NIUS Lecture Notes

On

Disordered Systems

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BRUGGEMAN'S EFFECTIVE MEDIUM THEORY

Consider a metal slab having conductivity σ_1 as shown in Fig.1(a)

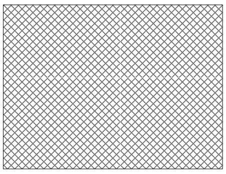


Fig.1(a)

Then,

$$\vec{j_1} = \sigma_1 \vec{E_0} \tag{1}$$

where $\vec{j}$: Current passing through the metal
and $\vec{E_0}$: Applied electric field
Isotropy is assumed. σ_1 is a scalar.
Consider another metal slab of conductivity σ_2 as shown in Fig.1(b)

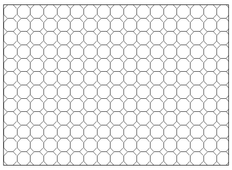


Fig.1(b)

$$\vec{j_2} = \sigma_2 \vec{E_0} \tag{2}$$

Now, consider a random mixture of the two metals individually described by equations (1) and (2), and having concentrations C_1 and C_2 respectively.
What is the resultant(i.e. effective) conductivity σ_{eff} of this random mixture of the two metals?(refer Fig.2)

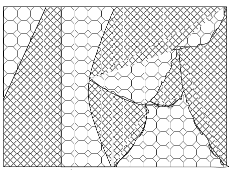


Fig.2

The problem was attempted by
Faraday (1837)
Maxwell (1871) Treatise on Elec. & Magn. Vol. I, Pg. 440, Sec. 3
J.C.Maxwell Garnet (1904) etc. Philos. Trans. R. Soc. Lond. 203, 385 (1904)
The first and perhaps the simplest approximation is

$$\sigma_{eff} = C_1\sigma_1 + C_2\sigma_2 \tag{3}$$

This is currently known as "Virtual Crystal Approximation"(VCA).
Bruggeman had an entirely novel idea. He conducted the following "thought-experiment"(Gedanken-Versuch):
Note: $C_1 + C_2 = 1$

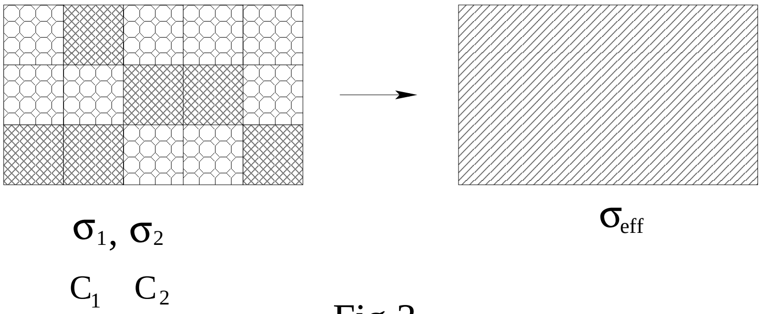


Fig.3

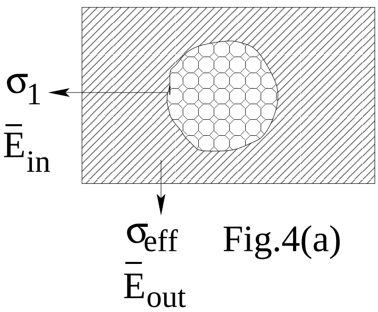


Fig.4(a)

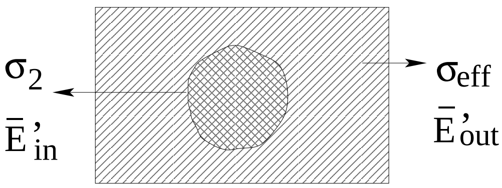


Fig.4(b)

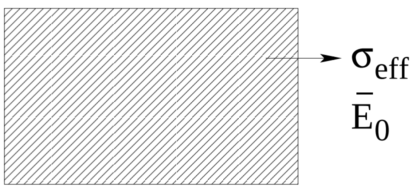


Fig.4(c)

On an average $\langle \bar{E}_{out}, \bar{E}'_{out} \rangle = \bar{E}_0$
i.e.

