Contributions of Particle Size and Index of Refraction to the Humidity Dependence of Aerosol Scattering

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OUTLINE

1) Aerosol scattering cross section σ_{sp}, dependencies on h, λ

2) Hygroscopic factor for light scattering $F_{sp}(h_1, h_2, \lambda)$

3) Size dependence of the radius ratio ξ (Kelvin effect)

4) Index of refraction m of substances of interest

5) Dependence of scattering efficiency Q_{sp} on m

6) Gamma approximation for scattering efficiency Q_{Γ}.

7) Dependence of scattering efficiency Q_{sp} on h and λ.

7) Dependence of scattering cross section σ_{sp} on λ, Ångström expnt $\mathring{a}_{sp}$

8) Ångström exponent $\mathring{a}_{sp}$ for gamma approximation Q_{Γ}

9) Putting it all together: contributions to $F_{sp}(h_1, h_2, \lambda)$ from ξ, m

10) Conclusions

AEROSOL SCATTERING CROSS SECTION

The scattering cross section at wavelength λ of an aerosol composed of *spherical particles* of the same uniform composition is given by

$$\sigma_{\mathrm{sp}} = \int \pi r^2 Q_{\mathrm{sp}}\left(\frac{r}{\lambda}, m\right)\frac{dN}{dr}dr$$

This can be written in a form that explicitly shows dependences on h, λ:

$$\sigma_{\mathrm{sp}}(h, \lambda) = \int \pi\left[r(h)\right]^2 Q_{\mathrm{sp}}\left(\frac{r(h)}{\lambda}, m(h, \lambda)\right)\frac{dN}{dr}dr\ ,$$

where the fractional relative humidity $h \equiv$ RH/100%.

With increase in relative humidity, r increases (the particles grow) and m decreases (the particles become more dilute).

We will assume that $m(h, \lambda) \equiv m(h)$, fairly accurate for visible light.

HYGROSCOPIC FACTOR FOR LIGHT SCATTERING

The hygroscopic factor for light scattering is typically described by the ratio of aerosol scattering cross section at two values of *h*:

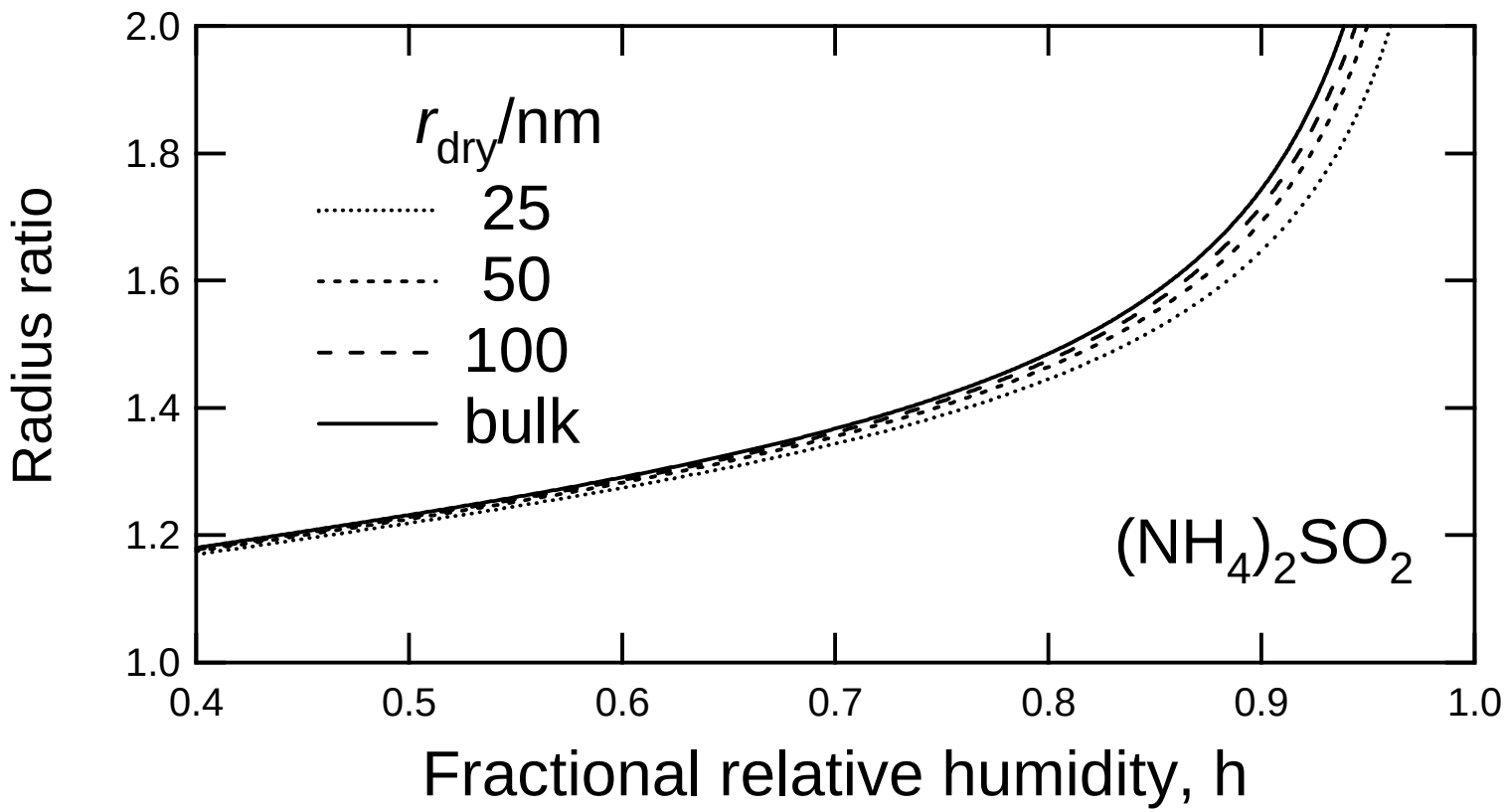
$$F_{sp}\left(h_1, h_2, \lambda\right) \equiv \frac{\sigma_{sp}\left(h_2, \lambda\right)}{\sigma_{sp}\left(h_1, \lambda\right)} = \frac{\int \pi\left[r\left(h_2\right)\right]^2 Q_{sp}\left(\frac{r\left(h_2\right)}{\lambda}, m\left(h_2\right)\right)\frac{dN}{dr}dr}{\int \pi\left[r\left(h_1\right)\right]^2 Q_{sp}\left(\frac{r\left(h_1\right)}{\lambda}, m\left(h_1\right)\right)\frac{dN}{dr}dr}$$

This can also be written as

$$F_{sp}\left(h_1, h_2, \lambda\right) = \frac{\int \pi\left[\frac{r\left(h_2\right)}{r\left(h_1\right)}\right]^2 \left[r\left(h_1\right)\right]^2 Q_{sp}\left(\frac{r\left(h_2\right)}{\lambda}, m\left(h_2\right)\right)\frac{dN}{dr\left(h_1\right)}dr\left(h_1\right)}{\int \pi\left[r\left(h_1\right)\right]^2 Q_{sp}\left(\frac{r\left(h_1\right)}{\lambda}, m\left(h_1\right)\right)\frac{dN}{dr\left(h_1\right)}dr\left(h_1\right)}$$

SIZE DEPENDENCE OF RADIUS RATIO

$\xi(h) \equiv r(h)/r_{\mathrm{dry}}$ depends on h and on r_{dry}—this latter is the Kelvin effect.



