PARAMETERIZATION OF AEROSOL PROPERTIES ON RELATIVE HUMIDITY

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DOE ARM Aerosol Working Group
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MOTIVATION

- Calculation of aerosol forcing in specific situations and representation of aerosol forcing in climate models requires calculation of light scattering by aerosol particles, and thus knowledge of **radius *r*** and **refractive index *n***:

$$\sigma_{\mathrm{s,p}} = \int f(\lambda)\left[\int \pi r^2 Q_{\mathrm{sca}}\left(r/\lambda, n\right)\frac{dN(r)}{dr}dr\right]d\lambda$$

- Additionally, knowledge of **density ρ** is necessary
  - to relate **radius *r*** to concentration: $\frac{r}{r_{\mathrm{dry}}} = \left(\frac{\rho_{\mathrm{dry}}}{\rho}\frac{1}{x_{\mathrm{s}}}\right)^{1/3}$
  - to relate aerodynamic radius to (geometric) **radius *r***: $\frac{r}{r_{\mathrm{aero}}} = \left(\frac{1\,\mathrm{g\,cm^{-3}}}{\rho}\right)^{1/2}$

PROBLEM

- These quantities (***r***, ***n***, and ρ) are typically parameterized in terms of concentration (**molality *m***, **solute mass fraction *x***, or **solute mole fraction n_s**), none of which is readily available in field situations or to modelers.

- However, the controlling quantity is **relative humidity *rh***.

- To obtain **radius *r*** at a given **relative humidity *rh*** requires:

1) invert for x_s: $a_w \equiv rh = 1 - 0.6366x_s + 0.8624x_s^2 - 11.58x_s^3 + 15.18x_s^4$

2) substitute for ρ: $\rho = 1 + 0.741x_s - 0.3741x_s^2 + 2.252x_s^3 - 2.06x_s^4$

3) substitute for **radius *r***: $\frac{r}{r_{dry}} = \left(\frac{\rho_{dry}}{\rho}\frac{1}{x_s}\right)^{1/3}$

- Such a procedure is cumbersome and yields little insight.

GOAL

- To determine ***simple but accurate*** parameterizations for **radius *r***, **refractive index *n***, and **density ρ**, of aerosol particles of different solutes in terms of **relative humidity *rh***.

PARAMETERIZATION CONSIDERATIONS

*There is always a tradeoff between **accuracy** and **simplicity***

- Advantages to simple expressions over more complicated ones:
  - Physical insight and recognition of trends and patterns.
  - Stable extrapolation possible.
  - Possible path forward for mixing rules.
  - Decreased computational burden.
  - Less chance of errors in coding or listing coefficients.

- High accuracy is often not justified because of
  - Measurement issues (RH not accurately known).
  - Uncertainties in particle composition.
    - internal mixtures
    - surface-active substances
    - insoluble inclusion
  - Uncertainties or errors in original data.
  - Paucity of data in supersaturated range.

ACCURACY GOALS

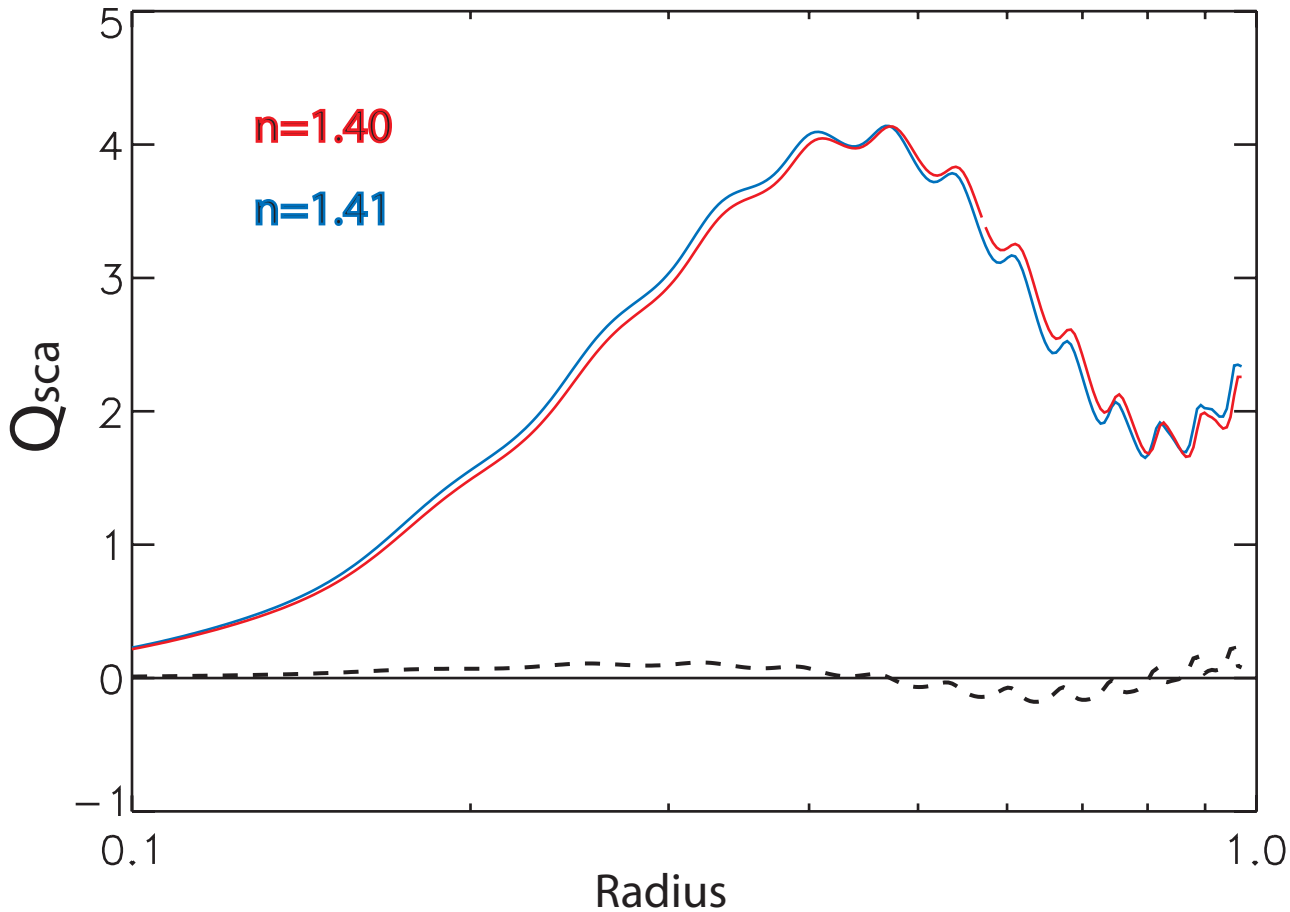
- Radius: ~2-3%

  Equivalent to ±0.02 in *rh* at *rh* = 0.75, or ±0.01 in *rh* at *rh* = 0.90.
  Radius ratio varies by >5× (i.e., 500%) over the range of *rh* up to 0.99.
  Radius varies by more than ±20% within radius bin 0.1-0.15 μm.
  Extensive quantities (Q_{sca}, forcing) depend on dN/dr (larger uncertainty).

- Index of Refraction: ~0.01

  Equivalent to Δr = 2-3% at n = 1.40, as pertinent quantity is $(n\text{-}1)r/\lambda$.
  n_w varies by ~0.01 over visible wavelengths.
  Difference in Q_{sca} for Δn = 0.01 small, smoothed by size distribution.

CHANGE in Q_{sca} for $\Delta n = 0.01$



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- Density: ~5%

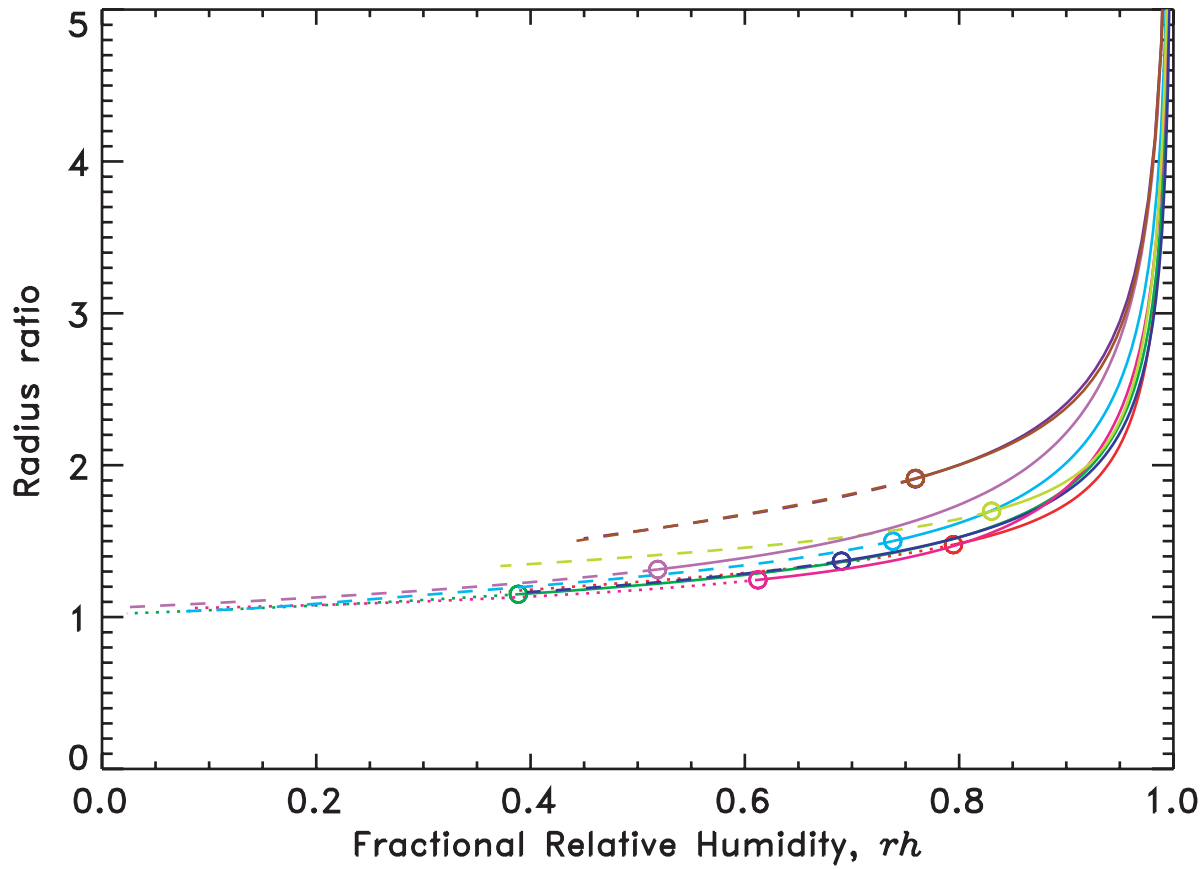
  As $\frac{r}{r_{dry}} = \left(\frac{\rho_{dry}}{\rho}\frac{1}{x_s}\right)^{1/3}$ and $\frac{r}{r_{aero}} = \left(\frac{1\,\mathrm{g\,cm^{-3}}}{\rho}\right)^{1/2}$, ±5% in $\rho \Rightarrow$ ±2-3% in radius.

