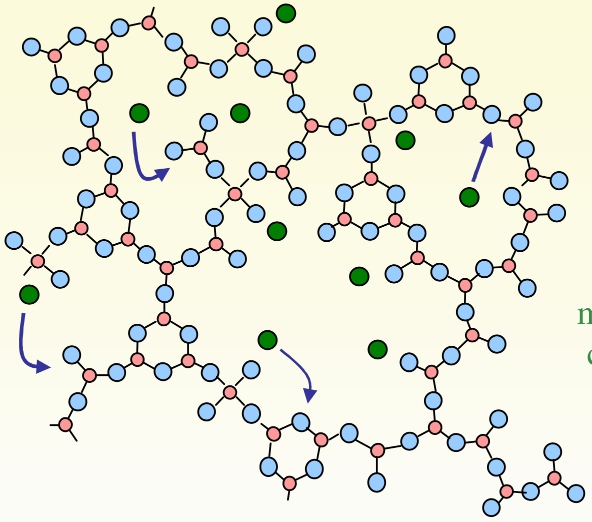
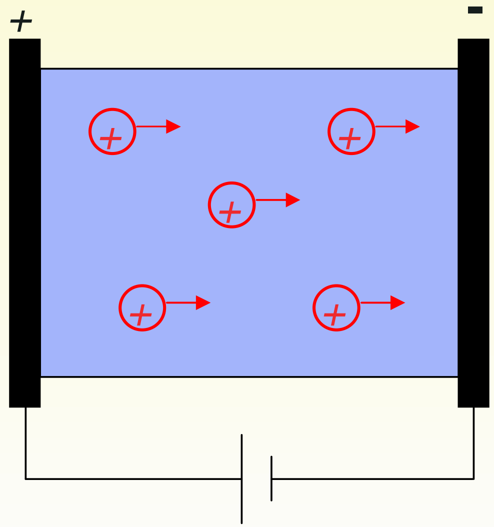
Ionically Conducting Materials:
Bulk Ion Dynamics and Electrode Polarisation





Bernhard Roling

Department of Chemistry, University of Marburg

Philipps Universität Marburg

Outlook

1. Introduction about Ionically Conducting Materials
   (Crystals, Glasses, Polymer Electrolytes, Ionic Liquids)

2. Simplest Equivalent Circuit for Ion Conductor between Blocking Electrodes: Admittance, Impedance, Capacitance and Modulus Spectra

3. Bulk Ion Dynamics and Linear Response Theory

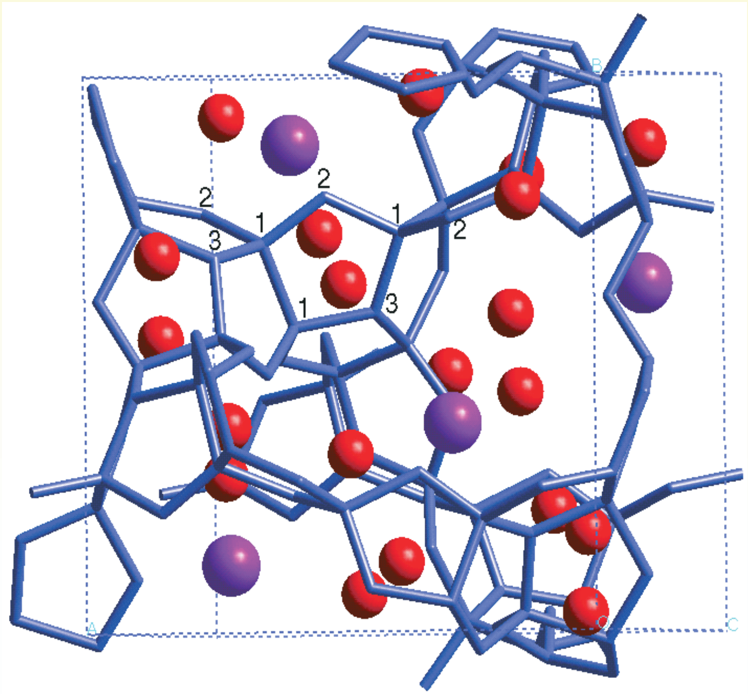
4. Double Layer Capacitance of Diluted and Concentrated Electrolytes

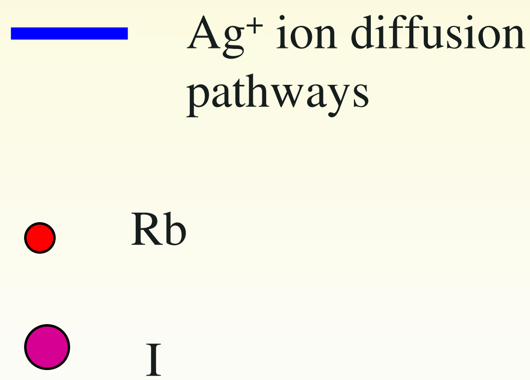
5. Conclusions

1. Introduction about Ionically Conducting Materials

Crystalline ion conductors

$RbAg_4I_5$: Ag^+ ion conductor with σ = 0,3 S/cm at ambient temperatures

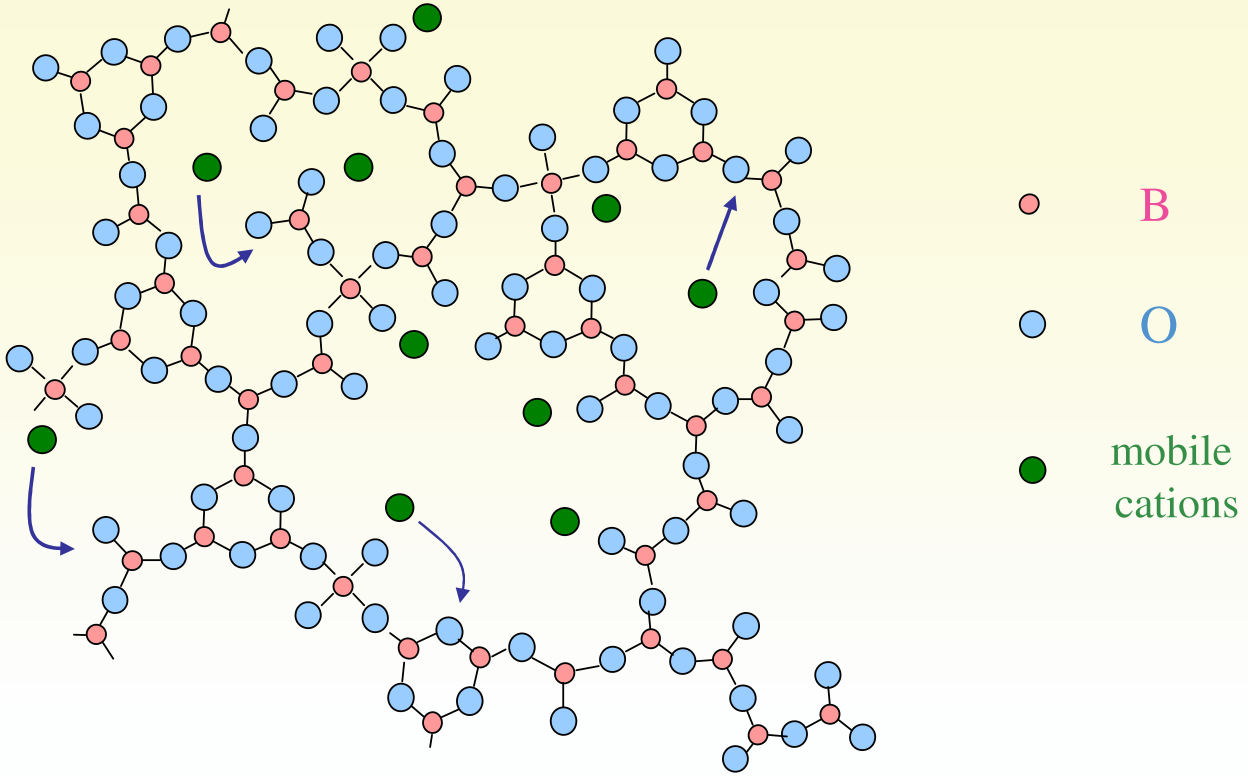




From: Stefan Adams, Habilitations thesis, Göttingen, 2000

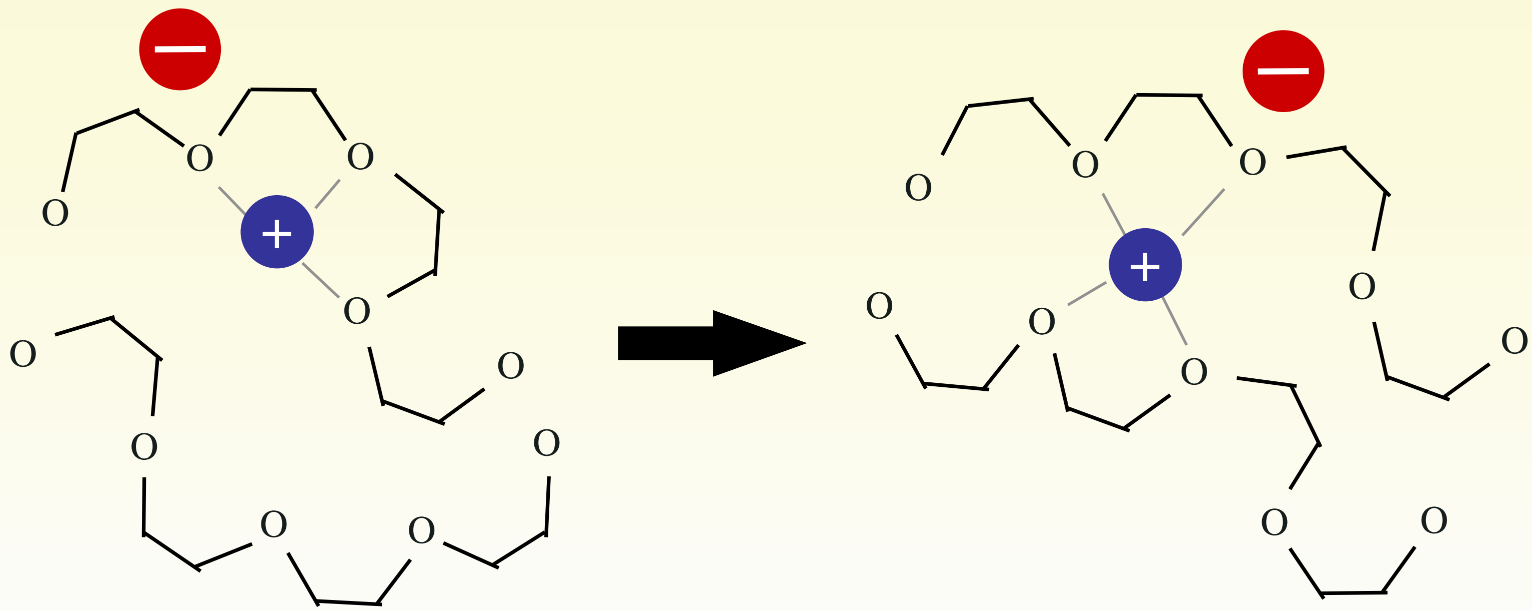
- Only 1/3 of all Ag^+ sites are occupied by Ag^+ ions.
- Weak chemical bonds between Ag^+ ions und Rb/I matrix.

Ionically conducting glasses



- Ions move in a rigid amorphous matrix
- Disorder causes broad distribution of site energies and hopping barriers.

