NOTES 1: Electrostatic Behavior of Solids#1

Solids are good at storing mechanical potential energy associated with the microscopic forces between atom (ionic or covalent bonds). A small compression of expansion of the solid entails a big change of energy. Solids are also good at storing other forms of potential energy, especially in electric and magnetic fields. We start with a look at electrostatic energy and the forces associated with it. This is one of the oldest branches of physics and engineering, and fundamental to the understanding of solid-state electronics.

Energy and electric fields

In presence of externally applied electric field, $\vec{E}_0$, there are two terms that contribute to *electrical* potential energy inside a solid:

(a) Work done by external field alone

$$\delta W = dU_E = d\left(\frac{\varepsilon_0}{2}\int |\vec{E}_0|^2 dV\right)$$

where U_E is the energy stored per unit volume.

(b) Potential energy from alignment of microscopic dipoles

$$\delta W = \vec{E}_{in} \cdot d\left(\vec{P}_e \cdot V\right)$$

where $\vec{P}_e \rightarrow$ polarization per unit volume, $\vec{E}_{in} \rightarrow$ electric field inside solid

For the purpose of solid-state analysis, we can subtract out the first term since it is there even without the solid present. The 1st law of thermodynamics then becomes

$$dU = TdS - PdV + \vec{E}_{in} \bullet d(\vec{P}_e \cdot V)$$

By definition: $E_{in} = \dfrac{1}{V}\dfrac{\partial U}{\partial |\vec{P}_e|}$ intensive variable

↑

derivative taken along $\vec{P}_e$ direction

and we have a susceptibility (thermodynamic)

$$\chi = \frac{V\partial\vec{P}_e}{\partial|\vec{E}_0|}\quad\text{electric susceptibility}$$

The more common electrical susceptibility is given by

$$\chi_e = \frac{V \partial \vec{P}_e}{\varepsilon_0 \partial |\vec{E}_0|} \equiv \frac{\chi}{\varepsilon_0}$$

$\varepsilon_0 \rightarrow$ permittivity of vacuum

- $\vec{E}_{in}$ and $\vec{P}_e$ are to be thought of as *macroscopic averages* over a volume much larger than the atoms but smaller than the solid itself.

- Solids generally form dipoles in 3 different ways

   (a) Microscopic dipoles are <u>induced</u> by applied field
   (b) Permanent internal dipoles are <u>aligned</u> by applied field
   (c) Free carriers (as in metals or semimetals) displace to create a large induced dipole extending over the entire solid sample.