$$C_1 \bar{E}_{out} + C_2 \bar{E}'_{out} = \bar{E}_0 \tag{4}$$

i.e. on an average there should be no further "scattering".
The problem is "How to implement this idea?"
To do this, we need to solve the "single inclusion" problem in Figs. 4(a) and 4(b). This is a two dimensional problem and no azimuthal dependence is needed to be considered.
Consider fig.4(a)
The potential in the effective medium is

$$\nabla^2 U_{out} = 0$$

$$U_{out}(r) = \sum_{l=0}^{\infty} \left(a_l r^l + \frac{b_l}{r^{l+1}} \right) P_l(\cos\theta)$$

We set constant term

$$a_0 = 0$$

Since there is no net charge on sphere,

$$b_0 = 0$$

At large distance, the electric field $= \bar{E}_0$
$\therefore$ At large distance, the potential $=\bar{E}_0 r \cos\theta (= -\bar{E}_0 z)$
$\therefore a_2, a_3, \cdots = 0$
$a_1 = -E_0$

$$U_{out}(r) = -\bar{E}_0 r \cos\theta + \frac{b_1}{r^2}\cos\theta + \frac{b_2}{r^3} P_2 \cos\theta + \frac{b_3}{r^4} P_3 \cos\theta + \cdots \tag{5}$$

$$U_{in}(r) = \sum_{l=0}^{\infty} \left(c_l r^l + \frac{d_l}{r^{l+1}} \right) P_l(\cos\theta)$$

as $r \to 0$, $U_{in}(r)$ is finite. $\therefore d_l = 0 \ \forall \ l$
Constant term is set to zero, $c_0 = 0$. (since zero can be redefined.)
Now, the spherical inclusion is small and we take the electric field inside it to be uniform, viz $\bar{E_{in}}$
$\therefore c_1 \neq 0, \qquad c_2 = c_3 = \cdots = 0.$

$$\bar{E}_{in} z = c_1 r \cos\theta$$

$$\therefore U_{in} = c_1 r \cos\theta \tag{6}$$

At the interface

$$U_{in}(r) = U_{out}(r) \tag{7}$$

(Continuity of potential)

$$\sigma_1 \bar{E}_{in}^{\perp} = \sigma_{eff} \bar{E}_{out}^{\perp} \tag{8}$$

(Continuity of current in normal direction)
(7) $\Rightarrow$

$$c_1 a \cos\theta = -E_0 a \cos\theta + \frac{b_1}{a^2}\cos\theta + \frac{b_2}{a^3} P_2(\cos\theta) + \frac{b_3}{a^4} P_3(\cos\theta) + \cdots$$

From the orthonormality of Legendre polynomials

$$b_2 = b_3 = b_4 = \cdots = 0$$

$$\therefore c_1 a = -E_0 a + \frac{b_1}{a^2} \tag{9}$$

Eq. (8) implies

$$\sigma_1 \left(-\frac{\partial U_{in}}{\partial r} \right) = \sigma_{eff} \left(-\frac{\partial U_{out}}{\partial r} \right)$$

$$\therefore \sigma_1 c_1 = \left(-E_0 - \frac{2b_1}{a^3}\right)\sigma_{eff}$$

i.e.

$$-\sigma_1 c_1 = \sigma_{eff}\left(E + \frac{2b_1}{a^3}\right) \tag{10}$$

Eliminating c_1 from (9) and (10),

$$\sigma_1\left(\frac{b_1}{a^2} - E_0 a\right) + a\sigma_{eff}\left(E_0 + \frac{2b_1}{a^3}\right) = 0$$

$$\therefore b_1\left(\frac{\sigma_1}{a^2} + \frac{2\sigma_{eff}}{a^2}\right) = E_0 a(\sigma_1 - \sigma_{eff})$$

$$\therefore b_1 = E_0 a^3\left(\frac{\sigma_1 - \sigma_{eff}}{\sigma_1 + 2\sigma_{eff}}\right)$$

