Notes on Electrostatics: Multipoles and Macroscopic Media

Compiled from handwritten notes

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1 Multipole Expansion

1.1 Electrostatic Potential

For a localized charge distribution $\rho(\vec{x}')$, the potential at a point $\vec{x}$ outside a sphere of radius R that encloses the entire distribution can be expressed using an expansion in spherical harmonics.

$$\Phi(\vec{x}) = \frac{1}{4\pi\epsilon_0} \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \frac{4\pi}{2l+1} q_{lm} \frac{Y_{lm}(\theta, \phi)}{r^{l+1}}$$

This is the multipole expansion. The terms are named as follows:

- $l = 0$ is the monopole term.

- $l = 1$ are the dipole terms.

- $l = 2$ are the quadrupole terms.

The potential is fundamentally given by the integral over the charge distribution:

$$\Phi(\vec{x}) = \frac{1}{4\pi\epsilon_0} \int \frac{\rho(\vec{x}')}{|\vec{x} - \vec{x}'|} d^3x'$$

By expanding the term $|\vec{x} - \vec{x}'|^{-1}$ for $r' < r$ (where $r = |\vec{x}|$ and $r' = |\vec{x}'|$),

$$\frac{1}{|\vec{x} - \vec{x}'|} = 4\pi \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \frac{1}{2l+1} \frac{r'^l}{r^{l+1}} Y_{lm}^*(\theta', \phi') Y_{lm}(\theta, \phi)$$

we find that the coefficients q_{lm}, known as the multipole moments, are given by:

$$q_{lm} = \int Y_{lm}^*(\theta', \phi') r'^l \rho(\vec{x}') d^3x'$$

The lowest order moments are related to more familiar quantities:

- **Monopole moment:** For $l = 0, m = 0$, $q_{00} = \int Y_{00}^* r'^0 \rho \, d^3x' = \frac{1}{\sqrt{4\pi}} \int \rho \, d^3x' = \frac{q}{\sqrt{4\pi}}$, where q is the total charge.

$$q_{00} = \frac{1}{\sqrt{4\pi}} \int \rho(\mathbf{x}') \, d^3x' = \frac{1}{\sqrt{4\pi}} q \qquad (4.4)$$

$$\left.\begin{array}{l} q_{11} = -\sqrt{\dfrac{3}{8\pi}} \int (x' - iy')\rho(\mathbf{x}') \, d^3x' = -\sqrt{\dfrac{3}{8\pi}} (p_x - ip_y) \\[2ex] q_{10} = \sqrt{\dfrac{3}{4\pi}} \int z'\rho(\mathbf{x}') \, d^3x' = \sqrt{\dfrac{3}{4\pi}} p_z \end{array}\right\} \qquad (4.5)$$

$$\left.\begin{array}{l} q_{22} = \dfrac{1}{4}\sqrt{\dfrac{15}{2\pi}} \int (x' - iy')^2\rho(\mathbf{x}') \, d^3x' = \dfrac{1}{12}\sqrt{\dfrac{15}{2\pi}} (Q_{11} - 2iQ_{12} - Q_{22}) \\[2ex] q_{21} = -\sqrt{\dfrac{15}{8\pi}} \int z'(x' - iy')\rho(\mathbf{x}') \, d^3x' = -\dfrac{1}{3}\sqrt{\dfrac{15}{8\pi}} (Q_{13} - iQ_{23}) \\[2ex] q_{20} = \dfrac{1}{2}\sqrt{\dfrac{5}{4\pi}} \int (3z'^2 - r'^2)\rho(\mathbf{x}') \, d^3x' = \dfrac{1}{2}\sqrt{\dfrac{5}{4\pi}} Q_{33} \end{array}\right\} \qquad (4.6)$$

Figure 1:

- **Electric dipole moment:**

$$\vec{p} = \int \vec{x}'\rho(\vec{x}')d^3x'$$

- **Traceless quadrupole moment tensor:**

$$Q_{ij} = \int (3x_i'x_j' - r'^2\delta_{ij})\rho(\vec{x}')d^3x'$$

In rectangular coordinates, the expansion of the potential is:

$$\Phi(\vec{x}) = \frac{1}{4\pi\epsilon_0}\left[\frac{q}{r} + \frac{\vec{p}\cdot\vec{x}}{r^3} + \frac{1}{2}\sum_{i,j}Q_{ij}\frac{x_ix_j}{r^5} + \dots\right]$$

1.2   Electric Field Components

In terms of spherical coordinates, the electric field components from the multipole expansion are:

$$E_r = -\frac{\partial\Phi}{\partial r} = \frac{1}{4\pi\epsilon_0}\sum_{l,m}\frac{4\pi(l+1)}{2l+1}q_{lm}\frac{Y_{lm}(\theta,\phi)}{r^{l+2}}$$

$$E_\theta = -\frac{1}{r}\frac{\partial\Phi}{\partial\theta} = -\frac{1}{4\pi\epsilon_0}\sum_{l,m}\frac{4\pi}{2l+1}\frac{q_{lm}}{r^{l+2}}\frac{\partial}{\partial\theta}Y_{lm}(\theta,\phi)$$

$$E_\phi = -\frac{1}{r\sin\theta}\frac{\partial\Phi}{\partial\phi} = -\frac{1}{4\pi\epsilon_0}\sum_{l,m}\frac{4\pi}{2l+1}\frac{q_{lm}}{r^{l+2}}\frac{im}{\sin\theta}Y_{lm}(\theta,\phi)$$

2   The Electric Field of a Dipole

For a dipole $\vec{p}$ located at the origin and aligned along the z-axis ($p_z = p, p_x = p_y = 0$), the field components simplify to:

$$E_r = \frac{2p\cos\theta}{4\pi\epsilon_0 r^3}, \quad E_\theta = \frac{p\sin\theta}{4\pi\epsilon_0 r^3}, \quad E_\phi = 0$$

In general vector form, the dipole field $\vec{E}(\vec{x})$ from a dipole $\vec{p}$ at a point $\vec{x}_0$ is often written for points outside the dipole source ($\vec{x} \neq \vec{x}_0$):

$$\vec{E}_{out}(\vec{x}) = \frac{1}{4\pi\epsilon_0}\left[\frac{3\vec{n}(\vec{n}\cdot\vec{p}) - \vec{p}}{|\vec{x} - \vec{x}_0|^3}\right]$$

where $\vec{n}$ is a unit vector from $\vec{x}_0$ to $\vec{x}$.

