Particle Phase State and Aerosol Liquid Water Greatly Impact Secondary Aerosol Formation: Insights into Phase Transition and Role in Haze Events

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Abstract. The particle-phase state is crucial for reactive gas uptake, heterogeneous, and multiphase chemical reactions, thereby impacting secondary aerosol formation. This study provides valuable insights into the significance of particle-phase transition and aerosol liquid water (ALW) in winter particulate growth. Our findings reveal that particles predominantly exist as semi-solid or solid during clean winter days with ambient relative humidity (RH) below 30%. However, non-liquid to liquid phase transition occurs when the ALW mass fraction exceeds 15% (dry mass) at transition RH thresholds of 40-60%. During haze episodes, the transformation rates of sulfate and nitrate aerosols rapidly increase through phase transition and increased ALW by 48% and 11%, respectively, resulting in noticeable increases in secondary inorganic aerosols (SIA). The presence of abundant ALW, favored by elevated RH and higher proportion of SIA, facilitates heterogeneous and aqueous processes in liquid particles, leading to a substantial increase in the formation of secondary organic aerosols and elevated aerosol
oxidation. Consequently, the overall hygroscopicity parameters exhibit a substantial enhancement with a mean value of 23%. These results highlight phase transition as a key factor initiating the positive feedback loops between ALW and secondary aerosol formation during haze episodes over the North China Plain. Accurate predictions of secondary aerosol formation necessitate explicit consideration of the particle-phase state in chemical transport models.
1 Introduction

Submicron particles are ubiquitous in the nature, having great impacts on climate, visibility, and human health (Shiraiwa et al., 2011; Ravishankara, 1997; Pöschl, 2005; Lelieveld et al., 2015; Seinfeld et al., 2016; Hu et al., 2021). Phase state, a key parameter of particles, plays profound roles in the mass transport of reactive molecules between the gas phase and the particle phase (Marshall et al., 2018; Shiraiwa et al., 2011). This, in turn, influences the gas-particle partitioning of semi-volatile materials (Shiraiwa et al., 2013; Li and Shiraiwa, 2019), multiphase reaction rates of chemical species (Zhang et al., 2018; Mu et al., 2018), and even the ice nucleating activities of organic aerosols (OA) (Murray et al., 2010; Knopf and Alpert, 2023). Aerosol liquid water (ALW) contributes a substantial fraction of the mass in sub-micrometer particles on a global basis (Nguyen et al., 2016). Atmospheric particles with the presence of condensed water serve as suspended vessels of multiphase chemical reactions, leading to significant impacts on secondary aerosol formation, particle size growth, and air quality (Wu et al., 2018; Hodas et al., 2014; Liu et al., 2019). Therefore, a comprehensive understanding of particle-phase state and ALW is crucial for better evaluation of the related environmental effects.

In the real atmosphere, the particle-phase state varies significantly among solid, semi-solid, and liquid under different conditions, which specifically influenced by ambient relative humidity (RH), temperature, and aerosol chemical composition. For example, the atmospheric particles in the tropical rainforest over central Amazonia, which primarily consisted of secondary organic aerosols (SOA) derived from oxidation of isoprene, were observed to be in liquid state at RH > 80% (Bateman et al., 2016), but more non-liquid particles occurred with the impact of anthropogenic pollutants (Bateman et al., 2017). Liu et al. (2019) reported that particles with high mass fraction of inorganics and high RH were prone to be liquid in a subtropical coastal megacity. However, non-liquid particles appeared at RH < 60% in Beijing (Liu et al., 2017). Moisture can drive an RH-induced glass transition in particles, leading to a liquid state.
and a significant water uptake at high RH in the lower atmosphere (Mikhailov et al., 2009). Moreover, organic aerosols might be in solid state at upper tropospheric temperatures that below about 210 K (Koop et al., 2011). Therefore, the changing features of aerosol composition and ambient RH may alter the ALW and trigger the phase state variation. More studies are needed to clarify the relationship between aerosol composition, particle-phase state, and ALW.

