TOPIC # 6 …

How does carbonaceous particle composition, shape, and size affect optical properties in the air and when sampled on a filter?

How might optical properties of particles in the air differ from those collected on a filter?

How might filter transmittance and reflectance change during heating as particle morphology and composition change?

Why might optical transmission and reflectance give different pyrolysis corrections?

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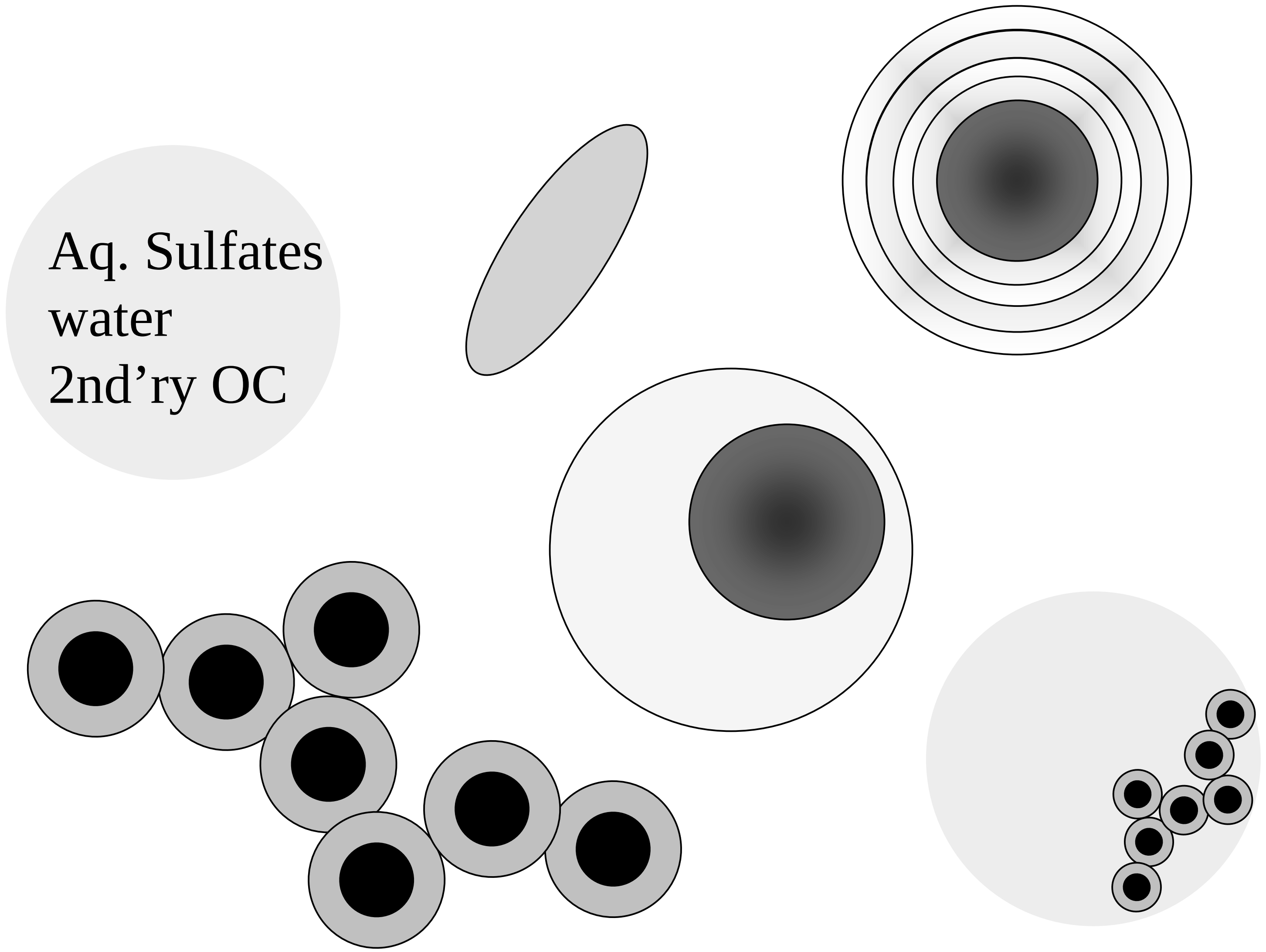
OVERVIEW

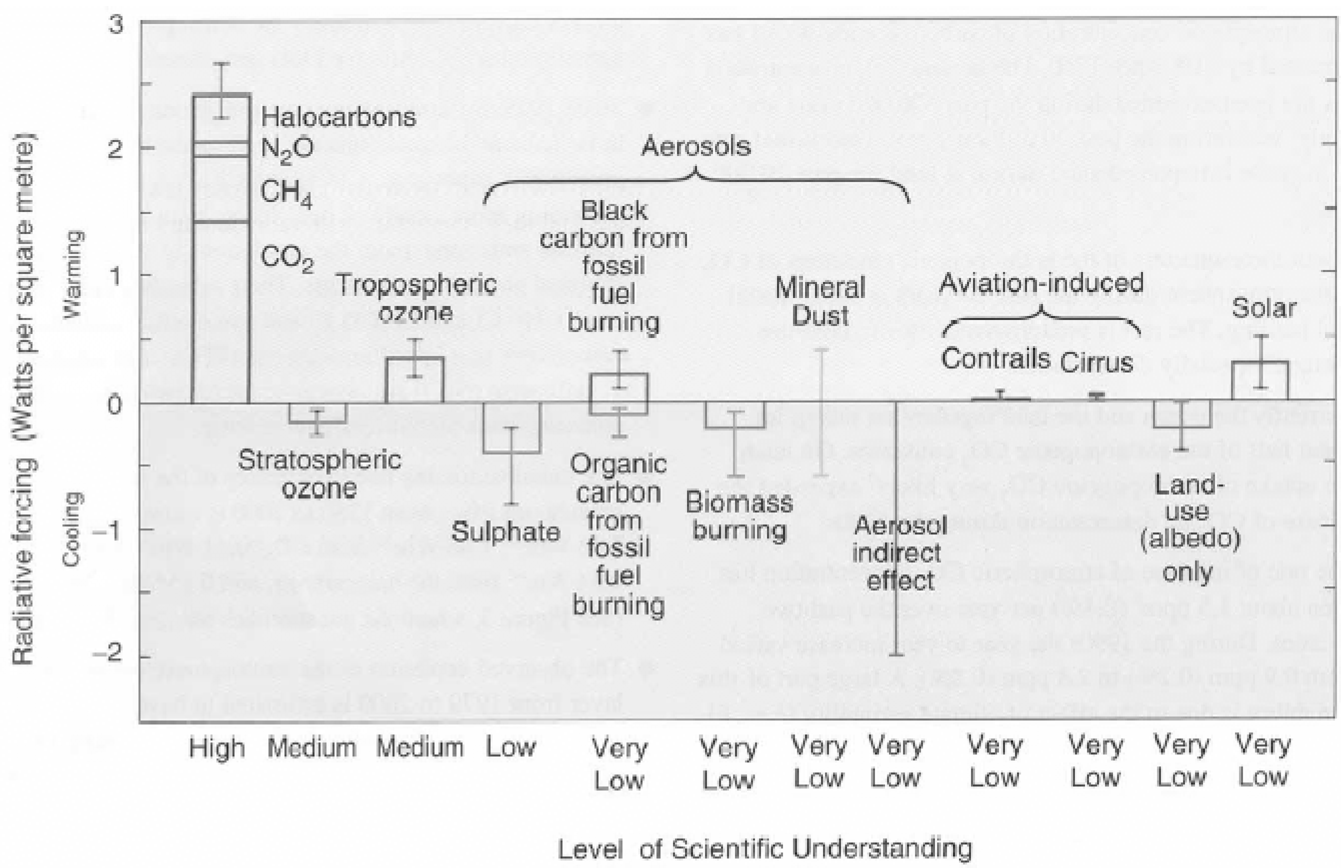
- Filter-based measurements of absorption
- Some pitfalls of measurements on filter deposits
- Effects of aggregation
- Effects of internal mixing
- Summary and suggested needs