   To obtain the complete field, including the point $\vec{x} = \vec{x}_0$, we must consider the behavior of the field inside the source. The full field includes a contact term involving a Dirac delta function. This can be derived by analyzing the integral of the field over a small sphere.

   Consider an integral of an electric field $\vec{E}(\vec{x}')$ over a spherical volume V of radius R centered at the origin.

- If the sphere completely encloses a polarization density $\vec{P}(\vec{x}')$ (where $\vec{p} = \int \vec{P}dV$), we have:

$$\int_{r'<R} \vec{E}(\vec{x}')d^3x' = -\frac{\vec{p}}{3\epsilon_0}$$

- If the charge is all exterior to the sphere ($r' > R$), the average field inside the sphere is related to the field at the center:

$$\int_{r'<R} \vec{E}(\vec{x}')d^3x' = \frac{4\pi}{3}R^3\vec{E}(0)$$

These considerations lead to the conclusion that the complete dipole field must be written as:

$$\vec{E}(\vec{x}) = \frac{1}{4\pi\epsilon_0}\left[\frac{3\vec{n}(\vec{p}\cdot\vec{n}) - \vec{p}}{|\vec{x} - \vec{x}_0|^3} - \frac{4\pi}{3}\vec{p}\delta(\vec{x} - \vec{x}_0)\right]$$
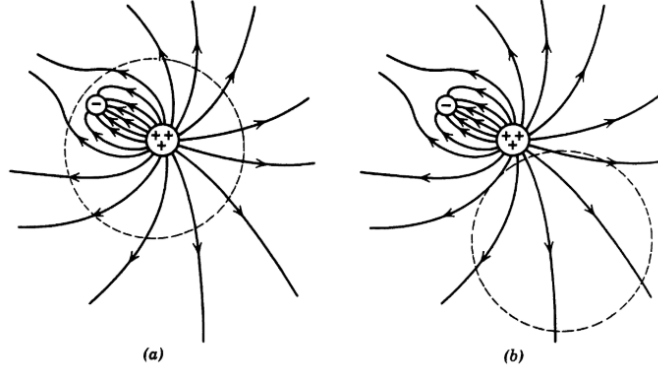
3   Energy of a Charge Distribution in an External Field

Consider a localized charge distribution $\rho(\vec{x})$ placed in an external potential $\Phi(\vec{x})$. The electrostatic energy is:

$$W = \int \rho(\vec{x}')\Phi(\vec{x}')d^3x'$$

We expand the external potential $\Phi(\vec{x}')$ in a Taylor series around an origin $\vec{x}' = 0$ located within the charge distribution.

$$\Phi(\vec{x}') = \Phi(0) + \vec{x}'\cdot\nabla\Phi(0) + \frac{1}{2}\sum_{i,j}x_i'x_j'\frac{\partial^2\Phi}{\partial x_i\partial x_j}(0) + \dots$$

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Figure 4.1 Two configurations of charge density and the spheres within which the volume integral of electric field is to be calculated.

Figure 2:

Utilizing $\vec{E} = -\nabla\Phi$, this becomes:

$$\Phi(\vec{x}') = \Phi(0) - \vec{x}' \cdot \vec{E}(0) - \frac{1}{2}\sum_{i,j} x_i' x_j' \frac{\partial E_j}{\partial x_i}(0) + \dots$$

Since the external field is source-free in the region of the charge distribution, $\nabla \cdot \vec{E} = 0$, or $\sum_i \partial E_i/\partial x_i = 0$. This allows for a simplification of the quadrupole term. Substituting the expansion into the energy integral gives:

$$W = q\Phi(0) - \vec{p} \cdot \vec{E}(0) - \frac{1}{6}\sum_{i,j} Q_{ij} \frac{\partial E_j}{\partial x_i}(0) + \dots$$

3.1   Interaction Energy of Two Dipoles

For two dipoles $\vec{p}_1$ and $\vec{p}_2$ separated by vector $\vec{x}_{12}$, the interaction energy is the energy of one dipole in the field of the other. For instance, the energy of $\vec{p}_2$ in the field of $\vec{p}_1$ is $W_{12} = -\vec{p}_2 \cdot \vec{E}_1(\vec{x}_2)$. This gives the result:

$$W_{12} = \frac{1}{4\pi\epsilon_0} \frac{\vec{p}_1 \cdot \vec{p}_2 - 3(\vec{n} \cdot \vec{p}_1)(\vec{n} \cdot \vec{p}_2)}{|\vec{x}_1 - \vec{x}_2|^3}$$

where $\vec{n}$ is the unit vector along $\vec{x}_{12}$.

4.3 Elementary Treatment of Electrostatics with Ponderable Media

We note that $\nabla \times \vec{E} = 0$, by $\nabla \times \vec{E}_{micro} = 0$.

The electric polarization $\vec{P}$ is given by

$$\vec{P}(\vec{x}) = \sum_i N_i \langle \vec{p}_i \rangle \quad \text{(dipole moment per unit volume)}$$

where $\vec{p}_i$ is the dipole moment of the i-th type of molecule in the medium.

