Short wave radiative impact of liquid-liquid phase separation in "Brown Carbon" aerosols

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Abstract. Atmospheric aerosol particles may undergo liquid-liquid phase separation (LLPS) when exposed to varying relative humidity. In this study, we model how the change in morphology affects the short wave radiative forcing, in particular for particles containing organic carbon as a molecular absorber, often termed "brown carbon" (BrC). Preferentially, such an absorber will redistribute to the organic phase after LLPS. We limited our investigation to particle diameters between 0.04 – 0.5 μm, atmospherically relevant organic-to-inorganic mass ratios typical for aged aerosol (1:4 < OIR < 4:1), and absorptivities ranging from zero (purely scattering) to highly absorbing brown carbon. For atmospherically relevant O:C ratios, core-shell morphology is expected for phase-separated particles. We compute the scattering and absorption cross-sections for realistic eccentric core-shell morphologies. For the size range of interest here, we show that assuming the core-shell morphology to be concentric is sufficiently accurate and numerically much more efficient than averaging over eccentric morphologies. In the UV-region, where BrC absorbs strongest, phase-separated particles may exhibit a scattering cross-section up to 50 % larger than those of homogenously mixed particles, while their absorption cross-section is up to 20 % smaller. Integrating over the full solar spectrum, due to the strong wavelength dependence of BrC absorptivity, limits the short wave radiative impact of LLPS. For particles with very substantial BrC absorption there will be a radiative forcing enhancement of 4 %-11.8 % depending on the Ångström exponent of BrC absorptivity. However, for those of moderate absorptivity, LLPS will have no significant short-wave radiative impact.

1 Introduction

Among many other impacts, atmospheric aerosols influence the radiation budget of the Earth directly through scattering and absorption (and less importantly emission) of incoming shortwave solar and outgoing infrared radiation. Aerosols can also affect climate indirectly through their interaction with clouds. Depending on their optical properties, aerosols contribute mostly to the cooling of our planet (IPCC, 2013) but when they are highly absorptive (e.g., soot) may also contribute to warming (e.g. Ramanathan et al., 2001). Anthropogenic aerosols are dominated by sulfate, organic carbon, black carbon (soot), nitrate and dust. According to the fifth Intergovernmental Panel on Climate Change report (IPCC, 2013), anthropogenic aerosols produce a net cooling effect, where radiative forcing due to aerosol–radiation interactions is assessed

to be –0.35 (–0.85 to +0.15) Wm^{-2}. Despite dedicated research efforts, aerosols remain one of the main sources of uncertainty for climate prediction.

Although organic aerosol particles are mainly characterized as only scattering as they are largely transparent in the visible region of the solar spectrum, a significant fraction of carbonaceous aerosols absorb solar and terrestrial radiation. Black

5 carbon (BC) is by far the most well known absorbing component of the atmospheric aerosols, which strongly absorbs light over a broad wavelength range from UV to IR. It has only been in recent years that a new class of organic matter was identified, which exhibit significant though weaker absorptive properties compared to BC. This absorbing fraction of organic matter is referred to as Brown Carbon (BrC) (Pöschl, 2005; Andreae and Gelencser, 2006; Ramanathan et al., 2007; Laskin et al., 2015). In contrast to BC, the absorptivity of BrC has a very strong wavelength dependence with high absorption in the

10 near-UV region, but absorption decreasing rapidly towards longer wavelengths (Andreae and Gelencser, 2006; Bond and Bergstrom, 2006; Ramanathan et al., 2007; Feng et al., 2013; Laskin et al., 2015). Several studies have suggested that at shorter wavelength, BrC can significantly contribute to the total aerosol absorption or even dominate it in certain geographic regions (Yang et al., 2009; Bond et al., 2011; Zhang et al., 2011; Chung et al., 2012; Feng et al., 2013; Laskin et al., 2015). Despite recent interest and extensive research regarding the impact of BrC on radiative forcing (e.g., Arnott et al., 2003;

15 Ramanathan et al., 2007; Alexander et al., 2008; Feng et al., 2013; Lack and Cappa, 2010; Lang-Yona et al., 2010; Lack et al., 2012; Ma and Thompson, 2012; Nakayama et al., 2010; Langridge et al., 2013; Saleh et al., 2013; Laskin et al., 2015; Tang et al., 2016), the magnitude of BrC absorption as well as its wavelength dependence is not yet well-established and its assignment to different sources and its oxidation lifetime is far from being fully characterized.

In addition to the limited knowledge associated with the optical properties of organic carbon, our current understanding with

20 respect to aerosol compositions, physical state, and morphology is insufficient to accurately quantify the direct radiative effect of such aerosols. In particular, particle phase and morphology need to be investigated, since they influence the scattering and absorption of radiation (e.g., Baumgardner and Clarke, 1998; Martin et al., 2004; Lewis et al., 2009; Lack and Cappa, 2010). Experiments and modelling studies have shown that as ambient relative humidity (RH) decreases, deliquesced aerosols can exist not only as a one-phase system containing organics, inorganic salts and water in a homogeneous mixture,

25 but often as two-phase systems, where one aqueous phase is dominated by the organic material while the other aqueous phase is predominantly inorganic, e.g. containing inorganic salts (Pankow, 2003; Marcolli and Krieger, 2006; Ciobanu et al., 2009 and 2010; Bertram et al., 2011; Krieger et al., 2012). This phenomenon is referred to as liquid-liquid phase separation (LLPS). The relative humidity (SRH) at which the transition from well mixed to liquid-liquid phase separated occurs depends on the O:C ratio of the organic as well as on the nature of the inorganic salts but typically occurs in a range between

30 70 % RH and 95 % RH (Song et al., 2012, You et al. 2012). In recent years, laboratory studies using model mixtures to represent tropospheric aerosols (Ciobanu et al., 2009; Bertram et al., 2011; Song et al., 2012a, Song et al., 2012b), or secondary organic aerosol (SOA) produced from smog chamber experiments (Smith et al., 2012) and filter samples collected

during field measurement campaigns (You et al., 2012) imply that liquid-liquid phase separation (LLPS) is a common feature in mixed organic/inorganic particles. When two aqueous phases coexist in a particle, they may form different morphologies, such as core-shell or partially engulfed, depending on which configuration yields the lowest total surface free energy (Kwamena et al. 2010, Qiu and Molinero, 2015). According to Song et al. (2012b) and (2013), for aged aerosols with

5 moderate to high oxygen-to-carbon (O:C) ratio, core-shell is the dominated morphology. For further information, see the Faraday Discussion on this very topic (Faraday Discuss. 2013, 165). Besides consequences for hygroscopicity (Hodas et al., 2015), a core-shell configuration alters the optical properties of the particles in particular for organic phases containing absorbing molecules, such as BrC since the absorbing BrC material will always reside in the organic shell.

Brown Carbon is referring to the light-absorbing fraction of the organic carbon that has a wavelength dependent absorptivity.

10 Emission sources of BrC are not very well characterized. The primary emissions are mainly linked to biomass burning, smoldering combustion and biogenic emissions from humic matter, plant debris and other bio-aerosols (Andreae and Gelencser, 2006; Alexander et al., 2008; Chakrabarty et al., 2010; Kirchstetter and Thatcher, 2012). Field measurements have also associated BrC to secondary organic aerosol (SOA) that form by gas to particle partitioning of semi-volatile organic compounds presenting in the biomass burning smoke (Hecobian et al., 2010; Saleh et al., 2013). As SOA ages

15 through oxidation processes, it may become significantly more absorbing in the near-UV region of the solar spectrum (Bones et al., 2010; Updyke et al., 2012; Laskin et al., 2015), implying that heterogeneous chemistry producing BrC in the condensed phase.

