Physics 153 (Hoffman)
Lecture #6
Tues, Feb 17, 2009

Polarization

Last time:

1. Solved Laplace's eqn by separation of variables
   - Cartesian: obtain sines & cosines, or exponentials, along each direction
     these are complete & orthogonal → we can form full solution
   - Spherical: obtain polynomials in r, Legendre polynomials in θ
     $$\varphi(r,\theta) = \sum_{\ell=0}^{\infty} \left(A_\ell r^\ell + \frac{B_\ell}{r^{\ell+1}}\right) P_\ell(\cos\theta)$$
     these are complete & orthogonal too → solve for A_ℓ, B_ℓ
2. Started multipole expansion:
   Try to express the potential $\varphi(r)$ of a localized charge configuration as a sum of powers of r: $\varphi(r) = \sum_{n=1}^{\infty} c_n \frac{1}{r^n}$

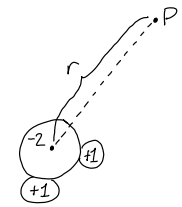
Goals for today:

1. Wrap up multipole expansion
2. Focus on dipoles: what is force & torque on a dipole?
3. Where does a dipole come from? → linear polarizability
4. How does a polarized object arise? behave?
5. Microscopic vs. macroscopic field

Multipole Expansion: a convenient way to estimate the "far field" of a charge distribution by writing $\varphi(r)$ as a sum of powers $1/r^n$

Start by looking at an arbitrary small charge distribution (e.g. H_2O)

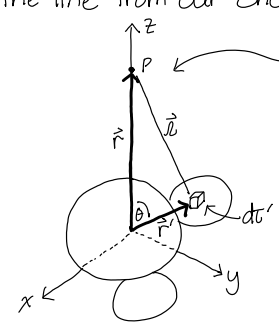
What is the $\vec{E}$-field at an arbitrary point P, far away?



(far away means $r \gg$ size of charge distribution)

We need to pick a coordinate system to get started (we'll try to get a coordinate-independent formula later).

Arbitrarily pick an origin somewhere within the charge distribution. Then for ease of calculation, let's orient our coordinates so the z-axis lies along the line from our chosen origin to point P.



The potential here is:
$$\varphi(\vec{r}) = \frac{1}{4\pi\varepsilon_0}\int \frac{\rho(\vec{r}')\,d\tau'}{\mathscr{r}}$$

The only distance which doesn't change as we integrate over our charge distribution is $\vec{r}$. The vector $\vec{r}$ depends only on our choice of origin and on P, so our goal is going to be to pull all of the $\vec{r}$-dependence out of the integral.

Law of cosines: $\mathscr{r} = (r^2 + r'^2 - 2rr'\cos\theta)^{1/2}$

$$\Rightarrow \varphi(\vec{r}) = \int \rho(\vec{r}\,')(r^2 + r'^2 + 2rr'\cos\theta)^{-1/2}\, d\tau'$$

Remember we're looking for the "far field" so $r \gg r'$.

$$\frac{1}{(r^2+r'^2-2rr'\cos\theta)^{1/2}} = \frac{1}{r\left[1+\left(\frac{r'}{r}\right)^2 - 2\frac{r'}{r}\cos\theta\right]^{1/2}}$$

$$= \frac{1}{r}\Big[1 + \underbrace{\left(\frac{r'}{r}\right)^2 - 2\frac{r'}{r}\cos\theta}_{\text{this should be small!}}\Big]^{-1/2}$$

Use the Taylor expansion: $(1+\varepsilon)^{-1/2} = 1 - \frac{1}{2}\varepsilon + \frac{3}{8}\varepsilon^2 + \ldots$

$$= \frac{1}{r}\left\{1 - \frac{1}{2}\left[\left(\frac{r'}{r}\right)^2 - 2\frac{r'}{r}\cos\theta\right] + \frac{3}{8}\left[\left(\frac{r'}{r}\right)^2 - 2\frac{r'}{r}\cos\theta\right]^2 + \ldots\right\}$$

The $\frac{r'}{r}$ terms will be $\ll 1$, and the $\left(\frac{r'}{r}\right)^2$ terms will be $\ll$ the $\frac{r'}{r}$ terms, and so on.

