PHY 712 Electrodynamics
10-10:50 AM MWF Olin 103

Notes for Lecture 11 --

Complete reading Chapter 4 (Sec. 4.5-4.7 in JDJ)

A. Microscopic ←→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 2024

(Preliminary schedule -- subject to frequent adjustment.)

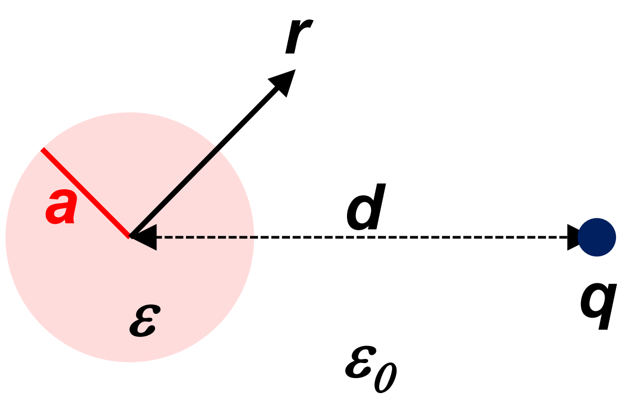
	Lecture date	JDJ Reading	Topic	HW	Due date
1	Wed: 01/17/2024	Chap. 1 & Appen.	Introduction, units and Poisson equation	#1	01/19/2024
2	Fri: 01/19/2024	Chap. 1	Electrostatic energy calculations	#2	01/29/2024
3	Mon: 01/22/2024	Chap. 1	Electrostatic energy calculations	#3	01/29/2024
4	Wed: 01/24/2024	Chap. 1 & 2	Electrostatic potentials and fields	#4	01/29/2024
5	Fri: 01/26/2024	Chap. 1 - 3	Poisson's equation in 2 and 3 dimensions	#5	01/29/2024
6	Mon: 01/29/2024	Chap. 1 - 3	Brief introduction to numerical methods	#6	02/05/2024
7	Wed: 01/31/2024	Chap. 2 & 3	Image charge constructions	#7	02/05/2024
8	Fri: 02/2/2024	Chap. 2 & 3	Poisson equation in cylindrical geometries		
9	Mon: 02/05/2024	Chap. 3 & 4	Spherical geometry and multipole moments	#8	02/12/2024
10	Wed: 02/07/2024	Chap. 4	Dipoles and Dielectrics	#9	02/12/2024
11	Fri: 02/09/2024	Chap. 4	Dipoles and Dielectrics	#10	02/12/2024
12	Mon: 02/12/2024	Chap. 5	Magnetostatics		

PHY 712 -- Assignment #10

Assigned: 2/9/2024 Due: 2/12/2024

Finish reading Chapter 4 in **Jackson** .

1. Work problem 4.9(a) in **Jackson**. Hint: It may be convenient to use a coordinate system with the origin at the center of the dielectric sphere. Also, you may benefit from considering the case where $\varepsilon/\varepsilon_0=1$ to check that your expression makes sense.



Note that for $r < d$:

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

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:

$$\Phi(\mathbf{r}) = \frac{1}{4\pi\varepsilon_0}\left(\frac{\mathbf{p}\cdot\mathbf{r}}{r^3}\right)$$

Electrostatic field from single dipole:

$$\mathbf{E}(\mathbf{r}) = \frac{1}{4\pi\varepsilon_0}\left(\frac{3\mathbf{r}\ (\mathbf{p}\cdot\mathbf{r}) - r^2\mathbf{p}}{r^5} - \frac{4\pi}{3}\mathbf{p}\delta^3(\mathbf{r})\right)$$

(Assuming that p is located at the origin.)

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: $\mathbf{D}(\mathbf{r}) \equiv \varepsilon_0 \mathbf{E}(\mathbf{r}) + \mathbf{P}(\mathbf{r})$

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

Review continued

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

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

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

$\varepsilon = \varepsilon_0 (1 + \chi_e)$ represents the dielectric function of the material

Boundary value problems in dielectric materials

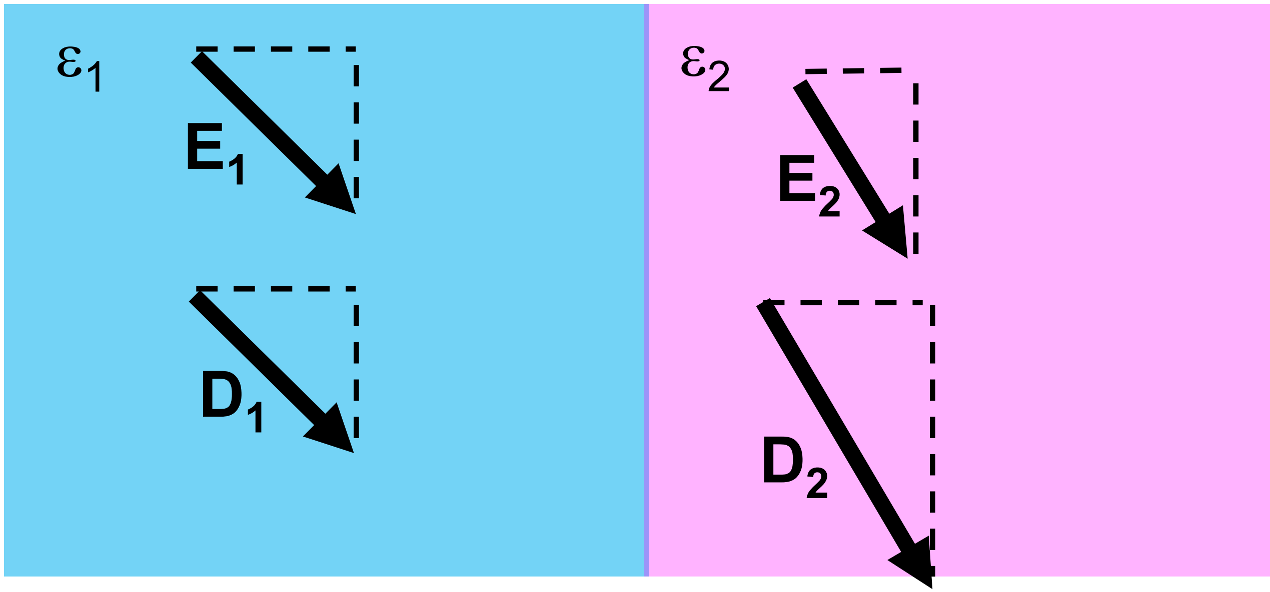
For $\rho_{\text{mono}}(\mathbf{r}) = 0$

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

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

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

Boundary value problems in the presence of dielectrics – example:



