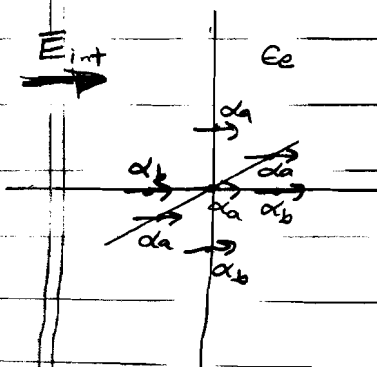
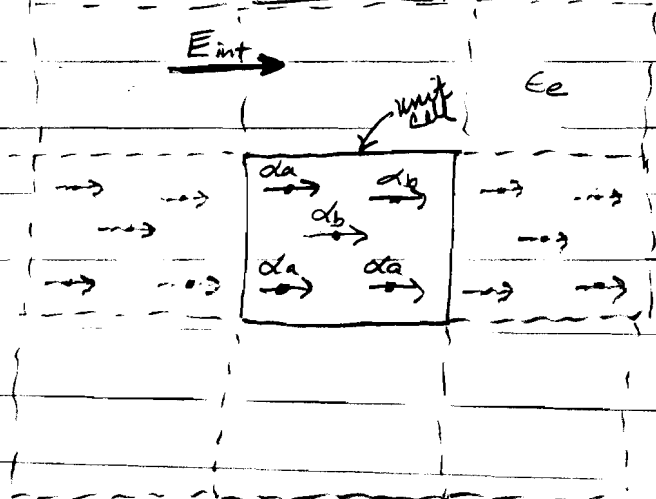


We can use the analysis of the SC lattice of polarizable dipole moments in the previous lecture to derive very useful and famous "mixing formulas" often used in effective electromagnetic materials. There are a few important formulas (such as Maxwell Garnett and Bruggeman) that commonly are derived in separate methods. Here we'll follow Aspnes' method and derive all 4 these formulas in a unified approach.

To accomplish this, we wish now to consider a "heterogeneous material", that is, one comprised by multiple phases of materials. Specifically, let's consider a three-phase system, which is a system containing two different types of particle polarizabilities plus the background material.

Aspnes says to randomly assign different polarizabilities α_a & α_b randomly to the pts. in the lattice. Alternatively, let's create a SC lattice with a large u.c. containing many α_a & α_b randomly located in the u.c.

Fig. 1

Aspnes:Alternatively:

The quest now is to repeat the derivation in the past lecture and determine the volume averaged quantities \bar{P} & \bar{E} for this lattice containing α_a & α_b . From these averaged field quantities, mixing formulas can be analytically derived, such as the Clausius-Mossotti eqn, etc...

Following Aspnes in Section II of his paper, he states that

$$\bar{E}_{loc} = \bar{E}_{int} \quad (1)$$

for this multiphase lattice of Fig. 1. Is this exactly true or an approximation/assumption?

Following (16)-(19) in the previous lecture

$$\bar{P} = \frac{1}{V} \int_V \left\{ \sum_i \left[\sum_j \alpha_{a,j} \bar{E}_{loc} \delta(\bar{r} - \bar{R}_{i,j}) + \sum_k \alpha_{b,k} \bar{E}_{loc} \delta(\bar{r} - \bar{R}_{i,k}) \right] \right\} dV \quad (2)$$

\uparrow Sum over all u.c.'s in V
 "a" particles in u.c. # i.
 "b" particles in u.c. # i

If $\bar{E}_{loc} \approx \bar{E}_{int}$ (and \bar{E}_{int} is uniform), then (2) becomes

$$\bar{P} \approx \frac{1}{V} \int_V \sum_i [N_a \alpha_a + N_b \alpha_b] \bar{E}_{int} dV = \frac{N_a}{V_{uc.}} \alpha_a \bar{E}_{int} + \frac{N_b}{V_{uc.}} \alpha_b \bar{E}_{int} \quad (3)$$

where N_a & N_b are the total number of a & b particles, respectively, in a unit cell.

Alternatively, (3) can be written as

$$\underline{\underline{\bar{P} \approx (n_a \alpha_a + n_b \alpha_b) \bar{E}_{int}}} \quad (4)$$

where n_a and n_b are the number densities of a & b particles in the lattice.