Amorphous salt-in-polymer electrolytes



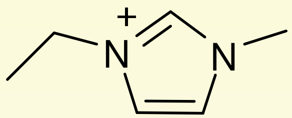
Polyethylene oxide +

salt, e.g. $LiClO_4$

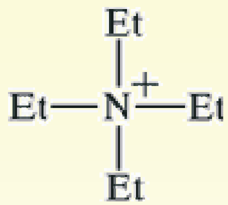
Ion transport is assisted by
polymer segmental motion

Ionic Liquids

Typical Cations



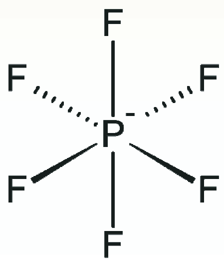
Imidazolium cation



Pyrrolidinium cation

Tetraalkylammonium cation

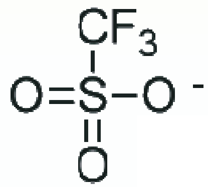
Typical Anions



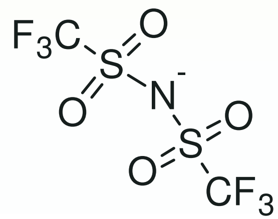
Hexafluorophosphate anion

$[BF_4]^-$

Tetrafluoroborate anion



Triflate anion



Bis(trifluoromethan-sulfonyl)imide anion (TFSI)

Important physico-chemical properties

- low vapour presssure
- non-flammable
- high thermal stability
- high ionic conductivity (10^{-3} – 10^{-2} S/cm at 298 K)
- broad electrochemical window (up to 5-6 V)

$\Downarrow$

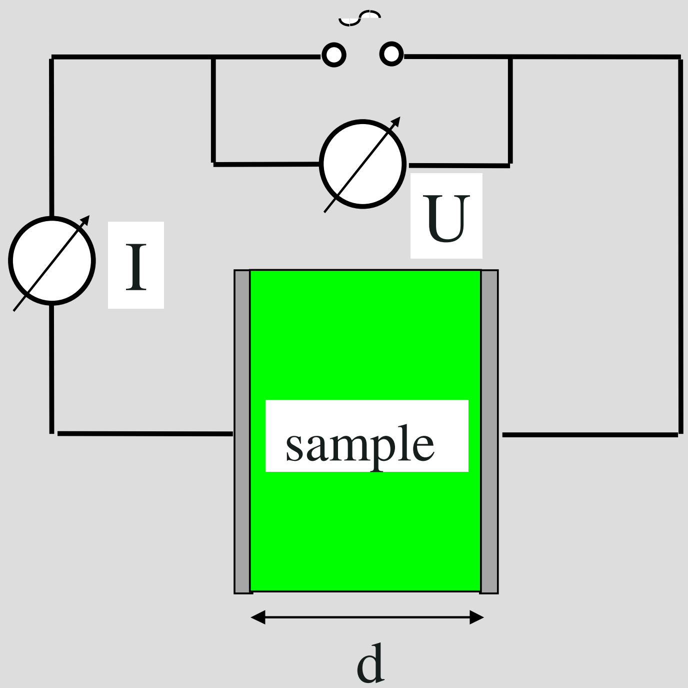
Application as electrolytes in batteries, supercapacitors,

fuel cells and dye-sensitized solar cells

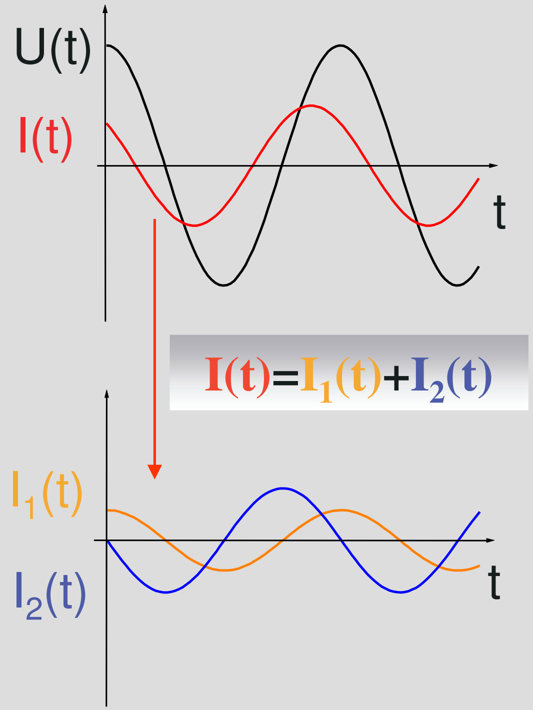
$\longrightarrow$ higher performance

$\longrightarrow$ higher safety

2. Simplest Equivalent Circuit for Ion Conductor between Blocking Electrodes: Admittance, Impedance, Capacitance and Modulus Spectra



A = contact area between sample and electrodes



Admittance $\hat{Y}(\omega) = Y'(\omega) + iY''(\omega)$

$Y'(\omega) = I_{0,1} / U_0$ (Energy dissipation)

$Y''(\omega) = I_{0,2} / U_0$ (Energy storage)

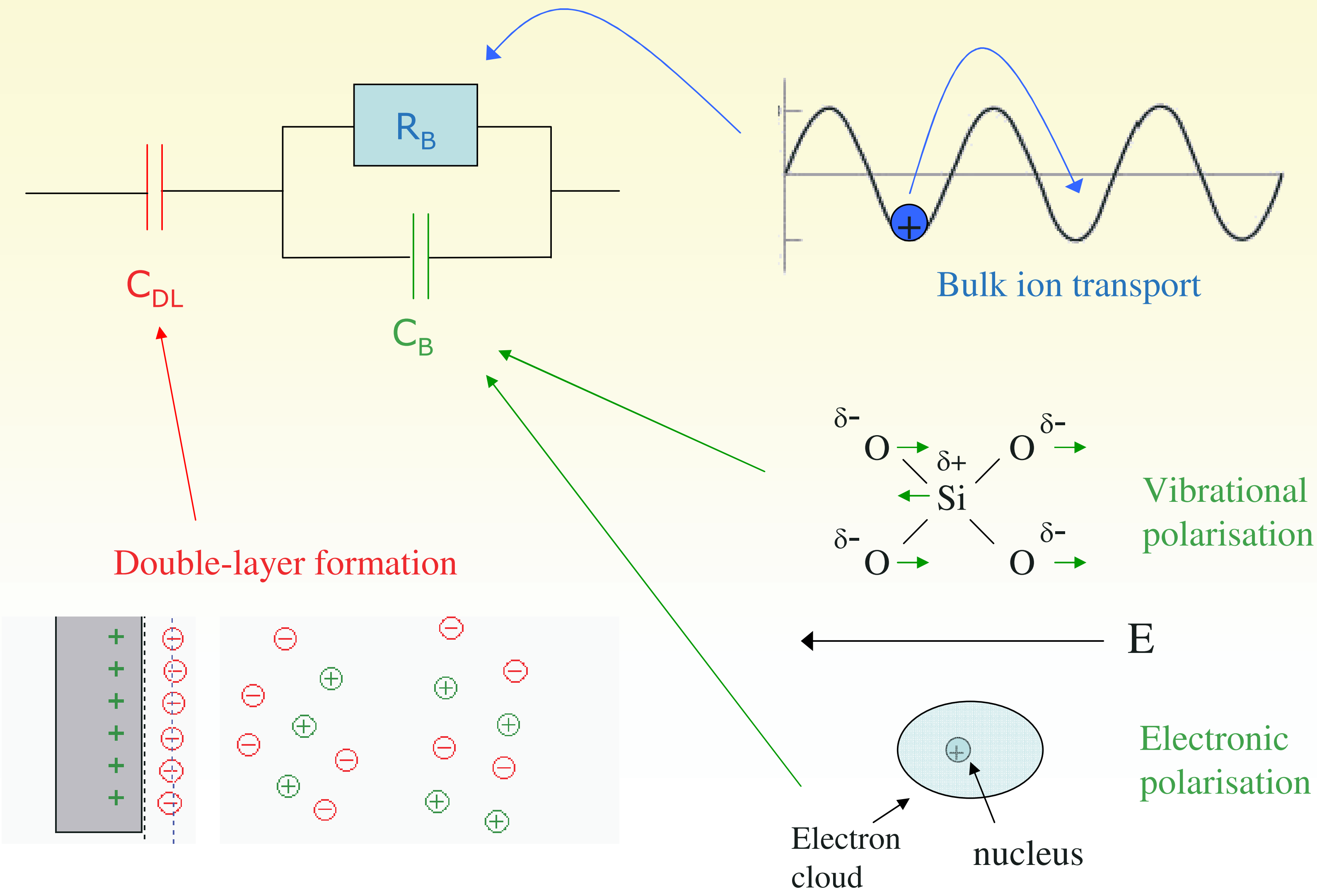
Other quantities

Impedance $$\hat{Z}(\omega) = \frac{1}{\hat{Y}(\omega)} = Z'(\omega) + i\ Z''(\omega)$$

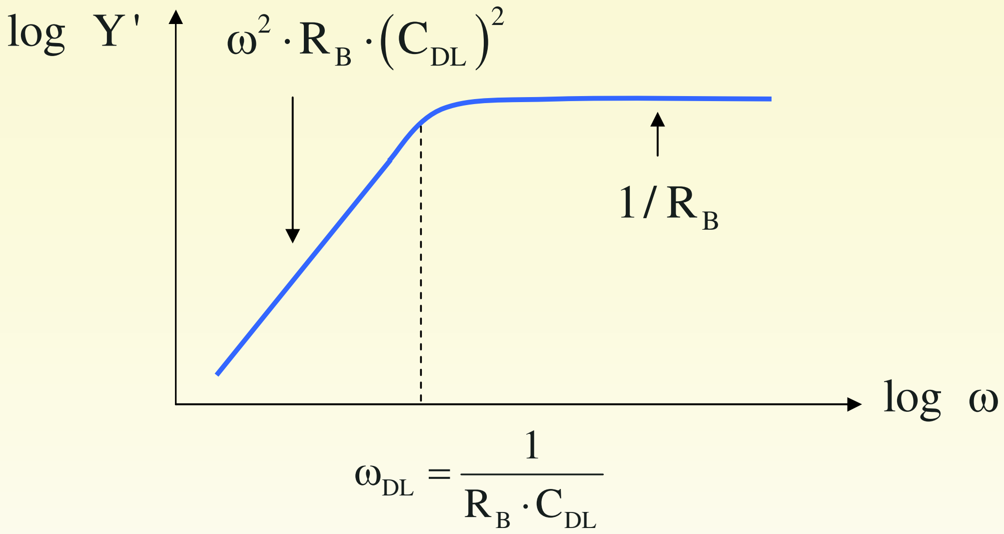
Capacitance $$\hat{C}(\omega) = \frac{\hat{Y}(\omega)}{i\omega} = C'(\omega) - i\ C''(\omega)$$

(Non-specific)
Modulus $$\hat{M}(\omega) = \frac{1}{\hat{C}(\omega)} = M'(\omega) + i\ M''(\omega)$$

