## Multipoles and Energy

Consider a localized charge distribution $\rho(\vec{r})$ in an __external__ potential $\Phi(\vec{r})$. [No part of $\Phi(\vec{r})$ is due to $\rho(\vec{r})$.] The interaction potential energy is:

$$U = \int d^3\vec{r} \; \rho(\vec{r})\Phi(\vec{r})$$

This will not contain any infinite self-energies.

Expand the potential in a Taylor Series:

$$\Phi(\vec{r}) = \Phi(0) + \vec{r}\cdot\vec{\nabla}\Phi(\vec{r})\Big|_{\vec{r}=0} + \frac{1}{2}\sum_i\sum_j x_i x_j \frac{\partial^2}{\partial x_i \partial x_j}\Phi(\vec{r})\Big|_{\vec{r}=0} + \cdots$$

In the linear term write: $\vec{\nabla}\Phi(\vec{r})\Big|_{\vec{r}=0} = -\vec{E}(0)$

Add to the quadratic term: $-\frac{1}{6}r^2 \vec{\nabla}\cdot\vec{E}(\vec{r})\Big|_{\vec{r}=0} = 0$ since $\vec{\nabla}\cdot\vec{E} = 0$, this changes nothing.

$$\Phi(\vec{r}) = \Phi(0) - \vec{r}\cdot\vec{E}(0) - \frac{1}{6}\sum_i\sum_j \left(3x_i x_j - r^2\delta_{ij}\right)\frac{\partial E_j(\vec{r})}{\partial x_i}\Big|_{\vec{r}=0} + \cdots$$

$$U = q\Phi(0) - \vec{\mu}\cdot\vec{E}(0) - \frac{1}{6}\sum_i\sum_j Q_{ij}\frac{\partial E_j(\vec{r})}{\partial x_i}\Big|_{\vec{r}=0} + \cdots$$

Notice how the different multipole moments of $\rho(\vec{r})$ combine in the energy with $\Phi(\vec{r})$. We illustrate with the interaction potential energy of two dipoles.

To use the formalism we just developed, we must relegate one dipole $(\vec{\mu}_1)$ to $\rho(\vec{r})$ and the other $(\vec{\mu}_2)$ to $\Phi(\vec{r})$.

If $\vec{\mu}_2$ is at the origin then

$$\Phi(\vec{r}) = \frac{\vec{\mu}_2 \cdot \vec{r}}{\rho^3}$$

If $\vec{\mu}_2$ is at $\vec{r}\,'$ then

$$\Phi(\vec{r}) = \frac{\vec{\mu}_2 \cdot (\vec{r} - \vec{r}\,')}{|\vec{r} - \vec{r}\,'|^3}$$

The first dipole $\vec{\mu}_1$ will combine with the electric field due to the second in the energy $U$.

$$\vec{E}(\vec{r}) = -\vec{\nabla}\Phi(\vec{r}) = \frac{3\hat{n}(\vec{\mu}_2 \cdot \hat{n}) - \vec{\mu}_2}{|\vec{r} - \vec{r}\,'|^3} \qquad \text{where } \hat{n} = \frac{\vec{r} - \vec{r}\,'}{|\vec{r} - \vec{r}\,'|}$$

$$U_{12} = U_{21} = \frac{\vec{\mu}_1 \cdot \vec{\mu}_2 - 3(\hat{n} \cdot \vec{\mu}_1)(\hat{n} \cdot \vec{\mu}_2)}{|\vec{r}_1 - \vec{r}_2|^3} \qquad \text{where } \hat{n} = \frac{\vec{r}_1 - \vec{r}_2}{|\vec{r}_1 - \vec{r}_2|}$$
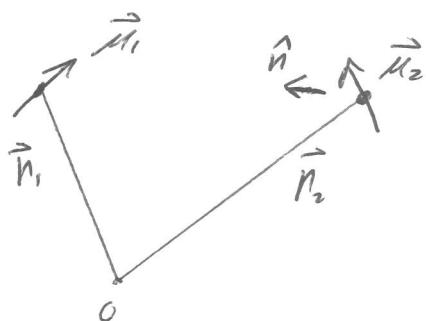


$U_{12} > 0$ is repulsion

$U_{12} < 0$ is attraction

We are skipping

F) <u>Variational Techniques</u>

and going on to

G) <u>Electrostatics in a Dielectric Medium</u>

The electrostatic potential at point $\vec{r}$ due to a volume charge density is

$$\underline{\Phi}(\vec{r}) = \int_V dV' \frac{k\rho(\vec{r}')}{|\vec{r}-\vec{r}'|}$$

this is a strictly true equation — no approximations have been made. In particular, it holds at the microscopic level.

