Lecture 4:
Microscopic Picture of Ion Transport

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Fall 2023 MSE 5007
Solid State Ionics

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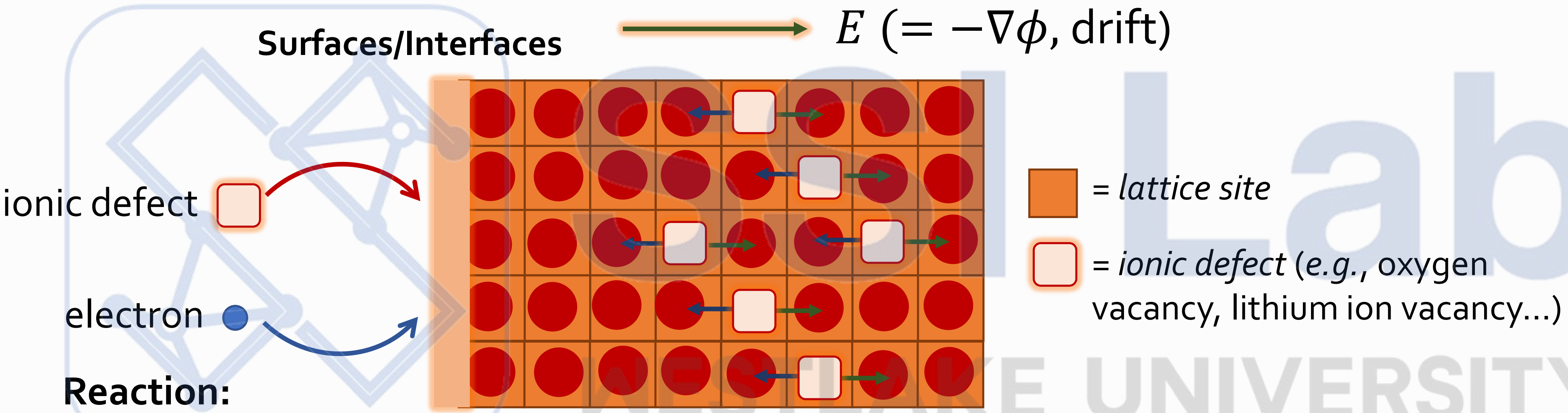
Diffusion and reactions in solid states w/ the picture of ionic defects



Reaction:
concerted ion & electron incorporation

Ion motion: *drift* + *diffusion*
(similar to electrons/holes in semiconductor physics)

Things we will discuss in this lecture

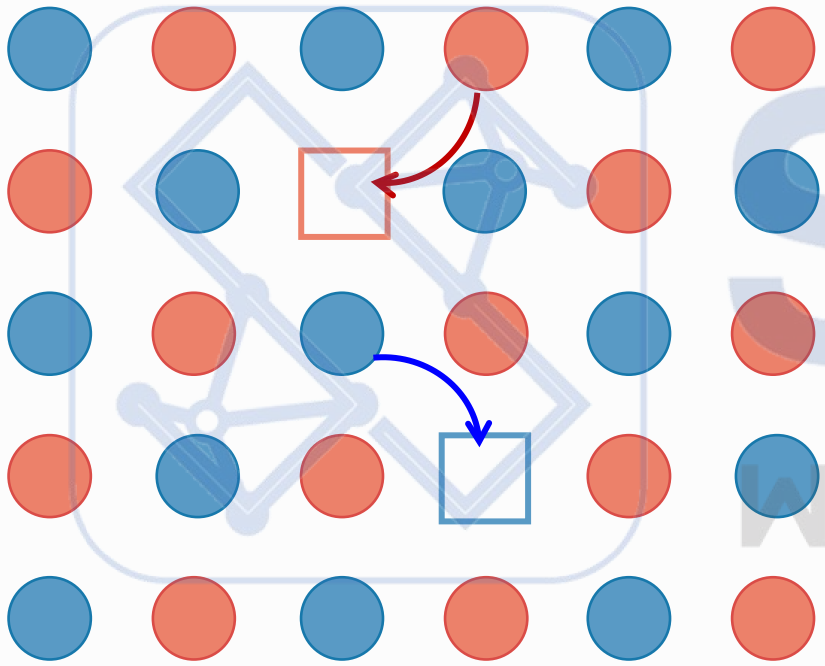
Microscopic picture of ion transport:

- What are the microscopic mechanisms for ionic migration based on the type of ionic defects?
- How to derive the Fick's law from the microscopic picture of ion migration?
- How to reach the Nernst-Einstein relation (correlating the diffusivity and the mobility) from the microscopic picture of ion transport?

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

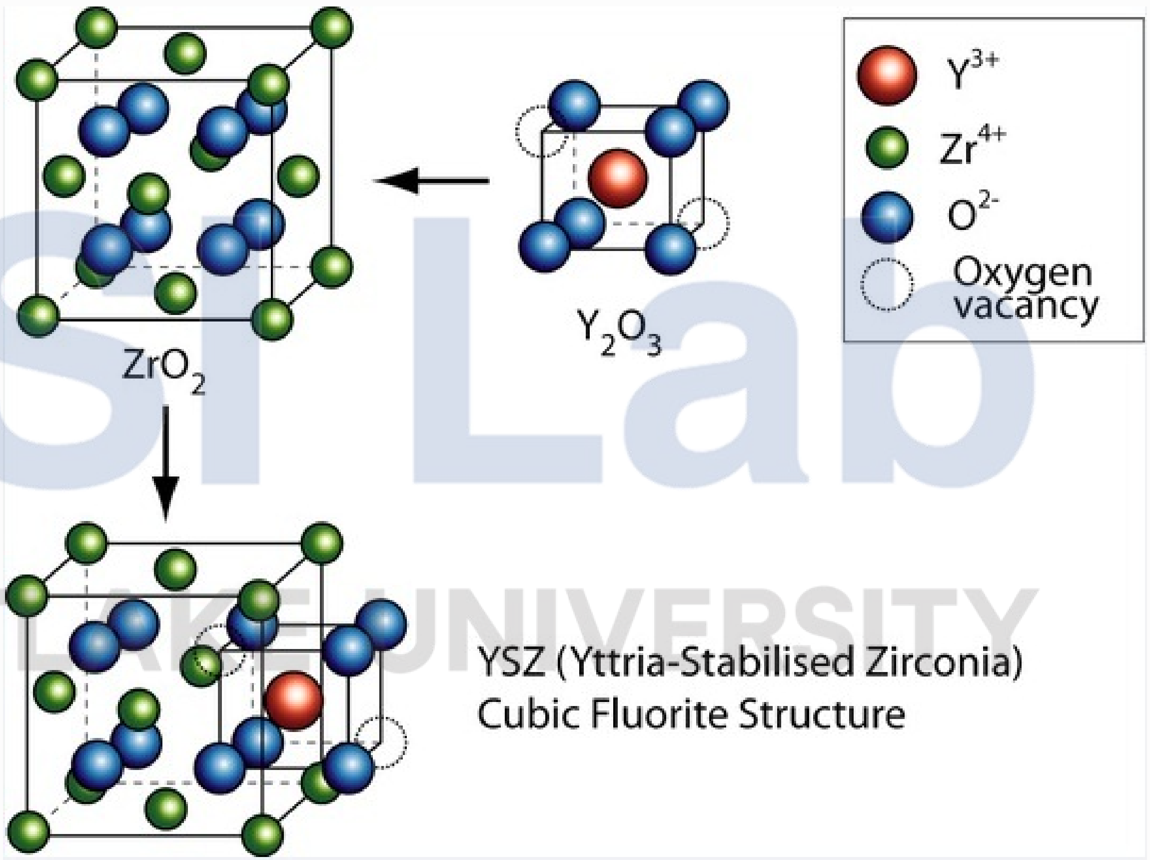
Mechanisms of ionic defect migration in crystals

Vacancy mechanism



Cation
(*e.g.*, Ni^{2+})

