

**PHY 712 Electrodynamics**  
**9-9:50 AM MWF Olin 103**

**Plan for Lecture 10:**

**Complete reading of Chapter 4**

**A. Microscopic  $\leftrightarrow$  macroscopic polarizability**

**B. Clausius-Mossotti equation**

**C. Electrostatic energy in dielectric media**

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**Course schedule for Spring 2015**

(Preliminary schedule -- subject to frequent adjustment.)

Lecture date	JDJ Reading	Topic	Assign.	Due date
1 Mon: 01/12/2015	Chap. 1	Introduction, units and Poisson equation	#1	01/23/2015
2 Wed: 01/14/2015	Chap. 1	Electrostatic energy calculations	#2	01/23/2015
Fri: 01/16/2015	No class	NAWH out of town		
Mon: 01/19/2015	No class	MLK Holiday		
3 Wed: 01/21/2015	Chap. 1	Poisson equation and Green's theorem	#3	01/23/2015
4 Fri: 01/23/2015	Chap. 1 & 2	Green's functions in Cartesian coordinates	#4	01/26/2015
5 Mon: 01/26/2015	Chap. 1 & 2	Brief introduction to grid solution methods	#5	01/28/2015
6 Wed: 01/28/2015	Chap. 2	Method of images	#6	01/30/2015
7 Fri: 01/30/2015	Chap. 3	Cylindrical and spherical geometries	#7	02/02/2015
8 Mon: 02/02/2015	Chap. 4	Multipole analysis	#8	02/04/2015
9 Wed: 02/04/2015	Chap. 4	Dipoles and dielectrics	#9	02/06/2015
10 Fri: 02/06/2015	Chap. 4	Dipoles and dielectrics	#10	02/09/2015

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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:

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

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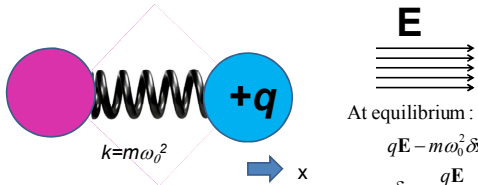
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Microscopic origin of dipole moments

- Polarizable isotropic atoms/molecules
- Charge anisotropic molecules

Polarizable isotropic atoms/molecules



At equilibrium :

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

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

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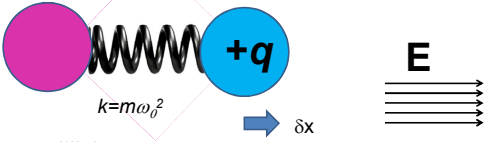
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Polarizable isotropic atoms/molecules – continued:



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 :

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

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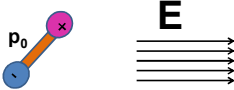
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Alignment of molecules with permanent dipoles  $\mathbf{p}_0$ :



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

$$\langle \mathbf{p}_{mol} \rangle = \frac{\mathbf{E} \int d\Omega p_0 \cos\theta e^{-p_0 E \cos\theta / kT}}{\int d\Omega e^{-p_0 E \cos\theta / kT}}$$

$$= \frac{1}{3} \frac{p_0^2}{kT} \mathbf{E} \equiv \epsilon_0\gamma_{mol}\mathbf{E}$$

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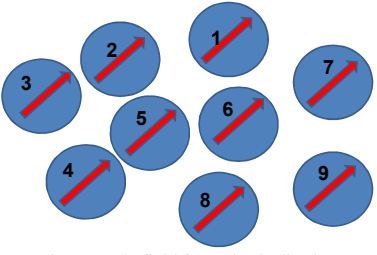
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Field due to collection of induced dipoles



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

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

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

Electrostatic field from single dipole:

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

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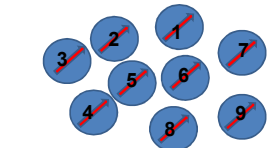
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Field due to collection of induced dipoles -- continued



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

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

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

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

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

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

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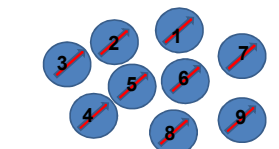
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Field due to collection of induced dipoles -- continued



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

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

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

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

Claussius-Mossotti equation

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

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Example of the Clausius-Mossotti equation –

Pentane (C<sub>5</sub>H<sub>12</sub>) at various densities

Density (g/cm <sup>3</sup> )	Mol/m <sup>3</sup>	$\epsilon/\epsilon_0$	$3V^*(\epsilon/\epsilon_0 - 1)/(\epsilon/\epsilon_0 + 2)$
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

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

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Re-examination of electrostatic energy in dielectric media

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

In terms of displacement field:

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

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

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

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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:

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

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

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

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

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

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

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

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

By contrast, the concept of the polarization of a periodic solid is not unique:

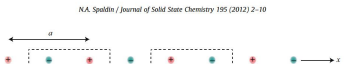


Fig. 1. One-dimensional chain of alternating anions and cations, spaced a distance  $a/2$  apart, where  $a$  is the lattice constant. The dashed lines indicate two representative unit cells which are used in the text for calculation of the polarization.

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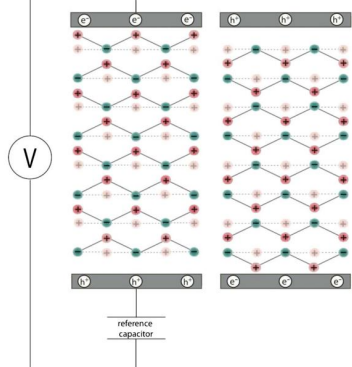
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$\Delta P$  example



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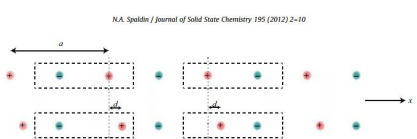
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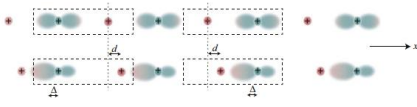
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$\Delta P$  example -- linear visualization



Effects on the electronic distribution



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