

## Electrostatics with Dielectrics (Garg: Chap 15)

Basics (from previous chapters):

$$\vec{\nabla} \cdot \vec{D} = 4\pi\rho \quad (\rho = \rho_{\text{free}}) \quad \vec{\nabla} \times \vec{E} = 0$$

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

We'll use  $\vec{D} = \epsilon\vec{E}$  (not a law, not general, good enough for now)

Then, equivalently

$$\epsilon\vec{E} = \vec{E} + 4\pi\vec{P} \quad \text{or} \quad \vec{P} = \frac{\epsilon-1}{4\pi}\vec{E} \equiv \chi_e\vec{E} \quad \chi_e = \frac{\epsilon-1}{4\pi}$$

"electric susceptibility"

Boundary Value Problems with Dielectrics:

Since  $\vec{\nabla} \times \vec{E} = 0 \Rightarrow \vec{E} = -\nabla\phi$  still.

Then  $\vec{\nabla} \cdot \vec{D} = \epsilon\vec{\nabla} \cdot \vec{E}$  (assume  $\epsilon = \text{uniform in medium}$ )  $\Rightarrow \vec{\nabla}^2\phi = -4\pi\rho/\epsilon$

At interfaces:



$\phi$  is continuous (so  $\vec{E} = -\nabla\phi$  is finite)

$$\phi_1 = \phi_2$$

$$\text{And } (\vec{D}_2 - \vec{D}_1) \cdot \hat{n}_1 = 4\pi\sigma \quad (\sigma = \sigma_{\text{free}})$$

$$\Rightarrow \epsilon_2 \frac{\partial\phi_2}{\partial n} = \epsilon_1 \frac{\partial\phi_1}{\partial n}$$

Note  $E_{t1} = E_{t2}$  (tangential), from  $\vec{\nabla} \times \vec{E} = 0$ .

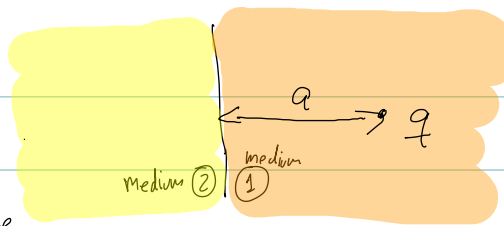
follows from continuity  $\phi_1 = \phi_2$

(Note that this does not imply  $\frac{\partial\phi_1}{\partial n} = \frac{\partial\phi_2}{\partial n}$ ).

Example:

Find  $\vec{E}$

(or  $\vec{D}$ ) everywhere.



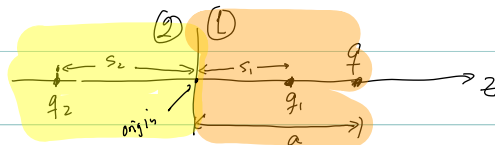
At the expense of just doing busy work, we do  $\frac{1}{2}$  example. This one has a solution using method of images. In contrast to analogous conductor case — where we know  $\vec{E} = 0$  in the conductor, so only need to determine  $\vec{E}$  outside, where the free charge is located — here we want  $\vec{E}$  (or, equivalently  $\phi$ ) both in regions ① & ② of the figure.

So now we need

(i) image charge in ② plus  $q$  in ① to give  $\phi$  in ①. (call image  $q_2$ )

(ii) image charge in ①, say  $q_1$ , to give  $\phi$  in ②

By symmetry place all in same axis,  $\perp$  to plane interface:



$$\text{In } \textcircled{1} \quad \phi_1(\vec{r}) = \frac{1}{\epsilon_1} \left[ \frac{q}{|\vec{r} - a\hat{z}|} + \frac{q_2}{|\vec{r} + s_2\hat{z}|} \right]$$

$$\text{In } \textcircled{2} \quad \phi_2(\vec{r}) = \frac{1}{\epsilon_2} \frac{q_1}{|\vec{r} - s_1\hat{z}|}$$

The factors of  $\frac{1}{\epsilon}$  are so that  $(\vec{\nabla} \cdot \vec{D} = \rho_{\text{free}}, \vec{D} = \epsilon \vec{E}, \vec{E} = -\vec{\nabla} \phi \Rightarrow \vec{\nabla} \cdot \phi = -\rho_{\text{free}}/\epsilon)$ .