Simplest circuit representing an ionic conductor between blocking electrodes



Real part of admittance

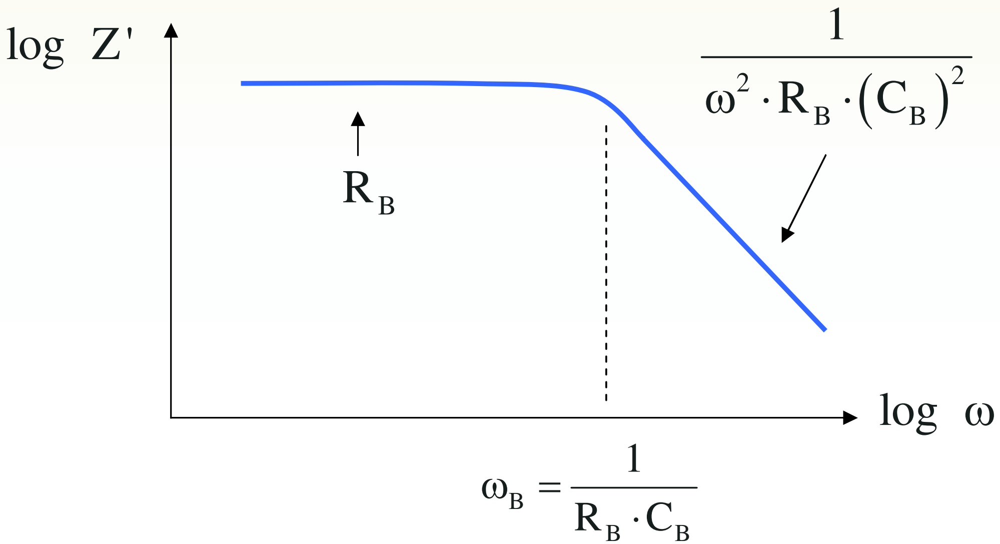


- Bulk ionic dc conductivity

$$\sigma_{dc} = \frac{1}{R_B} \cdot \frac{d}{A}$$

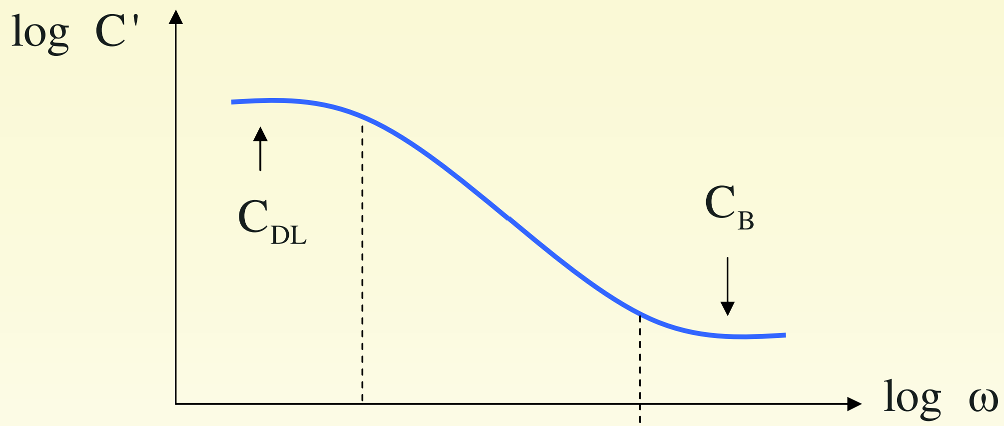
- No information about C_B

Real part of impedance



No information about C_{DL}

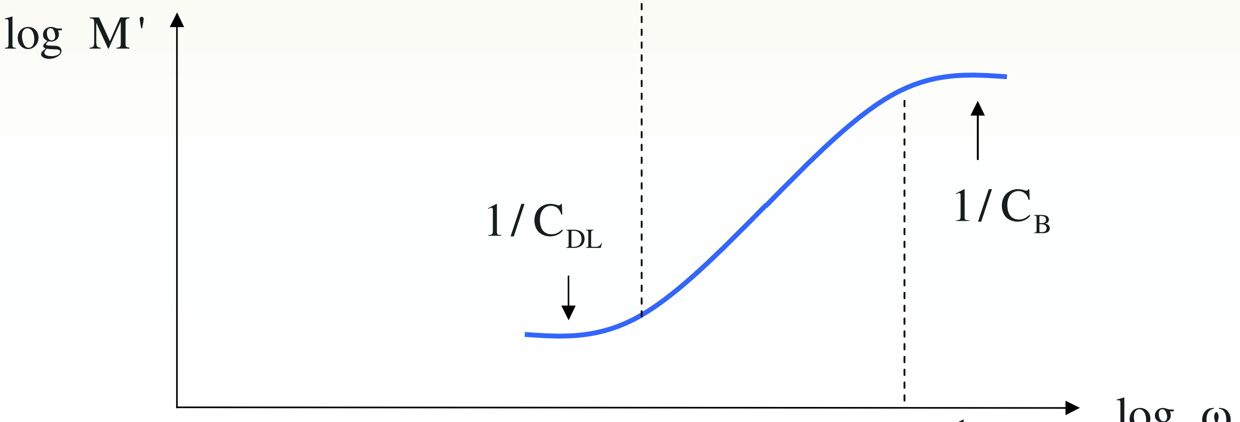
Real part of capacitance



$$\omega_{DL} = \frac{1}{R_B \cdot C_{DL}}$$

Real part of modulus

$$\omega_{avg} = \sqrt{\frac{1}{(R_B \cdot C_B)\cdot(R_B \cdot C_{DL})}} = \sqrt{\omega_B \cdot \omega_{DL}}$$



$$\omega_B = \frac{1}{R_B \cdot C_B}$$

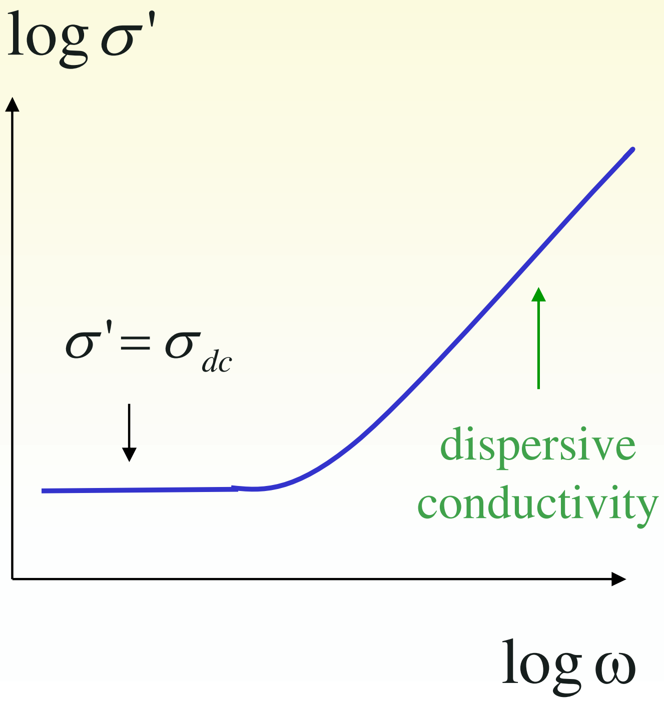
3. Bulk Ion Dynamics and Linear Response Theory

$$\sigma'(\omega) = Y'(\omega)\cdot\frac{d}{A}$$

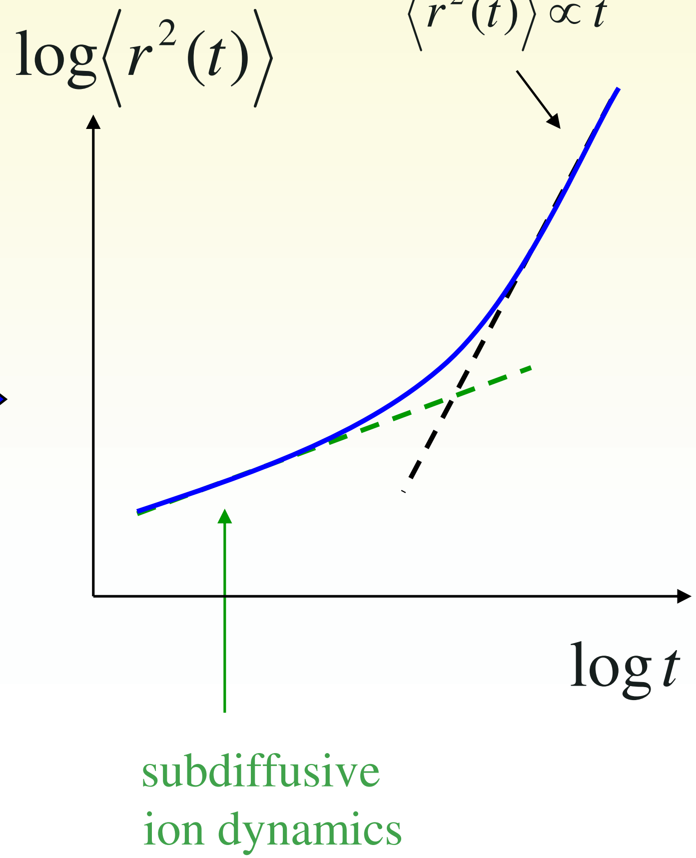
$\langle r^2(t)\rangle$ = mean square displacement of ions

