Effective medium approach to inhomogeneous systems (hetero-/nanostructures)

v. 2
11.5.2021

Josef Humlíček, humlicek@physics.muni.cz

- Linear optical response: bulk and nanostructured materials

- Average fields and effective permittivity for small contrast

    3D, 2D and 1D systems

- Established mixing rules

- Tests of EMA:

    macroscopic scale (glass spheres in liquids)

    ↓

    molecular scale (water solutions of sucrose)

- Differences between mixing rules for binary dielectric mixtures

- EMA and exact solutions for layered structures

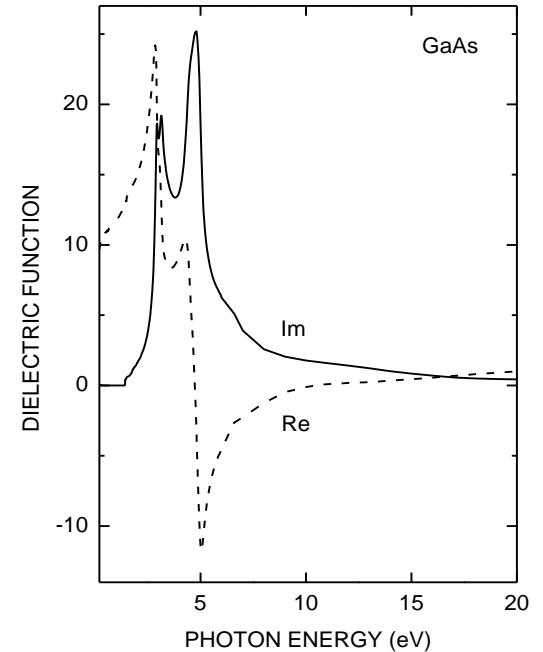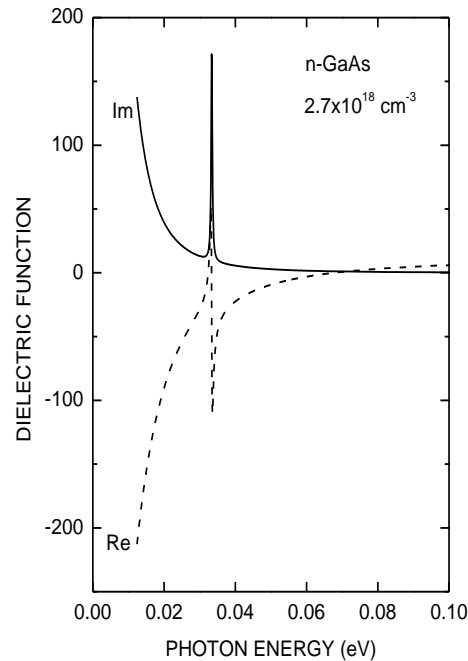- Resonant behavior of EMA mixtures, example of negative refraction

Linear optical response of bulk

electrons, phonons, ... optical response functions, complex ε, σ, N in the long-wavelength limit

$\lambda >> a$
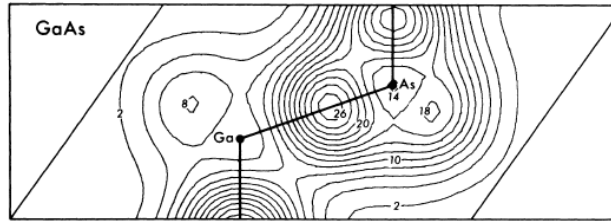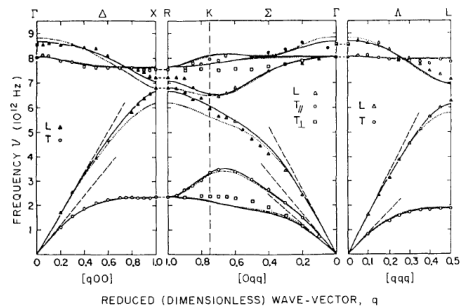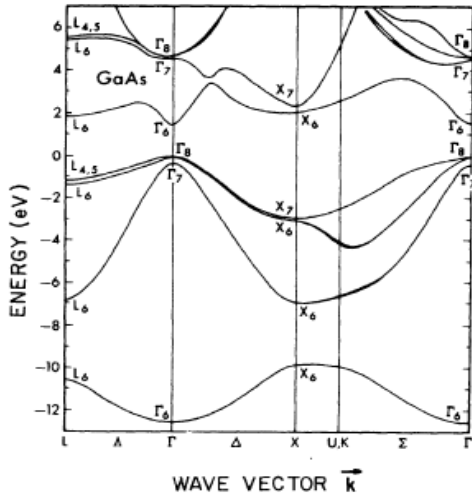
doped GaAs

(nano)structured media

layers, thicknesses << wavelength
e.g., multiple quantum wells
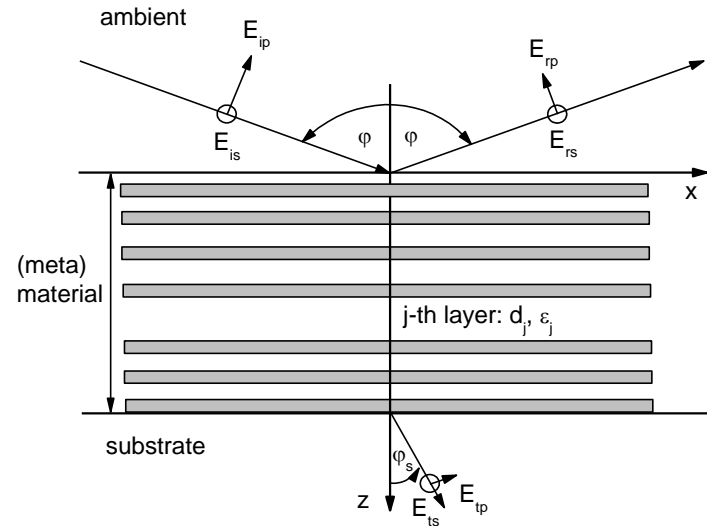
inclusions, dimensions << wavelength
e.g., ensembles of quantum dots or wires
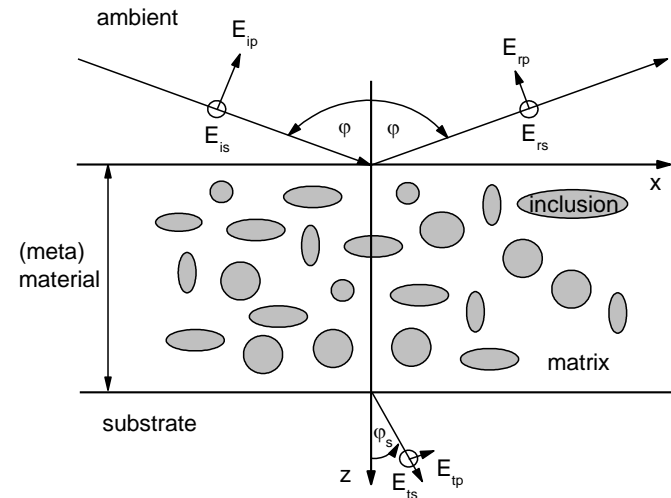
a continuum with
effective permittivity

$$\langle \boldsymbol{D} \rangle = \varepsilon_{eff} \langle \boldsymbol{E} \rangle$$

(nano)structured media

Example: multilayers in AlGaN/GaN/AlGaN/Aln/Si HEMTS

metamaterials in buffers between AlGaN/GaN channel and AlN/Si substrate, studied in IR

(nano)structured media

building up the screening charges,
planar interfaces
two limiting cases

E_{ext}

(∥)   (⊥)
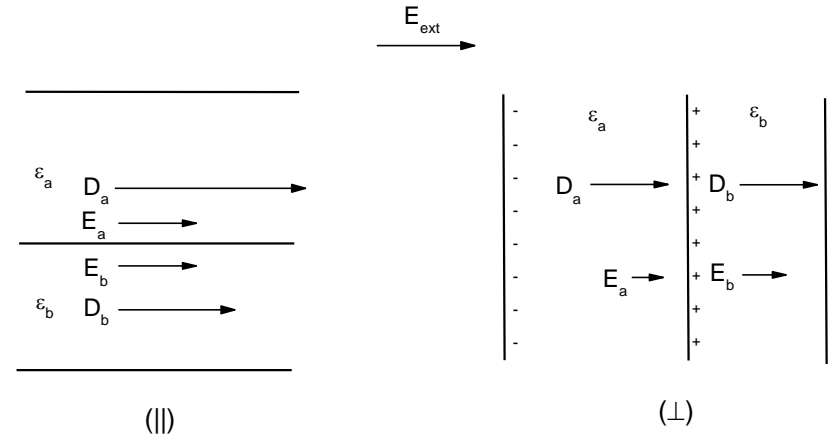
$$\varepsilon_{eff} = \langle\varepsilon\rangle = (1-f)\varepsilon_a + f\varepsilon_b.$$

