

Chapter 4 Multipoles, Electrostatics of Macroscopic Media, Dielectrics

Multipole Expansion

- The potential from a charge density outside a sphere can be written as

$$\Phi(\mathbf{r}) = \frac{1}{4\pi\epsilon_0} \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} \frac{4\pi}{2\ell+1} q_{\ell}^m \frac{Y_{\ell}^m(\theta, \phi)}{r^{\ell+1}} \quad \Leftarrow \text{multipole expansion}$$

- $\ell=0$: monopole term, $\ell=1$: dipole terms, $\ell=2$: quadrupole terms, etc.

- The problem is to determine q_{ℓ}^m in terms of the charge density $\rho(\mathbf{r}')$.

$$\begin{aligned} \Phi(\mathbf{r}) &= \frac{1}{4\pi\epsilon_0} \int \frac{\rho(\mathbf{r}')}{r} d^3x' \quad \Leftarrow r = |\mathbf{r} - \mathbf{r}'| \\ &= \frac{1}{4\pi\epsilon_0} \sum_{\ell m} \frac{4\pi}{2\ell+1} \left(\int Y_{\ell}^{*m}(\theta', \phi') r'^{\ell} \rho(\mathbf{r}') d^3x' \right) \frac{Y_{\ell}^m(\theta, \phi)}{r^{\ell+1}} \end{aligned}$$

$$\Rightarrow q_{\ell}^m = \int Y_{\ell}^{*m}(\theta', \phi') r'^{\ell} \rho(\mathbf{r}') d^3x' \quad \Leftarrow \text{multipole moments}$$

$$\begin{aligned} \Rightarrow q_0^0 &= \frac{1}{\sqrt{4\pi}} \int \rho(\mathbf{r}') d^3x' = \frac{q}{\sqrt{4\pi}}, \quad q_1^0 = \sqrt{\frac{3}{4\pi}} \int z' \rho(\mathbf{r}') d^3x' = \sqrt{\frac{3}{4\pi}} p_z \\ \Rightarrow q_1^{\pm 1} &= \mp \sqrt{\frac{3}{8\pi}} \int (x' \mp i y') \rho(\mathbf{r}') d^3x' = \mp \sqrt{\frac{3}{8\pi}} (p_x \mp i p_y) \end{aligned}$$

$$q_2^0 = \frac{1}{4} \sqrt{\frac{5}{\pi}} \int (3 z'^2 - r'^2) \rho(\mathbf{r}') d^3 x' = \frac{1}{4} \sqrt{\frac{5}{\pi}} Q_{33}$$

$$q_2^{\pm 1} = \mp \frac{1}{2} \sqrt{\frac{15}{2\pi}} \int z' (x' \mp i y') \rho(\mathbf{r}') d^3 x' = \mp \frac{1}{6} \sqrt{\frac{15}{2\pi}} (Q_{13} \mp i Q_{23})$$

$$q_2^{\pm 2} = \frac{1}{4} \sqrt{\frac{15}{2\pi}} \int (x' \mp i y')^2 \rho(\mathbf{r}') d^3 x' = \frac{1}{12} \sqrt{\frac{15}{2\pi}} (Q_{11} \mp 2i Q_{12} - Q_{22})$$

- For a real charge density the moments with $m < 0$ are $q_\ell^{-m} = (-1)^m q_\ell^{*m}$
- Electric dipole moment: $\mathbf{p} = \int \mathbf{r}' \rho(\mathbf{r}') d^3 x'$
- Traceless quadrupole moment tensor:

$$Q_{ij} = \int (3 x'_i x'_j - \delta_{ij} r'^2) \rho(\mathbf{r}') d^3 x' \Rightarrow \mathbf{Q} = \int (3 \mathbf{r}' \otimes \mathbf{r}' - r'^2 \mathbb{I}) \rho(\mathbf{r}') d^3 x'$$

- The ℓ^{th} multipole coefficients [$(2\ell+1)$ in number] are linear combinations of the corresponding multipoles expressed in rectangular coordinates.
- In the Cartesian coordinates $\Phi(\mathbf{r}) = \frac{1}{4\pi\epsilon_0} \left(\frac{q}{r} + \frac{\mathbf{p} \cdot \mathbf{r}}{r^3} + \frac{1}{2} \frac{\mathbf{r} \cdot \mathbf{Q} \cdot \mathbf{r}}{r^5} + \dots \right)$
by direct Taylor series expansion of $\frac{1}{|\mathbf{r} - \mathbf{r}'|}$.

- The electric field components for a given multipole with definite ℓ, m are

$$E_r = \frac{\ell+1}{2\ell+1} \frac{q_\ell^m}{\epsilon_0 r^{\ell+2}} Y_\ell^m(\theta, \phi)$$

$$E_\theta = -\frac{1}{2\ell+1} \frac{q_\ell^m}{\epsilon_0 r^{\ell+2}} \frac{\partial}{\partial \theta} Y_\ell^m(\theta, \phi)$$

$$E_\phi = \frac{1}{2\ell+1} \frac{q_\ell^m}{\epsilon_0 r^{\ell+2}} \frac{i m}{\sin \theta} Y_\ell^m(\theta, \phi)$$

- For a dipole \mathbf{p} $\mathbf{p} = p \hat{\mathbf{z}}$ $\Rightarrow E_r = \frac{2 p \cos \theta}{4 \pi \epsilon_0 r^3}, E_\theta = \frac{p \sin \theta}{4 \pi \epsilon_0 r^3}, E_\phi = 0$ along the z -axis:

$$\Rightarrow \mathbf{E}(\mathbf{r}) = \frac{1}{4 \pi \epsilon_0} \frac{3(\mathbf{p} \cdot \hat{\mathbf{n}}) \hat{\mathbf{n}} - \mathbf{p}}{|\mathbf{r} - \mathbf{r}_0|^3} \Leftarrow -\frac{1}{4 \pi \epsilon_0} \nabla \frac{\mathbf{p} \cdot (\mathbf{r} - \mathbf{r}_0)}{|\mathbf{r} - \mathbf{r}_0|^3} \Leftarrow \hat{\mathbf{n}} \equiv \frac{\mathbf{r} - \mathbf{r}_0}{|\mathbf{r} - \mathbf{r}_0|}$$

- The Cartesian multipole moments are $\frac{(\ell+1)(\ell+2)}{2}$ in number and for $\ell > 1$ are more numerous than the $(2\ell+1)$ spherical components.

- The root of the differences lies in the different rotational transformation properties of the 2 types of multipole moments; the Cartesian tensors are reducible, the spherical are irreducible. [Problem 4.3]

- Note that for $\ell=2$ we have recognized the difference by defining a traceless Cartesian quadrupole moment.
- In general the multipole moment coefficients depend on the choice of origin.
- For a *point charge* e located at $\mathbf{x}_0=(r_0, \theta_0, \phi_0)$, the multipole moments are

$$q_\ell^m = e r_0^\ell Y_\ell^{*m}(\theta_0, \phi_0) \leftarrow \begin{array}{c} \text{nonvanishing} \\ \text{in general} \end{array} \Rightarrow q_0^0 = \frac{e}{\sqrt{4\pi}} \leftarrow \begin{array}{c} \text{only one independent} \\ \text{of the location} \end{array}$$

- For 2 point charges $+e$ and $-e$ at \mathbf{r}_0 and \mathbf{r}_1 , the multipole moments are

$$q_\ell^m = e [r_0^\ell Y_\ell^{*m}(\theta_0, \phi_0) - r_1^\ell Y_\ell^{*m}(\theta_1, \phi_1)] \Rightarrow q_0^0 = 0$$

$$\Rightarrow q_1^0 = \sqrt{\frac{3}{4\pi}} e (z_0 - z_1), \quad q_1^1 = -\sqrt{\frac{3}{8\pi}} e [(x_0 - x_1) - i(y_0 - y_1)]$$

independent of the location, depend only on the relative position

Theorem: The values of q_ℓ^m for the *lowest nonvanishing multipole moment* of any charge distribution are indep. of the choice of origin, but all higher multipole moments do in general depend on the location of the origin. [Problem 4.4]

- Consider a localized charge distribution $\rho(\mathbf{r}')$ that gives rise to an electric field throughout space. Wish to calculate the integral of \mathbf{E} over the volume of a sphere

$$\int_{r < R} \mathbf{E}(\mathbf{r}) d^3x = - \int_{r < R} \nabla \Phi d^3x = - \oint_{r=R} \Phi \hat{\mathbf{r}} R^2 d\Omega \quad \Downarrow \quad \mathbb{r} = |\mathbf{r} - \mathbf{r}'| \\ = -\frac{R^2}{4\pi\epsilon_0} \int \rho(\mathbf{r}') d^3x' \oint_{r=R} \frac{\hat{\mathbf{r}} d\Omega}{\mathbb{r}} \quad \Leftarrow \quad \Phi = \frac{1}{4\pi\epsilon_0} \int \frac{\rho(\mathbf{r}')}{\mathbb{r}} d^3x'$$

$$\hat{\mathbf{r}} = \sin \theta (\cos \phi \hat{\mathbf{x}} + \sin \phi \hat{\mathbf{y}}) + \cos \theta \hat{\mathbf{z}} = \sqrt{\frac{2\pi}{3}} [Y_1^{-1}(\hat{\mathbf{x}} + i\hat{\mathbf{y}}) - Y_1^1(\hat{\mathbf{x}} - i\hat{\mathbf{y}}) + \sqrt{2} Y_1^0 \hat{\mathbf{z}}]$$

$$\frac{1}{\mathbb{r}} = \sum \frac{r_-^\ell}{r_+^{\ell+1}} P_\ell(\cos \gamma) \quad \Leftarrow \quad (r_-, r_+) = (\min(r', R), \max(r', R)) \\ \cos \gamma = \cos \theta \cos \theta' + \sin \theta \sin \theta' \cos(\phi - \phi')$$

$$\Rightarrow \int_{r=R} \frac{\hat{\mathbf{r}} d\Omega}{\mathbb{r}} = \frac{r_-}{r_+^2} \int \cos \gamma \hat{\mathbf{r}} d\Omega = \frac{4\pi}{3} \frac{r_-}{r_+^2} \hat{\mathbf{r}}' \quad \Leftarrow \quad \text{only the } \ell=1 \text{ term survives}$$

$$\Rightarrow \int_{r < R} \mathbf{E}(\mathbf{r}) d^3x = -\frac{R^2}{3\epsilon_0} \int \frac{r_-}{r_+^2} \rho(\mathbf{r}') \hat{\mathbf{r}}' d^3x' \quad \Leftarrow \quad \hat{\mathbf{r}}' = \frac{\mathbf{r}'}{r'}$$

- If the sphere completely encloses the charge density,

$$r_- = r', \quad r_+ = R \quad \Rightarrow \quad \int_{r < R} \mathbf{E}(\mathbf{r}) d^3x = -\frac{\mathbf{p}}{3\epsilon_0}$$

where \mathbf{p} is the electric dipole moment of the charge distribution with respect to the center of the sphere.

