Radial Growth and Optical Properties of Hygroscopic Absorbing Aerosols at High Relative Humidity

Ernie R. Lewis (Brookhaven National Laboratory, elewis@bnl.gov)
Arthur J. Sedlacek III (Brookhaven National Laboratory, sedlacek@bnl.gov)
Timothy B. Onasch (Aerodyne Research, Inc., onasch@aerodyne.com)

INTRODUCTION

The equilibrium relative humidity, and thus radial growth, of an aerosol particle is determined by vapor pressure lowering due to solutes (Raoult effect) and surface tension (Kelvin effect).

The radius of an aerosol particle depends on the relative humidity and the mass of solute (or equivalently, r_{dry}).

At RH approaching 100%, the Kelvin effect becomes increasingly important, depending on the size of the particle.

$$h = a_w\left(r/r_{dry}\right)\exp\left(r_\sigma/r\right)$$

The radius occurs in both the Raoult term and the Kelvin term, complicating finding an explicit expression for the radius in terms of RH. It is usually found through an iterative approach.

h	fractional relative humidity (RH/100%)
r_{dry}	mass-equivalent dry radius
σ	surface tension
$r_\sigma \equiv \frac{2\sigma\bar{v}_w}{RT}$	surface tension length, ~1.05 nm
$\bar{v}_w$	partial molal volume of water, $\sim M_w/\rho_w$
a_w	water activity

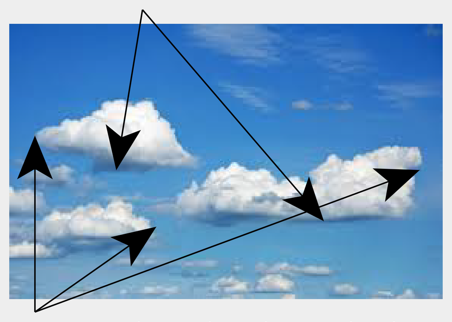
An explicit expression for radius in terms of RH and solute mass would be useful in models and would clearly illustrate the relative importance of the two effects and the dependences on RH and r_{dry}.

Here an explicit expression is presented of the form

$$r/r_{dry} = function\left(h, r_{dry}\right)$$

Where Is This Important?

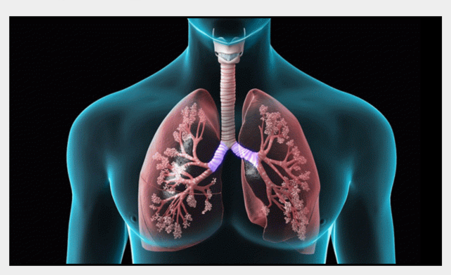
1) Clouds: just below cloud base (LCL), RH is near 100%.



The "twilight zone" at cloud edges is important for Earth's radiative balance, but challenges cloud-screening algorithms.

2) Fog creates safety/economic concerns, is difficult to forecast.

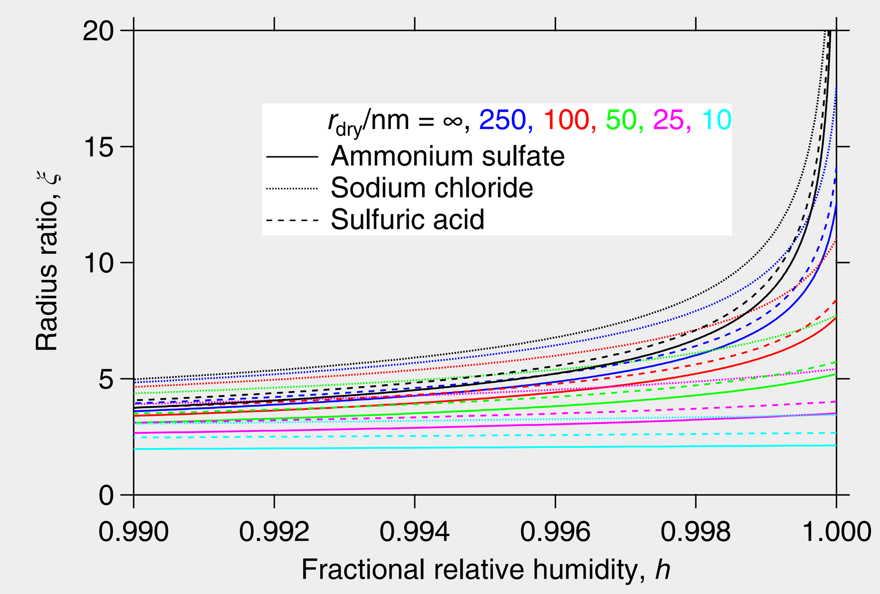
3) Lungs: human lungs are at 99.5% RH. The extent to which particles enter the lung depends on their size and on the RH.



