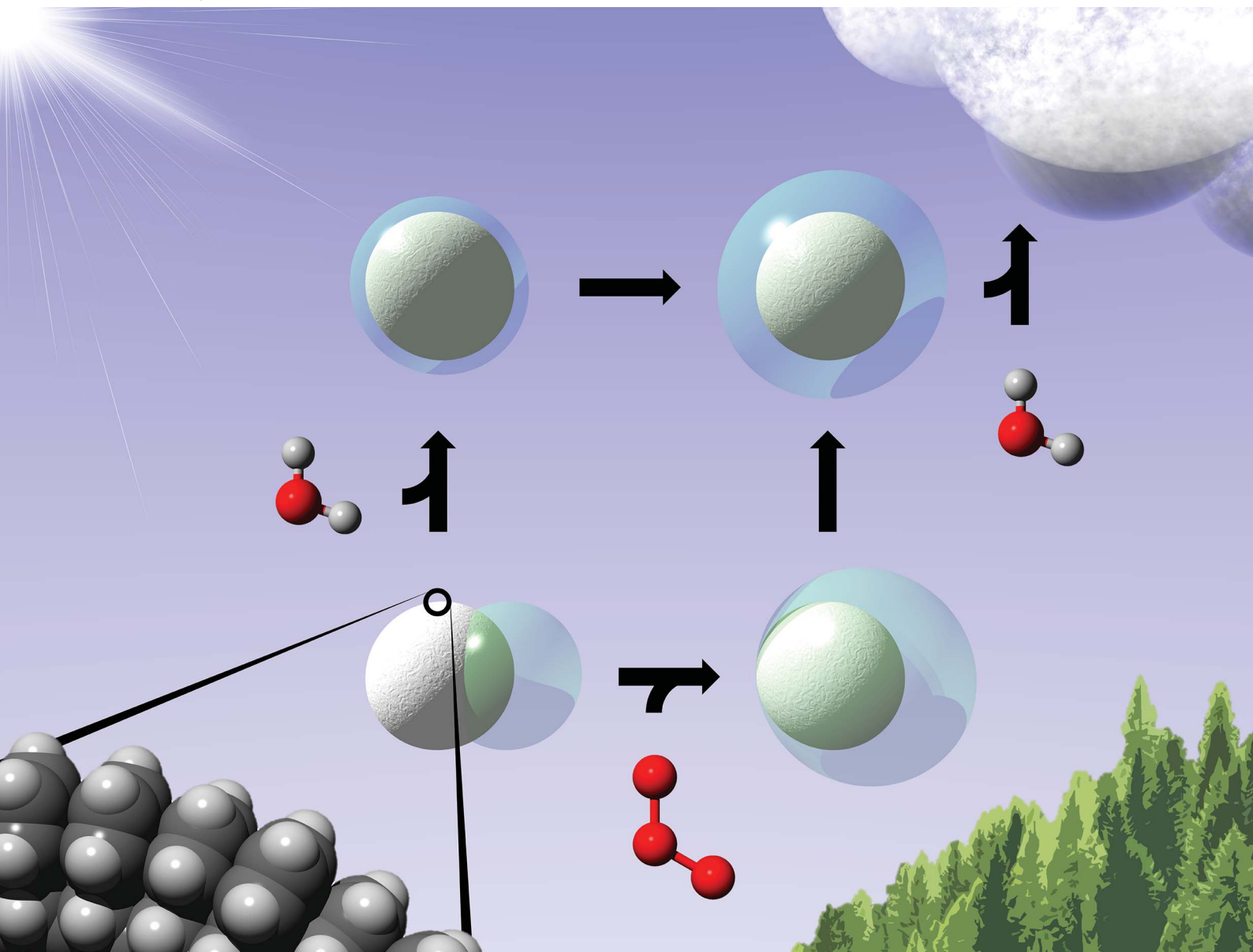


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## Partitioning of secondary organic aerosol onto nanoplastics leading to hygroscopic partially-engulfed particles†