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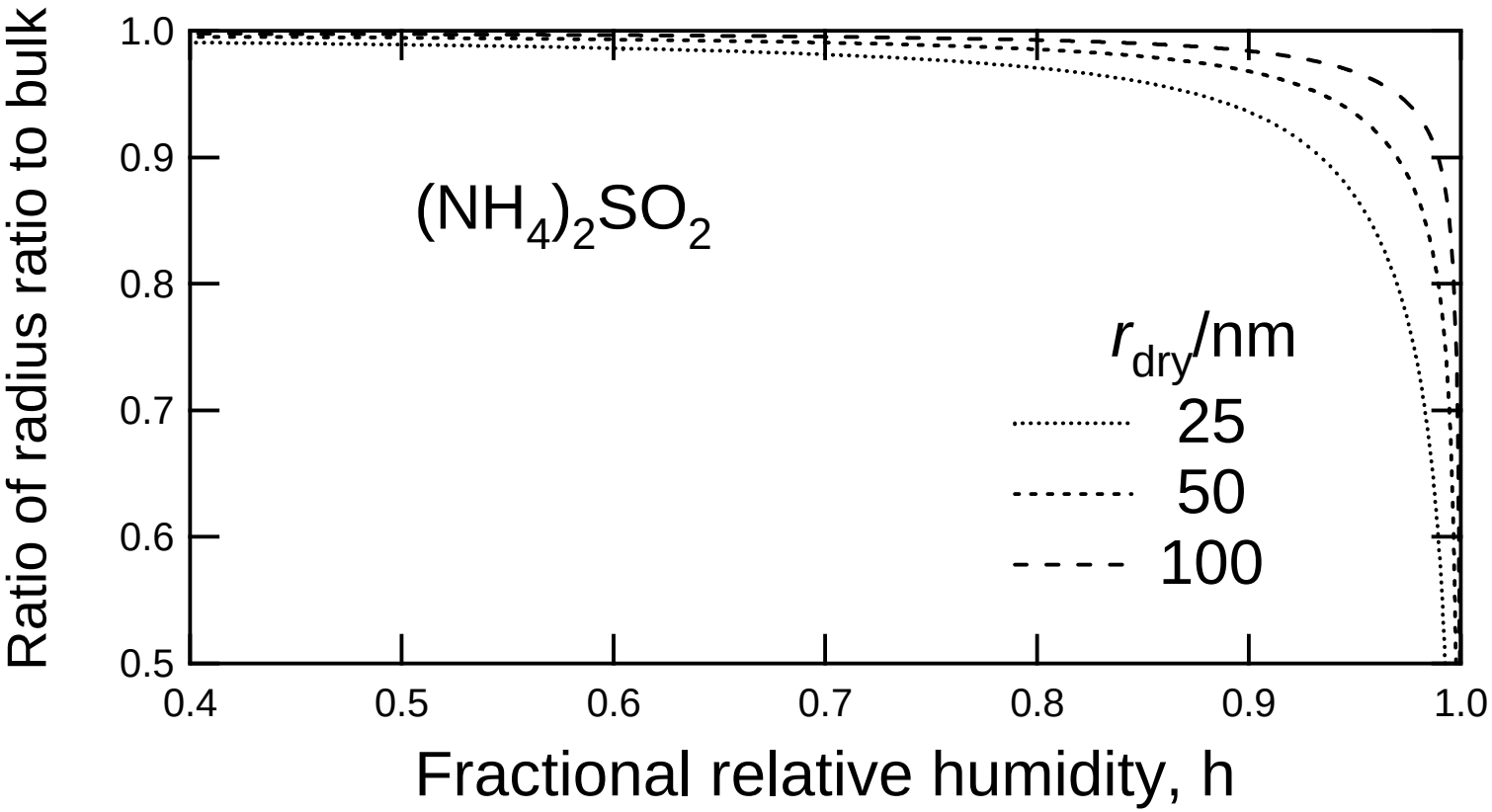
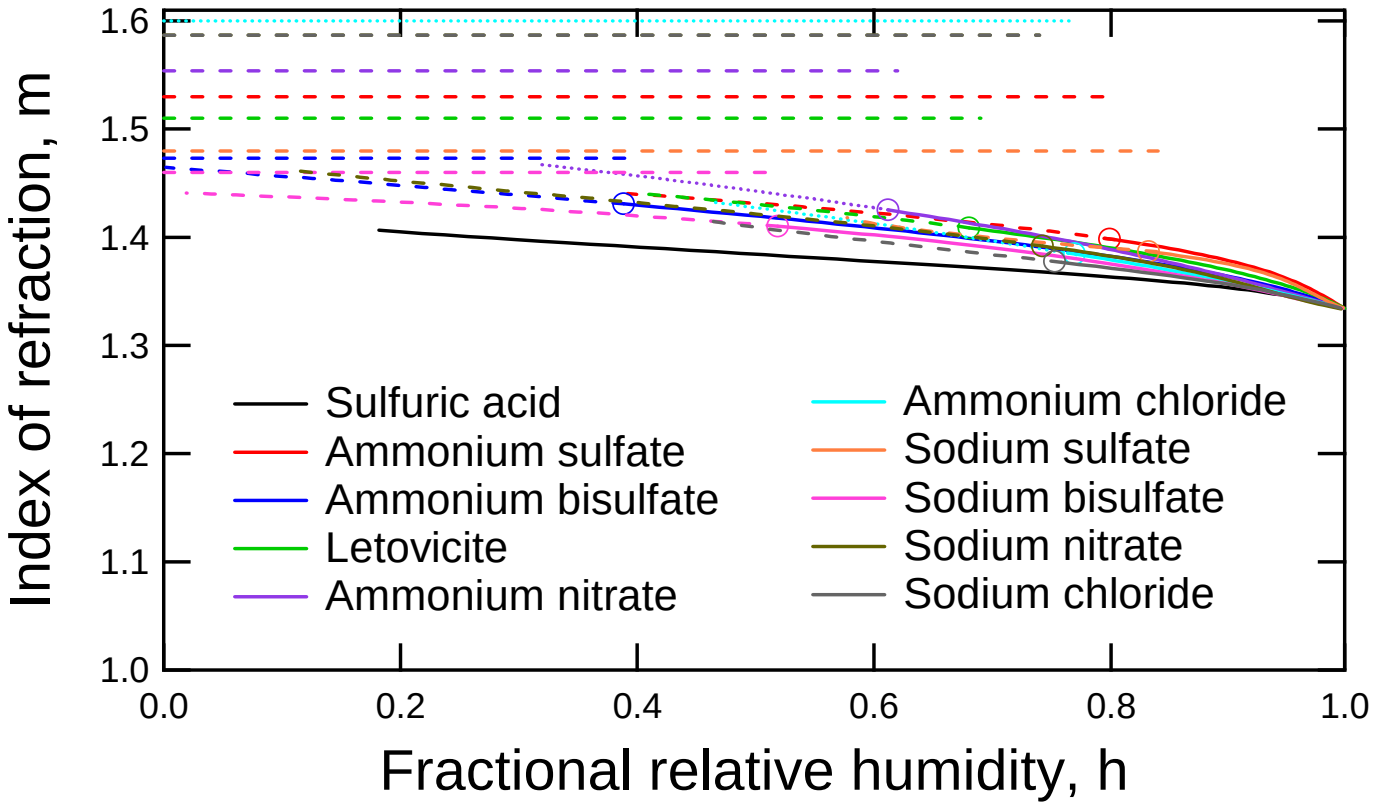


Thus for particles of the size that contribute most to scattering, $\xi(h)$ is nearly independent of r_{dry} and can be taken out of the integral.

HYGROSCOPIC FACTOR FOR LIGHT SCATTERING

$$F_{\mathrm{sp}}\left(h_1, h_2, \lambda\right) = \left[\frac{\xi\left(h_2\right)}{\xi\left(h_1\right)}\right]^2 \frac{\int \pi\left[r\left(h_1\right)\right]^2 Q_{\mathrm{sp}}\left(\frac{r\left(h_2\right)}{\lambda}, m\left(h_2\right)\right)\frac{dN}{dr\left(h_1\right)}dr\left(h_1\right)}{\int \pi\left[r\left(h_1\right)\right]^2 Q_{\mathrm{sp}}\left(\frac{r\left(h_1\right)}{\lambda}, m\left(h_1\right)\right)\frac{dN}{dr\left(h_1\right)}dr\left(h_1\right)}$$

INDEX OF REFRACTION OF SUBSTANCES



1) There is little absorption, so the indices of refraction are real.
2) For many inorganic solutes, *m* ranges from 1.33 to ~1.60.

