

PHY 712 Electrodynamics

10-10:50 AM MWF Olin 103

Plan for Lecture 11:

Complete reading of Chapter 4

- A. Microscopic \leftrightarrow macroscopic polarizability and dielectric function
- B. Clausius-Mossotti equation
- C. Electrostatic energy in dielectric media
- D. Comment on “modern theory of polarization”

Course schedule for Spring 2023

(Preliminary schedule -- subject to frequent adjustment.)

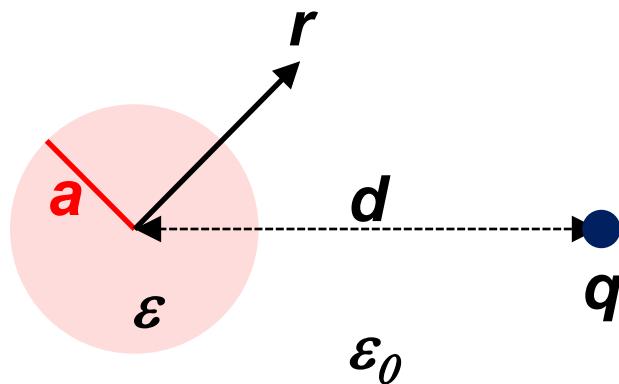
	Lecture date	JDJ Reading	Topic	HW	Due date
1	Mon: 01/9/2023	Chap. 1 & Appen.	Introduction, units and Poisson equation	#1	01/13/2023
2	Wed: 01/11/2023	Chap. 1	Electrostatic energy calculations	#2	01/18/2023
3	Fri: 01/13/2023	Chap. 1	Electrostatic energy calculations thanks to Ewald	#3	01/18/2023
	Mon: 01/16/2023		MLK Holiday -- no class		
4	Wed: 01/18/2023	Chap. 1 & 2	Electrostatic potentials and fields	#4	01/20/2023
5	Fri: 01/20/2023	Chap. 1 - 3	Poisson's equation in 2 and 3 dimensions	#5	01/23/2023
6	Mon: 01/23/2023	Chap. 1 - 3	Brief introduction to numerical methods	#6	01/25/2023
7	Wed: 01/25/2023	Chap. 2 & 3	Image charge constructions	#7	01/30/2023
8	Fri: 01/27/2023	Chap. 2 & 3	Cylindrical and spherical geometries		
9	Mon: 01/30/2023	Chap. 3 & 4	Spherical geometry and multipole moments	#8	02/01/2023
10	Wed: 02/01/2023	Chap. 4	Dipoles and Dielectrics	#9	02/03/2023
11	Fri: 02/03/2023	Chap. 4	Dipoles and Dielectrics	#10	02/06/2023
12	Mon: 02/06/2023	Chap. 5	Magnetostatics		

PHY 712 -- Assignment #10

February 3, 2023

Finish reading Chapter 4 in **Jackson** .

1. Work problem 4.9(a) in **Jackson**. It is probably most convenient to use a coordinate system with the origin at the center of the dielectric sphere.



Note that

$$\frac{1}{|\mathbf{r} - \mathbf{d}|} = \sum_{\ell=0}^{\infty} \frac{r^{\ell}}{d^{\ell+1}} P_{\ell}(\hat{\mathbf{r}} \cdot \hat{\mathbf{d}})$$

Review -- Focus on dipolar fields:

Dipole moment \mathbf{p} :

$$\mathbf{p} \equiv \int d^3r' \mathbf{r}' \rho(\mathbf{r}')$$

For r outside the extent of $\rho(\mathbf{r})$:

Electrostatic potential from single dipole:

$$\Phi(\mathbf{r}) = \frac{1}{4\pi\epsilon_0} \left(\frac{\mathbf{p} \cdot \mathbf{r}}{r^3} \right)$$

Electrostatic field from single dipole:

$$\mathbf{E}(\mathbf{r}) = \frac{1}{4\pi\epsilon_0} \left(\frac{3\mathbf{r} (\mathbf{p} \cdot \mathbf{r}) - r^2 \mathbf{p}}{r^5} - \frac{4\pi}{3} \mathbf{p} \delta^3(\mathbf{r}) \right)$$

Now consider a distribution of dipoles and monopoles --

Electric polarization $\mathbf{P}(\mathbf{r})$ due to collection of dipoles :

$$\mathbf{P}(\mathbf{r}) \equiv \sum_i \mathbf{p}_i \delta^3(\mathbf{r} - \mathbf{r}_i)$$

Monopole electric charge density $\rho_{\text{mono}}(\mathbf{r})$:

$$\rho_{\text{mono}}(\mathbf{r}) \equiv \sum_i q_i \delta^3(\mathbf{r} - \mathbf{r}_i)$$

Define Displacement field: $\mathbf{D}(\mathbf{r}) \equiv \epsilon_0 \mathbf{E}(\mathbf{r}) + \mathbf{P}(\mathbf{r})$

Macroscopic form of Gauss's law: $\nabla \cdot \mathbf{D}(\mathbf{r}) = \rho_{\text{mono}}(\mathbf{r})$

Review continued

Many materials are polarizable and produce a polarization field in the presence of an electric field with a proportionality constant χ_e :

$$\mathbf{P}(\mathbf{r}) = \varepsilon_0 \chi_e \mathbf{E}(\mathbf{r})$$

$$\mathbf{D}(\mathbf{r}) \equiv \varepsilon_0 \mathbf{E}(\mathbf{r}) + \mathbf{P}(\mathbf{r}) = \varepsilon_0 (1 + \chi_e) \mathbf{E}(\mathbf{r}) \equiv \varepsilon \mathbf{E}(\mathbf{r})$$