SUBSTANCES OF INTEREST

Substance	**Formula**	**MW** g mol^{-1}	**Density** g cm^{-3}	ν
Ammonium sulfate	$(NH_4)_2SO_4$	132.14	1.77	3
Ammonium bisulfate	NH_4HSO_4	115.11	1.78	3
Letovicite	$(NH_4)_3\,H(SO_4)_2$	247.25	1.83	6
Ammonium nitrate	NH_4NO_3	80.04	1.73	2
Sodium nitrate	$NaNO_3$	84.99	2.26	2
Sodium sulfate	Na_2SO_4	142.04	2.68	3
Sodium bisulfate	$NaHSO_4$	120.06	2.44	3
Sodium chloride	NaCl	58.44	2.17	2
Sea salt		62.79	2.2	2

Also H_2SO_4, NH_4Cl, possibly others.

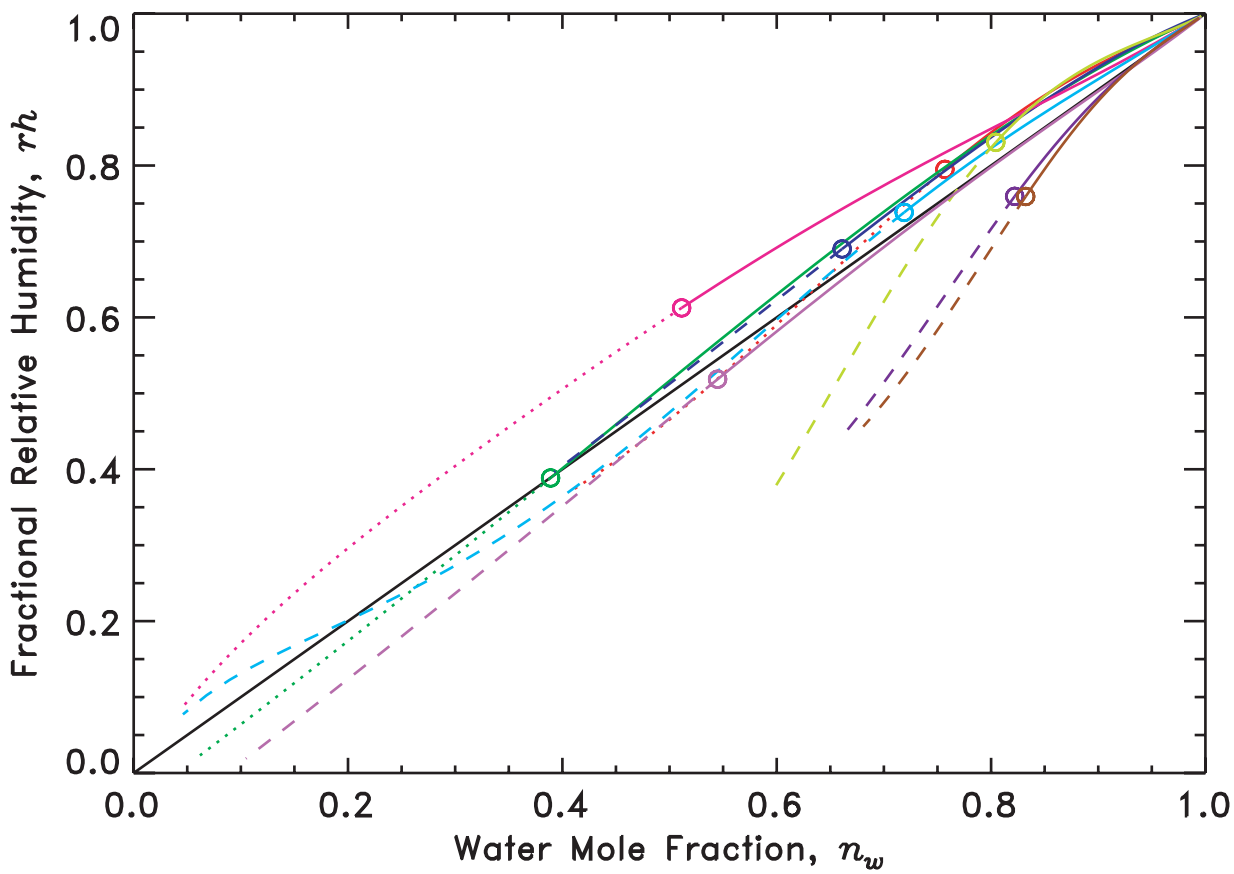
RADIUS RATIO r/r_{dry}



- Varies by more than a factor of 5 up to $rh = 0.99$
- ±3% in radius ratio equivalent to ±0.03 in rh at 0.75, ±0.01 in rh at 0.90

RADIUS RATIO r/r_{dry}

- Raoult assumes $rh \equiv a_{\mathrm{w}} = n_{\mathrm{w}}$ (mole fraction water)



- Raoult assumption fairly accurate, especially for *rh* near 1.0

RADIUS RATIO r/r_{dry}

Exact:

$$\frac{r}{r_{\mathrm{dry}}} = \left(\frac{\rho_{\mathrm{dry}}}{\rho} \frac{\nu M_{\mathrm{w}}}{M_{\mathrm{s}}} \right)^{1/3} \left[\left(\frac{M_{\mathrm{s}}}{\nu M_{\mathrm{w}}} - 1 \right) + \frac{1}{1 - n_{\mathrm{w}}} \right]^{1/3}$$

Assume

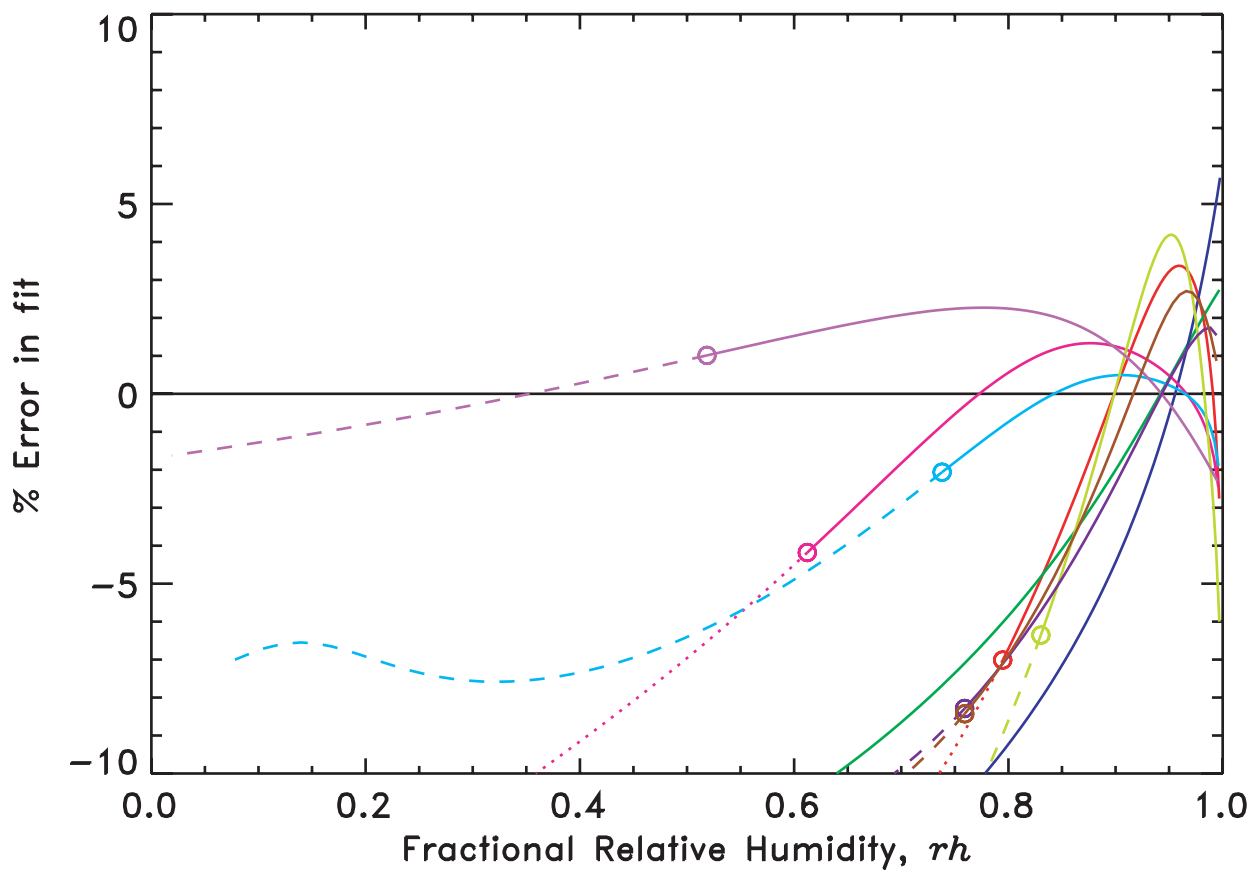
$$\frac{r}{r_{\mathrm{dry}}} = \left(\frac{\rho_{\mathrm{dry}}}{\rho_{\mathrm{w}}} \frac{\nu M_{\mathrm{w}}}{M_{\mathrm{s}}} \right)^{1/3} \left[\cancel{\left(\frac{M_{\mathrm{s}}}{\nu M_{\mathrm{w}}} - 1 \right)} + \frac{1}{1 - rh} \right]^{1/3}$$

