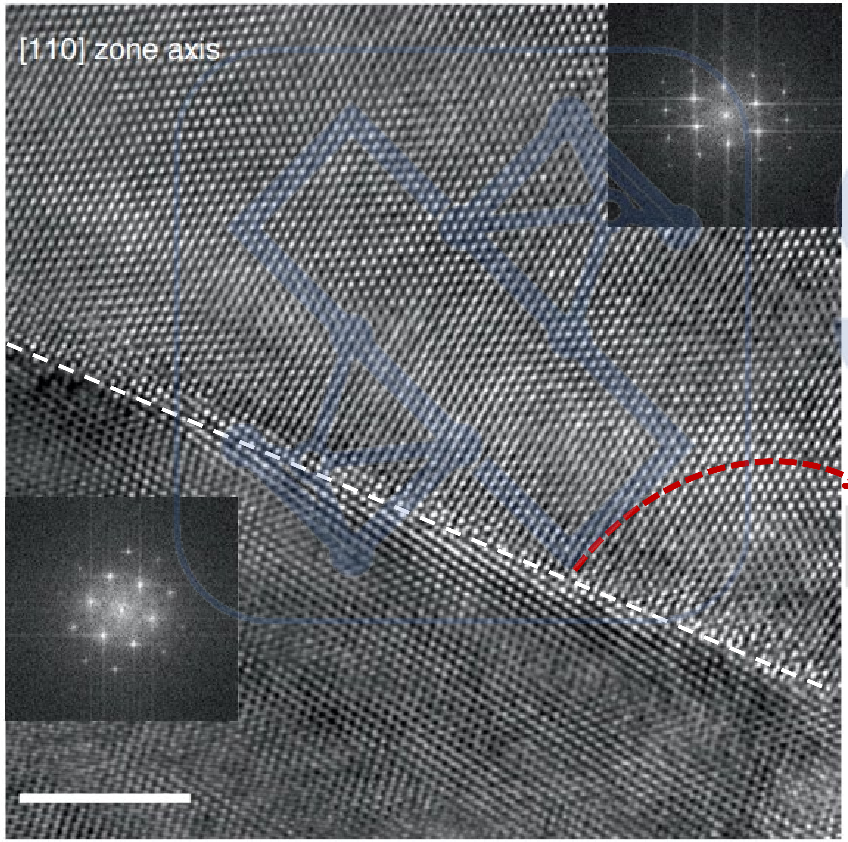
Independent on the core charge Q_{core}

Dependent on the core charge Q_{core}

In both cases, a higher bulk concentration $c_{i,\infty}$ → shorter SCL width (*faster screening*)

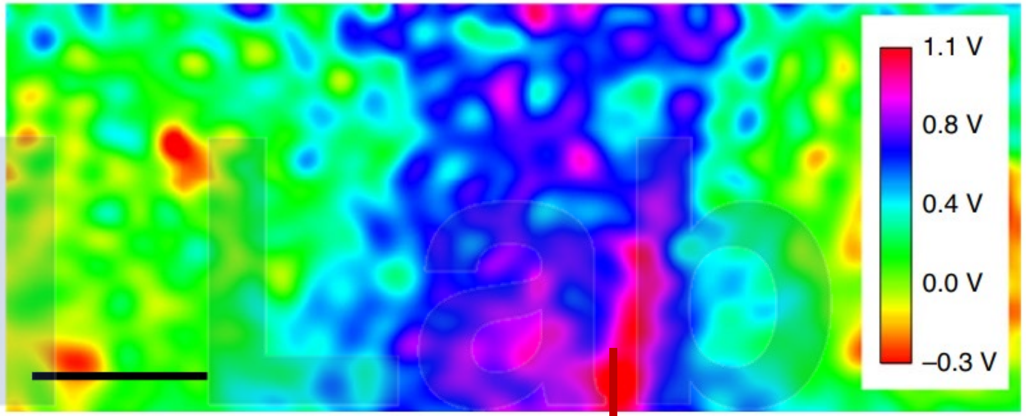
Can we see the potential profile in the real space?

0.2% at. Sm-doped $CeO_{2-\delta}$

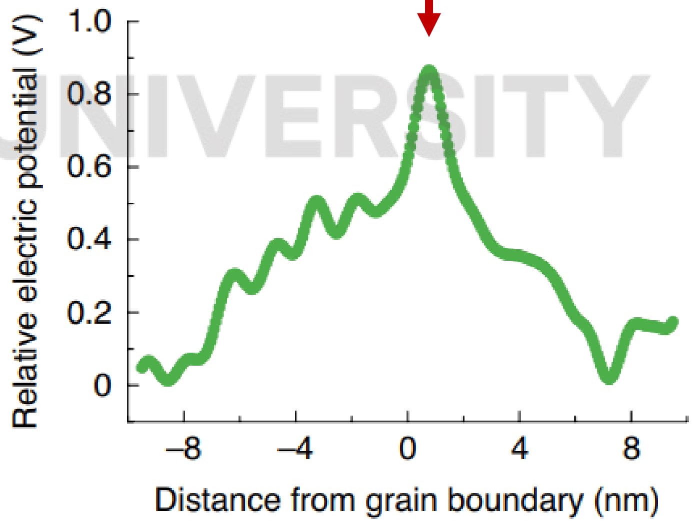


Grain boundary (GB) "core"

Electron holography in TEM



$\phi(x)$



Things we have discussed in this lecture

Space charge layers:

- What is the physical picture and assumptions of the space charge layer theory?
- What are the difference between the Gouy-Chapman and Mott-Schottky cases?
- How to model the distribution of ionic/electronic defects in the space charge layers?
- What are the effects of space charge layers on the conductivity of bulk (poly-crystalline)materials?

Goal of this lecture: you should be able to answer the questions above now (hopefully) :)

End of Lecture 6-7

Solid State Ionics Fall 2022

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