diffusive ion dynamics

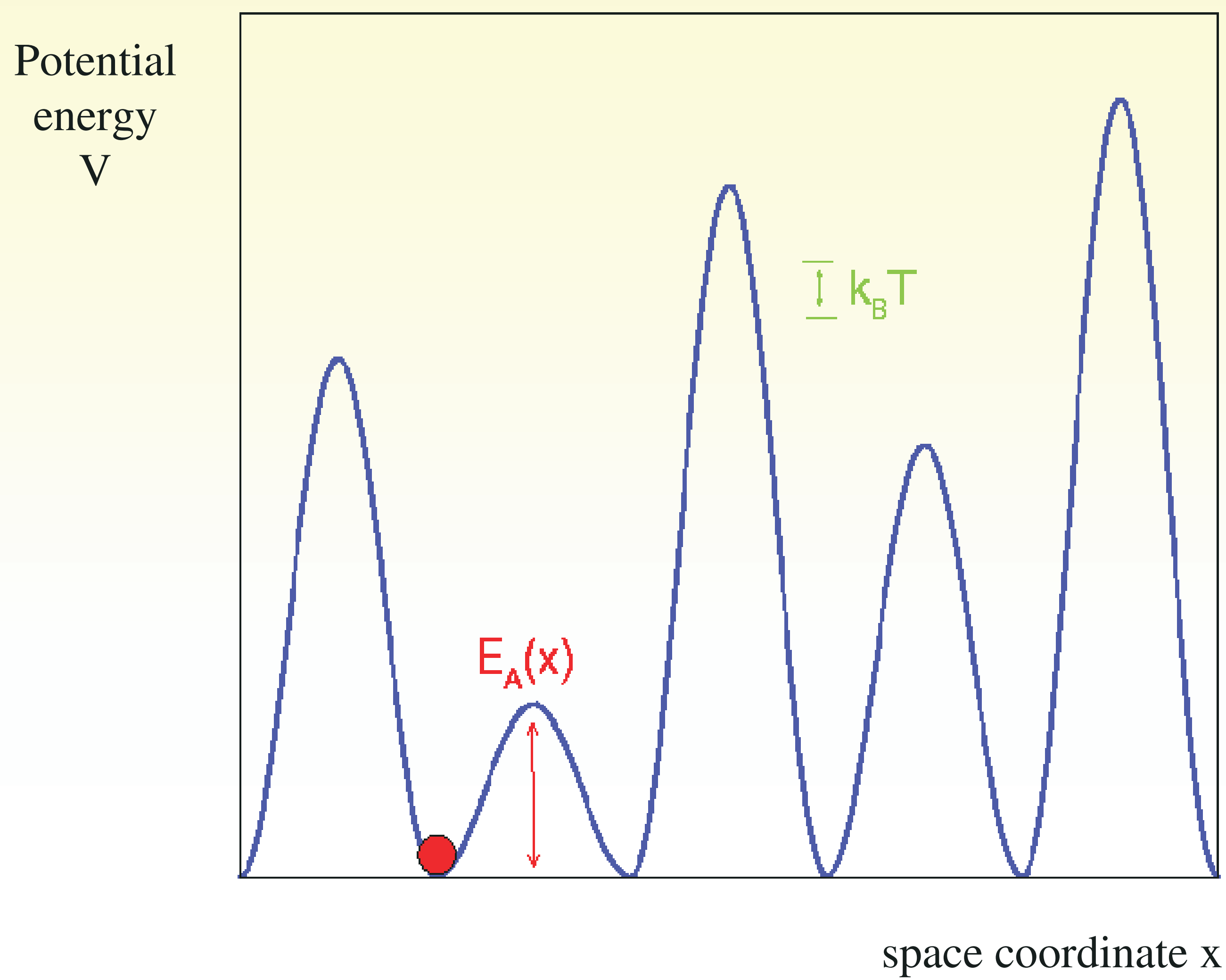
$\langle r^2(t)\rangle \propto t$



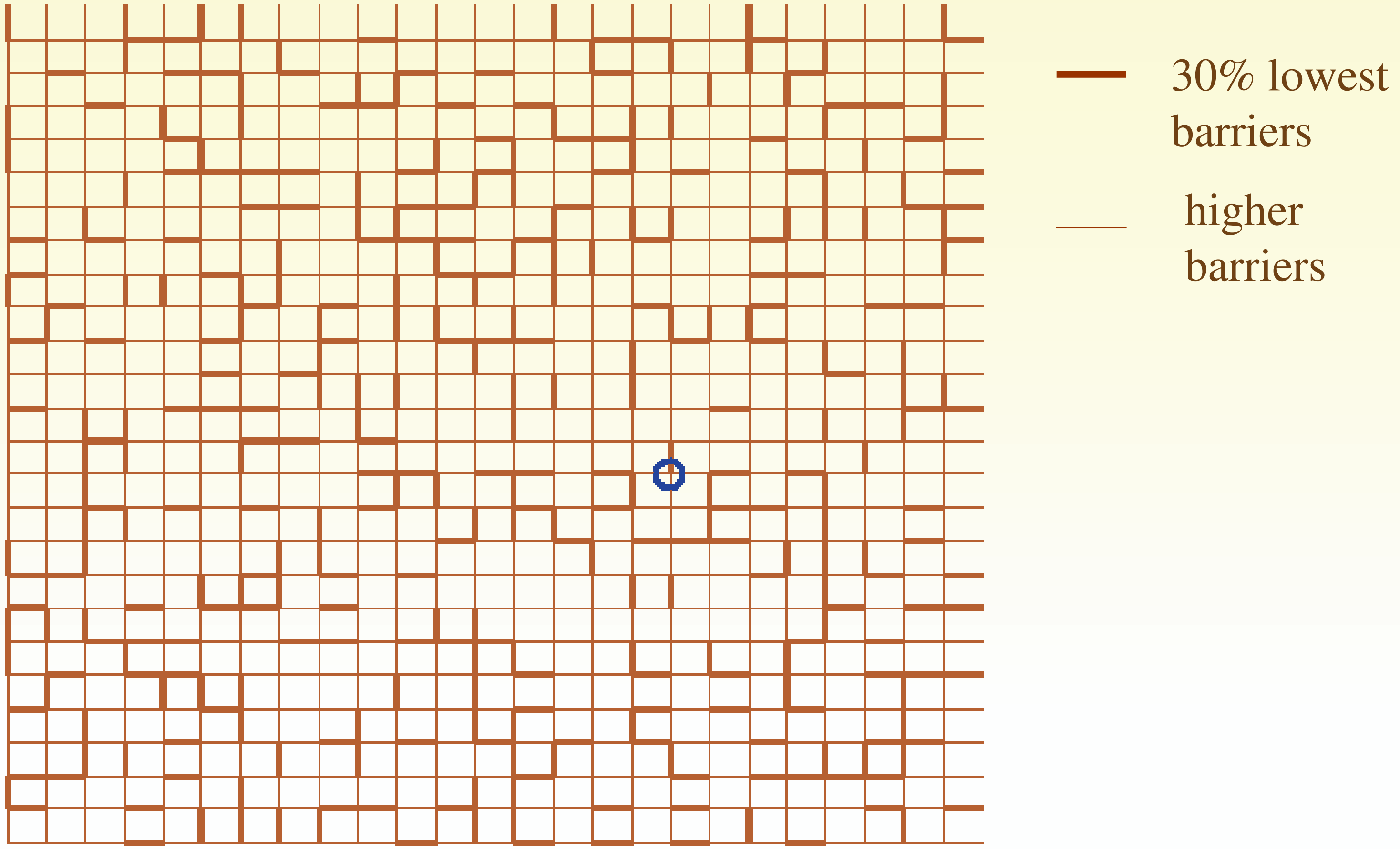
Linear response theory



Random barrier model

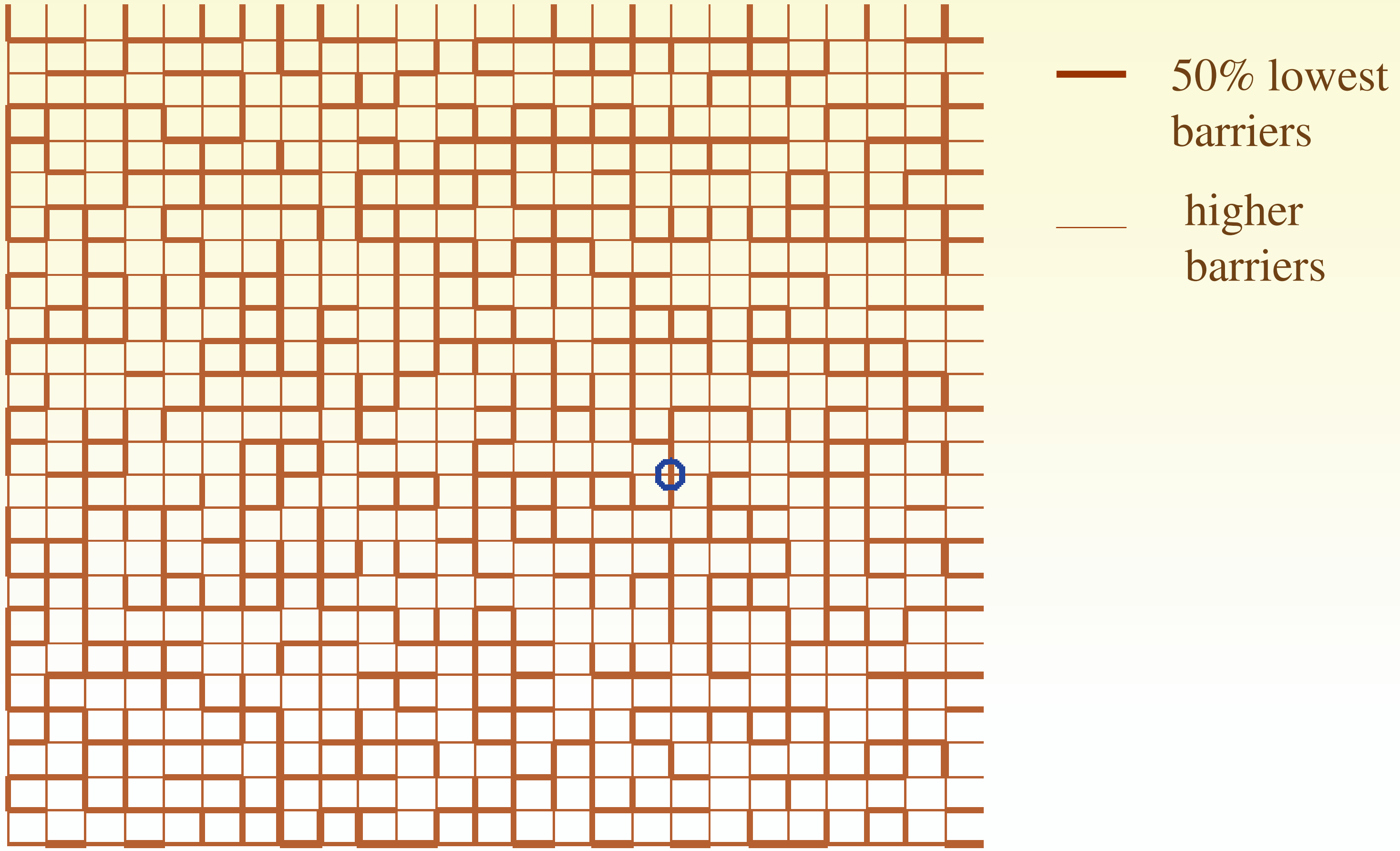


Ion transport pathways in 2D random barrier model



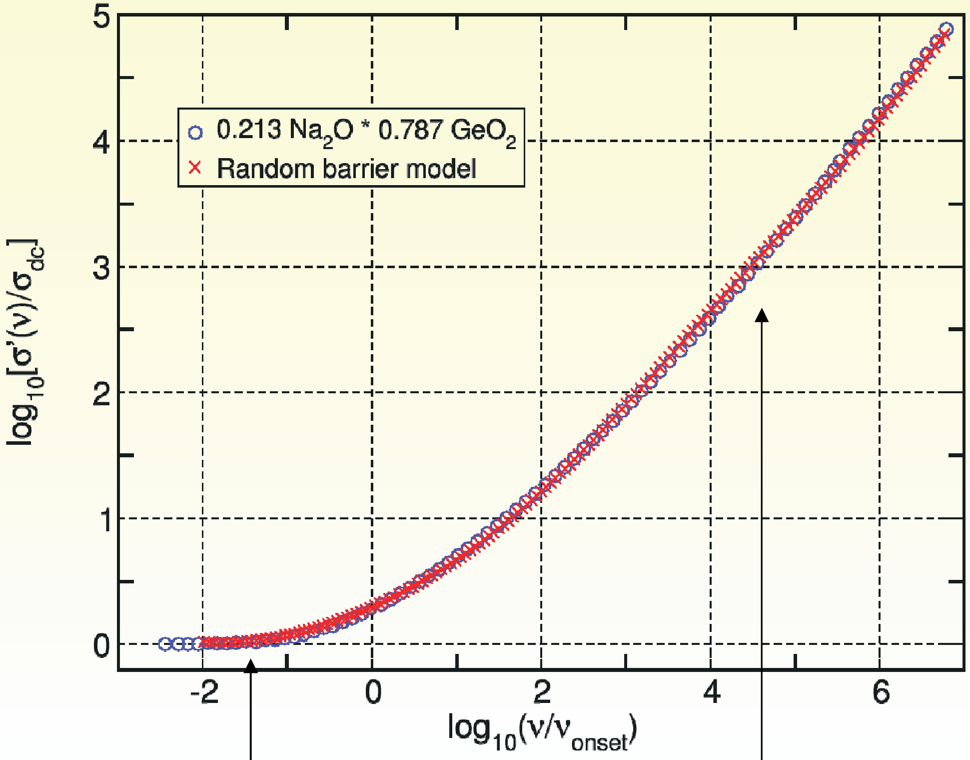
If the ions carry out hops exclusively over the 30% lowest barriers, the movements remain localised.

Ion transport pathways in 2D random barrier model



- Subdiffusive movements on short time scales
- Diffusive movements on long time scales.