Thus,

$$\frac{r}{r_{\mathrm{dry}}} = \left(\frac{\rho_{\mathrm{dry}}}{\rho_{\mathrm{w}}} \frac{\nu M_{\mathrm{w}}}{M_{\mathrm{s}}} \right)^{1/3} \left[\frac{1}{1 - rh} \right]^{1/3} = \frac{c}{(1 - rh)^{1/3}}$$

RADIUS RATIO r/r_{dry} – Fit with p=1/3 (Raoult)

$$\frac{r}{r_{\mathrm{dry}}} \approx \frac{c}{(1-rh)^{1/3}}$$



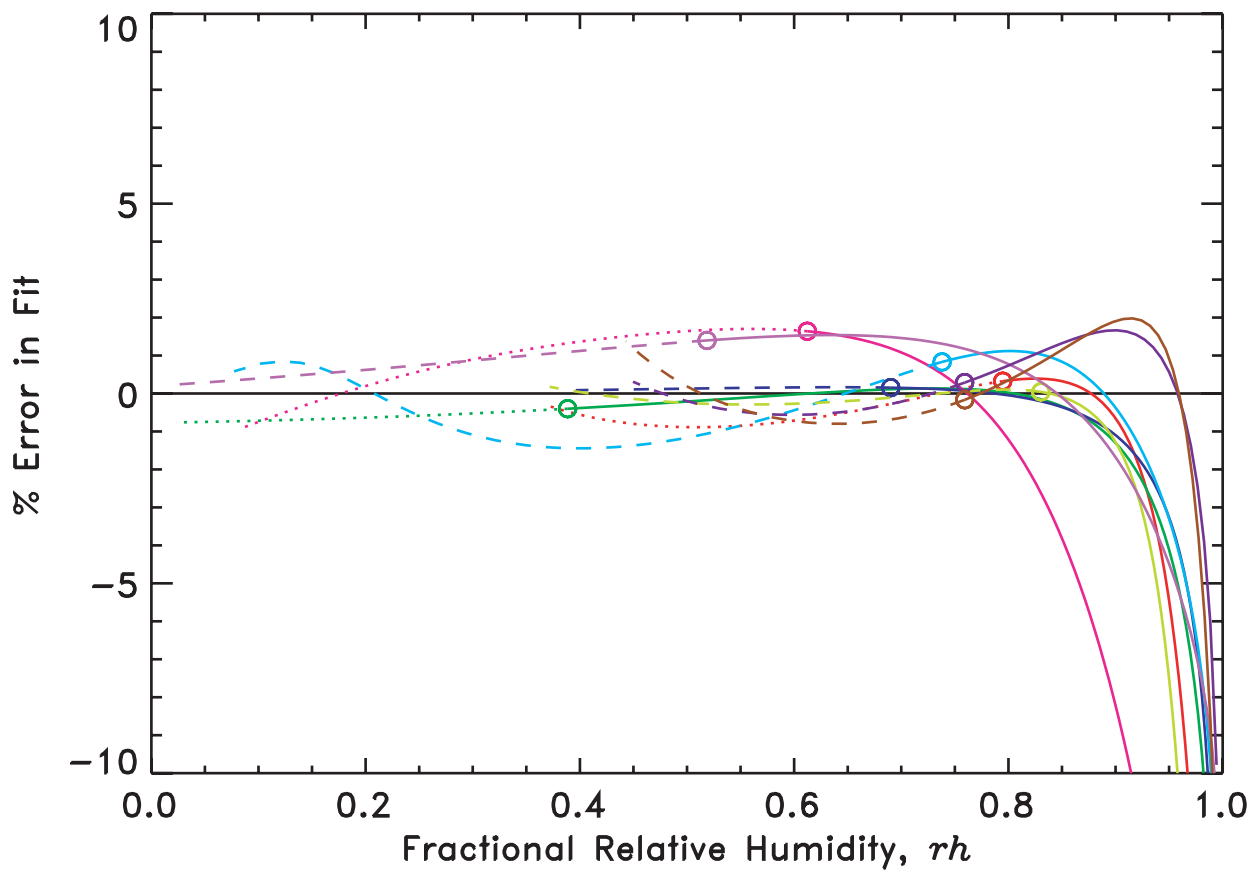
- Accurate to within ~3% for $rh > 0.9$, not so good for $rh < 0.9$
- Much of the error for $rh > 0.9$ is due to electrolytic (Debye) effects

COEFFICIENT c for $\dfrac{r}{r_{\mathrm{dry}}} \approx \dfrac{c}{(1-rh)^{1/3}}$

Substance	c	$\left(\dfrac{\rho_{\mathrm{dry}}}{\rho_{\mathrm{w}}}\dfrac{\nu M_{\mathrm{w}}}{M_{\mathrm{s}}}\right)^{1/3}$
Ammonium sulfate	**0.81**	0.90
Ammonium bisulfate	**0.84**	0.94
Letovicite	**0.81**	0.93
Ammonium nitrate	**0.87**	0.92
Sodium nitrate	**0.94**	0.99
Sodium sulfate	**0.88**	1.01
Sodium bisulfate	**1.04**	1.03
Sodium chloride	**1.09**	1.10
Sea salt	**1.09**	1.08

RADIUS RATIO r/r_{dry} — Fit with variable p

$$\frac{r}{r_{\mathrm{dry}}} \approx \frac{c}{(1-rh)^p}$$



- Accurate to within 2% for most substances for $rh < 0.9$

COEFFICIENTS c, p for $\frac{r}{r_{\mathrm{dry}}} \approx \frac{c}{(1-rh)^p}$

Substance	c	p
Ammonium sulfate	**1.05**	**0.22**
Ammonium bisulfate	**1.01**	**0.26**
Letovicite	**1.03**	**0.24**
Ammonium nitrate	**1.03**	**0.22**
Sodium nitrate	**1.02**	**0.29**
Sodium sulfate	**1.23**	**0.18**
Sodium bisulfate	**1.06**	**0.31**
Sodium chloride	**1.29**	**0.28**
Sea salt	**1.30**	**0.27**

RADIUS RATIO r/r_{dry}

Exact:

$$\frac{r}{r_{\mathrm{dry}}} = \left(\frac{\rho_{\mathrm{dry}}}{\rho} \frac{\nu M_{\mathrm{w}}}{M_{\mathrm{s}}} \right)^{1/3} \left[\left(\frac{M_{\mathrm{s}}}{\nu M_{\mathrm{w}}} - 1 \right) + \frac{1}{1 - n_{\mathrm{w}}} \right]^{1/3}$$