From (9),

$$c_1 = -E_0 + \frac{1}{a^3}E_0 a^3\left(\frac{\sigma_1 - \sigma_{eff}}{\sigma_1 + 2\sigma_{eff}}\right)$$

$$= -E_0\left[\frac{\sigma_1 + 2\sigma_{eff} - \sigma_1 + \sigma_{eff}}{\sigma_1 + 2\sigma_{eff}}\right]$$

$$= -E_0\frac{3\sigma_{eff}}{\sigma_1 + 2\sigma_{eff}}$$

We are mainly interested in b_1,

$$U_{out}(r) = -E_0 r\cos\theta - \frac{E_0}{r^2}a^3\left(\frac{\sigma_{eff} - \sigma_1}{\sigma_1 + 2\sigma_{eff}}\right)\cos\theta$$

$$\therefore \bar{E}_{out} = -\frac{\partial U_{out}}{\partial z} = \bar{E}_0 - a^3\left(\frac{\sigma_{eff} - \sigma_1}{\sigma_1 + 2\sigma_{eff}}\right)\left(-\frac{\partial}{\partial z}\left(\frac{\bar{E}_0.\bar{r}}{r^3}\right)\right)$$

Similarly,

$$\bar{E}'_{out} = \bar{E}_0 - a^3\left(\frac{\sigma_{eff} - \sigma_2}{\sigma_2 + 2\sigma_{eff}}\right)\left(-\frac{\partial}{\partial z}\left(\frac{\bar{E}_0.\bar{r}}{r^3}\right)\right)$$

Using eq.(4),

$$C_1\frac{(\sigma_{eff} - \sigma_1)}{\sigma_1 + 2\sigma_{eff}} + C_2\frac{(\sigma_{eff} - \sigma_2)}{\sigma_2 + 2\sigma_{eff}} = 0 \tag{11}$$

This is BRUGGEMAN'S EFFECTIVE MEDIUM RESULT.
We can go a step further and solve for σ_{eff}, from (11),

$$C_1(\sigma_2 + 2\sigma_{eff})(\sigma_{eff} - \sigma_1) + C_2(\sigma_1 + 2\sigma_{eff}(\sigma_{eff} - \sigma_2) = 0$$

$$\therefore C_1(-\sigma_1\sigma_2 + \sigma_2\sigma_{eff} + 2\sigma_{eff}^2 - 2\sigma_1\sigma_{eff}) + C_2(-\sigma_1\sigma_2 + \sigma_1\sigma_{eff} + 2\sigma_{eff}^2 - 2\sigma_2\sigma_{eff}) = 0$$

Note that $C_1 + C_2 = 1$

$$\therefore 2\sigma_{eff}^2 + \sigma_{eff}\{(1 - 3C_1)\sigma_1 + (1 - 3C_2)\sigma_2\} - \sigma_1\sigma_2 = 0$$

Let

$$r = (3C_1 - 1)\sigma_1 + (3C_2 - 2)\sigma_2 \tag{12}$$

$$\therefore 2\sigma_{eff}^2 - r\sigma_{eff} - \sigma_1\sigma_2 = 0$$

$$\therefore \sigma_{eff} = \frac{r \pm (r^2 + 8\sigma_1\sigma_2)^{1/2}}{4}$$

Now, $\sigma_1, \sigma_2, \sigma_{eff} \geq 0$ ($\not< 0$)
Hence,

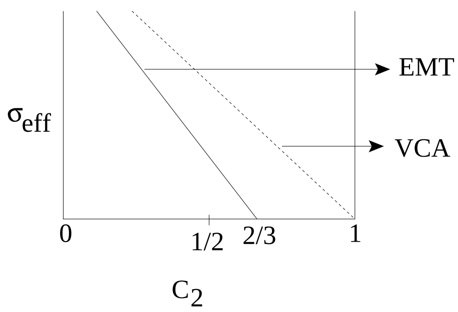
$$(r^2 + 8\sigma_1\sigma_2)^{1/2} > r$$

So, we must choose the +ve sign.

$$\therefore \sigma_{eff} = \frac{r + (r^2 + 8\sigma_1\sigma_2)^{1/2}}{4} \tag{13}$$

Analysis of the Result:

1. The Percolation Threshold:
   Consider a mixture of good and poor conductors.
   Let $\sigma_2 \simeq 0$(poor conductor)
   $r \simeq (3C_1 - 1)\sigma_1$
   Let $C_1 \simeq \frac{1}{3}$
   i.e. the good conductor has a low concentration of 1/3 and the poor conductor predominates.
   $\therefore r \simeq 0$
   $\therefore \sigma_{eff} \simeq 0$
   VCA result of eq.(3)$\Rightarrow$
   $\sigma_{eff} = 0$ if $C_1 \to 0$



