

Syllabus

1. Introduction

2. Fluids

1. General Characteristics
2. Dispersions
3. Thermodynamics
4. Transport Phenomena
5. Solutions
6. Surface Tension
- 7. Electrical Properties**
8. Optical Properties
9. Biological Fluids

Physics of Microfluidic Systems

1. Navier-Stokes Equation
2. Laminar and Turbulent Flow
3. Fluid Dynamics
4. Fluid Networks
5. Transport of Heat
6. Interfacial Surface Tension
7. Electrokinetics

2.7. Electrical Properties

- Distinction
 - **Gases**
 - **Liquids**
- (Direct) current
 - **Electric field** $E = U / L$
 - Response: motion of free charge carriers
 - **Ions**
 - **Electrons**
- **Gases**
 - Plasma-like state
- **Liquids**
 - Electrolytes containing solvated ions



2.7. Electrical Properties

2.7.1. Gas Discharges

2.7.2. Conductivity in Liquids and Solutions

2.7.3. Electrochemical Cells

2.7.4. Dielectric Properties



2.7.1. Gas Discharges

- Constant generation of charge carriers

$$Q_N = \alpha_q t$$

- Equal number N of positive and negative charge carriers
- Charge generation rate α_q

- Recombination rate

$$\frac{dQ_N}{dt} = \beta Q_N^2$$

- Constant of recombination β

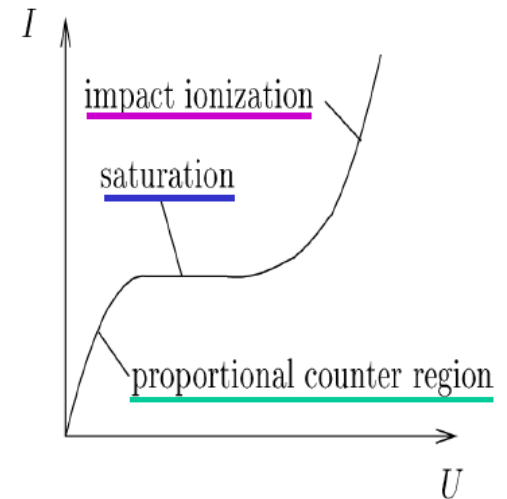
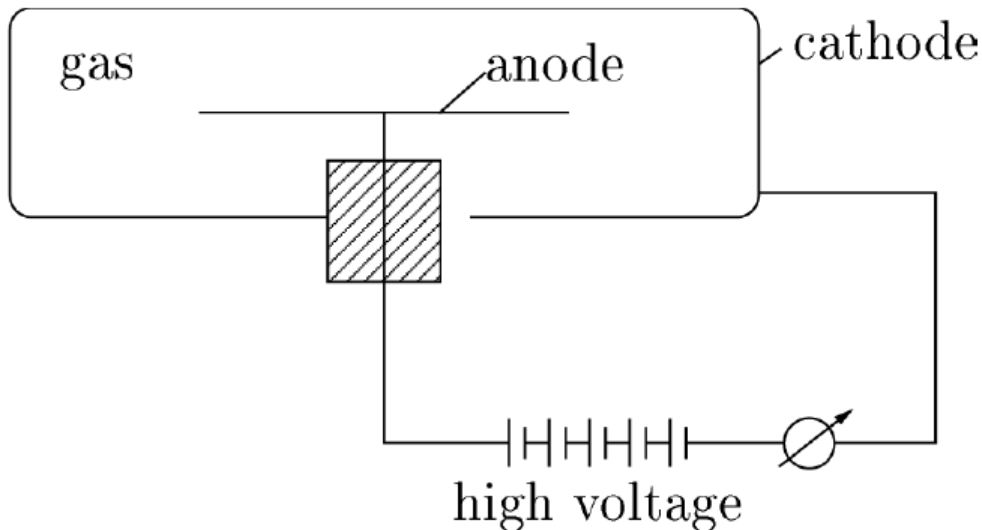
- Stationary concentration