Despite the fact that the presence of LLPS has been observed and studied by a number of research groups, its impact on the radiative properties of mixed aerosol particles with molecular absorbers has so far not been quantified. In previous optical

20 modeling studies, mostly focusing on the optical properties of particles containing soot inclusions, typically volume mixing approximations for the optical properties were employed or the morphology were assumed to be that of a spherical symmetric, concentric core-shell. In this paper, we apply a Mie-code developed for calculating the scattering properties of a non-symmetric cluster of spheres (Mackowski, 2013, http://eng.auburn.edu/users/dmckwski/scatcodes/) to calculate the ratio in optical efficiencies between homogeneous and phase-separated particles. We vary size, absorptivity of BrC, organic to

25 inorganic ratio over ranges typical for aged atmospheric aerosol in the accumulation mode and show first, that the average optical efficiencies of an ensemble of phase separated particles with a random eccentric inclusion are well represented by those calculated for a simple concentric core shell particle. Second, we take advantage of this finding and calculate the radiative forcing caused by phase separated aerosol particles relative to homogenously mixed once in a thin aerosol layer approximation (Nemesure and Schwartz, 1998).

30

2 Eccentric versus concentric core shell morphology

We first want to discuss the difference in scattering and absorption accounting for differences in morphology for liquid-liquid phase separated particles. In particular, we investigate the difference between a symmetric core shell morphology compared to one with an eccentric inclusion. To represent typical aged atmospheric aerosol containing BrC we choose the

5 inorganic salt to be ammonium sulfate, representing the most abundant inorganic salt in continental aerosols, and light-absorbing organic carbon material representing BrC. We choose to study three organics to inorganic ratios (OIR), 1:4, 1:1, and 4:1, from inorganic rich to organic rich, which cover the typical range observed with aerosol mass spectrometry (AMS) (Zhnag et al., 2007).

To account for the absorptivity of BrC values the imaginary part of the refractive index (k) for BrC are taken from various

10 studies (Kirchstetter et al., 2004; Chen and Bond, 2010; Feng et al., 2013) that measured k for different SOA at different locations, spanning a wide range from non-absorbing organic material ($k = 0$) to highly absorbing organic matter ($k = 0.168$ at 355 nm). The real part of the refractive index (n) for BrC at dry condition is taken as 1.65 (Hoffer et al., 2006). We use simple volume mixing to calculate the real part of BrC at 70 % RH, the size of the core relative to the shell for the different OIRs (see Fig. 1) as well as to calculate the refractive indices for the phase-separated particles (see Tables A1 and A2 in

15 Appendix A).

For about 20 years numerical calculations for scattering and absorption of a host sphere containing a non-concentrically positioned smaller sphere have been computationally feasible. In particular, the T-matrix approach of Mackowski and Mishchenko (1996) and (2011) solves the problem of obtaining random-orientation properties of clusters of spheres in a

20 numerically efficient manner. In our context, it has been applied in recent years for computing scattering and absorption of morphologically complex soot containing aerosol (e.g., Mishchenko et al., 2013, Cheng et al., 2014). Here, we use the Multiple Sphere T Matrix (MSTM) version 3.0 (Mackowski, 2013, http://eng.auburn.edu/users/dmckwski/scatcodes/) to compute fixed and random oriented scattering and absorption cross sections as well as the asymmetry parameter for eccentric core shell liquid-liquid phase separated aerosol with a molecular absorber in the organic phase.

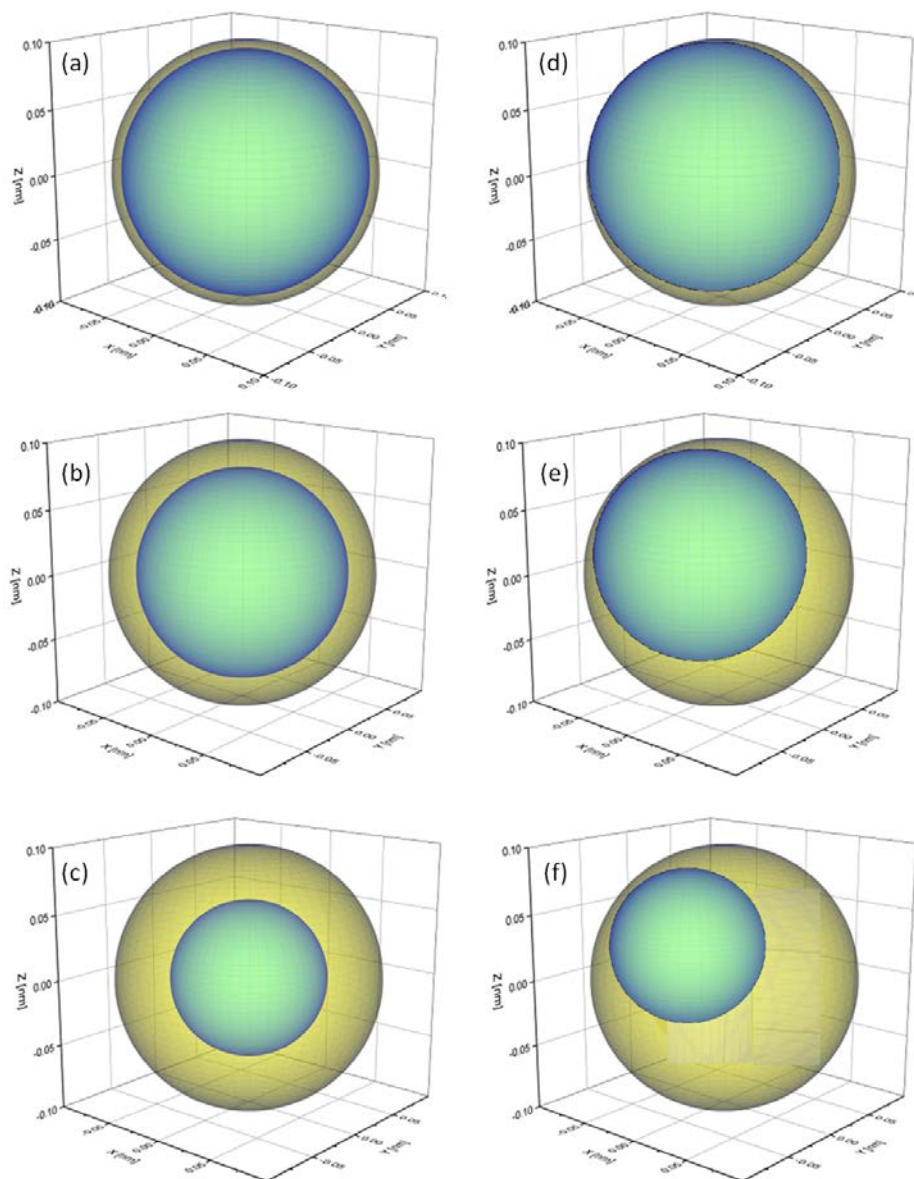



Figure 1: Schematic of a phase separated particle with a 75 nm radius to illustrate the thickness of the organic shell at (a): OIR = 1:4, (b): OIR = 1:1, and (c) OIR = 4:1 for concentric core-shell morphologies. (d) - (f) same for a single realization of an eccentric core-shell morphology. The calculations in this work use typically 500 such realizations, randomly oriented (with different distances of the inclusion from the center of the particles and different azimuth and polar angles) .The direction of incoming light is along the z-axis.

The computational costs of calculating cross sections increase substantially, when going from highly symmetric core shell morphology, to a given eccentric core position relative to the incident light, and even more when random orientational

averaging with random positioning of the core within the shell volume is required. Hence, we investigated systematically how the orientational averaged cross-sections for the eccentric morphologies differ from the cross section for the concentric morphology. We performed this comparison for particles with properties ranging within the limits of OIR, size and absorptivity discussed above.