For now, let's keep up to the $\left(\frac{r'}{r}\right)^2$ terms, although in principle we could continue this expansion to $\left(\frac{r'}{r}\right)^3$, etc.

Grouping terms, we're left with

$$(r^2+r'^2-2rr'\cos\theta)^{-1/2} = \frac{1}{r}\Big[1 + \frac{r'}{r}\cos\theta + \left(\frac{r'}{r}\right)^2 \frac{(3\cos^2\theta - 1)}{2} + \text{higher order terms}\Big]$$

Do these look familiar?
Hint: check lecture #5

Ah-hah! Now we can take r out of the integral:

$$\varphi(\vec{r}) = \frac{1}{4\pi\varepsilon_0}\int \frac{\rho(\vec{r}\,')d\tau'}{\mathscr{r}} = \frac{1}{4\pi\varepsilon_0}\left\{\frac{1}{r}\underbrace{\int \rho(\vec{r}\,')d\tau'}_{K_0} + \frac{1}{r^2}\underbrace{\int \rho(\vec{r}\,')r'\cos\theta\, d\tau'}_{K_1}\right.$$

$$\left. + \frac{1}{r^3}\underbrace{\int \rho(\vec{r}\,')r'^2\frac{(3\cos\theta - 1)}{2}d\tau'}_{K_2} + \ldots\right\}$$

Each of the K integrals now depends only on the structure of the charge distribution, not on the choice of point P. We've pulled the P-dependence out of the integrals, so now we have a prescription for finding φ at any point, based on a few integrals that we have to compute only once for a given charge distribution.

$$\varphi(\vec{r}) = \frac{1}{4\pi\varepsilon_0}\left\{\frac{1}{r}K_0 + \frac{1}{r^2}K_1 + \frac{1}{r^3}K_2 + \ldots\right\}$$

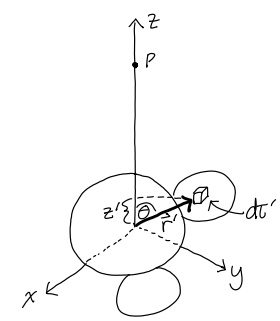
these terms are getting rapidly smaller

For the "far field", $\varphi(\vec{r})$ is dominated by the first non-vanishing term, given by the first non-vanishing K-integral.

$K_0 = \int \rho(\vec{r}\,')d\tau' =$ total charge in the distribution
→ vanishes for a neutral molecule
(called the "monopole moment" of the charge distribution)

$$K_1 = \int \rho(\vec{r}\,')\underbrace{r'\cos\theta}_{\text{this is just } z'}d\tau'$$

⇒ K_1 measures the relative displacement, in the direction towards P, of the positive & negative charge



Clearly, K_1 doesn't depend on our choice of origin in the x-y direction, but what about z?

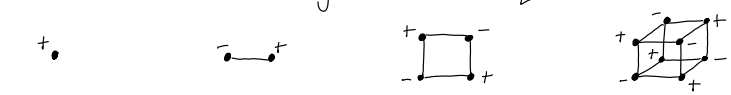
Choice of origin:

Does K_1 depend on our choice of origin in the z-direction?
Answer (proved rigorously in last lecture notes):

K_1 is a coordinate-independent property of a neutral molecule, called the "dipole moment"

If the charge distribution is not neutral, then the dipole moment is not a unique property - in this case, it does depend on choice of origin.