Continuity at interface  $\Rightarrow \phi_1(\vec{r}) = \phi_2(\vec{r})$  on  $\vec{r} = (x, y, 0)$ .

No surface charge:  $\epsilon_1 \frac{\partial \phi_1}{\partial z} = \epsilon_2 \frac{\partial \phi_2}{\partial z}$  on  $\vec{r} = (x, y, 0)$

$$\frac{q}{\sqrt{x^2+y^2+a^2}} + \frac{q_2}{\sqrt{x^2+y^2+s_2^2}} = \frac{\epsilon_1/\epsilon_2 q_1}{\sqrt{x^2+y^2+s_1^2}}$$

and

$$\frac{aq}{(x^2+y^2+a^2)^{3/2}} - \frac{s_2 q_2}{(x^2+y^2+s_2^2)^{3/2}} = \frac{s_1 q_1}{(x^2+y^2+s_1^2)^{3/2}}$$

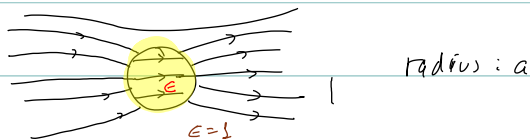
To satisfy for arbitrary  $\rho^2 = x^2 + y^2 \Rightarrow s_1^2 = s_2^2 = a^2 \Rightarrow s_1 = s_2 = a$  since we chose  $s_1 > 0$  &  $s_2 > 0$ .

Then  $q + q_2 = \frac{\epsilon_1}{\epsilon_2} q_1$  and  $q - q_2 = q_1$

$$\Rightarrow q_1 = \frac{2}{1 + \epsilon_1/\epsilon_2} q \quad q_2 = \frac{1 - \epsilon_1/\epsilon_2}{1 + \epsilon_1/\epsilon_2} q$$

(Now one can compute  $\vec{E}, \vec{D}, \vec{P} \dots$ )

Dielectric sphere in uniform external electric field



Much like for conductor.

Sphere suggest use spherical coordinates: center at center of sphere,  $\hat{z} = \hat{E}_0$ .

Azimuthal symmetry  $\Rightarrow Y_{lm}$  with  $m=0$  only  $\rightarrow P_l^0$ .

inside sphere  $\phi_{in}(\vec{r}) = \sum_{l=0}^{\infty} A_l r^l P_l(\cos\theta)$  (no  $\frac{1}{r^{l+1}}$  terms because  $r=0$  included in this region)

outside sphere  $\phi_{out}(\vec{r}) = -E_0 r \cos\theta + \sum_{l=0}^{\infty} B_l \frac{1}{r^{l+1}} P_l(\cos\theta)$   
external applied  $\vec{E}_0 = \text{constant}$

Conditions:

$$\phi_{in} = \phi_{out} \Big|_{r=a} \quad A_l a^l = B_l \frac{1}{a^{l+1}} \quad \text{except } l=1: \quad A_1 a = -E_0 a + \frac{B_1}{a^2}$$

$$\epsilon \frac{\partial \phi_{in}}{\partial r} \Big|_a = \frac{\partial \phi_{out}}{\partial r} \Rightarrow \epsilon A_l a^{l-1} = -(l+1) B_l a^{-(l+2)} \quad \text{except } l=1: \quad \epsilon A_1 = -E_0 - 2 B_1 a^{-3}$$

$$\Rightarrow A_2 = B_2 = 0 \quad \text{except } l=1: \quad \begin{aligned} \epsilon A_1 - a^{-1} B_1 &= -a E_0 \\ \epsilon A_1 + 2a^{-3} B_1 &= -E_0 \end{aligned} \Rightarrow \begin{aligned} A_1 &= -\frac{3}{\epsilon+2} E_0 \\ B_1 &= \frac{\epsilon-1}{\epsilon+2} a^3 E_0 \end{aligned}$$

Hence  $\Phi_{in}(\vec{r}) = -\frac{3}{\epsilon+2} E_0 r \cos\theta \rightarrow$  uniform  $\vec{E} = \frac{3}{\epsilon+2} \vec{E}_0$  inside sphere!

