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 functions and susceptibility

B. Clausius-Mossotti equation

C. Electrostatic energy in dielectric media

D. Comment on "modern theory of polarization"

Course schedule for Spring 2025

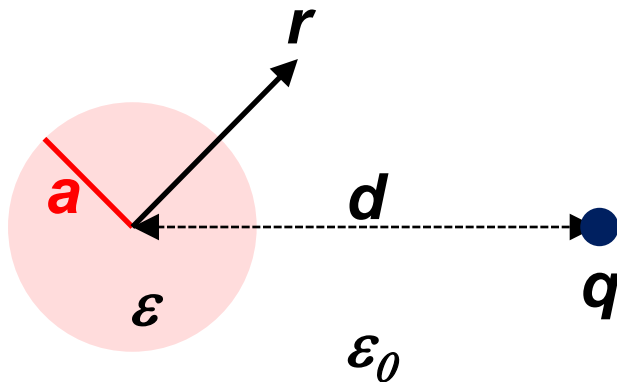## (Preliminary schedule -- subject to frequent adjustment.)

	Lecture date	JDJ Reading	Topic	HW	Due date
1	Mon: 01/13/2025	Chap. 1 & Appen.	Introduction, units and Poisson equation	#1	01/15/2025
2	Wed: 01/15/2025	Chap. 1	Electrostatic energy calculations	#2	01/17/2025
3	Fri: 01/17/2025	Chap. 1	Electrostatic energy calculations	#3	01/22/2025
	Mon: 01/20/2025	No Class	Martin Luther King Jr. Holiday		
4	Wed: 01/22/2025	Chap. 1	Electrostatic potentials and fields	#4	01/24/2025
5	Fri: 01/24/2025	Chap. 1 - 3	Poisson's equation in multiple dimensions		
6	Mon: 01/27/2025	Chap. 1 - 3	Brief introduction to numerical methods	#5	01/29/2025
7	Wed: 01/29/2025	Chap. 2 & 3	Image charge constructions	#6	01/31/2025
8	Fri: 01/31/2025	Chap. 2 & 3	Poisson equation in cylindrical geometries	#7	02/03/2025
9	Mon: 02/03/2025	Chap. 3 & 4	Spherical geometry and multipole moments	#8	02/05/2025
10	Wed: 02/05/2025	Chap. 4	Dipoles and Dielectrics	#9	02/07/2025
11	Fri: 02/07/2025	Chap. 4	Dipoles and Dielectrics	#10	02/10/2025
12	Mon: 02/10/2025	Chap. 5	Magnetostatics		

PHY 712 -- Assignment #10

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 $r < d$:

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

Review -- Focus on dipolar fields:

Dipole moment **p**:

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

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 monopoles and dipoles --

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

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

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

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

It will be convenient to define some new electrostatic fields --

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

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

Electrostatic potential for a single monopole charge q

and a single dipole $\mathbf{p}$:

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

Electrostatic potential for collections of monopole charges q_i

and dipoles $\mathbf{p}_i$:

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

$$\Phi(\mathbf{r}) \quad = \frac{1}{4\pi\varepsilon_0}\left(\int d^3r' \frac{\rho_{mono}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}+\int d^3r'\frac{\mathbf{P}(\mathbf{r}')\cdot(\mathbf{r}-\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|^3}\right)$$

Note: $\int d^3r'\frac{\mathbf{P}(\mathbf{r}')\cdot(\mathbf{r}-\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|^3}=\int d^3r'\ \mathbf{P}(\mathbf{r}')\cdot\nabla'\frac{1}{|\mathbf{r}-\mathbf{r}'|}=-\int d^3r'\frac{\nabla'\cdot\mathbf{P}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$

Coarse grain representation of macroscopic distribution of dipoles -- continued:

Electrostatic potential for collections of monopole charges q_i and dipoles $\mathbf{p}_i$:

$$\Phi(\mathbf{r}) = \frac{1}{4\pi\varepsilon_0}\left(\int d^3r'\frac{\rho_{mono}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} - \int d^3r'\frac{\nabla'\cdot\mathbf{P}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\right)$$

$$-\nabla^2\Phi(\mathbf{r}) = \nabla\cdot\mathbf{E}(\mathbf{r}) = \frac{1}{\varepsilon_0}\left(\rho_{mono}(\mathbf{r}) - \nabla\cdot\mathbf{P}(\mathbf{r})\right)$$

$$\Rightarrow \nabla\cdot\left(\underbrace{\varepsilon_0\mathbf{E}(\mathbf{r}) + \mathbf{P}(\mathbf{r})}\right) = \rho_{mono}(\mathbf{r})$$

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

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

More relationships due to the properties of materials --

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

Note: In practice, some dielectric functions may be dependent on time and/or space.

