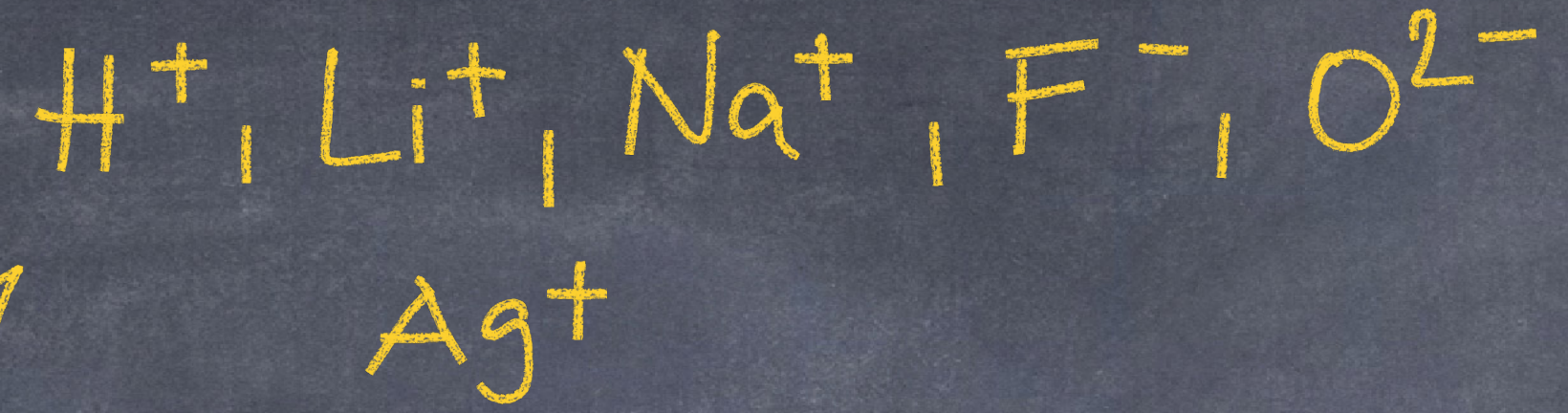


Ion Migration in Solids (Models, Methods, Materials)

Solid State Ionics 2024, LONDON

Some remarks:



migration vs diffusion
(hopping)

Ion Migration in Solids (Models, Methods, Materials)

isotope effects?
?

crystalline
amorphous
polymers
hybrid
materials
etc.

Solid State Ionics 2024, LONDON

hopping concepts

non-nuclear vs nuclear

fast
ion conductors

microscopic vs macroscopic

1820 M. Faraday: diffusion processes in solids

- phase transformations
- Oxidation, Corrosion of solids
- sintering
- growth of
- ion dynamics



Crystalline

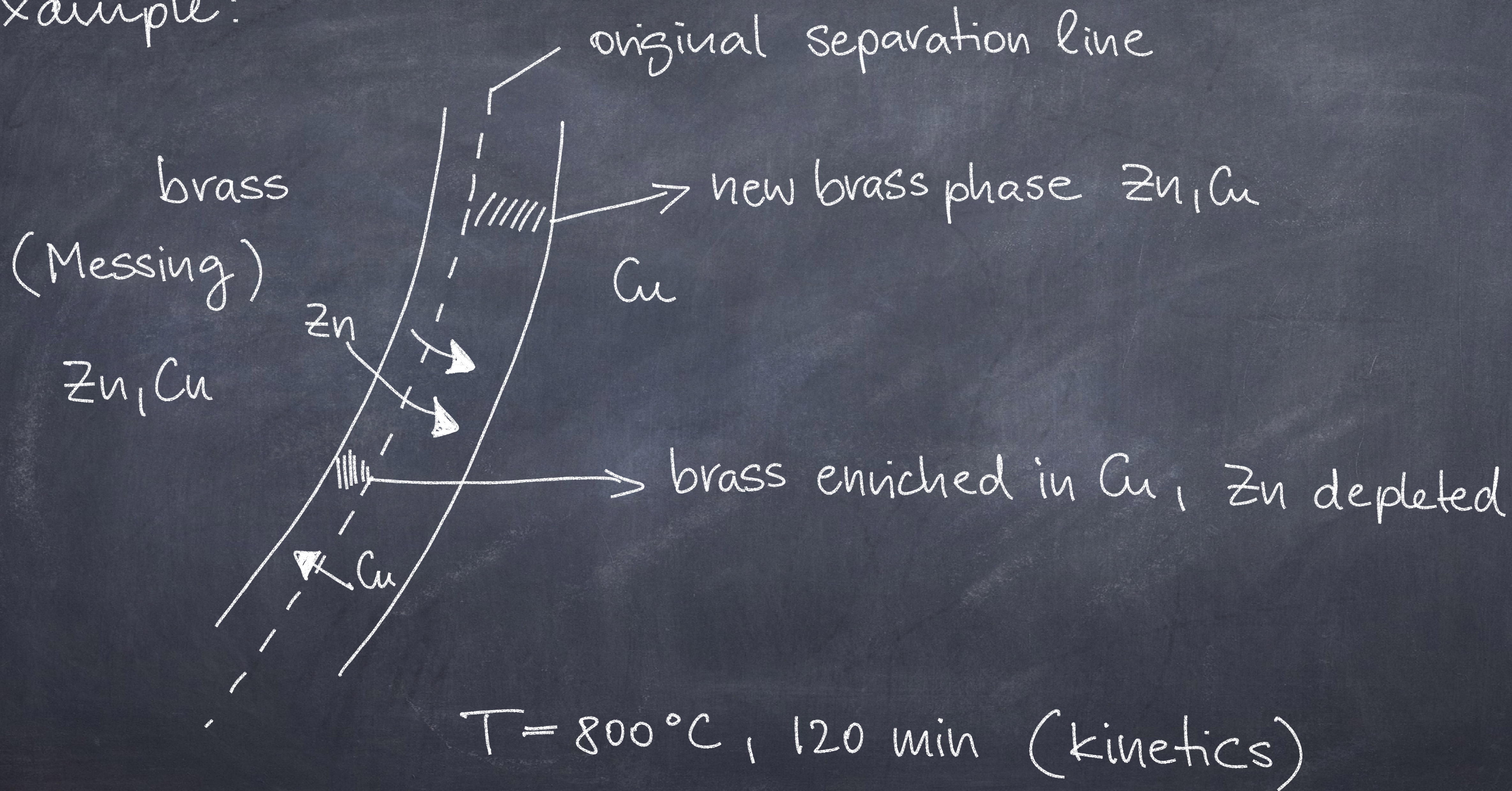
Amorphous,
glassy

Lave, 192

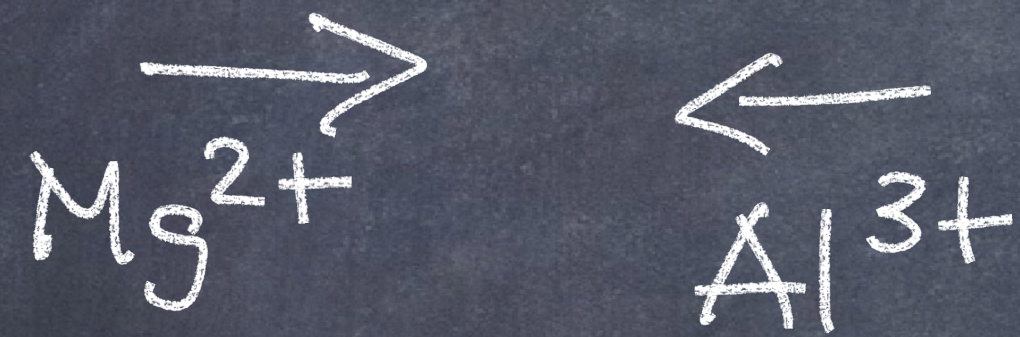
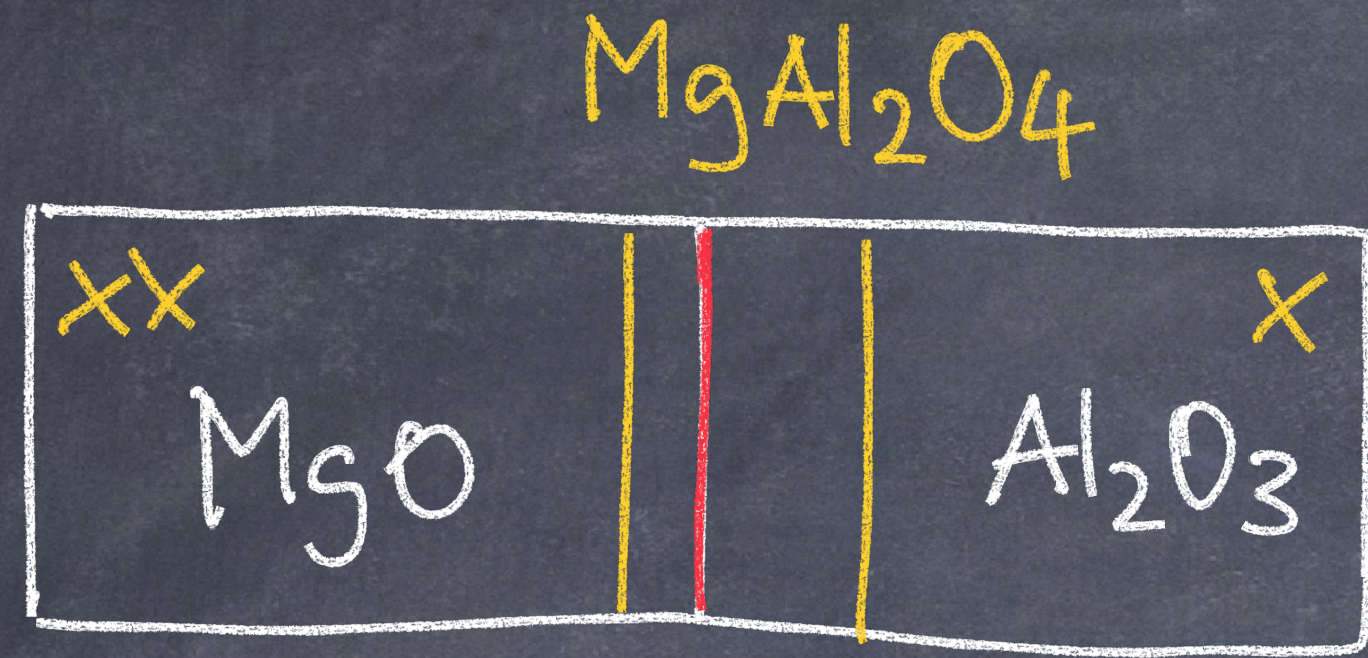
X-ray diffraction

atomic structure of solids

Example:

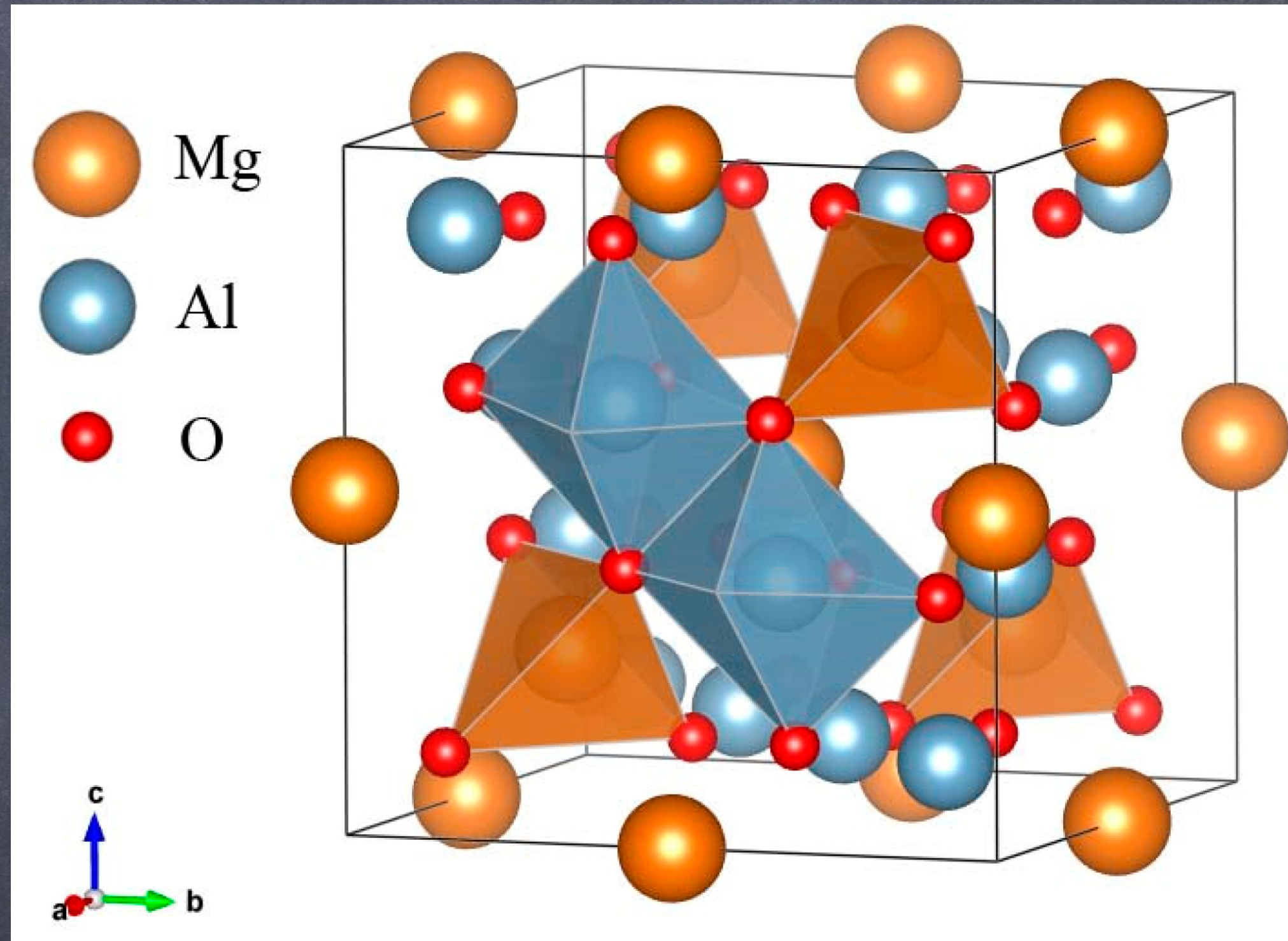


Example: Formation of the $MgAl_2O_4$ Spinel

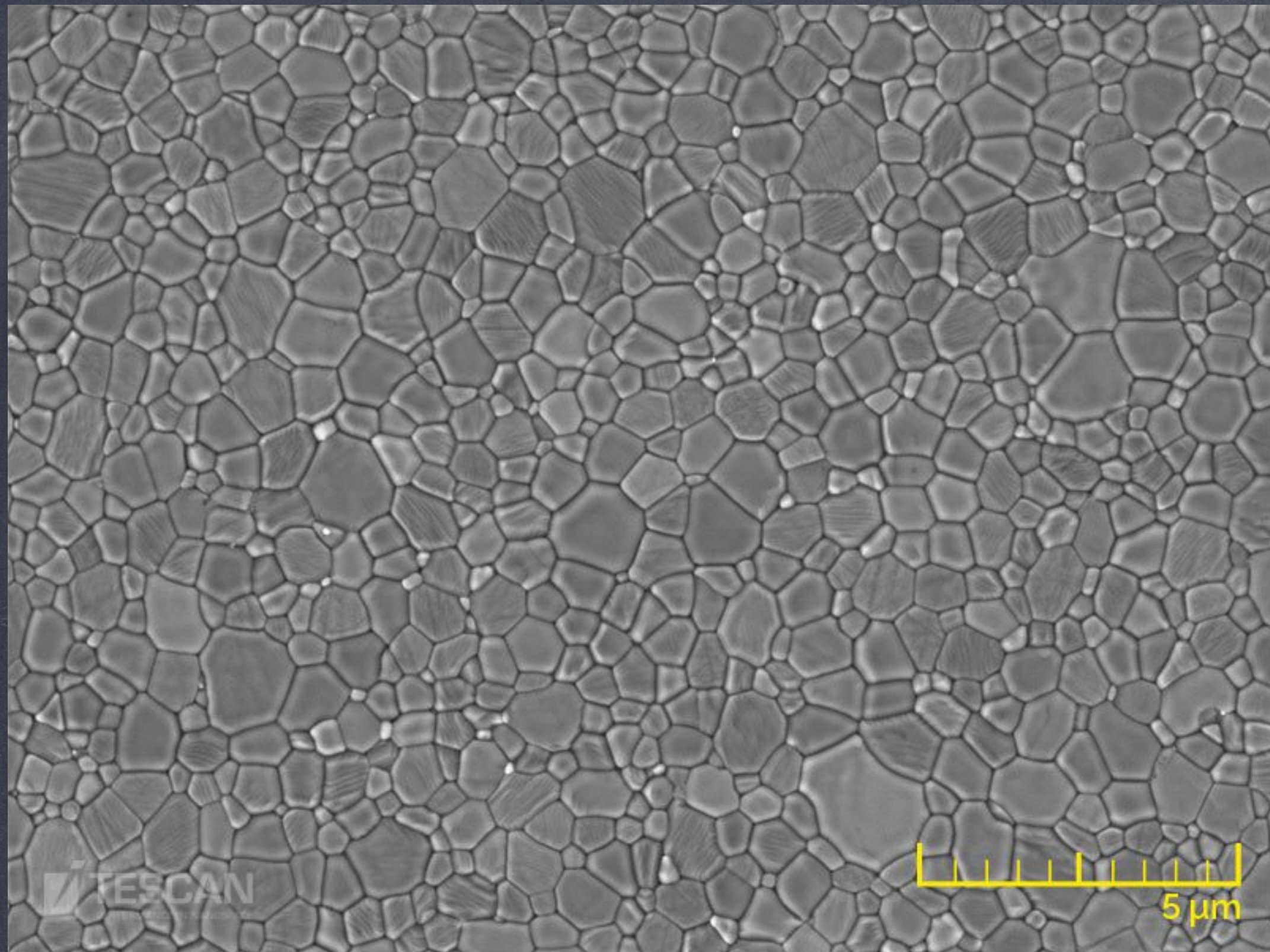


Mg^{2+} $\frac{1}{8}$ of all tetrahedral sites occupied

Al^{3+} $\frac{1}{2}$ of the octahedral sites occupied



O^{2-}
 padding
 x hexagonal
 xx cubic



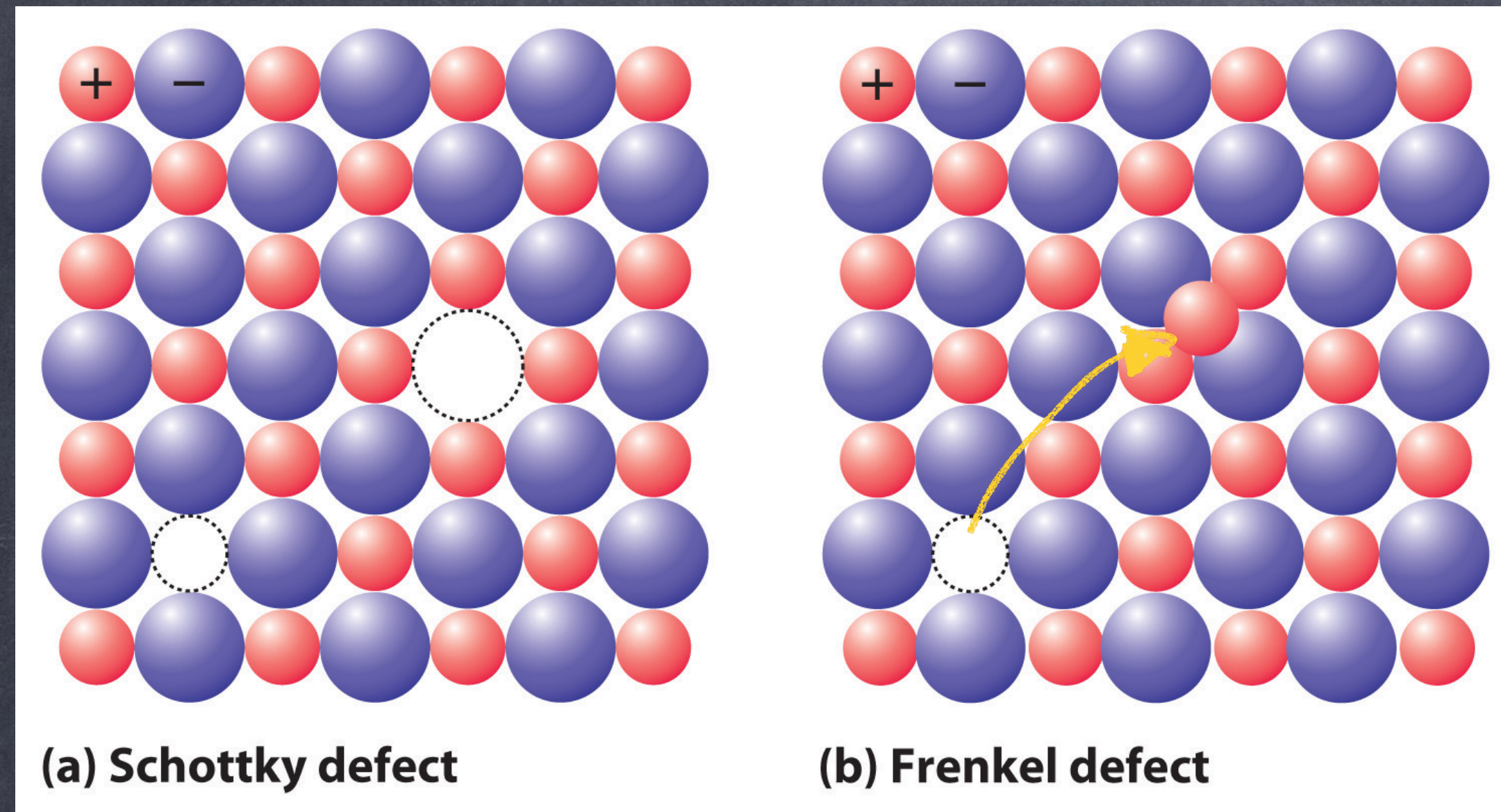
a sintered ceramic

- polycrystalline
- grains and
- grain boundaries

Sintering at high temperatures:
and pressures

MgO ($T > 1700^{\circ}\text{C}$)

Ionic conduction through defects



○ vacancy



interstitial site

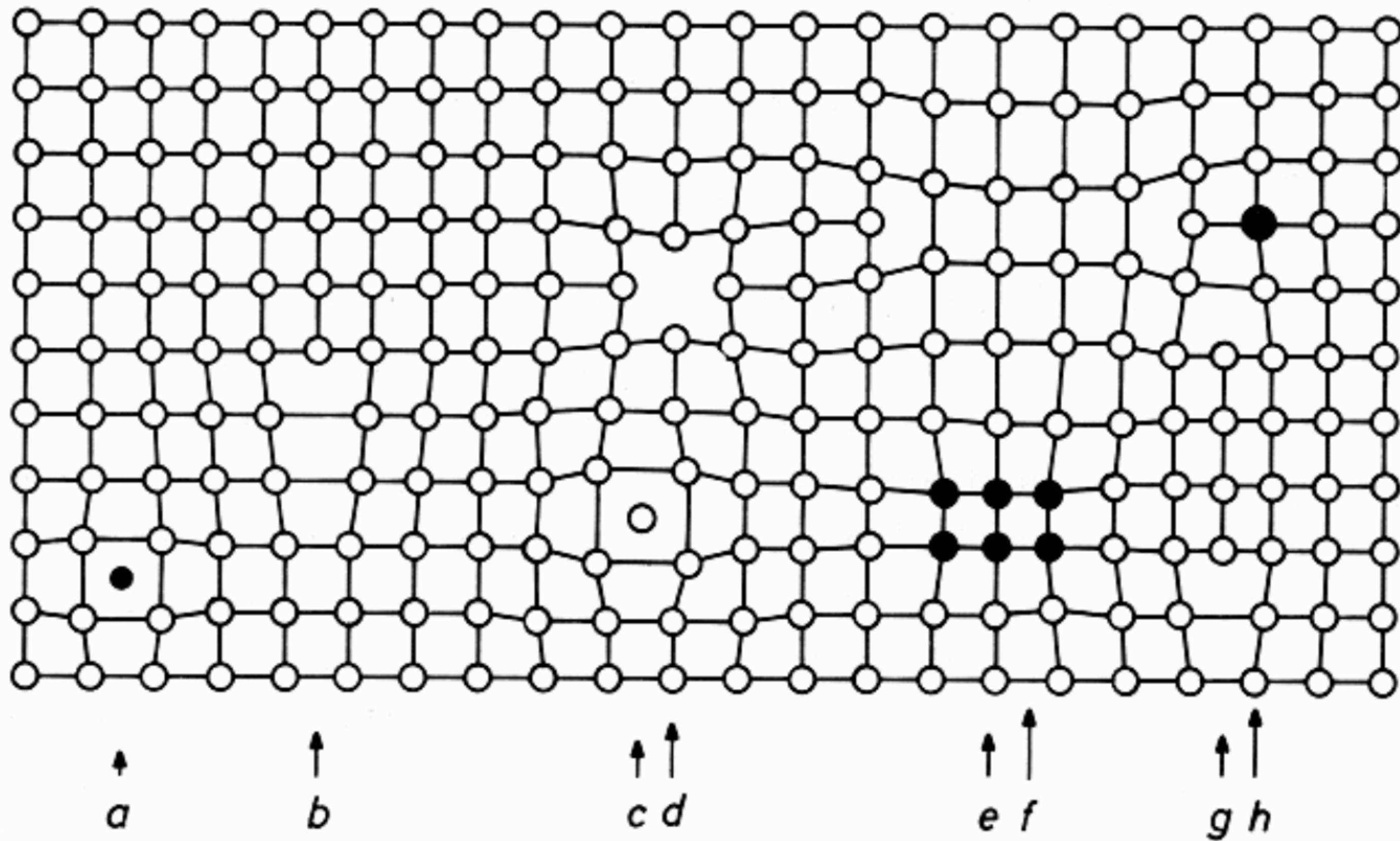
MgO
NaCl

AgI, AgCl
AgBr, CaF₂
BaF₂

AgCl : Ag⁺ on interstitial
cation Frenkel defect site

CaF₂ : F⁻ on interstitial
anion Frenkel defect site

more types of defects:

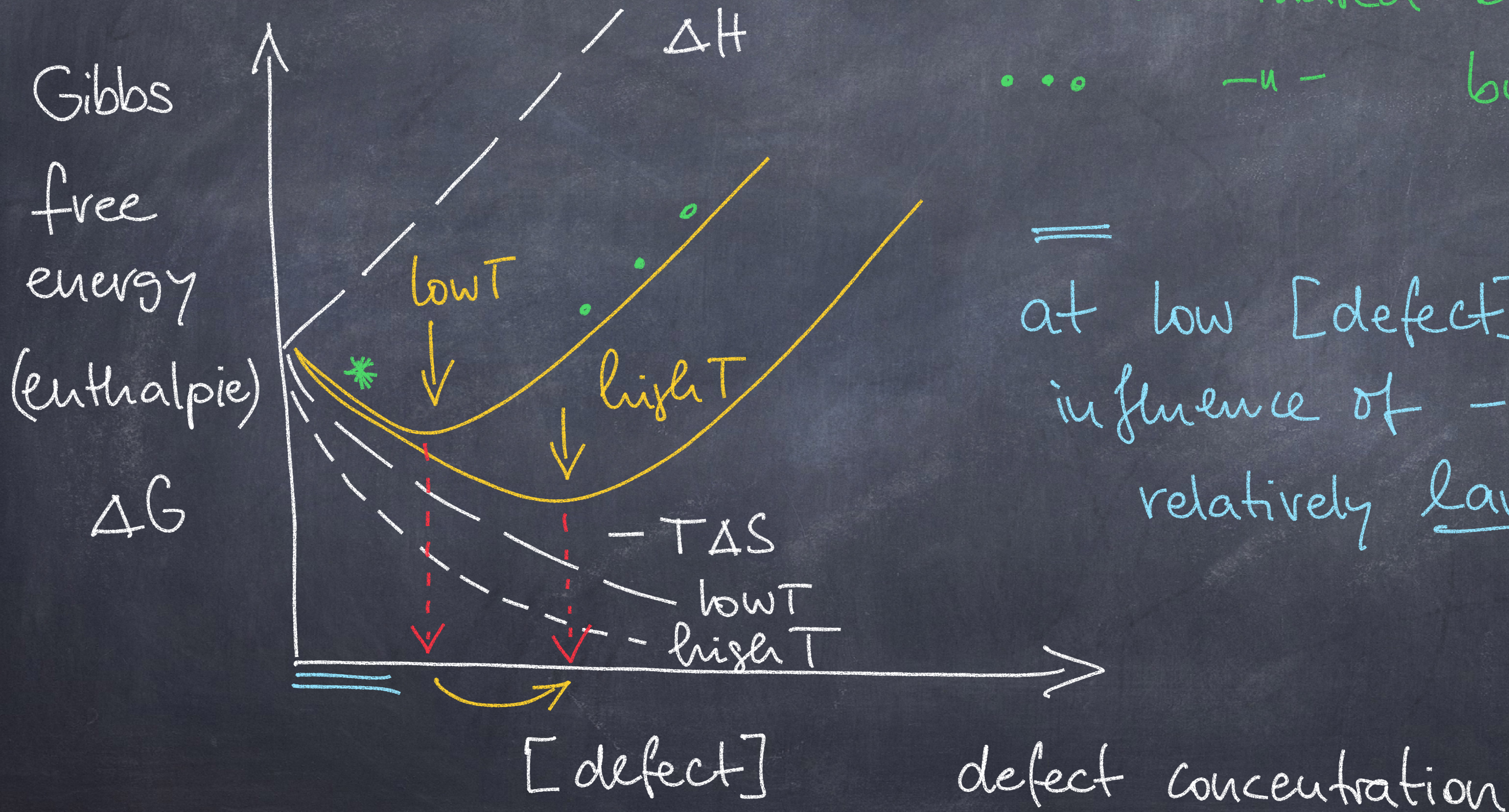


5 Types of crystal defects and impurities:-a) Interstitial impurity atom, b) Edge dislocation, c) Self interstitial atom, d) Vacancy, e) Precipitate of impurity atoms, f) Vacancy type dislocation loop, g) Interstitial type dislocation loop, h) Substitution impurity atom 2

Look at the arrangements of the ions next to a defect!

5 types

formation of defect:

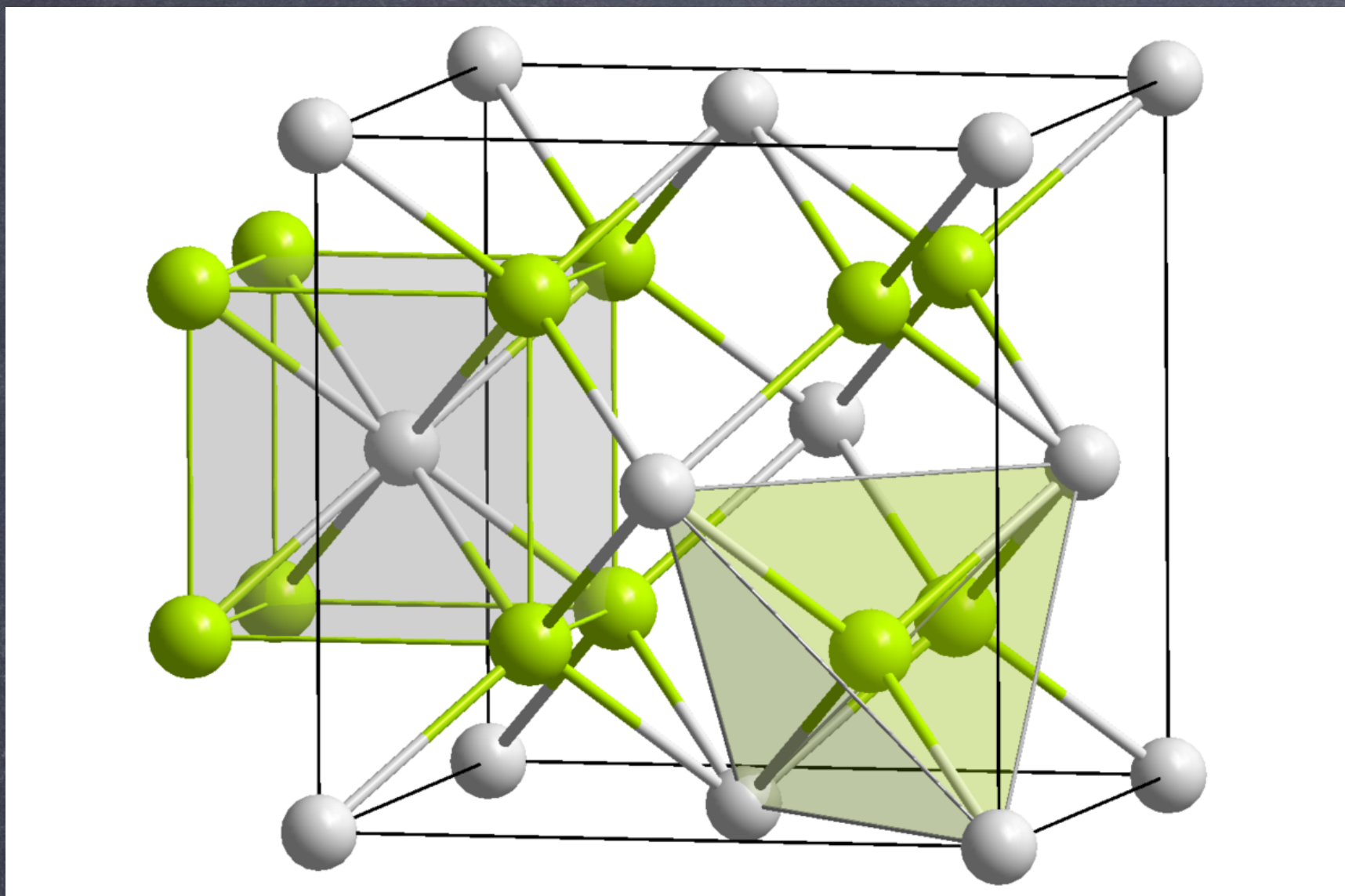


T dependence

* dominated by $-T\Delta S$
 ... -u- by ΔH

= at low [defect] the influence of $-T\Delta S$ is relatively large!

CaF_2

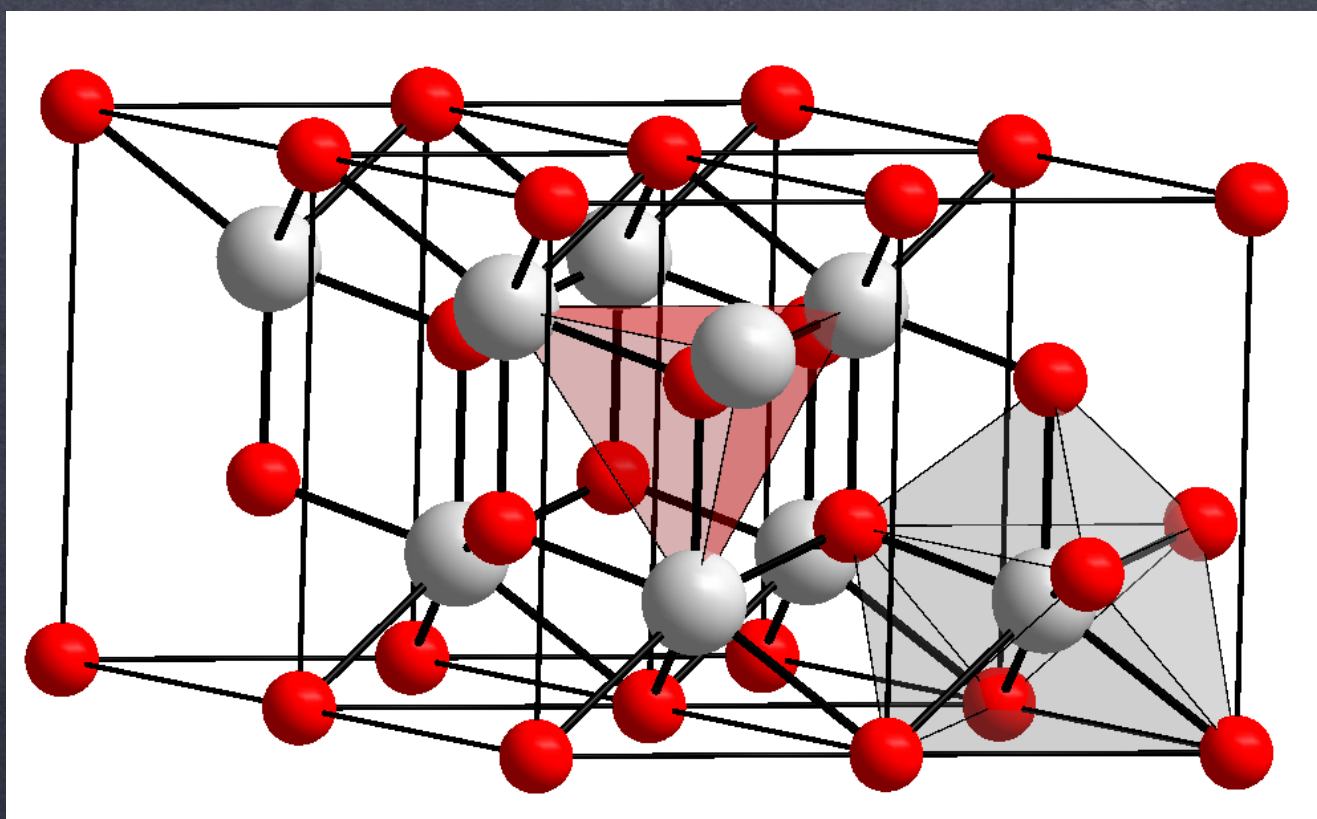
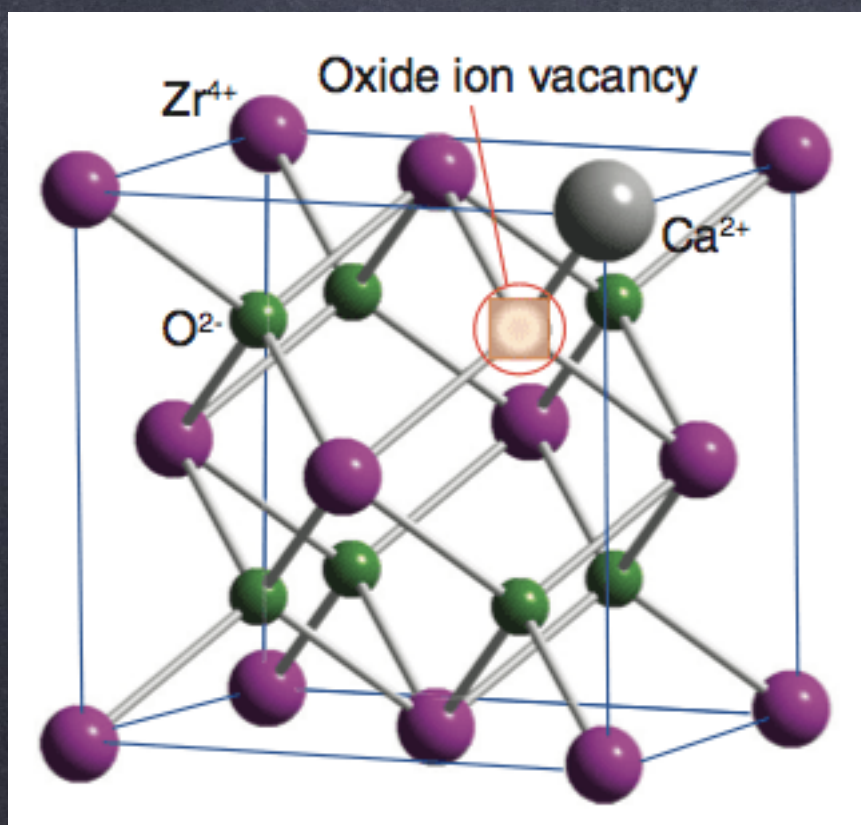


anions on tetrahedral sites
(small volume)

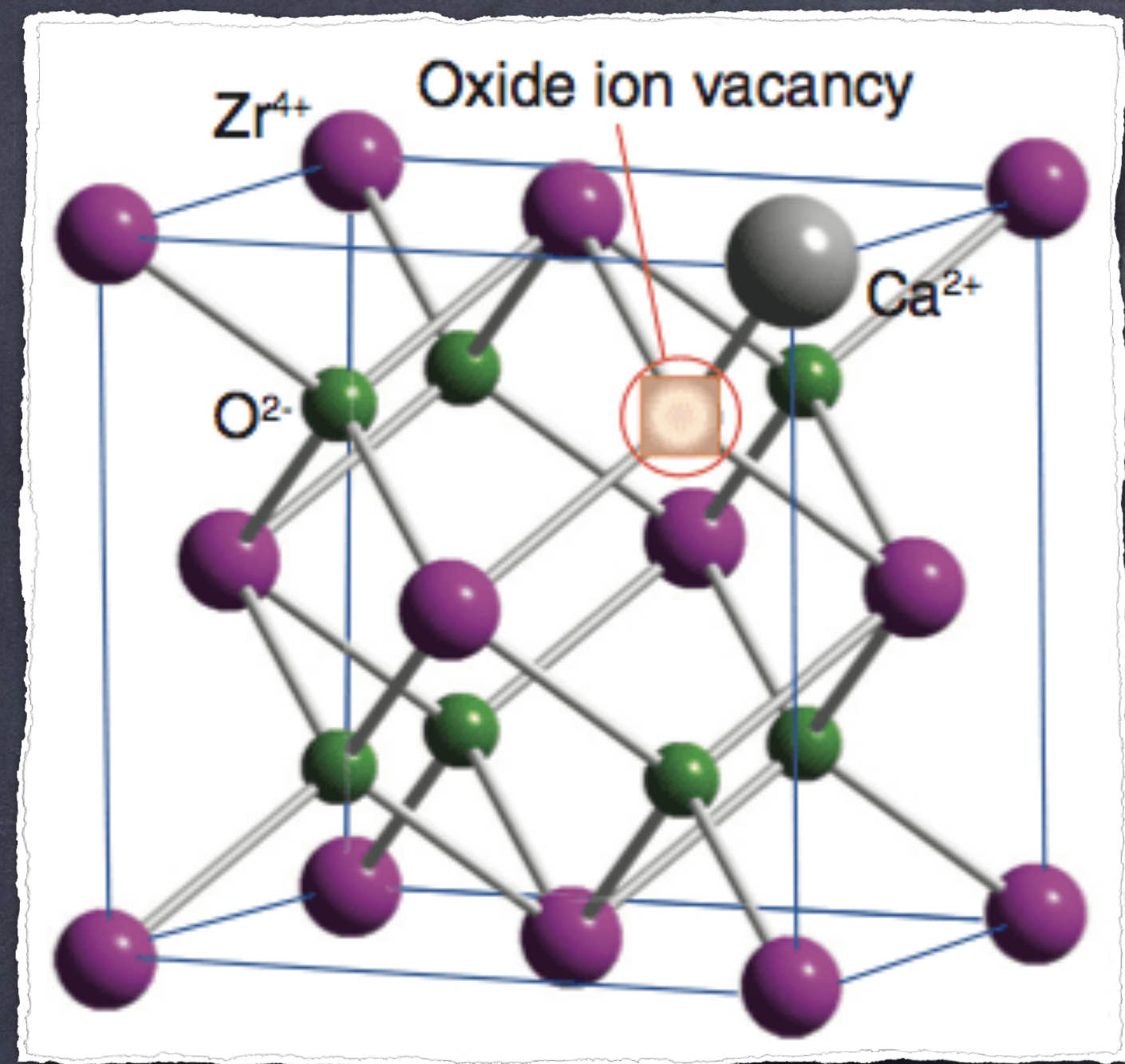
empty octahedral sites

see also CeO_2 , ZrO_2 , ThO_2

ZrO_2



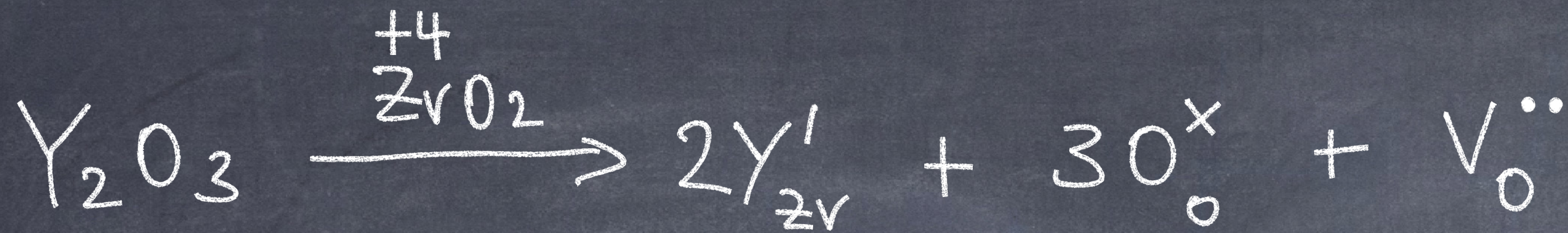
CeO_2



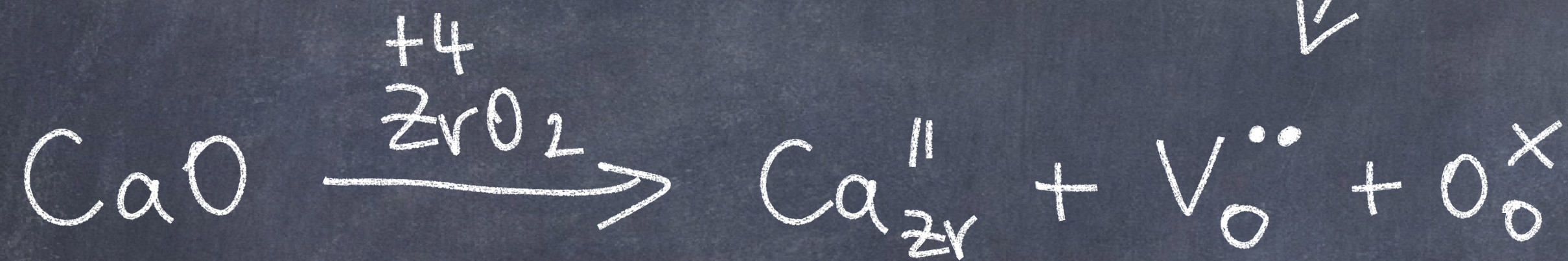
Zr^{4+} is replaced with Ca^{2+} :
to ensure charge neutrality, an
oxygen vacancy is formed.

O^{2-} uses this vacancy for diffusion!

What happens if you replace 2 Zr^{4+} with 2 Y^{3+}
ions?



$$[V_o''] = \frac{1}{2} [Y'_{Zr}]$$



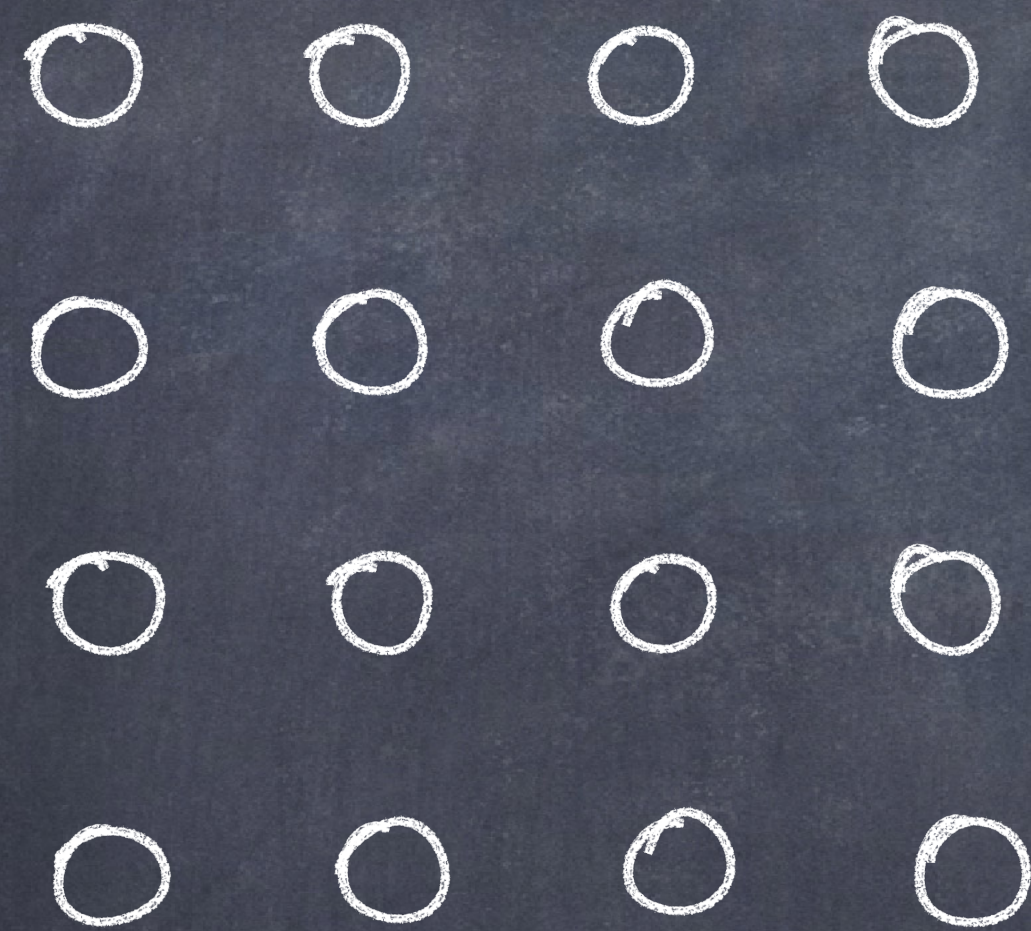
$$[V_o''] = [Ca''_{Zr}]$$

formation of O vacancies

Kröger-Vink notation!