First, we used the MSTM code with random positioning of the center of the inorganic core within the organic shell to check how many realizations of fixed positions are needed for convergence of the mean cross sections. Figure 2a shows the distribution of scattering efficiency (Q_{scat}) for a particular choice of particle parameters comparing 10000 (locations) realizations (red columns, which refer to the Q_{scat} of individual particles with their core located at random positions within

10 the volume of the shell) with 500 realizations (green columns).

Scattering efficiency (Q_{scat}) is expressed as the ratio of the scattering cross-section, σ_{scat} to the geometrical cross-section of the particle, $\sigma_{geometric}$:

$$Q_{scat} = \frac{\sigma_{scat}}{\sigma_{geometric}},$$

for spherical particles with radius r, $\sigma_{geometric} = \pi r^2$.

15 As illustrated in Fig. 2b the mean of the scattering efficiencies converges rapidly with the number of the realizations used to calculate this mean. The same holds true for absorption efficiencies. Conservatively, in the following we use 500 different positions of the inclusion within the particle to determine the averaged Q_{scat} and Q_{abs} for the particles with eccentric core-shell morphology.

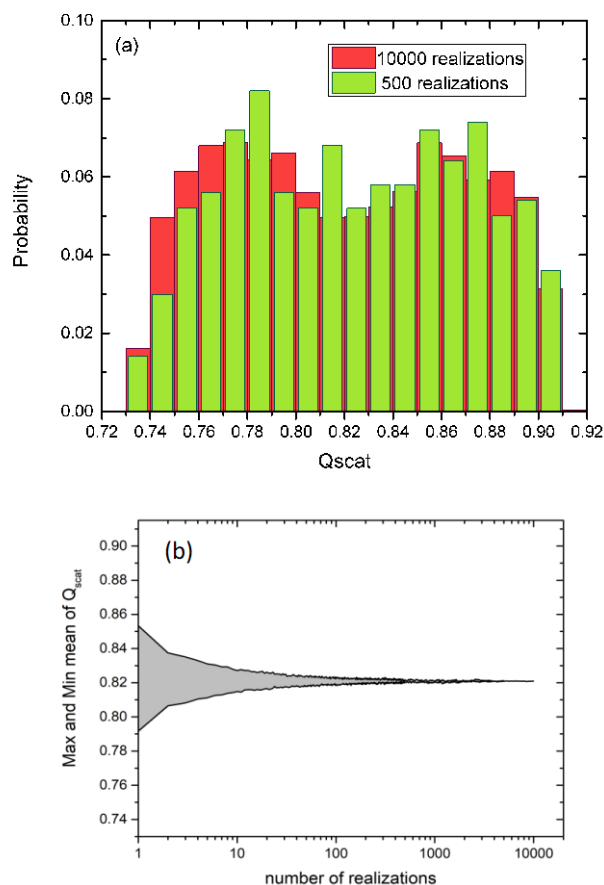
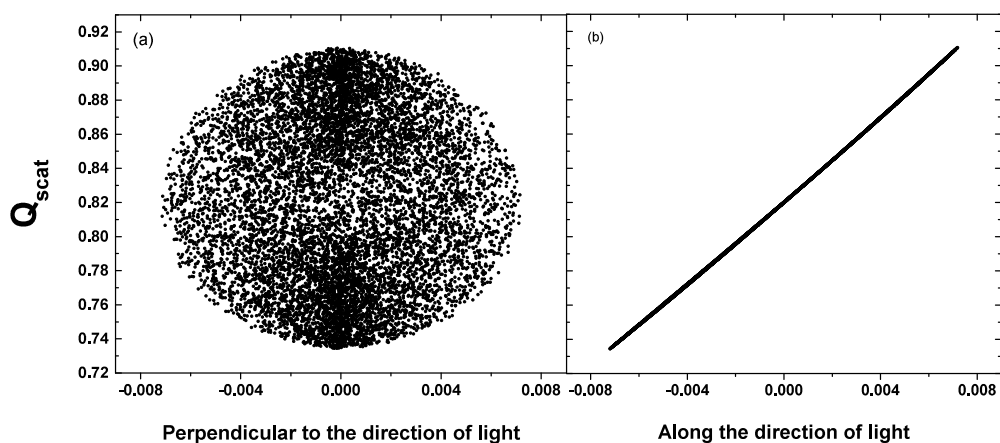



Figure 2 (a): Probability distribution of Q_{scat} for a phase separated particle with the eccentric core positioned at 500 random locations (green columns) and 10000 random locations (red column) within a 100 nm particle at OIR = 1:4 and k = 0.168. (b): Maximum and minimum of the mean for Q_{scat} for random realization of the position with the number of realizations used for the calculation. Optical properties, size and OIR are identical in (a) and (b).

It is evident from Fig. 2a that there is a range in scattering efficiency with the position of the center of the inclusion as the width of the distribution is more than 20 % of the mean of the scattering efficiency. Figure 3 shows Q_{scat} versus the core center perpendicular to the direction of the incoming radiation and along the direction of the radiation. (Please, note that the incoming radiation is randomly polarized for all calculations). Obviously, the scattering efficiency changes significantly with the position of the core along the incoming light axis. It is smallest for the core position facing the incoming light and largest with the core being located at the opposing position to the incoming light with an almost linear dependence for at least this particular set of parameters. The almost linear dependence of the efficiency along the light axis and random dependence perpendicular to it suggests that a concentric core-shell calculation of the scattering efficiency may be an excellent

approximation for the mean of a mono-disperse particle ensemble with random eccentric positions. In addition it suggests that the mean of the efficiency for an inclusion randomly distributed in the volume of the particle is not very different from one where the inclusion sticks to the surface of the particle at random positions.

5 **Figure 3. The change in Q_{scat} perpendicular to the direction of light (panel a) and along the direction of light (panel b) for particle with OIR = 1:4, k = 0.168, r = 100 nm over 10000 realizations.**

For these particular particle parameter choices, this is really the case as Fig. 4 shows the mean scattering efficiency for the
10 eccentric morphology as well as the one for a concentric core-shell with the standard deviation on an enlarged scale. The mean values for eccentric core-shell (with its center randomly placed in the volume) and eccentric core-shell (with its center position randomly placed such that it touches the surface) are very similar and only differ in the 4th decimal place and the value for a concentric core-shell is about 0.5 % lower. This emphasizes that the concentric core-shell model may be a good approximation for calculating the mean value for a distribution of particles with randomly located eccentric cores within
15 either volume or surface for the OIR range and refractive indices typical of aged aerosol and particles in the accumulation size range. Let us note parenthetically, that very similar behavior is exhibit when plotting the absorption efficiency instead of the scattering efficiency.

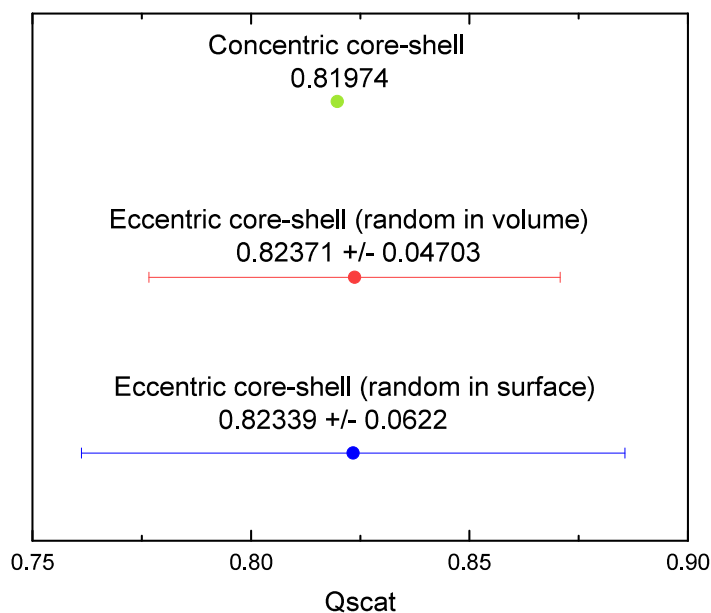



Figure 4.: Q_{scat} mean value and standard deviation (SD) for eccentric core-shell (over 10000 realizations) within the volume (blue dot), Q_{scat} mean value and SD for eccentric core-shell (over 10000 realizations) on random surface (red dot), and Q_{scat} for concentric core-shell (green dot).

