Day 16: Clausius-Mossotti, Boundary conditions, and example(s)

Linking the microscopic (often quantum dominated) and macroscopic pictures of physics is one of history's greatest challenges. Stat mech is often about this. Here we'll do it for polarization.

We know $\vec{P}(x) = n\vec{p}$, where n is the number density of atoms

And $\vec{p} = \alpha \vec{E}$, where $\vec{E}$ is all the field acting on the dipole. In a solid this is $\vec{E}_{applied}$ and also the $\vec{E}$ from nearby atoms.

If we restrict our model to gases, only $\vec{E}_{applied}$ matters and

$$\vec{p} = \alpha \vec{E}_{app}, \qquad \vec{P} = n\alpha \vec{E}_{app}. \quad \text{Also, by definition,} \quad \vec{P} = \chi_e \varepsilon_0 \vec{E}$$

We can figure out n (moles and whatnot), and can measure χ_e with capacitors, but you can't easily measure α for a single atom or molecule. The above gets us

$$n\alpha\vec{E} = \chi_e\varepsilon_0\vec{E} = \qquad \alpha = \frac{\chi_e \varepsilon_0}{n} \quad \text{(for gases)}$$

So we can infer a <u>microscopic</u> parameter from macroscopic ones.

Now if we don't have a gas, it gets trickier.

$\vec{p}$ is polarized by the fields made by everything but itself, so we say

(1) $$\vec{p} = \alpha\left(\vec{E}_{total} - \vec{E}_{self}\right)$$ and explicitly subtract out its own field

What is $\vec{E}_{self}$? Let's approximate the atom as a conducting sphere. We once derived that for such we have

$$\vec{p} = 4\pi a^3 \varepsilon_0 \vec{E}_{applied} \qquad \text{(a is atomic radius)}$$

And the field in a polarized conductor exactly cancels out, so

$$\vec{E}_{self} = -\vec{E}_{applied} = -\frac{\vec{p}}{4\pi a^3 \varepsilon_0}$$

Now, in a dense material, the number of atoms per volume is roughly $1/_{\text{volume per atom}}$, so $n = \frac{1}{\frac{4}{3}\pi a^3}$ and

$$\vec{E}_{self} = -\frac{n\vec{p}}{3\varepsilon_0} = -\frac{\vec{P}}{3\varepsilon_0} \quad \text{big } \vec{P}$$

Put this into (1) to get

$$\vec{P} = n\alpha\left(\vec{E} + \frac{\vec{P}}{3\varepsilon_0}\right) \Rightarrow \vec{P}\left(1 - \frac{n\alpha}{3\varepsilon}\right) = n\alpha\vec{E}$$

$$\Rightarrow \quad \vec{P} = \frac{n\alpha \vec{E}}{\left(1 - \frac{n\alpha}{3\varepsilon_0}\right)}$$

And since $\vec{P} = \chi\varepsilon_0 \vec{E}$ we infer

$$\chi_e = \frac{n\alpha/\varepsilon_0}{1 - n\alpha/3\varepsilon_0}$$

Invert this to get

$$\alpha = \frac{\varepsilon_0}{n}\left(\frac{\chi_e}{1+\chi_e/3}\right)$$

and since the dielectric "constant" is defined by $K = 1+\chi_e$ we get

$$\boxed{\alpha = \frac{3\varepsilon_0}{n}\,\frac{K-1}{K-2}}$$

Which works for solids and liquids Better than it has any business working given the guys that made it barely knew atoms existed, period.

You get to try numbers in the homework.

Boundary Conditions

The boundary conditions regarding $\vec{E}$ still work. At an interface,

$$E_{above\parallel} = E_{below\parallel}, \qquad E_{above\perp} - E_{below\perp} = \sigma/\varepsilon_0$$

But σ is $\sigma_{bound} + \sigma_{free}$, which we don't always know.
So let's get conditions on $\vec{D}$.

<u>If</u> $\vec{\nabla}\times\vec{P} = 0$ so that $\vec{\nabla}\times\vec{D} = 0$, we know $\oint \vec{D}\cdot d\vec{l} = 0 \ \forall$ paths,
so $D_{above\parallel} = D_{below\parallel}$

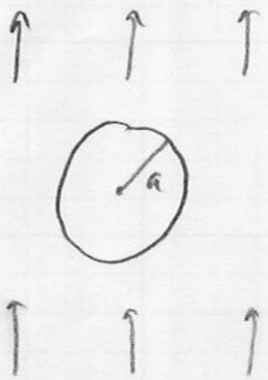
But that's <u>not</u> 100% general.

What is? The condition on $E_\perp$ was derived from Gauss's Law, and we have $\oint \vec{D}\cdot d\vec{A} = q_f$, so

$$D_{above\perp} - D_{below\perp} = \sigma_f$$

Where σ_f is usually more accessible than $\sigma_f + \sigma_b$.