- Natural sources $\alpha_q = 10^6 \text{ m}^{-3} \text{ s}^{-1}$
- Recombination $\beta = 10^{-12} \text{ m}^3 \text{ s}^{-1}$
- Charge carrier density $\rho_N = 10^9 \text{ m}^{-3}$ **very small**

$$Q_{N,\infty} = \sqrt{\frac{\alpha_q}{\beta}}$$

2.7.1. Gas Discharges

- Ionization chamber
 - Measuring electrical properties of gas
 - Ionic mobility μ
 - Current $I(U)$



2.7.1. Gas Discharges

- **Stationary drift velocity**

$$v = \mu |E|$$

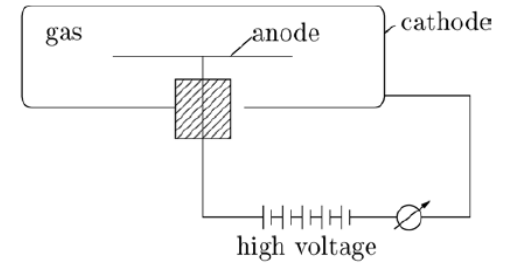
- Collisions with neutral atoms
- Superimposed upon thermal velocity $v_T \gg v$
- Time between collisions $\tau = \frac{l_{\text{mfp}}}{v_T}$
- Acceleration $a = q |E| / m$
- Mean velocity

$$\bar{v} = \frac{1}{2} a \tau = \frac{q |E| l_{\text{mfp}}}{2m v_T}$$

- Assuming total loss of kinetic energy upon collision
- Comparison of factors yields (with $q = e$)

$$\mu = \frac{e l_{\text{mfp}}}{2m v_T}$$

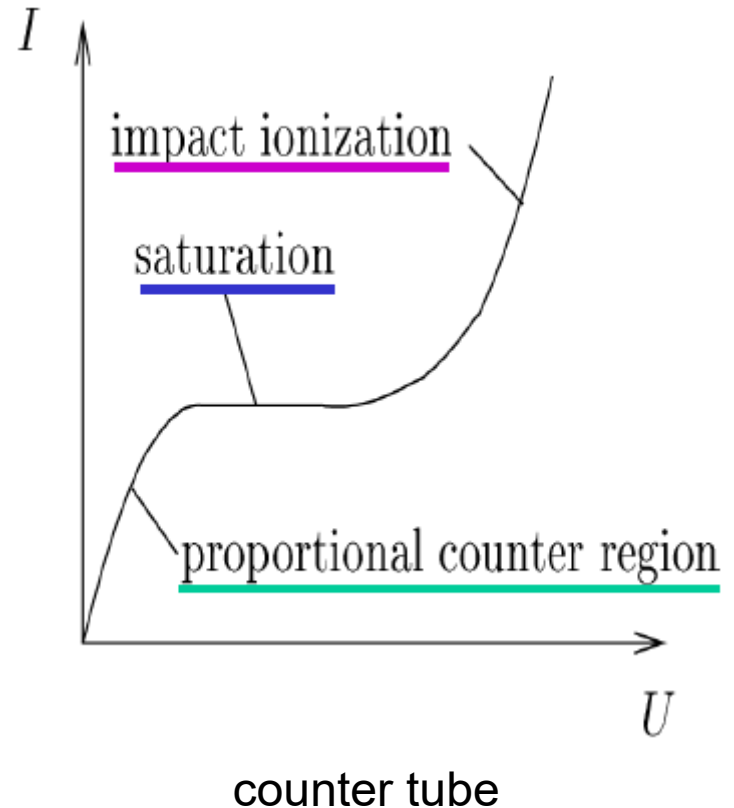
Ionic mobility



$$v = \mu E$$

2.7.1. Gas Discharges

- **Proportional region** (low U)
 - Stationary charge carrier density
Current density scales in Ohmic fashion with electric field strength
- **Region of saturation**
 - All ions generated in active region reach electrode
- **Region of impact ionization**
 - High field strength in vicinity of wire anode in Geiger-Müller tube
 - Charge amplified in avalanche of electron impact ionizations
 - Additional electrons ionize atoms while proceeding to anode



