From microphotonics to nanophotonics … and back!

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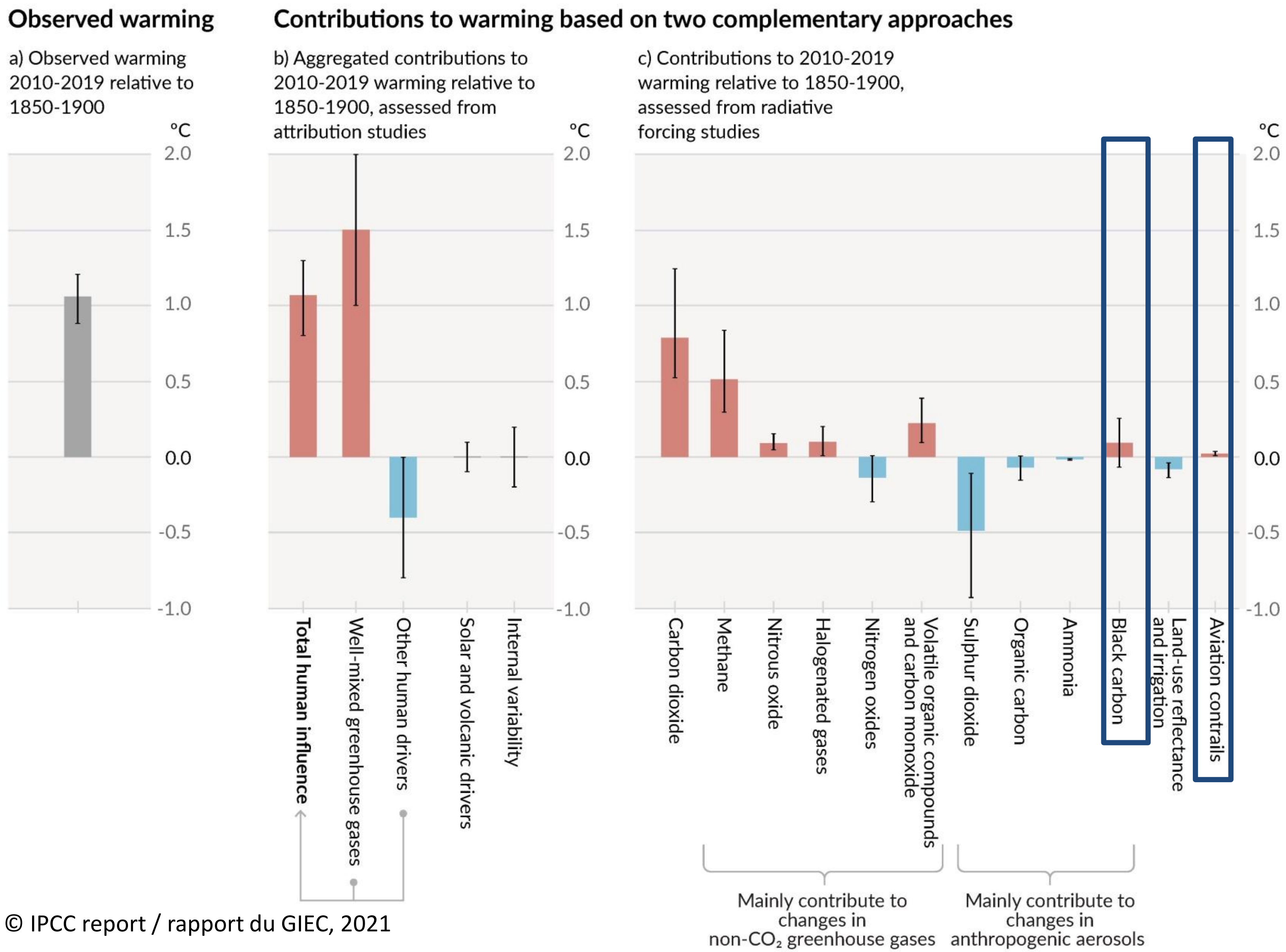
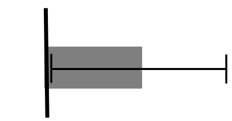
Context: impact of black carbon (BC) on global warming



Soot / black carbon

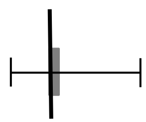
Impact on:

- Global warming
- Health
- Chemistry of intersideral media



0,40 Wm^{-2} © IPCC, 2014

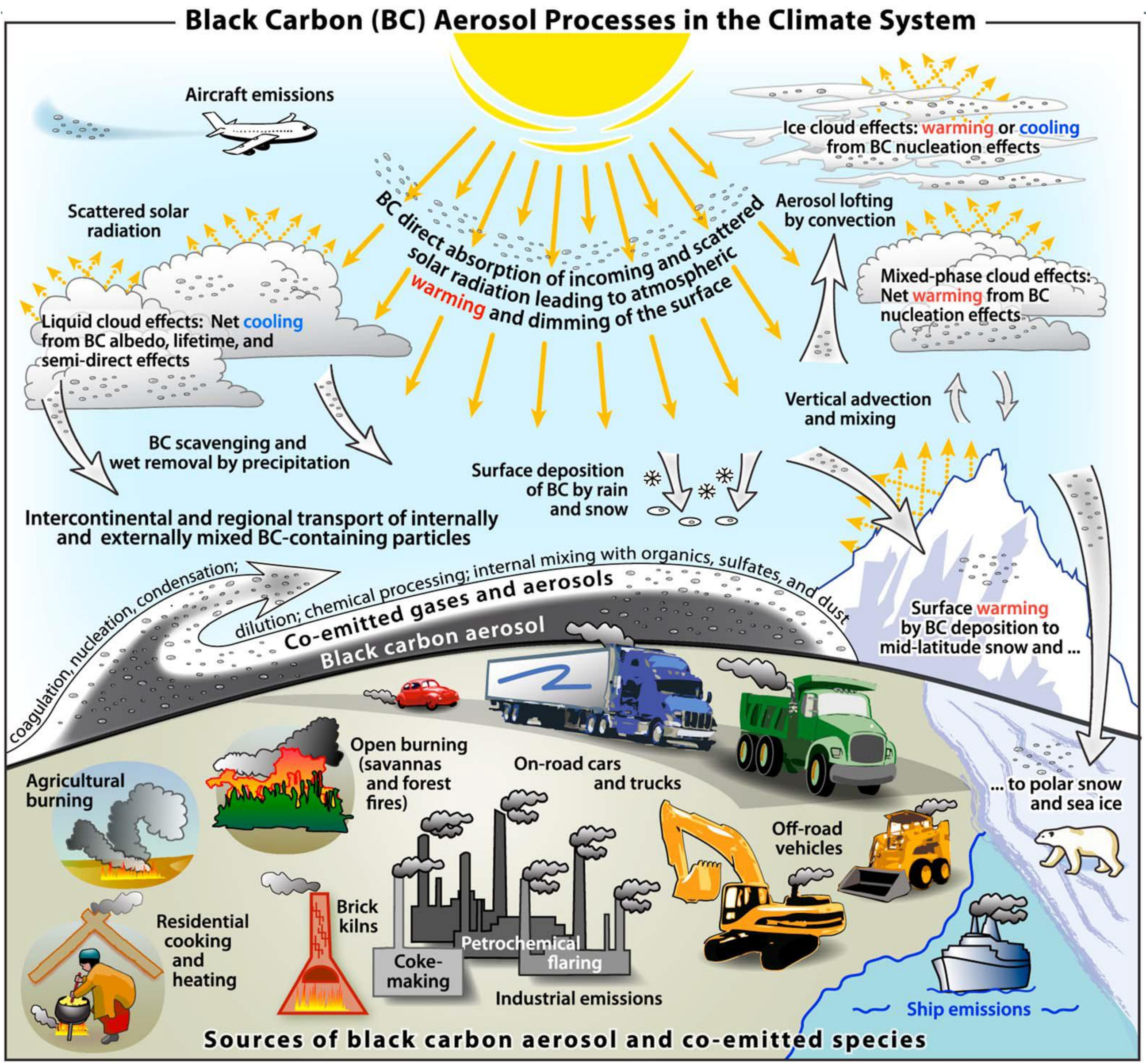
[+0,05 to 0,8 Wm^{-2}]



0,063 Wm^{-2} © IPCC, 2021

[-0,28 to 0,42 Wm^{-2}]

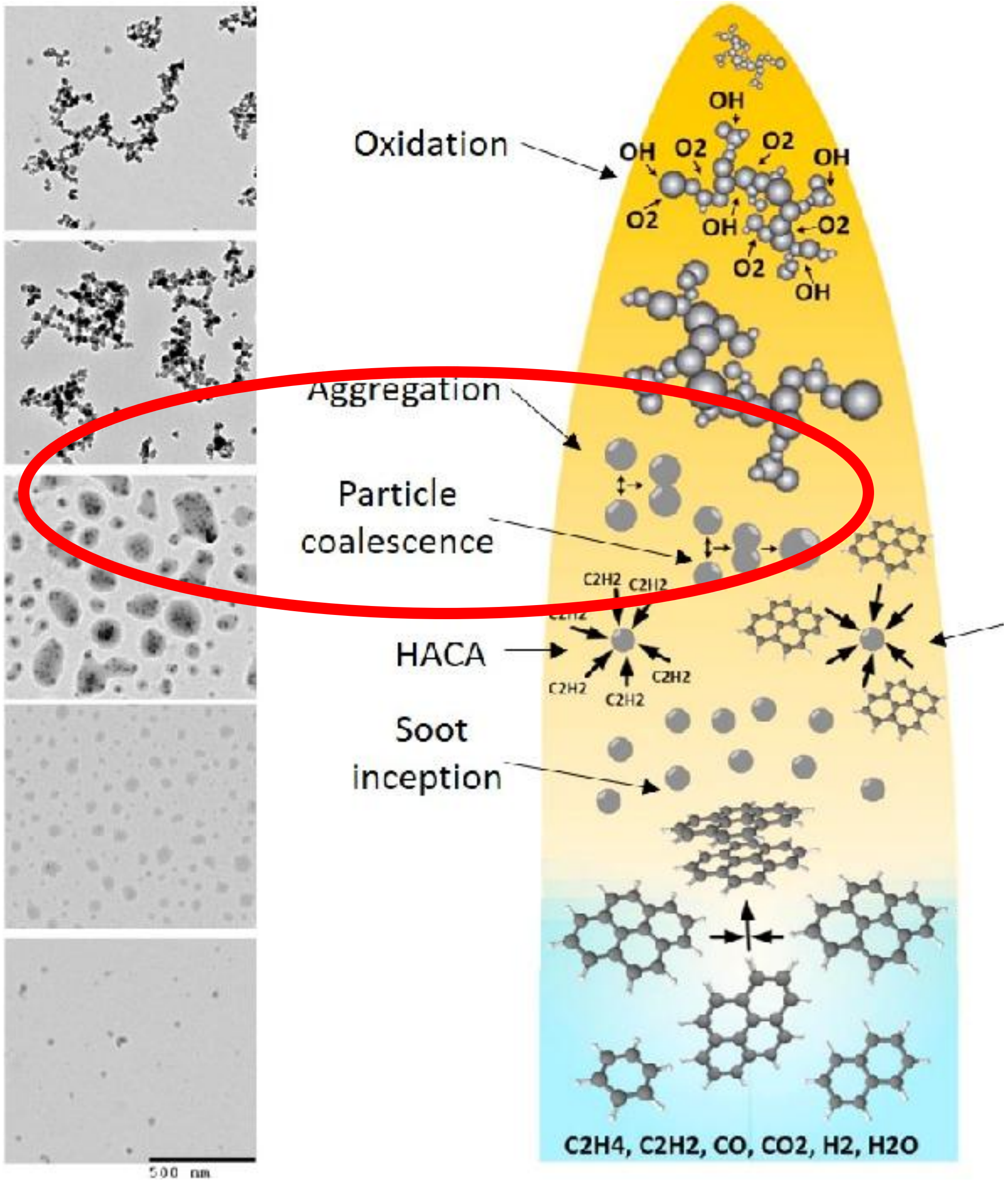
Context



- OC and BC form an important component of atmospheric Particulate Matter (PM)
- Carbonaceous particles interact with UV and visible solar radiations, impacting on the global Earth's radiative balance (direct effect)
- Also act as cloud condensation nuclei or ice nuclei, thus playing an essential role in cloud formation (indirect effect)

Bond et al., JGR Atmos., **118**, 2013

Context



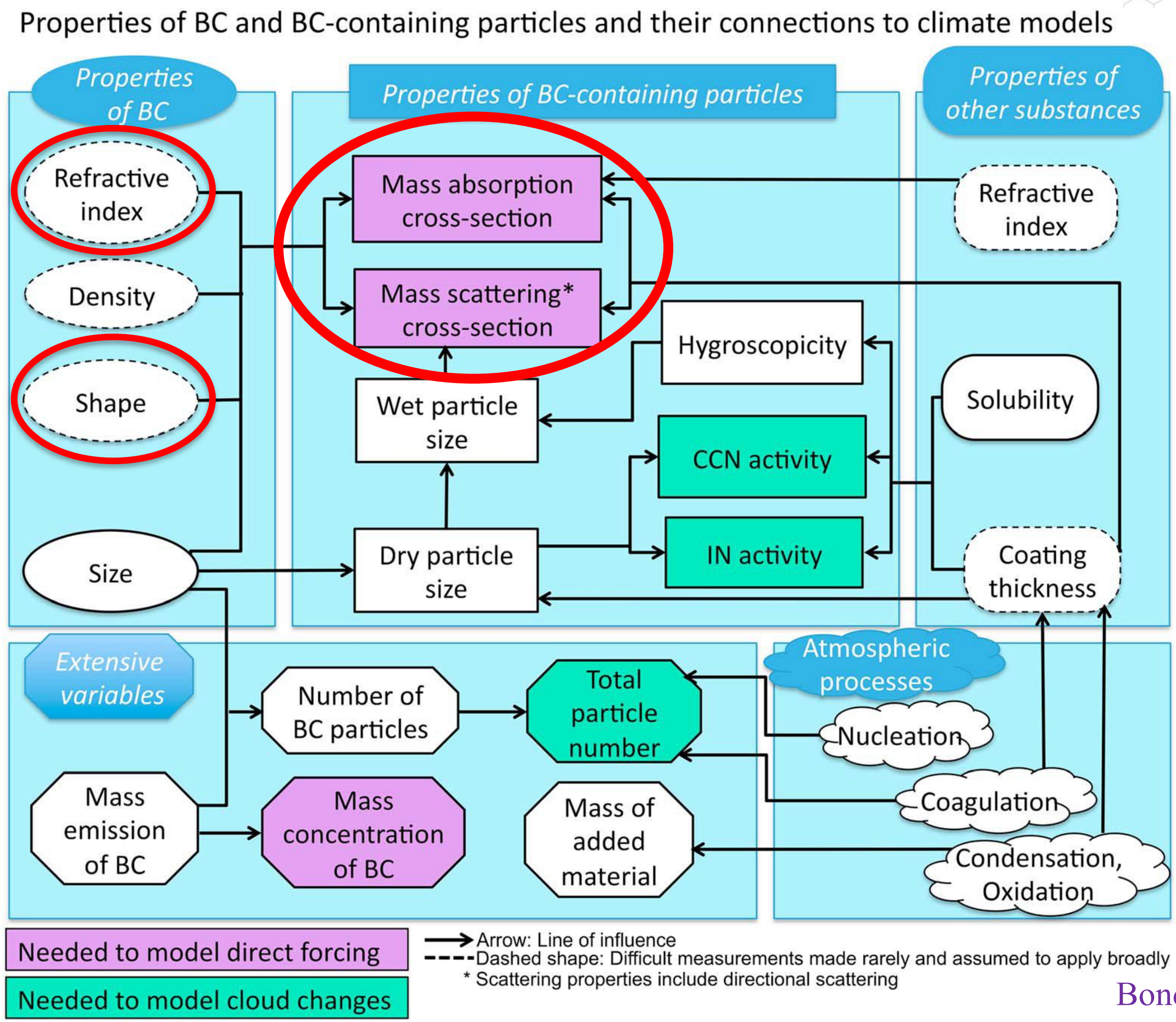
- It is expected that **optical properties** of BC would depend on the **morphology** of these aggregates, on their coating, and on the refractive index of the corresponding materials

- It has been shown that **overlapping and necking** between primary nanoparticles forming BC aggregates could have a strong **influence** on their **optical properties**

- Taking into account, as precisely as possible, all these ingredients in theoretical approaches with the goal of interpreting experimental measurements and/or observations still **remains challenging**

Wang et al., Int. J. Hydrogen Energy, **46**, 2021

Context



Bond et al., JGR Atmos., **118**, 2013

Key ingredients of atmospheric models:

Cross-sections of a particle, divided by its mass (MAC, MSC)

Classically, X-sections computed thanks to macroscopic quantities (refractive index, shape)

We compute them from atomistic information (polarizabilites, positions)

Goal: give macroscopic infos for climate models from atomistic simulations

Outline

I. Definitions

II. Wave equations

III. Green's "functions" and their singular part

IV. General volume integral equation

V. Discrete Dipole Approximation (microphotonics)

VI. DDA at the molecular scale $\Rightarrow$ DADI Model (nanophotonics)

VII. Optical indices from molecular information (and back!)

VIII. Conclusions and perspectives

IX. References

I - Definitions

a) Maxwell equations, constitutive relations, polarization, magnetization

Microscopic Maxwell equations

$$\begin{cases} \mathrm{div}\big(\vec{e}(\vec{r},t)\big) = \dfrac{\sum_i q_i \delta\big(\vec{r}-\vec{r}_i(t)\big)}{\varepsilon_0} \\ \overrightarrow{\mathrm{curl}}\big(\vec{e}(\vec{r},t)\big) = -\dfrac{\partial \vec{b}}{\partial t}(\vec{r},t) \\ \mathrm{div}\left(\vec{b}(\vec{r},t)\right) = 0 \\ \overrightarrow{\mathrm{curl}}\left(\vec{b}(\vec{r},t)\right) = \mu_0 \sum_i q_i \vec{v}_i \delta\big(\vec{r}-\vec{r}_i(t)\big) + \varepsilon_0\mu_0 \dfrac{\partial \vec{e}}{\partial t}(\vec{r},t) \end{cases}$$