Divergence theorem extended:

$$\int \nabla \cdot \mathbf{v} d^3 x = \oint \mathbf{v} \cdot d\mathbf{a}$$

Let $\mathbf{v} \rightarrow f \mathbf{c}$ where \mathbf{c} is a constant vector $\Rightarrow \nabla \cdot \mathbf{c} = 0$

$$\Rightarrow \int \nabla \cdot (f \mathbf{c}) d^3 x = \int (\mathbf{c} \cdot \nabla f + f \nabla \cdot \mathbf{c}) d^3 x = \mathbf{c} \cdot \int \nabla f d^3 x$$
$$\oint f \mathbf{c} \cdot d\mathbf{a} = \mathbf{c} \cdot \oint f d\mathbf{a}$$

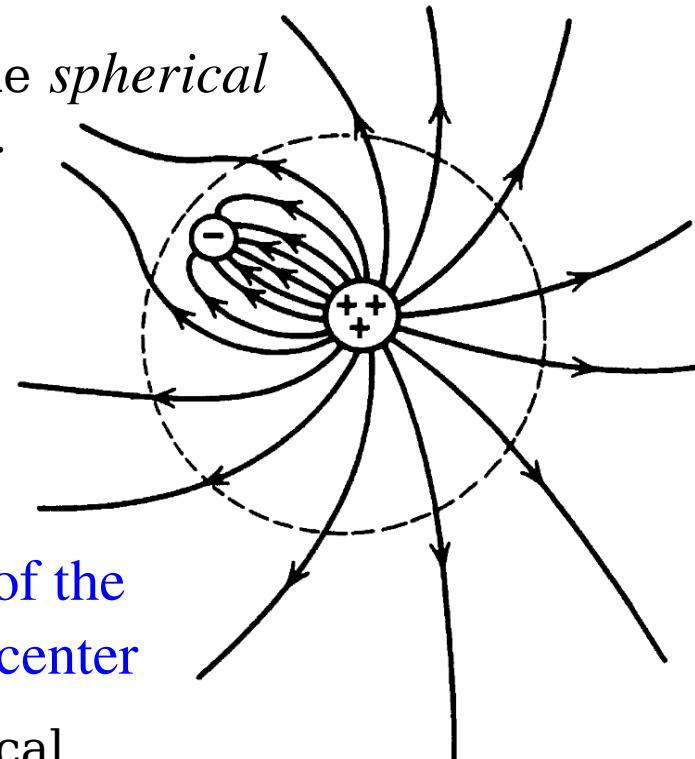
$$\Rightarrow \int_v \nabla f d^3 x = \oint_s f d\mathbf{a} \Leftarrow \mathbf{c} \text{ can be any constant.}$$

- This volume integral is independent of the size of the *spherical* region of integration provided all the charge is inside.

- With the charge all exterior to the sphere $\Rightarrow r_< = R, r_> = r'$

$$\Rightarrow \int_{r < R} \mathbf{E}(\mathbf{r}) d^3x = -\frac{R^3}{3\epsilon_0} \int \frac{\rho(\mathbf{r}')}{r'^2} \hat{\mathbf{r}'} d^3x'$$

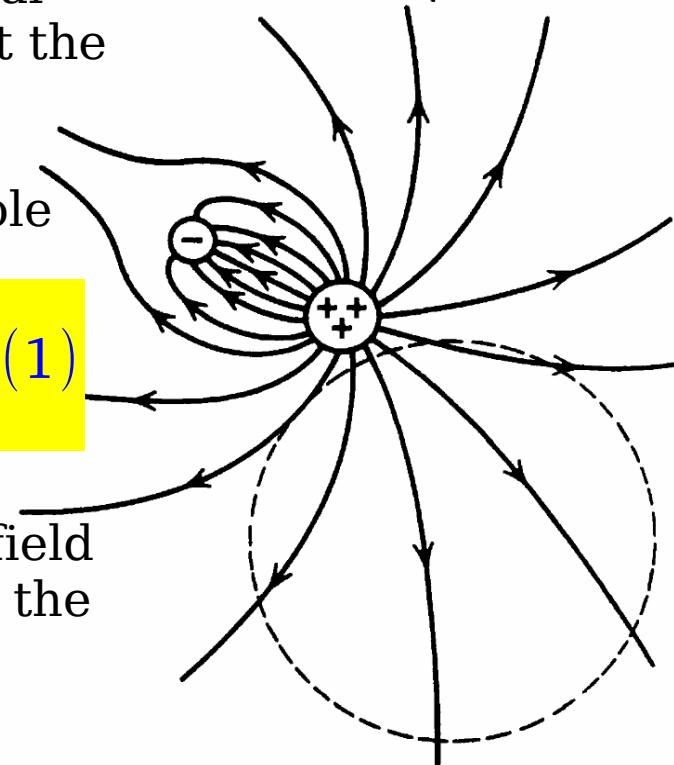
$$= \frac{4\pi}{3} R^3 \mathbf{E}(0) \Leftarrow \text{the definition of the } \mathbf{E} \text{ field at the center}$$



- The average value of the electric field over a spherical volume containing no charge is the value of the field at the center of the sphere.
- Modification of the eqn for the electric field of a dipole

$$\mathbf{E}(\mathbf{r}) = \frac{1}{4\pi\epsilon_0} \left(\frac{3\hat{\mathbf{n}}(\mathbf{p} \cdot \hat{\mathbf{n}}) - \mathbf{p}}{|\mathbf{r} - \mathbf{r}_0|^3} - \frac{4\pi}{3} \mathbf{p} \delta(\mathbf{r} - \mathbf{r}_0) \right) \quad (1)$$

- The added delta function does not contribute to the field away from the site of the dipole. Its purpose is to yield the required volume integral.



A point dipole with dipole moment \mathbf{p} is located at the point \mathbf{x}_0 . From the properties of the derivative of a Dirac delta function, show that for calculation of the potential Φ or the energy of a dipole in an external field, the dipole can be described by an effective charge density

$$\rho_{\text{eff}}(\mathbf{x}) = -\mathbf{p} \cdot \nabla \delta(\mathbf{x} - \mathbf{x}_0) \quad [\text{Problem 4.2}]$$

Since the dipole \mathbf{p} is a point dipole located at \mathbf{x}_0 , we can consider it as a constant dipole during the derivation. The potential due to \mathbf{p} is $\Phi(\mathbf{x}) = \frac{1}{4\pi\epsilon_0} \frac{\mathbf{p} \cdot (\mathbf{x} - \mathbf{x}_0)}{|\mathbf{x} - \mathbf{x}_0|^3}$. In the problem we are asked to transform it into $\Phi(\mathbf{x}) = \frac{1}{4\pi\epsilon_0} \int \frac{\rho_{\text{eff}}(\mathbf{x}')}{|\mathbf{x} - \mathbf{x}'|} d^3x'$. We can achieve the goal with the following manipulations:

$$\begin{aligned} \Phi(\mathbf{x}) &= \frac{\mathbf{p} \cdot (\mathbf{x} - \mathbf{x}_0)}{4\pi\epsilon_0 |\mathbf{x} - \mathbf{x}_0|^3} = -\frac{\mathbf{p}}{4\pi\epsilon_0} \cdot \nabla \left(\frac{1}{|\mathbf{x} - \mathbf{x}_0|} \right) = -\frac{\mathbf{p}}{4\pi\epsilon_0} \cdot \int \nabla \left(\frac{1}{|\mathbf{x} - \mathbf{x}'|} \right) \delta(\mathbf{x}' - \mathbf{x}_0) d^3x' \\ &= \frac{\mathbf{p}}{4\pi\epsilon_0} \cdot \int \nabla' \left(\frac{1}{|\mathbf{x} - \mathbf{x}'|} \right) \delta(\mathbf{x}' - \mathbf{x}_0) d^3x' = -\frac{\mathbf{p}}{4\pi\epsilon_0} \cdot \int \frac{\nabla' \delta(\mathbf{x}' - \mathbf{x}_0)}{|\mathbf{x} - \mathbf{x}'|} d^3x' \\ &= \frac{1}{4\pi\epsilon_0} \int \frac{-\mathbf{p} \cdot \nabla' \delta(\mathbf{x}' - \mathbf{x}_0)}{|\mathbf{x} - \mathbf{x}'|} d^3x' = \frac{1}{4\pi\epsilon_0} \int \frac{\rho_{\text{eff}}(\mathbf{x}')}{|\mathbf{x} - \mathbf{x}'|} d^3x', \end{aligned}$$

where $\rho_{\text{eff}}(\mathbf{x}) = -\mathbf{p} \cdot \nabla \delta(\mathbf{x} - \mathbf{x}_0)$.

The energy of \mathbf{p} in the external electric field \mathbf{E} is $W = -\mathbf{p} \cdot \mathbf{E}(\mathbf{x}_0)$. In the problem we are asked to transform it into $W = \int \rho_{\text{eff}}(\mathbf{x}) \Phi(\mathbf{x}) d^3x$. We can achieve the goal with the

following manipulations:

$$\begin{aligned} W &= -\mathbf{p} \cdot \mathbf{E}(\mathbf{x}_0) = -\mathbf{p} \cdot \int \mathbf{E}(\mathbf{x}) \delta(\mathbf{x} - \mathbf{x}_0) d^3x = \mathbf{p} \cdot \int \delta(\mathbf{x} - \mathbf{x}_0) \nabla \Phi(\mathbf{x}) d^3x \\ &= -\mathbf{p} \cdot \int \Phi(\mathbf{x}) \nabla \delta(\mathbf{x} - \mathbf{x}_0) d^3x = \int [-\mathbf{p} \cdot \nabla \delta(\mathbf{x} - \mathbf{x}_0)] \Phi(\mathbf{x}) d^3x = \int \rho_{\text{eff}}(\mathbf{x}) \Phi(\mathbf{x}) d^3x, \end{aligned}$$

where $\rho_{\text{eff}}(\mathbf{x}) = -\mathbf{p} \cdot \nabla \delta(\mathbf{x} - \mathbf{x}_0)$ again.