ε represents the dielectric function of the material

Boundary value problems in dielectric materials

For $\rho_{\text{mono}}(\mathbf{r}) = 0$

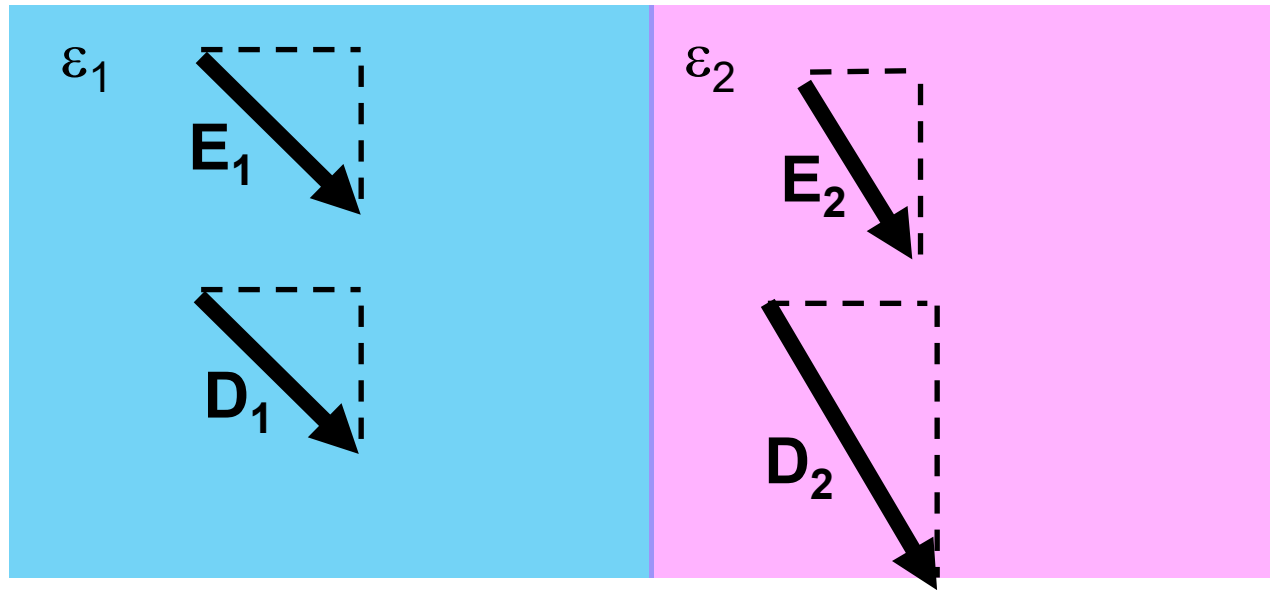
$$\nabla \cdot \mathbf{D}(\mathbf{r}) = 0 \quad \text{and} \quad \nabla \times \mathbf{E}(\mathbf{r}) = 0$$

\Rightarrow At a surface between two dielectrics, in terms of surface normal $\hat{\mathbf{r}}$:

$$\hat{\mathbf{r}} \cdot \mathbf{D}(\mathbf{r}) = \text{continuous} = \hat{\mathbf{r}} \times \mathbf{E}(\mathbf{r})$$

Boundary value problems in the presence of dielectrics

– example:



$$\text{For } \frac{\epsilon_2}{\epsilon_1} = 2$$

$$\text{For } \rho_{\text{mono}}(\mathbf{r}) = 0: \quad \nabla \cdot \mathbf{D}(\mathbf{r}) = 0 \quad \text{and} \quad \nabla \times \mathbf{E}(\mathbf{r}) = 0$$

\Rightarrow At a surface between two dielectrics, in terms of surface normal $\hat{\mathbf{r}}$:

$$\hat{\mathbf{r}} \cdot \mathbf{D}(\mathbf{r}) = \text{continuous} = \hat{\mathbf{r}} \times \mathbf{E}(\mathbf{r})$$

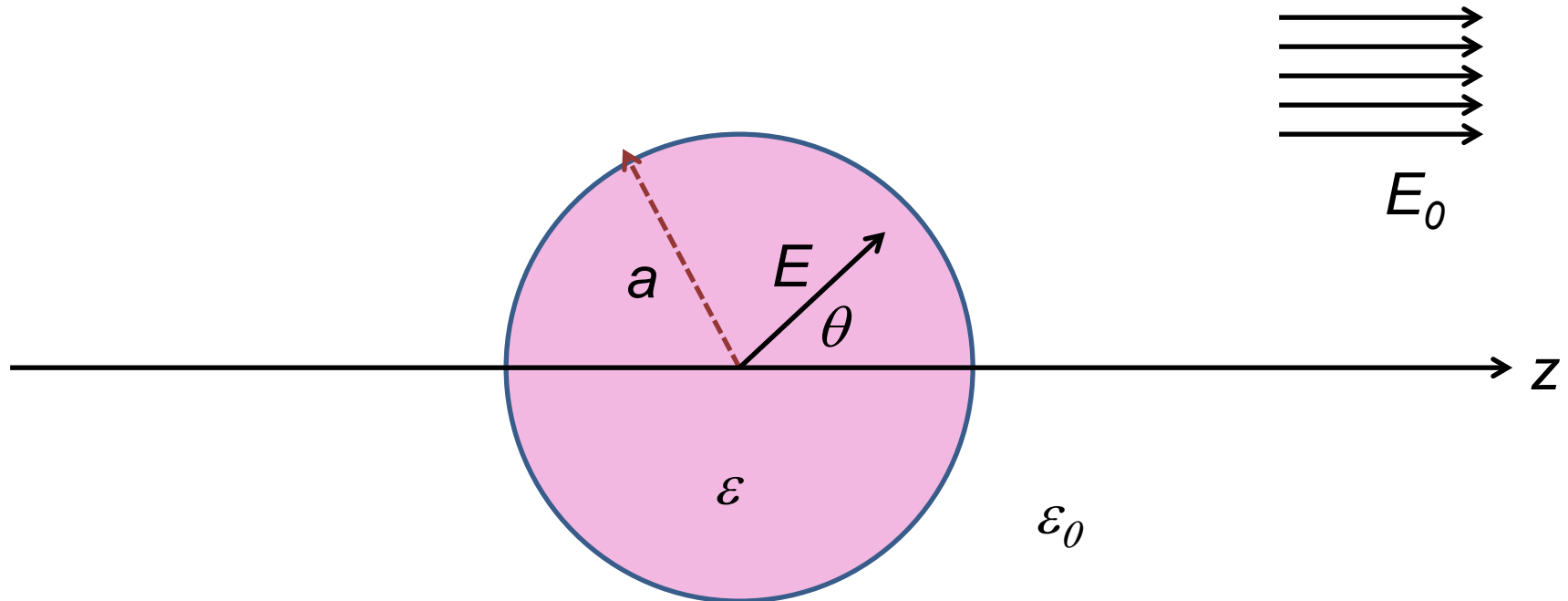
$$D_{1n} = D_{2n} \quad \epsilon_1 E_{1n} = \epsilon_2 E_{2n}$$

For isotropic dielectrics:

$$E_{1t} = E_{2t} \quad \frac{D_{1t}}{\epsilon_1} = \frac{D_{2t}}{\epsilon_2}$$

Boundary value problems in the presence of dielectrics

– example:



$$\nabla \cdot \mathbf{D}(\mathbf{r}) = 0 \quad \text{and} \quad \nabla \times \mathbf{E}(\mathbf{r}) = 0 \quad \text{At } r = a: \quad \epsilon \frac{\partial \Phi_{<}(\mathbf{r})}{\partial r} = \epsilon_0 \frac{\partial \Phi_{>}(\mathbf{r})}{\partial r}$$

$$\text{For } r \leq a \quad \mathbf{D}(\mathbf{r}) = -\epsilon \nabla \Phi(\mathbf{r})$$

$$\text{For } r > a \quad \mathbf{D}(\mathbf{r}) = -\epsilon_0 \nabla \Phi(\mathbf{r})$$

$$\frac{\partial \Phi_{<}(\mathbf{r})}{\partial \theta} = \frac{\partial \Phi_{>}(\mathbf{r})}{\partial \theta}$$