To test this hypothesis over a wide parameter range, we compare mean scattering and absorption efficiencies for particles with eccentric core-shell morphology (with the inorganic core randomly placed at 500 different positions within the volume of the particle) with the corresponding concentric core-shell morphology.

10   As the efficiencies for scattering and absorption are strongly dependent on the size of the particle (Bohren and Huffman, 2008; Van de Hulst, 1957) for accumulation mode particles, we need to come up with a relative measure for the comparison of the two morphologies. The dependence is illustrated in Fig. 5 for a particle with $k = 0.168$, and OIR = 1:4. Here, the homogeneous particle is more efficient in absorbing the incoming light as particle size is increasing compared to the equivalent phase-separated one. In contrast, the phase-separated particle scatters light about 20 % more efficiently for
15   particles above 400-nm diameter.

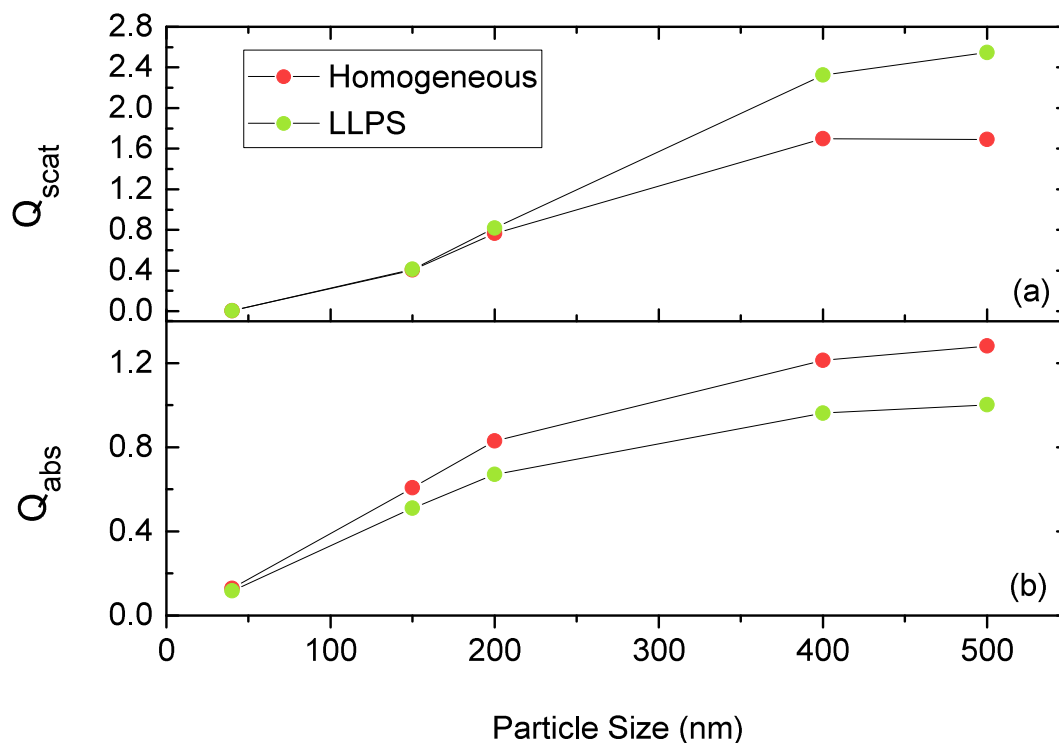



Figure 5: Q_{scat} **(panel a), and** Q_{abs} **(panel b) calculated for phase separated (LLPS) and homogeneous particles ranging from 40-500 nm at OIR = 1:4, and** k **= 0.168 using the eccentric core-shell Mie-code at** λ **= 355 nm. The red and green dots show the results for the same system at specific particle size for homogenous and phase separated (LLPS) particles respectively. The lines are only**
5 **meant to guide the eye.**

Since we are interested in the impact of LLPS on aerosol scattering and absorption, we take the internally mixed, homogeneous particle as reference and plot in the following always the ratio of the LLPS morphology to the homogeneous particle for all calculated efficiencies. This way, the strong size dependence of the efficiencies seen in Fig. 5 for both
10 morphologies cancels each other out and the emphasis is put instead on the effect of morphological change. These ratios may be understood as an empirical factor that could be used to correct calculations for homogeneous particles if those of equivalent phase separated particles are needed.

In Figure 6, we have calculated the ratio of scattering efficiencies for the LLPS morphology over the ones for the homogenous morphology for both, the eccentric case and the concentric case. As the computations for a concentric core-
15 shell morphology are computationally very efficient, those were calculated with for a small spacing in particle size whereas the calculations for the eccentric morphologies were done only for a few particles sizes. The analogues ratios for absorption efficiencies are plotted in the right column.