$\langle\ \rangle \rightarrow$

Macroscopic Maxwell equations

$$\begin{cases} \mathrm{div}\left(\vec{D}(\vec{r},t)\right) = \rho_{free}(\vec{r},t) \\ \overrightarrow{\mathrm{curl}}\left(\vec{E}(\vec{r},t)\right) = -\dfrac{\partial \vec{B}}{\partial t}(\vec{r},t) \\ \mathrm{div}\left(\vec{B}(\vec{r},t)\right) = 0 \\ \overrightarrow{\mathrm{curl}}\left(\vec{H}(\vec{r},t)\right) = \vec{j}_{free}(\vec{r},t) + \dfrac{\partial \vec{D}}{\partial t}(\vec{r},t) \end{cases}$$

Constitutive relations: $\boxed{\vec{D} \equiv \varepsilon_0 \vec{E} + \vec{P}}$ and $\boxed{\vec{H} \equiv \vec{B}/\mu_0 - \vec{M}}$ $\vec{P}$: **polarization**, $\vec{M}$: **magnetization**

with $\langle \vec{e}(\vec{r},t)\rangle = \vec{E}(\vec{r},t)$, $\langle \vec{b}(\vec{r},t)\rangle = \vec{B}(\vec{r},t)$,

*Rem: **Different** from Jackson-book-1998, §6.6*

$\boxed{\langle \sum_i q_i \delta(\vec{r}-\vec{r}_i)\rangle = \rho_{free}(\vec{r},t) - \mathrm{div}\vec{P}(\vec{r},t)}$ and $\boxed{\langle \sum_i q_i \vec{v}_i \delta(\vec{r}-\vec{r}_i)\rangle = \vec{j}_{free}(\vec{r},t) + \frac{\partial \vec{P}}{\partial t} + \overrightarrow{\mathrm{curl}}\left(\vec{M}\right)}$

Linear susceptibilities: $\vec{P}(\omega) = \varepsilon_0 \bar{\bar{\chi}}_e(\omega)\vec{E}(\omega)$ and $\vec{M}(\omega) = \bar{\bar{\chi}}_m(\omega)\vec{H}(\omega)$

Linear permittivity: $\bar{\bar{\varepsilon}}(\omega) = \varepsilon_0 \bar{\bar{\varepsilon}}_r(\omega) = \varepsilon_0 \left(\bar{\bar{1}} + \bar{\bar{\chi}}_e(\omega)\right)$, linear permeability: $\bar{\bar{\mu}}(\omega) = \mu_0 \bar{\bar{\mu}}_r(\omega) = \mu_0 \left(\bar{\bar{1}} + \bar{\bar{\chi}}_m(\omega)\right)$

Remark: $\vec{P}(t) = \varepsilon_0 \int_0^\infty \bar{\bar{\chi}}_e(\tau)\vec{E}(t-\tau)d\tau$ with integration from 0 and not $-\infty$ because of causality $\Rightarrow$ *Kramers-Kronig relations*

I - Definitions

b) Structural units, permanent microscopic multipoles

- ***Structural units*** *= stable ensemble of charges (atoms, ions, molecules, unit cells), carrying multipoles*

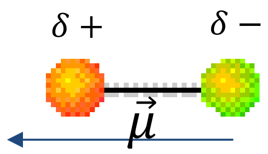
Permanent electric dipole moment: $\vec{\mu} = q(\vec{r}_+ - \vec{r}_-)$ for 2 opposite charges $\pm q$.

For some arbitrary structural unit composed of ***N* charges q_i located at** $\{\vec{r}_i\}_{i=1,\dots,N}$, the permanent multipole moments are (with α, β or γ = *x, y or z*):

α, β ou γ = *x, y* ou *z*

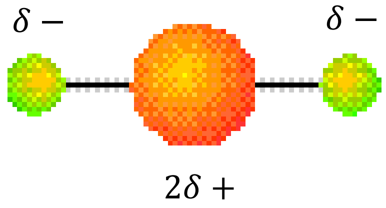
Monopole (ion)

$$q = \sum_{i=1}^{N} q_i$$



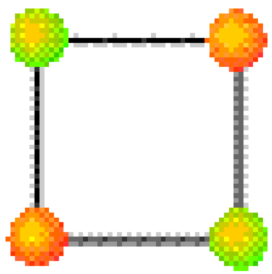
Dipole (HF, H_2O)

$$\mu_\alpha = \sum_{i=1}^{N} q_i r_{i,\alpha}$$

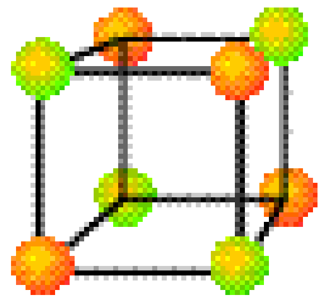


Quadrupole (CO_2)

$$Q_{\alpha\beta} = \sum_{i=1}^{N} q_i \left[\frac{3}{2} r_{i,\alpha} r_{i,\beta} - \frac{1}{2} r_i^2 \delta_{\alpha,\beta}\right]$$

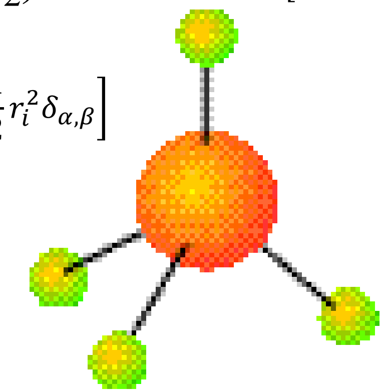


Quadrupole



Octupole

$$\Omega_{\alpha\beta\gamma} = \sum_{i=1}^{N} q_i \left[\frac{5}{2} r_{i,\alpha} r_{i,\beta} r_{i,\gamma} - \frac{1}{2} r_i^2 \left(r_{i,\alpha}\delta_{\beta,\gamma} + r_{i,\beta}\delta_{\alpha,\gamma} + r_{i,\gamma}\delta_{\alpha,\beta}\right)\right]$$



Octupole

Generalization: $$M^{(n)}_{\underbrace{\alpha,\dots,\nu}_{n\ indices}}(\vec{r}_0) \equiv \frac{(-1)^n}{n!} \sum_{i=1}^{N} q_i \|\vec{r}_i - \vec{r}_0\|^{2n+1} \frac{\partial}{\partial(\vec{r}_i - \vec{r}_0)_\nu} \cdots \frac{\partial}{\partial(\vec{r}_i - \vec{r}_0)_\alpha} \left(\frac{1}{\|\vec{r}_i - \vec{r}_0\|}\right)$$

c) Induced dipoles : electronic polarizabilities, local field

When some set of charges is submitted to an electric field, the positive charges are attracted in the direction of the field and the negative charges in the opposite direction.

$\Rightarrow$ The barycenters of the positive and negative charges separate

$\Rightarrow$ Creation of an induced dipole

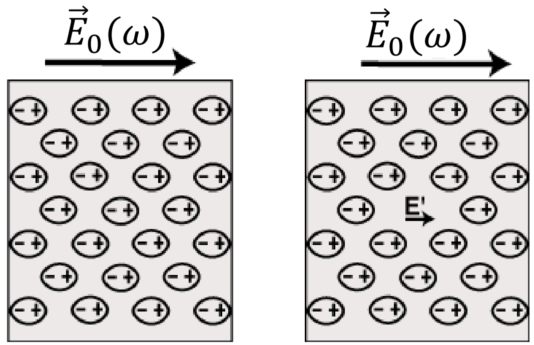
$\Rightarrow$ In the linear response approximation: $\boxed{\vec{p}_{ind} = \bar{\bar{\alpha}}\vec{E}_{loc}}$

General case: the polarizability $\bar{\bar{\alpha}}$ is represented by a (3×3) matrix

Most of the time, after averaging: isotropic (scalar) polarizability

SI unit of α: F.m^2 (ou J^{-1}C^{2}m^2 ou A^2 s^4 kg^{-1}),

SI unit of $\alpha/4\pi\varepsilon_0$: m^3 !!! $\alpha/4\pi\varepsilon_0$ ~ volume of the system



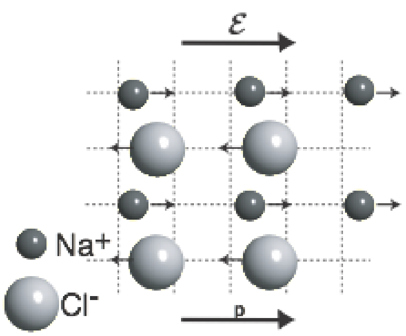
$$\vec{p}_{at,i}(\omega) = \bar{\bar{\alpha}}_i(\omega)\vec{E}_{loc,i}(\omega)$$

On each atom, the local field is:

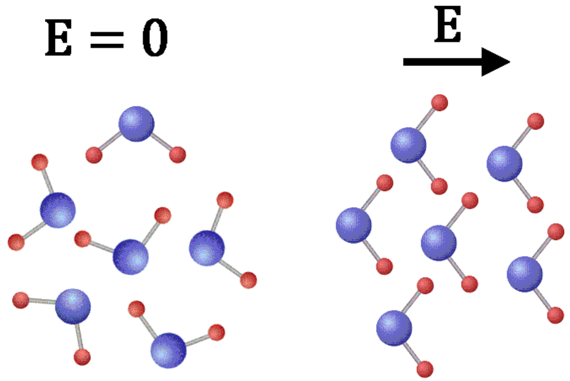
$$\vec{E}_{loc,i}(\omega) = \vec{E}_{ext}(\omega) + \sum_{i \neq j} \vec{E}_{j \to i}\left(\{\vec{p}_{at,k \neq i}(\omega)\}\right)$$

$\Rightarrow$ **The dipoles/fields must be computed self-consistently!**

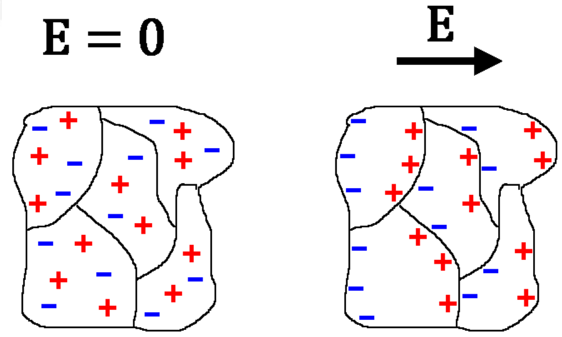
d) Other types of polarization



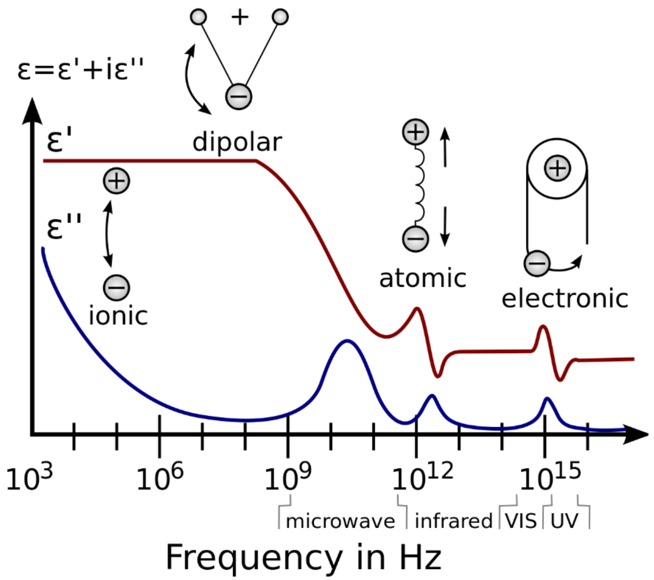
Ionic, $\tau \sim 10^{-10}$ to 10^{-13} s (IR-visible)



Orientation, T-dependent, very effective in polar liquids



Grain boundaries, electrode/sample interface $\tau \sim 10^{-2}$ to 10^{2} s



Previous mechanisms have different characteristic times

- At low frequencies, all mechanisms contribute
- If frequency ↑, oscillations of $\vec{E}$ too fast for polarization to follow (Inertia (mass) of atoms > inertia of e^-)

⇒ electronic polarization (polarizability) alone at high frequencies (optical, UV), then $\varepsilon_r \approx 1$.

Absorption: energy of $\vec{E}$ redistributed over material motions and electronic excitations. Modeled by complex permittivity: $\varepsilon = \varepsilon' + i\varepsilon"$

⇒ complex optical index: $m = n + i\kappa$

https://en.wikipedia.org/wiki/Dielectric_spectroscopy#/media/File:Dielectric_responses.svg

e) macroscopic multipoles

- Permanent multipole moments of the charge distribution (note integral instead of sum):

$$\Pi^{(m)}_{\alpha,\beta,\dots,\mu}(\vec{r}_0,\omega) \equiv \left[\frac{(2m-1)!!}{m!}\right] \times \int (\vec{r}\,'-\vec{r}_0)_\alpha (\vec{r}\,'-\vec{r}_0)_\beta \cdots (\vec{r}\,'-\vec{r}_0)_\mu \rho(\vec{r}\,',\omega) d\vec{r}\,'$$

$$\rho_{bound} = \Pi^{(1)}_{ij}\nabla_i E_j + \Pi^{(2)}_{ijk}\nabla_i\nabla_j E_k + \Pi^{(3)}_{ijkl}\nabla_j\nabla_k\nabla_l E_i + \cdots$$

$$\vec{J}_{bound,i} = \Theta^{(1)}_{ij} E_j + \Theta^{(2)}_{ijk}\nabla_j E_k + \Theta^{(3)}_{ikjl}\nabla_k\nabla_l E_j + \cdots$$

Can also be used when ρ comes from DFT!...

$$\vec{P}(\vec{r}) = \left\langle \sum_n \vec{p}_n \delta(\vec{r}-\vec{r}_n) \right\rangle + \vec{\nabla}\cdot\left\langle \sum_n \bar{\bar{Q}}_n \delta(\vec{r}-\vec{r}_n) \right\rangle + (\vec{\nabla}\otimes\vec{\nabla}) : \left\langle \sum_n \Omega^{(3)}_n \delta(\vec{r}-\vec{r}_n) \right\rangle + \cdots$$

- Dipolar approximation:

$$\boxed{\vec{P} \approx \langle \textstyle\sum_n \vec{p}_n \delta(\vec{r}-\vec{r}_n) \rangle}$$

$\vec{p}_n$ dipole of structural unit n located at $\vec{r}_n$

Note: Quadrupoles, octupoles, etc… are included in polarization contrarily to approach of Jackson's book. Easier for electromechanical terms in constitutive relations derived from a generalized enthalpy:

Dipolar order — Quadrupolar order

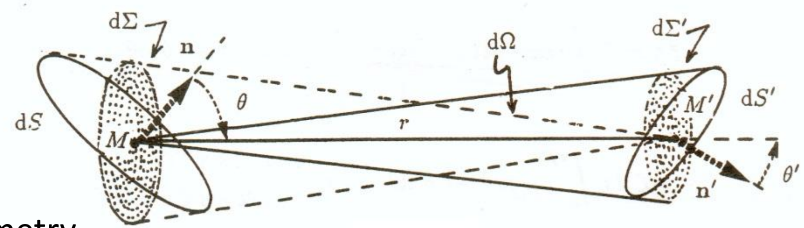
Ex: $D_i = -(\partial W^L/\partial E_i)_{S,\nabla S,\nabla E} = \varepsilon_{ij}E_j + e_{ikl}S_{kl} + t_{ijk}E_{j,k} + f_{klij}S_{kl,j} + \cdots$

Permittivity — Piezo — Circular anisotropy, gyrotropy — flexoelectricity

$$Q_{ij} = t_{ikj}E_k + f_{klij}S_{kl}$$

I - Definitions

f) SI radiometry units



From https://en.wikipedia.org/wiki/Radiometry

SI radiometry units

Quantity	Symbol	SI unit	Abbr.	Notes
Radiant energy	*Q*	joule	J	energy
Radiant flux	*Φ*	watt	W	radiant energy per unit time, also called *radiant power*
Radiant intensity	*I*	watt per steradian	$W \cdot sr^{-1}$	power per unit solid angle
Radiance	*L*	watt per steradian per square metre	$W \cdot sr^{-1} \cdot m^{-2}$	power per unit solid angle per unit *projected* source area. called *intensity* in some other fields of study.
Irradiance	*E*, *I*	watt per square metre	$W \cdot m^{-2}$	power incident on a surface. sometimes confusingly called "intensity".
Radiant exitance / Radiant emittance	*M*	watt per square metre	$W \cdot m^{-2}$	power emitted from a surface.
Radiosity	*J* or J_λ	watt per square metre	$W \cdot m^{-2}$	emitted plus reflected power leaving a surface
Spectral radiance	L_λ or L_ν	watt per steradian per metre^3 *or* watt per steradian per square metre per hertz	$W \cdot sr^{-1} \cdot m^{-3}$ *or* $W \cdot sr^{-1} \cdot m^{-2} \cdot Hz^{-1}$	commonly measured in $W \cdot sr^{-1} \cdot m^{-2} \cdot nm^{-1}$
Spectral irradiance	E_λ or E_ν	watt per metre^3 *or* watt per square metre per hertz	$W \cdot m^{-3}$ *or* $W \cdot m^{-2} \cdot Hz^{-1}$	commonly measured in $W \cdot m^{-2} \cdot nm^{-1}$