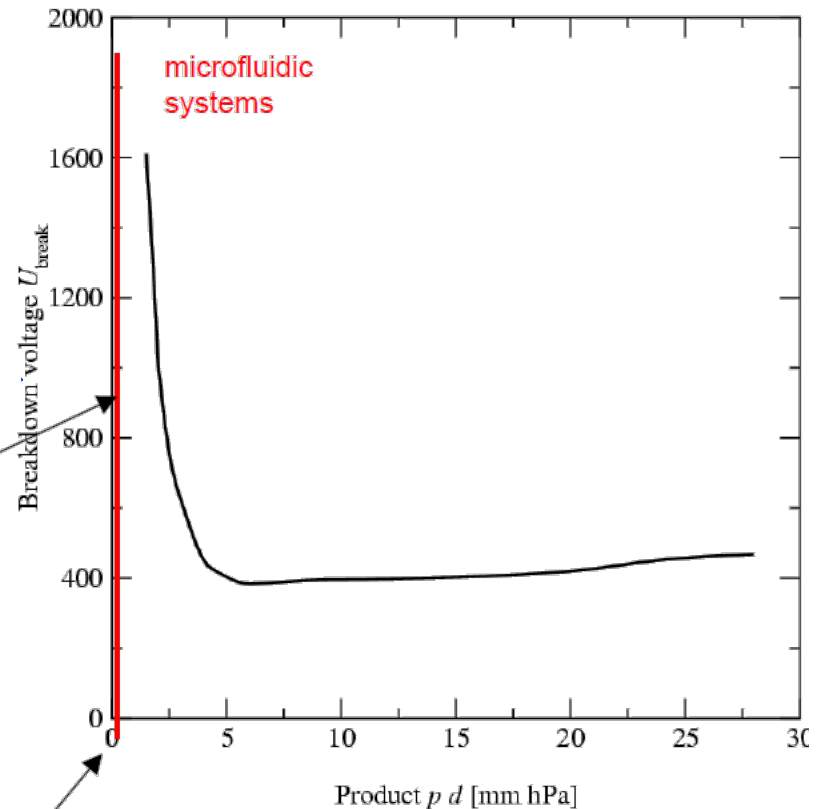
2.7.1. Gas Discharges - Breakdown Voltage

- Paschen curve

- Break through voltage U_{break}
- Product pd
 - Electrode spacing d
 - Pressure p

- Example

- Standard pressure 1013 hPa
- „Microscopic“ distances
- 10 μm - 100 μm
- $pd = 0.01$ to 0.1 mm hPa
- Part below minimum
- At fixed d , U_{break} sharply decreases with pressure p



Physics valid?

2.7. Electrical Properties

2.7.1. Gas Discharges

2.7.2. Conductivity in Liquids and Solutions

2.7.3. Electrochemical Cells

2.7.4. Dielectric Properties



2.7.2. Conductivity in Liquids and Solutions

- Velocities of anions and cations
 - Limit of high dilution: independent migration of ions

$$v_+ = \mu_+ |E|$$

$$v_- = -\mu_- |E|$$

- Stationary case

- Equal electrical “pull” and frictional forces: $F_D = -F_E$

cation	$\mu_+ / 10^{-4} \text{ cm}^2 \text{ s}^{-1} \text{ V}^{-1}$	anion	$\mu_- / 10^{-4} \text{ cm}^2 \text{ s}^{-1} \text{ V}^{-1}$
H ⁺	36.30	OH ⁻	20.50
Li ⁺	4.01	F ⁻	5.70
Na ⁺	5.19	Cl ⁻	7.91
K ⁺	7.62	Br ⁻	8.13
Ag ⁺	6.41	I ⁻	7.95
Ca ²⁺	6.16	NO ₃ ⁻	7.40
Cu ²⁺	7.92	CO ₃ ²⁻	7.46
NH ₄ ⁺	7.60	SO ₄ ²⁻	8.25

