We thank reviewer 2 for her/his comments and suggestions, in particular, we are grateful for her/him pointing out our neglect of surface albedo in the atmospheric implication section. We will reply to point by point below.

P1L29-31: Add the reference of Bond et al. (2013) and change the sentence also referring to the surface albedo (e.g., Chylek and Wong, 1995) and changing the unclear wording "may also contribute to warming". Does this mean that in addition to cooling they also cause warming?

We agree with the reviewer that surface albedo is very important for evaluating whether an aerosol is heating of cooling. We will add this to the sentence.
However, while purely scattering aerosol particles will cool the surface, strong absorbing aerosol can heat the planet. The sentence reads in the manuscript: "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)." That was not meant "in addition", but "instead". We will rephrase the sentence.

Changes to the manuscript: We will rephrase the sentence to: "Depending on their optical properties, size and albedo of the surface, aerosols mostly cool our planet (IPCC, 2013). However, those which are highly absorptive (e.g., soot particles) can lead to heating (e.g. Ramanathan et al., 2001, Bond et al., 2013). We will add the reference Bond et al. (2013).

P3L9: "Brown Carbon is referring to the light-absorbing fraction of the organic carbon that has a wavelength dependent absorptivity." This is a very poor definition of BrC because the key definition is that the imaginary part of the refractive index (not the absorptivity) is wavelength dependent and increases toward shorter wavelengths (e.g., Moosmuller et al., 2011).

We will take the advice of the reviewer and will change the sentence. However, while we agree that the sentence is a bit misleading with brown carbon being no single compound, it is clear that if nevertheless approximating it as such, its molar absorptivity would be indeed wavelength dependent, as the absorption coefficient is directly proportional to the imaginary part of the refractive index.

Changes to the manuscript: Sentence will be revised to: "Brown Carbon is referring to the light-absorbing fraction of the organic carbon that has a wavelength dependent imaginary part

of the refractive index, which increases towards shorter wavelengths"

P4L13: "We use simple volume mixing. . .". This needs some explanation of effective medium theories, why the volume mixing rule was chosen, and what its accuracy is. A good starting point would be Chylek et al. (1988).

In this section of the manuscript, we just want to show that the concentric core-shell model is a good approximation for calculating the mean value for a distribution of particles with randomly located eccentric cores. While the magnitude of the calculated efficiencies depend strongly on the real part of the refractive index, the core shell model is always a good for various assumed refractive indices. Hence we used simple volume mixing here (in contrast to what we do in appendix B, for estimating the atmospheric implications), just for illustration.

Changes to the manuscript: We will add a sentence stating this after line 15: (Note, we use the volume mixing approximation just to illustrate the effect of morphology in this section, for this purpose any effective medium approximation could be used.)

P7 Fig. 2: (1) Explain exactly what is meant here with random location and how it is realized computationally; (2) Give the complex refractive index both for the particle and the inclusion here and elsewhere; (3) "100 nm particle": Does "100 nm" refer to particle radius, diameter, circumference or something else; please state explicitly here and elsewhere!

Answer to (1). After LLPS there is only a certain volume accessible for the spherical core if we assume core-shell morphology, i.e. that the core is completely embedded in the spherical particle. We did two types of randomized calculations for the position of the core within the shell: (1) if the core remains always attached to the inside surface of the particle, the radial distance between center of core and center of the particle remains fixed and we used a random number generator to draw random numbers for both, the polar and the azimuthal angle to place the core within the particle in a spherical coordinate system. (The light is always parallel to the z-axis.) (2) If the core is not attached, we also varied the distance between core center and particle center, i.e. the radial coordinate in the spherical coordinate system, by using a random number scaled such that the core access the volume within the particle with equal probability.

Answer to (2). These are given in Table A1. However, we agree that it is helpful to have those in the figure captions.

Answer to (3). We use always diameter, when writing about the size of the particle in the text.