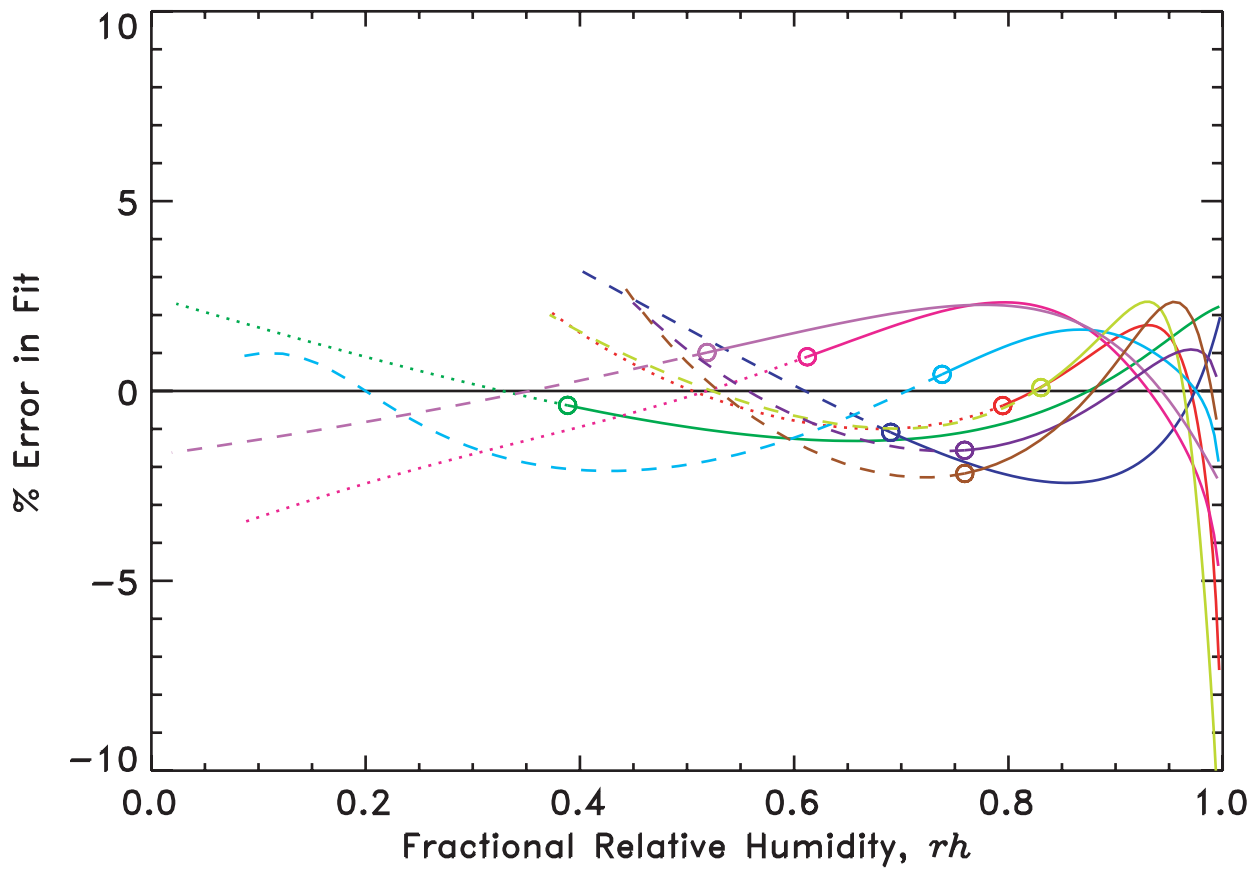
Try

$$\frac{r}{r_{\mathrm{dry}}} = c \left[b + \frac{1}{1 - rh} \right]^{1/3}$$

$$c = \left(\frac{\rho_{\mathrm{dry}}}{\rho_{\mathrm{w}}} \frac{\nu M_{\mathrm{w}}}{M_{\mathrm{s}}} \right)^{1/3} \qquad b = \left(\frac{M_{\mathrm{s}}}{\nu M_{\mathrm{w}}} - 1 \right)$$

RADIUS RATIO r/r_{dry} — General Fit

$$\frac{r}{r_{\mathrm{dry}}} \approx c\left(b + \frac{1}{1-rh}\right)^{1/3}$$

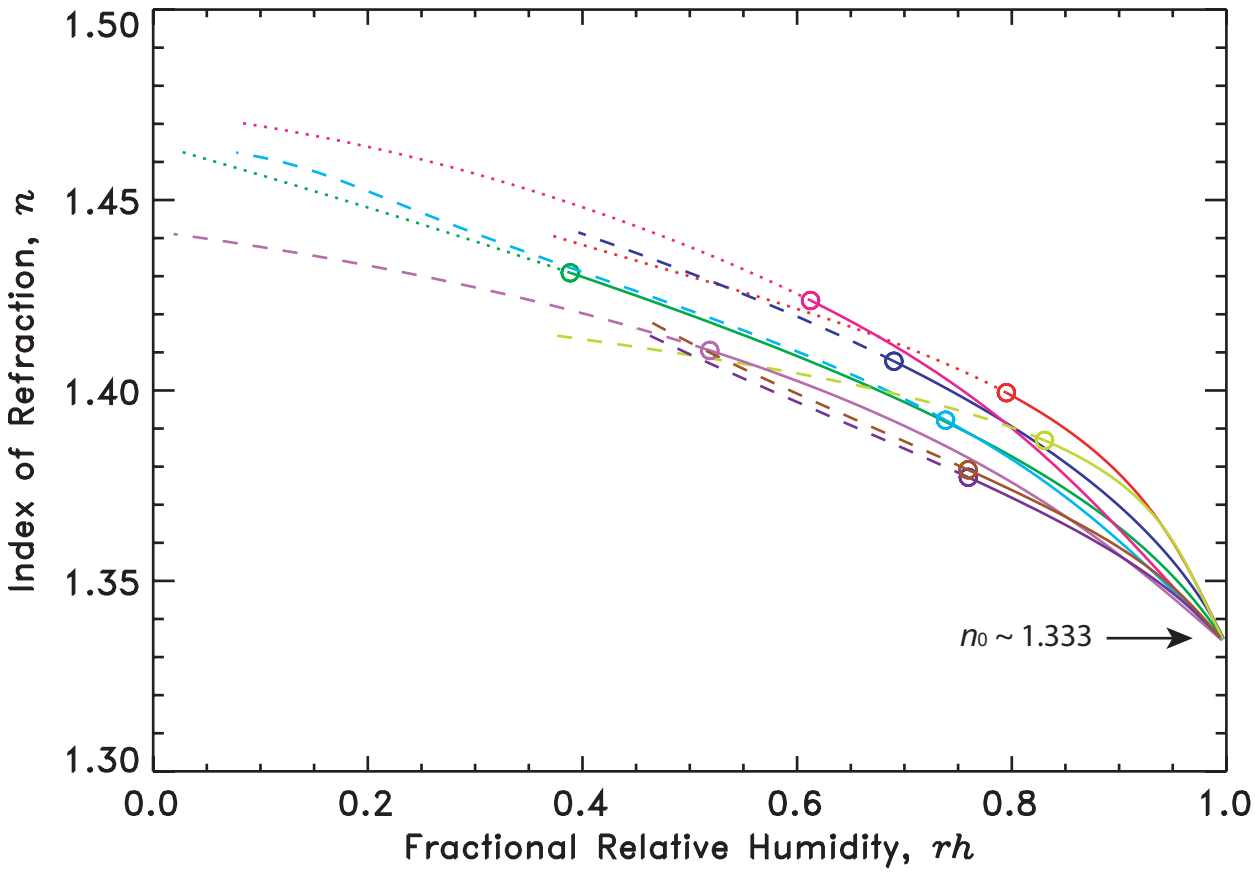


- Accurate to within ~3% over entire range of $rh < 1$
- Physically based

COEFFICIENTS c for $\dfrac{r}{r_{\mathrm{dry}}} \approx c\left(b + \dfrac{1}{1-rh}\right)^{1/3}$

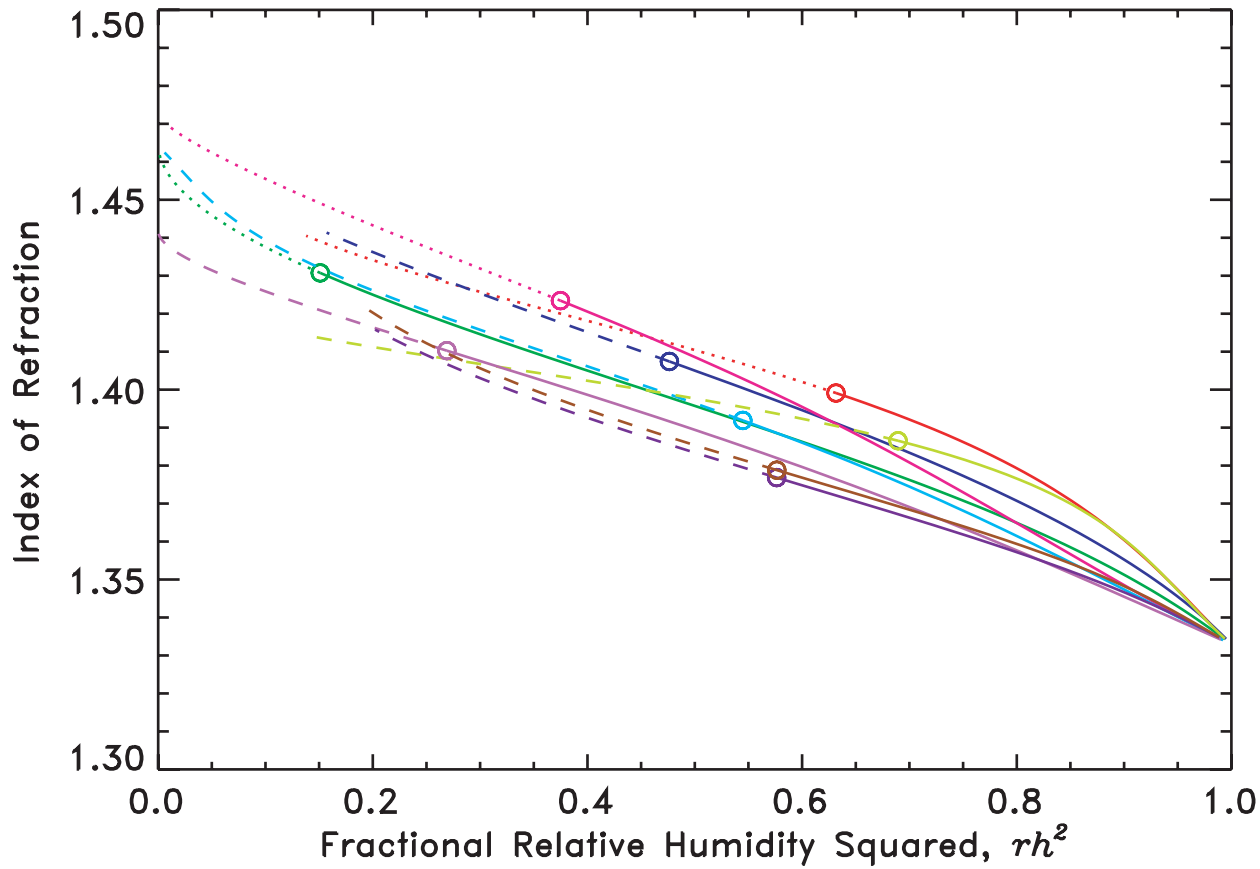
Substance	c	$\left(\dfrac{\rho_{\mathrm{dry}}}{\rho_{\mathrm{w}}}\dfrac{\nu M_{\mathrm{w}}}{M_{\mathrm{s}}}\right)^{1/3}$	b	$\left(\dfrac{M_{\mathrm{s}}}{\nu M_{\mathrm{w}}}-1\right)$
Ammonium sulfate	**0.77**	0.90	**2.1**	1.4
Ammonium bisulfate	**0.84**	0.94	**0.95**	1.1
Letovicite	**0.78**	0.93	**2.0**	1.3
Ammonium nitrate	**0.85**	0.92	**0.65**	1.2
Sodium nitrate	**0.94**	0.99	**0.3**	1.4
Sodium sulfate	**0.82**	1.01	**3.0**	1.6
Sodium bisulfate	**1.04**	1.03	**0.0**	1.2
Sodium chloride	**1.08**	1.10	**1.2**	0.6
Sea salt	**1.07**	1.08	**1.2**	0.7