Intensité énergétique

Luminance énergétique

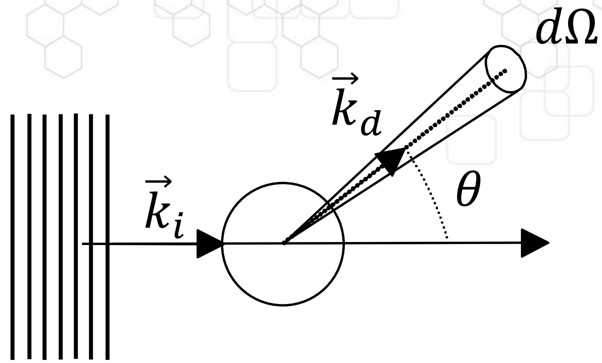
éclairement énergétique

exitance

I - Definitions

g) cross-sections (i)

Scattering of a plane wave



Nb of photons scattered in $d\Omega$ per unit time ⟵ $$dN_d = \phi(x) d\Omega \left(\frac{d\sigma}{d\Omega}\right)_{sca}$$

Scattering differential cross-section

$\phi(x)$ = Incident flux of photons per area unit (Irradiance on the scattering object)

– Total scattering cross-section : (unit: 1 barn = 10^{-28} m^2)

$$\sigma_{sca} = \int_0^{\pi} \int_0^{2\pi} \left(\frac{d\sigma}{d\Omega}\right)_{sca} d\varphi \sin\theta \, d\theta$$

Absorption of a plane wave

Nb of photons absorbed in Sdz per time unit ⟵ $$dN_a = \phi(x)\sigma_a dN(dx)$$

Nb of absorbing entities in $Sdx = \rho_{at} S dx$

Absorption cross-section

$$d\phi(x) = \phi(x+dx) - \phi(x) = -dN_a/S = -\phi(x)\sigma_a \rho_{at} dx$$

- **Beer**-Lambert(-Bouguer) law: $\Phi_\lambda(\rho \cdot x) = \Phi_\lambda(0) \exp\left(-(\alpha_\lambda/\rho) \cdot (\rho \cdot x)\right)$
- α_λ/ρ: Mass Absorption Cross-section of the material for wavelength λ (in cm^2 / g) = MAC_λ

Outline

I. Definitions

II. Wave equations

III. Green's "functions" and their singular part

IV. General volume integral equation

V. Discrete Dipole Approximation (microphotonics)

VI. DDA at the molecular scale $\Rightarrow$ DADI Model (nanophotonics)

VII. Optical indices from molecular information (and back!)

VIII. Conclusions and perspectives

IX. References

II – Wave equations

a) **Scalar and vector** wave equations for the electric field

- Recall Maxwell equations: $\mathrm{div}\left(\vec{D}(\vec{r},t)\right) = \rho_{free}(\vec{r},t)$ (MG), $\overrightarrow{\mathrm{curl}}\left(\vec{E}(\vec{r},t)\right) = -\frac{\partial \vec{B}}{\partial t}(\vec{r},t)$ (MF), $\mathrm{div}\left(\vec{B}(\vec{r},t)\right) = 0$ (MGM) and $\overrightarrow{\mathrm{curl}}\left(\vec{H}(\vec{r},t)\right) = \vec{j}_{free}(\vec{r},t) + \frac{\partial}{\partial t}\vec{D}(\vec{r},t)$ (MA)
- Using $\vec{B} = \mu_0[\vec{H} + \vec{M}]$ in $\overrightarrow{\mathrm{curl}}$(MF), then $\vec{\nabla} \times \vec{\nabla} \times \vec{E} = \vec{\nabla}(\vec{\nabla} \cdot \vec{E}) - \Delta\vec{E}$ and $\vec{D} = \varepsilon_0\vec{E} + \vec{P}$ in (MG) and finally (MA), we get the scalar wave equation:

$$\Delta\vec{E}(\vec{r};t) + \left(\frac{1}{c^2}\right)\frac{\partial^2}{\partial t^2}\vec{E}(\vec{r};t) = \mu_0\frac{\partial}{\partial t}\vec{j}_{tot}(\vec{r};t) + \overrightarrow{\mathrm{grad}}\left(\frac{\rho_{tot}(\vec{r};t)}{\varepsilon_0}\right)$$

with $\vec{j}_{tot} = \vec{j}_{free} + \partial\vec{P}/\partial t + \overrightarrow{\mathrm{rot}}(\vec{M})$ and $\rho_{tot} = \rho_{free} - \mathrm{div}(\vec{P})$.

- For monochromatic waves, with $\exp(-i\omega t)$ convention, in a linear medium such that $\vec{D} = \varepsilon_0\bar{\bar{\varepsilon}}_r\vec{E}$ and $\vec{B} = \mu_0\bar{\bar{\mu}}_r\vec{H}$, $\overrightarrow{\mathrm{curl}}((\bar{\bar{\mu}}_r)^{-1}$ MF) then (MA) ⇒ vector wave equation for $\vec{E}(\vec{r};\omega)$:

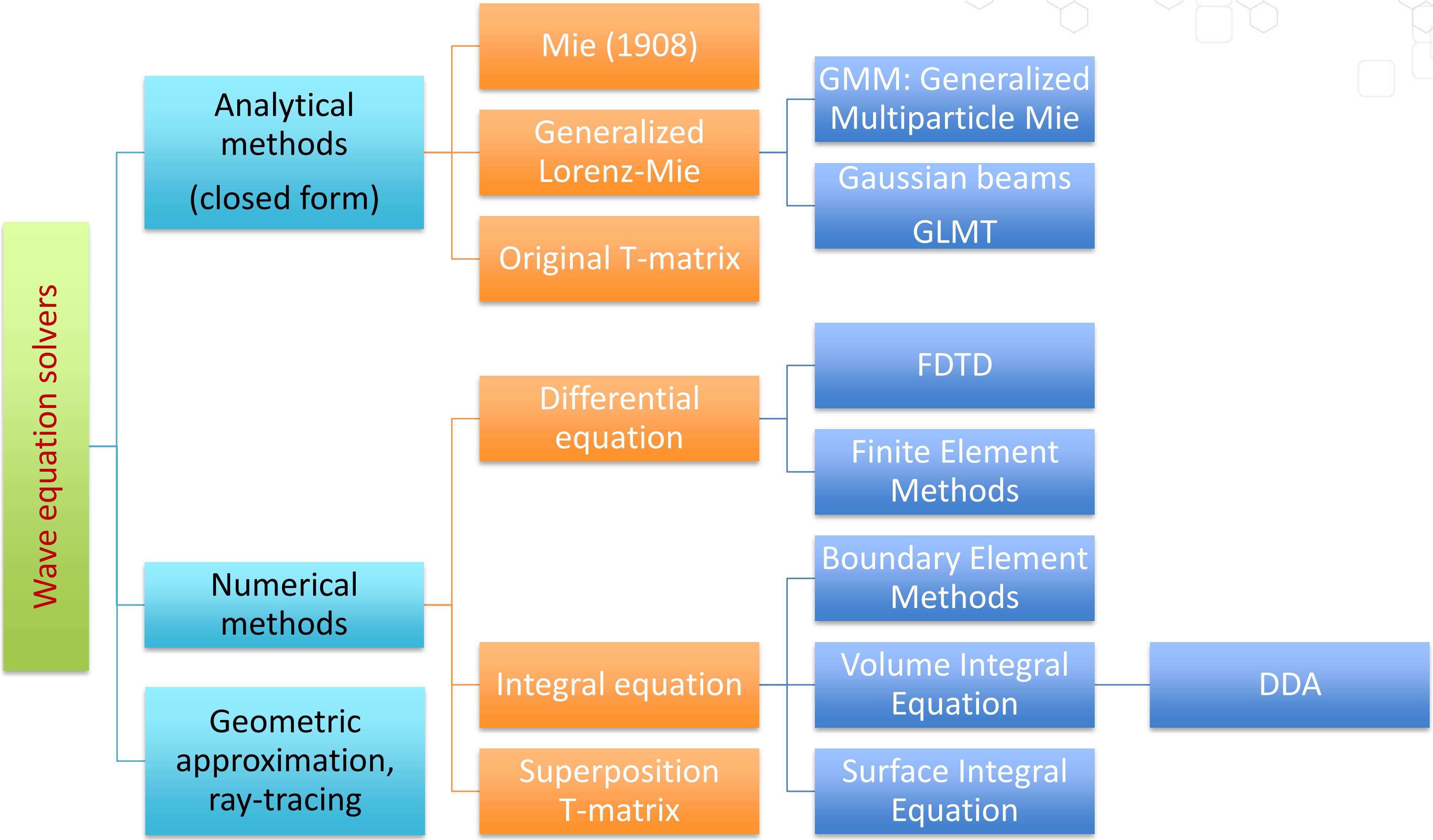
$$\overrightarrow{\mathrm{curl}}\left[(\bar{\bar{\mu}}_r)^{-1}(\vec{r};\omega)\overrightarrow{\mathrm{curl}}\left(\vec{E}(\vec{r};\omega)\right)\right] - \left(\frac{\omega^2}{c^2}\right)\bar{\bar{\varepsilon}}_r(\vec{r};\omega)\vec{E}(\vec{r};\omega) = i\omega\mu_0\vec{j}_{free}(\vec{r};\omega)$$

- For a magnetically homogeneous scatterer verifying the local form of Ohm's law $\vec{j}_{free} = \bar{\bar{\sigma}}\vec{E}$, we can define an effective permittivity $\boldsymbol{\bar{\bar{\varepsilon}}_{r,eff}(\vec{r};\omega) = \bar{\bar{\varepsilon}}_r(\vec{r};\omega) + i\,\bar{\bar{\sigma}}(\vec{r};\omega)/(\omega\varepsilon_0)}$. Then, in a *linear, homogeneous, isotropic* **B**ackground, we have:

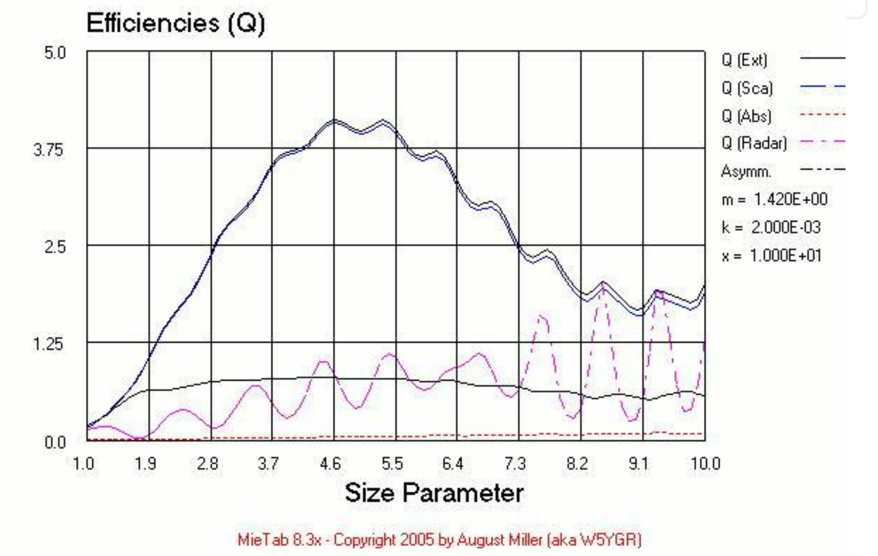
$$\vec{\nabla} \times \vec{\nabla} \times \vec{E}(\vec{r};\omega) - \left(\frac{\omega^2}{c^2}\right)\mu_{r,B}(\omega)\,\varepsilon_{r,B}(\omega)\vec{E}(\vec{r};\omega) = \left(\frac{\omega^2}{c^2}\right)\left[\bar{\bar{\mu}}_r(\omega)\,\bar{\bar{\varepsilon}}_{r,eff}(\vec{r};\omega) - \mu_{r,B}(\omega)\,\varepsilon_{r,B}(\omega)\right]\vec{E}(\vec{r};\omega)$$

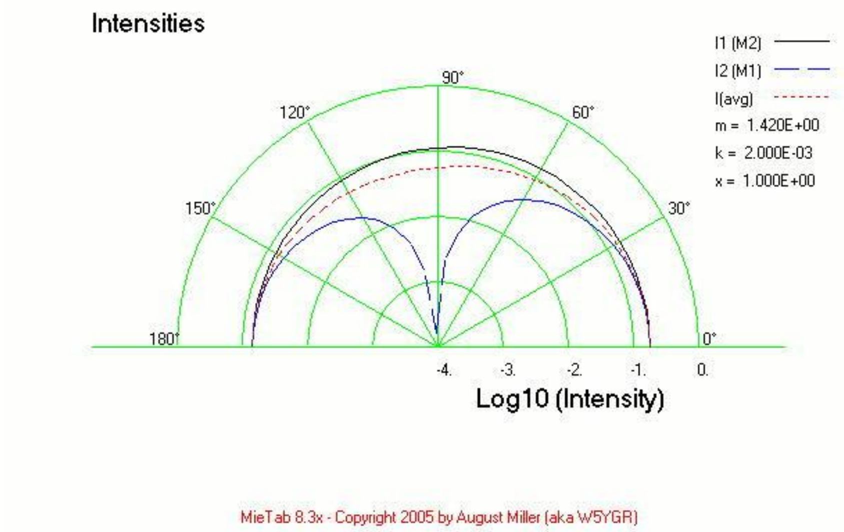
II – Wave equations

b) Panorama of solvers



- Mie Scattering (1908) and GLMT
  - Expansion of the solution on a basis of spherical vector wave function
  - Initially scattering of a plane wave by an homogeneous sphere
  - Exact solution whatever the size of the sphere
  - Extended for stratified spheres or infinite cylinders, or other geometries in cases where radial and angular dependence are separable.
  - The reference to test other methods (many different implementations available freely)
  - Extended for Gaussian incident beams and eccentric inclusion (G. Gouesbet et al.)





II – Wave equations

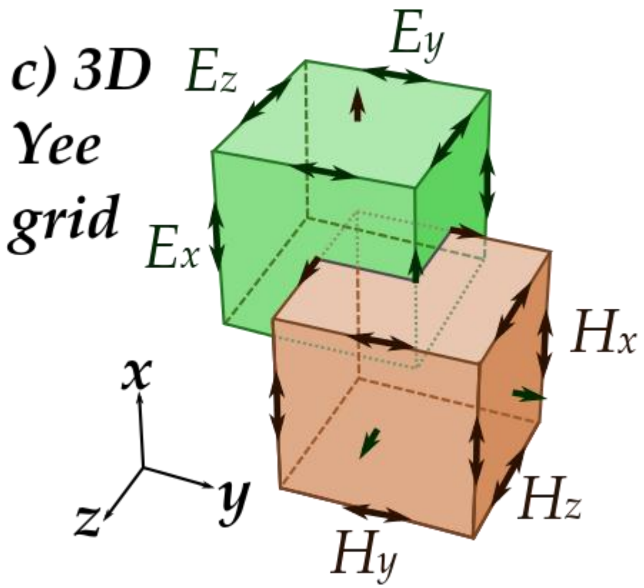
c) “Exact” solutions

- T-Matrix (Waterman - 1965, 1971)
  - Origin in an extended boundary condition method (null-field method)
  - Expansion of the fields on a basis of spherical vector wave function, with a Transition matrix connecting the expansion coefficients of the incident and scattered waves
  - can be applied to the entire scatterer as well as to separate parts of a composite scatterer
  - scattering by anisotropic, bi-isotropic or chiral objects, agglomerates, discrete random media, layered and composite materials, clusters of homogeneous and layered spheres, clusters of non-spherical monomers, particles with one or several inclusions, … (cf. 2010 paper below)
  - Used in various fields including planetary atmospheres or rings, combustion fires, biological cells or tissues,…
  - Limited in the range of optical index times relative size which can be used without instabilities in the computations
  - Can be much faster than DDA

Review by Mishchenko, Travis, Mackowski, JQSRT, **55**(5):535–575 (1996) **+ 111**(11):1700–1703 (2010)
See also https://www.giss.nasa.gov/staff/mmishchenko/t_matrix_database.html
https://www.researchgate.net/profile/Michael_Mishchenko

- FDTD (Yee-1966)
  - Finite Difference, Time Domain: direct time integration of the Maxwell equations in a finite domain.
  - $\vec{\nabla} \times \vec{E} = -\frac{\partial \vec{B}}{\partial t} \Rightarrow \Delta B_z = \left(\frac{\Delta E_x}{\Delta y} - \frac{\Delta E_y}{\Delta x}\right) \Delta t$
  - Useful for an arbitrary broadband incident beam / pulse (easier to describe in the time domain)

  BUT
  - Requires gridding of whole region of space, not only the scatterer. Far-field extensions are available for FDTD, but require some amount of post-processing
  - Dispersion not so easy (and fast) to take into account, but possible



Cf. https://en.wikipedia.org/wiki/Finite-difference_time-domain_method

Outline

I. Definitions

II. Wave equations

III. Green's "functions" and their singular part

IV. General volume integral equation

V. Discrete Dipole Approximation (microphotonics)

VI. DDA at the molecular scale $\Rightarrow$ DADI Model (nanophotonics)

VII. Optical indices from molecular information (and back!)

VIII. Conclusions and perspectives

IX. References

III – Green's "functions" and their singular part

a) **Scalar** wave equation and its corresponding Green's generalized function

- For monochromatic waves, with $\exp(-i\omega t)$ convention, the scalar wave equation is:

$$\Delta\vec{E}_{macro}(\vec{r};\omega) + \left(\frac{\omega^2}{c^2}\right)\vec{E}_{macro}(\vec{r};\omega) = -i\omega\mu_0\vec{J}_{tot} + \overrightarrow{\text{grad}}\left(\frac{\rho_{tot}}{\varepsilon_0}\right)$$

with $\vec{J}_{tot} = \vec{J}_{free}(\vec{r};\omega) - i\omega\vec{P}(\vec{r};\omega) + \overrightarrow{\text{rot}}\left(\vec{M}(\vec{r};\omega)\right)$ and $\rho_{tot} = \rho_{free}(\vec{r};\omega) - \text{div}[\vec{P}(\vec{r},\omega)]$