- Independent of the type of atomic dipole, the response mechanism is the same and can be drawn graphically as shown below:
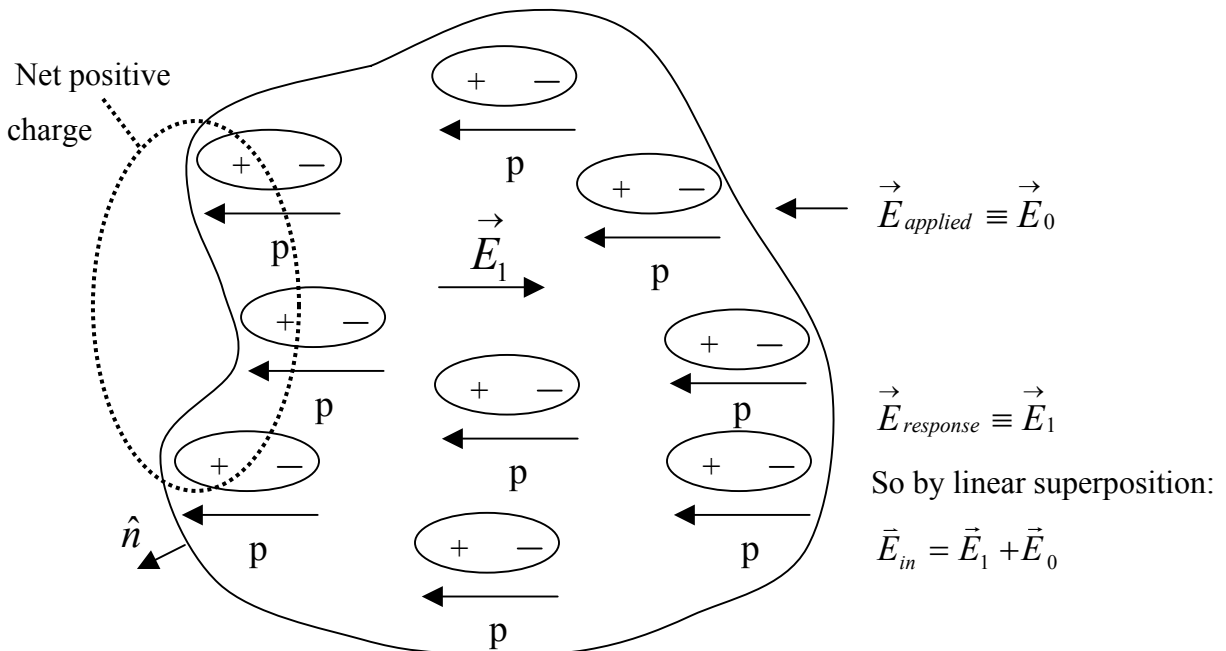
(Note: Kittel defines $\vec{E} = \vec{E}_{in}$)

- The physics of dielectrics is largely the study of $\vec{P}_e$ and how it depends on:

   (a) geometrical (i.e., shape) effects of the solid sample
   (b) microscopic nature of the solid

Before getting into these effects, we need one important result from electrostatics

Polarization Theorem

The distribution of microscopic dipoles shown in the above figure leads to a simple relation between the polarization vector and the microscopic dipole moment: $\vec{P}_e = n \cdot \vec{p}$. It is assumed that $\vec{P}_e$ is averaged over enough dipoles to get a "macroscopic" result, and that the $\vec{p}$ do not change appreciably over this volume.

It is also clear from the figure that the applied electric field will induce a net surface charge as the microscopic dipoles are induced. If $\vec{P}_e$ in the solid sample is uniform (we will see the sample conditions that create this shortly), every negatively charged end of a microscopic dipole must be effectively neutralized by being very close to the positive end of a neighboring dipole. And every positively charge end of a dipole must be effectively neutralized by being very close to the negative end of a neighboring dipole. So there can be no net charge Q, even though $\vec{P}_e$ is distinctly nonzero. But at the surfaces, there is "dangling" charge; i.e., negative or positive ends of dipoles that are not neutralized by opposite charges. The negative ones are enclosed by the dotted ellipse in the above figure. It turns out that the surface charge density is given exactly by[1]

$$\sigma_b = \vec{P}_e \cdot \hat{n} \qquad (1)$$

where $\hat{n}$ is the normal unit vector to the surface at each point, $\vec{P}_e$ is the polarization vector at that point, and the subscript "b" stands for bound, meaning that charge can move over distances only on a microscopic scale.

If the $\vec{P}_e$ in a solid is non-uniform, then an additional contribution to the net charge can build up owing to a imperfect neutralization of each microscopic dipole. Electrostatic theory then shows that

$$\rho_b = -\vec{\nabla} \cdot \vec{P}_e \qquad (2)$$

where ρ_b is the bulk charge density. In most *isotropic* solids ρ_b is small because $\vec{P}_e$ is uniform. But in highly anisotropic solids (particularly non-cubic crystals), spatial variation of $\vec{P}_e$ can result in significant ρ_b.