Boundary value problems in the presence of dielectrics

– example -- continued:

$$\Phi_{<}(\mathbf{r}) = \sum_{l=0}^{\infty} A_l r^l P_l(\cos \theta)$$

$$\Phi_{>}(\mathbf{r}) = \sum_{l=0}^{\infty} \left(B_l r^l + \frac{C_l}{r^{l+1}} \right) P_l(\cos \theta)$$

$$\text{At } r = a: \quad \epsilon \frac{\partial \Phi_{<}(\mathbf{r})}{\partial r} = \epsilon_0 \frac{\partial \Phi_{>}(\mathbf{r})}{\partial r}$$

$$\frac{\partial \Phi_{<}(\mathbf{r})}{\partial \theta} = \frac{\partial \Phi_{>}(\mathbf{r})}{\partial \theta}$$

$$\text{For } r \rightarrow \infty \quad \Phi_{>}(\mathbf{r}) = -E_0 r \cos \theta$$

Solution -- only $l = 1$ contributes

$$B_1 = -E_0$$

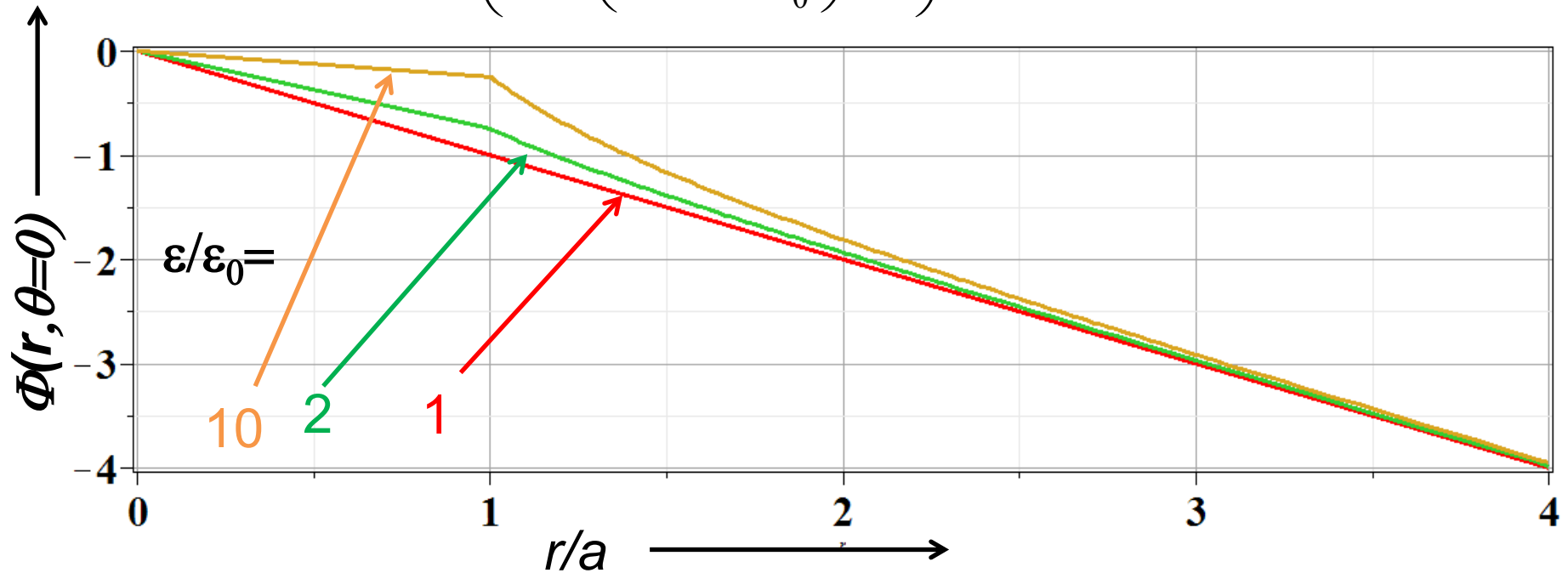
$$A_1 = - \left(\frac{3}{2 + \epsilon / \epsilon_0} \right) E_0$$

$$C_1 = \left(\frac{\epsilon / \epsilon_0 - 1}{2 + \epsilon / \epsilon_0} \right) a^3 E_0$$

Boundary value problems in the presence of dielectrics – example -- continued:

$$\Phi_{<}(\mathbf{r}) = -\left(\frac{3}{2 + \epsilon / \epsilon_0}\right) E_0 r \cos \theta$$

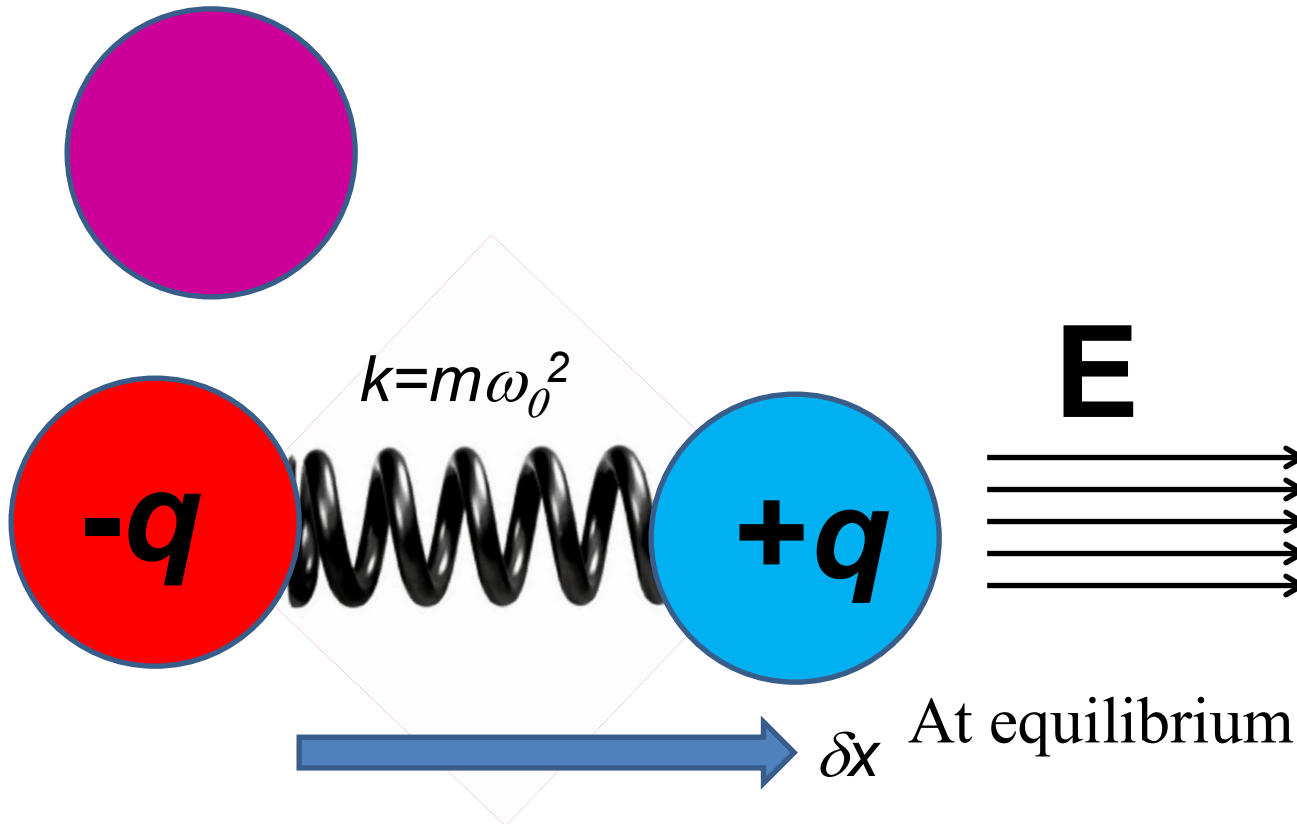
$$\Phi_{>}(\mathbf{r}) = -\left(r - \left(\frac{\epsilon / \epsilon_0 - 1}{2 + \epsilon / \epsilon_0}\right) \frac{a^3}{r^2}\right) E_0 \cos \theta$$