Changes to the manuscript: We will add the explanation given in (2) to the text in page 6 line 7.
"We did two types of randomized calculations for the position of the core within the shell. (1) Random position attached to inner surface: the core remains always attached to the inside surface of the particle, hence in a spherical coordinate system the radial distance between center of core and center of the particle remains fixed. We used a random number generator to draw random numbers for both, the polar and the azimuthal angle to place the core within the particle in the spherical coordinate system. The light is always parallel to the z-axis of a corresponding Cartesian coordinate system. (2) Random position within the volume: if the core is not attached, we also varied the distance between core center and particle center, i.e. the radial coordinate in the spherical coordinate system, by using a random number scaled such that the core access the volume within the particle with equal probability."

P12L22 – P17L12: "3 Atmospheric Implications". This section is flawed and in need of major revision! The reference Charlson et al. (1991) discusses only radiative forcing by non-absorbing (i.e., sulfate) aerosols; the reference Nemesure and Schwartz (1998) is in the "grey" literature and should be replace with a peer-reviewed reference such as Chylek and Wong (1995). In addition, the authors pick the wrong equation fromNemesure and Schwartz (1998) that doesn't account for the albedo of the underlying surface. In reality, the radiative forcing in the optically thin aerosol layer case depends on one extensive aerosol parameter (AOD), two intensive aerosol parameters (SSA and upscatter fraction), and the albedo of the underlying surface or scene. The equation for this can be found in Nemesure and Schwartz (1998) p. 532, left column just above the right column header "Results" or in the peer reviewed literature (Chylek and Wong; 1995; eq. 8), with further discussion of validity and assumptions to be found in Hassan et al. (2015), Moosmuller and Ogren (2017), and Moosmuller and Sorensen (2018). Of specific interest would be to plot the ratio (LLPS/homogeneous) of the dominating intensive aerosol forcing parameter SSA as function of particle diameter such as done in Fig. 6 for Qscat and Qabs.

Again, we would like to thank the reviewer very much for pointing this out. Our data of Fig. 8 and Fig. 9 are calculations for the albedo being 0, i.e. a completely absorbing surface. We will add corresponding figures for the case of a perfectly reflecting surface as well as a figure showing the effect of surface albedo on the ratio of LLPS to

homogenous forcing for the OIR, size and k with the strongest
overall effect. We will also follow the suggestion to plot the
ratio of SSA for the two morphologies and will use this
additional figure to start the discussion in the atmospheric
implications section.

Changes to the manuscript: Since there will be considerable
changes for this section, we do not list all changes here, but
refer to the completely revised atmospheric implications
section. In addition, the last sentence of the abstract will
be modified to reflect these changes to:

"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 for the case of
small surface albedos and a decrease of up to 18 % for
surfaces with high reflectivity. However, for those of
moderate absorptivity, LLPS will have no significant short-
wave radiative impact."

We add the revised version of the atmospheric implication
section here for completeness.

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 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 Chylek and Wong (1995) (see also Nemesure and Schwartz, 1998; compare to
Charlson et al., 1991 for a purely scattering aerosol), the intrinsic properties that dictate the
shortwave direct radiative forcing in the thin aerosol layer approximation for absorbing
aerosol particles are their scattering and absorption cross-sections and the fraction of
radiation scattered by aerosol into the upper hemisphere, the up-scattering fraction. Here,
the ratio of scattering efficiency to extinction efficiency, the single scattering albedo (SSA) ω,
determines the portion of total extinction due to scattering (e.g.: Moosmüller and Sorensen,
2018):

$$\omega = \frac{Q_{scat}}{Q_{ext}} = \frac{Q_{scat}}{Q_{scat}+Q_{abs}}$$
(1)