The polarization theorem states that no matter what the shape of a solid sample or its microscopic composition, that the electric field outside the sample can be calcualted just simply from σ_b and ρ_b by:

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[1] See any good book on Electrostatics, such as P. Lorrain and D. Corson, "Electromagnetic Fields and Waves, 2nd Ed. (Freeman and Company, San Francisco, 1970).
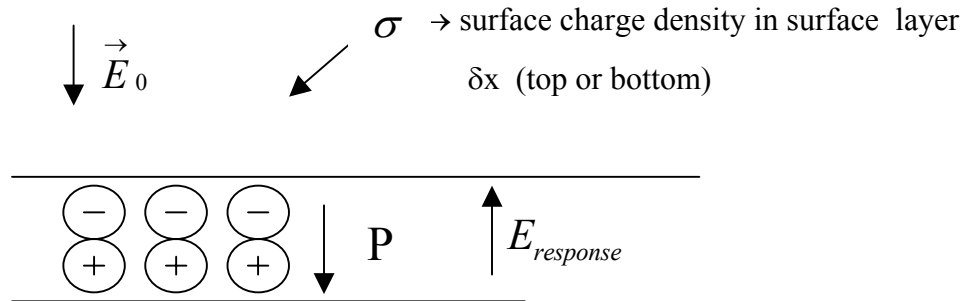
$$\vec{E} = -\frac{1}{4\pi\varepsilon_0}\vec{\nabla}\left\{\int_S \frac{\sigma_b dS'}{r} + \int_V \frac{\rho_b dV'}{r}\right\}$$

where dS' and dV' are the surface and volume differentials, respectively.

Geometrical Effects

- These arise from the existence in all solids of <u>surface charges</u>, and the dependence of the electric field on these charges.

<u>Example from electrostatics: the slab</u>

$\sigma \rightarrow$ surface charge density in surface layer

$\vec{E}_0$ $\qquad\qquad\qquad\qquad$ δx (top or bottom)

From Poisson equation: $\qquad \dfrac{dE}{dx} = \dfrac{\rho}{\varepsilon_0}$ or $E = \int_{out}^{in} \dfrac{\rho}{\varepsilon_0}dx$

$$E_{in} - E_0 = \frac{\rho}{\varepsilon_0}\delta x = \frac{\sigma}{\varepsilon_0} = E_{response} \equiv E_1$$

$E_{in} = E_0 + \dfrac{\sigma}{\varepsilon_0}$ $\qquad$ $\sigma < 0$ for E_0 as shown (negative charge on top)
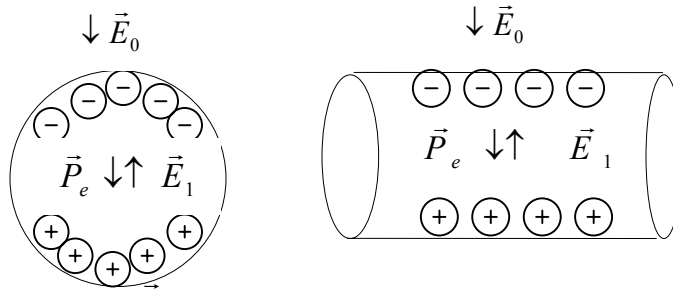
$$\Longrightarrow \qquad |E_{in}| < |E_0|$$

- We call $\vec{E}_1$ the "depolarization" field

From (1) above, $\left|\vec{E}_1\right| \equiv \dfrac{\sigma}{\varepsilon_0} = \dfrac{\vec{P}_e \cdot \hat{n}}{\varepsilon_0}$ $\qquad$ where $\vec{P}_e \rightarrow$ macroscopic internal polarization vector

So we have $\vec{E}_1 = \dfrac{-\vec{P}_e}{\varepsilon_0} \equiv -N\dfrac{\vec{P}_e}{\varepsilon_0}$ $\qquad \Rightarrow N \equiv$ depolarization factor $= 1$ for slab

Other important geometries

- sphere (below left) and cylinder (below right)

Sphere: $\vec{E}_1 = -\frac{1}{3}\frac{\vec{P}_e}{\varepsilon_0}$ $\Rightarrow N = 1/3$ for sphere

