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):

\[ \overline{\varepsilon} = f_A \varepsilon_A + f_B \varepsilon_B \]

- 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
  \[ \bar{\varepsilon} = f_A \varepsilon_A + f_B \varepsilon_B \]

- Series capacitors
  \[ \bar{\varepsilon}^{-1} = f_A \varepsilon_A^{-1} + f_B \varepsilon_B^{-1} \]
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$_2$O$_3$ 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-Al₂O₃ composites**

- Steep rise at $f \sim 0.2$ to $0.3$
- Connected with the tunneling contribution
- The temperature coefficient of resistance changes sign at $f \sim 0.7$
- Smooth crossover between tunneling and metallic conduction
Tunneling between metal particles

- Electron tunneling – the particles become charged
- Charging energy ($s \sim r$)
  \[ E_c = \frac{e^2}{4\pi\varepsilon_0\varepsilon_i} \frac{s}{s + r} \sim \frac{C}{s} \]
- Low applied fields
  \[ \sigma = \sigma_0 \exp(-2\alpha s - E_c / k_B T) \]
- Max of $\sigma$ 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$_2$O$_3$

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, $f_c$

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

• Percolation theory: Frequency dependence

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

- Critical exponents (theory)
  - $t = 1.9 \pm 0.1$
  - $s = 0.73 \pm 0.01$
  - $u = \frac{t}{t+s} = 0.72 \pm 0.02$
- 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 $\mathbf{E}$- and $\mathbf{H}$-fields are almost constant over a length of the order of a particle size.
- Materials treated as homogeneous on length scales $\sim \lambda$.
- Quasistatic approximation (electrostatics sufficient for small particles).
- Basis of effective medium theories (EMT).
Spheres in continuous matrix

- Consider dielectric function (permittivity)
- Static case ($\omega=0$)
- Quasistatic approx:
- Can be extended to frequency dependent case as long as
  \[ \text{max (n)} \frac{2\pi r}{\lambda} \ll 1 \]
  where max (n) is the largest of the refractive indices

- Particles of A in matrix B
- Electric field
  \[ E_A = E_B + E_p = E_B - \frac{P}{3\varepsilon_0} \]
- Compare the average fields $E_{av}$ and $D_{av}$
- The effective dielectric permittivity is given as
  (Maxwell, 1872)
  \[ \bar{\varepsilon} = \frac{D_{av}}{E_{av}} \]
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 $\varepsilon$
• 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: $S(\text{coated sphere})=0$
• Bruggeman: $f_A S_A(\text{sphere}) + f_B S_B(\text{sphere}) = 0$
• Rule of thumb: $r \ll \frac{\lambda}{20}$
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 $\sim 0.15$.
• 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 $\varepsilon$

- Wiener bounds: Only $\varepsilon_A$ and $\varepsilon_B$ known
  \[
  \overline{\varepsilon} = \int_A \varepsilon_A + \int_B \varepsilon_B \quad \overline{\varepsilon^{-1}} = \int_A \varepsilon_A^{-1} + \int_B \varepsilon_B^{-1}
  \]

- Arcs/lines in the complex plane encompassing an allowed region

- Hashin-Shtrikman bounds: Also $f_A$ and $f_B$ known

\[
\overline{\varepsilon} = \varepsilon_B \frac{L\varepsilon_A + (1 - L)\varepsilon_B + (1 - L)f_A(\varepsilon_A - \varepsilon_B)}{L\varepsilon_A + (1 - L)\varepsilon_B - Lf_A(\varepsilon_A - \varepsilon_B)}
\]

\[
\overline{\varepsilon} = \varepsilon_A \frac{L\varepsilon_B + (1 - L)\varepsilon_A + (1 - L)f_B(\varepsilon_B - \varepsilon_A)}{L\varepsilon_B + (1 - L)\varepsilon_A - Lf_B(\varepsilon_B - \varepsilon_A)}
\]

$0 \leq L \leq 1$
Bounds for isotropic materials

• More narrow bounds still (Bergman-Milton)

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

\[
\varepsilon_h = x \varepsilon_A + (1-x) \varepsilon_B \quad \text{or}
\]

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

• 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

- $\varepsilon_A$ and $\varepsilon_B$ 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- SiO₂
- Metallic behaviour: <25 % SiO₂
- Dielectric behaviour: >35 % SiO₂
- Localized plasmon (LP) absorption at $\lambda \sim 400$-500 nm
- Sharp LP predicted by MG theory

Source: Abeles et al
Ex: Au-SiO$_2$

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

Source: Abeles et al
Exp: Dielectric function

- Au-Al$_2$O$_3$ (amorphous)
- $\varepsilon=(n+ik)^2$

Source: Craighead and Sievers
Ex: Au-MgO

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

Source: Craighead and Sievers
Ex: Co-Al$_2$O$_3$

- 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

\[ \bar{\varepsilon} = \varepsilon_B (1 + \int_0^1 \frac{g(x)}{(\varepsilon_B/(\varepsilon_A - \varepsilon_B)) + x} \, dx) \]

- Sum rules for the spectral density \( g(x) \)

\[ g(0) + \int_0^1 g(x) \, dx = f_A \]
\[ \int_0^1 xg(x) \, dx = (1 - f_A) L \]

- 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 \( \varepsilon_A \) is negative and its absolute value is larger than that of the imaginary part.
Ex: Co-Al$_2$O$_3$ composite

- From R and T measurements: $300 \text{ nm} < \lambda < 2500 \text{ nm}$
- 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
- \( x \cdot g(x) \) 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 \( \lambda(f, L) \) or \( \lambda(<f>) \)
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