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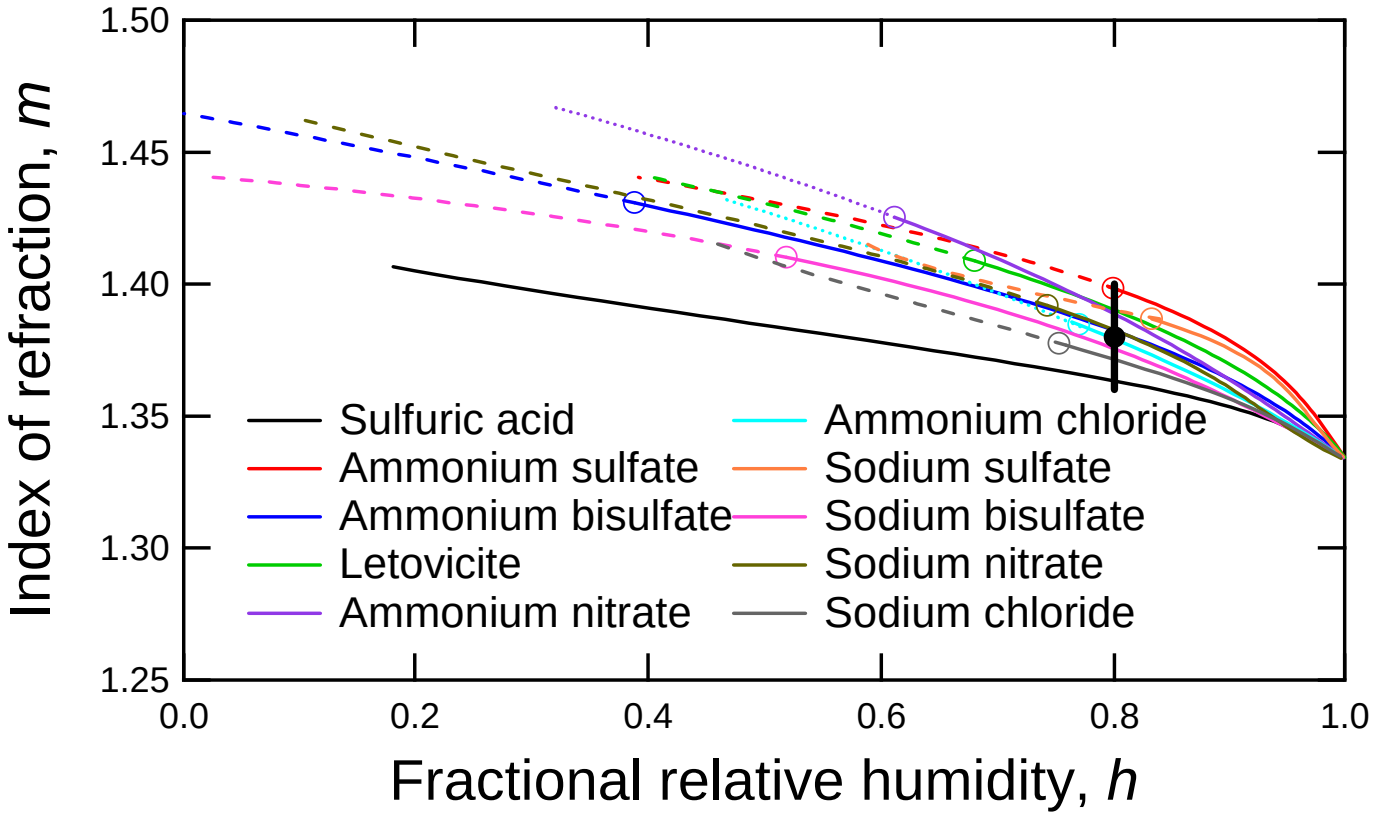
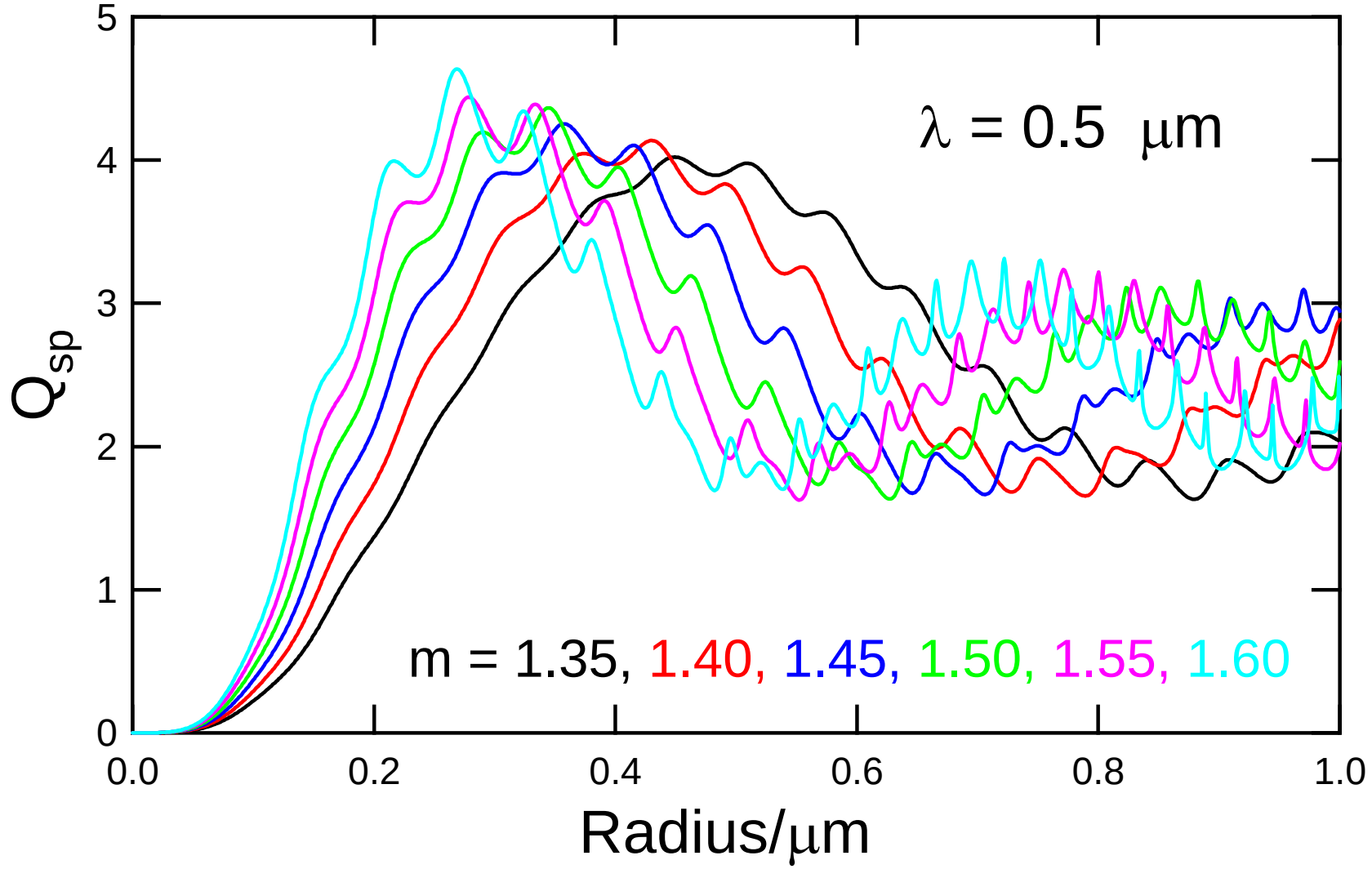


1) There is little absorption, so the indices of refraction are real.
2) For many inorganic solutes, *m* ranges from 1.33 to ~1.60.
3) For solutions of many inorganic solutes, *m* ranges from 1.33 to ~1.47.
4) For given *h*, the range is much narrower; $h = 0.8 \Rightarrow m = 1.38 \pm 0.02$.