Cylinder: $\vec{E}_1 = \frac{1}{2}\frac{\vec{P}_e}{\varepsilon_0}$ ($\perp$ to z axis) $\Rightarrow N = 1/2$ for cylinder

- Important theorem from electrostatics states that ellipsoids, in general, have the property that a uniform $\vec{P}_e$ yields a uniform $\vec{E}_{in}$. Hence the

$$E_{1x} = N_x \frac{-P_X}{\varepsilon_0} \qquad\qquad E_{1y} = N_y \frac{-P_y}{\varepsilon_0} \qquad\qquad E_{1z} = N_z \frac{-P_z}{\varepsilon_0}$$

subject to the constraint that $N_X + N_Y + N_Z = 1$. The values of each N map one-to-one into the principal axes of the ellipsoid. This is an amazing result that requires some higher level math (solving Laplaces eqn in ellipsoidal coordinates). By so doing, another result is found: the depolarization field $\vec{E}_1$ in an ellipsoid is always uniform when the external field $\vec{E}_0$ is uniform. However, $\vec{E}_1$ is not necessarily parallel to $\vec{E}_0$. The same statement can be made about spheroids. But $\vec{E}_1$ becomes parallel to $\vec{E}_0$ when the ellipsoid "degenerates" into a sphere.

Electric susceptibility, displacement vector, and dielectric constant

By definition: $\vec{P}_e \equiv \chi_e \varepsilon_0 \vec{E}_{in}$

so that $$\vec{P}_e = \chi_e \varepsilon_0 (\vec{E}_0 + \vec{E}_1) = \chi_e \varepsilon_0 \left(\vec{E}_0 - \frac{N\vec{P}_e}{\varepsilon_0} \right)$$

$$\vec{P}_e\left(1 + \chi_e N\right) = \chi_e \varepsilon_0 \vec{E}_0$$

or
$$\vec{P}_e = \frac{\chi_e \varepsilon_0 \vec{E}_0}{1 + N\chi_e}$$

- Another useful macroscopic field vector, particularly when there are free charges present, is the displacement vector $\vec{D}$. This is well defined in the following way: we consider the general case of a solid that can have significant bound charge density, ρ_b, and signficant free charge represented by density ρ_f. (a good example is a heavily doped semiconductor). The generalized Gauss equation in this case is given by

$$\vec{\nabla} \cdot \vec{E} = \frac{\rho}{\varepsilon_0} = \frac{\rho_b + \rho_f}{\varepsilon_0} = \frac{-\vec{\nabla} \cdot \vec{P} + \rho_f}{\varepsilon_0}$$

where the last step follows from (2). Rearrangement leads to

$$\vec{\nabla} \cdot (\varepsilon_0 \vec{E} + \vec{P}) = \rho_f \equiv \vec{\nabla} \cdot \vec{D}$$

Hence, we see that $\vec{D}$ is related to the spatial variation of the free charge density only.

- The dielectric constant (also called the relative permittivity) is used to gauge the strength of $\vec{D}$ relative to $\vec{E}_{in}$)

$$\varepsilon_r \equiv \frac{\vec{D}}{\varepsilon_0 \vec{E}_{in}} = \frac{\varepsilon_0 \vec{E}_{in} + \vec{P}_e}{\varepsilon_0 \vec{E}_{in}} = 1 + \frac{\vec{P}_e}{\varepsilon_0 \vec{E}_{in}} = 1 + \chi_e$$

This is defined so that ε_r increases as the response of the solid increases. If $\vec{P}_e$ is parallel to $\vec{E}_{in}$ (as is usually the case), then $\varepsilon_r > 1$. And since $\vec{E}_1$ is generally opposed to $\vec{P}_e$ and therefore opposed to $\vec{E}_0$, this is sometimes used to justify the label dielectric since "dia" means across or opposite in Latin (but note: more generally, the "dia" in dielectric means that the material opposes or blocks the flow of current).