Some μparticles of interest



National Aerosol-Climate Interactions Program
http://www-c4.ucsd.edu/NACIP/

The Global Mean Radiative Forcing of the Climate System for the Year 2000, Relative to 1750



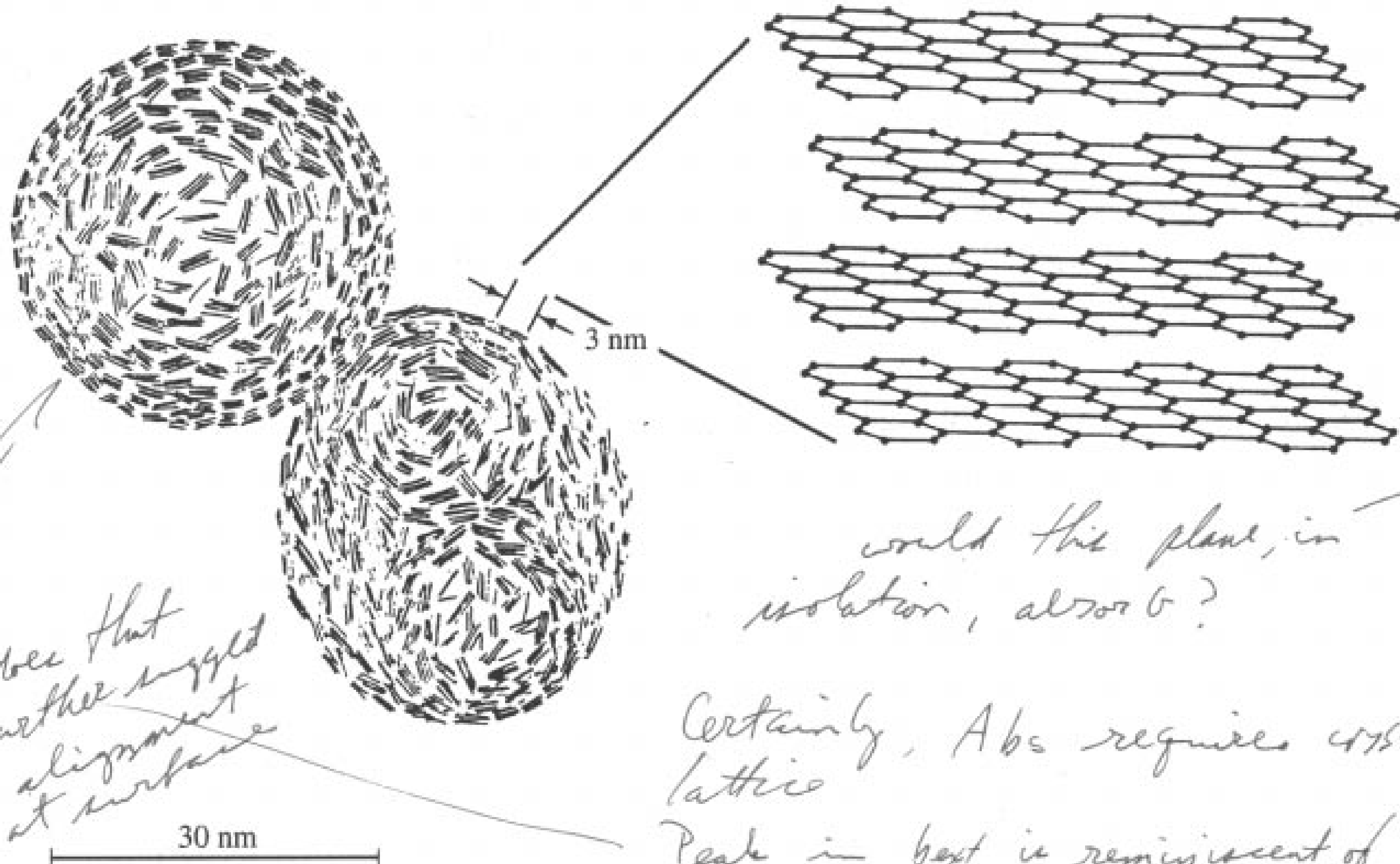
Absorption (scattering) cross section:

$$\frac{\text{total radiant flux aborbed (scattered)}}{\text{incident flux density}}$$

(Mass-) Specific absorption cross section:

$$\alpha = \frac{C_{abs}}{mass} = \frac{\langle C_{abs} \rangle}{mass\ of\ particles} = \frac{\langle C_{abs} \rangle}{\rho V}$$

α of Cabot Corp.'s Monarch 61 carbon black in air is <u>not</u> 9.68 m^2/gram



does that further suggest alignment at surface

would this plane, in isolation, absorb?

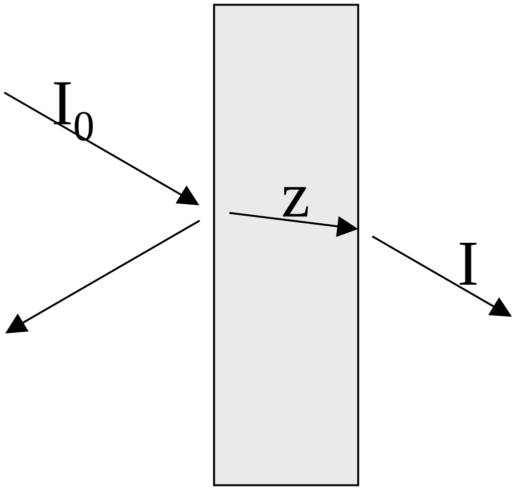
Certainly. Abs requires crystal lattice

Peak in best is reminiscent of plasmon resonance

FIGURE 13.1 Schematic of soot microstructure.

Seinfeld & Pandis
Atmospheric Chemistry and Physics

Filter methods and associated problems:

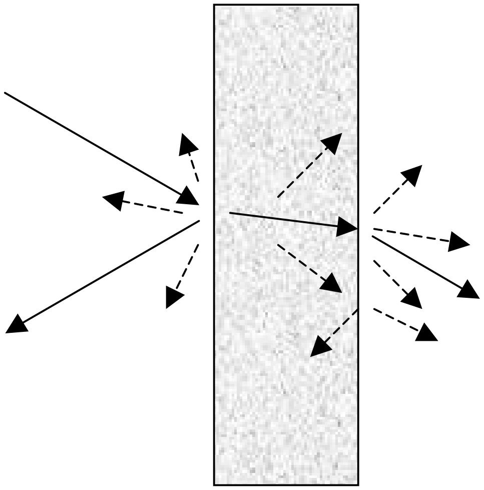


Idealized absorption spectroscopy:

$$I = I_0 \exp(-b_{abs}\, z) \quad = \; I_0 \exp(-\tau_{abs})$$

$$b_{abs} = \sigma_{abs}\,(m^2)\;\; N_{molecules}\,(m^{-3})$$

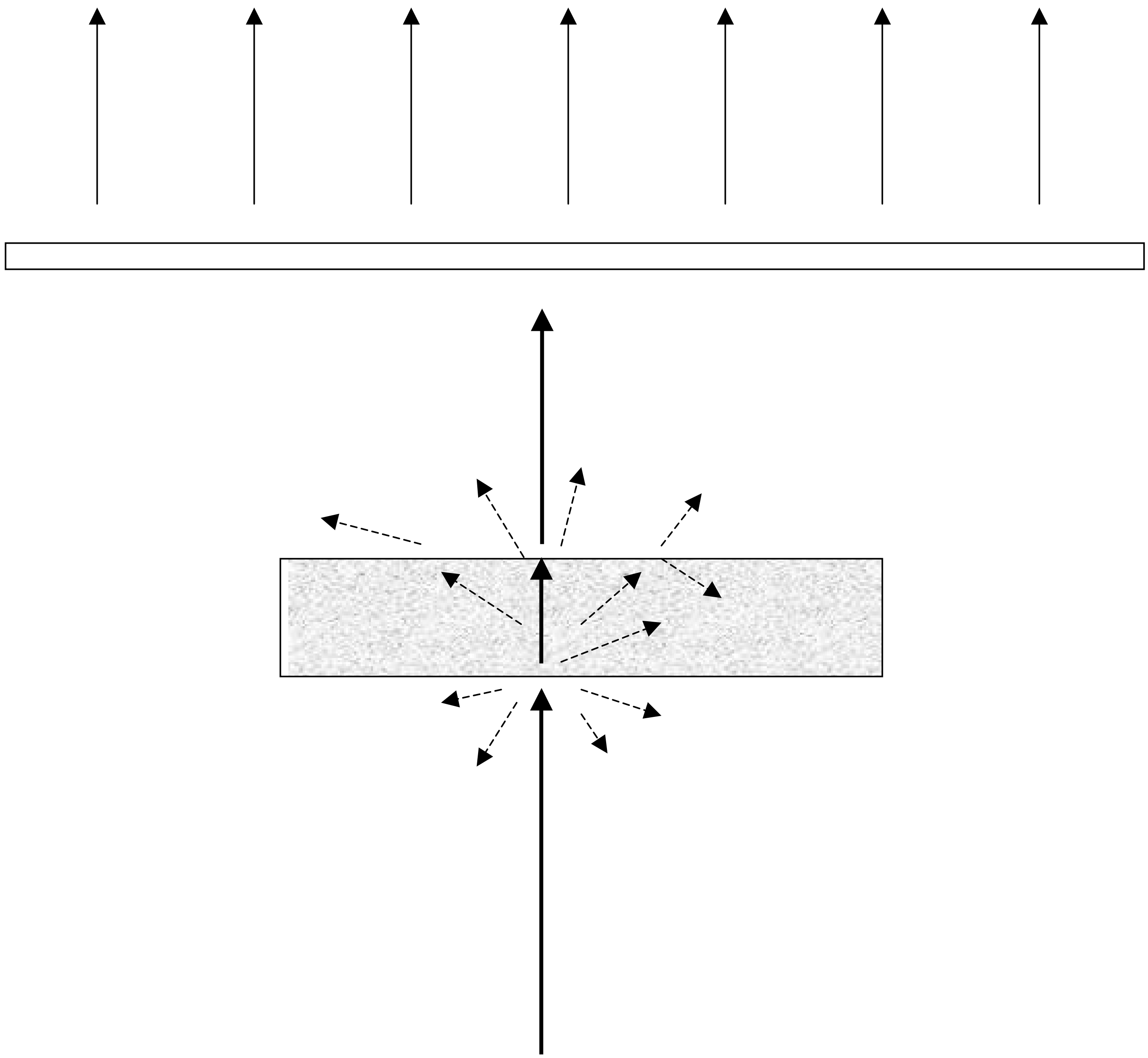
$$T = \frac{I}{I_0} \quad \text{or} \quad T = \frac{I\,(\text{with sample})}{I\,(\text{blank})}$$

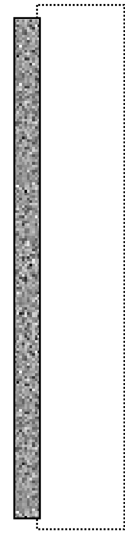


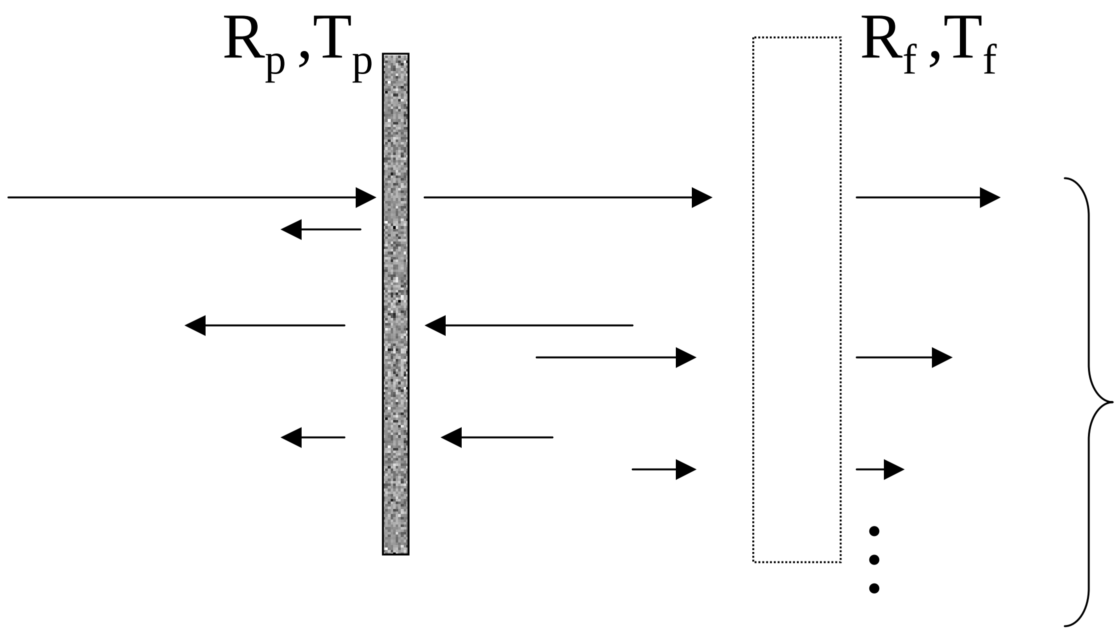
Particles
in the single scattering limit:

$$I = I_0 \exp(-b_{ext}\, z) \quad = \; I_0 \exp(-\tau)$$

$$b_{ext} = \langle C_{sca} + C_{abs} \rangle\;(m^2)\;\; N_{particles}\,(m^{-3})$$







$$\frac{T_p T_f}{1 - R_p R_f}$$

Use diffuse, not directional, quantities

Effects of particle spacing: Coherence

More rigorously, the electric field transmitted by a slab of noninteracting particles is

$$E_T = 1 - \lambda \mathrm{N}\,\mathrm{C}_{\mathrm{ext}}/2 \qquad \text{Intensity} \propto |E_T|^2$$

The fundamental assumption in Beer - Lambert spectroscopy is that this approximates the expansion $\mathrm{e}^{-\mathrm{x}} = 1 - \mathrm{x} + \frac{1}{2}\mathrm{x}^2 - \Lambda$ to first order ($\mathrm{N}\,\mathrm{C}_{\mathrm{ext}}$ is $\mathrm{b}_{\mathrm{ext}}$).