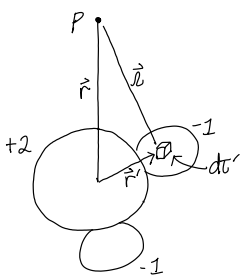
Summary: if $K_0 \neq 0$ then potential behaves like $1/r$ at large distances ("monopole")
if $K_0 = 0$ but $K_1 \neq 0$ then potential behaves like $1/r^2$ at large distances ("dipole moment")
if $K_1 = K_0 = 0$ but $K_2 \neq 0$ then potential behaves like $1/r^3$ at large distances ("quadrupole moment")



Monopole	Dipole	Quadrupole	Octupole
$\varphi \propto \frac{1}{r}$	$\varphi \propto \frac{1}{r^2}$	$\varphi \propto \frac{1}{r^3}$	$\varphi \propto \frac{1}{r^4}$

Remember: this description (decomposition into "moments", or powers of $1/r^n$) is only useful in the "far field" for large r.

φ from a dipole:



The dipole contribution to the potential at P is:

$$\varphi_{dip}(\vec{r}) = \frac{1}{4\pi\varepsilon_0 r^2}\int \rho(\vec{r}')\underbrace{r'\cos\theta}_{\text{this is just the projection of } \vec{r}' \text{ onto } \vec{r}}\, d\tau'$$

$= \vec{r}' \cdot \hat{r}$

depends only on charge distribution

depends only on direction & distance of P → we can pull this out of integral

$$\varphi_{dip}(\vec{r}) = \frac{\hat{r}}{4\pi\varepsilon_0 r^2} \cdot \underbrace{\int \rho(\vec{r}')\,\vec{r}'\,d\tau'}_{\text{this is a vector quantity } \equiv \text{ dipole moment } \equiv \vec{p}}$$

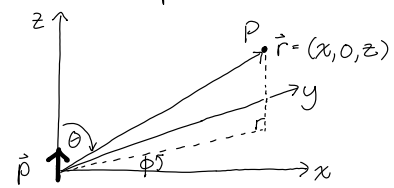
Now, finally, we can write $\varphi(\vec{r})$ in a coordinate-independent way:

$$\varphi(\vec{r}) = \frac{\hat{r}\cdot\vec{p}}{4\pi\varepsilon_0 r^2} \quad \text{where } \vec{p} = \int \rho(\vec{r}')\,\vec{r}'\,d\tau'$$

this is the dominant "far-field" potential for a neutral molecule.

$\vec{E}$ from a dipole:

$\vec{E} = -\vec{\nabla}\varphi$, so you can derive the $\vec{E}$-field of a dipole but to take the gradient it's easiest to go back into a coordinate system, e.g. choose the origin at the center of the dipole $\vec{p}$, and choose the z-axis to lie along the direction of $\vec{p}$.



What are the components of $\vec{E}$ at point $\vec{r}$?

$$\varphi(\vec{r}) = \frac{\hat{r}\cdot\vec{p}}{4\pi\varepsilon_0 r^2} = \frac{p\cos\theta}{4\pi\varepsilon_0 r^2}$$

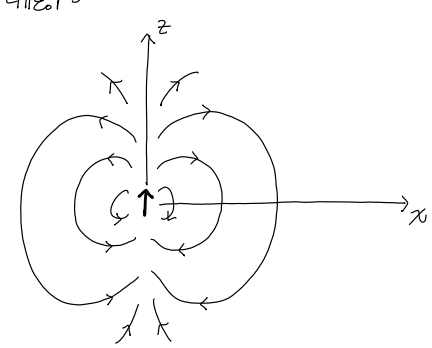
The components of $\vec{E}$ follow from $\vec{E} = -\vec{\nabla}\varphi$

$$E_r = -\frac{\partial\varphi}{\partial r} = \frac{2p\cos\theta}{4\pi\varepsilon_0 r^3}$$

$$E_\theta = -\frac{1}{r}\frac{\partial\varphi}{\partial\theta} = \frac{p\sin\theta}{4\pi\varepsilon_0 r^3}$$

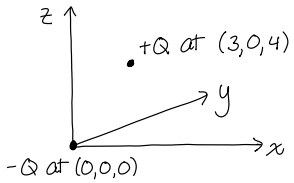
$$E_\phi = -\frac{1}{r\sin\theta}\frac{\partial\varphi}{\partial\phi} = 0$$

$$\Rightarrow \vec{E}_{dip}(r,\theta) = \frac{p}{4\pi\varepsilon_0 r^3}\left(2\cos\theta\,\hat{r} + \sin\theta\,\hat{\theta}\right)$$