Microscopic Effects
- At the atomic level, the electric field is a superposition of the external field $\vec{E}_0$, the response field $\vec{E}_1$ (due to geometry and surface charges), *and* the field due to other

atomic dipoles in the vicinity. While complicated, it is the interaction between neighboring dipoles that makes the electrostatics of solids so interesting.

$$\vec{E}_{local} = \vec{E}_{in} + \vec{E}_{dipoles} = \vec{E}_0 + \vec{E}_1 + \vec{E}_{dipoles}$$

Recall that Maxwell's equations, including the Poisson equation as a special case, are scalable to all dimensions including sub-atomic. The exact expression for the electric field from a neighboring atomic dipole is thus the same as from a macroscopic dipole:

$$\vec{E}(\vec{r}) = \frac{3(\vec{p}\cdot\vec{r})\vec{r} - r^2\vec{p}}{4\pi\varepsilon_0 r^5}$$

Unfortunately this is very difficult to evaluate, so it is common in solid-state theory to make approximations. The simplest and most common is the "spherical atom approximation" by which all of the charge comprising the atomic (or molecular) dipole moment $\vec{p}$ is assumed to be located inside a sphere, for which we already know that the internal electric field will be uniform if the external field is uniform.

We then now think of $\vec{E}_{local}$ as the field at the atomic (or molecular) site caused by charge from everywhere else in the solid other than the chosen atom (or molecule). This can be depicted as in Fig. 1 by a "virtual elimination" of the sphere representing the atom and then calculating the field (note: the virtual elimination is done in such a way that the charge distribution on the rest of the solid is not perturbed). The calculation of $\vec{E}_{local}$ now proceeds by the principle of *linear superposition* – arguably one of the most important principles in all of electromagnetism and all of solid-state theory, for that matter. By this principle, the effect of the charges in the solid without the spherical atom is equivalent to the effect of all the charges in the homogeneous solid *minus* the effect of the charges inside the spherical atom. The first effect is just $\vec{E}_{in}$. The second effect, represented by $\vec{E}_{sphere}$ is one of the most important results from electrostatic theory, which can be stated two ways depending on the spatial variation of the charge in the spherical atom:

Fig. 1.
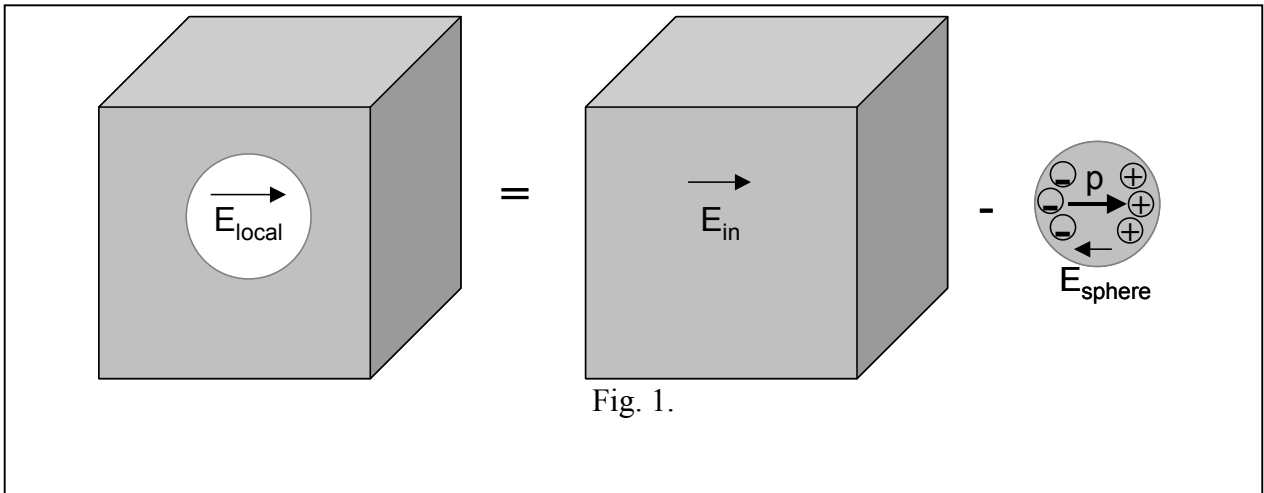
(1)   If the charge is homogeneous and the atom (or molecule) is big enough, then