Radius Ratio

The radius ratio r/r_{dry} at 100% RH ranges from 2-3 to 12-17 for AS, SC, and sulfuric acid as r_{dry} increases from 10 to 250 nm.

For r_{dry} = 10 nm, the radius ratio is ~2-3, nearly independent of RH over this range. For larger r_{dry}, this ratio shows a much stronger dependence on RH.



Expression for r/r_{dry}

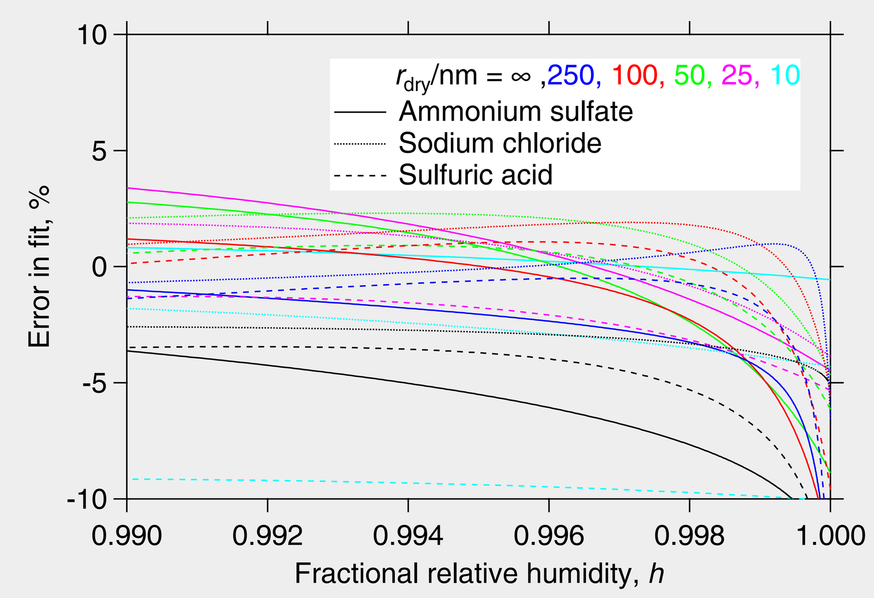
An expression for the radius ratio r/r_{dry} in terms of RH and r_{dry} is found by merging the solutions in two limits:
1) when Kelvin effect is unimportant, and
2) when RH=100%.

This expression yields r/r_{dry} as an explicit function of RH and r_{dry}, is finite at 100% RH, and contains a single adjustable parameter for each substance - ammonium sulfate: a = 0.78, sodium chloride: a = 1.04, sulfuric acid: a = 0.84.

$$\frac{r}{r_{dry}} = \frac{a}{\left[1-h+\left(\frac{r_{\sigma,0}}{a r_{dry}}\right)^{3/2}\right]^{1/3}}$$

This expression is extremely accurate - for r_{dry} from 10-250 nm and RH from 99% up to greater than 99.9%, it yields results within a few percent of the actual value, which ranges over more than 10x.

This is remarkable for an expression with one free parameter!



Importance of the Kelvin Effect

The importance of the Kelvin effect depends on both RH and r_{dry}. The criterion for when neglect of the Kelvin effect results in more than a 5% increase in the radius ratio is that

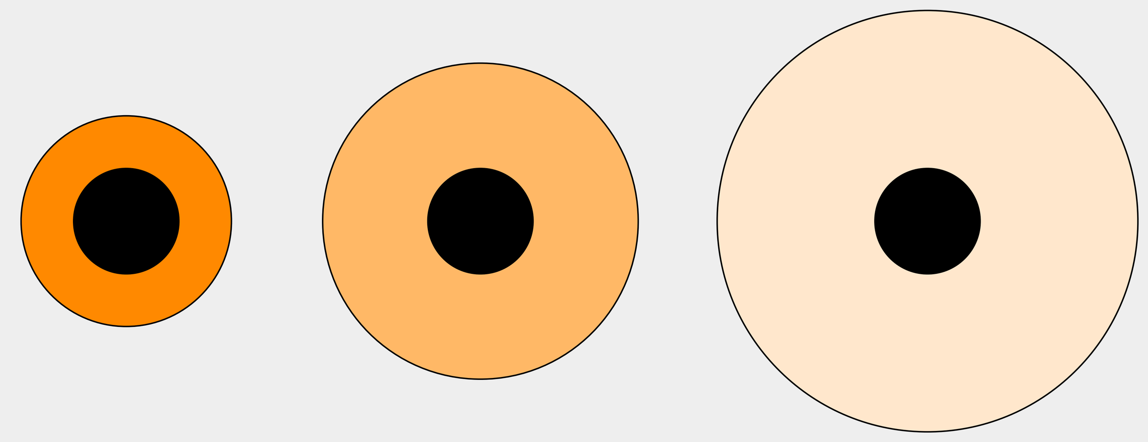
$$h_{crit} < 1 - (3.5\ \text{nm}/r_{dry})^{3/2}$$

For r_{dry} = (25, 50, 100) nm, h_{crit} = (0.95, 0.98, 0.994).