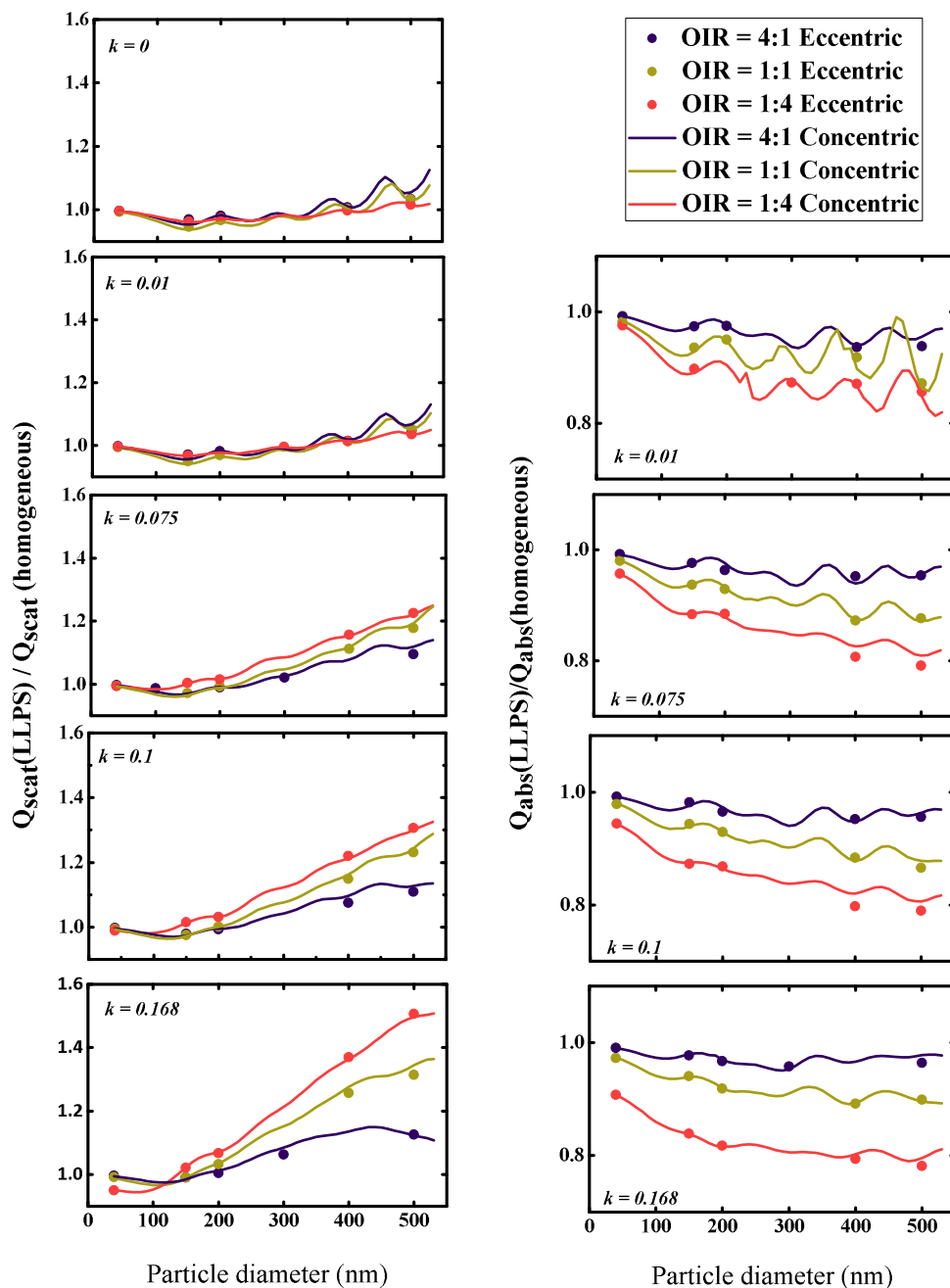



Figure 6. Left row: ratio of Q_{scat} for LLPS morphology over homogenous morphology as function of particle diameter for OIR = 1:4, 1:1, 4:1, with increasing k from top to bottom, k = 0, 0.01, 0.075, 0.1, and 0.168. **Right row:** corresponding absorption efficiency ratios. Dots represent calculations with random orientation of an eccentric core shell for the phase-separated particles; lines are calculations for the corresponding symmetric core-shell morphology (for details, see Tables A1 and A2).

Clearly, the effect of phase separation increases with particle size: the ratio of scattering efficiencies increases whereas the ratio of absorption efficiencies decreases. All calculations have been performed for a wavelength of 355 nm, hence particles much smaller than this wavelength are close to Rayleigh scattering and become less sensitive to internal morphology. Hence,

5 we expect all ratios to approach 1 for very small particle sizes. Also apparent are periodicities in both the ratio for scattering as well as the ratio of absorbing efficiencies showing a period with size of about 100 to 150 nm presumably related to half-integral ratios of size to wavelength. These dampen out with increasing absorptivity.

However, the overall effect of increasing absorptivity is to enhance the differences between phase-separated particles relative to homogeneous ones.

10 The most significant trend is the dependence of the efficiency ratios on the organic to inorganic ratio. For the absorption efficiency, the particles with the lowest organic volume (OIR = 1:4) show the strongest deviation for the LLPS morphology relative to the homogenous particle. As the organic fraction decreases in the particle, the effect of redistribution of the absorbing molecules into the organic phase yield a stronger contrast in the imaginary part of the refractive index between shell and core. This increase in contrast influences both absorption and scattering efficiency ratios (see Appendix A).

Most importantly, the extensive comparison between mean of eccentric core-shell realizations with concentric core shell calculations indicate that a concentric core-shell model is sufficient for estimating the ratios between scattering and absorption efficiencies for particles smaller than 500 nm in diameter and the ranges in OIR, and absorptivity under consideration here. This approximation becomes less accurate with increasing particle size but stays within 2.8 % at

20 maximum and is better than 1 % for most of the parameter range relevant here.

3 Atmospheric implications

In the previous section, we showed that concentric core shell calculations are sufficient to approximate the radiative impact of LLPS for a typical atmospheric aerosol containing a molecular absorber like Brown carbon. Utilizing this insight allows

25 us to perform integration over the UV-VIS part of the solar spectrum in a numerically efficient manner. In this section, we calculate the ratio of radiative forcing caused by a phase separated versus a homogeneously mixed aerosol in the thin aerosol layer approximation for mono-disperse aerosol.

According to Nemesure and Schwartz (1998), the properties that dictate the shortwave radiative forcing in the thin aerosol layer approximation (Charlson et al., 1991) are the scattering cross-section and the up-scattering fraction.

30 We follow their line of argumentation and calculate the radiative forcing of an optically thin aerosol layer (per unit area and unit vertical height, Δz) as:

$$\Delta F(\theta_0) = \left(F^\downarrow \cos \theta_0\right)\left(Q_{ext} \frac{1}{\cos \theta_0}\right) \omega \, \beta(\theta_0) \, C \, \Delta z \tag{1}$$

With $\left(F^\downarrow \cos \theta_0\right)$ being the incident direct beam flux at the top of the scattering volume, θ_0 being the solar zenith angle (SZA), $Qext$ the extinction efficiency, ω the single scattering albedo, $\beta(\theta_0)$ the up-scatter fraction and C the concentration of

5 the particles.

Since the extinction efficiency is the sum of scattering and absorption efficiencies, $Qext = Qscat + Qabs$, and the single scattering albedo is the ratio of scattering over extinction efficiencies:

10 $$\omega = \frac{Q_{scat}}{Q_{scat} + Q_{abs}} = \frac{Q_{scat}}{Q_{ext}} \tag{2}$$

Eq. (1) simplifies to:

$$\Delta F(\theta_0) = F^\downarrow \, Q_{scat} \, \beta(\theta_0) \, C \, \Delta z \tag{3}$$

The up-scatter fraction, β, is a function of particle size and accounts for the asymmetry of the phase function. It has a value of 0.5 for small particle in Rayleigh regime and decreases as the size of the particle increases. The up-scattering fraction for accumulation-mode particles (0.1 μm $< r <$ 1μm) that dominates aerosols mass and light scattering properties in the

20 atmosphere, β may be approximated for isotropic incoming radiation by $\beta = \frac{1}{2}\left(1 - \frac{7}{8} g\right)$ (Wiscombe and Grams, 1976), with g being the asymmetry parameter, i.e. the average cosine of the scattering angle ($g = \int_{4\pi} P \cos\theta \, d\Omega$, P being the normalized phase function). Since we are only interested in calculating the ratio of the radiative forcing for the LLPS morphology relative to homogenous morphology, we take this approximation for the up-scatter fraction and calculate the ratio as:

$$Ratio \; \Delta F = \frac{\int_{\lambda 1}^{\lambda 2}\left(F^\downarrow(\lambda) \, Q_{scat}^{LLPS}(\lambda) \, \beta^{LLPS}(\lambda)\right) d\lambda}{\int_{\lambda 1}^{\lambda 2}\left(F^\downarrow(\lambda) \, Q_{scat}^{Homo}(\lambda) \, \beta^{LLPS}(\lambda)\right) d\lambda} \tag{4}$$

30 An example of the relevant factors of Eq. (4) are shown in Fig. 7 for a particle for which we expect a significant effect of morphology based on the results presented in Fig. 6. Its OIR is equal to 1:4, it has a diameter of 200 nm, an imaginary part of

the refractive index of $k = 0.168$ at 355 nm. We take the wavelength dependence of the imaginary part of the refractive index (see Appendix B) to be given by its Ångström exponent (AAE) in the following power law relationship:

$$k(\lambda) = k_{355} \left(\frac{\lambda}{\lambda_{355}}\right)^{-AAE}$$

In the example shown in Fig. 7, AAE is equal to 2 (see Fig. B3 in Appendix B).

To estimate the real part of the refractive index for a typical aged aerosol particle we assume it to consist of aqueous ammonium sulfate and secondary organic matter. The Lorenz-Lorenz relation (Born & Wolf, 1959) is utilized to estimate the

10   real part of the refractive index based on parameterizations for the refractive index of ammonium sulfate and the organic matter for dry conditions and for 70 % RH as explained in detail in Appendix B.