For $\dfrac{\varepsilon_2}{\varepsilon_1} = 2$

Specifically,

$\varepsilon_2 = 2\varepsilon_0$

$\varepsilon_1 = \varepsilon_0$

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

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

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

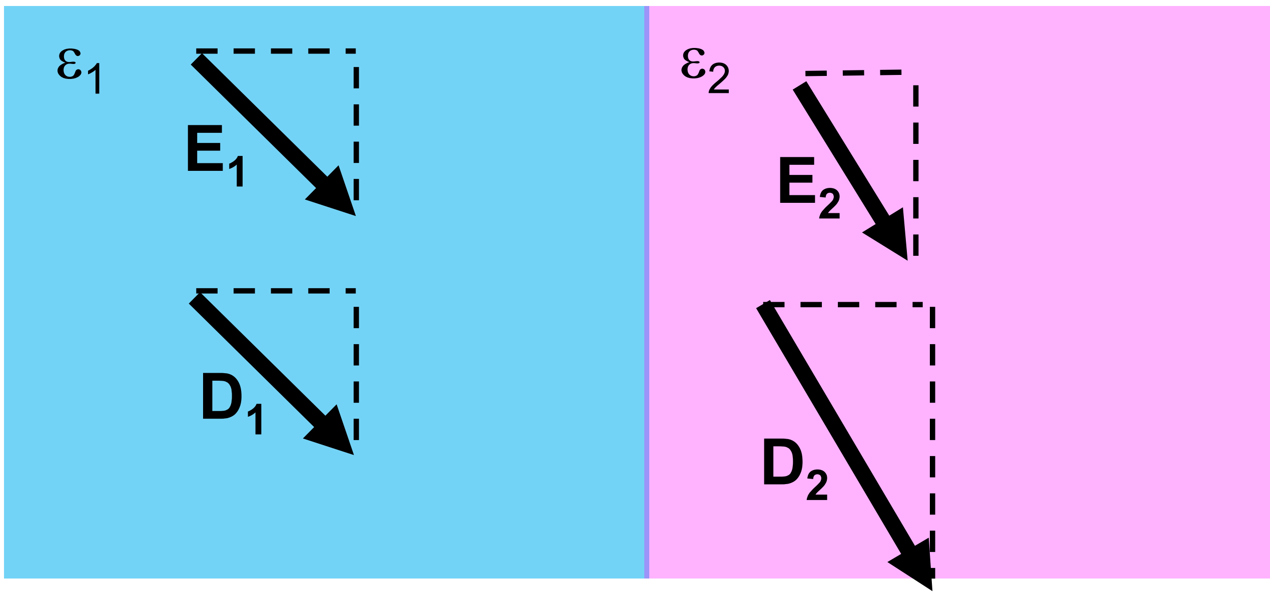
For isotropic dielectrics:

$$D_{1n} = D_{2n} \qquad \varepsilon_1 E_{1n} = \varepsilon_2 E_{2n}$$

$$E_{1t} = E_{2t} \qquad \frac{D_{1t}}{\varepsilon_1} = \frac{D_{2t}}{\varepsilon_2}$$

More details

$$\mathbf{D}_1 = \varepsilon_1 \mathbf{E}_1 \qquad \mathbf{D}_2 = \varepsilon_2 \mathbf{E}_2$$



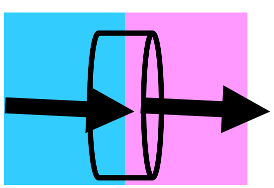
For $\frac{\varepsilon_2}{\varepsilon_1} = 2$

Specifically,

$\varepsilon_2 = 2\varepsilon_0$

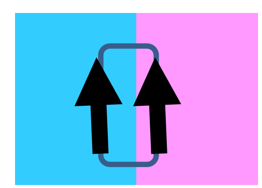
$\varepsilon_1 = \varepsilon_0$

$$\int dV \; \nabla \cdot \mathbf{D} = \int d\mathbf{A} \cdot \mathbf{D} = 0$$



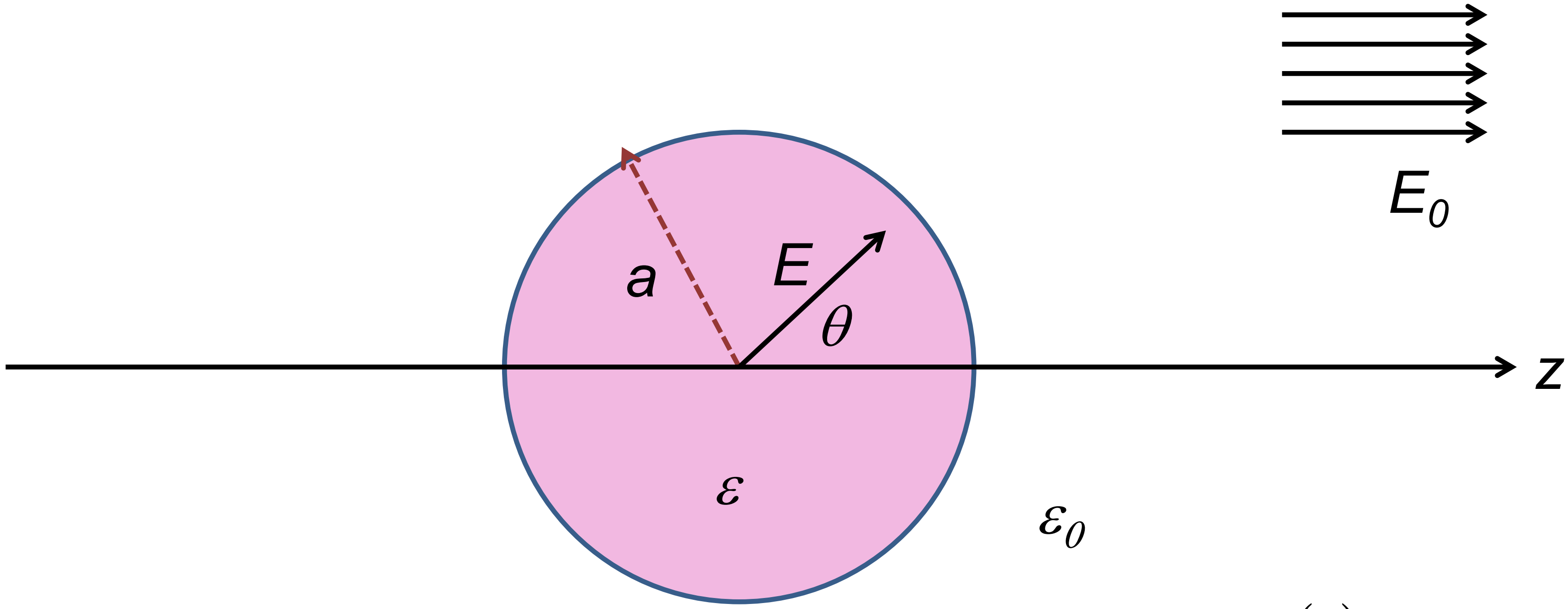
$$D_{1n} = D_{2n}$$

$$\int d\mathbf{A} \; \nabla \times \mathbf{E} = \int d\ell \cdot \mathbf{E} = 0$$



$$E_{1t} = E_{2t}$$

Boundary value problems in the presence of dielectrics – example:



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

For $r \le a \quad \mathbf{D}(\mathbf{r}) = -\varepsilon \nabla \Phi(\mathbf{r})$

For $r > a \quad \mathbf{D}(\mathbf{r}) = -\varepsilon_0 \nabla \Phi(\mathbf{r})$

At $r = a$:

$$\varepsilon \frac{\partial \Phi_<(\mathbf{r})}{\partial r} = \varepsilon_0 \frac{\partial \Phi_>(\mathbf{r})}{\partial r}$$

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

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

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

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

At $r = a$: $\quad \varepsilon \dfrac{\partial \Phi_<(\mathbf{r})}{\partial r} = \varepsilon_0 \dfrac{\partial \Phi_>(\mathbf{r})}{\partial r}$

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

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

Solution -- only $l = 1$ contributes

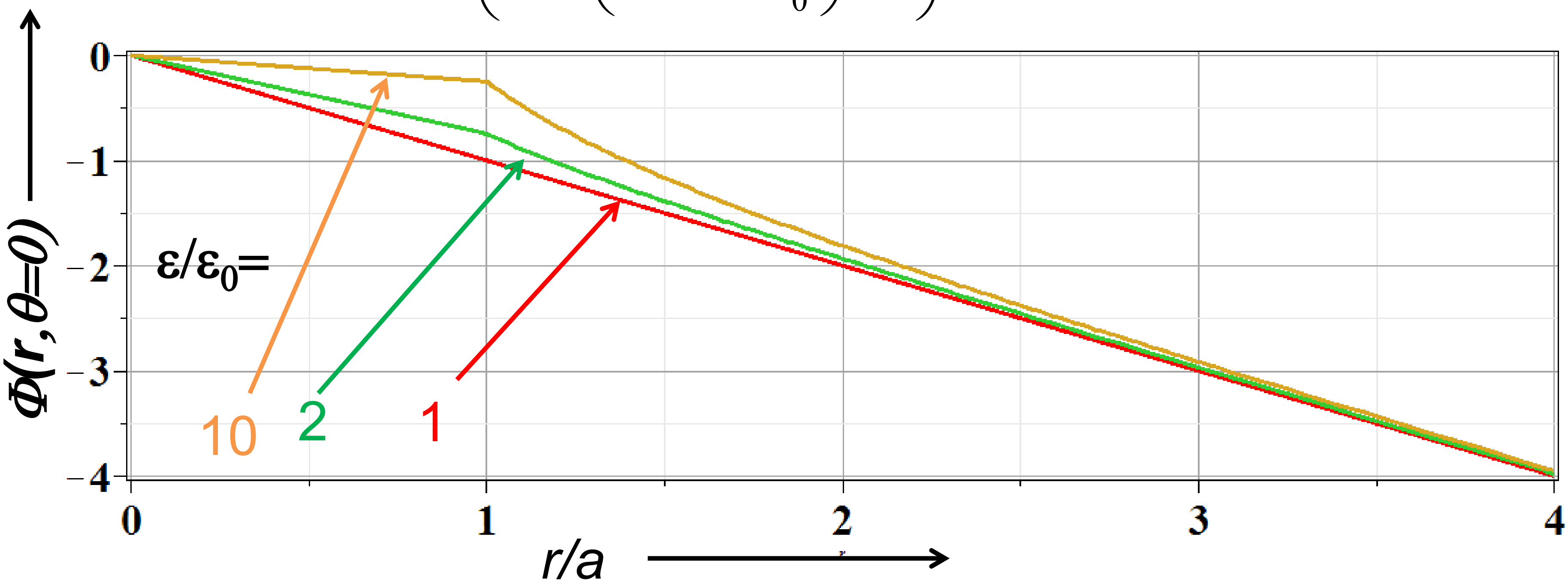
$$B_1 = -E_0$$

$$A_1 = -\left(\frac{3}{2 + \varepsilon / \varepsilon_0} \right) E_0 \qquad C_1 = \left(\frac{\varepsilon / \varepsilon_0 - 1}{2 + \varepsilon / \varepsilon_0} \right) a^3 E_0$$

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

$$\Phi_{<}(\mathbf{r}) = -\left(\frac{3}{2+\varepsilon/\varepsilon_0}\right)E_0\, r\cos\theta$$

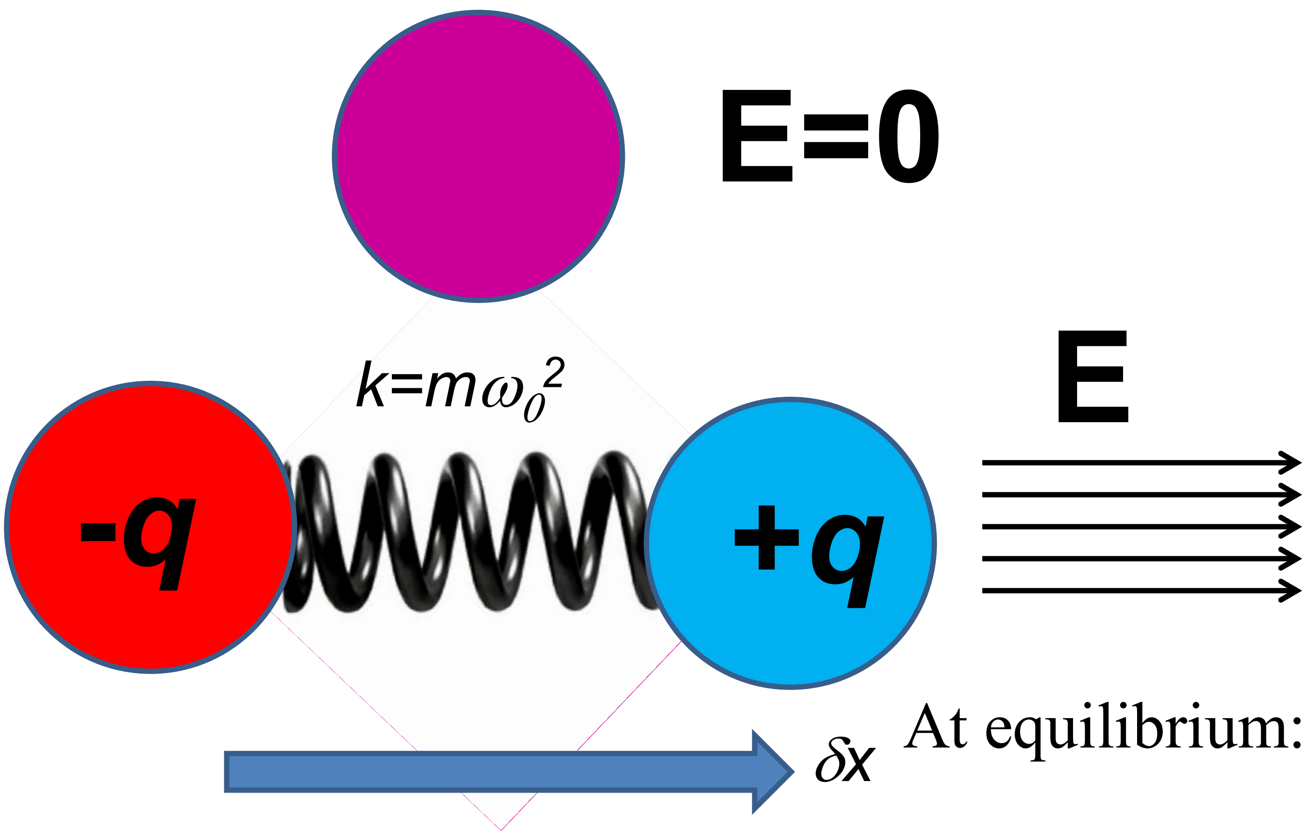
$$\Phi_{>}(\mathbf{r}) = -\left(r - \left(\frac{\varepsilon/\varepsilon_0 - 1}{2+\varepsilon/\varepsilon_0}\right)\frac{a^3}{r^2}\right)E_0\cos\theta$$