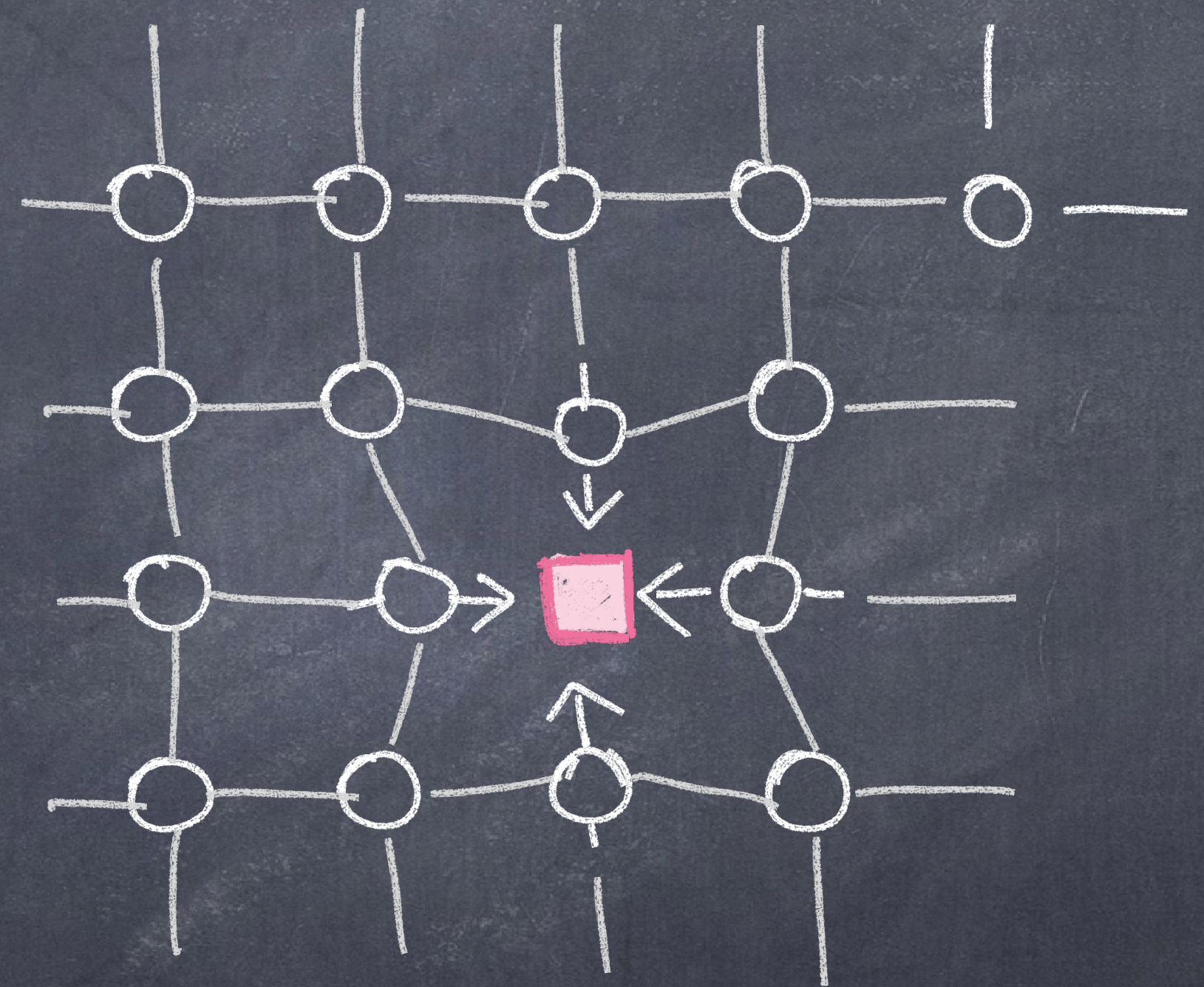
Jumping of ions

... remember your lessons on thermodynamics



$$S = k_B \cdot \ln \Omega$$

$$\Omega = 1$$

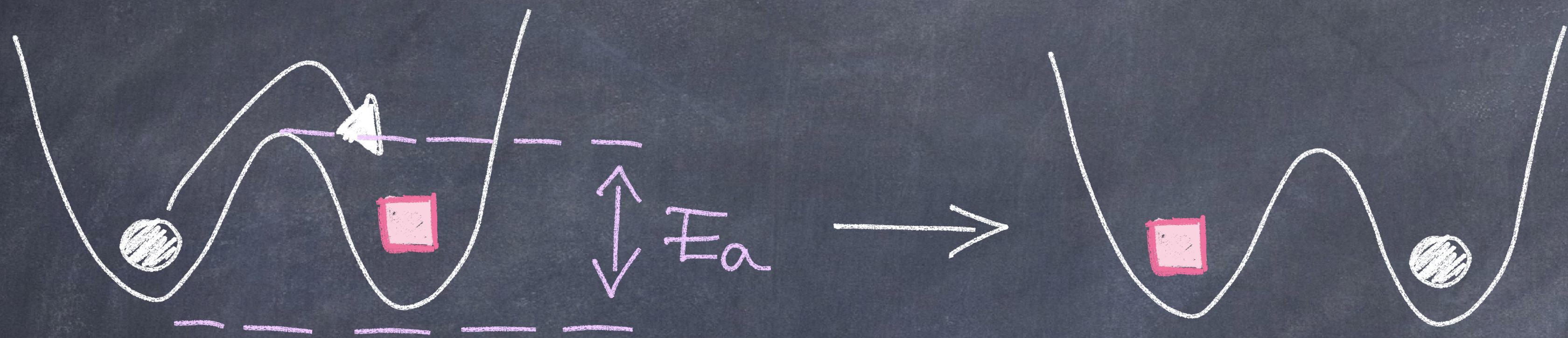


perfect crystal

$T \rightarrow 0K$

 : vacant site

What happens on the Ångström length scale?



fully homo-
geneous
potential
landscape

E_a : activation energy

$$E_a = E_m + E_f$$

$$\tau^{-1} = \tau_0^{-1} \exp\left(-\frac{E_a}{k_B T}\right)$$

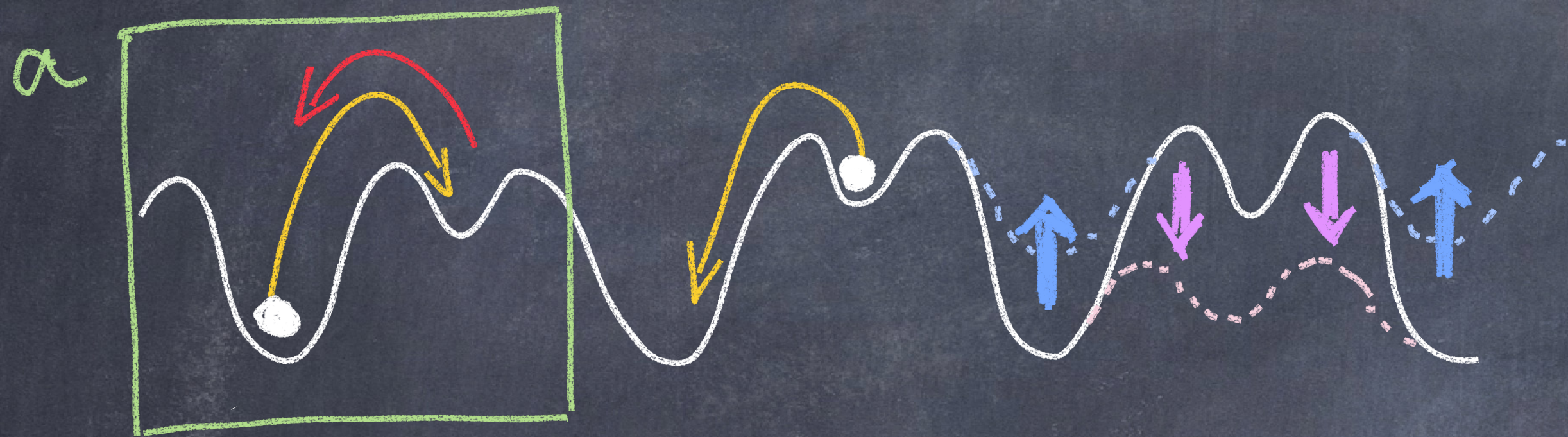
$\frac{1}{\tau}$: jump rate

Potential potential landscapes

s: symmetric
a: asymmetric



regular



regular / transition states
oct. - tetr. - oct. (Li_xTiS_2)

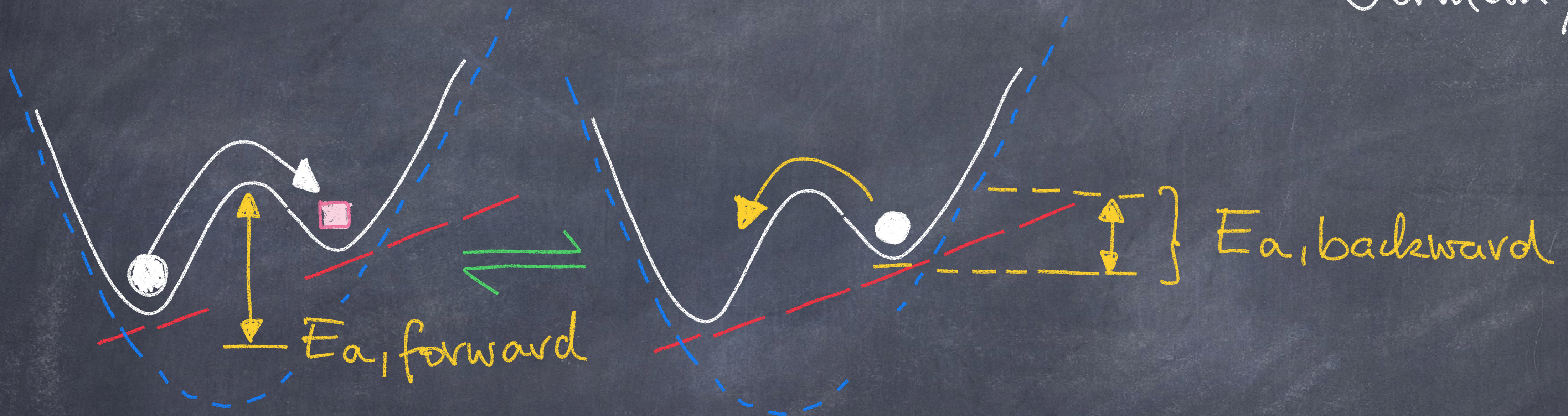


irregular (glasses)

— short range vs. long range —

just introduce some asymmetry

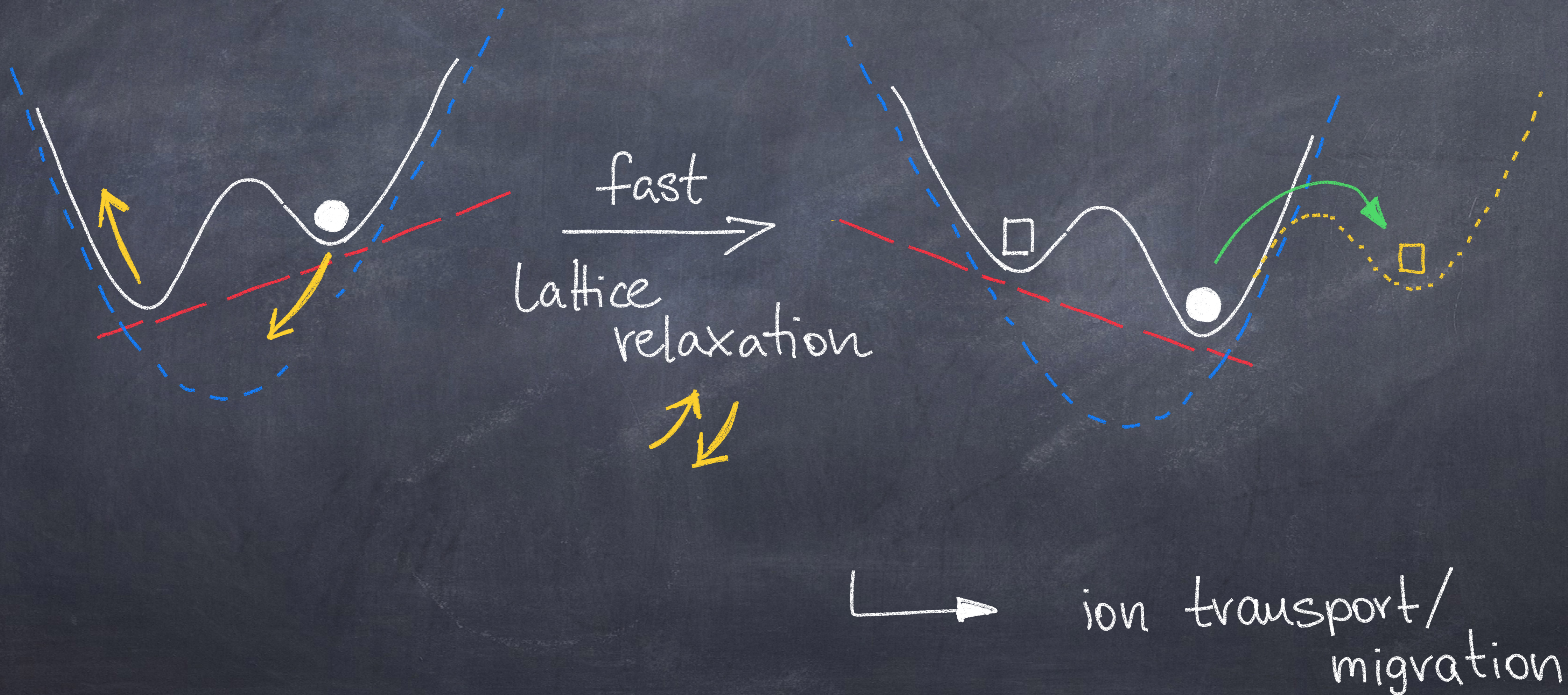
Funke, Münster,
Germany



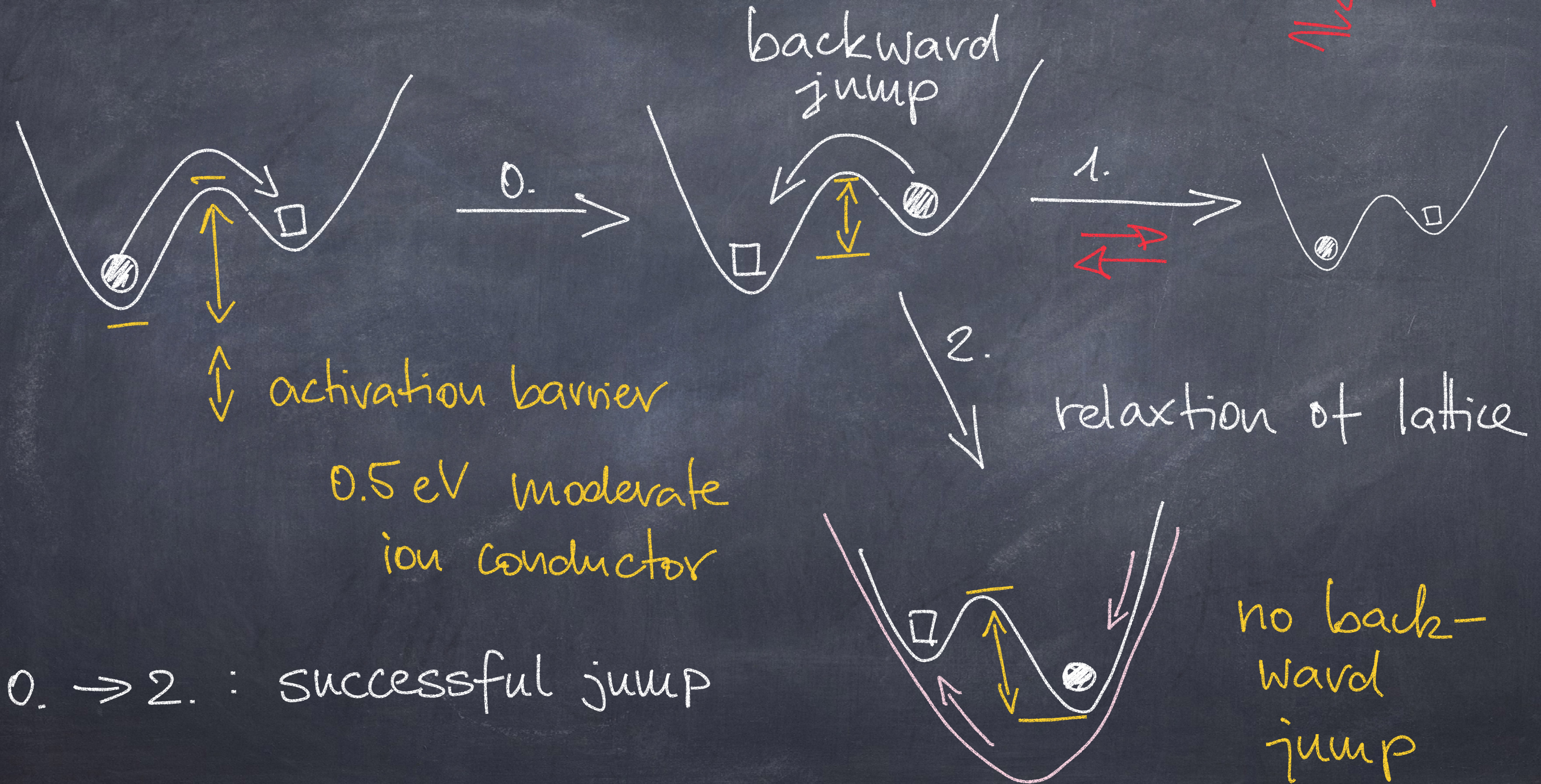
localised motion, no long-range ion
transport

RELAXATION VS. BACKWARD JUMP(S)

a concept



jumps and relaxation



0. → 2. : successful jump

number of jumps per second :

10^9 s^{-1} extremely fast
 10^6 s^{-1} fast
 10^4 s^{-1} slow to moderate
 $< 10^4 \text{ s}^{-1}$ poor conductor

\updownarrow E_a / activation energy
 $< 0.5 \text{ eV}$

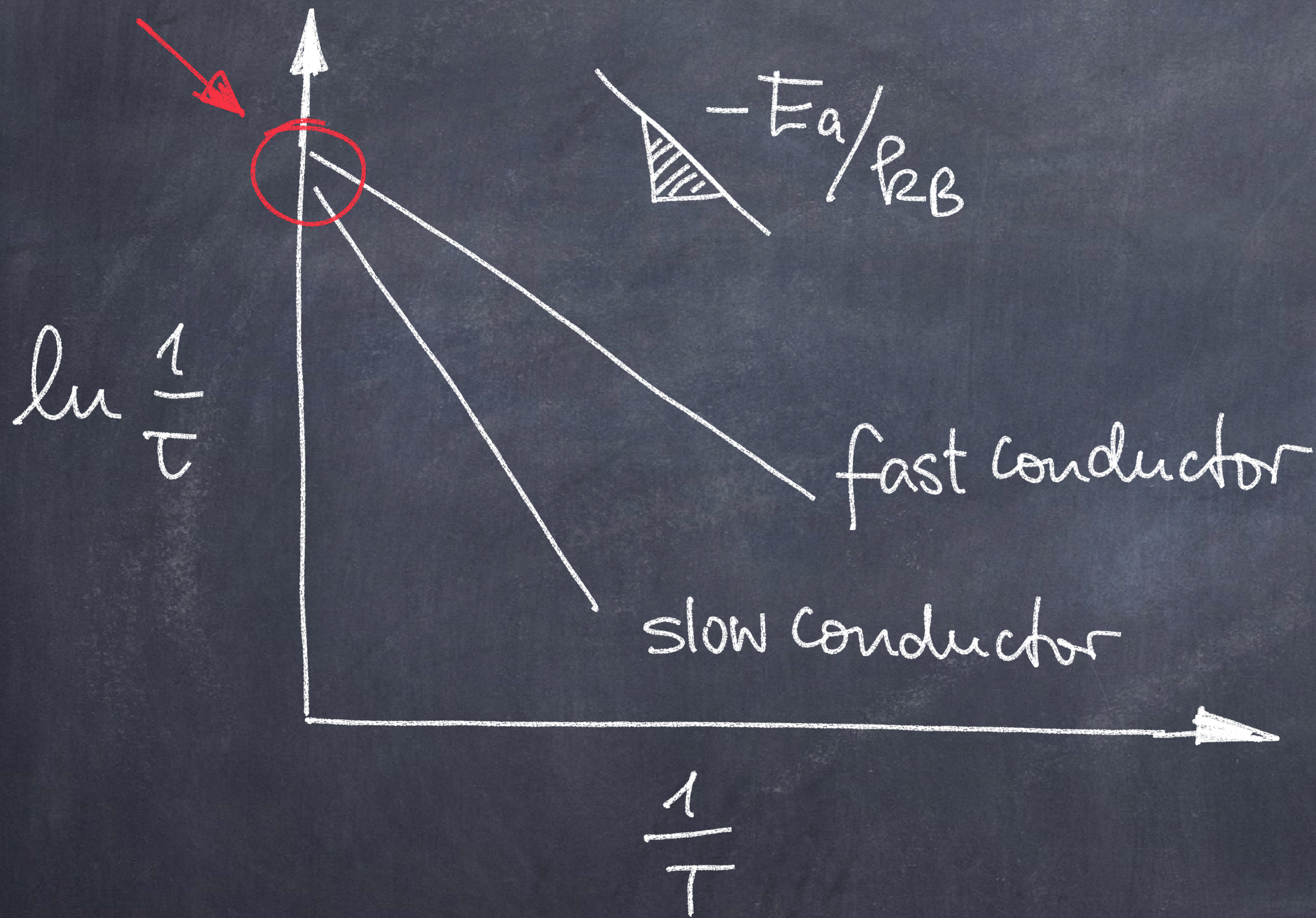
0.5 eV

$> 0.5 \text{ eV} \dots 1.0 \text{ eV}$
or higher

$$\text{jump rate } \frac{1}{\tau} = \frac{1}{\tau_0} e^{-E_a / (k_B \cdot T)}$$

\uparrow pre-factor contains attempt frequency

attempt frequency: $\frac{1}{\tau_0} \approx 10^{14} \text{ s}^{-1}$ (phonon frequencies)

