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SPRING COLLEGE IN MATERIALS SCIENCE ON 'CERAMICS AND COMPOSITE MATERIALS'

(17 April - 26 May 1989)

POROUS MEDIA

(Lecture I and II)

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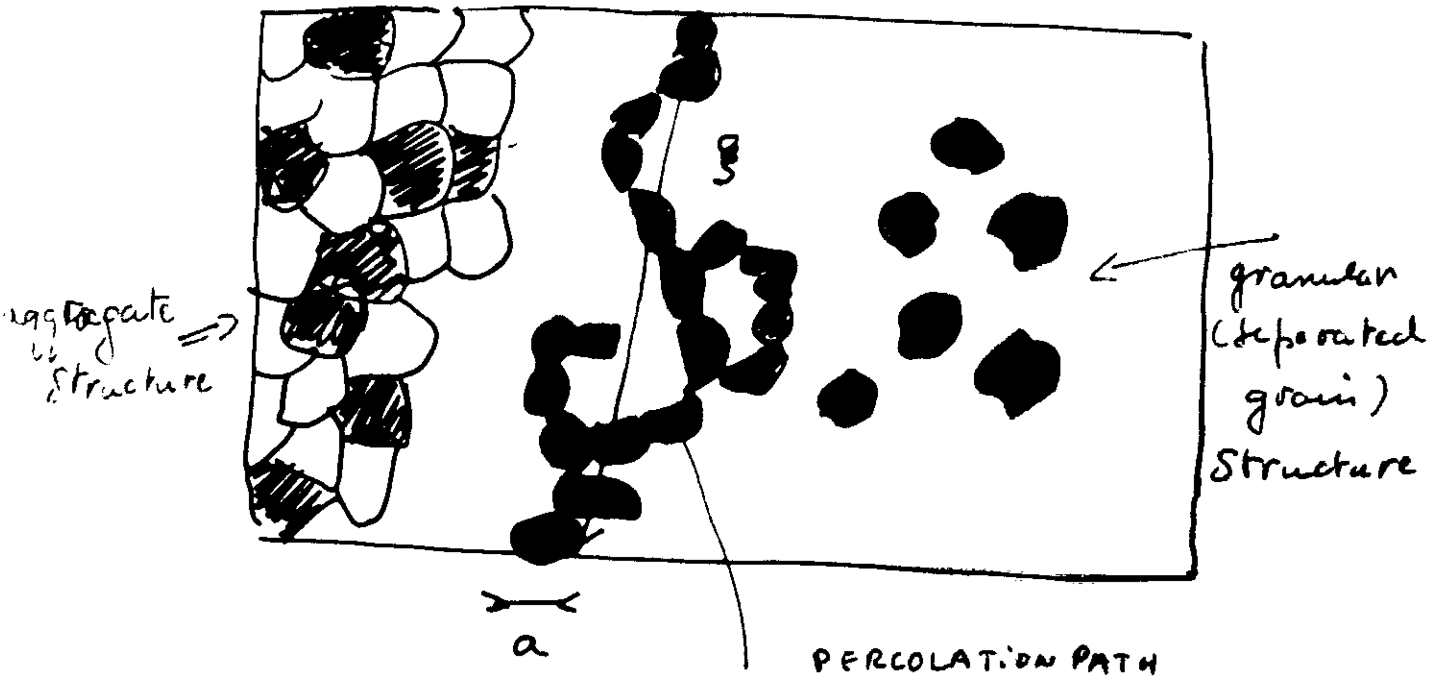
AIM OF THE COURSE

INCOMPLETE REVIEW OF SOME OF THE METHODS USED TO DESCRIBE THE MACROSCOPIC PROPERTIES OF INHOMOGENEOUS COMPOSITE MATERIALS FROM THE KNOWLEDGE OF THE PROPERTIES OF THE CONSTITUANTS AND THE MICROGEOMETRY OF THE COMPOSITE.

THE OBJECTIVE IS TO OPEN THE DOORS OF THE FIELD HOPING THAT IT WILL GIVE YOU THE TASTE TO GO FURTHER.



λ, ξ, a, L

λ light or "probe" wavelength

ξ Correlation length: characteristic linear size of an average cluster

a "grain" typical size

INHOMOGENEOUS MACROSCOPIC MEDIA

$L \leq 10\,\text{Å}$

MICROSCOPIC

$10\,\text{Å} < L <$ grainsize

MESOSCOPIC

grainsize $< L <$ cluster size (ξ)

MACROSCOPIC

$L >$ cluster size

Characteristic length of the probe (λ)

light (spectroscopic, optical measurement)

optical or electron microscope

tunneling microscope

light X-ray neutron scattering

METALS, SEMICONDUCTORS CRYSTALLINE MATERIALS	WELL ESTABLISHED THEORIES
AMORPHOUS MATERIALS	RATHER WELL ESTABLISHED
MACROSCOPIC RANDOM MEDIA	NO TEXT BOOKS STILL TIME OF THE PIONNERS

WHY ? A NEW GEOMETRY IS REQUIRED

MANY PHENOMENA ARE DOMINATED BY AN UNDERLYING PHASE TRANSFORMATION (PERCOLATION) OR (AND) IRREVERSIBLE GROWTH PROCESSES

NEW LANGUAGE HAD TO BE INVENTED. TERMINOLOGY COMES FROM THE THEORY OF THERMODYNAMIC PHASE TRANSITION AND CRITICAL PHENOMENA

PHYSICS OF MACROSCOPIC RANDOM MEDIA IS DOMINATED BY CONCEPTS LIKE

FRACTAL DIMENSION
MULTIFRACTAL DISTRIBUTION
SELF SIMILARITY
CRITICAL EXPONENTS
SCALING LAWS.

① MEAN FIELD THEORIES

② PERCOLATION THEORY

=> BRIEF INTRODUCTION TO FRACTAL PHYSICS.

① MEAN FIELD THEORIES.

THE PROBLEM IS HOW TO CALCULATE THE EFFECTIVE PROPERTY OF THE COMPOSITE P^* IF WE KNOW THE INDIVIDUAL PROPERTIES OF THE CONSTITUENTS P_A and P_B AND THE "CONCENTRATION" OF A and B.

EXAMPLE.

$$\underset{?}{\varepsilon^*(\omega)} \Longleftarrow \begin{cases} \varepsilon_A(\omega) = \varepsilon_A'(\omega) + i\,\varepsilon_A''(\omega) & f_A = f \\ \varepsilon_B(\omega) = \varepsilon_B'(\omega) + i\,\varepsilon_B''(\omega) & 1-f_A = f_B \end{cases}$$

$$\varepsilon_A''(\omega) = \frac{i\,\sigma_A(\omega)}{\varepsilon_0\,\omega}$$

A CONDUCTOR (METALLIC OR IONIC)

B ISOLANT OR CONDUCTOR $(\sigma_B \ll \sigma_A)$

OTHER EXAMPLES

ELASTIC PROPERTIES (bulk modulus K
Shear modulus μ
Youngs modulus Y)

TO TREAT SUCH PROBLEMS ONE HAS VARIOUS APROACHES

① $\lambda \gg \xi \gg a$

QUASI STATIC APPROXIMATION -> MEAN FIELD THEORIES

② $\lambda \sim a$

GEOMETRIC APPROXIMATION (OPTICS)

③ IF $a \ll \lambda \ll \xi$

CLOSE TO PERCOLATION THRESHOLD

THEORY OF PERCOLATION

SIMILAR TO A PHASE TRANSITION (ONE CANNOT NEGLECT FLUCTUATIONS)

$\boxed{\text{MEAN FIELD THEORY TO BE USED DEPEND ON MICROGEOMETRY}}$

① MAXWELL-GARNET (1904) ISOLATED GRAIN STRUCTURE (OXYDE COATING)
NO PHASE TRANSITION.

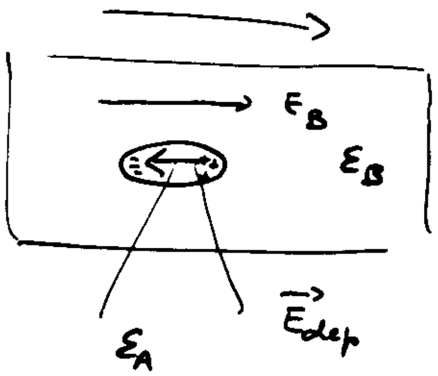
② BRUGGEMAN (1935) AGGREGATE STRUCTURE
PHASE TRANSITION AT PERCOLATION THRESHOLD

③ SYMMETRIZED MAXWELL GARNET (P. Sheng 80 + Brouers (86))

④ for ROCKS and POLYMERS. DIFFERENTIAL EFFECTIVE MEDIUM THEORY

MAXWELL - GARNETT

ELECTROSTATIC.



$$\vec{E}^{A}_{dep} = -g\,\frac{\epsilon_A - \epsilon_B}{(1-g)\,\epsilon_B + g\,\epsilon_A}\,\vec{E}_B$$

$$= -g\,\frac{P_A}{\epsilon_0}$$

g depolarization factor depends on shape of inclusion

$\longrightarrow$

 Sphere $g = 1/3$

 oblate $g \Rightarrow 1$

 prolate $g \to 0$

$$\vec{E}_A = \vec{E}_B + \vec{E}_{dep} = \vec{E}_B\,\frac{\epsilon_B}{(1-g)\epsilon_B + g\,\epsilon_A}$$

If $g \to 0$ (prolate) $\quad \bar{E}_{dep} = 0 \quad \bar{E}_A = \bar{E}_B$

CONTINUITY OF FIELD

$g \to 1$ (oblate) $\quad \bar{E}_{dep} = \frac{\epsilon_A - \epsilon_B}{\epsilon_A}\,\epsilon_B$

$$\bar{E}_A = \bar{E}_B\,\frac{\epsilon_B}{\epsilon_A}$$

CONTINUITY OF INDUCTION

SUPPOSE WE HAVE CONCENTRATION f OF A INCLUSIONS

$$\bar{E}_{eff} = f\,\bar{E}_A + (1-f)\,\bar{E}_B$$

$$= f\,\bar{E}_B \frac{\epsilon_B}{\epsilon_B(1-g) + g\,\epsilon_A} + (1-f)\,\bar{E}_B$$

$$\bar{E}_{eff} = \bar{E}_B \frac{(1-g+fg)\epsilon_B + g(1-f)\epsilon_A}{(1-g)\epsilon_B + g\,\epsilon_A} \quad (1)$$

Now the effective dielectric constant is determined using the two relations (1) and (2)

$$\bar{D}_{eff} = \epsilon_{eff}\,\bar{E}_{eff} = f\,\epsilon_A\,\bar{E}_A + (1-f)\,\epsilon_B\,\bar{E}_B$$

$$\epsilon_{MG} = \epsilon_{eff} = \epsilon_B \frac{g\,\epsilon_A + (1-g)\epsilon_B + f(1-g)(\epsilon_A - \epsilon_B)}{g\,\epsilon_A + (1-g)\epsilon_B - fg\,(\epsilon_A - \epsilon_B)}$$

$$\epsilon_{MG} = \epsilon_B \frac{1 + f(1-g)\alpha^{MG}}{1 - fg\,\alpha^{MG}} \simeq \epsilon_B\left[1 + f(1-g)\alpha^{MG} + O(f^2)\right]$$

$$\alpha^{MG} = \frac{\epsilon_A - \epsilon_B}{(1-g)\epsilon_B + g\,\epsilon_A}$$

IF ϵ_B insulator ϵ_A metal (Drude).

CONDITION $(1-g)\epsilon_B + g\,\epsilon_A = 0$

→ Surface plasmon mode

(responsible absorption of Solar radiation in cermets)

IN MICROSCOPIC SCALE MG ≡ CLAUSIUS MOSOTI FORMULA ($g = 1/3$).

MAXWELL-GARNETT CANNOT DESCRIBE INSULATOR-METAL TRANSITIO

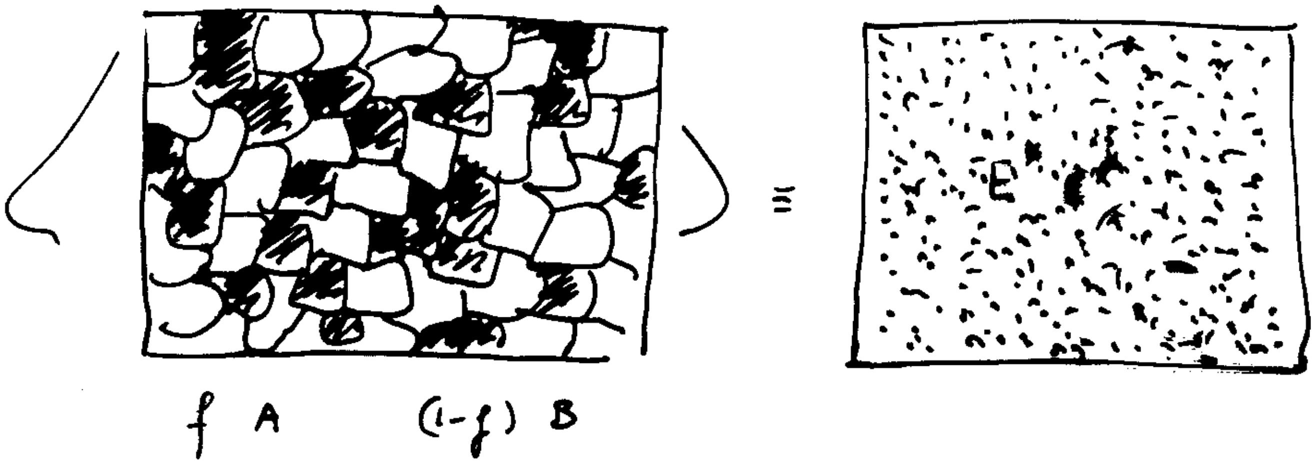
FOR D.C. CONDUCTIVITY $\varepsilon_A \to \sigma_A$

$\varepsilon_B \to \sigma_B$

$\sigma_B \neq 0$ ALWAYS A CONDUCTOR

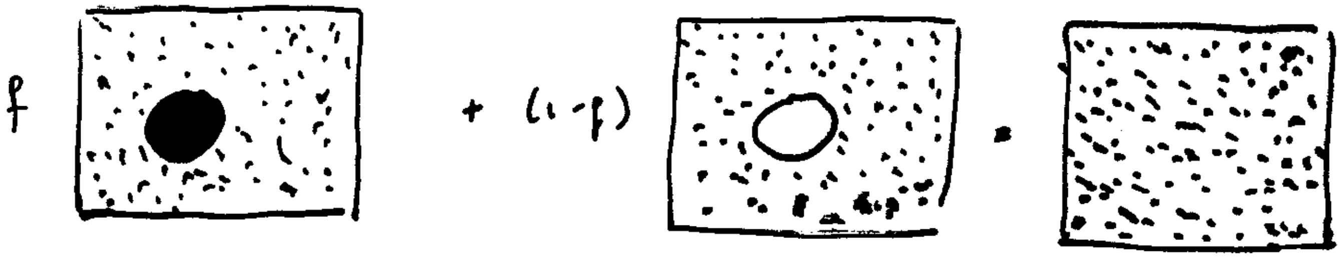
$\sigma_B = 0$ ALWAYS AN INSULATOR.