REFRACTIVE INDEX *n* vs. *rh*



- Not linear
- For given *rh* the spread in *n* is only ±0.02 among substances

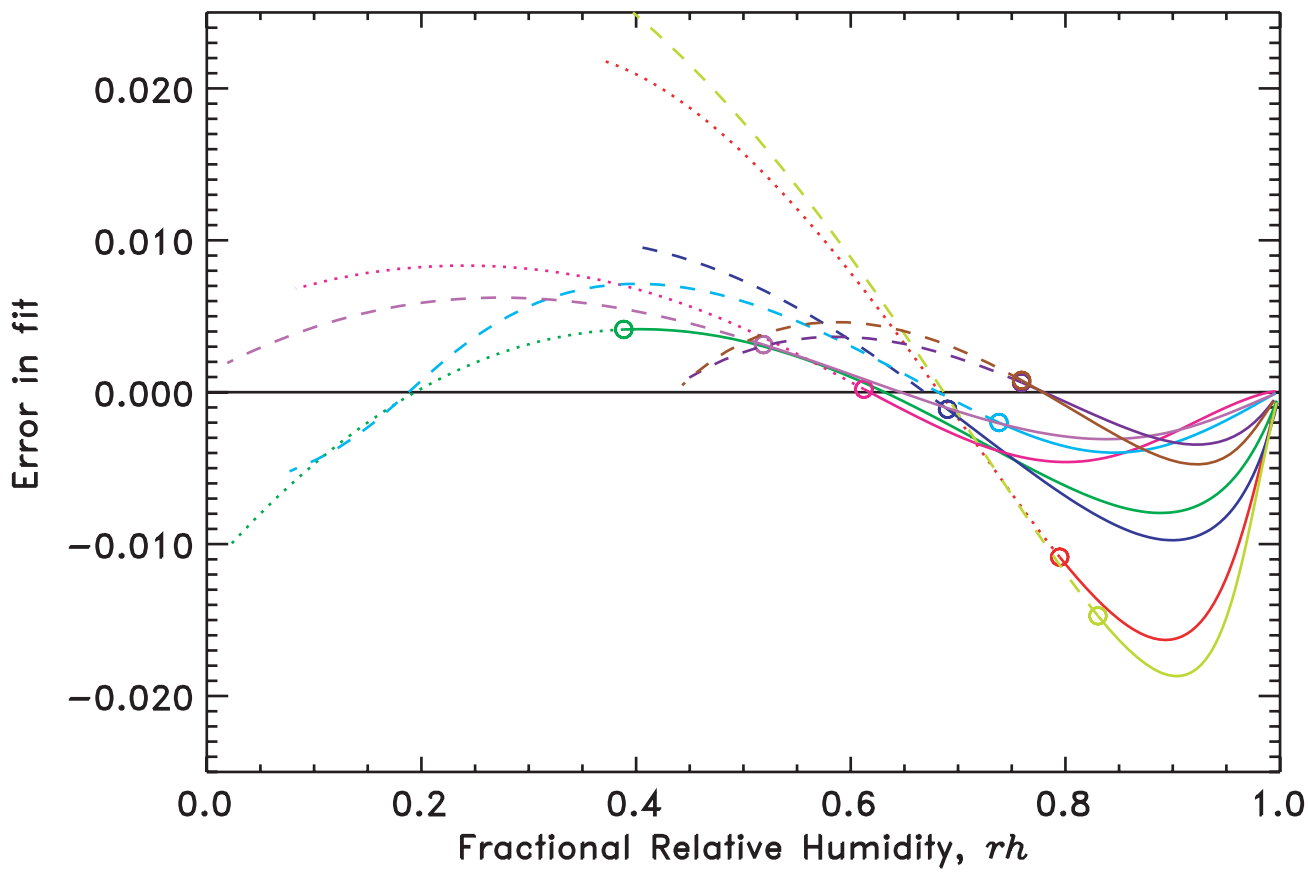
REFRACTIVE INDEX n vs. rh^2



- Nearly linear
- Fit as $n = n_{\mathrm{w}} + c\left(1 - rh^2\right)$ (purely empirical)

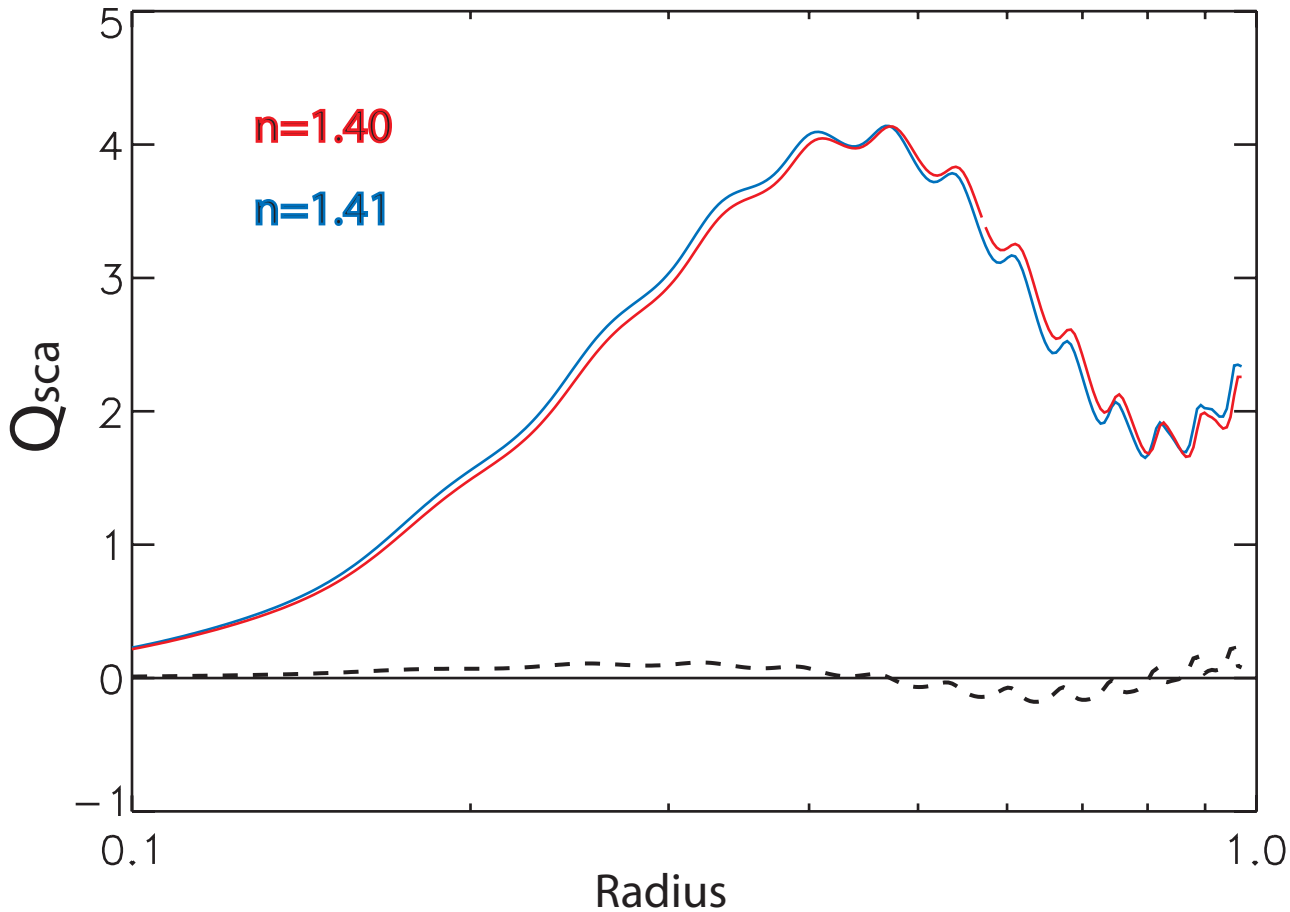
ACCURACY of FIT

$$n = n_{\mathrm{w}} + c\left(1 - rh^2\right)$$



- Single-parameter fit $n = n_{\mathrm{w}} + c\left(1 - rh^2\right)$ accurate to ~0.01