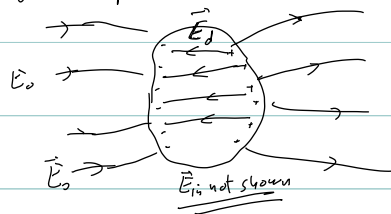
$$\Phi_{out} = \underbrace{-E_0 r \cos\theta}_{\text{external } \vec{E}_0} + \underbrace{\frac{\epsilon-1}{\epsilon+2} E_0 a \left(\frac{a}{r}\right)^2 \cos\theta}_{\text{dipole-induced: } \vec{d}_{in} = \frac{\epsilon-1}{\epsilon+2} a^3 \vec{E}_0}$$

Note  $\vec{P} = \frac{\epsilon-1}{4\pi} \vec{E} = \frac{\epsilon-1}{4\pi} \left(\frac{3}{\epsilon+2}\right) \vec{E}_0 = \frac{1}{4\pi a^3} \left(\frac{\epsilon-1}{\epsilon+2} a^3 \vec{E}_0\right) = \frac{\vec{d}_{in}}{\text{Volume}}$

Depolarization: If  $\vec{E}_{in} = \vec{E}_0 + \vec{E}_d \rightarrow$  "depolarization"

$\Rightarrow$  we get  $\vec{E}_d = \left(\frac{3}{\epsilon+2} - 1\right) \vec{E}_0 = -\frac{\epsilon-1}{\epsilon+2} \vec{E}_0 = -\frac{4\pi}{3} \vec{P}$   
 $\downarrow$  "depolarization coefficient"

$\vec{E}_d$  is the field produced by surface charges from aligned dipoles



In our example one can check this: use that  $\sigma_{pol} = \vec{P} \cdot \hat{n}$  on the surface to compute  $\vec{E}_d$  directly: first  $\Phi_d(\vec{r}) = \int_{\partial V} \frac{\sigma(\vec{r}')}{|\vec{r}-\vec{r}'|} d^2r'$  and then take  $\vec{E}_d = -\vec{\nabla} \Phi_d$ . The

result gives  $\vec{E}_d$  as above.

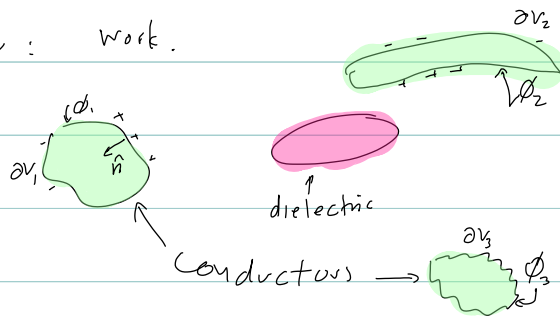
(The calculation uses  $\frac{1}{|\vec{r}-\vec{r}'|} = \sum_{l=0}^{\infty} \sum_{m=-l}^l \frac{4\pi}{2l+1} \frac{r^l}{r'^{l+1}} Y_{lm}^*(\hat{r}) Y_{lm}(\hat{r}')$  at  $r' = a > r$

and the integral, with  $\sigma(\vec{r}') = \vec{P} \cdot \hat{n} = P \cos\theta$  picks up only  $l=1, m=0$  term, so

$$\Phi(\vec{r}) = \frac{4\pi}{3} P r \cos\theta$$

# Thermodynamics with dielectrics

For 1st law: work.



Add charge  $\delta Q_a$  to conductors held at fixed  $\phi_a$ , adiabatically (no heat exchange)

$$\begin{aligned} \delta W &= \sum_a \phi_a \delta Q_a \\ &= - \sum_a \frac{1}{4\pi} \int_{\partial V_a} \phi \delta \vec{D} \cdot \hat{n} \, d\vec{s} && \text{(recall } \sigma = \vec{D} \cdot (-\hat{n}) \\ & && \text{with } (-\hat{n}) \text{ pointing away from conductor)} \\ &= - \frac{1}{4\pi} \int_V \vec{\nabla}(\phi \delta \vec{D}) \cdot d\vec{r} && \text{(by Gauss's theorem)} \end{aligned}$$