$$\vec{E}_{sphere} = \frac{-\vec{P}}{3\varepsilon_0}$$, identical to the depolarization field for a macroscopic sphere.

(2)   If the charge is inhomogeneous, as one would certainly expect in any real atom or

molecule), we can take a spatial average over the sphere and find $\vec{E}_{sphere} \rightarrow \vec{E}_{ave} = \frac{-\vec{p}}{4\pi\varepsilon_0 R^3}$

where R is the radius of the sphere.[2]   Note that the dipole moment here is generalized from the

simple case of two displaced (and opposite charges). It is now given by $\vec{p} = \int \rho(\vec{r}) \cdot \vec{r} \cdot dV$

where $\rho(\vec{r})$ is the charge distribution and $\vec{r}$ defines the position where the charge occurs

relative to some origin within the sphere .   But because $V_{sphere} = (4/3)\pi R^3$, we find

$$\vec{E}_{ave} = \frac{-\vec{p}}{3\varepsilon_0 V} \approx \frac{-\vec{P}}{3\varepsilon_0}$$. The last step is an approximation because spheres can not fill space !

This important consequence of the "spherical atom approximation" is called the Lorentz

condition. (the super-smart guy that Einstein once said he admired most amongst all his

colleagues). So in total, we get the very useful result that connects the microscopic to the

macroscopic:

$$\vec{E}_{local} = \vec{E}_{in} - \vec{E}_{sphere} \approx \vec{E}_0 + \vec{E}_1 + \frac{\vec{P}_e}{3\varepsilon_0} .$$

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[2]   See practically any undergradute book on Electricity and Magnetism, such as P. Lorrain and D. Corson, Electromagnetic Fields and Waves, 2nd ed. (W.H. Freeman, New York, 1970), Sec. 2.13

Important comments:

(1) In general $\vec{E}_1$ opposes $\vec{E}_0$ but $\vec{P}_e/3\varepsilon_0$ supports $\vec{E}_0$. Hence $\vec{E}_{local}$ is generally larger in magnitude than $\vec{E}_{in}$

(2) Because atoms (or molecules) rarely, if ever, have spherical charge distributions, a more general expression is often used:

$$\vec{E}_{local} = \vec{E}_{in} - \vec{E}_{sphere} \approx \vec{E}_0 + \vec{E}_1 + \frac{b\vec{P}_e}{\varepsilon_0} \qquad \text{where } 0 < b < 1.$$

Electrostatic Feedback Loop

- To complete the microscopic formulation, we need two more relations

  $\vec{P}_e = \rho\vec{p}_{atomic}$, $\rho \rightarrow$ density of atomic (or molecular) dipoles

  $\vec{p}_{atomic} = \alpha_e\vec{E}_{local}$, $\alpha_e \rightarrow$ electric polarizability, which assumes a linear response.

