

## New Multiphase Chemical Processes Influencing Atmospheric Aerosols, Air Quality, and Climate in the Anthropocene

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Hang Su, Yafang Cheng,\* and Ulrich Pöschl



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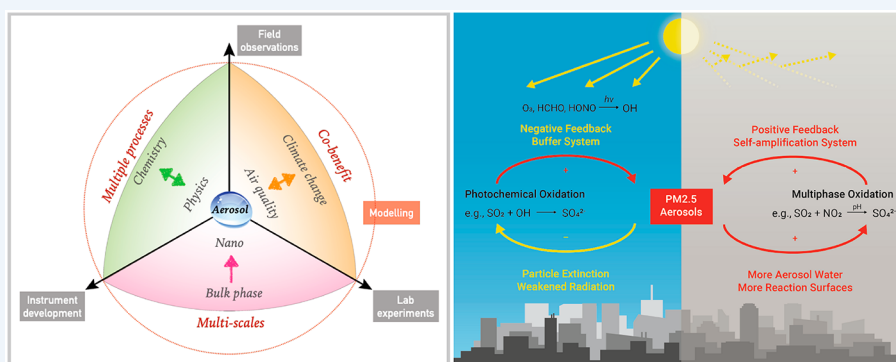


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**CONSPECTUS:** Atmospheric aerosols and fine particulate matter (PM<sub>2.5</sub>) are strongly affecting human health and climate in the Anthropocene, that is, in the current era of globally pervasive and rapidly increasing human influence on planet Earth. Poor air quality associated with high aerosol concentrations is among the leading health risks worldwide, causing millions of attributable excess deaths and years of life lost every year. Besides their health impact, aerosols are also influencing climate through interactions with clouds and solar radiation with an estimated negative total effective radiative forcing that may compensate about half of the positive radiative forcing of carbon dioxide but exhibits a much larger uncertainty. Heterogeneous and multiphase chemical reactions on the surface and in the bulk of solid, semisolid, and liquid aerosol particles have been recognized to influence aerosol formation and transformation and thus their environmental effects. However, atmospheric multiphase chemistry is not well understood because of its intrinsic complexity of dealing with the matter in multiple phases and the difficulties of distinguishing its effect from that of gas phase reactions.

Recently, research on atmospheric multiphase chemistry received a boost from the growing interest in understanding severe haze formation of very high PM<sub>2.5</sub> concentrations in polluted megacities and densely populated regions. State-of-the-art models suggest that the gas phase reactions, however, are not capturing the high concentrations and rapid increase of PM<sub>2.5</sub> observed during haze events, suggesting a gap in our understanding of the chemical mechanisms of aerosol formation. These haze events are characterized by high concentrations of aerosol particles and high humidity, especially favoring multiphase chemistry. In this Account, we review recent advances that we have made, as well as current challenges and future perspectives for research on multiphase chemical processes involved in atmospheric aerosol formation and transformation. We focus on the following questions: what are the key reaction pathways leading to aerosol formation under polluted conditions, what is the relative importance of multiphase chemistry versus gas-phase chemistry, and what are the implications for the development of efficient and reliable air quality control strategies? In particular, we discuss advances and challenges related to different chemical regimes of sulfate, nitrate, and secondary organic aerosols (SOAs) under haze conditions, and we synthesize new insights into the influence of aerosol water content, aerosol pH,

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phase state, and nanoparticle size effects. Overall, there is increasing evidence that multiphase chemistry plays an important role in aerosol formation during haze events. In contrast to the gas phase photochemical reactions, which are self-buffered against heavy pollution, multiphase reactions have a positive feedback mechanism, where higher particle matter levels accelerate multiphase production, which further increases the aerosol concentration resulting in a series of record-breaking pollution events. We discuss perspectives to fill the gap of the current understanding of atmospheric multiphase reactions that involve multiple physical and chemical processes from bulk to nanoscale and from regional to global scales. A synthetic approach combining laboratory experiments, field measurements, instrument development, and model simulations is suggested as a roadmap to advance future research.

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## 1. INTRODUCTION

The term “Anthropocene” has been suggested to describe the current geological epoch, in which human activities are exerting increasing impacts on the planet’s climate and ecosystems.<sup>5</sup> Production of anthropogenic aerosols and fine particulate matter is among the activities that strongly affect human health and climate in the Anthropocene.<sup>5,6</sup> Unlike the well-known positive radiative forcing of carbon dioxide and other long-lived greenhouse gases, the radiative forcing of atmospheric aerosols is highly uncertain, depending on particle composition, properties, and interactions with clouds. Poor air quality associated with high aerosol particle concentrations is among the leading health risks worldwide.<sup>7</sup> In addition, aerosols of biological origin (e.g., airborne viruses and bacteria, fungal spores, and pollen) are essential for the reproduction and spread of organisms across various ecosystems and for transmission between humans, animals, and plants.<sup>8</sup>

Multiphase and heterogeneous chemical reactions on the surface and in the bulk of aerosol particles can influence the composition and gas-particle partitioning of atmospheric aerosols.<sup>6</sup> The challenge in understanding atmospheric multiphase chemistry comes from its intrinsic complexity of dealing with the matter in multiple phases and the difficulties of distinguishing the effects of small amounts of particulate matter from the rates and uncertainties of chemical reactions between gas phase species that are typically more abundant. Moreover, the rates of multiphase reactions depend on matrix effects and multicomponent interactions that are not affecting the mono-, bi-, and termolecular reactions that dominate atmospheric gas phase chemistry. Thus, experimental results obtained for multiphase reactions are more difficult to interpret and to extrapolate between laboratory and atmospheric conditions.<sup>9</sup>