Microscopic origin of dipole moments

- Polarizable atoms/molecules
- Anisotropic charged molecules aligned in random directions

Polarizable systems

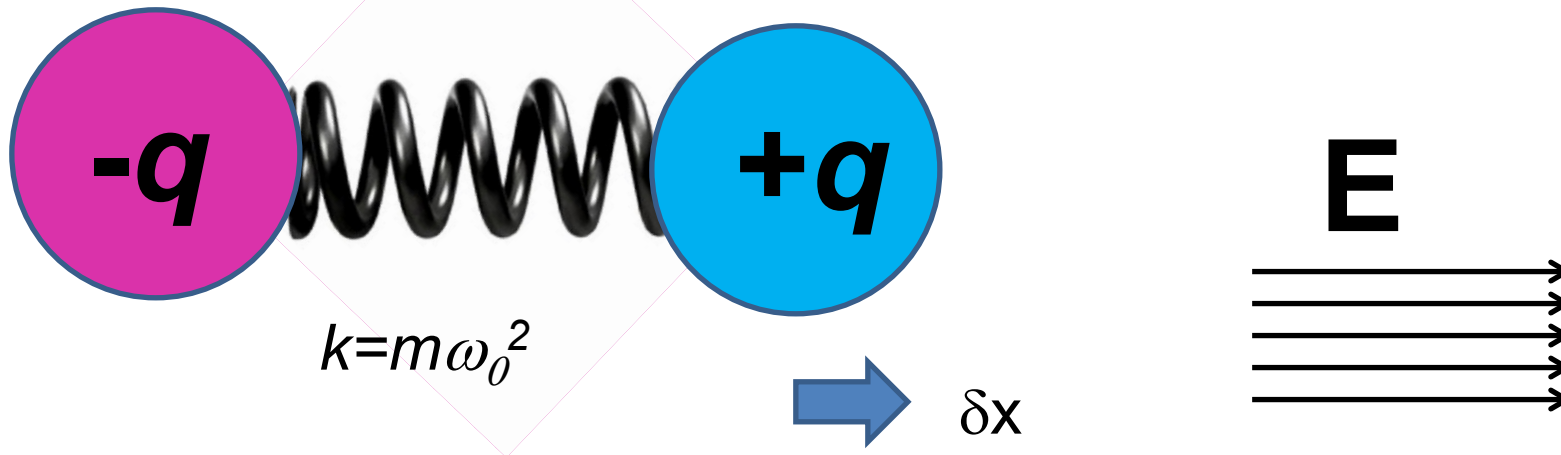


At equilibrium:

$$q\mathbf{E} - m\omega_0^2\delta\mathbf{x} = 0$$

$$\delta\mathbf{x} = \frac{q\mathbf{E}}{m\omega_0^2}$$

Polarizable atoms/molecules – continued:



At equilibrium:

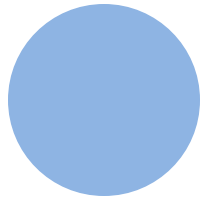
$$q\mathbf{E} - m\omega_0^2\delta\mathbf{x} = 0$$

$$\delta\mathbf{x} = \frac{q\mathbf{E}}{m\omega_0^2}$$

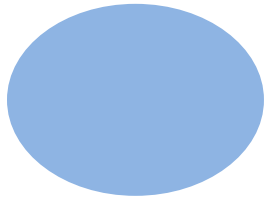
Induced dipole moment:

$$p = q\delta\mathbf{x} = \frac{q^2}{m\omega_0^2}\mathbf{E} \equiv \epsilon_0\gamma_{mol}\mathbf{E} \quad \Rightarrow \quad \gamma_{mol} = \frac{q^2}{m\omega_0^2\epsilon_0}$$

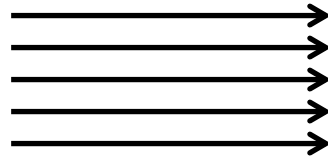
For a neutral atom



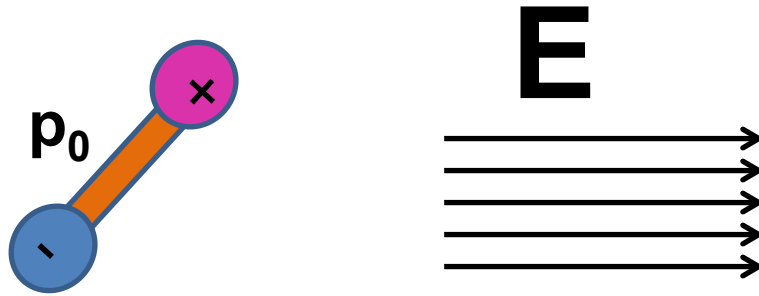
$$E=0$$



E



Alignment of molecules with permanent dipoles \mathbf{p}_0 :