DEPENDENCE OF Q_{sp} ON INDEX OF REFRACTION



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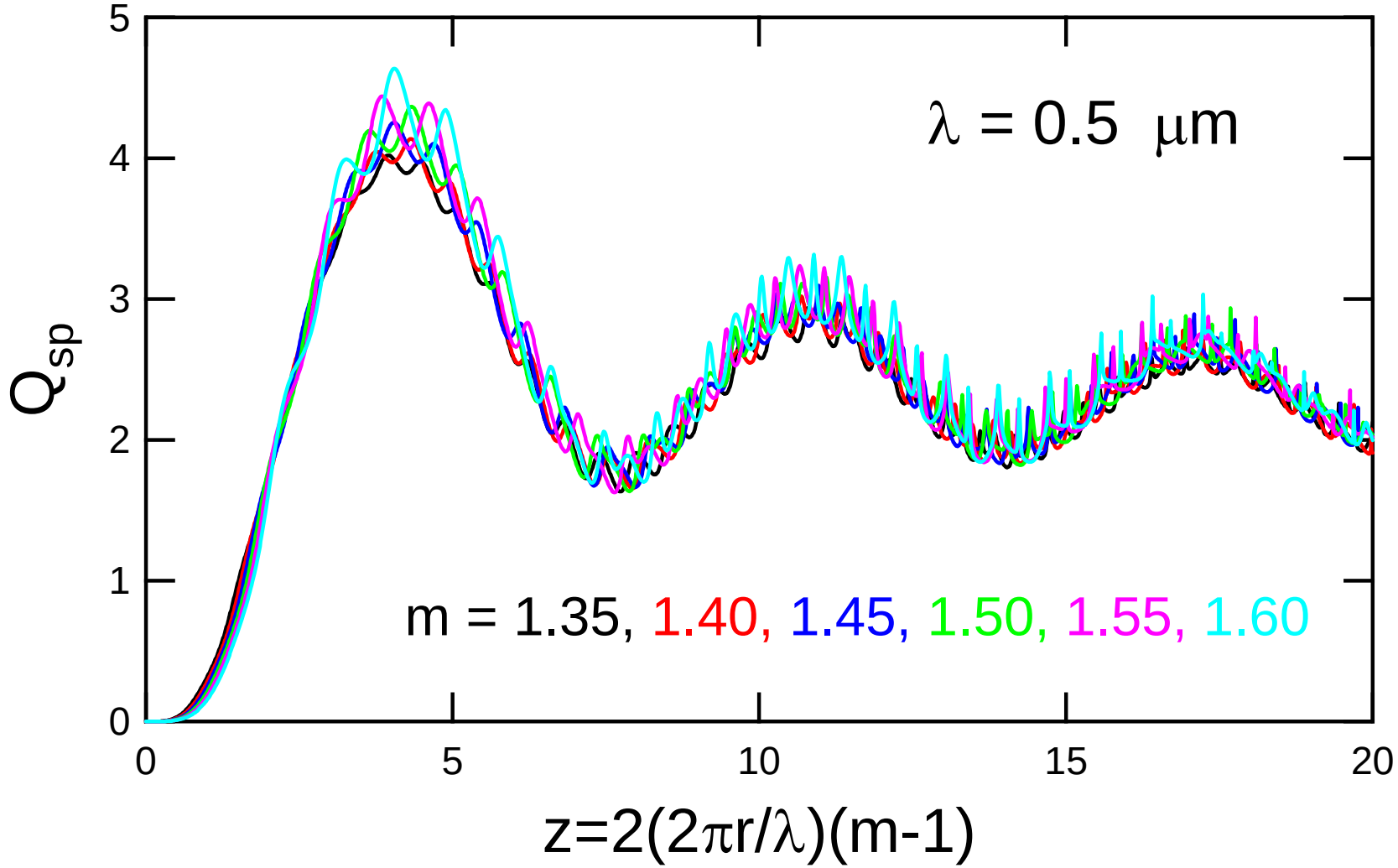
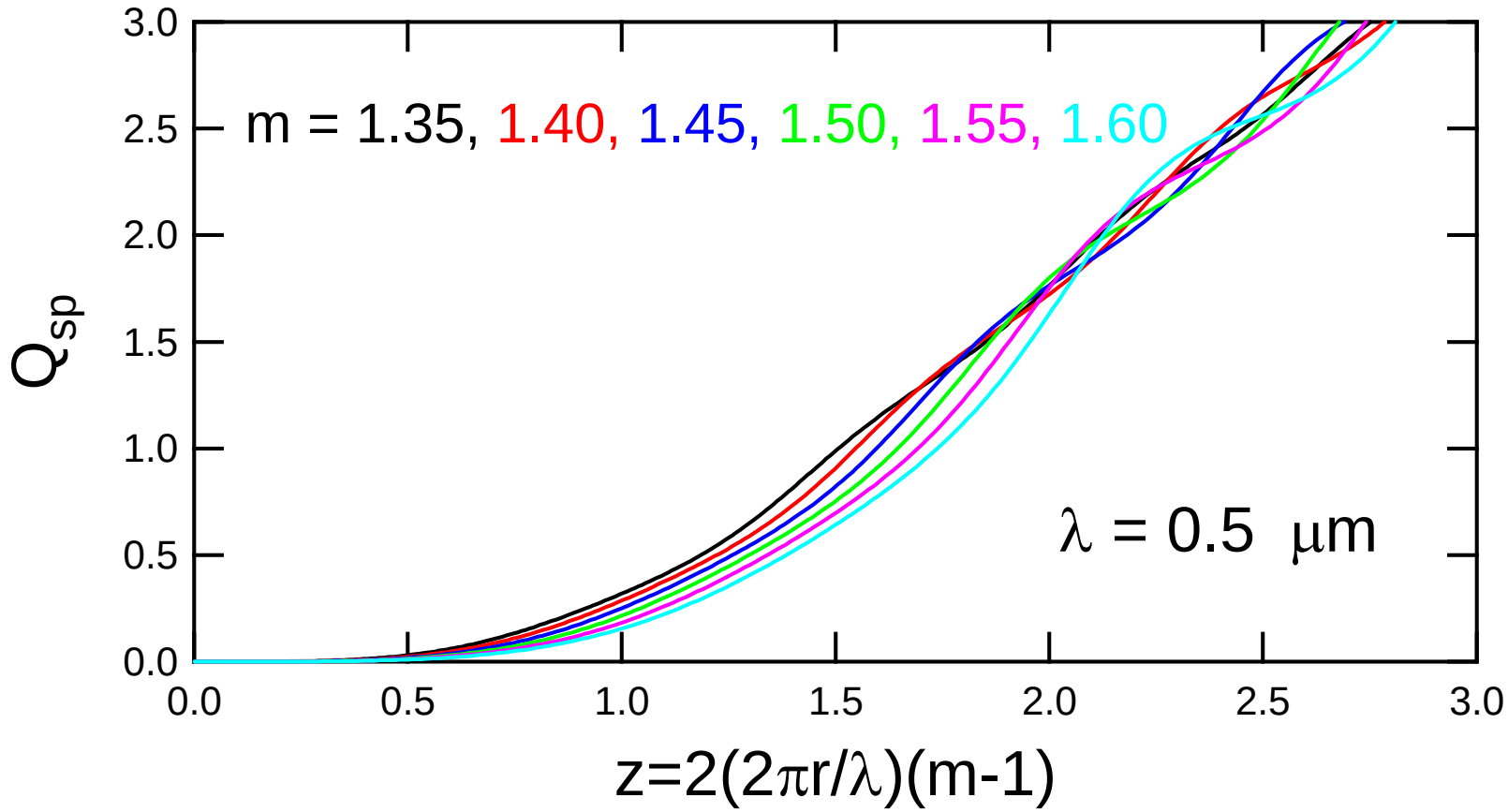