- We can now show the macroscopic and microscopic relationships graphically through the "dielectric feedback loop", with $\vec{E}_0$ being the input
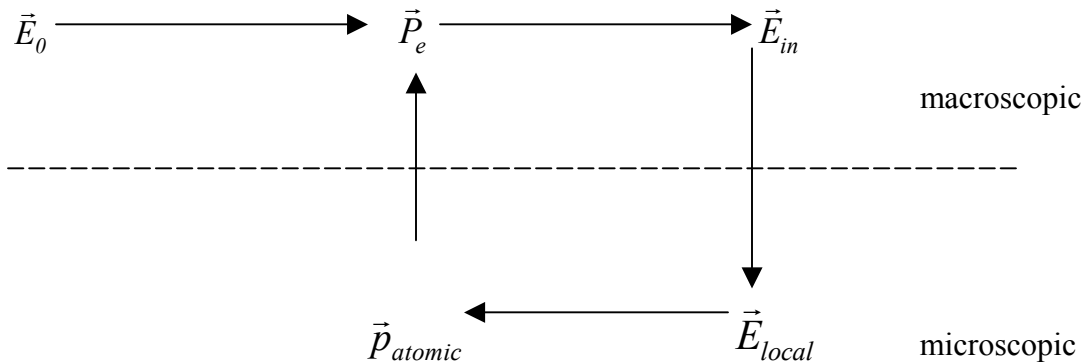
Macroscopic-to-Microscopic Formulae: Clausius-Mosotti Relation

We know $\vec{E}_{local} \approx \vec{E}_{in} + \vec{P}_e/3\varepsilon_0$. So we can relate the atomic polarizabilities to the

macroscopic susceptibility $\vec{P}_e = \sum_j \rho_j \vec{p}_j = \sum_j \rho_j \alpha_j \vec{E}_{local}$

$j \rightarrow$ dipole type; $\rho_j \rightarrow$ density of that dipole type

Thus,
$$\vec{P}_e = \sum_j \rho_j \alpha_j \left(\vec{E}_{in} + \vec{P}_e / 3\varepsilon_0 \right)$$

Solving, we get $\vec{P}_e \left(1 - \dfrac{1}{3\varepsilon_0} \sum_j \rho_j \alpha_j \right) = \sum_j \rho_j \alpha_j \vec{E}_{in}$,   or $\vec{P}_e = \dfrac{\vec{E}_{in} \sum \rho_j \alpha_j}{1 - \dfrac{1}{3\varepsilon_0} \sum_j \rho_j \alpha_j}$

$$\Rightarrow \quad \chi \equiv \frac{\vec{P}_e}{\varepsilon_0 \vec{E}_{in}} = \frac{\sum \rho_j \alpha_j / \varepsilon_0}{1 - \dfrac{1}{3\varepsilon_0} \sum \rho_j \alpha_j}$$

This is a very useful connection equation !   But what most books fail to mention is that this is

exactly the form as the gain of a two-port feedback system, generally written as $G_F = \dfrac{G}{1 - GH}$

where $G = X_{out}/X_{in}$ is the "open-loop" (i.e., without feedback) gain, X is the "signal" (could be

current or voltage), and $H \equiv X_F/X_{out}$ is the unitless feedback factor.[3]   In our case, G

corresponds to $\sum_j \rho_j \alpha_j / \varepsilon_0$ and H = 1/3 !

Back to solid-state theory, we have by definition $\varepsilon = 1 + \chi$. So,

$$\varepsilon - 1 = \frac{\sum \rho_j \alpha_j / \varepsilon_0}{1 - \dfrac{1}{3\varepsilon_0} \sum \rho_j \alpha_j} \; ; \quad \text{or} \quad \varepsilon = 1 + \frac{\sum \rho_j \alpha_j / \varepsilon_0}{1 - \dfrac{1}{3} \sum \rho_j \alpha_j}$$

Algebraic rearrangement yields: $\sum \dfrac{1}{\varepsilon_0} \rho_j \alpha_j \left(-\dfrac{2}{3} - \dfrac{\varepsilon}{3} \right) = 1 - \varepsilon$

or $\sum_j \dfrac{\rho_j \alpha_j}{3\varepsilon_0} = \dfrac{\varepsilon - 1}{\varepsilon + 2}$ The famous Clausis-Mosotti relation

Example 1: Dielectric Sphere, uniform applied field, one dipole type α

From depolarization factor for sphere, $N = \tfrac{1}{3}$, $\vec{E}_{in} = \vec{E}_0 - \dfrac{\vec{P}_e}{3\varepsilon_0}$

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[3] See any good book on Electronic Circuit Theory, e.g., "Electronics: Circuits and Devices" by R.J. Smith (Wiley, New York, 1973), Chap. 14. This was Prof. Brown's undergraduate text.

