PHY 712 Electrodynamics
11-11:50 AM MWF Olin 107

Plan for Lecture 10:

Complete reading of Chapter 4

A. Microscopic ←→macroscopic polarizability

B. Clausius-Mossotti equation

C. Electrostic energy in dielectric media

Course schedule for 2013

(Preliminary schedule -- subject to frequent adjustment.)

Date	JDJ Reading	Topic	Assign.
01-16(Wed)	Chap. 1	Introduction, units and Poisson equation.	#1
01-18(Fri)	Chap. 1	Electronstatic energy calculations	#2
01-21(Mon)	*No class*	*MKL Holiday*	
01-23(Wed)	Chap. 1	Poisson Equation and Green's Functions	#3
01-25(Fri)	Chap. 1 & 2	Green's Theorem and Functions	#4
01-28(Mon)	Chap. 1 & 2	Brief introduction to numerical methods	#5
01-30(Wed)	Chap. 2	Method of images	#6
02-01(Fri)	Chap. 3	Cylindrical and spherical geometries	#7
02-04(Mon)	Chap. 4	Multipole moments	#8
02-06(Wed)	Chap. 4	Dipoles and dielectrics	#9
02-08(Fri)	Chap. 4	Microscopic and macroscopic polarizability	

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 :

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

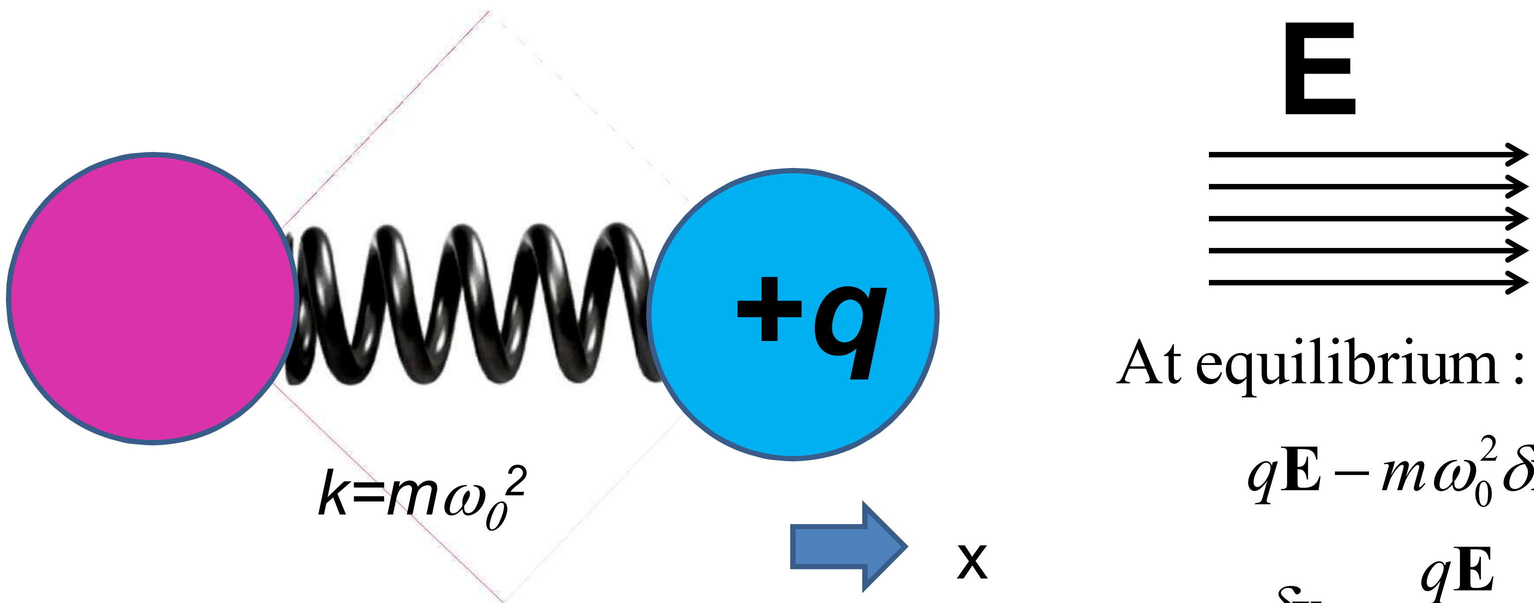
Electrostatic field from single dipole :