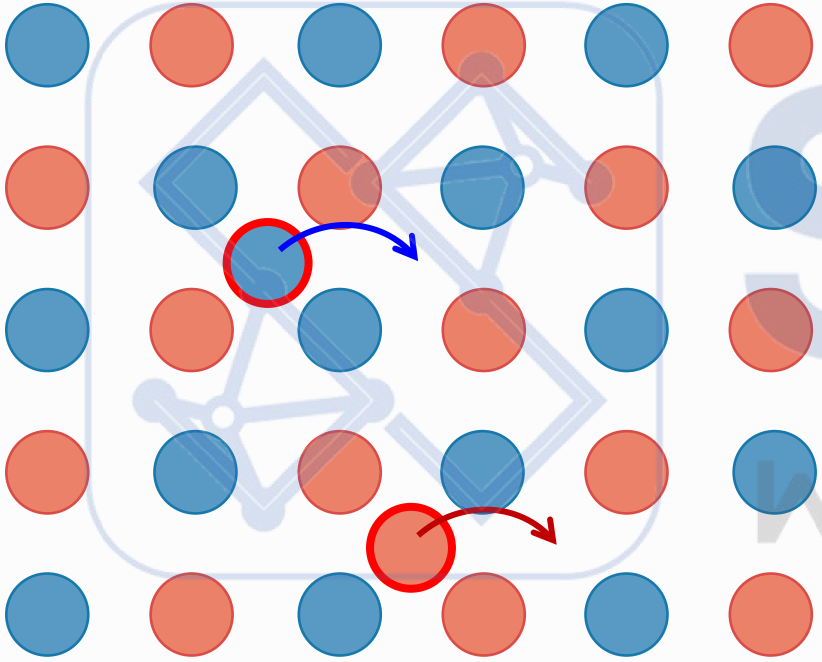
Anion
(*e.g.*, O^{2-})



***Ionic defects** are needed for ion migration in crystals.*

Mechanisms of ionic defect migration in crystals

Interstitial mechanism

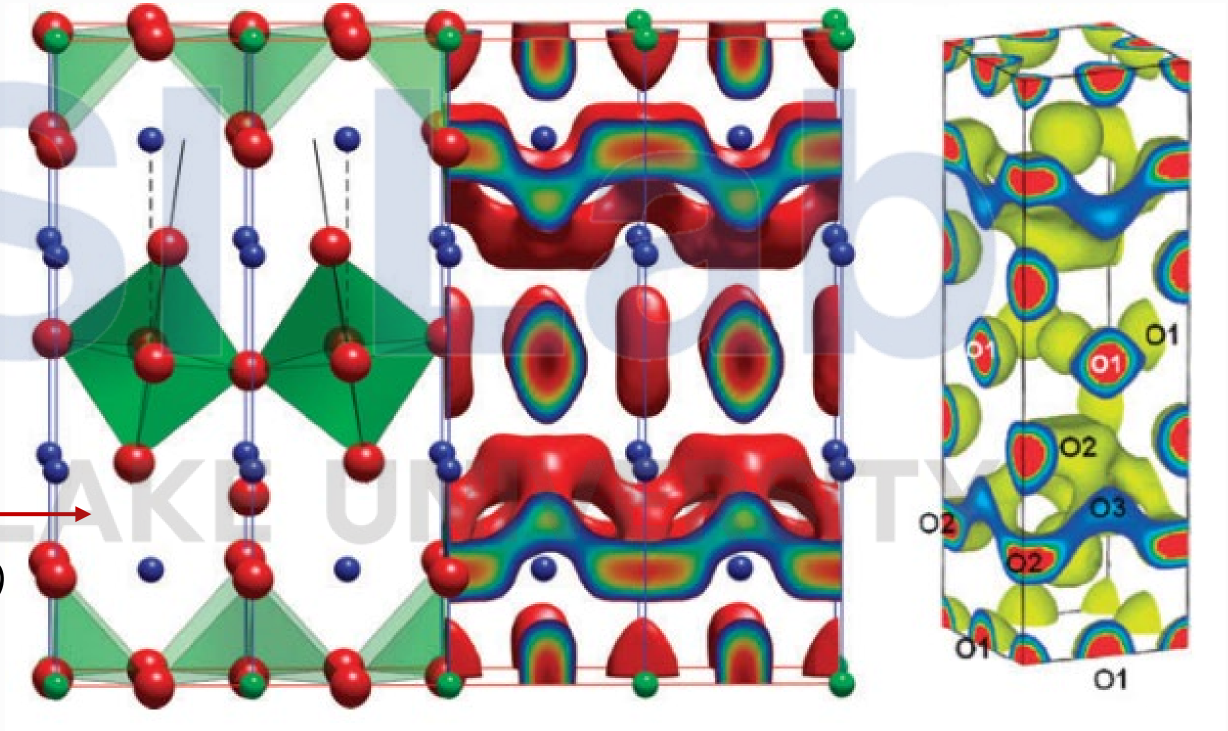


Cation
(*e.g.*, Ni^{2+})

Anion
(*e.g.*, O^{2-})

$Pr_2NiO_{4+\delta}$

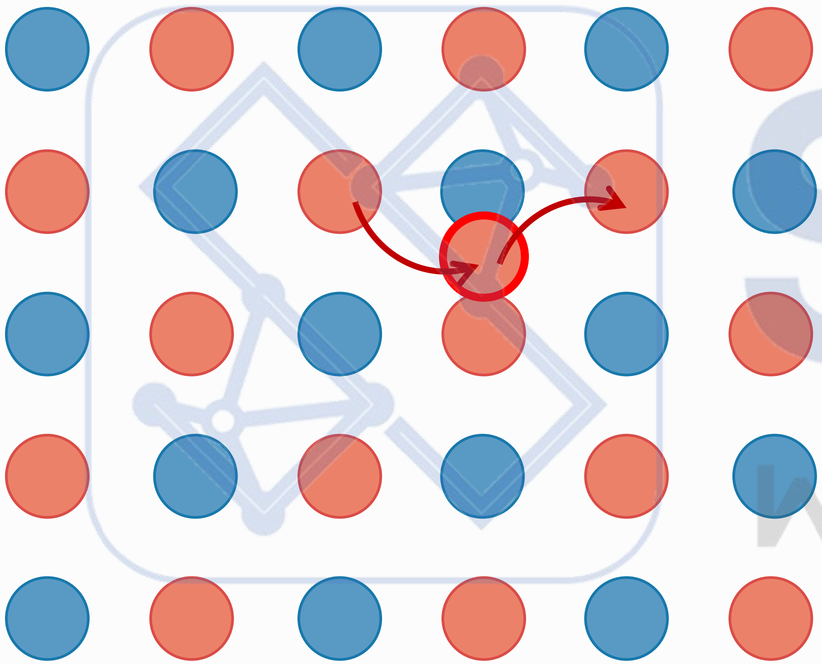
extra oxide ions (interstitials)