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Nanoplastics have been shown to be emitted into the atmosphere over land and the ocean and transported long distances to remote regions. During their atmospheric lifetime, nanoplastics may influence climate directly by absorbing and scattering sunlight and indirectly by enhancing ice or liquid cloud formation. Bare nanoplastics will not influence liquid cloud formation, since they are hydrophobic, but nanoplastics internally mixed with hygroscopic species during atmospheric aging have the potential to act as cloud condensation nuclei. Here, we report measurements of hygroscopic growth of initially 100, 200, and 250 nm polystyrene nanoplastics internally mixed with secondary organic aerosol (SOA) from the ozonolysis of  $\alpha$ -pinene in a smog chamber. SOA formation and water uptake were quantified using parallel differential mobility analyzers at <10 and 90% relative humidity (RH), respectively. Interestingly, early in each experiment, at low SOA volumes, the mobility diameters of the humidified particles became smaller than those of the dry particles, despite certain water uptake. This discrepancy indicates that the particles at low RH have a non-spherical, partially-engulfed morphology. When they are humidified, the SOA takes up water, becomes less viscous, and coalesces around the nanoplastic, so the coated particles adopt a spherical morphology. Eventually, the SOA volume is high enough that the dry particles are also spherical, and the apparent volume of water scales linearly with the volume of SOA, as expected. A fit to measurements during this stage gives a hygroscopicity parameter of 0.02. Together, these observations have important implications on both the direct and indirect climate effects of nanoplastics in the atmosphere.

### 1. Introduction

Plastic particles with dimensions in the range of nanometers have been observed in the atmosphere.<sup>1–3</sup> These nanoplastics

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#### Environmental significance

Plastic particles with dimensions in the nanometer range, or nanoplastics, are emitted over land and the ocean into the atmosphere, where they are exposed to condensable products of the gas-phase oxidation of volatile organic compounds. These products can partition onto the particles, transforming the initially hydrophobic nanoplastics into potential cloud condensation nuclei. Here, we report appreciable hygroscopic growth, a prerequisite for cloud droplet activation, of polystyrene nanoplastics coated with secondary organic aerosol from the ozonolysis of  $\alpha$ -pinene. Furthermore, we provide compelling evidence that under certain conditions, coating through partitioning can lead to partially-engulfed, rather than core-shell, morphologies, which may impact the direct and indirect climate effects of nanoplastics.

may be emitted into the environment directly or form from larger plastic pollution through chemical and physical processes.<sup>4–6</sup> They are small enough to be entrained over terrestrial sources, so their emission may increase with wind speed.<sup>7,8</sup> They can also be emitted over oceans,<sup>9–11</sup> where they tend to be concentrated at the sea surface microlayer, due to their low densities, ideally situated to be incorporated into sea spray aerosol upon wave breaking.<sup>12–14</sup> Because of their small dimensions, they can reside in the atmosphere for weeks, sometimes transported to remote regions, including the Arctic.<sup>15,16</sup> In turn, through wet and dry deposition, the nanoplastics are transferred from the atmospheric to the aquatic and terrestrial environments,<sup>7,17,18</sup> where they can continue to have a wide range of harmful influences on organisms.<sup>19–21</sup>

While they are in the atmosphere, nanoplastics may have direct and indirect effects on climate, by absorbing and scattering solar and terrestrial radiation and by influencing cloud formation, respectively.<sup>22,23</sup> Though all nanoplastics will scatter visible radiation, only those that are colored will strongly absorb at visible wavelengths. It is conceivable that colored nanoplastics whiten during their atmospheric lifetime, due to light-driven processing. Atmospheric aging is likely to also influence the indirect effects of nanoplastics, as the bare hydrophobic particles accumulate hygroscopic components. Bare and





was  $1 \text{ L min}^{-1}$ , so  $0.7 \text{ L min}^{-1}$  was drawn from the laboratory through a filter.