Use  $\vec{\nabla} \cdot \delta \vec{D} = 0$  ( $\rho_{free} = 0$ ) and  $\vec{E} = -\vec{\nabla} \phi \Rightarrow$  (Note: recall  $\vec{\nabla}_x \vec{E} = -\frac{1}{4\pi} \vec{E} \cdot \frac{\partial \vec{D}}{\partial \vec{r}} + \dots$ )

$$\boxed{\delta W = \frac{1}{4\pi} \int_V \vec{E} \cdot \delta \vec{D} \, d\vec{r}}$$

Thermodynamic potentials:

let  $S = \text{entropy}$ ,  $T = \text{temperature}$ ,  $U = \text{internal energy}$

$$\Rightarrow \text{1st law is } \boxed{\delta U = \underbrace{T \delta S}_{\text{heat!}} + \frac{1}{4\pi} \int_V \vec{E} \cdot \delta \vec{D} \, d\vec{r}} \quad U = U(S, \vec{D})$$

Now,  $F = F(T, \vec{D})$  "free energy" with  $F = U - TS$

$$\text{(so that } \delta F = -S \delta T + \frac{1}{4\pi} \int_V \vec{E} \cdot \delta \vec{D} \, d\vec{r}$$

$$\text{or } \tilde{U} = \tilde{U}(S, \vec{E}) \quad \text{with } \tilde{U} = U - \frac{1}{4\pi} \int_V \vec{E} \cdot \vec{D} \, d\vec{r}$$

$$\text{and } \tilde{F} = \tilde{F}(T, \vec{E}) \quad \text{with } \tilde{F} = \tilde{U} - TS$$

Now,  $\int_V \vec{E} \cdot \vec{D}$  in  $U - \tilde{U}$  has interesting interpretation:

$$\begin{aligned} \frac{1}{4\pi} \int_V \vec{E} \cdot \vec{D} \, d\vec{r} &= -\frac{1}{4\pi} \int_V \vec{\nabla} \phi \cdot \vec{D} \, d\vec{r} = -\frac{1}{4\pi} \int_V \vec{\nabla}(\phi \vec{D}) \, d\vec{r} \quad (\text{since } \rho_{free} = 0) \\ &= -\frac{1}{4\pi} \int_{\partial V} \phi \vec{D} \cdot \hat{n} \, dS \\ &= \sum_a \phi_a Q_a \end{aligned}$$

points out of V as in figure previous page

2x the energy in the conductors

$$\text{So } (\delta F)_T = (\delta U)_S = \sum_a \phi_a \delta Q_a$$

ie. "at fixed T"

$$\text{And } \tilde{F} = F - \sum_a \phi_a Q_a \Rightarrow (\delta \tilde{F})_T = (\delta \tilde{U})_S = -\sum_a \delta \phi_a Q_a$$

Hold  $\begin{pmatrix} T \text{ \& } Q_a \\ T \text{ \& } \phi_a \\ S \text{ \& } Q_a \\ S \text{ \& } \phi_a \end{pmatrix}$  fixed, system relaxes to minimum of  $\begin{pmatrix} F \\ \tilde{F} \\ U \\ \tilde{U} \end{pmatrix}$  in equilibrium

Free energy in linear media: For  $D_i = \epsilon_{ij} E_j$

$$\Rightarrow \vec{E} \cdot \delta \vec{D} = \frac{1}{2} \delta(\vec{E} \cdot \vec{D}) = \beta \vec{E} \cdot \vec{D} \text{ so } \delta U \sim \int \vec{E} \cdot \delta \vec{D} \text{ can be integrated}$$