IF METAL-INSULATOR $\Longrightarrow$ <u>BRUGGEMAN APPROXIMATION</u>.



HOW TO DETERMINE E^* AND ε^*

<u>SELF CONSISTENT CONDITION</u>.



The effective field E^* is given by

$$E^* = f E_A + (1-f) E_B \qquad (1)$$

$$E_{A(B)} = \frac{\epsilon^* E^*}{g\,\epsilon_{A(B)} + (1-g)\,\epsilon^*} = E^* - \frac{g(\epsilon_{A(B)} - \epsilon^*)\,E^*}{g\,\epsilon_{A(B)} + (1-g)\,\epsilon^*} \qquad (2$$

$$P_{A(B)} = \varepsilon_0\, \alpha^{Br}_{A(B)}\, E^* \qquad (3)$$

$$\alpha^{Br}_{A(B)} = \frac{\epsilon_A - \epsilon^*}{(1-g)\,\epsilon^* + g\,\epsilon_{A(B)}} \qquad (4)$$

Introducing (2) into (1), one gets

$$\epsilon^* = f\epsilon^* - \frac{f g(\epsilon_A - \epsilon^*)\,E^*}{g\,\epsilon_A + (1-g)\,\epsilon^*} + (1-f)E^* - \frac{(1-f)g\,(\epsilon_B - \epsilon^*)E^*}{g\,\epsilon_B + (1-g)\,\epsilon^*}$$

from which the following expression may be obtained

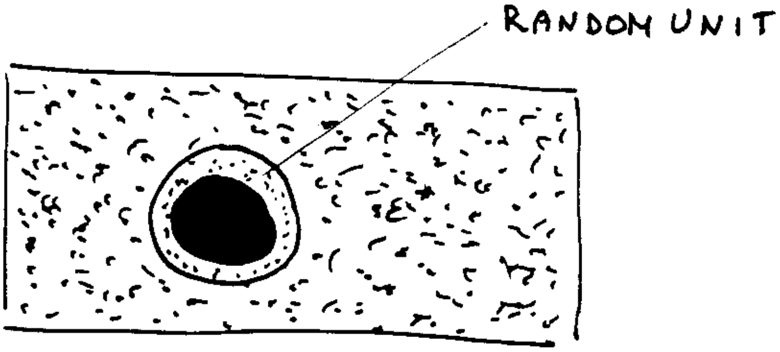
$$\boxed{f\,\frac{\epsilon_A - \epsilon^*}{\epsilon^* + g\,(\epsilon_A - \epsilon^*)} + (1-f)\,\frac{\epsilon_B - \epsilon^*}{\epsilon^* + g\,(\epsilon_B - \epsilon^*)} = 0}$$

THIS IS EQUIVALENT TO WRITE THE CONDITION

$\langle S(\theta = 0) \rangle$ IN THE DIPOLAR APPROXIMATON

S : Scattering amplitude in th MIE theory. of light scattering.

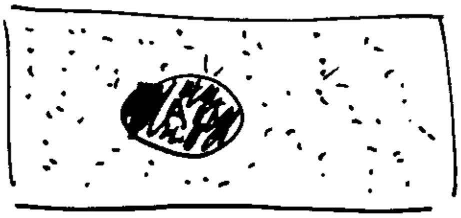
MAXWELL-GARNETT

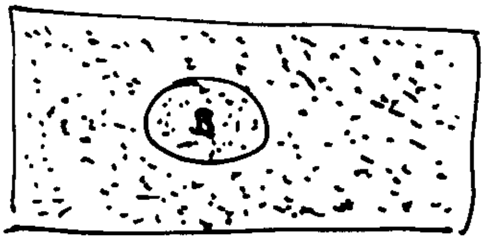


$S_{A,B}(\theta=0)=0$

Coated sphere or ellipsoid – ratio of volumes determines f_A.

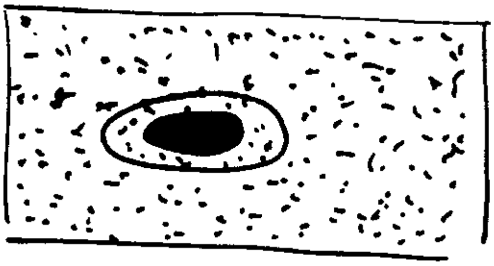
BRUGGEMAN



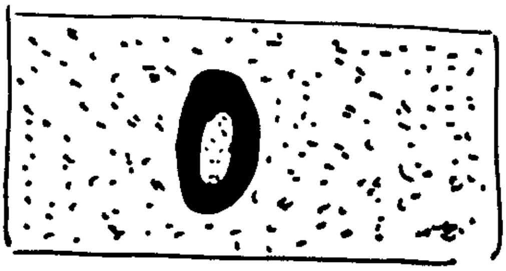


$$f\,S_A(\theta=0) + (1-f)\,S_B(\theta=0) = 0$$

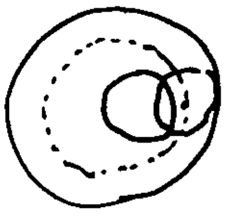
Symmetrized Maxwell. Garnett



$p_1 = \frac{u_1}{u_1+u_2}$



$p_2 = \frac{u_2}{u_1+u_2}$



$u_1 = (1-f^{1/3})^3$ $\qquad$ $u_2 = [1-(1-f)^{1/3}]^3$

$$p_1 S_A^{MG}(f) + (1-p_1) S_B^{MG}(f) = 0$$

D.C. Conductivity

$$\varepsilon_A = \varepsilon'_A + \frac{i\sigma_A}{\varepsilon_0 \omega}$$

$$\varepsilon_B = \varepsilon'_B \qquad \omega \to 0$$

$$\sigma_{MG} / \sigma_A = \frac{f(1-g)}{1-fg} \qquad \text{no threshold}$$

$$\sigma_{Br} / \sigma_A = \frac{f-g}{1-g} \qquad \text{threshold } f_c = g$$

$$= \frac{f(1-g_B) - (1-f)g_A}{(1-f)(1-g_A) + f(1-g_B)} \qquad f_c = \frac{g_A}{1-g_B+g_A}$$

$$\sigma_{MGS} / \sigma_A = F\sigma_2$$

$$\sigma_2 = \frac{f(1-g_2)}{1-fg_2} \qquad F = \frac{g_2 - p_2 + p_2(g_1-g_2)}{g_2 - 1 + p_2(g_1-g_2)}$$

Percolation threshold $p_2^c = \frac{g_2}{1+g_2-g_1}$

$$\to f_c(p_2^c)$$

cf Brouers F. J. Phy. C 19 7183 (1986)

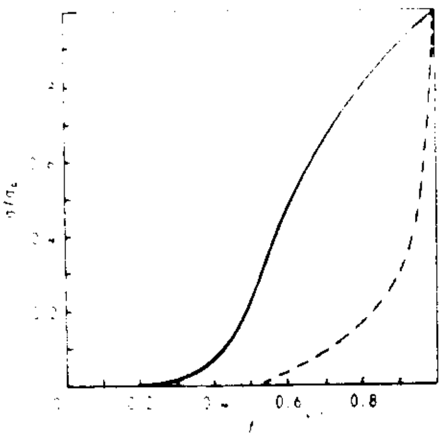


Figure 3. The normalised conductivity as a function of metal volume fraction for three sets of (g_1, g_2) values in the symmetrised Maxwell–Garnett approximation $(g_1 \geq g_2)$. Full curve, (0.333, 0.004); dotted curve, (0.333, 0.333); chain curve, (0.333, 0.945).

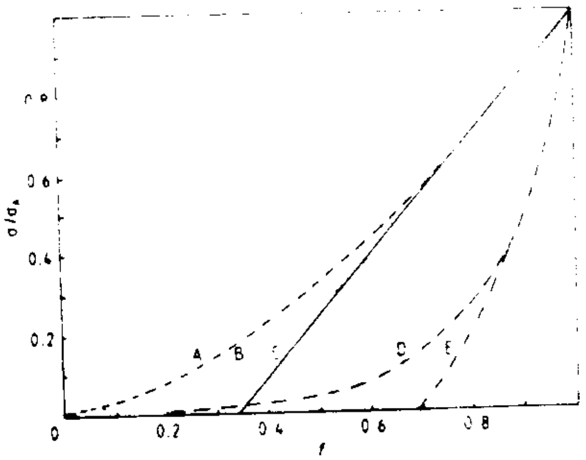


Figure 4. The orientationally averaged normalised conductivity as a function of metal volume fraction for several sets of depolarisation factors (g_A, g_B) in the Bruggeman approximation. (g_A, g_B): C, (0.333, 0.333); B, (0.004, 0.004), (0.004, 0.333), (0.333, 0.004); A, (0.945, 0.004), (0.945, 0.333); D, (0.004, 0.945); E, (0.333, 0.945).

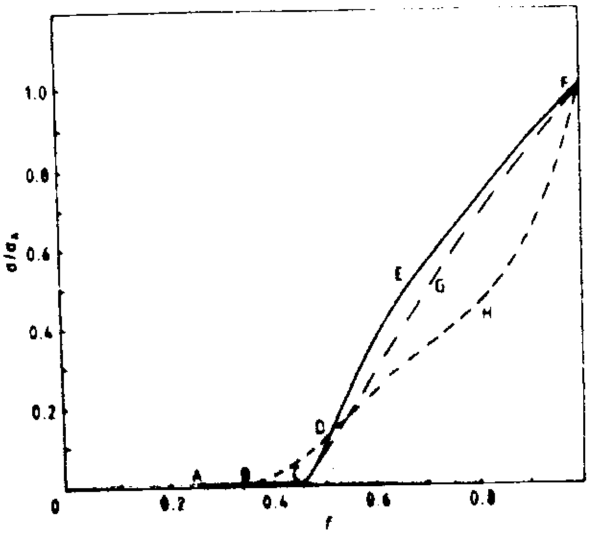


Figure 5. The orientationally averaged normalised conductivity as a function of metal volume fraction for several sets of depolarisation factors (g_1, g_2) in the symmetrised Maxwell–Garnett approximation.

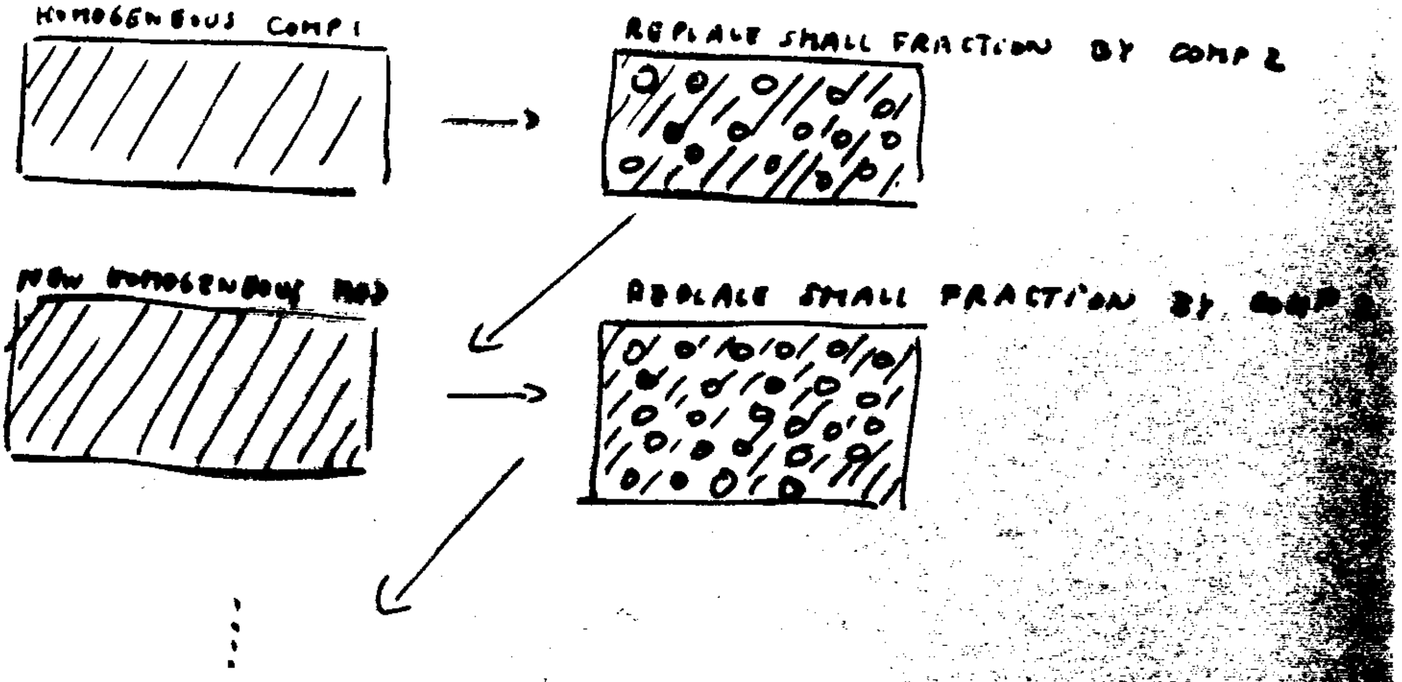
DIFFERENTIAL EFFECTIVE MEDIUM THEORY

For porous media like rocks which can be viewed as a fluid-solid composite system that is in the vicinity of a percolation threshold.

f_1 ϵ_1 is the conducting fluid.
f_2 ϵ_2 is the rock (non-conducting)

Bruggeman =>

$$(1-f_2)\frac{\epsilon-\epsilon_1}{2\epsilon+\epsilon_1} - f_2\frac{\epsilon-\epsilon_2}{2\epsilon+\epsilon_2} = 0$$



Small amount $f_2 = \Delta\varphi \longrightarrow \Delta\epsilon = \epsilon - \epsilon_1$

$$\Delta\epsilon = 3\epsilon_1\left(\frac{\epsilon_2-\epsilon_1}{\epsilon_2+2\epsilon_1}\right)\Delta\varphi$$

next -> $\epsilon_1 \to \epsilon$

$$\Delta\epsilon = 3\epsilon\left(\frac{\epsilon_2-\epsilon}{\epsilon_2+2\epsilon}\right)\Delta\varphi'$$