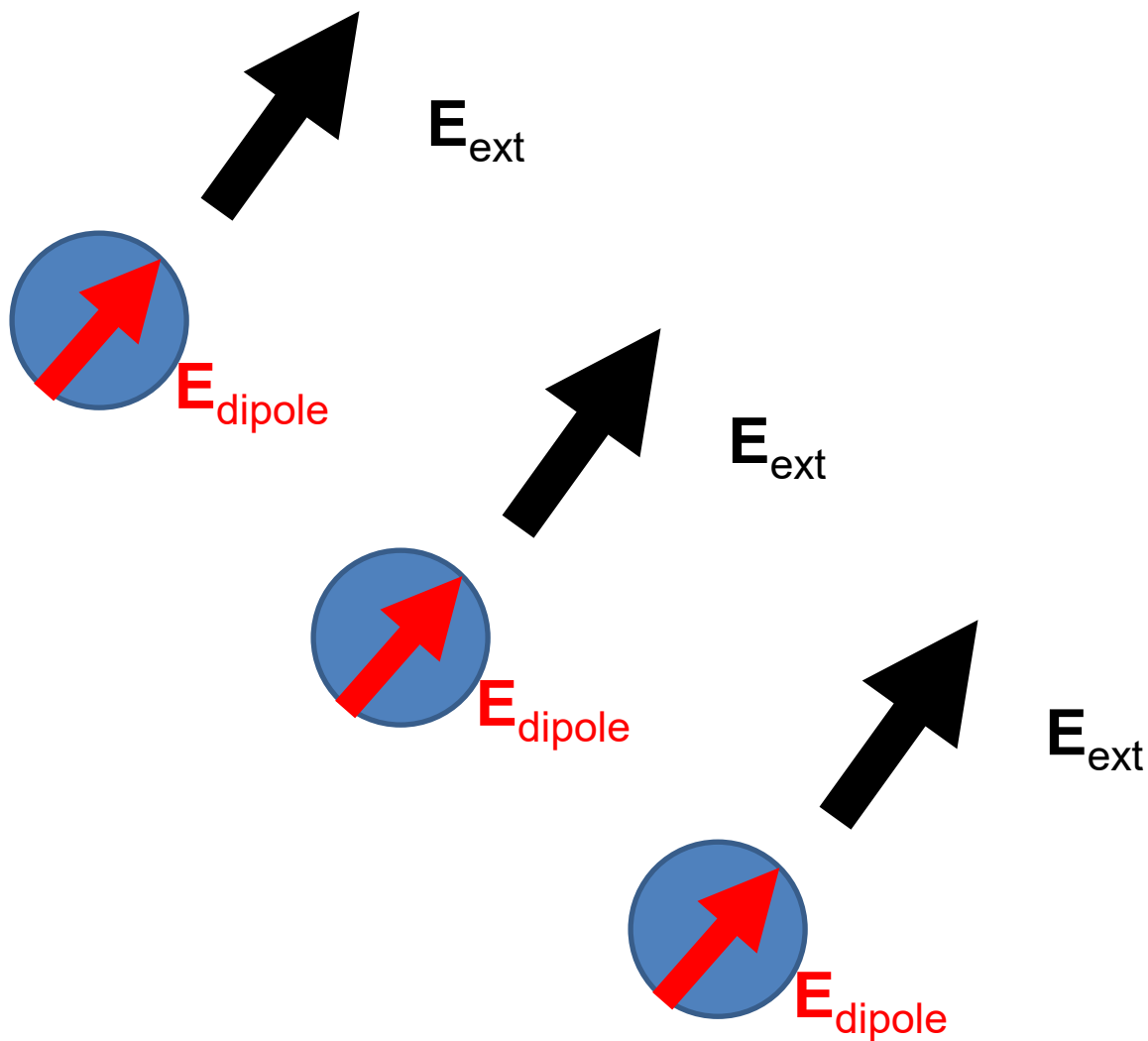


For a freely rotating dipole its average moment in an electric field, estimated assuming a Boltzmann distribution:

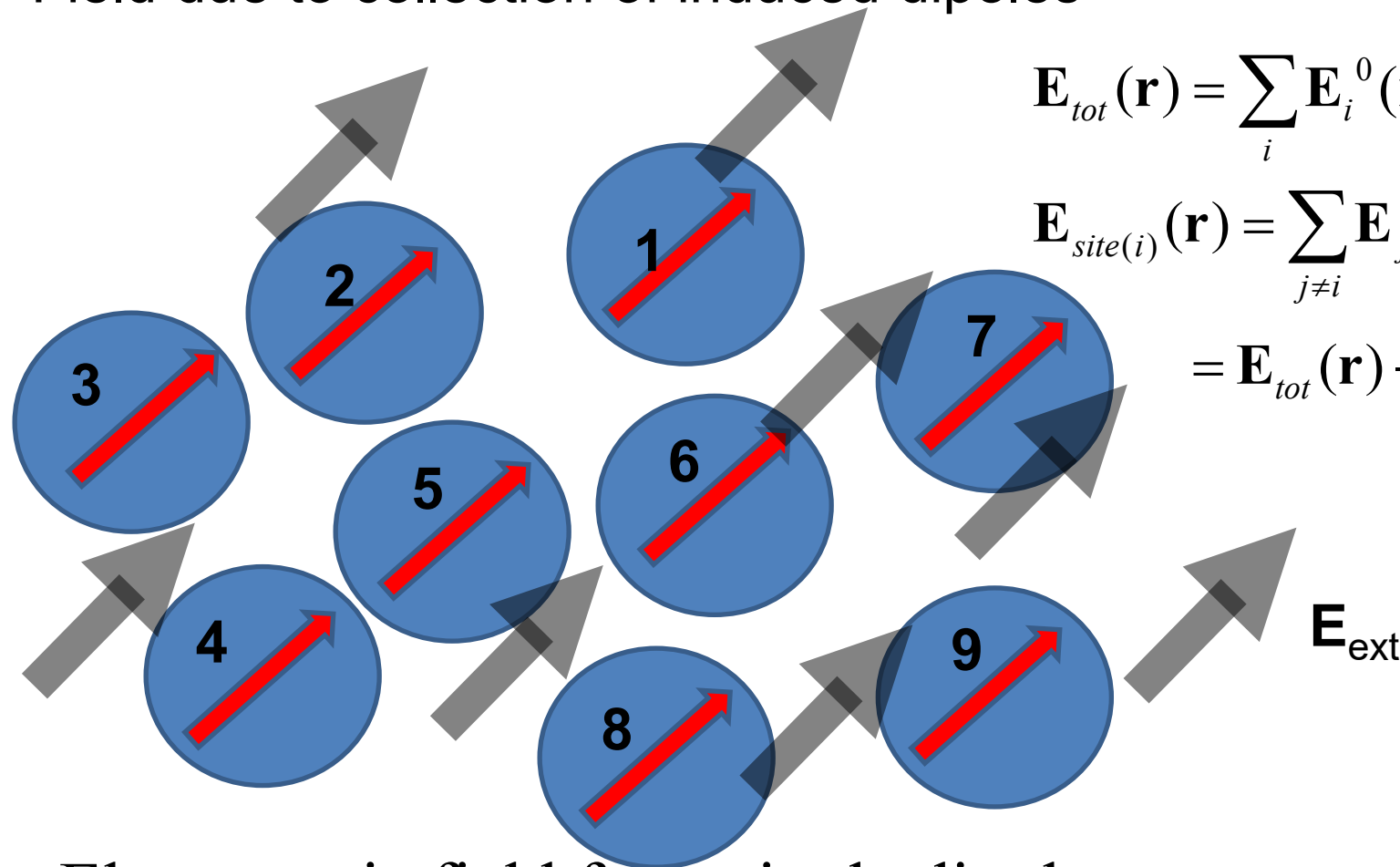
$$\langle \mathbf{p}_{mol} \rangle = \frac{\int d\Omega p_0 \cos \theta e^{p_0 E \cos \theta / kT}}{\int d\Omega e^{p_0 E \cos \theta / kT}} \approx \frac{1}{3} \frac{p_0^2}{kT} \mathbf{E} \quad \text{for} \quad \frac{p_0 E}{kT} \ll 1$$

$$\langle \mathbf{p}_{mol} \rangle \approx \frac{1}{3} \frac{p_0^2}{kT} \mathbf{E} \equiv \epsilon_0 \gamma_{mol} \mathbf{E} \quad \Rightarrow \quad \gamma_{mol} \approx \frac{1}{3} \frac{p_0^2}{kT \epsilon_0}$$