Example: physical dipole

Compute the dipole moment of this charge distribution:



Solution:

$$\vec{p} = \int \rho(\vec{r}\,')\vec{r}\,' d\tau' = -Q(0,0,0) + Q(3,0,4) = Q(3,0,4)$$

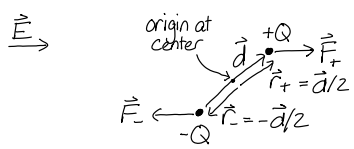
$$|\vec{p}| = Q|(3,0,4)| = 5Q \quad ; \quad \hat{p} = (3/5, 0, 4/5)$$

↖ in general, for a simple physical dipole consisting of equal & opposite charges Q separated by some distance d,

$\vec{p} = Q\vec{d}$ where $\vec{d}$ points from $-Q$ to $+Q$

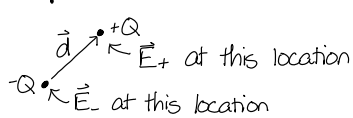
Note: origin doesn't matter!

Torque on a dipole from applied $\vec{E}$:



$$\vec{\tau} = \vec{r}_+ \times \vec{F}_+ + \vec{r}_- \times \vec{F}_- = \vec{d}/2 \times Q\vec{E} + (-\vec{d}/2) \times (-Q\vec{E}) = Q\vec{d} \times \vec{E} = \vec{p} \times \vec{E}$$

Force on a dipole from non-uniform $\vec{E}$:



$$\vec{F} = Q\vec{E}_+ - Q\vec{E}_- = Q(\vec{E}_+ - \vec{E}_-)$$

Taylor expand $\vec{E}(\vec{r})$ around $\vec{E}_-$: $\vec{E}(\vec{r}) = \vec{E}_- + (\vec{r}\cdot\vec{\nabla})\vec{E} + \ldots$

$$\vec{F} = Q[\vec{E}_- + (\vec{d}\cdot\vec{\nabla})\vec{E} - \vec{E}_-] = Q(\vec{d}\cdot\vec{\nabla})\vec{E} = (\vec{p}\cdot\vec{\nabla})\vec{E}$$

Energy of a dipole

Example: Griffiths 4.7

Show that the energy of an ideal dipole $\vec{p}$ at point $\vec{r}$ in an electric field $\vec{E}$ is given by $U = -\vec{p}\cdot\vec{E}$.

Solution: We bring both charges $\pm Q$ in from some reference point (typically from infinity, where $\varphi_0 = 0$, but all that really matters is that we bring both charges in from reference points with the same φ_0, i.e. $\varphi_{0+} = \varphi_{0-}$)

$$U = Q\varphi(\vec{r}+\vec{d}) - Q\varphi(\vec{r}) = Q[\varphi(\vec{r}+d) - \varphi(\vec{r})]$$

$$= Q\Big[\underbrace{-\int_{\vec{r}}^{\vec{r}+\vec{d}} \vec{E}\cdot d\vec{l}}_{\text{as } \vec{d}\to 0 \text{ this reduces to } \vec{E}\cdot\vec{d}}\Big]$$

$$= -Q\vec{d}\cdot\vec{E}$$

$$= -\vec{p}\cdot\vec{E}$$

Follow-up: what's the energy difference between $\vec{p}$ that's perfectly aligned with $\vec{E}$ and $\vec{p}$ that's perfectly misaligned?

Answer: $2pE$

(perfect alignment is the lowest energy configuration)

Where does a physical dipole come from?

First of all, let's restrict our discussion to insulators: materials where we can't strip all the negative charges and move them far from the positive charges. We're going to have approximate local charge neutrality, so these are the types of materials where the dipoles are going to be the most relevent terms. We call these materials **dielectrics**. They come in 2 basic types:

1. induced dipoles, in non-polar molecules (e.g. hydrogen atom)
   → $\vec{E}$ will cause ⊕ and ⊖ to separate
2. permanent dipoles (eg. H_2O)
   → will rotate to align with $\vec{E}$

Induced dipoles:

Estimate the polarizability of a typical atom:

In response to an applied field $\vec{E}$, the "center of gravity" of the negative charge cloud will shift by Δz.