Table 2.1. Ionic mobilities μ_i in water solution at $T = 298 \text{ K}$

2.7.2. Conductivity in Liquids and Solutions

- Current densities

$$j_+ = z_+ (+e)(+v_+)c_+ = z_+ e \mu_+ |\mathbf{E}| c_+$$

$$j_- = z_- (-e)(-v_-)c_- = z_- e \mu_- |\mathbf{E}| c_-$$



- Law of **Kohlrausch**
 - High dilution limit
 - Charge carrier concentrations c_i
 - Relative charge z_i
 - **Both** carrier types contribute **constructively**
- Electrolytic conductivity

$$\sigma_E = \frac{j}{|\mathbf{E}|} = e (z_+ \mu_+ c_+ + z_- \mu_- c_-)$$

- Measured at AC (for avoiding polarization)

2.7.2. Conductivity in Liquids and Solutions

optional

- Overall electric neutrality
 - Electrolyte always neutral on macroscale
 - Valid down to **Debye radius**
 - Distance where **thermal energy** roughly equals **Coulomb energy**

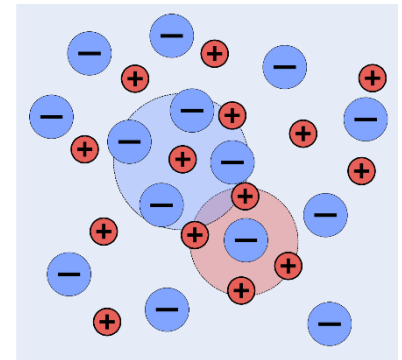


$$r_D = \sqrt{\frac{k_B T \epsilon \epsilon_0}{e^2 \sum_i c_i z_i^2}}$$

- **Ionic strength**

- Coulomb coupling capability per unit volume

$$s_q = e^2 \sum_i c_i z_i^2$$



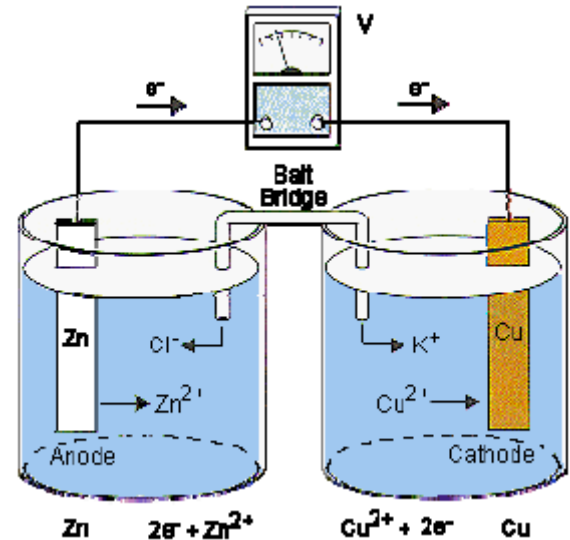
2.7. Electrical Properties

2.7.1. Gas Discharges

2.7.2. Conductivity in Liquids and Solutions

2.7.3. Electrochemical Cells

2.7.4. Dielectric Properties



2.7.3. Electrochemical Cells

- Galvanic Cell

- **Chemical energy** converted into **voltage difference U**

- Example: Daniell cell

- Zn-electrode in ZnSO_4 solution

- Cu-electrode in CuSO_4 solution

- Semipermeable membrane or KCl salt bridge

- Blocks metal ions Zn^{2+} and Cu^{2+} , while SO_4^{2-} passes membrane