Comparison: Ion Conducting Glasses vs. Random Barrier Model



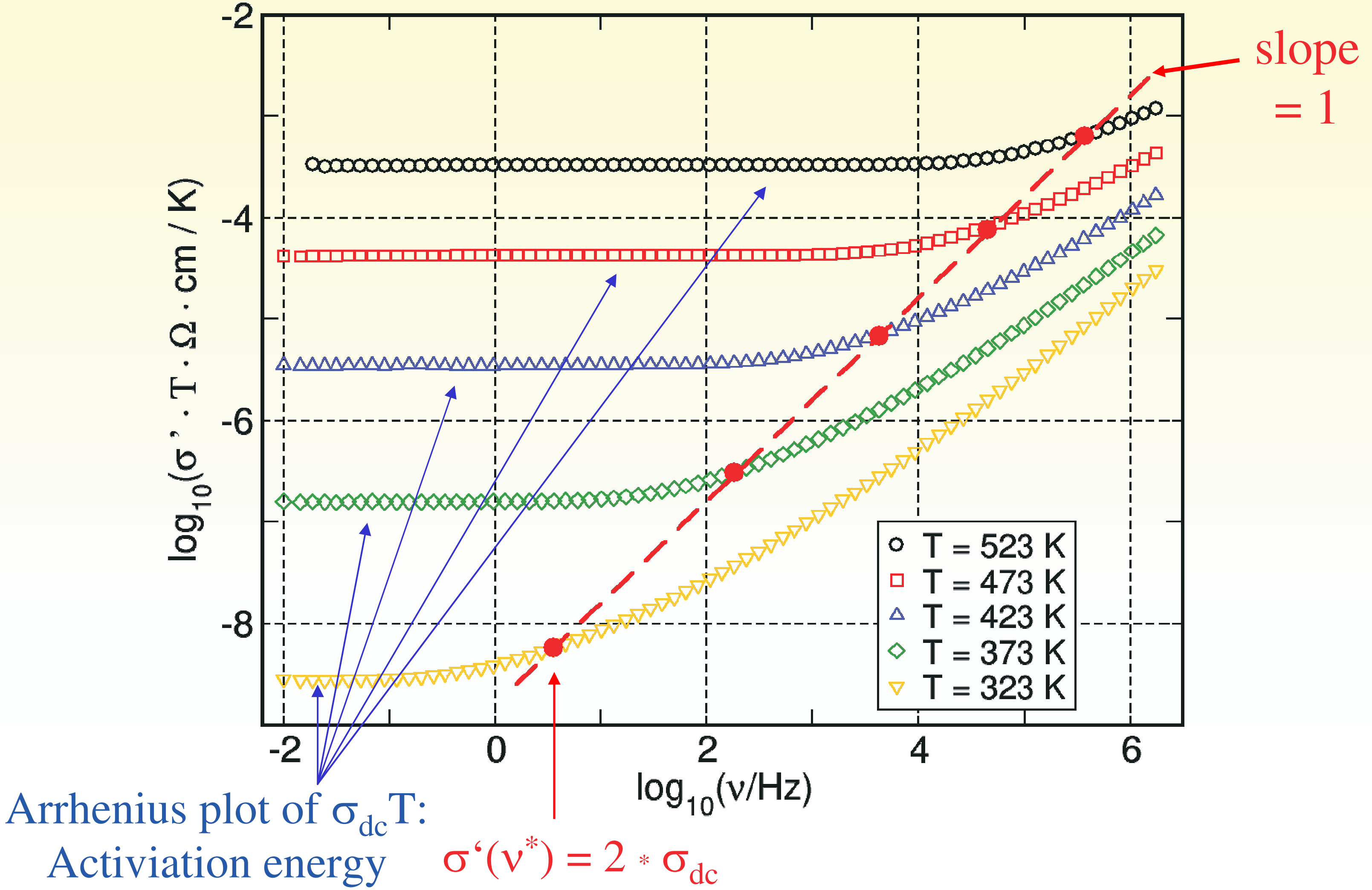
dc conductivity

dispersive conductivity

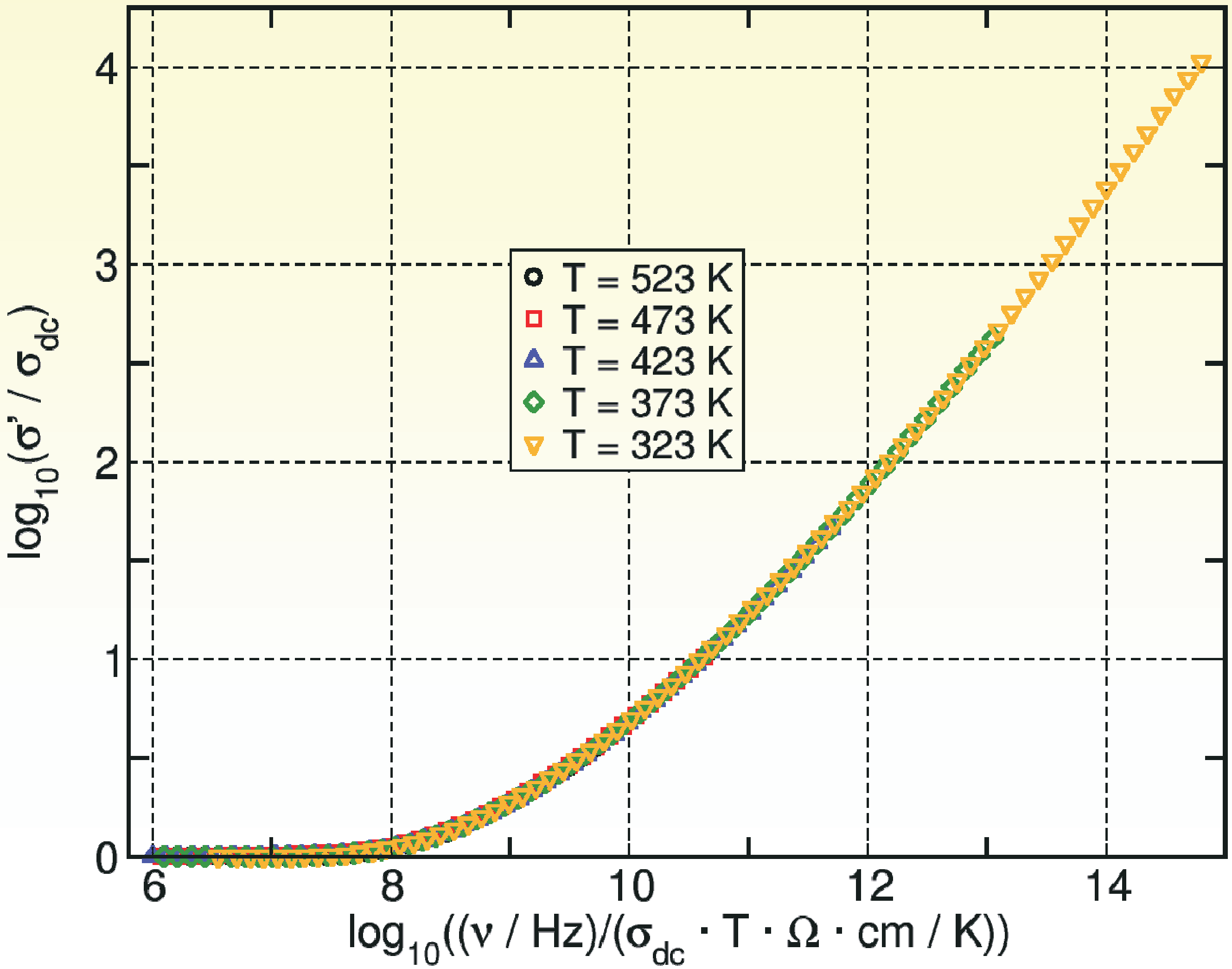
B. Roling,
Phys. Chem. Chem. Phys.
3 (2001) 5093.

See also:
J. C. Dyre, T. Schroeder,
Rev. Mod. Phys.
72 (2000) 873.

Conductivity spectra of a 0.213 Na_2O * 0.787 GeO_2 glass

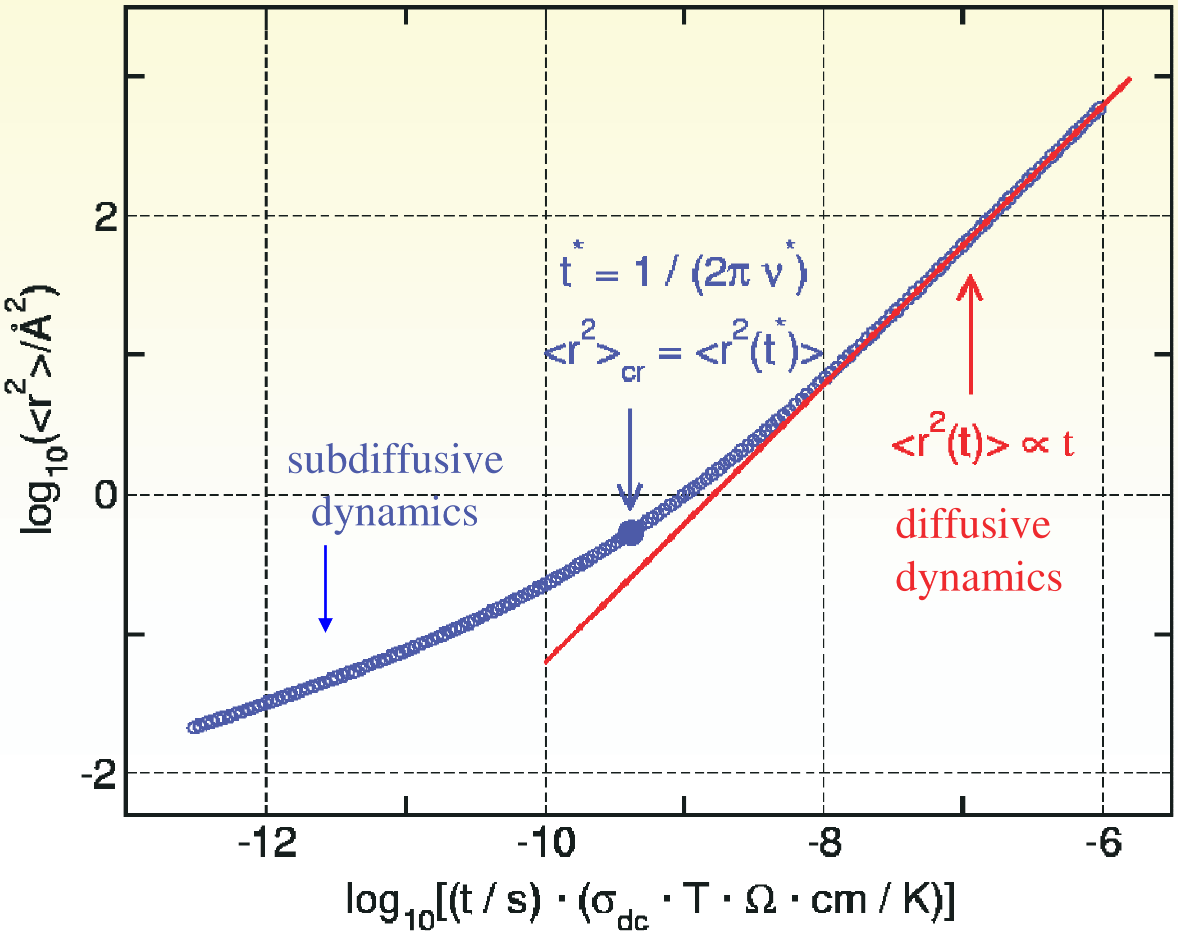


Summerfield scaling



Master curve of the time-dependent mean square displacement of the mobile Na^+ ions, $\langle r^2(t) \rangle$

0.213 Na_2O * 0.787 GeO_2 glass

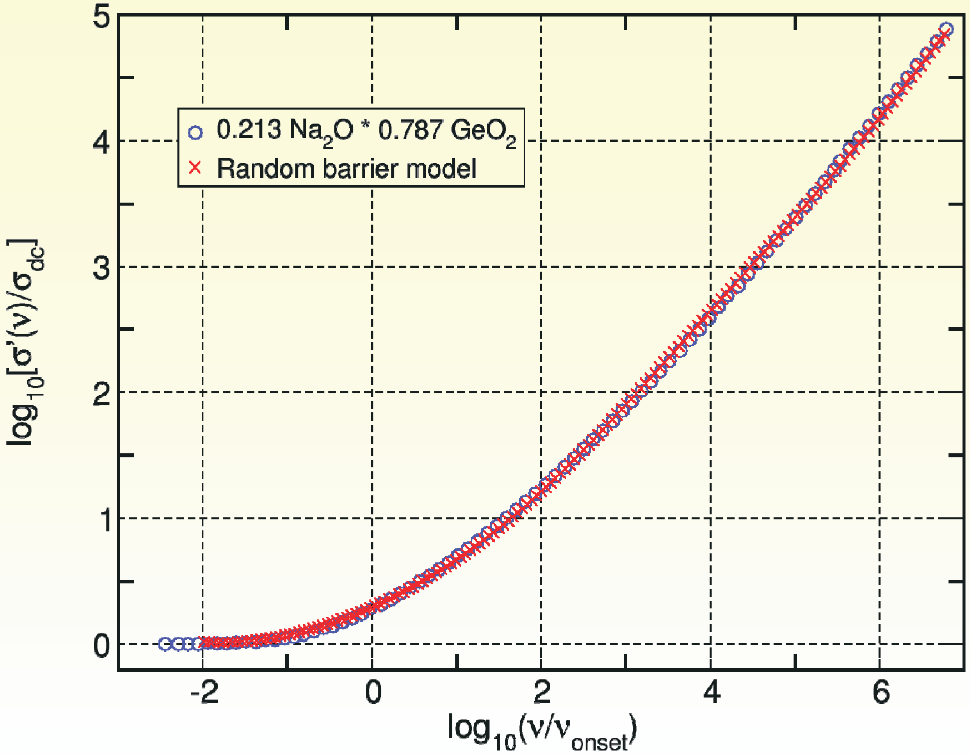


$$R \equiv \sqrt{\langle r^2 \rangle_{cr}}$$

“Spatial extent of subdiffusive dynamics“

For most glasses, R is independent of temperature.