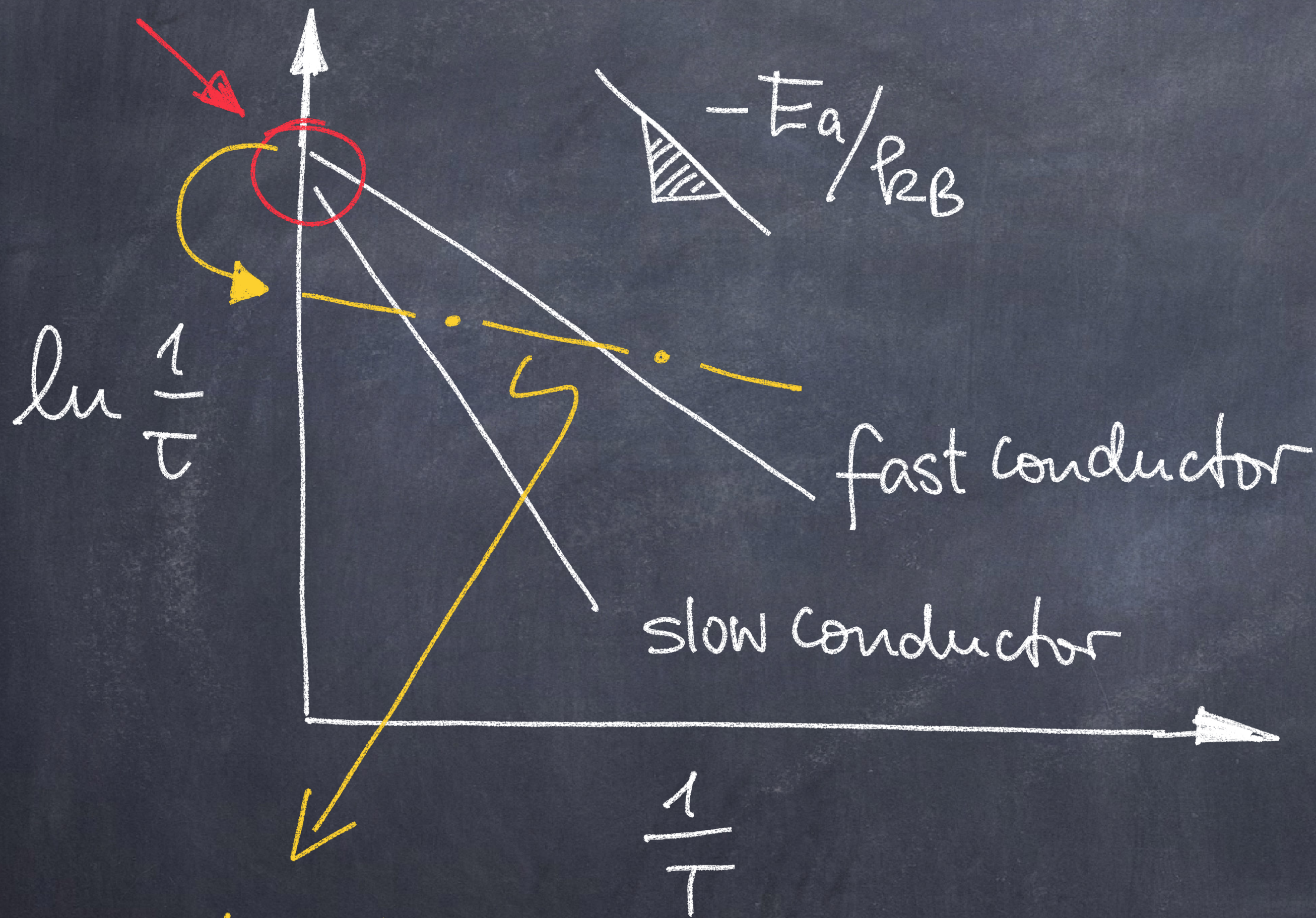


$$\frac{1}{\tau} = \frac{1}{\tau_0} e^{-\frac{E_a}{k_B T}}$$

$$\ln \frac{1}{\tau} \propto -\frac{E_a}{k_B} \cdot \frac{1}{T}$$

- change E_a or
- manipulate $\frac{1}{\tau_0}$!

attempt frequency: $\frac{1}{\tau_0} \approx 10^{14} \text{ s}^{-1}$ (phonon frequencies)



$$\frac{1}{\tau} = \frac{1}{\tau_0} e^{-\frac{E_a}{k_B T}}$$

$$\ln \frac{1}{\tau} \propto -\frac{E_a}{k_B} \cdot \frac{1}{T}$$

very low E_a
 very low $\frac{1}{\tau_0}$ (Meyer-Neldel)

- change E_a or
- manipulate $\frac{1}{\tau_0}$!

$\frac{1}{\tau}$ and the Einstein diffusion coefficient D_{sd}

$$D_{sd} = \frac{a^2}{2d \cdot \tau}$$

$d = 1, 2, 3$ dimensionality
($d \in \mathbb{N}$)
1,6 : fractal?

$$D_{sd}^{3D} = \frac{a^2}{6 \cdot \tau}$$

$d=2$ 2D diffusion, e.g.
Lit in Li6InCl3

a : jump distance



an approximation

D can be converted into a conductivity σ

$$D = \frac{\sigma k_B T}{N q^2}$$

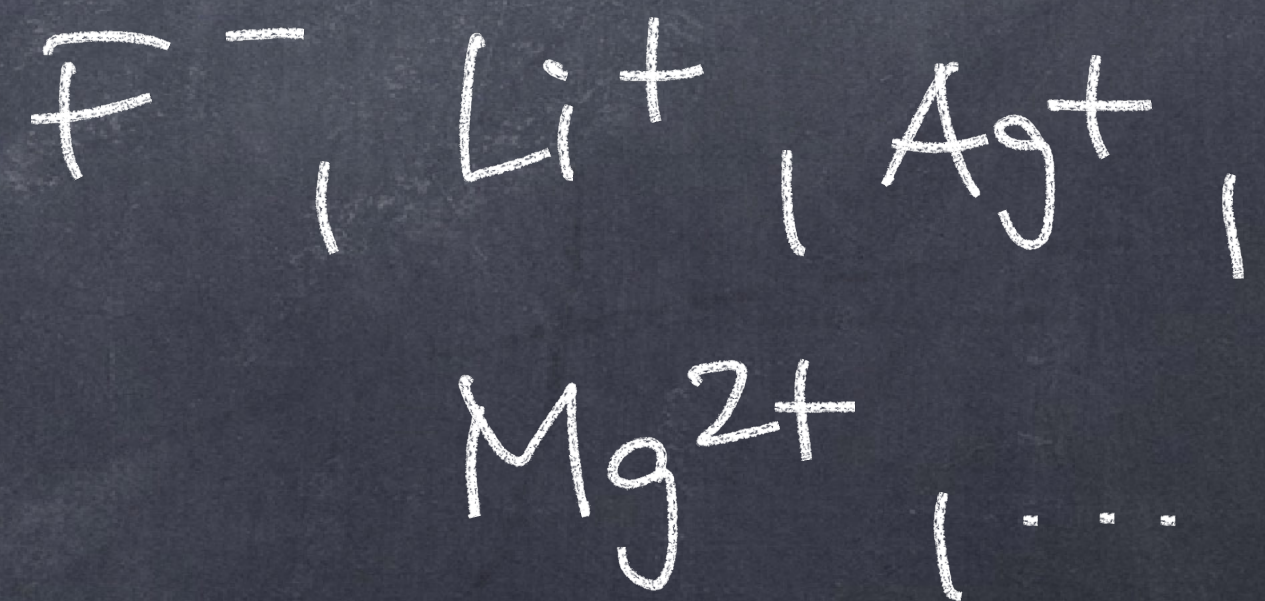


Solid state diffusion coefficient based on the

NERNST-EINSTEIN
equation

N: no. of charge carriers /
volume

q: charge of the mobile
species

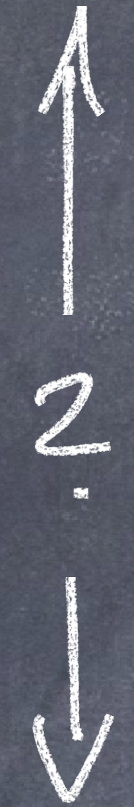


T: Tracer

$$D_T = D_0 e^{-E_a / (k_B T)}$$

macroscopic diffusion

$$D_T = \underline{H_R} D = H_R \frac{2 \cdot k_B T}{N \cdot q^2}$$



$$D_T = \underline{f} \cdot D_{SD}$$

$$D_{SD} = \frac{a^2}{2d\tau}$$

microscopic (view)

f: correlation factor $(0 < f \leq 1)$

H_R : Haven ratio

... taken together:

$$D_{\text{tracer}} = H_r \frac{\sigma k_B T}{N q^2} = f a^2 / (6\tau)$$

$$\tau^{-1} = (H_r / f) \frac{6k_B T}{N q^2 a^2} \cdot \sigma$$

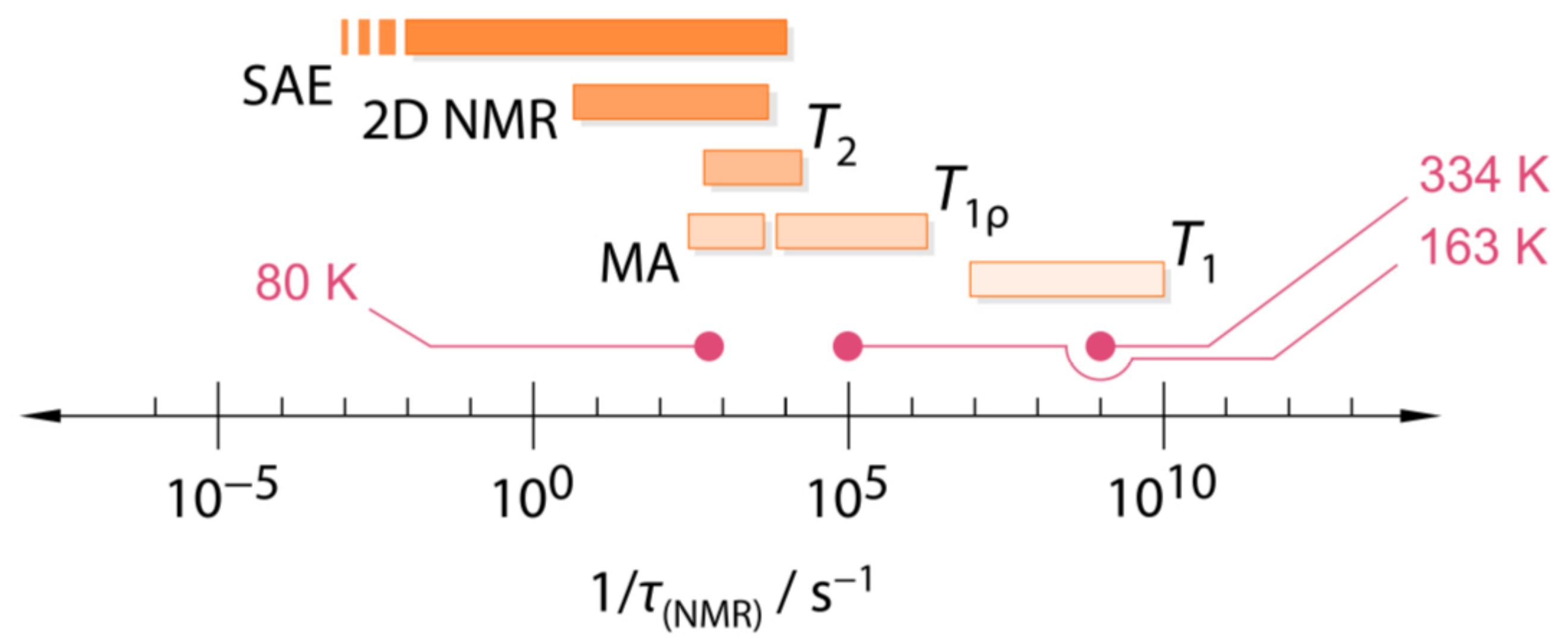
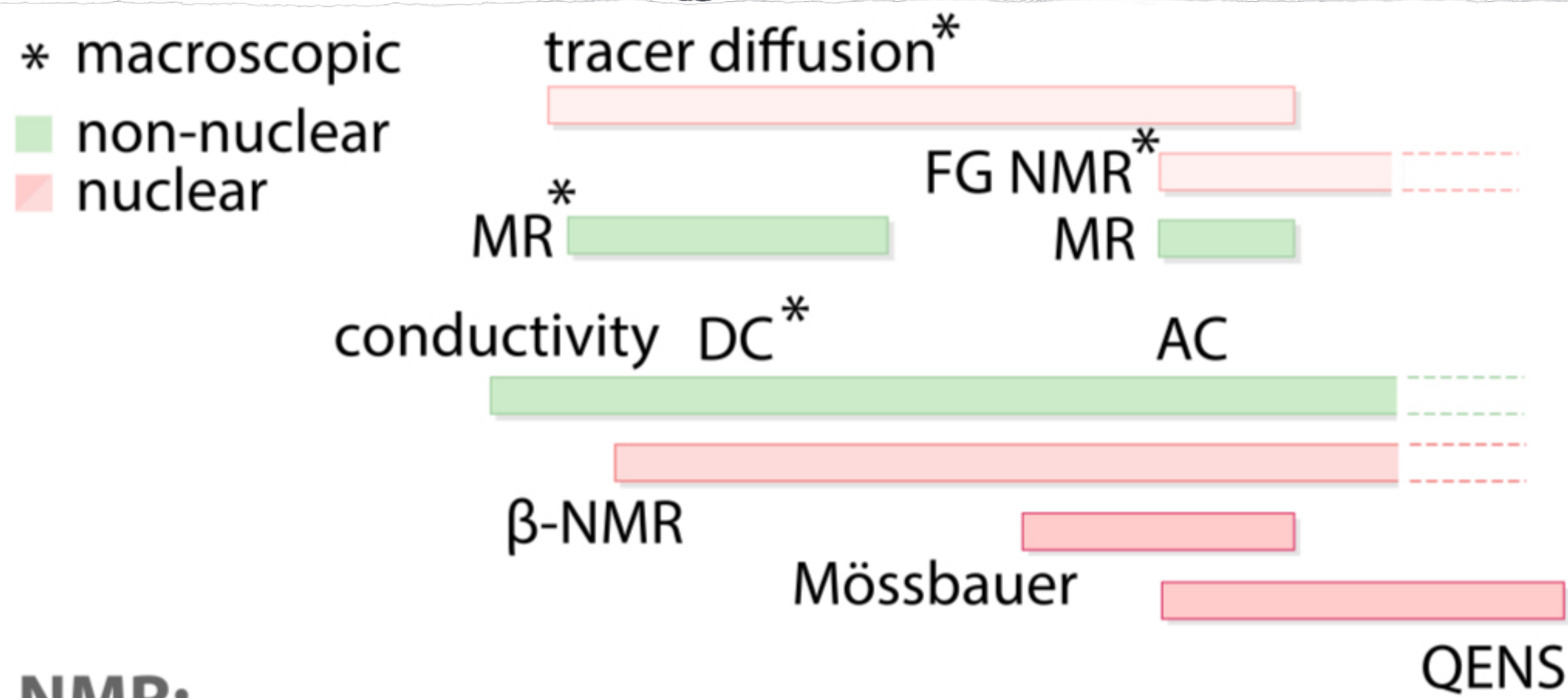


- simple diffusion mechanism
- uncorrelated (random) jump diffusion

METHODS:

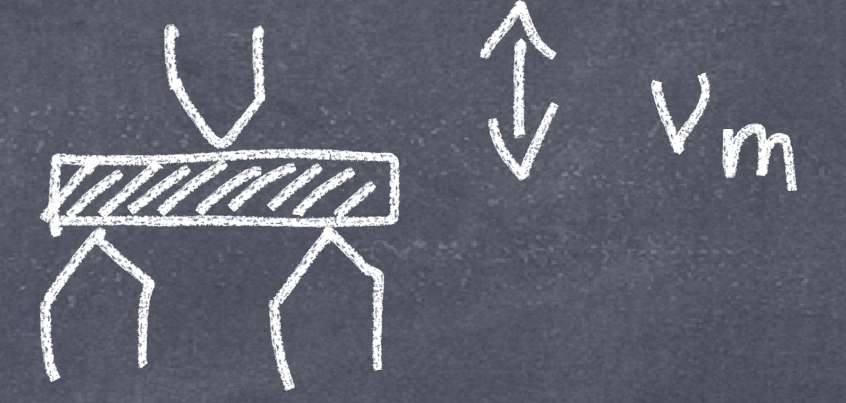
How to measure

D or τ^{-1} ?



FG: field gradient (NMR)