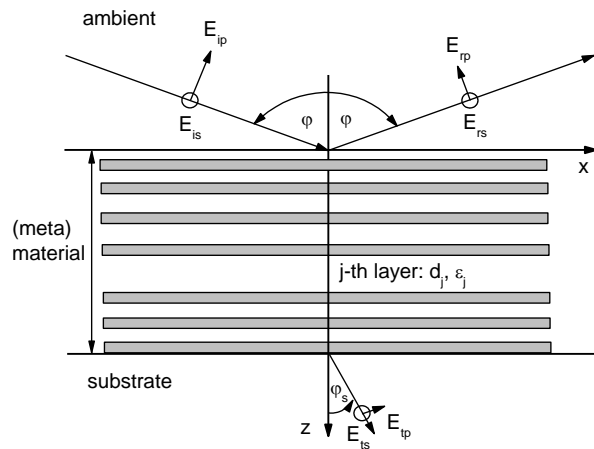$$1/\varepsilon_{eff} = (1-f)/\varepsilon_a + f/\varepsilon_b.$$

curved interfaces, sphere (ellipsoids)
sparsely distributed in a matrix

Maxwell-Garnett – the nanotechnology of 1904
J.C.M. Garnett, Philos. Trans. R. Soc. Lond. 203, 385 (1904)
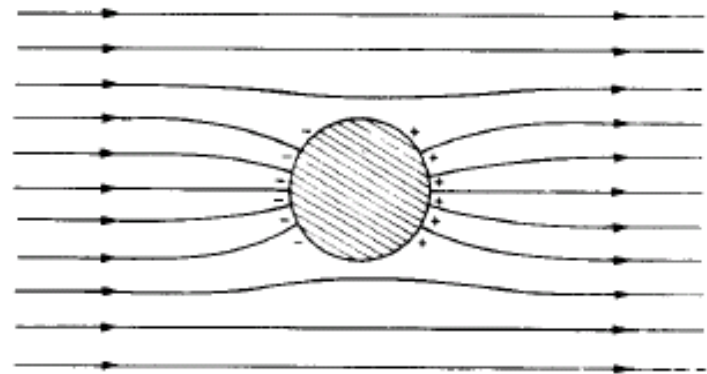
$$\varepsilon_{eff} = \frac{\langle D\rangle}{\langle E\rangle} = \varepsilon_a + f(\varepsilon_b - \varepsilon_a)\frac{3\varepsilon_a}{\varepsilon_b + 2\varepsilon_a - f(\varepsilon_b - \varepsilon_a)}.$$

A general results for small contrast

LLL – Landau, Livshitz, Looyenga

The average field quantities,

$$\langle \boldsymbol{D} \rangle = \varepsilon_{eff} \langle \boldsymbol{E} \rangle,$$

calculated for a general mixture with a **small difference of the permittivities** of the components (Landau-Livshitz, Electrodynamics of continuous media):

$$\boldsymbol{E}(\boldsymbol{r}) = \langle \boldsymbol{E} \rangle + \delta \boldsymbol{E}(\boldsymbol{r}), \quad \varepsilon(\boldsymbol{r}) = \langle \varepsilon \rangle + \delta \varepsilon(\boldsymbol{r}).$$

Neglecting higher-order terms in Taylor expansions leads to

$$\langle \varepsilon^{1/3} \rangle^3 = \langle (\langle \varepsilon \rangle + \delta \varepsilon)^{1/3} \rangle^3 \approx \langle \varepsilon \rangle - 3 \langle \varepsilon \rangle \frac{1 \cdot 2}{3 \cdot 6} \frac{\langle (\delta \varepsilon)^2 \rangle}{\langle \varepsilon \rangle^2},$$

i.e., the "LL" formula

$$\varepsilon_{eff} = \langle \varepsilon \rangle - \frac{\langle (\delta \varepsilon)^2 \rangle}{3 \langle \varepsilon \rangle}.$$

This can be further approximated by

$$\varepsilon_{eff} = \langle \varepsilon^{1/3} \rangle^3,$$

which was derived in a different way by Looyenga (1965); the "LL(L)" formula.

A general results for small contrast

LLL – Landau, Livshitz, Looyenga

LLL (called usually Looyenga) is very popular biochemistry/biology environment:
• very simple and easy to handle,
• the optical contrast in the (complex) mixtures is typically small.

The (3D) averaging of LL can be fairly easily repeated in reduced dimensions:

$$\varepsilon_{eff} = \langle \varepsilon \rangle - \frac{\langle (\delta \varepsilon)^2 \rangle}{D \langle \varepsilon \rangle},$$

where D =3, 2, 1 for the 3D, 2D, and 1D mixtures, respectively.

Interestingly, for $D=1$ (lamellar structure with fields perpendicular to interfaces):

$$\varepsilon_{eff}\big|_{1D} = \langle \varepsilon^{-1} \rangle^{-1}.$$

This is exact for the long-wavelength averaging for general lamellar structures, not restricted to the low contrast of constituents.

A general results for small contrast

LLL – Landau, Livshitz, Looyenga

For binary mixtures with the volume fraction *f* of the components *a* and *b*:

$$f_a = V_a /(V_a + V_b), \ f_b = V_b /(V_a + V_b) = 1 - f_a \equiv f.$$

The average permittivity:

$$\langle \varepsilon \rangle = (1 - f)\varepsilon_a + f\varepsilon_b = \varepsilon_a + f(\varepsilon_b - \varepsilon_a),$$

the deviations from the mean:

$$\delta\varepsilon_a = \varepsilon_a - \langle \varepsilon \rangle = f(\varepsilon_a - \varepsilon_b), \quad \delta\varepsilon_b = \varepsilon_b - \langle \varepsilon \rangle = (1 - f)(\varepsilon_b - \varepsilon_a),$$

the mean of the squared deviation:

$$\langle (\delta\varepsilon)^2 \rangle = (1 - f)(\delta\varepsilon_a)^2 + f(\delta\varepsilon_b)^2 = f(1 - f)(\varepsilon_b - \varepsilon_a)^2,$$

and the LL formula:

$$\varepsilon_{eff} = \varepsilon_a + f(\varepsilon_b - \varepsilon_a) - \frac{f(1 - f)(\varepsilon_b - \varepsilon_a)^2}{D[\varepsilon_a + f(\varepsilon_b - \varepsilon_a)]}.$$

Examples of established mixing rules

Some of them implicit:

(e.g., solution of quadratic equation for Bruggeman and CPA)

Table 3.1 Effective medium rules for binary mixtures

Effective medium	ε_{eff}	f
Layer stack, planes parallel to E	$(1-f)\varepsilon_a + f\varepsilon_b$	$\dfrac{\varepsilon_{eff}-\varepsilon_a}{\varepsilon_b-\varepsilon_a}$
Layer stack, planes perp. to E	$\dfrac{\varepsilon_a\varepsilon_b}{(1-f)\varepsilon_b + f\varepsilon_a}$	$\dfrac{\varepsilon_{eff}-\varepsilon_a}{\varepsilon_b-\varepsilon_a}\dfrac{\varepsilon_b}{\varepsilon_{eff}}$
LLL (small contrast)	$[(1-f)\varepsilon_a^{1/3} + f\varepsilon_b^{1/3}]^3$	$\dfrac{\varepsilon_{eff}^{1/3}-\varepsilon_a^{1/3}}{\varepsilon_b^{1/3}-\varepsilon_a^{1/3}}$
Maxwell Garnett (dilute spheres)	$\varepsilon_a + f(\varepsilon_b-\varepsilon_a)\dfrac{3\varepsilon_a}{\varepsilon_b+2\varepsilon_a - f(\varepsilon_b-\varepsilon_a)}$	$\dfrac{\varepsilon_{eff}-\varepsilon_a}{\varepsilon_b-\varepsilon_a}\dfrac{\varepsilon_b+2\varepsilon_a}{\varepsilon_{eff}+2\varepsilon_a}$
Rayleigh (dilute cylinders)	$\varepsilon_a + f(\varepsilon_b-\varepsilon_a)\dfrac{2\varepsilon_a}{\varepsilon_b+\varepsilon_a - f(\varepsilon_b-\varepsilon_a)}$	$\dfrac{\varepsilon_{eff}-\varepsilon_a}{\varepsilon_b-\varepsilon_a}\dfrac{\varepsilon_b+\varepsilon_a}{\varepsilon_{eff}+\varepsilon_a}$
Maxwell Garnett (dilute aligned ellipsoids)	$\varepsilon_a + f(\varepsilon_b-\varepsilon_a)\dfrac{\varepsilon_a}{\varepsilon_a+L(1-f)(\varepsilon_b-\varepsilon_a)}$	$\dfrac{\varepsilon_{eff}-\varepsilon_a}{\varepsilon_b-\varepsilon_a}\dfrac{\varepsilon_a+L(\varepsilon_b-\varepsilon_a)}{\varepsilon_a+L(\varepsilon_{eff}-\varepsilon_a)}$
Bruggeman (spheres)	$2\varepsilon_{eff}^2 + \varepsilon_{eff}[(3f-2)\varepsilon_a + (1-3f)\varepsilon_b] - \varepsilon_a\varepsilon_b = 0$	$\dfrac{\varepsilon_{eff}-\varepsilon_a}{\varepsilon_b-\varepsilon_a}\dfrac{\varepsilon_b+2\varepsilon_{eff}}{3\varepsilon_{eff}}$
CPA (spheres)	$3\varepsilon_{eff}^2 + \varepsilon_{eff}[4(f-1)\varepsilon_a + (1-4f)\varepsilon_b] - (1-f)\varepsilon_a(\varepsilon_b-\varepsilon_a) = 0$	$\dfrac{\varepsilon_{eff}-\varepsilon_a}{\varepsilon_b-\varepsilon_a}\dfrac{3\varepsilon_{eff}+\varepsilon_b-\varepsilon_a}{4\varepsilon_{eff}-\varepsilon_a}$