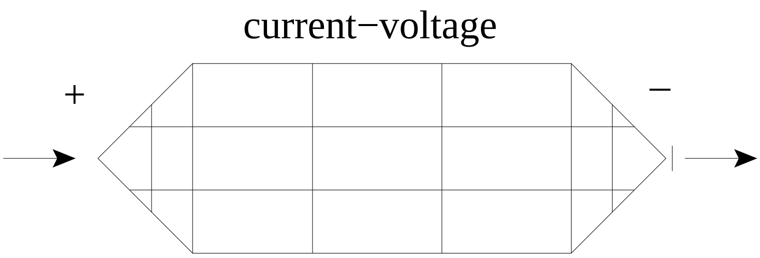
   Let us call P_c = percolation threshold, as the concentration of good conductor, when current ceases (i.e. $\sigma_{eff} = 0$)
   $P_c = 1/3 = 33\%$(3-dim)
   Thus EMT predicts a PERCOLATION THRESHOLD !
   Thus, enough conductor (1/3), put into an insulator, makes it conducting.
   enough insulator (2/3), put into a conductor, makes it insulating.
   agrees with observations:-

   (i) In metallurgy.

   (ii) Leaking roof (a common monsoon problem in India) Cement, Gravel, sand.
   Sand concentration > 33%

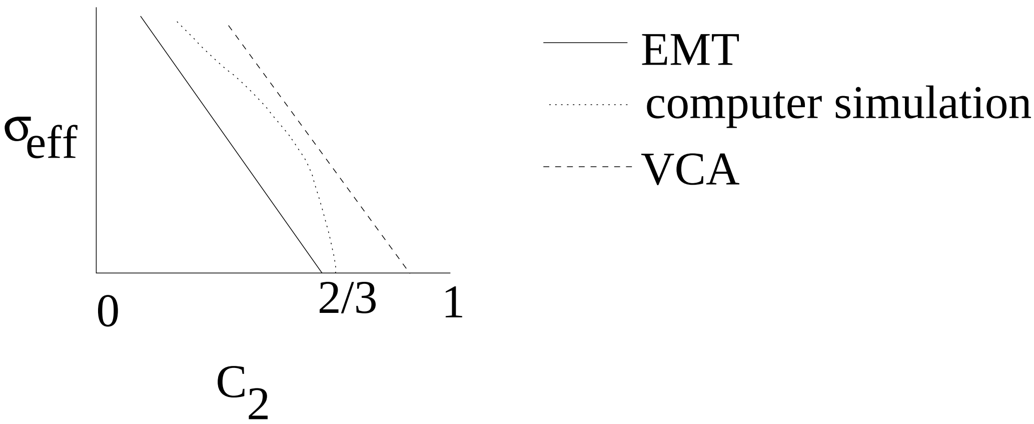
(iii) Surahi

Consider a resistor network (non-directed percolation)
Remove bonds at random.



Computer experiments give $P_c = 15$ to 17% in 3 - dim.
In fact P_c is different when you have directed percolation.
Note that such results don't work in the case of neural transmission. Thus $P_c \simeq 0$ like VCA. But VCA is not supposed to be operative in this case & the agreement is purely coincidental.

2. Slope at percolation threshold



This is important in critical phenomenon

$$\frac{\partial \sigma_{eff}}{\partial C_2} = \frac{\partial \sigma_{eff}}{\partial C_1}\frac{\partial C_1}{\partial C_2} = \frac{\partial \sigma_{eff}}{\partial C_1}\left(\frac{\partial (1-C_2)}{\partial C_2}\right) = -\frac{\partial \sigma_{eff}}{\partial C_1}$$

VCA:

$$\left.\frac{\partial \sigma_{eff}}{\partial C_2}\right|_{\sigma_2=0} = -\frac{\partial}{\partial C_1}(C_1\sigma_1 + 0)$$
$$= -\sigma_1$$

$\therefore$ approaches zero with a negative slope of value σ_1.

EMT:

$$\left.\frac{\partial \sigma_{eff}}{\partial C_2}(\sigma_2 = 0)\right|_{c_2=2/3} = -\frac{1}{4}\left.\left[\frac{\partial r}{\partial C_1} + \frac{\partial r}{\partial C_1}\right]\right|_{c_1=1/3}$$

$$= -\frac{1}{2}\frac{\partial r}{\partial c_1}$$
$$= -\frac{1}{2}\frac{\partial}{\partial c_1}[\sigma_1(3c_1 - 1)]$$
$$= -\frac{3}{2}\sigma_1$$

Both are linear. Computer experiments, show non-linearity.

