Electrical and optical properties III

Composites

Outline

- Mixtures of two or more materials on the nano- or micro scale
- Metal-insulator mixtures most studied
- DC conductivity
- AC conductivity, percolation, fractals
- Optical properties, effective medium theories
- Light scattering

Effective physical properties

- ”Mixing rules” or effective medium theories
- Common description for:
- Optical and electrical properties (complex dielectric permittivity or refractive index)
- Magnetic permeability
- Thermal conductivity
- Mechanical properties (bulk and shear moduli)

Two-phase composites

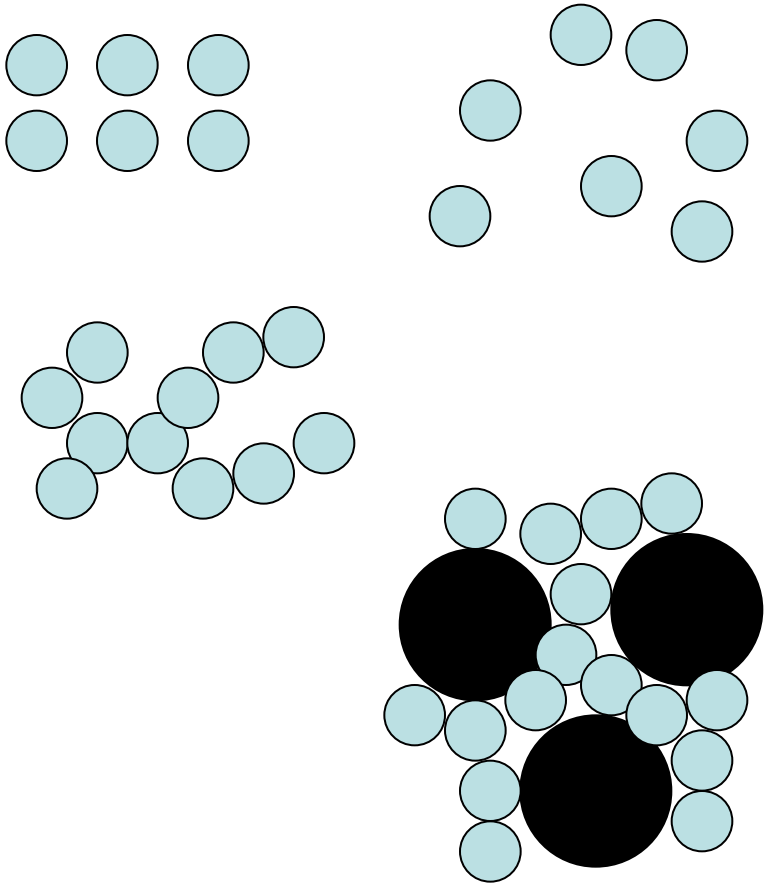
- Case of effective dielectric permittivity. The simplest mixing rule (phases A and B):

$$\bar{\varepsilon} = f_A \varepsilon_A + f_B \varepsilon_B$$

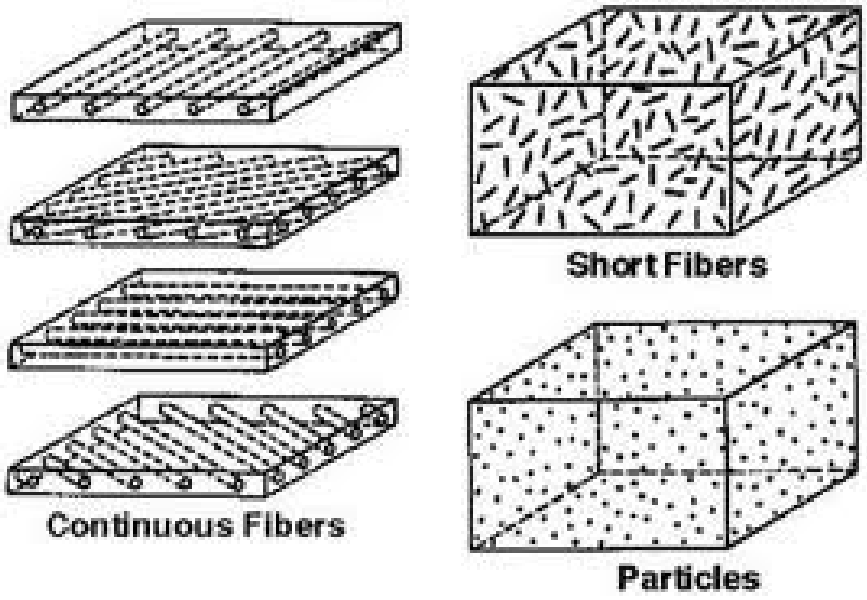
- Volume fractions of A and B: f_A, f_B
- During the 1800's and early 1900's many such relations were derived
- Mosotti, Clausius, Maxwell, Lorenz, Lorentz, Rayleigh, Maxwell Garnett, Wiener, Wagner, Bruggeman…

Microstructure in very important!