Now consider a superposition of dipoles in an electric field



Field due to collection of induced dipoles



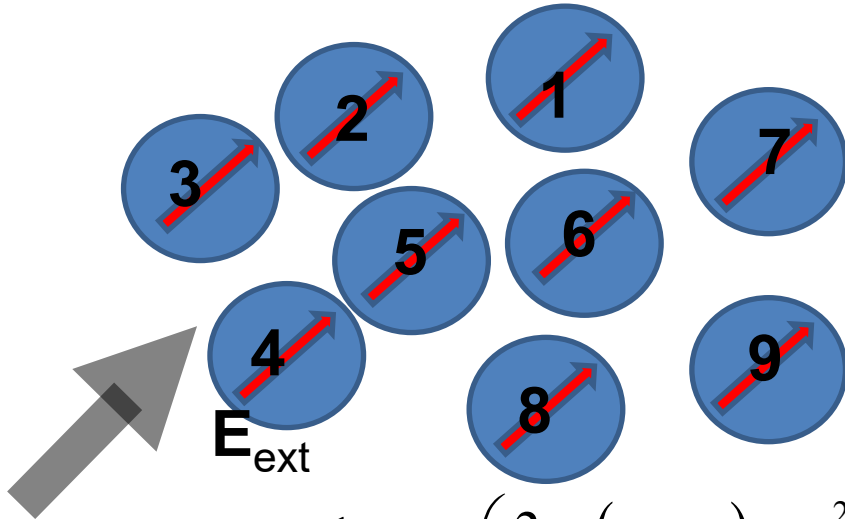
$$\mathbf{E}_{tot}(\mathbf{r}) = \sum_i \mathbf{E}_i^0(\mathbf{r}) + \mathbf{E}_{ext}(\mathbf{r})$$

$$\begin{aligned} \mathbf{E}_{site(i)}(\mathbf{r}) &= \sum_{j \neq i} \mathbf{E}_j^0(\mathbf{r}) + \mathbf{E}_{ext}(\mathbf{r}) \\ &= \mathbf{E}_{tot}(\mathbf{r}) - \mathbf{E}_i^0(\mathbf{r}) \end{aligned}$$

Electrostatic field from single dipole:

$$\mathbf{E}_i^0(\mathbf{r}) = \frac{1}{4\pi\epsilon_0} \left(\frac{3\mathbf{r} (\mathbf{p}_i \cdot \mathbf{r}) - r^2 \mathbf{p}_i}{r^5} - \frac{4\pi}{3} \mathbf{p}_i \delta^3(\mathbf{r} - \mathbf{r}_i) \right)$$

Field due to collection of induced dipoles -- continued



$$\mathbf{E}_{tot}(\mathbf{r}) = \sum_i \mathbf{E}_i^0(\mathbf{r}) + \mathbf{E}_{ext}(\mathbf{r})$$

$$\begin{aligned} \mathbf{E}_{site(i)}(\mathbf{r}) &= \sum_{j \neq i} \mathbf{E}_j^0(\mathbf{r}) + \mathbf{E}_{ext}(\mathbf{r}) \\ &= \mathbf{E}_{tot}(\mathbf{r}) - \mathbf{E}_i^0(\mathbf{r}) \end{aligned}$$

$$\mathbf{E}(\mathbf{r})_{tot} = \frac{1}{4\pi\epsilon_0} \sum_i \left(\frac{3\mathbf{r}(\mathbf{p}_i \cdot \mathbf{r}) - r^2 \mathbf{p}_i}{r^5} - \frac{4\pi}{3} \mathbf{p}_i \delta^3(\mathbf{r} - \mathbf{r}_i) \right) + \mathbf{E}_{ext}(\mathbf{r})$$

$$\mathbf{E}(\mathbf{r})_{site(i)} = \frac{1}{4\pi\epsilon_0} \left(\sum_{j \neq i} \frac{3\mathbf{r}(\mathbf{p}_j \cdot \mathbf{r}) - r^2 \mathbf{p}_j}{r^5} \right) + \mathbf{E}_{ext}(\mathbf{r}) = \mathbf{E}(\mathbf{r})_{tot} - (\mathbf{E}_i^0(\mathbf{r}))_{site(i)}$$

$$\langle \mathbf{E}_{site(i)} \rangle = \langle \mathbf{E}_{tot} \rangle + \frac{1}{V} \frac{1}{3\epsilon_0} \langle \mathbf{p} \rangle = \langle \mathbf{E}_{tot} \rangle + \frac{1}{3\epsilon_0} \langle \mathbf{P} \rangle$$

Averaging:

$$\langle \rangle \rightarrow \frac{1}{V} \int d^3r$$

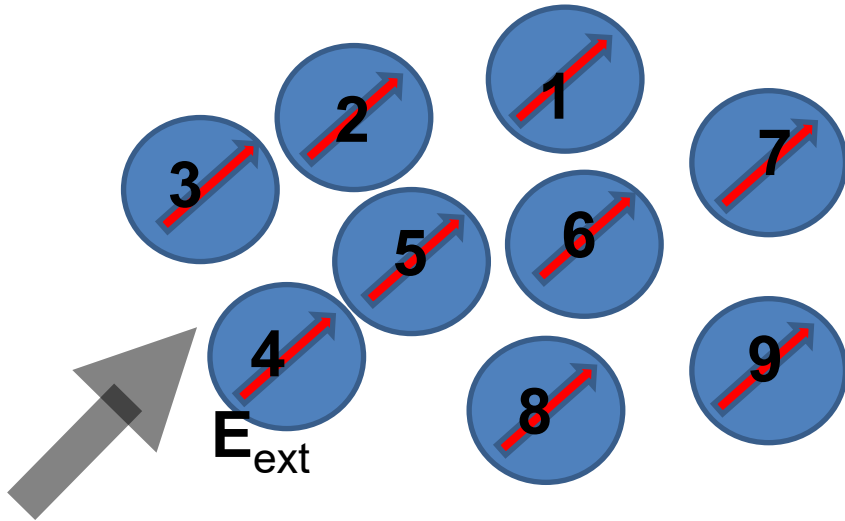
Field due to collection of induced dipoles -- continued