- Define corresponding Green's (generalized) function (solution of

$$\Delta G_{vac}(\vec{r},\vec{r}';\omega) + (\omega^2/c^2)G_{vac}(\vec{r},\vec{r}';\omega) = \delta(\vec{r}-\vec{r}')$$

for the appropriate vacuum boundary conditions, which force us to keep only the outgoing (retarded) spherical wave):

$$\boxed{G_{vac}(\vec{r},\vec{r}' \neq \vec{r};\omega) = -\frac{\exp\left(i\left(\frac{\omega}{c}\right)|\vec{r}-\vec{r}'|\right)}{4\pi|\vec{r}-\vec{r}'|}}$$

- Following Yaghjian-PIEEE-1980, we use the equation coming from the continuity of the total charge density function $\vec{\nabla}\cdot\vec{J}_{tot}(\vec{r};\omega) - i\omega\rho_{tot}(\vec{r};\omega) = 0$ to get $\Delta\vec{E}(\vec{r};\omega) + (\omega^2/c^2)\vec{E}(\vec{r};\omega)$ $= -i\omega\mu_0\vec{J}_{tot}(\vec{r};\omega) + \vec{\nabla}[\vec{\nabla}\cdot\vec{J}_{tot}(\vec{r};\omega)]/(i\omega\varepsilon_0)$, which gives:

$$\Delta\left[\vec{E}(\vec{r};\omega) - \frac{\vec{J}_{tot}(\vec{r};\omega)}{i\omega\varepsilon_0}\right] + (\omega^2/c^2)\left[\vec{E}(\vec{r};\omega) - \frac{\vec{J}_{tot}(\vec{r};\omega)}{i\omega\varepsilon_0}\right] = \frac{\vec{\nabla}\wedge[\vec{\nabla}\wedge\vec{J}_{tot}(\vec{r};\omega)]}{i\omega\varepsilon_0}$$

- Hence, general solution is $\boxed{\vec{E}(\vec{r};\omega) = \lim_{\delta\to 0}\int_{V_j - V_\delta} G(\vec{r},\vec{r}';\omega)\left[\frac{\vec{\nabla}'\wedge[\vec{\nabla}'\wedge\vec{J}_{tot}(\vec{r}';\omega)]}{i\omega\varepsilon_0}\right]d\vec{r}' + \frac{\vec{J}_{tot}(\vec{r};\omega)}{i\omega\varepsilon_0}}$

b) **Vector** wave equations and their corresponding dyadic Green's generalized function

In vacuum, we have

$$\vec{\nabla}\wedge\left[\vec{\nabla}\wedge\left(\vec{E}(\vec{r};\omega)\right)\right]-(\omega^2/c^2)\vec{E}(\vec{r};\omega)=i\omega\mu_0\vec{J}_{free}(\vec{r};\omega)$$

and

$$\vec{\nabla}\wedge\left[\vec{\nabla}\wedge\left(\vec{H}(\vec{r};\omega)\right)\right]-(\omega^2/c^2)\vec{H}(\vec{r};\omega)=\vec{\nabla}\wedge\vec{J}_{free}(\vec{r};\omega)$$

In Yaghjian-PIEEE-1980, two dyadic tensors are introduced:

- The dyadic Green's function for the electric field in vacuum $\bar{\bar{G}}_e$, solution of:

$$\vec{\nabla}\wedge\left[\vec{\nabla}\wedge\left(\bar{\bar{G}}_e(\vec{r},\vec{r}';\omega)\right)\right]-(\omega^2/c^2)\bar{\bar{G}}_e(\vec{r},\vec{r}';\omega)=\delta(\vec{r}-\vec{r}')\bar{\bar{1}}$$

- The dyadic Green's function for the magnetic field in vacuum $\bar{\bar{G}}_{\mathrm{m}}$, solution of:

$$\vec{\nabla}\wedge\left[\vec{\nabla}\wedge\left(\bar{\bar{G}}_m(\vec{r},\vec{r}';\omega)\right)\right]-(\omega^2/c^2)\bar{\bar{G}}_m(\vec{r},\vec{r}';\omega)=\vec{\nabla}\wedge\left(\delta(\vec{r}-\vec{r}')\bar{\bar{1}}\right)$$

Both functions must also respect the boundary (radiative) conditions corresponding to vacuum (!…) and it can be proved that (Yaghjian-PIEEE-1980) :

$$\bar{\bar{G}}_e(\vec{r},\vec{r}'\neq\vec{r};\omega)=\frac{1}{4\pi k^2}\vec{\nabla}\wedge\vec{\nabla}\wedge\left(\psi\bar{\bar{I}}\right)=\frac{1}{4\pi}\left(\bar{\bar{I}}+\vec{\nabla}\otimes\vec{\nabla}/k^2\right)\psi$$

$$\bar{\bar{G}}_m(\vec{r},\vec{r}'\neq\vec{r};\omega)=-\frac{1}{4\pi}\vec{\nabla}\wedge\left(\psi\bar{\bar{I}}\right)$$

with $\psi=\psi(\vec{r},\vec{r}'\neq\vec{r};\omega)=e^{ik|\vec{r}-\vec{r}'|}/|\vec{r}-\vec{r}'|$

c) Electric **vector** wave equation in l.h.i. medium and its corresponding Green's generalized function

- Recall that for monochromatic waves with $\exp(-i\omega t)$ convention, in a linear, *magnetically homogeneous* medium, the vector wave equation for the electric field is:

$$\vec{\nabla}\times\vec{\nabla}\times\vec{E}(\vec{r};\omega)-\left(\frac{\omega^2}{c^2}\right)\mu_{r,B}(\omega)\,\varepsilon_{r,B}(\omega)\vec{E}(\vec{r};\omega)=\left(\frac{\omega^2}{c^2}\right)\left[\bar{\bar{\mu}}_r(\omega)\,\bar{\bar{\varepsilon}}_{r,\mathrm{eff}}(\vec{r};\omega)-\mu_{r,B}(\omega)\,\varepsilon_{r,B}(\omega)\right]\vec{E}(\vec{r};\omega)$$

- Let's define $\bar{\bar{G}}_{\mathrm{e},B}$ the dyadic Green's (generalized) function of the electric vector wave equation, in the ω space, for a *linear, homogeneous, isotropic* **B**ackground material (such that $\boxed{k_B^2=\mu_{r,B}\varepsilon_{r,B}\,\omega^2/c^2}$ and $\boxed{\bar{\bar{m}}^2\equiv\bar{\bar{\mu}}_r\bar{\bar{\varepsilon}}_{r,eff}/\mu_{r,B}\varepsilon_{r,B}}$).
  $\bar{\bar{G}}_{\mathrm{e},B}$ is solution of:

$$\vec{\nabla}\times\vec{\nabla}\times\left[\bar{\bar{G}}_{\mathrm{e},B}(\vec{r},\vec{r}\,';\omega)\right]-k_B^2\bar{\bar{G}}_{\mathrm{e},B}(\vec{r},\vec{r}\,';\omega)=+\delta(\vec{r}-\vec{r}\,')\bar{\bar{1}}$$

- $\bar{\bar{G}}_{\mathrm{e},B}$ is related to the solution $G_B(\vec{r},\vec{r}\,'\neq\vec{r};\omega)=-\exp(ik_B|\vec{r}-\vec{r}\,'|)/(4\pi|\vec{r}-\vec{r}\,'|)$ of the scalar wave equation in ω space by: $\bar{\bar{G}}_B(\vec{r},\vec{r}\,'\neq\vec{r};\omega)=-\left(\bar{\bar{1}}+\vec{\nabla}\otimes\vec{\nabla}/k_B^2\right)G_{\mathrm{e},B}(\vec{r},\vec{r}\,'\neq\vec{r};\omega)$

- For the non-singular part, this leads to:

$$\boxed{\bar{\bar{G}}_{\mathrm{e},B}(\vec{r},\vec{r}\,';\omega)=\left(\frac{1}{k_B^2}\right)\frac{e^{ik_B|\vec{r}-\vec{r}\,'|}}{4\pi|\vec{r}-\vec{r}\,'|^5}\begin{pmatrix}(3-3ik_B|\vec{r}-\vec{r}\,'|-(k_B|\vec{r}-\vec{r}\,'|)^2)(\vec{r}-\vec{r}\,')\otimes(\vec{r}-\vec{r}\,')\\-(1-ik_B|\vec{r}-\vec{r}\,'|-(k_B|\vec{r}-\vec{r}\,'|)^2)|\vec{r}-\vec{r}\,'|^2\bar{\bar{1}}\end{pmatrix}}$$

- In order to deal with the singular part, we define the dyadic propagator (interaction tensor):

$$\boxed{\bar{\bar{T}}_{\mathrm{e},B}(\vec{r},\vec{r}\,';\omega)\equiv\left(\frac{1}{\varepsilon_0\varepsilon_{r,B}}\right)k_B^2\bar{\bar{G}}_{\mathrm{e},B}(\vec{r},\vec{r}\,';\omega)}$$

d) Imaginary part of the singularity

$$\bar{\bar{T}}_{e,B}(\vec{r},\vec{r}';\omega) \equiv \left(\frac{1}{\varepsilon_0\varepsilon_{r,B}}\right) k_B^2 \bar{\bar{G}}_{e,B}(\vec{r},\vec{r}';\omega) = \frac{e^{ik_B|\vec{r}-\vec{r}'|}}{4\pi\varepsilon_0\varepsilon_{r,B}|\vec{r}-\vec{r}'|^5}\begin{pmatrix} [3(\vec{r}-\vec{r}')\otimes(\vec{r}-\vec{r}')-|\vec{r}-\vec{r}'|^2\bar{\bar{1}}] \\ -ik_B|\vec{r}-\vec{r}'|[3(\vec{r}-\vec{r}')\otimes(\vec{r}-\vec{r}')-|\vec{r}-\vec{r}'|^2\bar{\bar{1}}] \\ -k_B^2|\vec{r}-\vec{r}'|^2[(\vec{r}-\vec{r}')\otimes(\vec{r}-\vec{r}')-|\vec{r}-\vec{r}'|^2\bar{\bar{1}}] \end{pmatrix}$$

If we integrate the imaginary part of $\bar{\bar{T}}_B$ over a small spherical volume of radius δ, we have:

$$\iiint_{d\tau(\vec{r})} \mathrm{Im}[\bar{\bar{T}}_{e,B}(\vec{r},\vec{r}';\omega)]\, d\vec{r}'$$

$$= \frac{1}{4\pi\varepsilon_0\varepsilon_{r,B}}\int_0^\delta \frac{\rho^2 d\rho}{\rho^3}(k_B\rho)\cos(k_B\rho)\int_0^\pi d\theta\,\sin\theta\int_0^{2\pi} d\varphi\,(\bar{\bar{1}}-3\vec{u}_r\otimes\vec{u}_r) + \frac{1}{4\pi\varepsilon_0\varepsilon_{r,B}}\int_0^\delta \frac{\rho^2 d\rho}{\rho^3}k_B^2\rho^2\sin(k_B\rho)\int_0^\pi d\theta\,\sin\theta\int_0^{2\pi} d\varphi\,(\bar{\bar{1}}-\vec{u}_r\otimes\vec{u}_r)$$

$$-\frac{1}{4\pi\varepsilon_0\varepsilon_{r,B}}\int_0^\delta \frac{\rho^2 d\rho}{\rho^3}\sin(k_B\rho)\int_0^\pi d\theta\,\sin\theta\int_0^{2\pi} d\varphi\,(\bar{\bar{1}}-3\vec{u}_r\otimes\vec{u}_r)$$

Since $\int_0^\pi d\theta\,\sin\theta\int_0^{2\pi} d\varphi\,(\vec{u}_r\otimes\vec{u}_r) = (4\pi/3)\bar{\bar{1}}$ so that $\int_0^\pi d\theta\,\sin\theta\int_0^{2\pi} d\varphi\,(\bar{\bar{1}}-3\vec{u}_r\otimes\vec{u}_r) = \bar{\bar{0}}$ and $\int_0^\pi d\theta\,\sin\theta\int_0^{2\pi} d\varphi\,(\bar{\bar{1}}-\vec{u}_r\otimes\vec{u}_r)$ $= (8\pi/3)\bar{\bar{1}}$, we have:

$$\iiint_{d\tau(\vec{r})} \mathrm{Im}[\bar{\bar{T}}_{e,B}(\vec{r},\vec{r}';\omega)]\, d\vec{r}' = \frac{1}{4\pi\varepsilon_0\varepsilon_{r,B}}\int_0^\delta \frac{\rho^2 d\rho}{\rho^3}k_B^2\rho^2\sin(k_B\rho)\,(8\pi/3)\bar{\bar{1}} = \frac{2}{3\varepsilon_0\varepsilon_{r,B}}\bar{\bar{1}}\times\int_0^{k_B\delta} x\sin x\,dx$$

$$= \frac{2}{3\varepsilon_0\varepsilon_{r,B}}\bar{\bar{1}}\times[\sin(k_B\delta)-k_B\delta\cos(k_B\delta)]$$

Now let us note that $\vec{r}\to\vec{r}'$ means $\delta\to 0$. Furthermore, $\sin(a)-a\cos(a) \underbrace{\sim}_{a\to 0} a^3/3-a^5/30+O(a^7)$, so that to first non-zero order:

$\iiint_{d\tau(\vec{r})} \mathrm{Im}[\bar{\bar{T}}_{e,B}(\vec{r},\vec{r}';\omega)]\, d\vec{r}' = \frac{k_B^3}{6\pi\varepsilon_0\varepsilon_{r,B}}\bar{\bar{1}}\times\left(\frac{4}{3}\pi\delta^3\right)$. Hence it is as if we would have a constant $\boxed{\mathrm{Im}[\bar{\bar{T}}_{e,B}(\vec{r},\vec{r};\omega)] = \frac{k_B^3}{6\pi\varepsilon_0\varepsilon_{r,B}}\bar{\bar{1}}}$

e) Real part of the singularity

If we integrate the real part of $\overline{\overline{T}}_B$ over a small spherical volume of radius δ, small enough so that we can consider that the electric field is constant inside, we have:

$$\iiint_{d\tau(\vec{r})} \mathrm{Re}\left[\overline{\overline{T}}_{\mathrm{e},B}(\vec{r},\vec{r}';\omega)\right] d\vec{r}'$$

$$= -\frac{1}{4\pi\varepsilon_0\varepsilon_{r,B}}\int_0^\delta \frac{\rho^2 d\rho}{\rho^3}\cos(k_B\rho)\int_0^\pi d\theta\ \sin\theta\int_0^{2\pi} d\varphi\left(\overline{\overline{1}} - 3\vec{u}_r\otimes\vec{u}_r\right) - \frac{1}{4\pi\varepsilon_0\varepsilon_{r,B}}\int_0^\delta \frac{\rho^2 d\rho}{\rho^3}(k_B\rho)\sin(k_B\rho)\int_0^\pi d\theta\ \sin\theta\int_0^{2\pi} d\varphi\left(\overline{\overline{1}} - 3\vec{u}_r\otimes\vec{u}_r\right)$$

$$+\frac{1}{4\pi\varepsilon_0\varepsilon_{r,B}}\int_0^\delta \frac{\rho^2 d\rho}{\rho^3}k_B^2\rho^2\cos(k_B\rho)\int_0^\pi d\theta\ \sin\theta\int_0^{2\pi} d\varphi\left(\overline{\overline{1}} - \vec{u}_r\otimes\vec{u}_r\right)$$

The singularity is the first term since the ρ integral diverges (due to the 0 boundary) and the angular part is zero whereas the other terms are finite and $\to 0$ when $\delta \to 0$.

However, the singularity is the same as that of the static term ($k_B = 0$) since the difference remains finite!