- Prevents direct e-exchange between Cu^{2+} and Zn

- Overall redox reaction

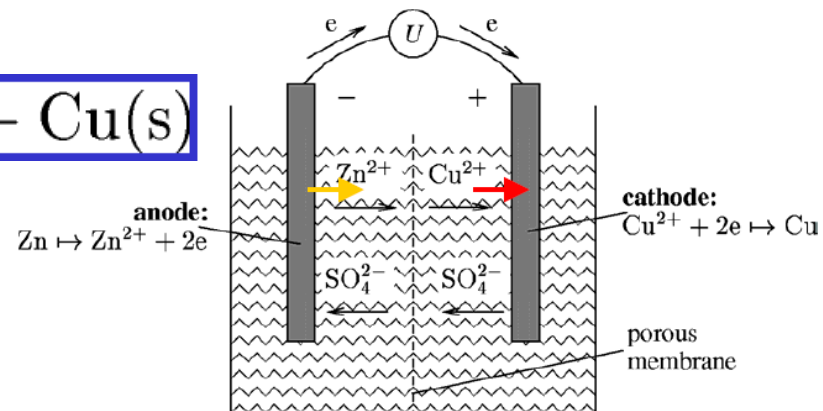
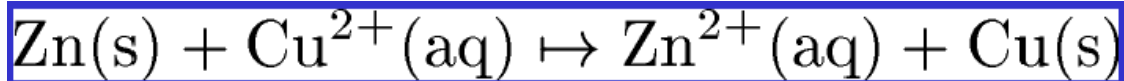


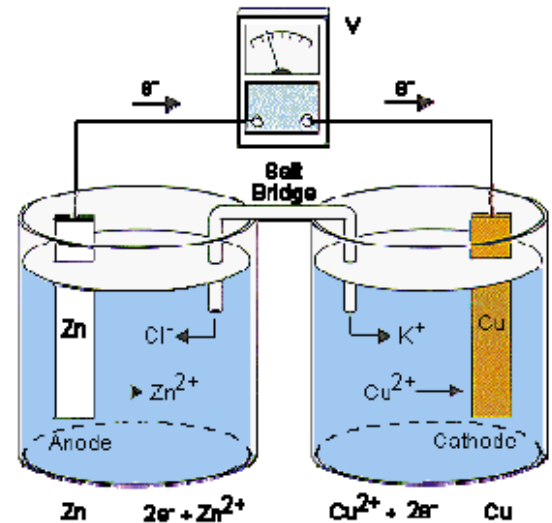
Fig. 2.29. Principle of a galvanic cell. In this so-called Daniell element, the electromotric force (EMF) makes an electric current flows between the two half-cells separated by a permeable membrane. In the left half-cell, a Zn-anode dips into a ZnSO_4 solution and on the right, the Cu-cathode in CuSO_4 solution

2.7.3. Electrochemical Cells

- Electromotive force (EMF)
 - Voltage produced by galvanic cell

$$U_{\text{EMF}} = U_{\text{anode}} - U_{\text{cathode}}$$

- Often specified for standard conditions
 - $a = 1$ (activity, effective concentration)
 - $c = 1 \text{ mol l}^{-1}$
 - $T = 25^\circ\text{C}$
 - $p = 1013 \text{ hPa}$
- Daniell element
at standard conditions: $U_0 = 1.10 \text{ V}$
- Reference: standard hydrogen electrode



2.7.3. Electrochemical Cells

optional

- Maximum energy
 - Galvanic cell operating at U_{EMF}
 - Moles of redox pair n
 - Electrons produced per reaction z

$$E = zn\mathcal{F}U_{\text{EMF}}$$

- Faraday constant
 - Relates moles to charge

$$\mathcal{F} = 96486.7 \text{ C mol}^{-1}$$

- Change in Gibbs enthalpy
 - $U_{\text{EMF}} > 0$ for spontaneous process $\Delta G < 0$

$$\Delta G = -zn\mathcal{F}U_{\text{EMF}}$$



- Nernst equation

- **Potential** under **non-standard** conditions

$$U_{\text{EMF}} = U_{\text{EMF}}^0 - \frac{R_{\text{g}}T}{c\mathcal{F}} \ln k_c$$