Microscopic origin of dipole moments

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

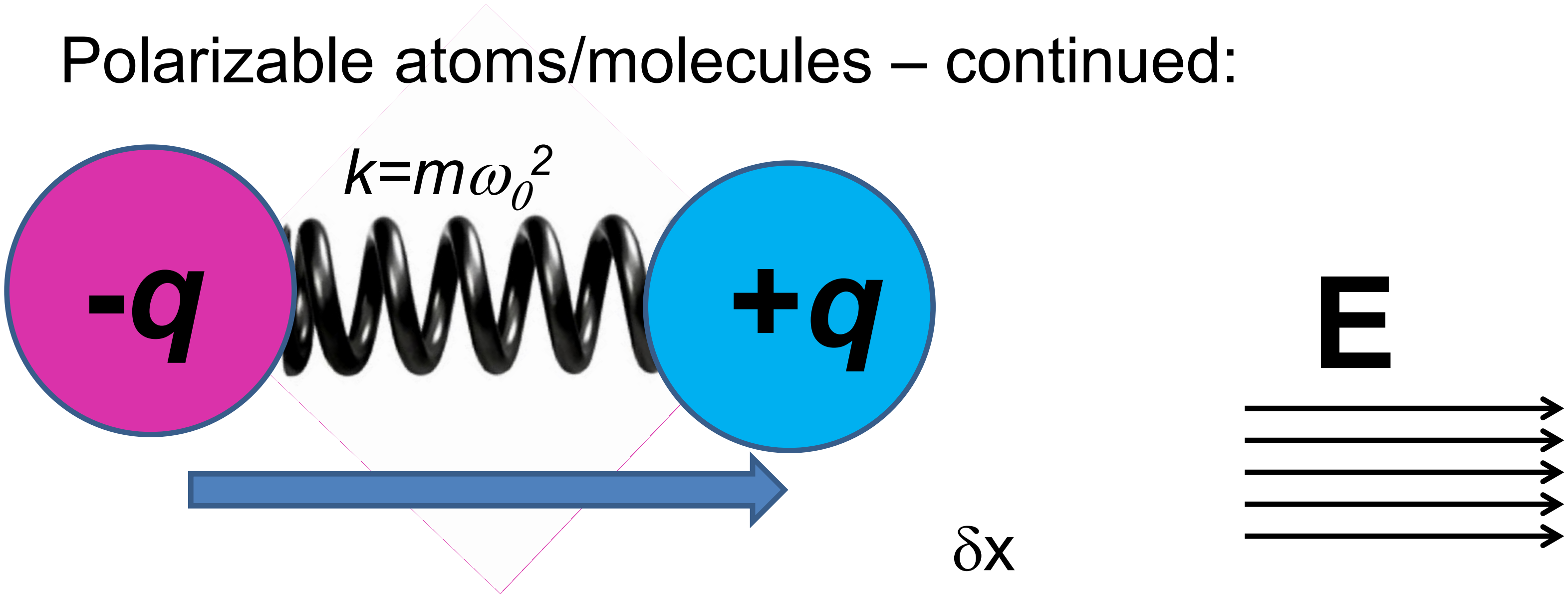
Polarizable systems



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:

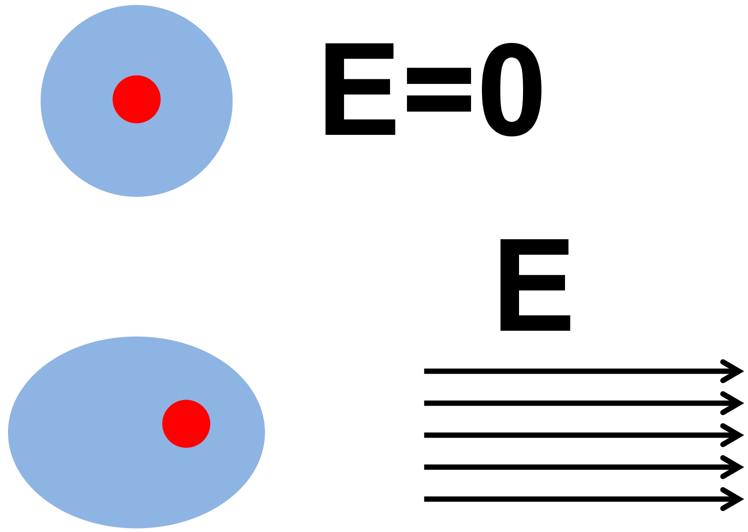
$$q\mathbf{E} - m\omega_0^2 \delta\mathbf{x} = 0$$

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

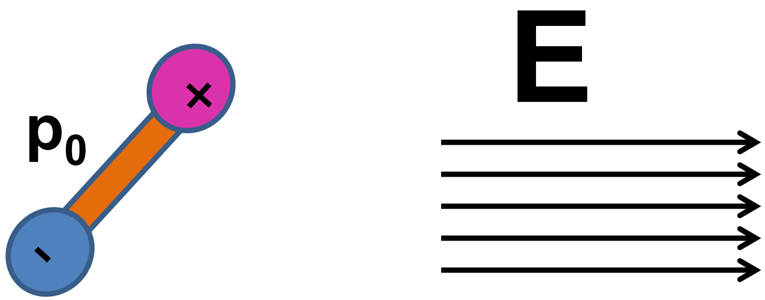
Induced dipole moment:

$$p = q\delta\mathbf{x} \;= \frac{q^2}{m\omega_0^2}\mathbf{E} \equiv \varepsilon_0 \gamma_{mol} \mathbf{E} \quad \Rightarrow \gamma_{mol} = \frac{q^2}{m\omega_0^2 \varepsilon_0}$$