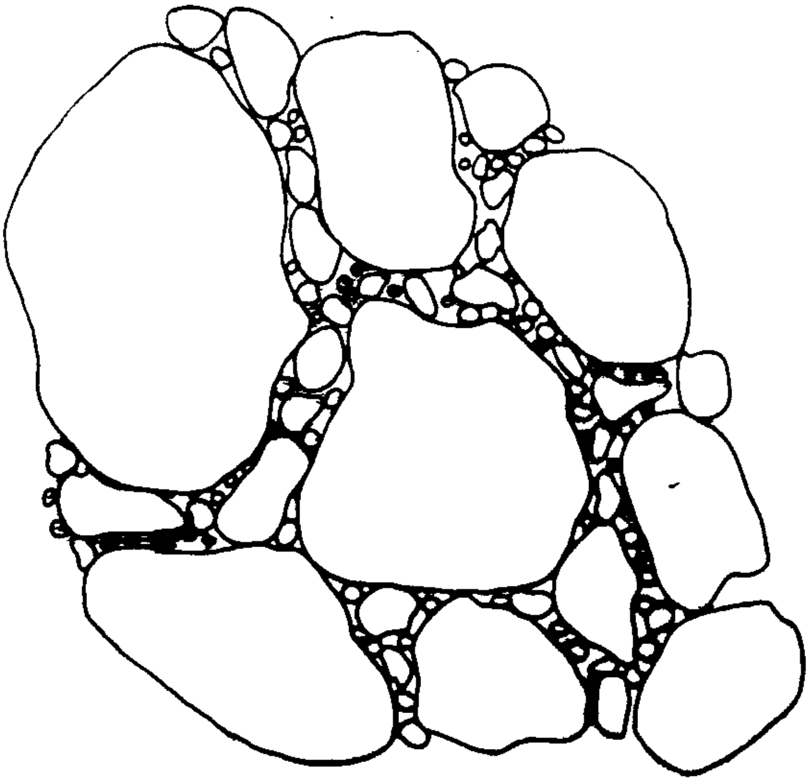


FIG. 8

[illegible] $\Delta\psi'$ is the [illegible] of composite replaced by 2

The actual amount of component 2 added in the replacement step is given by

$$\Delta\psi' = (1-\psi)\,\Delta\psi$$

one gets
$$\frac{1}{3\varepsilon}\left(\frac{\epsilon_2 + 2\epsilon}{\epsilon_2 - \epsilon}\right) d\varepsilon = \frac{d\psi}{1-\psi}$$

Direct integration yields

$$1-\psi = \left(\frac{\varepsilon/\varepsilon_1 - \varepsilon_2/\varepsilon_1}{1 - \varepsilon_2/\varepsilon_1}\right)\left(\frac{\varepsilon_1}{\varepsilon}\right)^{1/3} \leftarrow (g).$$

For d.c. conductivity of rocks $\quad \varepsilon = \varepsilon' + \frac{i\sigma}{\varepsilon_0\omega}$

In the limit $\omega \to 0 \qquad (\sigma_2 = 0,\ \sigma_1 = \sigma_f)$

$$\Rightarrow \quad \sigma = \sigma_f\, \phi^{\frac{1}{1-g}} \qquad \phi = 1-\psi$$

$$\sigma = \sigma_f\, \phi^{3/2}$$

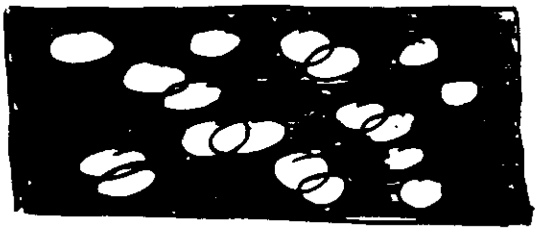
$$\frac{1}{1-g} = m$$

If one makes an average over the shape distribution

$$m \simeq 2 \qquad \text{(Archie's Law)}$$

NOTE The experimental value of $m \sim 2$ is also very close to the value given by percolation theory on a lattice [illegible]

ELASTIC DEPLETION TRANSITION.



DEPLETED CONTINUUM

"SWISS-CHEESE" ELLEPTICAL HOLES ARE CUT RANDOMLY IN AN ISOTROPIC TWO DIMENSIONAL ELASTIC CONTINUUM
MAJOR/MINOR AXES a / b

2 self consistent mean field theory

1) host and inclusions are treated symmetrically
2) " " " " " asymmetrically

Elastic Constant K bulk modulus
μ shear modulus

$\Downarrow \quad \Leftarrow$ holes

k^*, μ^* function $(1-p)$ of holes

If we make an isotropic average over all directions the invariants for 2D

$$P = \frac{1}{2} \sum_{ij} T_{iijj}$$

$$Q = \frac{1}{2} \sum_{ij} \left(T_{ijij} - \frac{1}{2} T_{iijj} \right)$$

T_{ijkl} tensor relating homogeneous strains outside of the inclusions to those inside

P and Q depend on shape and model of both inclusion and hole.

Ex Circles and Needles $K (k_1)$ $\mu (\mu_1)$ host (inclusion)

	P	Q
Circle	$\frac{k+\mu}{k_1+\mu}$	$\frac{2(k+\mu)\mu}{k\mu + (k+2\mu)\mu_1}$
Needle	$\frac{k+\mu_1}{k_1+\mu_1}$	$\frac{1}{2}\left[\frac{k_1+\mu}{k_1+\mu_1} + \frac{\mu}{\mu_1}\right]$

Symmetric approx.

$$\sum_i c_i P_{eff}^{(i)} (k_{eff} - k_i) = 0$$

$$\sum_i c_i Q_{eff}^{(i)} (\mu_{eff} - \mu_i) = 0$$

hole $k_i = \mu_i = 0$

$$\frac{k_{eff}}{k_1} = \frac{1-\alpha/p}{1-\alpha} \quad ; \quad \frac{\mu_{eff}}{\mu} = \frac{1-\beta/p}{1-\alpha}$$

$$\alpha = \left[\frac{1-P_{eff}^{(1)}}{P_{eff}^{(2)}}\right]^{-1} ; \quad \beta = \left[\frac{1-Q_{eff}^{(1)}}{1-Q_{eff}^{(2)}}\right]^{-1}$$

=> Percolation threshold

$$p^* = 2\left\{1 + \left[2(a+b)^2/\sqrt{a^2+b^2}\right\}^{-1}\right.$$

Asymmetric approx:
$$p^* = \left[1 + \frac{ab}{a^2+b^2}\right]^{-1}$$

both approaches $\Rightarrow$ $\boxed{p^* + \sigma^* = 1}$

$$\sigma^* = \frac{k^* - \mu^*}{k^* + \mu^*}$$ Poisson ratio at percolation

Both k^* and $\mu^* \to 0$ but the ratio is finite.

$$\sigma^* = \frac{k^*/\mu^* - 1}{k^*/\mu^* + 1}$$

Conclusion p^* and k^*/μ^* depend on geometries but not on the initial values.

Ratio of the longitudinal to transverse sound velocities is

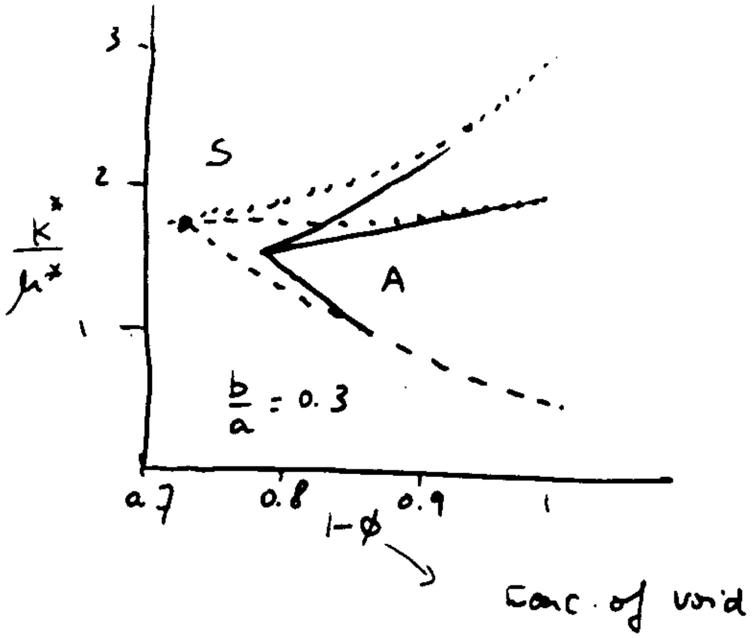
$$\frac{V_L^2}{V_T^2} = 1 + \frac{k}{\mu}$$

at the transition point

$$\left[\frac{V_L^2}{V_T^2}\right]^* = 1 + \frac{k^*}{\mu^*} = \frac{2}{p^*}$$

of course $$\frac{k^*}{\mu^*} = \left[\frac{2(a+b)^2}{a^2+b^2}\right]^{1/2}$$

$$\frac{k^*}{\mu^*} = \frac{(a+b)^2}{a^2+b^2}$$



Young's Modulus

$$E^* = E(1-3\phi)$$

$$(\sigma^* - 1/3) = (\sigma - 1/3)(1-3\phi)$$

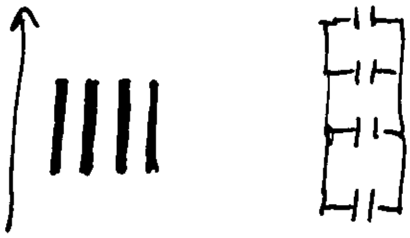
$$\bar{z}^* = \Sigma(1-2\phi)$$

Bounds

Limits should be applied to estimate the intrinsic uncertainities in the model parameter that result from our inability to specify the actual microstructure exactly.

Wiener bounds (Absolute bounds if $a \ll \lambda$ $(< 0.1\lambda)$)

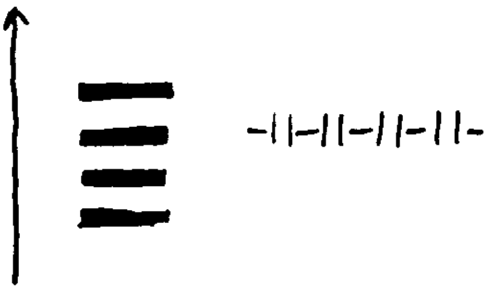
laminar
E uniform



$$\varepsilon = f\varepsilon_A + (1-f)\varepsilon_B \qquad (1)$$

no screening of the field

D uniform



$$\frac{1}{\varepsilon} = f\frac{1}{\varepsilon_A} + (1-f)\frac{1}{\varepsilon_B} \qquad (2)$$

maximum screening

They are absolute bounds because no matter what the microstructure there can never be less screening than no screening, nor more screening than maximum screening.

The Wiener bounds hold for the case of complex ε irrespective of structure. Only ε_A and ε_B need to be known. As f_A and $1-f_A$ are varied Eq (1) traces out a straight line between ε_A and ε_B. While Eq (2) becomes a circular arc joining ε_A and ε_B.

Wiener bounds are absolute limit to ε for a composite material even if nothing is known about the volume fraction or microstructure of the composite.

Hashin - Shtrikman

The Maxwell-Garnett expressions (host A and host B) provide absolute limits to ε for a two phase composite if the macroscopic composition $f_A = 1 - f_B$ is known.

Bergman - Milton bounds

Analytic representation of the composite dielectric constant allows to derive additional limits

All the bounds can be expressed most simply in the following way

The composite dielectric constant is written as

$$\varepsilon = \frac{\varepsilon_A \varepsilon_B + \bar{\varepsilon}\left(f_A \varepsilon_A + f_B \varepsilon_B\right)}{\bar{\varepsilon} + \left(f_A \varepsilon_B + f_B \varepsilon_B\right)}$$

where

$$\bar{\varepsilon} = \frac{(1-g)\,\varepsilon_H}{g}$$

g is the screening parameter of range 0-1

ε_H is the host dielectric function.

Wiener bounds

are given by $g = 0$ and $g = 1$ for $0 \leq f_A \leq 1$

Haskin - Shrikman

are given by the Maxwell-Garnett lines for $0 \leq g \leq 1$ $\quad \varepsilon_H = \varepsilon_A$, $\varepsilon_H = \varepsilon_B$

Bergman - Milton bounds

For a known composition f and screening value
($g = 1/2$ for 2D or $g = 1/3$ for 3D)

are given by imposing the Wiener bounds on ε_H

i.e. $\varepsilon_H = x\,\varepsilon_A + (1-x)\,\varepsilon_B$

and $\varepsilon_H^{-1} = x\,\frac{1}{\varepsilon_A} + (1-x)\,\frac{1}{\varepsilon_B}$

where x is a structural parameter

$0 < x < 1$ and is related to the pair and three-point correlation function of the material.

MORE PRECISE BOUNDS

for a value of x, one writes the Bergman-Milton bounds for $0 < g < 1$.

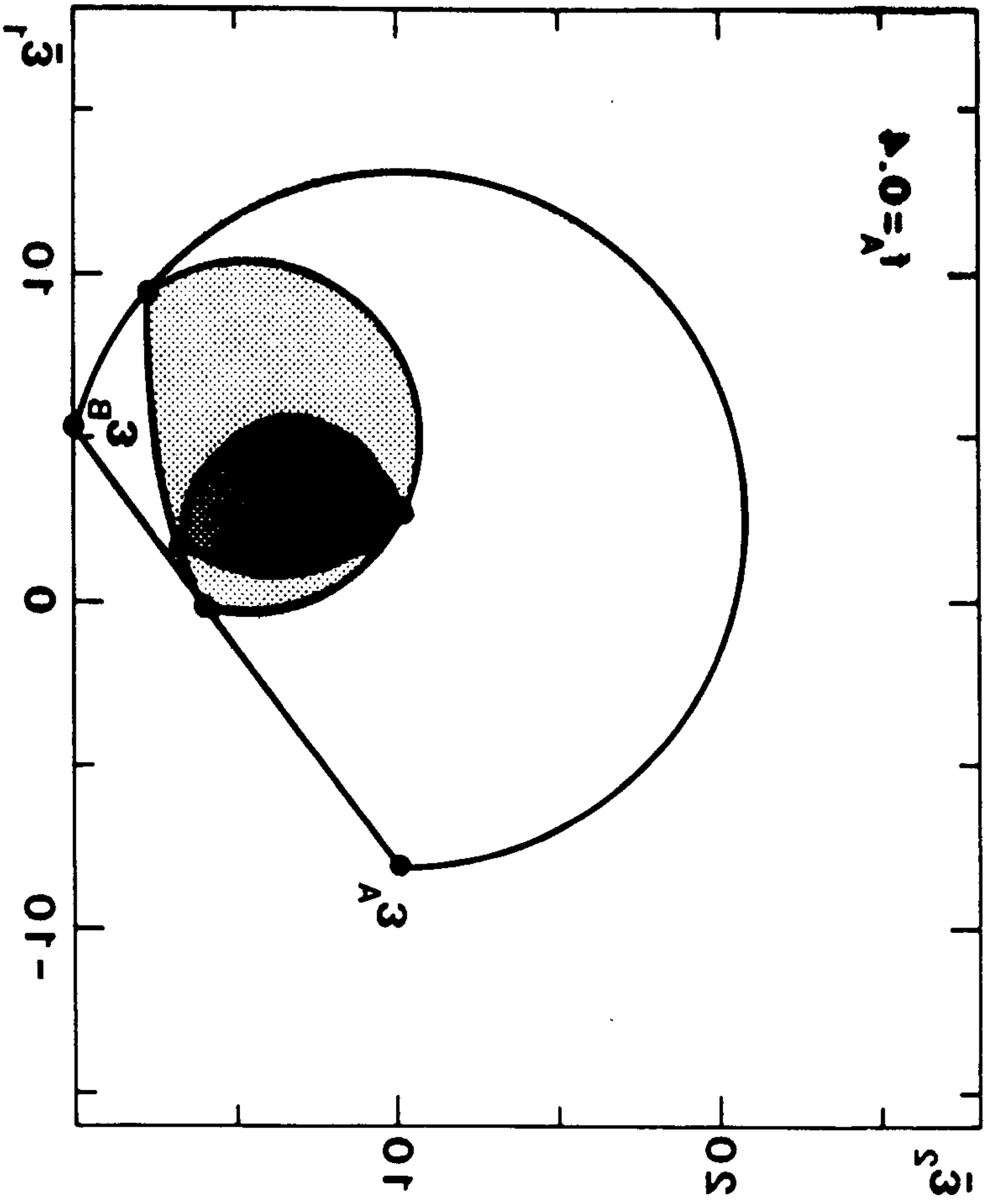
Remarks and Conclusions.