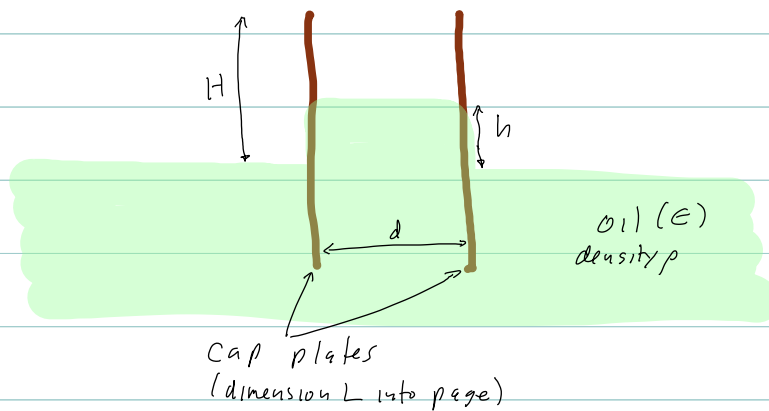
$$\text{If } F_0 = \text{free energy at zero field} \Rightarrow F - F_0 = \int \frac{1}{4\pi} \vec{E} \cdot \vec{D} \, d\vec{r} = \frac{1}{2} \sum_a \phi_a Q_a$$

$$\text{similarly } \tilde{F} - \tilde{F}_0 = -\frac{1}{2} \sum_a \phi_a Q_a$$

The difference in sign is the familiar effect that the plates of a capacitor held at fixed charge attract ( $F = F(T, Q)$  decreases  $\rightarrow$  goes towards equilibrium - for  $Q_a$  decreasing  $\rightarrow$  move conductors closer) but capacitors held at fixed potential repel ( $\tilde{F} = \tilde{F}(T, \phi_a)$  decreases for  $Q$  increasing, but larger  $Q$  requires moving plates apart to keep  $\phi_a$  fixed).

What about the dielectric? We used  $\vec{D}$  throughout and even assumed linearity ( $D_i = \epsilon_{ij} E_j$ ), but it is hidden is  $\sum \phi_a Q_a$  which depends on free charge  $Q_a$  — but  $\phi_a$ 's actually will depend on  $\epsilon$ .

Example: see text for details, here only rough:



Isolated:  $S = \text{constant}$ .  $V$  fixed  $\Rightarrow$  minimize  $\tilde{U}$  to find equilibrium.

Need gravitational potential energy\*  $= mgh = \frac{1}{2} \rho (Ldh) gh$

and subtract  $\frac{1}{8\pi} \int \vec{E} \cdot \vec{D}$ . Need  $\vec{E}$ .

$$\left. \begin{array}{c} \vec{E}_e \\ \vec{E}_\epsilon \end{array} \right\} E_e|_{\text{air}} = E_\epsilon|_{\text{oil}} \Rightarrow E = \frac{V}{d} \text{ everywhere}$$

$$\text{so } \int_V \vec{E} \cdot \vec{D} d^3x = [(H-h)Ld] \vec{E} \cdot (\epsilon \vec{E}) + [hLd] \vec{E} \cdot (\epsilon \vec{E}) = \left(\frac{V}{d}\right)^2 Ld [h(\epsilon-1) + \text{constant}]$$

(h-independent)

$$\text{Minimize (w.r.t. } h): \frac{\tilde{U}}{Ld} = \frac{1}{2} \rho g h^2 - \frac{1}{8\pi} \left(\frac{V}{d}\right)^2 (\epsilon-1) h$$

$$h_{\text{eff}} = \frac{\frac{1}{8\pi} \left(\frac{V}{d}\right)^2 (\epsilon-1)}{\rho g}$$

$$* \frac{1}{2} \text{ from } \int_0^h dz \rho L dz$$

If  $\epsilon$  depends on  $T$  and on its volume  $\epsilon = \epsilon(T, V)$  (depends on  $V$  because it may change if compressed, ie if under pressure) then we can write (assuming  $\vec{D} = \epsilon \vec{E}$ )

$$\tilde{F}(V, T, E) = \tilde{F}(V, T, 0) - \frac{1}{8\pi} V_0 E^2 \epsilon(V, T)$$

↑  
assumed  $\vec{E}$  = uniform and  
only on volume  $V_0$

Since  $\delta \tilde{F} = -S \delta T - \frac{1}{8\pi} \int \vec{D} \cdot \vec{E} \Rightarrow S = - \frac{\partial \tilde{F}}{\partial T}$

and  $\tilde{U} = \tilde{F} + ST$

$$\Rightarrow S(V, T, E) = S(V, T, 0) + \frac{1}{8\pi} V_0 E^2 \frac{\partial \epsilon}{\partial T}$$

$$\text{and } \tilde{U}(V, T, E) = \tilde{U}(V, T, 0) - \frac{1}{8\pi} V_0 E^2 \left( \epsilon - T \frac{\partial \epsilon}{\partial T} \right)$$



Exercise 97.2 (electrostriction)

$\epsilon$  depends on  $p$  (for some materials)

Apply uniform  $E$  to volume  $V$  of dielectric; in such cases  
what is the change in volume  $\Delta V$  of material?