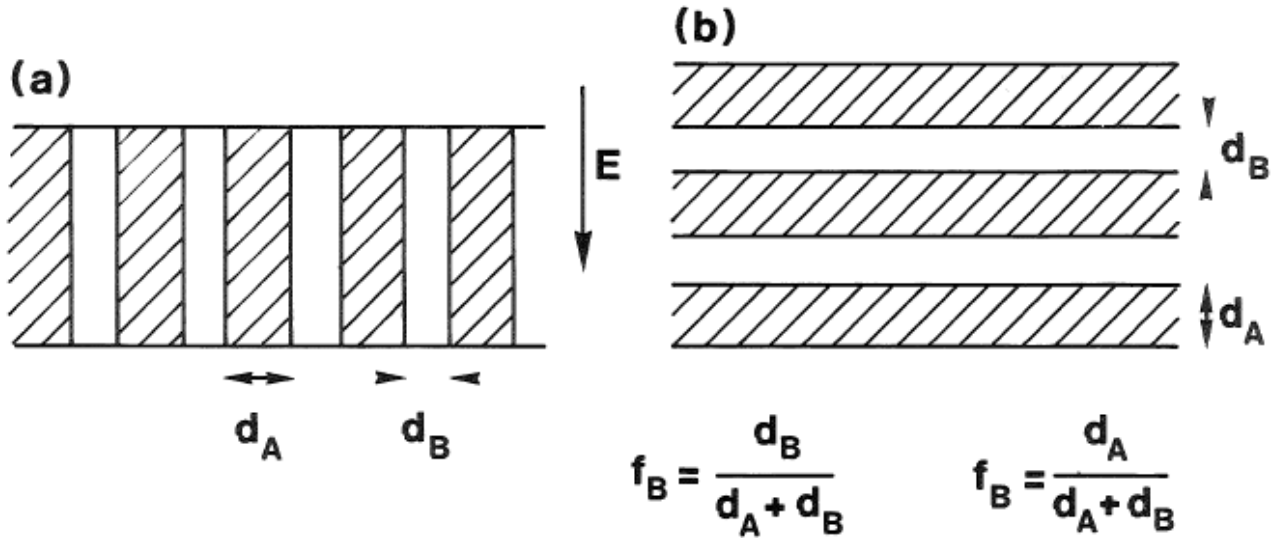
- Ordered and disordered



- Different particle shapes



Rigorous Wiener bounds



- Parallel capacitors

$$\overline{\varepsilon} = f_A \varepsilon_A + f_B \varepsilon_B$$

- Series capacitors

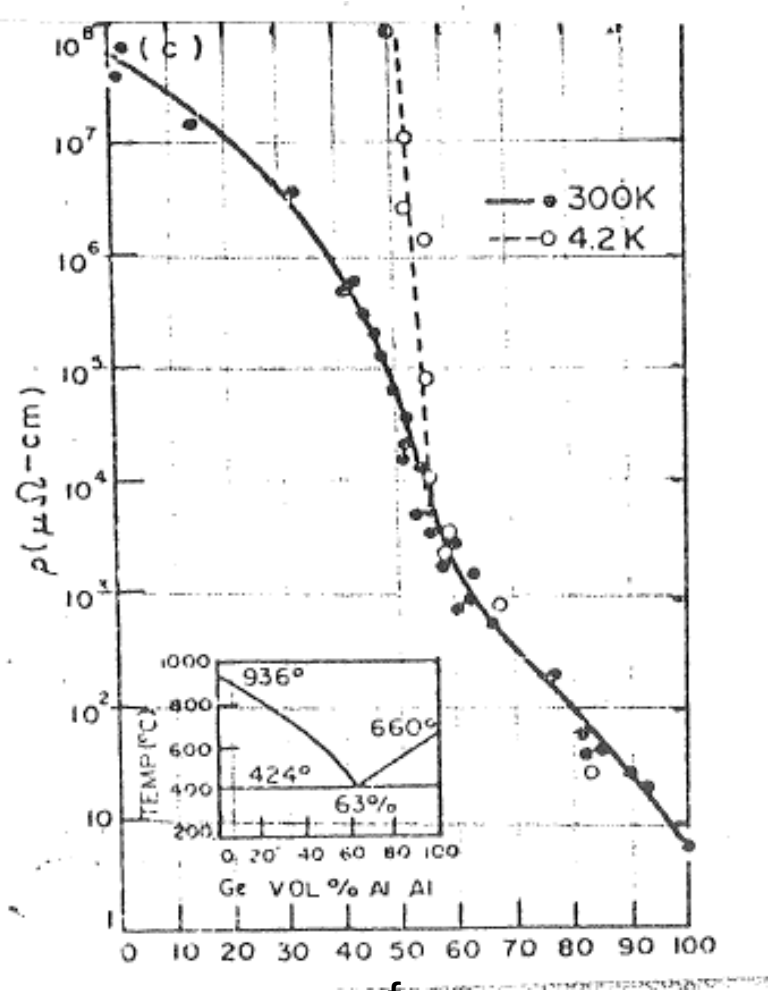
$$\overline{\varepsilon}^{-1} = f_A \varepsilon_A{}^{-1} + f_B \varepsilon_B{}^{-1}$$

DC conductivity

- Composites from materials with widely differing resistivities
- Metal-insulator, metal-semiconductor
- By tailoring the composition every intermediate resistivity can be achieved
- Metal-insulator transition – percolation threshold
- Metallic conduction above the percolation threshold
- Tunneling between metal particles below the percolation threshold

Ex: Al-Ge composites

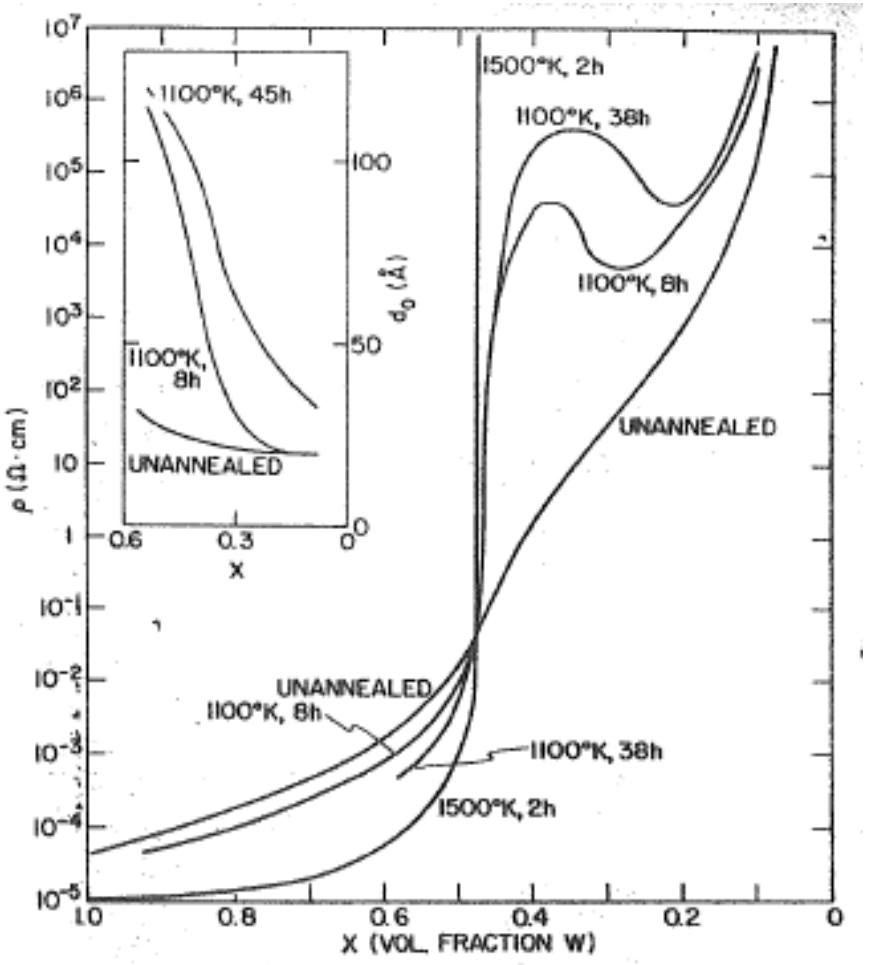
- Low T – sharp metal-insulator transition at ~50 % Al
- High critical volume fraction – Ge tends to coat the Al particles
- Room temp. – we see a rising tunneling contribution below the transition



Source: Deutscher et al

Ex: W-Al_2O_3 composites

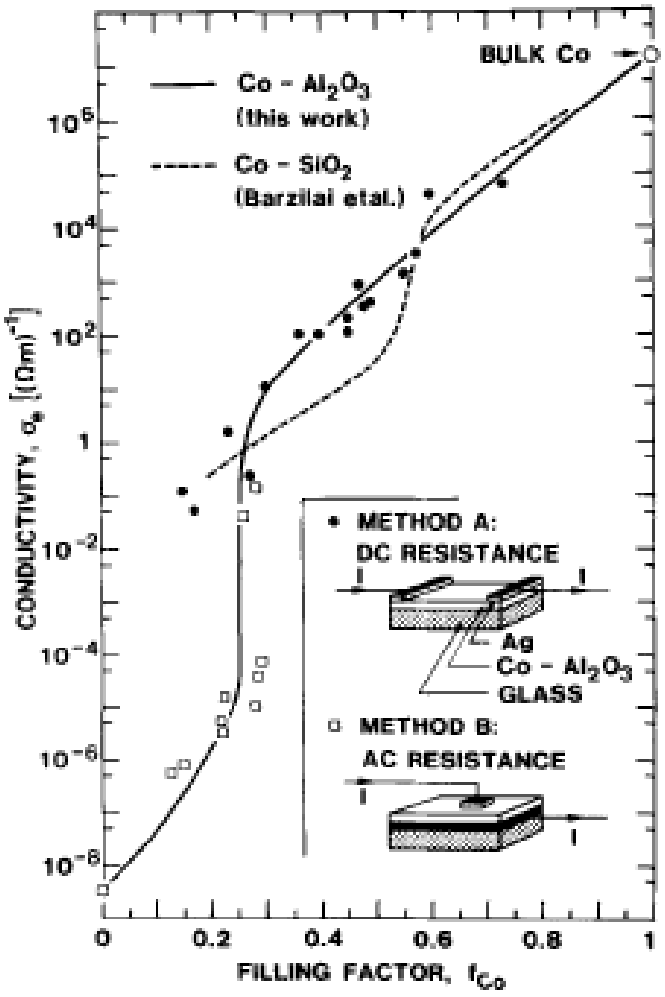
- Resistivity at T=300K
- Metal-insulator transition at f~0.5 . Insulator coats metal particles
- Annealing – particle size increases – larger separations between particles – much lower tunneling contribution – sharper transition
- Inset: W grain size