- If ε_A and ε_B are similar ε^* is determined by composition and independent of [illegible]

· If ε_A and ε_B are substantially ≠ ε^* is mostly determined by microstructure.

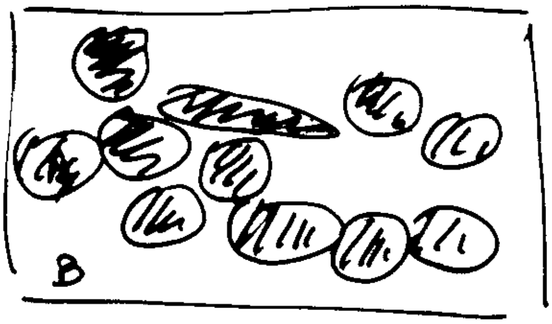
$\varepsilon_A/\varepsilon_B$ change with $\lambda \rightarrow$ two aspects.

BY INCORPORATING MORE STRUCTURAL INFORMATION, i.e. higher order correlation functions into the theory, a whole hierarchy of narrower bounds can be obtained.


$\bar{\omega}_l$
$\bar{\omega}_s$
ω_A
ω_B
$t_A=0.4$
-10
0
10
10
20

RELATION BETWEEN MICROSTRUCTURE AND PHYSICAL PROPERTIES OF INHOMOGENEOUS MATERIALS

—



$A_p B_{1-p}$

granular or aggregate ?

Short range order ? clustering ?

distribution of grain shape

distribution of size shape

distribution of intergrain distances

open, close porosity

roughness or smoothness of grains

If we know A and B How to determine $A_x B_{1-x}$

$$P^*(s) = F(s)$$

F depends on the microstructure

S depends on P_A/P_B

$s = S(P_A/P_B)$?

$F(s)$??

F scale dependent

USE OF THE BERGMAN-MILTON ANALYTIC REPRESENTATION OF A TWO COMPONENT COMPOSITE TO GET INFORMATION ON THE MICROSTRUCTURE OF THE COMPOSITE MATERIAL

THE TWO COMPONENTS ARE DESCRIBED BY

$$\epsilon_1(\omega) \quad \text{and} \quad \epsilon_2(\omega)$$

IT IS CONVENIENT TO INTRODUCE THE COMPLEX VARIABLE

$$s = \frac{\epsilon_1(\omega)}{\epsilon_1(\omega) - \epsilon_2(\omega)} = \left(1 - \frac{\epsilon_1(\omega)}{\epsilon_2(\omega)}\right)^{-1}$$

homogeneity requirement $\Rightarrow$

$\frac{\epsilon^*}{\epsilon_1}$ depends on $\frac{\epsilon_2}{\epsilon_1}$ and not on ϵ_1 and ϵ_2 individually

$$f = 1 - \frac{\epsilon^*}{\epsilon_1} = f\left(\frac{\epsilon_2}{\epsilon_1}\right) \quad \text{or} \quad f(s)$$

$$\frac{\epsilon^*}{\epsilon_1} = 1 - f(s) = Z(s)$$

SPECTRAL REPRESENTATION

$\Downarrow$

$$f(s) = \sum_n \frac{B_n}{s - s_n} \qquad s_n \geq 0$$

$$f(s) = \frac{A}{s} + \int_0^1 \frac{g(n)}{s-n}\, dn = \frac{A}{s} + G(s)$$

$$\varepsilon^* = \varepsilon_1 \left[1 - \frac{A}{s} - G(s) \right]$$

$$G(s) = \int_0^1 \frac{g(n)}{s-n}\, dn$$

$g(n)$ IS THE SPECTRAL DENSITY WHICH IS DETERMINED BY THE STATISTICAL GEOMETRY DOES NOT DEPEND ON THE MATERIAL PROPERTIES $\varepsilon_1(\omega)$ AND $\varepsilon_2(\omega)$ NOR ON THE FREQUENCY.

IF WE KNOW $g(n)$

WE CAN WRITE

$$\sigma^* = \sigma_1 \left[1 - \frac{A}{S} - G(s) \right] \quad \text{with} \quad S = \frac{\sigma_1}{\sigma_1 - \sigma_2}$$

FOR CONDUCTIVITY.

$$\lambda^* = \lambda_1 \left[1 - \frac{A}{s} - G(s) \right] \quad \text{with} \quad s_\lambda = \frac{\lambda_1}{\lambda_1 - \lambda_2}$$

FOR HEAT CONDUCTIVITY

.....

SOME PROPERTIES OF THE SPECTRAL DENSITY $g(n)$ FOLLOWS FROM PERTURBATION THEORY.

THE WEAK COUPLING EXPANSION OF ε^* IN POWERS OF $\varepsilon_1 - \varepsilon_2$ CORRESPONDS TO THE EXPANSION OF $f(s)$ IN INVERSE POWERS OF s.

WE FIND $$G(s) = \sum_{j=1}^{\infty} g_j s^{-j}$$

WITH $$g_j = \int_0^1 n^{j-1} g(n) dn$$

IF s IS LARGE $\varepsilon_1 \simeq \varepsilon_2$ ONE KNOWS THE SOLUTION

$$G(s) = \frac{x}{s} + \frac{x(1-x)}{3s^2} + O(1/s^3)$$

$$\int_0^1 g(n)\,dn = x \qquad \int_0^1 n\,g(n)\,dn = \frac{1}{3}x(1-x)$$

The COEFFICIENTS $$C_1 = x$$

$$C_2 = \frac{x(1-x)}{3}$$

ARE <u>CORRELATION FUNCTIONS</u>

THE SPECTRAL DENSITY $g(n)$ IS COMPLETELY DETERMINED BY THE STATISTICAL GEOMETRY. $g(n)$ DOES NOT DEPEND ON THE MATERIAL PROPERTIES ε_1, ε_2 NOR ON THE FREQUENCY ω

VARIOUS MODELS AND APPROXIMATIONS

MAXWELL-GARNETT

BRUGGEMAN

MAXWEL- GARNET (GENERALISED) ≡ PING SHENG

$$g(n) = -\frac{1}{\pi} \lim_{s \to 0} \mathrm{Im} \left[1 - \frac{\epsilon^*}{\epsilon} \right]$$

LOW CONCENTRATION APPROXIMATION

$$g(n) = x \, \delta(n - \tfrac{1}{3})$$

CLAUSIUS MOSOTTI ≡ MAXWELL GARNETT

$$g(n) = x \, \delta(n - s_0) \qquad s_0 = \frac{1}{3}(1-x)$$

BRUGGEMAN

$$g^{EMT}_{(n)} = \frac{1}{4\pi x n} \left[-9n^2 + 6(1+x)n - (3x-1)^2 \right]^{1/2}$$

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Percolation threshold and conductivity in metal–insulator composite mean-field theories

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Abstract. Using a proper space average, we have calculated systematically the DC conductivity and percolation threshold of cermet thin films and a granular composite in various mean-field theories. The results emphasise the decisive role of the composite microgeometry which has to be considered together with other effects neglected in effective medium theories. They should help in the interpretation of the growing number of experimental data on cermets, composite and porous materials.

1. Introduction

The relationship between the microstructure and the optical and transport properties is one of the most important and interesting aspects of the physics of composite materials.

Cermet thin films used to fabricate selective surfaces for solar photothermal energy conversion are made of a mixture of metal (for instance Cr, Au, Pt, Co, ...) and insulator (Cr_2O_3, Al_2O_3, SiO_2 ...).

When the metal concentration or metal volume fraction f is small, the system is made of metallic grain inclusions in an insulating matrix. By contrast when f tends to one, the system appears as a mixture of insulating inclusions in a metallic matrix.

For a critical value of f, called the *percolation threshold* f_c, the system undergoes an insulator–metal transition. In the vicinity of f_c, the dielectric constant and therefore the optical properties exhibit dramatic changes and as a consequence it is possible to prepare films whose reflectivity can vary from zero to one in a narrow range of frequencies. The condition for an efficient selective surface is that this transition occurs for frequencies lying between the solar spectrum and the infrared black-body radiation spectrum of the collector.

The grain formation in these films is the result of several processes, essentially surface diffusion and coalescence and as a consequence the final microgeometry depends on the nature of the cermet constituents and of the film preparation.

One interesting aspect of these systems is the dependence of f_c and therefore of the conductivity on the microgeometry and in particular the shape and distribution of grains. This is an important property in its own right since it determines the concentration of inclusions for which dramatic changes in the electrical and optical properties occur. The study of the insulator–metal transition and its related critical exponents can give important clues to the microstructure.

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In Co–SiO$_2$ for instance, f_c is about 0.55 while it is about 0.25 for Co–Al$_2$O$_3$. This difference has to be related to the different microgeometry of the two materials (Niklasson and Granqvist 1984, Barzilai *et al* 1981).

It is therefore of interest to have an overall picture of the dependence of these properties on the nature and shape of inclusions.

Another interesting related problem is the relation between the electrical resistivity of a rock and its pore fluid content. An empirical equation that relates conductivity and porosity was first proposed by Archie (1942) and has become known as Archie's law:

$$\sigma_R = a\sigma_w \varphi^m$$

where σ_w is the water conductivity and a and m are empirical parameters that vary with the rock microgeometry. The exponent m appears to be non-universal and can vary from 1.5 to 4. a is generally assumed to be of the order of one.

The main difficulty with percolation in that system is that the usual percolation models require a finite critical threshold. There is currently a discussion (Balberg 1986) about the existence of a strictly zero or a very small partial porosity.

In some simple porous rock models, it can be shown that in the case of a large aspect ratio, one can obtain φ_c values which can be made as small as desired. Balberg (1986) has also argued that ordinary percolation theory can account for the zero pore space threshold as well as for the power-law behaviour derived from available experimental data. In all these problems, effective medium theories are natural reference points with which percolation theory results can be compared.

It is therefore of interest to have an overall picture of the variation of DC conductivity and percolation threshold with the aspect ratio of particles in the various mean-field theories proposed so far.

In §§ 2 and 3, we recall the two basic Maxwell–Garnett (Garnett 1904, 1906) and Bruggeman (1935) theories as well as the expression for the DC conductivity and the percolation threshold of an ellipsoidal inclusion. In § 4 the same quantities are expressed in the symmetrised Maxwell–Garnett approximation.

In § 5 we introduce an average of randomly oriented spheroids valid for any concentration and calculate the variation of percolation threshold and DC conductivity with the aspect ratio and depolarisation factor. These results are commented on in the conclusion. An Appendix deals with a proof of the equivalence of two different symmetrised Maxwell–Garnett approximations.

2. Aggregate and separate grain structure

As discussed in a number of recent papers (Niklasson and Granqvist (1984) and references therein), granular composite films generally can be described by one of the two distinct microstructures: an *aggregate structure* where the metal and insulator grains are inter-dispersed and topologically equivalent and a *separated grain structure* where the metal and insulator exhibit an asymmetric topology consisting of either metallic inclusions in an insulating matrix or insulating inclusions in a conducting matrix.

3. Bruggeman and Maxwell–Garnett approximations

This dichotomy finds its counterpart in the two main theoretical approaches which have been used to interpret the optical and transport properties of these materials.

The traditional ideas of the effective medium approximation have been introduced in this problem, namely a random unit is subjected to an, as yet unknown, effective medium which is determined to be such that the resulting extra perturbation vanishes on the average over all possibilities of the random unit. If this perturbation is taken to be the Lorenz–Mie scattering amplitude in the direction of the impinging light beam $S(\theta=0)$. Niklasson and Granqvist (1984) have shown that one can obtain elegantly the various mean-field approximations. The condition

$$\langle S(\theta=0)\rangle = 0 \tag{1}$$

first introduced by Stroud and Pan (1978) is a generalisation of the optical theorem to non-homogeneous systems.

If the random unit is a sphere of component A (concentration f, dielectric constant $\varepsilon_A(\omega)$ or component B (concentration $1-f$, dielectric constant $\varepsilon_B(\omega)$) embedded in an effective medium (dielectric constant $\varepsilon^*(\omega)$) (see figure 1), the condition (1) reads in this case:

$$fS_A(\theta=0) + (1-f)S_B(\theta=0) = 0. \tag{2}$$

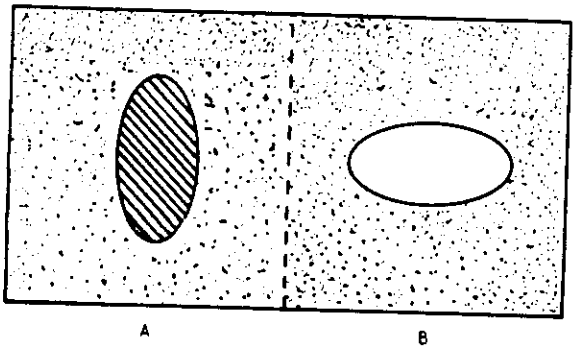

Figure 1. Random units A and B in the effective medium (Bruggeman approximation).

