**PHASE STATE OF ATMOSPHERIC NANOPARTICLES: GEOMETRIC ANALYSIS OF THE FREE VOLUME ACCESSIBLE TO SMALL MOLECULES**

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**ABSTRACT**

We analyze atomistically-detailed structures of atmospheric nanoparticles using Delaunay tessellation followed by Monte Carlo integration to relate free volume to their phase state. The nanoparticles studied consist of water, organic molecules (such as cis-pinonic acid), and inorganic species (such as sulfate and ammonium ions). We investigate the effect of relative humidity and organic content of the particle on its free and accessible volume to diffusing molecules. Our analysis provides information concerning the distribution of empty pores in the nanoparticle, the available volume in which a guest molecule (e.g., water) can reside, and the connection of the corresponding cavities. Indirectly, our geometric analysis provides accurate measures of the nanoparticle's shape, surface area, and total volume.

Unoccupied and accessible volumes in the organic islands of the nanoparticles, or at their interfaces with other substances, are larger than those in their aqueous or inorganic domains. Pores accessible to a water molecule are mostly located in the nanoparticles’ intermediate and outer regions that are dominated by organic molecules. As the organic mass fraction of the nanoparticle increases and the relative humidity (RH) decreases there are larger pores accessible to a water molecule. The free volume in the pure inorganic domains is reduced at high RH, as do the organic-inorganic interfacial domains, implying a full separation of organic molecules from inorganic ions (with the latter showing a strong preference to accumulate in the internal areas of the nanoparticle).

Under the same circumstances, cis-pinonic acid was found to form a single island in the external area of the nanoparticle with a density almost equal to that in its pure bulk phase. The inorganic mass, on the other hand, tends to form a single continuous island with a density very close to that of ammonium sulfate, indicating the existence of a solid-like phase at the particle’s center. At lower RH water can be found in several islands of similar size. At higher levels of RH, on the other hand, water shows a tendency to form one large island, with several smaller islands around it.

**KEYWORDS:** Atmospheric Nanoparticles, Geometric Analysis, Free Volume

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