If the molecules have a net charge e_i and there is macroscopic excess or free charge, the charge density at the macroscopic level will be:

$$\rho(\vec{x}) = \sum_i N_i \langle e_i \rangle + \rho_{excess}$$

where the first term is usually zero.

By superposition of small volume element ΔV

$$\Delta\Phi(\vec{x}; \vec{x}') = \frac{1}{4\pi\epsilon_0} \left[\frac{\rho(\vec{x}')\Delta V}{|\vec{x}-\vec{x}'|} + \frac{\vec{P}(\vec{x}') \cdot (\vec{x}-\vec{x}')}{|\vec{x}-\vec{x}'|^3} \Delta V \right]$$

where $\vec{x}$ is outside ΔV.

We treat ΔV as $d^3 x'$

$$\Phi(\vec{x}) = \frac{1}{4\pi\epsilon_0} \int d^3 x' \left[\frac{\rho(\vec{x}')}{|\vec{x}-\vec{x}'|} + \vec{P}(\vec{x}') \cdot \nabla'\left(\frac{1}{|\vec{x}-\vec{x}'|} \right) \right]$$

$$= \frac{1}{4\pi\epsilon_0} \int d^3 x' \frac{1}{|\vec{x}-\vec{x}'|} \left[\rho(\vec{x}') - \nabla' \cdot \vec{P}(\vec{x}') \right]$$

With $\vec{E} = -\nabla\Phi$, we have the first Maxwell equation:

$$\nabla \cdot \vec{E} = \frac{1}{\epsilon_0}(\rho - \nabla \cdot \vec{P})$$

With the definition of electric displacement $\vec{D}$

$$\vec{D} = \epsilon_0 \vec{E} + \vec{P}$$

which implies

$$\nabla \cdot \vec{D} = \rho$$

If the polarization is non-uniform, there can be a net increase/decrease of charge within any small volume.

We suppose the medium is isotropic, $\vec{P} \parallel \vec{E}$

$$\implies \vec{P} = \epsilon_0 \chi_e \vec{E}$$

where χ_e is the electric susceptibility of the medium and thus $\vec{D} = \epsilon \vec{E}$ where $\epsilon = \epsilon_0(1 + \chi_e)$ is the electric permittivity. $\epsilon/\epsilon_0 = 1 + \chi_e$ is the dielectric constant. Therefore we obtain:

$$\nabla \cdot \vec{E} = \rho/\epsilon$$

The normal components of $\vec{D}$ and the tangential components of $\vec{E}$ on either side of an interface satisfy the boundary conditions.

$$\begin{cases} (\vec{D}_2 - \vec{D}_1) \cdot \vec{n}_{21} = 0 \\ (\vec{E}_2 - \vec{E}_1) \times \vec{n}_{21} = 0 \end{cases}$$

where $\vec{n}_{21}$ is a unit normal to the surface directed from region 1 to region 2.
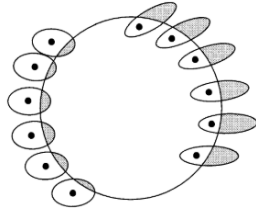
Figure 4.2 Origin of polarization-charge density. Because of spatial variation of polarization, more molecular charge may leave a given small volume than enters it. Only molecules near the boundary are shown.

Figure 3:

4.4 Boundary-Value Problems with Dielectrics

We, to illustrate the method of images, consider a point charge, q, embedded in a semi-infinite dielectric ϵ_1 a distance d away from a plane interface that separates the first medium from another semi-infinite dielectric ϵ_2.
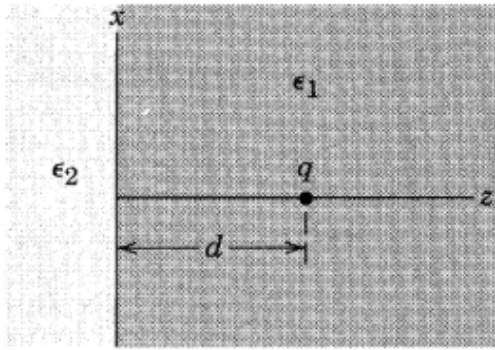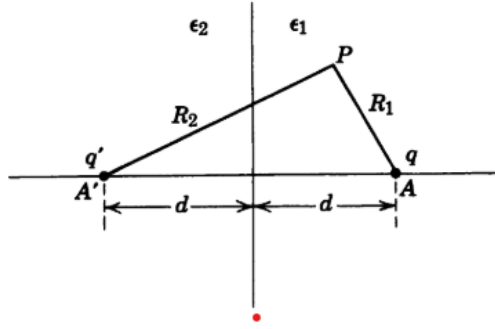

Figure 4.3

Figure 4:

We have:

$$\begin{cases} \epsilon_1 \nabla \cdot \vec{E} = \rho, & z > 0 \\ \epsilon_2 \nabla \cdot \vec{E} = 0, & z < 0 \end{cases}$$

$$\nabla \times \vec{E} = 0, \quad \text{everywhere}$$

The boundary:

$$\lim_{z \to 0^+} \begin{pmatrix} \epsilon_1 E_z \\ E_x \\ E_y \end{pmatrix} = \lim_{z \to 0^-} \begin{pmatrix} \epsilon_2 E_z \\ E_x \\ E_y \end{pmatrix}$$

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Figure 4.4

Figure 5:

For $z > 0$ the potential at a point P by (p, ϕ, z)

$$\Phi = \frac{1}{4\pi\epsilon_1} \left(\frac{q}{R_1} + \frac{q'}{R_2} \right), \quad z > 0$$

where $R_1 = \sqrt{\rho^2 + (d-z)^2}$, $R_2 = \sqrt{\rho^2 + (d+z)^2}$.