Parfitt *et al.*, ***PCCP***, 2010

Mechanisms of ionic defect migration in crystals

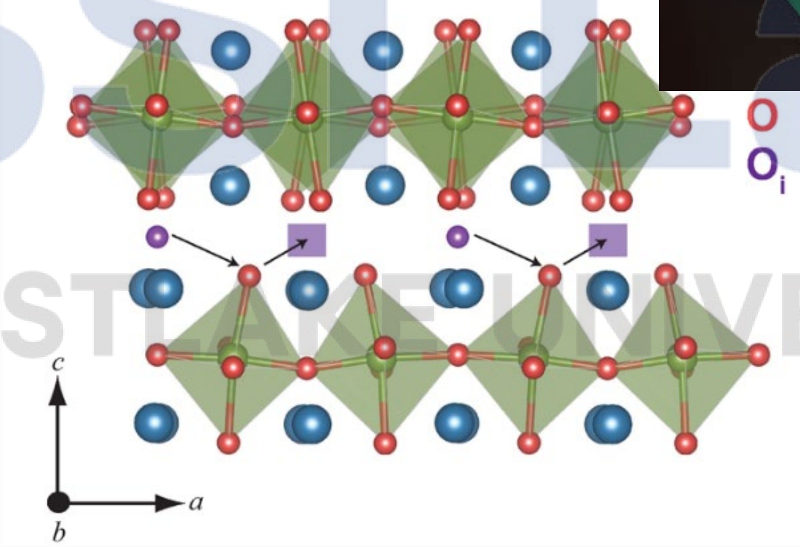
Interstitialcy mechanism

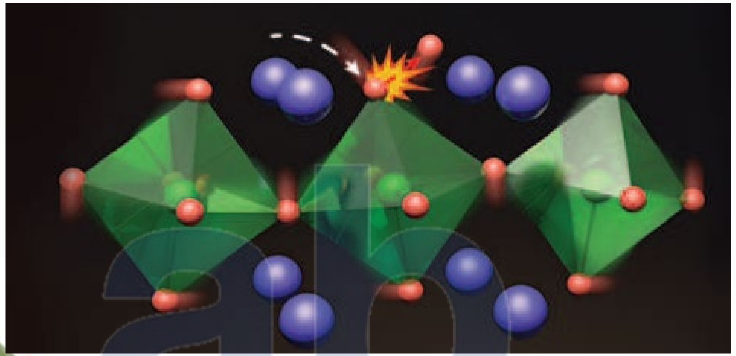


Cation
($e.g.$, Ni^{2+})

Anion
($e.g.$, O^{2-})

$Ln_2NiO_{4+\delta}$
Ln = Pr, Nd, La ...



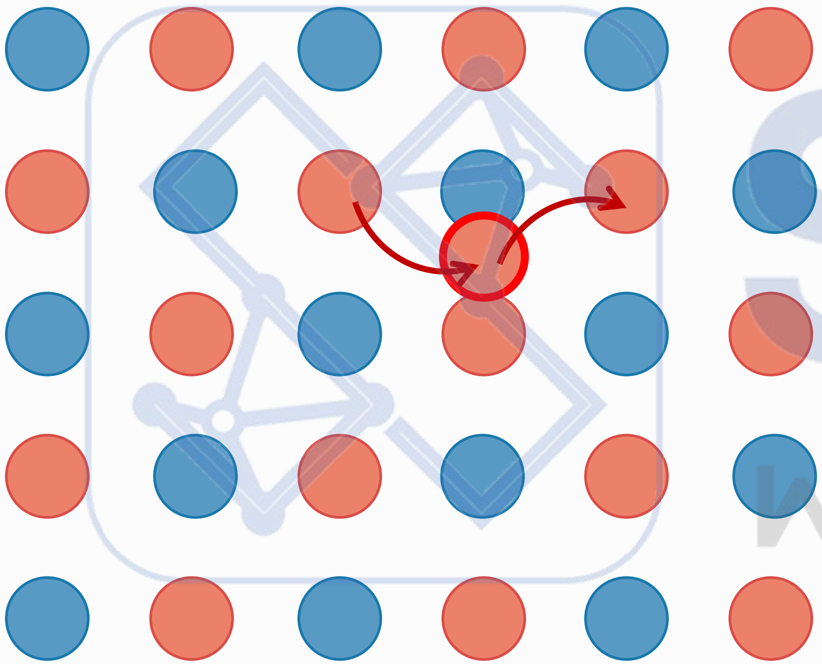


Oxide ion transport through ***"concerted motion"*** of multiple ions/ionic defects.

Li & Benedek, ***Chem. Mater.***, 2015

Mechanisms of ionic defect migration in crystals

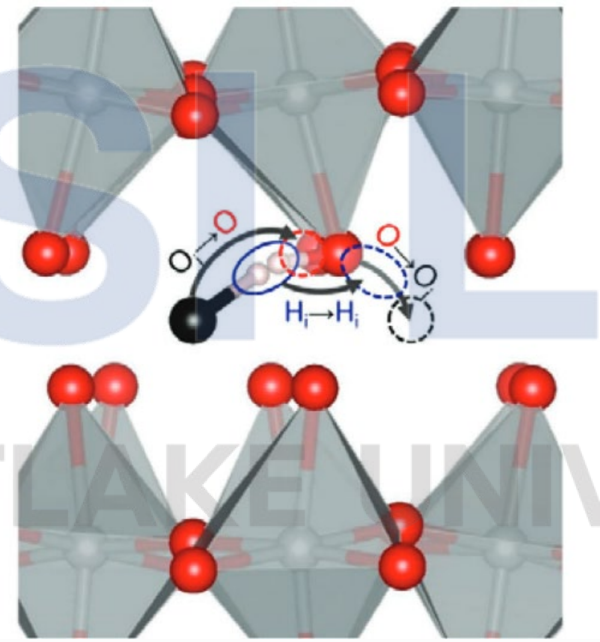
Interstitialcy mechanism



Cation
(*e.g.*, Ni^{2+})

Anion
(*e.g.*, O^{2-})

$La_2NiO_{4+\delta}$ *w/ protons*



Zhong, Norby, Han *et al.*, ***Adv. Energy Mater.***, 2022

Protons forms "-OH" group with oxygen interstitials.

Cooperative proton-oxide ion transport via interstitialcy mechanism.

Protons on lattice oxygen site → $OH_O^{\bullet}$

Protons on oxygen interstitial → OH_i'

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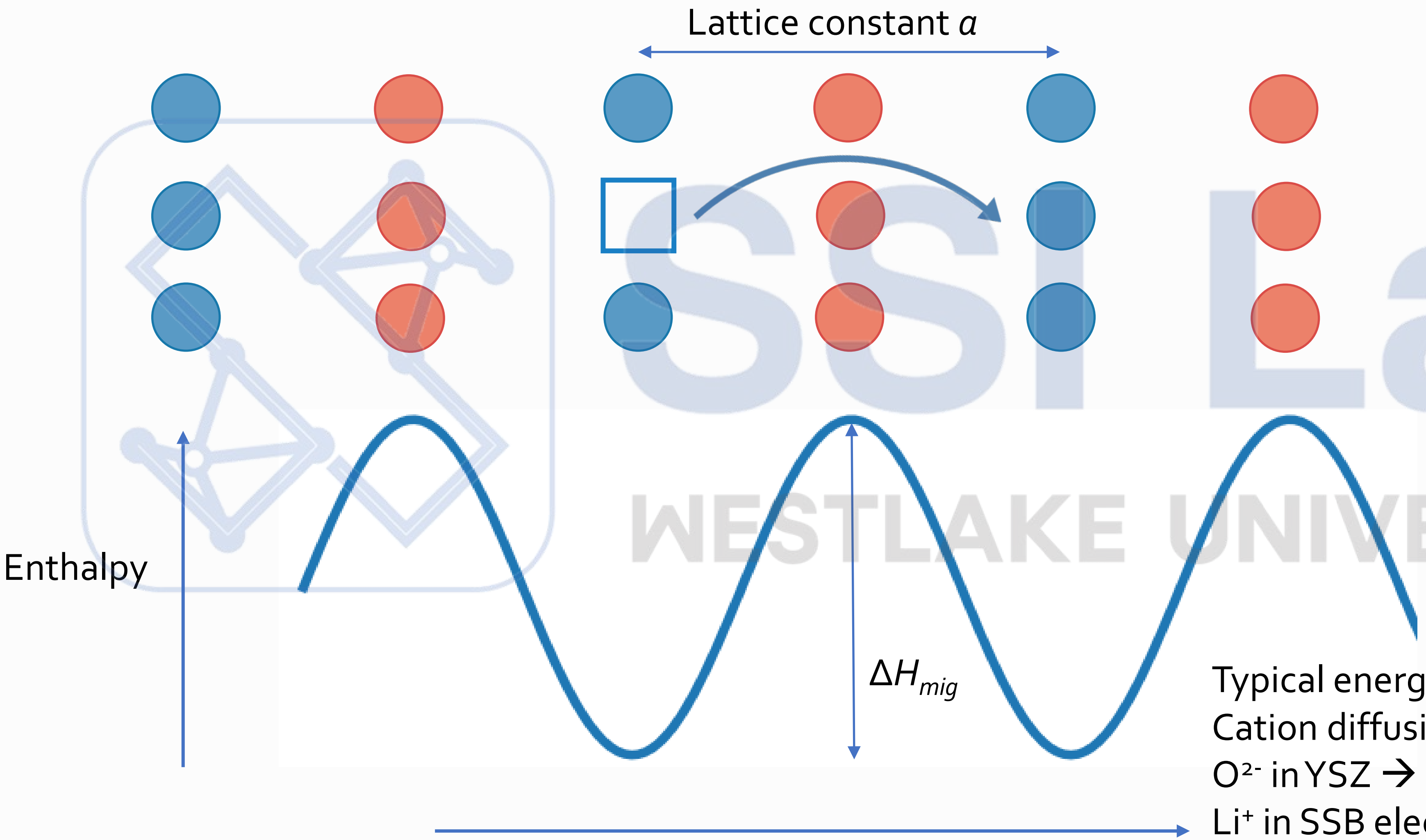
Ion migration and energy barriers