By transforming the volume integral into a surface integral of the static term, we define:

$$\int_{\delta V}\mathrm{Re}\left[\overline{\overline{T}}_{\mathrm{e},B}(\vec{r},\vec{r}';\omega)\right] d\vec{r}' \approx \int_{\delta V}\vec{\nabla}\otimes\vec{\nabla}\left(\frac{1}{4\pi\varepsilon_0\varepsilon_{r,B}|\vec{r}-\vec{r}'|}\right)d\vec{r}' = \vec{\nabla}\otimes\int_{\delta V} -\vec{\nabla}'\left(\frac{1}{4\pi\varepsilon_0\varepsilon_{r,B}|\vec{r}-\vec{r}'|}\right)d\vec{r}'$$

$$\int_{\delta V}\mathrm{Re}\left[\overline{\overline{T}}_{\mathrm{e},B}(\vec{r},\vec{r}';\omega)\right] d\vec{r}' \approx -\frac{1}{4\pi\varepsilon_0\varepsilon_{r,B}}\vec{\nabla}\otimes\oiint_{\delta S}\frac{1}{|\vec{r}-\vec{r}'|}\overrightarrow{dS'}_{ext} = \boxed{\frac{1}{4\pi\varepsilon_0\varepsilon_{r,B}}\oiint_{\delta S}\frac{\vec{r}-\vec{r}'}{|\vec{r}-\vec{r}'|^3}\otimes\overrightarrow{dS'}_{ext} \equiv -\frac{\overline{\overline{L}}}{\varepsilon_0\varepsilon_{r,B}}}$$

Conclusion: (to first order in both Re and Im), it is **as if**:

$$\boxed{\overline{\overline{T}}_{e,B}(\vec{r},\vec{r}'\to\vec{r};\omega) = -\frac{\overline{\overline{L}}\delta(\vec{r}-\vec{r}')}{\varepsilon_0\varepsilon_{r,B}} + \frac{2}{3}i\frac{k_B^3}{4\pi\varepsilon_0\varepsilon_{r,B}}\overline{\overline{1}}}$$

$\overline{\overline{L}}$ is the tensor of Lorentz depolarization factors

Outline

I. Definitions

II. Wave equations

III. Green's "functions" and their singular part

IV. General volume integral equation

V. Discrete Dipole Approximation (microphotonics)

VI. DDA at the molecular scale $\Rightarrow$ DADI Model (nanophotonics)

VII. Optical indices from molecular information (and back!)

VIII. Conclusions and perspectives

IX. References

IV - General Integral equation for the electric field

a) Solution as a function of polarization contrast

Supposing that the scatterer is non-magnetic, in a linear homogeneous background and does not carry free currents, we rewrite the wave equation in the scatterer as (*cf.* § II-a):

$$\vec{\nabla}\times\left(\vec{\nabla}\times\vec{E}\right)-\frac{\omega^2}{c^2}\varepsilon_{r,B}\vec{E}=\frac{\omega^2}{c^2}\left(\bar{\bar{\varepsilon}}_{r,sca}-\varepsilon_{r,B}\bar{\bar{1}}\right)\vec{E}=k_B^2\frac{\Delta\vec{P}}{\varepsilon_0\varepsilon_{r,B}}$$

We can now introduce the Green's "function" of the background, solution of:

$$\vec{\nabla}\times\vec{\nabla}\times\left[\bar{\bar{G}}_B(\vec{r},\vec{r}\,';\omega)\right]-k_B^2\bar{\bar{G}}_B(\vec{r},\vec{r}\,';\omega)=+\delta(\vec{r}-\vec{r}\,')\bar{\bar{1}}$$

With the appropriate boundary conditions and $k_B^2=\varepsilon_{r,B}\,\omega^2/c^2$

The solution of this equation can be written as:

$$\begin{aligned}\bar{\bar{G}}_B(\vec{r},\vec{r}\,'\neq\vec{r};\omega) &= \left(\bar{\bar{1}}+\frac{\vec{\nabla}\otimes\vec{\nabla}}{k_B^2}\right)\frac{\exp(ik_B|\vec{r}-\vec{r}\,'|)}{4\pi|\vec{r}-\vec{r}\,'|}\\ &= \frac{\exp(i\alpha)}{4\pi\alpha^2|\vec{r}-\vec{r}\,'|}\begin{bmatrix}(3-3\mathrm{i}\alpha-\alpha^2)\vec{u}\otimes\vec{u}\\ -(1-\mathrm{i}\alpha-\alpha^2)\bar{\bar{1}}\end{bmatrix}\end{aligned}$$

With $\alpha\equiv k_B|\vec{r}-\vec{r}\,'|$ and $\vec{u}\equiv(\vec{r}-\vec{r}\,')/|\vec{r}-\vec{r}\,'|$.

IV - General Integral equation for the electric field

b) Volume integral solution

Then, taking inspiration from A. D. Yaghjian, Proc. IEEE, 68, 248-263 (1980), the solution of the wave equation in the scatterer can be written as:

$$\vec{E}(\vec{r}\,;\omega) = \vec{E}_{inc}(\vec{r}\,;\omega) +$$

$$\lim_{\delta V\to 0}\int_{V_{scatterer}-\delta V} \bar{\bar{T}}_{e,B}(\vec{r},\vec{r}\,'\,;\omega)\,\Delta\vec{P}(\vec{r}\,'\,;\omega)d\vec{r}\,'$$

$$-\,\bar{\bar{L}}\,\frac{\left(\bar{\bar{\varepsilon}}_{r,sca}(\vec{r}\,;\omega)-\varepsilon_{r,B}\bar{\bar{1}}\right)}{\varepsilon_0\varepsilon_{r,B}}\vec{E}(\vec{r}\,;\omega)$$

with $\vec{E}_{inc}(\vec{r}\,;\omega) = \int_{V_{sources}} \bar{\bar{G}}_{sources}(\vec{r},\vec{r}\,'\,;\omega)\, i\omega\mu_0\vec{j}_{free}d\vec{r}\,'$ and $\bar{\bar{L}} = \frac{1}{4\pi}\oint\!\!\!\oint_{S_\delta(\vec{r})}\frac{(\vec{r}\,'-\vec{r})}{|\vec{r}\,'-\vec{r}|^3}\otimes d\vec{S'}_{ext}$

$\bar{\bar{L}}$ is the tensor of Lorenz depolarization factors. It reduces to $\bar{\bar{L}} = \bar{\bar{1}}/3$ if $S_\delta(\vec{r})$ is a sphere centered at $\vec{r}$.

Note that, formally, in the electrostatically small limit ($\Delta\vec{P}(\vec{r}\,'\,;\omega)$ constant in δV), we could have defined $\bar{\bar{L}} = -\int_{\delta V} k_B^2\bar{\bar{G}}_B(\vec{r},\vec{r}\,'\,;\omega)\,d\vec{r}\,'$. However, this volume integral is ill-defined, but can be transformed into a well-defined (because $\vec{r}$ is not at the surface) surface integral, using the divergence theorem. Furthermore, it can be shown that the volume δV around $\vec{r}$, enclosed by the surface $S_\delta(\vec{r})$, can be any shape provided its characteristic size δ is small enough that the retardation effects can be neglected, so that $\lim_{\omega\to 0} k_B^2\bar{\bar{G}}_B(\vec{r},\vec{r}\,';\omega)$ can be employed to compute it. In fact the singularity of $\lim_{\omega\to 0} k_B^2\bar{\bar{G}}_B(\vec{r},\vec{r}\,';\omega)$ is essentially the same as that of $k_B^2\bar{\bar{G}}_B(\vec{r},\vec{r}\,';\omega)$ when $\vec{r}\to\vec{r}\,'$.

IV - General Integral equation for the electric field

c) Discretization of the volume integral solution

Several methods of solution of the volume integral equation exist (including the method of moments or the generalized multipole method).

Here, as an example, we follow O.J.F. Martin and N.B. Piller, Phys. Rev. E, 58, 3909-3915 (1998)) and discretize the volume of the scatterer by "electrically small volumes" (i.e. such that $\Delta\vec{P}(\vec{r}'\,;\omega) = \varepsilon_0\left(\bar{\bar{\varepsilon}}_{r,sca}(\vec{r}'\,;\omega) - \varepsilon_{r,B}\bar{\bar{1}}\right)\vec{E}(\vec{r}\,';\omega)$ and $\bar{\bar{G}}_{e,B}(\vec{r},\vec{r}'\,;\omega)$ can be considered constant in that volume):

$$\forall i = 1,\dots,N \quad \vec{E}(\vec{r}_i;\omega) \approx \vec{E}_{inc}(\vec{r}_i;\omega) + \sum_{\substack{j=1\\ j\neq i}}^{N} \bar{\bar{G}}_{e,B}\left(\vec{r}_i,\vec{r}_j;\omega\right)\frac{\omega^2}{c^2}\left[\frac{\Delta\vec{P}(\vec{r}_j;\omega)}{\varepsilon_0}\right]V_j$$

$$+\frac{\bar{\bar{M}}_i}{\varepsilon_{r,B}}\left[\frac{\Delta\vec{P}(\vec{r}_i;\omega)}{\varepsilon_0}\right] - \frac{\bar{\bar{L}}}{\varepsilon_{r,B}}\left[\frac{\Delta\vec{P}(\vec{r}_i;\omega)}{\varepsilon_0}\right]$$

with: $\bar{\bar{M}}_i = \lim_{\delta V\to 0}\int_{V_i-\delta V} k_B^2\bar{\bar{G}}_{e,B}(\vec{r}_i,\vec{r}'\,;\omega)\,d\vec{r}' = \frac{2}{3}\left[\left(1 - ik_B R_{j,\mathrm{eff}}\right)\exp\left(ik_B R_{j,\mathrm{eff}}\right) - 1\right]\bar{\bar{1}}$,

for an equivalent sphere of radius $R_{i,\mathrm{eff}} = \sqrt[3]{3V_i/4\pi}$. Also, $k_B^2 = \varepsilon_{r,B}\,\omega^2/c^2$ and $\bar{\bar{L}} = \bar{\bar{I}}/3$.

IV - General Integral equation for the electric field

c) Discretization of the volume integral solution

Several other improved methods of discretization have been proposed:

- Peltoniemi, *J. Quant. Spectrosc. Radiat. Transfer*, **55**(5), 637-647 (1996) proposed some more complicated calculations which do not need the “electrically small” approximation

- “filtered coupled dipole” (FCD) method: Piller & Martin, IEEE Transactions on Antennas and Propagation, 46, 1126–1137 (1998) and Gay-Balmaz & Martin, *Comp. Phys. Comm.*, **144**, 111–120 (2002). Convolution by a smoothing function to filter out high spatial frequency (as in the process that goes from microscopic fields to macroscopic fields).
  Useful for targets with large refractive indices where the classical point dipole method fails according to Yurkin at al. Phys. Rev. E, **82**, 036703 (2010).
  (now implemented in ADDA and DDSCAT (since v7.3, cf. § 14.2 of manual))

All these methods can be rewritten using point dipoles induced by the incident waves:

$$\Delta\vec{P}(\vec{r}_n;\omega)V_n = \vec{p}_n(\omega) = \bar{\bar{\alpha}}_n(\omega)\vec{E}_{loc}(\vec{r}_n;\omega)$$

Outline

I. Definitions

II. Wave equations

III. Green's "functions" and their singular part

IV. General volume integral equation

V. Discrete Dipole Approximation (microphotonics)

VI. DDA at the molecular scale $\Rightarrow$ DADI Model (nanophotonics)

VII. Optical indices from molecular information (and back!)

VIII. Conclusions and perspectives

IX. References

1rst DDA paper: E. M. Purcell and C. R. Pennypacker, *Ap. J.*, **186**, 705-714 (1973), see also Draine-ApJ-1988 and Draine-Flatau-JOSAA-1994 (refs at end of this presentation)

- DDA is a general method to compute scattering and absorption of electromagnetic waves by particles of arbitrary geometry and composition.
- The shape of a particle is represented as a finite array of finite continuum dielectric volumes of possibly different compositions, without net charge
- When the particle is submitted to an incident monochromatic field $\vec{E}_{inc}(\vec{r};\omega)e^{-i\omega t}$, there is a creation of discrete induced dipoles in the discretized continuum volumes:

$$\varepsilon_0 V_n\left(\bar{\bar{\varepsilon}}_{r,sca}(\vec{r}_n;\omega)-\varepsilon_{r,B}\bar{\bar{1}}\right)\vec{E}(\vec{r}_n;\omega)=\Delta\vec{P}(\vec{r}_n;\omega)V_n=\vec{p}_n(\omega)=\bar{\bar{\alpha}}_n(\omega)\vec{E}_{loc}(\vec{r}_n;\omega)$$

- In the “electrically small” approximation: $(\bar{\bar{\alpha}}_i)^{-1}\vec{p}_i=\vec{E}_{loc}(\vec{r}_i;\omega)\approx\vec{E}_{inc}(\vec{r}_i;\omega)+\sum_{\substack{n=1\\n\neq i}}^{N}\bar{\bar{T}}_{e,B}(\vec{r}_i,\vec{r}_n;\omega)\vec{p}_n$

  with $\bar{\bar{T}}_{e,B}(\vec{r},\vec{r}';\omega)=\bar{\bar{G}}_{e,B}(\vec{r},\vec{r}';\omega)\frac{\omega^2}{\varepsilon_0 c^2}=k_B^2\bar{\bar{G}}_{e,B}(\vec{r},\vec{r}';\omega)\frac{1}{\varepsilon_0\varepsilon_{r,B}}$ since $k_B^2=\varepsilon_{r,B}\,\omega^2/c^2$

- Hence, the effective dipoles can be computed by solving the linear system:

$$\forall i=1,\ldots,N\quad\left[(\bar{\bar{\alpha}}_i)^{-1}\delta_{in}-\sum_{\substack{n=1\\n\neq i}}^{N}\bar{\bar{T}}_{e,B}(\vec{r}_i,\vec{r}_n;\omega)\right]\vec{p}_n=\vec{E}_{inc}(\vec{r}_i;\omega)$$

- Once the effective dipoles have been computed, derived quantities can be computed, e.g.

$$\vec{E}(\vec{r}\,;\omega)=\vec{E}_{inc}(\vec{r}\,;\omega)+\sum_{j=1}^{N}\bar{\bar{T}}_{e,B}^{\infty}(\vec{r},\vec{r}_j;\omega)\vec{p}_j(\omega)$$

V – Discrete Dipole Approximation

b) Some comments on the linear system to solve

- The effective dipoles are computed by solving the linear system:

$$\forall i = 1, \dots, N \quad \left[(\bar{\bar{\alpha}}_i)^{-1} \delta_{in} - \sum_{\substack{n=1 \\ n \neq i}}^{N} \bar{\bar{T}}_{e,B}(\vec{r}_i, \vec{r}_n; \omega) \right] \vec{p}_n = \vec{E}_{inc}(\vec{r}_i; \omega)$$

- The results depend notably from the prescription taken for the diagonal elements (effective polarizabilities). (dependence ↑ if N ↓).This problem has been discussed not only in the context of DDA but also of near-field optics (see e.g. Draine-Goodman-ApJ-1993, Lakhtakia-IJIMW-1993, Peltoniemi-JQSRT-1996, Martin-Piller-PRE-1998, Gutkowicz-Krusin-Draine-Arxiv-2004, Yurkin-Hoekstra-JQSRT-2007, Albaladejo et al.-OE-2010, Massa et al.-JOSAA-2014)

- In the most popular DDA codes (ADDA and DDSCAT), the discretization is done on a regular grid so that a FFT can be employed to speed up the linear system solution by changing the scaling of the algorithm for $O(N_{iter} N \ln N)$ instead of $O(N^3)$. Hence millions of discretization points can be used (using a cluster).

- The maximal admissible grid step d is such that $|m|kd \sim 1$ (with $m = \sqrt{\varepsilon_{r,sca}/\varepsilon_{r,B}}$ the complex relative optical index and $k = \omega/c$), $|m-1| \leq 3^+$ and d ↓ as $\mathrm{Im}(m)$ ↑
(cf. DDSCAT manual 7.3 § 2)

- NB: The DDA system can be found by optimizing the self-interaction energies + the interaction energies between dipoles, with respect to the dipoles moments.

V – Discrete Dipole Approximation

c) Effective polarizability as a function of optical index: radiative correction

In his seminal 1988 article (Draine-ApJ-1988), Bruce Draine states that the radiative correction to the absorption cross-section can be easily obtained in the case where the polarizability is a scalar!

Indeed, if one defines $\vec{p}_j = \bar{\bar{\alpha}}_j \vec{E}_{ext,j} = \bar{\bar{\alpha}}_j^0 \left(\vec{E}_{ext,j} + \vec{E}_{rad,j}\right)$ (cf. Eq. (2.02) of Draine-ApJ-1988),

then one finds $\alpha_j = \frac{\alpha_j^0}{1-\left(\frac{2}{3}\right) i k^3 \alpha_j^0}$ (CGS-Gauss units), (cf. Eq. (2.03) of Draine-ApJ-1988)

which is also $\alpha_j = \alpha_j^0 / \left[1 - \left(\frac{2}{3}\right) i k^3 \left(\frac{\alpha_j^0}{4\pi\varepsilon_0}\right)\right]$ (MKSA units), where $\boldsymbol{\alpha_j^0} = (4\pi\varepsilon_0)\left(\frac{3(V_{tot}/N)}{4\pi}\right)\frac{(\varepsilon_r - 1)}{(\varepsilon_r + 2)}$ **is the polarizability computed from the usual Clausius Mossotti quasi-static approximation**

A crucial observation for the generalization of this correction to non-cubic and non-amorphous cases is that this relation is simpler with inverses:

$\frac{4\pi\varepsilon_0}{\alpha_j} = \frac{4\pi\varepsilon_0}{\alpha_j^0} - \frac{2}{3} i k^3$ (MKSA) or $\frac{1}{\alpha_j} = \frac{1}{\alpha_j^0} - \frac{2}{3} i k^3$ (CGS-Gauss) (in Draine's paper the background medium is vacuum)

Draine-ApJ-1988 : "The Discrete Dipole Approximation and its Application to Interstellar Graphite Grains", B. T. Draine, Astrophys. J., **333**, 848-872 (1988)

V – Discrete Dipole Approximation

c) Effective polarizability as a function of optical index: generalized Lorenz (1869) – Lorentz (1878) relation

- Recall that : $\varepsilon_0 V_n\left(\bar{\bar{\varepsilon}}_{r,sca}(\vec{r}_n;\omega) - \varepsilon_{r,B}\bar{\bar{1}}\right)\vec{E}(\vec{r}_n;\omega) = \Delta\vec{P}(\vec{r}_n;\omega)V_n = \vec{p}_n(\omega) = \bar{\bar{\alpha}}_n(\omega)\vec{E}_{loc}(\vec{r}_n;\omega)$,
  with $\vec{E}_{loc}(\vec{r}_n;\omega) \approx \vec{E}_{inc}(\vec{r}_i;\omega) + \sum_{\substack{n=1\\n\neq i}}^{N} \bar{\bar{T}}_B(\vec{r}_i,\vec{r}_n;\omega)\vec{p}_n$ in the "electrically small" approximation.

- Pb: how to relate the macroscopic field $\vec{E}(\vec{r}_n;\omega)$ and the local field $\vec{E}_{loc}(\vec{r}_n;\omega)$, so as to compute $\bar{\bar{\alpha}}_n(\omega)$ as a function of $\bar{\bar{\varepsilon}}_{r,sca}(\vec{r}_n;\omega)$ (or the reverse)?