Source: Abeles et al

Ex: Co-Al_2O_3 composites

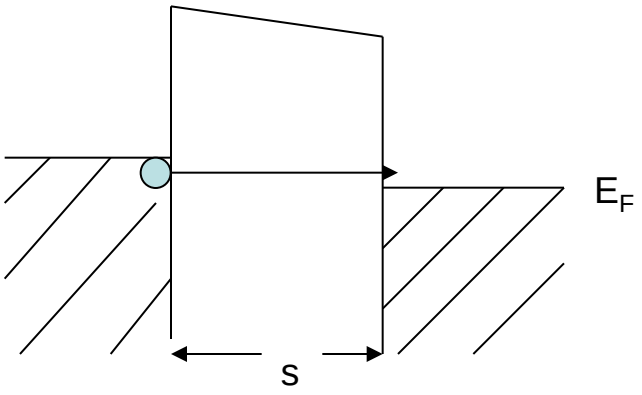
- Steep rise at f ~0.2 to 0.3
- Connected with the tunneling contribution
- The temperature coefficient of resistance changes sign at f~0.7
- Smooth crossover between tunneling and metallic conduction



Tunneling between metal particles

- Electron tunneling – the particles become charged
- Charging energy (s~r)

$$E_c = \frac{e^2}{4\pi\varepsilon_0\varepsilon_i}\frac{s/2r}{s+r} \sim C/s$$



- Low applied fields

$$\sigma = \sigma_0 \exp(-2\alpha s - E_c / k_B T)$$

- Max of σ when

$$s_M = (C/2\alpha k_B T)^{1/2}$$

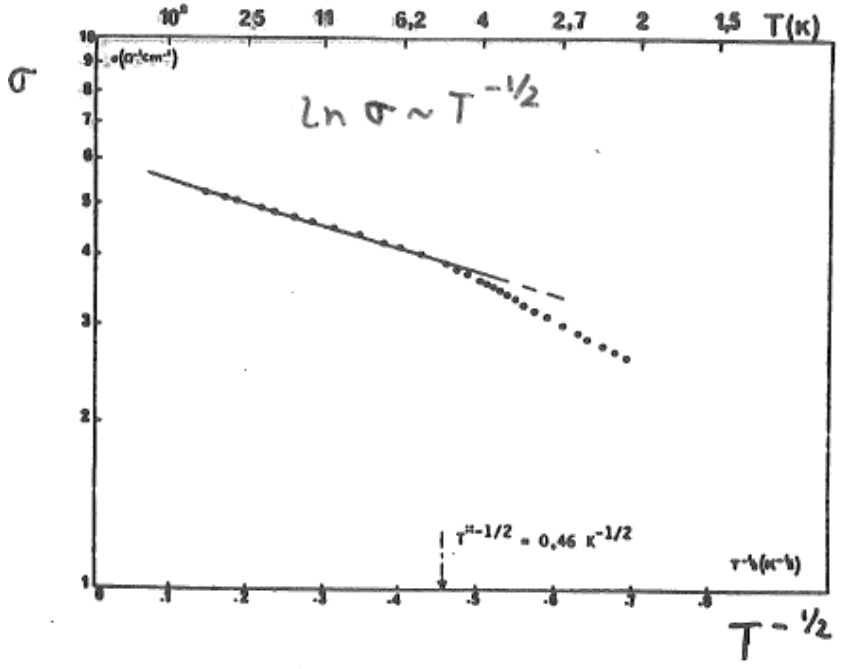
- Mott type expression

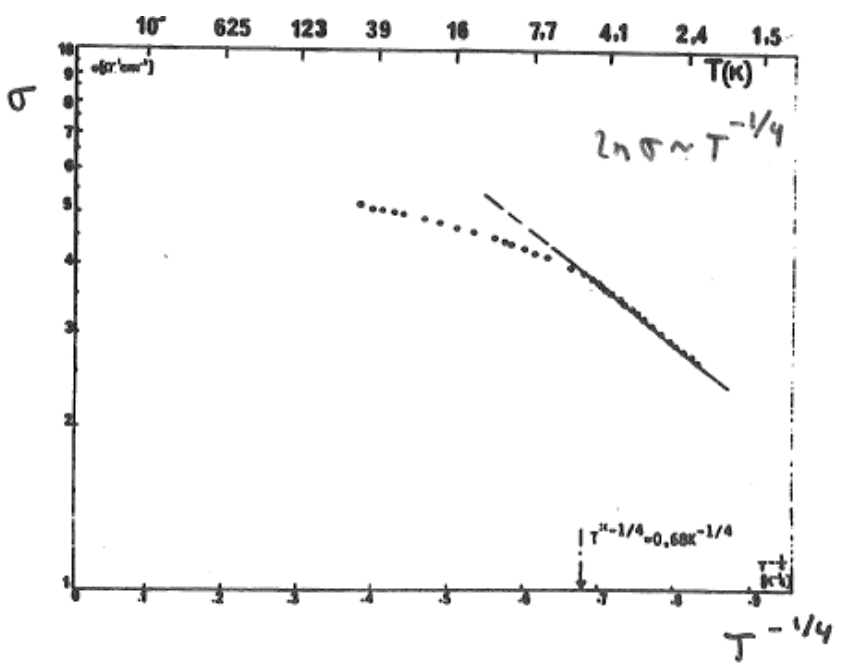
$$\sigma = \sigma_0 \exp(-(T_p/T)^{1/2})$$

- Different at very low temperatures

Ex: Au-Al_2O_3

Experiments often show crossover to VRH behaviour





Source: Khatami, Thesis, 1985

AC electrical properties

- Low f – insulating region: Particle-particle tunneling as well as localized states in the insulator
- Complex behaviour typical of insulators
- Intermediate f: Tunneling conductivity, ”quasi-dc”
- High f – metallic region: Metallic conduction
- Metal-insulator crossover at the percolation threshold: Scaling behaviour as predicted by percolation theory

Percolation theory: ac conductivity

- Metal-insulator composites: random structure of conducting and insulating regions
- Can be mapped onto a random RC-network
- Percolation theory: DC conductivity and dielectric constant close to the percolation threshold, f_c

$$\sigma_{DC} \sim (f - f_c)^t \qquad \varepsilon_{DC} \sim \left| f - f_c \right|^{-s}$$

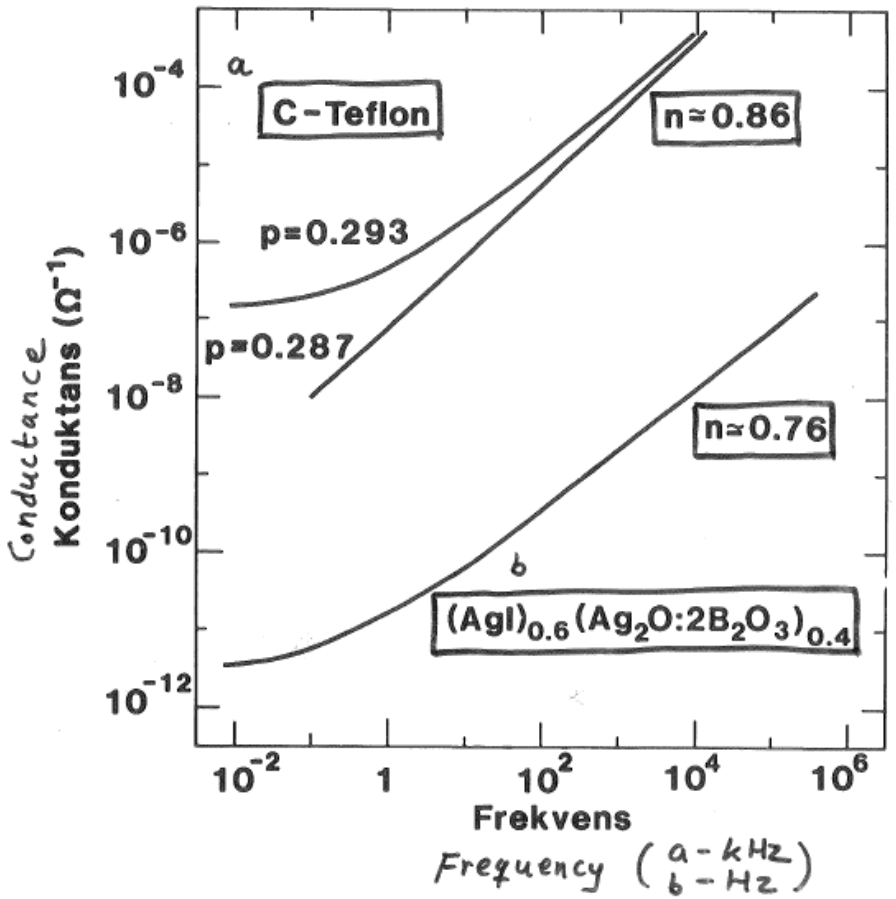
- Percolation theory: Frequency dependence

$$\sigma(\omega) \sim \omega^{t/(t+s)} \quad , \omega >> \sigma_m \left| f - f_c \right|^{t+s} / \varepsilon_i$$

Experiments on composites

- Critical exponents (theory)
- t = 1.9 +/- 0.1
- s = 0.73 +/- 0.01
- u = t/t+s = 0.72 +/- 0.02
- Frequency exponent u is influenced by distributions of resistances and Coulomb interactions

Data from: Song et al; Brantervik et al.



