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Effect of particle mixing morphology on aerosol scattering and absorption: A discrete dipole modeling study

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ABSTRACT

Atmospheric aerosol particles may undergo phase separation due to differences in miscibility. This alters the morphology of particles such that they are no longer well-mixed, simple spheres. As a result, scattering and absorption of sunlight in Earth's atmosphere could be affected. In turn, this may alter direct climate forcing by aerosols. In this work we examine the impact of phase separation on aerosol optics for the bi-sphere, core–shell, and engulfed morphologies. We find bi-spherical particles often exhibit very different scattering and absorption cross-sections for a mid-visible wavelength (0.53 μm) relative to an equivalent, volume-weighted spherical case. Optical differences are largely driven by the particle shape, rather than differences in refractive index between phases. However, when averaged across a typical urban particle size distribution, the differences in light scattering largely vanish and bi-sphere and volume equivalent models generally agreed to within 10% for dielectric particles. For particles that are light absorbing, the bi-sphere and volume averaged cases often yielded dissimilar results with the volume-averaged case reflecting absorption >10% more than the phase separated particles. This was particularly true for bi-spheres in which one component particle is strongly light absorbing. Core–shell and engulfed morphologies yield volume scattering efficiencies within a few percent of volume-weighted spheres. However, modeled light absorption between the phase separated and volume averaged models frequently differ by >20% when inclusions absorb light strongly. Therefore, modeling light absorption of mixed-phase particles through the volume-mixing rule cannot be recommended.

Introduction

Recent research has discovered that airborne particles dispersed in Earth's atmosphere likely undergo phase separation driven by differences in solubility and molecular polarity [1–7]. Such internally mixed particles are often described as containing an 'organic' component and an inorganic or aqueous component that phase separate. The 'organic' phase is largely nondescript, being comprised of potentially hundreds of compounds. A fraction of the organic materials may be light absorbing compounds. The inorganic phase is often modeled as ammonium sulfate or ammonium nitrate as these materials have historically been present in atmospheric aerosol in significant quantities. For particles that do phase separate there are many possible morphologies, however, two specific models have emerged. First, a core–shell arrangement can result in which a spherical core of material is coated with a concentric shell of the phase-separated material. A second possibility has been termed 'engulfed' in which phase separated droplets form an interface of variable surface area at the droplet surfaces.

For this work, we consider several of the possible morphologies. One extreme morphology is when particle materials form two spheres (or near spheres) that touch on edge, but remain phase separated. Here, we model this type of particle as a true bi-sphere, in which droplets touch at a single point on their surface. We also consider core–shell morphology, and 'engulfed' particles in which a film of phase-separated material accumulates on the surface of the second solvent. Fig. 1 illustrates micrographs of several phase-separated particles that have appeared in previous literature along with sketches of the particle types and particle categories considered in this report.

Our laboratory has a strong interest in the measurement and modeling of aerosol optics [8–16]. Given the apparent inclination for materials in aerosols to phase separate, it is important to understand how this phase separation may influence optical properties of aerosols. Phase separated particles may exhibit additional interfaces of differing refractive index and/or increased surface area relative to homogeneous particles. As a result, the light