- Let us suppose that to get the total macroscopic field, we just need to add the contribution of the considered discretization element : $\vec{E}(\vec{r}_i;\omega) \approx \vec{E}_{loc}(\vec{r}_i;\omega) + \bar{\bar{T}}_{e,B}(\vec{r}_i,\vec{r}_i;\omega)\vec{p}_i = \vec{E}_{inc}(\vec{r}_i;\omega) + \sum_{n=1}^{N}\bar{\bar{T}}_{e,B}(\vec{r}_i,\vec{r}_n;\omega)\vec{p}_n$
  with $\bar{\bar{T}}_{e,B}(\vec{r},\vec{r}\,';\omega) = k_B^2\bar{\bar{G}}_{e,B}(\vec{r},\vec{r}\,';\omega)/\varepsilon_0\varepsilon_{r,B} = \bar{\bar{G}}_{e,B}(\vec{r},\vec{r}\,';\omega)\frac{\omega^2}{\varepsilon_0 c^2}$ and $\bar{\bar{T}}_{e,B}(\vec{r}_i,\vec{r}_i;\omega) = \frac{1}{\varepsilon_0 V_i}\left(\frac{\bar{\bar{M}}_i - \bar{\bar{L}}}{\varepsilon_{r,B}}\right)$
  $\left(\bar{\bar{T}}_{e,B}(\vec{r},\vec{r}\,' \to \vec{r};\omega) = -\frac{\bar{\bar{L}}\delta(\vec{r}-\vec{r}\,')}{\varepsilon_0\varepsilon_{r,B}} + i\,\frac{2}{3}\frac{k_B^3}{(4\pi\varepsilon_0)\varepsilon_{r,B}}\bar{\bar{1}}\right)$

- **Generalized Lorenz-Lorentz relation:** $\boxed{\vec{E}_{loc}(\vec{r}_i;\omega) \approx \left\{\bar{\bar{1}} + \frac{(\bar{\bar{L}}-\bar{\bar{M}}_i)}{\varepsilon_{r,B}}\Delta\bar{\bar{\varepsilon}}_r(\vec{r}_i;\omega)\right\}\vec{E}(\vec{r}_i;\omega)}$

- Hence, $\varepsilon_0 V_i\left(\bar{\bar{\varepsilon}}_{r,sca}(\vec{r}_i;\omega) - \varepsilon_{r,B}\bar{\bar{1}}\right)\vec{E}(\vec{r}_i;\omega) = \vec{p}_i = \bar{\bar{\alpha}}_i\vec{E}_{loc}(\vec{r}_i;\omega) = \bar{\bar{\alpha}}_i\left(\bar{\bar{1}} + \bar{\bar{T}}_{e,B}(\vec{r}_i,\vec{r}_i;\omega)\bar{\bar{\alpha}}_i\right)^{-1}\vec{E}(\vec{r}_i;\omega)$

- Finally, one recovers a generalized version of the radiative correction pointed out in Draine-ApJ-1988:
  $\varepsilon_0 V_i\left(\bar{\bar{\varepsilon}}_{r,sca}(\vec{r}_i;\omega) - \varepsilon_{r,B}\bar{\bar{1}}\right) = \bar{\bar{\alpha}}_i\left(\bar{\bar{1}} + \bar{\bar{T}}_{e,B}(\vec{r}_i,\vec{r}_i;\omega)\bar{\bar{\alpha}}_i\right)^{-1}$ or $\boxed{(\bar{\bar{\alpha}}_i)^{-1} = \left(\bar{\bar{\alpha}}_i^{(0)}\right)^{-1} - \bar{\bar{T}}_{e,B}(\vec{r}_i,\vec{r}_i;\omega)}$
  with $\bar{\bar{\alpha}}_i^{(0)}(\omega) = \varepsilon_0 V_i\left(\bar{\bar{\varepsilon}}_{r,sca}(\vec{r}_i;\omega) - \varepsilon_{r,B}\bar{\bar{1}}\right)$

V – Discrete Dipole Approximation

c) Effective polarizability as a function of optical index: final anisotropic expression

We showed that: $(\bar{\bar{\alpha}}_i)^{-1} = \left(\varepsilon_0 V_i\left(\bar{\bar{\varepsilon}}_{r,sca}(\vec{r}_i;\omega) - \varepsilon_{r,B}\bar{\bar{1}}\right)\right)^{-1} - \bar{\bar{T}}_{e,B}(\vec{r}_i,\vec{r}_i;\omega) = \left(\bar{\bar{\alpha}}_i^{(0)}\right)^{-1} - \bar{\bar{T}}_B(\vec{r}_i,\vec{r}_i\,;\omega)$

Since $\bar{\bar{T}}_{e,B}(\vec{r}_i,\vec{r}_i\,;\omega) = \frac{1}{\varepsilon_0 V_i}\left(\frac{\bar{\bar{M}}_i - \bar{\bar{L}}}{\varepsilon_{r,B}}\right)$, this can be recast in the form (beware that $\bar{\bar{\alpha}}_i^{(0)} \neq \bar{\bar{\alpha}}_i(0)$!):

$$(\bar{\bar{\alpha}}_i)^{-1} = \left(\bar{\bar{\alpha}}_i(0)\right)^{-1} - \frac{\bar{\bar{M}}_i}{\varepsilon_0\varepsilon_{r,B}V_i}$$

With $\left(\bar{\bar{\alpha}}_i(0)\right)^{-1} = \left(\varepsilon_0 V_i\left(\bar{\bar{\varepsilon}}_{r,sca}(\vec{r}_i;\omega) - \varepsilon_{r,B}\bar{\bar{1}}\right)\right)^{-1} + \frac{\bar{\bar{L}}}{\varepsilon_0\varepsilon_{r,B}V_i} = \left(\bar{\bar{\alpha}}_i^{(CM)}\right)^{-1}$

At first order $\mathrm{Im}\left(\frac{\bar{\bar{M}}_i}{\varepsilon_0\varepsilon_{r,B}V_i}\right) = i\,\frac{2}{3}\frac{k_B^3}{(4\pi\varepsilon_0)\varepsilon_{r,B}}\bar{\bar{1}}$, so that we have:

$$\left(\frac{\bar{\bar{\alpha}}_i}{(4\pi\varepsilon_0)}\right)^{-1} = \left(\frac{\bar{\bar{\alpha}}_i^{(CM)}}{(4\pi\varepsilon_0)}\right)^{-1} - i\,\frac{2}{3}\frac{k_B^3}{\varepsilon_{r,B}}\bar{\bar{1}}$$

which generalizes Draine's relation with vacuum as background: $\frac{4\pi\varepsilon_0}{\alpha_j} = \frac{4\pi\varepsilon_0}{\alpha_j^0} - \frac{2}{3}ik^3$

Note that for an anisotropic background, $\left(\frac{1}{\varepsilon_0}\sum_j N_j\bar{\bar{\alpha}}_j^{(\mathrm{CM})}\right)^{-1} = (\bar{\bar{\varepsilon}}_i - \bar{\bar{\varepsilon}}_m)^{-1} + (\bar{\bar{\varepsilon}}_m)^{-1}\bar{\bar{L}}$

V – Discrete Dipole Approximation

b) summary

- Separation of a continuous medium into a finite set of polarizable volumes
- Approximation: polarizable volumes = point particles with dipoles $\vec{p} = f\left(\vec{E}_{loc}\right)$
- Interactions between $\vec{p} \Rightarrow$ system of linear equations (size = $3 \times N_{dip}$)
- Resolution of the system $\Rightarrow$ fields/dipoles on all atoms
- fields/dipoles on all atoms $\Rightarrow$ cross sections, asymmetries, degree of polarization,…
- Input = geometry of the system (position of the dipoles) and effective dipole polarizabilities (!...) method applicable for objects of any shape or for periodic structures. Materials can be inhomogeneous and anisotropic!
- Results are all the more precise as the discretization is fine, but RAM requirements and computing time increase very quickly!
- High-performance and open-access codes available $\Rightarrow$ many interesting results

Outline

I. Definitions

II. Wave equations

III. Green's "functions" and their singular part

IV. General volume integral equation

V. Discrete Dipole Approximation (microphotonics)

VI. DDA at the molecular scale $\Rightarrow$ DADI Model (nanophotonics)

VII. Optical indices from molecular information (and back!)

VIII. Conclusions and perspectives

IX. References

VI - DDA at the molecular scale ⇒ DADI Model

a) A short historical point

- 1rst DDA paper:

"Scattering and Absorption of Light by Nonspherical Dielectric Grains", E. M. Purcell and C. R. Pennypacker, *Ap. J.*, **186**, 705-714 (1973)

- DDA at the atomic scale is often called PDI (Point Dipole Interaction)

"An Atom-Dipole Interaction Model for Molecular Polarizability, Application to Polyatomic Molecules and Determination of Atom Polarizabilities", J. Applequist, J. R. Carl and K.-K. Fung, *J.A.C.S.*, **94**, 2952–2960 (1972)

$$\begin{bmatrix} \alpha_1^{-1} & \mathbf{T}_{12} \cdots \mathbf{T}_{1N} \\ \mathbf{T}_{21} & \alpha_2^{-1} \cdots \mathbf{T}_{2N} \\ \cdot & \\ \cdot & \\ \cdot & \\ \mathbf{T}_{N1} & \cdot \quad \cdot \quad \cdot \quad \alpha_N^{-1} \end{bmatrix} \begin{bmatrix} \mu_1 \\ \mu_2 \\ \cdot \\ \cdot \\ \cdot \\ \mu_N \end{bmatrix} = \begin{bmatrix} \mathbf{E}_1 \\ \mathbf{E}_2 \\ \cdot \\ \cdot \\ \cdot \\ \mathbf{E}_N \end{bmatrix} \qquad (4)$$

- But in fact this approach can be traced to:

"Molecular refractivity and atomic interaction",

L. Silberstein, *Phil. Mag.*, **33**, 92–128 (1917)

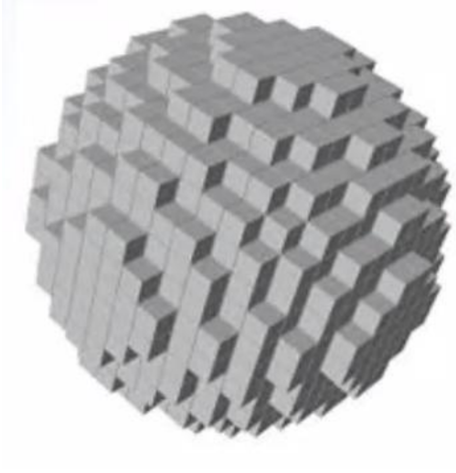
b) Principle of the method

Similarly to DDA, we can compute **dipoles** on each atom i with DADI model by solving the following system of equations, for all i from 1 to N:

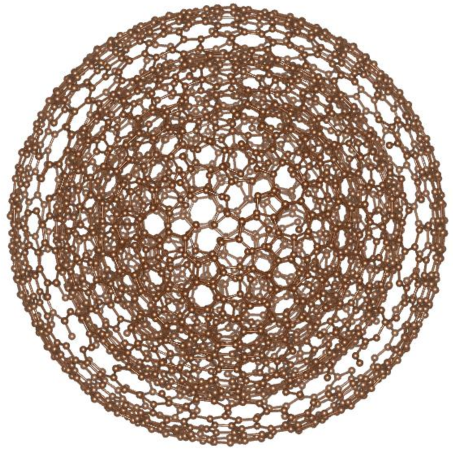
$$\vec{p}_i(\omega) = \bar{\bar{\alpha}}_i(\omega)\vec{E}_0(\vec{r}_i,\omega) + \sum_{j=1}^{N} \bar{\bar{\alpha}}_i(\omega)\bar{\bar{T}}(\vec{r}_i,\vec{r}_j,\omega)\vec{p}_j(\omega)$$

where $\bar{\bar{\alpha}}_i(\omega)$ is the atomic polarizabilities tensor, $\vec{E}_0(\vec{r}_i,\omega)$ the incident electric field applied to the particle and $\bar{\bar{T}}(\vec{r}_i,\vec{r}_{j\neq i},\omega)$ that can be computed with the double gradient of the generalized Green's function for the Helmholtz equation:

$$\bar{\bar{T}}(\vec{r}_i,\vec{r}_{j\neq i},\omega) = -\frac{1}{\varepsilon_0}\left(\vec{\nabla}_{\vec{r}_i} \otimes \vec{\nabla}_{\vec{r}_j} + \frac{\omega^2}{c^2}\bar{\bar{I}}\right)\left(-\frac{e^{i\frac{\omega}{c}|\vec{r}_i-\vec{r}_j|}}{4\pi|\vec{r}_i-\vec{r}_j|}\right)$$



DDA vs DADI



In DADI the point dipoles are supposed to represent atoms much smaller than the discretization volumes used in DDA, the $i = j$ terms of the interaction tensor $\bar{\bar{T}}$ are assumed to simplify to:

$$\bar{\bar{T}}(\vec{r}_i,\vec{r}_i,\omega) = i\frac{2}{3}\frac{\omega^3}{c^3}\frac{1}{4\pi\varepsilon_0}\bar{\bar{I}}$$

Once the values of dipoles are self-consistently computed, they are used to compute various optical quantities of interest (such as Müller matrix or the extinction, diffusion and absorption cross-sections).

VI - DDA at the molecular scale ⇒ DADI Model

c) First geometrical model

Soot = chemical units C_y randomly scattered on n concentric spheres

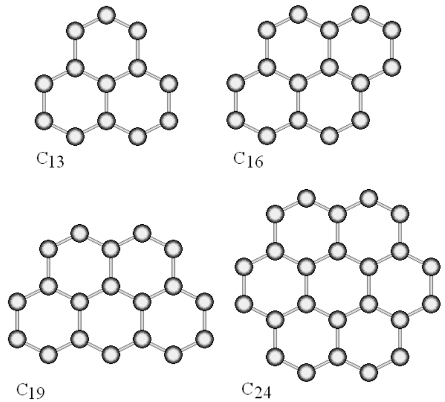
Total number of atoms: N

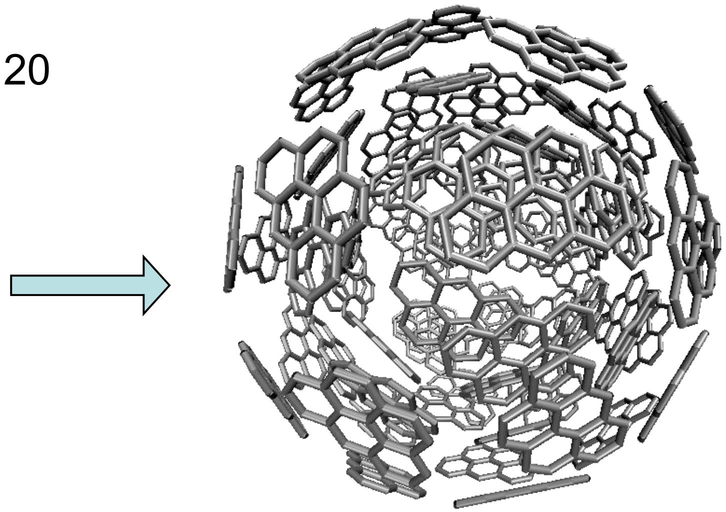
$R_n = R_0 + 0.34 \times (n-1)$ nm [*, **]

$R_n \approx 1 - 8$ nm

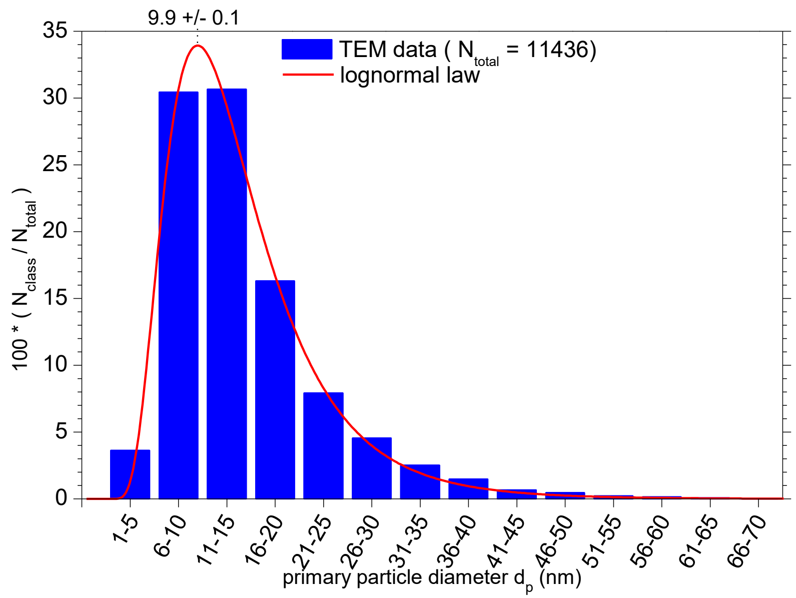
$R_0 \approx 1$ nm

$y = 13$ to 24, $n \approx 1 - 20$





$\varnothing_{th} \approx 2 - 16$ nm



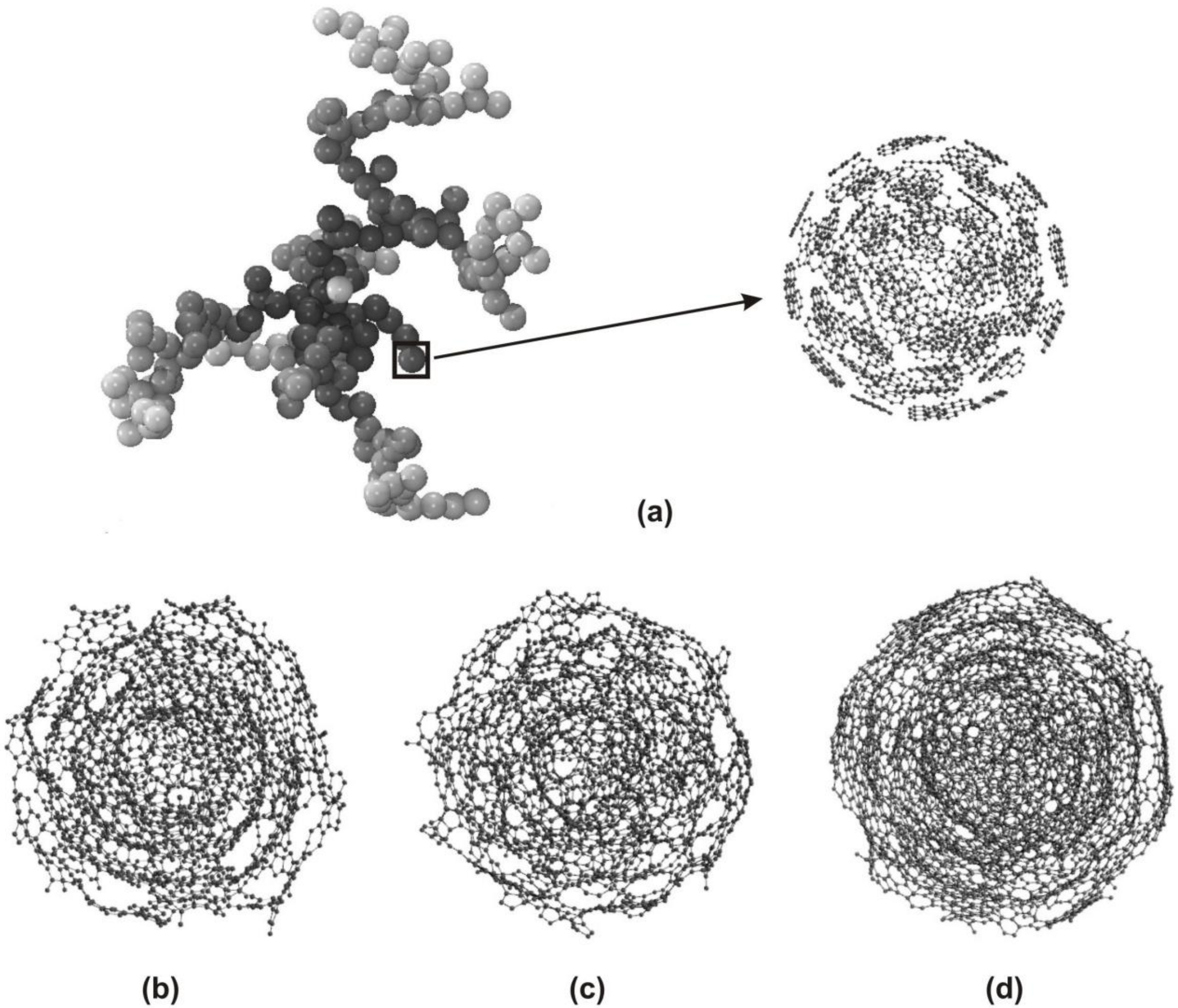
$\varnothing_{exp} \approx 6 - 20$ nm (*)

[*] F. Douce, Étude de la formation des particules de suie à partir de constituants représentatifs du gazole, thèse de doctorat, Université d'Orléans (2001).