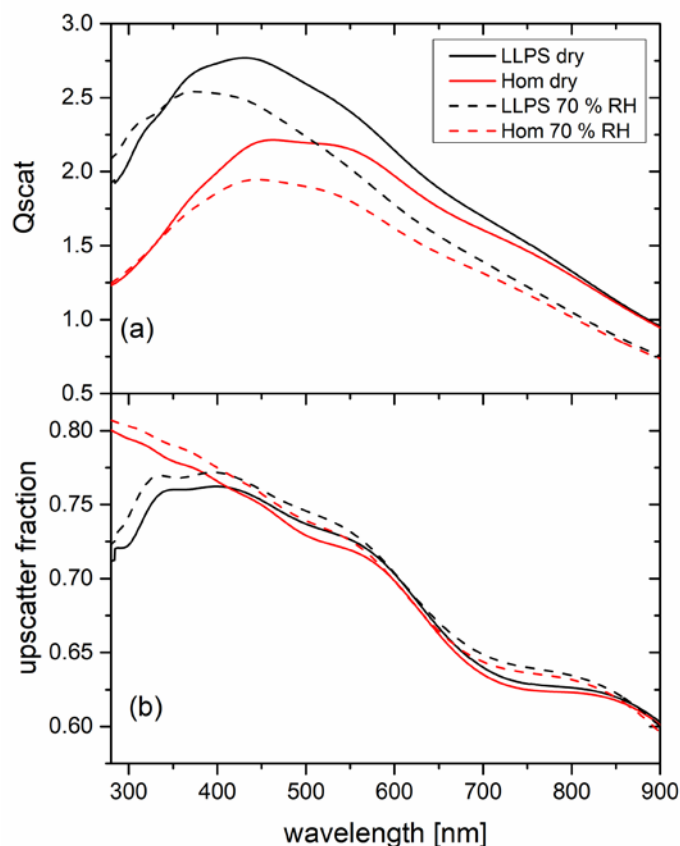



Figure 7 (a): Scattering efficiency for the homogeneous morphology (red) and LLPS morphology (black) under dry and wet conditions (solid and dashed line, respectively) for particles of identical size (200 nm) and AAE = 2. (b): Up-scatter fraction for the homogeneous particle (red) and LLPS particle (black) under dry and wet conditions (solid and dashed line, respectively).

Panel (a) in Fig. 7 shows the scattering efficiency for both, dry conditions and at a relative humidity of 70 %. As discussed above, the LLPS morphology yields larger scattering efficiencies especially at shorter wavelengths at which the differences in refractive indices are more significant. The up-scatter fraction shown in panel (b) for LLPS morphology is about 10 % smaller than for the homogeneous morphology at near UV-wavelength (λ = 290 nm) but they merge for the wavelengths

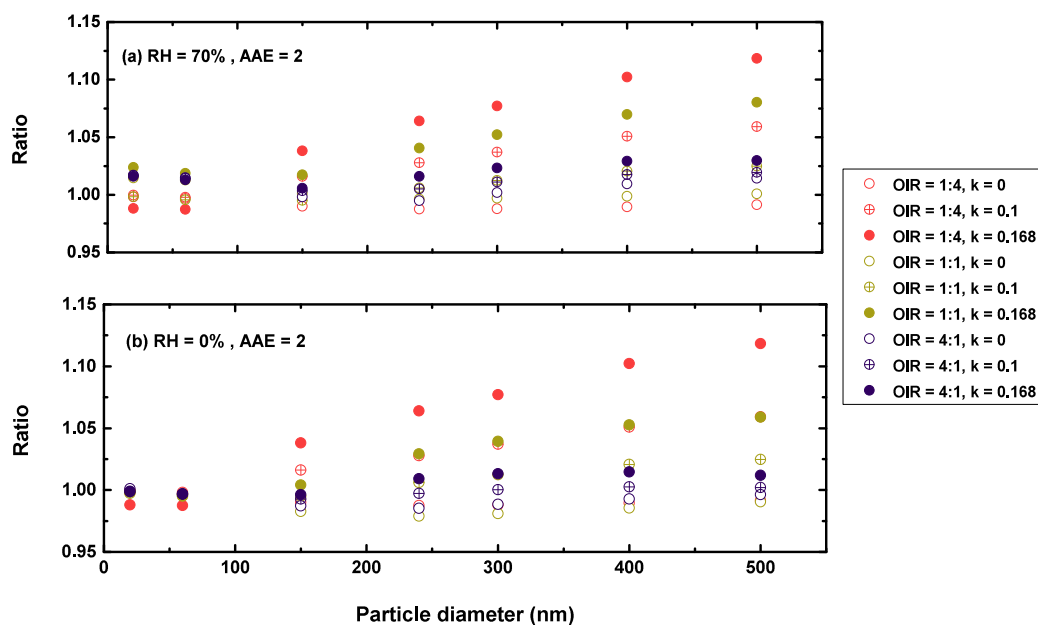
10   above 400 nm.

For calculating the net ratio in radiative forcing of phase-separated particles relative to homogeneously mixed ones, we utilize Eq. (4). Here, the product of up-scatter fraction and scattering efficiency integrated over the solar spectrum for both, LLPS morphology and homogeneous morphology, yields the net ratio that quantifies the effect of morphology on radiative

forcing. For the solar spectrum we used the spectral irradiance according to ASTM G173-03 (ASTM, 2012) and integrated Eq. (4) from 290 nm to 900 nm, see Appendix C.

The ratio is shown as a function of particle radius under dry and wet (70 % RH) conditions in Figs. 8a and 8b respectively. These calculations were done as in the example of Fig. 7 but for different scenarios with OIR = 1:4, 1:1, 4:1, k = 0, 0.1, 0.1,

5   and 0.168.

Figure 8 shows the results for the case where AAE is equal to 2. This corresponds to highly absorbing BrC and will give the largest radiative forcing impact possible by mixed BrC particles. Figure 9 depicts the result for a less strongly absorbing BrC where AAE is equal to 6.

10   **Figure 8: Ratio of radiative forcing of LLPS to homogenous case under 70 % RH (a) and dry condition (b) for AAE = 2.**

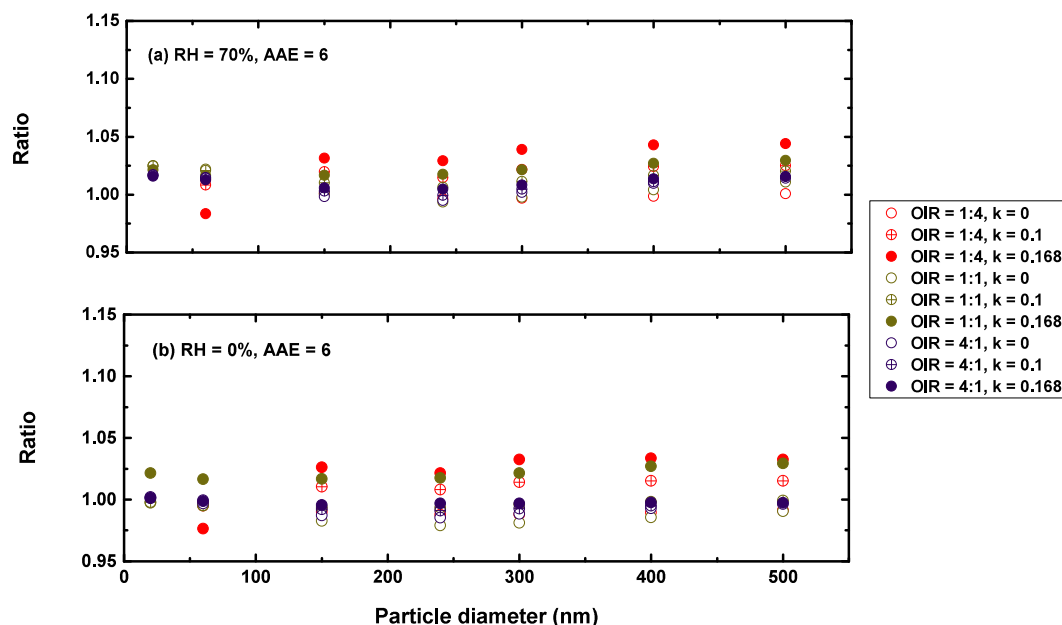



Figure 9: Ratio of radiative forcing of LLPS to homogenous case under 70 % RH (a) and dry condition (b) for AAE = 6.