Typical energy barriers:

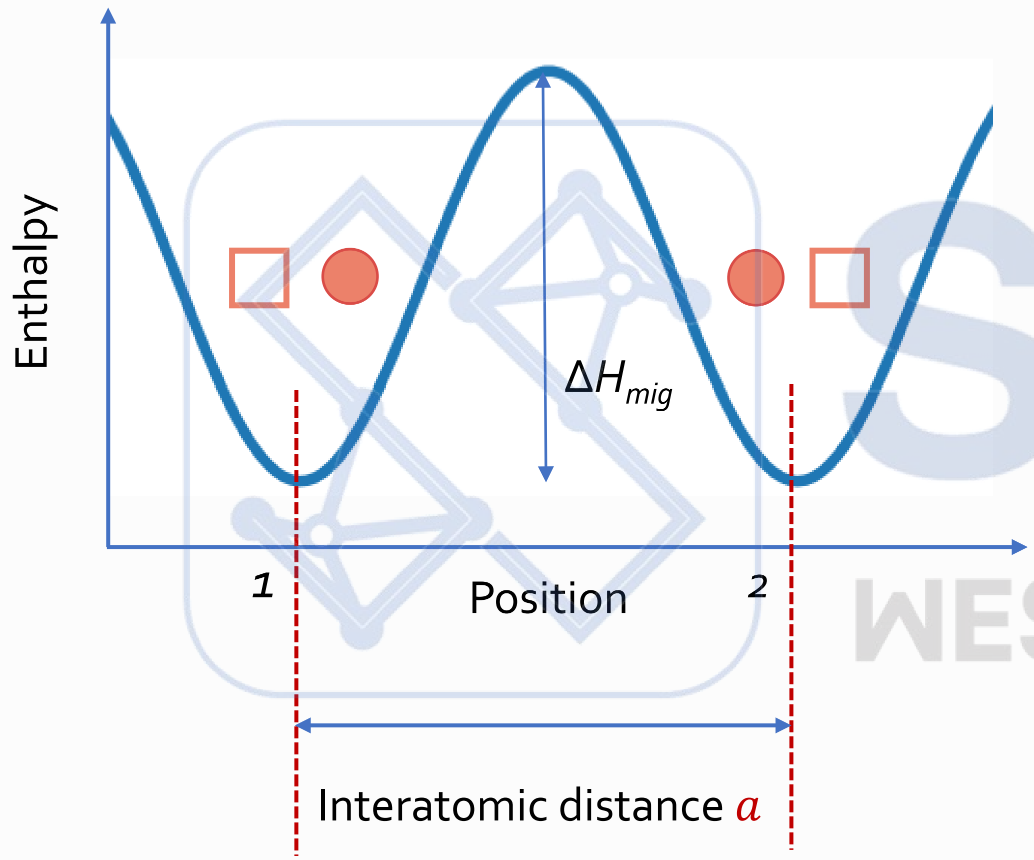
Cation diffusion in metal oxides → ~5-10 eV

O^{2-} in YSZ → ~ 1 eV

Li^{+} in SSB electrolyte → ~ 0.2 eV

k_BT *at RT* → 26 meV

Hop frequency, attempt frequency and mean free time



$$\Gamma = \nu \exp(-\frac{\Delta H_{mig}}{k_B T})$$

Hop frequency

Attempt frequency

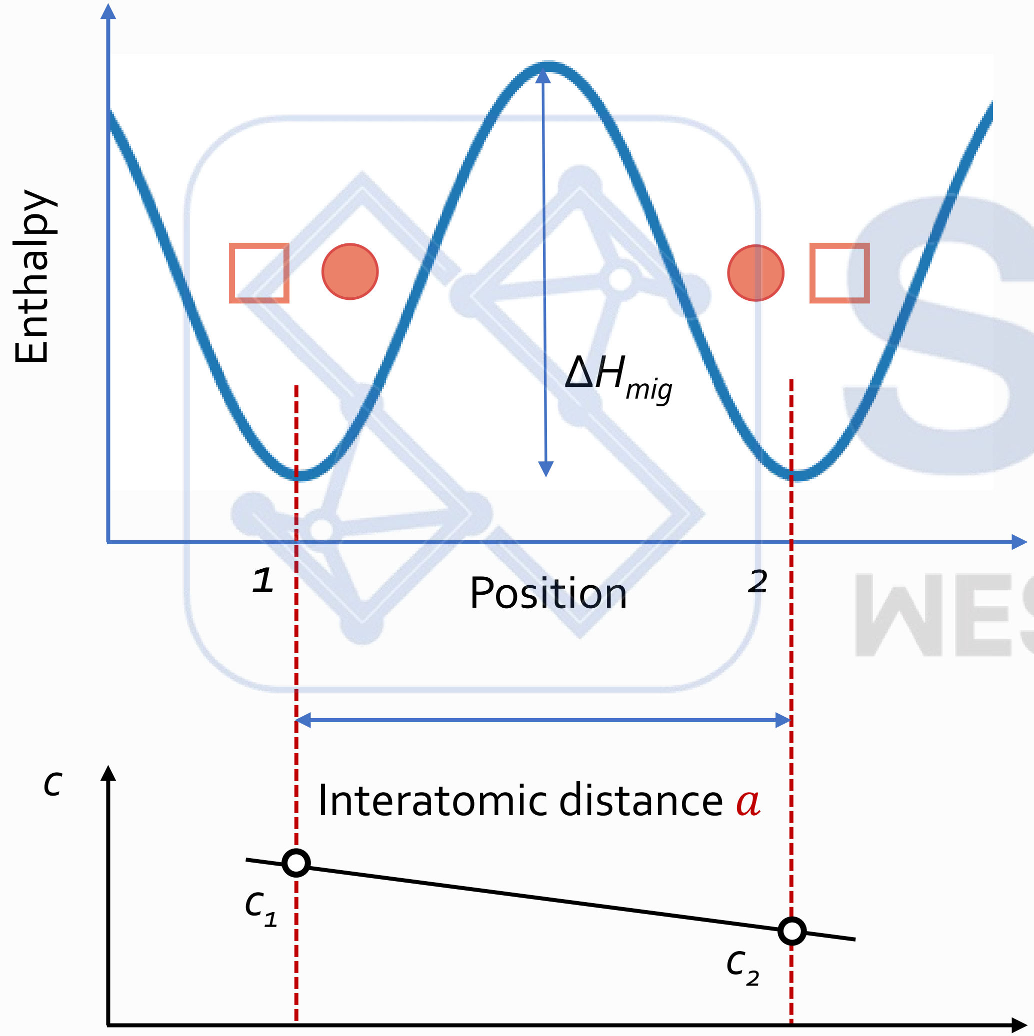
"*success rate*" (Boltzmann probability)

$$\Gamma = \frac{1}{\tau}$$

Hop frequency (unit: s^{-1})