MR: mechanical relaxation



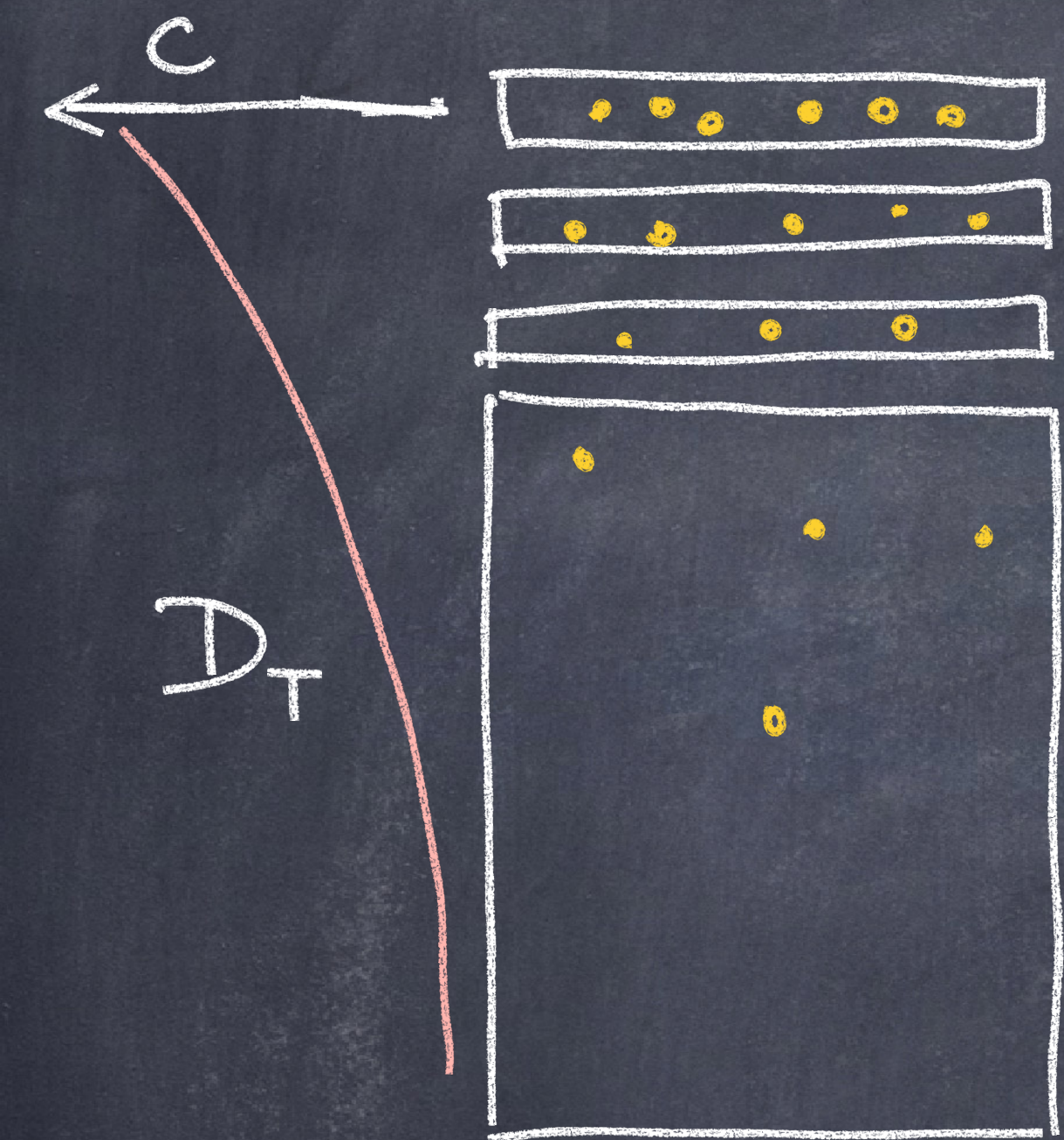
QENS: quasi elastic neutron scattering

$T_{1,2,\rho}$: relaxation NMR

MA: motional averaging

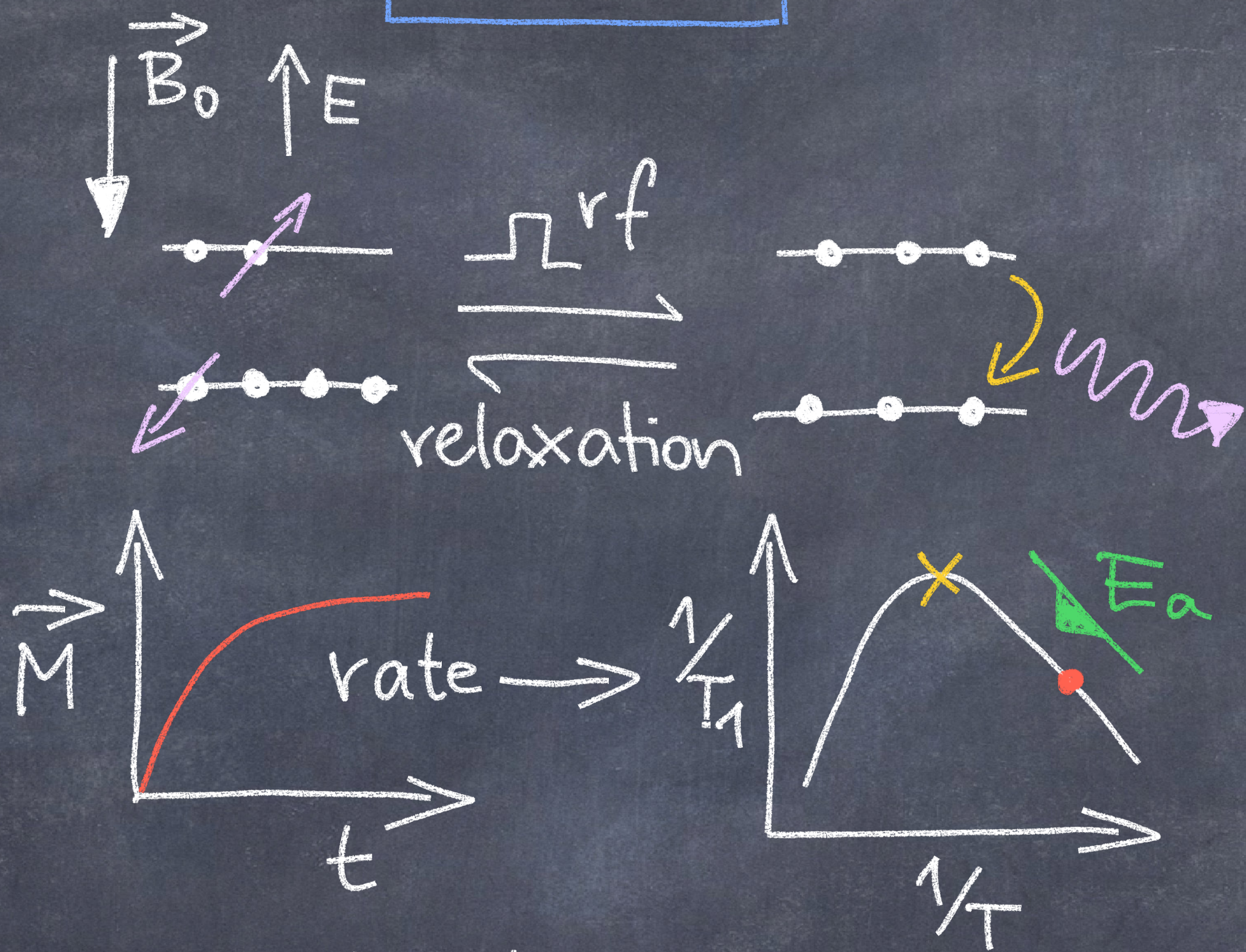
SAE: Spin-alignment NMR

TRACER



- radio tracer
- measure concentration profile

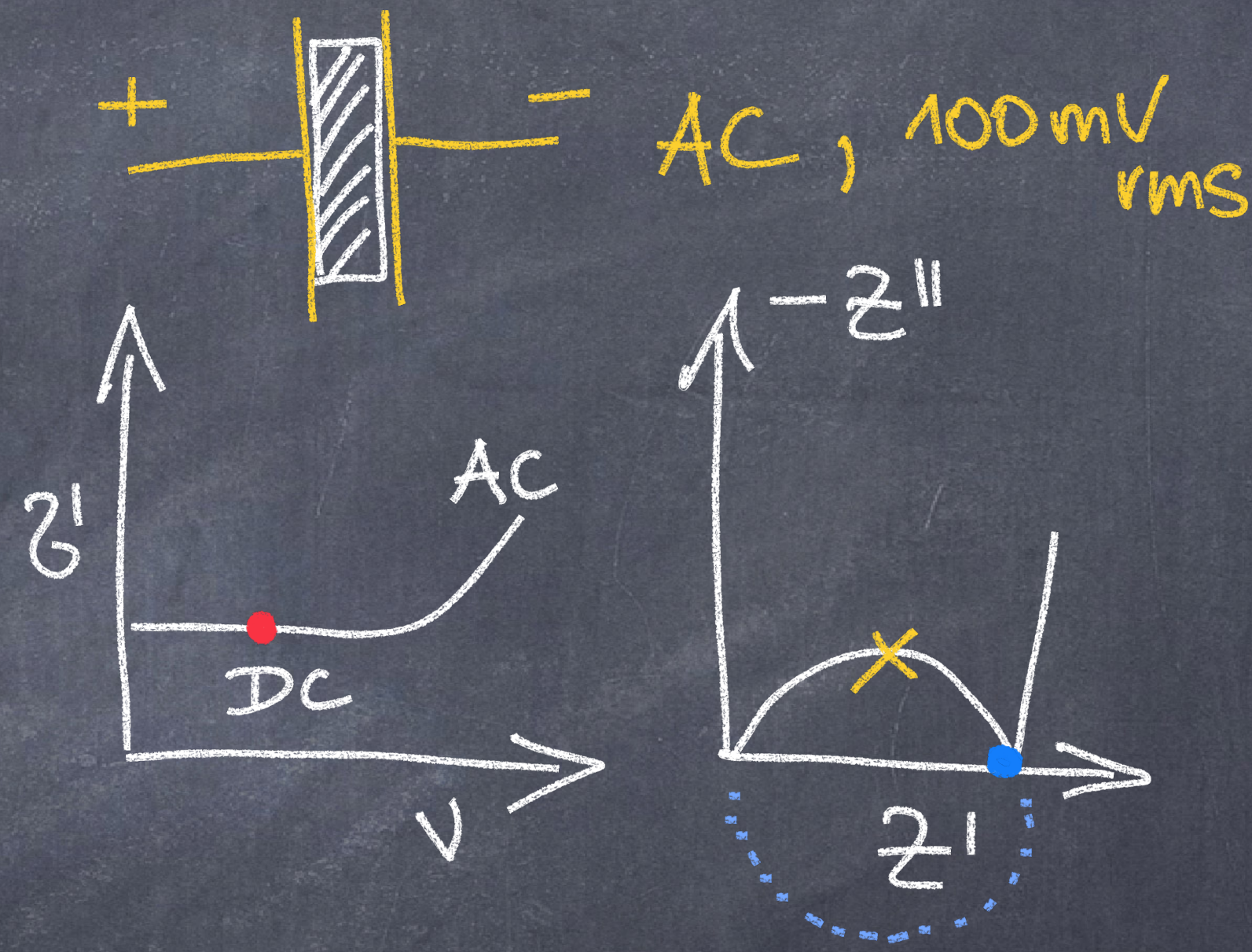
NMR



- measure relaxation rates

$x : \tau_c \omega_0 \approx 1$

CONDUCTIVITY AC, DC



- conductivity or impedence

$x : \omega_e CR \approx 1$

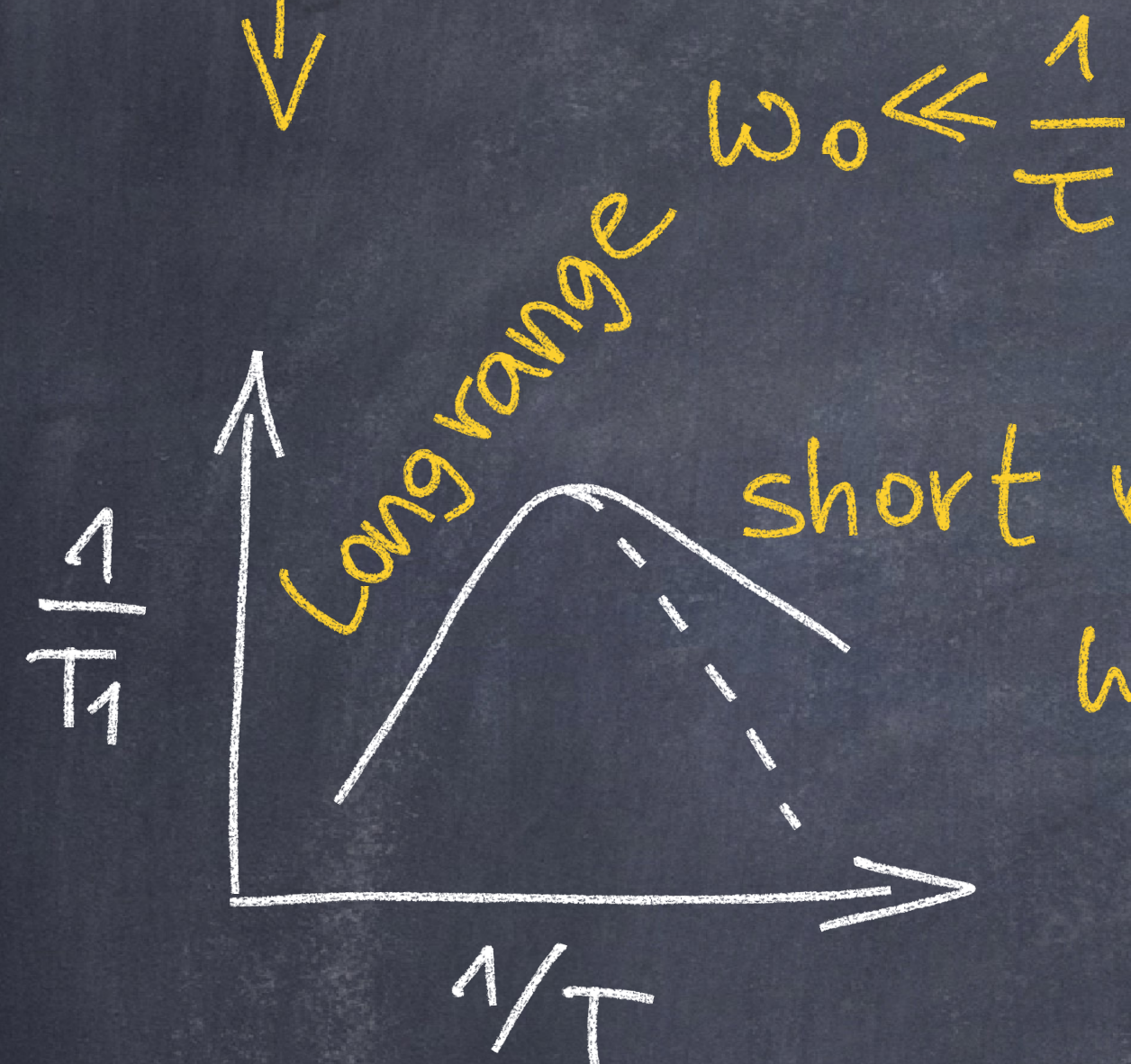
- short range vs. long range

- correlated vs uncorrelated

- grain boundary vs bulk (intragrain)

- ionic vs electronic

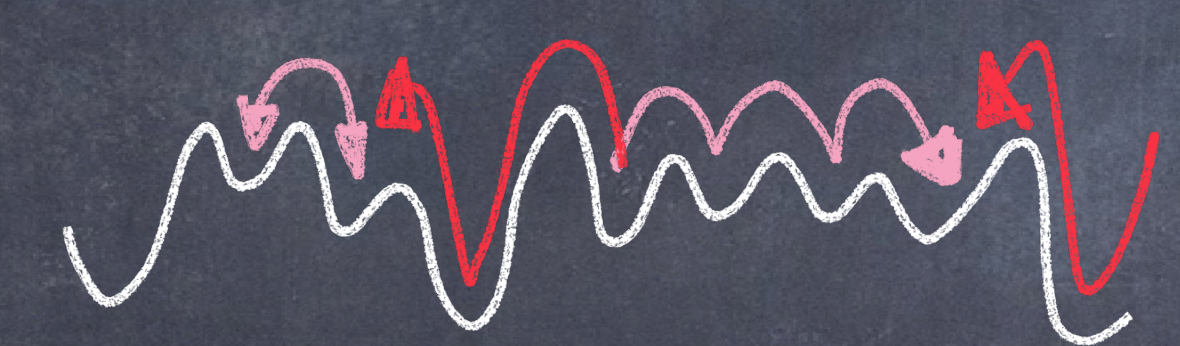
- dimensionality



$$\omega_0 \ll \frac{1}{\tau}$$

$$\omega_0 \gg \frac{1}{\tau}$$

NMR



no. of events (jumps)

per time

ω_0 : Larmor frequency

at low T: many jumps over low barriers (high probability)



- short range vs. long range

- correlated vs uncorrelated

- grain boundary vs bulk (intragrain)

- ionic vs electronic

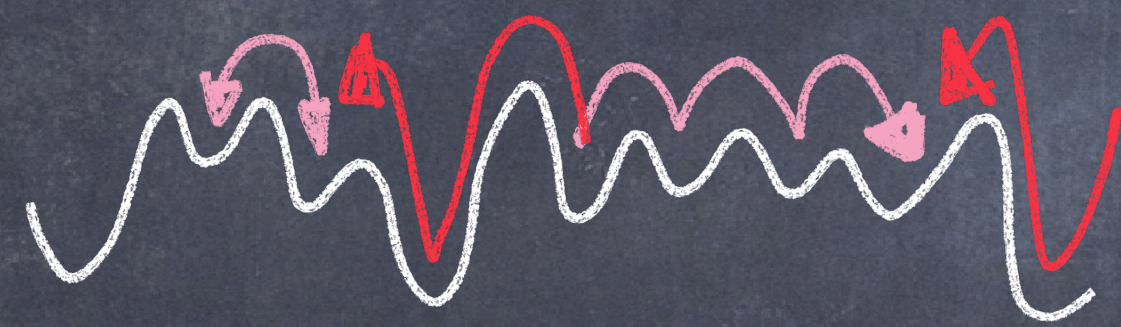
- dimensionality



$$\omega_0 \ll \frac{1}{\tau}$$

$$\omega_0 \gg \frac{1}{\tau}$$

NMR



no. of events (jumps)

per time

ω_0 : Larmor frequency



high T: probability to detect jumps over high barriers increases

- short range vs. long range

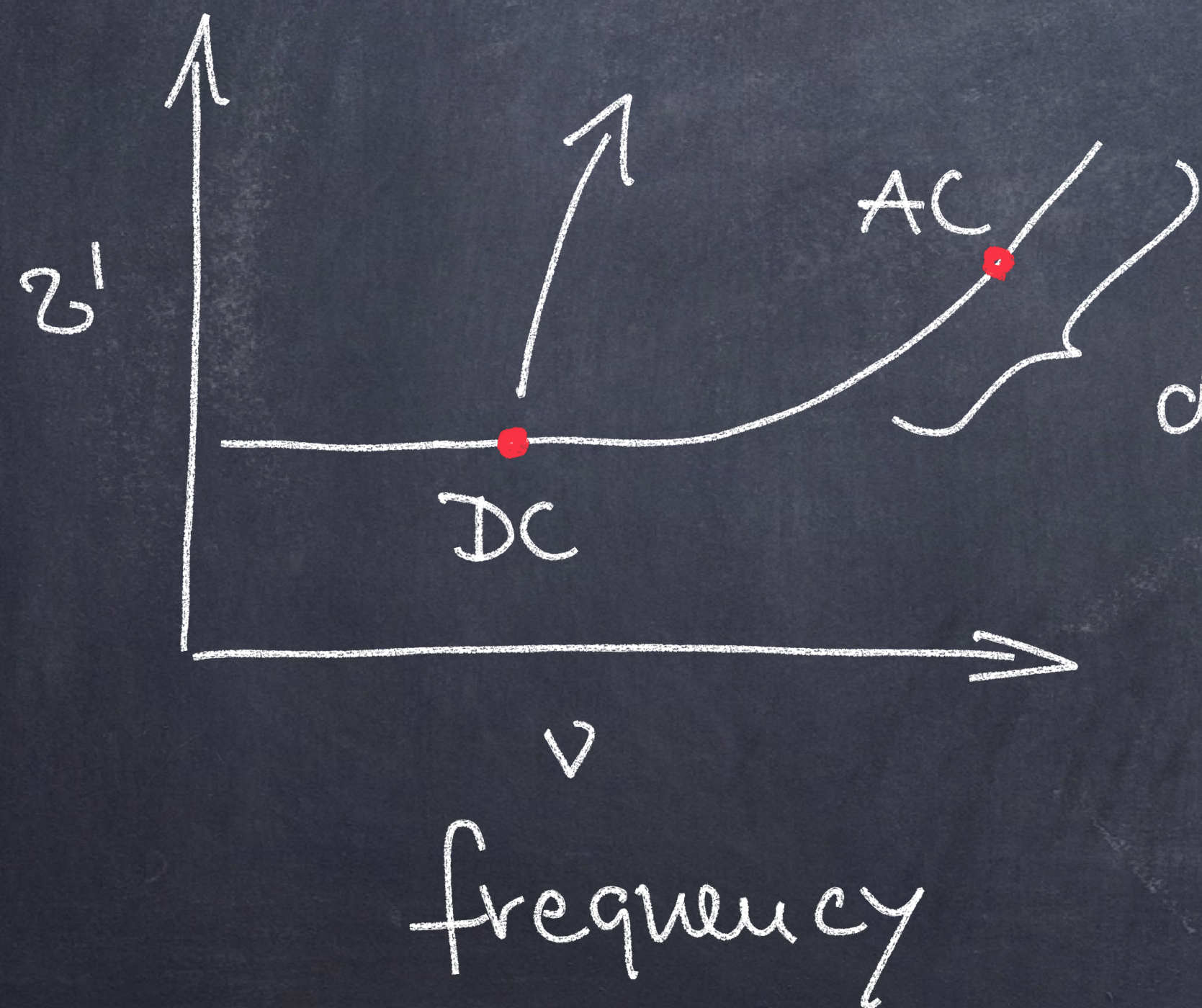
- correlated vs uncorrelated

- grain boundary vs bulk (intragrain)

- ionic vs electronic

- dimensionality

successful jumps



$$Z_{DC} = f(T)$$
$$Z_{AC} = f(T)$$

dispersive region

forward, backward jumps

localised motions,

NCL behaviour at low T

- short range vs. long range

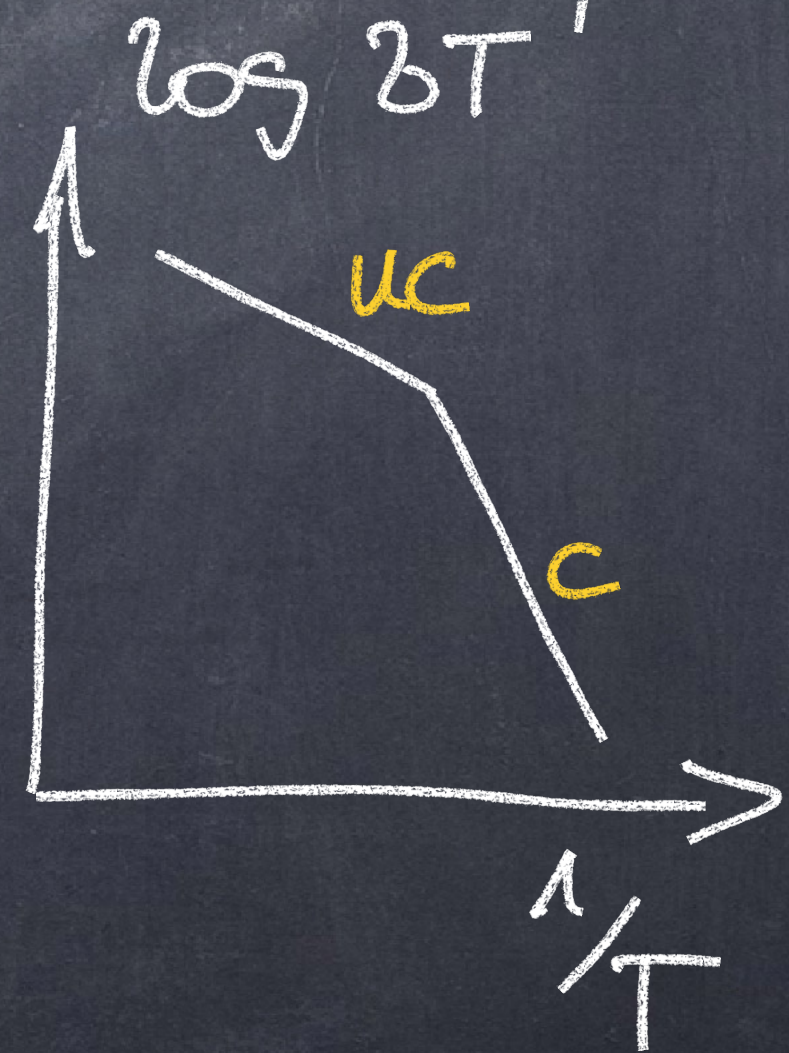
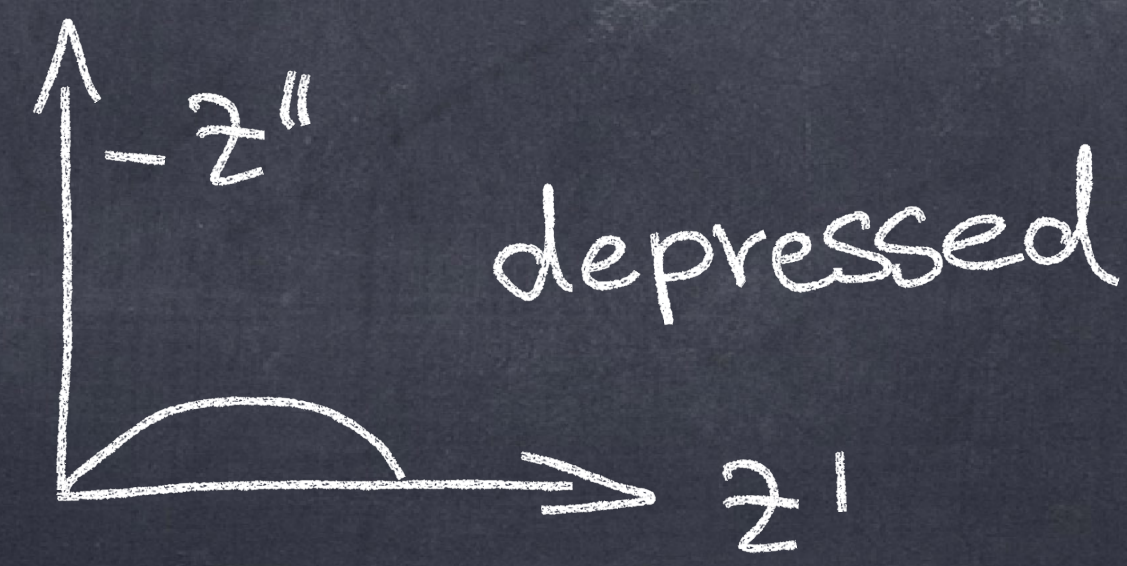
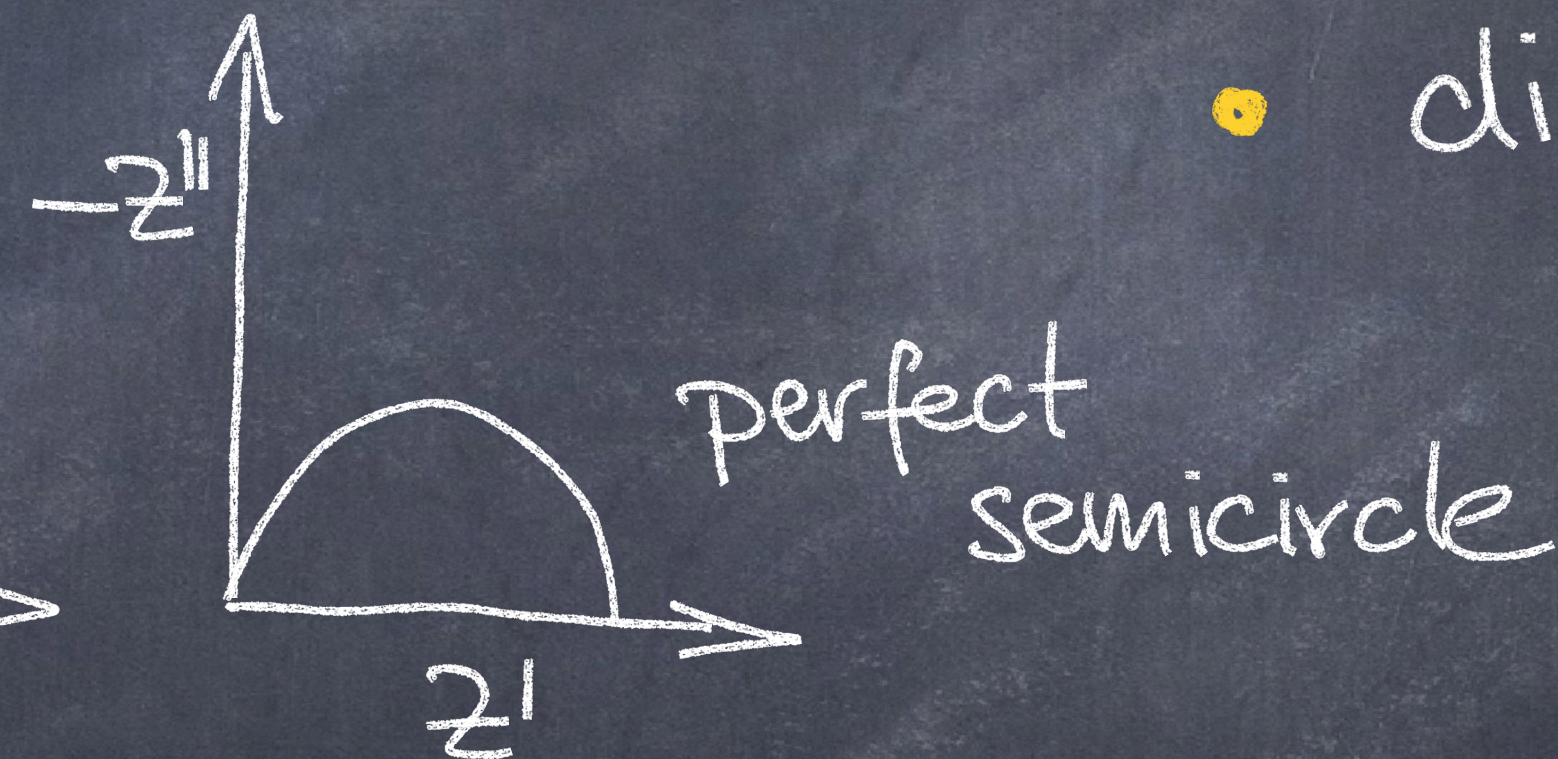
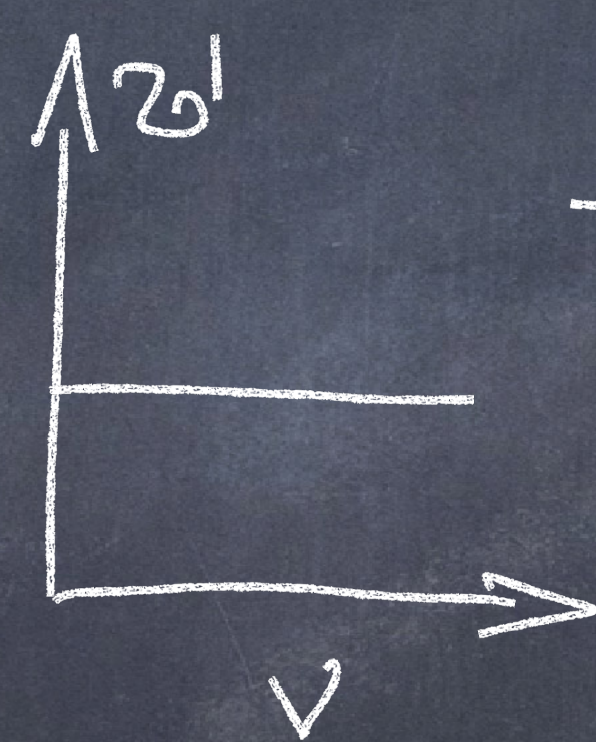
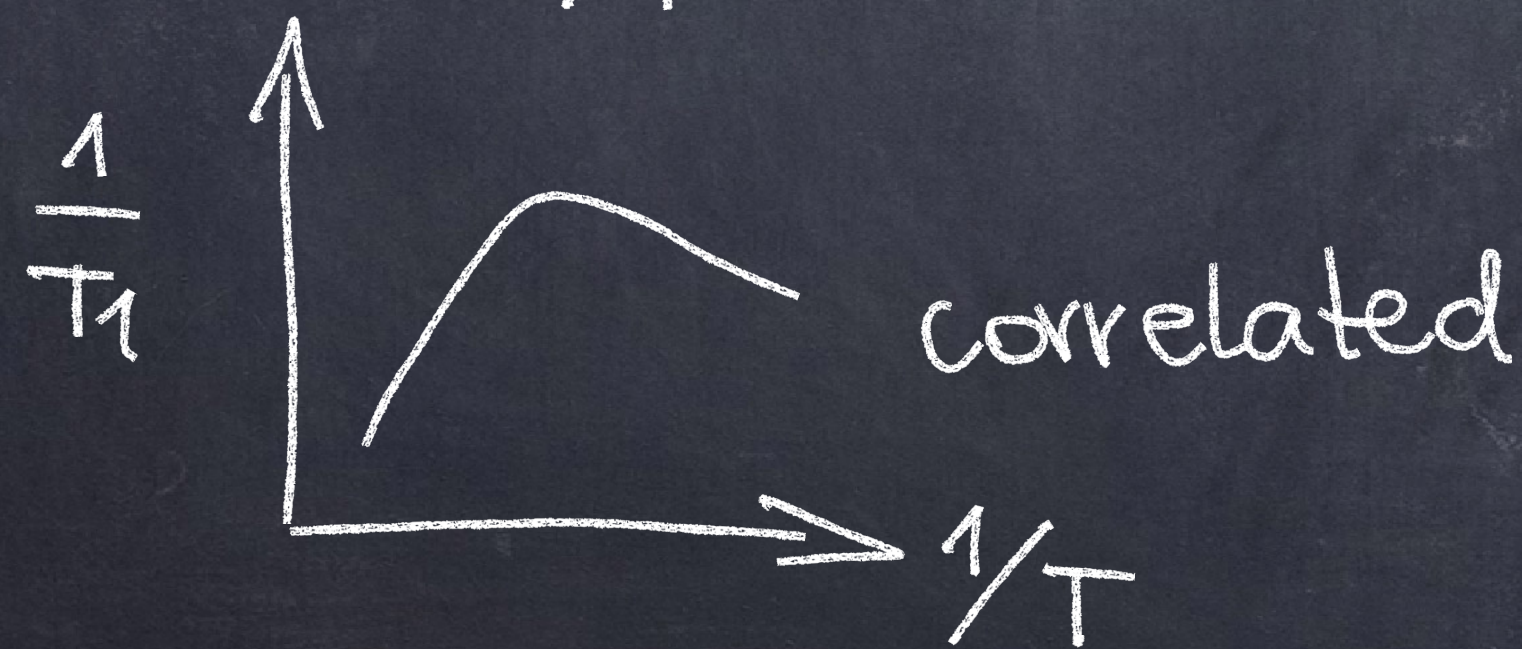
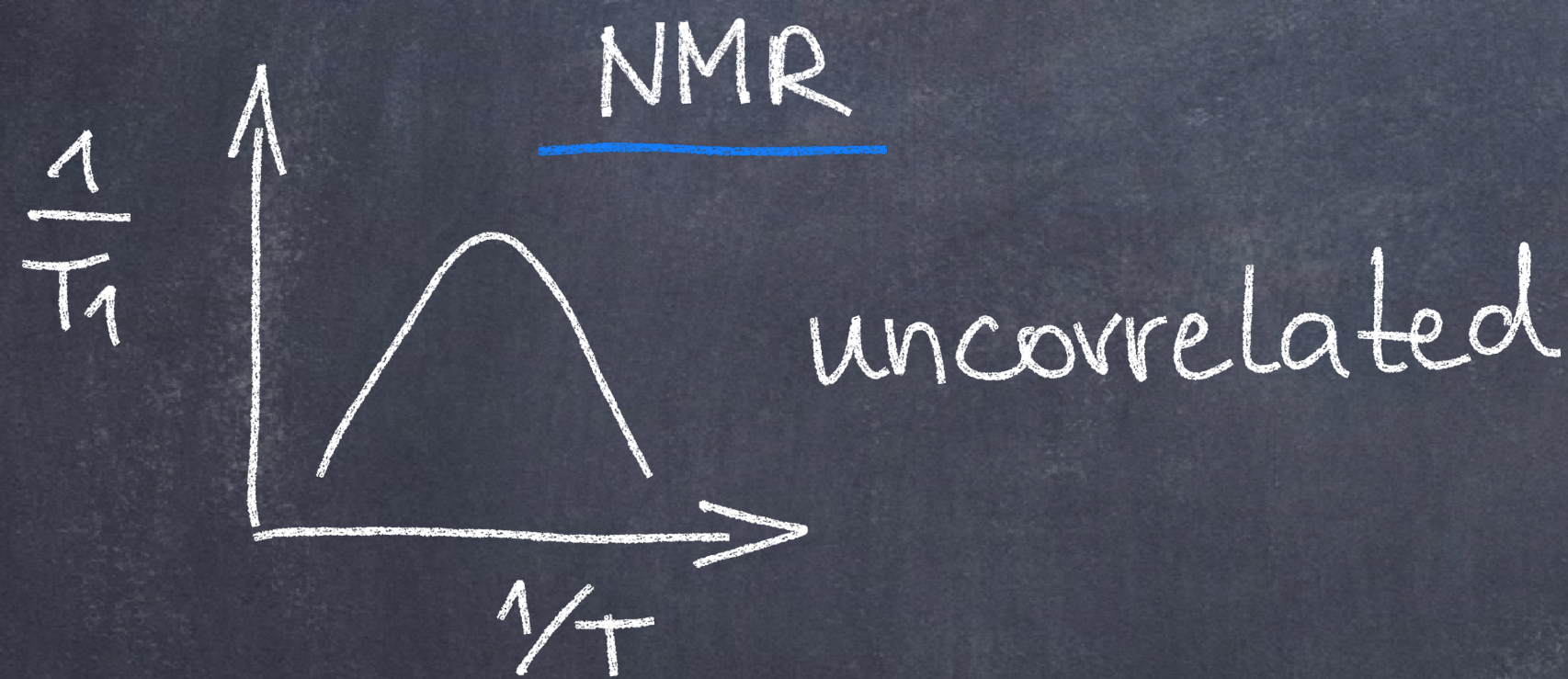
- correlated ^c vs uncorrelated ^{uc}