For the examples of Fig. 6, the ratio of the single scattering albedos of the two morphologies
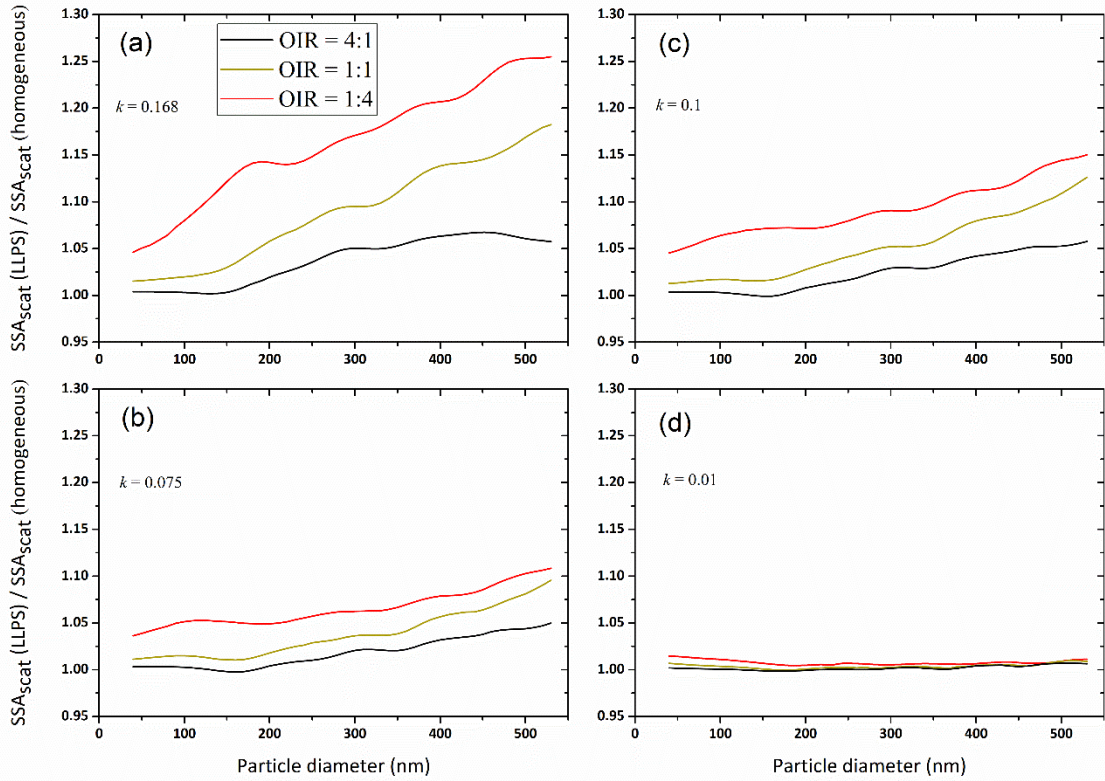are shown in Fig. 7.

Figure 7. Ratios of *SSA* for LLPS morphology over homogenous morphology as function of particle diameter for OIR = 1:4, 1:1, 4:1, with decreasing absorption from (a) to (d), *k* = 0.168, 0.1, 0.075, 0.01 (same parameters as in Fig. 6, for details, see Tables A1 and A2). Here, we show only the data calculated for concentric core shell morphologies.

For all OIR and absorptivities, a phase-separated particle has a larger single scattering albedo compared to a corresponding homogeneous particle, up to 25% larger for the strong absorbing case and a large particle diameter. However, for weakly absorbing particles (k <= 0.01) the effect is negligible, as expected. As in Fig. 6, the strongest enhancement is observed for the OIR 1:4 case, i.e. the one with the largest redistribution of absorbing molecules upon LLPS.

Following Chylek and Wong's (1995) line of argumentation, we calculate the direct radiative forcing, *ΔF_R*, of an optically thin aerosol layer in a cloud free atmosphere (per unit area and unit vertical height, Δz) as:

$$\Delta F_R = -\frac{S_0}{4}\sigma\{(1-a)^2 2\beta Q_{scat} - 4aQ_{abs}\}\,\Delta z \qquad (2)$$

With $\frac{S_0}{4}$ being the globally averaged solar flux at the top of the scattering volume, σ the geometric cross section, a being the surface albedo and β the up-scatter fraction. The up-scatter fraction, β, is a function of particle size and accounts for the asymmetry of the scattering phase function. It has a value of 0.5 for small particles in the 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 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 use this approximation for the up-scatter fraction and calculate the ratio of the short wave radiative forcing for the different morphologies as:

$$Ratio \, \Delta F_R = \frac{\int_{\lambda 1}^{\lambda 2} \Delta F_R^{LLPS}(\lambda) \, d\lambda}{\int_{\lambda 1}^{\lambda 2} \Delta F_R^{Hom}(\lambda) \, d\lambda}$$
(3)