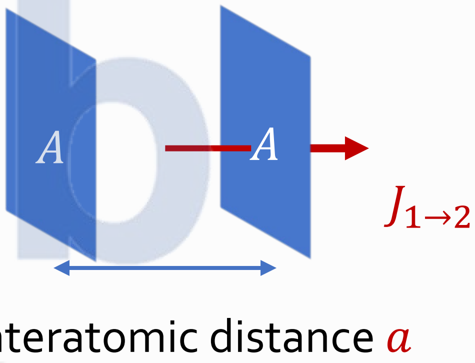
"Mean free time" (unit: s)

Microscopic origin of Fick's law



$$J = J_{1\to 2} - J_{2\to 1}$$

$$J_{1\to 2} = \frac{\frac{1}{2}N_1\Gamma}{A} = \frac{\frac{1}{2}c_1 aA\Gamma}{A} = \frac{1}{2}c_1 a\Gamma$$



$$J = \frac{1}{2}c_1 a\Gamma - \frac{1}{2}c_2 a\Gamma$$

$$= \frac{1}{2}(c_1 - c_2)a\Gamma$$

$$= -\frac{1}{2}\frac{\Delta c}{a}a^2\Gamma$$

$$\frac{\Delta c}{a} \to \frac{\partial c}{\partial x}$$

Compared with $J = -D\frac{\partial c}{\partial x}$

$$D = \frac{1}{2}a^2\Gamma$$

If $c_1 = c_2 = c$, then *exchange flux* $J_{exch} = \frac{1}{2}ca\Gamma$

Microscopic expression of diffusivity

$$D = \frac{1}{2} a^2 \Gamma$$

Microscopic expression of diffusivity (diffusion coefficient)

Beyond 1D → $D = \frac{1}{CN} a^2 \Gamma$

CN = coordination number, *i.e.*, the # of nearest neighbor for ion hop

$$\Gamma = \nu \exp\left(-\frac{\Delta H_{mig}}{k_B T}\right)$$

→

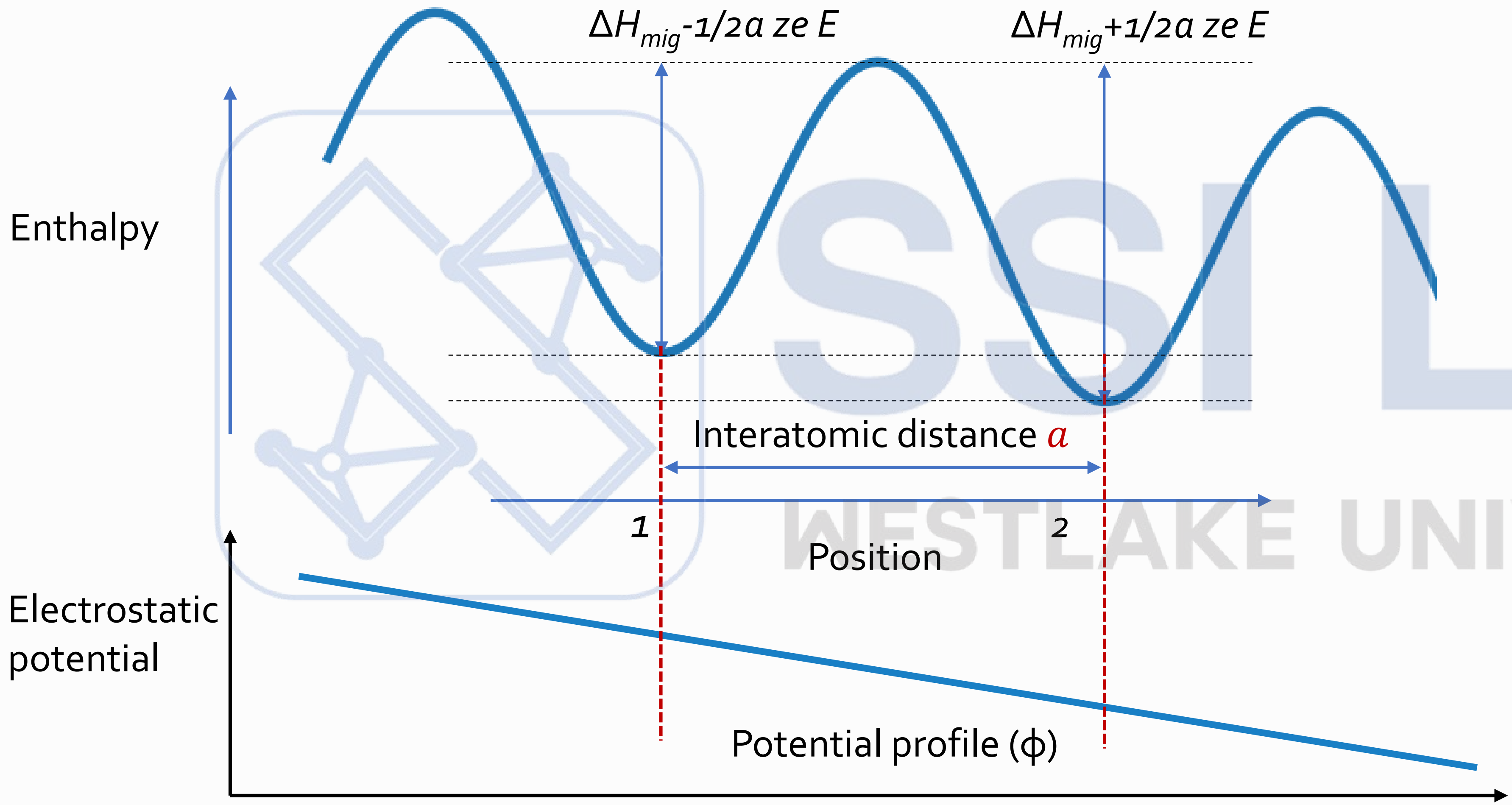
$$D = \frac{1}{CN} a^2 \nu \exp\left(-\frac{\Delta H_{mig}}{k_B T}\right)$$

Pre-factor *Thermal activation*

$$D = D_0 \exp\left(-\frac{\Delta H_{mig}}{k_B T}\right)$$

$$D_0 = \frac{1}{CN} a^2 \nu$$

Migration under an electric field



$$E = -\frac{\partial \phi}{\partial x} \longrightarrow \vec{E}$$

*How much energy is **a ze E** term?*

- Interatomic distance a ~ 1 nm
- If Δϕ = 1 V, across a length l = 1 mm → E = 10 V/cm

aeE = *10^-6^ eV* (*very small*)

Compared with k_BT = 26 meV at RT

i.e., normally migration barrier is **NOT sensitive** to applied electric field.

However, if l = 10 nm, then E = 1 MV/cm, *aeE* = 0.1 *eV* (*e.g.*, the case of memristors)

Migration under an electric field

Recall the *exchange flux* $J_{exch} = \frac{1}{2}ca\Gamma = \frac{1}{2}cav\,\exp(-\frac{\Delta H_{mig}}{k_BT})$

$$J = J_{1\to2} - J_{2\to1} = \frac{1}{2}cav\,\exp(-\frac{\Delta H_{mig} - 1/2\,zeaE}{k_BT}) - \frac{1}{2}cav\,\exp(-\frac{\Delta H_{mig} + 1/2\,zeaE}{k_BT})$$

Note: in this case, the concentrations at position 1&2 are the same (c), however, the migration barriers are different.

$$J = \frac{1}{2}cav\,\exp(-\frac{\Delta H_{mig}}{k_BT})(\exp\left(\frac{1/2\,zeaE}{k_BT}\right) - \exp\left(\frac{-1/2\,zeaE}{k_BT}\right))$$

$eaE \ll k_BT$ for low-field condition

$$\exp\left(\frac{1/2\,zeaE}{k_BT}\right) \sim 1 + \frac{1/2\,zeaE}{k_BT}$$

$$J = \underbrace{\frac{1}{2}cav\,\exp\left(-\frac{\Delta H_{mig}}{k_BT}\right)}_{\Gamma}\frac{zeaE}{k_BT} = \frac{1}{2}ca\Gamma\frac{zeaE}{k_BT}$$