At the position A, the charge q'' results in the potential for $z < 0$.

$$\Phi = \frac{1}{4\pi\epsilon_1} \frac{q''}{R_1}, \quad z < 0$$

Since

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

$$\frac{\partial}{\partial \rho} \left(\frac{1}{R_1} \right)_{z=0} = \frac{\partial}{\partial \rho} \left(\frac{1}{R_2} \right)_{z=0} = \frac{-\rho}{(\rho^2 + d^2)^{3/2}}$$
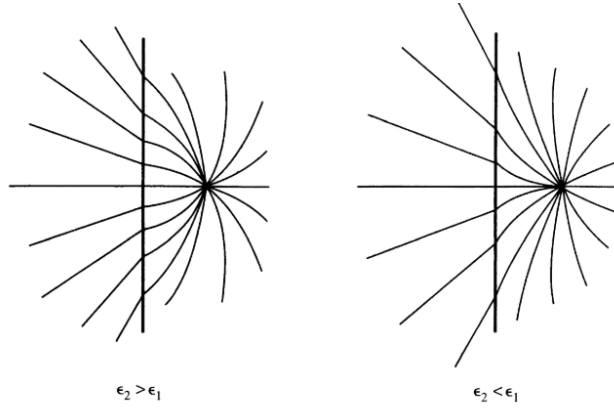
we obtain:

$$\begin{cases} q - q' = q'' \\ \frac{1}{\epsilon_1}(q - q') = \frac{1}{\epsilon_2} q'' \end{cases} \implies q' = -\left(\frac{\epsilon_2 - \epsilon_1}{\epsilon_2 + \epsilon_1} \right) q$$

$$\implies q'' = \left(\frac{2\epsilon_2}{\epsilon_1 + \epsilon_2} \right) q$$

Since $\vec{P} = \epsilon_0 \chi_e \vec{E}$, we obtain $-\nabla \cdot \vec{P} = -\epsilon_0 \chi_e \nabla \cdot \vec{E} = 0$ at the surface, χ_e takes a discontinuous jump so that $\nabla \chi_e = (\epsilon_1 - \epsilon_0)/\epsilon_0$ as z passes through $z = 0 \implies$ on the plane $z = 0$: $\sigma_{pol} = -(\vec{P}_2 - \vec{P}_1) \cdot \vec{n}_{21}$ where $\vec{n}_{21}$ is the unit normal from dielectric 1 to dielectric 2, $\vec{P}_i$ is the polarization in the dielectric i at $z = 0$.

Since $\vec{P}_1 = (\epsilon_1 - \epsilon_0)\vec{E}_1 = -(\epsilon_1 - \epsilon_0)\nabla\Phi(z \to 0^+)$, we have

$$\sigma_{pol} = \frac{-q}{\epsilon_0} \frac{\epsilon_0(\epsilon_2 - \epsilon_1)}{\epsilon_1(\epsilon_2 + \epsilon_1)} \frac{d}{(\rho^2 + d^2)^{3/2}}$$

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Figure 4.5 Lines of electric displacement for a point charge embedded in a dielectric ϵ_1 near a semi-infinite slab of dielectric ϵ_2.

Figure 6:

In the limit $\epsilon_2 \gg \epsilon_1$, the dielectric ϵ_2 behaves much like a conductor since the electric field becomes very small.

We consider another example that a dielectric sphere of radius a with ϵ/ϵ_0 placed in an initially uniform electric field $\vec{E}_0$.
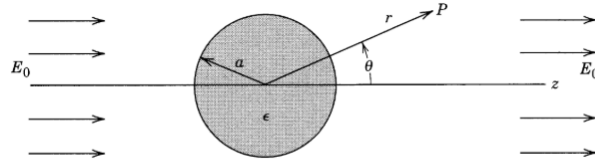
Figure 4.6

Figure 7:

Inside:

$$\Phi_{in} = \sum_{l=0}^{\infty} A_l r^l P_l(\cos\theta)$$

Outside:

$$\Phi_{out} = \sum_{l=0}^{\infty} \left[E_0 r^l + C_l r^{-(l+1)} \right] P_l(\cos\theta)$$

At infinity:

$$\Phi \to -E_0 z = -E_0 r \cos\theta$$

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4   Boundary Value Problem for a Dielectric Sphere

We consider a dielectric sphere of radius a and permittivity ϵ placed in a uniform electric field $\vec{E}_0 = E_0\hat{z}$. The potential must satisfy Laplace's equation, and the solutions can be expressed in terms of Legendre polynomials. The boundary conditions at the surface of the sphere $(r = a)$ are:

4.1   Boundary Conditions

1. The tangential component of the electric field $\vec{E}$ is continuous.

$$\text{Tangential E:} \quad -\frac{1}{a}\frac{\partial \Phi_{in}}{\partial \theta}\bigg|_{r=a} = -\frac{1}{a}\frac{\partial \Phi_{out}}{\partial \theta}\bigg|_{r=a}$$

2. The normal component of the electric displacement field $\vec{D}$ is continuous (assuming no free surface charge).

$$\text{Normal D:} \quad -\epsilon\frac{\partial \Phi_{in}}{\partial r}\bigg|_{r=a} = -\epsilon_0\frac{\partial \Phi_{out}}{\partial r}\bigg|_{r=a}$$

4.2   Solving for the Potentials

The general solutions for the potential inside and outside the sphere are:

$$\Phi_{in}(r, \theta) = \sum_{l=0}^{\infty} A_l r^l P_l(\cos\theta)$$

$$\Phi_{out}(r, \theta) = -E_0 r \cos\theta + \sum_{l=0}^{\infty} \frac{C_l}{r^{l+1}} P_l(\cos\theta)$$

where $-E_0 r \cos\theta$ is the potential of the applied uniform field.

Applying the boundary conditions and using the orthogonality of the Legendre polynomials $(P_l(\cos\theta))$, we can solve for the coefficients A_l and C_l.