The volume fraction of the component a is $1-f$, that of the component b is f. L is the depolarization factor of Eq. (3.30). For the Bruggeman and CPA models the effective permittivity results from the solution of the quadratic equation given in the table

Example: glass spheres in CCl_4

Measurements of Reynolds (Thesis, London 1955)
of glass spheres dispersed in carbon tetrachloride, quoted by Looyenga

long-wavelength limit - low frequencies (≤1 GHz, λ_{vac} ≥ 300 cm)
diameter of the glass beads ≤ 1 mm

TABLE I

Measurements of J. A. Reynolds (Thesis, London 1955), quoted by Van Beek[1]); Glass spheres ($\varepsilon_2 = 4.594$) dispersed in carbon tetrachloride ($\varepsilon_1 = 2.228$)

| v_2	dielectric constant			
	exp.	eq. (1)	eq. (2)	eq. (17)
0.05	2.317	2.317	2.317	2.320
0.10	2.411	2.409	2.410	2.415
0.15	2.510	2.503	2.506	2.513
0.20	2.611	2.601	2.605	2.613
0.25	2.714	2.702	2.708	2.716
0.30	2.824	2.806	2.814	2.821
0.35	2.949	2.913	2.924	2.929

Example: glass spheres in CCl$_4$

The slightly bowed composition dependence follows the predictions of various variants of EMA
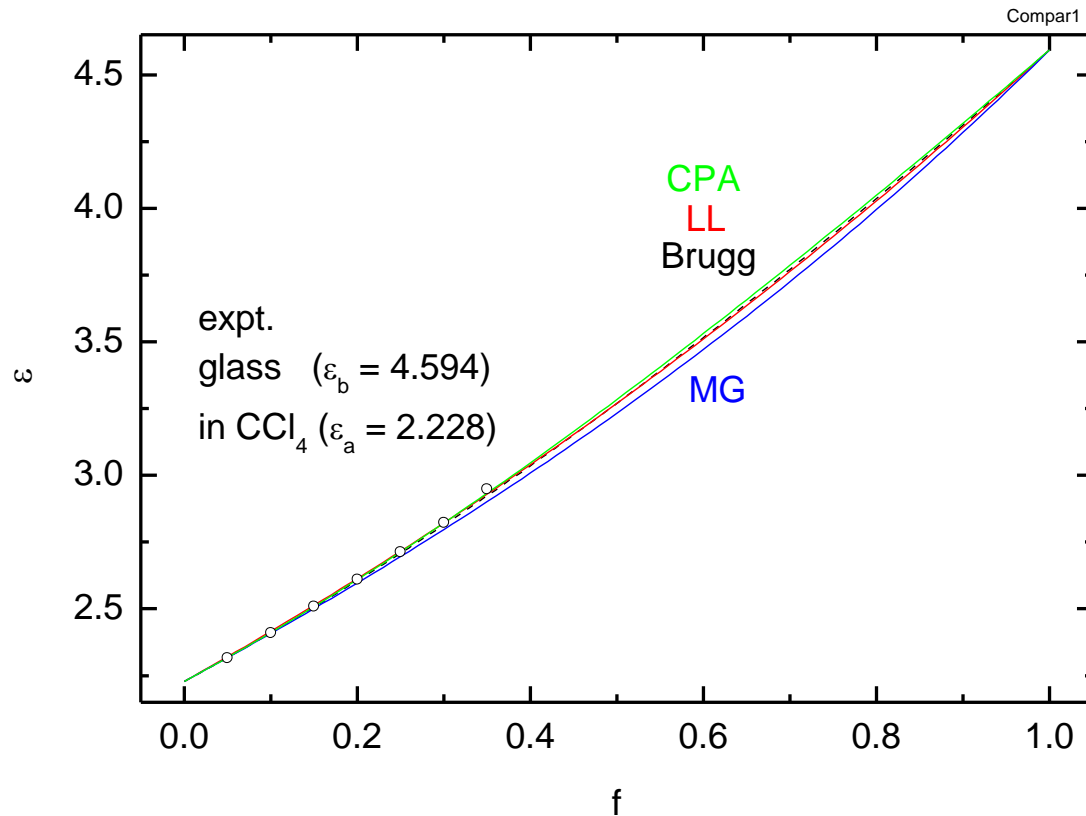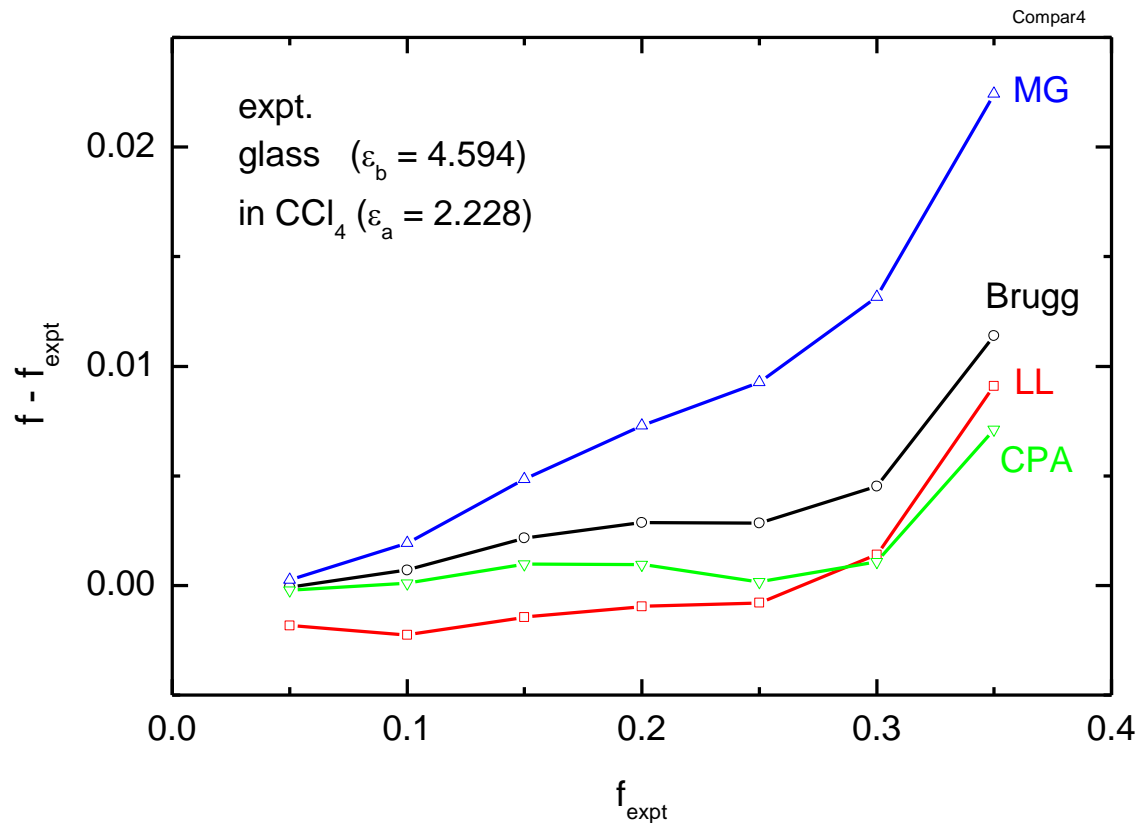
Example: glass spheres in CCl$_4$

A closer look at the deviations from measured values:
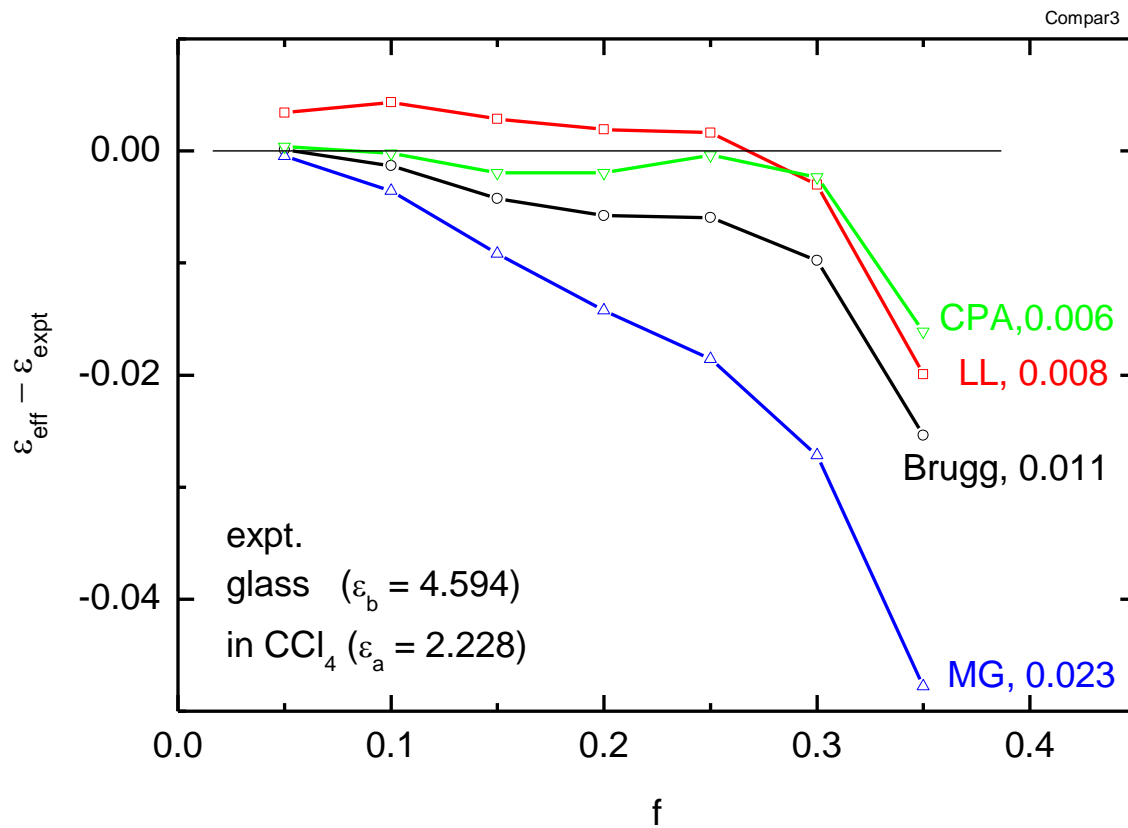
Example: glass spheres in CCl_4

The typical use of EMA is an estimation of the volume fractions

how do different mixing formulae perform in the case of the known concentrations?