Multipole Expansion of the Energy of a Charge Distribution in an External Field

- For a localized charge distribution in an external potential, the electrostatic energy of the system is

$$W = \int \rho(\mathbf{r}) \Phi(\mathbf{r}) d^3x$$

$$\Phi(\mathbf{r}) = \Phi(0) + \mathbf{r} \cdot \nabla \Phi(0) + \frac{1}{2} \sum_{i,j} x^i x^j \frac{\partial^2 \Phi}{\partial x^i \partial x^j}(0) + \dots$$

$$= \Phi(0) - \mathbf{r} \cdot \mathbf{E}(0) - \frac{1}{2} \sum_{i,j} x^i x^j \frac{\partial E_j}{\partial x^i}(0) + \dots \Leftarrow \mathbf{E} = -\nabla \Phi$$

$$= \Phi(0) - \mathbf{r} \cdot \mathbf{E}(0) - \sum_{i,j} \frac{3x^i x^j - r^2 \delta^{ij}}{6} \frac{\partial E_j}{\partial x^i}(0) + \dots \Leftarrow \nabla \cdot \mathbf{E} = 0 \text{ for the external field}$$

$$\Rightarrow W = q \Phi(0) - \mathbf{p} \cdot \mathbf{E}(0) - \frac{1}{6} \sum_{i,j} Q^{ij} \frac{\partial E_j}{\partial x^i}(0) + \dots$$

- This expansion shows the characteristic way in which the various multipoles interact with an external field—the charge with the potential, the dipole with the electric field, the quadrupole with the field gradient, and so on.
- In nuclear physics the quadrupole interaction is of particular interest. The magnitudes and signs of the electric quadrupole moments reflect the nature of the forces between neutrons and protons, as well as the shapes.

- A nuclear state has associated with it a quantum-mechanical charge density, which depends on the quantum numbers (J, M, α) but is cylindrically symmetric about the z axis. Thus the only non-vanishing quadrupole moment is q_2^0 or Q_{33} .

- The quadrupole moment of a nuclear state is defined as
$$Q_{J M \alpha} \equiv \frac{Q_{33}}{e} = \frac{1}{e} \int (3 z^2 - r^2) \rho_{J M \alpha}(\mathbf{r}) d^3 x$$
- The states of different M value for the same J will have different quadrupole moments and so a degeneracy in M value will be removed by the quadrupole coupling to the "external" electric field. Detection of these small energy differences allows the determination of the quadrupole moment of the nucleus.
- The interaction energy between 2 dipoles

$$W_{12} = -\mathbf{p}_1 \cdot \mathbf{E}_2 = \frac{\mathbf{p}_1 \cdot \mathbf{p}_2 - 3(\hat{\mathbf{n}} \cdot \mathbf{p}_1)(\hat{\mathbf{n}} \cdot \mathbf{p}_2)}{4 \pi \epsilon_0 |\mathbf{r}_1 - \mathbf{r}_2|^3} \quad \Leftarrow (1) \quad \& \quad \hat{\mathbf{n}} \equiv \frac{\mathbf{r}_1 - \mathbf{r}_2}{|\mathbf{r}_1 - \mathbf{r}_2|}$$

- The dipole-dipole interaction is attractive or repulsive, depending on the dipoles' orientation. For fixed orientation and separation of the dipoles, the value of the interaction, averaged over the relative positions of the dipoles, is zero.
- If the moments are generally parallel, attraction (repulsion) occurs when the moments are oriented more parallel (perpendicular) to the line joining their centers. For anti-parallel moments the reverse is true.

A localized distribution of charge has a charge density

[Problem 4.7a]

$$\rho(\mathbf{r}) = \frac{1}{64\pi} r^2 e^{-r} \sin^2 \theta$$

(a) Make a multipole expansion of the potential due to this charge density and determine all the nonvanishing multipole moments. Write down the potential at large distances as a finite expansion in Legendre polynomials.

Rewrite the charge density

$$\rho(\mathbf{r}) = \frac{1}{64\pi} \frac{r^2}{e^r} \sin^2 \theta = \frac{1}{64\pi} \frac{r^2}{e^r} (1 - \cos^2 \theta) = \frac{1}{96\pi} \frac{r^2}{e^r} [P_0(\cos \theta) - P_2(\cos \theta)].$$

This charge density is not so “localized,” thus a multipole expansion of the potential is valid only at large distance. Since this charge density is azimuthally symmetric, we can foresee that only the $m = 0$ multipole moments $q_{\ell 0}$ are nonvanishing.

(a) With Eq. (4.3) in the context, the multipole moments are

$$\begin{aligned} q_{\ell m} &= \int Y_{\ell m}^*(\theta, \phi) r^\ell \rho(\mathbf{r}) d^3 r \\ &= \frac{\delta_{0m}}{48} \sqrt{\frac{2\ell+1}{4\pi}} \int_0^\infty \int_0^\pi P_\ell(\cos \theta) r^\ell \frac{r^2}{e^r} [P_0(\cos \theta) - P_2(\cos \theta)] r^2 \sin \theta d\theta dr \\ &= \frac{\delta_{0m}}{48} \sqrt{\frac{2\ell+1}{4\pi}} \int_0^\infty \frac{r^{\ell+4}}{e^r} dr \int_{-1}^1 P_\ell(u) [P_0(u) - P_2(u)] du \end{aligned}$$

$$= \frac{\delta_{0m}}{48} \sqrt{\frac{2\ell+1}{4\pi}} (\ell+4)! \frac{2(\delta_{0\ell} - \delta_{2\ell})}{2\ell+1} = \delta_{0m} \left(\frac{\delta_{0\ell}}{2\sqrt{\pi}} - 3\delta_{2\ell} \sqrt{\frac{5}{\pi}} \right),$$

where $\int_0^\infty \frac{r^n}{e^r} dr = n!$ and the orthogonality condition (3.21) of the Legendre polynomials are used. Hence the nonvanishing multipole moments are $q_{00} = \frac{1}{2\sqrt{\pi}}$, $q_{20} = -3\sqrt{\frac{5}{\pi}}$. And the potential is

$$\begin{aligned} \Phi(\mathbf{x}) &= \frac{1}{4\pi\epsilon_0} \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} \frac{4\pi}{2\ell+1} q_{\ell m} \frac{Y_{\ell m}}{r^{\ell+1}} = \frac{1}{2\sqrt{\pi}\epsilon_0} \frac{Y_{00}}{r} - \frac{3}{\sqrt{5\pi}\epsilon_0} \frac{Y_{20}}{r^3} \\ &= \frac{1}{4\pi\epsilon_0 r} \left[P_0(\cos\theta) - \frac{6}{r^2} P_2(\cos\theta) \right], \quad r \gg 1. \end{aligned}$$

Elementary Treatment of Electrostatics with Ponderable Media

- Much of electrostatics concerns itself with charges and fields in ponderable media whose respective electric responses must be taken into account.
- When an averaging is made of the homogeneous equation $\nabla \times \mathbf{E}_{\text{micro}} = 0 \Rightarrow \nabla \times \mathbf{E} = 0 \Rightarrow$ the electric field is still derivable from a potential
- If an electric field is applied to a medium, the molecular charge density in the medium will be distorted. The multipole moments will be different from what they were in the absence of the field. The dominant molecular multipole with the applied fields is the dipole.

$$\mathbf{P}(\mathbf{r}) = \sum N_i \langle \mathbf{p}_i \rangle \Leftarrow \text{the electric polarization (dipole moment per unit volume)}$$

- If the molecules have a net charge and there is macroscopic excess or free charge, the charge density at the macroscopic level is

$$\rho(\mathbf{r}) = \sum N_i \langle e_i \rangle + \rho_{\text{excess}} \Leftarrow \langle e_i \rangle = 0 \text{ usually} \Rightarrow \rho(\mathbf{r}) \approx \rho_{\text{excess}}$$

- If we now look at the medium from a macroscopic point of view, without higher macroscopic multipole moment densities, the potential caused in ΔV is

$$\Delta \Phi(\mathbf{r}, \mathbf{r}') = \frac{1}{4 \pi \epsilon_0} \left(\frac{\rho(\mathbf{r}')}{\mathbf{r}} \Delta V + \mathbf{P}(\mathbf{r}') \cdot \frac{\hat{\mathbf{r}}}{\mathbf{r}^2} \Delta V \right) \Leftarrow \mathbf{r} \notin \Delta V$$

$$\text{where } \vec{\mathbf{r}} = \mathbf{r} - \mathbf{r}', \quad \mathbf{r} = |\vec{\mathbf{r}}|, \quad \hat{\mathbf{r}} = \frac{\vec{\mathbf{r}}}{\mathbf{r}}$$

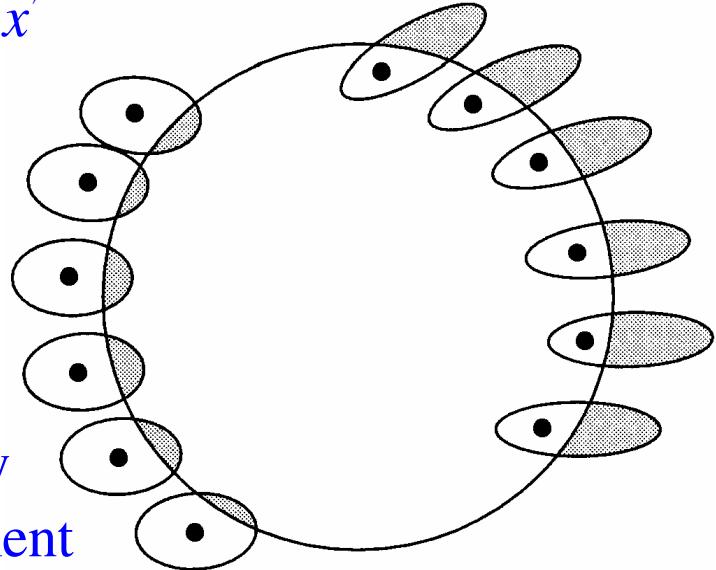
$$\Rightarrow \Phi(\mathbf{r}, \mathbf{r}') = \frac{1}{4\pi\epsilon_0} \int \left(\frac{\rho(\mathbf{r}')}{\mathbf{r}} + \mathbf{P}(\mathbf{r}') \cdot \nabla' \frac{1}{\mathbf{r}} \right) d^3 x'$$

$$= \frac{1}{4\pi\epsilon_0} \int \frac{\rho(\mathbf{r}') - \nabla' \cdot \mathbf{P}(\mathbf{r}')}{\mathbf{r}} d^3 x'$$

$$\Rightarrow \nabla \cdot \mathbf{E} = \frac{\rho - \nabla \cdot \mathbf{P}}{\epsilon_0} \quad \Leftarrow \quad \mathbf{E} = -\nabla \Phi$$

$\rho - \nabla \cdot \mathbf{P}$: effective charge density

$$\Rightarrow \nabla \cdot \mathbf{D} = \rho \quad \Leftarrow \quad \mathbf{D} \equiv \epsilon_0 \mathbf{E} + \mathbf{P} \quad \text{electric displacement}$$



- The divergence of \mathbf{P} in the effective charge density comes from that if the polarization is nonuniform there can be a net increase or decrease of charge within any small volume.
- Assume the response of the system to an applied field is *linear* and the medium is *isotropic* $\Rightarrow \mathbf{P} = \epsilon_0 \chi_e \mathbf{E} \Leftarrow \chi_e$: electric susceptibility
- $\mathbf{D} = \epsilon \mathbf{E} \Leftarrow \epsilon = \epsilon_0 (1 + \chi_e) \Rightarrow \epsilon_r \equiv \frac{\epsilon}{\epsilon_0} = 1 + \chi_e$: dielectric constant $\Rightarrow \mathbf{P} = (\epsilon - \epsilon_0) \mathbf{E}$
- $\nabla \cdot \mathbf{E} = \frac{\rho}{\epsilon}$ for a uniform dielectric $\Leftarrow \epsilon$ is independent of position
- All problems in the medium are reduced to those earlier ones, except that the electric fields produced by given charges are reduced by a factor ϵ_r^{-1} . The reduction comes from a polarization of the atoms that produce fields in opposition to that of the given charge.