In the second branch, the particles were conditioned at high RH, specifically  $90 \pm 2\%$ , using a Nafion membrane humidifier (Perma Pure, MD-110-48S-4) before being classified. After they passed through the humidifier, the particles were directed through a length of copper tubing to allow 30 s for equilibration at high RH. The particles were then directed to the second DMA, which was equipped the same as the first, with the same flow rates. The sheath flow of this DMA was set to  $90 \pm 2\%$  RH, to match the humidified sample flow, using a second membrane humidifier. For each particle size spectrum (see Fig. S2†), or measurement distribution function,<sup>39,40</sup> the sample and sheath RH values agreed to within 2% during collection. The CPC sampled from the two DMAs alternately.

### 3. Results and discussion

Since our focus is on bare and SOA-coated nanoplastics, it was important that the initial particles were spherical with a uniform surface. In a previous study, a similar surfactant in aqueous suspensions of polystyrene was shown to form much smaller, hygroscopic particles, less than 100 nm in mobility diameter, externally mixed with the nanoplastics.<sup>34</sup> A comparison of the manufacturer-reported diameters, measured in suspension, and our mobility diameters, measured after aerosolization, are consistent with an external mixture (see Table S1†). To ensure the surface of the nanoplastics was uniform, we heated the particles to 473 K in the thermal denuder before injection into the smog chamber. If trace amounts of surfactant were present, this elevated temperature would promote desorption from the particle surface. Furthermore, this temperature is well above the glass transition temperature of polystyrene, 380 K, but below the melting point, 513 K.<sup>41</sup> Bispheres of polystyrene with point contacts have been shown to undergo coalescence to form spheres when heated above the glass transition temperature, due to surface tension, as the material becomes less viscous.<sup>33</sup> If any surface features were present, the decreased viscosity of the particles when heated would be expected to result in perfectly spherical particles upon cooling and vitrification. Volatility differential mobility analysis was performed by varying the temperature of the thermal denuder, and while no significant changes in mobility diameter were observed (see Fig. S3†), a slight drop is discernible for initially 100 nm particles just above the glass transition temperature (see Fig. S4†). Also, no water uptake to the conditioned polystyrene was observed, indicating that no traces of hygroscopic surfactant were present. Together, these observations confirm that the conditioned nanoplastics were spherical with a uniform surface.

The coatings of SOA were formed by gas-phase oxidation of  $\alpha$ -pinene in the smog chamber. A representative experiment with initially 250 nm nanoplastics is shown in Fig. 1. SOA formation as a function of time is quantified here in terms of the diameter growth factor, Gfd, which is the ratio of the mobility diameter during reaction to that of the bare nanoplastics (see ESI†). At reaction time zero, the particles in the



Fig. 1 Diameter growth factor and apparent coating thickness as functions of reaction time in the smog chamber for a representative experiment with initially 250 nm nanoplastics.