Let us first discuss the case for a perfectly absorbing surface, i.e. albedo a equal zero. The last term in the curly bracket of Eq. (2) vanishes. The relevant factors of Eq. (2) for this albedo 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) into account by using a single Ångström exponent (AAE) in the following power law relationship:

$$k(\lambda) = k_{355} \left(\frac{\lambda}{\lambda_{355}}\right)^{-AAE}$$
(4)

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

We also need to estimate the real part of the refractive index for a typical aged aerosol particle. Her, 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 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.
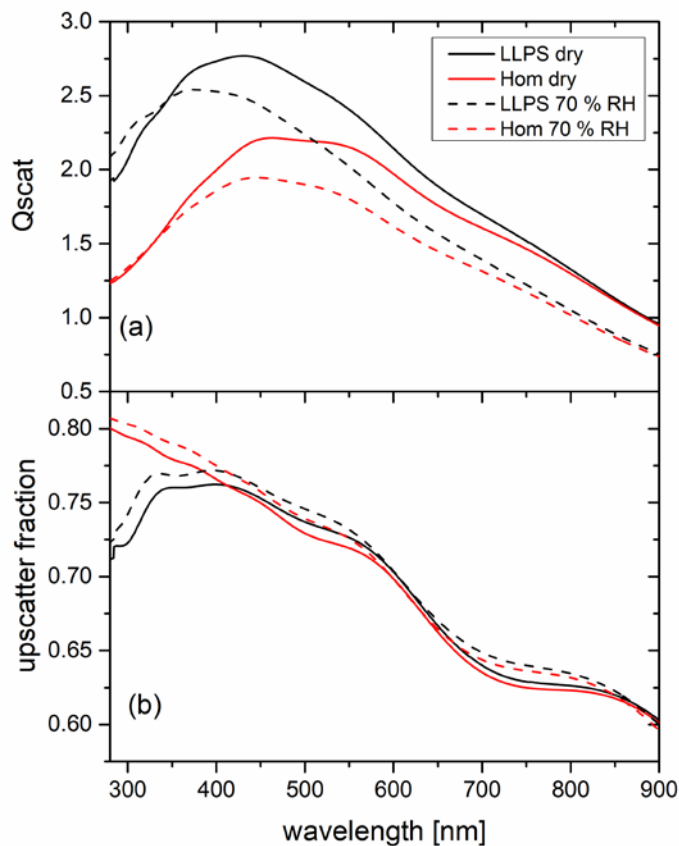
Figure 7 Shown are calculations for the limiting low albedo case. OIR 1:4, diameter 200 nm, *k* = 0.168 at 355 nm. (a): Scattering efficiency for the homogeneous morphology (red) and LLPS morphology (black) under dry and wet conditions (solid and dashed line, respectively) for particles of identical diameter (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 above 400 nm.