Comparison: Ion Conducting Glasses vs. Random Barrier Model



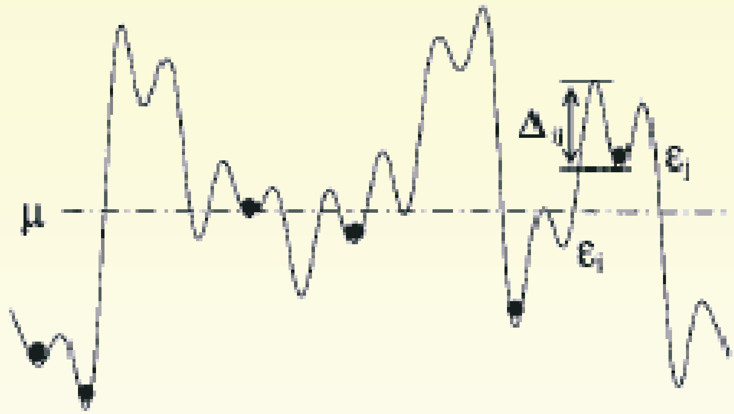
B. Roling,
Phys. Chem. Chem. Phys.
3 (2001) 5093.

See also:
J. C. Dyre, T. Schroeder,
Rev. Mod. Phys.
72 (2000) 873.

However: Random Barrier Model: $\left\langle r^2 \right\rangle_{cr} \propto T^{-1.3}$ (Pathway structure depends on on temperature.)

Most ion conducting glasses: $\left\langle r^2 \right\rangle_{cr}$ independent of T

Random site-energy model with hard-core interactions between particles



S. D. Baranovskii,
H. Cordes,
J. Chem. Phys.
111 (1999) 7546

Empty site can only be occupied by a single ion. $\Rightarrow$ Fermi statistics

$$\Rightarrow \quad \left\langle r^2 \right\rangle_{cr} \propto T^{-0.3}$$

The number of mobile ions that can hop to an empty site close to the Fermi level is proportional to T.

Random barrier model
with Coulomb interactions between mobile ions

Monte Carlo simulations:

$$\left\langle r^2 \right\rangle_{cr} \propto T^{\gamma}$$

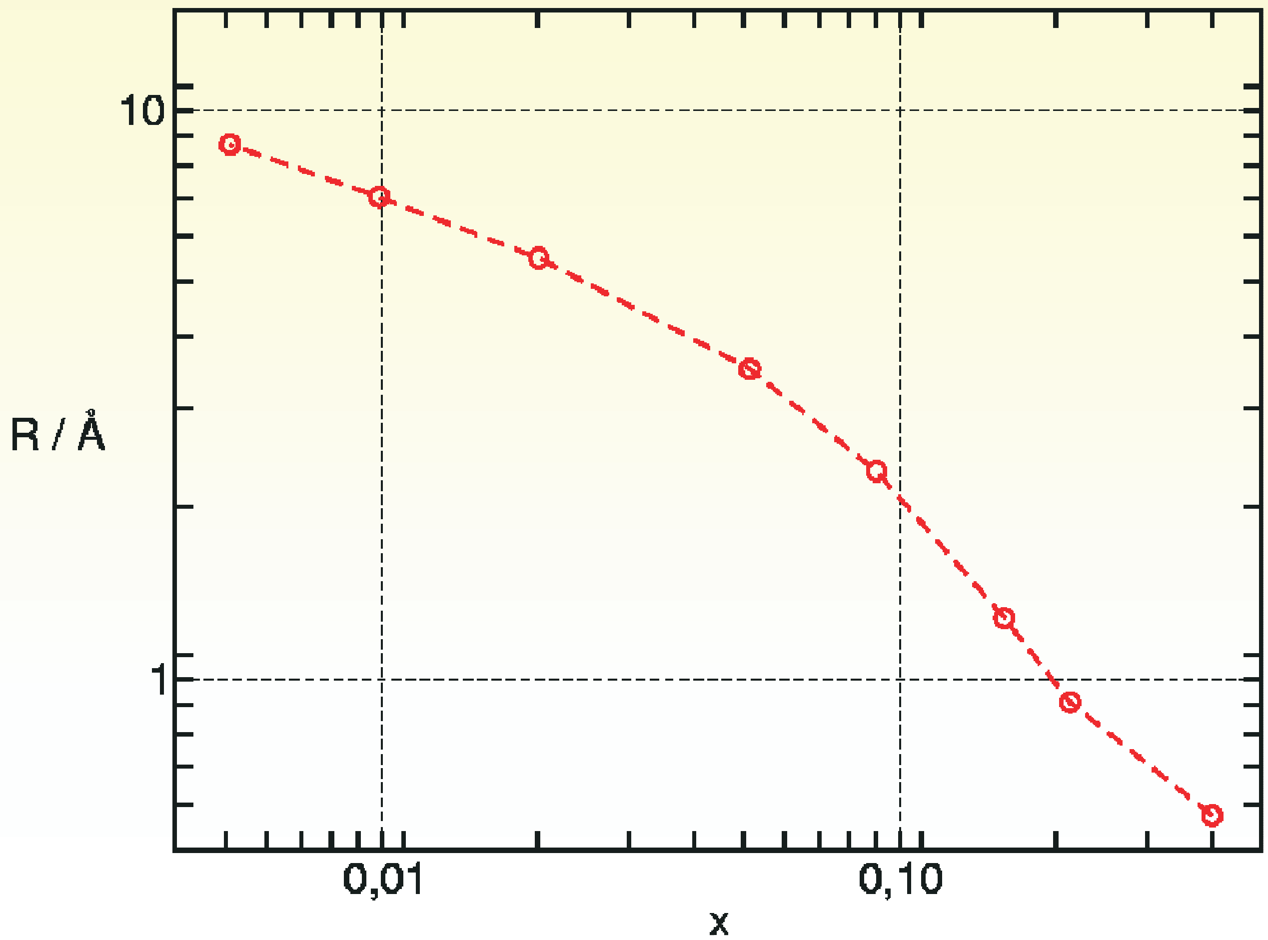
- without Couloub interactions: $\gamma = -1.3$

- with increasing strength of Coulomb interaction:
  γ increases (i.e. becomes more positive)

B. Roling, *Phys. Chem. Chem. Phys.* **3** (2001) 5093

Spatial extent of subdiffusive ion dynamics $R \equiv \sqrt{\left\langle r^2 \right\rangle_{cr}}$

for x $Na_2O * (1 - x)$ GeO_2 glasses



B. Roling, C. Martiny, S. Brückner, *Phys. Rev. B* **63** (2001) 214203.

Assumption: Typical hopping distance of Na^+ ions: $d \approx 3\ \mathring{A}$
(Molecular dynamics simulations)

Glass with x = 0.005: R > d

⟶ At the crossover time t^*, the ions have moved, on the average, over *several hopping distances*.

Glass with x = 0.40: R < d

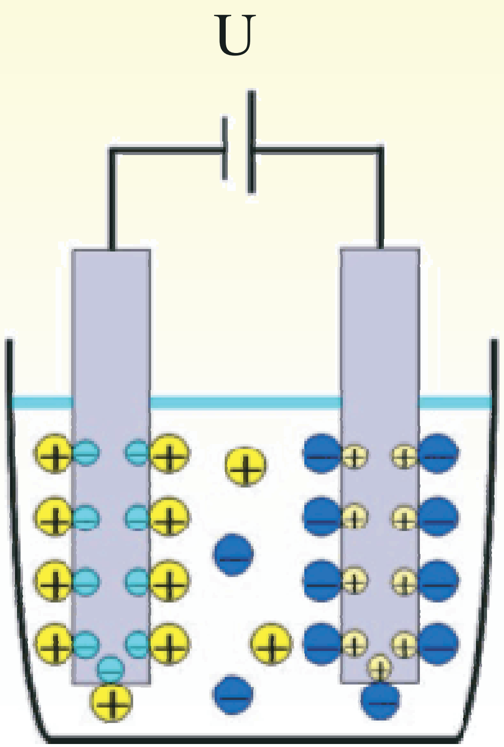
⟶ At the crossover time t^*, only a *small fraction of ions* have left their original sites.

⬇

Despite the quasi-universal shape of the conductivity spectra, the microscopic mechanisms of the ion transport depend strongly on glass composition.

4. Double Layer Capacitance of Diluted and Concentrated Electrolytes

Energy storage in electrochemical supercapacitors



Stored energy

$$E = \frac{1}{2} \cdot C \cdot U^2$$

C = double layer capacitance

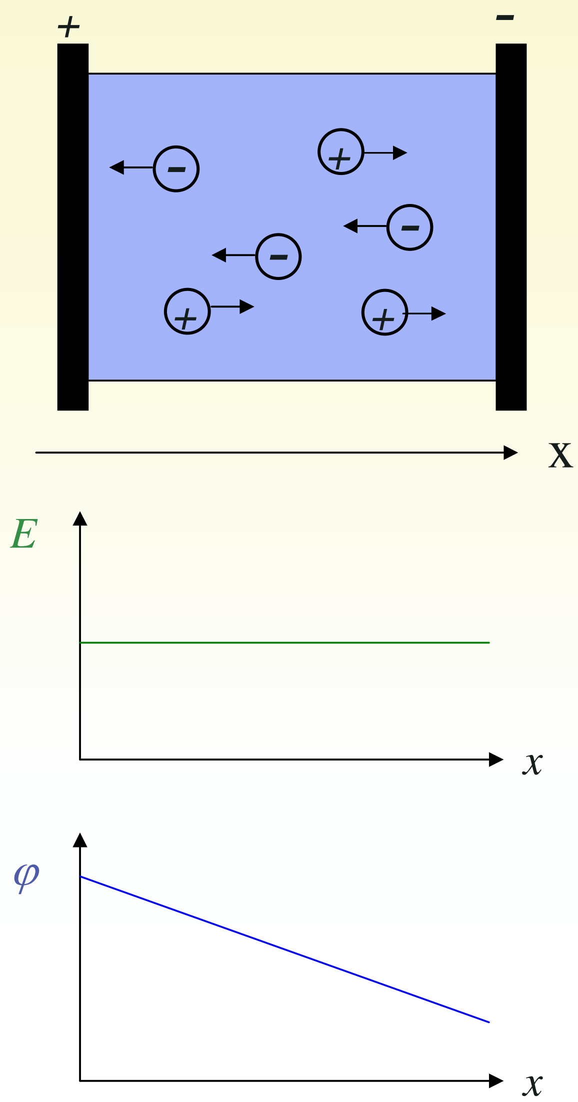
U = voltage

Power

$$P = \frac{U^2}{R}$$

R = electrolyte resistance

Mean-field approaches for diluted electrolyte solutions



Charge density

$$\rho(x) = \frac{Q(x)}{V} =$$

$$N_{V,+}(x) \cdot z_+ \cdot e + N_{V,-}(x) \cdot z_- \cdot e$$

$$= 0$$

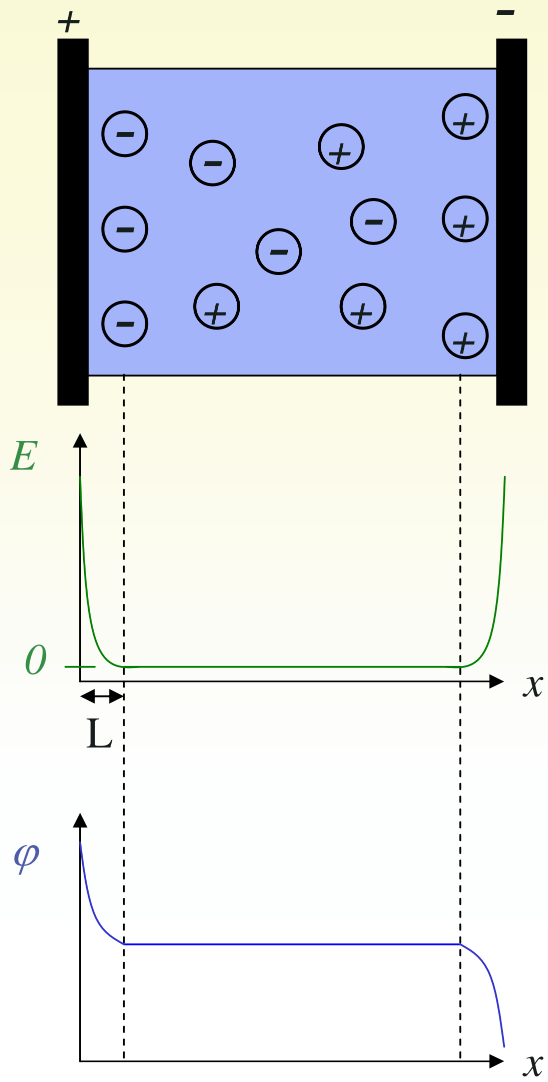
Poisson equation

$$\frac{dE(x)}{dx} = \frac{\rho(x)}{\varepsilon_0 \cdot \varepsilon_r} = 0$$

ε_0 = vacuum permittivity

ε_r = relative permittivity

$$\frac{d^2\varphi(x)}{dx^2} = -\frac{\rho(x)}{\varepsilon_0 \cdot \varepsilon_r} = 0$$



close to the electrodes:

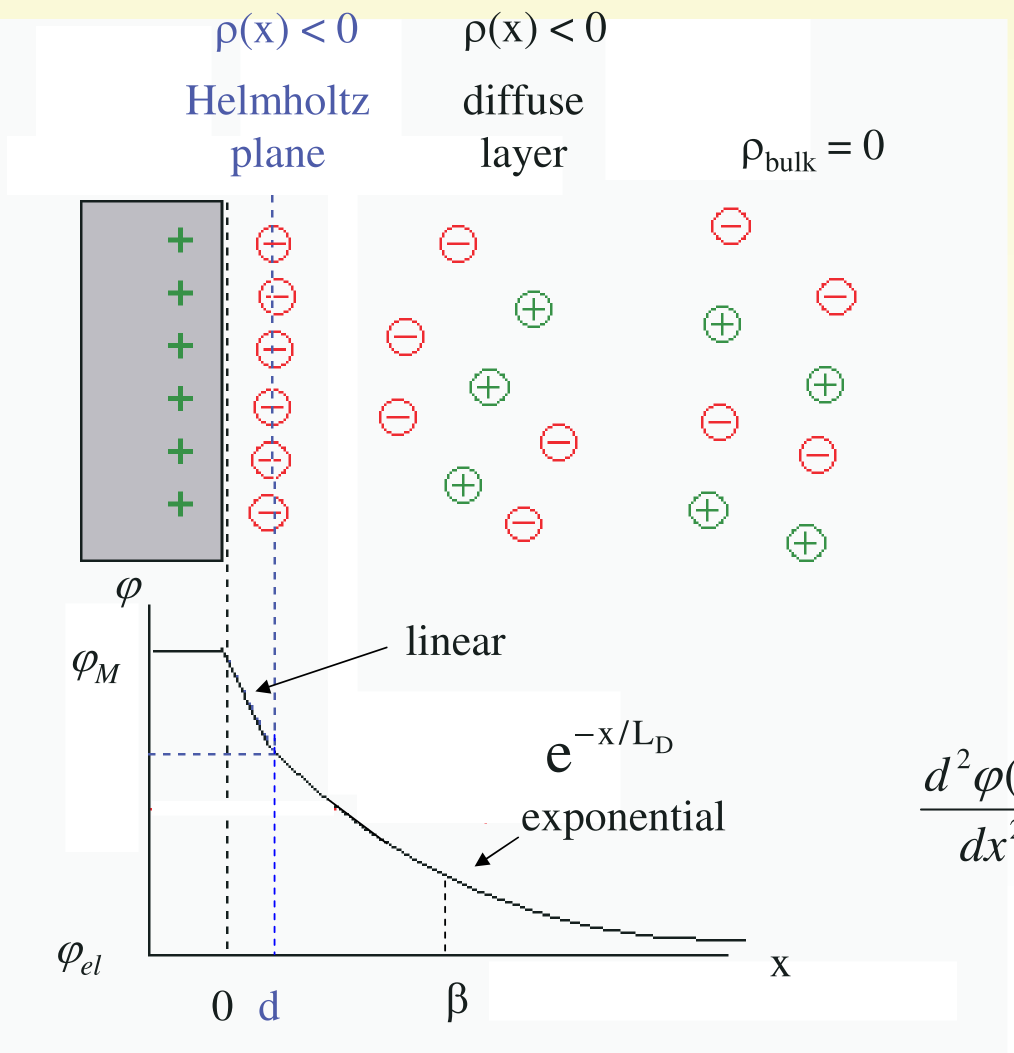
$$\rho(x) \neq 0$$

in the bulk: $\rho(x) = 0$

$$\frac{dE(x)}{dx} = \frac{\rho(x)}{\varepsilon_0 \cdot \varepsilon_r}$$

$$\frac{d^2\varphi(x)}{dx^2} = -\frac{\rho(x)}{\varepsilon_0 \cdot \varepsilon_r}$$

Now in more detail….



$$\frac{d^2\varphi(x)}{dx^2} = -\frac{\rho(x)}{\varepsilon_0 \cdot \varepsilon_r}$$

Capacitance of the double layer

Integral capacitance per area $$K_A = \frac{C}{A} = \frac{Q/A}{\Delta\varphi} \quad \text{with} \quad \Delta\varphi = \varphi_M - \varphi_{el}$$

Helmholtz layer $$K_A^{HL} = \frac{\varepsilon_0 \cdot \varepsilon_r}{d}$$

Diffuse layer $$K_A^{diffuse} = \ldots..$$ (see next slides)

⬇

$$\frac{1}{K_A} = \frac{1}{K_A^{HL}} + \frac{1}{K_A^{diffuse}}$$

Gouy-Chapman theory for diffuse layer

Poisson $$\frac{d^2\varphi(x)}{dx^2} = -\frac{\rho(x)}{\varepsilon_0 \cdot \varepsilon_r}$$

Boltzmann $$\rho(x) = N_{V,+,bulk} \cdot z_+ \cdot e \cdot \exp\left(-\frac{z_+ \cdot e \cdot [\varphi(x) - \varphi_{el}]}{kT}\right) + N_{V,-,bulk} \cdot z_- \cdot e \cdot \exp\left(-\frac{z_- \cdot e \cdot [\varphi(x) - \varphi_{el}]}{kT}\right)$$

mean-field approach

Solution for 1-1 electrolyte with $z_+ = 1$, $z_- = -1$, $N_V = N_{V,+,\,bulk} = N_{V,-,bulk}$

$$\frac{Q}{A} = \frac{\varepsilon_0 \cdot \varepsilon_r \cdot 2 \cdot kT}{e \cdot L_D} \cdot \sinh\left(\frac{e \cdot \Delta\varphi}{2 \cdot kT}\right)$$

with $L_D = \sqrt{\dfrac{\varepsilon_0 \cdot \varepsilon_r \cdot kT}{2 \cdot N_V \cdot e^2}}$ Debye length

1-1 electrolyte at **small** potential differences Δφ

$$e \cdot \Delta\varphi < kT \longrightarrow \sinh\left(\frac{e \cdot \Delta\varphi}{2 \cdot kT}\right) \approx \frac{e \cdot \Delta\varphi}{2 \cdot kT}$$

$$\longrightarrow \frac{Q}{A} = \frac{\varepsilon_0 \cdot \varepsilon_r}{L_D} \cdot \Delta\varphi \longrightarrow \boxed{\mathrm{K}_{\mathrm{A}}^{\mathrm{diffuse}} = \frac{\varepsilon_0 \cdot \varepsilon_\mathrm{r}}{\mathrm{L}_\mathrm{D}} \equiv \mathrm{C}_\mathrm{D}}$$

Debye capacitance

for

$$\Delta\varphi < 0.025 \text{ eV}$$

at 25 °C

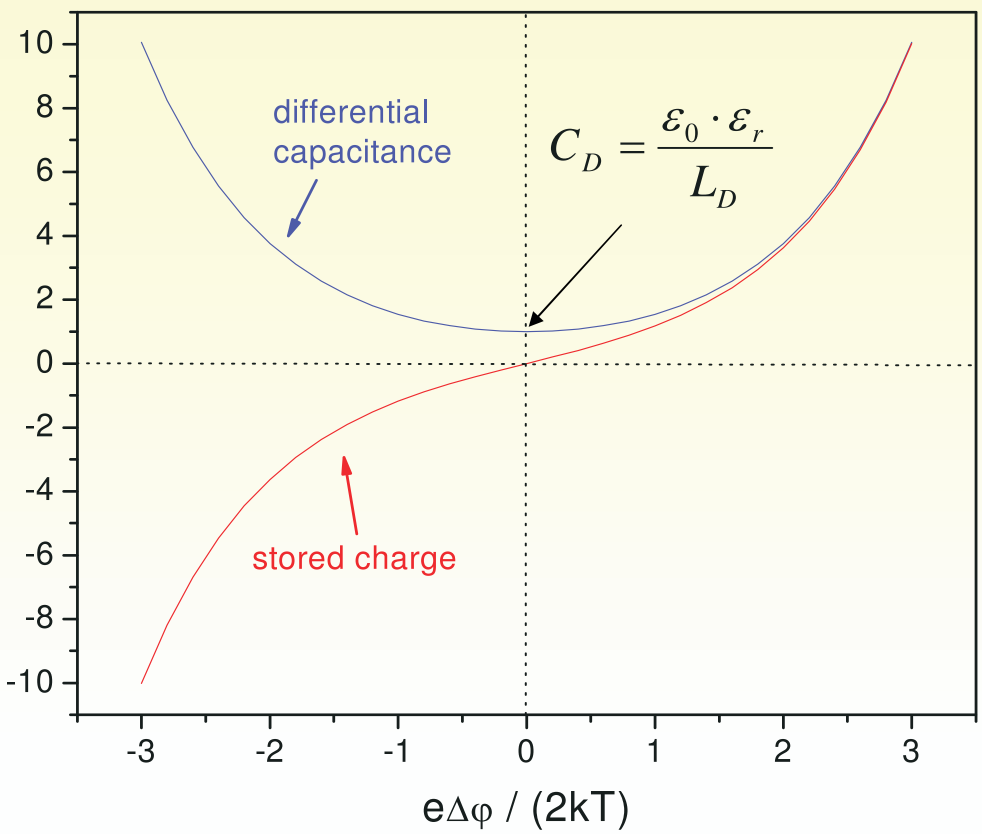
1-1 electrolyte at **large** potential differences Δφ

$$\frac{Q}{A} = \frac{\varepsilon_0 \cdot \varepsilon_r \cdot 2 \cdot kT}{e \cdot L_D} \cdot \sinh\left(\frac{e \cdot \Delta\varphi}{2 \cdot kT}\right)$$

→ Differential capacitance

$$\boxed{\mathrm{C}_\mathrm{A}^{\mathrm{diffuse}} \equiv \frac{\mathrm{d}(Q/A)}{\mathrm{d}(\Delta\varphi)} = \frac{\varepsilon_0 \cdot \varepsilon_\mathrm{r}}{\mathrm{L}_\mathrm{D}} \cdot \cosh\left(\frac{\mathrm{e} \cdot \Delta\varphi}{2 \cdot \mathrm{kT}}\right) = \mathrm{C}_\mathrm{D} \cdot \cosh\left(\frac{\mathrm{e} \cdot \Delta\varphi}{2 \cdot \mathrm{kT}}\right)}$$

Stored charge and differential capacitance



At highly positive and negative electrode potentials:
Strong accumulation of counter ions at the electrode.