- If there are different media juxtaposed, we must consider the boundary conditions on \mathbf{D} and \mathbf{E} at the interfaces between media

$$\begin{aligned} (\mathbf{D}_2 - \mathbf{D}_1) \cdot \hat{\mathbf{n}}_{21} &= \sigma \\ (\mathbf{E}_2 - \mathbf{E}_1) \times \hat{\mathbf{n}}_{21} &= 0 \end{aligned} \quad \leftarrow \quad \begin{array}{l} \sigma : \text{macroscopic surface-charge density} \\ \text{on the boundary surface} \end{array}$$

$$\begin{aligned} \Rightarrow D_2^\perp - D_1^\perp &= \sigma \\ \mathbf{E}_2^\parallel &= \mathbf{E}_1^\parallel \end{aligned}$$

- The boundary conditions are valid for time-varying as well as static fields.

Polarization Charges

- For polarized material with polarization \mathbf{P} , we would like to know what the field is produced by this object.

- For a single dipole \mathbf{p} : $\Phi(\mathbf{r}) = \frac{1}{4\pi\epsilon_0} \frac{\mathbf{p} \cdot \hat{\mathbf{r}}}{r^2}$

- For dipole moment $d\mathbf{p} = \mathbf{P} d\tau'$ in each volume element $d\tau'$, the total potential

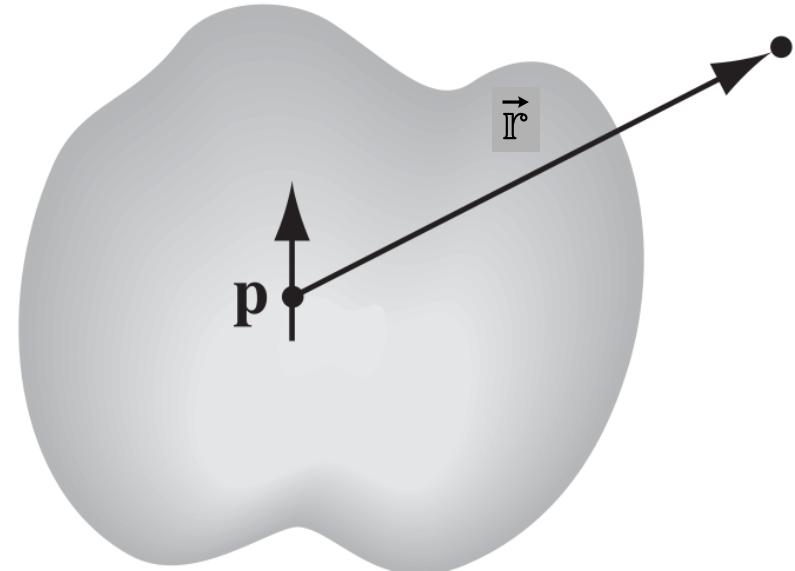
$$\Phi(\mathbf{r}) = \frac{1}{4\pi\epsilon_0} \int \frac{\hat{\mathbf{r}} \cdot d\mathbf{p}}{r^2} = \frac{1}{4\pi\epsilon_0} \int_V \frac{\hat{\mathbf{r}} \cdot \mathbf{P}(\mathbf{r}')}{r^2} d\tau' \Leftarrow \hat{\mathbf{r}} = \mathbf{r} - \mathbf{r}' \Leftarrow \mathbf{r}': \text{source coordinates}$$

$$= \frac{1}{4\pi\epsilon_0} \int_V \mathbf{P} \cdot \nabla' \frac{1}{r} d\tau' \Leftarrow \frac{\hat{\mathbf{r}}}{r^2} = \nabla' \frac{1}{r} = -\nabla \frac{1}{r} \Downarrow d\mathbf{a}' = \hat{\mathbf{n}} d\mathbf{a}'$$

$$= \frac{1}{4\pi\epsilon_0} \left(\int_V \nabla' \cdot \frac{\mathbf{P}}{r} d\tau' - \int_V \frac{\nabla' \cdot \mathbf{P}}{r} d\tau' \right) = \frac{1}{4\pi\epsilon_0} \left(\oint_S \frac{\mathbf{P}}{r} \cdot d\mathbf{a}' - \int_V \frac{\nabla' \cdot \mathbf{P}}{r} d\tau' \right)$$

$$= \frac{1}{4\pi\epsilon_0} \oint_S \frac{\sigma_{\text{pol}}}{r} d\mathbf{a}' + \frac{1}{4\pi\epsilon_0} \int_V \frac{\rho_{\text{pol}}}{r} d\tau' \Leftarrow \sigma_{\text{pol}} \equiv \mathbf{P} \cdot \hat{\mathbf{n}}, \quad \rho_{\text{pol}} \equiv -\nabla \cdot \mathbf{P}$$

- The potential (and hence also the field) of a polarized object is the same as that produced by a volume charge density $\rho_{\text{pol}} = -\nabla \cdot \mathbf{P}$ plus a surface charge density $\sigma_{\text{pol}} = \mathbf{P} \cdot \hat{\mathbf{n}}$

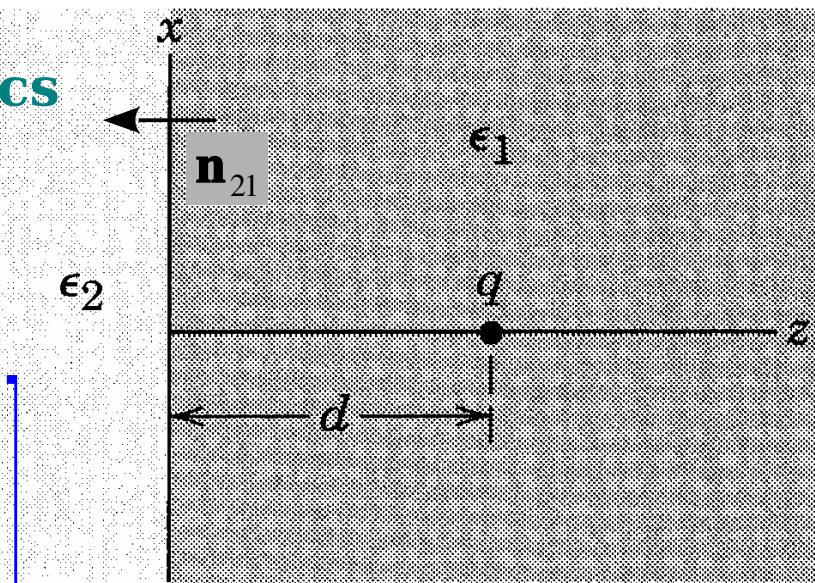


Boundary-Value Problems with Dielectrics

- Find the appropriate solution to the equations

$$\begin{aligned} \epsilon_1 \nabla \cdot \mathbf{E} &= \rho, \quad z > 0 \quad \& \quad \nabla \times \mathbf{E} = 0 \quad \text{everywhere} \\ \epsilon_2 \nabla \cdot \mathbf{E} &= 0, \quad z < 0 \end{aligned}$$

& the boundary condition $\lim_{z \rightarrow 0^+} \begin{bmatrix} \epsilon_1 E_z \\ E_x \\ E_y \end{bmatrix} = \lim_{z \rightarrow 0^-} \begin{bmatrix} \epsilon_2 E_z \\ E_x \\ E_y \end{bmatrix}$



- $\nabla \times \mathbf{E} = 0$ everywhere $\Rightarrow \mathbf{E}$ is derivable from a potential $\Rightarrow \mathbf{E} = -\nabla \Phi$

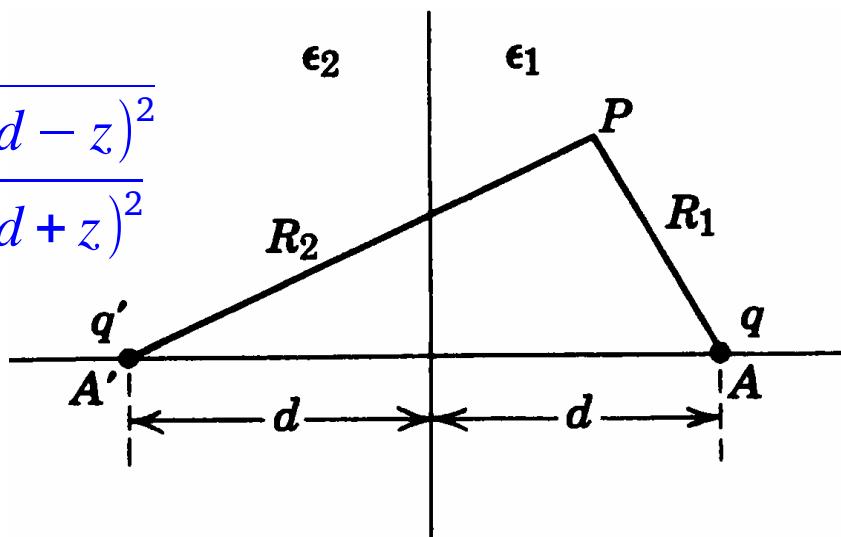
- Use the image method

$$\Phi = \frac{1}{4\pi\epsilon_1} \left(\frac{q}{R_1} + \frac{q'}{R_2} \right), \quad z > 0 \quad \leftarrow \begin{aligned} R_1 &= \sqrt{\rho^2 + (d-z)^2} \\ R_2 &= \sqrt{\rho^2 + (d+z)^2} \end{aligned}$$