- grain boundary vs bulk (intragrain)

- ionic vs electronic

CONDUCTIVITY

- dimensionality



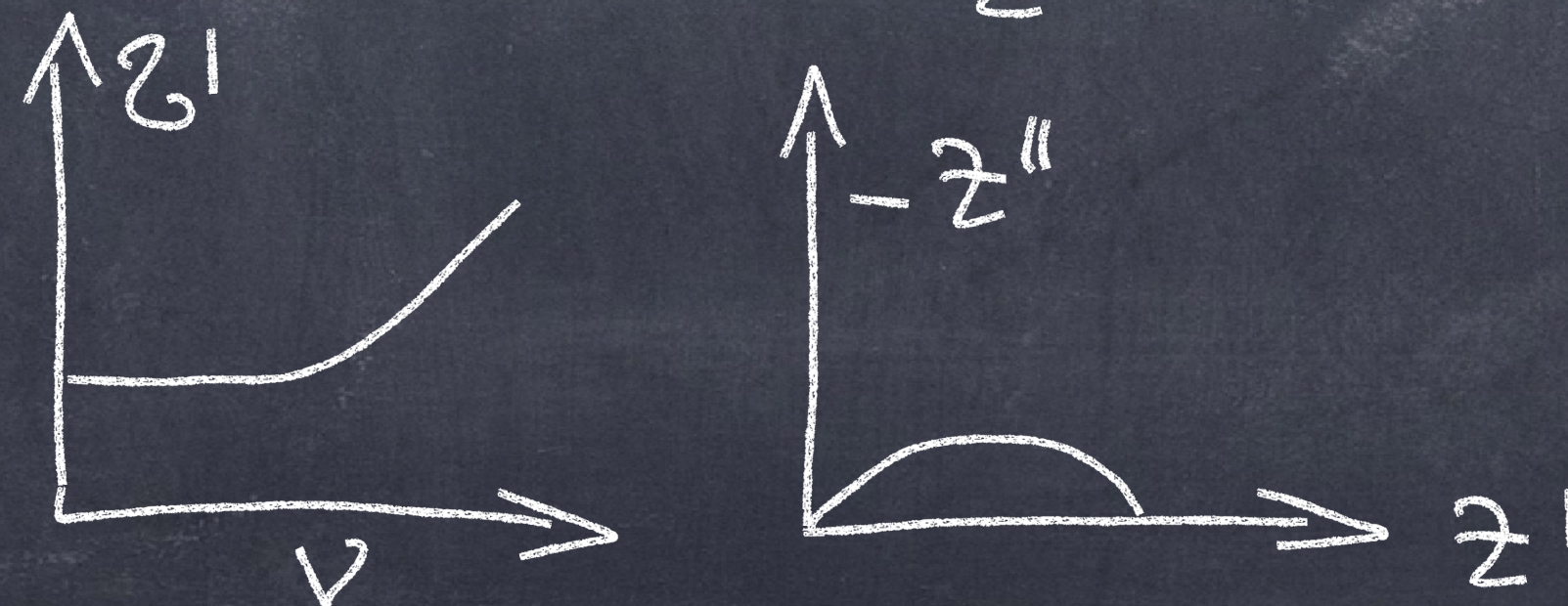
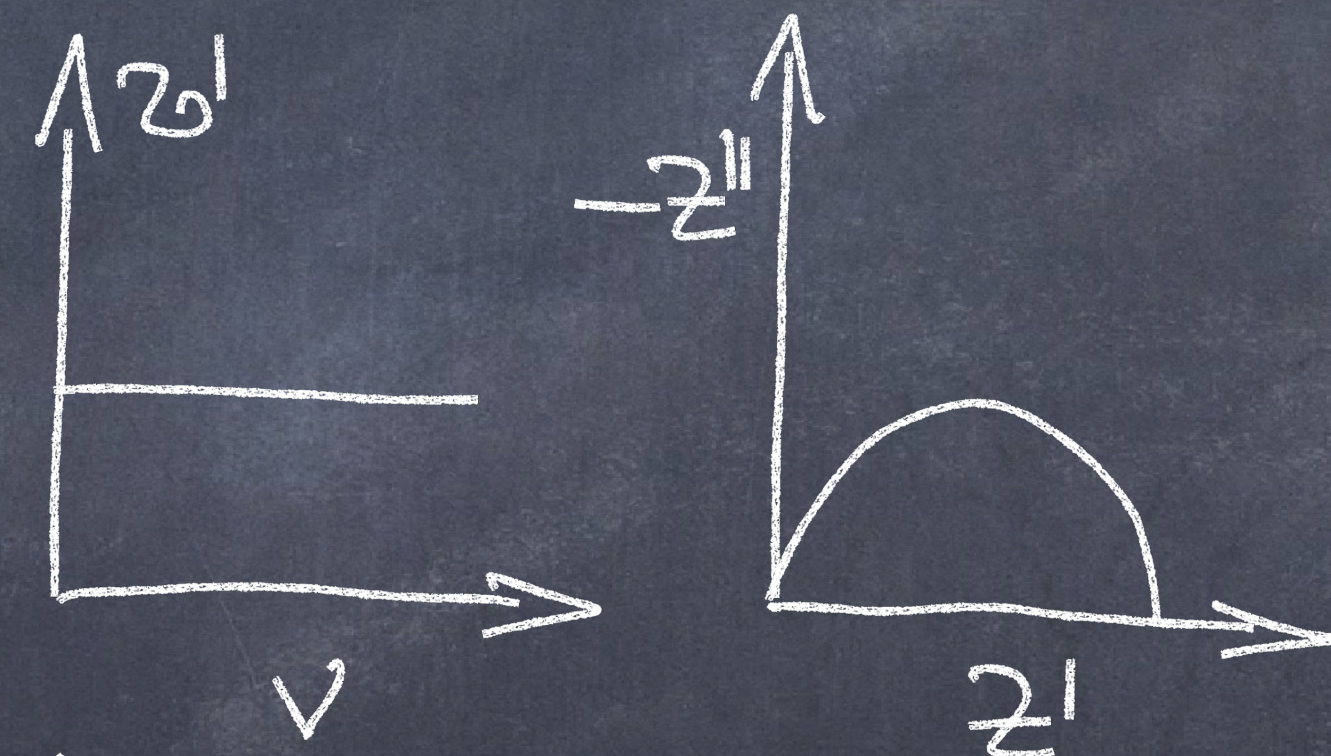
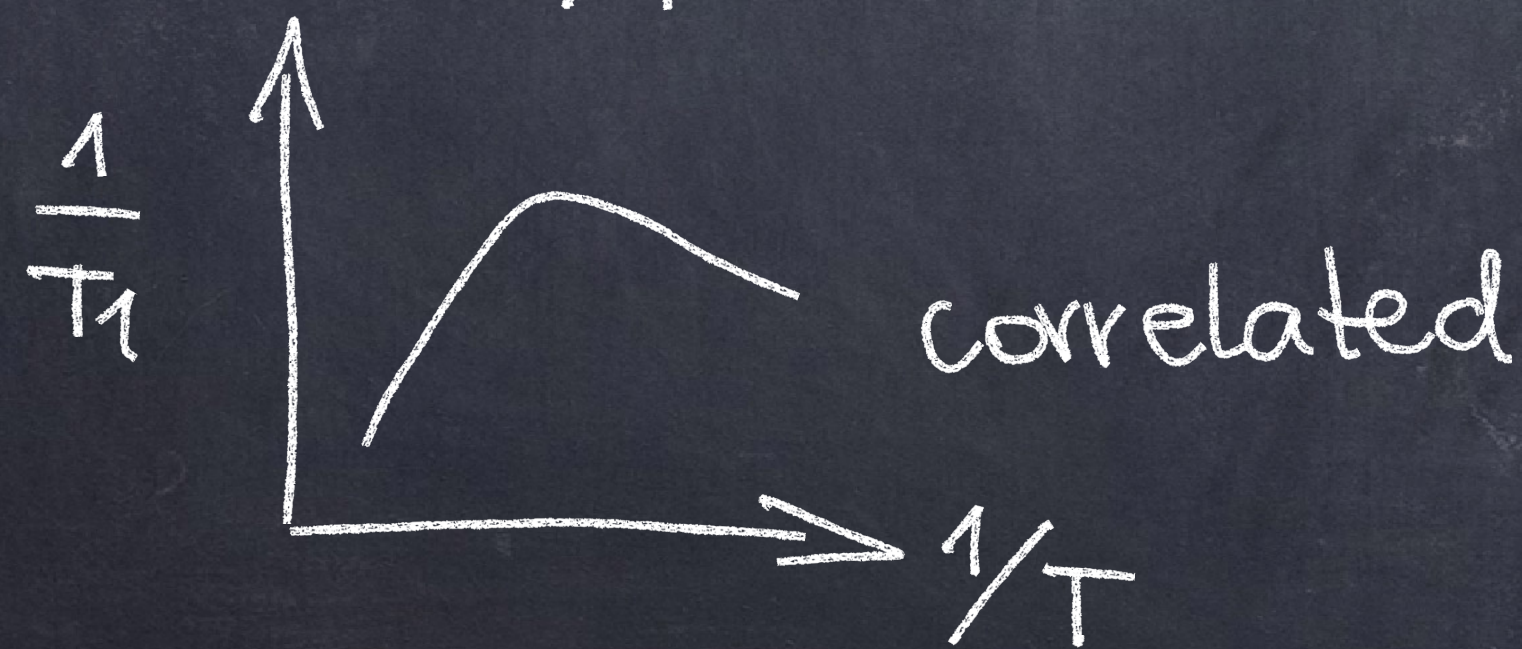
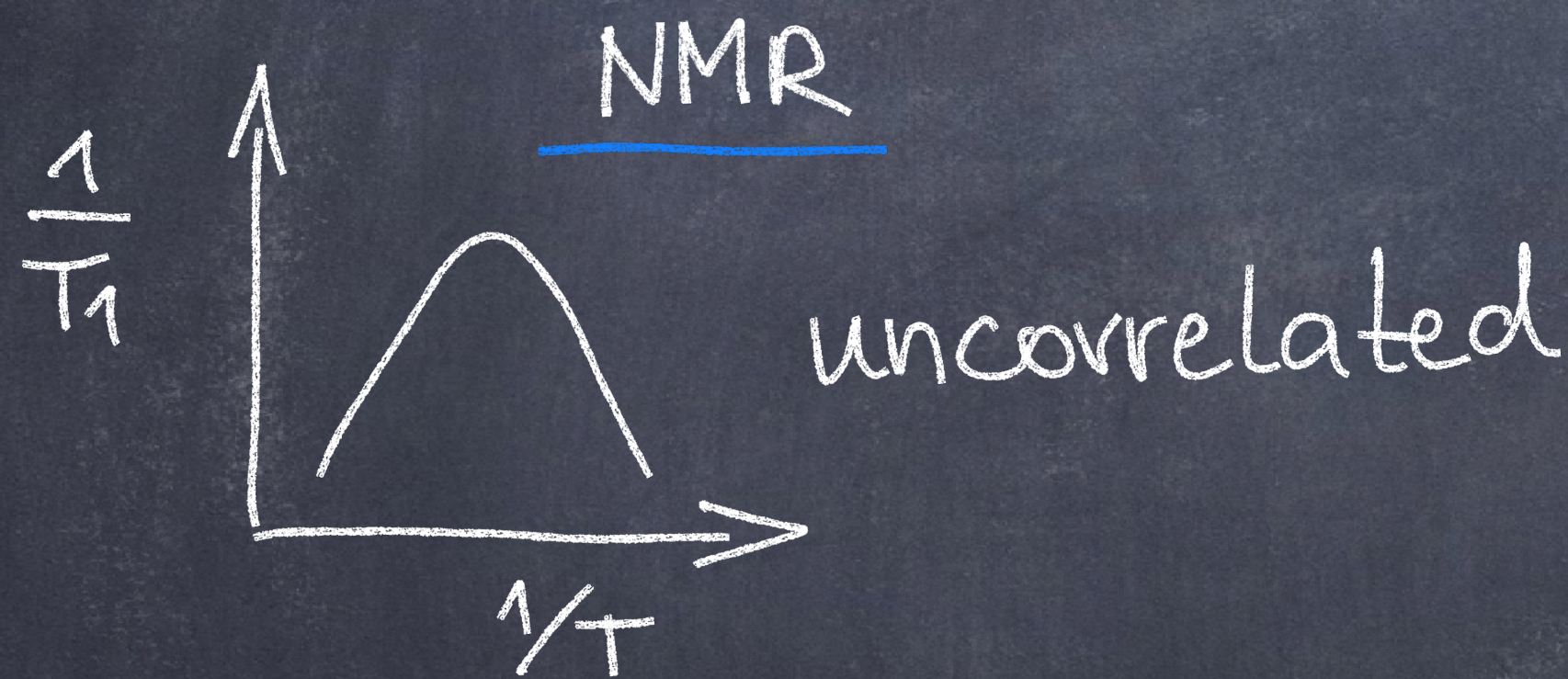
- short range vs. long range

- correlated ^c vs uncorrelated ^{uc}

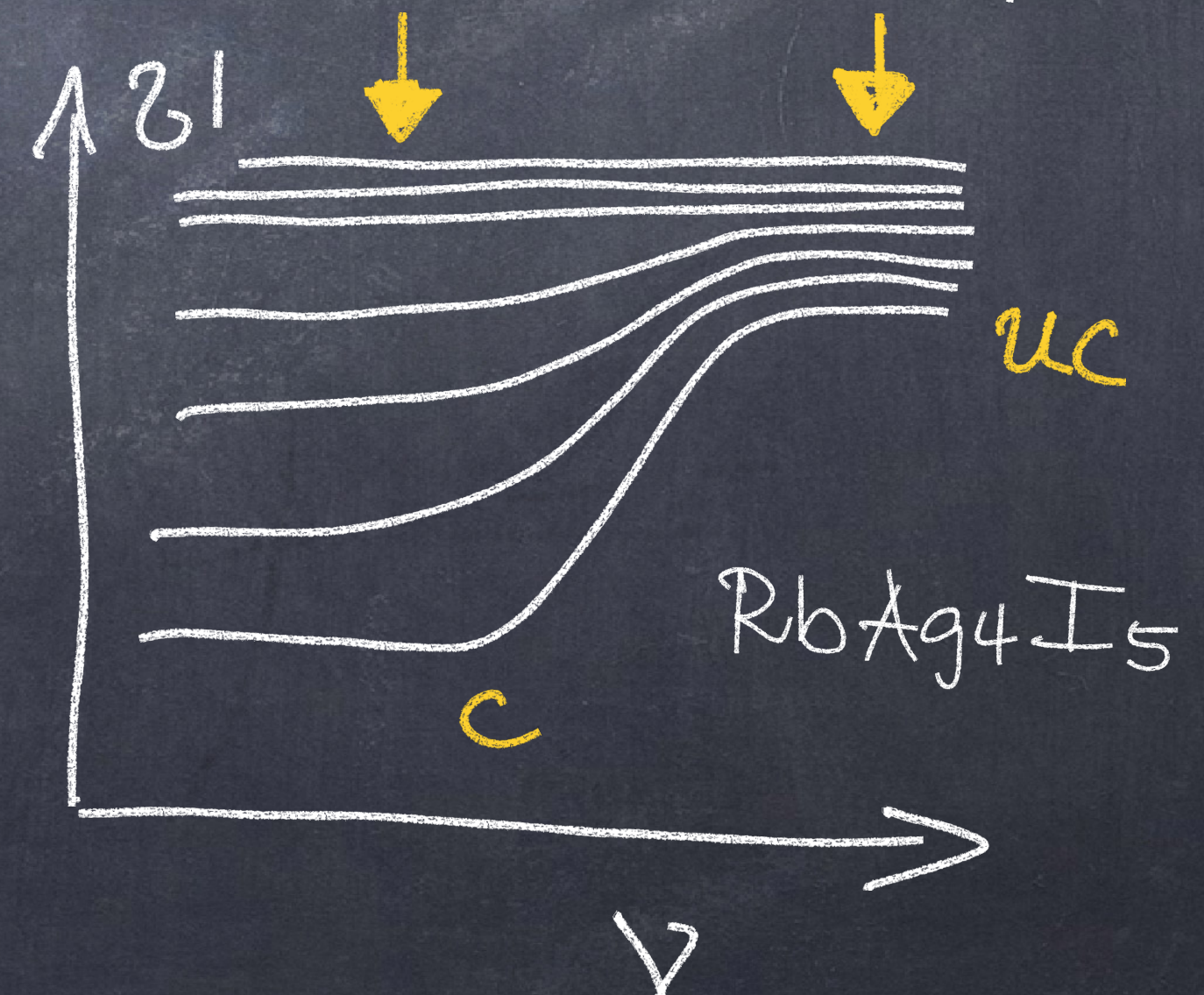
- grain boundary vs bulk (intragrain)