Optical properties

- We consider two component materials
- If the particle size << wavelength of light then the **E**- and **H**-fields are almost constant over a length of the order of a particle size
- Materials treated as homogeneous on length scales ~ λ
- Quasistatic approximation (electrostatics sufficient for small particles)
- Basis of effective medium theories (EMT)

Spheres in continuous matrix

- Consider dielectric function (permittivity)
- Static case (ω=0)
- Quasistatic approx:
- Can be extended to frequency dependent case as long as

  max (n) $2\pi r/\lambda << 1$

  where max (n) is the largest of the refractive indices

- Particles of A in matrix B
- Electric field

$$E_A = E_B + E_p = E_B - P/3\varepsilon_0$$

- Compare the average fields E_{av} and D_{av}
- The effective dielctric permittivity is given as

  (Maxwell, 1872)

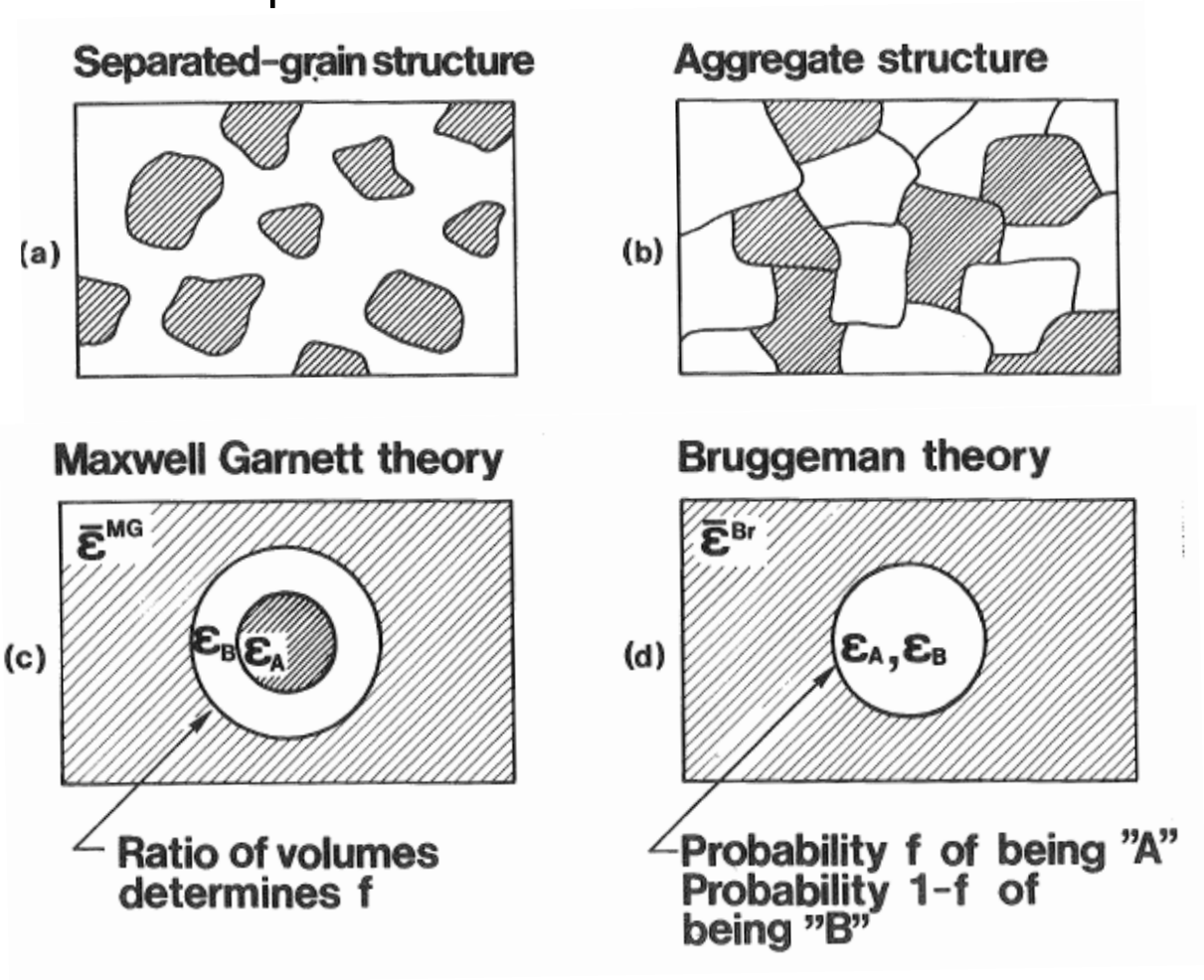
$$\bar{\varepsilon} = D_{av} / E_{av}$$

Complex dielectric function

- Optical transmittance and reflectance depends on the effective complex and frequency-dependent dielectric function
- Different microstructures lead to different expressions for the complex ε
- Microstructural models: Random Unit Cells
- Limit theorems give bounds in the complex plane
- Influence of microstructure can be represented by a spectral density.

Random Unit Cells (RUC)

- Two often used simple cases:



Derivation of EMT's

- RUC's can be used to systematically derive EMT's
- They account for the important aspects of a given microstructure
- Can be extended to nonspherical shapes
- Criterion: The RUC should be invisible in an optical experiment when embedded in the effective medium
- Light scattering S=0
- Maxwell Garnett: S(coated sphere)=0
- Bruggeman: $f_A S_A(\text{sphere}) + f_B S_B(\text{sphere}) = 0$
- Rule of thumb: $r <\sim \lambda/20$

Some simple EMT´s

- Maxwell Garnett (MG) theory

$$\bar{\varepsilon} = \varepsilon_B \frac{\varepsilon_A + 2\varepsilon_B + 2f_A(\varepsilon_A - \varepsilon_B)}{\varepsilon_A + 2\varepsilon_B - f_A(\varepsilon_A - \varepsilon_B)}$$

- Particles in continuous matrix (often amorphous)
- No percolation threshold
- Can be extended by incorporating information from pair distribution function

- Bruggeman (BR) theory

$$f_A \frac{\varepsilon_A - \bar{\varepsilon}}{\varepsilon_A + 2\bar{\varepsilon}} + (1 - f_A) \frac{\varepsilon_B - \bar{\varepsilon}}{\varepsilon_B + 2\bar{\varepsilon}} = 0$$

- Random mixtures of A and B
- Percolation threshold f_c=1/3 for spheres
- Different for other shapes
- If RUC's are coated spheres: f_c=0.50

Physical interpretation

- Mixture of metal and insulator nanocrystals: Random distribution – **BR theory**. Not good close to f_c, which should be at ~0.15.
- Insulator crystallites << metal ones: They will preferentially be situated between the metal particles, and hence f_c increases.
- Metal nanocrystals and amorphous insulator: Metal particles preferentially coated by insulator. **MG theory** is a good approximation at low f, and we have a high f_c

Rigorous bounds on complex ε

- Wiener bounds: Only ε_A and ε_B known

$$\bar{\varepsilon} = f_A\varepsilon_A + f_B\varepsilon_B \qquad \bar{\varepsilon}^{-1} = f_A\varepsilon_A^{-1} + f_B\varepsilon_B^{-1}$$