First Boundary Condition (Tangential E):   For each l, the coefficients of $P_l(\cos\theta)$ must be equal.

$$A_1 a = -E_0 a + \frac{C_1}{a^2} \quad \text{(for } l = 1\text{)}$$

$$A_l a^l = \frac{C_l}{a^{l+1}} \quad \text{(for } l \neq 1\text{)}$$

Second Boundary Condition (Normal D):   Similarly, for each l, we match coefficients.

$$\epsilon A_1 = -\epsilon_0(-E_0) - \epsilon_0\frac{2C_1}{a^3} \implies (\epsilon/\epsilon_0)A_1 = E_0 - \frac{2C_1}{a^3} \quad \text{(for } l = 1\text{)}$$

$$\epsilon(lA_l a^{l-1}) = -\epsilon_0\left(-(l+1)\frac{C_l}{a^{l+2}}\right) \implies (\epsilon/\epsilon_0)lA_l = (l+1)\frac{C_l}{a^{2l+1}} \quad \text{(for } l \neq 1\text{)}$$

Combined Equations: For $l \neq 1$, combining the two conditions gives $A_l = C_l = 0$. For $l = 1$, we solve the system of two equations for A_1 and C_1:

$$A_1 = -\frac{3}{\epsilon/\epsilon_0 + 2} E_0$$

$$C_1 = \left(\frac{\epsilon/\epsilon_0 - 1}{\epsilon/\epsilon_0 + 2} \right) a^3 E_0$$

4.3 Final Potentials and Fields

Therefore, the potentials are:

$$\Phi_{in} = A_1 r \cos\theta = -\frac{3}{\epsilon/\epsilon_0 + 2} E_0 r \cos\theta \tag{1}$$

$$\Phi_{out} = -E_0 r \cos\theta + \frac{C_1}{r^2} \cos\theta = -E_0 r \cos\theta + \left(\frac{\epsilon/\epsilon_0 - 1}{\epsilon/\epsilon_0 + 2} \right) \frac{a^3 E_0}{r^2} \cos\theta \tag{2}$$

The electric field inside the sphere is uniform:

$$\vec{E}_{in} = -\nabla\Phi_{in} = -A_1 \hat{z} = \frac{3}{\epsilon/\epsilon_0 + 2} \vec{E}_0$$

For a dielectric with $\epsilon > \epsilon_0$, the field inside, E_{in}, is less than the applied field E_0.

The potential outside, Φ_{out}, is the sum of the potential of the applied field E_0 and the potential of an electric dipole at the origin with dipole moment:

$$\vec{p} = 4\pi\epsilon_0 C_1 \hat{z} = 4\pi\epsilon_0 \left(\frac{\epsilon/\epsilon_0 - 1}{\epsilon/\epsilon_0 + 2} \right) a^3 \vec{E}_0$$

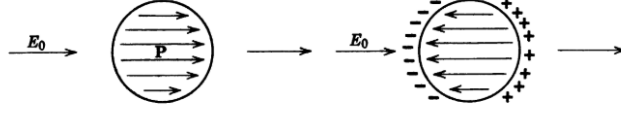oriented in the direction of the applied field.

5 Polarization and Bound Charge

The polarization $\vec{P}$ inside the dielectric is given by:

$$\vec{P} = (\epsilon - \epsilon_0)\vec{E}_{in} = \epsilon_0(\epsilon/\epsilon_0 - 1)\vec{E}_{in} = 3\epsilon_0 \left(\frac{\epsilon/\epsilon_0 - 1}{\epsilon/\epsilon_0 + 2} \right) \vec{E}_0$$

The bound surface charge density σ_{pol} is:

$$\sigma_{pol} = \vec{P} \cdot \hat{r} = P \cos\theta = 3\epsilon_0 \left(\frac{\epsilon/\epsilon_0 - 1}{\epsilon/\epsilon_0 + 2} \right) E_0 \cos\theta$$

Figure 4.7 Dielectric sphere in a uniform field E_0, showing the polarization on the left and the polarization charge with its associated, opposing, electric field on the right.

Figure 8:

6 Molecular Polarizability and the Clausius-Mossotti Equation

6.1 The Local Field

The internal field $\vec{E}_i$ experienced by a molecule can be written as the sum of the field from nearby molecules, $\vec{E}_{near}$, and the field from more distant molecules, $\vec{E}_p$, which can be treated as a continuum.

$$\vec{E}_i = \vec{E}_{near} + \vec{E}_p$$

For a spherical cavity of radius R carved out of a uniformly polarized dielectric, the field $\vec{E}_p$ due to the polarization outside the cavity is:

$$\vec{E}_p = \frac{\vec{P}}{3\epsilon_0}$$

The field due to all dipoles at the origin for a cubic array is shown to be zero by symmetry.

$$\vec{E}_{near} = 0$$

This holds for amorphous substances and most materials as well. Thus, the local field is:

$$\vec{E}_i = \vec{E}_{macro} + \vec{E}_p = \vec{E} + \frac{\vec{P}}{3\epsilon_0}$$

where $\vec{E}$ is the macroscopic average field.

6.2 Derivation

The macroscopic polarization $\vec{P}$ is the total dipole moment per unit volume, which can be written as:

$$\vec{P} = N\langle\vec{p}_{mol}\rangle$$

where N is the number of molecules per unit volume and $\langle\vec{p}_{mol}\rangle$ is the average molecular dipole moment.

We define the molecular polarizability γ_{mol} as the ratio of the average molecular dipole moment to ϵ_0 times the local field at the molecule.

$$\langle\vec{p}_{mol}\rangle = \epsilon_0\gamma_{mol}\vec{E}_i$$

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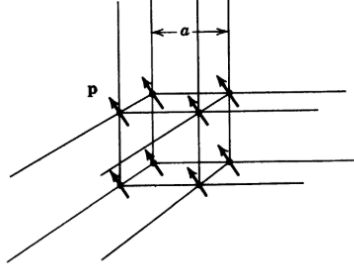
Figure 4.9 Calculation of the internal field: contribution from nearby molecules in a simple cubic lattice.