Double layer formation in ionic liquids

Gouy-Chapman theory NOT applicable:

In concentrated systems, the finite volume of the ions and the individual interactions between the ions play an important role.

A. A. Kornyshev, *J. Phys. Chem. B* **111** (2007) 5545-5557.

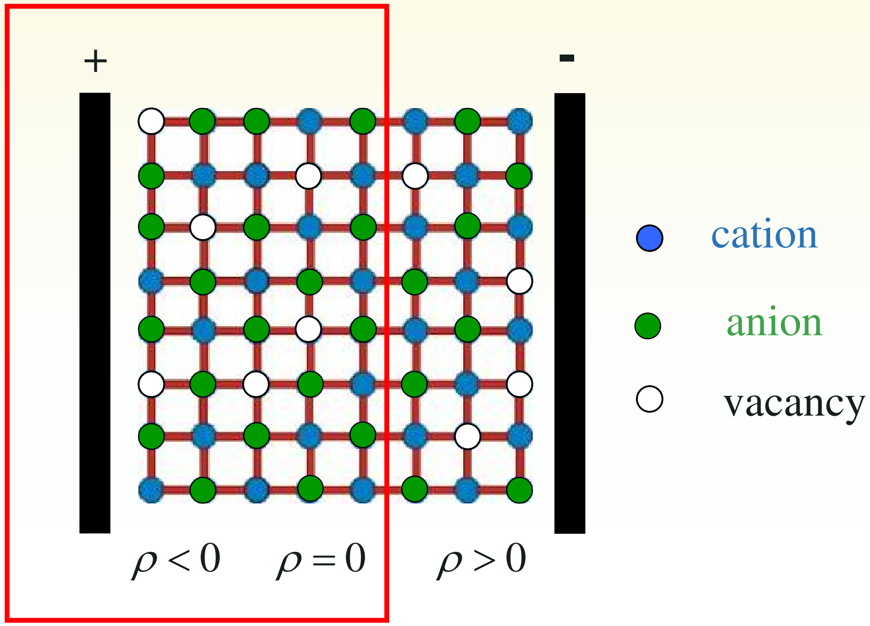
Mean-field lattice gas model

- Hard-core interactions between ions are implicitely taken into account.
- Individual Coulomb interactions are neglected.
- Model parameters:

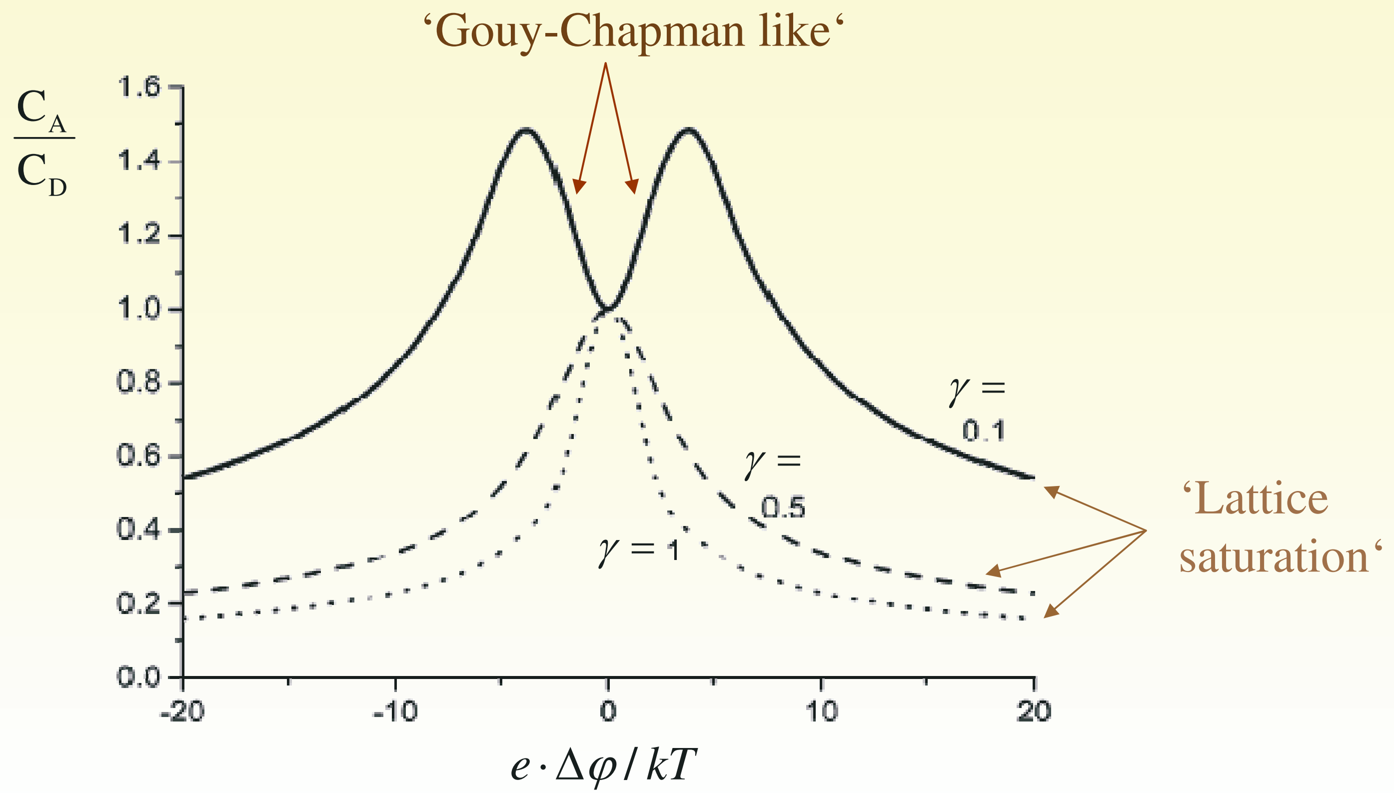
  (i) $e \cdot \Delta\varphi / kT$

  (ii) ratio of occupied sites

  $\gamma = 0...1$



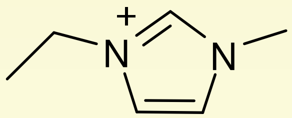
Kornyshev's results for differential capacitance of double layer



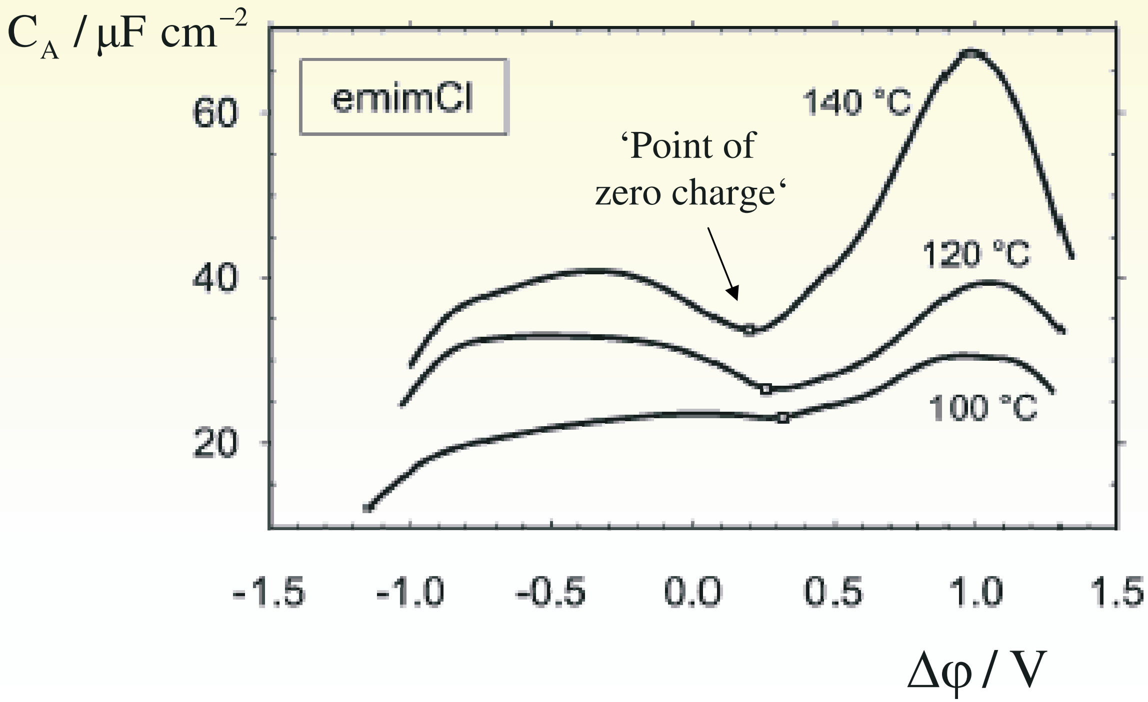
At highly positive and negative electrode potentials:
Since ion concentration at the electrodes cannot become much higher than in the bulk, the thickness of the double layer has to increase with increasing potential.

$\longrightarrow$ 'Lattice saturation'

Experimental results for double layer capacitance



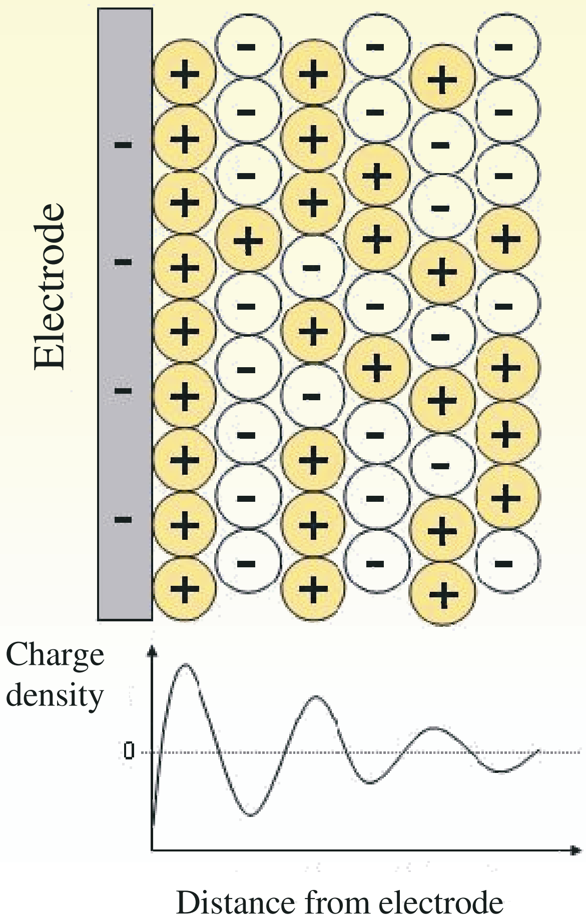
Cl^- at glassy carbon electrode



Lockett et al., *J. Phys. Chem. C* **112** (2008) 7486.

Similar to Kornyshev's results for $\gamma = 0.1$!

Structure of Double Layer from Molecular Dynamics Simulations



Charge density oscillations and ‘Overscreening effect‘:

“Too much“ positive charge in the first layer at the negative electrode.

Seems to be a universal interfacial phenomenon in dense ionic systems.

However: Influence on differential capacitance not yet well understood.

5. Conclusions

Bulk ion dynamics:

- Vast amount of experimental data
- Many well established models
- However, no model can describe all experimental features.
- Still, many basic experimental results are not fully understood.

Review article on open questions in this field: J. C. Dyre, P. Maass, B. Roling, D. L. Sidebottom, *Rep. Prog. Phys.* **72** (2009) 046501.

Electrode polarisation in concentrated electrolytes
(Ionic liquids and solid electrolytes)

- Reliable experimental data are scarce.
  (Impurities may have strong impact on results!)
- Currently, new model approaches are being developed and
  sophisticated molecular dynamics simulations are being carried out.
- Apart from purely electrostatic double layer charge storage,
  pseudocapacitive processes play an important role.

Talk about electrode polarisation in ILs: Ionic Solids Session, tomorrow, 12.00-12.30