First, we conclude from these calculations that the effect of morphology for purely scattering aerosol is negligible, smaller
than 2 % for all sizes and organic to inorganic ratios. Second, there is not much difference between dry and moderately
humid conditions (remember, that at high RH (beyond SRH) we expect the particle to homogeneously mixed). Third, as
expected from the results discussed in the previous section, the greatest effect is calculated when the organic fraction is the
lowest (OIR = 1:4), k has the largest value (0.168) and the size is on the upper size range of the accumulation mode.
However, even here the increase is only about 12 %. For an AAE more likely to occur in aged aerosol, i.e. AAE = 6, this
increase reduces to 4 %. Based on the results shown in Figs 8-9, the impact for cases where AAE is lower than 6 is
negligible. Since even an AAE of 6 is considered to be characteristic of a strongly absorbing brown carbon, our overall
conclusion is that liquid-liquid phase separation has no significant effect on direct short-wave aerosol forcing.

4 Conclusions

Using both eccentric and concentric core-shell model calculations for scattering and absorption efficiencies of single aerosol
particles with an inorganic non-absorbing core and an absorbing organic shell at different volume ratios, sizes and
absorptivity revealed that a concentric core-shell model is a good approximation for calculating these efficiencies. Applied to
liquid-liquid phase separation for atmospheric relevant OIR and sizes typical of the accumulation mode we showed that the

largest impact resulted from the case where organic fraction had the lowest contribution in the mixed particle (OIR = 1:4) and formed a very thin shell around the inorganic core and was highly absorbing (k = 0.168). Once integrated over the solar spectrum, taking into account the typical spectral dependence of BrC, the effect of morphology on radiative forcing substantially decreased to about a few percent. Overall, we conclude that the effect of liquid-liquid phase separation on short wave radiative forcing is rather small and the correct value of AAE is the greatest source of uncertainty when estimating for the impact.

Appendices

Appendix A. Calculating refractive indices for homogenous and phase-separated particles

Tables A1 and A2 show the values for the refractive indices, $n + i\,k$, at selected imaginary refractive indices ($k = 0.168$ in
5   Table A1 and $k = 0.01$ in Table A2) set for the homogenous particle. The corresponding size of the core in the LLPS
morphology as well as the refractive indices were calculated using simple volume mixing. These values are used as inputs
for the calculations shown in Fig. 6.

Table A1: Calculated values for relative size of the core to shell for phase-separated particles and refractive indices ($k = 0.168$) for
10   **homogenous and LLPS case at different size and OIRs using volume mixing**.

Particle Size (nm)	OIR	Morphology	r_{shell} (nm)	r_{core} (nm)	n_{core}	n_{shell}	k_{core}	k_{shell}
40	1:1	homogeneous	-		1.5		0.168	
		LLPS	20	15.87	1.429	1.571	0	0.336
40	1:4	homogeneous	-		1.457		0.168	
		LLPS	20	18.57	1.429	1.571	0	0.84
40	4:1	homogeneous	-		1.543		0.168	
		LLPS	20	11.69	1.429	1.571	0	0.21
200	1:1	homogeneous	-	-	1.5		0.168	
		LLPS	100	79.37	1.429	1.571	0	0.336
200	1:4	homogeneous	-	-	1.457		0.168	
		LLPS	100	92.8	1.429	1.571	0	0.84
200	4:1	homogeneous	-	-	1.543		0.168	
		LLPS	100	58.9	1.429	1.571	0	0.21
500	1:1	homogeneous	-	-	1.5		0.168	
		LLPS	250	198.4	1.429	1.571	0	0.336
500	1:4	homogeneous	-	-	1.457		0.168	
		LLPS	250	232	1.429	1.571	0	0.84
500	4:1	homogeneous	-	-	1.543		0.168	
		LLPS	250	146.2	1.429	1.571	0	0.21

Table A2: Calculated values for relative size of the core to shell for phase-separated particles and refractive indices (k = 0.01) for homogenous and LLPS case at different size and OIRs using volume mixing.

Particle Size (nm)	OIR	Morphology	r_{shell} (nm)	r_{core} (nm)	n_{core}	n_{shell}	k_{core} (nm)	k_{shell} (nm)
40	1:1	homogeneous	-	-	1.5		0.01	
		LLPS	20	15.87	1.429	1.571	0	0.02
40	1:4	homogeneous	-	-	1.457		0.01	
		LLPS	20	18.57	1.429	1.571	0	0.05
40	4:1	homogeneous	-	-	1.543		0.01	
		LLPS	20	11.69	1.429	1.571	0	0.0125
200	1:1	homogeneous	-	-	1.5		0.01	
		LLPS	100	79.37	1.429	1.571	0	0.02
150	1:4	homogeneous	-	-	1.457		0.01	
		LLPS	75	69.6	1.429	1.571	0	0.05
200	4:1	homogeneous	-	-	1.543		0.01	
		LLPS	100	58.9	1.429	1.571	0	0.0125
500	1:1	homogeneous	-	-	1.5		0.01	
		LLPS	250	198.4	1.429	1.571	0	0.02
500	1:4	homogeneous	-	-	1.457		0.01	
		LLPS	250	232	1.429	1.571	0	0.05
500	4:1	homogeneous	-	-	1.543		0.01	
		LLPS	250	146.2	1.429	1.571	0	0.0125

Appendix B. Estimating the refractive index for the calculations of section 3.

The real part of the refractive index for a liquid solution may be estimated in terms of the refractivity of the solution based
on the Lorentz-Lorenz relation (Born & Wolf, 1959). The refractivity, to a good approximation, is a linear superposition of
the molar refractivities of the solution's components. While refractive index data as well as density data are available for
aqueous ammonium sulfate (AS) solutions (Tang & Munkelwitz, 1994), we choose the refractive index and density
parameterizations of Lienhard et al. (2015) to be representative for the secondary organic matter (SOM) in our model
calculations. As the molar refractivities depend strongly on wavelength, we parameterize the SOM molar refractivity
wavelength dependence based on the parameterization given in Liu et al. (2013) and the ones for aqueous ammonium sulfate
on the parameterization by Semmler et al., (2018). Finally, we use ideal mixing of the two binary systems to calculate the
refractive index of the ternary system. The resulting refractive indices for the ternary system with different OIR under dry
conditions are shown in Fig. B1.