For a neutral atom



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

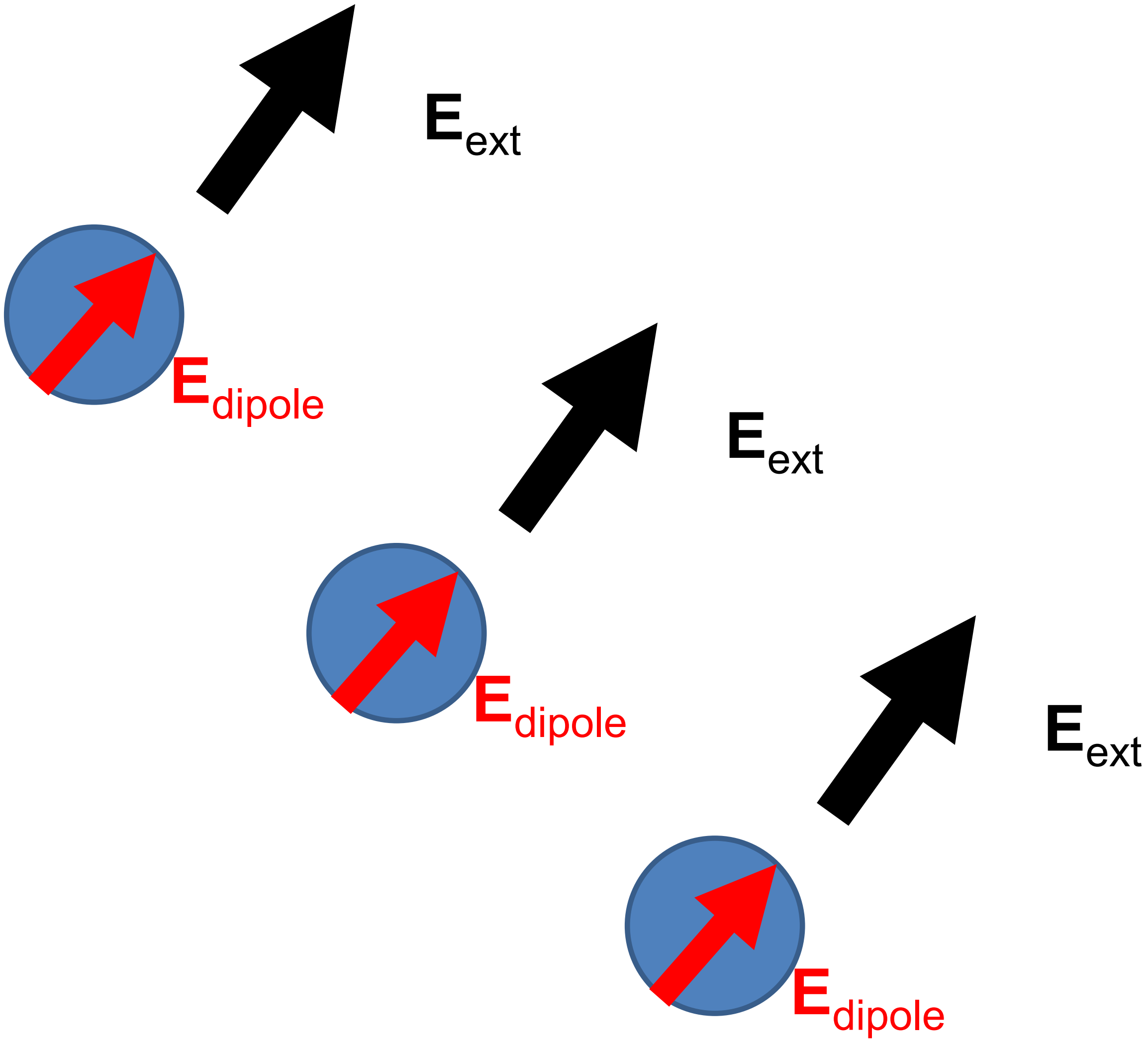


For a freely rotating dipole its average moment in an electric field, estimated assuming a Boltzmann distribution:

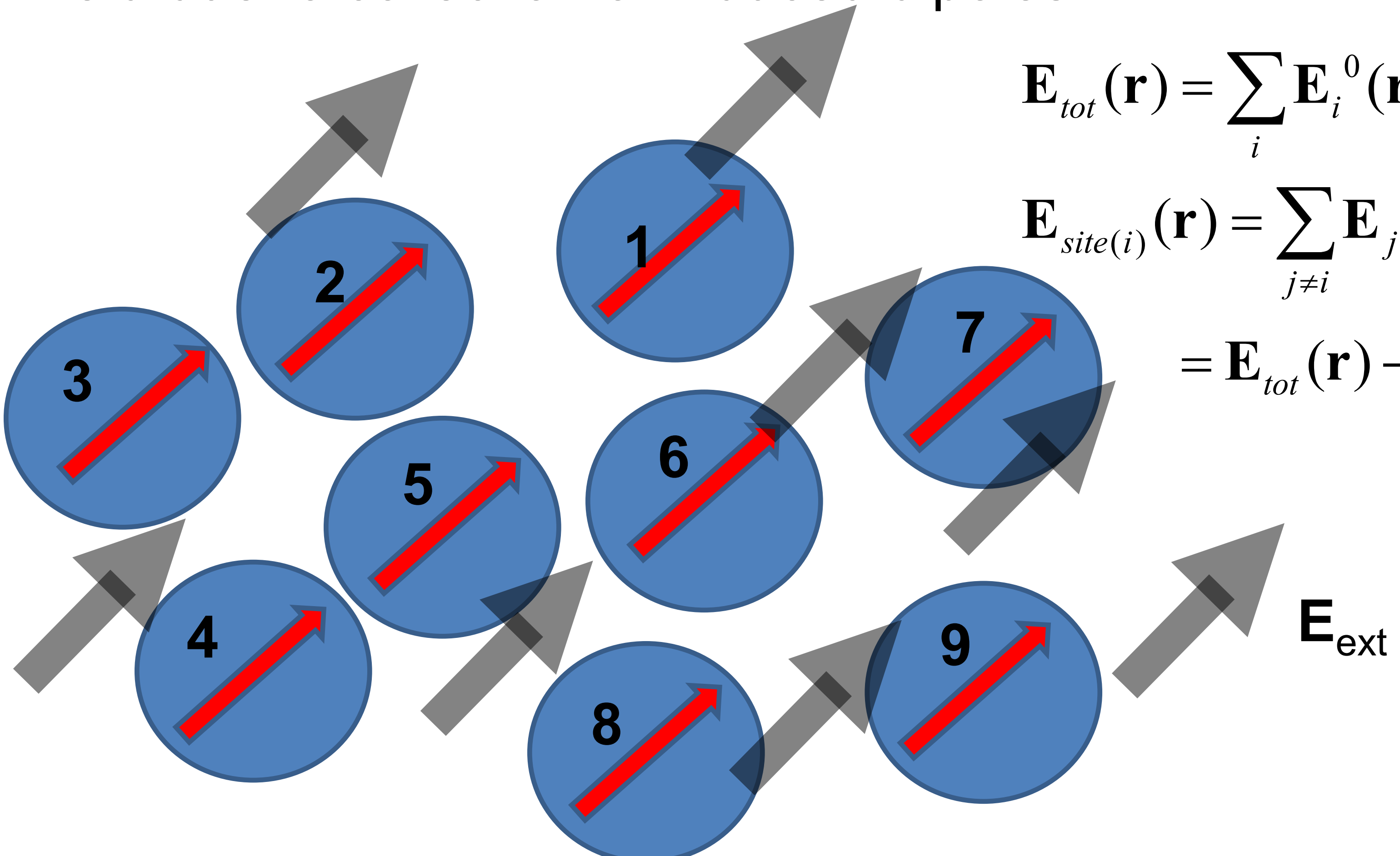
$$\langle \mathbf{p}_{mol} \rangle = \frac{\int d\Omega \;\; p_0 \cos\theta e^{p_0 E \cos\theta / kT}}{\int d\Omega e^{p_0 E \cos\theta / kT}} \approx \frac{1}{3}\frac{p_0^2}{kT}\mathbf{E} \text{ for } \frac{p_0 E}{kT} \ll 1$$