CHANGE in Q_{sca} for $\Delta n = 0.01$



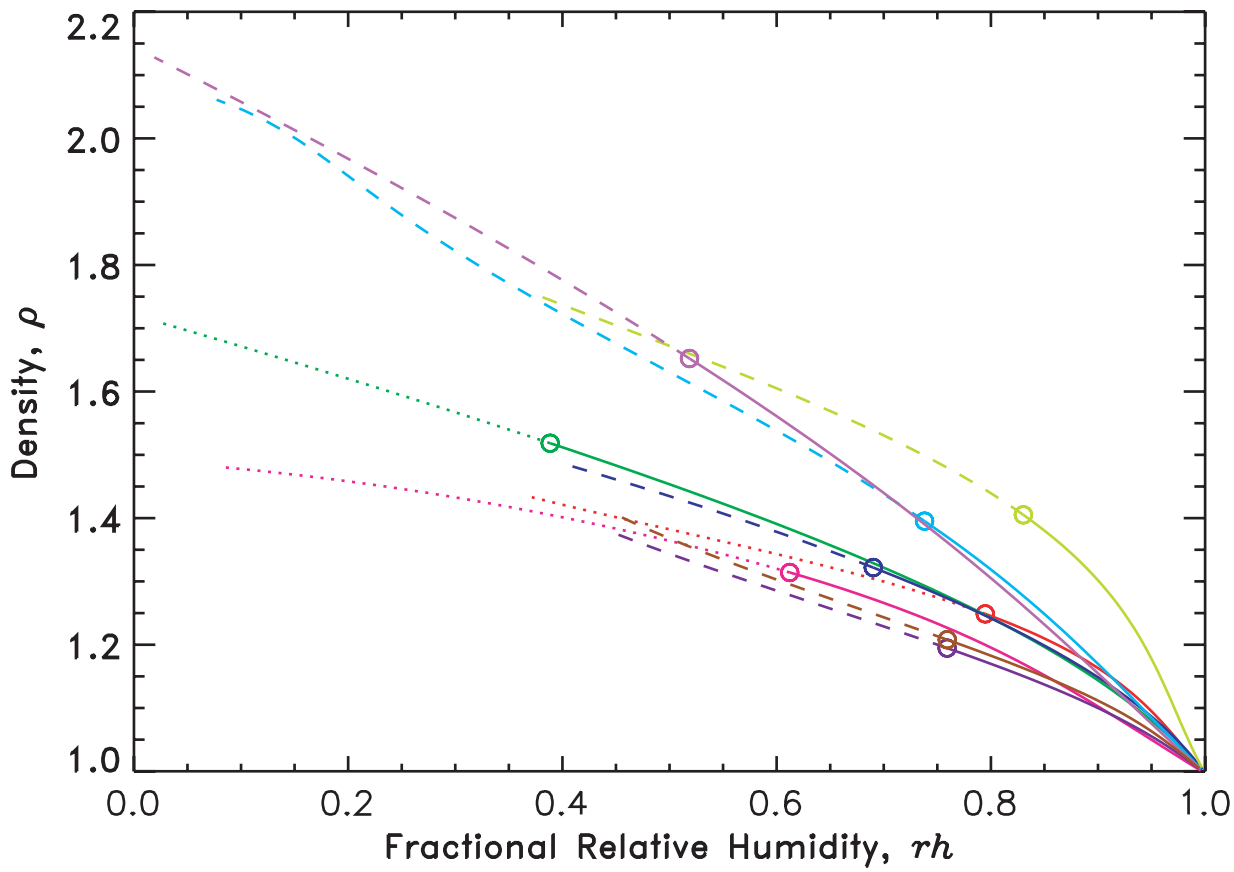
$\Delta n = 0.01$ at $n = 1.40 \Rightarrow \Delta r = 2\text{-}3\%$

COEFFICIENTS c for $n = n_{\mathrm{w}} + c\left(1 - rh^2\right)$

Substance	c
Ammonium sulfate	0.150
Ammonium bisulfate	0.120
Letovicite	0.140
Ammonium nitrate	0.145
Sodium nitrate	0.125
Sodium sulfate	0.125
Sodium bisulfate	0.110
Sodium chloride	0.105
Sea salt	0.110

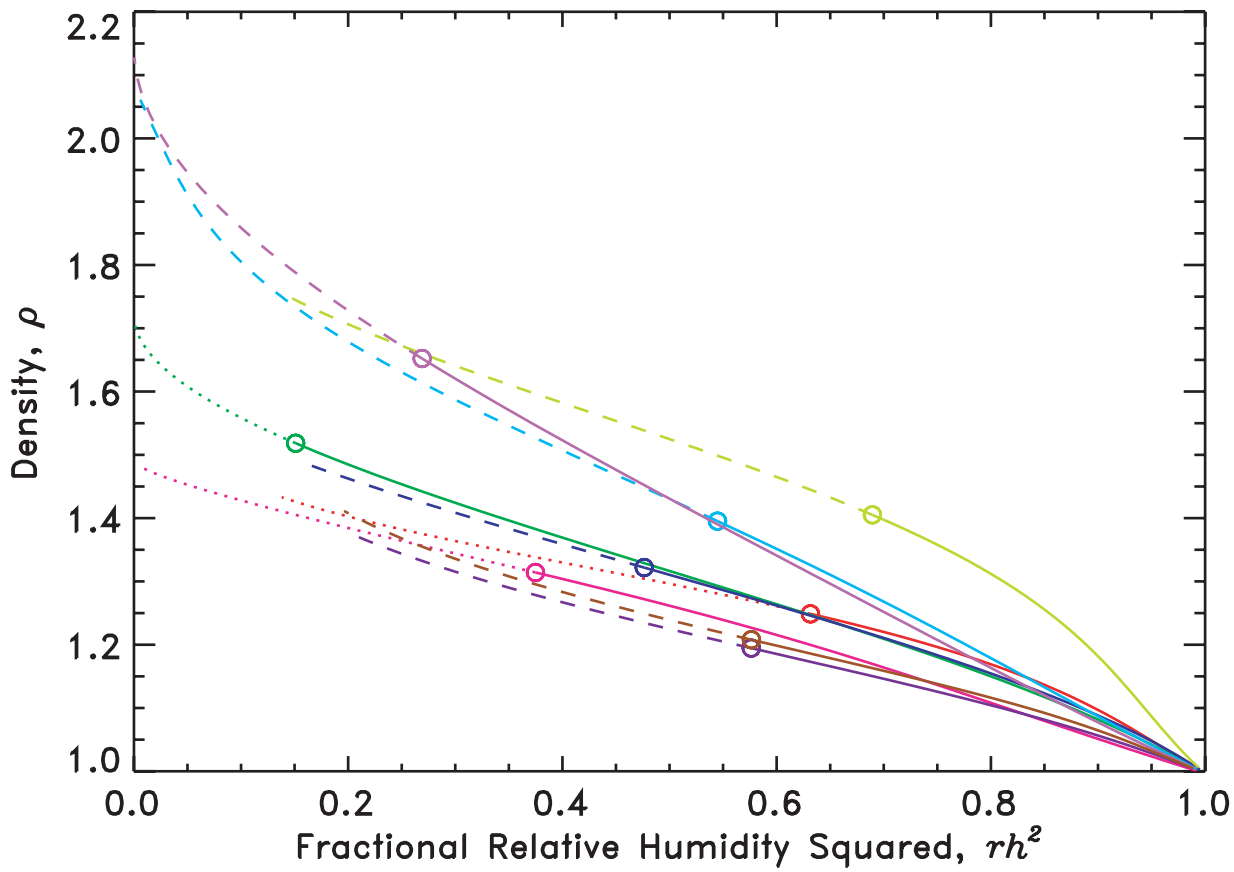
- $n \approx 1.333 + 0.125\left(1 - rh^2\right)$ matches all substances to ~0.02

DENSITY ρ vs. rh



- Not linear

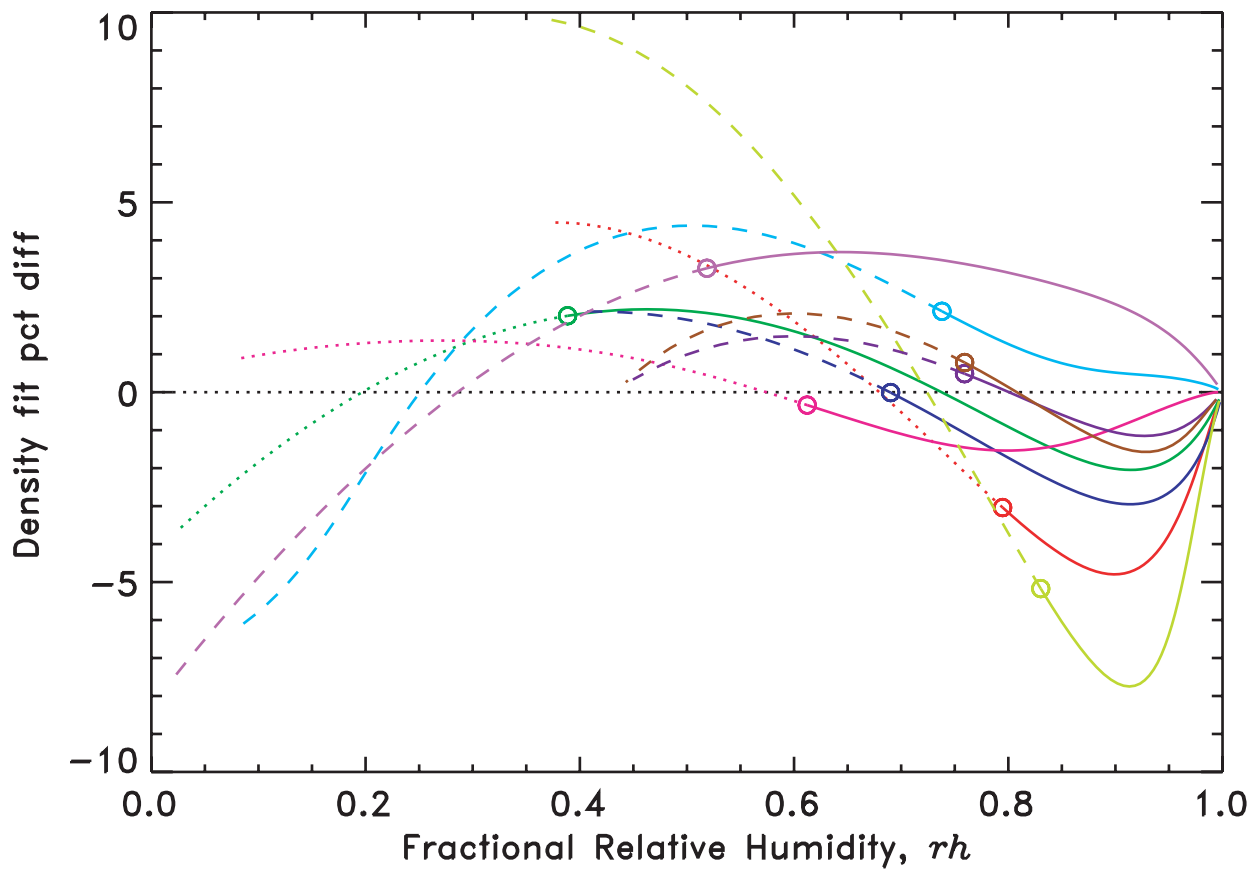
DENSITY ρ vs. rh^2



- Nearly linear
- Fit as $\rho = \rho_{\mathrm{w}} + c\left(1 - rh^2\right)$ (purely empirical)