In the presence of matter, some charges are free to move (for example, the conduction band electrons in a conductor or semiconductor) while other charges are bound to fixed sites (for example, the net negative charge in a $Cl^-$ ion).

The free charge is distributed over <u>macroscopic</u> distances whereas the bound charge is distributed over <u>microscopic</u> distances.

Suppose we have molecules at sites $\vec{r}_\alpha$. Then

$$\rho_{total}(\vec{r}) = \rho_{free}(\vec{r}) + \sum_\alpha \rho_\alpha(\vec{r})$$

where $\rho_\alpha(\vec{r})$ is the charge density within the $\alpha^{\underline{th}}$ molecule — it is non-zero only in a small volume about $\vec{r}_\alpha$ which we may take to be the center of mass of the molecule (although this is not critical)

$$\Phi(\vec{r}) = \int dV' \frac{\rho_{free}(\vec{r}')}{|\vec{r}-\vec{r}'|} + \sum_\alpha \int dV' \frac{\rho_\alpha(\vec{r}')}{|\vec{r}-\vec{r}'|}$$

(still no approximations)

Next we make a <u>molecular</u> multipole expansion of the second term. For the $\alpha^{\underline{th}}$ molecule,

$$\int dV' \frac{\rho_\alpha(\vec{r}')}{|\vec{r}-\vec{r}'|} = \int dV' \frac{\rho_\alpha(\vec{r}')}{|(\vec{r}-\vec{r}_\alpha)-(\vec{r}'-\vec{r}_\alpha)|}$$

where we expand about $\vec{r}_\alpha$

$$= \sum_{m=0}^\infty \frac{(-1)^m}{m!} \sum_{\substack{i_1,...i_m \\ =1}}^3 Q_{i_1...i_m}^{(\alpha)} \frac{\partial^m}{\partial x_{i_1}...\partial x_{i_m}} \frac{1}{|\vec{r}-\vec{r}_\alpha|}$$

in Cartesian multipoles, for example.

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The reducible multipole moment tensor components are

$$\overline{Q}^{(\alpha)}_{i_1 \ldots i_m} = \int dV' \, \rho_\alpha(\vec{r}') \, (x'_{i_1} - x_{\alpha i_1}) \cdots (x'_{i_m} - x_{\alpha i_m})$$

Generally, it is sufficient to consider only the lowest two moments:

m=0: $\quad q_\alpha = \int dV' \, \rho_\alpha(\vec{r}') \quad\quad$ molecular charge

m=1: $\quad \vec{\mu}_\alpha = \int dV' \, \rho_\alpha(\vec{r}')(\vec{r}' - \vec{r}_\alpha) \quad\quad$ molecular dipole moment

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$$\overline{\phi}(\vec{r}) = \int dV' \, \frac{\rho_{free}(\vec{r}')}{|\vec{r} - \vec{r}'|} + \sum_\alpha \frac{q_\alpha}{|\vec{r} - \vec{r}_\alpha|} + \sum_\alpha \vec{\mu}_\alpha \cdot \frac{(\vec{r} - \vec{r}_\alpha)}{|\vec{r} - \vec{r}_\alpha|^3}$$

now we have made our first approximation — we drop the multipoles beyond the dipole.

For our second approximation, we consider a special physical scale:
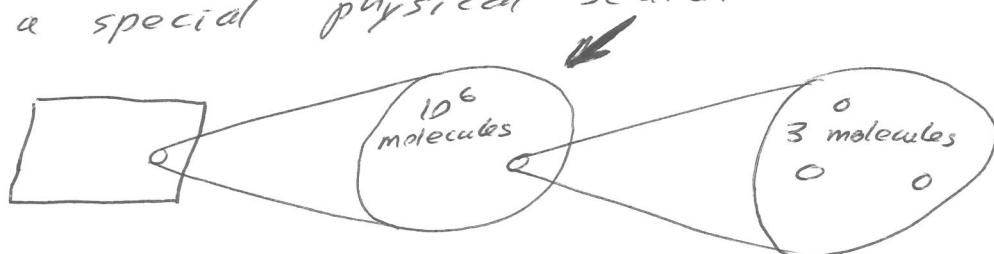


We consider a region that is macroscopically small (so calculus works) but microscopically large (so we can approximate the charge inside as a continuous distribution.)