Example: water solution of sucrose

Feynman, Leighton, Sands: The Feynman Lectures on Physics, Vol. 2 (Addison-Wesley, Reading, 1964)
§32-5 "The index of a mixture"

invokes Clausius-Mossotti relation for the effect of local field on induced dipoles

32–5 The index of a mixture

There is another prediction of our theory of the index of refraction that we can check against experiment. Suppose we consider a mixture of two materials. The index of the mixture is not the average of the two indexes, but should be given in terms of the sum of the two polarizabilities, as in Eq. (32.34). If we ask about the index of, say, a sugar solution, the total polarizability is the sum of the polarizability of the water and that of the sugar. Each must, of course, be calculated using for N the number per unit volume of the molecules of the particular kind. In other words, if a given solution has N_1 molecules of water, whose polarizability is α_1, and N_2 molecules of sucrose ($C_{12}H_{22}O_{11}$), whose polarizability is α_2, we should have that

$$3\left(\frac{n^2 - 1}{n^2 + 2}\right) = N_1\alpha_1 + N_2\alpha_2. \qquad (32\ 37)$$

Example: water solution of sucrose

Space filling model of the sucrose ($C_{12}H_{22}O_{11}$) molecule
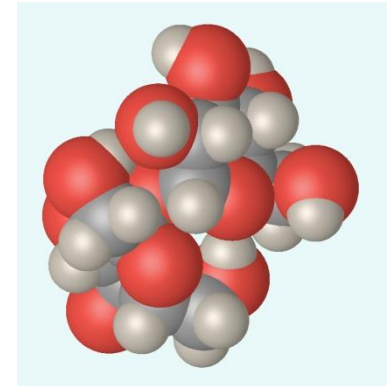
Feynman, Leighton, Sands: The Feynman Lectures on Physics, Vol. 2 (Addison-Wesley, Reading, 1964)

§32-5 "The index of a mixture"

Table 32–2

Refractive index of sucrose solutions, and comparison with predictions of Eq. (32.37).

Data from Handbook

A	B	C	D	E	F	G	H	J
Fraction of sucrose by weight	density (gm/cm^3)	n at 20°C	Moles of sucrose[d] per liter, N_2/N_0	Moles of water[e] per liter, N_1/N_0	$3\left(\dfrac{n^2-1}{n^2+2}\right)$	$N_1\alpha_1$	$N_2\alpha_2$	$N_0\alpha_2$ (gm/liter)
0[a]	0.9982	1.333	0	55.5	0 617	0 617	0	—
0.30	1.1270	1.3811	0.970	43.8	0 698	0.487	0.211	0 213
0.50	1.2296	1.4200	1.798	34 15	0.759	0.379	0.380	0 211
0 85	1.4454	1.5033	3.59	12 02	0.886	0.1335	0.752	0 210
1.00[b]	1.588	1.5577[c]	4 64	0	0.960	0	0.960	0.207

[a] pure water
[c] average (see text)
[e] molecular weight of water = 18

[b] sugar crystals
[d] molecular weight of sucrose = 342

Example: water solution of sucrose, density data (no optics)

Extensive data available (importance in food industry)

International Critical Tables of Numerical Data, Physics, Chemistry and Technology, First Electronic Edition (Knovel, Norwich, New York 2003). Vol. 2, pp. 334-355.

Measurements of the density (mass per unit volume), masses/molecule and concentrations:

$$\rho = \frac{N_w m_w + N_s m_s}{V} = c_w m_w + c_s m_s,$$

The total volume V is shared by the *apparent volumes*, $V = V_w + V_s$;

assuming the apparent volume of the water molecule to be that of the pure water having the density ρ_w (the better the more dilute the solution is):

$$V_s = \frac{N_w m_w + N_s m_s}{\rho} - \frac{N_w m_w}{\rho_w}.$$

Using the mass fraction of sugar (independent of temperature and pressure):

$$f_M = \frac{N_s m_s}{N_w m_w + N_s m_s},$$

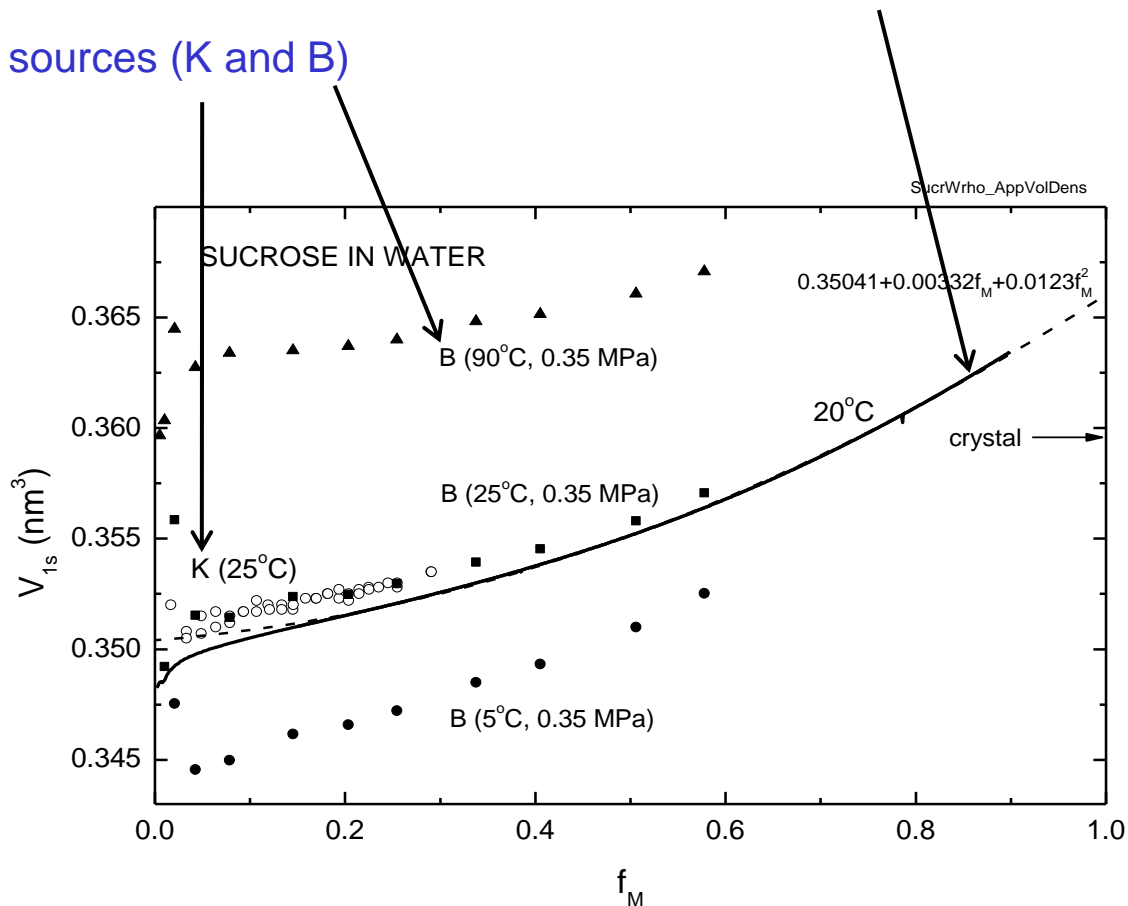we get the apparent volume of one succrose molecule, $\quad V_{1s} \equiv \frac{V_s}{N_s} = \left(\frac{1}{\rho} - \frac{1 - f_M}{\rho_w} \right) \frac{m_s}{f_M}.$

Example: water solution of sucrose, density data (no optics)

Measured apparent volume of one succrose molecule

International Critical Tables of Numerical Data, Physics, Chemistry and Technology, First Electronic Edition (Knovel, Norwich, New York 2003). Vol. 2, pp. 334-355.