[**] F. Moulin, Modélisation morphologique des suies émises par les avions, thèse de doctorat, université de Franche-Comté (2007).

VI - DDA at the molecular scale ⇒ DADI Model

d) improved spherule model thanks to molecular dynamics



(a) S_{units} containing 2147 C atoms, scattered by units on concentric spheres

(b), (c) and (d) S_{holes} nanoparticles containing 2133, 2206 and 3774 C atoms, respectively, relaxed by Molecular dynamics (AIREBO potential).

VI - DDA at the molecular scale ⇒ DADI Model

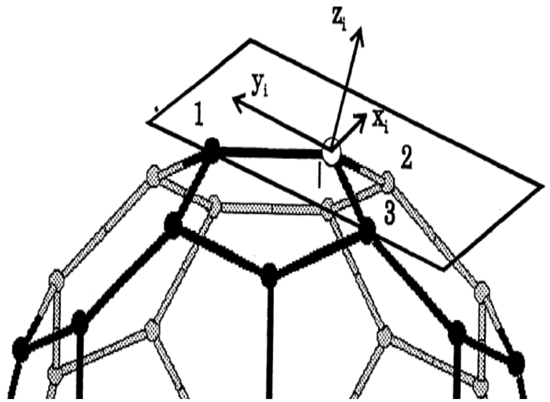
e) Anisotropic dipole polarizabilities

- The difference between DDA and PDI lies essentially in the diagonal elements of the matrix for which we need « true » complex atomic polarizabilities (+ discretization points = atomic positions which are not on a regular grid…).

- For carbonaceous soot, we convert Draine's tabulated values for the frequency dependent dielectric constant of graphite into anisotropic carbon polarizabilities using depolarizing factors computed by Senet et al. (Kirchberg-1994), $L_{\perp} = 0.803$ and $L_{\parallel} = 1 - 2 \times 0.803 = -0.606$, $\parallel$ and $\perp$ meaning here $\parallel$ and $\perp$ to the graphite plane: $\sum_i N_i \frac{(\overleftrightarrow{\alpha_i})_{xx}}{\varepsilon_0} = \frac{(\overleftrightarrow{\chi_e})_{xx}}{(1+L_{xx}\times(\overleftrightarrow{\chi_e})_{xx})}$

- For curved structures, we define a local graphite plane around a given atom, using the 3 nearest neighbors and compute a rotation matrix $\bar{\bar{R}}$ to connect the local frame to the absolute frame. Then the polarizability matrix in the absolute frame is given by:

$$\overleftrightarrow{\alpha}_C = {}^tR \begin{pmatrix} \alpha_{C//} & 0 & 0 \\ 0 & \alpha_{C//} & 0 \\ 0 & 0 & \alpha_{C\perp} \end{pmatrix} R$$



- In cases when the atom does not have 3 nearest neighbors, we take a scalar polarizability equal to

$$\alpha_{C,iso} = \left(2\alpha_{C,\parallel} + \alpha_{C,\perp}\right)/3$$

VI - DDA at the molecular scale ⇒ DADI Model

f) Anisotropic dipolar polarizabilities in the quasi-static limit (i)

- Pb : When $R \to 0$, the propagators diverge.
  The interactions between ions and/or atoms cannot be considered as interactions between point multipoles any more!

⇒ It is then necessary to regularize the (static) propagator for the small distances

- Idea (often used in quantum chemistry): suppose that the charge distributions are spherically symmetrical with a Gaussian radial dependence

⇒ convolution of the classical propagator with one Gaussian (GMI), or two (GMM), depending on whether we only want the field at one point or if we need the interaction energy between 2 multipoles :

$$\tilde{T}_0^{(0)}(\vec{r}_i, \vec{r}_j) \equiv \iint \frac{\exp\left[-\frac{(\vec{r}_1 - \vec{r}_i)^2}{R_i^2}\right]}{\pi^{3/2} R_i^3} \frac{1}{4\pi\varepsilon_0 |\vec{r}_1 - \vec{r}_2|} \frac{\exp\left[-\frac{(\vec{r}_2 - \vec{r}_j)^2}{R_j^2}\right]}{\pi^{3/2} R_j^3} d\vec{r}_1 d\vec{r}_2$$

$$= \frac{\operatorname{erf}\left(|\vec{r}_i - \vec{r}_j| / \sqrt{R_i^2 + R_j^2}\right)}{\left(4\pi\varepsilon_0 |\vec{r}_i - \vec{r}_j|\right)}$$

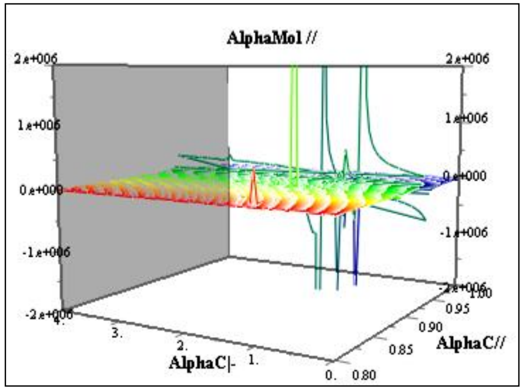
- Thanks to the possibility to invert gradients and integrals on different variables, the higher order propagators can be deduced from $T^{(0)}$ by successive differentiation.

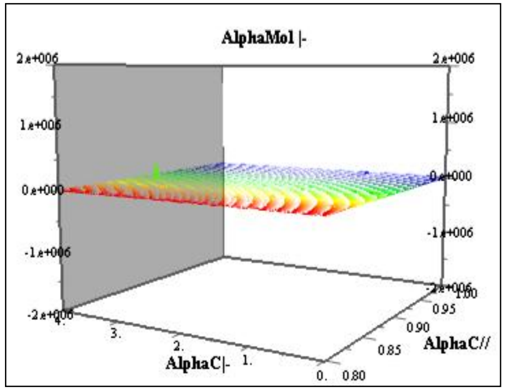
f) Anisotropic dipolar polarizabilities in the quasi-static limit (ii)

Influence of the propagator regularization on the polarizability catastrophes

- a and b: ∥ and ⊥ polarizabilities of a (13,7) nanotube, as a function of $\alpha_{C//}$ and $\alpha_{C\perp}$

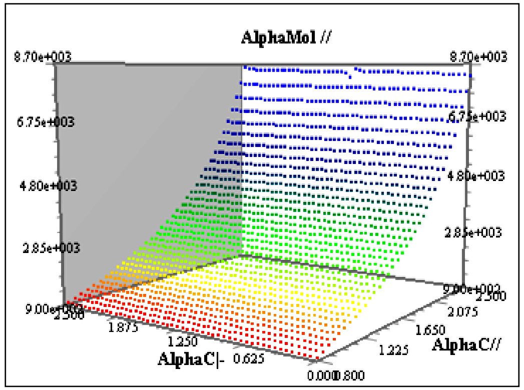
without regularization

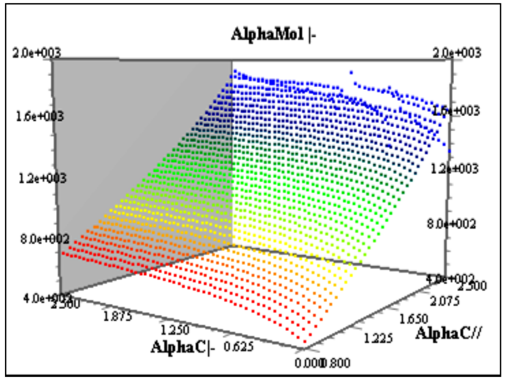




- c and d: ∥ and ⊥ polarizabilities of a (13,7) nanotube, as a function of $\alpha_{C//}$ and $\alpha_{C\perp}$

with regularization

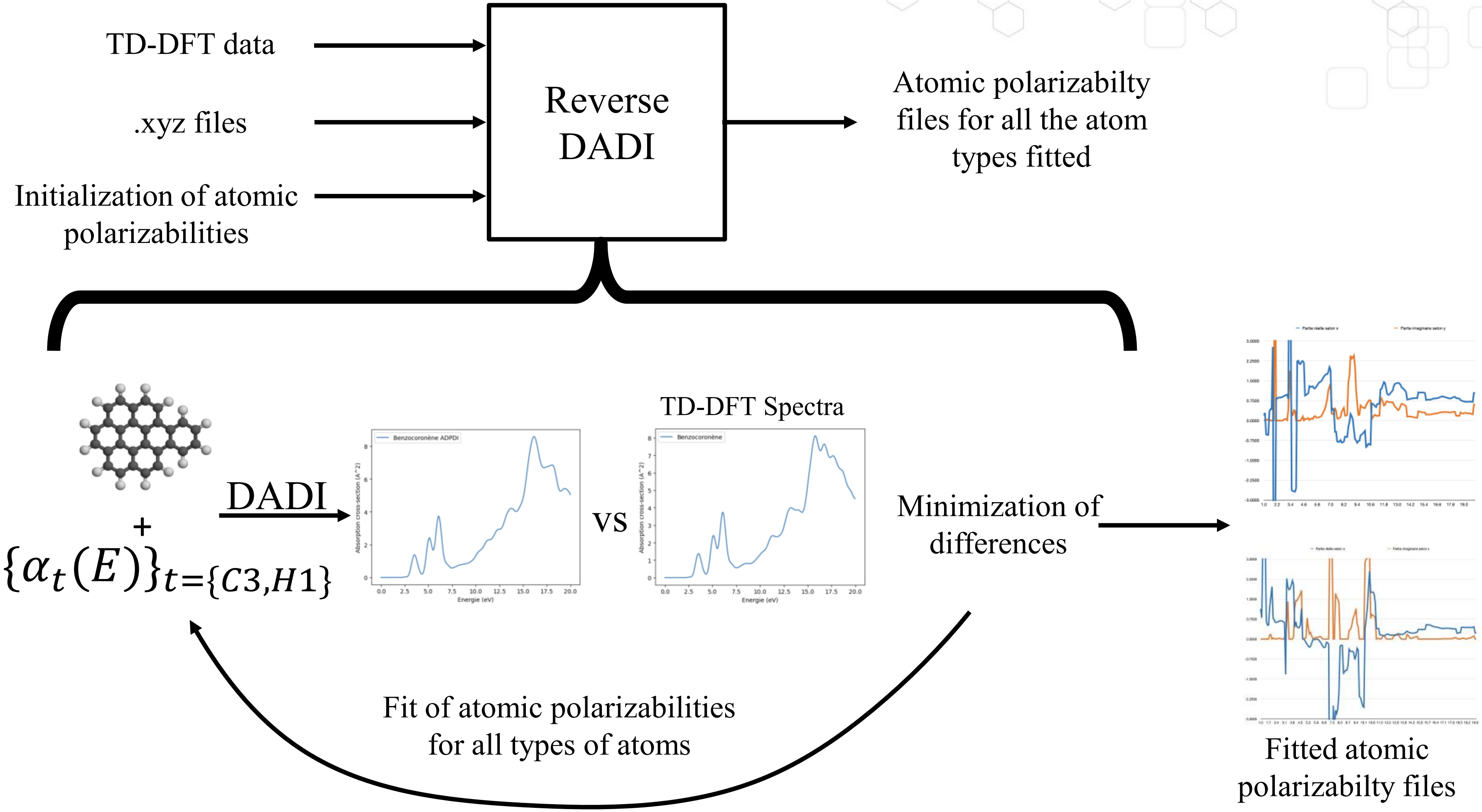




Rachel Langlet, PHD Thesis, Besançon, 2004

VI - DDA at the molecular scale ⇒ DADI Model

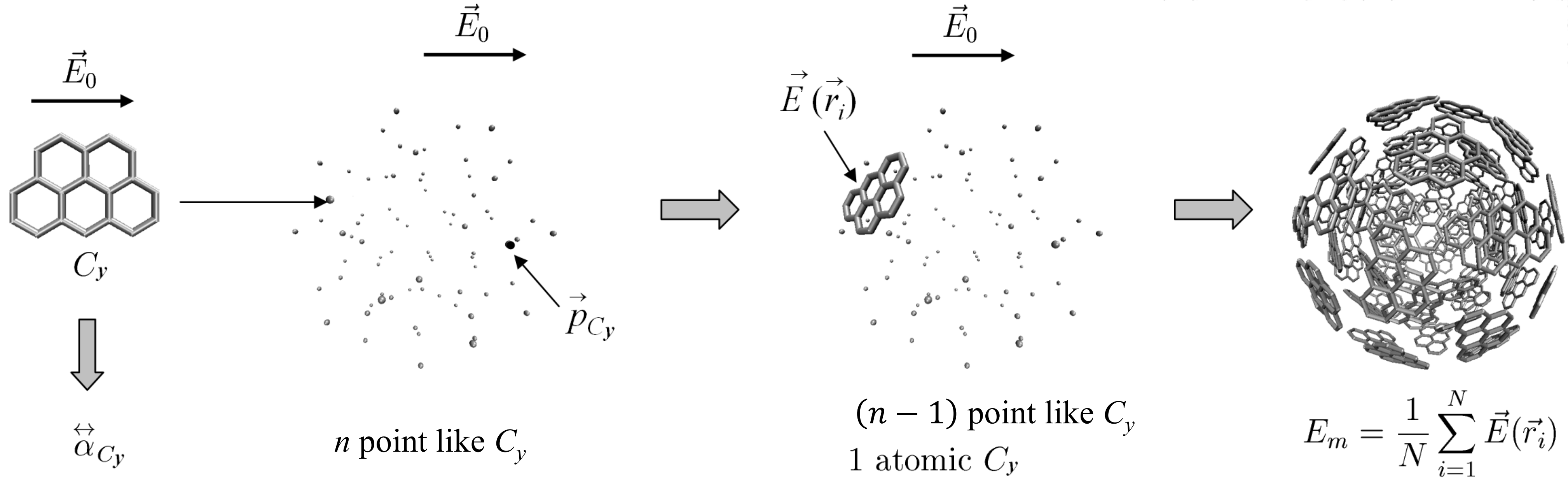
g) Reverse-DADI (Rérat M. et al., Theor. Chem. Acc., **141** (2022), Brosseau-Habert N. et al., JQSRT, **329**, (2024))



- With DADI, we compute optical response from atomic polarizabilities
- With reverse-DADI, we compute atomic polarizabilities from a database of molecular polarizabilities of small molecules, calculated with TD-DFT

VI - DDA at the atomic scale

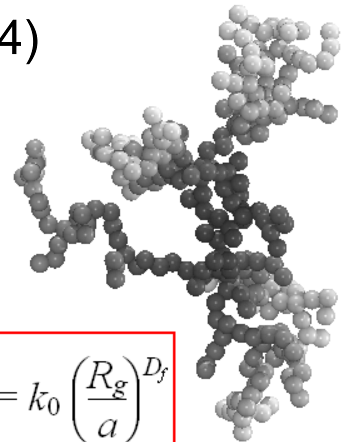
h) multi-step (iterative) procedure



The unique $3N \times 3N$ matrix is replaced by n matrices with size $3y \times 3y$ (y = 13 to 24)

$$\forall i = 1, \dots, y \qquad \vec{E}(\vec{r}_i) = \left[\vec{E}_0(\vec{r}_i) + \sum_{j=1}^{n-1} \overleftrightarrow{T}(\vec{r}_i, \vec{r}_j; \omega)\vec{p}_{C_y}(\vec{r}_j)\right] + \sum_{j=1}^{y} \overleftrightarrow{T}(\vec{r}_i, \vec{r}_j; \omega)\overleftrightarrow{\alpha}_C(\vec{r}_j)\vec{E}(\vec{r}_j)$$