3. The theory is enormously successful in the metallic regime, away from the percolation threshold.

4. A look at VCA result: $\sigma_{eff} = C_1\sigma_1 + C_2\sigma_2$
   This philosophy is widely used.
   Vegard's law in crystal structure:
   Ga metal has an interatomic distance d_1
   As insulator has an interatomic distance d_2
   $GaAs$ semiconductor has an interatomic distance $\frac{1}{2}(d_1 + d_2)$
   $Cu_{1-C}Ni_C$ has an interatomic distance $Cd_{Ni} + (1 - C)d_{Cu}$ etc.
   Going beyond VCA result in an intuitive way.

$$\sigma_{eff} = C_1\sigma_1 + C_2\sigma_2 + C_1C_2(a_1\sigma_1 + a_2\sigma_2)$$
$$= VCA \ + \ NORDHEIMS\ RULE \ (1931)$$

:Ensures $C_2 = 0, \ \sigma_{eff} = \sigma_1$
$C_2 = 0, \ \sigma_{eff} = \sigma_1$

   This rule is often found.
   "Band bowing" is one example.(in semiconductors)

5. The theory goes under the name of "Coherent Potential Approximation" (CPA) when applied to elementary excitations in substitutionally disordered solids:
   Electrons (Soven 1967)
   Phonons (Tayler 1967)

   This theory is not applicable to positionally disordered systems.

6. Confusion of terms:
   "Effective Medium Theory"
   "Effective Medium Approximation"
   "Coherent Potential Approximation"
   "Coherent Medium Approximation"

Further References:

1. Bruggeman in his paper also works out the case for dimensionalities $d = 1, 2$.

$$C_1\frac{\sigma_1 - \sigma_{eff}}{\sigma_1 + (d-1)\sigma_{eff}} + C_2\frac{\sigma_2 - \sigma_{eff}}{\sigma_2 + (d-1)\sigma_{eff}} = 0$$

   One could derive this and work out its implications.

2. One could extend the theory to an n-component mixture

$$\sum_{i=1}^{n} C_i \frac{\sigma_i - \sigma_{eff}}{\sigma_1 + (d-1)\sigma_{eff} = 0}$$

Given above, this is trivial.

3. D.Polder and J.H.Van Santen, Physica Utrecht 12, 257 (1946) have worked out the problem for ellipsoids instead of spheres.

4. D.Stroud Phys. Rev. B 12 3368 (1975)He has considered the conductivity of the spherical regions to be tensorial and not merely isotropic.

5. D.Stroud (above reference) & B.E.Springett-(Phys. Rev. Lett. 31,1463 (1973)) have focussed on the ac case.

6. S.Kirkpatrick Rev. Mod. Physics 45, 574 (1973) has applied the Brugemann idea to random resistor networks. In these networks. In these networks the absence (or presence) of resistors is chosen stochastically, but their positions are laid out in a periodic array. The way Kirkpatrick proceeds is as follows. View each possible choice of resistor as embedded in an otherwise uniform network of "effective"resistors. The resistor under consideration will have an excess or deficit voltage, compared to the effective resistors far from it. The effective resistor value is then chosen so that the average voltage deviation vanishes.

7. An excellent overview is provided by Rolf Landauer in "Electrical Conductivity in Inhomogeneous media".

8. The method has been widely used in many areas as outlined above .An application to the effective viscosity of a random distribution of spheresin a fluid is by
G.K.Batchelor, J-Fluid Mech. 52,245 (1972)
G.K.Batchelor, J-7-Green, J-Fl. Mech. 56, 401 (1972)
G.K.Batchelor, Ann.Rev. Fluid Mech. 6.227 (1974)
H.C.Brinkman, Appl. Sci. Res. A1,27 (1947)

9. Bruggeman's idea has been applied to calculation of the elasticity of polycrystalline rocks by
E.Kroner: J.Mechs. Phys.-Solids 15,319-339 (1967)
L.Thompsen: J.GeoPhys. Res. 77, 315-327, (1972).