- Arcs/lines in the complex plane encompassing an allowed region
- Hashin-Shtrikman bounds: Also f_A and f_B known

$$\bar{\varepsilon} = \varepsilon_B \frac{L\varepsilon_A + (1-L)\varepsilon_B + (1-L)f_A(\varepsilon_A - \varepsilon_B)}{L\varepsilon_A + (1-L)\varepsilon_B - Lf_A(\varepsilon_A - \varepsilon_B)}$$

$0 \le L \le 1$

$$\bar{\varepsilon} = \varepsilon_A \frac{L\varepsilon_B + (1-L)\varepsilon_A + (1-L)f_B(\varepsilon_B - \varepsilon_A)}{L\varepsilon_B + (1-L)\varepsilon_A - Lf_B(\varepsilon_B - \varepsilon_A)}$$

Bounds for isotropic materials

- More narrow bounds still (Bergman-Milton)

$$\bar{\varepsilon} = \frac{\varepsilon_A \varepsilon_B + 2\varepsilon_h (f_A \varepsilon_A + f_B \varepsilon_B)}{2\varepsilon_h + f_A \varepsilon_B + f_B \varepsilon_A}$$

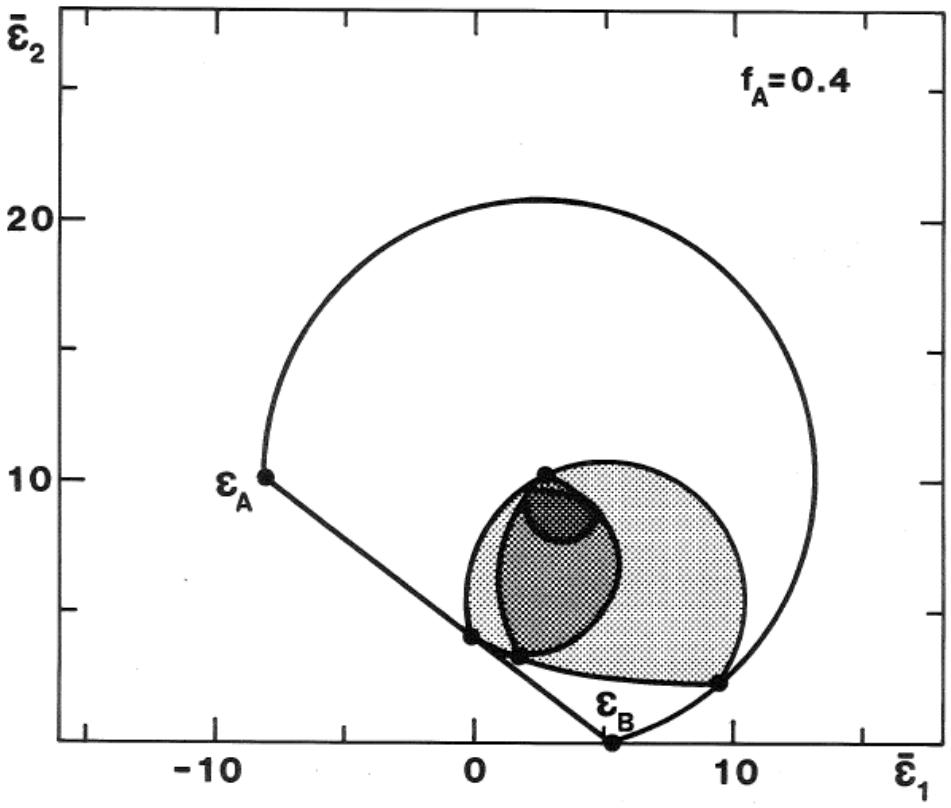
$$\varepsilon_h = x\varepsilon_A + (1-x)\varepsilon_B \quad or$$

$$\varepsilon_h^{-1} = x\varepsilon_A^{-1} + (1-x)\varepsilon_B^{-1}$$

- The parameter x ($0 \leq x \leq 1$) can be obtained from integrals over the pair and three-point distribution functions of the composite
- If x is known – another set of bounds and so on…

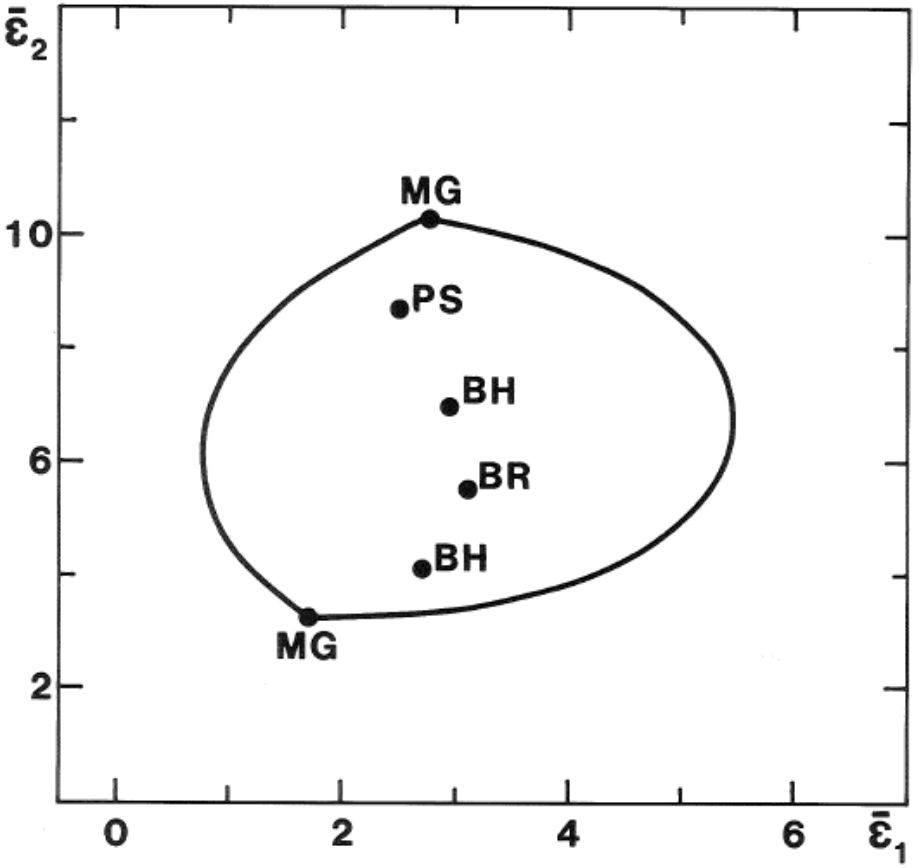
Example of bounds

- ε_A and ε_B given
- Wiener bounds
- HS bounds (anisotropic in general)
- BM bounds (isotropy)
- Next order bounds with x=0.1