Using the dipolar approximation of $S(\theta)$ for a sphere (Van de Hulst 1981) (1) leads to a relation which allows the calculation of the effective medium $\varepsilon^*(\omega)$:

$$f\frac{\varepsilon_A-\varepsilon^*_{BA}}{\varepsilon_A+2\varepsilon^*_{BA}} + (1-f)\frac{\varepsilon_B-\varepsilon^*_{BA}}{\varepsilon_B+2\varepsilon^*_{BA}} = 0. \tag{3}$$

This is the approximation known as the *Bruggeman approximation* (BA) (Bruggeman 1935). The BA is analogous to the CPA theory of random alloys and applies to the *aggregate structure*.

If the random unit is a coated sphere, for instance an internal sphere A of radius r_A surrounded by an external sphere B of radius r_B with a volume fraction $f=(r_A/r_B)^3$, using the dipolar approximation of $S(\theta=0)$ for a coated sphere having this compositional geometry, the condition $S^{CS}_{AB}(0)=0$ yields the expression

$$\varepsilon^*_{MG} = \varepsilon_B\frac{\varepsilon_A+2\varepsilon_B+2f(\varepsilon_A-\varepsilon_B)}{\varepsilon_A+2\varepsilon_B-f(\varepsilon_A-\varepsilon_B)} \tag{4}$$

which is the *Maxwell–Garnett approximation* (MG) (Garnett 1904, 1906) for an A inclusion in a B host. If instead one considers a B inclusion in a A host, by making the replacement A ⇄ B and $f \to 1-f$, one gets an analogous relation for the inverted structure. One can calculate the DC conductivity in these two approximations by using the relation between dielectric constant and conductivity in the limit $\omega \to 0$. This is equivalent to replacing ε_A by i and ε_B by 0. In that case the effective ε^* is the ratio of the composite conductivity to the pure A conductivity. For the BA, one gets:

$$\sigma_\mathrm{BA}/\sigma_\mathrm{A} = (3f-1)/2. \tag{5}$$

The percolation threshold is $f_\mathrm{c} = 1/3$.

In the MG, for an A (metallic) inclusion in B (insulator), the system is always an insulator and $f_\mathrm{c} = 1$. For a B inclusion in A, in contrast

$$\sigma_\mathrm{MG}/\sigma_\mathrm{A} = 2f/(3-f) \tag{6}$$

and the relative conductivity varies from 0 to 1 without percolation threshold ($f_\mathrm{c} = 0$).

Since the shape of inclusions in cermets are far from being spherical, the theory can be extended to ellipsoidal inclusions. If g is the depolarisation factor in the direction of the field, equations (3)–(6) become respectively:

$$f\frac{\varepsilon_\mathrm{A}-\varepsilon^*_\mathrm{BA}}{\varepsilon^*_\mathrm{BA}+g(\varepsilon_\mathrm{A}-\varepsilon^*_\mathrm{BA})}+(1-f)\frac{\varepsilon_\mathrm{B}-\varepsilon^*_\mathrm{BA}}{\varepsilon^*_\mathrm{BA}+g(\varepsilon_\mathrm{B}-\varepsilon^*_\mathrm{BA})}=0 \tag{3'}$$

$$\varepsilon^*_\mathrm{MG}=\varepsilon_\mathrm{B}\frac{g\varepsilon_\mathrm{A}+(1-g)\varepsilon_\mathrm{B}+f(1-g)(\varepsilon_\mathrm{A}-\varepsilon_\mathrm{B})}{g\varepsilon_\mathrm{A}+(1-g)\varepsilon_\mathrm{B}-fg(\varepsilon_\mathrm{A}-\varepsilon_\mathrm{B})} \tag{4'}$$

$$\sigma_\mathrm{BA}/\sigma_\mathrm{A}=(f-g)/(1-g) \qquad (f_\mathrm{c}=g) \tag{5'}$$

$$\sigma_\mathrm{MG}/\sigma_\mathrm{A}=f(1-g)/(1-fg) \qquad (f_\mathrm{c}=0). \tag{6'}$$

In the BA the two depolarisation factors are not necessarily the same. In that case (3′) becomes

$$f\frac{\varepsilon_\mathrm{A}-\varepsilon^*_\mathrm{BA}}{\varepsilon^*_\mathrm{BA}+g_\mathrm{A}(\varepsilon_\mathrm{A}-\varepsilon^*_\mathrm{BA})}+(1-f)\frac{\varepsilon_\mathrm{B}-\varepsilon^*_\mathrm{BA}}{\varepsilon^*_\mathrm{BA}+g_\mathrm{B}(\varepsilon_\mathrm{B}-\varepsilon^*_\mathrm{BA})}=0 \tag{3''}$$

and

$$\frac{\sigma_\mathrm{BA}}{A}=\frac{f(1-g_\mathrm{B})-(1-f)g_\mathrm{A}}{(1-f)(1-g_\mathrm{A})+f(1-g_\mathrm{B})} \qquad \left(f_\mathrm{c}=\frac{g_\mathrm{A}}{1-g_\mathrm{B}+g_\mathrm{A}}\right). \tag{5''}$$

The percolation threshold volume fraction depends on the shape of the random units. This is illustrated for spheroids by considering the two following limiting cases. If $g_{\mathrm{A(B)}}$ is the depolarisation factor of random unit A (B) in the direction of the minor (major) axis of the oblate (problate) spheroidal unit

For $g_\mathrm{A} \to 0$ (problate spheroids) $\qquad f_\mathrm{c} \to 0$ for any g_B

For $g_\mathrm{B} \to 1$ (oblate spheroids) $\qquad f_\mathrm{c} \to 1$ for any g_A.

4. Symmetrised Maxwell–Garnett approximation

For small concentrations of inclusions (f close to 1 or to 0), it appears that a number of composite films are better described by the separated grain structure. Since the MG approximation is unable to describe the metal–insulator transition, symmetrised MG approximations have been proposed by introducing an average over the two following random units: an inclusion of A coated by a shell of B and an inclusion of B coated by a shell of A. Using this picture the film can be modelled as a mixture of two types of coated ellipsoids. Dielectric-coated metal ellipsoids are denoted as type 1 units and metal-coated insulator ellipsoids are denoted as type 2 units (see figure 2). The problem is to

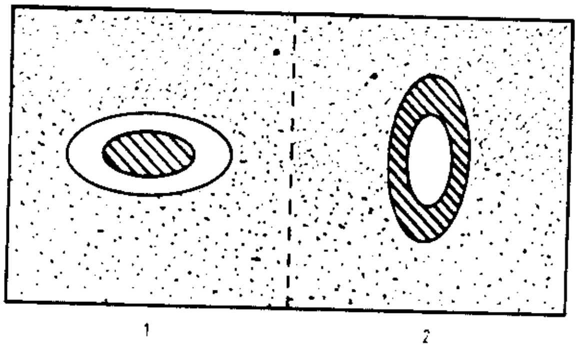

Figure 2. Random units 1 and 2 in the effective medium (symmetrised Maxwell–Garnett approximation).

evaluate the proportion of these two random units for a given value of the filling factor. Sheng (1980) has introduced a probabilistic growth model where the probability of occurrence of these two units as a function of f is given by the number of possible configurations of each type of units. This number is given by the volume available to the internal ellipsoid in the external ellipsoid. In the case of coated confocal spheroidal units, these probabilities are (Sheng 1980)

$$p_1 = u_1/(u_1 + u_2) \quad \text{and} \quad p_2 = u_2/(u_1 + u_2) \tag{7}$$

$$u_1 = (1 - f^{1/3})^3 \quad \text{and} \quad u_2 = [1 - (1 - f)^{1/3}]^3.$$

For spherical inclusions ($g = 1/3$), two schemes have been used to apply the Sheng approximation. Niklasson and Granqvist (1984) have used the condition (1) i.e.

$$p_1 S_1(\theta = 0) + p_2 S_2(\theta = 0) = 0 \tag{8}$$

where $S_1(\theta = 0)$ and $S_2(\theta = 0)$ are the scattering amplitudes for types 1 and type 2 respectively. Gibson and Buhrman (1983) have calculated the dielectric constant of type 1 and type 2 units in the MG ε_1^* and ε_2^* and then introduced these two values in the Bruggeman formula (3) with $\varepsilon_A = \varepsilon_1^*$ and $\varepsilon_B = \varepsilon_2^*$ and $f = p_1$. It can be shown that these approximations yield the same second-order equation for ε^* (see Appendix) and are therefore identical.

In the case of coated confocal spheroidal units when the depolarisation factors in the direction of the field are respectively g_1 and g_2, the same method can be used and again it can be shown that the two schemes give the same results. In particular, the conductivity of the composite material can be written:

$$\sigma^*/\sigma_A = F\sigma_2 \tag{9}$$

Formulae for the relation between depolarisation factors and axial ratios for spheroids are found in Landau and Lifshitz (1960).

5. Average for randomly oriented spheroids

Any application of this formalism to cermets requires some average of the randomly oriented spheroids. If this is done over the three spheroid axes the Buggeman self-consistent equation (1) reads:

$$f\{\tfrac{1}{3}S_{Ax} + \tfrac{2}{3}S_{Ay}\} + (1-f)\{\tfrac{1}{3}S_{Bx} + \tfrac{2}{3}S_{By}\} = 0 \tag{13}$$

where

$$S_{Ai}(i = x, y) = \frac{\varepsilon_A - \varepsilon^*}{\varepsilon^* + g_{Ai}(\varepsilon_A - \varepsilon^*)}. \tag{14}$$

g_{Ax} is the depolarisation factor of random unith A in the direction of the minor (major) axis of the oblate (prolate) spheroid unit and

$$g_{Ay} = \tfrac{1}{2}(1 - g_{Ax}) \qquad S_{Bi} = S_{Ai}(A \rightleftarrows B, f \rightleftarrows 1-f).$$

In a similar manner the self-consistent equation (8) for confocally coated spheroids can be written:

$$p_1\{\tfrac{1}{3}S_{1x} + \tfrac{2}{3}S_{1y}\} + p_2\{\tfrac{1}{3}S_{2x} + \tfrac{2}{3}S_{2y}\} = 0 \tag{15}$$

where

$$S_{1i}(i = x, y) = \frac{[g_{1i}(f-1)(\varepsilon_A - \varepsilon_B) - \varepsilon_B](\varepsilon_B - \varepsilon^*) - f\varepsilon_B(\varepsilon_A - \varepsilon_B)}{[g_{1i}(f-1)(\varepsilon_A - \varepsilon_B) - \varepsilon_B][\varepsilon^* + g_{1i}(\varepsilon_B - \varepsilon^*)] - g_{1i}f\varepsilon_B(\varepsilon_A - \varepsilon_B)}. \tag{16}$$

g_{1x} is the depolarisation factor of random unit 1 in the direction of the minor (major) axis of the oblate (prolate) spheroid random unit and

$$g_{1y} = \tfrac{1}{2}(1 - g_{1x}) \qquad S_{2i} = S_{1i}(A \rightleftarrows B, 1 \rightleftarrows 2, f \rightleftarrows 1-f).$$

In contrast to previous average treatment (Granqvist and Hunderi 1977) this procedure is valid for any volume fraction f. If we replace ε_A by i and $\varepsilon_B = 0$, the composite conductivity of the averaged Bruggeman and averaged symmetrised Maxwell–Garnett approximation can be calculated for any set of values (g_A, g_B) or (g_1, g_2) as a function of f and the percolation threshold f_c may be determined. The results of the calculations are shown in figures 4 and 5 and in tables 1 and 2. Figure 4 exhibits the averaged Bruggeman results. Figure 5 exhibits the averaged symmetrised Maxwell–Garnett approximation. The curve for the couple of values $(g_1 = 0.33,\ g_2 = 0.945)$ and $(g_1 = 0.333,\ g_2 = 3.7 \times 10^{-3})$ correspond to the case considered by Sheng (1980). One can verify that the results based on (15) and (16) are very close to the ones derived from the slightly more complicated expressions of that paper.

The comparison of the two figures emphasises the qualitative difference between the two fundamental composite systems mean-field approximations as far as the dependence of conductivity and metal–insulator transition on microgeometry is concerned. This has to be present in mind when interpreting cermet optical and conductivity data.

From the examination and the comparison of figures 4 and 5 a few conclusions may be drawn:

where σ_2 is the MG conductivity for the conductive coated spheroid 2:

$$\sigma_2 = f(1 - g_2)/(1 - fg_2) \tag{10}$$

and F is a statistical factor depending on p_2 and the two gs:

$$F = \frac{g_2 - p_2 + p_2(g_1 - g_2)}{g_2 - 1 + p_2(g_1 - g_2)}. \tag{11}$$

The percolation threshold f_c is given by:

$$f_c = f(p_2^c) \qquad \text{(obtained from (7))}$$

and

$$p_2^c = g_2/(1 + g_2 - g_1). \tag{12}$$

The shape of the function σ^*/σ_A and the values of the percolation threshold depend decisively on the values of g_1 and g_2 and therefore on the shape of the inclusions. This is illustrated by considering the two extreme limiting cases:

$$g_1 \rightarrow 1 \text{ (oblate spheroids)} \qquad \text{where } p_2^c = f_c = 1 \text{ for any } g_2$$

and

$$g_2 \rightarrow 0 \text{ (prolate spheroids)} \qquad \text{where } p_2^c = f_c = 0 \text{ for any } g_1.$$

The variation of the composite conductivity (9) expressed as a fraction of the metallic component bulk conductivity is plotted in figure 3.

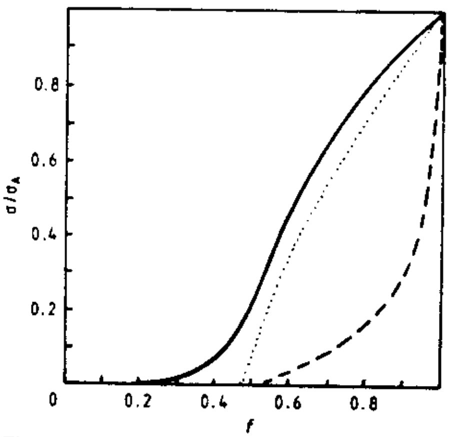

Figure 3. The normalised conductivity as a function of metal volume fraction for three sets of (g_1, g_2) values in the symmetrised Maxwell–Garnett approximation. (g_1, g_2): Full curve, (0.333, 0.004); dotted curve, (0.333, 0.333); chain curve, (0.333, 0.945).

To make the comparison with the work of Sheng (1980) easier we have chosen the following values: for the random unit 1, $g_1 = 0.333$ (spherical random unit); $g_2 = 0.945$ and $g_2 = 3.7 \times 10^{-3}$, values of the depolarisation factor corresponding respectively to an oblate (prolate) spheroid random unit whose minor (major) and major (minor) axes of the elliptic cross section are 0.035 and $(0.035)^{-1}$.