Boundary value problems in dielectric materials

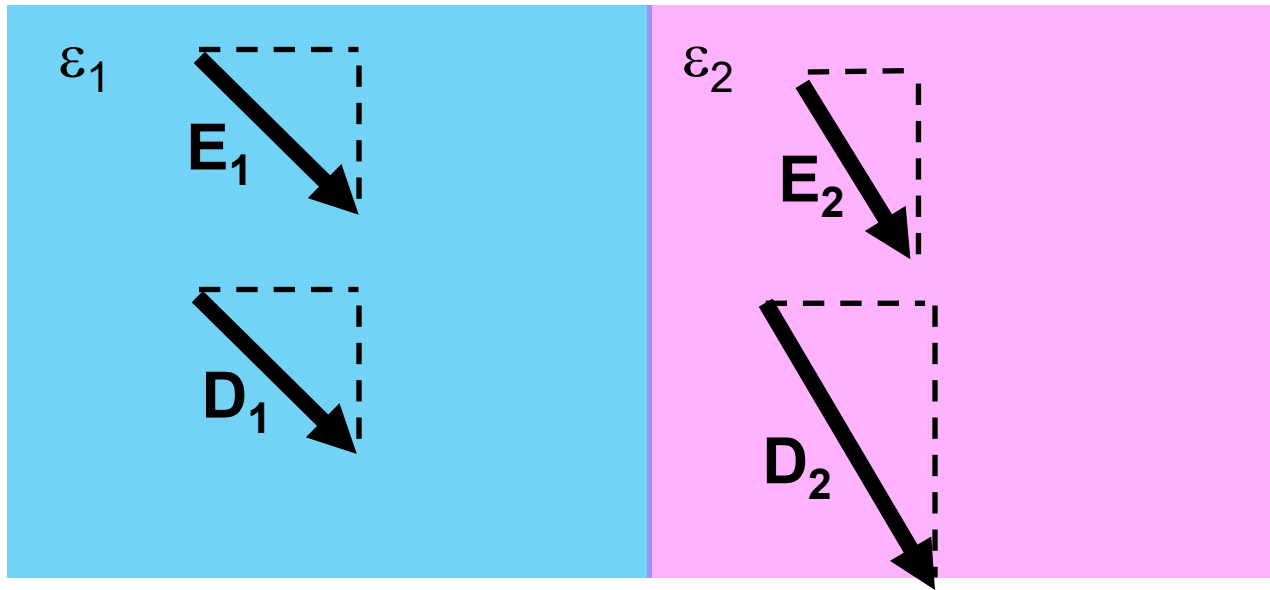For $\rho_{\text{mono}}(\mathbf{r}) = 0$

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

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

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

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

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

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

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

For isotropic dielectrics:

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

More details

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

ε_1

$\mathbf{E_1}$

$\mathbf{D_1}$

ε_2

$\mathbf{E_2}$

$\mathbf{D_2}$

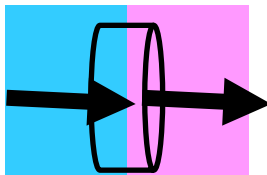For $\dfrac{\varepsilon_2}{\varepsilon_1} = 2$

Specifically,
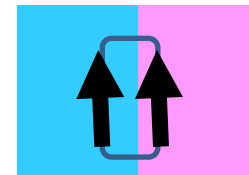
$\varepsilon_2 = 2\varepsilon_0$

$\varepsilon_1 = \varepsilon_0$

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

$$D_{1n} = D_{2n} \qquad\qquad\qquad\qquad E_{1t} = E_{2t}$$

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

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

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

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

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

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

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

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

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

$$\text{For } r \to \infty \quad \Phi_>(\mathbf{r}) = -E_0 r \cos\theta$$
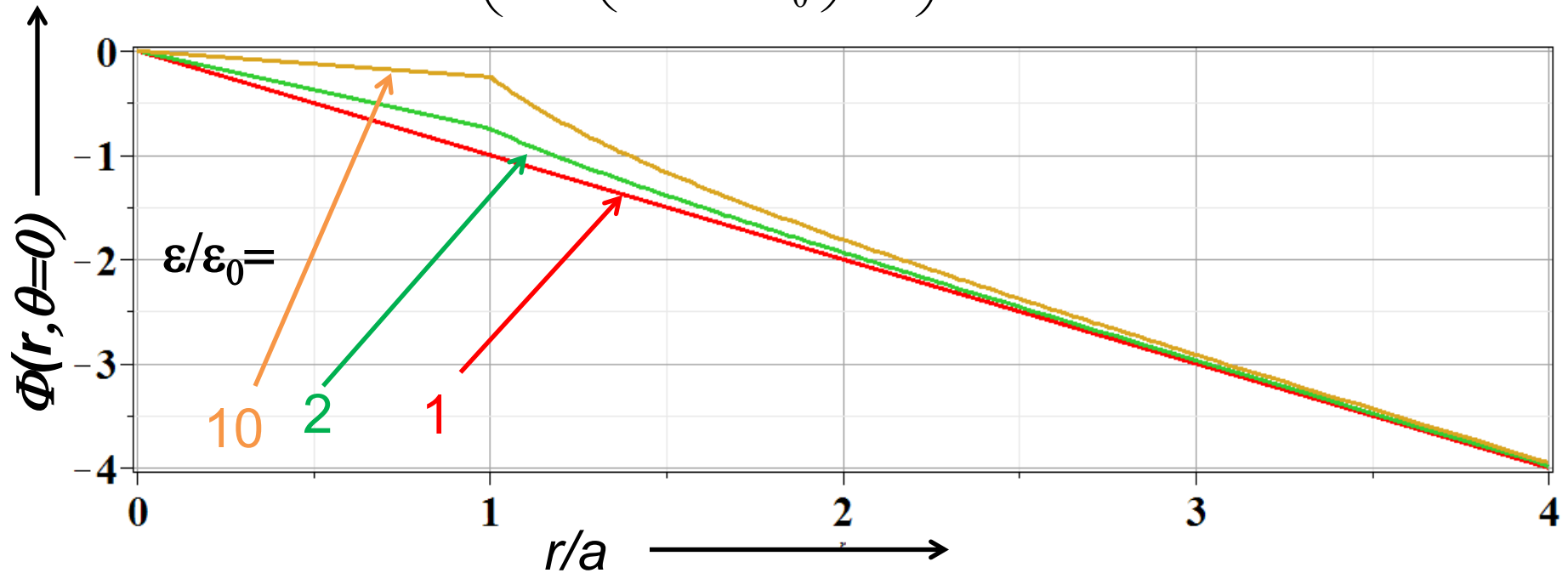
Solution -- only $l = 1$ contributes