We "smear out" the charges $q_\alpha$ and dipoles $\vec{\mu}_\alpha$ over a region that is still small compared to the bulk of the material:

$$\vec{r}_\alpha \rightarrow \vec{r}\,'$$

$$q_\alpha \rightarrow \rho_{mol}(\vec{r}\,')\, dV' \left.\begin{array}{c}\\ \\ \\ \\ \\ \end{array}\right\} \begin{array}{c}continuum \\ limits\end{array}$$

$$\vec{\mu}_\alpha \rightarrow \vec{P}(\vec{r}\,')\, dV'$$

where $\rho_{mol}(\vec{r}\,')$ is the <u>macroscopic</u> molecular charge density and $\vec{P}(\vec{r}\,')$ is the <u>macroscopic</u> molecular dipole moment density, also called the "polarization."

The potential which results from the continuum approximation is called the macroscopic electrostatic potential. Its negative gradient is the macroscopic electrostatic field.

$$\underset{macro}{\underline{\Phi}(\vec{r})} = \int dV'\, \frac{\rho_{free}(\vec{r}\,') + \rho_{mol}(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|} - \int dV'\, \vec{P}(\vec{r}\,') \cdot \vec{\nabla}\frac{1}{|\vec{r}-\vec{r}\,'|}$$

We define the combination:

$$\rho_{free}(\vec{r}\,') + \rho_{md}(\vec{r}\,') \equiv \rho_{true}(\vec{r}\,')$$

to be the <u>true</u> charge density.

Let's integrate the polarization term by parts:

$$\vec{P}(\vec{r}') \cdot \vec{\nabla} \frac{1}{|\vec{r}-\vec{r}'|} = - \vec{P}(\vec{r}') \cdot \vec{\nabla}_{r'} \frac{1}{|\vec{r}-\vec{r}'|}$$

$$= - \vec{\nabla}_{r'} \cdot \left[ \frac{\vec{P}(\vec{r}')}{|\vec{r}-\vec{r}'|} \right] + \frac{\vec{\nabla}_{r'} \cdot \vec{P}(\vec{r}')}{|\vec{r}-\vec{r}'|}$$

Then we use the divergence theorem as follows:

$$\underline{\Phi}_{macro}(\vec{r}) = \int dV' \frac{\rho_{true}(\vec{r}')}{|\vec{r}-\vec{r}'|} + \oint_{S} ds' \frac{\hat{n} \cdot \vec{P}(\vec{r}')}{|\vec{r}-\vec{r}'|}^{0} - \int dV' \frac{\vec{\nabla}_{r'} \cdot \vec{P}(\vec{r}')}{|\vec{r}-\vec{r}'|}$$

If we take the surface $S$ out to infinity, where the charge and polarization vanish, the surface integral will vanish.

$$\vec{E}_{macro}(\vec{r}) = - \vec{\nabla} \underline{\Phi}_{macro}(\vec{r})$$

$$\vec{\nabla} \cdot \vec{E}_{macro}(\vec{r}) = - \nabla^2 \underline{\Phi}_{macro}(\vec{r}) = - \int dV' \underbrace{\nabla^2 \frac{1}{|\vec{r}-\vec{r}'|}}_{-4\pi \delta^3(\vec{r}-\vec{r}')} \left[ \rho_{true}(\vec{r}') - \vec{\nabla}_{r'} \cdot \vec{P}(\vec{r}') \right]$$

$$= 4\pi \rho_{true}(\vec{r}) - \vec{\nabla} \cdot 4\pi \vec{P}(\vec{r})$$

The divergence of the macroscopic Electric field does not satisfy a simple Maxwell equation, like the microscopic $\vec{E}$ field.

We define the macroscopic displacement field

$$\vec{D}(\vec{r}) = \vec{E}_{macro}(\vec{r}) + 4\pi \vec{P}(\vec{r})$$

$$\boxed{\vec{\nabla} \cdot \vec{D}(\vec{r}) = 4\pi \rho_{true}(\vec{r})}$$

This is the first of our Maxwell equations in __matter.__

The source of $\vec{D}$ is __true__ charge only, not __bound__ charge.

If we define: $-\vec{\nabla} \cdot \vec{P}(\vec{r}) = \rho_{polar}(\vec{r})$

to be the "polarization charge" then we set

$$\vec{\nabla} \cdot \vec{E}_{macro} = 4\pi \left[ \rho_{true}(\vec{r}) + \rho_{polar}(\vec{r}) \right]$$

Since the macroscopic electric field is derived from the macroscopic potential,

$$\vec{E}_{macro}(\vec{r}) = -\vec{\nabla} \Phi_{macro}(\vec{r})$$

the curl of $\vec{E}_{macro}$ vanishes

$$\vec{\nabla} \times \vec{E}_{macro}(\vec{r}) = -\vec{\nabla} \times \vec{\nabla} \Phi_{macro}(\vec{r}) = 0$$

$$\boxed{\vec{\nabla} \times \vec{E}_{macro}(\vec{r}) = 0}$$

This is the second Maxwell equation in matter.