$G = F + pV$  Gibbs free energy

$\tilde{G}$  idem with  $E$  as variable.

As above  $d\tilde{G} = V dp + \dots$   $V = \frac{\partial \tilde{G}}{\partial p}$

$$V(p, T, E) = V(p, T, 0) - \frac{1}{8\pi} V_0 E^2 \left( \frac{\partial \epsilon}{\partial p} \right)_T$$

$$\Rightarrow \frac{V(p, T, E) - V(p, T, 0)}{V_0} = \frac{\Delta V}{V} = - \frac{1}{8\pi} E^2 \left( \frac{\partial \epsilon}{\partial p} \right)_T$$

## Models of $\epsilon$

(Rarefied) gases. First look at collections of molecules that are so far apart (small number density  $n$ ) that the  $\vec{E}$  from some molecules on any one molecule is negligible compared to the applied field (for numbers quantifying this see text).

① Non-polar molecules/atoms (like He,  $H_2$ )

$$\text{If } \vec{d} = \alpha \vec{E} \text{ for one molecule } \Rightarrow \vec{P} = n\vec{d} = n\alpha \vec{E}$$

$$\Rightarrow \chi_e = n\alpha \quad \epsilon = 1 + 4\pi n\alpha$$

At STP,  $n = 2.7 \times 10^{19} \text{ cm}^{-3}$ . And  $\alpha \sim 1 \text{ \AA}^3$

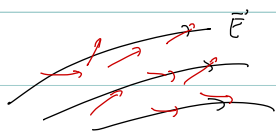
(For H one can use OM to calculate,  $\alpha = \frac{9}{2} a_0^3$   $a_0 = \text{Bohr's radius}$ )

$$\text{and } \alpha_H = 6.7 \times 10^{-25} \text{ cm}^3 = 0.67 \text{ \AA}^3.$$

$$\text{Then } n\alpha \sim 10^{-5} \quad \text{and } \epsilon - 1 \sim 10^{-4}$$

② Polar molecules (like  $H_2O$ )

These can be polarized too, so have an  $\alpha \vec{E}$  contribution as above. But also have a permanent  $\vec{d}_0$  dipole moment



Thermal fluctuations about alignment with  $\vec{E}$ . Need thermal average  $\langle \vec{d} \rangle$ .

Assume  $\vec{E} = \text{uniform}$  (on scale of interest).  $U(\theta) = -\vec{d}_0 \cdot \vec{E} = -d_0 E \cos\theta$

$$\langle \vec{d} \rangle = \frac{\int d\Omega (d_0 \cos\theta \hat{E}) e^{d_0 E \cos\theta / k_B T}}{\int d\Omega e^{d_0 E \cos\theta / k_B T}}; \quad \frac{d_0 E}{k_B T} \ll 1 \rightarrow \text{expand in powers to linear order}$$

since  $\int d\Omega \cos\theta = 0$

$$\Rightarrow \langle \vec{d} \rangle = \hat{E} \frac{\int d\Omega d_0 \cos\theta \left( \frac{d_0 E \cos\theta}{k_B T} \right)}{\int d\Omega} = \frac{d_0^2 \vec{E}}{3k_B T}$$

The rest is as above:  $\chi = n \left( \alpha + \frac{d_0^2}{3k_B T} \right)$

$$\epsilon = 1 + 4\pi n \left( \alpha + \frac{d_0^2}{3k_B T} \right)$$

Plot vs  $1/T \rightarrow$  get both  $\alpha$  and  $d_0$ !