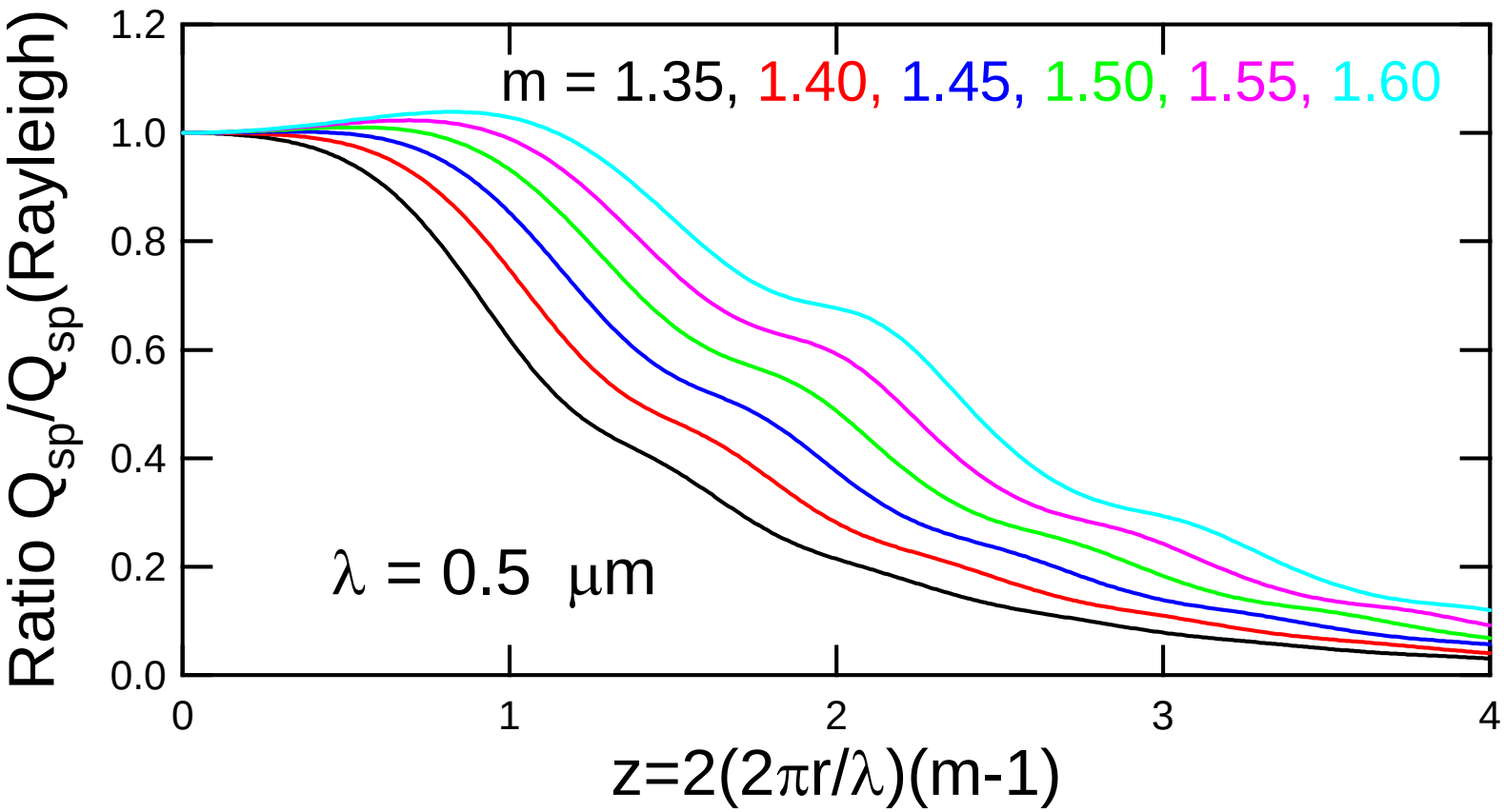
DEPENDENCE OF Q_{sp} ON INDEX OF REFRACTION

This dependence is less accurate for $z < 2 \Rightarrow r < \sim 0.13\text{-}0.22\ \mu m$:



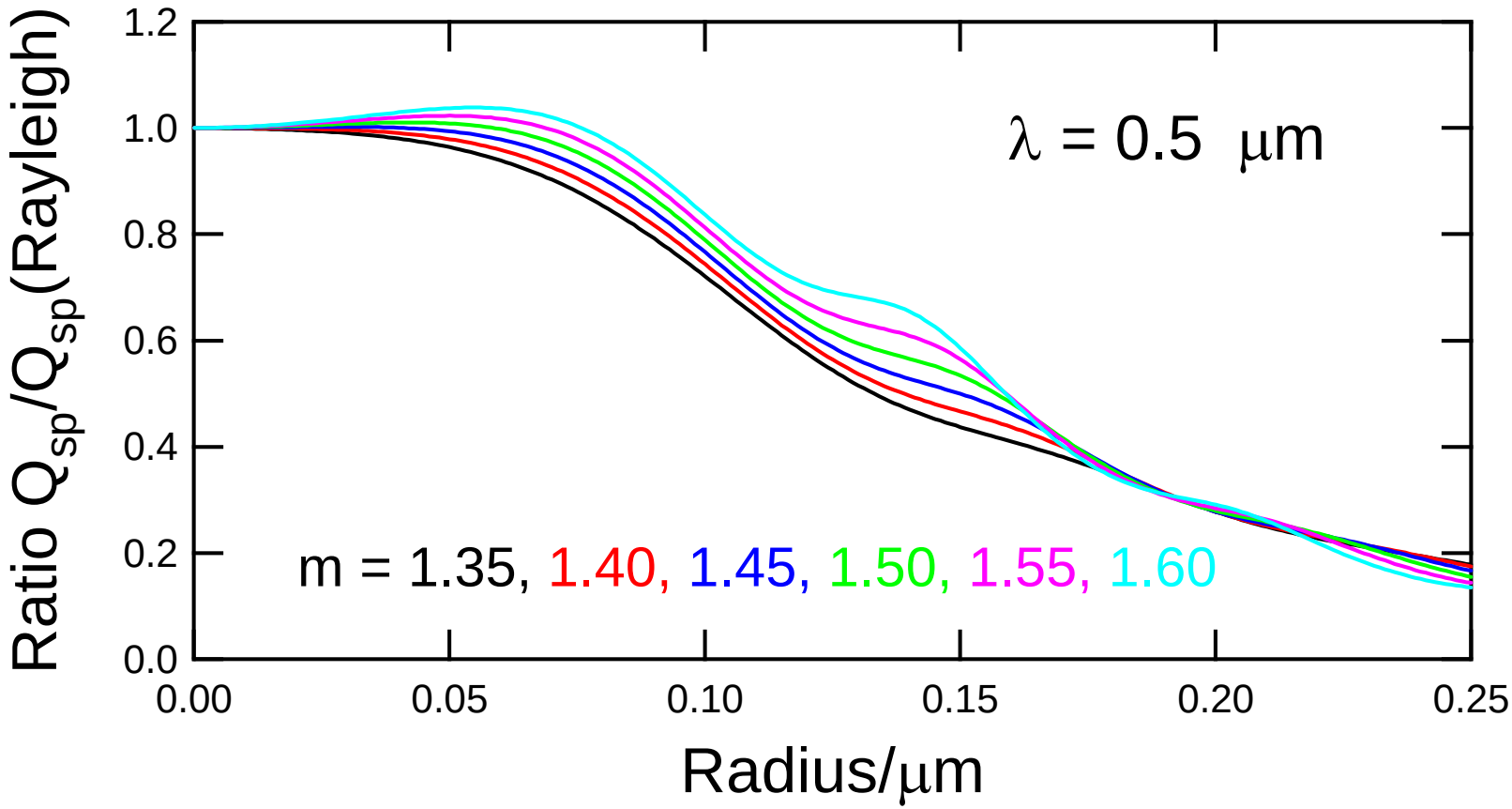
DEPENDENCE OF Q_{sp} ON INDEX OF REFRACTION

Rayleigh scattering is inaccurate for $z > 0.5$-1.0:

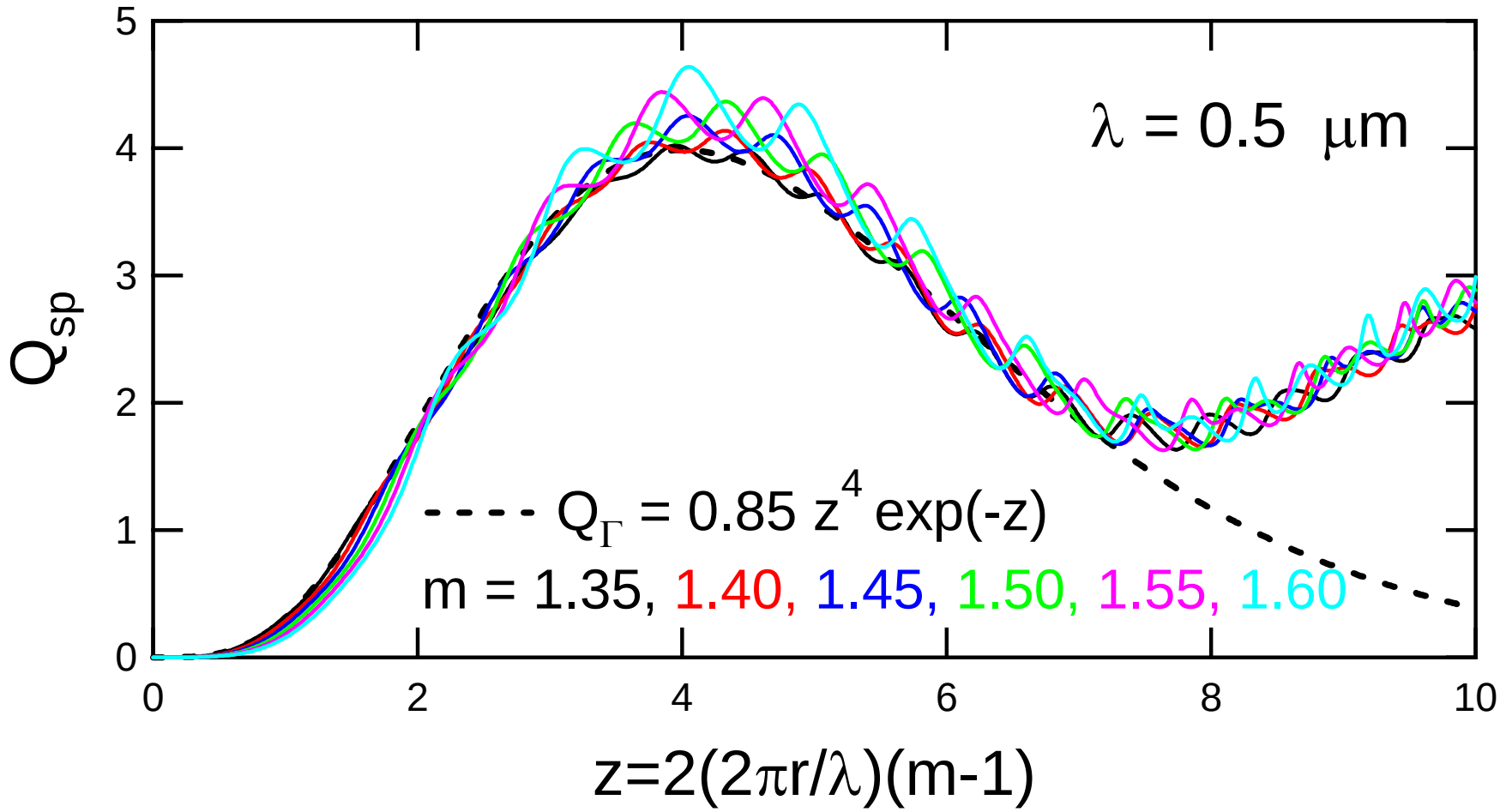


DEPENDENCE OF Q_{sp} ON INDEX OF REFRACTION

Rayleigh scattering is inaccurate for z > 0.5-1.0, or r > ~0.06-0.08 μm:

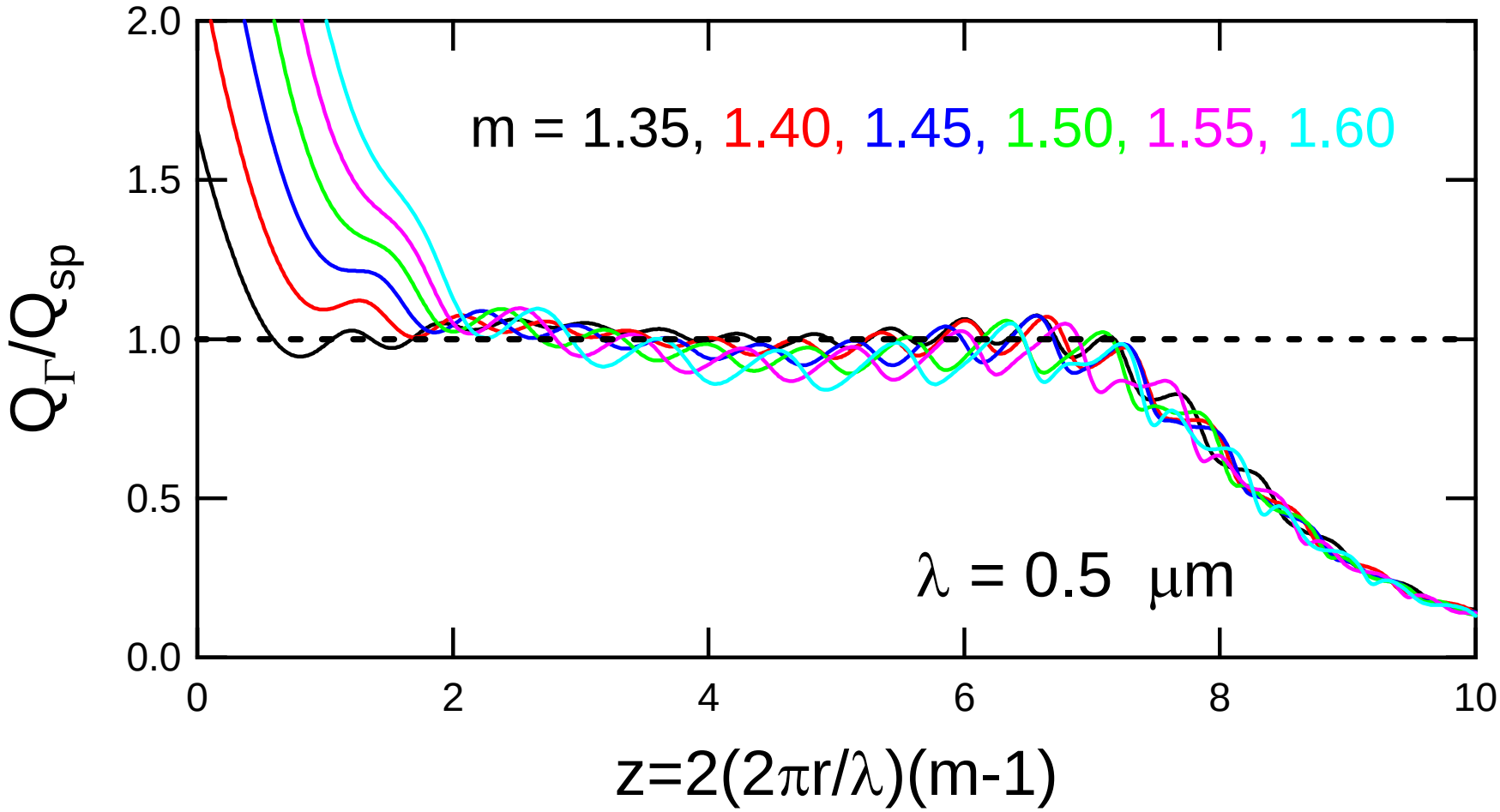


GAMMA APPROXIMATION FOR $Q_{sp}(z)$



wiggles don't matter

GAMMA APPROXIMATION FOR $Q_{sp}(z)$



$Q_\Gamma(z) = 0.85 z^4 e^{-z}$ is an accurate approximation for $2 < z < 7$.

DEPENDENCE OF Q_{sp} ON INDEX OF REFRACTION

For particle sizes that contribute most to light scattering in the visible, Q_{sp} depends mainly on $z \equiv 2(2\pi r/\lambda)(m\text{-}1)$, and $Q_{sp}(z)$ depends weakly on m; thus

$$Q_{sp}\left(\frac{r}{\lambda}, m\right) \approx Q_{sp}(z) \equiv Q_{sp}\left(2\left[\frac{2\pi r(h)}{\lambda}\right]\left[m(h)-1\right]\right).$$

A change in h is equivalent to a change in wavelength λ!