Δz is limited by the restoring force of the positive nucleus pulling back on the negative charge cloud.

If a is a typical atom dimension, then $E_{int} \sim e/a^2$ is a typical internal field holding the atom together.

The fractional distortion of the atom in the presense of the applied field should be equal to the fractional change in the total field experienced by the charge cloud in the presense of the applied external field:

$$\frac{\Delta z}{a} \sim \frac{E_{applied}}{E_{internal}} = \frac{E_{app}}{e/a^2}$$

$$\Rightarrow \Delta z \sim \frac{a^3}{e} E_{app}$$

$$\vec{p} = e\Delta z \sim a^3 \vec{E}_{app}$$

$$\Rightarrow \alpha \equiv \text{polarizability} \sim a^3$$

The main point to take from this is that for a typical atom (or non-polar molecule) the induced dipole moment is to a good approximation linear in the applied field.

Polar materials (e.g. H_2O, composed of polar molecules)

→ acquire a net polarization when the applied field rotates some of the molecular dipoles $\vec{p}$ along the field direction

Note that not <u>all</u> of the dipoles align. Thermal excitations are always causing most of the H_2O molecules to randomly orient.

<u>Equipartition Theorem:</u> predicts that every available degree of freedom will have energy $\frac{1}{2}k_BT$

where k_B = boltzmann's constant $= 1.381\times10^{-23}$ J/K and T is a temperature in Kelvin

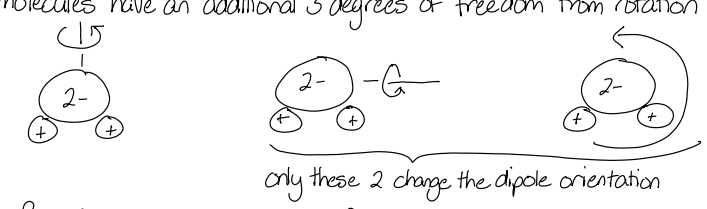
e.g. Helium atom at room temperature (~300K) will have 3 degrees of freedom: x translational motion, y, and z, with $\frac{1}{2}k_BT$ of kinetic energy each

⇒ total translational kinetic energy of an average single He is

$$\frac{1}{2}m(v_x^2+v_y^2+v_z^2) = \frac{1}{2}mv^2 = \frac{3}{2}k_BT$$

$$\Rightarrow v = \sqrt{\frac{3k_BT}{m}} \approx 1.36 \text{ km/s}$$

H_2O molecules have an additional 3 degrees of freedom from rotation:



The fractional polarization of water will be on order:

$$\frac{\text{average energy gained by rotating one molecule}}{\text{thermal energy in the relevant degrees of freedom}}$$

$$= \frac{pE}{k_BT} \leftarrow \text{on average, molecule has to turn } 90°$$

≈ 2 degrees of freedom

⇒ average polarization of a water molecule in applied field $\vec{E}$ is:

$$p\left(\frac{p\vec{E}}{k_BT}\right) = \frac{p^2}{k_BT}\vec{E}$$

Polarization $\vec{P}$

We've just given plausible arguments that both nonpolar substances and polar gases & liquids acquire a net polarization which is linear in applied magnetic field.

(Note: it seems pretty clear that a single molecule would polarize linearly in an applied field, but it's not at all clear why this linearity should hold for dense materials where each molecule must be influenced by strong fields from its neighbors as well as the applied external field. But, the linearity does hold.)

Let $\vec{P}$ = dipole moment $\vec{p}$ per unit volume

We've just argued that $\vec{P} \propto \vec{E}$.