- k_c constant of mass action law

- Dependency on molar concentration c

- Galvanic cells with equal parameters
- Except concentration of solvated ions

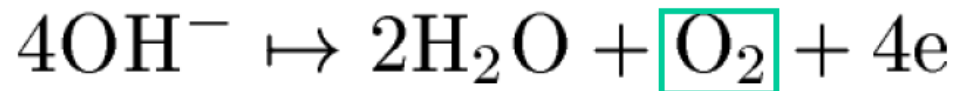


$$k_c = \frac{c^x(\text{X})c^y(\text{Y})}{c^v(\text{V})c^w(\text{W})}$$

2.7.3. Electrochemical Cells

optional

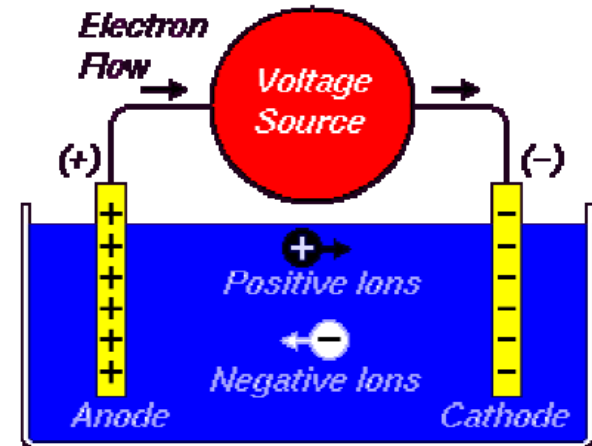
- Electrolytic cells
 - Reversal of spontaneous redox reaction
 - Voltage source $U > -U_{EMF}$
 - „Electrolysis“
 - **Electrical** energy → **Chemical** energy
 - E.g., rechargeable batteries
- Electrolysis of water
 - Protons reduced to H_2 gas at cathode
 - Hydroxide ions oxidized at anode



- Faraday's Law

$$q = \mathcal{F}zn$$

charge moles



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2.7.4. Dielectric Properties

- Poisson equation (sources of E -field: charge density ρ_q)

- Vacuum conditions

$$\nabla \cdot \mathbf{E} = \frac{1}{\epsilon_0} \rho_q(\mathbf{r}, t)$$

- $\epsilon_0 = 8.8542 \times 10^{-12} \text{ C V}^{-1} \text{ m}^{-1}$

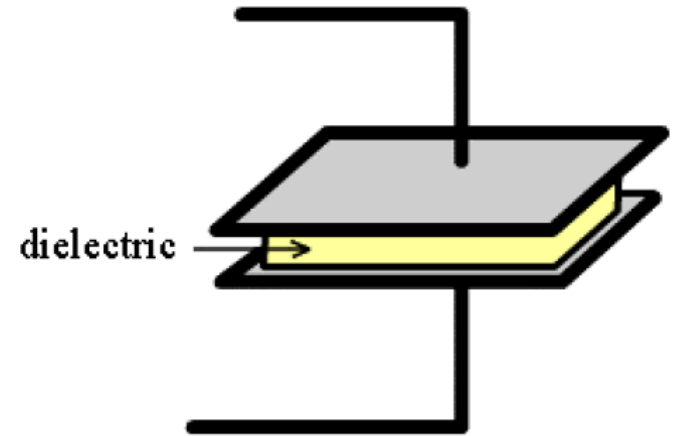
- Capacity

$$C_q = q/U$$

- Parallel plate capacitor in vacuum

$$C_{q,0} = \epsilon_0 A/d$$

- Cross sectional area A
- Distance between plates d



2.7.4. Dielectric Properties

- Dielectric permittivity
 - Dielectric medium between plates
 - Capacity enhanced by factor of $\varepsilon = C_q/C_{q,0} > 1$
 - **Relative** permittivity ε
 - **Absolute** permittivity $\varepsilon\varepsilon_0$
- Molecular dipole moments
 - Charge q , spaced by vector $d\hat{e}_r$.