$$B_1 = -E_0$$

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

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

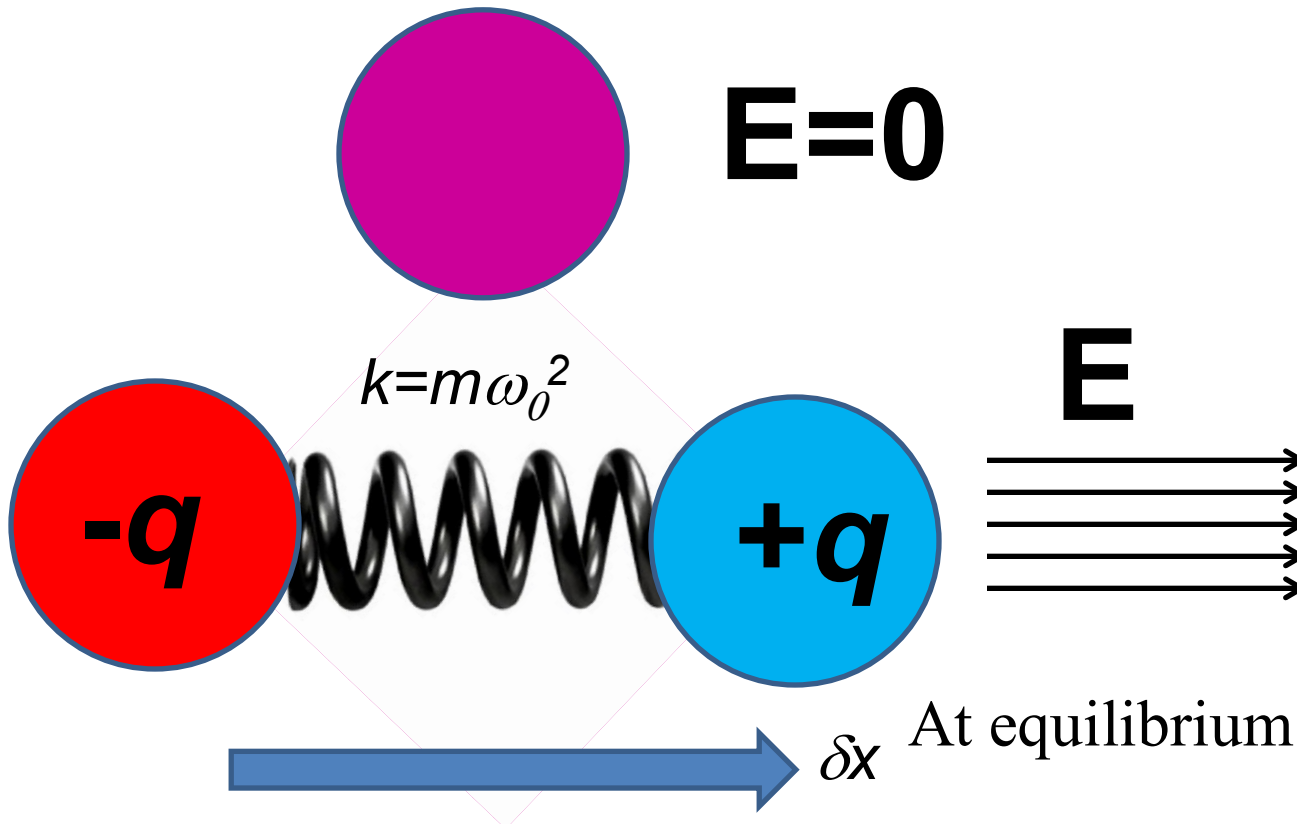$$\Phi_<(\mathbf{r}) = -\left(\frac{3}{2 + \varepsilon / \varepsilon_0}\right) E_0 \, r \cos\theta$$