For calculating the net ratio in radiative forcing of phase-separated particles relative to homogeneously mixed ones, we utilize Eq. (3). Here, the product of up-scatter fraction and scattering efficiency integrated over the short wave solar spectrum for both, LLPS morphology and homogeneous morphology, yields the net ratio that quantifies the effect of morphology on direct 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. 8(a) and 8(b), 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, 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 in the visible range of the solar spectrum, where AAE is chosen to be equal 6.
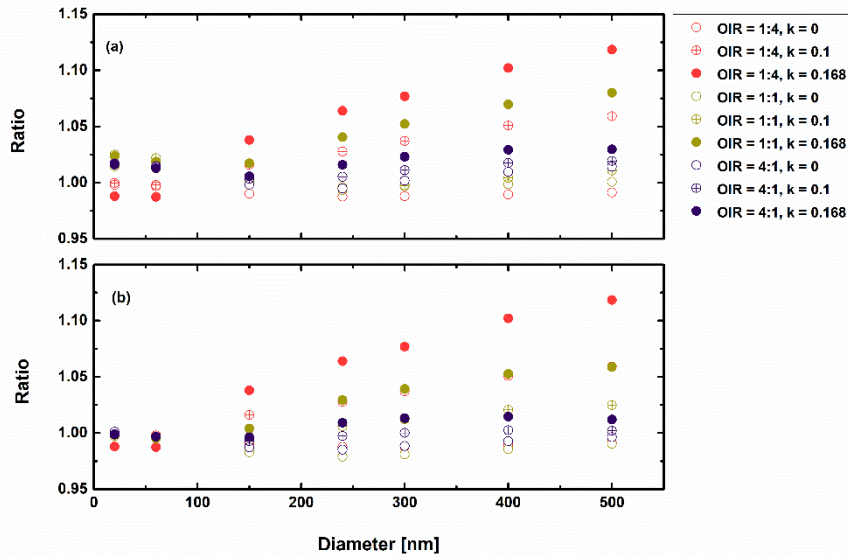

Figure 8: Ratio of radiative forcing of LLPS to homogenous case under 70 % RH (a) and dry condition (0 % RH). (b) both for AAE = 2 and albedo *a* = 0.
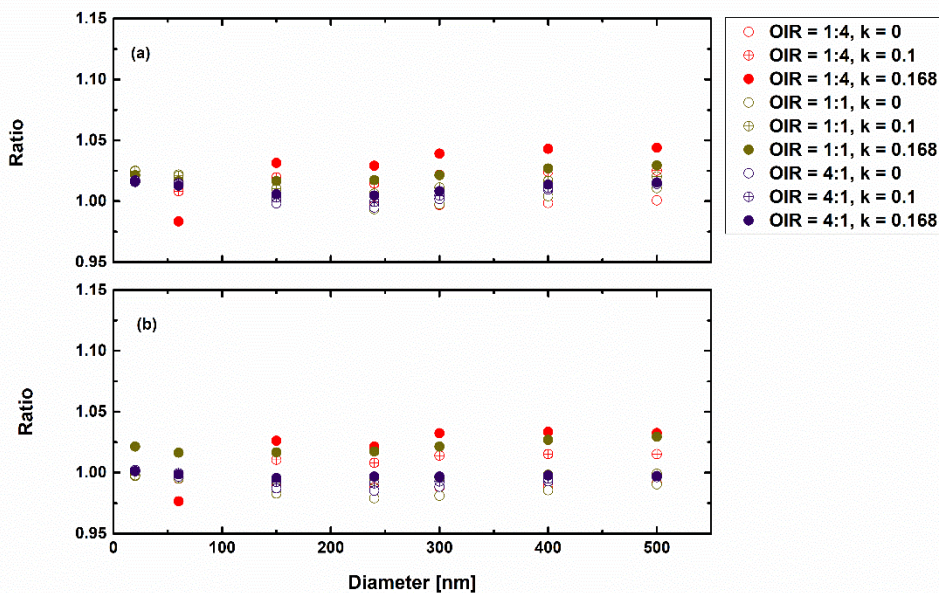

Figure 9: Ratio of radiative forcing of LLPS to homogenous case under 70 % RH (a) and dry condition (b) for AAE = 6 and albedo *a* = 0.

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 be 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 for low albedos.