Ion migration under an electric field

$$J = \frac{1}{2} ca\Gamma \frac{zeaE}{k_B T}$$

Recall $D = \frac{1}{2} a^2 \Gamma$

$$J = cD \frac{zeE}{k_B T}$$

Since J is the flux of ions (unit: #/(cm² · s)), we need to convert to the flux of charge (unit: C/(cm² · s)))

$$J_{chg} = J\, ze = c\, ze\, D \frac{zeE}{k_B T}$$

Plug in the expression of conductivity: $\sigma = c\, ze\, M$ → Mobility

$$J_{chg} = \sigma \frac{D}{M} \frac{ze}{k_B T} E$$

Compared with Ohm's law: $J_{chg} = \sigma E$

We finally reach the Nernst-Einstein relation: $\frac{D}{M} = \frac{k_B T}{ze}$ or if the unit is per mole: $\frac{D}{M} = \frac{RT}{zF}$

Nernst-Einstein relation

The **Nernst-Einstein** relation $\frac{D}{M} = \frac{k_B T}{ze}$ relates the diffusivity D and the mobility M

Recall $D = D_0 \exp(-\frac{\Delta H_{mig}}{k_B T})$

We have: $M = \frac{ze}{k_B T} D = \frac{ze}{k_B T} D_0 \exp(-\frac{\Delta H_{mig}}{k_B T})$

$$M = \frac{A}{T} \exp(-\frac{\Delta H_{mig}}{k_B T})$$

$$\sigma = c\, ze\, M = cze \frac{A}{T} \exp\left(-\frac{\Delta H_{mig}}{k_B T}\right)$$

$$\sigma = \frac{\sigma_0}{T} \exp\left(-\frac{\Delta H_{mig}}{k_B T}\right)$$

Assumption: *const. c*

Compare ***mobilities*** of ionic and electronic defects in $SrTiO_3$

Ionic (oxygen vacancy)	$\mu_V = 1.0 \times 10^4 (T^{-1}/K^{-1}) \times \exp\left(-\frac{0.86\ eV}{k_B T}\right) cm^2 V^{-1} s^{-1}$
Electronic (electrons & holes)	$\mu_n = 4.5 \times 10^5 (T/K)^{-2.2} cm^2 V^{-1} s^{-1}$ $\mu_p = 8.9 \times 10^5 (T/K)^{-2.36} cm^2 V^{-1} s^{-1}$

Guo, Fleig & Maier, ***SSI***, 2002

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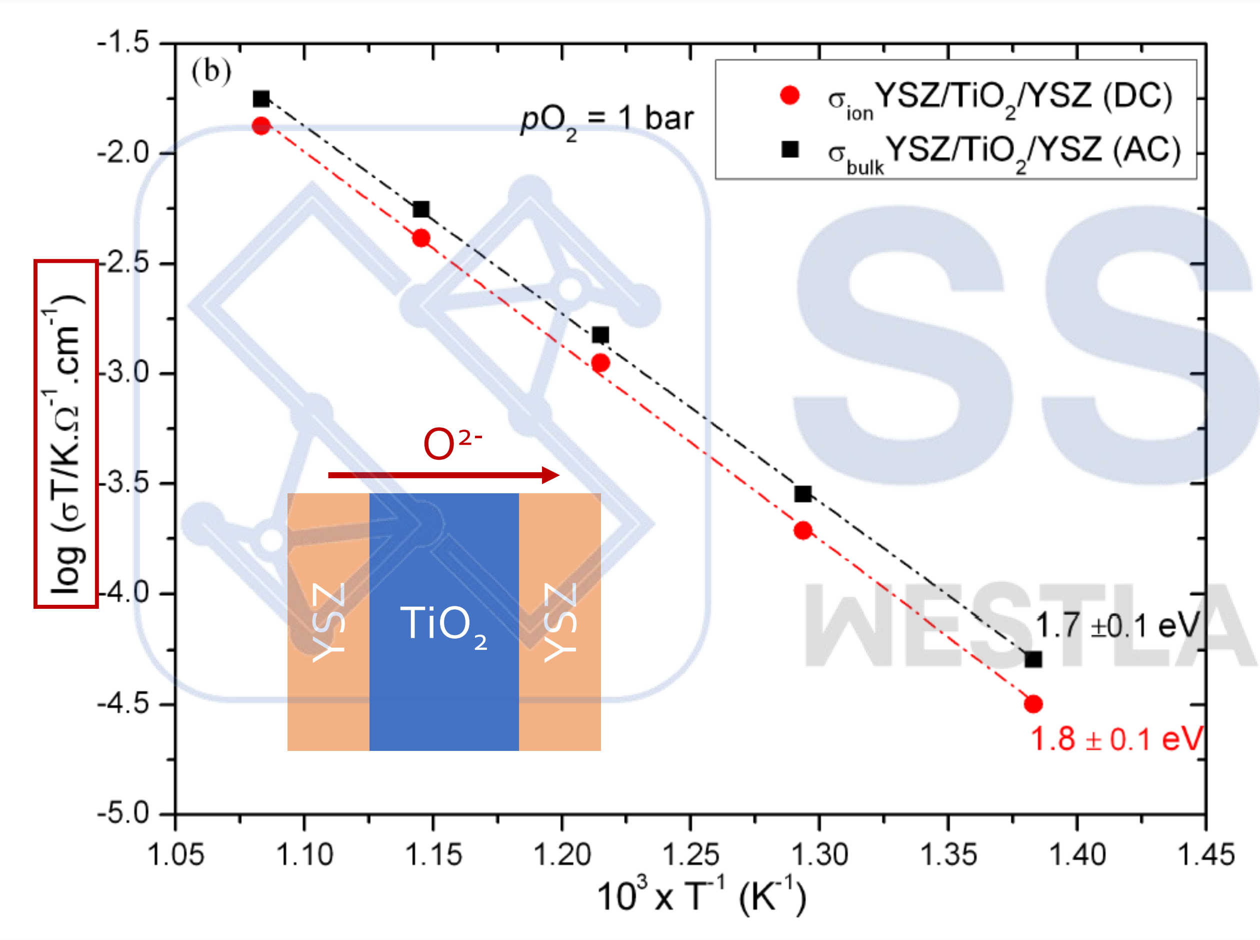
Temperature dependence of ionic conductivity



PhD Thesis, Kiran Adepalli, Max-Planck Institute for Solid State Research (2013)

$$\sigma = \frac{\sigma_0}{T}\exp\left(-\frac{\Delta H_{mig}}{k_B T}\right)$$

- Linear relationship of lnσT ~ 1/T;
- Slope → ΔH_{mig} (again, assuming ionic defect concentration does not change).