Two other sources (K and B)

Example: water solution of sucrose – effective medium

Polarization of the solution in <u>optical wave</u>, EMA treatment:

the increase of apparent volume V_s with increasing mass fraction, due to the formation of voids between adjacent sucrose molecules, small enough to prevent filling with water (?) →

three components of the mixture, water, succrose and voids.

trying LLL formula for a small optical contrast;

with volume fractions of water, sugar, and voids

$$f_w, \ f_s, \ \text{and} \ f_v, \quad f_w + f_s + f_v = 1,$$

the cube root of effective permittivity of the mixture is

$$\varepsilon_{eff}^{\ 1/3} = \ \langle \varepsilon^{1/3} \rangle = f_w \varepsilon_w^{\ 1/3} + f_s \varepsilon_s^{\ 1/3} + f_v.$$

Example: water solution of sucrose

Very precise refractive index data of the solution available for the sodium line 589.3 nm, at 20C, www.icumsa.org, ICUMSA Method SPS-3 (2000), up to mass fraction of 85%; note the small level of noise (msd of 1.3E-5 from the cubic polynomial)

Voids_fvICUMSA-InvRhoF
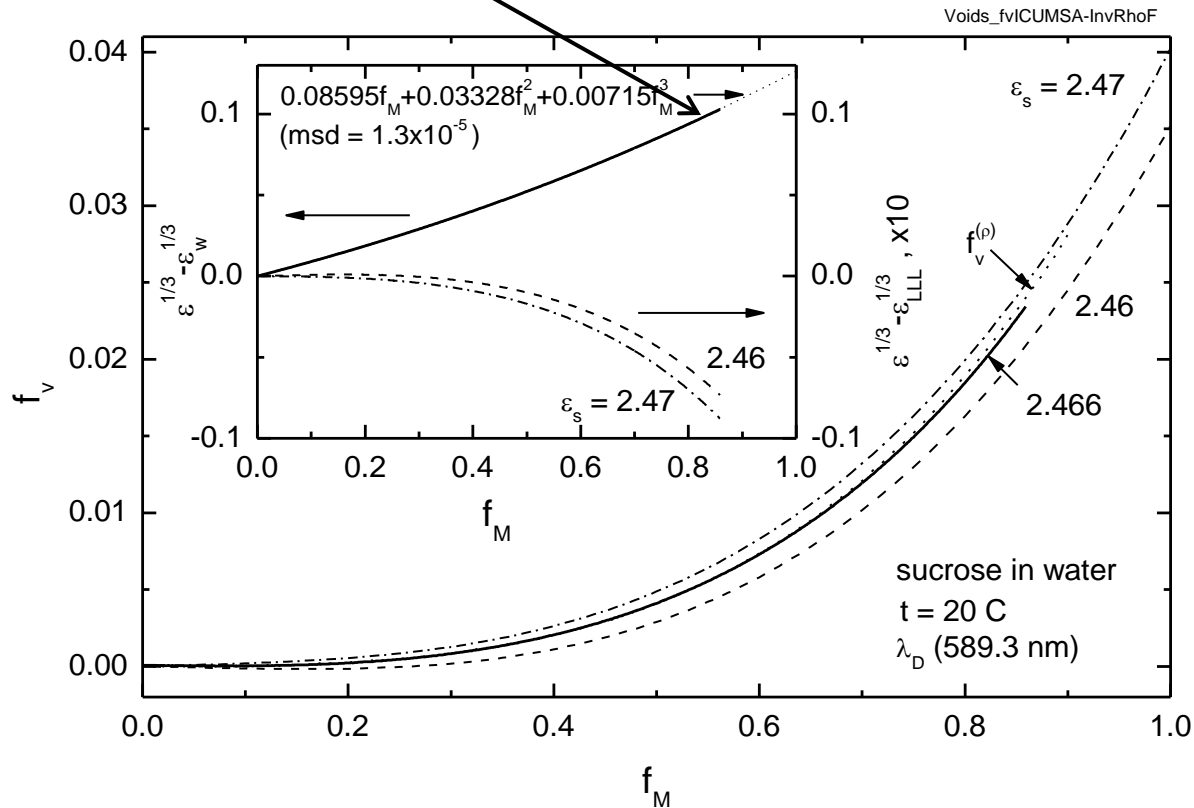
Example: water solution of sucrose

Small optical contrast,

permittivity of   1.77686 for pure water,
to   2.26196 at f_M=0.85,
$\rightarrow$ the sucrose component in EMA below about 2.5,

suggests effective ε from LL or LLL formula;
written in terms of the volume fraction of voids:

$$f_v = \frac{\varepsilon_s^{1/3} - \varepsilon^{1/3}}{\varepsilon_s^{1/3} - 1} - f_w \frac{\varepsilon_s^{1/3} - \varepsilon_w^{1/3}}{\varepsilon_s^{1/3} - 1}.$$

Note:
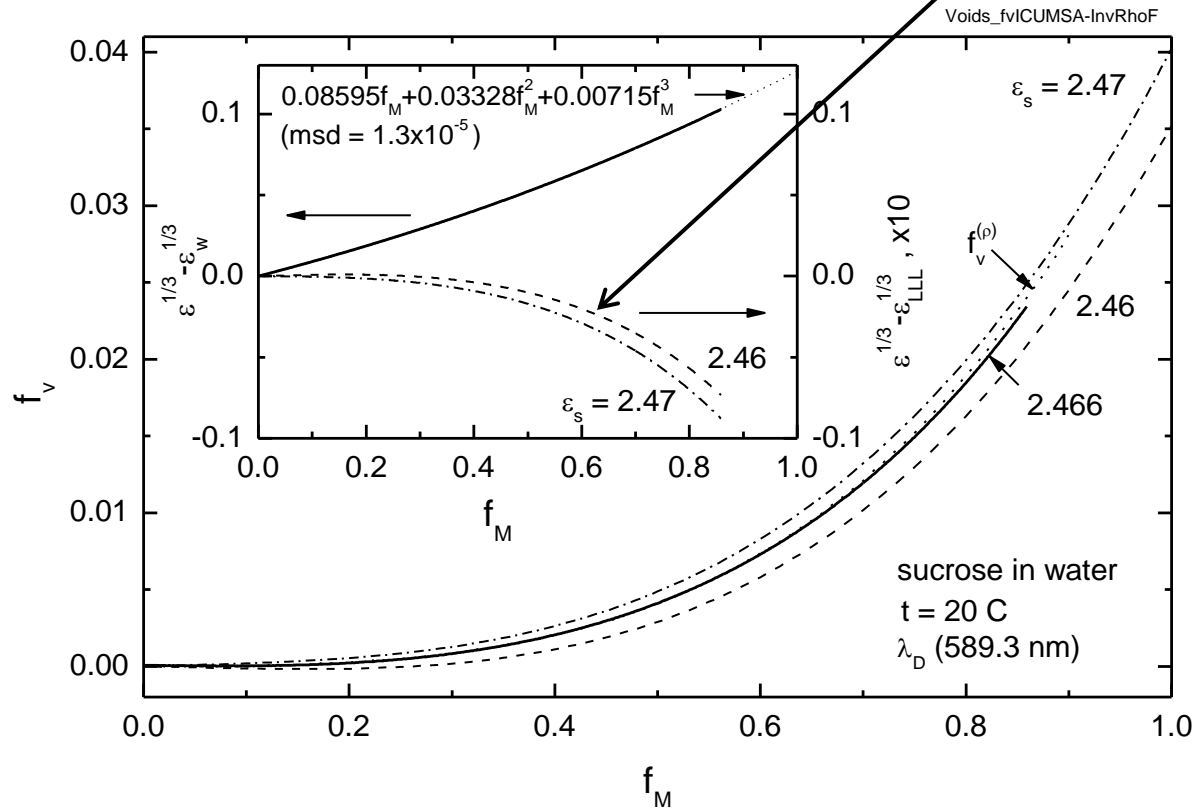ε_s is the permittivity of the hypothetical 100% sugar solution (not a crystal).