$$\Phi = \frac{1}{4\pi\epsilon_2} \frac{q''}{R_1}, \quad z < 0$$

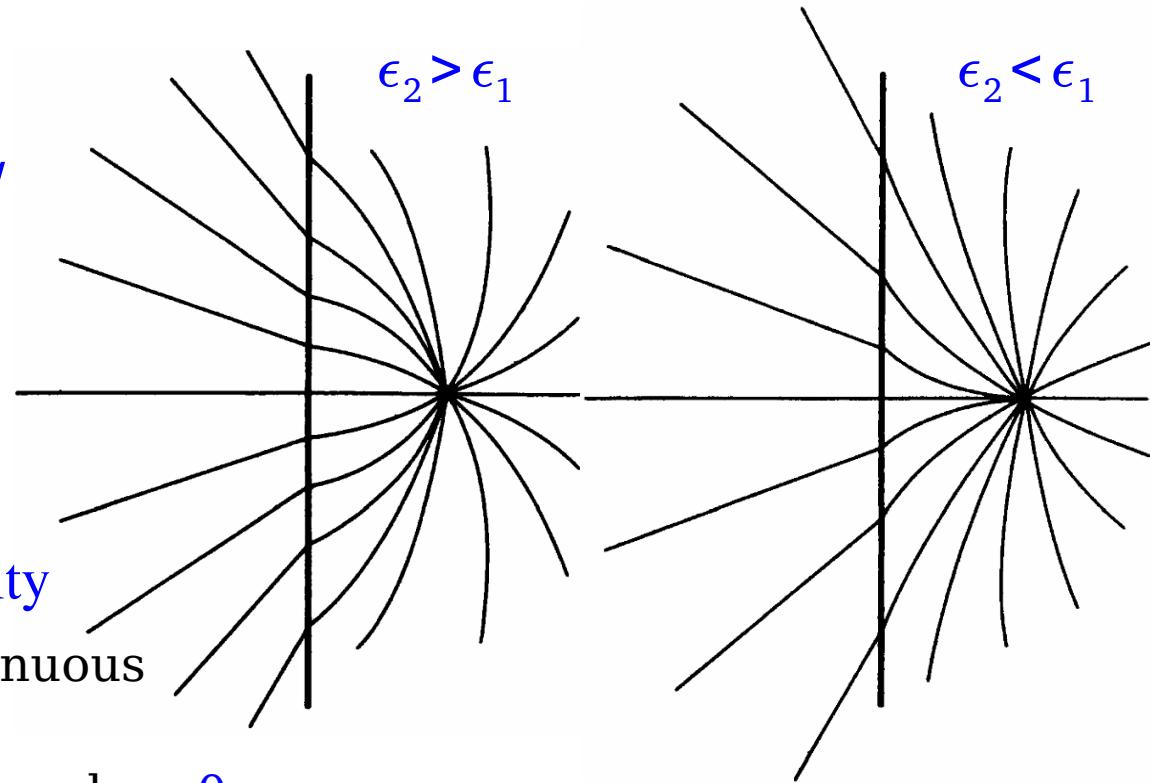
$$\frac{\partial}{\partial z} \frac{1}{R_1|_{z=0}} = - \frac{\partial}{\partial z} \frac{1}{R_2|_{z=0}} = \frac{d}{\sqrt{(\rho^2 + d^2)^3}}$$

$$\frac{\partial}{\partial \rho} \frac{1}{R_1|_{z=0}} = - \frac{\partial}{\partial \rho} \frac{1}{R_2|_{z=0}} = - \frac{\rho}{\sqrt{(\rho^2 + d^2)^3}}$$



$$\begin{aligned}
 \Rightarrow q - q' &= q'' \Rightarrow q' = -\frac{\epsilon_2 - \epsilon_1}{\epsilon_2 + \epsilon_1} q \\
 \Rightarrow \frac{q + q'}{\epsilon_1} &= \frac{q''}{\epsilon_2} \Rightarrow q'' = 2 \frac{\epsilon_2}{\epsilon_2 + \epsilon_1} q \\
 \Rightarrow \rho_{\text{pol}} &\equiv -\nabla \cdot \mathbf{P} = -\epsilon_0 \chi_e \nabla \cdot \mathbf{E} \\
 &\propto q \delta(z - d)
 \end{aligned}$$

the polarization-charge density



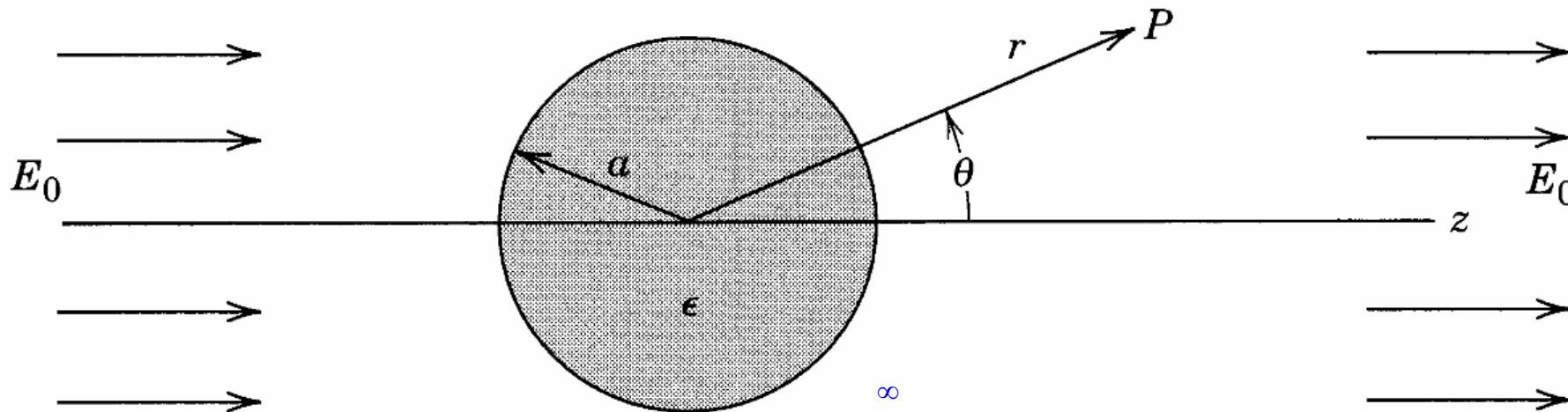
- At the surface, χ_e takes a discontinuous

jump, $\Delta \chi_e = \frac{\epsilon_2 - \epsilon_1}{\epsilon_0}$ as z passes through $z=0$

$$\Rightarrow \sigma_{\text{pol}} = (\mathbf{P}_1 - \mathbf{P}_2) \cdot \hat{\mathbf{n}}_{21} = -\frac{q}{2\pi} \frac{\epsilon_0(\epsilon_2 - \epsilon_1)}{\epsilon_1(\epsilon_2 + \epsilon_1)} \frac{d}{\sqrt{(\rho^2 + d^2)^3}} \quad \leftarrow \quad \begin{aligned} \mathbf{P}_i &= (\epsilon_i - \epsilon_0) \mathbf{E}_i \\ &= (\epsilon_0 - \epsilon_i) \nabla \Phi(0^\pm) \end{aligned}$$

- In the limit $\epsilon_2 \gg \epsilon_1$ the dielectric ϵ_2 behaves much like a conductor in that $\mathbf{E}_2 \rightarrow 0$

$$\Rightarrow \sigma_{\text{pol}} \rightarrow -\frac{q}{2\pi} \frac{\epsilon_0}{\epsilon_1} \frac{d}{\sqrt{(\rho^2 + d^2)^3}} = \frac{\epsilon_0}{\epsilon_1} \sigma_{\text{conducting surface}}$$



$$\Phi_{\text{in}} = \sum_{\ell=0}^{\infty} A_{\ell} r^{\ell} \quad P_{\ell}(\cos \theta) \text{ inside}$$

- Axial symmetry of the geometry

$$\Phi_{\text{out}} = \sum_{\ell=0}^{\infty} \left(B_{\ell} r^{\ell} + \frac{C_{\ell}}{r^{\ell+1}} \right) P_{\ell}(\cos \theta) \text{ outside}$$

- $\Phi(r \rightarrow \infty) \rightarrow -E_0 z = -E_0 r \cos \theta \Rightarrow B_1 = -E_0 \text{ & other } B_{\ell} \text{'s} = 0$

$$\bullet \text{tangential E: } -\frac{1}{a} \frac{\partial \Phi_{\text{in}}}{\partial \theta} \Big|_{r=a} = -\frac{1}{a} \frac{\partial \Phi_{\text{out}}}{\partial \theta} \Big|_{r=a} \Rightarrow \begin{aligned} A_1 &= -E_0 + \frac{C_1}{a^3} \\ A_{\ell} &= \frac{C_{\ell}}{a^{2\ell+1}} \text{ for } \ell \neq 1 \end{aligned}$$

$$\bullet \text{normal D: } -\epsilon \frac{\partial \Phi_{\text{in}}}{\partial r} \Big|_{r=a} = -\epsilon_0 \frac{\partial \Phi_{\text{out}}}{\partial r} \Big|_{r=a} \Rightarrow \begin{aligned} \epsilon_r A_1 &= -E_0 - 2 \frac{C_1}{a^3} \Leftarrow \epsilon_r = \frac{\epsilon}{\epsilon_0} \\ \epsilon_r \ell A_{\ell} &= -(\ell+1) \frac{C_{\ell}}{a^{2\ell+1}} \text{ for } \ell \neq 1 \end{aligned}$$

$$A_1 = -\frac{3}{\epsilon_r + 2} E_0$$

$$\Rightarrow C_1 = \frac{\epsilon_r - 1}{\epsilon_r + 2} a^3 E_0 \quad \Rightarrow$$