Relative permittivity: $(\sum \vec{p})/V = \varepsilon_0 \overleftrightarrow{\chi}_e \vec{E}_m = \varepsilon_0(\overleftrightarrow{\varepsilon}_r - \overleftrightarrow{1})\vec{E}_m$



$$N = k_0 \left(\frac{R_g}{a}\right)^{D_f}$$

R. Langlet, M. R. Vanacharla, S. Picaud & M. Devel, *JQSRT*, **110**, 1615-1627 (2009)
Bottom-up multi-step approach to study the relations between the structure and the optical properties of carbon soot nanoparticles

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IV. General volume integral equation

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VII – Optical indices in the Rayleigh Approximation

a) X-sections from a complex scalar polarizability modeled by a single oscillator (i)

- Taking into account radiative corrections for bound charges, Jackson-3rd ed. gives expressions for the absorption and extinction cross-section of a single atom:

  - Eq. (16.77)

$$C_{sca} = 6\pi c^2 \frac{\omega^4}{\omega_0^4}\left[\frac{\Gamma^2(1+\omega^2\tau^2)}{\left(\omega_0^2-\omega^2\right)^2+\omega^2\Gamma_{tot}^2}\right]$$

$$\approx 6\pi c^2 \frac{\omega^4}{\omega_0^4}\left[\frac{\Gamma^2}{\left(\omega_0^2-\omega^2\right)^2+\omega^2\Gamma_{tot}^2}\right]$$

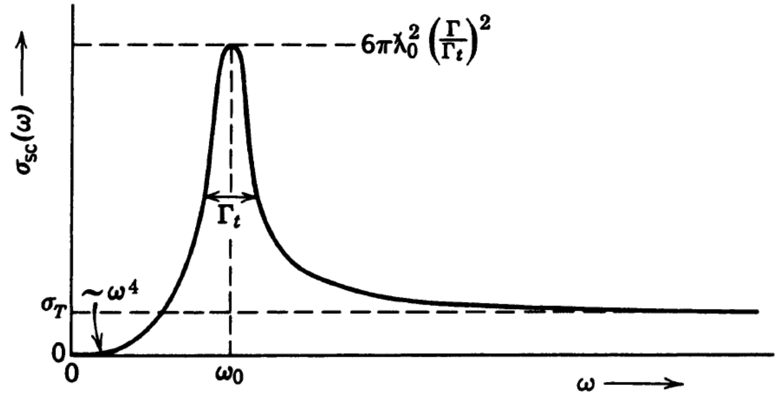

Figure 16.2 Total cross section for the scattering of radiation by an oscillator as a function of frequency. σ_T is the Thomson free-particle scattering cross section.

  - Eq. (16.78)

$$C_{ext} = \frac{4\pi}{k}\mathrm{Im}\left(f\left(\vec{\epsilon}' = \vec{\epsilon}, \vec{k}' = \vec{k}\right)\right) = 6\pi c^2 \frac{\omega^2}{\omega_0^2}\left[\frac{\Gamma\left((\Gamma_{tot}-\Gamma)+\omega^2\Gamma/\omega_0^2\right)}{(\omega_0^2-\omega^2)^2+\omega^2\Gamma_{tot}^2}\right]$$

with ω_0 the fluorescence resonance angular frequency, such that $\omega_0^2 = \beta/m$ (with $\beta \approx (d^2V/dr^2)$ the 2nd derivative of the potential energy between the bound electron and the nucleus), If we now introduce $\tau = (2/3)\left(e^2/4\pi\varepsilon_0 mc^3\right)$ the characteristic time of the exponential law for average spontaneous emission, we can define $\Gamma = \omega_0^2\tau$ the width due to the radiative self-interaction energy, Γ_{tot} the width due to all the energy losses (radiative or not) and $\Gamma' = \Gamma_{tot} - \Gamma$ the width due to the non-radiative effects

a) X-sections from a complex scalar polarizability modeled by a single oscillator (ii)

Let us remark that both expressions can be recast into the form ($k = \omega/c$) (Exercise 16.13 for C_{ext}):

$$C_{ext} = 4\pi k \times \mathrm{Im}\left(\frac{\alpha}{(4\pi\varepsilon_0)}\right)$$

$$C_{sca} = \frac{8\pi k^4}{3}\left|\frac{\alpha}{(4\pi\varepsilon_0)}\right|^2$$

Using an atomic dynamical linear dipolar polarizability:

$$\frac{\alpha}{(4\pi\varepsilon_0)} \equiv \frac{3}{2}\frac{c^3\tau}{\omega_0^2}(1 - i\omega\tau)\frac{\omega_0^2}{(\omega_0^2 - \omega^2) - i\omega\Gamma_{tot}}$$

with ω_0 the fluorescence resonance angular frequency, τ the characteristic time of the exponential law for average spontaneous emission, $\Gamma = \omega_0^2\tau$ the width due to the radiative self-interaction energy, Γ_{tot} the width due to all the energy losses (radiative or not).

This can be compared to expressions given in Draine-ApJ-1988 for a single dipole:

$$C_{ext} = \frac{k}{\varepsilon_0\left\|\vec{E}_{0,inc}\right\|^2}\mathrm{Im}\left(\vec{p}(\vec{r})\cdot\vec{E}^*_{0,inc}\exp(-i\vec{k}\cdot\vec{r})\right)$$

$$C_{sca} = \frac{k^4}{\left\|\vec{E}_{0,inc}\right\|^2(4\pi\varepsilon_0)^2}\int d\Omega\left|\{[\vec{p} - \hat{n}(\hat{n}\cdot\vec{p})]\exp(-ik\hat{n}\cdot\vec{r})\}\right|^2$$

It is found to be the same, by setting $\vec{p}(\vec{r}) = \alpha\vec{E}_{inc}(\vec{r}) = \alpha\vec{E}_{0,inc}\exp\left(i\vec{k}\cdot\vec{r}\right)$ and $\vec{E}_{0,inc}\cdot\hat{n} = E_{0,inc}\sin\theta$

VII – Optical indices in the Rayleigh Approximation

b) Formula with a complex polarizability modeled by a set of oscillators

For a single dynamical polarizability, we have:

$$\frac{\alpha}{(4\pi\varepsilon_0)} = \frac{3}{2}\frac{c^3\tau}{\omega_0^2}(1 - i\omega\tau)\frac{\omega_0^2}{(\omega_0^2 - \omega^2) - i\omega\Gamma_{tot}}$$

For a set of independent oscillators (possibly several oscillators for the same atom), we then define

$$\frac{\alpha_{part}}{(4\pi\varepsilon_0)} \equiv \sum_j f_j \frac{3}{2}\frac{c^3}{\omega_j^2}(1 - i\omega\tau_j) \times \frac{\Gamma_j}{(\omega_j^2 - \omega^2) - i\omega\Gamma_{j,tot}}$$

with $\omega_j = \sqrt{\beta_j/m_j^*}$, the resonance frequency of the j^th^ oscillator of strength f_j (such that $\sum_j f_j = 1$), $\Gamma_j = \omega_j^2\tau_j$ the radiative width corresponding to the relaxation time τ_j, and $\Gamma_{j,tot}$ the total width (radiative+non-radiative).

This can be compared to expressions given in Draine-AA-1988:

$$C_{ext} = \frac{k}{\varepsilon_0\left\|\vec{E}_{0,inc}\right\|^2}\sum_{j=1}^{N}\mathrm{Im}\left(\vec{p}_j \cdot \vec{E}_{0,inc}^*\exp(-i\vec{k}\cdot\vec{r}_j)\right)$$

$$C_{sca} = \frac{k^4}{\left\|\vec{E}_{0,inc}\right\|^2(4\pi\varepsilon_0)^2}\int d\Omega\left|\sum_{j=1}^{N}\{[\vec{p}_j - \hat{n}(\hat{n}\cdot\vec{p}_j)]\exp(-ik\hat{n}\cdot\vec{r}_j)\}\right|^2$$

By defining α_{part} such that $\alpha_{part}\vec{E}_{0,inc} = \sum_j \vec{p}_j\exp(-i\vec{k}\cdot\vec{r}_j)$ (i.e. origin taken at the center of charge of the particle, we have trivially: $C_{ext} = 4\pi k \times \mathrm{Im}\left(\alpha_{part}/((4\pi\varepsilon_0))\right)$.

Pb: do we have $C_{sca} = \frac{8\pi k^4}{3}\left|\frac{\alpha_{part}}{(4\pi\varepsilon_0)}\right|^2$? What about C_{abs}?

- **Lemma: the average over all orientations of $R\bar{\bar{A}}R^T$, where R is a rotation matrix from the group SO(3), is: $\langle R\bar{\bar{A}}R^T \rangle = \frac{1}{3}\mathrm{Tr}(\bar{\bar{A}})\bar{\bar{1}}$**

This allows to show that the extinction and scattering cross-sections averaged on all the relative orientations of the incident field and the object are:

$$\langle C_{ext} \rangle = 4\pi k_B \times \mathrm{Im}\left(\frac{\alpha}{(4\pi\varepsilon_0\varepsilon_{r,B})}\right)$$

with $\alpha = \mathrm{Tr}(\bar{\bar{\alpha}}_{obj})/3$

$$\langle C_{sca} \rangle = \frac{8\pi}{3} k_B^4 \times \frac{1}{3}\mathrm{Tr}\left(\frac{\bar{\bar{\alpha}}_{obj}\bar{\bar{\alpha}}_{obj}{}^{\dagger}}{(4\pi\varepsilon_0\varepsilon_{r,B})^2}\right)$$

Proof: using Draine's expressions and $\forall j = 1, \dots, N \quad \vec{p}_j = \sum_{l=1}^{N} \bar{\bar{B}}_{j,l}\vec{E}_{inc,l} = \sum_{l=1}^{N} \bar{\bar{B}}_{j,l} \exp(i\vec{k}_{inc} \cdot \vec{r}_j)\, \vec{E}_{0,inc}$, we get $C_{ext} = \frac{4\pi k_B}{(4\pi\varepsilon_0\varepsilon_{r,B})|\vec{E}_{0,inc}|^2} \sum_{j=1}^{N} \mathrm{Im}\left(\exp(-i\vec{k}_{inc} \cdot \vec{r}_j)\, \vec{E}_{0,inc}^* \cdot \sum_{l=1}^{N} \bar{\bar{B}}_{j,l} \exp(i\vec{k}_{inc} \cdot \vec{r}_j)\, \vec{E}_{0,inc}\right) = \frac{4\pi k_B}{(4\pi\varepsilon_0\varepsilon_{r,B})} \sum_{j=1}^{N} \mathrm{Im}\big(\hat{e}_{0,inc}^*$ $\cdot \left[\sum_{j=1}^{N}\sum_{l=1}^{N} \bar{\bar{B}}_{j,l}\right]\hat{e}_{0,inc}\big) = \frac{4\pi k_B}{(4\pi\varepsilon_0\varepsilon_{r,B})} \sum_{j=1}^{N} \mathrm{Im}\left(\hat{e}_{0,inc}^* \cdot \bar{\bar{\alpha}}_{obj}(\omega)\hat{e}_{0,inc}\right)$

Furthermore, $C_{sca} = \frac{k_B^4}{(4\pi\varepsilon_0\varepsilon_{r,B})^2} \int \left|\sum_{j=1}^{N}\left[\sum_{l=1}^{N} \bar{\bar{B}}_{j,l}\hat{e}_{0,inc} - \hat{n}\left(\hat{n} \cdot \sum_{l=1}^{N} \bar{\bar{B}}_{j,l}\hat{e}_{0,inc}\right)\right]\right|^2 d\Omega = k_B^4 \left(\int \left|(\bar{\bar{1}} - \hat{n} \otimes \hat{n})\right|^2 d\Omega\right) \left|\frac{\bar{\bar{\alpha}}_{obj}(\omega)}{(4\pi\varepsilon_0\varepsilon_{r,B})}\hat{e}_{0,inc}\right|^2$ and thus $C_{sca} = \frac{8\pi}{3} k_B^4 \left|\frac{\bar{\bar{\alpha}}_{obj}(\omega)}{(4\pi\varepsilon_0\varepsilon_{r,B})}\hat{e}_{0,inc}\right|^2$. The above expressions are then found by using the Lemma.

d) Computation of optical indices suitable for Rayleigh approximation from computed cross-sections

- Recall that $\frac{C_{sca}}{V} = \frac{32\pi^4 a^3}{\lambda_0^4}\left|\frac{m^2-1}{m^2+2}\right|^2 \equiv \frac{24\pi^3 V}{\lambda_0^4} F(m)$ and $\frac{C_{ext}}{V} = \frac{6\pi}{\lambda_0}\mathrm{Im}\left(\frac{m^2-1}{m^2+2}\right) \equiv \frac{6\pi}{\lambda_0} E(m)$
- If we set $\boxed{z = \frac{m^2-1}{m^2+2} = \pm\sqrt{F(m) - E^2(m)} + iE(m)}$, we can compute $\boxed{m^2 = \frac{1+2z}{1-z}}$ from C_{sca} and C_{ext}, provided we know V!...
- Let us define $m = n + i\kappa$ so that $m^2 = n^2 - \kappa^2 + 2in\kappa$ (Rem: $|m^2| = |m|^2 = n^2 + \kappa^2$)
- We must have $\kappa > 0$, since we are interested by an absorbing medium and use the convention $\exp\left(i\omega(m\,x/c - t)\right)$. Hence $\boxed{\kappa = \sqrt{\left(|m^2| - \mathrm{Re}(m^2)\right)/2}}$
- Furthermore $E(m) = \mathrm{Im}\left(\frac{m^2-1}{m^2+2}\right) = 3\,\mathrm{Im}(m^2)/\left[(\mathrm{Re}(m^2)+2)^2 + \left(\mathrm{Im}(m^2)\right)^2\right]$, so that $\mathrm{Im}(m^2)$ is of the same sign as $E(m)$ or C_{ext}, hence >0. Then, $\mathrm{Im}(m^2) = 2n\kappa \Rightarrow n > 0$, so that

$$\boxed{n = \sqrt{\left(|m^2| + \mathrm{Re}(m^2)\right)/2}}$$

- Hence, the only remaining problem (apart from knowing V) is to choose whether $\mathrm{Re}(z) = \pm\sqrt{F(m) - E^2(m)}$ (+ is OK except (maybe) near resonance!)

Outline

I. Definitions

II. Wave equations

III. Green's "functions" and their singular part

IV. General volume integral equation

V. Discrete Dipole Approximation (microphotonics)

VI. DDA at the molecular scale $\Rightarrow$ DADI Model (nanophotonics)

VII. Optical indices from molecular information (and back!)

VIII. Conclusions and perspectives

IX. References

VIII – Conclusion and perspectives

a) Conclusions

- DDA and T-matrix remain the most popular methods for the simulation of the optical and radiative properties of soot particles, partly because there exist high quality, highly tested freely available codes.
- Atomistic multi-scale DDA model adaptable to all geometries (fractals,…)
- Uses same atomistic description as adsorption isotherm simulations
- Empty internal cavity not important for $R_{int} < R_{ext}/3$
- "Intensive" quantities reach limit quite fast
- Optical index mainly governed by the amount of chemical defects
- Polarization degree is much more sensitive to geometric parameters
- Need for better agreement between different methods of measurements of graphite permittivity component // to c axis $\Rightarrow$ common parameterization!

VIII – Conclusion and perspectives

b) Perspectives

- For DDA: There may still be some room for improvement of DDA by coupling Peltoniemi's approach with the high spatial frequency filtering method of Martin et al, to get improved diagonal matrix elements.
- For DADI,
  - **we need to fit dynamical polarizabilities for more elements (thanks to ab-initio computations for small molecules)**
  - **Systematic studies for polarization degree, efficiencies and asymetries**
  - **Inclusion of chemical defects CO, COOH…**
  - **parallel implementation**
  - **Necking**
  - **Systematic studies for optical index by varying the chemical content**
  - **Scattering by fractal soot in water micro-droplets to compare with *Absorption of light by soot particles in micro-droplets of water*. V.A. Markel , V. M. Shalaev. J. Quant. Spectr. Radiat. Transfer 63(2), 321-339, 1999**

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Interesting web sites

List adapted from the one compiled by Fabrice Onofri on his group web page:
http://iusti.univ-provence.fr/document.php?pagendx=12780&project=iusti

- University of Bremen (Germany) Thomas Wriedt's group: http://www.scattport.org/

  Essential site that compiles archives of codes for various simulation methods + newsletter
- Database of Optical Properties of small particles + codes + literature reviews + tutorials (Sobolev Astronomical Institute, http://www.astro.spbu.ru/DOP/)
- NASA Goddard Institute for Space Studies (Mishchenko & Travis web site https://www.giss.nasa.gov/staff/mmishchenko/t_matrix.html (also codes for Global Climate Modeling)
- Bruce T. Draine's pages for DDSCAT http://www.ddscat.org/
- Maxim Yurkin and Alfons Hoekstra ADDA https://github.com/adda-team/adda
- The HITRAN Database of spectroscopic parameters (https://www.cfa.harvard.edu/hitran//)
- ASTER spectral library, JPL, Caltech (https://speclib.jpl.nasa.gov/)
- IOFFE institute (Russia) n,k database : semiconductor, metals, oxides (http://www.ioffe.ru/SVA/NSM/nk/index.html)
- Jena - St. Petersburg Database of Optical Constants (http://www.astro.spbu.ru/JPDOC/1-entry.html)
- Ludmilla Kolokolova (Univ. of Maryland) http://www.astro.umd.edu/~elsnews/ (congresses, job postings)
- Optical Data from Sopra SA (http://www.sspectra.com/sopra.html)
- Research gate page of Olivier Martin: https://www.researchgate.net/profile/Olivier_Martin9