Wet deposition was early recognized as an important multiphase process efficiently removing trace gases and aerosol particles from the troposphere.<sup>10</sup> On the other hand, the aqueous phase oxidation of SO<sub>2</sub> was found to be an important source of sulfate.<sup>11</sup> The importance of multiphase processes for global atmospheric chemistry was further highlighted in the investigation of the Antarctic ozone hole and stratospheric ozone depletion.<sup>12</sup> Tropospheric ozone chemistry and the oxidation capacity and self-cleaning of the atmosphere were also found to be influenced by the uptake of reactive oxygen and nitrogen species like HO<sub>2</sub>, NO<sub>2</sub>, NO<sub>3</sub>, N<sub>2</sub>O<sub>5</sub>, and HNO<sub>3</sub> by aerosols and clouds.<sup>13,14</sup> Among recent scientific developments and challenges are the contributions of multiphase chemical reactions to the formation of sulfate, nitrate, and secondary organic aerosols (SOAs) in haze and fog and the role of aerosol pH and phase state.<sup>1,3,4,15–20</sup> Besides airborne particles, multiphase processes also occur at the planetary surface where they play a key role in the exchange and biogeochemical cycling of reactive species between the atmosphere, biosphere, and hydrosphere.<sup>6,21</sup> For example, HONO and OH radicals originate from chemical and biochemical processing of reactive nitrogen in biological organisms, materials, and soils.<sup>22–26</sup>

Due to increasingly severe air pollution in densely populated regions, there has been growing interest in understanding the formation of severe winter haze in polluted urban air. The very rapid increase and high concentrations of particulate matter during haze events cannot be explained by traditional models of gas phase and aqueous atmospheric chemistry.<sup>2</sup> On the other hand, haze events with extremely high PM<sub>2.5</sub> concentrations and suppression of gas phase photochemistry by aerosol dimming provide an opportunity to explore the mechanisms and effects of atmospheric multiphase chemistry.<sup>2</sup>

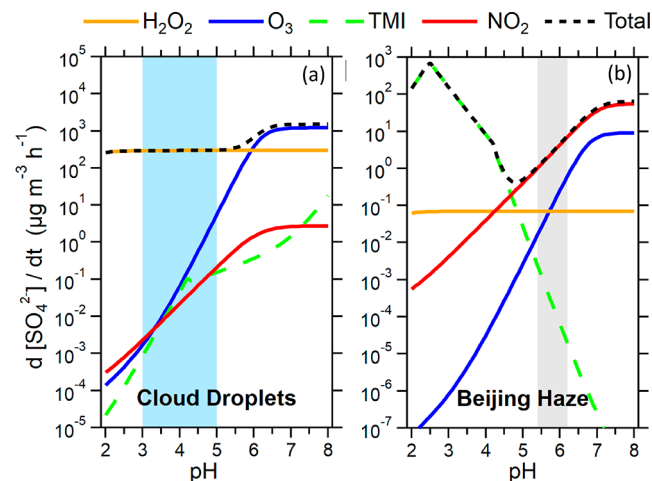
Our interest in atmospheric multiphase chemistry is stimulated by (a) the scientific challenge of explaining the formation of atmospheric aerosols and haze, (b) the aim to support the forecast and mitigation of air pollution, and (c) the desire to advance fundamental understanding of multiphase processes including phase transitions and nanosize effects. This

Account provides a review of our recent findings, current challenges, and future perspectives of multiphase chemical processes in atmospheric aerosols and haze.

## 2. RECENT DEVELOPMENTS

### 2.1. Sulfate and Nitrate Formation in Aerosol Water during Haze Events

In recent years, a severe and persistent winter haze has shrouded Beijing and the North China Plain, but the sources and formation pathways of particulate matter remained unclear.<sup>1,2,15</sup> Usually, gas phase photochemistry is assumed to play a central role in aerosol formation by transforming gaseous pollutants like SO<sub>2</sub>, NO<sub>x</sub>, and volatile organic compounds (VOCs) into particulate pollutants like sulfate, nitrate, and SOA. In severe haze, however, photochemistry is suppressed due to reduced solar radiation by the aerosol dimming effect. Nevertheless, enhanced production and accumulation of secondary particulate matter, especially sulfate, was observed under severe haze conditions.<sup>2</sup> Cheng et al.<sup>1</sup> discovered that high rates of sulfate production and large differences between observed and modeled sulfate concentrations were related to high aerosol water content (AWC), suggesting that aqueous phase oxidation in aerosol water, which follows different reaction pathways depending on aerosol pH and oxidant concentration levels, may play a key role. As shown in Figure 1, multiphase reactions of NO<sub>2</sub> and O<sub>3</sub> may



**Figure 1.** Aqueous-phase sulfate production by sulfur dioxide oxidation under characteristic conditions. Sulfate production rates for (a) cloud droplets and (b) Beijing haze plotted against pH values. Light blue and gray shaded areas indicate characteristic pH ranges for cloudwater under clean to moderately polluted conditions and aerosol water during severe haze episodes in Beijing, respectively. The colored lines represent sulfate production rates calculated for different aqueous-phase reaction pathways with oxidants: hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), ozone (O<sub>3</sub>), transition metal ions (TMIs), and nitrogen dioxide (NO<sub>2</sub>). The black lines represent the total reaction rates. Adapted from ref 1 under the terms of Creative Commons CC BY license.