$$A_\ell = C_\ell = 0 \text{ for } \ell \neq 1$$

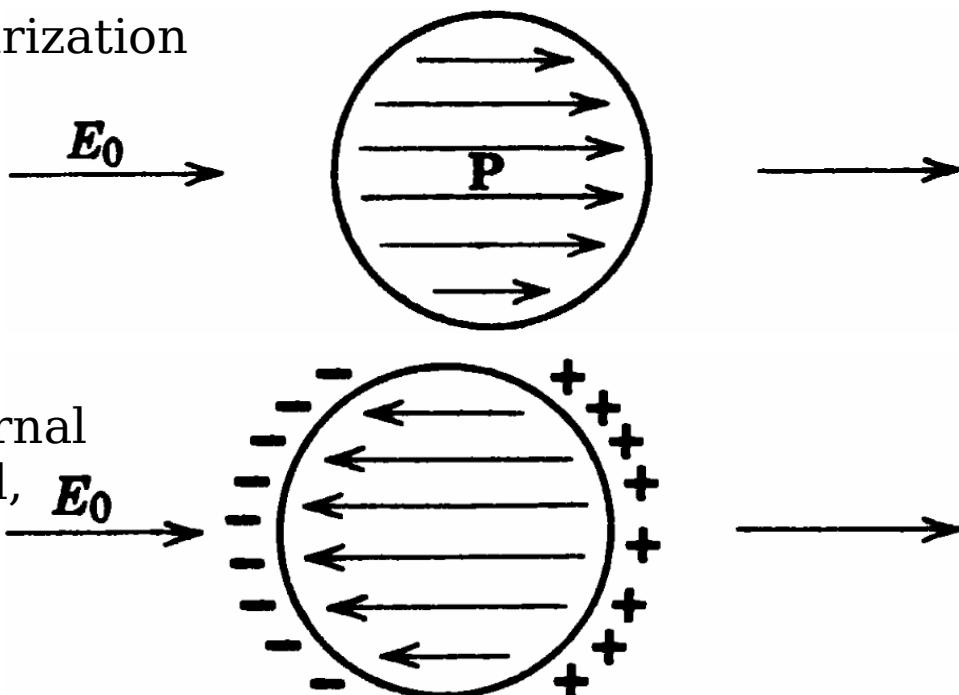
$$\begin{aligned} \Phi_{\text{in}} &= -\frac{3}{\epsilon_r + 2} E_0 r \cos \theta \Rightarrow E_{\text{in}} = \frac{3}{\epsilon_r + 2} E_0 \\ &\Rightarrow E_{\text{in}} < E_0 \text{ if } \epsilon > \epsilon_0 \\ \Phi_{\text{out}} &= -E_0 r \cos \theta + \frac{\epsilon_r - 1}{\epsilon_r + 2} \frac{a^3}{r^2} E_0 \cos \theta \\ &= \frac{p}{4 \pi \epsilon_0 r^3} - E_0 z \Leftarrow p = 4 \pi \epsilon_0 \frac{\epsilon_r - 1}{\epsilon_r + 2} a^3 E_0 \end{aligned}$$

- The dipole moment \mathbf{p} , oriented in the direction of the applied field, can be regarded as the volume integral of the polarization

$$\mathbf{P} = (\epsilon - \epsilon_0) \mathbf{E} = 3 \epsilon_0 \frac{\epsilon_r - 1}{\epsilon_r + 2} \mathbf{E}_0 = \text{constant} \quad \xrightarrow{\mathbf{E}_0}$$

$$\Rightarrow \sigma_{\text{pol}} = \mathbf{P} \cdot \hat{\mathbf{r}} = 3 \epsilon_0 \frac{\epsilon_r - 1}{\epsilon_r + 2} E_0 \cos \theta$$

- This can be thought as producing an internal field directed oppositely to the applied field, \mathbf{E}_0 , so reducing the field inside the sphere.



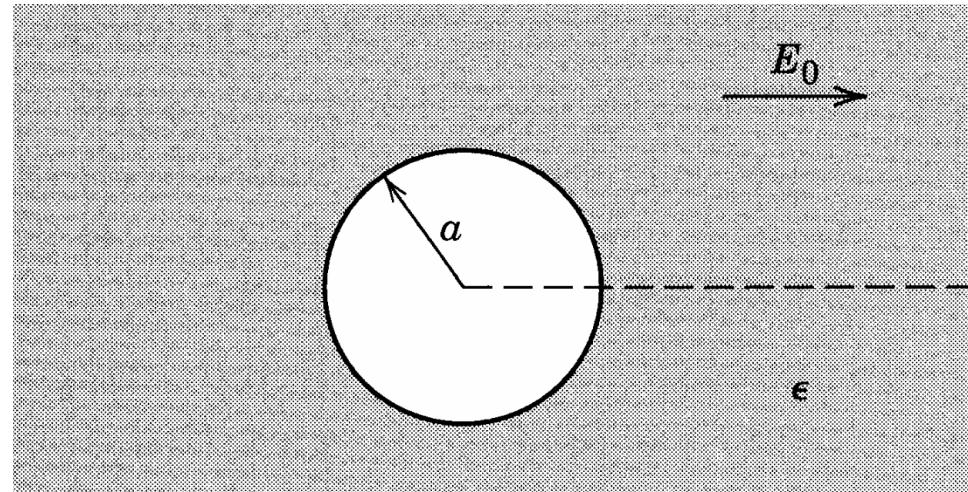
- The problem of a spherical cavity in a dielectric medium and with an applied electric field parallel to the z axis can be handled in exactly the same way as the dielectric sphere.

- The results for the cavity can be obtained from those of the sphere by the

$$\text{replacement } \epsilon_r \rightarrow \frac{1}{\epsilon_r} \iff \epsilon_r = \frac{\epsilon}{\epsilon_0}$$

$$E_{\text{in}} = \frac{3\epsilon_r}{2\epsilon_r + 1} E_0 \Rightarrow E_{\text{in}} > E_0 \quad \text{if} \quad \epsilon > \epsilon_0 \Rightarrow p = -4\pi\epsilon_0 \frac{\epsilon_r - 1}{2\epsilon_r + 1} a^3 E_0$$

the dipole orients oppositely to the applied field



Molecular Polarizability and Electric Susceptibility

- In dense media the polarization of neighboring molecules gives rise to an internal field \mathbf{E}_i in addition to the average macroscopic field \mathbf{E} , so that the total field at the molecule is $\mathbf{E} + \mathbf{E}_i$ and $\mathbf{E}_i = \mathbf{E}_{\text{near}} - \mathbf{E}_P$.
- Inside some macroscopically small, but microscopically large, volume V we subtract out the smoothed macroscopic equivalent of the nearby molecular contributions (\mathbf{E}_P) and replace it with the correctly evaluated contribution (\mathbf{E}_{near}). This difference is the extra internal field \mathbf{E}_i .
- For the volume chosen to be a sphere, the total dipole moment inside is $\mathbf{p} = \mathbf{P} V = \frac{4 \pi R^3}{3} \mathbf{P} \Leftarrow \text{assume } V \text{ is so small that } \mathbf{P} \text{ is essentially constant}$

$$\int_{r < R} \mathbf{E} d^3 x = -\frac{\mathbf{p}}{3 \epsilon_0} \Rightarrow \mathbf{E}_P = \frac{3}{4 \pi R^3} \int_{r < R} \mathbf{E} d^3 x = -\frac{\mathbf{P}}{3 \epsilon_0} \Rightarrow \mathbf{E}_i = \frac{\mathbf{P}}{3 \epsilon_0} + \mathbf{E}_{\text{near}}$$

- For atoms in a simple cubic lattice \mathbf{E}_{near} vanishes at any lattice site (by Lorentz).

Proof: $\mathbf{E}(0) = \sum_{i j k} \frac{3(\mathbf{p} \cdot \mathbf{r}_{ijk}) \mathbf{r}_{ijk} - \mathbf{r}_{ijk}^2 \mathbf{p}}{4 \pi \epsilon_0 r_{ijk}^5} \Leftarrow \mathbf{r}_{ijk} = (i a, j a, k a)$

$$\Rightarrow E_1 = \sum_{i j k} \frac{3(i^2 p_1 + i \cancel{j} p_2 + i \cancel{k} p_3) - (i^2 + j^2 + k^2) p_1}{4 \pi \epsilon_0 a^3 \sqrt{(i^2 + j^2 + k^2)^5}}$$

$$\sum_{i j k} \frac{i^2}{\sqrt{(i^2 + j^2 + k^2)^5}} = \sum_{i j k} \frac{j^2}{\sqrt{(i^2 + j^2 + k^2)^5}} = \sum_{i j k} \frac{k^2}{\sqrt{(i^2 + j^2 + k^2)^5}}$$

(by symmetry)

$$\Rightarrow E_1 = p_1 \sum_{i j k} \frac{3 i^2 - (i^2 + j^2 + k^2)}{\sqrt{(i^2 + j^2 + k^2)^5}} = 0 = E_2 = E_3$$

$$\Rightarrow \mathbf{E}_{\text{near}} = 0 \text{ for a simple cubic lattice}$$

- It seems plausible that $\mathbf{E}_{\text{near}} = 0$ also for completely random situations. Although it is not true, it is a good working assumption that $\mathbf{E}_{\text{near}} \approx 0$ for most materials.

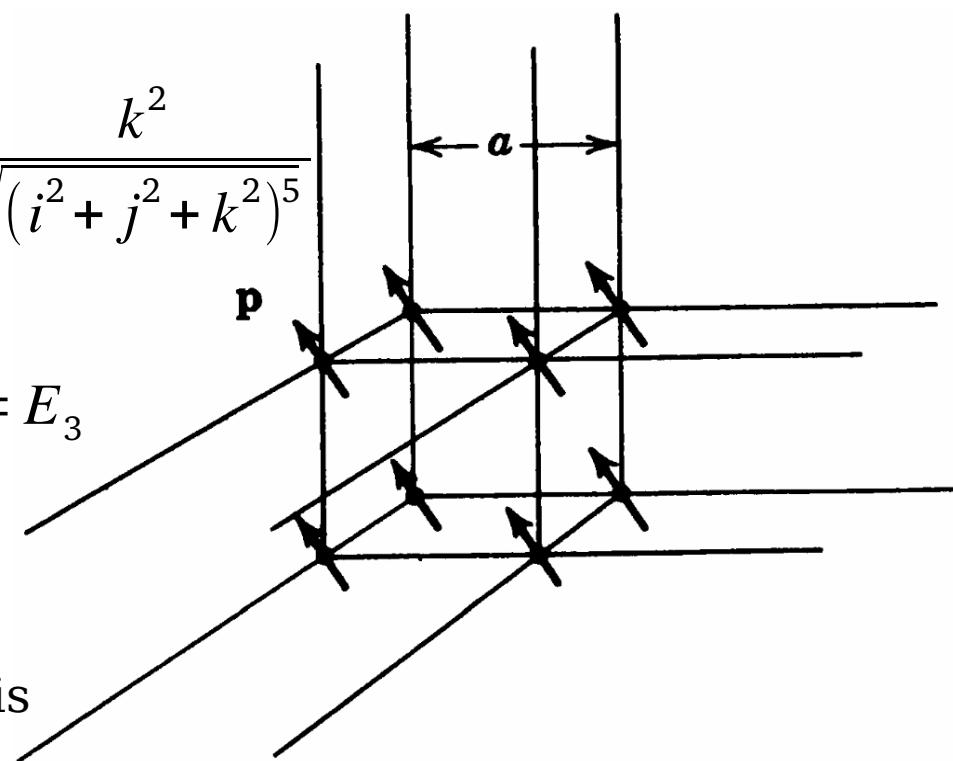
- The polarization vector $\mathbf{P} = N \langle \mathbf{p}_{\text{mol}} \rangle \Leftarrow \langle \mathbf{p}_{\text{mol}} \rangle$: average dipole moment of molecules

- This dipole moment is approximately proportional to the electric field acting on the molecule.