The electrostatic problem is now complicated by the presence of a second field, $\vec{P}$, in addition to the macroscopic electric field $\vec{E}_{macro}$. Generally, the polarization $\vec{P}$ is a function of $\vec{E}$. The specification of this functional relation is called the "constitutive equation." If we assume that $\vec{P}$ is an _analytic_ function of $\vec{E}$ (which need not be the case) then we have

$$P_i(\vec{E}) = P_i(0) + \sum_j \frac{\partial P_i}{\partial E_j}\bigg|_{\vec{E}=0} E_j + \cdots$$

$$\uparrow$$
$$\vec{E}=0, \; \underline{\underline{not}} \; \vec{r}=0$$

If the electric field is sufficiently weak, then we may neglect terms beyond the linear. For most materials, the polarization in the absence of field is zero: $P_i(0) = 0$. However, there are materials such as some waxes called "ferro-electrics" (the electric analog of ferro-magnets) for which a polarization exists independent of $\vec{E}$ field.

"Electrets" can be made out of such materials just as magnets can be made of ferro-magnetic material. We will not consider electrets further.

From now on, $P_i(0) = 0$ and we have the linear constitutive relation:

$$P_i = \sum_j \chi_{ij} E_j \qquad \text{or in vector form}$$

$$\vec{P} = \underline{\underline{\chi}} \, \vec{E}$$

$\chi_{ij}$ is the _electric susceptibility_ matrix (or tensor)

$$\chi_{ij} = \left. \frac{\partial P_i(\vec{E})}{\partial E_j} \right|_{\vec{E}=0} = \chi_{ji} \qquad \text{it is } \underline{symmetric}$$

Off-diagonal matrix elements will produce a polarization in a direction other than the $\vec{E}$ field direction. Piezzo-electric crystals are an example of a material with this property.

We limit our discussion to isotropic materials for which

$$\chi_{ij} = \chi_e \, \delta_{ij}$$

$\chi_e$ is the electric susceptibility,

$\epsilon$ is the dielectric constant.

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

$$\vec{D} = \vec{E} + 4\pi \vec{P} = \epsilon \, \vec{E}$$

$$\epsilon = 1 + 4\pi \chi_e$$

## Boundary conditions at a dielectric interface

We have two field equations:

$$\vec{\nabla} \times \vec{E}_{macro} = 0 \qquad\qquad \vec{\nabla} \cdot \vec{D} = 4\pi \, \rho_{true}$$

Consider a medium in which there is a discontinuity in $\epsilon$. Suppose the rectangle in the diagram is the cross-section of a Gaussian pillbox.
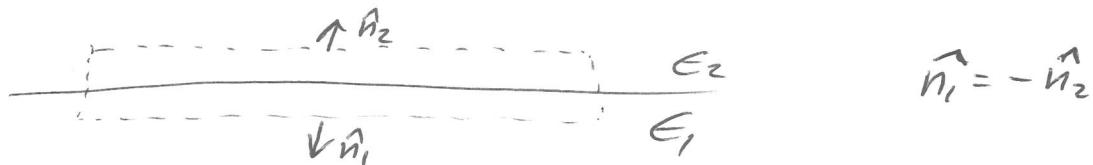


$$0 = \int_V dV \; \vec{\nabla} \times \vec{E} = \oint_S ds \; \hat{n} \times \vec{E} = \oint_S ds \left[ \hat{n}_1 \times \vec{E}_1 + \hat{n}_2 \times \vec{E}_2 \right]$$

$$\Rightarrow \hat{n}_1 \times (\vec{E}_1 - \vec{E}_2) = 0$$

the _tangential_ component of $\vec{E}$ is continuous across a dielectric boundary.

$$4\pi \, Q_{true} = \int_V dV \; \vec{\nabla} \cdot \vec{D} = \oint_S ds \left[ \hat{n}_1 \cdot \vec{D}_1 + \hat{n}_2 \cdot \vec{D}_2 \right]$$

$$\Rightarrow \hat{n}_1 \cdot (\vec{D}_1 - \vec{D}_2) = 4\pi \, \sigma_{true}$$

the _normal_ component of $\vec{D}$ is continuous across a dielectric boundary if there is no _true_ charge there.

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