Example: Spherical solid dielectric in a uniform field



We have a neutral sphere of radius a filled with a dielectric with dielectric "constant" κ and permittivity ε.

Then we apply an external field of the form $\vec{E} = E_0 \hat{k}$, which means far away we'll have

$$V(r,\theta) = -E_0 r\cos\theta \quad (\text{or } -E_0 z)$$

In spherical coordinates, for systems with no ϕ dependence, the general solution for the potential looks like:

$$V(r,\theta) = \sum_{\ell=0}^{\infty} \left(A_\ell r^\ell + B_\ell r^{(-\ell-1)}\right) P_\ell(\cos\theta)$$

To find the potential everywhere, we need to adapt this to two regions separately. For $r<a$, the potential ought to stay finite, so we need all the $r^{-\ell-1}$ terms to go away:

$$V(r,\theta)_{in} = \sum_{\ell=0}^{\infty} C_\ell r^\ell P_\ell(\cos\theta)$$

Outside, we have to allow for the possibility that V blows up at large r on account of the applied field, so we <u>can't</u> exclude all the r^ℓ terms:

$$V(r,\theta)_{out} = \sum_{\ell=0}^{\infty} A_\ell r^\ell P_\ell(\cos\theta) + B_\ell r^{-\ell-1} P_\ell(\cos\theta)$$

To fix our constants, we need boundary conditions. We certainly have

$$V_{out}(a,\theta) = V_{in}(a,\theta) \qquad (1)$$

We also have

$$V_{out}(r,\theta) \rightarrow -E_0 r\cos\theta \quad \text{for large } r \qquad (2)$$

We technically have $E_{1\perp} - E_{2\perp} = (\sigma_f + \sigma_b)/\varepsilon_0$,

but it's not very helpful since we won't know σ_b till after we've solved the problem.

We do, however, know that

$$D_{1\perp} - D_{2\perp} = \sigma_f$$

And $\sigma_f = 0$, and $D = \varepsilon E$, so if we let $D_1 = D_{out} = \varepsilon_0 E_{out}$, we have

$$\varepsilon_0 E_{out\perp} - \varepsilon E_{in\perp} = 0$$

$$\Rightarrow \quad \boxed{\varepsilon_0 \frac{\partial V_{out}}{\partial r}\bigg|_{r=a} = \varepsilon \frac{\partial V_{in}}{\partial r}\bigg|_{r=a}} \qquad (3)$$

Note that since $\varepsilon = \varepsilon_0(1+\chi_e)$, $\varepsilon = \varepsilon_0$ in vacuum.

Let's use (2) first, since it's a pretty severe constraint. For large r, $V_{out} \to -E_0 r\cos\theta$. Only $P_1(\cos\theta)$ has that kind of θ-dependence, so it must be the case that A_1 is the only nonzero A_ℓ. One might also guess that holds for the B_ℓ, but that's not as obvious, so let's leave that be. Then we have

$$V_{out}(r,\theta) = A_1 r P_1(\cos\theta) + \sum_{\ell=0}^{\infty} B_\ell r^{(-\ell-1)} P_\ell(\cos\theta)$$

Let's use (1) next. We get:

$$A_1 a P_1(\cos\theta) + \sum_{\ell=0}^{\infty} B_\ell a^{(-\ell-1)} P_\ell(\cos\theta) = \sum_{\ell=0}^{\infty} C_\ell a^\ell P_\ell(\cos\theta)$$

This has to hold for all θ, so the terms involving each independent $P_\ell(\cos\theta)$ need to match individually. This works out slightly differently for $\ell=1$ and $\ell \neq 1$. For $\ell=1$:

$$A_1 a P_1(\cos\theta) + B_1 a^{-2} P_1(\cos\theta) = C_1 a P_1(\cos\theta)$$

$$\Rightarrow \quad \boxed{A_1 a + B_1/a^2 = C_1 a}$$

For $\ell \neq 1$: $$B_\ell a^{-\ell-1} P_\ell(\cos\theta) = C_\ell a^\ell P_\ell(\cos\theta)$$

$$\Rightarrow \quad \boxed{B_\ell = C_\ell a^{2\ell+1}} \qquad (4)$$

Finally, let's use condition (3). r-derivatives of V are easy enough, but again we get slightly different answers for $l=1$ and $l \neq 1$. For $l=1$:

$$\varepsilon_0 A_1 P_1(\cos\theta) + \varepsilon_0(-2) B_1 a^{-3} P_1(\cos\theta) = \varepsilon C_1 P_1(\cos\theta)$$

$$\Rightarrow \quad \boxed{\varepsilon_0 A_1 - \frac{2\varepsilon_0 B_1}{a^3} = \varepsilon C_1}$$

For $l \neq 1$ we get:

$$\varepsilon_0 (-l-1) a^{(-l-2)} B_l \cancel{P_l(\cos\theta)} = \varepsilon l a^{l-1} C_l \cancel{P_l(\cos\theta)}$$

Substituting from (4), we get:

$$\varepsilon_0(-l-1) a^{(-l-2)} C_l a^{2l+1} = \varepsilon l a^{(l-1)} C_l$$

$$\Rightarrow \quad \left[\varepsilon_0 (-l-1) \cancel{a^{l-1}}\right] C_l = \left[\varepsilon l \cancel{a^{l-1}}\right] C_l$$

$$\Rightarrow \quad \varepsilon_0(-l-1) C_l = \varepsilon l C_l$$

ε is arbitrary, so this has to hold for all ε. But in general $\varepsilon_0(-l-1) \neq \varepsilon l$, so it must be the case that all C_l (and therefore all B_l) are zero if $l \neq 1$. Had we guessed that up front, we'd have been right.