Typical numbers

steam at 400K,  $n = 10^{19} \text{ cm}^{-3}$ ,  $\frac{d_0^2}{3k_B T} \approx 2.1 \times 10^{-23} \text{ cm}^3$

so  $\epsilon - 1 \approx 4\pi \times 2.1 \times 10^{-4} \sim 2 \times 10^{-3}$

and  $d_0 \sim 2 \times 10^{-18} \text{ esu}\cdot\text{cm}$

Back to rarefied approximation.

Dipole field  $E_{\text{dip}} \sim \frac{d}{r^3}$ . With density  $n$ , typical distance

is  $n^{-1/3}$  so  $E_{\text{dip}} \sim \frac{d}{(n^{-1/3})^3} = n d = n \alpha E$

So  $\frac{E_{\text{dip}}}{E} = n \alpha$  (or  $n \left( \alpha + \frac{d_0^2}{3k_B T} \right)$  for polarizable case)

So approximation is good provided  $\frac{\epsilon - 1}{4\pi} \ll 1$ .

## Dense dielectrics.

If  $n \gg 1$  the field of nearby molecules on a molecule cannot be neglected. (Compared to the ambient  $\vec{E}$ ). We need to go back to the microscopic description in terms of  $\vec{e}$ .

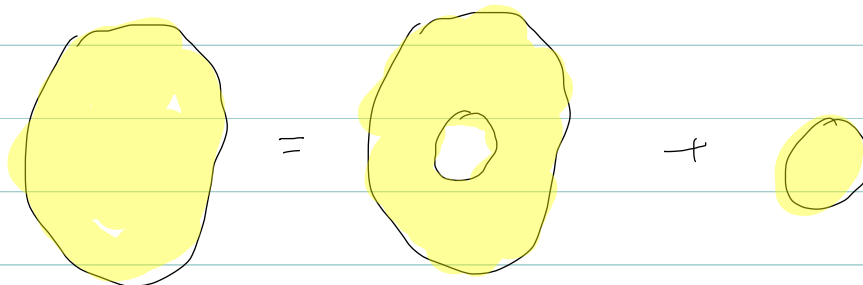
Now, we break the effect of  $\vec{e}$  into two pieces

$$\vec{e} = \vec{e}_{\text{near}} + \vec{e}_{\text{far}}$$

where  $\vec{e}_{\text{near}}$  is from a ball of radius  $a$  around the molecule of interest, and  $\vec{e}_{\text{far}}$  from outside the ball. The ball is large enough that the effect of molecules outside the ball can be averaged as the field due to a polarizable material from which the ball has been removed, plus the applied field:

$$\vec{e}_{\text{far}} = \vec{E}_{\text{far}}$$

Here is the picture:



Yet  $a$  is small enough that the field  $\vec{E}_{\text{far}}$  is uniform in it.

If  $\vec{E}$  is the macroscopic field at the center of the ball we can write :

$$\vec{E} = \vec{E}_{\text{far}} + \vec{E}_{\text{near}}$$

where  $\vec{E}_{\text{near}}$  is the field we would have if the ball is in an applied uniform external field  $\vec{E}_{\text{far}}$ .

But from the example in pp. 3-4 of this note, the field in the ball is

$\vec{E} = \vec{E}_0 + \vec{E}_d$  where  $\vec{E}_0$  is the applied uniform field and  $\vec{E}_d$  is the depolarization field

$\vec{E}_d = -\frac{4\pi}{3}\vec{P}$ . In our case  $\vec{E}_0 = \vec{E}_{far}$  and  $\vec{E} = \vec{E}_{near}$  so

$$\vec{E} = \vec{E}_{far} + \vec{E}_{near} = \vec{E}_{far} - \frac{4\pi}{3}\vec{P}$$

$$\Rightarrow \vec{E}_{far} = \vec{E} + \frac{4\pi}{3}\vec{P}$$

We still have to account for  $\vec{E}_{near}$ . This depends on the specific arrangement of molecules inside the ball.