But by definition: $\qquad \vec{P}_e \equiv \chi \varepsilon_0 \vec{E}_{in}$

So, $\qquad\qquad \vec{E}_{in} = \vec{E}_0 - \dfrac{\chi}{3} \vec{E}_{in}$, $\qquad$ or $\qquad \vec{E}_{in} = \dfrac{\vec{E}_0}{1 + \chi/3}$

and $\qquad\qquad\qquad \vec{P}_e = \dfrac{\chi \varepsilon_0 \vec{E}_0}{1 + \chi/3}$

But since $\vec{E}_0$ is uniform, so is $\vec{E}_{in}$ and $\vec{P}_e$

At the microscopic level $\vec{E}_{local} = \vec{E}_{in} + \dfrac{\vec{P}_e}{3\varepsilon_0}$

or $\qquad\qquad\qquad \vec{E}_{local} = \vec{E}_0 - \dfrac{\vec{P}_e}{3\varepsilon_0} + \dfrac{\vec{P}_e}{3\varepsilon_0} = \vec{E}_0$

The microscopic local field equals the (macroscopic) applied field !

So that the induced (or aligned) atomic dipoles are

$$\vec{p} \equiv \alpha \vec{E}_{local} = \alpha \vec{E}_0$$

Example 2: Dielectric slab in uniform applied field, one dipole type $\underline{\alpha}$

Depolarization factor $N = 1 \Rightarrow \vec{E}_{in} = \vec{E}_0 - \dfrac{\vec{P}_e}{\varepsilon_0} \Rightarrow \vec{E}_{in} = \vec{E}_0 - \chi \vec{E}_{in}$ or $\vec{E}_{in} = \dfrac{\vec{E}_0}{1 + \chi}$

and thus: $\qquad\qquad \vec{P}_e = \dfrac{\chi \varepsilon_0 \vec{E}_0}{1 + \chi}$

At the microscopic level: $\qquad \vec{E}_{local} = \vec{E}_0 - \dfrac{\vec{P}_e}{\varepsilon_0} + \dfrac{\vec{P}_e}{3\varepsilon_0} = \vec{E}_0 - \dfrac{2\vec{P}_e}{3\varepsilon_0}$

or $\qquad\qquad \vec{E}_{local} = \vec{E}_0 - \dfrac{2\chi \vec{E}_0}{3(1 + \chi)} = \vec{E}_0 \left[\dfrac{3 + \chi}{3(1 + \chi)} \right] = \vec{E}_0 \left(\dfrac{1 + \chi/3}{1 + \chi} \right)$

$$\vec{p} \equiv \alpha \vec{E}_{local} = \vec{E}_0 \alpha \left(\dfrac{1 + \chi/3}{1 + \chi} \right) = \vec{E}_0 \alpha \left(\dfrac{1 + (\rho\alpha/3\varepsilon_0)(1 - \rho\alpha/3\varepsilon_0)^{-1}}{1 + (\rho\alpha/3\varepsilon_0)(1 - \rho\alpha/3\varepsilon_0)^{-1}} \right)$$

or $\qquad\qquad \vec{p} = \vec{E}_0 \alpha \left(\dfrac{1 - \rho\alpha/3\varepsilon_0 + \rho\alpha/3\varepsilon_0}{1 - \rho\alpha/3\varepsilon_0 + \rho\alpha/\varepsilon_0} \right) = \vec{E}_0 \alpha \left[\dfrac{1}{1 + 2\rho\alpha/3\varepsilon_0} \right]$