The volume fraction of water is

$$f_w = \frac{\rho}{\rho_w}(1 - f_M).$$

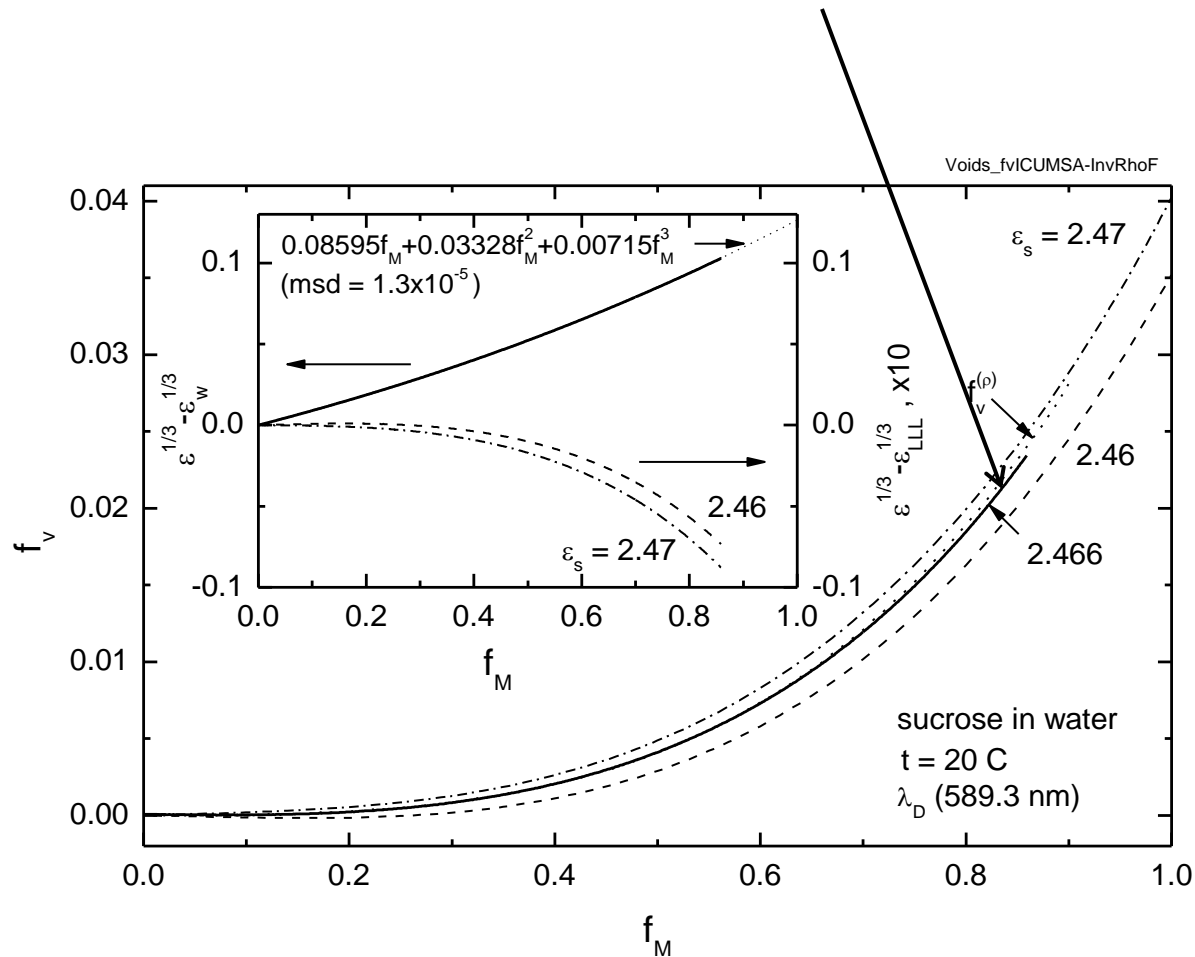# Example: water solution of sucrose

The value of ε_s :
the zero slope of the $f_v(f_M)$ dependence for $f_M \rightarrow 0$, which occurs for $\varepsilon_s = 2.466$

Example: water solution of sucrose

Test of the LLL approximation:
comparison of the volume fraction of voids with that from the density

Voids_fvICUMSA-InvRhoF

$\varepsilon_s = 2.47$

$0.08595 f_M + 0.03328 f_M^2 + 0.00715 f_M^3$
(msd = 1.3×10^{-5})

$\varepsilon^{1/3} - \varepsilon_w^{1/3}$

$\varepsilon^{1/3} - \varepsilon_{LLL}^{1/3}$, x10

$f_v^{(\rho)}$

2.46

2.466

2.46

$\varepsilon_s = 2.47$

f_M

f_v

sucrose in water
t = 20 C
λ_D (589.3 nm)

f_M

Example: water solution of sucrose

Fairly good agreement of optical data with EMA for the very small volume of the sugar molecule (0.35 nm^3 at RT) !

Confirms the basic lines of Feynman's approach, except for the use of polarizability of the succrose molecules, obtained from the average of refractive indices of (anisotropic) crystal.

Selected concerns:

- uncertainty in choosing the "EMA rule",

- oversimplified introduction of the voids
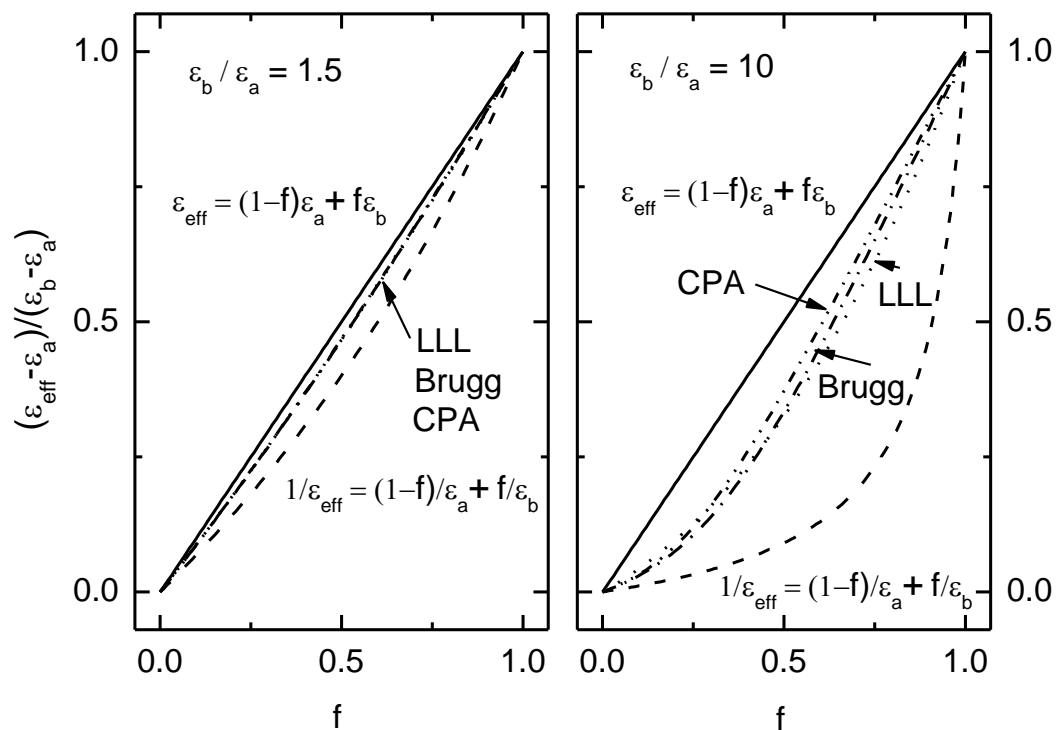   (also in the apparent free volume from the density),

- ...

Differences between mixing rules for binary dielectric mixtures

Normalized differences for real dielectric functions of *a* and b
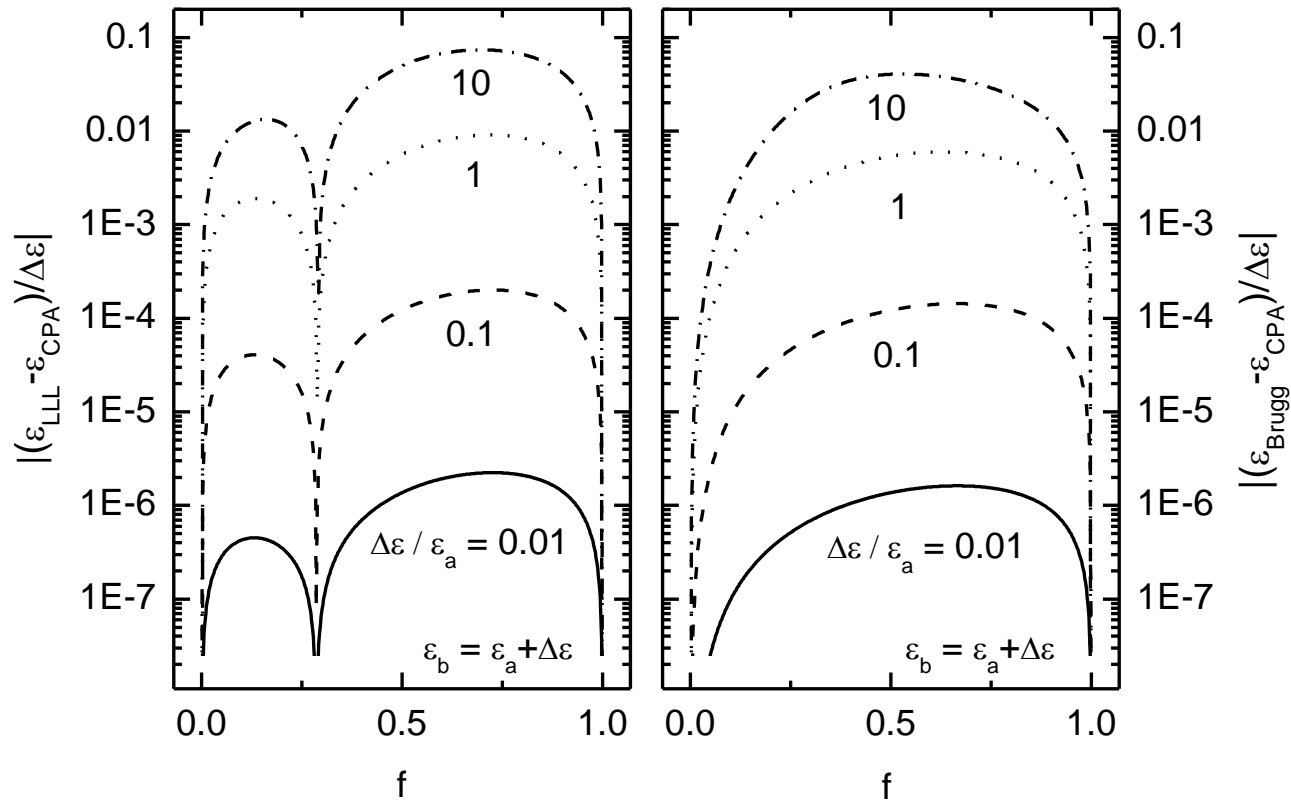planar structures (parallel and perpendicular) form Wiener bounds

small contrast
(2.466/1.777 ≈ 1.39 for sugar/water)

large contrast
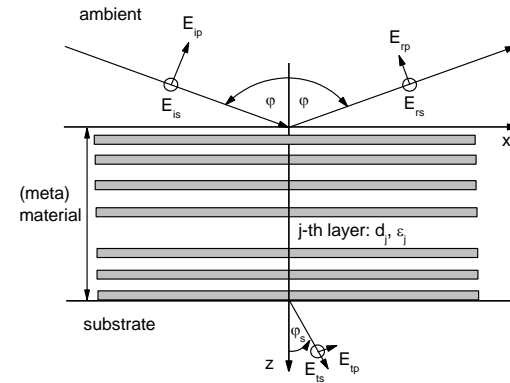(12/1 for silicon/voids in IR)