dominate in aerosol water at pH > 4.5, while reactions of transition metal ions (TMIs) and H<sub>2</sub>O<sub>2</sub> may prevail at pH < 4.5.<sup>1</sup> A main contribution of Cheng et al.<sup>1</sup> was to bring multiphase haze chemistry in aerosols to people's attention and suggest its inclusion in state of the art atmospheric models in addition to the present cloud chemistry. Together with concurrent laboratory proofs of sulfate formation in aerosol water,<sup>15</sup> our study has triggered a series of laboratory and modeling studies to

further constrain the chemical kinetics of the aforementioned reactions, to identify new reaction pathways and evaluate their impact.

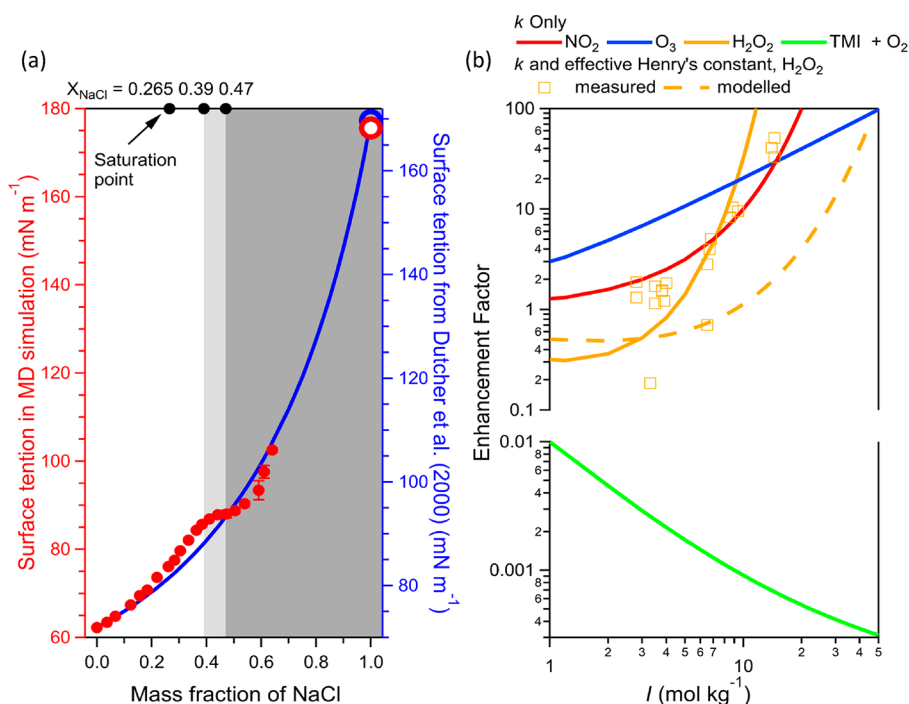
While the relevance of aqueous phase reactions in aerosol water has become widely accepted, the dominant pathways of SO<sub>2</sub> oxidation under haze conditions are still under debate. Understanding the chemical regime and major reaction pathways not only is a scientific challenge but also matters for air pollution forecasting and mitigation. For example, reducing emissions of NO<sub>x</sub> will lead to a cobenefit of decreasing both nitrate and sulfate formation when SO<sub>2</sub> oxidation is dominated by NO<sub>2</sub>. On the other hand, reducing emissions of NH<sub>3</sub> may reduce aerosol pH, which leads to a decrease of sulfate production when SO<sub>2</sub> oxidation is dominated by NO<sub>2</sub> or O<sub>3</sub> but to an increase when the TMI reaction pathway dominates (Figure 1).

Atmospheric chemistry and transport models (CTMs) usually consider two main pathways of particulate nitrate production: (1) gas phase oxidation of NO<sub>2</sub> by OH radicals forming HNO<sub>3</sub>, which partitions into the particle phase, and (2) gas phase reactions of NO<sub>2</sub> with O<sub>3</sub> leading to the formation of nitrate radicals and N<sub>2</sub>O<sub>5</sub>, followed by hydrolysis of N<sub>2</sub>O<sub>5</sub> in the aqueous phase. Haze conditions with high concentrations of PM<sub>2.5</sub> and high humidity favor the hydrolysis of N<sub>2</sub>O<sub>5</sub> in aerosol water. Despite the well-established mechanism, quantitative predictions remain challenging because the relevant kinetic parameters may vary with environmental conditions. For example, reactive uptake coefficients (γ) for N<sub>2</sub>O<sub>5</sub> on atmospheric aerosols varied over a wide range of 10<sup>-5</sup> to 10<sup>-1</sup> and were more strongly correlated with aerosol water content than with other parameters.<sup>16</sup> Zheng et al.<sup>27</sup> had to adopt high uptake coefficients close to 0.1 (similar to mineral dust) to reproduce the observed nitrate concentrations during severe haze in Beijing, while observation-based closure studies revealed uptake coefficients from 0.009 to 0.072 in Beijing and southern China.<sup>28,29</sup> It is desirable to improve the parametrization of γ for a better understanding of nitrate formation and its environmental impact.<sup>30,31</sup>