$$\langle \mathbf{p}_{mol} \rangle \approx \frac{1}{3}\frac{p_0^2}{kT}\mathbf{E} \equiv \varepsilon_0 \gamma_{mol} \mathbf{E} \qquad \Rightarrow \gamma_{mol} \approx \frac{1}{3}\frac{p_0^2}{kT\varepsilon_0}$$

Now consider a superposition of dipoles in an electric field



Field due to collection of induced dipoles



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

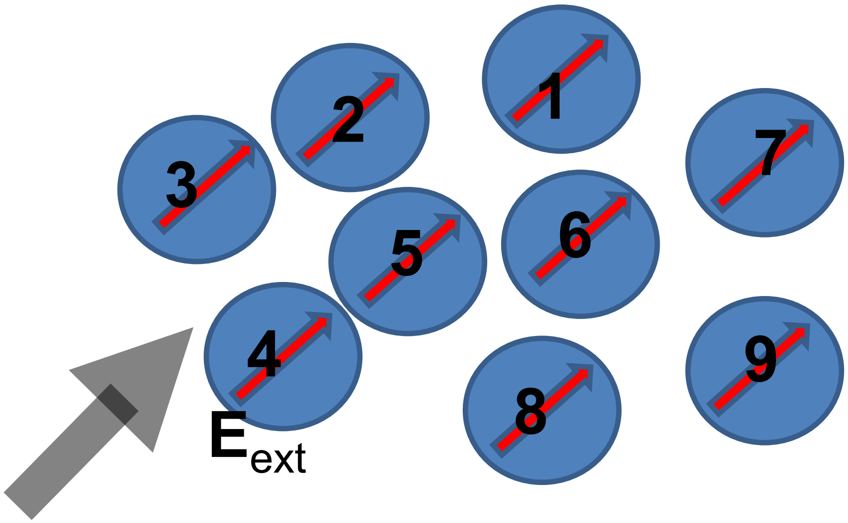
$$\mathbf{E}_{site(i)}(\mathbf{r}) = \sum_{j\neq i} \mathbf{E}_j{}^0(\mathbf{r}) + \mathbf{E}_{ext}(\mathbf{r})$$

$$= \mathbf{E}_{tot}(\mathbf{r}) - \mathbf{E}_i{}^0(\mathbf{r})$$

Electrostatic field from single dipole:

$$\mathbf{E}_i^0(\mathbf{r}) = \frac{1}{4\pi\varepsilon_0}\left(\frac{3(\mathbf{r}-\mathbf{r}_i)(\mathbf{p}_i\cdot(\mathbf{r}-\mathbf{r}_i)) - |\mathbf{r}-\mathbf{r}_i|^2\mathbf{p}_i}{|\mathbf{r}-\mathbf{r}_i|^5} - \frac{4\pi}{3}\mathbf{p}_i\delta^3(\mathbf{r}-\mathbf{r}_i)\right)$$

Field due to collection of induced dipoles -- continued



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

$$\mathbf{E}_{site(i)}(\mathbf{r}) = \sum_{j\neq i} \mathbf{E}_j^{\,0}(\mathbf{r}) + \mathbf{E}_{ext}(\mathbf{r})$$

$$= \mathbf{E}_{tot}(\mathbf{r}) - \mathbf{E}_i^{\,0}(\mathbf{r})$$

$$\mathbf{E}(\mathbf{r})_{tot} = \frac{1}{4\pi\varepsilon_0}\sum_i \left(\frac{3(\mathbf{r}-\mathbf{r}_i)\ (\mathbf{p}_i\cdot(\mathbf{r}-\mathbf{r}_i)) - |\mathbf{r}-\mathbf{r}_i|^2\,\mathbf{p}_i}{|\mathbf{r}-\mathbf{r}_i|^5} - \frac{4\pi}{3}\mathbf{p}_i\delta^3(\mathbf{r}-\mathbf{r}_i)\right) + \mathbf{E}_{ext}(\mathbf{r})$$

$$\mathbf{E}(\mathbf{r})_{site(i)} = \frac{1}{4\pi\varepsilon_0}\left(\sum_{j\neq i} \frac{3(\mathbf{r}-\mathbf{r}_j)\ (\mathbf{p}_j\cdot(\mathbf{r}-\mathbf{r}_j)) - |\mathbf{r}-\mathbf{r}_j|^2\,\mathbf{p}_j}{|\mathbf{r}-\mathbf{r}_j|^5}\right) + \mathbf{E}_{ext}(\mathbf{r}) = \mathbf{E}(\mathbf{r})_{tot} - \left(\mathbf{E}_i^0(\mathbf{r})\right)_{site(i)}$$

$$\langle \mathbf{E}_{site(i)} \rangle = \langle \mathbf{E}_{tot} \rangle + \frac{1}{V}\frac{1}{3\varepsilon_0}\langle \mathbf{p} \rangle = \langle \mathbf{E}_{tot} \rangle + \frac{1}{3\varepsilon_0}\langle \mathbf{P} \rangle$$

Averaging:

$$\langle\ \rangle \to \frac{1}{V}\int_V d^3r$$

Field due to collection of induced dipoles -- continued

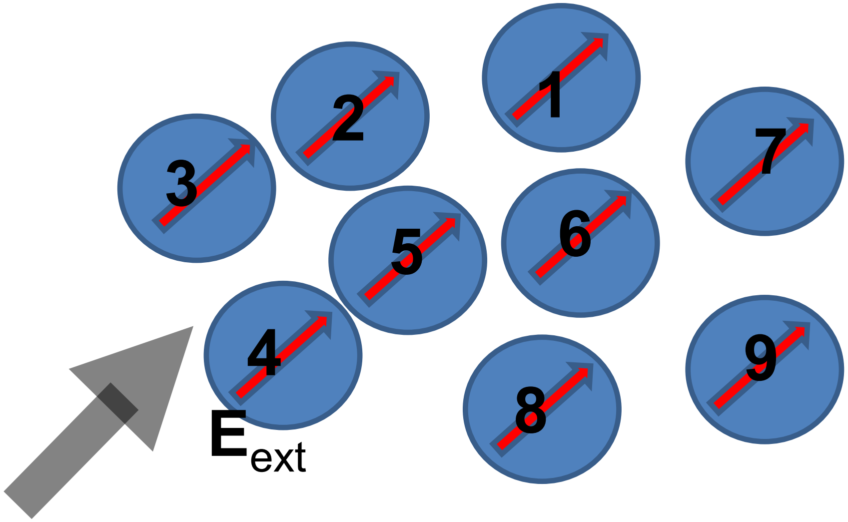
$$\mathbf{E}(\mathbf{r})_{site(i)} = \mathbf{E}(\mathbf{r})_{tot} - \left(\mathbf{E}_i^0(\mathbf{r})\right)_{site(i)}$$