Second, we may discuss in a similar manner the high albedo limit, i.e. *a* = 1. Fig. 10 and 11 show the corresponding results.
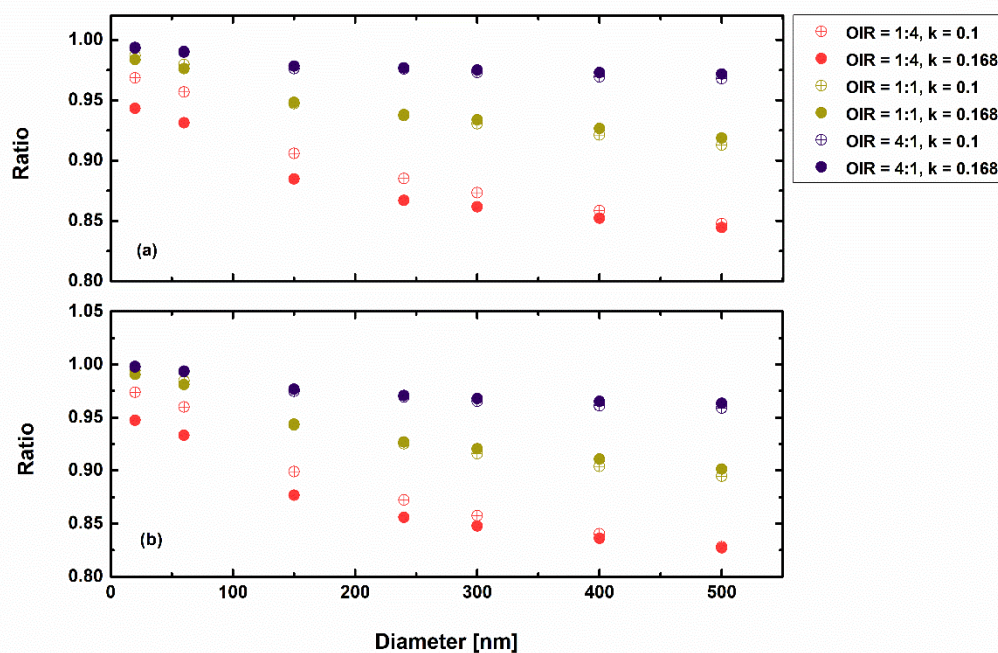

Figure 10: Ratio of radiative forcing of LLPS to homogenous case under 70 % RH (a) and dry condition (0 % RH). (b) both for AAE = 2 and albedo *a* = 1.

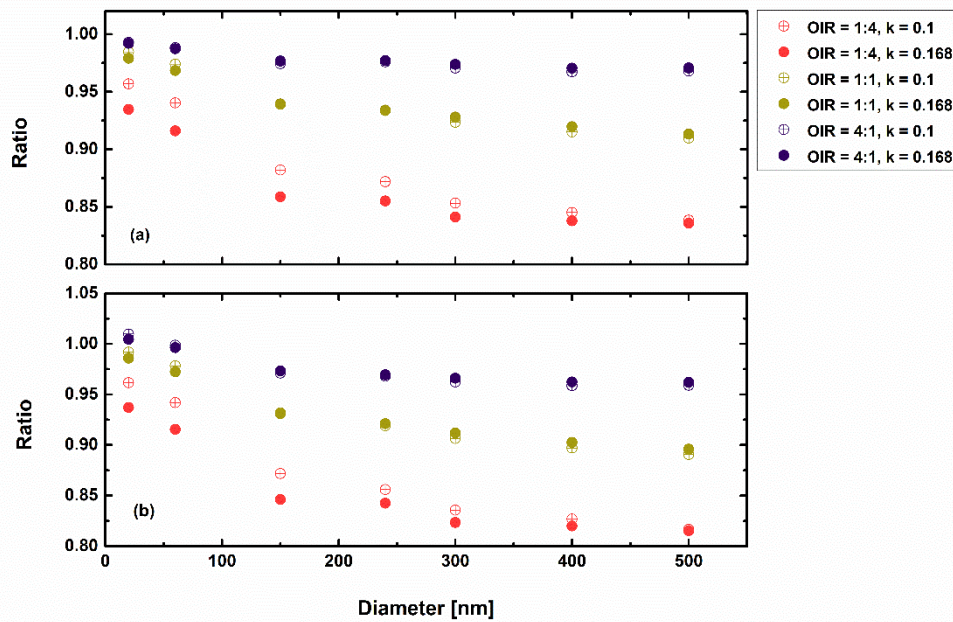**Figure 9: Ratio of radiative forcing of LLPS to homogenous case under 70 % RH (a) and dry condition (b) for AAE = 6 and albedo a = 1.**

Again, there are only small differences when comparing the humid and dry cases as well as between the AAE = 6 and AAE = 2 cases. However, the LLPS morphology shows a smaller forcing compared to the homogeneous morphology because Q_{abs} is the decisive parameter for a highly refractive surface (compare Eq. (3) and Fig. 6). Overall, the maximum reduction is 20% for the largest sizes considered here and the OIR equal 1:4 as expected from the discussion above.