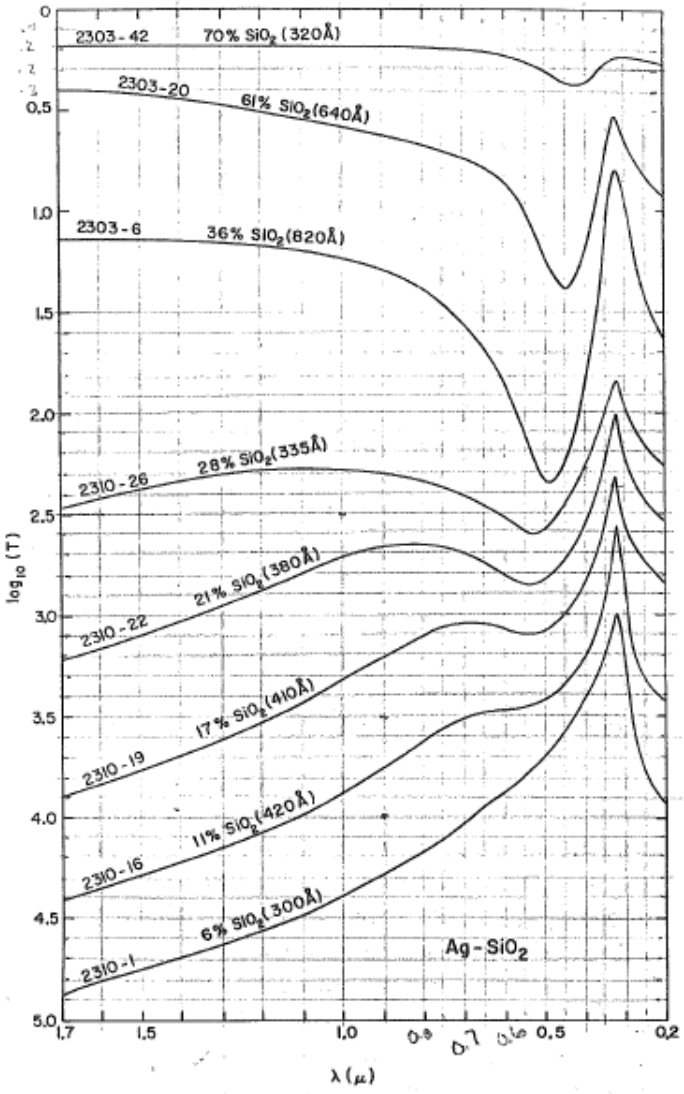
Isotropic materials

- Isotropic bounds and some EMT's
- Input values as in previous figure
- MG – Maxwell Garnett
- BR – Bruggeman
- PS – Ping Sheng (BR for coated spheres)
- BH - Bruggeman-Hanai



Exp: Transmittance

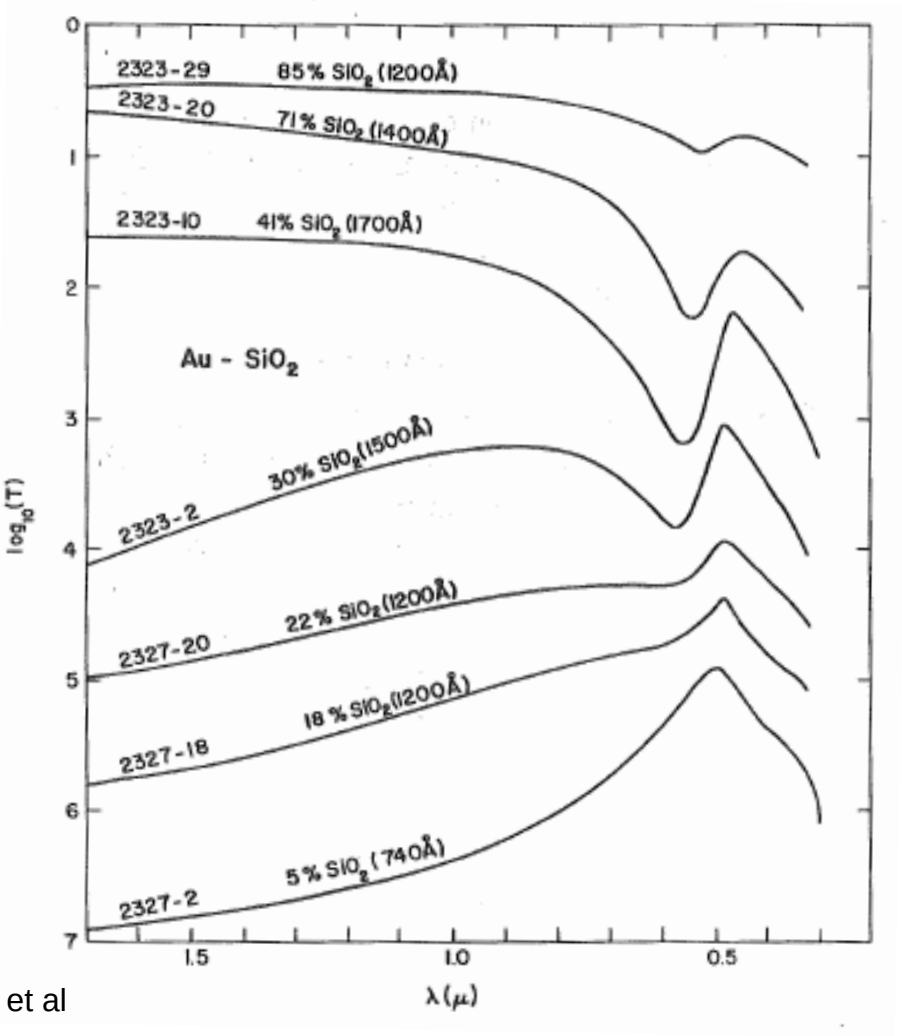
- Clear-cut case: Noble metal composites
- Ex: Ag- SiO_2
- Metallic behaviour: <25 % SiO_2
- Dielectric behaviour: >35 % SiO_2
- Localized plasmon (LP) absorption at λ ~ 400-500 nm
- Sharp LP predicted by MG theory



Source: Abeles et al

Ex: Au-SiO_2

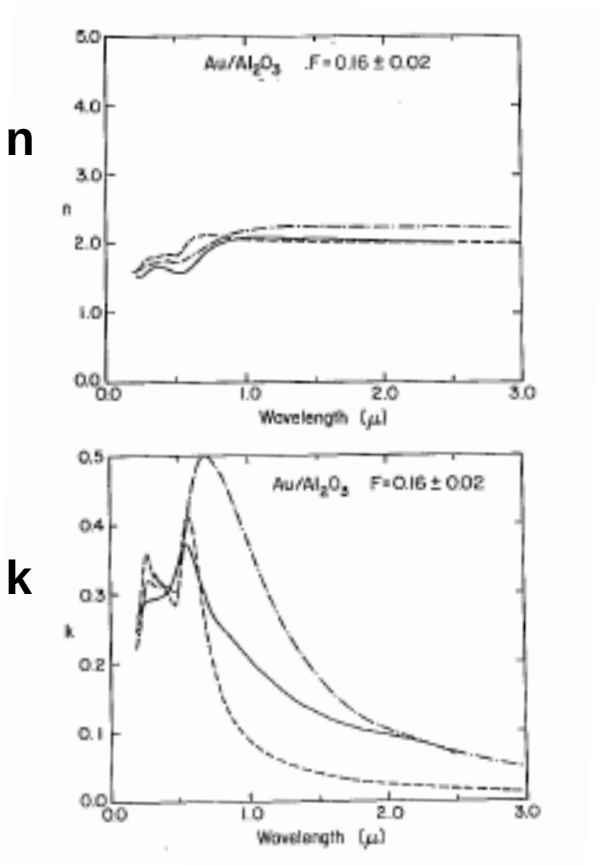
- Dielectric and metallic regions
- Metal-insulator transition around f_{Au}~0.6 to 0.7
- Localized plasma absorption at 500-600 nm
- Diminishes in the metallic region
- Percolation threshold higher than most theories predict (PS at ~0.5 may be OK)