- ionic vs electronic

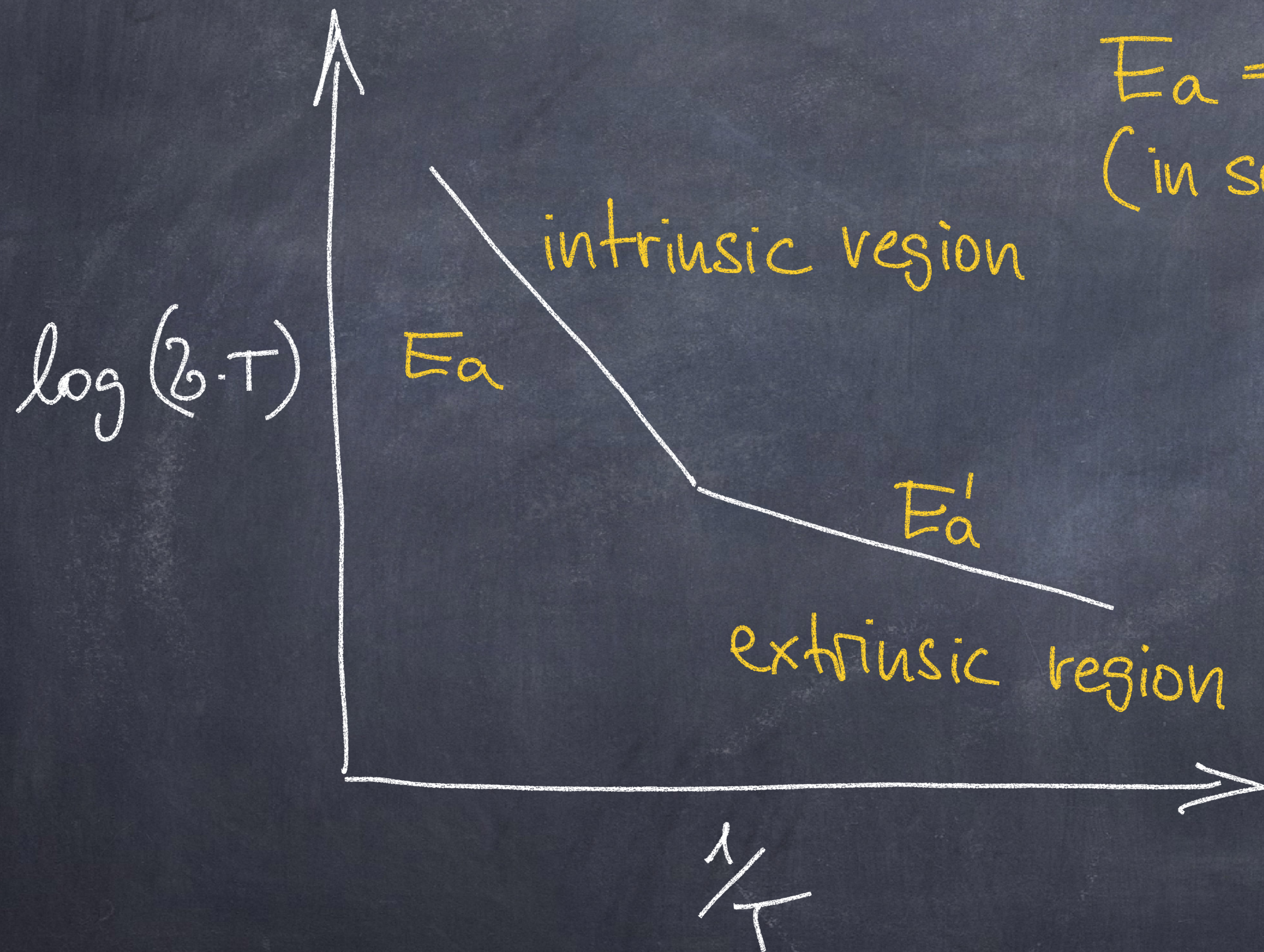
CONDUCTIVITY



- dimensionality



ζ : conductivity
 can also directly be measured : impedance spectroscopy



$E_a = 2 \cdot E'_a$
 (in some cases)

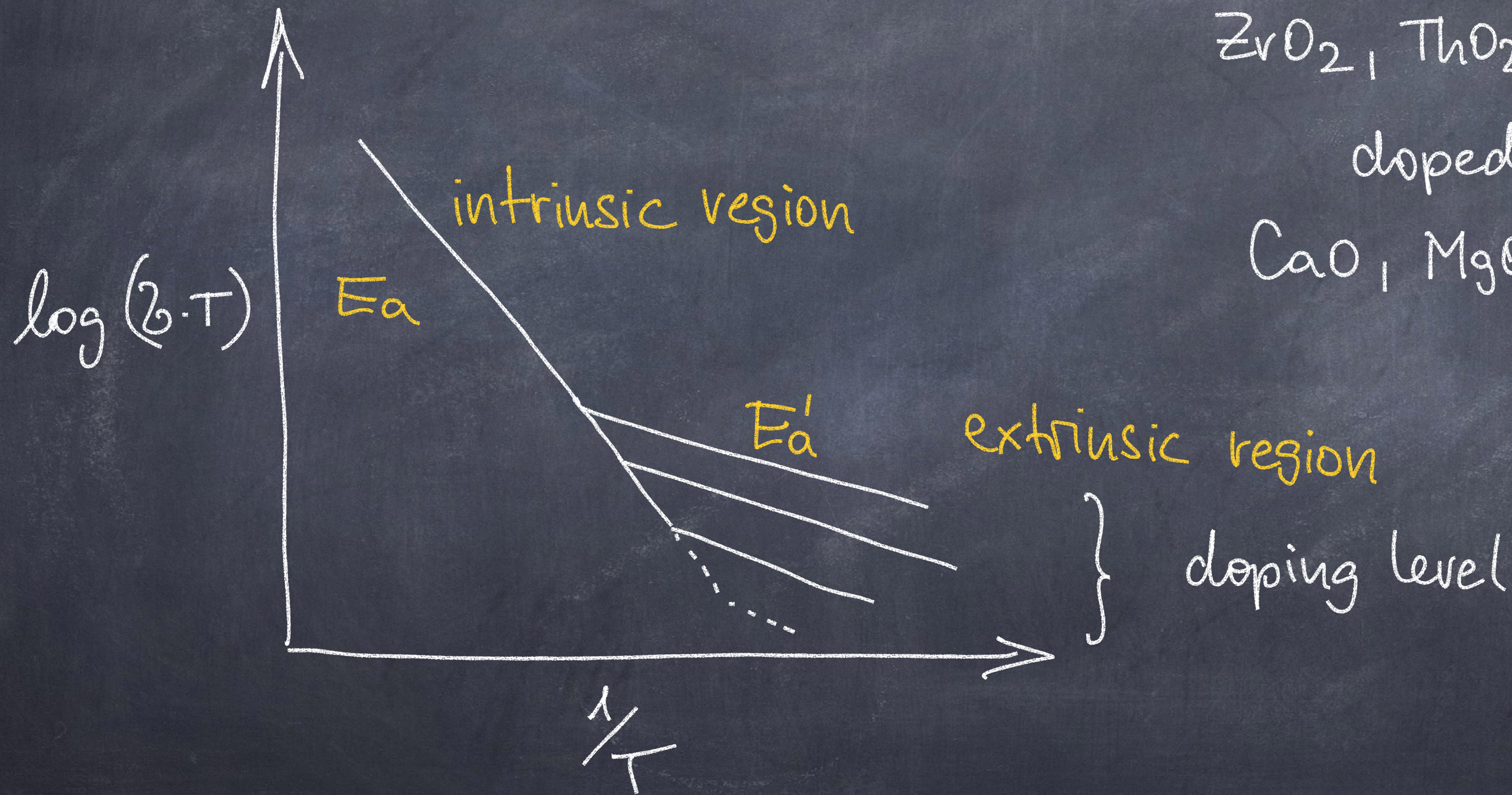
$$\zeta = \frac{\zeta_0}{T} e^{-E_a / (k_B \cdot T)}$$

plot $\ln(\zeta \cdot T)$ vs $\frac{1}{T}$

or

$\log(\zeta \cdot T)$ vs $\frac{1}{T}$

... polycrystalline samples and single crystals:



ZrO_2, ThO_2, CeO_2

doped with

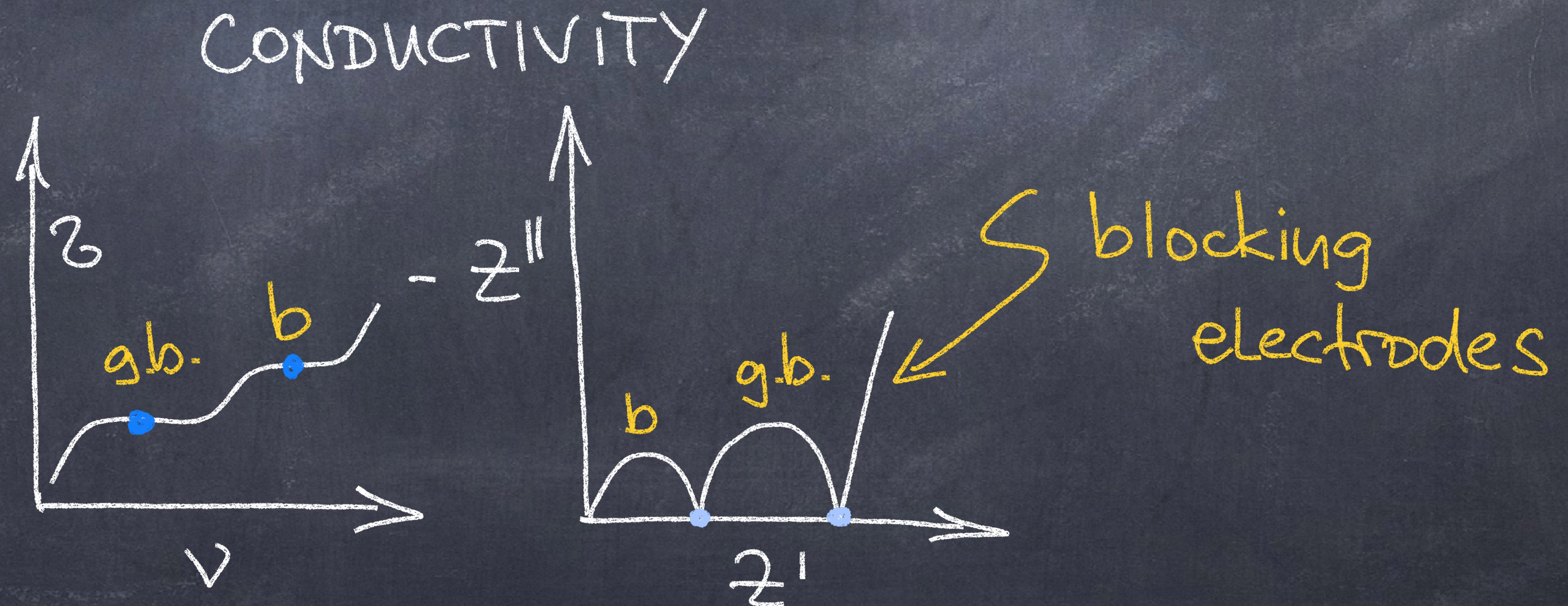
$CaO, MgO, Y_2O_3, Sc_2O_3,$
 Ln_2O_3, \dots

- short range vs. long range
 - correlated vs uncorrelated
 - grain boundary vs bulk (intragrain)
 - ionic vs electronic
 - dimensionality



NMR
needs many spins
in g.b.
regions

- nanocrystalline materials

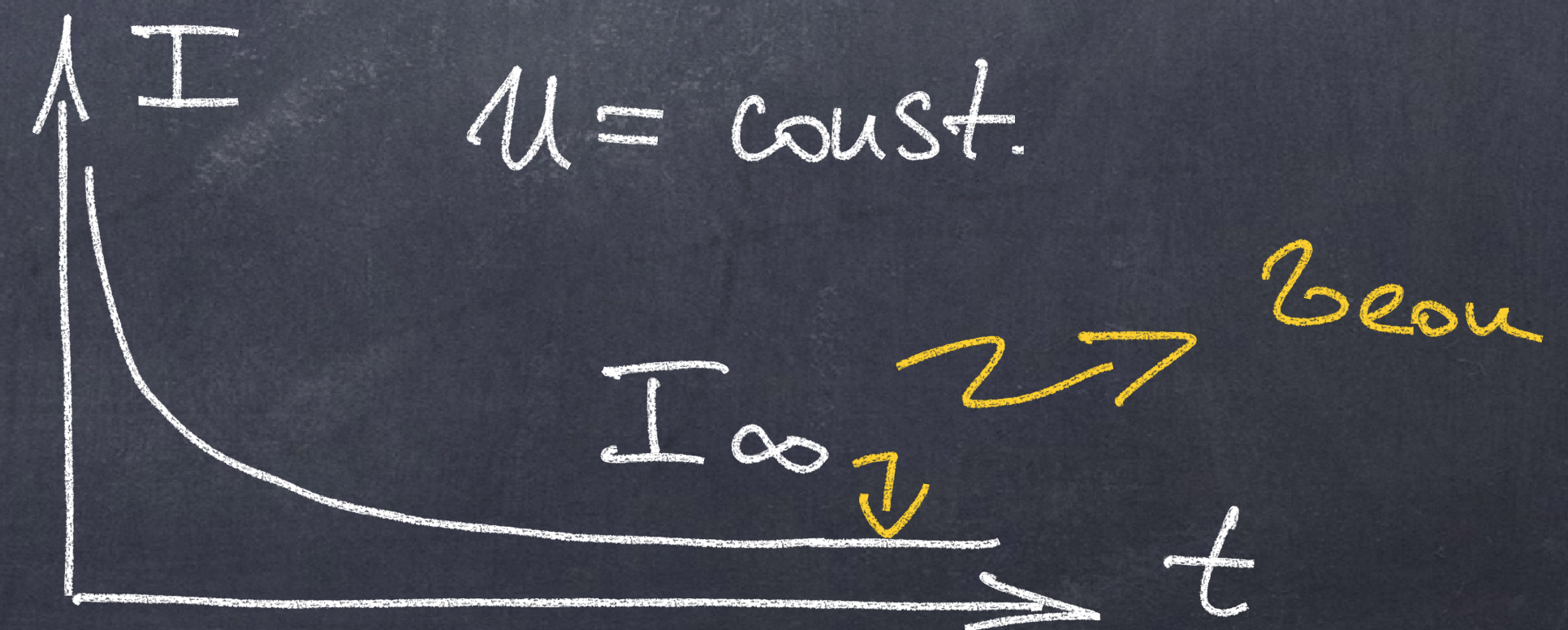


- short range vs. long range
 - correlated vs uncorrelated
 - grain boundary vs bulk (intragrain)
 - ionic vs electronic

NMR (^7Li , ^{23}Na , ^1H , ...) is sensitive to ionic dynamics

Conductivity: $\sigma_{\text{ion}} < \sigma_{\text{total}}$

Chronoamperometric meas.
(polarisation)



- short range vs. long range

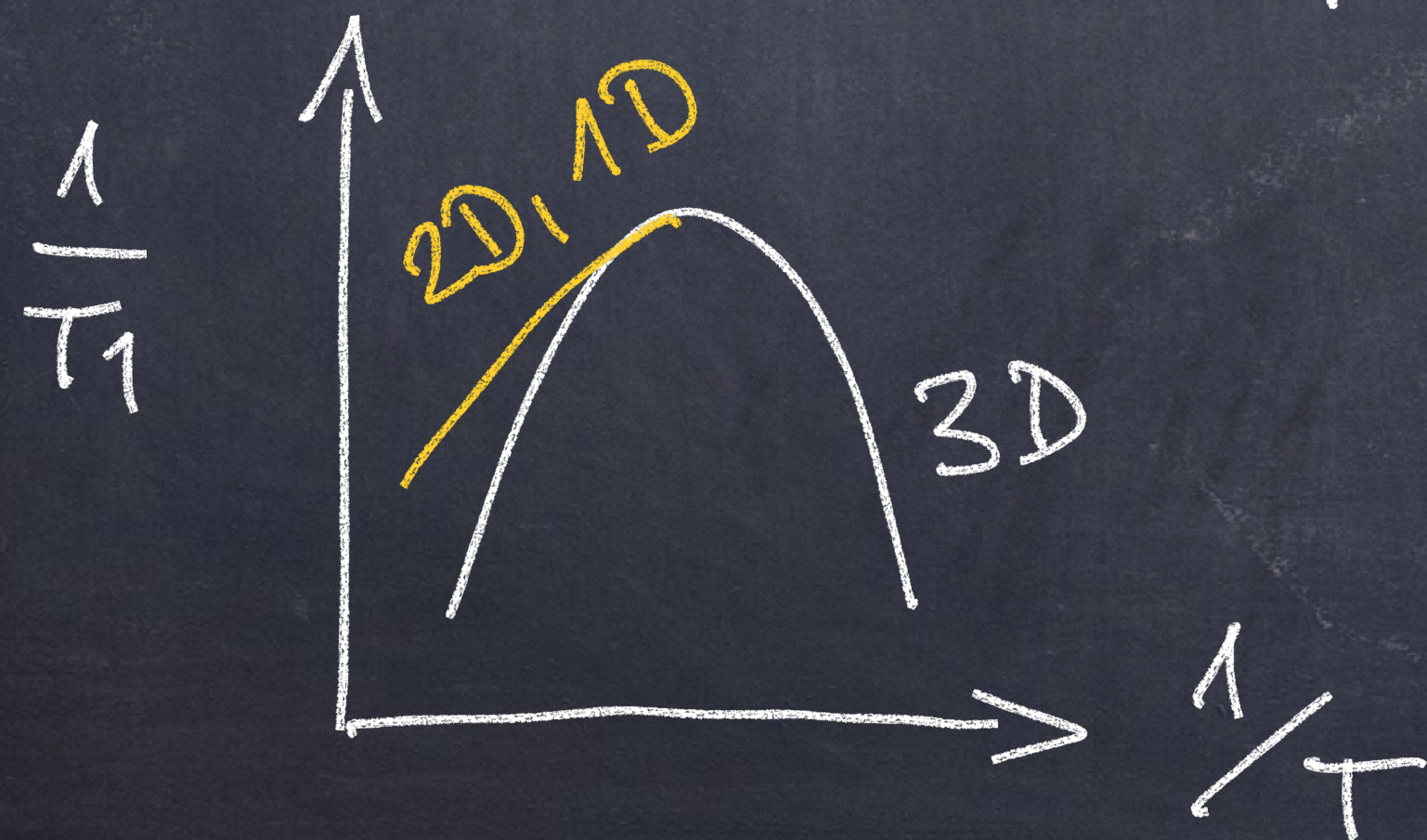
- correlated vs uncorrelated

- grain boundary vs bulk (intragrain)

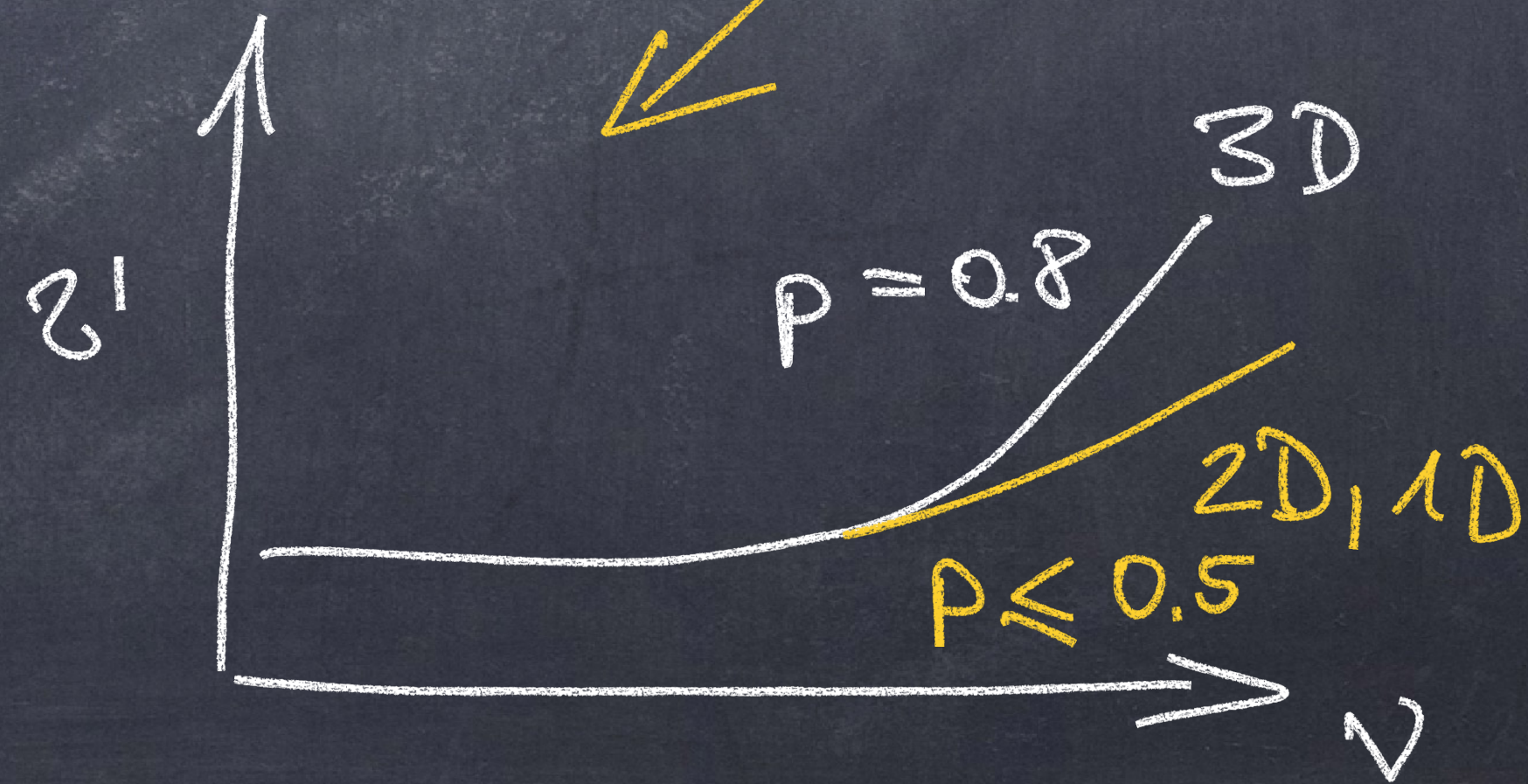
- ionic vs electronic

NMR:

$\frac{1}{T_1} \propto J(\omega_0)$; J_{1D}, J_{2D}, J_{3D}
spectral density
function



COND.:



$z' \propto \nu^p$

- dimensionality

$p = 0.8$

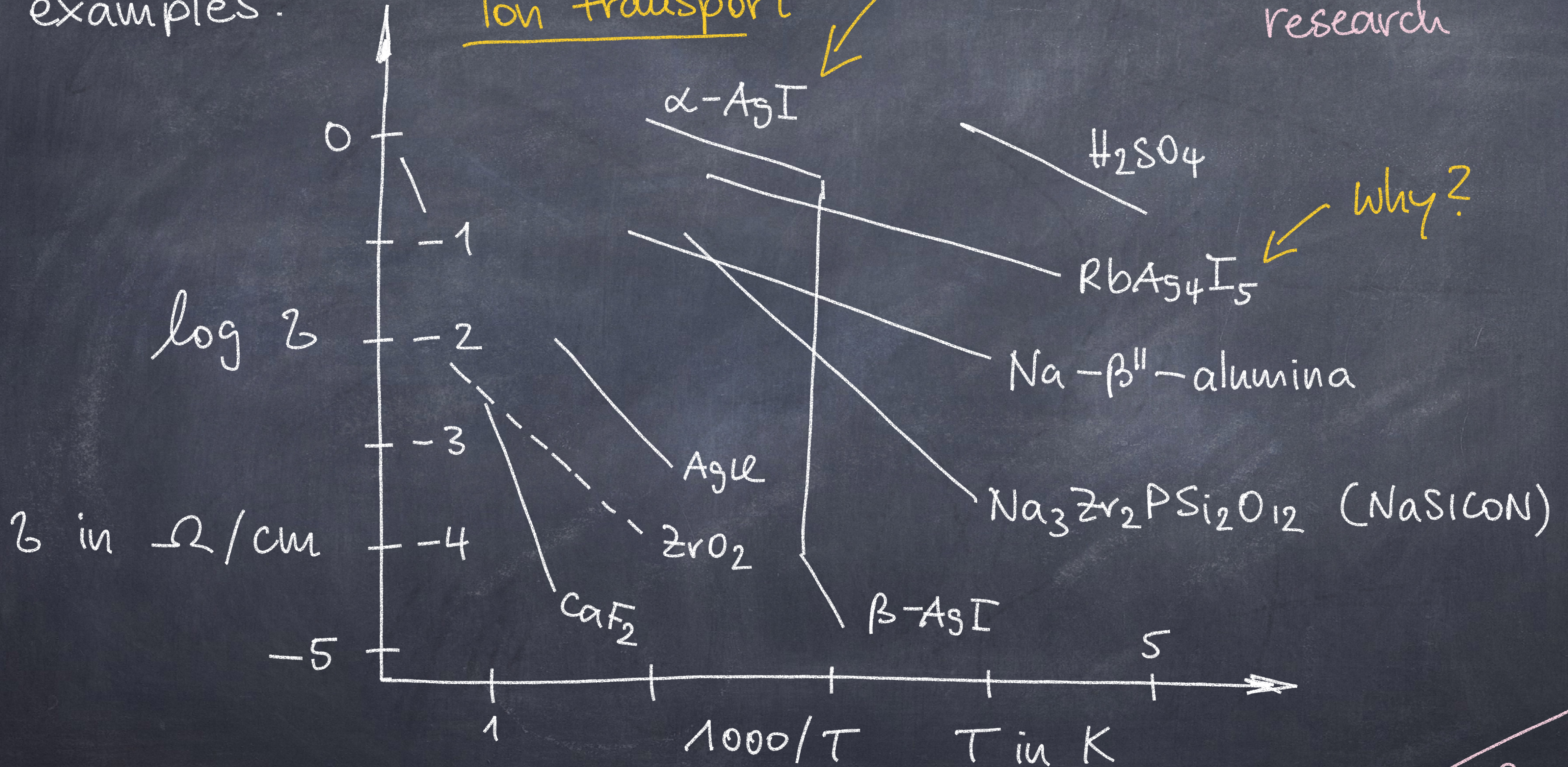
$p \leq 0.5$

Some examples:

origins of fast ion transport

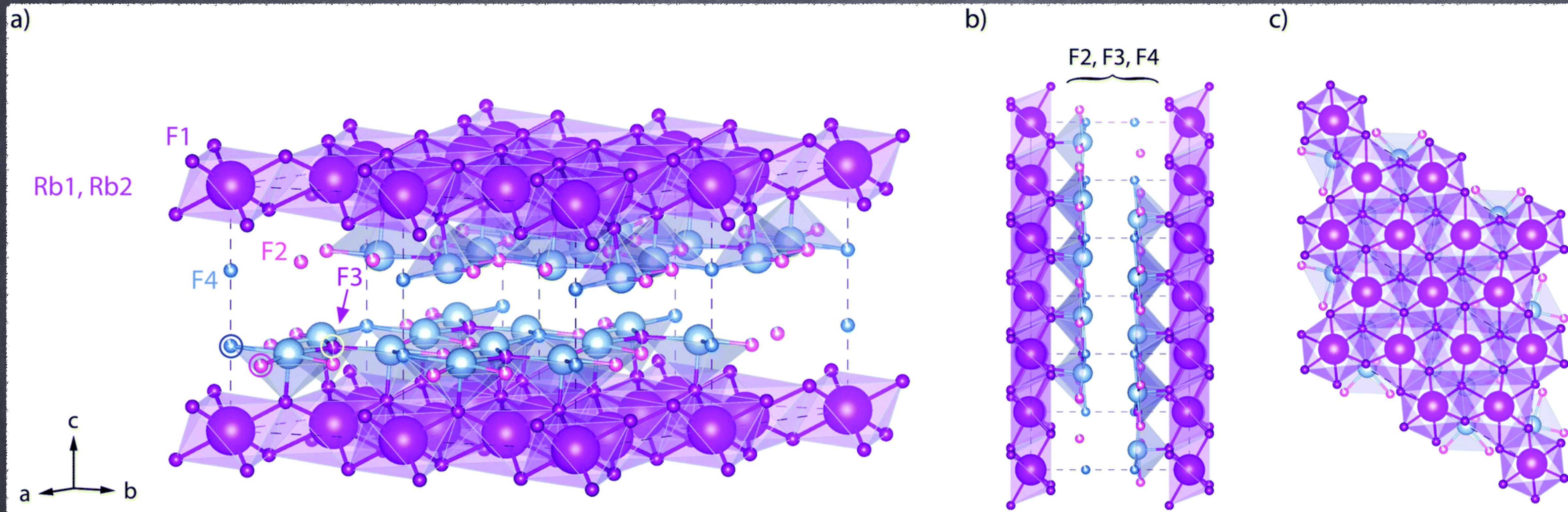
Why?