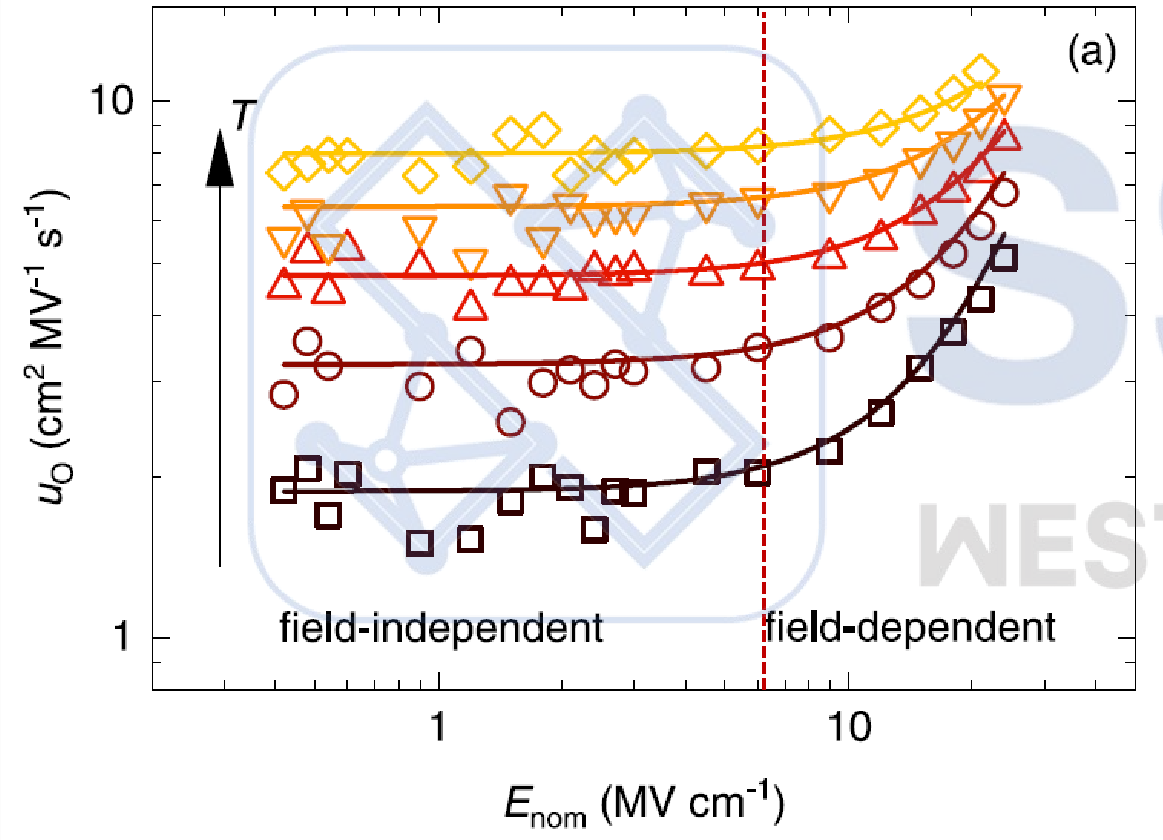
Note:

- If the range of varying temperature is not too large, then lnσ ~ 1/T is almost linear.
- *Be careful what the activation energy actually mean.* If the concentration is a function of temperature, then $E_a = \Delta H_{mig} + \Delta H_f$

Formation energy

The case of high electric field: field-dependent mobility

Simulated field-dependent mobility of oxide ions in $SrTiO_3$



Kemp & de Souza, ***PRM***, 2021

Recall:

$$J = \frac{1}{2} cav \exp\left(-\frac{\Delta H_{mig}}{k_B T}\right)\left(\exp\left(\frac{1/2\, zeaE}{k_B T}\right) - \exp\left(\frac{-1/2\, zeaE}{k_B T}\right)\right)$$

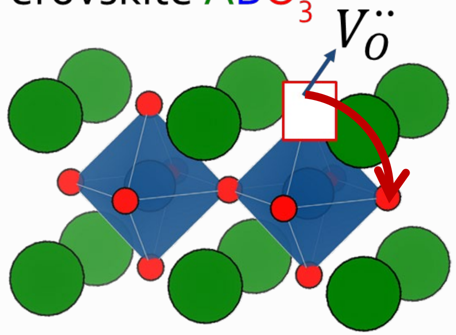
What if $1/2\, zeaE \sim k_B T$? Then the linearization breaks down.

For $SrTiO_3$, the threshold electric field is given by:

$$E_{th} = \frac{2k_B T}{zea} \sim 0.9\ MV/cm$$

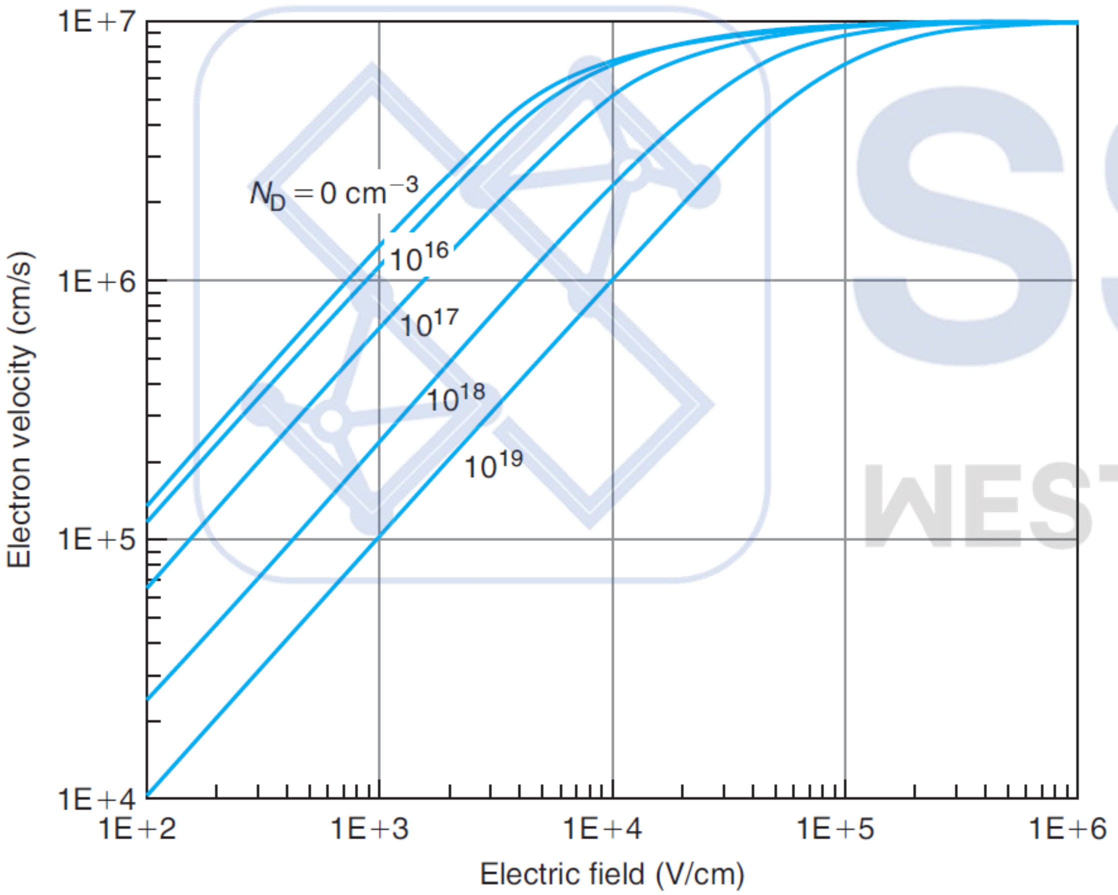
$$(z = 2, a = \frac{\sqrt{2}}{2} d_{(100)} = 2.76\ \text{Å})$$

Perovskite ABO_3



Comparing the temperature dependence of mobility

For electrons in semiconductors, mobility *decreases* with increasing electric field after a threshold.