Suppose the molecules are electric dipoles all of same magnitude and all aligned, and placed in a cubic lattice.

$$\vec{E}_{near} = \sum_n \frac{3(\vec{r}_n \cdot \vec{d})\vec{r}_n - r_n^2 \vec{d}}{r_n^5}$$

where  $\vec{r}_n$  are the locations of the vertices on the cubic lattice centered at the molecule of interest. This vanishes. To see this in a pedestrian way, take  $\vec{r} = b(n, m, k)$

and consider  $\sum \frac{3r_i r_j - \delta_{ij} r^2}{r^5}$ :

$$i=j=1 \quad \frac{1}{b^3} \sum_{n,m,k} \frac{3n^2 - (n^2 + m^2 + k^2)}{(n^2 + m^2 + k^2)^{5/2}} = \frac{1}{b^3} \sum_{n,m,k} \frac{2n^2 - m^2 - k^2}{(n^2 + m^2 + k^2)^{5/2}}$$

$$n^2 + m^2 + k^2 = 1 \Rightarrow 8 \frac{1}{b^3} [(2-0) + (0-1) + (0-1)] = 0 \quad (8 \text{ is from } \pm 1\text{'s in } (n,m,k) = (\pm 1, 0, 0), (0, \pm 1, 0), (0, 0, \pm 1)).$$

$$n^2 + m^2 + k^2 = 2 \Rightarrow \frac{1}{b^3} [(2-1-0) + (2-0-1) + (0-1-1)] = 0 \quad (\text{from here on, ignore multiplicity}).$$

$$n^2 + m^2 + k^2 = 3 \Rightarrow \frac{1}{b^3} [(2-1-1)] = 0$$

and so on

$$\text{For } i \neq j \quad \frac{1}{b^3} \sum_{n,m,k} \frac{3nm}{(n^2 + m^2 + k^2)^{5/2}} = \frac{1}{b^3} \sum_{n,m,k} 3n \sum_m \frac{m}{(n^2 + m^2 + k^2)^{5/2}} = 0 \quad \text{from } m = \pm |m| \text{ pairs.}$$

Whether  $\vec{E}_{near}$  vanishes depends on the specific lattice.

For a liquid with dipoles at random locations  $\langle \vec{E}_{near} \rangle = 0$  too. This follows from

$$\langle r_i r_j \rangle = \frac{1}{3} \delta_{ij} r^2$$

on average.

Assuming  $\vec{E}_{near}$  vanishes, then  $\vec{E} = \vec{E}_{near} + \vec{E}_{far} = \vec{E}_{far} = \vec{E}_{for} = \vec{E} + \frac{4\pi}{3} \vec{P}$

Using  $\vec{P} = \frac{\epsilon - 1}{4\pi} \vec{E}$  then

$$\vec{E} = \left(1 + \frac{1}{3}(\epsilon - 1)\right) \vec{E} = \frac{\epsilon + 2}{3} \vec{E}$$

To finish the calculation take  $\alpha =$  molecular polarizability

$n =$  number density, so  $\vec{P} = n\alpha \vec{E} = n\alpha \frac{\epsilon + 2}{3} \vec{E}$ .

This gives  $\chi_e = n\alpha \frac{\epsilon + 2}{3}$  and therefore

$$\epsilon = 1 + 4\pi n\alpha \frac{\epsilon + 2}{3}$$

$$\text{or } \epsilon \left(1 - \frac{4\pi n\alpha}{3}\right) = 1 + \frac{8\pi n\alpha}{3} \Rightarrow \epsilon = \frac{1 + \frac{8\pi n\alpha}{3}}{1 - \frac{4\pi n\alpha}{3}}$$

$$\text{or } \boxed{\epsilon = 1 + \frac{4\pi n\alpha}{1 - \frac{4\pi n\alpha}{3}}} \quad \text{"Clausius-Mossotti"}$$

One can determine  $\alpha$  from a dilute gas of a material and then compute  $\epsilon$  for a liquid (dense) of the same material. It works pretty well. See table 15.3. For example

for  $\text{CS}_2$   $\epsilon$  (Clausius-Mossotti) = 2.75 vs  $\epsilon$  (exp) = 2.64 (at  $n = 10^{22} \text{ cm}^{-3}$ ).

The CM formula fails as  $\frac{n \pi \alpha}{3} \rightarrow 1$ . For polar materials this is the case. But this is far beyond the scope of our study here.