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

Plan for Lecture 10:

Complete reading of Chapter 4

A. Microscopic ←→ macroscopic polarizability

B. Clausius-Mossotti equation

C. Electrostatic energy in dielectric media

Course schedule for Spring 2017

(Preliminary schedule -- subject to frequent adjustment.)

	Lecture date	JDJ Reading	Topic	HW	Due date
1	Wed: 01/11/2017	Chap. 1	Introduction, units and Poisson equation	#1	01/18/2017
2	Fri: 01/13/2017	Chap. 1	Electrostatic energy calculations	#2	01/18/2017
	Mon: 01/16/2017		*MLK Holiday - no class*		
3	Wed: 01/18/2017	Chap. 1	Poisson equation and Green's theorem	#3	01/20/2017
4	Fri: 01/20/2017	Chap. 1 and 2	Poisson equation in 2 and 3 dimensions	#4	01/23/2017
5	Mon: 01/23/2017	Chap. 1 and 2	Brief introduction to grid solution methods	#5	01/25/2017
6	Wed: 01/25/2017	Chap. 2	Method of images	#6	01/27/2017
7	Fri: 01/27/2017	Chap. 3	Cylindrical and spherical geometries	#7	01/30/2017
8	Mon: 01/30/2017	Chap. 3 & 4	Multipole analysis	#8	02/01/2017
9	Wed: 02/01/2017	Chap. 4	Dipoles and dielectrics	#9	02/03/2017
10	Fri: 02/03/2017	Chap. 4	Dipoles and dielectrics	#10	02/06/2017
11	Mon: 02/06/2017				
12	Wed: 02/08/2017				
13	Fri: 02/10/2017				
14	Mon: 02/13/2017				

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:

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

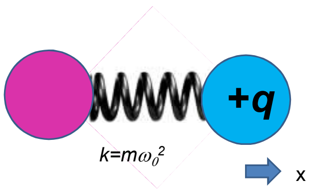
Electrostatic field from single dipole:

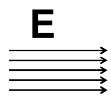
$$\mathbf{E}(\mathbf{r}) = \frac{1}{4\pi\varepsilon_0}\left(\frac{3\mathbf{r}(\mathbf{p}\cdot\mathbf{r}) - r^2\mathbf{p}}{r^5} - \frac{4\pi}{3}\mathbf{p}\delta^3(\mathbf{r})\right)$$

Microscopic origin of dipole moments

- Polarizable isotropic atoms/molecules
- Charge anisotropic molecules

Polarizable isotropic atoms/molecules



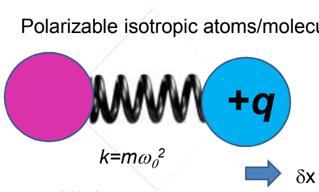


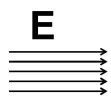
At equilibrium:

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

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

Polarizable isotropic atoms/molecules – continued:





At equilibrium:

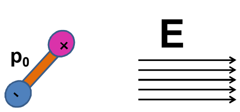
$$q\mathbf{E} - m\omega_0^2 \delta\mathbf{x} = 0$$

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

Induced dipole moment:

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

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

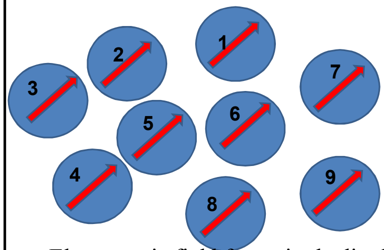


For a freely rotating dipole its average moment in an electric field, estimated assuming a Boltzmann distribution:

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

$$= \frac{1}{3}\frac{p_0^2}{kT}\mathbf{E} \equiv \varepsilon_0 \gamma_{mol}\mathbf{E} \quad \Rightarrow \gamma_{mol} = \frac{1}{3}\frac{p_0^2}{kT\varepsilon_0}$$

Field due to collection of induced dipoles



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

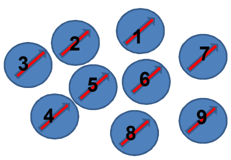
$$\mathbf{E}_{site(i)} = \sum_{j \neq i} \mathbf{E}_j^{\,0} + \mathbf{E}_{ext}$$

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

Electrostatic field from single dipole:

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

Field due to collection of induced dipoles -- continued



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

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

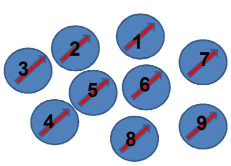
$$= \mathbf{E}_{tot} - \mathbf{E}_i^{\,0}$$

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

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

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

Field due to collection of induced dipoles -- continued



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

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

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

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

Claussius-Mossotti equation

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

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:

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

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

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

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

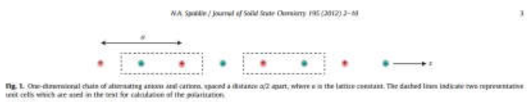
Note: In general **P** is highly dependent on the boundary values; often it is more convenient/meaningful to calculate Δ**P**.

Comment on the “Modern Theory of Polarization”
-- continued

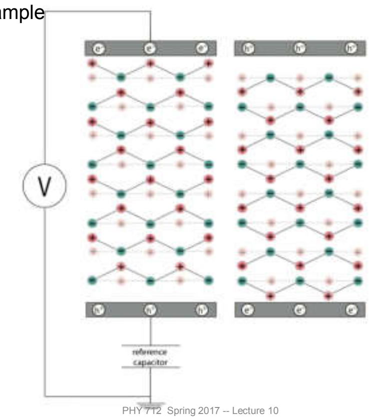
$$\nabla \cdot \Delta\mathbf{P} = \Delta\rho_{bound} = \Delta\rho^{nuclear}_{bound} + \Delta\rho^{electronic}_{bound}$$

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

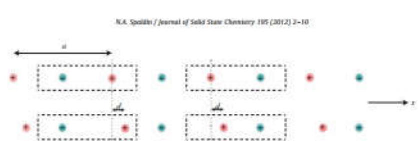
By contrast, the concept of the polarization of a periodic solid is not unique:



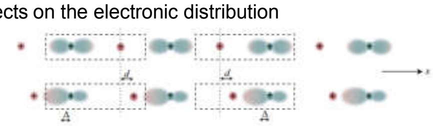
ΔP example



ΔP example -- linear visualization



Effects on the electronic distribution



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