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

$\varepsilon/\varepsilon_0=$

10   2   1

Microscopic origin of dipole moments
  ➢ Polarizable atoms/molecules
  ➢ Anisotropic charged molecules aligned in random directions

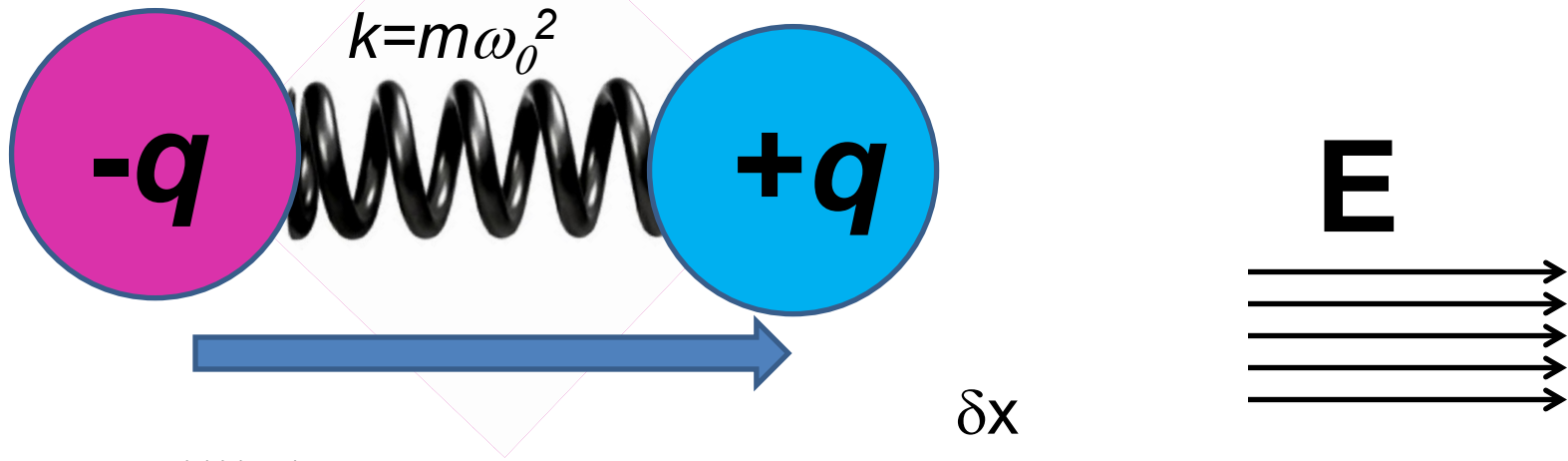Polarizable systems

E=0

$k=m\omega_0^2$

E

-q

+q

δx 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:

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

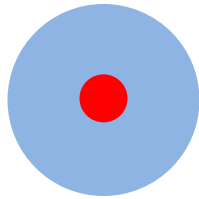$$\delta\mathbf{x} = \frac{q\mathbf{E}}{m\omega_0^2}$$

Induced dipole moment:

$$p = q\delta\mathbf{x} = \frac{q^2}{m\omega_0^2}\mathbf{E} \equiv \varepsilon_0 \gamma_{mol}\mathbf{E}$$
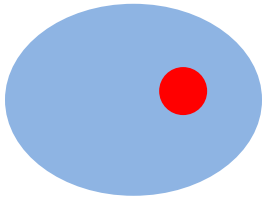
Molecular susceptibility for this model:

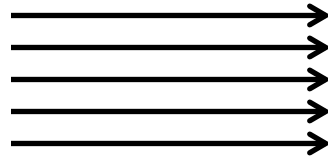$$\Rightarrow \gamma_{mol} = \frac{q^2}{m\omega_0^2 \varepsilon_0}$$
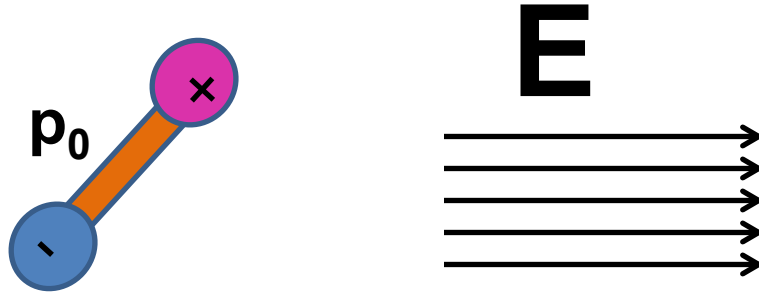
For a neutral atom