$$= \mathbf{E}(\mathbf{r})_{tot} - \frac{1}{4\pi\varepsilon_0}\left(\frac{3(\mathbf{r}-\mathbf{r}_i)\left(\mathbf{p}_i\cdot(\mathbf{r}-\mathbf{r}_i)\right) - |\mathbf{r}-\mathbf{r}_i|^2\,\mathbf{p}_i}{|\mathbf{r}-\mathbf{r}_i|^5} - \frac{4\pi}{3}\mathbf{p}_i\delta^3(\mathbf{r}-\mathbf{r}_i)\right)$$

$$\left\langle \mathbf{E}_{site(i)} \right\rangle = \left\langle \mathbf{E}_{tot} \right\rangle - \left\langle \frac{1}{4\pi\varepsilon_0}\left(\frac{3(\mathbf{r}-\mathbf{r}_i)\left(\mathbf{p}_i\cdot(\mathbf{r}-\mathbf{r}_i)\right) - |\mathbf{r}-\mathbf{r}_i|^2\,\mathbf{p}_i}{|\mathbf{r}-\mathbf{r}_i|^5} - \frac{4\pi}{3}\mathbf{p}_i\delta^3(\mathbf{r}-\mathbf{r}_i)\right)\right\rangle$$

$$\left\langle \mathbf{E}_{site(i)} \right\rangle = \left\langle \mathbf{E}_{tot} \right\rangle + \frac{1}{V}\frac{1}{3\varepsilon_0}\left\langle \mathbf{p} \right\rangle = \left\langle \mathbf{E}_{tot} \right\rangle + \frac{1}{3\varepsilon_0}\left\langle \mathbf{P} \right\rangle$$

Field due to collection of induced dipoles -- continued



$$\langle \mathbf{E}_{site(i)} \rangle = \langle \mathbf{E}_{tot} \rangle + \frac{1}{3\varepsilon_0} \langle \mathbf{P} \rangle$$

$$\langle \mathbf{p} \rangle = \varepsilon_0 \gamma_{mol} \langle \mathbf{E}_{site} \rangle$$

$$\langle \mathbf{P} \rangle = \frac{1}{V} \langle \mathbf{p} \rangle = \frac{\varepsilon_0 \gamma_{mol}}{V} \left(\langle \mathbf{E}_{tot} \rangle + \frac{1}{3\varepsilon_0} \langle \mathbf{P} \rangle \right)$$

$$\langle \mathbf{P} \rangle = \frac{\varepsilon_0 \gamma_{mol}}{V} \frac{\langle \mathbf{E}_{tot} \rangle}{1 - \frac{\gamma_{mol}}{3V}} = \varepsilon_0 \chi_e \langle \mathbf{E}_{tot} \rangle$$

Claussius-Mossotti equation

$$\chi_e = \frac{\frac{\gamma_{mol}}{V}}{1 - \frac{\gamma_{mol}}{3V}} = \frac{\varepsilon}{\varepsilon_0} - 1 \qquad \gamma_{mol} = 3V \left(\frac{\varepsilon / \varepsilon_0 - 1}{\varepsilon / \varepsilon_0 + 2} \right)$$

Example of the Clausius-Mossotti equation –

Pentane (C_5H_{12}) at various densities

Density (g/cm3)	Mol/m3	ε/ε0	3V*(ε/ε0-1)/(ε/ε0+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

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

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:

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

$$W = \frac{1}{2}\int d^3r \ \nabla \cdot \mathbf{D} \ \Phi(\mathbf{r}) = \frac{1}{2}\int d^3r \ \nabla \cdot \left(\mathbf{D}(\mathbf{r}) \ \Phi(\mathbf{r})\right) - \frac{1}{2}\int d^3r \ \mathbf{D}(\mathbf{r}) \cdot \nabla\Phi(\mathbf{r})$$

$$= \qquad 0 \qquad + \ \frac{1}{2}\int d^3r \ \mathbf{D}(\mathbf{r}) \cdot \mathbf{E}(\mathbf{r})$$

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

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:

$$\varepsilon_0 \nabla \cdot \mathbf{E} = \rho_{tot} = \rho_{bound} + \rho_{mono}$$

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

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

$$\varepsilon_0 \mathbf{E} = \mathbf{D} + \mathbf{P}$$

Note: In general **P** is highly dependent on the boundary values; often it is more convenient/meaningful to calculate **ΔP**.