Collection over 24 hours @ 21.7 liters/minute through a filter

Aerosol material density : $1.8\ \mathrm{g/cm}^3$

Atmospheric concentration : $4\ \mu\mathrm{g/m}^3$

Area of sample $\approx 2.2\ \mathrm{cm}^2$,

Mass - specific extinction of the aerosol : $\approx 5\ \mathrm{m}^2/\mathrm{g}$, then $\lambda \mathrm{N}\,\mathrm{C}_{\mathrm{ext}}/2 \approx 1.6$

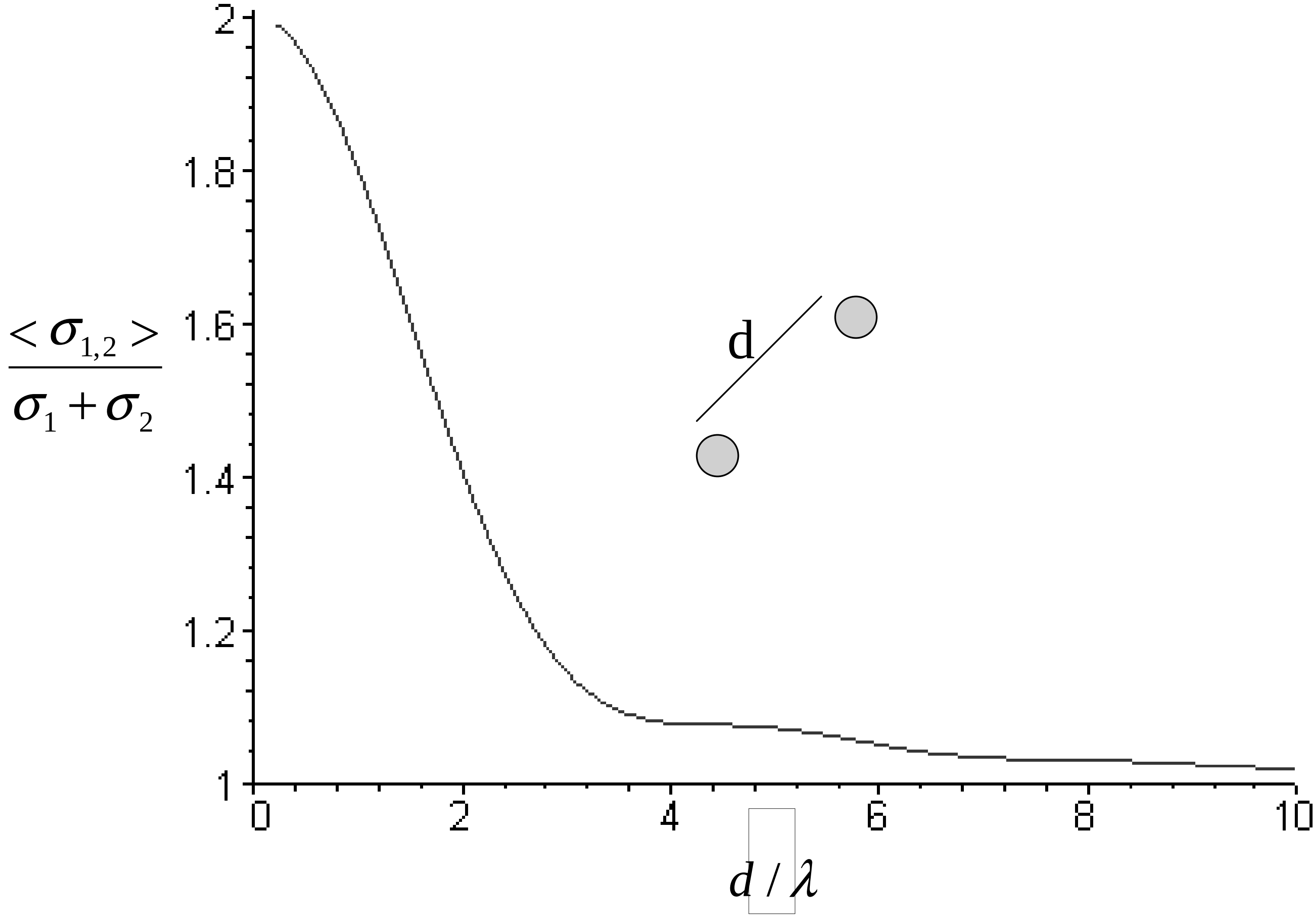
The exponential expression is meaningless, even if there is no influence from interparticle scattering.

Rather than voltage outputs related to abs. by

$$b_{\mathrm{abs}} = \frac{-1}{\ell} \ln \frac{V}{V'} \quad \left(= \frac{-1}{\ell} \ln \frac{A\Phi_0 \exp\left(-b_{\mathrm{abs}}\, \ell\right)}{A\Phi_0} \right)$$

the measurement actually relates to extinction as

$$\underline{b_{\mathrm{ext}}} \equiv \frac{2}{\ell} \left(1 - \sqrt{\frac{V}{V'}} \right)$$


$\frac{<\sigma_{1,2}>}{\sigma_1+\sigma_2}$
2
1.8
1.6
1.4
1.2
1
0
2
4
6
8
10
d
d/λ

Optical properties may be altered by:

(1) multiple scattering in the deposit/substrate system,
(2) alteration of absorption and scattering cross sections by electromagnetic coupling between particles,
(3) electromagnetic coupling of particles to filter surfaces,
(4) optical coherence between particles with separations comparable to the wavelength of the interrogating radiation,
(5) induced alignment of nonspherical particles along filter surfaces,
(6) shape distortion of liquid droplets, and
(7) reactions among different chemical species, especially over extended sampling times.

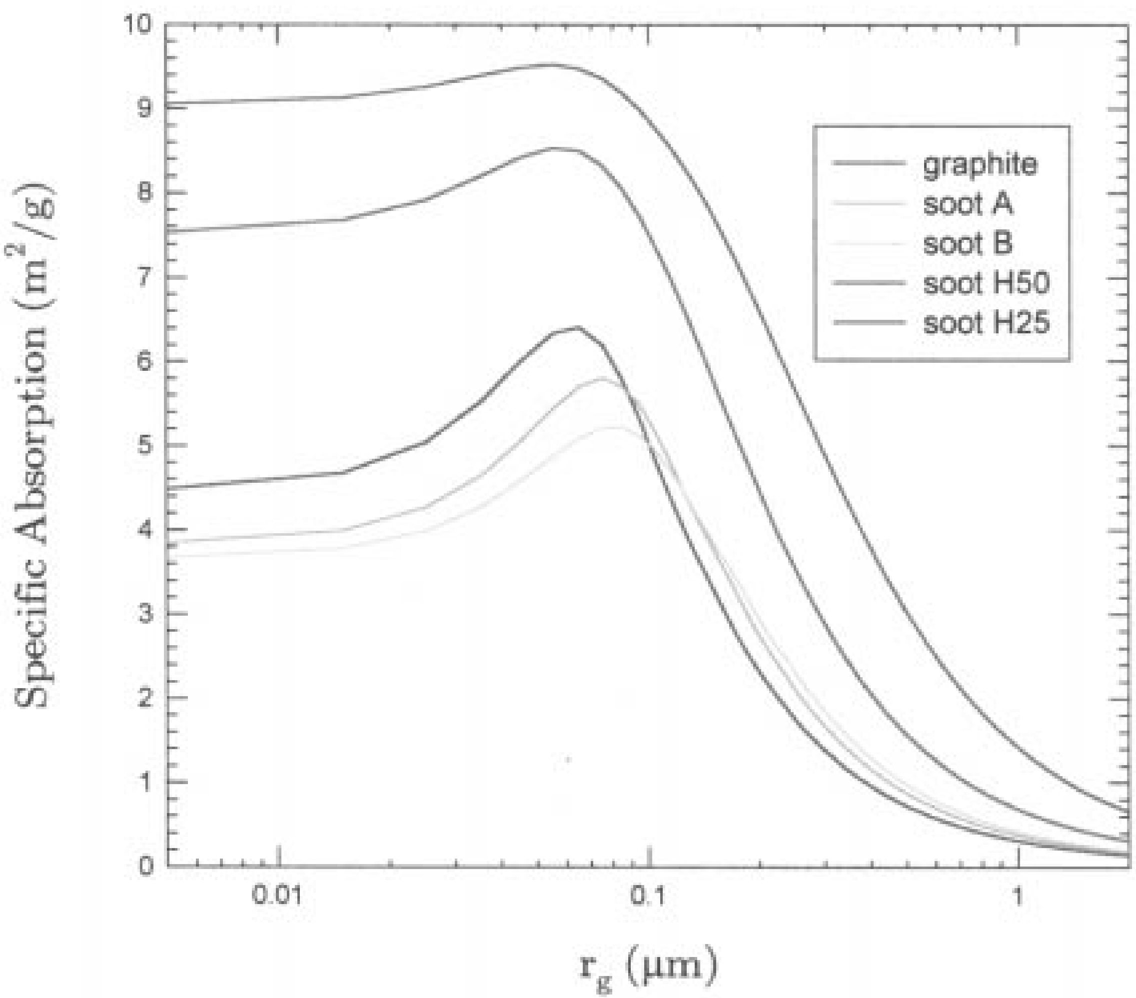
- effects of aggregation
- effects of mixing