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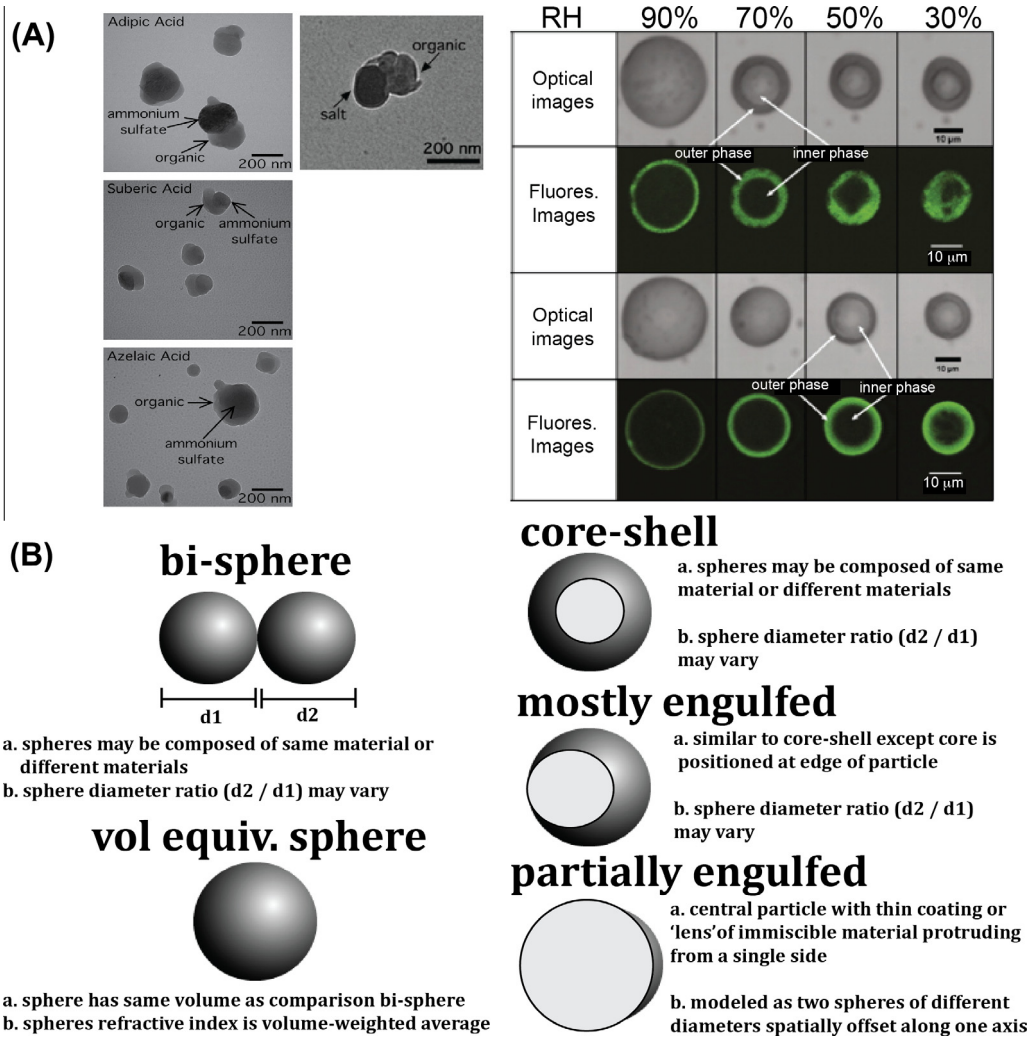

Fig. 1. (A) Micrographs from previous literature providing evidence for phase separation within atmospheric particulate matter. Micrographs are reprinted with permission from *Proc. Nat Acad Sci* 2012;109(33):13188–13193, *Anal Chem* 2014;86(5):2436–2442, and *J Am Chem Soc* 2013;135(43):16046–16049. The latter two figures are copyright American Chemical Society. (B) Particle models used for the discrete dipole modeling in this work. For the bi-sphere, core–shell, mostly engulfed, and partially engulfed cases the individual sphere diameters and refractive indices were varied.

scattering and absorption properties of the aerosol may be altered because of the biphasic behavior. In essence, the phase separation may cause increased or decreased scattering and absorption. Because aerosol scattering and absorption is believed to affect Earth's climate through direct radiative forcing, understanding the effect of phase separation upon radiative transfer is an important goal.

Lang-Yona et al. [17] have previously investigated core–shell geometries, but to the best of our knowledge this manuscript is one of the first to consider bi-spherical and engulfed geometries caused by phase separation. Here, we use a publically available discrete dipole code (ADDA) [18] to model light scattering and absorption for various phase-separated particles and compare results to volume-averaged equivalent spheres. We carefully constrain the modeling experiments to maintain constant particle volume for the comparison test cases, but simply distribute the volume amongst different shapes. Again, Fig. 1 presents explanatory drawings of each case along with micrographs that inspire each model. The micrographs have all appeared in previous literature. We constrain refractive indices used to reflect authentic aerosol components as much as possible.

Methods

Discrete-dipole modeling

Determination of light scattering and absorption cross-sections (C_{scat} or C_{abs}; μm^2) for individual particles were accomplished through the Amsterdam Discrete Dipole Approximation code [18] (ADDA) downloaded from https://code.google.com/p/a-dda/. This code allows the user to adjust the diameters and refractive index for each sphere independently. For this work, a wavelength of 0.53 microns was always used. Since the optical effects for particles may depend upon their orientation with respect to the incident light beam, averaging optical results for many orientations of the particle is required. The ADDA program treats this problem by sequentially varying three Euler angles (α, β, γ) that define the particles orientation with respect to the incident beam. Alpha was modified from 0° to 360° in 32 steps, beta from 0° to 180° in up to 17 steps, and gamma from 0° to 360° in up to 16 steps. Therefore, the optical cross sections and S_{11} element of the scattering matrix we report for bi-spheres represent values averaged over many orientations. The accuracy of discrete dipole computations