For the volume averaged \bar{E} , assuming that $\bar{E}_{loc} \approx \bar{E}_{int}$ as in (1), then following (20) - (26) in the previous lecture, we can show that

$$\bar{E} \approx \bar{E}_{int} - \left[\frac{N_a}{V_{uc}} \frac{4\pi}{3} \bar{p}_a + \frac{N_b}{V_{uc}} \frac{4\pi}{3} \bar{p}_b \right] = \bar{E}_{int} - \frac{4\pi}{3} [n_a \bar{p}_a + n_b \bar{p}_b] \bar{E}_{int} \quad (5)$$

Sub. (5) into (4)

$$\underline{\underline{\bar{E} \approx \bar{E}_{int} - \frac{4\pi}{3} \bar{P}}} \quad (6)$$

which is the same result we obtained for a two phase system in the previous lecture.

The microscopic field averaged quantities in (4) and (6) will be used ^{a number of} to obtain effective media equations for ϵ , as in the previous lecture.

Lorentz-Lorenz equation

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Using $\bar{P} \propto \bar{E}$ in (4) and (6), can easily show, similar to the last lecture, that

$$\frac{\epsilon-1}{\epsilon+2} = \frac{4\pi}{3} (n_a \alpha_a + n_b \alpha_b) = \frac{4\pi}{3} n_a \alpha_a + \frac{4\pi}{3} n_b \alpha_b \quad (7)$$

As we saw in (31) of the previous lecture, for a single particle (two phase) S.C. lattice system,

$$\frac{4\pi}{3} n \alpha = \frac{\epsilon-1}{\epsilon+2} \quad (8)$$

For this formula, all lattice points had the same polarizability. In our three phase system, only a fraction of the lattice sites have the same polarizability. For the "a" particles, this fraction is f_a and calculated as

$$f_a = \frac{n_a}{n_a + n_b} = \frac{N_a}{N_{tot}} \quad (9)$$

and for the "b" particles
$$f_b = \frac{n_b}{n_a + n_b} = \frac{N_b}{N_{tot}} \quad (10)$$

Using (8)-(10), we can express (7) alternatively as

$$\frac{\epsilon-1}{\epsilon+2} = f_a \frac{\epsilon_a-1}{\epsilon_a+2} + f_b \frac{\epsilon_b-1}{\epsilon_b+2} \quad (11)$$

f_i = volume fraction of the i^{th} phase, $i=a$ or b
for a three-phase system

This is the famous Lorentz-Lorenz formula. Alternatively, we can express this in MKS units as

$$\frac{\epsilon_{\text{eff}} - \epsilon_e}{\epsilon_{\text{eff}} + 2\epsilon_e} = f_a \frac{\epsilon_a - \epsilon_e}{\epsilon_a + 2\epsilon_e} + f_b \frac{\epsilon_b - \epsilon_e}{\epsilon_b + 2\epsilon_e} \quad (12)$$

Where ϵ_{eff} is the effective permittivity of the three phase system, ϵ_e is the permittivity of the ^{environment} (background) material, ϵ_a and ϵ_b are the permittivities of the phases a : b with volume fractions f_a : f_b , respectively. Note that we haven't said anything about the shapes of these particles,

Maxwell Garnett Mixing Formula

Returning now to the Clausius - Mosotti formula of the last lecture in eqn (32):

$$\frac{N\alpha}{3\epsilon_0} = \frac{\epsilon_{\text{eff}} - 1}{\epsilon_{\text{eff}} + 2} \cdot \frac{\epsilon_e}{\epsilon_e} = \frac{\epsilon_{\text{eff}} - \epsilon_e}{\epsilon_{\text{eff}} + 2\epsilon_e} \quad (13)$$

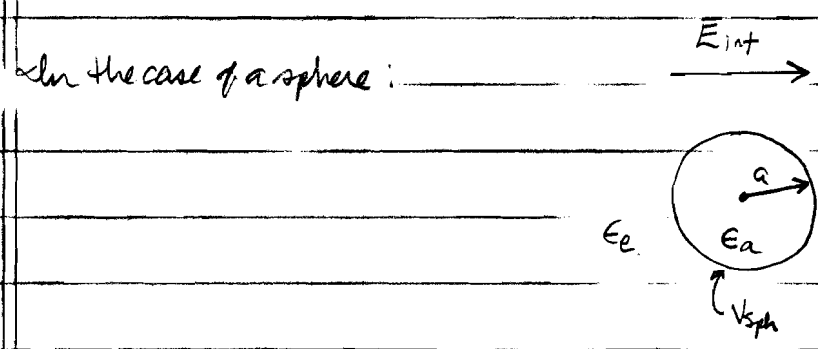
This Clausius - Mosotti equation contains references to microscopic descriptions of this two phase system such as the number density of the particles and their polarizabilities. For macroscopic engineering of artificial materials, these are always the most convenient quantities to work with.