Courtesy of National Park Service

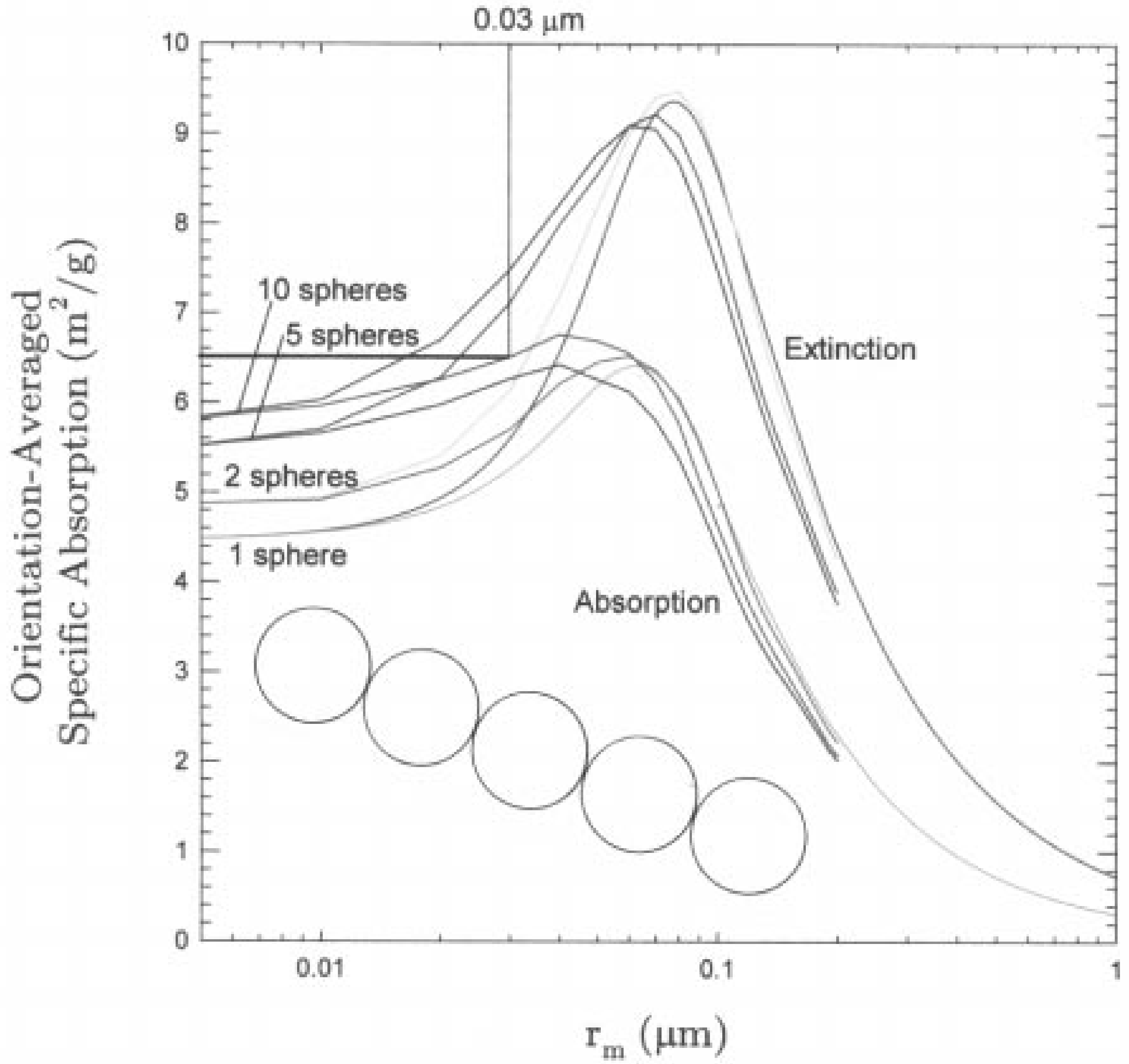
Table 1. Refractive indices for 5 classes of soot at $\lambda = 0.55\mu m$.

n	k	$\rho(g/cm^3)$	Classification	Major Refs.
1.25	0.25	0.625	soot H25	Horvath, 1993
1.50	0.50	1.125	soot H50	Horvath, 1993
1.80	0.50	1.800	soot B	Shettle and Fenn, 1979
1.95	0.66	2.000	soot A	Bergstrom, 1972
2.00	1.00	2.250	Graphitic	Weast, 1977