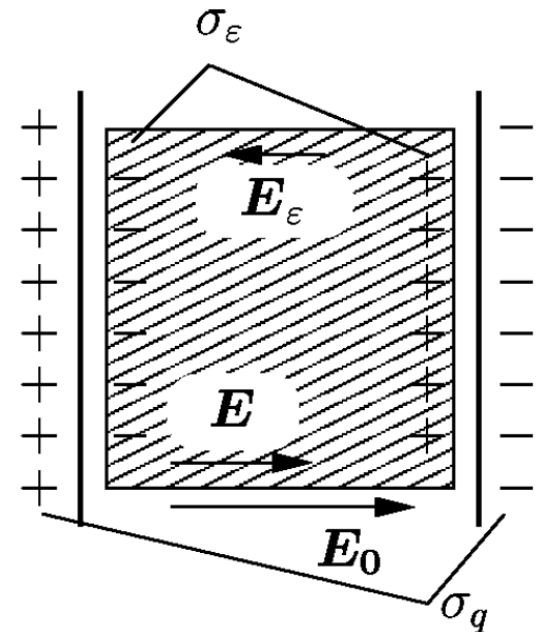
$$\mathbf{p}_q = qd\hat{e}_r$$

- Density of molecular dipole moments

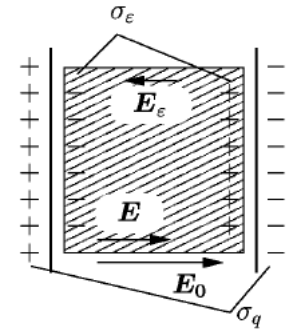
$$\mathbf{P}_q = \frac{d\mathbf{p}_q}{dV} = \xi_\varepsilon \mathbf{E}$$

- Dielectric susceptibility

$$\xi_\varepsilon = (\varepsilon - 1)\varepsilon_0$$



2.7.4. Dielectric Properties



material	temperature $\theta / ^\circ\text{C}$	relative permittivity ϵ
glass	20	5 – 10
silica glass	20	3.7
ethanol	20	25.8
water	18	81.1
air	0	1.000576
hydrogen	0	1.000264
nitrogen	0	1.000606

solids

liquids

gases

Table 2.1. Relative permittivities of selected materials, gases at 1013 hPa

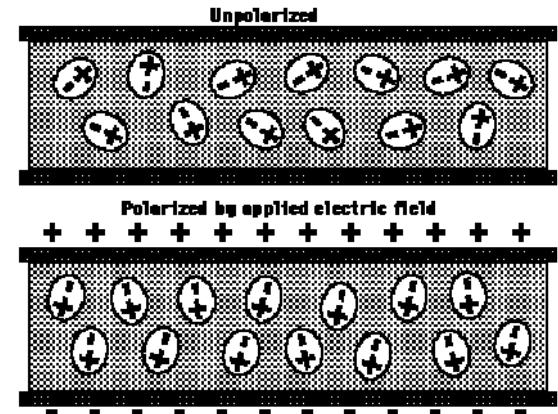
2.7.4. Dielectric Properties

optional

- Mechanisms of dielectric polarization
 - Dipole moment induced by external field E

$$\mathbf{p}_q = \frac{q^2}{k_{\text{elast}}} \mathbf{E} = \alpha_\epsilon \mathbf{E}$$