Figure 9:

Thus, since $\vec{E}_{near} \approx 0$:

$$\vec{P} = N\gamma_{mol}(\vec{E} + \frac{\vec{P}}{3\epsilon_0})$$

By definition, $\vec{P} = \epsilon_0 \chi_e \vec{E}$. Substituting this, we find:

$$\epsilon_0 \chi_e \vec{E} = N\gamma_{mol}(\vec{E} + \frac{\epsilon_0 \chi_e \vec{E}}{3\epsilon_0}) = N\gamma_{mol}\vec{E}(1 + \frac{\chi_e}{3})$$

Solving for χ_e:

$$\chi_e = \frac{N\gamma_{mol}}{1 - \frac{1}{3}N\gamma_{mol}}$$

Using the relation $\epsilon/\epsilon_0 = 1 + \chi_e$, we can rearrange to find:

$$\frac{\chi_e}{\chi_e + 3} = \frac{N\gamma_{mol}}{3}$$

Substituting $\chi_e = \epsilon/\epsilon_0 - 1$:

$$\frac{\epsilon/\epsilon_0 - 1}{\epsilon/\epsilon_0 + 2} = \frac{N\gamma_{mol}}{3}$$

which is the **Clausius-Mossotti equation**.

7 Models for Molecular Polarizability

The polarization of a collection of atoms or molecules can arise in two main ways:

(i) The applied electric field distorts the charge distributions and so produces an **induced dipole moment** in each molecule.

(ii) The applied field tends to line up the initially randomly oriented **permanent dipole moments** of the molecules. This is called orientation polarization.

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7.1   Induced Polarization

We consider a simple model where a charge e is bound harmonically (representing electrons and ions) and is under the action of a restoring force:

$$\vec{F} = -m\omega_0^2 \vec{x}$$

where ω_0 is the natural frequency of oscillation about equilibrium and m is the mass of the charge.

Under the action of an external electric field $\vec{E}$, the charge is displaced from its equilibrium by an amount $\vec{x}$. At the new equilibrium position, the restoring force balances the electric force:

$$m\omega_0^2 \vec{x} = e\vec{E}$$

The induced dipole moment is therefore:

$$\vec{p}_{mol} = e\vec{x} = \frac{e^2}{m\omega_0^2}\vec{E}$$

Thus, the electronic polarizability γ is given by:

$$\gamma = \frac{e^2}{m\omega_0^2}$$

If there is a set of charges e_j with mass m_j and natural frequency ω_j in each molecule, we have a total molecular polarizability:

$$\gamma_{mol} = \sum_j \frac{e_j^2}{m_j \omega_j^2}$$

Effect of Thermal Agitation

We now consider the thermal agitation of molecules, which could modify the induced dipole polarizability. For classical systems, we use the Boltzmann factor $f(H) = e^{-H/kT}$.

For a harmonically bound charge with an applied field $\vec{E}$ in the z-direction, the Hamiltonian is:

$$H = \frac{1}{2m}|\vec{P}|^2 + \frac{1}{2}m\omega_0^2 z^2 - eEz$$

where $\vec{P}$ is the momentum of the charged particle. The average value of the dipole moment in the z-direction is a statistical average over phase space:

$$\langle p_{mol} \rangle = \frac{\int d^3p \int d^3x (ez) f(H)}{\int d^3p \int d^3x f(H)} = \frac{\int d^3p \int d^3x (ez) e^{-H/kT}}{\int d^3p \int d^3x e^{-H/kT}}$$

We can simplify the Hamiltonian by completing the square, introducing a displaced coordinate $z' = z - \frac{eE}{m\omega_0^2}$:

$$H = \frac{1}{2m}|\vec{P}|^2 + \frac{1}{2}m\omega_0^2 \left(z - \frac{eE}{m\omega_0^2}\right)^2 - \frac{e^2E^2}{2m\omega_0^2}$$
$$= \frac{1}{2m}|\vec{P}|^2 + \frac{1}{2}m\omega_0^2 (z')^2 - \frac{e^2E^2}{2m\omega_0^2}$$

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Let's call the constant energy shift $E_0 = \frac{e^2 E^2}{2m\omega_0^2}$ and $H' = \frac{1}{2m}|\vec{P}|^2 + \frac{1}{2}m\omega_0^2(z')^2$. Then $H = H' - E_0$. The average dipole moment is:

$$\langle p_{mol} \rangle = \frac{\int d^3p \int d^3x' e(z' + \frac{eE}{m\omega_0^2})e^{-(H'-E_0)/kT}}{\int d^3p \int d^3x' e^{-(H'-E_0)/kT}}$$

Since H' is an even function of z', the first integral in the numerator vanishes: $\int z' e^{-H'/kT} d^3x' = 0$. The remaining terms, including the exponential factor $e^{E_0/kT}$, cancel out between the numerator and denominator.

$$\langle p_{mol} \rangle = e\left(\frac{eE}{m\omega_0^2}\right) = \frac{e^2 E}{m\omega_0^2}$$

The result is the same as the zero-temperature case and is independent of temperature. This means that for induced polarization, thermal effects do not change the average polarizability in this classical model.

7.2 Orientation Polarization

Suppose all molecules have a permanent dipole moment $\vec{p}_0$ which can be oriented in any direction in space. In the absence of a field, thermal agitation keeps the molecules randomly oriented so that there is no net dipole moment.