Hygroscopic Growth of Coated BC

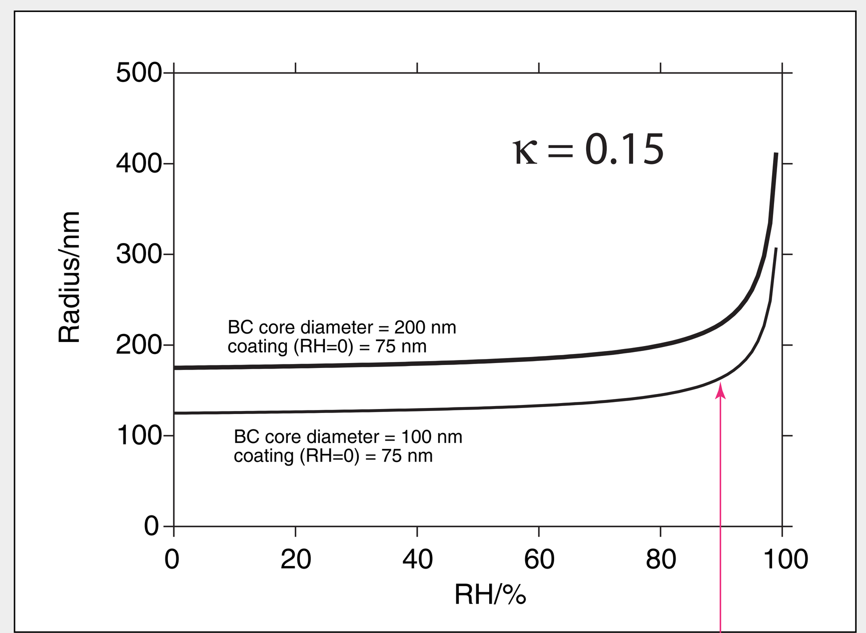
With increasing RH, a coated BC particle will increase in size, but the coating will become less absorbing due to dilution.

There are many mixing rules to predict the decrease in refractive index as a function of RH, but they give similar results.



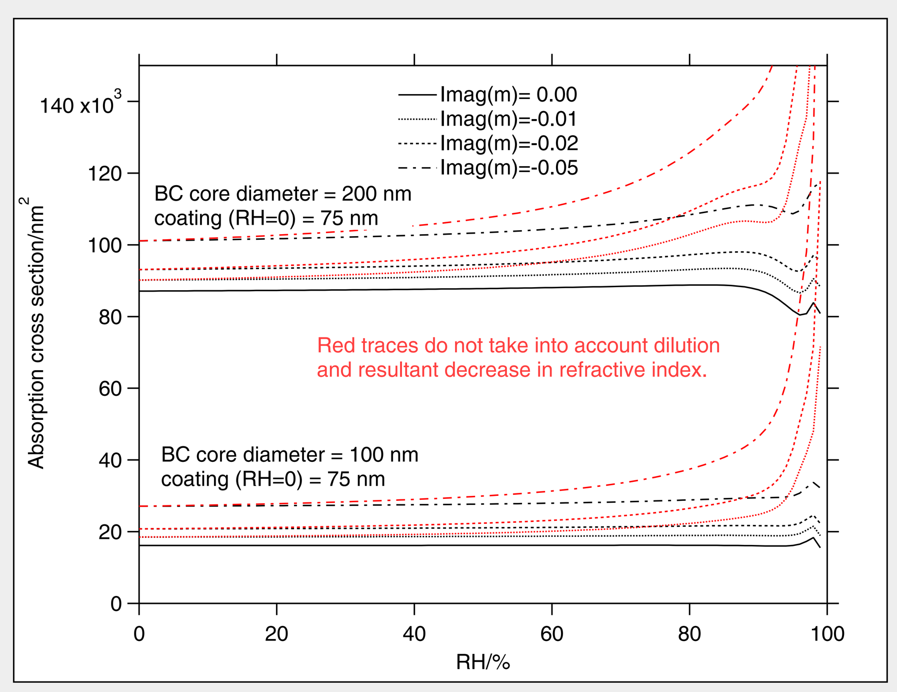
Increasing RH →

Hygroscopic Growth



Little radial growth until RH > 90%.

Absorption Cross Section Dependence on RH



Very little dependence of absorption cross section on RH!
Some resonance structure at RH > 95%
Fairly weak dependence on imaginary component of coating refractive index (although some additional absorption by coating).
Strong dependence on BC core diameter.
Necessary to include change in index of refraction due to dilution.