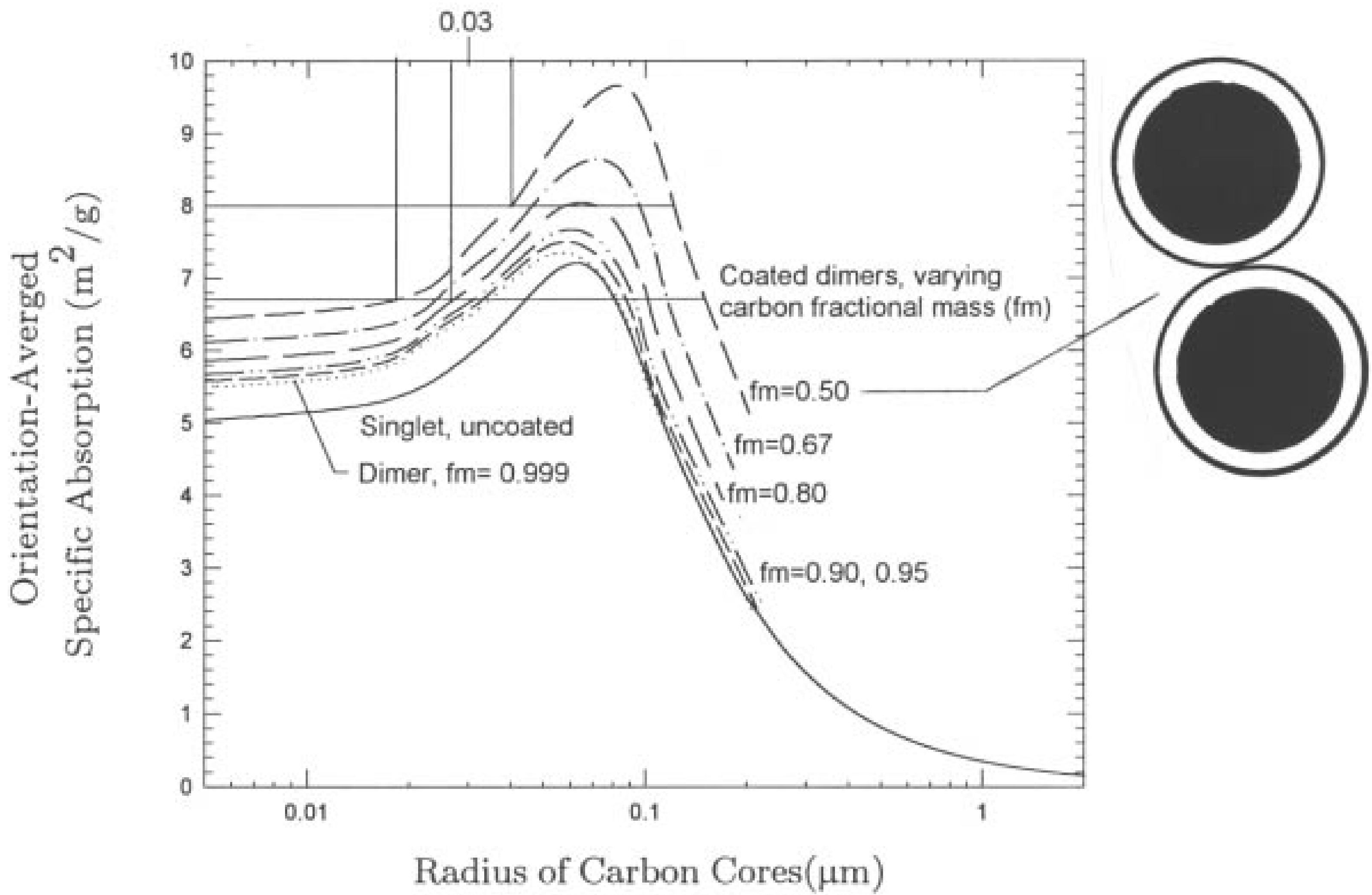
Specific absorption cross sections for the 5 Soot types listed in Table 1 as functions of geometric mean radius r_g. The radii of the monomers are lognormally distributed with $\sigma_g = 1.2$. Incident wavelength $\lambda = 0.55$ μm.



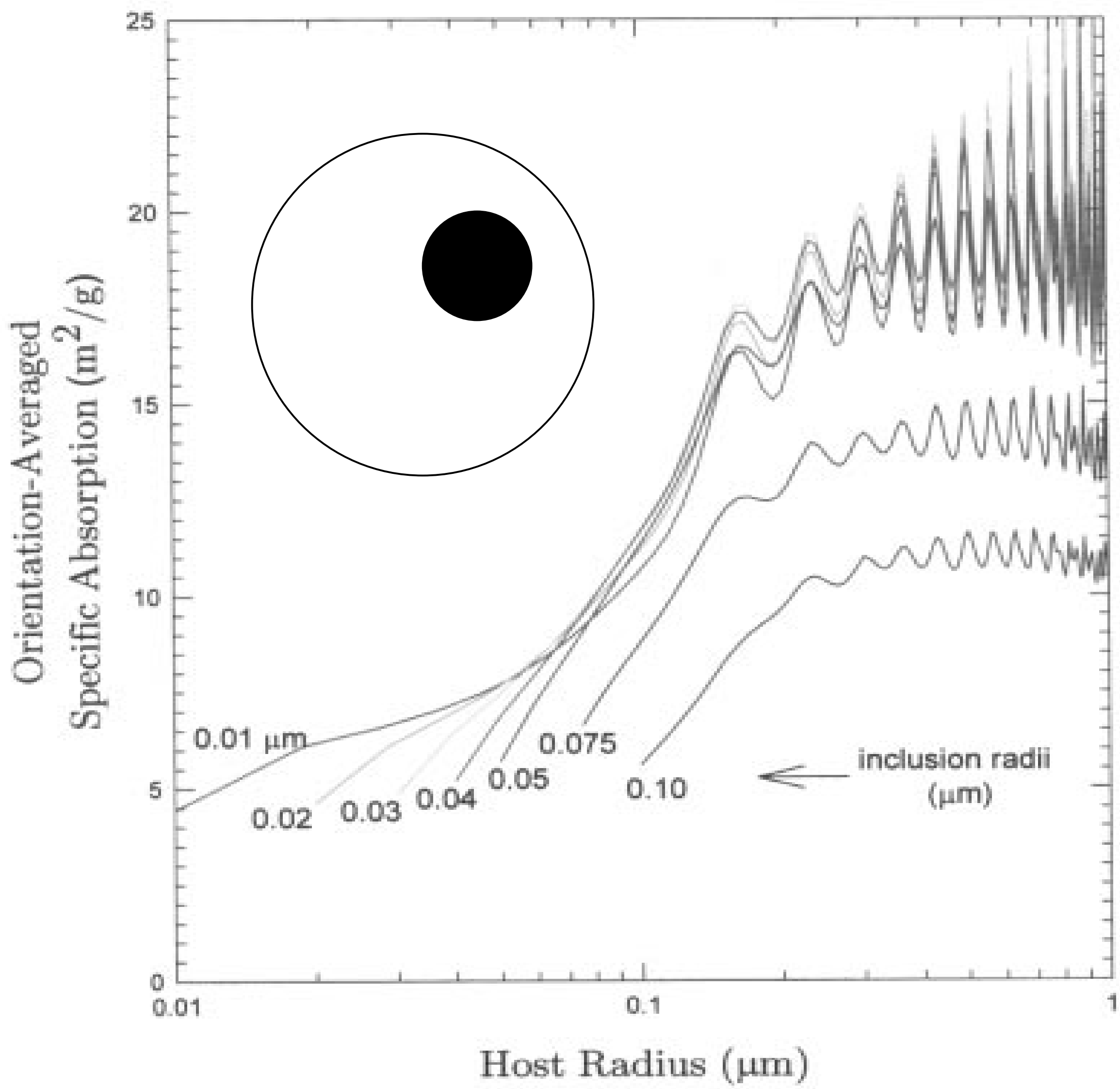
Specific extinction and absorption cross sections of <u>chain aggregates</u> of monodisperse graphitic carbon (ρ=2.25 g/cc, N=2+i) as functions of monomer radius r_m. Incident wavelength λ=0.55 μm.