### 2.2. Secondary Organic Aerosol Formation in Haze and Fog

Organic aerosols (OAs) consist of a wide range of organic compounds originating from direct emissions or secondary formation in the atmosphere (SOAs). SOAs can be produced by gas phase oxidation of VOCs and subsequent partitioning into the particle phase or by multiphase chemistry of VOCs and semivolatile organic compounds (SVOCs) in the condensed phase of aerosols, haze, fog, or clouds.<sup>32</sup>

Our recent study showed that the relative mass fraction of SOAs in PM<sub>2.5</sub> decreased with increasing PM<sub>2.5</sub> and AWC under severe haze conditions,<sup>2</sup> suggesting that multiphase reactions contribute less to the production of SOAs than to the production of inorganic aerosol components (sulfate and nitrate). Nevertheless, the ratio of SOA to black carbon (BC) (which reflects the relationship to primary emissions) remained at the same level during severe haze as during less polluted periods where gas phase photochemistry prevails.<sup>2</sup> Very low photooxidant levels (~1 ppbv O<sub>3</sub>) during the severe haze indicate that gas phase production of SOA was largely suppressed, and thus the sustained SOA/BC ratio suggests substantial SOA production by multiphase chemistry.<sup>2</sup> This is confirmed by the results of the recent field campaign McFan (multiphase chemistry in fogs and aerosols in the North China Plain).<sup>33</sup> In this campaign, SOA production in aerosol water was



**Figure 2.** (a) Concentration-dependent surface tension of NaCl solution determined by Molecular Dynamic simulations. (b) Influence of ionic strength ( $I$ ) on the rate of aqueous sulfate-producing reactions. The enhancement factor is defined as the ratio of the modeled or measured sulfate production rate coefficient for nonideal solutions to the modeled rate assuming ideal solution. Solid lines, only the  $I$ -dependence of the aqueous-phase rate constant ( $k$ ) was considered;<sup>1</sup> dashed lines, the  $I$ -dependence of both  $k$  and effective Henry's constant for  $\text{SO}_2$  and  $\text{H}_2\text{O}_2$  were considered;<sup>65</sup> squares, measured enhancement factor.<sup>65</sup> Adapted with permission from refs 1 and 42 under the Creative Commons CC BY license.

only 40% lower than that during fog events, although the fog water content was orders of magnitude larger.<sup>33</sup> This suggests a higher efficiency of SOA production in the highly concentrated aqueous solutions of haze droplets compared to the more dilute solutions in fog droplets, similar to previous parcel model simulation results,<sup>32</sup> which may be due to enhancement effects of ionic strengths and activities, due to aerosol pH, or due to different reaction pathways such as oligomerization<sup>32</sup> or the formation of organonitrates and organosulfates.<sup>34</sup>

### 3. CURRENT CHALLENGES

Ongoing debates about the competition and variable dominance of different reaction pathways of haze formation can be addressed and resolved in terms of different chemical regimes. Tao et al.<sup>35</sup> showed that different chemical regimes and reaction pathways of sulfate formation prevail in different regions of the North China Plain (NCP), depending on reactant concentrations and other atmospheric conditions.<sup>35</sup> Changes in the relative importance of different reaction pathways can be efficiently explained and described in terms of different chemical regimes, but the reliability of predictions is still limited by a lack of understanding of aerosol pH, nonideality effects at high ionic strength, and aerosol phase state.

#### 3.1. Aerosol pH and Ionic Strength

Aerosol acidity is a key factor regulating the chemistry of atmospheric particles and their effects on air quality, climate, and human health. The aqueous phase oxidation of  $\text{SO}_2$  is a good example of the importance of aerosol pH. It controls the partitioning of semivolatile acidic or basic compounds between the gas and particle phase and vice versa. After uptake into the aqueous phase of deliquesced aerosol particles and fog or cloud droplets,  $\text{SO}_2$  molecules form bisulfite ( $\text{HSO}_3^-$ ) and sulfite

( $\text{SO}_3^{2-}$ ) ions in proportions that depend on particle acidity and pH. Accordingly, the effective Henry's law coefficient for the gas–particle partitioning of  $\text{SO}_2$  and related S(IV) species,  $H_{\text{S(IV)}}^*$ , increases by a factor of  $\sim 10$  as aerosol pH increases by a unit. Moreover, pH can influence reaction rate coefficients and oxidation pathways of  $\text{SO}_2$  and the related S(IV) species. For example, the aqueous phase oxidation rate coefficient of S(IV) increases for  $\text{NO}_2$  but decreases for  $\text{H}_2\text{O}_2$  when the pH increases.<sup>1</sup> In addition, aerosol acidity can also influence the formation of secondary organic aerosols through formation of oligomers and high molecular weight species.<sup>36</sup>

Despite its importance, the scientific understanding of aerosol pH is still limited due to the lack of direct measurements. Aerosol pH values typically vary in the range of 0 to 6, with higher and lower outliers under special conditions, but most literature values are based solely on thermodynamic model calculations.<sup>1</sup> Good agreement between modeled and measured partitioning of pH-sensitive compounds like  $\text{NH}_4^+/\text{NH}_3$  is frequently used as model validation, but the partitioning of other pH-sensitive species like HCl and  $\text{HNO}_3$  is often not so well reproduced. Moreover, the partitioning of  $\text{NH}_4^+/\text{NH}_3$  is a necessary but not a sufficient condition for good model performance on aerosol pH, because it can be reached by adjustments of ionic balance without getting the pH values right.