Define a constant χ_e = **electric susceptibility** such that:

$$\vec{P} = \varepsilon_0 \chi_e \vec{E}$$

"susceptibility to electric polarization

χ_e is a material-dependent property

We'll see later that χ_e also depends on frequency:

No material can respond to an applied field and polarize instantly (it would violate special relativity).

non-polar dielectrics: shift of charge cloud (e^-) is pretty quick
→ cutoff frequency ~ 10^{16} Hz (adjusts in ~10^{-16} s)

polar dielectrics: rotation of comparatively massive nuclei is slow
→ cutoff frequency ~ 10^{11} Hz (adjusts in ~10^{-11} s)

But both of these time scales are really fast, so for now let's just consider the steady state effects, when $\vec{P}$ has already finished developing in response to a static $\vec{E}$.

The problem is still more complicated than it initially appears. $\vec{P}$ developes in response to an external $\vec{E}_{ext}$ but then $\vec{P}$ actually causes additional induced $\vec{E}_{ind}$. But now $\vec{P}$ must be proportional to the total $\vec{E}_{ext} + \vec{E}_{ind}$ which in turn causes more $\vec{P}$ and more changes to $\vec{E}$...

Field of a polarized object:

For now, let's not worry about this vicious $\vec{E} \to \vec{P} \to \vec{E} \to \vec{P} \to \vec{E} \to \vec{P}$ cycle. Let's start by just considering a single polarized object with polarization $\vec{P}$, and we won't worry about how it acquired its polarization. We'll compute the $\vec{E}$ produced by this object. That will at least give us the $\vec{P} \to \vec{E}$ part of the vicious cycle.

We got $\vec{E}(\vec{r})$ for a single $\vec{p}$ from $-\vec{\nabla}\varphi(\vec{r})$ where:

$$\varphi(\vec{r}) = \frac{\hat{r} \cdot \vec{p}}{4\pi\varepsilon_0 r^2}$$

So we can integrate over a whole polarized object to get:

$$\varphi(\vec{r}) = \frac{1}{4\pi\varepsilon_0} \int_V \frac{\hat{\mathscr{r}} \cdot \vec{P}(\vec{r}\,')}{\mathscr{r}^2} \, d\tau'$$

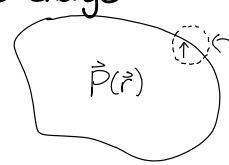
Griffiths uses a trick and integration by parts to arrive at:

$$\varphi(\vec{r}) = \frac{1}{4\pi\varepsilon_0} \int_S \frac{1}{\mathscr{r}} \vec{P} \cdot d\vec{a}' - \frac{1}{4\pi\varepsilon_0} \int_V \frac{1}{\mathscr{r}} (\vec{\nabla}' \cdot \vec{P}) \, d\tau'$$

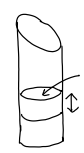
which is still not very enlightening, so let's look physically.

Suppose we have some object with polarization $\vec{P}$ (not even necessarily uniform $\vec{P}$).

Surface charge:



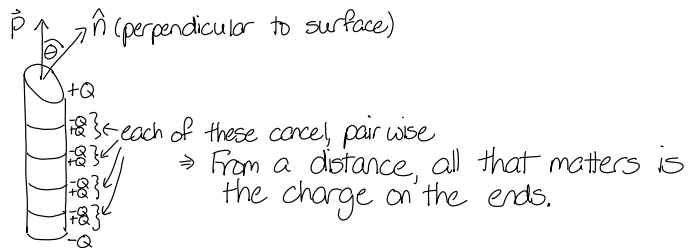
Consider part of the surface: pull out a tiny column, along the direction of $\vec{P}$, starting at the surface, and small enough so $\vec{P}$ ~ constant within.



each increment within the column has $\vec{p} = A d \vec{P}$

In fact, it is composed of many molecules, and thus many displaced charges, but from a distance it will appear as a single dipole with $-Q = -AP$ on bottom and $+Q = +AP$ on top, separated by $\vec{d}$.

The whole column is just a stack of these dipoles:



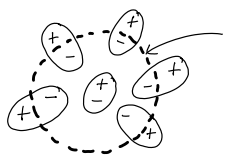
At the surface of area $A/\cos\theta$, the charge is $+Q = AP$.
⇒ surface charge density is:

$$\sigma = \frac{AP}{A/\cos\theta} = P\cos\theta = \vec{P}\cdot\hat{n}$$

We call this "bound charge" $\sigma_b = \vec{P}\cdot\hat{n}$ because the charge came from the insulator itself, so we're not free to move it.