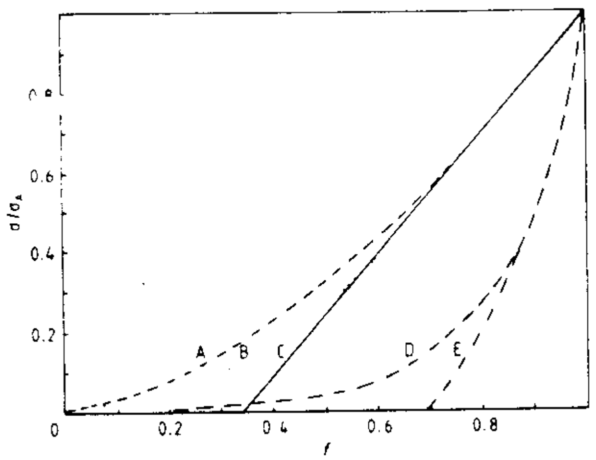

Figure 4. The orientationally averaged normalised conductivity as a function of metal volume fraction for several sets of depolarisation factors (g_A, g_B) in the Bruggeman approximation. (g_A, g_B): C, (0.333, 0.333); B, (0.004, 0.004), (0.004, 0.333), (0.333, 0.004); A, (0.945, 0.004), (0.945, 0.333); D, (0.004, 0.945); E, (0.333, 0.945).

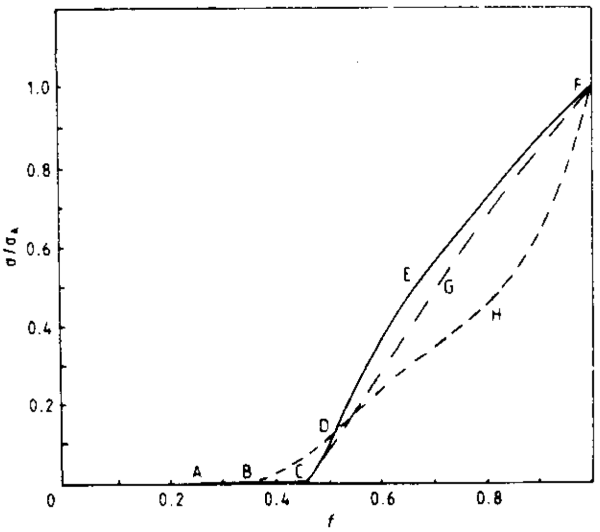

Figure 5. The orientationally averaged normalised conductivity as a function of metal volume fraction for several sets of depolarisation factors (g_1, g_2) in the symmetrised Maxwell–Garnett approximation.

g_1	g_2	
0.004	0.004	ABDEF
0.004	0.333	CDEF
0.004	0.945	BDHF
0.333	0.004	ABDEF
0.333	0.333	CDEF
0.333	0.945	BDHF
0.945	0.004	CGF
0.945	0.945	CHF

Table 1. The percolation threshold volume fraction in the orientationally averaged Bruggeman approximation. (The figures in brackets are the volume fractions corresponding to a normalised conductivity equal to 0.01.)

g_A \ g_B	4.3×10^{-4}	3.7×10^{-3}	0.05	0.333	0.700	0.945	0.984
4.3×10^{-4}	0.002 (0.048)	0.002 (0.048)	0.002 (0.046)	0.002 (0.043)	0.002 (0.054)	0.008 (0.169)	0.026 (0.394)
3.7×10^{-3}	0.017 (0.061)	0.017 (0.061)	0.017 (0.059)	0.016 (0.055)	0.020 (0.069)	0.068 (0.209)	0.190 (0.457)
0.05	0.171 (0.194)	0.170 (0.193)	0.167 (0.189)	0.156 (0.178)	0.190 (0.215)	0.455 (0.493)	0.727 (0.756)
0.333	0.357 (0.363)	0.356 (0.363)	0.350 (0.357)	0.333 (0.340)	0.387 (0.394)	0.692 (0.698)	0.877 (0.880)
0.700	0.252 (0.264)	0.252 (0.264)	0.247 (0.259)	0.233 (0.244)	0.278 (0.290)	0.378 (0.592)	0.813 (0.822)
0.945	0.063 (0.084)	0.063 (0.084)	0.061 (0.082)	0.057 (0.076)	0.071 (0.094)	0.215 (0.271)	0.466 (0.543)
0.984	0.019 (0.042)	0.019 (0.042)	0.019 (0.041)	0.017 (0.038)	0.022 (0.048)	0.074 (0.153)	0.204 (0.366)

(i) The coating of inclusion in the separated grain structure increases the value of the percolation volume fraction threshold.

(ii) For volume fraction $f > 0.5$, the departure from sphericity implies a decrease of the average conductivity. In the separated grain structure model, this effect is more pronounced for oblate random unit spheroids 2 (conductor-coated insulating inclusions). In the aggregate structure model, this effect is more pronounced for oblate insulating spheroid inclusions.

(iii) For volume fraction of <0.5, the percolation threshold f_c shifts to lower f for prolate random unit 2 in the first model and prolate random unit A in the second model.

Table 2. The percolation threshold volume fraction in the orientationally averaged symmetrised Maxwell–Garnett approximation. (The figures in brackets are the volume fractions corresponding to a normalised conductivity equal to 0.01.)

g_1 \ g_2	4.3×10^{-4}	3.7×10^{-3}	0.05	0.333	0.700	0.945	0.984
4.3×10^{-4}	0.164 (0.369)	0.259 (0.374)	0.398 (0.420)	0.461 (0.467)	0.430 (0.439)	0.331 (0.373)	0.264 (0.350)
3.7×10^{-3}	0.164 (0.369)	0.259 (0.374)	0.398 (0.420)	0.461 (0.466)	0.429 (0.439)	0.331 (0.372)	0.263 (0.350)
0.05	0.163 (0.367)	0.258 (0.373)	0.397 (0.418)	0.460 (0.465)	0.428 (0.437)	0.329 (0.371)	0.262 (0.349)
0.333	0.160 (0.363)	0.254 (0.369)	0.392 (0.413)	0.455 (0.460)	0.423 (0.433)	0.325 (0.367)	0.258 (0.345)
0.700	0.169 (0.376)	0.266 (0.381)	0.406 (0.428)	0.470 (0.475)	0.438 (0.447)	0.338 (0.380)	0.270 (0.357)
0.945	0.223 (0.446)	0.336 (0.453)	0.488 (0.507)	0.552 (0.556)	0.522 (0.528)	0.416 (0.454)	0.341 (0.427)
0.984	0.281 (0.512)	0.406 (0.520)	0.563 (0.579)	0.625 (0.628)	0.596 (0.601)	0.491 (0.525)	0.412 (0.494)

If the spheroid axis ratio is of the order of 100, the percolation threshold is zero and the system is conducting for any f in the Bruggeman approximation. In the separated grain model, the coating of the metallic inclusions does not allow any percolation paths for low values of the volume fraction and therefore the limit $f_c = 0$ is reached for very low values of g_{2c}.

Tables 1 and 2 give the percolation threshold for various values of (g_A, g_B^0 and (g_1, g_2) in the two models. Because of the presence of long tails for some values of the depolarisation factors, we have also given (between brackets) the values of f for which the cermet conductivity is one hundredth of the pure A conductivity. This can be of importance to compare experimental results with the theoretical curves.

6. Conclusions

In this paper we have discussed systematically the DC conductivity and percolation threshold in the various mean-field theories used to interpret the experimental data of composite thin films and cermets.

The aim was to have an overall picture of the dependence of these properties on the nature and shape of inclusions. The results presented in this paper should help in the interpretation of the growing number of experimental data on cermets, composite materials and porous materials.

We thought that this study was also necessary to assess the importance of effects not included in usual mean-field theories i.e. correlations and clustering effects, a detailed description of the microgeometry and multiple terms in the polarisability.

Acknowledgments

We would like to thank Professor F Abeles and Dr H L Theye for pleasant hospitality at the Laboratoire d'Optique des Solides, Paris, and Dr J Lafait, S Bertheir and J Rivory for useful discussions.

Appendix

For spherical inclusions ($g = \frac{1}{3}$), two schemes have been used to apply the symmetrised Maxwell–Garnett (MG) approximation with the Sheng (1980) coated spheroids probabilities p_1 and p_2 (7). Niklasson and Granqvist (1984) have used the zero average scattering function (8) while Gibson and Buhrman (1983) have calculated the dielectric constant of type 1 and type 2 units in the MG approximation ε_1^* and ε_2^* and then introduced these values in the Bruggeman formula (3) with $\varepsilon_A = \varepsilon_1^*$ and $\varepsilon_B = \varepsilon_2^*$ and $f = p_1$. The two procedures lead to the following second-order equations

$$A\varepsilon^{*2} + B\varepsilon^* + C = 0 \tag{A1}$$

where

$$A = 2[(1-f)(3-f)\varepsilon_A^2 - 2(f^2 - f - 3)\varepsilon_A\varepsilon_B + (2+f)f\varepsilon_B^2]$$

$$B = p_1 B_1 + p_2 B_2$$

$$B_1 = 2f(1-f)\varepsilon_A^3 + (8f^2 - 11f - 3)\varepsilon_A^2\varepsilon_B - (10f^2 - 13f + 6)\varepsilon_A\varepsilon_B^2 - 4f(1-f)\varepsilon_B^3$$

$$B_2 = B_1(f \rightleftarrows 1-f;\ \varepsilon_A \rightleftarrows \varepsilon_B)$$

$$C = -2(1+2f)f\varepsilon_A^3\varepsilon_B + (8f^2 - 8f - 3)\varepsilon_A^2\varepsilon_B^2 - 2(1-f)(3-2f)\varepsilon_A\varepsilon_B^3$$

and are therefore identical.

We have verified that this equivalence is also true for any value of g_1 and g_2.

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DIELECTRIC AND OPTICAL PROPERTIES CLOSE TO PERCOLATION THRESHOLD

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ABSTRACT

We analyze the dielectric and conductivity properties of a metal-insulator composite thin films or cermets close to the insulator-metal transition. Using the frequency dependent Bruggeman approximation it is possible to predict the existence of an optical threshold at a concentration p* slightly higher than the percolation threshold p_c. At that concentration defined by the vanishing of the real part of the dielectric constant and which depends on dimensionality and on the relaxation time τ, we show that the composite optical conductivity (or the optical absorption) is constant up to near infrared frequencies. This result can be related to the percolation scaling laws of a mixture of self-inductors and capacitors and for $\tau^{-1} \rightarrow 0$ is in agreement with a qualitative explanation based on real space renormalization group and scaling arguments.

Keywords Dielectric constant,metallic conductivity, percolation, effective medium theory, optical transition, scaling laws.

1.INTRODUCTION

The understanding of the disorder induced dispersive variation of the metallic or ionic conductivity in disordered materials[1-4], thin films, cermets,smokes, porous materials, polymers etc. is one of the most challenging problems in the field of inhomogeneous materials. For instance, close to the percolation threshold p_c, the interpretation of optical data or radio frequencies data of granular and cermet thin films requires an extension of the theory of percolation to mixtures of resistors, inductors and capacitors [5-8].

Two dimensional discontinuous metal films are obtained during early stages of film growth by evaporating and sputtering onto a non-conducting substrate. The deposited metal first form isolated islands. They undergo coalescence growth and then via surface diffusion and direct impingement as the film thickness increases they eventually form a continuous film. In this case the intervening insulator consists partly of the substrate and partly of the space between the metal islands above the substrate.

Granular metal consist of inhomogeneous mixtures of metal and non metal. Three dimensional composites are generally produced by co-evaporation or co-sputtering of a metal and an insulator. They are known as cermets.

Electrical properties of such systems vary continuously as composition is changed when the concentration of metal is small, the metal forms small isolated islands embedded in an insulating matrix and electrical conductivity is small and highly activated.
As the proportion of metal is increased, the islands grow and coalesce, the activation energy falls and eventually for a given thickness or given composition (percolation threshold) continuous metallic paths extending through the material are established. At this stage the system undergoes an "metal-insulator" transition to a conducting state. For higher metal concentrations the structure becomes that of a isolated insulating inclusions in a metallic matrix. The conductivity continues to improve as the proportion of insulator is reduced to zero.

Recently several papers[9-13] have been devoted to the behaviour of optical properties in the vicinity of the percolation threshold. The interessant experimental observation is that the near infrared transmittance and reflectance as well the optical absorption become frequency independent.

If the three groups agree on the strong correlation between the frequency independence of the three optical quantities and the presence of a percolation threshold in Al and Au granular films, the magnitude of the critical thicknesses for which this interesting phenomena occurs is strongly dependent of the thin film deposition technology, substrate conditions etc. The critical thickness is larger for conventional evaporation than for films in which the deposition is accompanied by ion bombardment as in sputtering.

In the case of reflectance, a qualitative explanation of this behaviour has been given by Yavil and Deutscher[9-10] in terms of the different length involved in the percolation process: the wavelength λ , the grain size and the correlation length ξ ,defined as the linear length above which the probability of two sites (grains) to belong to the same finite clusters decays exponentially and which diverges as $(p - p_c)^{-\nu}$ at percolation threshold. In the region $a \ll \lambda \ll \xi$. a real space renormalization group argument leads to a expression for the film transmittance given by :

$$T(p) = p_c\, T_m + (1 - p_c)\, T_i + (\lambda/2\pi a)^{1/\nu} (p - p_c)\,(T_i - T_m) \qquad (1)$$

where T_m and T_i are the average transmittances of the metallic and insulating region at percolation. The argument strongly rely on the assumption that $T_m = 0$ and $T_i = 1$ are independent of frequency. In the case of the optical absorption as discussed in Gadenne et al. (1988), the frequency (or wavelength) dependence of the corresponding quantity depends on an effective relaxation wavelength and its corresponding relaxation time τ which are strongly material and microgeometry dependent.

The purpose of the present paper is to show that although it cannot account correctly for the exact critical exponent and the correct behaviour in the vicinity of the percolation threshold, the Bruggeman approximation extended to finite frequency and which has been used widely to described composite materials and to model thin film layers systems is able to account for this frequency independence of the optical absorption in the far and near infrared region for a concentration p^* close to the percolation threshold p_c but which depend on the relaxation time τ. This result can be related to the percolation scaling laws of a mixture of self-inductors and capacitors and for $\tau^{-1} \rightarrow 0$,it is in agreement with the conclusions of the renormalization group argument of Yavil and Deutscher. This should not be too surprising since it has been shown recently[6-8] that the analytic effective medium approximations are in good agreement with the result obtained by numerical simulations if one except the immediate vicinity of the percolation threshold.

2. THE PERCOLATION OPTICAL THRESHOLD

A detailed analysis of the dielectric properties of a mixture of a metal ,supposed to obey a Drude law, and an insulator, represented by a constant dielectric constant, reveals the existence of a variety of interesting details which can lead to a deeper analysis of optical data of granular and cermet thin films.