Differences between mixing rules for binary dielectric mixtures

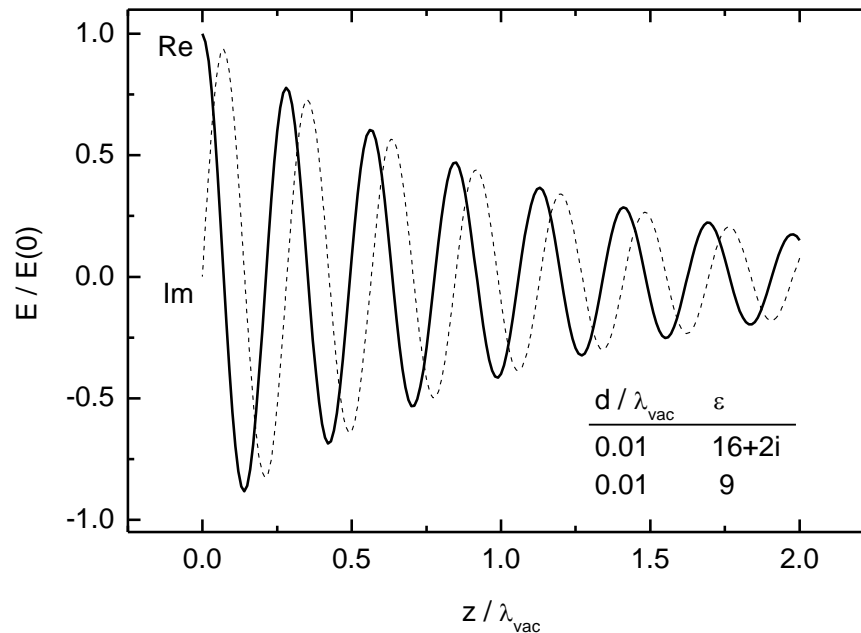comparison of LLL, Bruggeman and CPA for different contrasts

EMA and exact solutions for layered structures

planar interfaces between homogeneous slabs:

easy solutions of the wave equation (transfer matrices)

electric field inside the superlattice of absorbing/dielectric materials

d / λ_{vac}	ε
0.01	16+2i
0.01	9

EMA and exact solutions for layered structures

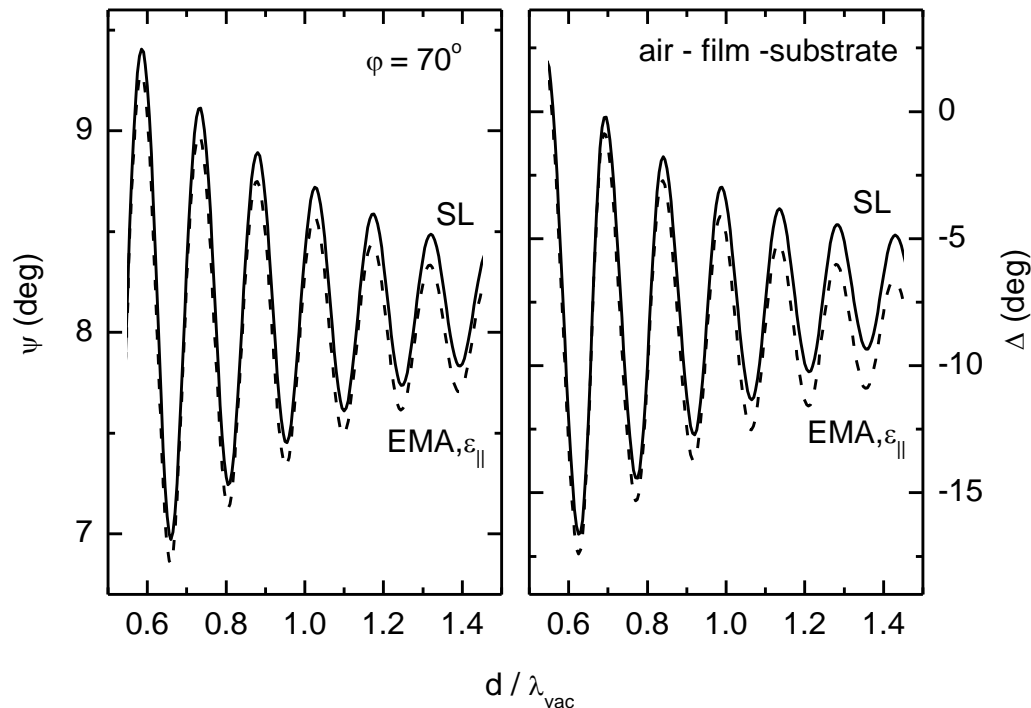oblique incidence, ellipsometric angles:
a (rather fine) superlattice of $d_1=d_2=l_{vac}/1000$
EMA for the field parallel to the interfaces
the total thickness of the film on the $\varepsilon = 6+2i$ substrate

$\rightarrow$ easily observable deviations

Resonant behavior of EMA mixtures

Spectacular behavior of the effective optical response possible,
can be traced down to the spectacular behavior of local fields.

Simple case with analytical solution:
the constant field inside an isolated ellipsoid in an infinite host medium,
easily transferrable to diluted mixtures.

The field intensity inside the ellipsoid *diverges* whenever

$$\frac{\varepsilon_b}{\varepsilon_a} = 1 - \frac{1}{L_u} \in (-\infty, 0 > .$$

L_u is the depolarization factor (semiaxes *u,v, w* of the ellipsoid)

$$L_u = \frac{uvw}{2} \int_0^\infty \frac{dt}{(t^2 + u^2)\sqrt{(t + u^2)(t + v^2)(t + w^2)}} \in \langle 0,1 \rangle$$

with the field along *u.*

Resonant behavior of EMA mixtures

In particular, the divergence occurs in

sphere:
$u=v=w$, $L_u=1/3$ for $\varepsilon_b = -2\varepsilon_a$;