chamber were bare polystyrene, and the Gfd is one. As reaction progresses, oxidation products began partitioning to the particle phase, so the Gfd increases. Since the DMA was operated at  $<10\%$  RH, like the chamber, water does not contribute to this growth. Since  $\alpha$ -pinene was introduced with an excess of hexane, which is an effective hydroxyl radical scavenger without significantly altering the distribution of SOA species or the production of  $\text{HO}_2$  radicals,<sup>42–44</sup> the SOA was strictly from the ozonolysis of  $\alpha$ -pinene. By the end of the experiment, after nearly 250 min, the Gfd of the dry particles is 1.34 (see Fig. 1). Assuming the SOA coating is uniformly distributed, the average coating thickness is about 40 nm across the surface of the initially 250 nm nanoplastics. Comparable coating thicknesses have been measured for solid carbonaceous particles, specifically black carbon, exposed to ambient air in Houston, USA, for 10 to 15 h.<sup>45</sup> The apparent volume growth factor, Gfv, can be calculated from this timeseries, assuming the particles are spherical for the entirety of the experiment (see ESI†). Since the reaction kinetics can vary slightly between experiments, this apparent Gfv, instead of reaction time, is used as an independent variable in the subsequent discussion. In turn, the mass growth factor, Gfm, can be calculated to reach 2.68 at the end of the experiment (see Fig. S5†). The densities of polystyrene,  $\alpha$ -pinene SOA, and water are taken as 1.05, 1.28, and  $1.00 \text{ g cm}^{-3}$ , respectively.<sup>46,47</sup> By the end of the experiment, the dry particles are 63% SOA by mass (see Fig. S6†). Importantly, given the second-order rate constant for the ozonolysis of  $\alpha$ -pinene,  $8.4 \times 10^{-17} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ,<sup>48</sup> and the upper limit for the mixing ratio of ozone, 20 ppb, 55% of the initial  $\alpha$ -pinene was still present at the end of the experiment. By design, these reaction conditions allowed slow, steady growth of the coatings and ensured their composition was relatively uniform, as first-generation products formed for the duration of the experiment.

Additional growth of the SOA-coated nanoplastics due to water uptake was measured by conditioning and classifying the particles at high RH. In  $\kappa$ -Köhler theory, water uptake is





governed by the hygroscopicity parameter  $\kappa$ ,<sup>49,50</sup> which is defined by its impact on water activity,  $a_w$ , according to eqn (1).

$$\frac{1}{a_w} = 1 + \kappa \frac{V_s}{V_w} \quad (1)$$

Here,  $V_s$  is the volume of the dry, water-soluble particle before uptake, and  $V_w$  is the volume of water after uptake. In the smog chamber experiments, only the SOA coating is water-soluble, so  $V_s$  is taken as the volume of SOA,  $V_{\text{SOA}}$ . Eqn (1) can be rearranged to relate the volume of water to  $V_{\text{SOA}}$  according to eqn (2).

$$V_w = \kappa \frac{a_w}{(1 - a_w)} V_{\text{SOA}} \quad (2)$$

Typically, individual  $\kappa$  values are reported for SOA from distinct precursors, although  $\kappa$  may increase slightly with further oxidative aging of the SOA, in terms of the oxygen-to-carbon ratio.<sup>51</sup> In hygroscopic tandem DMA experiments,  $V_{\text{SOA}}$  is held constant, by setting the voltage of the first DMA, and the activity of water is ramped up to increase the volume of water,  $V_w$ .<sup>52–54</sup> Here, in contrast, the volume of SOA is increased, and the activity of water is held constant. We assume that the activity of water is equal the saturation ratio, neglecting the Kelvin effect for the SOA-coated particles.<sup>49,50</sup> Since  $\kappa$  and  $a_w$  are steady, the volume of water taken up by the particles will increase linearly with the volume of SOA partitioned onto the polystyrene. Surprisingly, between 0 and about 100 min, the Gfd of the humidified particles is lower than that of the dry particles (see Fig. 1). At 125 min, the two timeseries intersect, and afterwards the humidified particles are larger than the dry particles, as expected. Towards the end of the experiment, the two timeseries increase proportionally. In one experiment, the parallel DMAs were interchanged to rule out instrumental artefacts, yielding the same trends.