Thus, there is an urgent need for direct measurements of aerosol pH, which are difficult to realize with traditional techniques because of the small sample volume of nanometer- and micrometer-sized aerosols. Raman microspectroscopy has been used to determine the pH in a range of  $-0.7$  to  $1.3$  for laboratory-generated aerosol particles of  $\text{MgSO}_4 + \text{H}_2\text{SO}_4$  in the size range of  $10$ – $30 \mu\text{m}$  collected on quartz substrates.<sup>37</sup> This method was also applied to particles composed of other conjugate acid–base pairs covering a pH range<sup>38</sup> from  $-1.3$  to

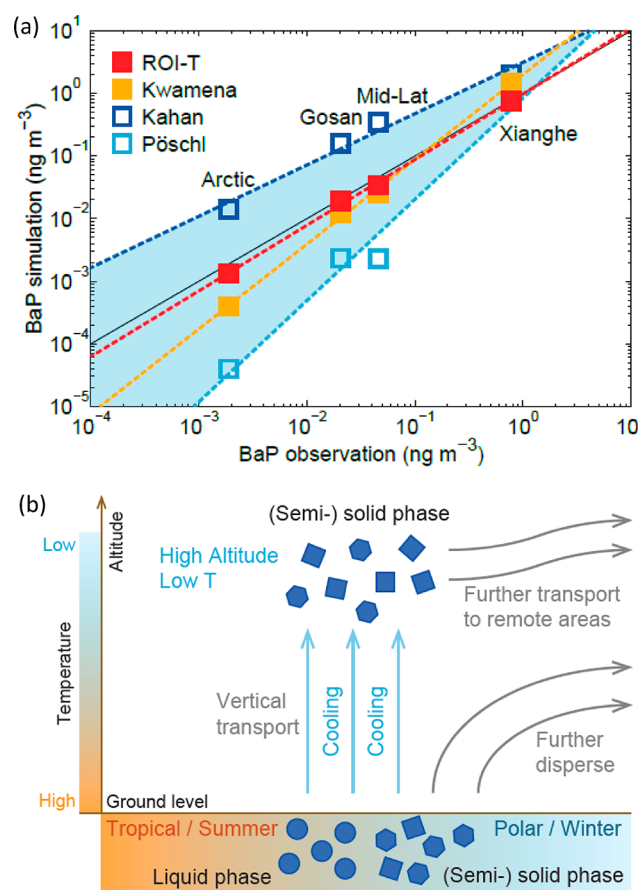
10, but so far the applications have been limited to lab systems of concentrated acid–base conjugates and it appears difficult to apply to atmospheric aerosol particles with smaller sizes, complex composition, and weak Raman signals. Surface-enhanced Raman spectroscopy and the introduction of nanometer-sized pH probes into the droplets can be used to enhance sensitivity, but ambient measurements remains an experimental challenge.<sup>39</sup> Recently, methods have been developed to collect aerosol samples on pH indicator papers<sup>40</sup> and to determine their pH over the atmospherically most relevant range<sup>41</sup> of 0–6. This approach is restricted to the collection of particle ensembles, but ongoing developments of microspectroscopic techniques are aimed at pH measurements of ambient airborne aerosols.

Compared to cloud and fog droplets, aerosol droplets can have extremely high solute concentrations and ionic strengths<sup>3</sup> up to several tens or a hundred moles per liter. The high concentrations and ionic strengths can lead to highly nonideal solution behavior and a strong influence on kinetic and thermodynamic parameters (reaction rate coefficients, surface tension, activity coefficients, etc.) (Figure 2).<sup>3,42</sup> For example, ionic strength can have a strong impact on the rate coefficients of S(IV) oxidation in aerosol water, and such effects need to be better constrained to assess and predict the relative importance of different reaction pathways and chemical regimes of sulfate formation.<sup>1</sup> On the other hand, aerosols might be the exclusive system to study and improve our fundamental understanding of physicochemical reactions under such high ionic strength, for example, aqueous ammonium sulfate droplets of diameter of ~6 nm reached a concentration of ~380 mol kg<sup>-1</sup> before crystallization,<sup>3</sup> about 1 order of magnitude more concentrated than the bulk saturated solution. Cheng et al.<sup>3</sup> developed a new analytical approach (differential Köhler analysis, DKA) to determine thermodynamic parameters of such systems, and more measurement techniques are in urgent need for these systems.

### 3.2. Aerosol Phase State and Nanosize Effects

Atmospheric aerosol particles can exist in liquid, solid, and semisolid phase states. The main factors controlling the phase state of aerosol particles include chemical composition, temperature, relative humidity, and particle size.<sup>3,43</sup> Phase transitions like melting, freezing, deliquescence, efflorescence and related changes in diffusivity, water uptake, particle size, and optical properties can strongly influence mass transport, the rate of multiphase chemical reactions, the atmospheric lifetime and dispersion of air pollutants, and the climate effects of aerosols.<sup>4,17,19,44</sup> For example, introducing an improved multiphase chemical reaction scheme with phase- and temperature-dependent kinetic parameters into regional and global CTMs led to greatly improved agreement between modeled and measured atmospheric concentrations of the hazardous polycyclic aromatic air pollutant benzo[a]pyrene (BaP; Figure 3).<sup>4</sup>