The Hamiltonian of one such molecule in an external field $\vec{E}$ is:

$$H = H_0 - \vec{p}_0 \cdot \vec{E}$$

where H_0 is a function of only the internal coordinates of the molecule. Using the Boltzmann factor, the average dipole moment is:

$$\langle \vec{p}_{mol} \rangle = \frac{\int (\vec{p}_0) e^{(-H_0 + \vec{p}_0 \cdot \vec{E})/kT} d\Omega}{\int e^{(-H_0 + \vec{p}_0 \cdot \vec{E})/kT} d\Omega}$$

We can cancel the $e^{-H_0/kT}$ term. Let's choose the z-axis along the direction of $\vec{E}$, so $\vec{p}_0 \cdot \vec{E} = p_0 E \cos\theta$. We are interested in the component of the average moment along $\vec{E}$:

$$\langle p_{mol} \rangle_z = \frac{\int (p_0 \cos\theta) e^{p_0 E \cos\theta/kT} d\Omega}{\int e^{p_0 E \cos\theta/kT} d\Omega}$$

where $d\Omega = \sin\theta d\theta d\phi$. In general, except at low temperatures, the argument of the exponential $(p_0 E/kT)$ is very small compared to unity. Hence, we can use the approximation $e^x \approx 1 + x$:

$$\langle p_{mol} \rangle_z \approx \frac{\int_0^{2\pi} d\phi \int_0^\pi (p_0 \cos\theta)(1 + \frac{p_0 E \cos\theta}{kT}) \sin\theta d\theta}{\int_0^{2\pi} d\phi \int_0^\pi (1 + \frac{p_0 E \cos\theta}{kT}) \sin\theta d\theta}$$

$$= \frac{2\pi p_0 \int_0^\pi (\cos\theta + \frac{p_0 E}{kT} \cos^2\theta) \sin\theta d\theta}{2\pi \int_0^\pi (1 + \frac{p_0 E}{kT} \cos\theta) \sin\theta d\theta}$$

Evaluating the integrals:

- $\int_0^\pi \cos\theta \sin\theta d\theta = 0$

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- $\int_0^\pi \cos^2\theta \sin\theta d\theta = [-\frac{1}{3}\cos^3\theta]_0^\pi = \frac{2}{3}$
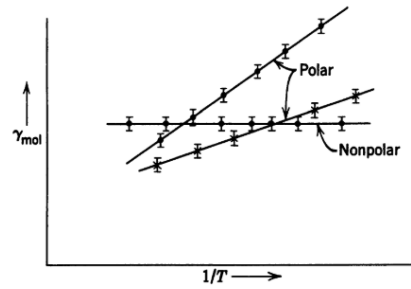
- $\int_0^\pi \sin\theta d\theta = 2$

The expression simplifies to:

$$\langle p_{mol}\rangle_z \approx \frac{p_0(\frac{p_0 E}{kT})\frac{2}{3}}{2} = \frac{p_0^2 E}{3kT}$$

This shows that the orientation polarization depends inversely on the temperature.

7.3 Total Molecular Polarizability

For both types of polarization, induced (γ_i) and orientation, present, the general form of molecular polarizability is the sum of the two effects:

Figure 4.10 Variation of molecular polarizability γ_{mol} with temperature for polar and nonpolar substances: γ_{mol} versus T^{-1}.

Figure 10:

$$\gamma_{mol} \approx \gamma_i + \frac{p_0^2}{3kT}$$

8 Electrostatic Energy in Dielectric Media

For a charge density $\rho(\vec{x})$ and a potential $\Phi(\vec{x})$, the energy of a system is:

$$W = \frac{1}{2}\int \rho(\vec{x})\Phi(\vec{x})d^3x$$

This is the energy required to form the final configuration of charge by assembling it bit-by-bit against the action of the existing electric field.

Let's consider the work done to accomplish some sort of charge change $\delta\rho$. The work done is:

$$\delta W = \int \delta\rho(\vec{x})\Phi(\vec{x})d^3x$$

In a dielectric, the free charge density ρ_f is related to the electric displacement field $\vec{D}$ by Gauss's law: $\nabla \cdot \vec{D} = \rho_f$. We can then relate a change in free charge to a change in displacement: $\delta\rho_f =$

$\nabla \cdot (\delta \vec{D})$. The energy change can be cast into a new form:

$$\delta W = \int (\nabla \cdot \delta \vec{D}) \Phi d^3 x$$

$$= - \int (\delta \vec{D}) \cdot (\nabla \Phi) d^3 x \quad \text{(using integration by parts)}$$

Since the electric field is the negative gradient of the potential, $\vec{E} = -\nabla \Phi$:

$$\delta W = \int \vec{E} \cdot \delta \vec{D} d^3 x$$

By allowing $\vec{D}$ to be brought from an initial value of $\vec{D} = 0$ to its final value $\vec{D}$, we can find the total work done, which is the stored electrostatic energy:

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

If the medium is linear, then $\vec{D} = \epsilon \vec{E}$, and we can write:

$$\vec{E} \cdot \delta \vec{D} = \frac{1}{\epsilon} \vec{D} \cdot \delta \vec{D} = \frac{1}{2\epsilon} \delta(\vec{D} \cdot \vec{D}) = \delta \left(\frac{1}{2} \vec{E} \cdot \vec{D} \right)$$

The total energy is then:

$$W = \int d^3 x \int_0^{\vec{D}} \delta \left(\frac{1}{2} \vec{E} \cdot \vec{D} \right) = \frac{1}{2} \int \vec{E} \cdot \vec{D} d^3 x$$

9 Energy of a Dielectric in an External Field

9.1 Derivation of the Interaction Energy

Suppose that initially the electric field $\mathbf{E}_0$ due to a certain distribution of charges ρ_f exists in a medium of electric susceptibility ϵ_0. The initial electrostatic energy is:

$$W_0 = \frac{1}{2} \int \mathbf{E}_0 \cdot \mathbf{D}_0 \, d^3 x$$

where $\mathbf{D}_0 = \epsilon_0 \mathbf{E}_0$.