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

Microscopic origin of dipole moments

- Polarizable isotropic atoms/molecules
- Charge anisotropic molecules

Polarizable isotropic atoms/molecules

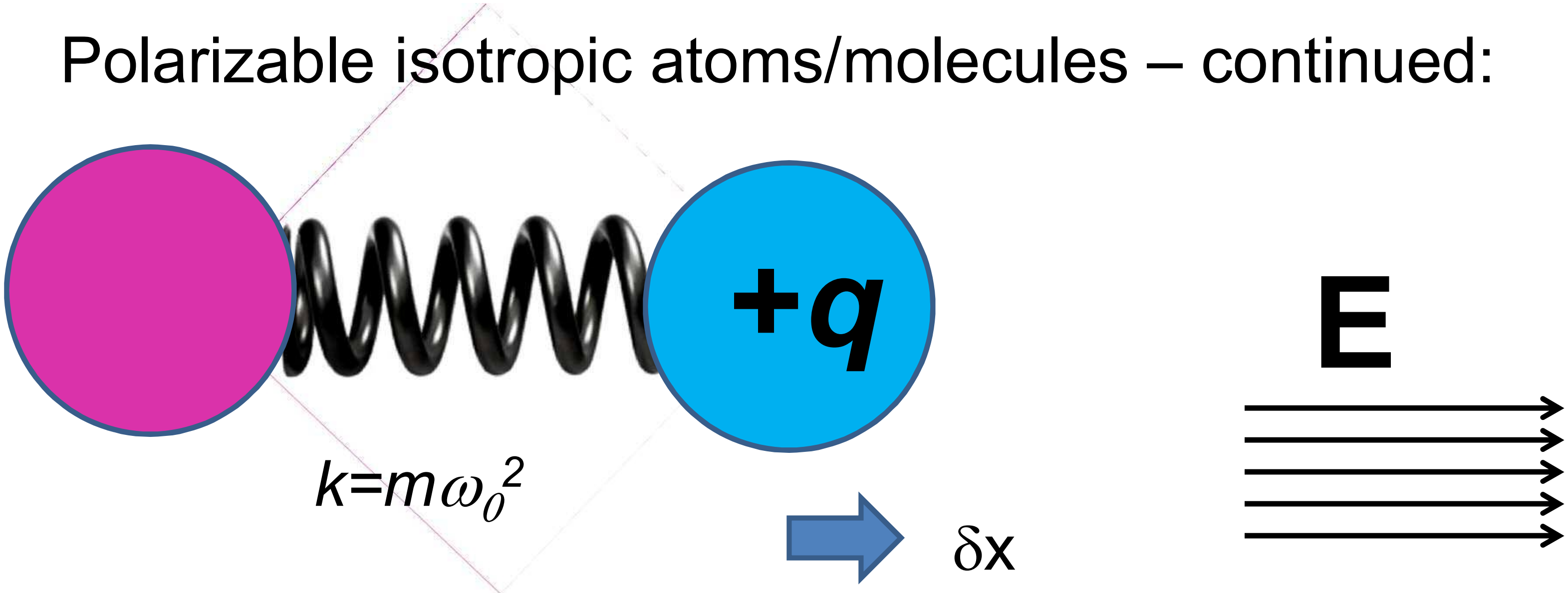


At equilibrium:

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

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

Polarizable isotropic atoms/molecules – continued:



At equilibrium:

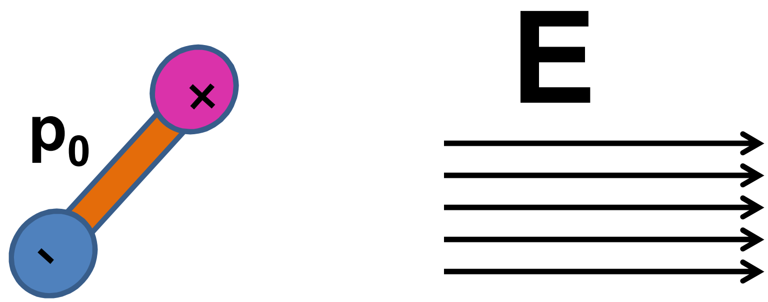
$$q\mathbf{E} - m\omega_0^2\delta\mathbf{x} = 0$$

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

Induced dipole moment:

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

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

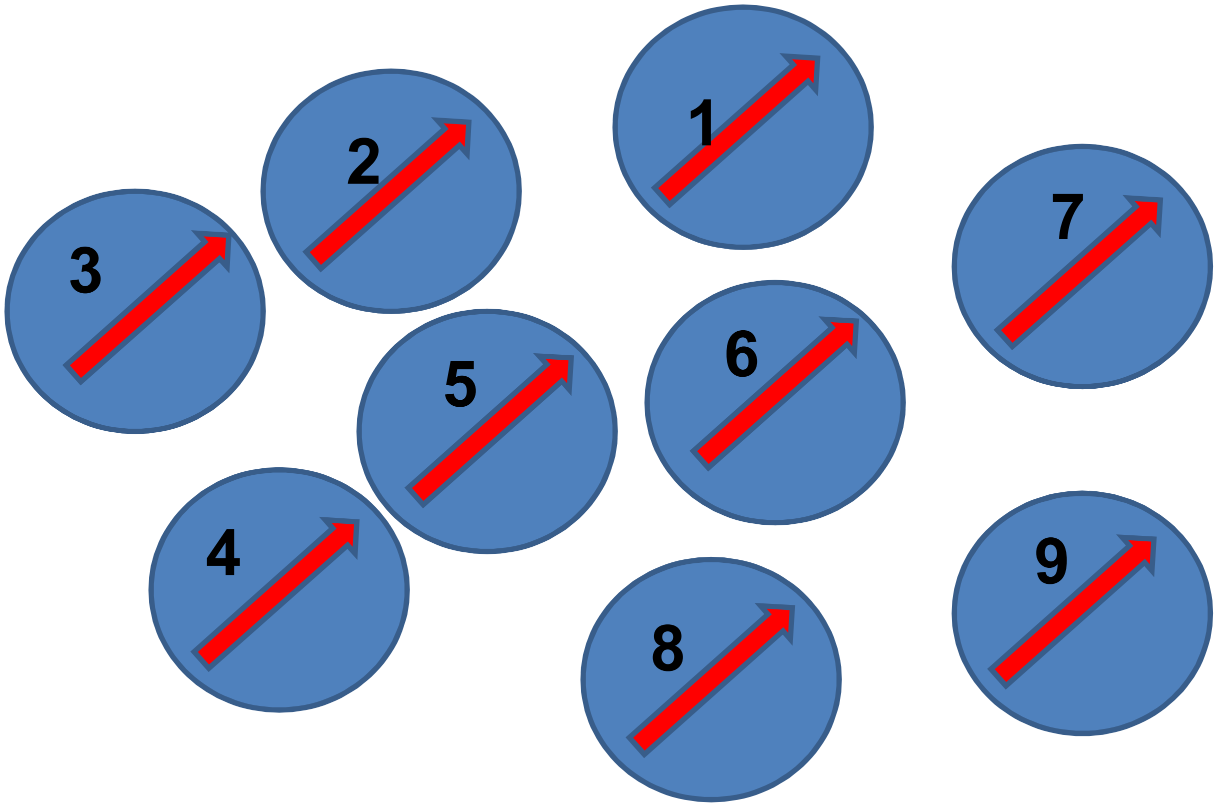


For a freely rotating dipole its average moment in an electric field, estimated assuming a Boltzmann distribution :

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

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

Field due to collection of induced dipoles



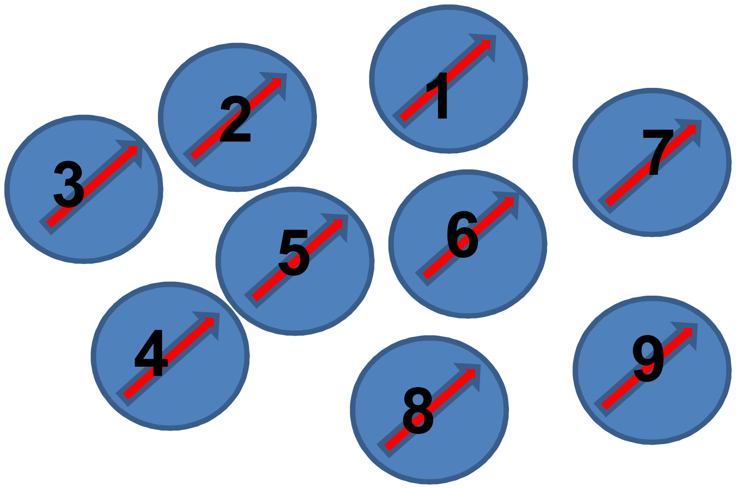
$$\mathbf{E}_{tot} = \sum_i \mathbf{E}_i^{\;0}$$

$$\mathbf{E}_{site(i)} = \sum_{j \neq i} \mathbf{E}_j^{\;0} = \mathbf{E}_{tot} - \mathbf{E}_i^{\;0}$$

Electrostatic field from single dipole:

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

Field due to collection of induced dipoles -- continued



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

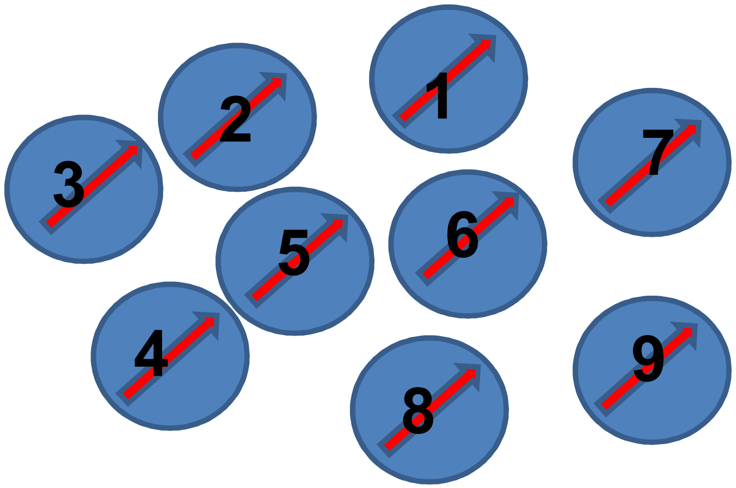
$$\mathbf{E}_{site(i)} = \sum_{j \neq i} \mathbf{E}_j^{\,0} = \mathbf{E}_{tot} - \mathbf{E}_i^{\,0}$$

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

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

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

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	e/e0	3V*(e/e0-1)/(e/e0+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

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)

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

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

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