E=0

E

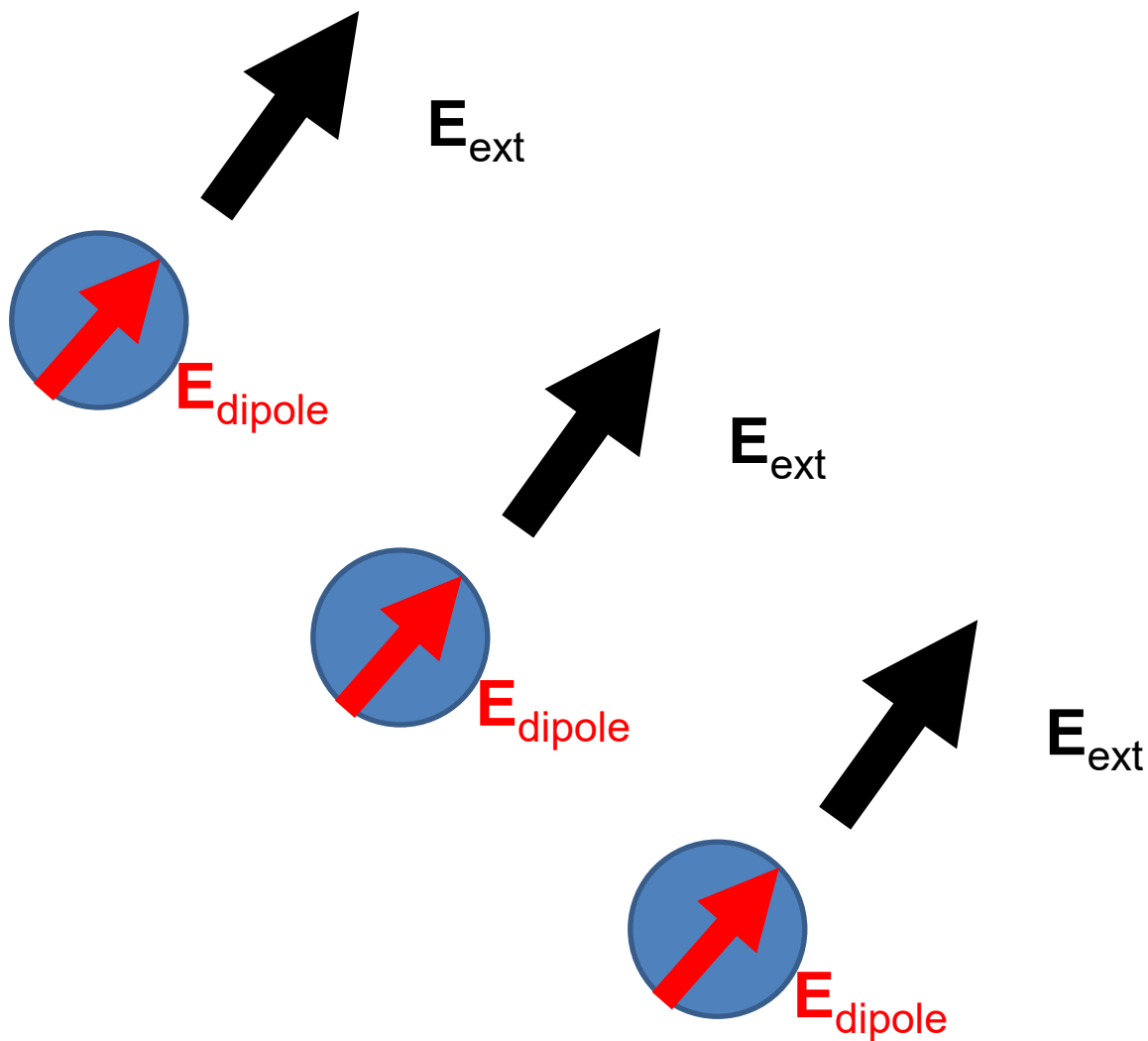Alignment of molecules with permanent dipoles $\mathbf{p}_0$:

E

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

$$\langle \mathbf{p}_{mol} \rangle = \frac{\int d\Omega \; p_0 \cos\theta \, e^{p_0 E \cos\theta / kT}}{\int d\Omega \, e^{p_0 E \cos\theta / kT}} \approx \frac{1}{3}\frac{p_0^2}{kT}\mathbf{E} \text{ for } \frac{p_0 E}{kT} \ll 1$$
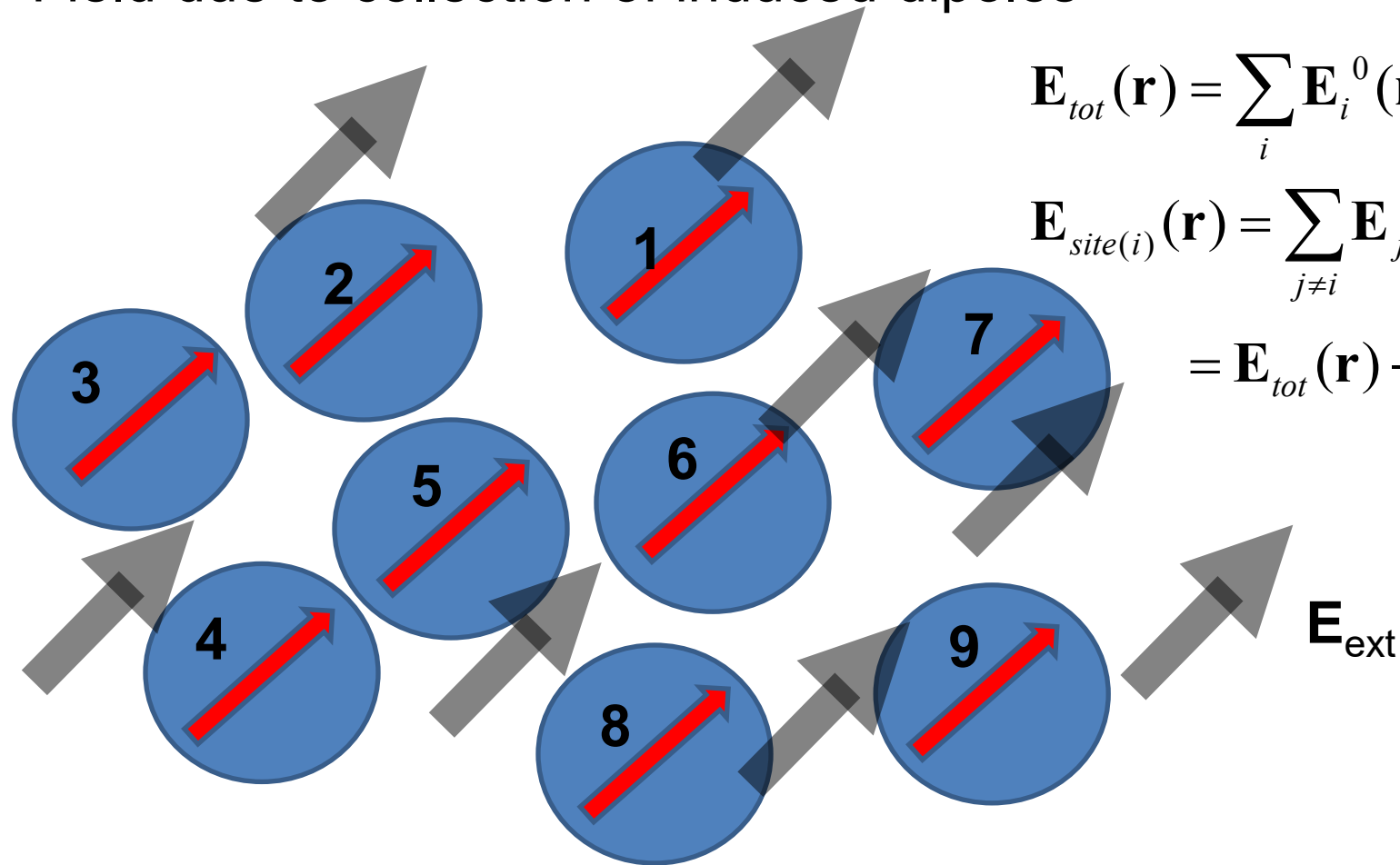
$$\langle \mathbf{p}_{mol} \rangle \approx \frac{1}{3}\frac{p_0^2}{kT}\mathbf{E} \equiv \varepsilon_0 \gamma_{mol} \mathbf{E} \qquad \Rightarrow \gamma_{mol} \approx \frac{1}{3}\frac{p_0^2}{kT\varepsilon_0}$$

Molecular susceptibility for this model:

Now consider a superposition of dipoles in an electric field

$\mathbf{E}_{ext}$

$\mathbf{E}_{dipole}$

$\mathbf{E}_{ext}$

$\mathbf{E}_{dipole}$

$\mathbf{E}_{ext}$

$\mathbf{E}_{dipole}$

Field due to collection of induced dipoles
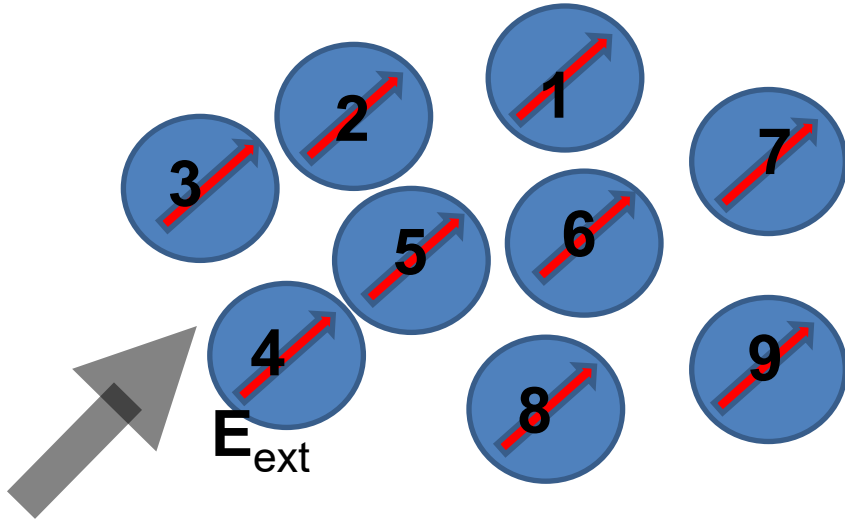
$$\mathbf{E}_{tot}(\mathbf{r}) = \sum_i \mathbf{E}_i^0(\mathbf{r}) + \mathbf{E}_{ext}(\mathbf{r})$$