In a volume V_1, from $\mathbf{E}_0$ to $\mathbf{E}$, the object is described by $\epsilon(\mathbf{r})$, which has the value ϵ_1 inside V_1 and ϵ_0 outside V_1. At the edge of the volume V_1, the new energy is:

$$W_1 = \frac{1}{2} \int \mathbf{E} \cdot \mathbf{D} \, d^3 x$$

where $\mathbf{D} = \epsilon \mathbf{E}$.

The difference in the energy is:

$$W = W_1 - W_0 = \frac{1}{2} \int (\mathbf{E} \cdot \mathbf{D} - \mathbf{E}_0 \cdot \mathbf{D}_0) \, d^3 x$$

$$= \frac{1}{2} \int (\mathbf{E} \cdot \mathbf{D} - \mathbf{E}_0 \cdot \mathbf{D}_0) \, d^3 x + \frac{1}{2} \int (\mathbf{E} + \mathbf{E}_0) \cdot (\mathbf{D} - \mathbf{D}_0) \, d^3 x$$

Since the free charge distribution is unchanged, $\nabla \cdot (\mathbf{D} - \mathbf{D}_0) = 0$. Also, since both fields are electrostatic, $\nabla \times \mathbf{E} = 0$ and $\nabla \times \mathbf{E}_0 = 0$, which implies $\nabla \times (\mathbf{E} + \mathbf{E}_0) = 0$. We can therefore write the sum of the fields as the gradient of a scalar potential:

$$\mathbf{E} + \mathbf{E}_0 = -\nabla \Phi$$

Then the second integral becomes:

$$I = -\frac{1}{2} \int \nabla \Phi \cdot (\mathbf{D} - \mathbf{D}_0)\, d^3x$$

Using integration by parts (and assuming fields vanish at infinity):

$$I = \frac{1}{2} \int \Phi \nabla \cdot (\mathbf{D} - \mathbf{D}_0)\, d^3x = 0$$

since $\nabla \cdot (\mathbf{D} - \mathbf{D}_0) = 0$. Consequently, the energy change simplifies to:

$$W = \frac{1}{2} \int (\mathbf{E} \cdot \mathbf{D}_0 - \mathbf{E}_0 \cdot \mathbf{D})\, d^3x$$

Outside the volume V_1, $\mathbf{D} = \epsilon_0 \mathbf{E} = \mathbf{D}_0$, so the integrand is zero. We only need to integrate over the volume of the dielectric, V_1:

$$W = \frac{1}{2} \int_{V_1} (\mathbf{E} \cdot (\epsilon_0 \mathbf{E}_0) - \mathbf{E}_0 \cdot (\epsilon_1 \mathbf{E}))\, d^3x$$

$$= \frac{1}{2} \int_{V_1} (\epsilon_0 - \epsilon_1) \mathbf{E} \cdot \mathbf{E}_0\, d^3x$$

By definition of the polarization vector $\mathbf{P} = \mathbf{D} - \epsilon_0 \mathbf{E} = (\epsilon_1 - \epsilon_0)\mathbf{E}$, we can write:

$$W = -\frac{1}{2} \int_{V_1} \mathbf{P} \cdot \mathbf{E}_0\, d^3x$$

9.2   Physical Interpretation and Force

The energy density of a dielectric placed in a field $\mathbf{E}_0$ whose sources are fixed is given by:

$$w = -\frac{1}{2} \mathbf{P} \cdot \mathbf{E}_0$$

The factor $\frac{1}{2}$ represents the energy density of a polarizable dielectric in an external field. We imagine a small generalized displacement of the body, which tends to move toward regions of increasing field $\mathbf{E}_0$, provided $\epsilon_1 > \epsilon_0$.

The change in field energy δW can be interpreted as a change in the potential energy of the body. There is a force acting on the body. For a generalized displacement $\delta \xi$:

$$F_\xi = -\left(\frac{\partial W}{\partial \xi} \right)_Q$$

where the subscript Q has been placed on the partial derivative to indicate that the sources of the field are kept fixed.

10 Energy Variations under Different Conditions

10.1 Constant Charge vs. Constant Potential

Let's consider two scenarios for the change in energy.

1. Fixed Charges (Disconnected Electrodes) The electrodes are disconnected from the batteries and the charges on them held fixed ($\delta\rho = 0$). The energy change is:

$$\delta W_1 = \frac{1}{2} \int \rho \delta \Phi_1 \, d^3x$$

2. Fixed Potential (Connected Batteries) Then the batteries are connected again to the electrodes to restore potentials to the original values. There will be a flow of charge $\delta\rho_2$ accompanying the potential change $\delta\Phi_2 = -\delta\Phi_1$. The energy change during this restoration is δW_2. The total energy change for the process at constant potential is $\delta W = \delta W_1 + \delta W_2$. It can be shown that $\delta W_2 = -2\delta W_1$. Consequently, the total change in energy at constant potential is:

$$\delta W = \delta W_1 + \delta W_2 = \delta W_1 - 2\delta W_1 = -\delta W_1$$

Symbolically, we write this important result as:

$$\delta W_V = -\delta W_Q$$

10.2 Force on a Dielectric at Constant Potential

If a dielectric with $\epsilon/\epsilon_0 > 1$ moves into a region of greater field strength, the energy increases. For a generalized displacement $d\xi$, the force is given by:

$$F_\xi = + \left(\frac{\partial W}{\partial \xi} \right)_V$$

Note the positive sign, which is a consequence of the system being held at constant potential (by a battery that can do work), in contrast to the constant charge (isolated system) case. A dielectric is therefore pulled into a region of stronger electric field.