Volume charge:

If the polarization is uniform, then all of the net charge will be bound at the surfaces, as above. But if $\vec{P}$ is non-uniform:



Any local volume will contain some heads and some tails of dipoles. If it contains more tails (if $\vec{\nabla}\cdot\vec{P} > 0$) the the local charge density is negative. (& vice versa)

Net bound charge in a volume is equal and opposite to the amount pushed out through the surface:

$$\int_V \rho_b \, d\tau = -\oint_S \sigma_b \, da = -\oint_S \vec{P}\cdot\hat{n}\, da = -\oint_S \vec{P}\cdot d\vec{a} = -\int_V (\vec{\nabla}\cdot\vec{P})\, d\tau$$

argument above — divergence thm

Since this is true for any volume, we have

$$\rho_b = -\vec{\nabla}\cdot\vec{P}$$

Potential from a polarized object, revisited:

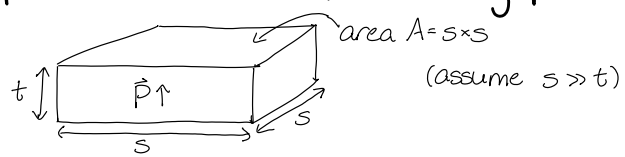
Now we look back at Griffiths' formula:

$$\varphi(\vec{r}) = \frac{1}{4\pi\varepsilon_0}\int_S \frac{1}{\mathscr{r}}\underbrace{\vec{P}\cdot d\vec{a}'}_{\substack{\text{surface charge:}\\ \sigma_b = \vec{P}\cdot\hat{n}}} - \frac{1}{4\pi\varepsilon_0}\int_V \frac{1}{\mathscr{r}}\underbrace{(\vec{\nabla}'\cdot\vec{P})}_{\substack{\text{bound charge:}\\ \rho_b = \vec{\nabla}\cdot\vec{P}}}\, d\tau'$$

So we see that this formula reverts to the more intuitive:

$$\varphi(\vec{r}) = \frac{1}{4\pi\varepsilon_0}\oint_S \frac{\sigma_b}{\mathscr{r}}\, da' + \frac{1}{4\pi\varepsilon_0}\int_V \frac{\rho_b}{\mathscr{r}}\, d\tau'$$

Example: what is $\vec{E}$ for from a uniformly polarized slab?



Solution:
$\vec{P}$ is uniform, so $\rho_b = 0$
$\sigma_b = \vec{P}\cdot\hat{n} = P$

Put the origin in the center of the slab and integrate:

$$\varphi(\vec{r}) = \frac{1}{4\pi\varepsilon_0}\int_{-s/2}^{s/2} dx' \int_{-s/2}^{s/2} dy' \frac{P}{\left[(x-x')^2 + (y-y')^2 + (z - t/2)\right]^{1/2}}$$
$$+ \frac{1}{4\pi\varepsilon_0}\int_{-s/2}^{s/2} dx' \int_{-s/2}^{s/2} dy' \frac{-P}{\left[(x-x')^2 + (y-y')^2 + (z + t/2)^2\right]^{1/2}}$$

Then compute $\vec{E} = -\vec{\nabla}\varphi$

What about $\vec{E}$ inside the slab?

Naively, we say this looks just like 2 parallel plates of charge, so if $s \gg t$ then we have

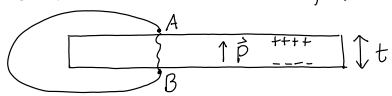
$$\vec{E} = \frac{\sigma_b}{\varepsilon_0}(-\hat{z}) = \frac{P}{\varepsilon_0}(-\hat{z}) = -\frac{1}{\varepsilon_0}\vec{P}$$

But wait! Inside there are actual point charges, so the actual field is going to vary wildly...