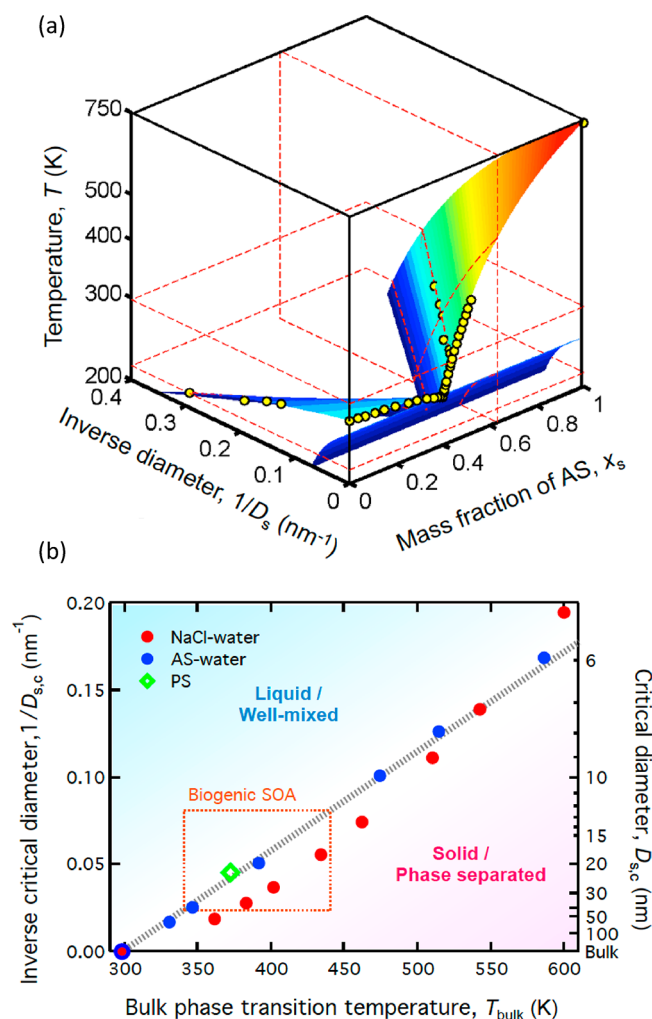
Inorganic salts usually undergo sharp liquid–solid phase transitions upon humidification and drying (deliquescence/efflorescence). However, organic substances often exhibit a gradual response to changes in temperature and humidity (hygroscopic growth), with gradual changes of viscosity and phase state between liquid, viscous or amorphous semisolid, and glassy solid with a wide range of diffusivity varying over several orders of magnitude.<sup>17–19,43,45</sup> Predictions of the glass transition temperature, viscosity, and diffusivity are of great importance for



**Figure 3.** (a) Comparisons of the ROI-T scheme and previous laboratory-derived schemes with global observations of benzo[a]pyrene (BaP, ng m<sup>-3</sup>). (b) Diagram of temperature/RH effects on BaP transport in ambient air. Reprinted with permission from ref 4 under the Creative Commons CC BY license.

assessing the physicochemical properties, interactions, and effects of organic aerosols in the atmosphere.<sup>4,46</sup> Ambient aerosols are usually a mixture of organic and inorganic species, and in addition to gradual or stepwise deliquescence and efflorescence transitions, they can exhibit liquid–liquid phase separations (LLPSs), which can influence the gas–particle partitioning of SOAs.<sup>47–49</sup>

In the nanometer size range, the particle diameter can have a strong impact on the humidity and temperature thresholds of liquid–solid phase transitions. Cheng et al.<sup>3</sup> extended traditional phase diagrams by including the inverse diameter as an additional dimension and parameter that has a similar effect as temperature on nanoparticle phase transitions (Figure 4). The new three-dimensional (3-D) phase diagram can be used to predict a critical diameter for liquid–solid phase transitions at constant composition and temperature and explain the observed size dependence of organic and inorganic aerosol phase state.<sup>18,20</sup> For different compounds and mixed systems, Cheng et al.<sup>3</sup> found that the inverse critical diameter depends nonlinearly on inverse phase transition temperature, which suggests a close connection between interfacial energy and phase transition enthalpy and can be combined with molecular dynamic simulations to provide insights into fundamental physicochemical relations and processes (Figure 4).<sup>3,42,50</sup>



**Figure 4.** (a) Three-dimensional liquid–solid equilibrium phase diagrams for the ammonium sulfate (AS)–water system in the coordinates of inverse diameter ( $1/D_s$ ), temperature ( $T$ ), and AS mass fraction ( $x_s$ ). The solid circles represent data of the bulk phase diagram of aqueous AS solution, size-dependent melting temperature of ice, and solubility of AS. The surfaces (colored by temperature) are estimated from polynomial fitting, showing the equilibrium between liquid and crystalline phases. (b) Dependence of critical diameter on bulk phase transition temperature. Inverse critical diameters of liquefaction at 298 K ( $D_{s,c}^{-1}$ ) are plotted against bulk phase transition temperatures ( $T_{\text{bulk}}$ ) for aqueous AS (blue solid circle), aqueous sodium chloride (NaCl, red solid circle), and low chain length polystyrene (PS, green open diamond). The data points are observations, and the dotted line is a linear fit to all data through the point of  $[298 \text{ K}, D_s^{-1} = 0]$ . The orange dashed line bounded area indicates the parameter range estimated for atmospheric biogenic secondary organic aerosol (SOA). Reprinted with permission from ref 3 under the Creative Commons CC BY license.