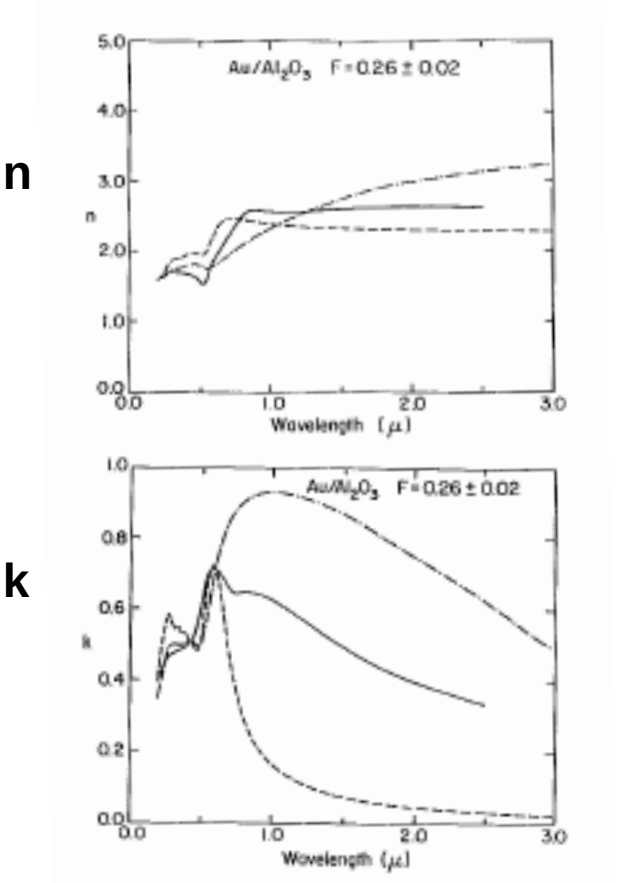
Source: Abeles et al

Exp: Dielectric function

- Au-Al_2O_3 (amorphous)
- $\varepsilon=(n+ik)^2$



Exp-full line
MG-dash
BR-dash-dot

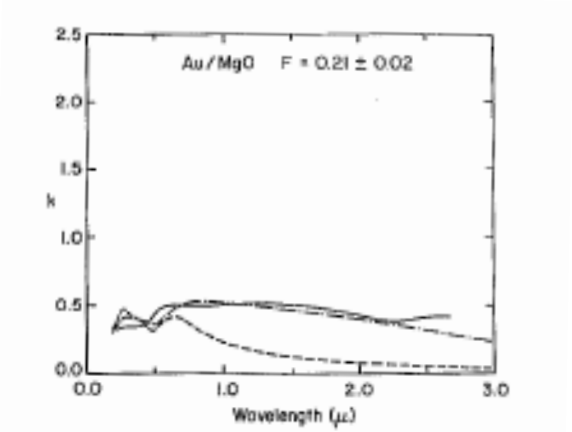


Source:Craighead and Sievers

Ex: Au-MgO

- Mixture of nanocrystals
- $\varepsilon=(n+ik)^2$

n



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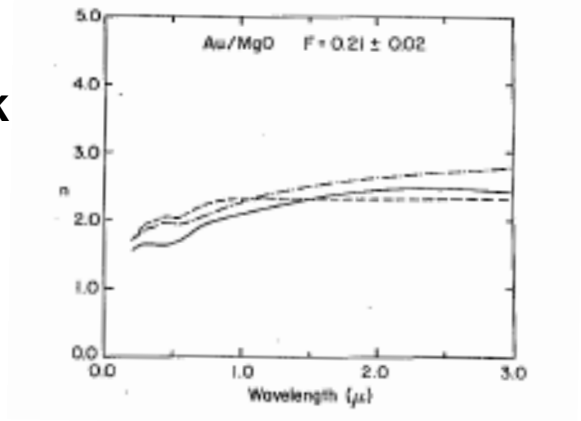
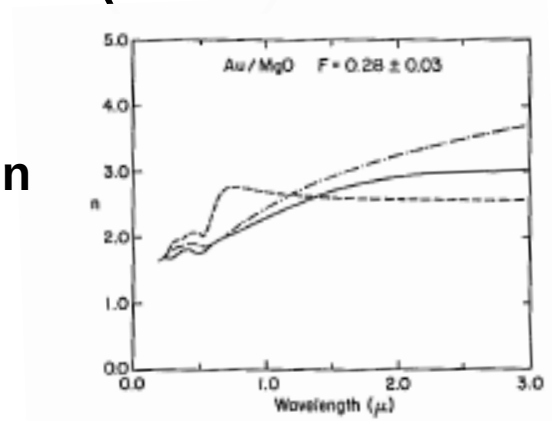


Exp-full line
MG-dash
BR-dash-dot

n



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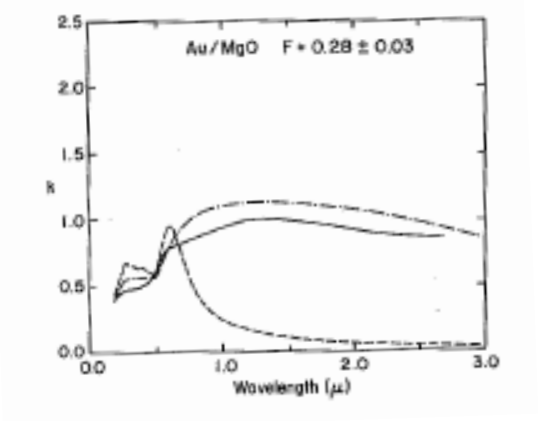
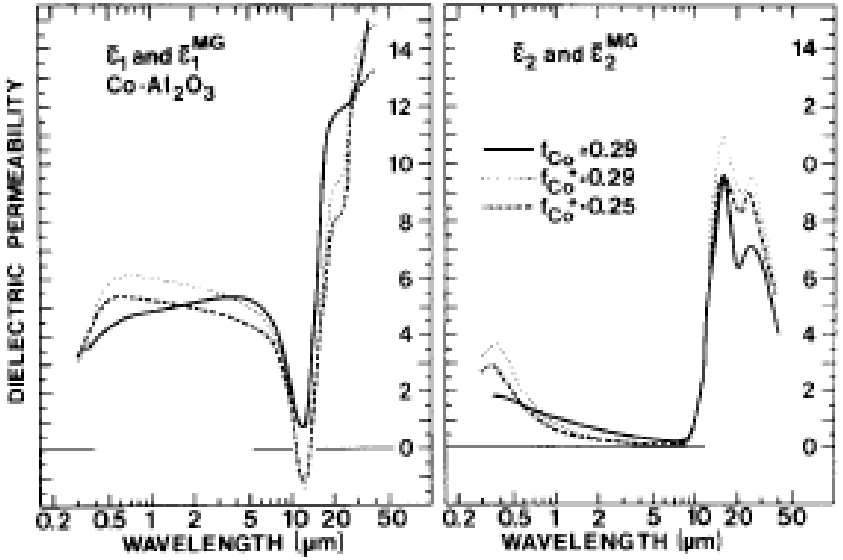
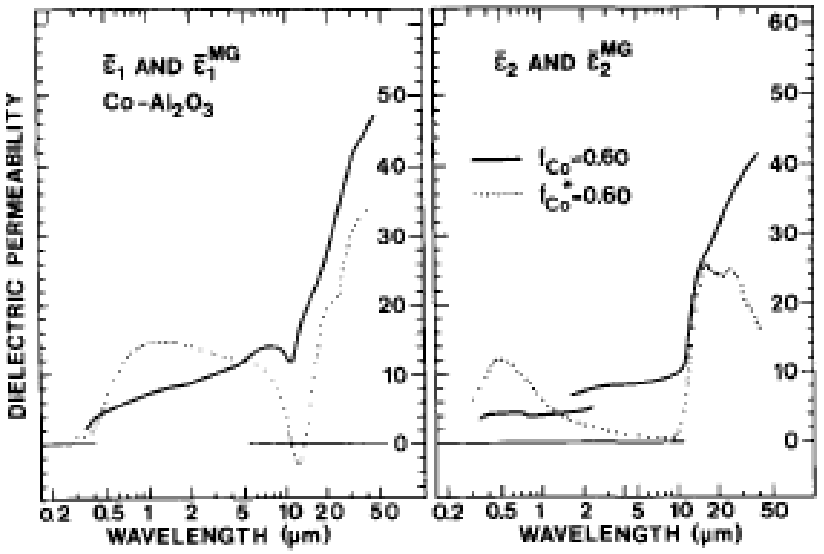


Source:Craighead and Sievers

Ex: Co-Al_2O_3

- Small f: MG quite good
- Vis-NIR-IR data





Transition region

- The distinction between MG and BR type composites is very useful for the dielectric region at low f.
- EMT's do not give a good description of the percolation region: Difficult to model exp f_c and critical exponents are not correct in BR theory
- Close to f_c the percolation correlation length can be $>\lambda$ and then the effective medium concept will fail.
- "Optical percolation": Descriptions with scaling theories, fractal impedance networks or general LCR networks have been attempted.