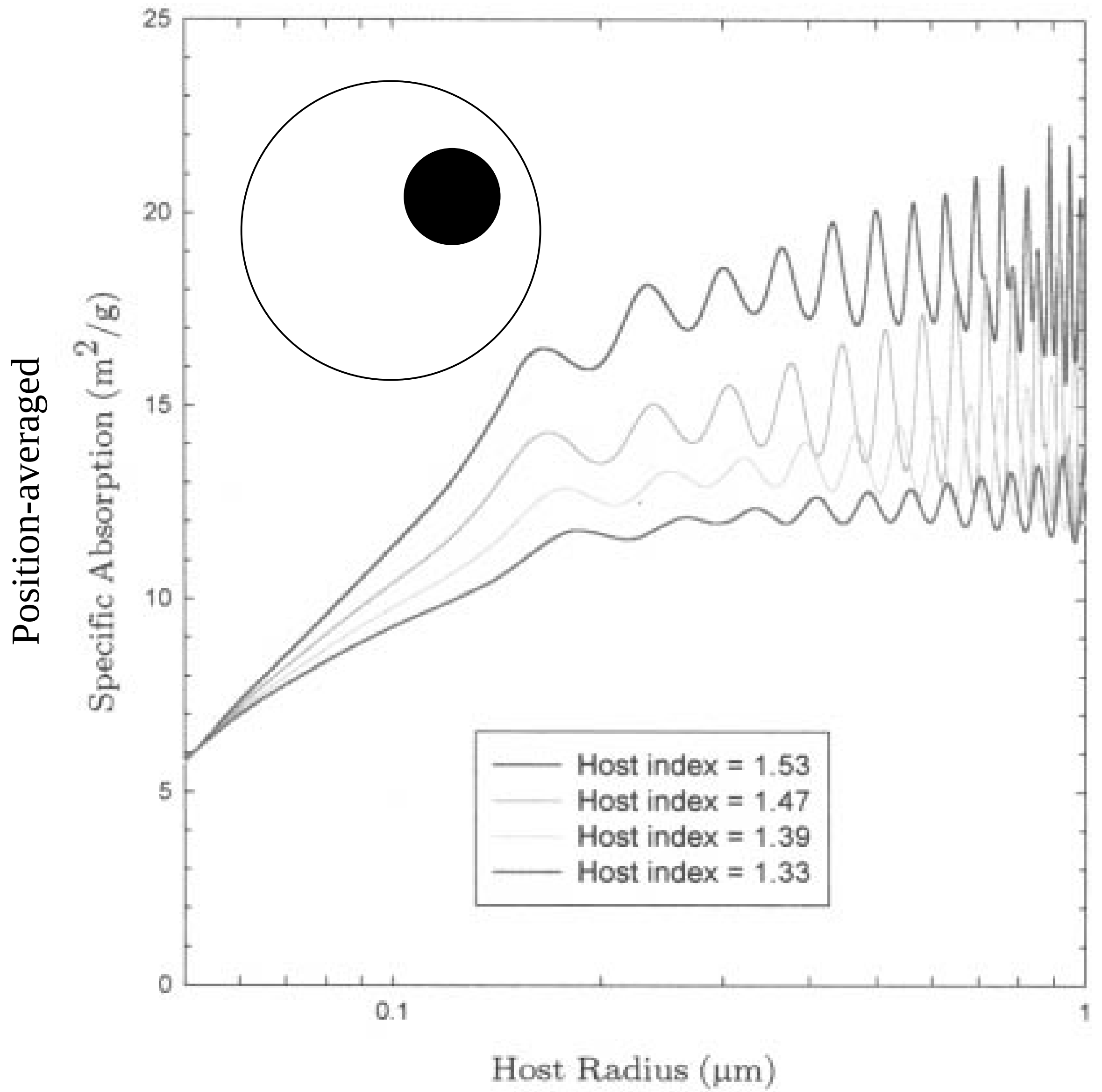
Specific absorption cross sections for coated amorphous carbon dimers as functions of radius r_g of the carbon cores. Incident wavelength $\lambda = 0.55\ \mu m$.



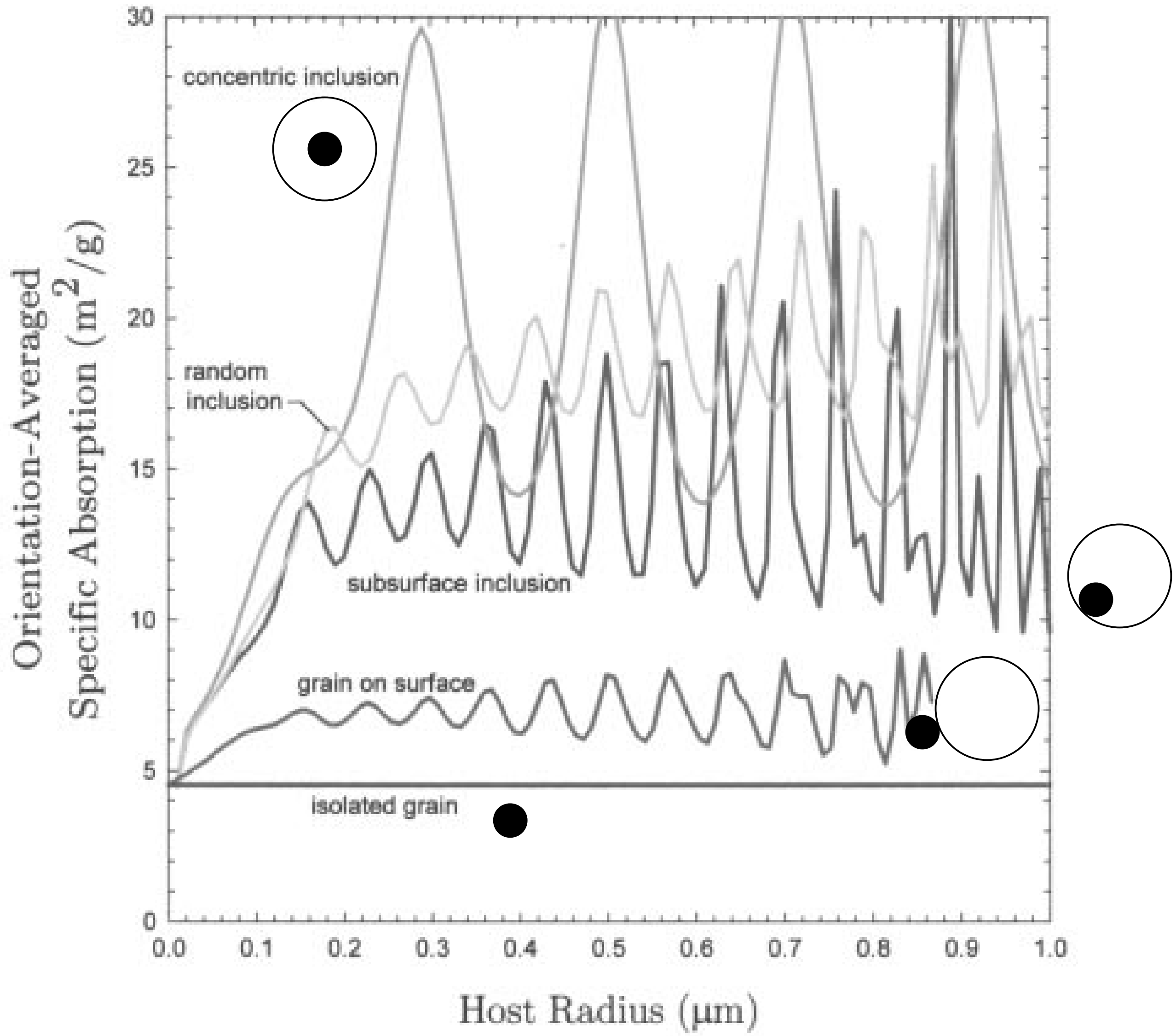
Position-averaged (or random inclusion) calculations of specific absorption for graphitic carbon spheres as a function of host size. Selected, constant inclusion radii.