#### 4. FUTURE PERSPECTIVES

A key question in studying aerosol multiphase reactions is how to identify and quantify their contribution to the budget of aerosol particles. This requires a closure study, the success of which is subject to the level of understanding and uncertainties in laboratory experiments, field measurements, and model simulations.

#### 4.1. Laboratory Experiments

Laboratory study is a common approach to study key parameters of certain multiphase reactions. A series of techniques have been developed including coated flow tube reactors, liquid jet, droplet, and bubble apparatuses, aerosol chambers, Knudsen cells, and single particle levitation technique. These techniques can be combined with different detectors to measure the loss or production of gas and aerosol phase compounds or other tracer signals in multiphase reactions, which is then used to further derive kinetics and thermodynamics of chemical reactions, mass accommodation coefficient, or condensed phase diffusivity.

These lab-determined reaction parameters are important to understand the impact of multiphase reactions. Uptake coefficient ( $\gamma$ ) is one of the most commonly used parameters in models. It represents the probability that molecules colliding with the surface are taken up by the condensed phase. However, there are a few caveats concerning its application in modeling atmospheric relevant reactions.

First, the lab system (one or a few gases and simple aerosols) differs from that in the real atmosphere (multiple gases and complex aerosols). This is often not an issue for atmospheric gas phase reactions mainly dealing with a single molecule or bimolecular or trimolecular collisions, of which the collision and reaction are hardly affected by the presence of other molecules due to the extremely low probability. In multiphase reactions, aerosols may concentrate other trace gases and increase their chance to interact and react with the target compound, resulting in a different reaction mechanism and uptake coefficient. In addition, the difference in aerosol compositions and mixing state may also lead to different reactivity in multiphase reactions.

Second, the lab experiment may not capture the sustainability and reversibility of multiphase reactions under ambient conditions. In the atmosphere, aerosol particles can have a lifetime from a few days to weeks, which is often longer than the time scale of lab experiments. Early studies suggest that the initial high uptake coefficient of  $\text{NO}_2$  on soot cannot be maintained over atmospherically relevant time scales.<sup>51,52</sup> Thus, the uptake coefficient determined by experiments with a reaction time of a few tens or hundreds of microseconds needs to be further evaluated before application in models.<sup>53,54</sup> In addition, in reversible uptake, aerosols can either act as a source or a sink depending on the gas concentration and ambient conditions. In this case, model parametrizations of gas uptake need to account for both adsorption–desorption and chemical reactions.<sup>55</sup>

Another potential problem may arise when studying multiphase photochemistry using filter-based methods. In these experiments, aerosol samples were collected on filters and exposed to UV or visible light to get an uptake coefficient or reaction rate at different light intensities. The photoenhanced reaction rate determined by a filter-based method may differ from the real reaction rate for aerosols because of the multiple scattering effects by the filter. This effect increases the chance for a photon to be absorbed (1.2–3.5 times higher),<sup>56</sup> resulting in a higher reaction rate. We recommend further investigation of this effect in aerosol kinetic studies.

#### 4.2. Model Simulations

Modeling is a key approach to evaluate and quantify the contribution and impact of multiphase reactions. Introducing models to assist analyses of lab and field measurement results can help in the following ways: (1) Models can aid understanding of detailed mechanisms and kinetics. The reaction rate

determined in the lab reflects a net effect of multiple processes and often shows a nonlinear feature. A kinetic multilayer model that explicitly resolves mass transport and chemical reaction at the surface and in the bulk of aerosol particles can reproduce these nonlinear features and extract underlying kinetic parameters.<sup>57</sup> (2) Models can detect missing sources or validate the current mechanism. The modeling results represent our expectations from the current knowledge. It is an effective way to validate a proposed mechanism through model–observation comparisons. While improved agreement often supports the importance of a certain mechanism, the presence of a gap implies a missing source or sink.<sup>58</sup> Note that introducing a new source or mechanism may not only influence the target compound but also change the budget of other relevant compounds or their other properties.<sup>59</sup> The latter also needs to be considered in the source and mechanism evaluation. (3) Models can help to quantify the impact of individual reaction pathways. This is often done by putting the lab-determined mechanism into a comprehensive 3-D model or a box model and estimating its impact through comparison with and without the new mechanism.

### 4.3. Field Experiments

Field measurements are carried out to measure the evolution of atmospheric compounds under real atmospheric conditions. Though field measurement results may not directly tell the mechanism, they provide a basis for further analysis:

- (1) Correlation studies of observed parameters are often used to detect potential precursors or mechanisms. Such correlations can be argued because variations of the target compound are also subject to processes other than multiphase chemistry, for example, change of air masses due to transport or gas phase chemistry. Furthermore, correlation does not imply causation, for example, the boundary layer development leads to a strong and similar diurnal variation for many pollutants.
- (2) Field measurements are often combined with model simulations to account for other processes. As aforementioned, this combination can help to detect missing sources or validate current mechanisms. People may argue that model simulations can be adjusted or tuned for better agreement at a single site. Thus, for a more robust validation, it is preferable to have a comparison at large spatial and temporal scales, for example, comparison of modeling results with worldwide long-term measurements.