It is for instance possible to predict the existence of a *percolation optical threshold* at a concentration $p^* > p_c$ characterized by the condition $\epsilon'(0) = 0$ (Evros and Shklovskii[14], Gadenne et al.[12]). We show in this paper that at this concentration p^*, the conductivity is constant up to the near infra-red frequencies (from $\omega = 0$ to a fraction of ω_p). At that concentration and in a range of frequencies up to τ^{-1}, the system behaves as a pure resistor. This transition occurs at p^* and not at p_c as this is sometimes assumed.

Let us calculate this optical threshold using the model of Lafait et al [15-16]

We start from the Bruggeman formula for the effective dielectric constant $\epsilon^*(\omega)$:

$$p\,\frac{\epsilon_m(\omega)-\epsilon^*(\omega)}{\epsilon^*(\omega)+g(\epsilon_m(\omega)-\epsilon^*(\omega))} + (1-p)\,\frac{\epsilon_d-\epsilon^*(\omega)}{\epsilon^*(\omega)+g(\epsilon_d-\epsilon^*(\omega))} = 0. \qquad (1)$$

p is the concentration of metal m. d is the insulator and g the depolarization factor which depends on the shape of the inclusions In the

case of spherical inclusions one has g=1/3 for three dimensional systems and g=1/2, for two dimensional systems.
We have :

$$\epsilon_m(\omega) = \left\{\epsilon_m(\infty) - \frac{\tau^2\omega_p^2}{\omega^2\tau^2+1}\right\} + i\,\frac{\tau^2\omega_p^2}{\omega\tau(\omega^2\tau^2+1)} \qquad (2)$$

and since $\tau\omega_p^2 = \frac{\tau ne^2}{\epsilon_0 m} = \sigma_m(0)$ the d.c. metallic conductivity of m.

$$\epsilon_m(\omega) = \left\{\epsilon_m(\infty) - \frac{\tau\sigma_m(0)}{\epsilon_0(\omega^2\tau^2+1)}\right\} + i\,\frac{\sigma_m(0)}{\epsilon_0\omega(\omega^2\tau^2+1)} = \epsilon'_m + \epsilon''_m \qquad (3)$$

We shall use in the numerical illustration the Lafait et al.[10] values: g=1/3 $\hbar\omega_p$ = 9.2 eV for the plasmon frequency, $\hbar/\tau$ = 0.06 eV for the inverse relaxation time, $\epsilon_m(\infty)$ = 6.5 and ϵ_d = 2.82 used to represent a gold based cermet.

As observed by Berthier et al.[16] (see also Brouers [17]) in the limit $\omega \to 0$, the Bruggeman approximation (1) yields for p > g :

$$\sigma^*(0) = \left[\frac{p-g}{1-g}\right]\sigma_m(0) \qquad (4)$$

and

$$\epsilon^*(0) = \left[\frac{p-g}{1-g}\right]\epsilon'_m(0) + \frac{p(1-p)}{(1-g)^2}\left[\frac{1-g}{p-g}\right]\epsilon'_d \qquad (5)$$

This is an exact result of the mean field approximation.It can be obtained by separating the real and imaginary parts in Equ. (1).
The percolation threshold is $p_c = g$. $\epsilon'(0)$ diverges for $p = g = p_c$. These results are in agreement with the percolation theory if we use the mean field conductivity and superconductivity exponents t = s = 1.

Since $\epsilon'_A(0)$ is strongly negative in the chosen numerical example $\epsilon'_A(0) \approx -20{,}000$, there is a characteristic concentration p* for which $\epsilon'^*(0)$ is zero (*optical threshold*). For p<p*, the behaviour is dominated by the dielectric divergence. For p>p* it is dominated by the metallic behaviour $\epsilon'^*(0) < 0$.

In Figures 1,2 and 3 we present the results of the calculation of the dielectric constant $\epsilon_1(\omega)$ the real and the imaginary part of the conductivity for the Lafait et al.[15-16] model for three concentrations below (p =0.337), at (p = p* =0.3385) and above (p = 0.34) the "optical threshold". In this example the percolation threshold p_c = 1/3. The behaviour obtained for the real part of the conductivity, the "optical conductivity" which is proportional to the optical absorption coefficient, is very similar to what has been observed by Gadenne 11-12) in granular discontinuous gold films of different thickness around the percolation threshold. The optical conductivity close to percolation exhibits a linear behaviour versus frequency (or wavelength). The slope of this variation is positive beyond $p^* \approx p_c$, negative below and vanishes at the optical cross-over percolation (p*) which coincides with the vanishing of ϵ_1^*.

In the chosen numerical example p_c = 1/3 and p* = 0.3385. The difference is small. However this value strongly depends on τ. Due to the grain size or the small film thickness $\hbar/\tau$ can be much higher see Ref.9. In Table I we give the values of p* for different values of $\hbar/\tau$.

$\hbar/\tau$	p* (s=1,t=1)	p* (s=0.75,t=1.95)
0.06 eV	0.3385	0.3515
0.6 eV	0.3875	0.438
3 eV	0.7560	0.791

Table I

We also report the values obtained with the correct exponents t and s i.e. by using

$$\left[\frac{p-p_c}{1-p_c}\right]^t \text{ and } \left[\frac{1-p_c}{p-p_c}\right]^s \text{ in (4) and (5)} .$$

Berthier et al. (1987) have interpreted their experimental data by fitting them to an effective Drude formula

$$\epsilon'^*(\omega) = \epsilon'^*(\infty) - \frac{\left[\frac{p-p_c}{1-p_c}\right]^t \omega_p^2 \tau}{1+\omega^2\tau} \qquad (6)$$

with $$\epsilon'^{*}(\infty) = \left[\frac{p-p_c}{1-p_c}\right]^{t} \epsilon'_m(\infty) + \frac{p(1-p)}{(1-p_c)^2}\left[\frac{1-p_c}{p-p_c}\right]^{s} \epsilon'_d \qquad (7)$$

We want to emphasize that this is only possible and physically justified for $p > p^*$, where a plasmon mode can be defined.

3. ELECTRICAL CIRCUIT ANALOGUE, UNIT POWER RESONANCE AND SCALING LAW.

To understand the behaviour of electrical and optical properties close to percolation threshold as well as to use numerical or circuit simulations it is convenient to represent a Drude conductor as a R- L -C system where the resistance $R \equiv 1/\sigma_m(0)$, the inductance $L \equiv \tau/\sigma_m(0) = m/ne^2$ and the capacitance $C_m \equiv \epsilon_0\epsilon'_m(\infty)$. The insulator is represented by a capacitor $C_d \equiv \epsilon_0\epsilon'_d$. One can define for the conductor and the mixture the following characteristic frequencies : the plasma frequency $\omega_p = \frac{1}{\sqrt{L_m\epsilon_0}}$, the relaxation frequency $\omega_{RL} = \tau^{-1} = R/L$, the Drude circuit resonance frequency $\omega_{LC_m} = \frac{1}{\sqrt{L_mC_m}}$ and the RC frequency $\omega_{RC_m} = 1/RC_m$ to which we have to add the composite characteristic frequencies $\omega_{RC_d} = 1/RC_d$ and $\omega_{LC_m} = \frac{1}{\sqrt{L_mC_d}}$. In these conditions using equation (5) the condition $\epsilon^*(0) = 0$ yields :

$$\left[\frac{p^*-p_c}{1-p_c}\right]^2 \left(\frac{L_m}{R_m^2} - C_m\right) = \frac{p^*(1-p^*)}{(1-p_c)^2} C_d \qquad (8)$$

or

$$\frac{(p^* - p_c)}{\sqrt{p^*(1-p^*)}} \sqrt{Q^2_{mix} - \frac{C_m}{C_d}} = 1 \qquad (9)$$

defining the quality factor of the mixture $Q^2_{mix} = \frac{1}{R^2_m} \frac{L_m}{C_d}$ (10)

and posing $A = Q^2_{mix} - \frac{C_m}{C_d}$, the solution of this equation is given by

$$p^* = \frac{2p_cA + 1 \pm \sqrt{4p_cA + 1 - 4Ap_c^2}}{2(A+1)} \qquad (11)$$

Since $p_c < 1$, p^* is always real and the numerical values obtained from (11) coincide with those of Table I.

If $p_c = 1$, as expected $p^* = 1$.

As already noticed in Table 1 if $R_m \rightarrow 0$, $p^* \rightarrow p_c$ and the optical transition occurs at the percolation threshold.

In the case $p_c = 1/2$ $\quad \frac{p^*-p_c}{p_c}\sqrt{A+1} = 1.$ (12)

If moreover $C_m = 0$, $\quad \frac{p^*-p_c}{p_c}\sqrt{Q^2_{mix}+1} = 1.$ (13)

Clerc et al.[7] have shown that for two-dimensional real $(RL)_pC_{1-p}$ circuits this last relation, established here for $\omega = 0$, holds up to $\omega \sim 1/\sqrt{LC}$.

If we define the effective quantities $L^* = \frac{p^*L_m}{(p^*-p_c)}$, $R^* = \frac{p^*R_m}{(p^*-p_c)}$ and

$C^* = C_d^* + C_m^*$ with $C_d^* = (1-p^*)\frac{C_d}{(p^*-p_c)}$ and $C_m^* = (p^*-p_c)\frac{C_m}{p^*}$ (the (1-p*) d-capacitors are coupled in parallel and the p* m-capacitors are coupled in series), the condition (8) is equivalent to $R^* = \sqrt{L^*/C^*}$.
In that particular situation the effective circuit is in unit power resonance ($Q^* = 1$) and the resulting equivalent impedance is $Z^* = \sqrt{L^*/C^*}$. For finite frequencies it is easy to show that the effective circuit is resistive up to frequencies $\omega \sim \omega_{L^*C^*} = \omega_{R^*C^*} = \omega_{L^*R^*} = \tau^{-1}$. This explains the behaviour of $\epsilon_1(\omega)$ and $\sigma(\omega)$ in Fig. (2). The real part of the dielectric is zero and the conductivity is constant up to τ^{-1}.

Using the electrical circuit analogue and a generalization to a mixture of self-inductors and capacitors of the scaling laws derived by Efros and Shklovskii[14] and Straley[18], it is moreover possible to show that at $p = p^*$, the d.c conductivity is very close to the optical conductivity in the near infrared region as observed numerically in Fig 2 and experimentally in the vicinity of the percolation threshold (Gadenne et al.[11-12]).

Equation (8) can be written

$$\sigma^{*2}(\omega=0,\, p^*) = \left[\frac{p^*-p_c}{1-p_c}\right]^2 \frac{C_m}{L_m} + \frac{p^*(1-p^*)}{(1-p_c)^2}\,\frac{C_d}{L_m} \qquad (14)$$

If $\left[\dfrac{p^*-p_c}{1-p_c}\right] \ll 1$ or $C_m = 0$ one has

$$\sigma^*(\omega=0,p^*) = \frac{\sqrt{p^*(1-p^*)}}{(1-p_c)}\sqrt{C_d\tau^{-1}\sigma_m(0)}$$

and since $\sigma_d = i\, C_d\omega$, and $\sigma_m(\omega \gg \tau^{-1}) \approx -i\dfrac{\sigma_m(0)}{\omega\tau}$

$$\sigma^*(\omega=0,p^*) = \frac{\sqrt{p^*(1-p^*)}}{(1-p_c)}\sqrt{\sigma_d(\omega)\sigma_m(\omega \gg \tau^{-1})} \qquad (15)$$

The right hand side of this expression is the conductivity close to the percolation threshold of the m-d composite in the region $\tau^{-1} \ll \omega$ given by the two conductors[18] scaling law $\sigma \sim \sigma_m(\sigma_m\sigma_d)^{t/(s+t)}$ of Efros and Shklovskii and Straley in the mean field approximation ($s=t=1$) or in two dimensional systems ($s = t$). Therefore in the Bruggeman approximation the optical threshold condition $\epsilon^{*\prime}(0) = 0$ is equivalent to the equality between the low frequency Drude conductivity and optical conductivity in the optical region close to percolation region as this is shown numerically in Fig.2..

4 CONCLUSION

A model used by Lafait et. al to interpret optical and infra-red properties of cermets and granular films has been analyzed in the region where a frequency independent behaviour of optical absorption, reflectivity and transmittivity has been observed. We confirm the conjecture of Gadenne et al.[12] that this remarkable behaviour coincides with the vanishing of ϵ' ,the real part of the dielectric constant (which in this region is difficult to measure accurately) and is the signature of a "percolation optical cross-over ". The cross-over concentration is close but different from the static percolation threshold p_c and depend on the microgeometry of the sample through the relaxation time τ. In real systems, it might not be easy to separate them.

Based on an effective medium theory, our treatment cannot be the complete answer to that problem. We believe that future efforts should be done in two directions.

a) Since the exact location of the optical cross-over appears to be dependent on the film microgeometry and its influence on the various scattering mechanisms, a detailed analysis of the correlation between the various microgeometries resulting from different nucleation and coalescence growth processes and the discrepancy between critical thicknesses (t^*) or coverage (p^*) reported by different groups using different preparation methods (evaporation and magnetron sputtering) should be pursued.

b) Numerical simulations on R-C-L electrical networks and measurement on real electrical circuits could be done to confirm the conclusions of our study and to determine the exact exponents for two and three dimensional composite systems.

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FIGURE CAPTIONS

Figure1. Real part of the dielectric constant (A) and real and imaginary part of the conductivity (B) for $p_c < p = 0.337 < p^*$.

Figure2. Real part of the dielectric constant (A) and real and imaginary part of the conductivity (B) for $p = p^* = 0.3385$

Figure3. Real part of the dielectric constant (A) and real and imaginary part of the conductivity (B) for $p = 0.340 > p^*$.