Bergman's spectral density

- It is possible to decouple the effect of nanostructure on the dielectric function from the properties of the phases A and B

$$\bar{\varepsilon} = \varepsilon_B \left(1 + \int_0^1 \frac{g(x)}{(\varepsilon_B / (\varepsilon_A - \varepsilon_B)) + x} dx\right)$$

- Sum rules for the spectral density g(x)

$$g(0) + \int_{0^+}^{1} g(x)dx = f_A \qquad \int_0^1 x g(x)dx = (1 - f_A)L$$

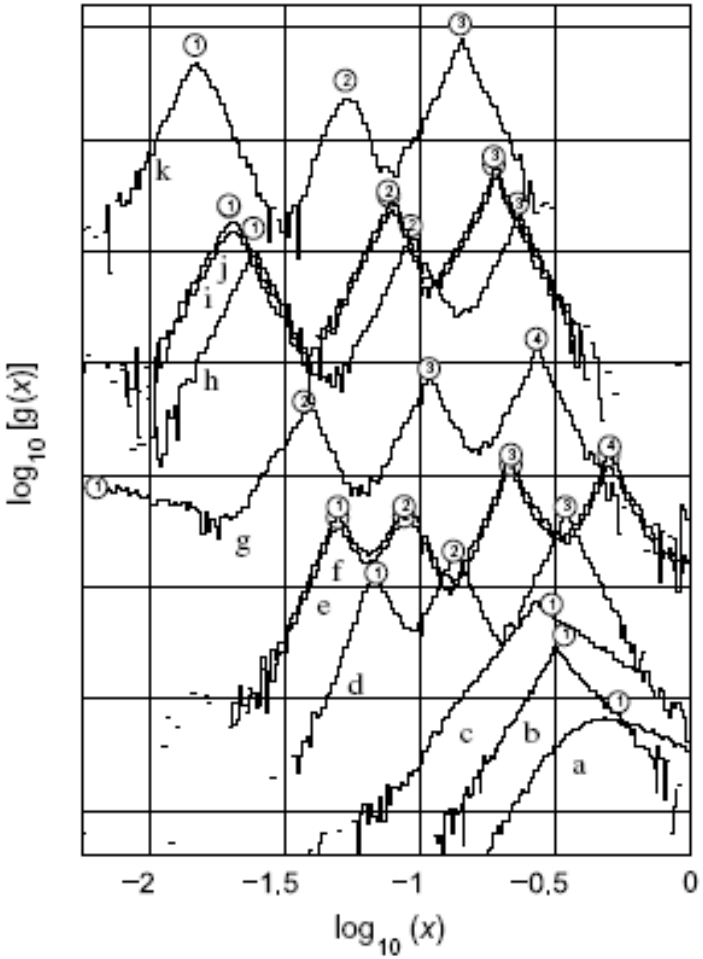
- We have separated out the percolation strength g(0)
- But relation between g(x) and nanostructure not known!

Spectral density function (SDF)

- This relation is in principle ”exact” and g(x) is determined by the detailed nanostructure.
- The SDF g(x) can only be computed if the nanostructure is known exactly
- Even so it is not known how to compute it, except in simple cases
- It is however possible to obtain g(x) from inversion of experimental data (dielectric function from R,T or ellipsometry) in a wide wavelength range
- Exp. data sensitive to g(x) when the real part of ε_A is negative and its absolute value is larger than that of the imaginary part

Ex: Co-Al_2O_3 composite

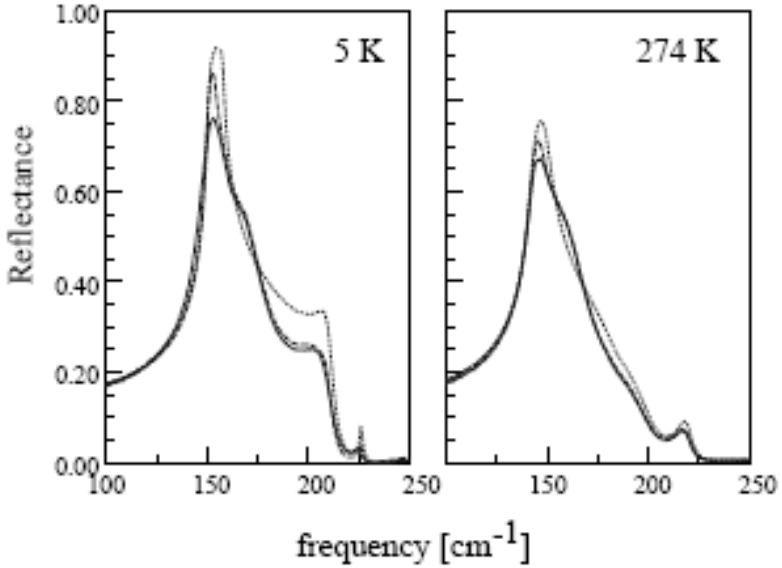
- From R and T measurements: 300 nm < λ < 2500 nm
- Volume fractions of Co, f: a:0.03, b:0.07, c:0.12, d:0.19, e:0.25, f:0.26, g:0.37, h:0.52, i:0.56, j:0.57, k:0.71.
- Low f: Peak corresponding to almost spherical particles
- f>0.15: Three or four peaks (structural resonances)
- Percolation strength cannot be reasonably estimated from optical data



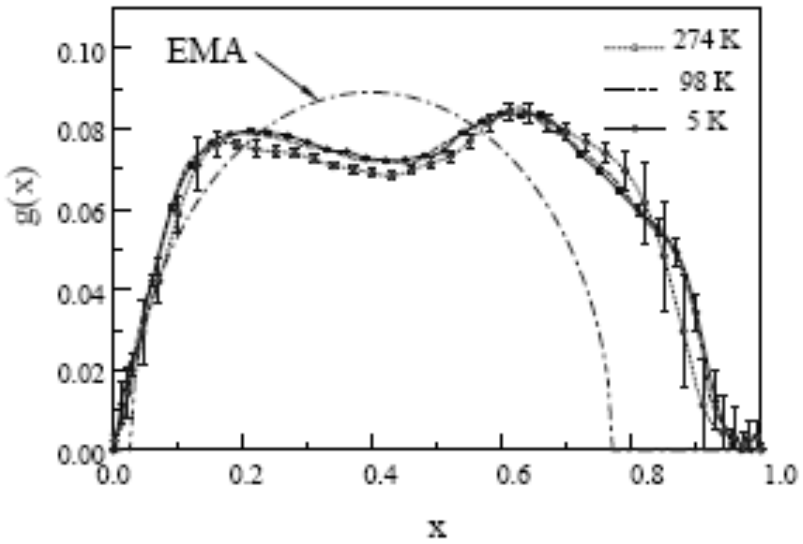
Source: Tuncer and Niklasson

Ex: KCl-diamond composite

- 20 % Diamond
- IR reflectance



- SDF compared to Bruggeman theory
- x g(x) is plotted



Source: Day and Sievers

A general effective medium theory?

- Use description of nanostructure in terms of local density distributions and local percolation probabilities
- Generalization of Bruggeman theory:

$$\int_0^1 \left[\lambda(f,L)\frac{\varepsilon_c(f)-\bar{\varepsilon}}{\varepsilon_c(f)+2\bar{\varepsilon}} + (1-\lambda(f,L))\frac{\varepsilon_{nc}(f)-\bar{\varepsilon}}{\varepsilon_{nc}(f)+2\bar{\varepsilon}}\right]\mu(f,L)df = 0$$

- Evaluate for L where the entropy function has a minimum
- Percolating cells – index c
- Non-percolating cells – index nc
- L → 0: Usual Bruggeman expression
- L→ infinity: No L-dependence; replace f by <f>
- Percolation threshold determined by λ(f,L) or λ(<f>)

Some applications

- Selectively solar absorbing coatings for solar collectors: Transition metal particles in an insulator matrix, high f (~0.5)
- Modeling of rough surfaces, e.g. in ellipsometry
- Columnar structures or ”sculptured” thin films: Extension of EMT’s to anisotropic structures
- High voltage insulation – field grading materials
- C-black and C-fiber composites (electrical properties)
- Thermal insulation
- Porous materials: Geological applications, cement