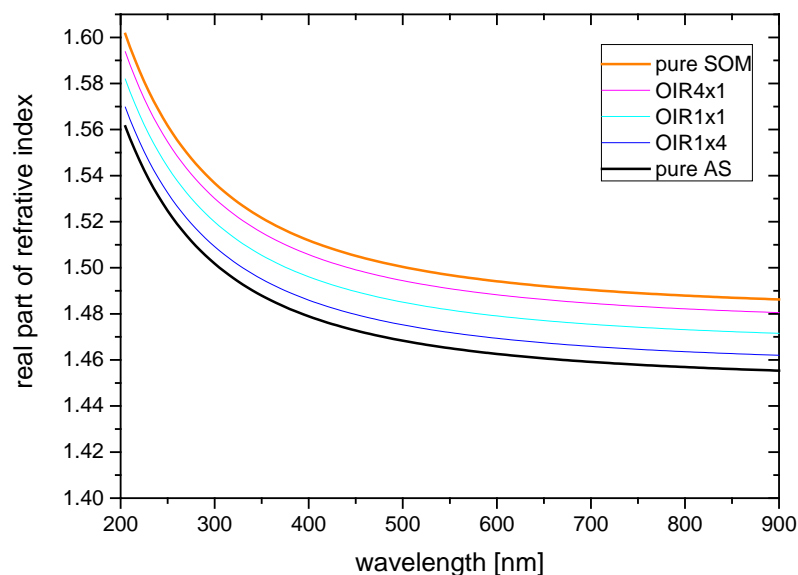



**Figure B1: Real part of refractive index, *n*, for aqueous mixtures of ammonium sulfate (AS) and secondary organic matter (SOM)
with varying OIR extrapolated to dry condition.**

To calculate the refractive indices at 70 % relative humidity we use the water activity of the binary aqueous solutions for AS (Tang & Munkelwitz, 1994) and SOM (Lienhard et al. 2015), and the Zdanovskii-Stokes-Robinson (ZSR) relation to calculate the water content of the AS-SOM mixture. This yields the refractive indices shown in Fig. B2.

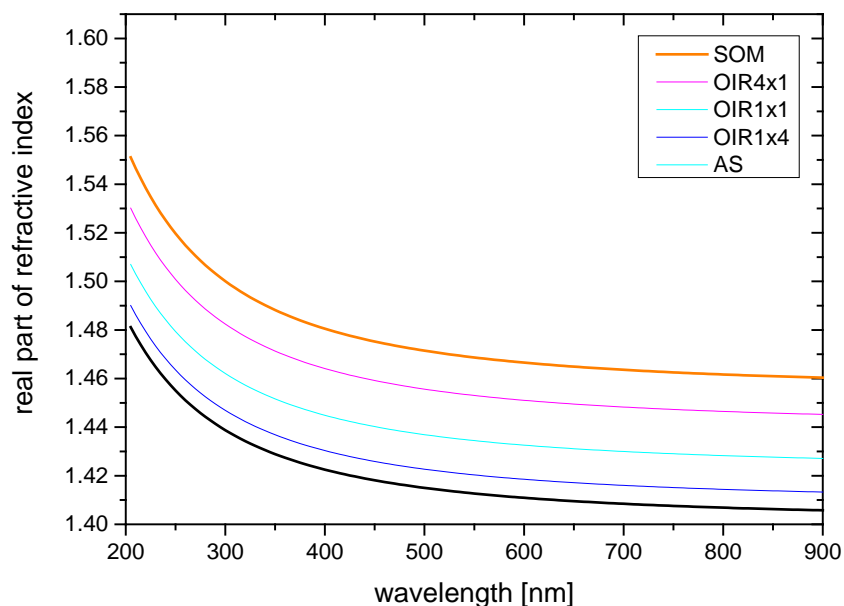



Figure B2: Real part of refractive index for mixtures of AS and SOM with varying OIR at 70 % RH.

Under humid conditions the real part of the refractive index decrease and, since AS takes up more water at 70 % compared to SOM, the difference in refractive index between AS rich mixtures to SOM rich mixtures increases when comparing humid to dry conditions.

The wavelength dependence of the imaginary part of the refractive index is shown in Fig. B3 for two Ångström exponents, with the k = 0.168 at λ = 355 nm.

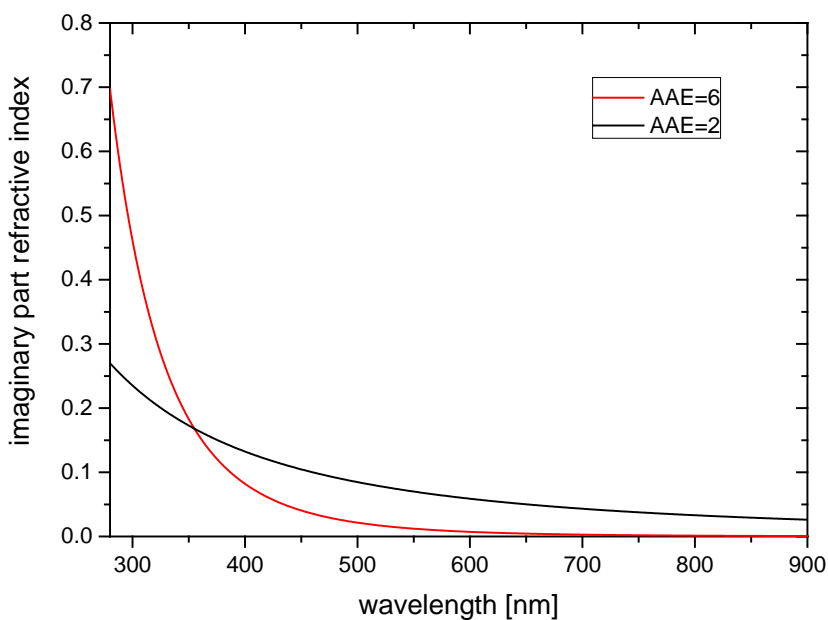



Figure B3: Wavelength dependence of the imaginary part of the refractive index for AAE equal to 2 and 6, respectively. $k = 0.168$ for $\lambda = 355$ nm.

Appendix C. Spectral Irradiance

For calculating the shortwave radiative forcing ratio defined in Eq. (4), spectral irradiance is needed as an input for performing the integration. Since we are interested in estimating the relevance of LLPS for radiative forcing and calculating only a ratio, the particular choice of irradiance data is not very important. We use the ASTM G173-03 (ASTM, 2012) as
10 spectral irradiance, which is plotted in Fig. C1.

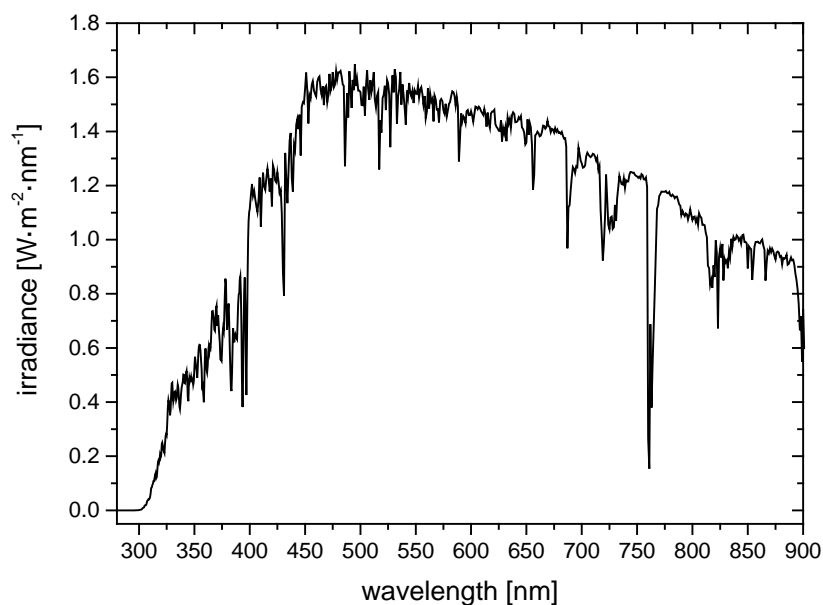



Figure C1: Direct spectral irradiance (ASTM G173-03).

The irradiance is for a solar zenith angle of 41.81°, the atmospheric conditions are those of the standard US atmosphere with

5   an ozone column of 340 DU and total column water vapor equivalent of 1.42 cm.

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