Current research



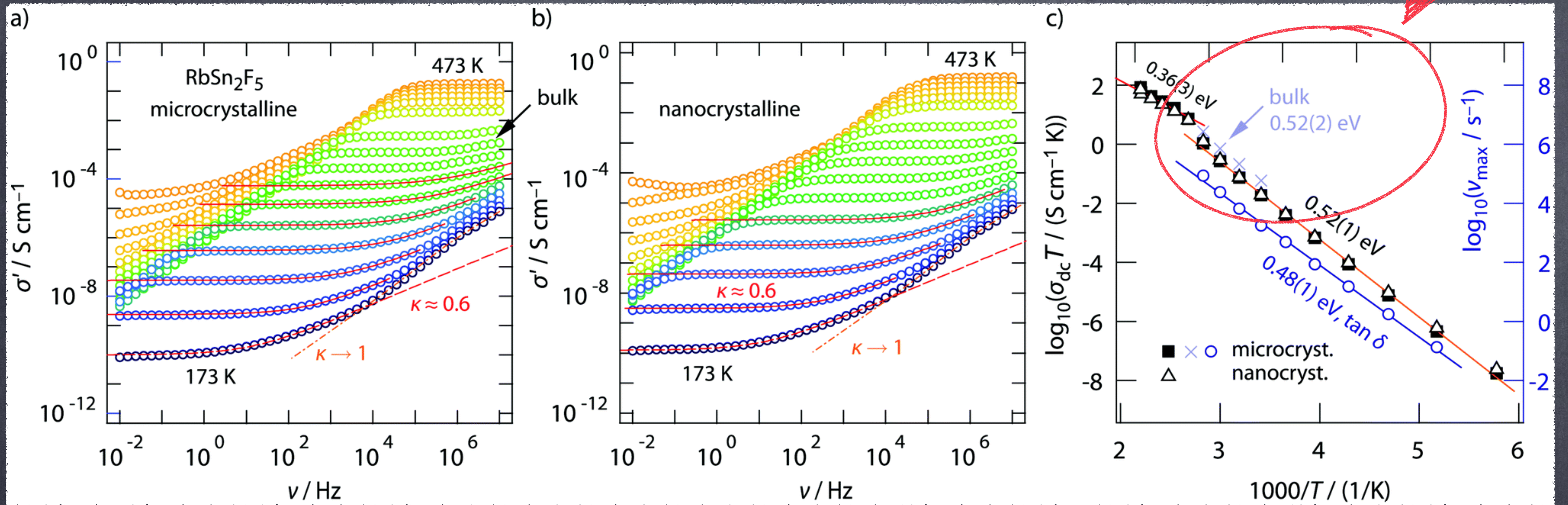
end

... a final example: RbSu_2F_5 (just few images)



a 2D ionic conductor?

Conductivity isotherms:



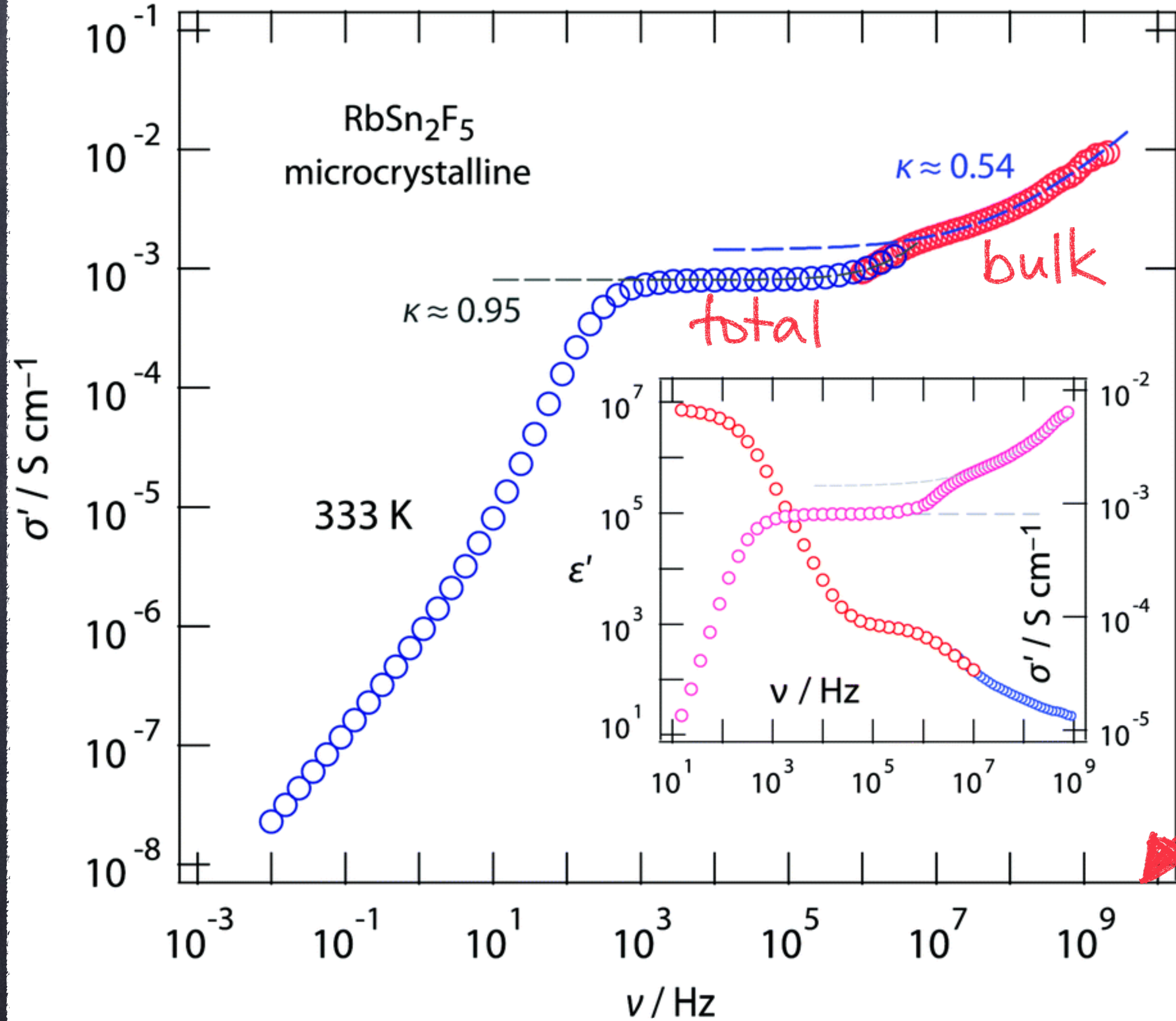
activation energy : $\sim 0.48 \text{ eV} \dots 0.52 \text{ eV}$ (F⁻)

bulk vs. g.b./total

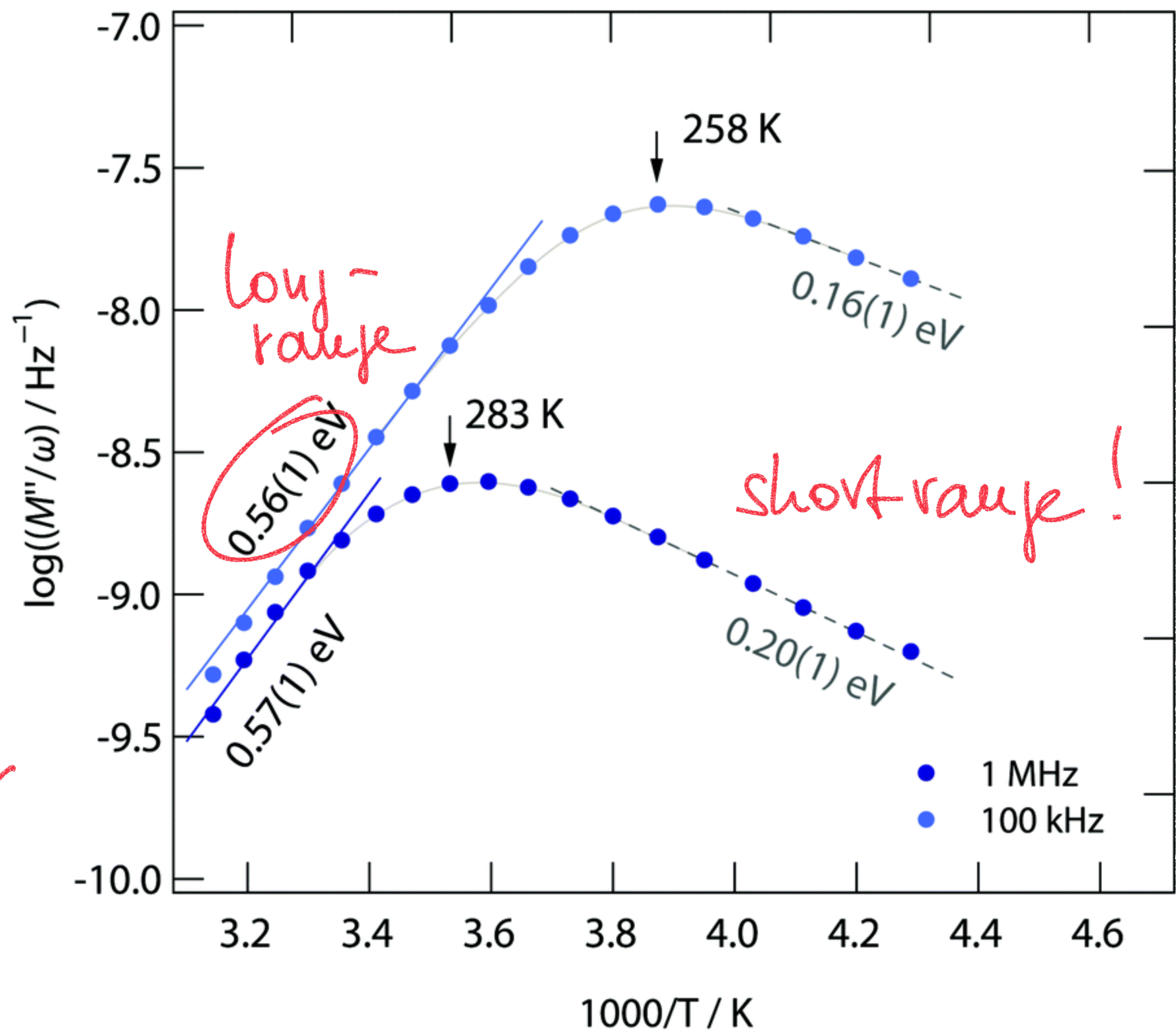
$M'' \propto \frac{1}{\omega}$: bulk!

a)

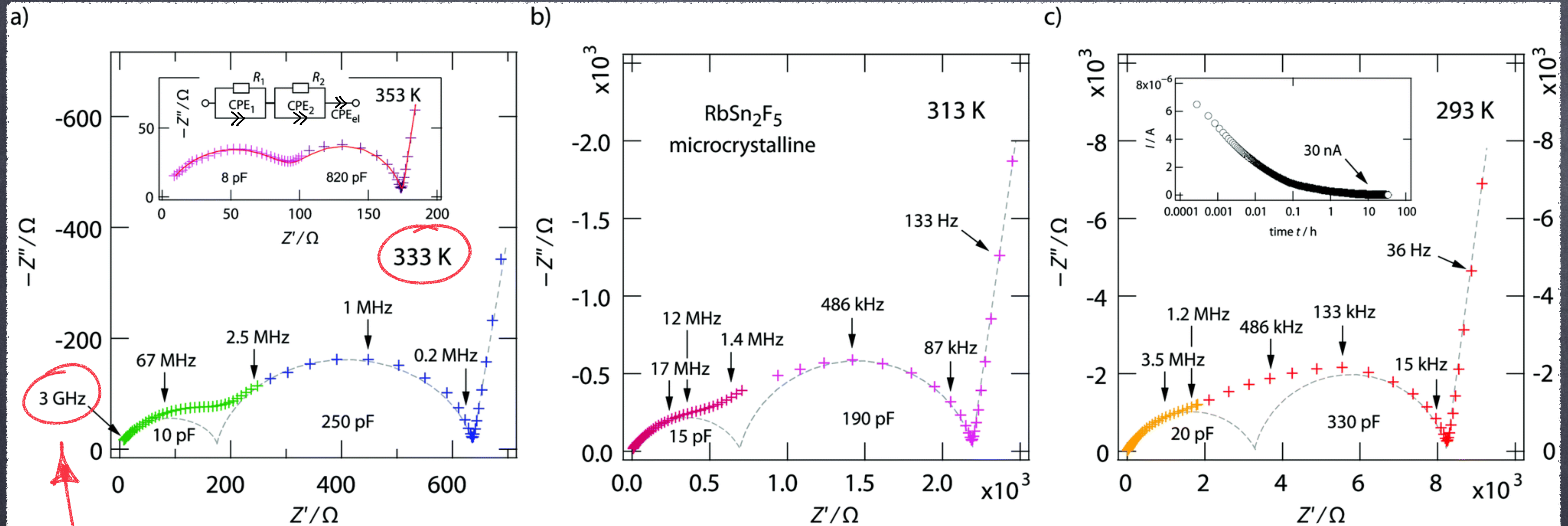
$\nu/\text{Hz} \rightarrow 10^9$



b)

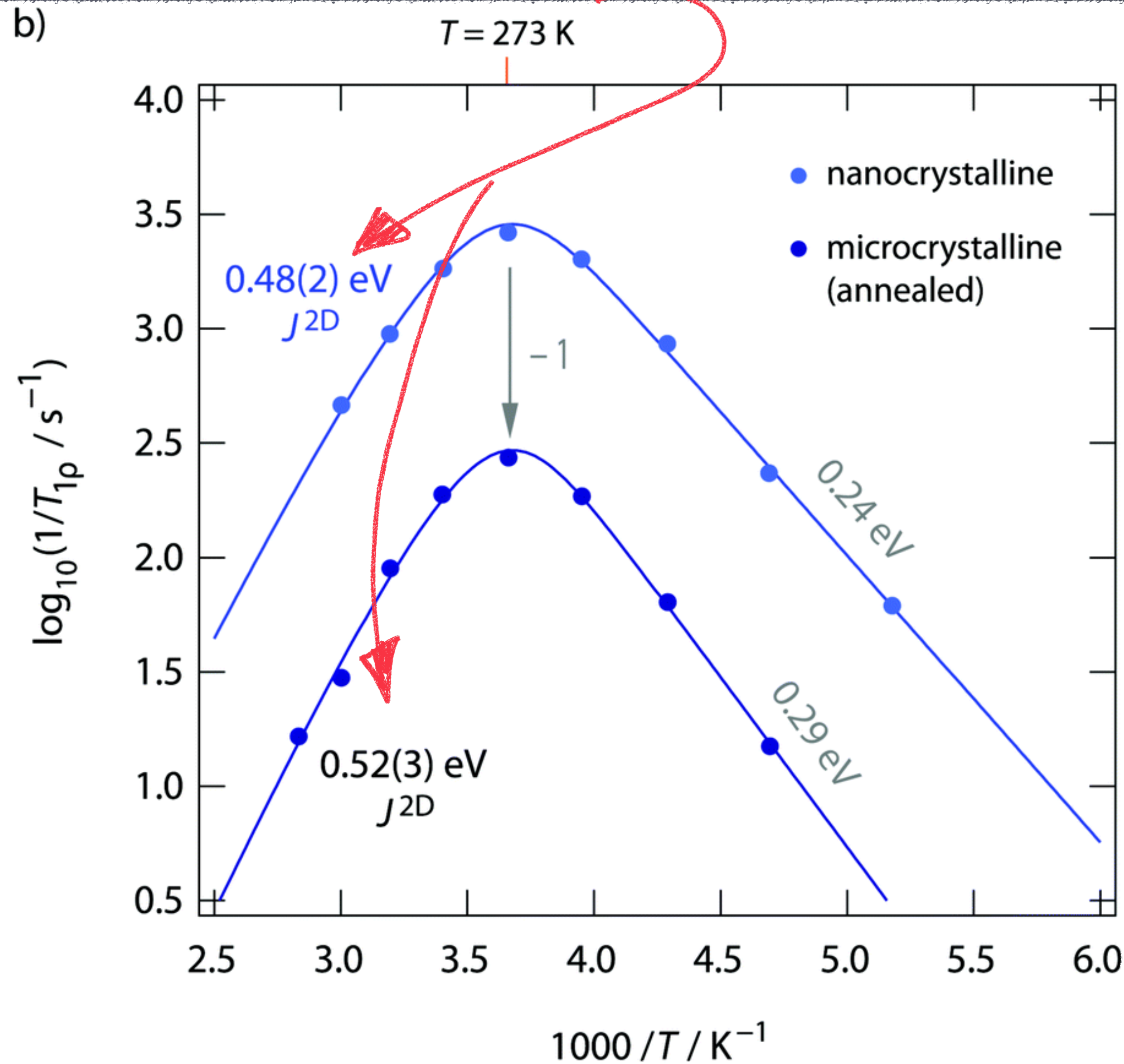
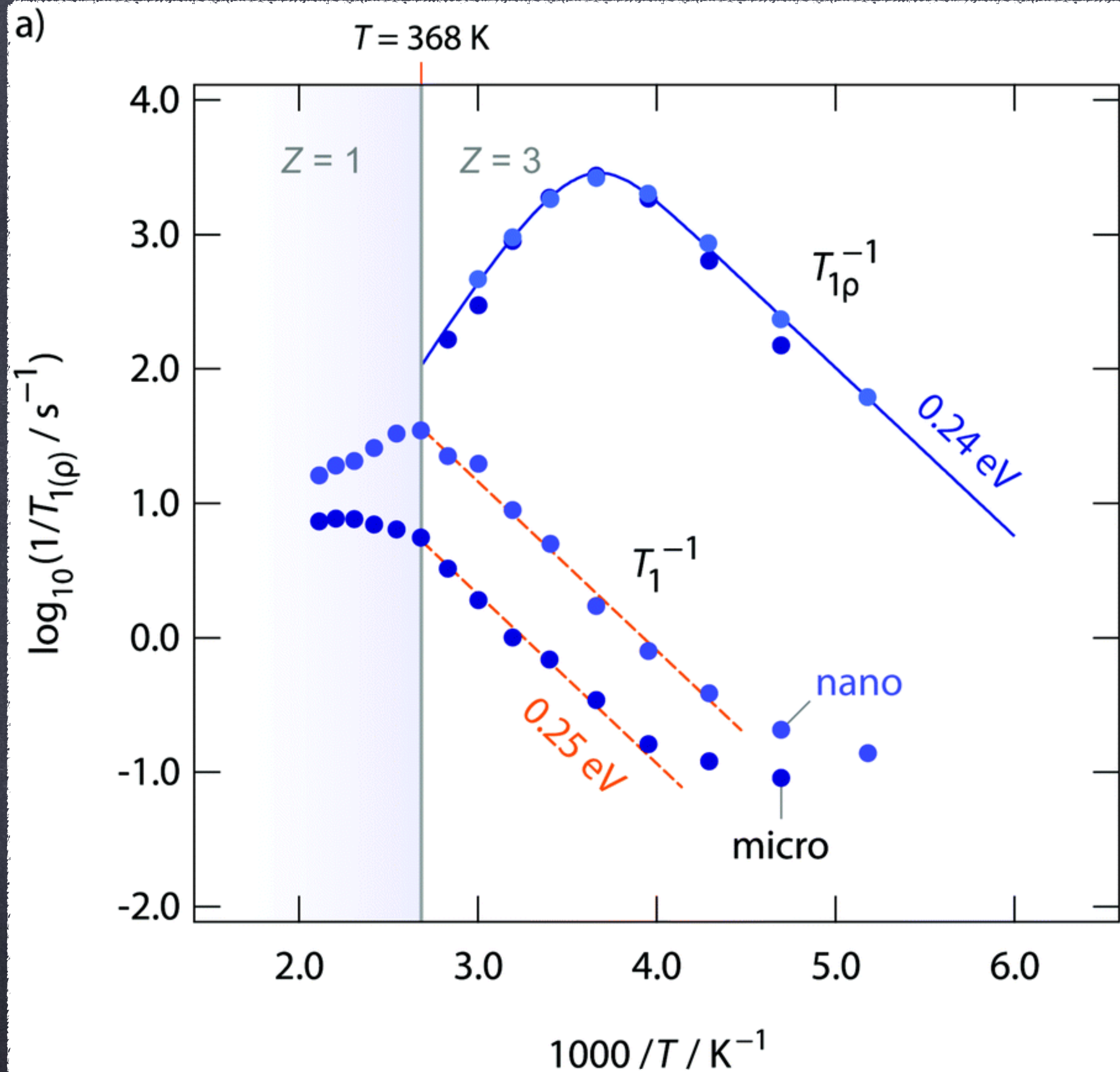


Nyquist plots:



3 GHz! apex: 67 MHz

NMR : 2D spectral density function J_{2D} (————)



→ consistent result! E_a, τ, D

Thank you!

... and all the best!