cylinder:
field perpendicular to its axis
$u=v$, $w\rightarrow\infty$, $L_u=1/2$ for $\varepsilon_b = -\varepsilon_a$;
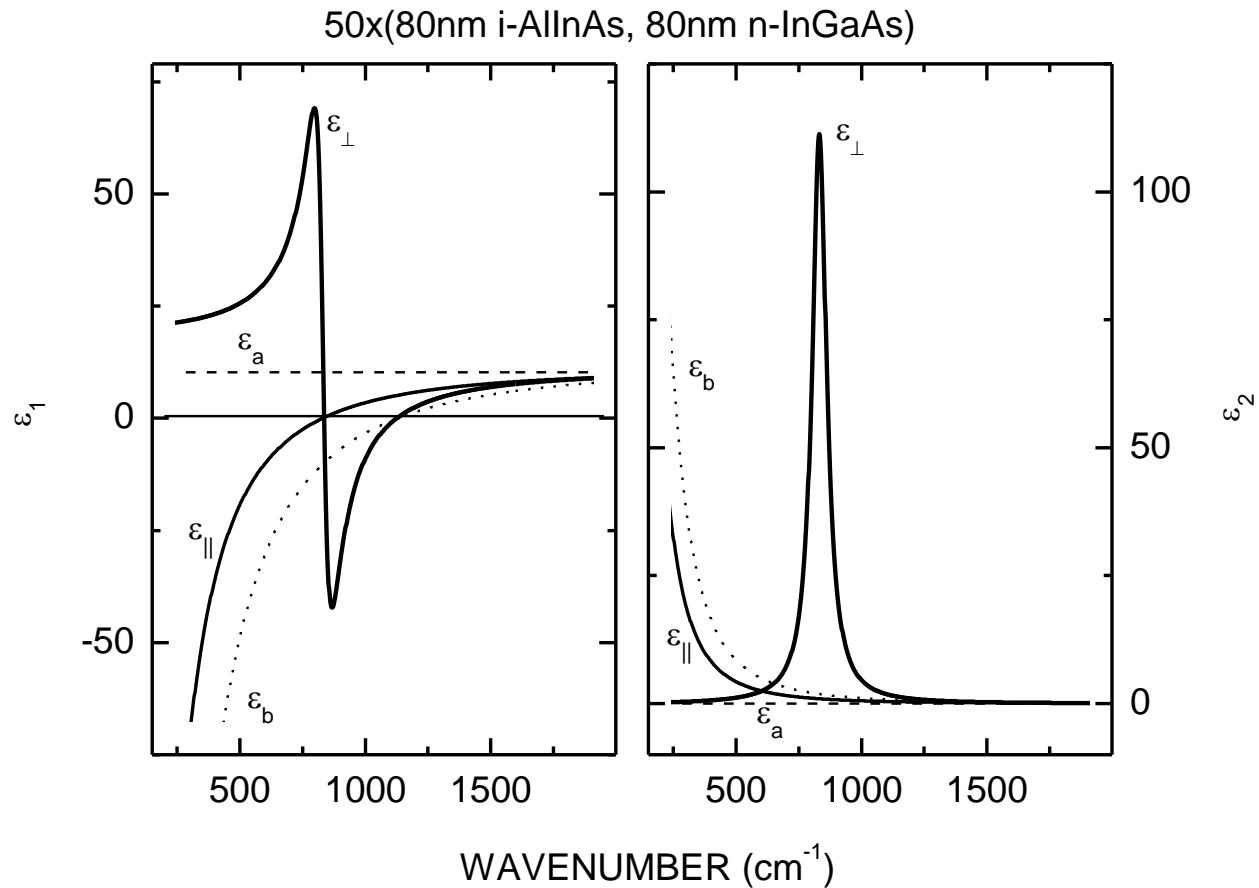
slab:
field perpendicular to the interface
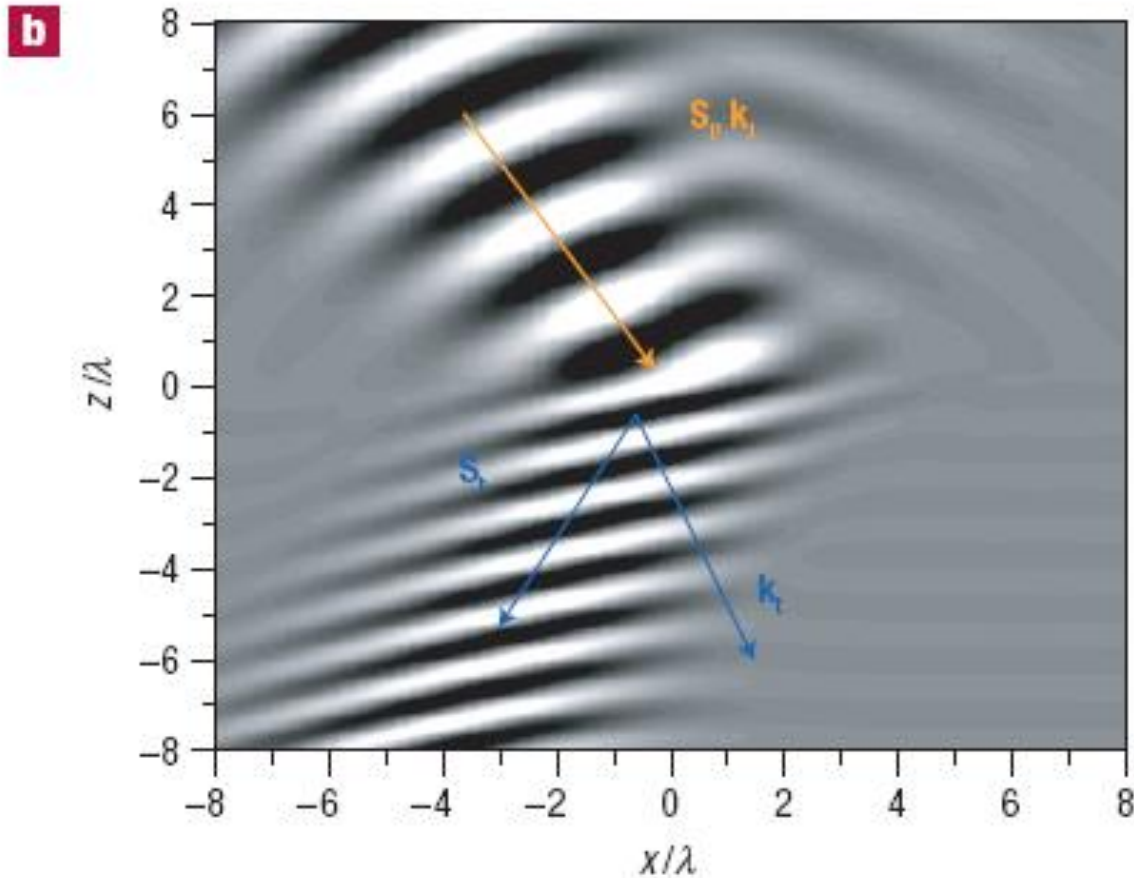$v=w\rightarrow\infty$, $L_u=1$ for $\varepsilon_b = 0$.

Resonant behavior of EMA mixtures

The IR resonance in undoped/doped SL (leading to negative refraction in a part of the IR spectrum):

50x(80nm i-AlInAs, 80nm n-InGaAs)

FDTD calculations (Hoffman et al.)

Figure 1 **Calculated dielectric function and beam refraction.** **a**, Dielectric function, $\varepsilon_\perp$ and $\varepsilon_\parallel$ of an n^+-i-n^+ heterostructure calculated using the effective medium theory and $n_d = 7.5 \times 10^{18}$ cm^{-3}. The inset shows the relative orientation of the dielectric function ($\varepsilon_\perp$ and $\varepsilon_\parallel$), the electric-field vectors (transverse electric, transverse magnetic) and the layered structure. **b**, Full numerical calculations demonstrating negative refraction of a monochromatic transverse-magnetic-polarized gaussian beam across an air–metamaterial interface. **c**, Calculations of the absorption coefficient for the transverse magnetic polarization, α_{TM}, and the figure of merit, FOM, as a function of wavelength for a metamaterial with the dielectric function shown in **a**. The portion shaded in yellow indicates the spectral region where the metamaterial exhibits negative refraction.

Directions of *E* and *D*, averaging (ε>0 in a, <0 in b)

note the flow of energy (Poynting vector p)
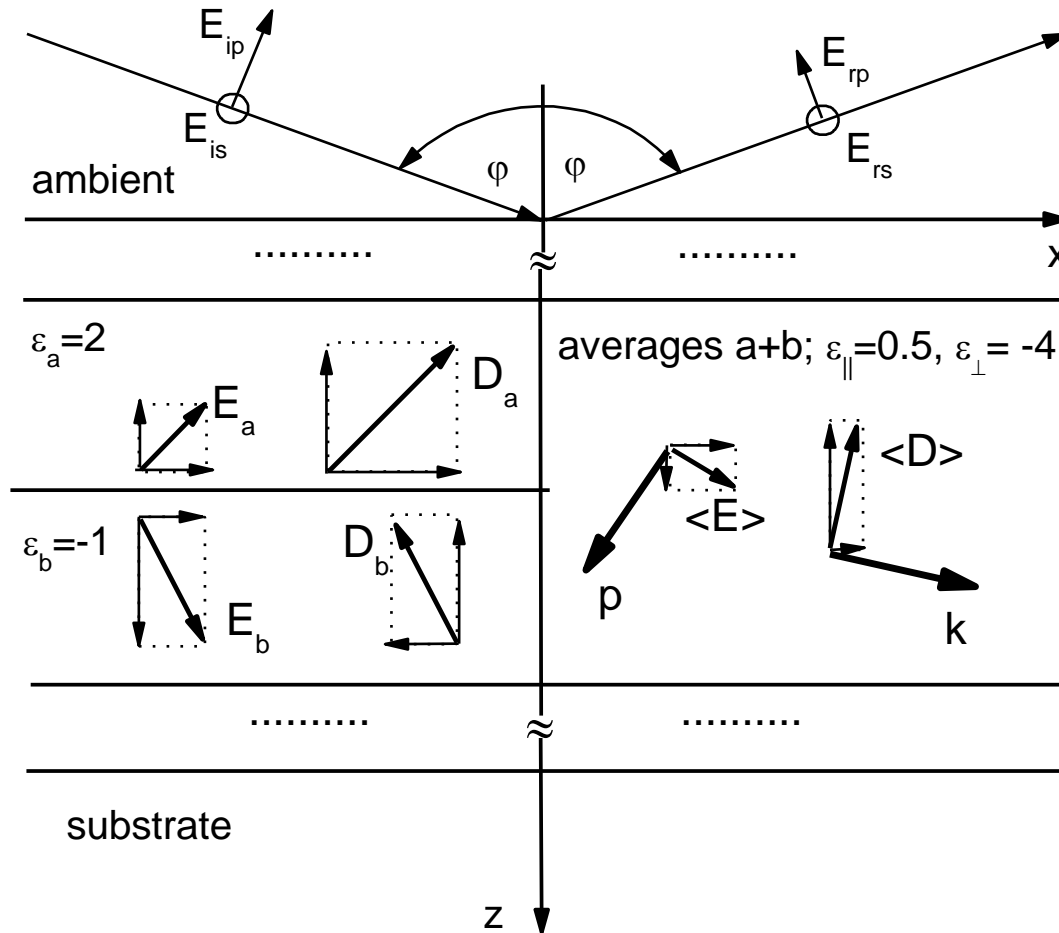
Main lessons to be taken

- EMA can be attractive and helpful.
- EMA can easily fail – if improperly used.
- <u>Using it with caution is recommended</u>.

A selection from the (vast) literature:

L.D. Landau and E.M. Lifshitz, *Electrodynamics of continuous media*, Second edition (Pergamon Press, Oxford, 1984), Sec. 9.

R.P. Feynman, R.B. Leighton, and M. Sands, *The Feynman Lectures on Physics*, Vol. II (Addison-Wesley, 1964), § 32-5.

A. Sihvola, *Electromagnetic mixing formulas and applications* (IEE, Stevenage, 1999).

D.E. Aspnes, Am. J. Phys. 50, 704 (1982).

Ellipsometry at the Nanoscale , M. Losurdo and K. Hingerl, eds., (Springer 2013).