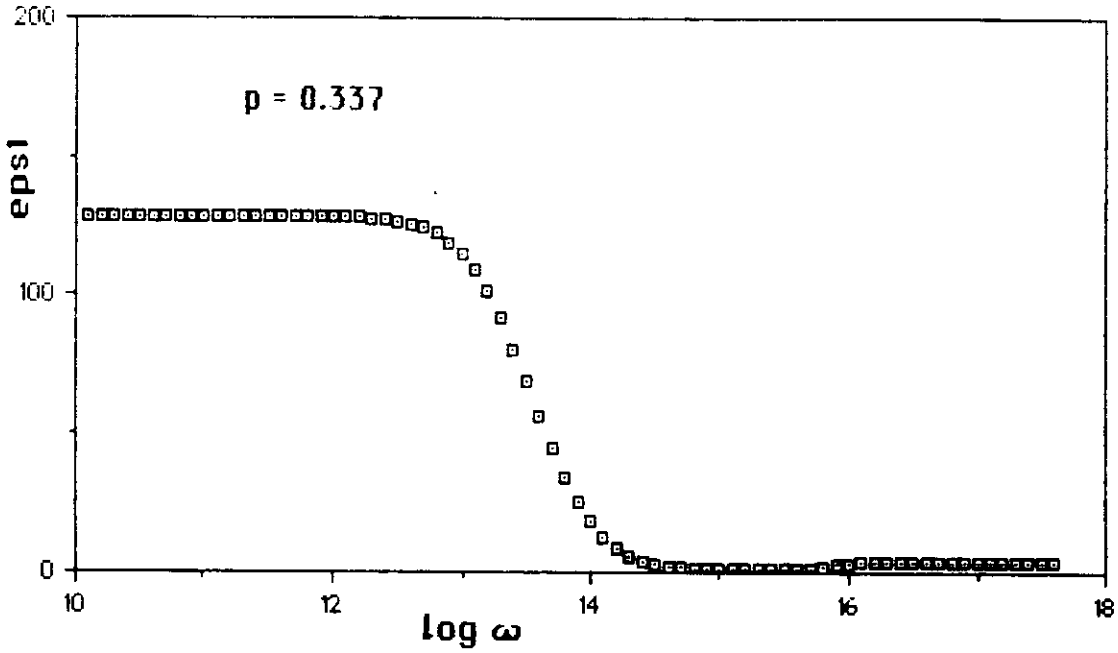

FIGURE 1A

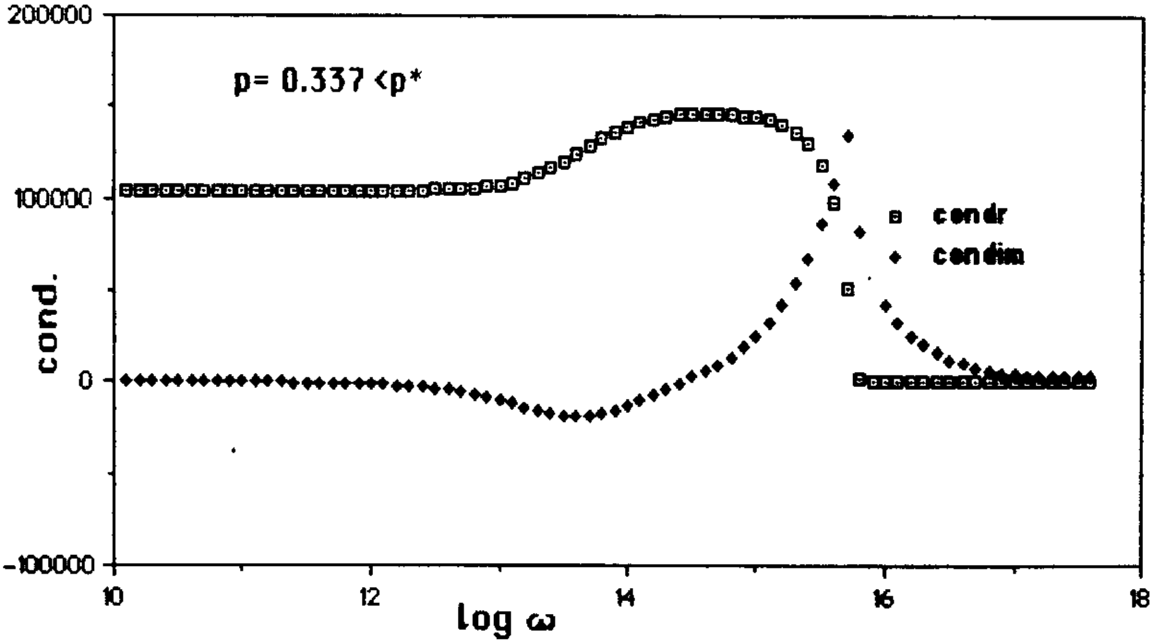

FIGURE 1B

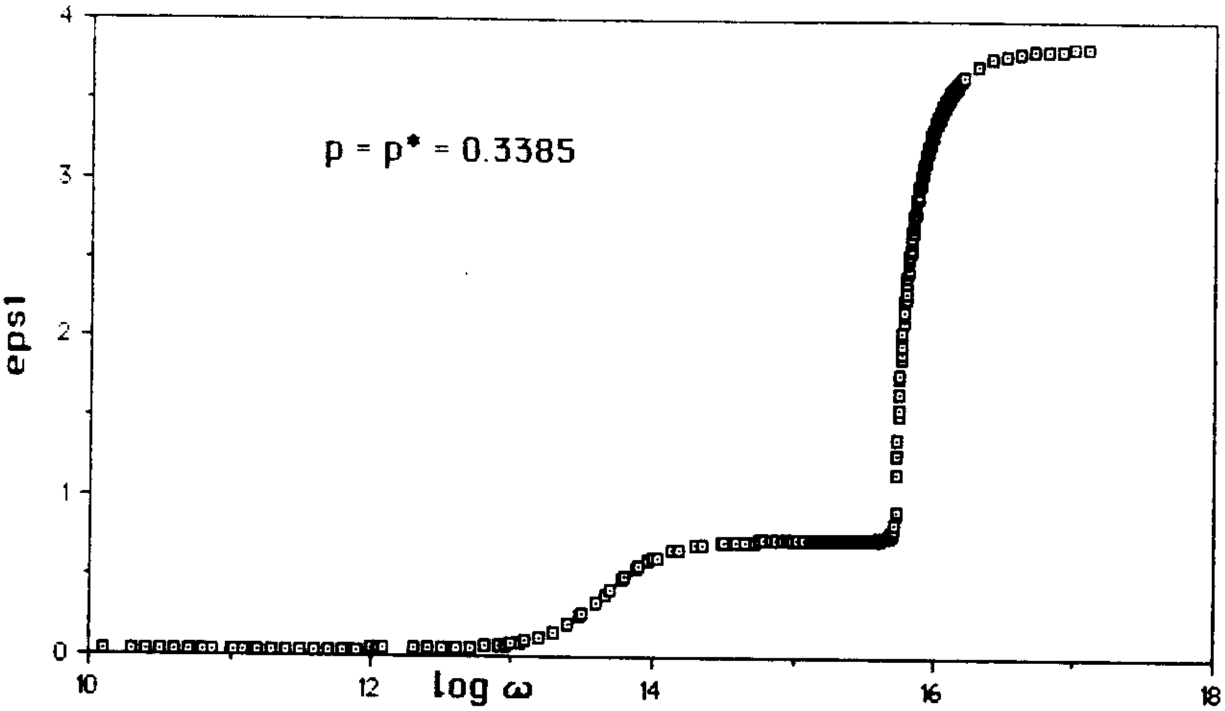

FIGURE 2 A

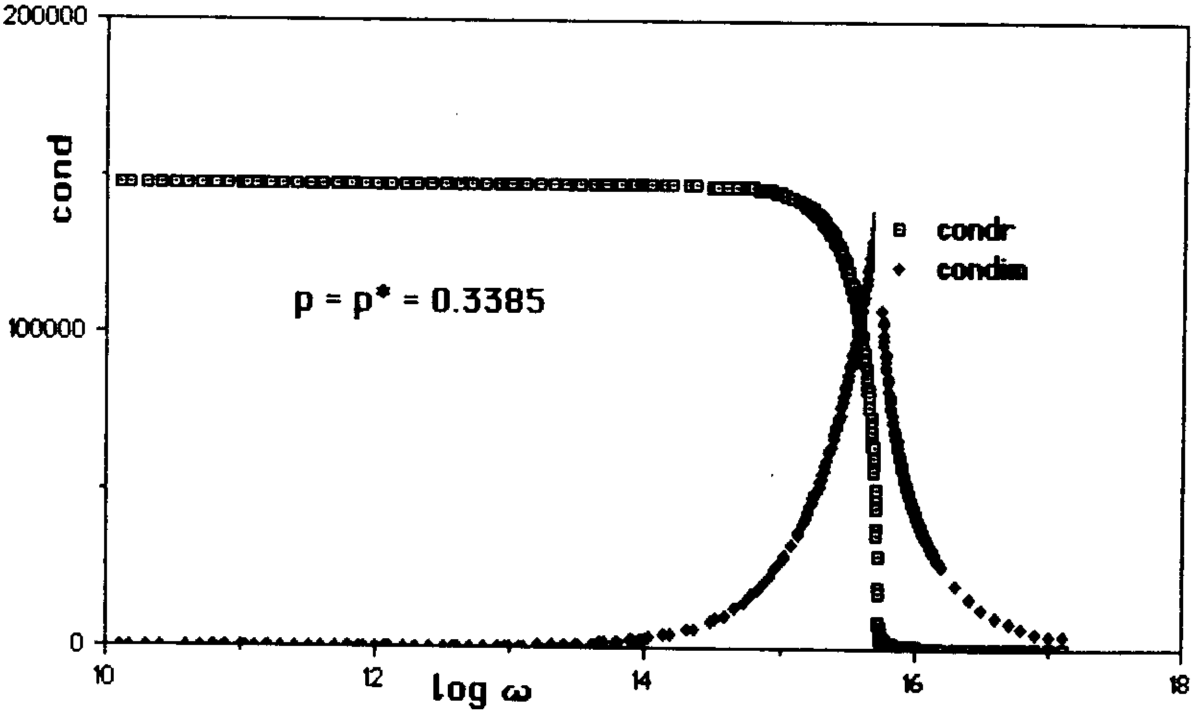

FIGURE 2B

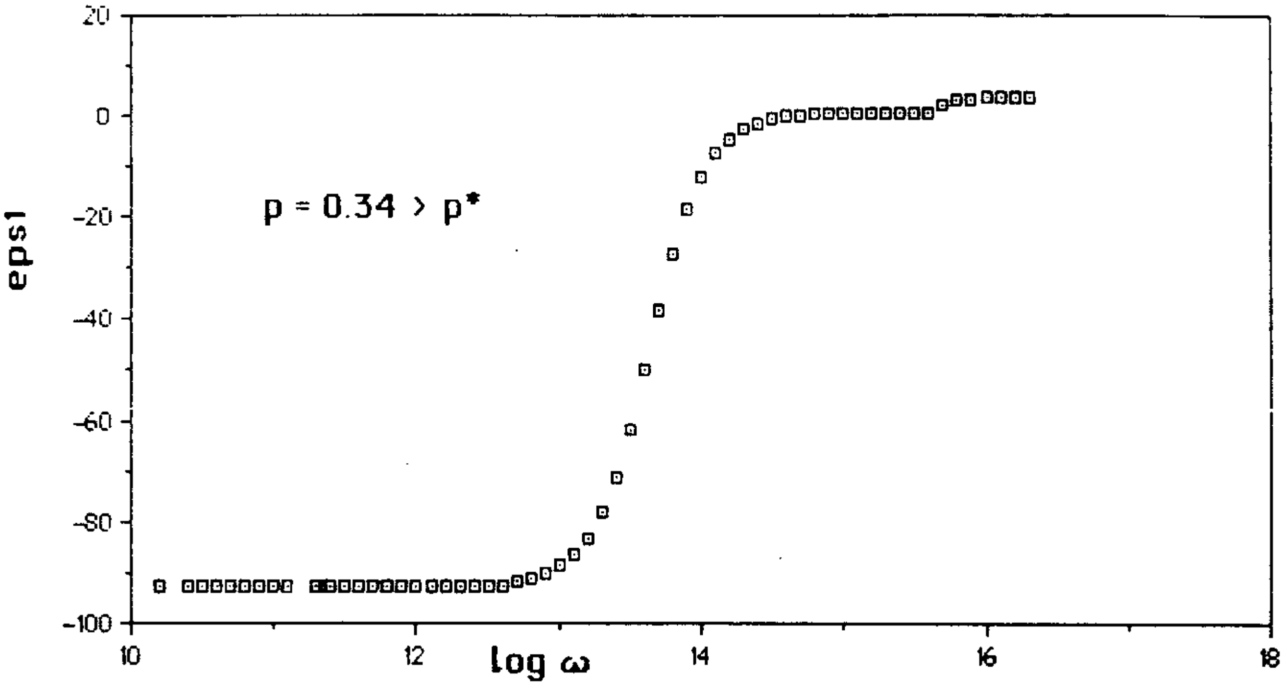

FIGURE 3A

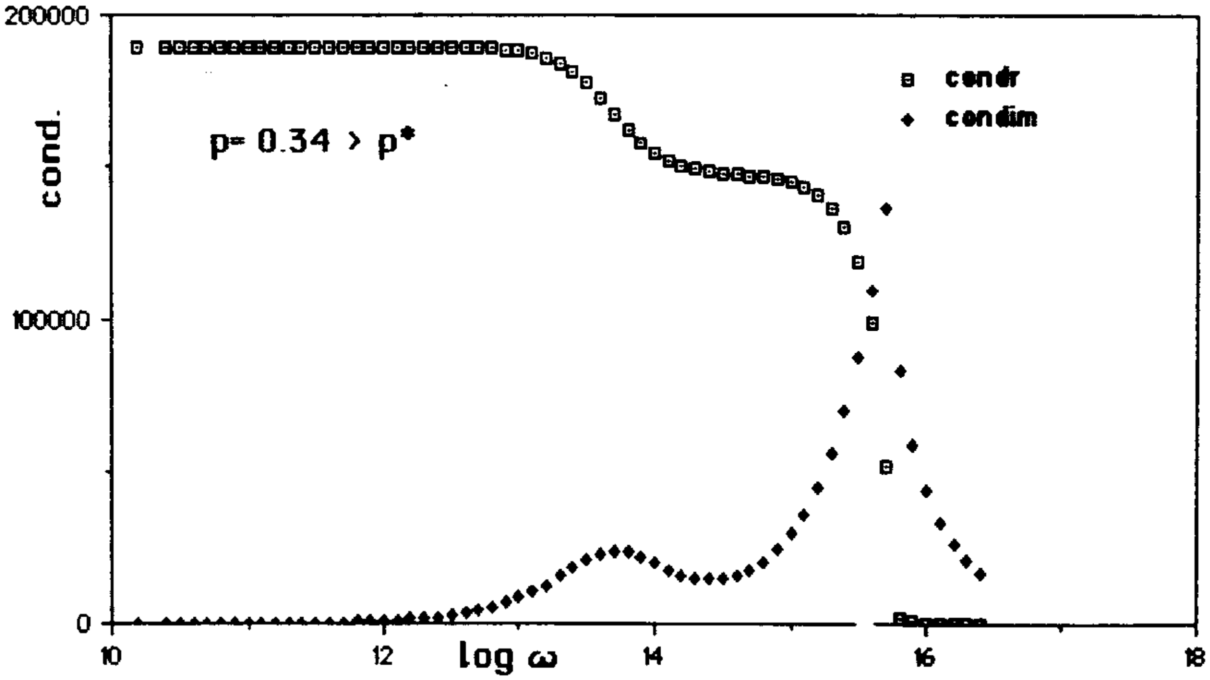

FIGURE 3B