# 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



Regular colloquium this week

## Zijie Yan, PhD

Chemical & Biomolecular Engineering
Clarkson University

## "Light-Driven Self-Organization of Nanoparticles into Artificial Materials"

**Wednesday, February 6, 2019, at 4:00 pm**
**George P. Williams, Jr. Lecture Hall (Olin 101)**

**Refreshments will be served at 3:30 pm in the Olin lounge.**
**All interested persons are cordially invited to attend.**



### Course schedule for Spring 2019

(Preliminary schedule -- subject to frequent adjustment.)

| | Lecture date | JDJ Reading | Topic | HW | Due date |
|---|---|---|---|---|---|
| 1 | Mon: 01/14/2019 | Chap. 1 & Appen. | Introduction, units and Poisson equation | #1 | 01/23/2019 |
| 2 | Wed: 01/16/2019 | Chap. 1 | Electrostatic energy calculations | #2 | 01/23/2019 |
| 3 | Fri: 01/18/2019 | Chap. 1 | Electrostatic potentials and fields | #3 | 01/23/2019 |
| | Mon: 01/21/2019 | No class | Martin Luther King Holiday | | |
| 4 | Wed: 01/23/2019 | Chap. 1 - 3 | Poisson's equation in 2 and 3 dimensions | | |
| 5 | Fri: 01/25/2019 | Chap. 1 - 3 | Brief introduction to numerical methods | #4 | 01/28/2019 |
| 6 | Mon: 01/28/2019 | Chap. 2 & 3 | Image charge constructions | #5 | 01/30/2019 |
| 7 | Wed: 01/30/2019 | Chap. 2 & 3 | Cylindrical and spherical geometries | | |
| 8 | Fri: 02/01/2019 | Chap. 3 & 4 | Spherical geometry and multipole moments | #6 | 02/04/2019 |
| 9 | Mon: 02/04/2019 | Chap. 4 | Dipoles and Dielectrics | #7 | 02/06/2019 |
| 10 | Wed: 02/06/2019 | Chap. 4 | Polarization and Dielectrics | | |
| 11 | Fri: 02/08/2019 | Chap. 5 | Magnetostatics | #8 | 02/11/2019 |
| 12 | Mon: 02/11/2019 | | | | |
| 13 | Wed: 02/13/2019 | | | | |
| 14 | Fri: 02/15/2019 | | | | |
| 15 | Mon: 02/18/2019 | | | | |

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:

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

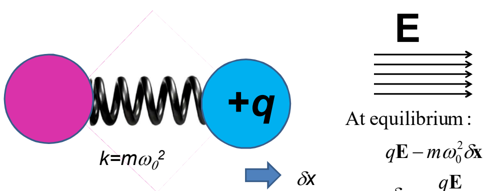
Electrostatic field from single dipole:

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



Microscopic origin of dipole moments
- Polarizable atoms/molecules
- Anisotropic charged molecules

Polarizable isotropic atoms/molecules



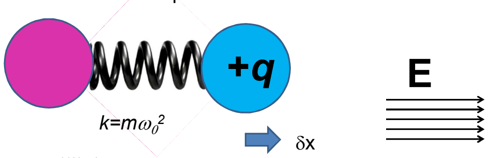

At equilibrium:

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

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



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 $\mathbf{p}_0$:

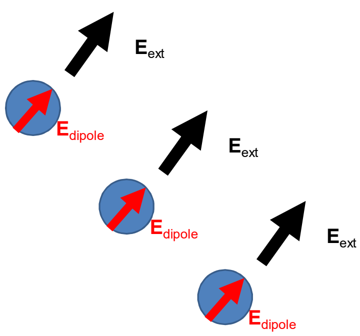

For a freely rotating dipole its average moment in an electric field, estimated assuming a Boltzmann distribution:

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

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

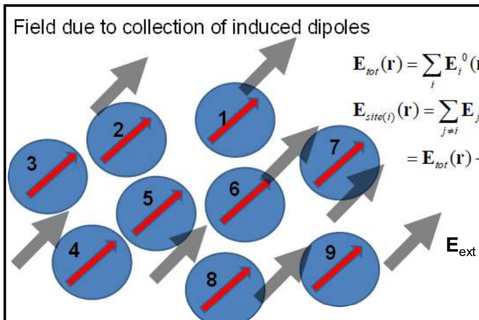


Superposition of dipoles






Field due to collection of induced dipoles




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

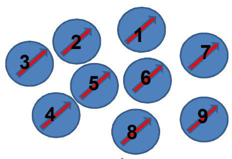
$$\mathbf{E}_{site(i)}(\mathbf{r}) = \sum_{j \neq i} \mathbf{E}_j^{\,0}(\mathbf{r}) + \mathbf{E}_{ext}(\mathbf{r})$$

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

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

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

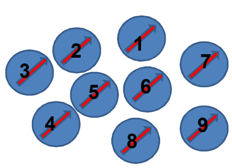
$$= \mathbf{E}(\mathbf{r})_{tot} - \frac{1}{4\pi\varepsilon_0}\left( \frac{3\mathbf{r}\,(\mathbf{p}_i\cdot\mathbf{r}) - r^2\mathbf{p}_i}{r^5} - \frac{4\pi}{3}\mathbf{p}_i\delta^3(\mathbf{r}-\mathbf{r}_i)\right)$$

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

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



## Field due to collection of induced dipoles -- continued




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

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

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

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

Claussius-Mossotti equation

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

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:

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

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

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

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



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

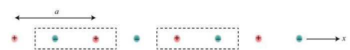
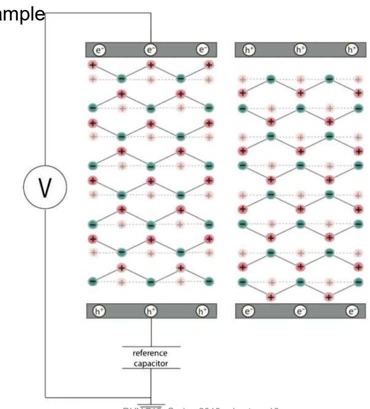



Fig. 1. One-dimensional chain of alternating anions and cations, spaced a distance a/2 apart, where a is the lattice constant. The dashed lines indicate two representative unit cells which are used in the text for calculation of the polarization.



$\Delta P$ example






$\Delta P$ example -- linear visualization

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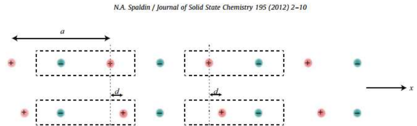
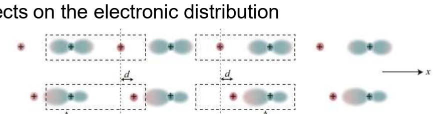



Effects on the electronic distribution

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