- Elastic constant $k_{\text{elast}} \approx (d/dr) F_{\text{Coul}}$
- Polarizability $\alpha_\epsilon \approx 2\pi\epsilon_0 r^3$
- Atomic radius r



- Relation between **microscopic** and **macroscopic** quantities

$$\rho N \alpha_\epsilon = (\epsilon - 1) \epsilon_0$$

- Law of **Clausius-Mossotti** (for liquids and solids)

- Takes non-negligible dipole-dipole interactions into account

$$\epsilon_0 \frac{\epsilon - 1}{\epsilon + 2} V_n = \frac{1}{3} N_A \alpha_\epsilon$$

2.7.4. Dielectric Properties

optional

- Dielectric relaxation

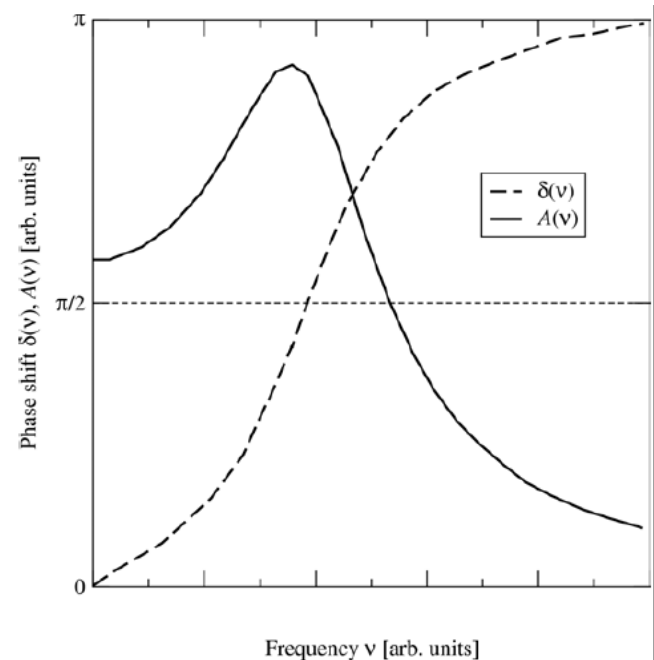
- Response time for adjustment of dipole moments to E -field
- Approx. 10^{-16} s for **induced** dipole moments
- Frequency-dependency negligible even for visible light
 - Field oscillation at approx. 10^{-14} s
- **Permanent** dipoles much slower
 - E.g., water 10^{-11} s for complete reversal
 - Response time even slower for solids

→ $\varepsilon = \varepsilon(\nu)$ for $\nu > 10^{10}$ Hz

→ **Phase shift** δ with respect to E -field

- **Complex dielectric permittivity**

$$\varepsilon^*(\nu) = |\varepsilon^*(\nu)| e^{i\delta(\nu)} = \varepsilon + i \frac{\sigma E}{\omega}$$



“microwave heater” (GHz)

Summary

Density of charge carriers in atmosphere:

$$Q_{N,\infty} = \sqrt{\frac{\alpha_q}{\beta}}$$

Drift velocity v and ionic mobility μ

$$v = \mu |\mathbf{E}|$$

$$v_+ = \mu_+ |\mathbf{E}|$$
$$v_- = -\mu_- |\mathbf{E}|$$

$$\mu = \frac{el_{\text{mfp}}}{2mv_T}$$

Electrolytic conductivity

$$\sigma_E = \frac{j}{|\mathbf{E}|} = e(z_+ \mu_+ c_+ + z_- \mu_- c_-)$$

EMF

$$U_{\text{EMF}} = U_{\text{anode}} - U_{\text{cathode}}$$

Capacity C_q

$$C_q = q/U$$

$$\varepsilon = C_q/C_{q,0} > 1$$

Dielectric permittivity ε

Dielectric susceptibility ξ_ε

$$C_{q,0} = \varepsilon_0 A/d$$

$$\xi_\varepsilon = (\varepsilon - 1)\varepsilon_0$$