HYGROSCOPIC FACTOR FOR LIGHT SCATTERING

The hygroscopic factor for light scattering can thus be written

$$F_{\mathrm{sp}}\left(h_1, h_2, \lambda\right) = \left[\frac{\xi\left(h_2\right)}{\xi\left(h_1\right)}\right]^2 \frac{\int \pi\left[r\left(h_1\right)\right]^2 Q_{\mathrm{sp}}\left(2\left[\frac{2\pi r\left(h_2\right)}{\lambda}\right]\left[m\left(h_2\right)-1\right]\right)\frac{dN}{dr\left(h_1\right)}dr\left(h_1\right)}{\int \pi\left[r\left(h_1\right)\right]^2 Q_{\mathrm{sp}}\left(2\left[\frac{2\pi r\left(h_1\right)}{\lambda}\right]\left[m\left(h_1\right)-1\right]\right)\frac{dN}{dr\left(h_1\right)}dr\left(h_1\right)}$$

Define λ_1 and λ_2 by

$$\begin{cases} 2\left[\frac{2\pi r\left(h_1\right)}{\lambda_1}\right]\left[m\left(h_1\right)-1\right] = 2\left[\frac{2\pi r\left(h_1\right)}{\lambda}\right]\left[m\left(h_1\right)-1\right] \\ 2\left[\frac{2\pi r\left(h_1\right)}{\lambda_2}\right]\left[m\left(h_1\right)-1\right] = 2\left[\frac{2\pi r\left(h_2\right)}{\lambda}\right]\left[m\left(h_2\right)-1\right] \end{cases}$$

HYGROSCOPIC FACTOR FOR LIGHT SCATTERING

With this definition,

$$F_{\mathrm{sp}}\left(h_1, h_2, \lambda\right) = \left[\frac{\xi\left(h_2\right)}{\xi\left(h_1\right)}\right]^2 \frac{\int \pi\left[r\left(h_1\right)\right]^2 Q_{\mathrm{sp}}\left(2\left[\frac{2\pi r\left(h_1\right)}{\lambda_2}\right]\left[m\left(h_1\right)-1\right]\right)\frac{dN}{dr\left(h_1\right)}dr\left(h_1\right)}{\int \pi\left[r\left(h_1\right)\right]^2 Q_{\mathrm{sp}}\left(2\left[\frac{2\pi r\left(h_1\right)}{\lambda_1}\right]\left[m\left(h_1\right)-1\right]\right)\frac{dN}{dr\left(h_1\right)}dr\left(h_1\right)}$$

where $\lambda_1 = \lambda$ and $\lambda_2 = \lambda \frac{r\left(h_1\right)}{r\left(h_2\right)}\left[\frac{m\left(h_1\right)-1}{m\left(h_2\right)-1}\right] \Rightarrow \frac{\lambda_2}{\lambda_1} = \frac{\xi\left(h_1\right)}{\xi\left(h_2\right)}\left[\frac{m\left(h_1\right)-1}{m\left(h_2\right)-1}\right]$.

But this can also be written as

$$F_{\mathrm{sp}}\left(h_1, h_2, \lambda\right) = \left[\frac{\xi\left(h_2\right)}{\xi\left(h_1\right)}\right]^2 \frac{\sigma_{\mathrm{sp}}\left(h_1, \lambda_2\right)}{\sigma_{\mathrm{sp}}\left(h_1, \lambda_1\right)}.$$

DEPENDENCE OF σ_{sp} ON WAVELENGTH

The wavelength dependence of σ_{sp} is characterized by the Ångström exponent for scattering by particles $\mathring{a}_{sp}$:

$$\mathring{a}_{sp} \equiv \frac{-\Delta \ln \sigma_{sp}}{\Delta \ln \lambda} = \frac{-\ln\left[\dfrac{\sigma_{sp}(\lambda_2)}{\sigma_{sp}(\lambda_1)}\right]}{\ln\left(\dfrac{\lambda_2}{\lambda_1}\right)}$$

Small particles => large $\mathring{a}_{sp}$ ($\mathring{a}_{sp}$ = 4 for Rayleigh scattering)
Large particles => small $\mathring{a}_{sp}$ ($\mathring{a}_{sp}$ = 0 for aerosol of large particles)
Most measurements yield $\mathring{a}_{sp}$ between 0 and 2.

The above definition can be inverted to yield

$$\frac{\sigma_{sp}(\lambda_2)}{\sigma_{sp}(\lambda_1)} = \left(\frac{\lambda_2}{\lambda_1}\right)^{-\mathring{a}_{sp}}$$

ÅNGSTRÖM EXPONENT FOR GAMMA APPROXIMATION

For $Q_\Gamma(z) = 0.85\, z^4\, e^{-z}$ and $\frac{dN}{dr} = r^{\left(\frac{1}{v_{\text{eff}}}-3\right)} e^{-\left(\frac{r}{r_{\text{eff}} v_{\text{eff}}}\right)}$, $\mathring{a}_{\text{sp}} = \frac{4 - z_{\text{eff}}}{1 + v_{\text{eff}}\, z_{\text{eff}}}$,

where $z_{\text{eff}} \equiv 2(2\pi r_{\text{eff}}/\lambda)(m\text{-}1)$.

For $m = 1.4$, $\lambda = 0.5\ \mu\text{m}$, $z_{\text{eff}} > 2 \Rightarrow r_{\text{eff}} > 0.2$

$z_{\text{eff}} > 2 \Rightarrow \mathring{a}_{\text{sp}} < \sim 1.5$ (for $v_{\text{eff}} = 0.2$)

Recall, most measurements yield values of $\mathring{a}_{\text{sp}}$ between 0 and 2.

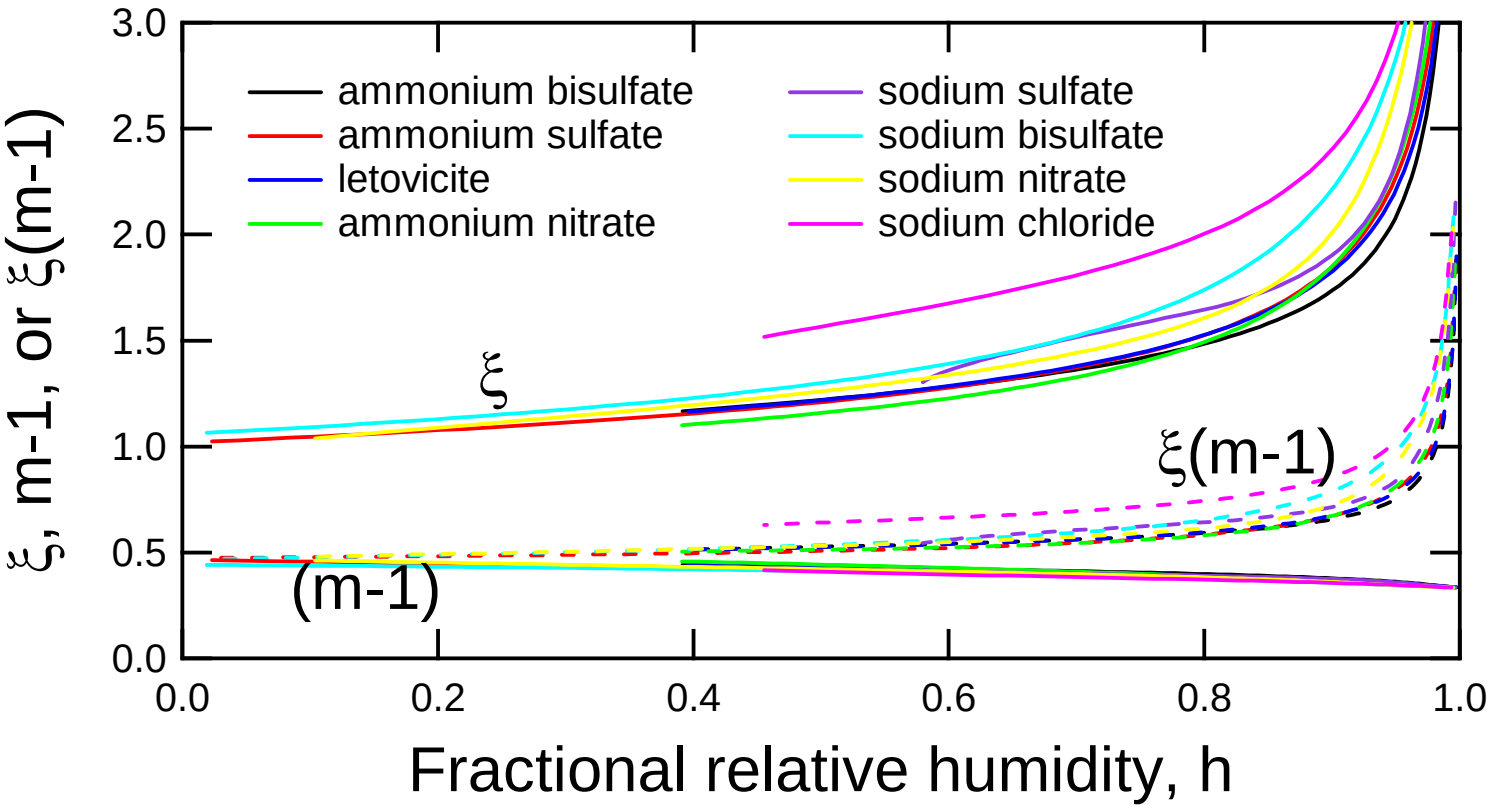
Thus the main contribution to light scattering in the visible is from particles with $z_{\text{eff}} > \sim 1.5 \Rightarrow$ $\underline{r_{\text{eff}} > \sim 0.1\text{-}0.15\ \mu\text{m}}$ and the approximation $Q_{\text{sp}}(z, m) = Q_{\text{sp}}(z)$ is accurate over most of this range.