$$\begin{aligned}\mathbf{E}(\mathbf{r})_{site(i)} &= \mathbf{E}(\mathbf{r})_{tot} - \left(\mathbf{E}_i^0(\mathbf{r})\right)_{site(i)} \\ &= \mathbf{E}(\mathbf{r})_{tot} - \frac{1}{4\pi\epsilon_0} \left(\frac{3\mathbf{r}(\mathbf{p}_i \cdot \mathbf{r}) - r^2\mathbf{p}_i}{r^5} - \frac{4\pi}{3}\mathbf{p}_i\delta^3(\mathbf{r} - \mathbf{r}_i) \right)\end{aligned}$$

$$\langle \mathbf{E}_{site(i)} \rangle = \langle \mathbf{E}_{tot} \rangle - \left\langle \frac{1}{4\pi\epsilon_0} \left(\frac{3\mathbf{r}(\mathbf{p}_i \cdot \mathbf{r}) - r^2\mathbf{p}_i}{r^5} - \frac{4\pi}{3}\mathbf{p}_i\delta^3(\mathbf{r} - \mathbf{r}_i) \right) \right\rangle$$

$$\langle \mathbf{E}_{site(i)} \rangle = \langle \mathbf{E}_{tot} \rangle + \frac{1}{V} \frac{1}{3\epsilon_0} \langle \mathbf{p} \rangle = \langle \mathbf{E}_{tot} \rangle + \frac{1}{3\epsilon_0} \langle \mathbf{P} \rangle$$

Field due to collection of induced dipoles -- continued



$$\langle \mathbf{E}_{\text{site}(i)} \rangle = \langle \mathbf{E}_{\text{tot}} \rangle + \frac{1}{3\epsilon_0} \langle \mathbf{P} \rangle$$

$$\langle \mathbf{p} \rangle = \epsilon_0 \gamma_{\text{mol}} \langle \mathbf{E}_{\text{site}} \rangle$$

$$\langle \mathbf{P} \rangle = \frac{1}{V} \langle \mathbf{p} \rangle = \frac{\epsilon_0 \gamma_{\text{mol}}}{V} \left(\langle \mathbf{E}_{\text{tot}} \rangle + \frac{1}{3\epsilon_0} \langle \mathbf{P} \rangle \right)$$

$$\langle \mathbf{P} \rangle = \frac{\epsilon_0 \gamma_{\text{mol}}}{V} \frac{\langle \mathbf{E}_{\text{tot}} \rangle}{1 - \frac{\gamma_{\text{mol}}}{3V}} = \epsilon_0 \chi_e \langle \mathbf{E}_{\text{tot}} \rangle$$

Claussius-Mossotti equation

$$\chi_e = \frac{\frac{\gamma_{\text{mol}}}{V}}{1 - \frac{\gamma_{\text{mol}}}{3V}} = \frac{\epsilon}{\epsilon_0} - 1 \quad \gamma_{\text{mol}} = 3V \left(\frac{\epsilon / \epsilon_0 - 1}{\epsilon / \epsilon_0 + 2} \right)$$

Example of the Clausius-Mossotti equation –

Pentane (C₅H₁₂) at various densities

Density (g/cm ³)	Mol/m ³	ϵ/ϵ_0	$3V^*(\epsilon/\epsilon_0-1)/(\epsilon/\epsilon_0+2)$
0.613	5.12536E+27	1.82	1.25646E-28
0.701	5.86114E+27	1.96	1.24084E-28
0.796	6.65544E+27	2.12	1.22536E-28
0.865	7.23236E+27	2.24	1.2131E-28
0.907	7.58353E+27	2.33	1.2151E-28

$$\gamma_{\text{mol}} = 1.2 \times 10^{-28} \text{ m}^3 = 0.12 \text{ nm}^3$$

Re-examination of electrostatic energy in dielectric media

$$W = \frac{1}{2} \int d^3r \rho_{mono}(\mathbf{r}) \Phi(\mathbf{r})$$

In terms of displacement field:

$$\nabla \cdot \mathbf{D} = \rho_{mono}(\mathbf{r})$$

$$\begin{aligned} W &= \frac{1}{2} \int d^3r \nabla \cdot \mathbf{D} \Phi(\mathbf{r}) = \frac{1}{2} \int d^3r \nabla \cdot (\mathbf{D}(\mathbf{r}) \Phi(\mathbf{r})) - \frac{1}{2} \int d^3r \mathbf{D}(\mathbf{r}) \cdot \nabla \Phi(\mathbf{r}) \\ &= 0 + \frac{1}{2} \int d^3r \mathbf{D}(\mathbf{r}) \cdot \mathbf{E}(\mathbf{r}) \end{aligned}$$

$$W = \frac{1}{2} \int d^3r \mathbf{D}(\mathbf{r}) \cdot \mathbf{E}(\mathbf{r})$$

Comment on the “Modern Theory of Polarization”

Some references:

- R. D.King-Smith and D. Vanderbilt, Phys. Rev. B 47, 1651 (1993)
- R. Resta, Rev. Mod. Physics **66**, 699 (1994)
- R. Resta, J. Phys. Condens. Matter 23, 123201 (2010)
- N. A. Spaldin, J. Solid State Chem. **195**, 2 (2012)

Basic equations :

$$\epsilon_0 \nabla \cdot \mathbf{E} = \rho_{tot} = \rho_{bound} + \rho_{mono}$$

$$\nabla \cdot \mathbf{P} = \rho_{bound}$$

$$\nabla \cdot \mathbf{D} = \rho_{mono}$$

$$\epsilon_0 \mathbf{E} = \mathbf{D} + \mathbf{P}$$

Note: In general \mathbf{P} is highly dependent on the boundary values; often it is more convenient/meaningful to calculate $\Delta\mathbf{P}$.

Comment on the “Modern Theory of Polarization”

-- continued

$$\nabla \cdot \Delta \mathbf{P} = \Delta \rho_{bound} = \Delta \rho_{bound}^{nuclear} + \Delta \rho_{bound}^{electronic}$$

$$\Delta \mathbf{P}^{electronic} = -\frac{e}{V_{crystal}} \sum_n \langle w_{n0} | \mathbf{r} | w_{n0} \rangle$$

Note: The concept of the polarization of a periodic solid is not unique:

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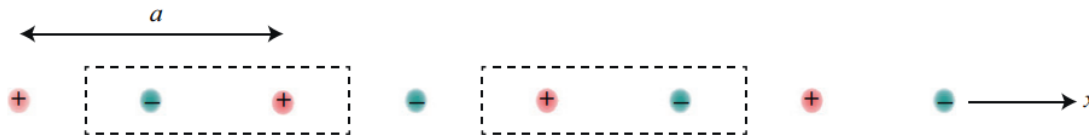
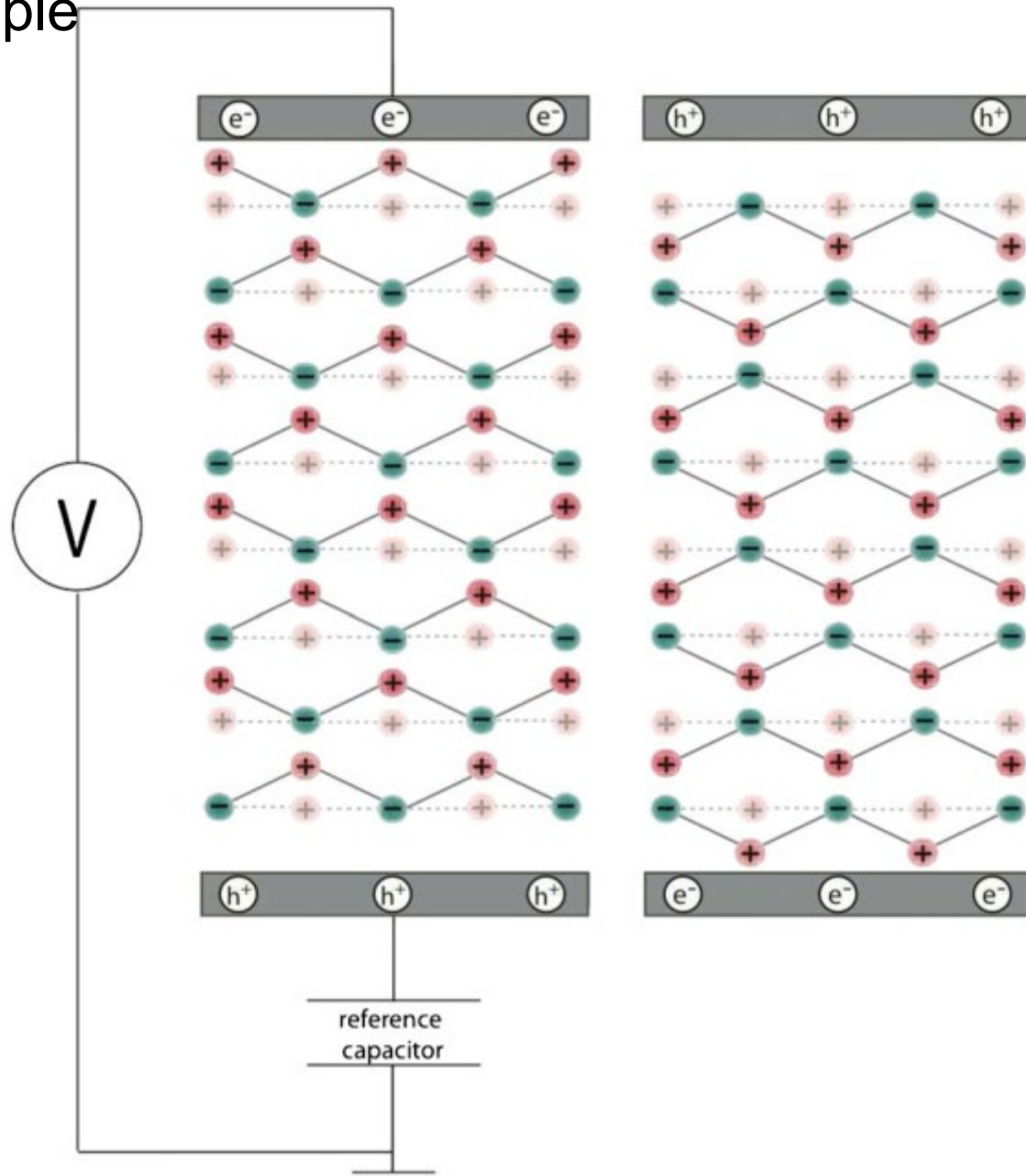


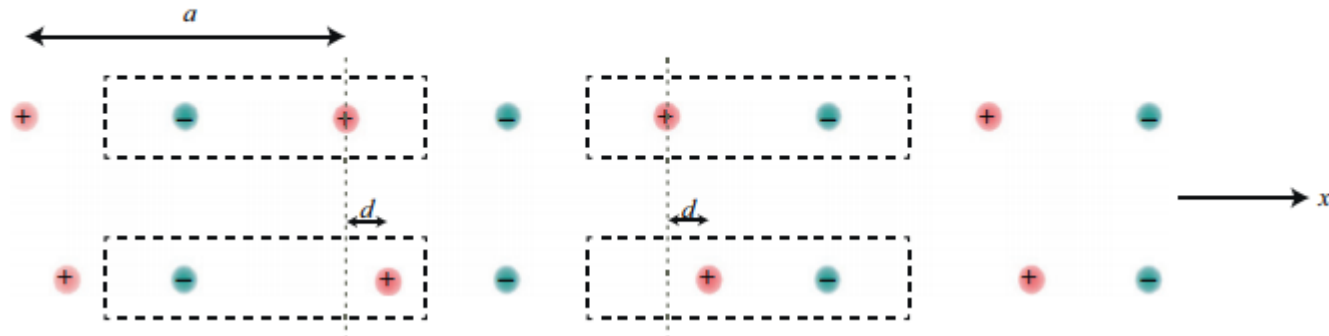
Fig. 1. One-dimensional chain of alternating anions and cations, spaced a distance $a/2$ apart, where a is the lattice constant. The dashed lines indicate two representative unit cells which are used in the text for calculation of the polarization.

ΔP example

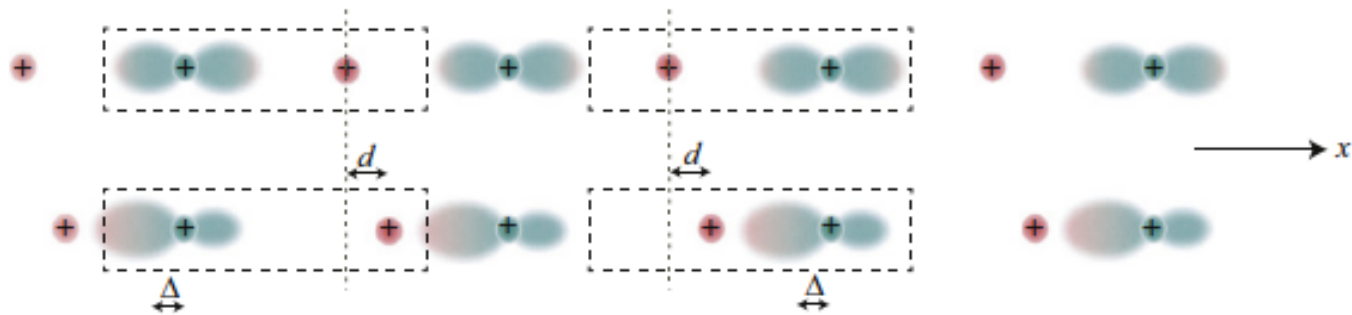


ΔP example -- linear visualization

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Effects on the electronic distribution



Na Cl