Comment on the "Modern Theory of Polarization" -- continued

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

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

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

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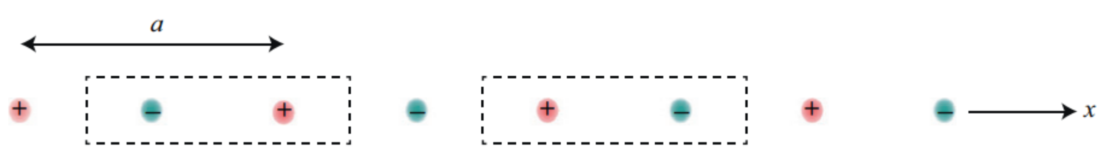
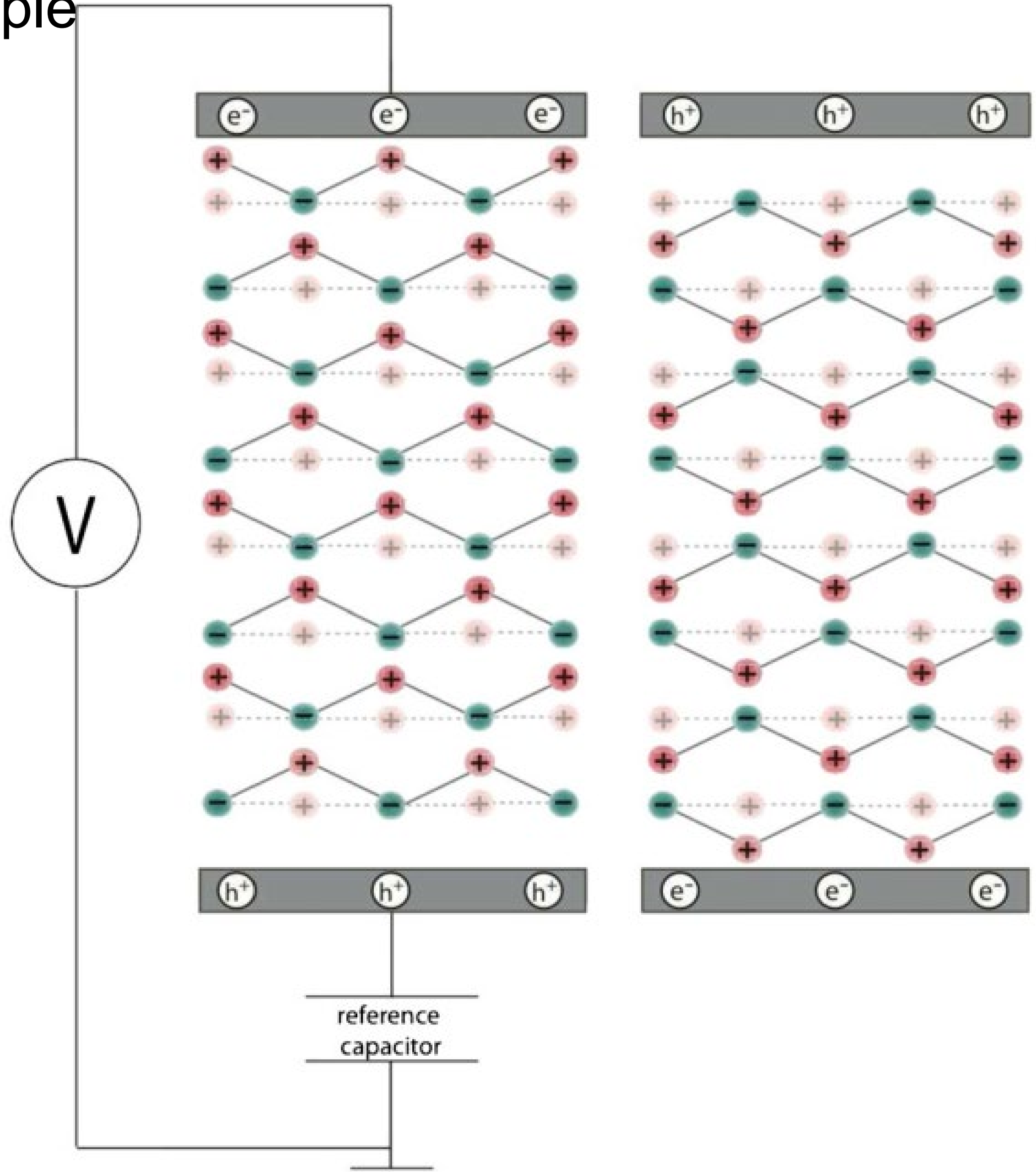


Fig. 1. One-dimensional chain of alternating anions and cations, spaced a distance $a/2$ apart, where a is the lattice constant. The dashed lines indicate two representative unit cells which are used in the text for calculation of the polarization.

ΔP example



ΔP example -- linear visualization

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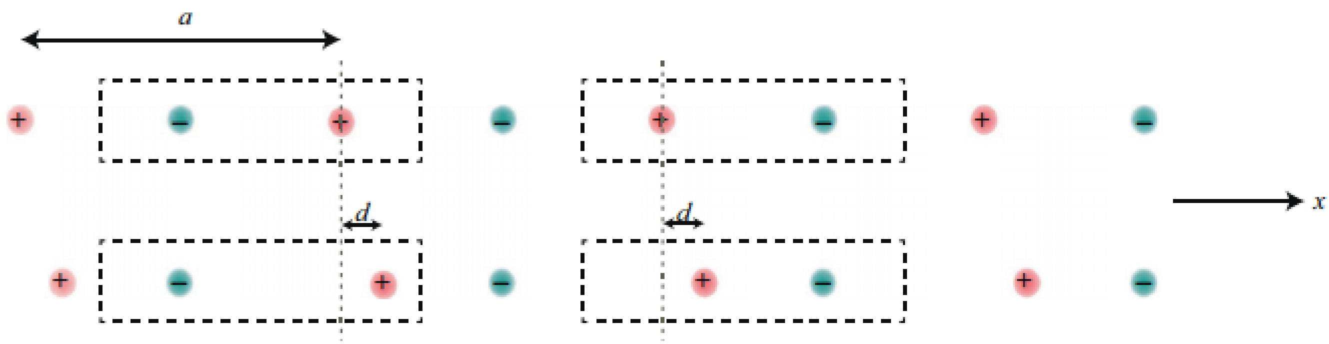
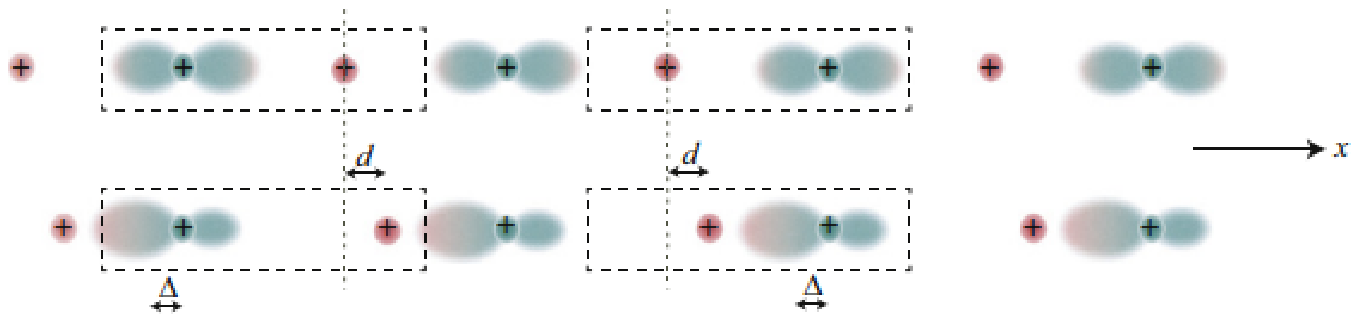


Effects on the electronic distribution



Na Cl

Summary of electrostatics – Chapter 1-4 in **Jackson**
By "statics" we mean that all properties are constant in time

Field equations in differential form:

$$\nabla \cdot \mathbf{E}(\mathbf{r}) = \frac{\rho(\mathbf{r})}{\varepsilon_0}$$

$$\nabla \cdot \mathbf{D}(\mathbf{r}) = \rho_{mono}(\mathbf{r}) \quad \text{where } \mathbf{D}(\mathbf{r}) = \varepsilon_0 \mathbf{E}(\mathbf{r}) + \mathbf{P}(\mathbf{r}) = \varepsilon \mathbf{E}(\mathbf{r})$$

$$\nabla \times \mathbf{E}(\mathbf{r}) = 0$$

Electrostatic potential:

$$\mathbf{E}(\mathbf{r}) = -\nabla \Phi(\mathbf{r}) \qquad \Phi(\mathbf{r}) = -\frac{\rho(\mathbf{r})}{\varepsilon_0}$$