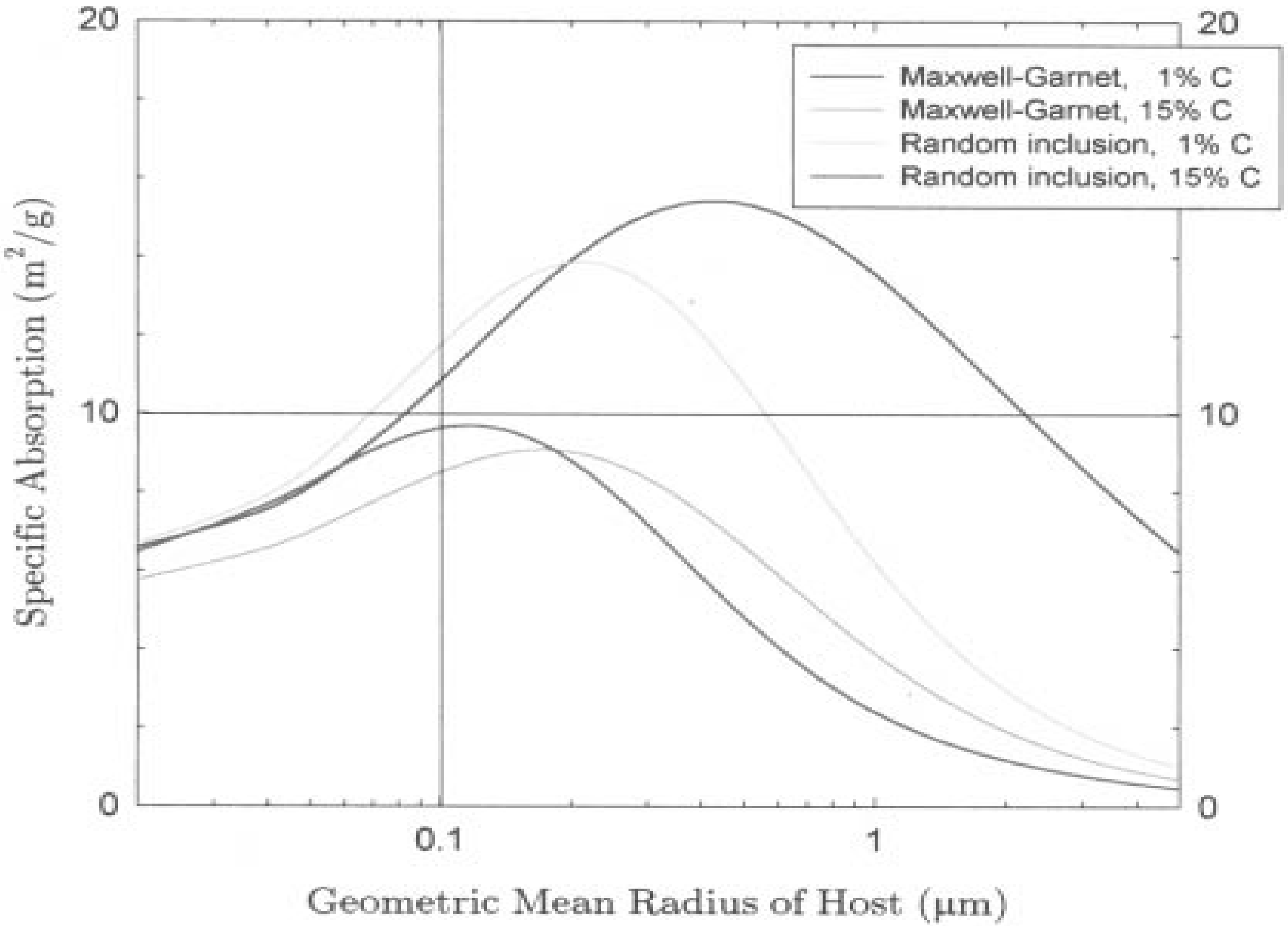
Specific absorption for 0.05 μm graphitic carbon inclusions in hosts of different refractive indices



Specific absorption for 0.01μm carbon inclusions:
Comparisons for different inclusion locations.

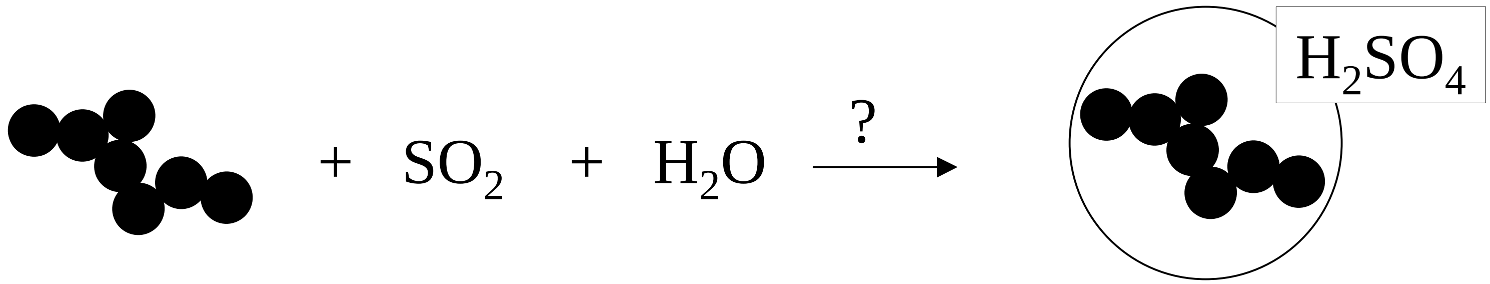


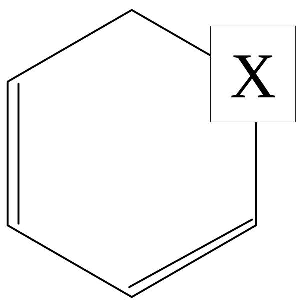
Maxwell-Garnet approximation compared with random inclusion calculations of the average specific absorption of graphitic carbon dispersed in dry, lognormally distributed $(NH_4)_2SO_4$. Geometric standard deviation = 2.0.



$R_g = 0.10\ \mu m \longrightarrow$ 0.80 µm mass median diameter

Mechanisms for making EC hygroscopic?





Do these make EC polar?

α of GC in H_2O is about 10 m^2/g, but 5-7 m^2/g in air.

Is α changed from its value in air by embedding in a filter deposit? Seems very likely if deposit is aqueous: Enhancement would be even greater if in $(NH_4)_2SO_4$ sol'n

What is needed?

A. More photoacoustic studies

B. More Trans/Nephelometer measurements
- Long-path Trans a la IMPROVE
- Short/folded path Trans to study humidification effects in photoacoustic work

A + **B** to improve filter-based measurements

Improved filter measurements for automated, real-time, reduced-cost monitoring of EC.

C. Optical models that better account for internal mixing, morphology, and filter artifacts.

D. IMPROVE-type analysis of EC for chem-based parameterization of soot optics ?

E. Increased use of Raman spectroscopy, along with IR spectroscopy

- Include this in studies of thermal evolution

F. Critical review of reference material by all authors *and* reviewers

G. Specific absorption of Porter, Stout, Coffee, other important light-absorbing OCs

Topic #6 Report / Research Strategy

Science team selected from RFP

Invite climate community participation

Invite combustion science community

Lab measurements on well-characterized particles

- Generated by investigators
- Provided by NIST

Theoretical analysis[+]

Characterize aging of soot

Include satellite remote sensing

Intercomparison of lab measurements & theoretical models

Targeted source and downwind measurement and analysis

Collocated measurements (e.g., @ IMPROVE and EPA sites)[+]

Method intercomparisons at selected super site

Products and clients:

Standardized fast/cheap/good measurement of EC for climate and visibility communities

Baseline for EC to assist TOA methods for climate, visibility and health communities

Caveat:
Make everything as simple as possible, but no simpler:
Protocols may require complementary measurements such as vibrational spectroscopy, optical particle counters, etc.