PHY 712 Electrodynamics
9-9:50 AM MWF Olin 105

Plan for Lecture 10:

Complete reading of Chapter 4

A. Microscopic ←→ macroscopic polarizability

B. Clausius-Mossotti equation

C. Electrostatic energy in dielectric media

Colloquium: Feb. ~~7~~ 8 ? at 4 PM

Posted on February 4, 2018

Postponed (probably by one day) due to airline difficulties:

WFU Physics Colloquium

TITLE: "Computational Engineering of Thermoelectric Materials"
SPEAKER: Professor Kristian Berland
Centre for Materials Science and Nanotechnology,
University of Oslo
TIME: Wed. Feb. ~~7~~ 8 ?, 2018, at 4:00 PM
PLACE: George P. Williams, Jr. Lecture Hall, (Olin 101)

Course schedule for Spring 2018

(Preliminary schedule -- subject to frequent adjustment.)

	Lecture date	JDJ Reading	Topic	HW	Due date
	Wed: 01/17/2018	No class	Snow		
1	Fri: 01/19/2018	Chap. 1 & Appen.	Introduction, units and Poisson equation	#1	01/26/2018
2	Mon: 01/22/2018	Chap. 1	Electrostatic energy calculations	#2	01/26/2018
3	Wed: 01/24/2018	Chap. 1	Poisson's equation and Green's theorem	#3	01/26/2018
4	Thu: 01/25/2018	Chap. 1 & 2	Poisson's equation in 2 and 3 dimensions		
5	Fri: 01/26/2018	Chap. 1 & 2	Brief introduction to numerical methods	#4	01/29/2018
6	Mon: 01/29/2018	Chap. 2	Method of image charges	#5	01/31/2018
7	Wed: 01/31/2018	Chap. 2 & 3	Cylindrical and spherical geometries	#6	02/02/2018
8	Fri: 02/02/2018	Chap. 3 & 4	Multipole analysis	#7	02/07/2018
9	Mon: 02/05/2018	Chap. 4	Dipoles and Dielectrics	#8	02/09/2018
10	Wed: 02/07/2018	Chap. 4	Dipoles and Dielectrics		
11	Fri: 02/09/2018	Chap. 1-4	Review		
12	Mon: 02/12/2018				
13	Wed: 02/14/2018				
14	Fri: 02/16/2018				
15	Mon: 02/19/2018				

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:

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

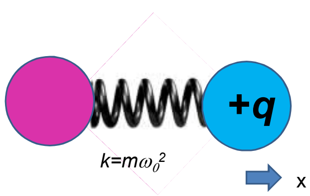
Electrostatic field from single dipole:

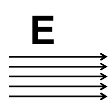
$$\mathbf{E}(\mathbf{r}) = \frac{1}{4\pi\varepsilon_0}\left(\frac{3\mathbf{r}(\mathbf{p}\cdot\mathbf{r}) - r^2\mathbf{p}}{r^5} - \frac{4\pi}{3}\mathbf{p}\delta^3(\mathbf{r})\right)$$

Microscopic origin of dipole moments

- Polarizable isotropic atoms/molecules
- Charge anisotropic molecules

Polarizable isotropic atoms/molecules



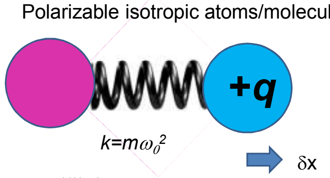


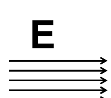
At equilibrium:

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

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

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:

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

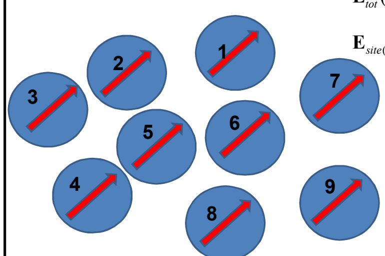
Alignment of molecules with permanent dipoles $\mathbf{p}_0$:

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

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

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

Field due to collection of induced dipoles



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

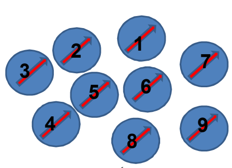
$$\mathbf{E}_{site(i)}(\mathbf{r}) = \sum_{j\neq i} \mathbf{E}_j^{\,0}(\mathbf{r}) + \mathbf{E}_{ext}(\mathbf{r})$$

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

Electrostatic field from single dipole:

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

Field due to collection of induced dipoles -- continued



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

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

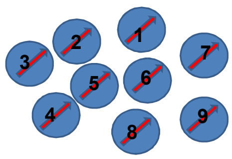
$$= \mathbf{E}_{tot}(\mathbf{r}) - \mathbf{E}_i^{\,0}(\mathbf{r})$$

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

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

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

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

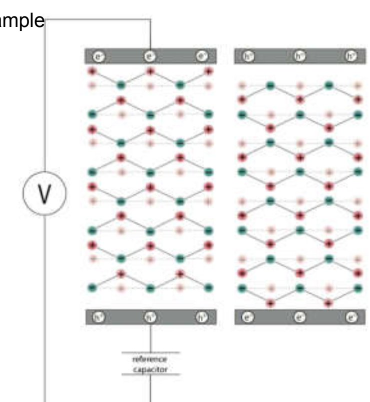
$$\nabla \cdot \Delta\mathbf{P} = \Delta\rho_{bound} = \Delta\rho^{nuclear}_{bound} + \Delta\rho^{electronic}_{bound}$$
$$\Delta\mathbf{P}^{electronic} = -\frac{e}{V_{crystal}} \sum_n \langle w_{n0} | \mathbf{r} | w_{n0} \rangle$$

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

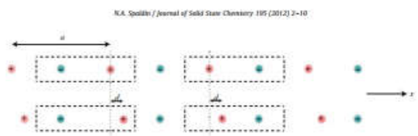
N.A. Spaldin / Journal of Solid State Chemistry 195 (2012) 2–10 3

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.

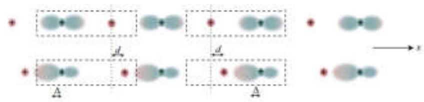
ΔP example



ΔP example -- linear visualization



Effects on the electronic distribution



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