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

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

$\mathbf{E}_{ext}$

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

E_ext

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

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

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

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

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

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

Averaging:

$$\left\langle \ \right\rangle \rightarrow \frac{1}{V}\int_V d^3r$$

Field due to collection of induced dipoles -- continued

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

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

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

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

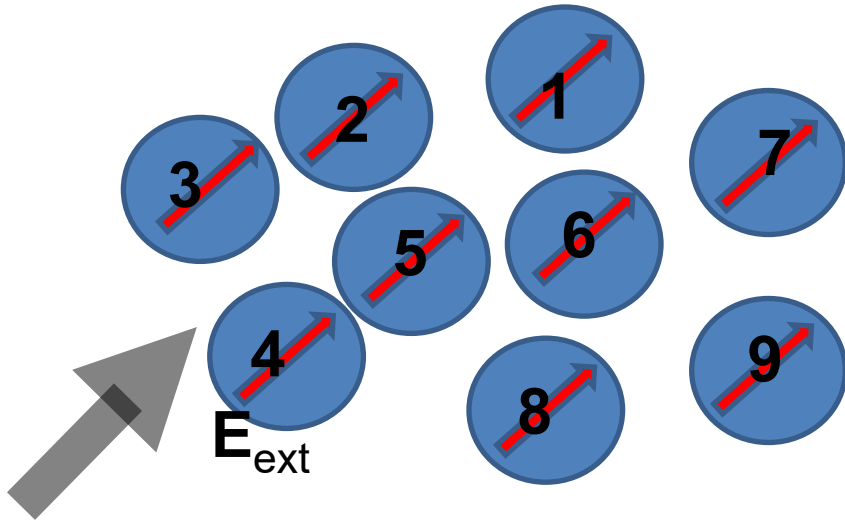# Field due to collection of induced dipoles -- continued

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

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

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

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

Claussius-Mossotti equation

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

Rudolf Julius Emmanuel Clausius

Quick Info

Born
2 January 1822
[Koslin, Prussia (now Koszalin, Poland)](#)

Died
24 August 1888
Bonn, Germany

Summary
Rudolf Clausius did important work in thermodynamics.

Ottaviano-Fabrizio Mossotti

Born	18 April 1791
	Novara, Italy
Died	20 March 1863 (aged 71)
	Pisa, Italy
Nationality	Italian
Known for	Clausius–Mossotti relation
Scientific career	
Fields	Physics, Mathematics
Doctoral advisor	Vincenzo Brunacci
Doctoral students	Enrico Betti

Example of the Clausius-Mossotti equation –

Pentane (C_5H_{12}) at various densities

Density (g/cm3)	Mol/m3	$\varepsilon/\varepsilon_0$	$3V*(\varepsilon/\varepsilon_0-1)/(\varepsilon/\varepsilon_0+2)$
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

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

Re-examination of electrostatic energy in dielectric media

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

In terms of displacement field:

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

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

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

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

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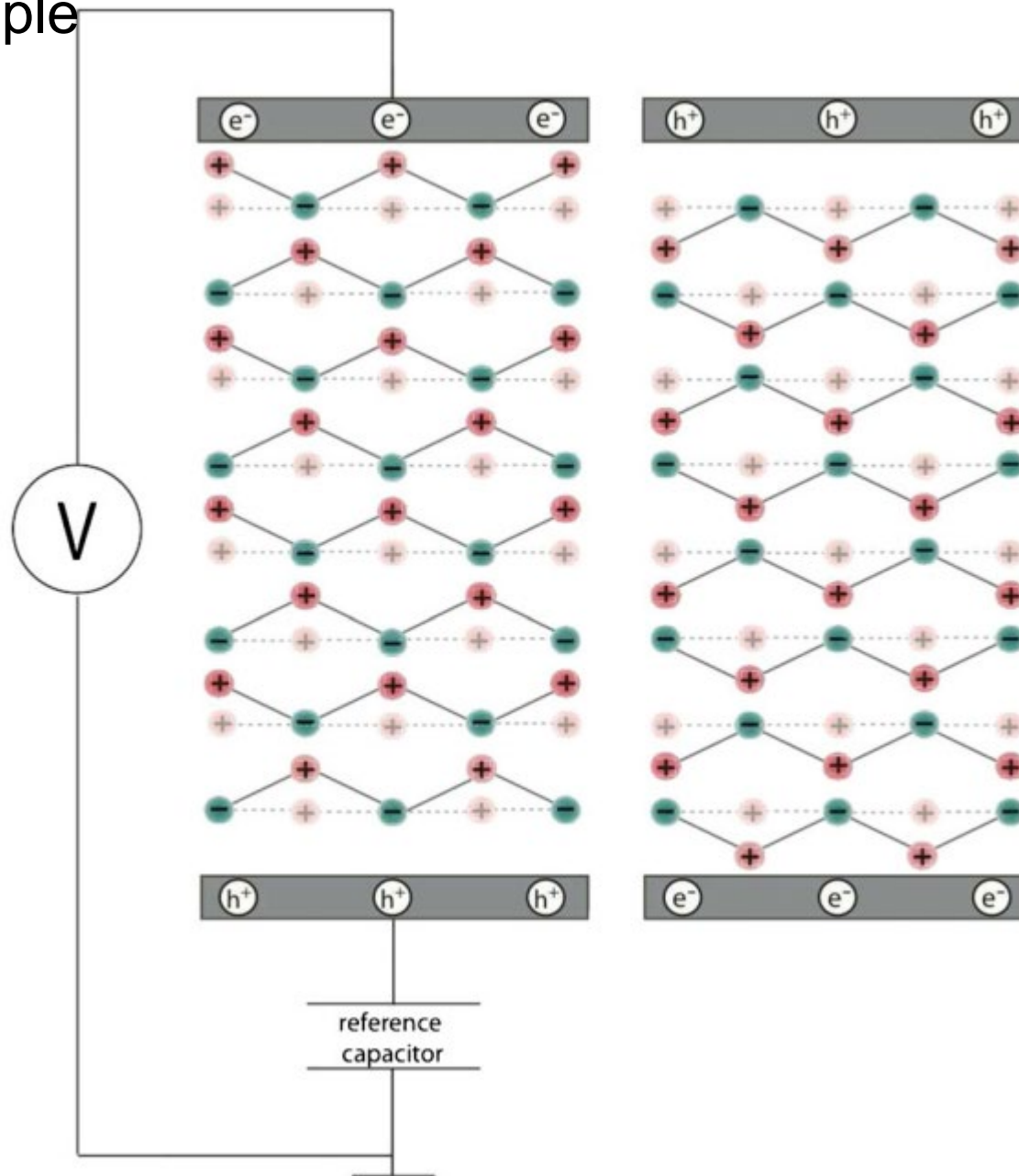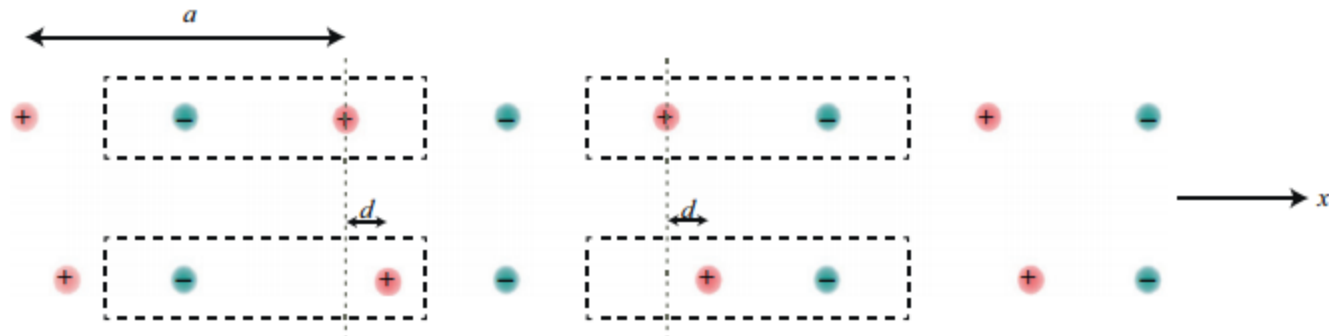
Fig. 1. One-dimensional chain of alternating anions and cations, spaced a distance $a/2$ apart, where a is the lattice constant. The dashed lines indicate two representative unit cells which are used in the text for calculation of the polarization.

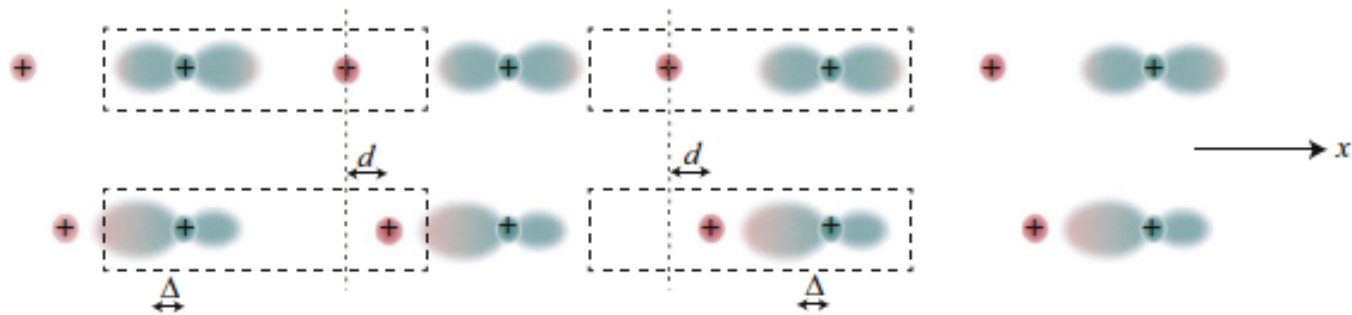# ΔP example

ΔP example   -- linear visualization

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:

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