So now we're down to our $l=1$ conditions:

$$A_1 a + B_1/a^2 = C_1 a$$

$$\varepsilon_0 A_1 - \frac{2\varepsilon_0 B_1}{a^3} = C_1 \varepsilon$$

We'll tap condition (2) one last time to get

$$A_1 r P_1(\cos\theta) = -E_0 r \cos\theta \quad \Rightarrow \quad \boxed{A_1 = -E_0}$$

Moving right along,

$$-E_0 a + B_1/a^2 = a C_1$$

$$-E_0 \varepsilon_0 - \frac{2\varepsilon_0 B_1}{a^3} = \varepsilon C_1$$

so $\quad C_1 = -E_0 + B_1/a^3$ from the first. Sub into the second:

$$-E_0 \varepsilon_0 - 2\varepsilon_0 B_1/a^3 = \varepsilon\left(-E_0 + B_1/a^3\right)$$

$$\Rightarrow \quad -E_0 \varepsilon_0 - 2\varepsilon_0 B_1/a^3 = -\varepsilon E_0 + \varepsilon B_1/a^3$$

$$\Rightarrow \quad (\varepsilon - \varepsilon_0) E_0 = \left(\frac{\varepsilon}{a^3} + 2\frac{\varepsilon_0}{a^3}\right) B_1$$

$$\Rightarrow \quad B_1 = \frac{(\varepsilon - \varepsilon_0)}{\frac{\varepsilon}{a^3} + \frac{2\varepsilon_0}{a^3}} = \frac{a^3(\varepsilon - \varepsilon_0)}{\varepsilon + 2\varepsilon_0} E_0$$

Here's a fun trick: $\varepsilon = K\varepsilon_0$, so $\varepsilon/\varepsilon_0 = K$. Divide top + bottom by ε_0:

$$B_1 = \frac{a^3\left(\frac{\varepsilon}{\varepsilon_0} - 1\right)}{\left(\varepsilon/\varepsilon_0 + 2\right)} E_0$$

$$\Rightarrow \quad \boxed{B_1 = \frac{(K-1)}{(K+2)} a^3 E_0}$$

Back substituting,

$$C_1 = -E_0 + \left(\frac{K-1}{K+2}\right) E_0 = \left[\frac{K-1}{K+2} - \frac{K+2}{K+2}\right] E_0$$

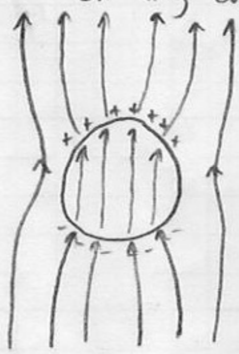
$$\boxed{C_1 = -\frac{3}{K+2} E_0}$$

Yielding, finally, $V_{in}(r,\theta) = -\dfrac{3E_0}{K+2} r\cos\theta = -\dfrac{3E_0}{K+2} z$

$$V_{out}(r,\theta) = -E_0 r\cos\theta + \frac{E_0 a^3}{r^2}\frac{(K-1)}{(K+2)}\cos\theta$$

We can see $\vec{E}_{inside} = -\dfrac{\partial V_{in}}{\partial z}\hat{k} = +\dfrac{3E_0}{K+2}\hat{k}$ Note this is basically $\vec{E}_{applied}$, but a little weaker since $K>1$. As $K \to \infty$ $E_{inside} \to 0$ (conducting limit)

In any event the polarized charges cancel out some of the applied field



Let's get $\vec{P}$ so we can check σ_b and σ_f.

$\vec{P}$ exists inside the sphere, so

$$\vec{P} = \chi_e \varepsilon_0 \left(\frac{3E_0}{K+2}\right)\hat{k} \quad \text{and} \quad \chi_e = K-1$$

$$\vec{P} = \frac{(K-1)}{(K+2)} 3\varepsilon_0 E_0 \hat{k}$$

And $\rho_b = -\vec{\nabla}\cdot\vec{P} = 0$, which we expect.

$$\sigma_b = \hat{n}\cdot\vec{P} = \hat{r}\cdot\hat{k}\,(\text{blar}) = 3\varepsilon_0 E_0 \frac{(K-1)}{(K+2)}\cos\theta$$

Which has the kind of θ dependence we expect