$$\langle \mathbf{p}_{\text{mol}} \rangle = \epsilon_0 \gamma_{\text{mol}} (\mathbf{E} + \mathbf{E}_i) \Leftarrow \gamma_{\text{mol}}: \text{molecular polarizability}$$

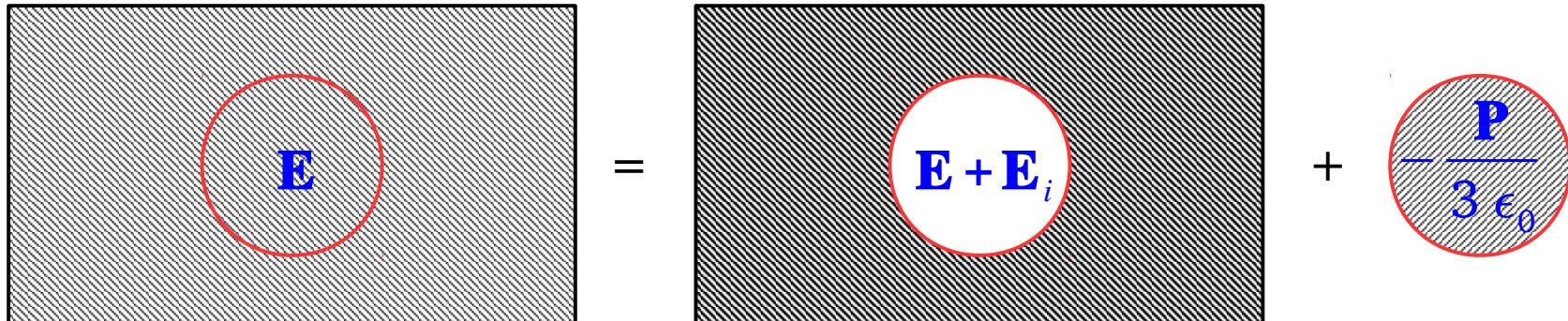
$$\Rightarrow \mathbf{P} = N \gamma_{\text{mol}} \left(\epsilon_0 \mathbf{E} + \frac{1}{3} \mathbf{P} \right) \text{ for } \mathbf{E}_{\text{near}} = 0 \Rightarrow \chi_e = \frac{3 N \gamma_{\text{mol}}}{3 - N \gamma_{\text{mol}}} \Leftarrow \mathbf{P} = \epsilon_0 \chi_e \mathbf{E}$$

$$\Rightarrow \gamma_{\text{mol}} = \frac{3}{N} \frac{\epsilon - \epsilon_0}{\epsilon + 2 \epsilon_0} \text{ Clausius-Mossotti equation} \Leftarrow \epsilon = \epsilon_0 (1 + \chi_e) = \epsilon_r \epsilon_0$$



Atomic/Molecular Polarizability and Electric Susceptibility

- Consider the relation between mircoscopically molecular properties, ie, the atomic/molecular polarizability γ_{mol} , and the macroscopically defined parameter, the electric susceptibility χ_e :



$$\mathbf{P} = \epsilon_0 \chi_e \mathbf{E}, \quad \frac{\mathbf{P}}{N} \Leftarrow \mathbf{p} = \epsilon_0 \gamma_{\text{mol}} (\mathbf{E} + \mathbf{E}_i) \Rightarrow \mathbf{E} = (\mathbf{E} + \mathbf{E}_i) + \left(-\frac{\mathbf{P}}{3 \epsilon_0} \right)$$

$$\Rightarrow \mathbf{E}_i = \frac{\mathbf{P}}{3 \epsilon_0} \Rightarrow \frac{\mathbf{P}}{\epsilon_0 \chi_e} = \frac{\mathbf{P}}{N \epsilon_0 \gamma_{\text{mol}}} - \frac{\mathbf{P}}{3 \epsilon_0} \Rightarrow \chi_e = \epsilon_r - 1 = \frac{3 N \gamma_{\text{mol}}}{3 - N \gamma_{\text{mol}}}$$

$$\Rightarrow \gamma_{\text{mol}} = \frac{3}{N} \frac{\epsilon_r - 1}{\epsilon_r + 2} \quad \text{Clausius-Mossotti equation}$$

- The relation holds best for dilute substances such as gases. For liquids & solids, the equation is only approximately valid, especially if the dielectric constant is large.

Models for the Molecular Polarizability

- The polarization of a collection of atoms or molecules can arise in 2 ways:
 1. the applied field distorts the charge distributions and so produces an induced dipole moment in each molecule;
 2. the applied field tends to line up the initially randomly oriented permanent dipole moments of the molecules.
- To estimate the induced moments we consider a simple model of harmonically bound charges (electrons & ions). Each charge e is bound under a restoring force

$$-e \mathbf{E} \leftarrow \mathbf{F} = -m \omega_0^2 \mathbf{r} \Rightarrow \mathbf{p}_{\text{mol}} = e \mathbf{r} = \frac{e^2}{m \omega_0^2} \mathbf{E} \quad (2)$$

$$\Rightarrow \gamma = \frac{e^2}{\epsilon_0 m \omega_0^2} \Rightarrow \gamma_{\text{mol}} = \frac{1}{\epsilon_0} \sum \frac{e_j^2}{m_j \omega_j^2}$$

- Since γ has the dimensions of a volume, its magnitude must be of the order of molecular dimensions or less, namely $\gamma_{\text{el}} \leq 10^{-29} \text{ m}^3$.
- Or, the binding frequencies of electrons in atoms must be of the order of light frequencies $\lambda_{\text{light}} \sim 3000 \text{ \AA} \Rightarrow \omega \simeq 6 \times 10^{15} \text{ s}^{-1} \Rightarrow \gamma_{\text{el}} \sim \frac{e^2}{\epsilon_0 m \omega^2} \sim 0.88 \times 10^{-29} \text{ m}^3$ consistent with the molecular volume estimate.

- For gases $N = 2.7 \times 10^{25} \text{ m}^{-3} \Rightarrow \chi_e \leq 10^{-3} \Rightarrow \frac{\epsilon}{\epsilon_0} \leq 1 + 10^{-3}$
 $\Rightarrow \epsilon_{\text{air}} = 1.00054 \epsilon_0, \epsilon_{\text{NH}_3} = 1.0072 \epsilon_0, \epsilon_{\text{CH}_3\text{OH}} = 1.0057 \epsilon_0, \epsilon_{\text{He}} = 1.000068 \epsilon_0$
- For solid or liquid dielectrics: $N = 10^{28} - 10^{29} / \text{m}^3 \Rightarrow \chi_e \sim 10^{\pm 1}$
- Thermal agitation of the molecules could modify the molecular polarizability.
- The probability distribution of particles in phase space for classical systems is

$$\text{Boltzmann factor } f(H) = e^{-\frac{H}{kT}} \Rightarrow \langle p_{\text{mol}} \rangle = \frac{\int e z f(H) d^3 x d^3 p}{\int f(H) d^3 x d^3 p}$$

- For a harmonically bound charge with an applied field in the \hat{z} direction

$$H = \frac{\mathbf{p}^2}{2m} + \frac{m}{2} \omega_0^2 \mathbf{r}^2 - e E z = \frac{\mathbf{p}^2}{2m} + \frac{m}{2} \omega_0^2 \mathbf{r}'^2 - \frac{e^2 E^2}{2m \omega_0^2} \Leftarrow \mathbf{r}' = \mathbf{r} - \frac{e E}{m \omega_0^2} \hat{\mathbf{z}}$$

$$\Rightarrow \langle p_{\text{mol}} \rangle = \frac{\int \left(\cancel{e/z'} + \frac{e^2 E}{m \omega_0^2} \right) f(H) d^3 x' d^3 p}{\int f(H) d^3 x' d^3 p} = \frac{e^2}{m \omega_0^2} E \Leftarrow \text{same as (2)}$$

- The 2nd type of polarizability is that caused by the partial orientation of random permanent dipole moments. The orientation polarization is important in "polar" substances such as HCl and H₂O.

- With an applied field there is a tendency to line up along the field in the configuration of lowest energy, thus there will be an average dipole moment.

- The Hamiltonian of a molecule $H = H_0 - \mathbf{p}_0 \cdot \mathbf{E} = H_0 - p_0 E \cos \theta$

$$\Rightarrow \langle p_{\text{mol}} \rangle = \frac{\int p_0 \cos \theta e^{\frac{\mathbf{p}_0 \cdot \mathbf{E}}{kT}} d\Omega}{\int e^{\frac{\mathbf{p}_0 \cdot \mathbf{E}}{kT}} d\Omega} \simeq \frac{1}{3} \frac{p_0^2}{kT} E \quad \begin{array}{l} \text{by expanding the exponentials} \\ \text{for } \frac{p_0 E}{kT} \ll 1 \end{array}$$

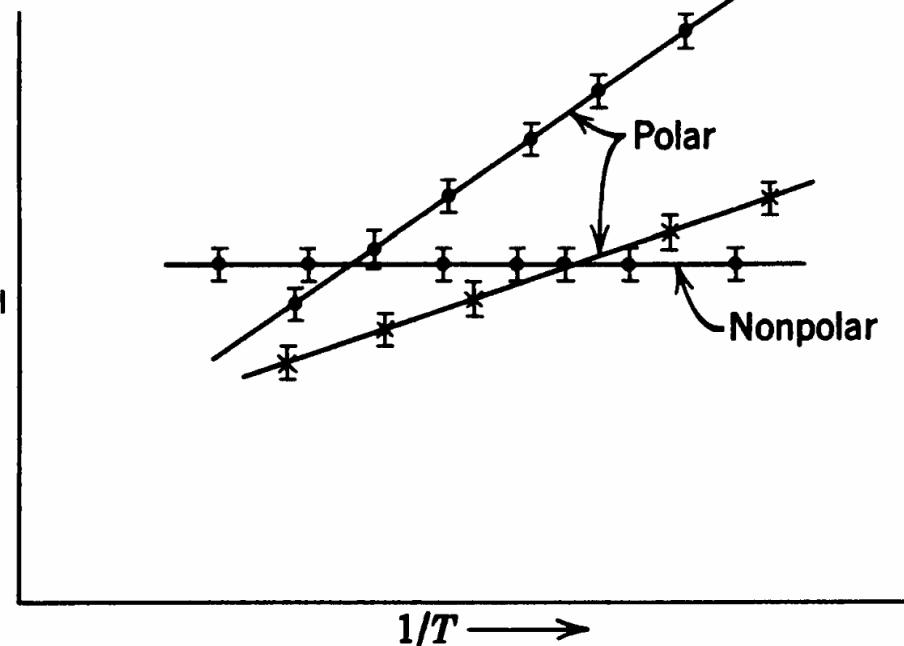
$$e^{\frac{\mathbf{p}_0 \cdot \mathbf{E}}{kT}} \approx 1 + \frac{p_0}{kT} E \cos \theta \Rightarrow \int e^{\frac{\mathbf{p}_0 \cdot \mathbf{E}}{kT}} d\Omega \approx 2\pi \int_{-1}^{+1} \left(1 + \frac{p_0}{kT} E \cos \theta \right) d\cos \theta = 4\pi$$

$$\Rightarrow \int p_0 \cos \theta e^{\frac{\mathbf{p}_0 \cdot \mathbf{E}}{kT}} d\Omega \approx 2\pi p_0 \int_{-1}^{+1} \left(\cos \theta + \frac{p_0}{kT} E \cos^2 \theta \right) d\cos \theta = \frac{4\pi}{3} \frac{p_0^2}{kT} E$$