For such macroscopic engineering, we can specialize (13) to a specific type of particle: particle shapes. Often, the α of a single, isolated particle is used in (13).

Will this be an approximation? Of course $\vec{p} = \alpha \vec{E}$ will depend on the effects of other particles, but does α itself change in the presence of other particles in the lattice?

For most particle shapes such an isolated α is not known analytically, much less α in the presence of a lattice of particles. However, α is known analytically for spherical & ellipsoidal shapes.

For other particle shapes, α can be calculated numerically. See Schwela, et al. "Polarizabilities of Platonic Solids."



$$\bar{p} = \alpha \bar{E}_{int} \quad (mks) \quad (14)$$

where

$$\alpha = V_{sph} (\epsilon_a - \epsilon_e) \cdot \frac{3\epsilon_e}{\epsilon_a + 2\epsilon_e} \quad (mks) \quad (15)$$

and $V_{sph} = \frac{4}{3} \pi a^3$ (16)

Substituting (15) \rightarrow (13)

$$\frac{n}{3\epsilon_e} V_{sph} (\epsilon_a - \epsilon_e) \cdot \frac{3\epsilon_e}{\epsilon_a + 2\epsilon_e} = \frac{\epsilon_{eff} - \epsilon_e}{\epsilon_{eff} + 2\epsilon_e}$$

or $\frac{\epsilon_{eff} - \epsilon_e}{\epsilon_{eff} + 2\epsilon_e} = n V_{sph} \frac{\epsilon_a - \epsilon_e}{\epsilon_a + 2\epsilon_e}$ (17)

But $n V_{sph} = \frac{\# \text{ particles}}{V_{uc.}} \cdot V_{sph} = N \frac{V_{sph}}{V_{uc.}} = f_a$ (18)
 \uparrow volume fraction of spheres

Therefore, (17) becomes

$$\frac{\epsilon_{\text{eff}} - \epsilon_e}{\epsilon_{\text{eff}} + 2\epsilon_e} = f_a \frac{\epsilon_a - \epsilon_e}{\epsilon_a + 2\epsilon_e} \quad (\text{MKS}) \quad (19)$$

Eqn (19) is the famous Maxwell Garnett mixing formula. It was actually first derived by James Clerk Maxwell in his *Treatise on the electrical conductivity of a two phase mixture of conducting spheres in a conducting background material.*

After some simple algebra, can solve for ϵ_{eff} as

$$\epsilon_{\text{eff}} = \epsilon_e + 3f \epsilon_e \frac{\epsilon_a - \epsilon_e}{\epsilon_a + 2\epsilon_e - f(\epsilon_a - \epsilon_e)} \quad (\text{MKS}) \quad (20)$$

Bruggeman Effective Medium Approximation

As Aspnes points out in eqn. (A) of his paper, the Lorentz-Lorentz & MG equations in (12) & (19), respectively, have the same general form as

$$\frac{\epsilon_{\text{eff}} - \epsilon_h}{\epsilon_{\text{eff}} + 2\epsilon_h} = f_a \frac{\epsilon_a - \epsilon_h}{\epsilon_a + 2\epsilon_h} + f_b \frac{\epsilon_b - \epsilon_h}{\epsilon_b + 2\epsilon_h} \quad (\text{MKS}) \quad (21)$$

where ϵ_h is "some sort of a" "host" material. In particular:

- For Lorentz-Lorentz: choose $\epsilon_h = \epsilon_e$ and we arrive at (12)

while • for Maxwell Garnett : choose $\epsilon_h = \epsilon_b$ and the last term in (21) vanishes and we're left with

$$\frac{\epsilon_{eff} - \epsilon_b}{\epsilon_{eff} + 2\epsilon_b} = f_a \frac{\epsilon_a - \epsilon_b}{\epsilon_a + 2\epsilon_b} \quad (MGS) \quad (22)$$

which we can recognize as the MGS formula for spheres of ϵ_a in a host (background) of ϵ_b .