PUTTING IT ALL TOGETHER

$$
\begin{aligned}
F_{\mathrm{sp}}\left(h_1, h_2, \lambda\right) &\equiv \frac{\sigma_{\mathrm{sp}}\left(h_2, \lambda\right)}{\sigma_{\mathrm{sp}}\left(h_1, \lambda\right)} \\
&= \left[\frac{\xi\left(h_2\right)}{\xi\left(h_1\right)}\right]^2 \frac{\sigma_{\mathrm{sp}}\left(h_1, \lambda_2\right)}{\sigma_{\mathrm{sp}}\left(h_1, \lambda_1\right)} \\
&= \left[\frac{\xi\left(h_2\right)}{\xi\left(h_1\right)}\right]^2 \left(\frac{\lambda_2}{\lambda_1}\right)^{-\mathring{a}_{\mathrm{sp}}} \\
&= \left[\frac{\xi\left(h_2\right)}{\xi\left(h_1\right)}\right]^2 \left\{\frac{\xi\left(h_1\right)}{\xi\left(h_2\right)}\left[\frac{m\left(h_1\right)-1}{m\left(h_2\right)-1}\right]\right\}^{-\mathring{a}_{\mathrm{sp}}} \\
&= \left[\frac{\xi\left(h_2\right)}{\xi\left(h_1\right)}\right]^{2+\mathring{a}_{\mathrm{sp}}} \left[\frac{m\left(h_2\right)-1}{m\left(h_1\right)-1}\right]^{\mathring{a}_{\mathrm{sp}}}
\end{aligned}
$$

WHICH FACTOR DOMINATES?

$$F_{sp}\left(h_1, h_2, \lambda\right) = \left[\frac{\xi\left(h_2\right)}{\xi\left(h_1\right)}\right]^2 \left\{\frac{\xi\left(h_2\right)}{\xi\left(h_1\right)}\left[\frac{m\left(h_2\right)-1}{m\left(h_1\right)-1}\right]\right\}^{\mathring{a}_{sp}}$$



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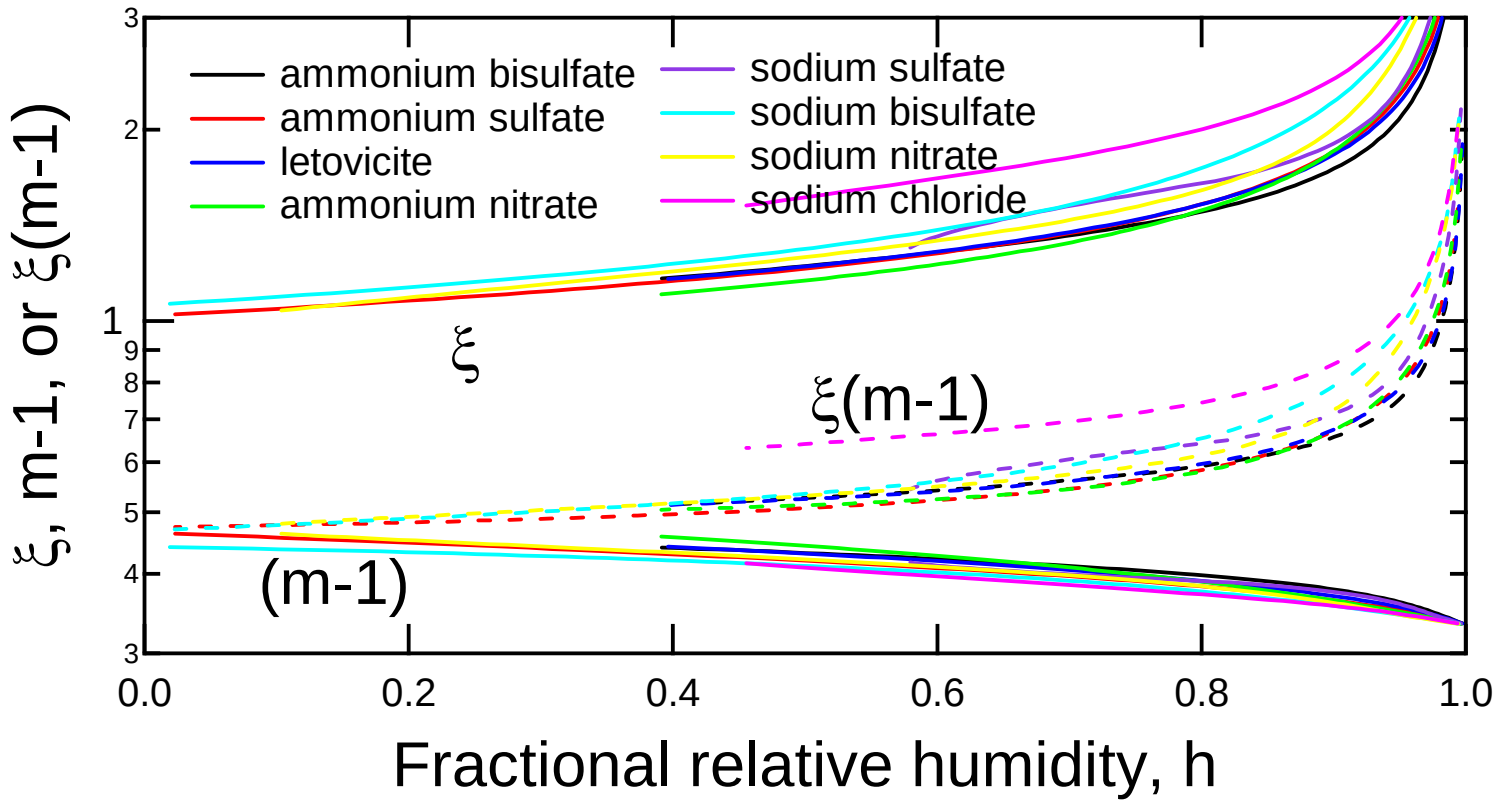

RH growth of radius dominates over RH decrease of refractive index!

LIMITATIONS, EXTENSIONS

1) The assumption $Q_{sp}(z, m) \approx Q_{sp}(z)$ may not be valid if scattering is mainly from sufficiently small particles (i.e., $\mathring{a}_{sp}$ is large, > ~2)

2) Dried particles may not be spherical, of uniform composition.

3) For crystalline particles, m may depend upon direction.

4) Numerical simulations required to test the limits of these results.

5) This analysis will be extended to organics substances.

CONCLUSIONS

1) The hygroscopic factor for light scattering at a given wavelength

$$F_{\mathrm{sp}}\left(h_1, h_2, \lambda\right) \equiv \frac{\sigma_{\mathrm{sp}}\left(h_2, \lambda\right)}{\sigma_{\mathrm{sp}}\left(h_1, \lambda\right)}$$

can be related to the ratio of scattering cross sections at two wavelengths.

2) The hygroscopic factor for light scattering can be expressed as

$$F_{\mathrm{sp}}\left(h_1, h_2, \lambda\right) = \left[\frac{\xi\left(h_2\right)}{\xi\left(h_1\right)}\right]^{2+\mathring{a}_{\mathrm{sp}}} \left[\frac{m\left(h_2\right)-1}{m\left(h_1\right)-1}\right]^{\mathring{a}_{\mathrm{sp}}} .$$

3) The contribution of particle size is greater than that of refractive index.