$$v = M\ E$$

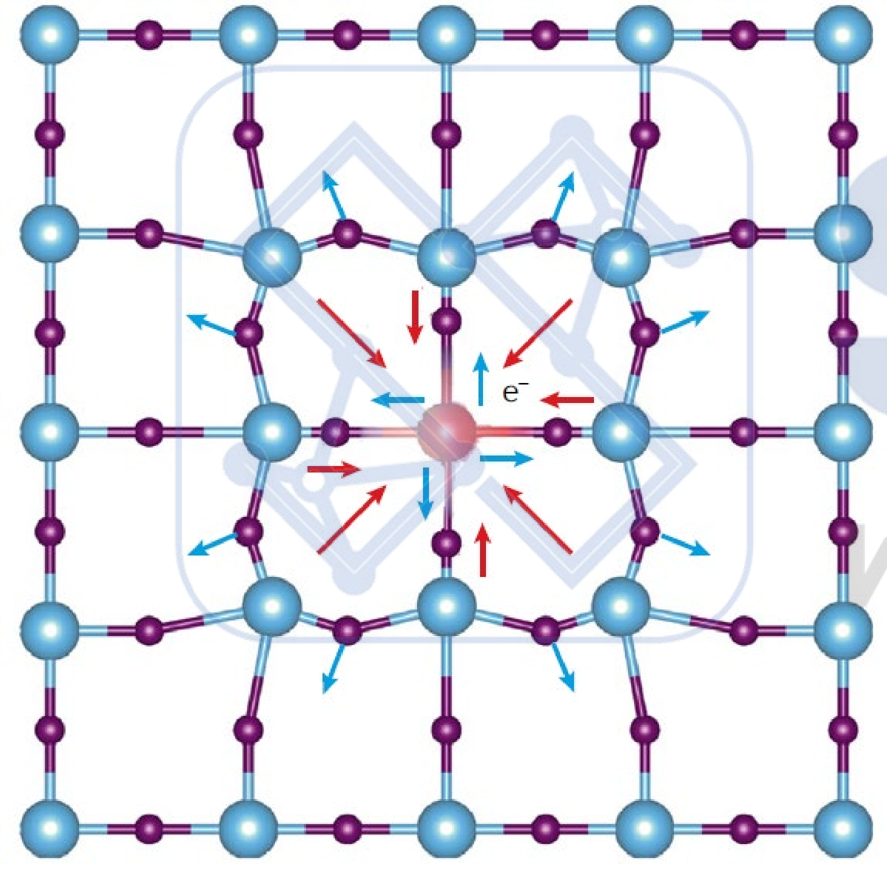
Velocity (cm/s) — Mobility (cm²/(V·s)) — Electric field (V/cm)

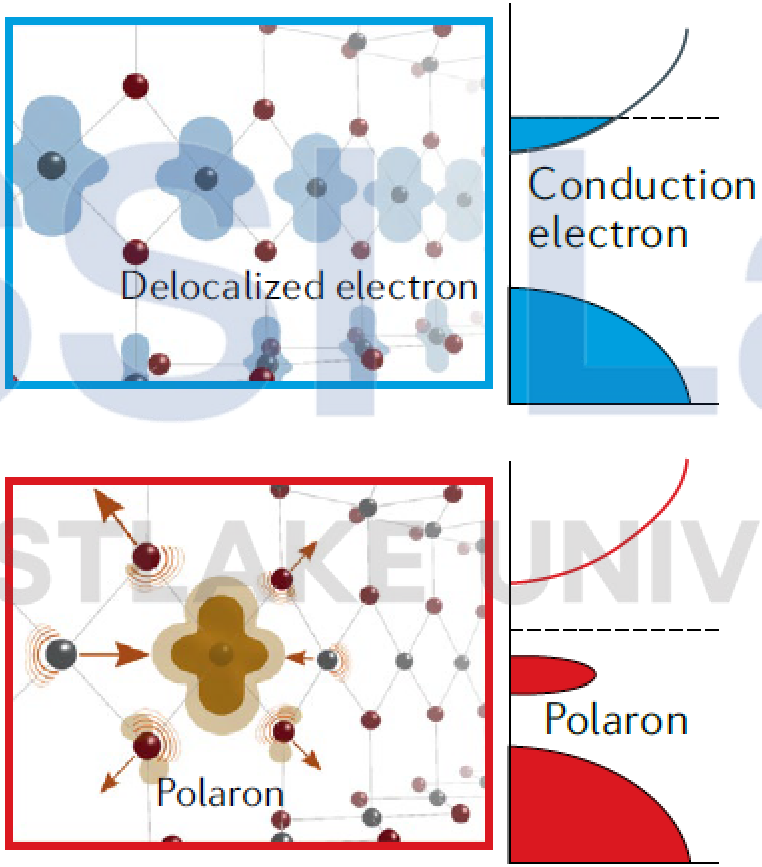
Electronic defects	*Saturation velocity* → mobility decreases linearly with electric field
Ionic defects	*Energy landscape distortion*→ mobility increases exponentially with electric field

* High electric field condition (*i.e.*, above a threshold electric field)

Polarons

Electron-phonon interaction → lattice distortion





Example:

Electrons & holes in Si

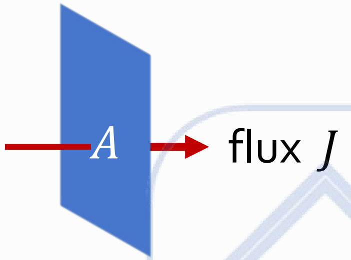
Example:

Ce^{3+} (Ce'_{Ce}) in $CeO_{2\text{-}\delta}$

Polarons in many ways behave very similarly to ionic defects.
E.g., the conductivity of polarons is thermally activated.

Franchini *et al.*, ***Nat. Mater. Rev.***, 2021

Irreversible thermodynamics: flux and driving force



Unit of flux: (mol/L) · cm³ / (cm² · s) = (mol/L)·cm/s (*or eV·cm/s*) ~ mol/(cm²·s)

(mol/L) → *concentration*; cm³ → *unit volume*; cm² → *unit area*; s → *time*

Irreversible thermodynamics

The rate of entropy production: $\Pi = T\frac{\delta S}{\delta t} = \sum_k J_k X_k$ (J_k → *flux*; X_k → *driving force*)

e.g., for diffusion: $\Pi = J\,(-\nabla\mu)$ Unit: J: mol/(cm²·s); $\nabla\mu$: (J/mol)/cm → Π: J/(cm³·s)

At equilibrium: $\Pi = 0$ (no flow) At "steady state": Π is minimized (constant flow) → $\nabla \cdot J = 0$

Linear flux-force relationships

driving force

flux ← $J = \beta X$

	Linear flux-force relationships
$J = D\,(-\nabla c)$	Fick's Law
$j = \sigma\,(-\nabla \phi)$	Ohm's Law
$f = \lambda\,(-\nabla T)$	Fourier's Law

* Linear relationships are valid "near-equilibrium"

$$J_i = -\frac{\sigma_i}{{z_i}^2 F^2} \nabla \tilde{\mu}_i$$

→ For charged particles (ions & electrons)

Electronic current density: $j_{e^-} = -F\,J_{e^-} = \frac{\sigma_{e^-}}{F} \nabla \tilde{\mu}_{e^-}$ $(z_{e^-} = -1)$

$j_{h^+} = F\,J_{h^+} = -\frac{\sigma_{h^+}}{F} \nabla \tilde{\mu}_{h^+}$ $(z_{h^+} = 1)$

Onsager reciprocity: electron-ion interference

$$J_i = \frac{\sigma_i}{{z_i}^2 F^2}(-\nabla\tilde{\mu}_i)$$ → For charged particles (ions & electrons)

L_i: connect flux with driving force;

flux of ionic species ← ; flux of electronic species ←

$$\begin{pmatrix} J_i \\ J_e \end{pmatrix} = \begin{pmatrix} L_{ii} & L_{ei} \\ L_{ie} & L_i \end{pmatrix} \begin{pmatrix} -\nabla\tilde{\mu}_i \\ -\nabla\tilde{\mu}_e \end{pmatrix}$$

→ driving force for ionic species; → driving force for electronic species

L_{mn}: connect flux with driving force;

$L_{ii} = \frac{\sigma_i}{{z_i}^2 F^2}$ $L_{ee} = \frac{\sigma_e}{F^2}$: Charge transport coefficient for ions and electrons

$L_{ei} = L_{ie} = ??$: cross-term; "interference" effect

Hong-Seok Kim and Han-Ill Yoo, *Phys. Rev. Lett.*, **97** (25), 2006

Things we have discussed in this lecture

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- What are the microscopic mechanisms for ionic migration based on the type of ionic defects?
- How to derive the Fick's law from the microscopic picture of ion migration?
- How to reach the Nernst-Einstein relation (correlating the diffusivity and the mobility) from the microscopic picture of ion transport?

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

End of Lecture 4
Solid State Ionics Fall 2023

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