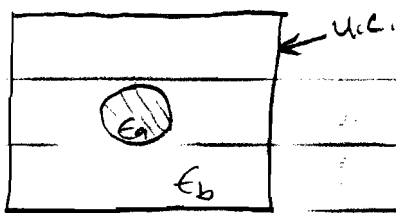
But! How (21) picks both of these formulas.

Now, this choice of $\epsilon_h = \epsilon_b$ makes good sense when $f_a < f_b$.

Say for spheres in a background material. But what if $f_a > f_b$?

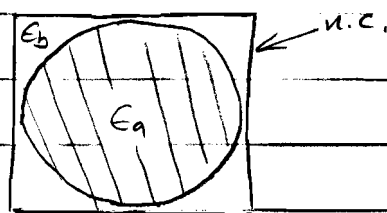
Which to call the "host" material?

$f_a < f_b$:



call $\epsilon_h = \epsilon_b$.

$f_a > f_b$:



call $\epsilon_h = ?$. What is the best choice for the host?

also this case with $f_a > f_b$, it is not so clear that ϵ_a is the appropriate choice as the "host" phase. Aspnes actually says that ϵ_b is the more appropriate choice.

However, depending on the choice of ϵ_a or ϵ_b as the host, the two mixing formulas will be different. The MG formula in (22) is not symmetrical for $\epsilon_a \leftrightarrow \epsilon_b$. More specifically, consider these results from Sihvola, "Electromagnetic Mixing Formulas and Applications," 1999:

Classical mixing approach 51

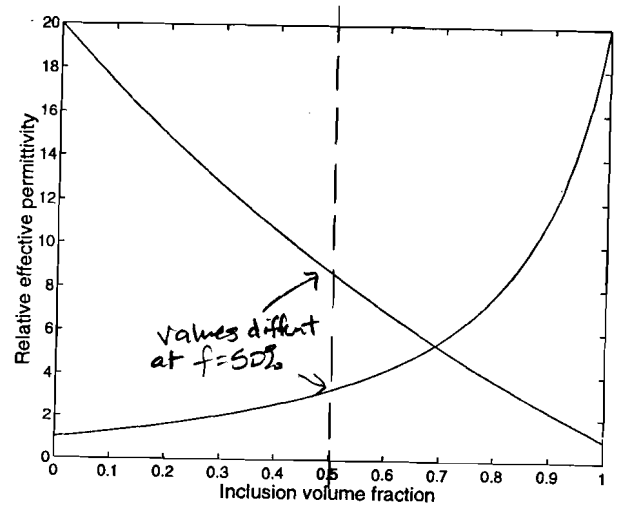


Figure 3.6: A comparison of complementary mixtures: the effective permittivity ϵ_{eff} is shown for two mixtures where the contrast between the phases is 20. The roles of inclusion and environment have been interchanged in the two models: $\epsilon_i = 20\epsilon_e$ in the rising curve and $\epsilon_e = 20\epsilon_i$ in the falling curve.

According to Agnes, Bruggeman resolved this dilemma by proposing that neither phases (a or b) should be given the preference as the "host". Rather, both phases a & b should be considered as being embedded in the effective medium (i.e., the "host") itself.

This is equivalent to choosing

$$\epsilon_h = \epsilon_{eff}$$

in (21) above. Making this substitution gives

$$\underline{0 = f_a \frac{\epsilon_a - \epsilon_{\text{eff}}}{\epsilon_a + 2\epsilon_{\text{eff}}} + f_b \frac{\epsilon_b - \epsilon_{\text{eff}}}{\epsilon_b + 2\epsilon_{\text{eff}}} \quad (\text{MRS}) \quad (24)}$$

where $f_a + f_b = 1$. This formula is called the Bruggeman mixing formula, or the effective medium approximation (EMA).

Eqn (24) is probably more appropriately called the symmetrical Bruggeman formula. With $\epsilon_a \leftrightarrow \epsilon_b$, $f_a \leftrightarrow f_b$ see that the formula is unchanged. (There are other Bruggeman formulas such as the asymmetrical Bruggeman formula.)