Up to here, we did only compare ratios for the different morphologies. For a surface albedo close to zero radiative forcing will be negative for a thin aerosol layer, whereas the forcing will turn positive for a highly reflecting surface for an absorbing aerosol. For intermediate albedos, the denominator of Eq. (3) (the forcing for the homogeneous morphology) will approach zero for a particular size and albedo combination, meaning that the effect of scattering and absorption at this surface albedo cancel out yielding a zero forcing. However, since the corresponding particles with LLPS morphology have a small but finite forcing it results in a very large ratio of the short wave radiative forcing for LLPS to homogenous morphology. This is illustrated in Fig. 12.
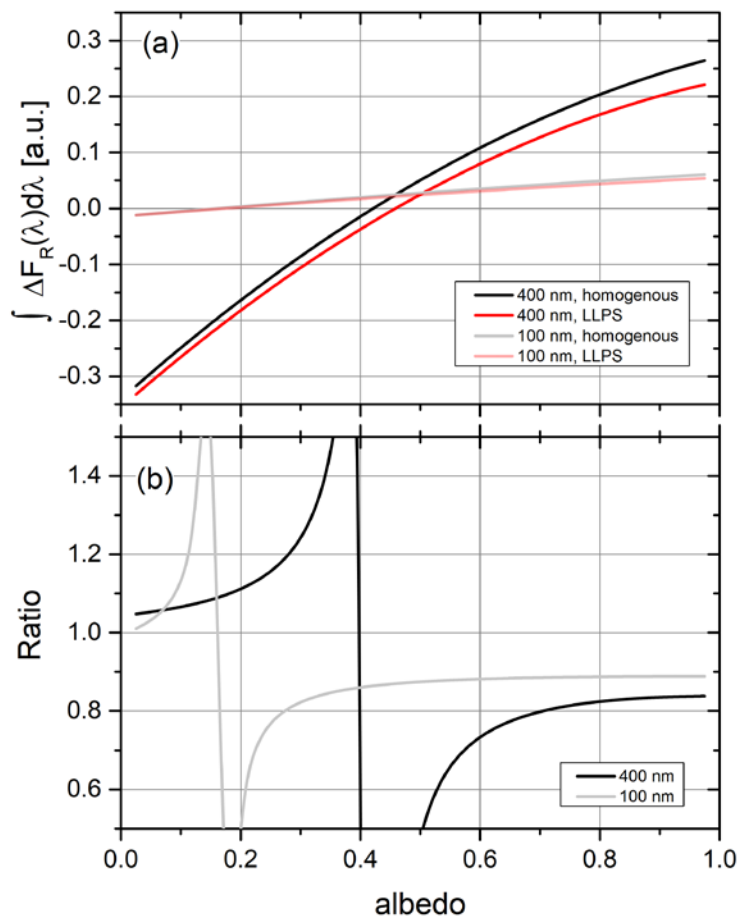
Figure 12 (a): Direct radiative forcing integrated over the visible solar spectrum for particles with OIR 1:4, AAE = 6, and k = 0.168 at 355 nm. Results for two diameters are shown. (b) Ratio of forcing for LLPS morphology to homogeneous morphology, see Eq. (3), for the data of (a).

Panel (a) shows clearly, that the albedo for which the direct radiative forcing vanishes, depend on the size of the particle, shifting to larger albedos with increasing particle size. This leads to poles in the ratio of forcing for the two morphologies as seen in panel (b) of Fig. 12. However, for a more realistic atmospheric situation where the thin aerosol layer will contain particles with sizes and refractive indices distributed over a significant range these poles will level out. Hence, we expect a smooth transition for the ratio of radiative with a larger negative forcing for LLPS morphology at low albedos to a smaller positive forcing at high albedos for LLPS morphology compared to homogeneous morphology.