What is the origin of these unexpected observations? The difference between the Gfd values for the dry and humidified particles is quantified in terms of the hygroscopic volume growth factor, HGfv.<sup>26,55</sup> When the ozonolysis in the chamber begins, the HGfv decreases, eventually to a minimum value of about 0.95, before beginning to increase (see Fig. S7†). It returns to unity when the timeseries of Gfd intersect, *e.g.*, at 125 min in Fig. 1. With further reaction, the HGfv increases rapidly to reach a plateau at about 1.07 after 150 min. If this trend in HGfv is plotted as a function of the apparent SOA coating volume, as shown in Fig. 2, the plateau occurs at a Gfv of about 2. Analogous trends for initially 100 and 200 nm nanoplastics are shown in Fig. S8.† The apparent volume of water can also be calculated from this timeseries. Note that the apparent volumes of SOA and water are based on the assumption that the particles are spherical throughout each experiment. Since the nanoplastics are spherical to begin the experiment, as described above, this assumption would be true if the coating occurred uniformly across the nanoplastic surface. The seeming loss of water from already dry particles that are non-volatile demonstrates that the coated particles adopt partially-engulfed, rather than core-shell, morphology at small SOA volumes. SOA from  $\alpha$ -pinene is known to be glassy at low RH but less viscous at high RH.<sup>56</sup> Consequently, the coated nanoplastics classified by the DMA at

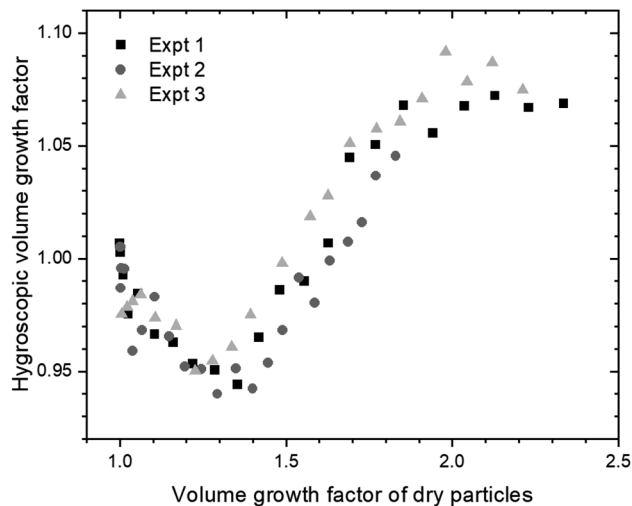


Fig. 2 Hygroscopic volume growth factor as a function of the volume growth factor of the dry particles, a measure of the SOA coating volume, for three experiments with initially 250 nm nanoplastics, illustrating intra- and inter-experiment variability. There is more scatter in the hygroscopic volume growth factor than in the individual time series of diameter growth factors, because the hygroscopic volume growth factor is a measure of the small difference between these time series.

low RH retained the non-spherical morphology of particles in the dry chamber, whereas those classified by the DMA at high RH coalesced to give spherical morphology. Importantly, although smaller values have been determined in the free molecular regime,<sup>57</sup> the dynamic shape factor,  $\chi$ , of bispheres in the continuum (or viscous) flow regime is known to be 1.10,<sup>58,59</sup> which is more than enough to allow for the degree of restructuring observed here and broadly consistent with partially-engulfed morphology at low RH.

The relationship between the volume of water and the volume of SOA, according to eqn (2), can further highlight these differences in morphology. Since  $\kappa$  and  $a_w$  are steady, the relationship should be linear. As shown in Fig. 3, the apparent volume of water drops below zero at early reaction times, *i.e.*, small SOA volumes. During this period, the particles in the chamber, at low RH, have partially-engulfed morphology. When they are humidified before classification in the second DMA, the SOA takes up water, transitions to liquid, and fully encapsulates the polystyrene to give spherical core-shell particles at all SOA coating volumes. At low RH, significantly more SOA volume must accumulate to fully encapsulate the polystyrene and give spherical particles; in this case, the polystyrene may be uncentered in the SOA coating. The apparent volume of water increases and returns to zero at the intersection of the Gfd timeseries for the dry and humidified particles. Once the particles become spherical at low RH, at large SOA volumes, the volume of water scales linearly with the SOA volume, as initially expected. The SOA volume required to reach spherical morphology at low RH increases with the diameter of the nanoplastics (see Fig. 3), because they must be fully encapsulated.





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