There is increasing interest in using isotope measurements or other tracers (e.g.,  $\text{N}_2\text{O}$  and  $\text{ClNO}_2$ ) to estimate the contribution of multiphase chemistry. Based on measurements of oxygen isotope (oxygen-17 excess of sulfate), it was suggested that reaction with  $\text{O}_3$  contributes ~20% of aqueous phase sulfate production, while the rest was contributed by reaction with  $\text{NO}_2$  and  $\text{TMI} + \text{O}_2$ .<sup>60</sup> This approach can be possible if there are only two pathways that contribute to the change of isotopic composition. While there are more relevant reactions, additional measurements or assumptions are needed to further constrain the equation.

## 5. OUTLOOK

Overall, there is increasing evidence of the importance of multiphase chemistry in aerosol formation during haze events. It is more efficient in producing inorganic aerosols than organic aerosols. The high ionic strength and distinct pH in aerosol

water can either increase or reduce the rate of certain reactions compared to that in cloudwater. While most studies agree that the  $\text{N}_2\text{O}_5$  reaction is the main pathway producing nitrate, a consensus has not been reached for sulfate and SOA formation. Model calculation and a few studies suggest that aerosols mostly stay in a liquid phase during severe haze events, but the range of RH and  $T$  to maintain the liquid phase in the presence of organic aerosols is not clear. To further advance understanding of atmospheric multiphase chemistry, we have the following suggestions:

- (1) To effectively identify the atmospherically relevant reactions and to validate laboratory-determined kinetics in the presence of other gases or mixtures of other aerosols, it is desirable to extend the current kinetic studies from a relatively simple reaction system to a system reflecting the complexity of the real atmosphere, for example, an environment chamber filled with real atmospheric gases and aerosols. Using multiple parallel chambers, we could condition the chamber (changing RH,  $T$ , or certain reactants) and determine reaction rate constants in analogy to laboratory kinetic studies. Such a chamber system also avoids the influence of complicated transport processes, which interfere with the real production rate. Instead of using a complex 3-D model for closure study, a simple box model can then be used to check whether the current understanding is still valid and to shed light on the potential missing mechanism.
- (2) New techniques and design of experiments are needed. As many chemical reaction rates strongly depend on aerosol pH, its direct measurement will advance our understanding and improve model predictions. More knowledge is also needed on the kinetics and thermodynamics in solutions of high ionic strength. The difficulty is that the change of ionic strength may also change aerosol pH due to its influence on the equilibrium of acid dissociations. Decoupling of these two effects could be a technical challenge in the design of experiments. Moreover, including phase state measurements will greatly complement the current data set in field campaigns, providing a basis for model validations.
- (3) We need to promote the establishment of a 3-D comprehensive observation network at a global scale through international collaborations and initiatives.<sup>61</sup> The long-term observation network could be designed (1) to have comprehensive measurement parameters to facilitate closure studies for mechanistic understanding as in the SMEAR station<sup>62</sup> and ATTO station<sup>63</sup> and (2) to include routine aircraft measurements, for example, the CARIBIC online aerosol measurement project<sup>64</sup> to provide 3-D in situ information for satellite and model validations.
- (4) We suggest more comparative studies of multiphase chemistry during hazy days with that at nighttime and in fogs. Nighttime is characterized by a high abundance of AWC and air pollutants, which is the same on hazy days except for more solar radiation. If solar radiation is going to influence multiphase reactions, we would see a difference between nighttime and hazy days. The comparison of hazy days with foggy days may also shed light on our understanding of the ionic strength effect.

## AUTHOR INFORMATION

### Corresponding Author

**Yafang Cheng** – Max Planck Institute for Chemistry, Mainz 55128, Germany; [orcid.org/0000-0003-4912-9879](https://orcid.org/0000-0003-4912-9879);  
Email: [yafang.cheng@mpic.de](mailto:yafang.cheng@mpic.de)

### Authors

**Hang Su** – Max Planck Institute for Chemistry, Mainz 55128, Germany; [orcid.org/0000-0003-4889-1669](https://orcid.org/0000-0003-4889-1669)

**Ulrich Pöschl** – Max Planck Institute for Chemistry, Mainz 55128, Germany; [orcid.org/0000-0003-1412-3557](https://orcid.org/0000-0003-1412-3557)

Complete contact information is available at:  
<https://pubs.acs.org/10.1021/acs.accounts.0c00246>

### Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

### Notes

The authors declare no competing financial interest.

### Biographies

**Hang Su** is a Group Leader at the Max Planck Institute for Chemistry, Germany. He received his B.S. at Fudan University and Ph.D. at Peking University. He received the Arne Richter Award for Outstanding Young Scientists from European Geosciences Union.

**Yafang Cheng** heads the Minerva independent research group at the Max Planck Institute for Chemistry. She received her B.S. at Wuhan University and Ph.D. at Peking University. She completed postdoctoral positions at Leibniz-Institute for Tropospheric Research and the University of Iowa and became a “Bairen” professor at Peking University. She received the Schmauss Award from the German Association of Aerosol Research (GAef). Cheng’s scientific research is focused on aerosols and their impact on air quality and climate.

**Ulrich Pöschl** is the director of the Multiphase Chemistry Department at the Max Planck Institute for Chemistry and professor at the Johannes Gutenberg University in Mainz, Germany. He studied chemistry at the Technical University of Graz, and he has worked as a researcher and lecturer at the Massachusetts Institute of Technology and at the Technical University of Munich. Pöschl’s scientific research is focused on the effects of multiphase processes in the earth system, climate, and public health.

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