Macroscopic vs. Microscopic $\vec{E}$-field

We're going to show that the macroscopic field is a local average of the microscopic field, and it's a legitimate quantity in its own right. Our argument may be a little more intuitive but not quite as rigorous as Griffiths.

Consider a slab of thickness t, viewed from the side:

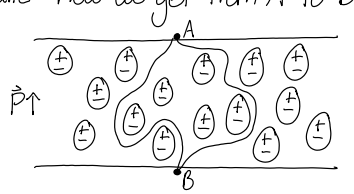


$\int_A^B \vec{E}\cdot d\vec{l}$ must be path-independent.

Since we don't yet know how to deal with the messy internal path, just consider the external one: the external field is just that of 2 charged plates.

$$\Rightarrow \int_A^B \vec{E}\cdot d\vec{l} = \varphi_A - \varphi_B = \frac{\sigma_b}{\varepsilon_0} t = \frac{1}{\varepsilon_0} P t$$

No matter how we get from A to B, the total path integral is constant.



$$\int_A^B \vec{E}\cdot d\vec{l} = \text{constant}$$

But this $\vec{E}$ is the <u>total</u> field, including the messy microscopic fields, and the path integral of this messy field, no matter which way we go, still gives us the clean value $\frac{1}{\varepsilon_0}Pt$.

$\Rightarrow$ We have to conclude that the spatially averaged field within the polarized slab must be $-\frac{1}{\varepsilon_0}\vec{P}$.

Denote $\langle \vec{E} \rangle_V$ = spatial average of $\vec{E}$ over volume V.

$$\langle \vec{E} \rangle_V = \frac{1}{V}\int_V \vec{E}\, d\tau$$

"macroscopic field" "microscopic field"

It turns out that $\langle \vec{E} \rangle$ is really all we <u>can</u> or <u>need to</u> talk about inside a material.

$\int_A^B \langle \vec{E} \rangle \cdot d\vec{l}$ is path-independent

$\Rightarrow \vec{\nabla} \times \langle \vec{E} \rangle = 0$

and $\langle \vec{E} \rangle = -\vec{\nabla}\langle \varphi \rangle$ for some potential function $\langle \varphi \rangle$

It can also be proven that $\vec{\nabla}\cdot\langle \vec{E} \rangle = \frac{1}{\varepsilon_0}\langle \rho \rangle$

Summary: $\langle \vec{E} \rangle$, $\langle \varphi \rangle$, and $\langle \rho \rangle$ are related to each other just like $\vec{E}$, φ, and ρ. Since we can't say anything useful, or do any productive quantitative calculations with the real microscopic $\vec{E}$, φ, and ρ anyhow, we will never actually talk about them again. So there is no ambiguity in dropping the $\langle\ \rangle$ and just writing $\vec{E}$, φ, and ρ for the spatially averaged quantities from here on.

Summary:

① Multipole expansion:

$$\varphi(\vec{r}) = \frac{1}{4\pi\varepsilon_0}\left\{\frac{1}{r}K_0 + \frac{1}{r^2}K_1 + \frac{1}{r^3}K_2 + \dots\right\}$$

K_0 = "monopole" = total charge
K_1 = "dipole" = charge × displacement from origin
K_2 = "quadrupole"

② Force on dipole: $\vec{F} = (\vec{p}\cdot\vec{\nabla})\vec{E}$; Torque on dipole: $\vec{\tau} = \vec{p}\times\vec{E}$
Energy of dipole: $U = -\vec{p}\cdot\vec{E}$

③ $\vec{P}$ = polarization per unit volume
In general, $\vec{P} \propto \vec{E}$

④ Polarized object: $\sigma_b = \vec{P}\cdot\hat{n}$; $\rho_b = \vec{\nabla}\cdot\vec{P}$

⑤ Inside dielectric, just worry about $\langle \vec{E} \rangle$, $\langle \varphi \rangle$, and $\langle \rho \rangle$

Next time: figure out the $\vec{E} \to \vec{P} \to \vec{E} \to \vec{P} \to \vec{E} \to \vec{P}$ ... problem