ACCURACY of FIT

$$\rho = \rho_{\mathrm{w}} + c\left(1 - rh^2\right)$$



- Single-parameter fit $\rho = \rho_{\mathrm{w}} + c\left(1 - rh^2\right)$ accurate to ~5% (except Na_2SO_4)

COEFFICIENT c for $\rho = \rho_{\mathrm{w}} + c\left(1 - rh^2\right)$

Substance	c
Ammonium sulfate	**0.58**
Ammonium bisulfate	**0.65**
Letovicite	**0.62**
Ammonium nitrate	**0.50**
Sodium nitrate	**0.94**
Sodium sulfate	**1.08**
Sodium bisulfate	**0.97**
Sodium chloride	**0.48**
Sea salt	**0.52**

SUMMARY

Simple expressions have been determined for **radius *r***, **index of refraction *n***, and **density ρ**, of aerosol particles of different solutes in terms of **relative humidity *rh*** that are accurate over the entire range of *rh*.

$$\frac{r}{r_{\mathrm{dry}}} = c\left(b + \frac{1}{1-rh}\right)^{1/3}$$, c = 0.8-1.1, b = 0.0-3.0 (accuracy ~2-3%)

$$n = n_{\mathrm{w}} + c\left(1 - rh^2\right)$$, c = 0.105-0.150 (accuracy ~0.01)

$$n = 1.333 + 0.125\left(1 - rh^2\right)$$ (accuracy ~0.02, independent of solute)

$$\rho = \rho_{\mathrm{w}} + c\left(1 - rh^2\right)$$, c = 0.5-1.1 g cm^{-3} (accuracy ~5%)

REFRACTIVE INDEX n

- Molal refractivity R defined by $R = V\left(\dfrac{n^2-1}{n^2+2}\right) \Rightarrow n = \left(\dfrac{2R/V+1}{1-R/V}\right)^{1/2}$

- R assumed additive when weighted by mole fraction y: $R = y_\mathrm{w}R_\mathrm{w} + y_\mathrm{s}R_\mathrm{s}$

- $V = \dfrac{y_\mathrm{w}\mathrm{M}_\mathrm{w} + y_\mathrm{s}\mathrm{M}_\mathrm{s}}{\rho} \Rightarrow \dfrac{R}{V} = \left(\dfrac{n^2-1}{n^2+2}\right) = \rho\,\dfrac{y_\mathrm{w}R_\mathrm{w} + y_\mathrm{s}R_\mathrm{s}}{y_\mathrm{w}\mathrm{M}_\mathrm{w} + y_\mathrm{s}\mathrm{M}_\mathrm{s}}$

- $$n = \left(\frac{2\dfrac{n_\mathrm{w}^2-1}{n_\mathrm{w}^2+2} + \dfrac{\rho_\mathrm{w}}{\rho} + 2y_\mathrm{s}\left(\dfrac{\mathrm{M}_\mathrm{s}}{\mathrm{M}_\mathrm{w}}\dfrac{n_\mathrm{s}^2-1}{n_\mathrm{s}^2+2} - \dfrac{n_\mathrm{w}^2-1}{n_\mathrm{w}^2+2}\right) + y_\mathrm{s}\dfrac{\rho_\mathrm{w}}{\rho}\left(\dfrac{\mathrm{M}_\mathrm{s}}{\mathrm{M}_\mathrm{w}} - 1\right)}{\dfrac{\rho_\mathrm{w}}{\rho} - \dfrac{n_\mathrm{w}^2-1}{n_\mathrm{w}^2+2} + y_\mathrm{s}\dfrac{\rho_\mathrm{w}}{\rho}\left(\dfrac{\mathrm{M}_\mathrm{s}}{\mathrm{M}_\mathrm{w}} - 1\right) - y_\mathrm{s}\left(\dfrac{\mathrm{M}_\mathrm{s}}{\mathrm{M}_\mathrm{w}}\dfrac{n_\mathrm{s}^2-1}{n_\mathrm{s}^2+2} - \dfrac{n_\mathrm{w}^2-1}{n_\mathrm{w}^2+2}\right)}\right)^{1/2}$$

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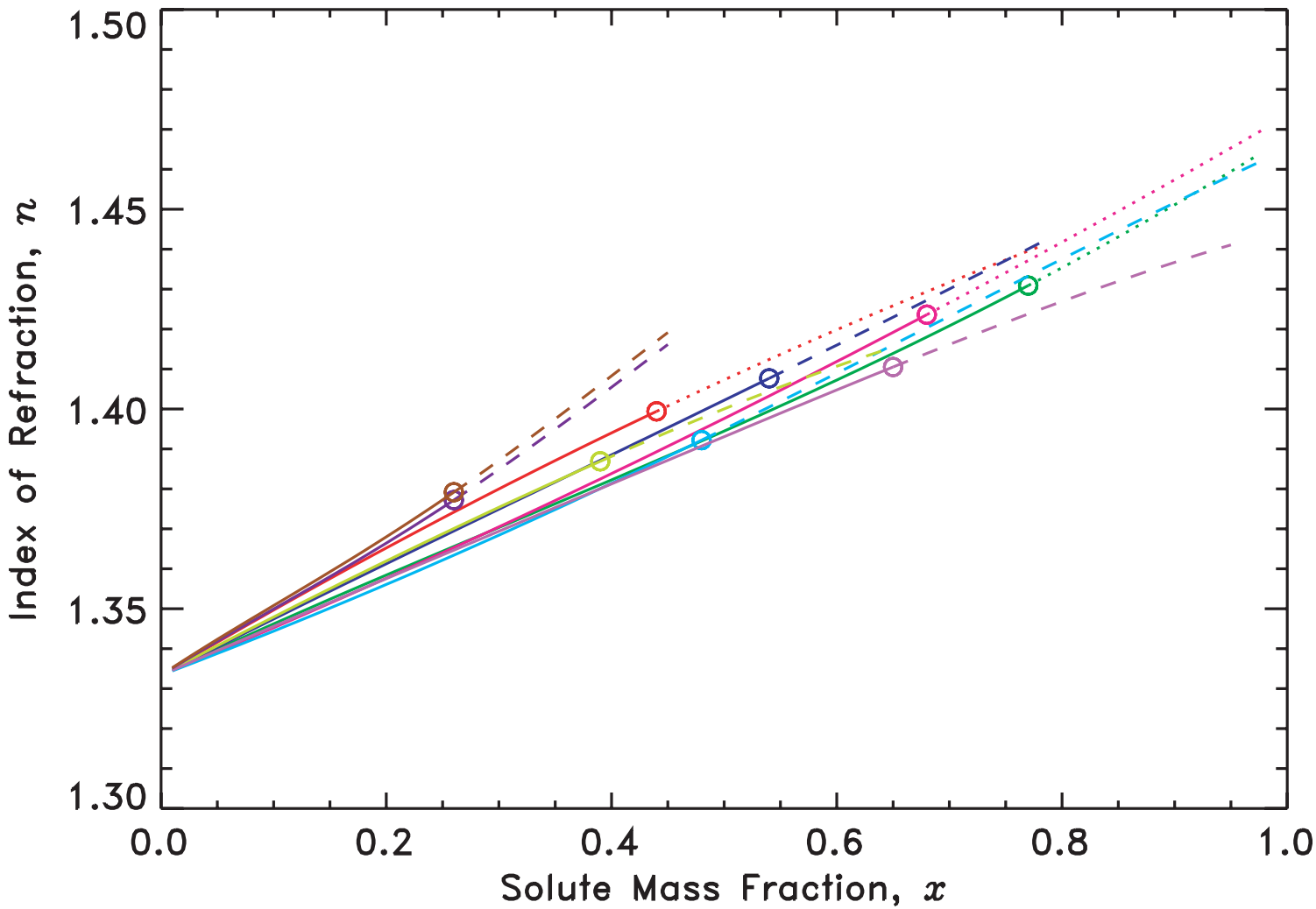
- $$n = \left(\frac{2\dfrac{n_\mathrm{w}^2-1}{n_\mathrm{w}^2+2} + \dfrac{\rho_\mathrm{w}}{\rho} + 2y_\mathrm{s}\left(\dfrac{\mathrm{M}_\mathrm{s}}{\mathrm{M}_\mathrm{w}}\dfrac{n_\mathrm{s}^2-1}{n_\mathrm{s}^2+2} - \dfrac{n_\mathrm{w}^2-1}{n_\mathrm{w}^2+2}\right) + y_\mathrm{s}\dfrac{\rho_\mathrm{w}}{\rho}\left(\dfrac{\mathrm{M}_\mathrm{s}}{\mathrm{M}_\mathrm{w}} - 1\right)}{\dfrac{\rho_\mathrm{w}}{\rho} - \dfrac{n_\mathrm{w}^2-1}{n_\mathrm{w}^2+2} + y_\mathrm{s}\dfrac{\rho_\mathrm{w}}{\rho}\left(\dfrac{\mathrm{M}_\mathrm{s}}{\mathrm{M}_\mathrm{w}} - 1\right) - y_\mathrm{s}\left(\dfrac{\mathrm{M}_\mathrm{s}}{\mathrm{M}_\mathrm{w}}\dfrac{n_\mathrm{s}^2-1}{n_\mathrm{s}^2+2} - \dfrac{n_\mathrm{w}^2-1}{n_\mathrm{w}^2+2}\right)}\right)^{1/2}$$

- To comparable accuracy n is additive when weighted by mass fraction x:

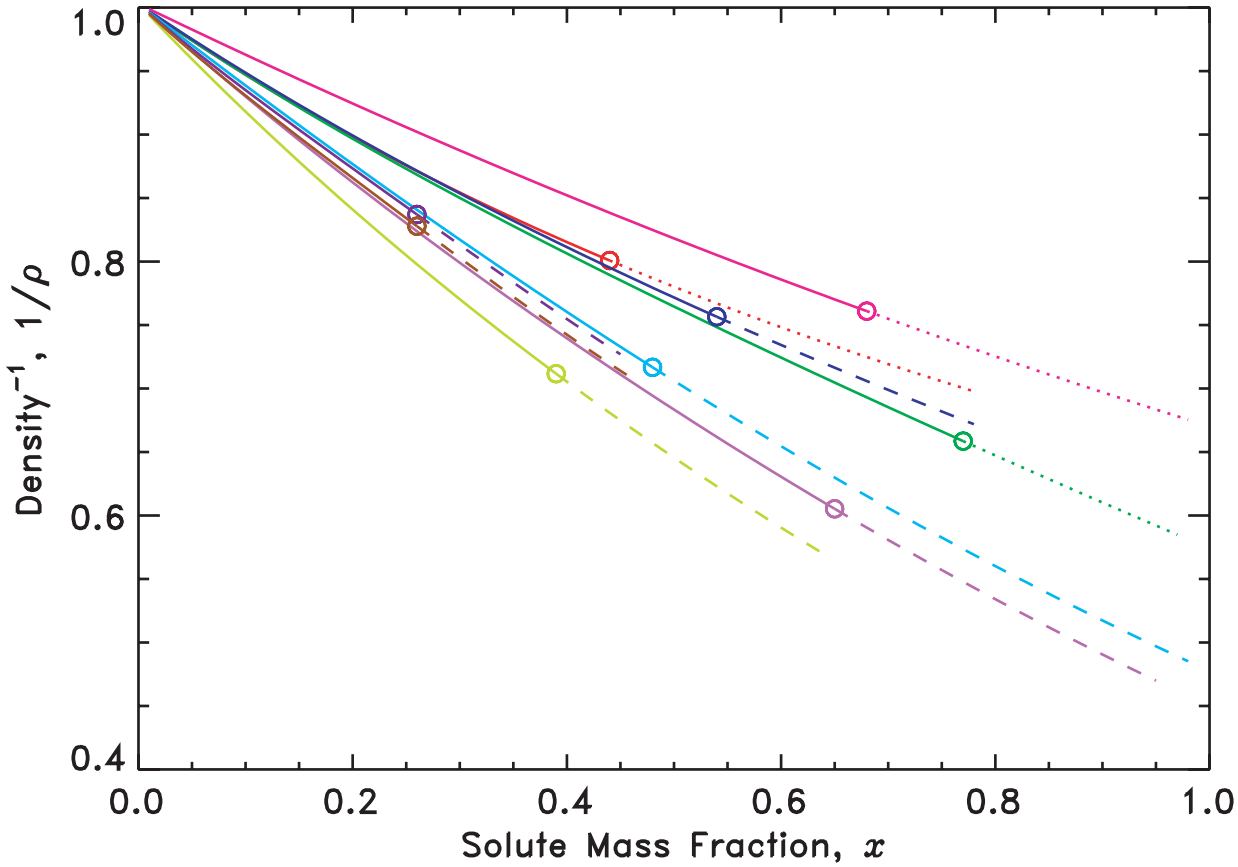
$$n = n_\mathrm{w}(1-x_\mathrm{s}) + n_\mathrm{s}x_\mathrm{s} = n_\mathrm{w} + x_\mathrm{s}\left(n_\mathrm{s} - n_\mathrm{w}\right)$$

REFRACTIVE INDEX n vs. x — Mixing Rule?



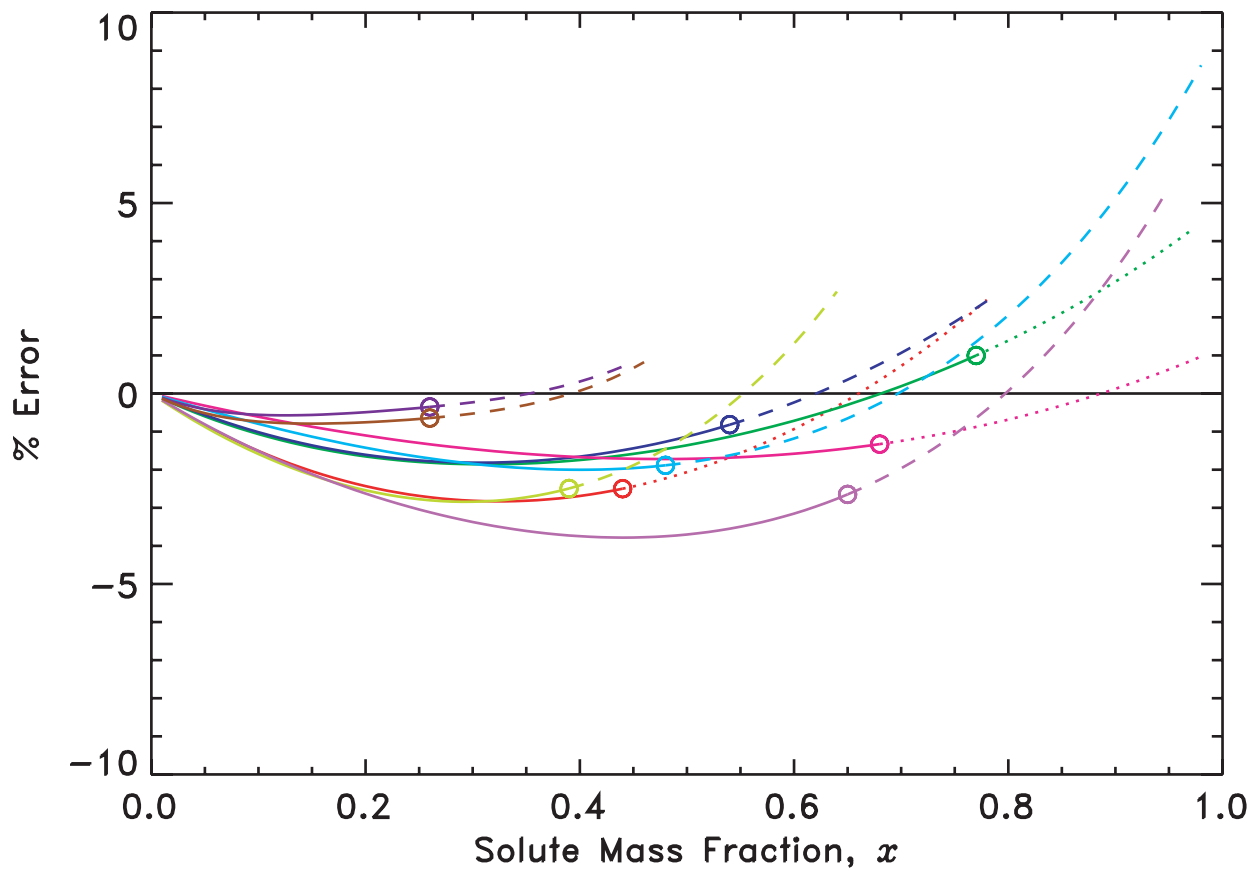
$$n = n_{\mathrm{w}}\left(1-\sum x_{\mathrm{s,i}}\right)+\sum n_{\mathrm{s,i}} x_{\mathrm{s,i}} = n_{\mathrm{w}} + \sum x_{\mathrm{s,i}}\left(n_{\mathrm{s,i}} - n_{\mathrm{w}}\right)$$

INVERSE DENSITY ρ^{-1} vs. x



- Nearly linear

ACCURACY OF LINEAR FIT OF ρ^{-1} vs. x



- Accurate to within 5%

APPARENT MOLAL VOLUME ϕ_V

- <u>Apparent molal volume</u> ϕ_V defined by $\phi_V = \dfrac{M_s}{\rho} + \dfrac{1000(\rho_w - \rho)}{m\rho\rho_w}$

- Equivalently, $$\phi_V = \frac{M_s}{\rho_w} + \frac{M_s(\rho_w - \rho)}{x\rho\rho_w}$$

- Or, $$\frac{1}{\rho} = \left(\frac{1}{\rho_w}\right) - x\left(\frac{1}{\rho_w} - \frac{\phi_V}{M_s}\right)$$

- Thus, linearity of $(1/\rho)$ vs. x implies constant ϕ_V

- In terms of density, $$\rho = \frac{\rho_w}{1 - x\left(1 - \rho_w \dfrac{\phi_V}{M_s}\right)}$$

- Ideal situation: $\phi_V = \dfrac{M_s}{\rho_s}$

APPARENT MOLAL VOLUME ϕ_V

Units: $cm^3\ mol^{-1}$

Substance	ϕ_V	M_s/ρ_s
Ammonium sulfate	**78**	75
Ammonium bisulfate	**63**	65
Letovicite	**138**	135
Ammonium nitrate	**53**	46
Sodium nitrate	**37**	38
Sodium sulfate	**43**	53
Sodium bisulfate	**50**	49
Sodium chloride	**22**	27
Sea salt	**22**	29

MIXING RULE for DENSITY

- Single solute:

$$\rho = \frac{\rho_{\mathrm{w}}}{1 - x\left(1 - \rho_{\mathrm{w}} \frac{\phi_{\mathrm{V}}}{M_{\mathrm{s}}}\right)}$$

- Mixture:

$$\rho = \frac{\rho_{\mathrm{w}}}{1 - \sum x_{\mathrm{i}} + \rho_{\mathrm{w}} \sum\left(x_{\mathrm{i}} \frac{\phi_{\mathrm{V,i}}}{M_{\mathrm{s,i}}}\right)} = \frac{\rho_{\mathrm{w}}}{1 - \sum\left[x_{\mathrm{i}}\left(1 - \rho_{\mathrm{w}} \frac{\phi_{\mathrm{V,i}}}{M_{\mathrm{s,i}}}\right)\right]}$$