- In general both types of polarization, induced and orientation, are present

$$\gamma_{\text{mol}} \simeq \gamma_i + \frac{1}{3\epsilon_0} \frac{p_0^2}{kT} \Rightarrow \text{in the form } a + \frac{b}{T}$$

Selected problems: 1, 9, 10, 13



Water vapor is a polar gas whose dielectric constant exhibits an appreciable temperature dependence. The following table gives experimental data on this effect. Assuming that water vapor obeys the ideal gas law, calculate the molecular polarizability as a function of inverse temperature and plot it. From the slope of the curve, deduce a value for the permanent dipole moment of the H_2O molecule (express the dipole moment in coulomb-meters). [Problem 4.12]

T(K)	Pressure (cm Hg)	$(\epsilon/\epsilon_0 - 1) \times 10^5$
393	56.49	400.2
423	60.93	371.7
453	65.34	348.8
483	69.75	328.7

The ideal gas law is $PV = nN_A kT$, where N_A is Avogadro's number and $k = 1.38 \times 10^{-23} \text{ J/K}$ is the Boltzmann constant. Thus $N = nN_A/V = P/kT$. According to the Clausius-Mossotti relation $\gamma_{\text{mol}} = \frac{3}{N} \frac{\epsilon/\epsilon_0 - 1}{\epsilon/\epsilon_0 + 2} = \frac{3kT}{P} \frac{\epsilon/\epsilon_0 - 1}{\epsilon/\epsilon_0 + 2}$. The corresponding γ_{mol} and $1/T$ are listed in the following table:

T(K)	P/10 ⁴ (N/m ²)	($\epsilon/\epsilon_0 - 1$) × 10 ⁵	$\gamma_{\text{mol}} \times 10^{28}$ (m ³)	10 ³ /T
393	7.531	400.2	2.878	2.544
423	8.123	371.7	2.668	2.364
453	8.711	348.8	2.500	2.208
483	9.299	328.7	2.353	2.070

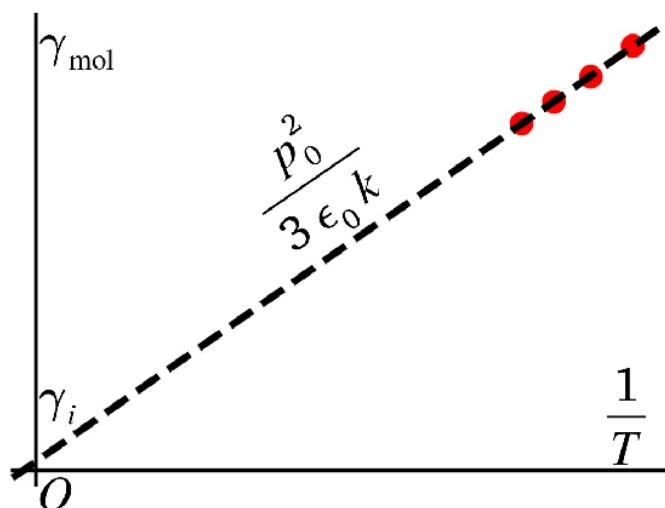


Fig. 4.5 Problem 4.12

From Eq. (4.82), γ_{mol} is expected to have a linear relation with $1/T$, i.e., $\gamma_{\text{mol}} \simeq \gamma_i + \frac{1}{3\epsilon_0} \frac{p_0^2}{kT}$. From the data curve (or with the least-square method), see Fig. 4.5, we can deduce the slope $\frac{p_0^2}{3\epsilon_0 k} = 1.106 \times 10^{-25} \text{ m}^3 \cdot \text{K}$. (And the induced molecular polarizability $\gamma_i = 5.982 \times 10^{-30} \text{ m}^3$.) This leads to $p_0 = 6.367 \times 10^{-30} \text{ C} \cdot \text{m}$.

Electrostatic Energy in Dielectric Media

- $W = \frac{1}{2} \int \rho(\mathbf{r}) \Phi(\mathbf{r}) d^3 x$ for the energy due to a charge density and a potential

cannot in general be used in our macroscopic description of dielectric media because work is done in a dielectric media not only to bring real (macroscopic) charge into position, but also to produce polarization in the medium.

- Consider a small change in the energy due to some sort of change in the macroscopic charge density existing in all space

$$\delta W = \int \delta \rho(\mathbf{r}) \Phi(\mathbf{r}) d^3 x = \int \mathbf{E} \cdot \delta \mathbf{D} d^3 x \quad \leftarrow \quad \mathbf{E} = -\nabla \Phi \\ \delta \rho = \nabla \cdot \delta \mathbf{D} \quad \leftarrow \quad \nabla \cdot \mathbf{D} = \rho$$

$$\Rightarrow W = \int d^3 x \int_0^D \mathbf{E} \cdot \delta \mathbf{D}$$

$$2 \mathbf{E} \cdot \delta \mathbf{D} = \delta (\mathbf{E} \cdot \mathbf{D}) \quad \begin{matrix} \text{if the medium} \\ \text{is linear} \end{matrix} \quad \Rightarrow \quad W = \frac{1}{2} \int \mathbf{E} \cdot \mathbf{D} d^3 x = \frac{1}{2} \int \rho \Phi d^3 x$$

- $W = \frac{1}{2} \int \rho(\mathbf{r}) \Phi(\mathbf{r}) d^3 x$ is valid macroscopically only if the behavior is linear.

- An interesting problem is the change in energy when a dielectric object with a linear response is placed in an electric field whose sources are fixed.

- The initial electrostatic energy $W_0 = \frac{1}{2} \int \mathbf{E}_0 \cdot \mathbf{D}_0 d^3 x \quad \leftarrow \quad \mathbf{D}_0 = \epsilon_0 \mathbf{E}_0$

- Introduce a dielectric object into the field $W_1 = \frac{1}{2} \int \mathbf{E} \cdot \mathbf{D} d^3 x \quad \leftarrow \quad \mathbf{D} = \epsilon \mathbf{E}$

$$\begin{aligned}
W &= \int \frac{\mathbf{E} \cdot \mathbf{D} - \mathbf{E}_0 \cdot \mathbf{D}_0}{2} d^3 x = \int \frac{\mathbf{E} \cdot \mathbf{D}_0 - \mathbf{E}_0 \cdot \mathbf{D}}{2} d^3 x + \int \frac{\mathbf{E} + \mathbf{E}_0}{2} \cdot (\mathbf{D} - \mathbf{D}_0) d^3 x \\
&\int (\mathbf{E} + \mathbf{E}_0) \cdot (\mathbf{D} - \mathbf{D}_0) d^3 x \\
&= - \int \nabla \Psi \cdot (\mathbf{D} - \mathbf{D}_0) d^3 x \Leftarrow \mathbf{E} + \mathbf{E}_0 = - \nabla \Psi \Leftarrow \nabla \times (\mathbf{E} + \mathbf{E}_0) = 0 \\
&= \int \Psi \nabla \cdot (\mathbf{D} - \mathbf{D}_0) d^3 x = 0 \Leftarrow \nabla \cdot (\mathbf{D} - \mathbf{D}_0) = 0 \Leftarrow \rho_0 \text{ is fixed} \\
&\Rightarrow W = \int \frac{\mathbf{E} \cdot \mathbf{D}_0 - \mathbf{E}_0 \cdot \mathbf{D}}{2} d^3 x = - \int_V \frac{\epsilon - \epsilon_0}{2} \mathbf{E} \cdot \mathbf{E}_0 d^3 x \quad (3) \quad \Rightarrow w = -\frac{1}{2} \mathbf{P} \cdot \mathbf{E}_0 \\
&= - \int_V \frac{\mathbf{P} \cdot \mathbf{E}_0}{2} d^3 x \Leftarrow \mathbf{P} = (\epsilon - \epsilon_0) \mathbf{E} \quad (4)
\end{aligned}$$

- The factor $\frac{1}{2}$ in the expression is because it represents the energy density of a polarizable dielectric in an external field, rather than a permanent dipole.
- (3) & (4) show that a dielectric body will tend to move toward regions of increasing field \mathbf{E}_0 provided $\epsilon > \epsilon_0$.
- Imagine a small generalized displacement of the body, then there will be a change in the energy, and this means that there is a force acting on the body:

$$F_\xi = - \frac{\partial W}{\partial \xi} \Big|_{Q=\text{const}}$$

- In practical situations the electric fields are often produced with *fixed potentials*.
- For linear media $W = \int \frac{\rho(\mathbf{r})\Phi(\mathbf{r})}{2} d^3x \Rightarrow \delta W = \int \frac{\rho\delta\Phi + \Phi\delta\rho}{2} d^3x \quad (5)$
- If the dielectric properties are not changed, the 2 terms in (5) are equal. If the dielectric properties are altered, the 2 contributions are not necessarily the same.
- The reason for the difference is the polarization charge. The change in dielectric properties can be thought of as a change in the polarization-charge density.
- The process of altering the dielectric properties with fixed potentials can be viewed as taking place in 2 steps. In the 1st step the dielectric properties are

changed with the charges held fixed: $\delta W_1 = \frac{1}{2} \int \rho \delta \Phi_1 d^3x$

- In the 2nd step the potentials are restored to the original values. There will be a flow of charge to change the potential $\delta\Phi_2 = -\delta\Phi_1$

$$\Rightarrow \delta W_2 = \frac{1}{2} \int (\rho \delta \Phi_2 + \Phi \delta \rho_2) d^3x = -2 \delta W_1$$

$$\Rightarrow \delta W = \delta W_2 + \delta W_1 = -\frac{1}{2} \int \rho \delta \Phi_1 d^3x \Rightarrow \delta W_V = -\delta W_Q$$

- If a dielectric with $\frac{\epsilon}{\epsilon_0} > 1$ moves into a region of greater field strength, the energy increases instead of decreases.

$$\Rightarrow F_\xi = + \frac{\partial W}{\partial \xi} \Big|_{V=\text{const}}$$