After the implementation of “China’s Action Plan for Air Pollution Prevention and Control” in 2013, emissions of primary particulate matter and several gaseous pollutants have greatly reduced. However, the contribution and proportion of secondary inorganic aerosols (SIA) and secondary organic aerosols (SOA) have become increasingly significant (Lei et al., 2021; Wang et al., 2021b), especially during haze episodes in winter. As mentioned, particles changes from solid to liquid with elevated RH conditions during heavy haze episodes (Liu et al., 2017). In liquid particles, the gas-particle mass transfer for reactive gases can be greatly facilitated due to increased diffusion coefficients, and the thermodynamic equilibrium of semi-volatile compounds may be impacted to contribute to secondary aerosol formation (Shiraiwa et al., 2011; Jia et al., 2023). A recent field study by Gkatzelis et al. (2021) pointed out that the gas-to-particle partitioning in liquid particles enhances the uptake of water-soluble gas compounds, resulting in a 15-25% contribution of SOA mass during particulate pollution in Beijing. Many studies have demonstrated that the abundant ALW and high RH condition can greatly impact secondary aerosol formation processes (Xu et al., 2017; Wang et al., 2021a; Gkatzelis et al., 2021). However, there is still a lack of understanding regarding the role of phase state variations in secondary particulate pollution. In this study, we conducted a one-month field campaign in Beijing during winter to investigate the relationship between particle-phase state, ALW, and the chemical and physical processes involved in haze formation.
2 Methodology

2.1 Instruments and Measurements

Field campaigns were conducted in Beijing from 15th December 2020 to 10th January 2021 at the Changping campus of Peking University (40°8′N, 116°6′E). A detailed description of the sampling site can be found in previous studies (Wang et al., 2020d). The instruments were situated in the air monitoring laboratory, located on the top floor of the main building. A weather station (Met One Instruments Inc., USA), a suite of automatic gas analyzers (O₃, SO₂, CO and NOₓ) from Thermo Scientific and an Aerodyne Quadrupole Aerosol Chemical Speciation Monitor (Q-ACSM) were operated according to standard protocols (Ng et al., 2011) and necessary information as described in Text S1.

The particle rebound fraction ($f$) was measured using a modified three-arm impactor (Bateman et al., 2014) coupled to a condensation particle counter (CPC, model 3772, TSI Inc.) with a time interval of 3 minutes, as described in our previous work (Liu et al., 2017; Meng et al., 2021). The three-arm impactor consisted of three parallel impactors with different designs. One of the impactors had no plate, while the others had plate equipped with an uncoated plate and a grease-coated plate, respectively. The no-plate impactor provided the total throughput rate, while the solid surface of the uncoated plate let particle rebound, and the sticky surface of the grease-coated plate captured all particles that struck it. To measure the $f$, a valve system with three solenoids and two actuators was used to ensure that the particle populations passing through the three impactors were sequenced and were measured by the CPC. Thus, rebound fraction, $f$, was defined as:

$$f = \frac{N_2 - N_3}{N_1 - N_3} \quad (1)$$

where $N_1$ was the whole particle population, $N_2$ was the population of particles that did not strike plus the rebounded particles from the impaction plate, and $N_3$ was the...
population of particles that did not strike the impaction plate. Prior to measurement, we dried the particles to below 30% RH using a silica gel diffusion dryer. Then, 300 nm mono-disperse particles were selected by a Differential Mobility Analyzer (DMA, TSI model 3080). An RH adjustment system with two RH probes and a Nafion RH conditioner was employed to measure the RH conditions (ambient RH and impactor RH), as well as to adjust the impactor RH to match the real atmospheric RH. Weekly calibrations using standard ammonium sulfate and daily flow check were conducted (Liu et al., 2021; Liu et al., 2019). Typically, \( f < 0.2 \) or 0.1 are referred to the completely phase transition from non-liquid to liquid state (Pajunoja et al., 2016; Liu et al., 2017).

In this study, we consider \( f < 0.2 \) in the case of liquid state. The time series of \( f \) with an initial time resolution is shown in Figure 1, while the data presented in other figures are all displayed as hourly averages.

### 2.2 Data Analysis

The mass concentrations of organic, sulfate, nitrate, ammonium, and chloride in non-refractory particles (NR-PM\(_1\)) were analyzed using the standard ACSM data analysis software (v.1.5.10). A collection efficiency (CE) of 0.5 was applied to the dataset (Xu et al., 2017; Matthew et al., 2008). Positive matrix factorization (PMF) was performed on the organic mass spectra using the Igor Pro based PMF2.exe algorithm to resolve primary organic aerosols (POA) and SOA factors. The data and error matrices were pretreated following methods from previous studies (Zhang et al., 2011; Zhang et al., 2017). The key diagnostic plots are provided in supplementary (Figure S1-S2).

The aerosol liquid water content contributed by inorganics (ALW\(_{\text{inorg}}\)) in PM\(_1\) was estimated using the ISORROPIA-II thermodynamic model (Fountoukis and Nenes, 2007) with input of aerosol chemical composition measured by Q-ACSM. The particles were assumed to be in metastable state, and the reverse mode was used to calculate the ALW\(_{\text{inorg}}\) due to absence of gaseous HNO\(_3\) and NH\(_3\). Besides, ALW associated with organics (ALW\(_{\text{org}}\)) was considered using a simplified equation of \( \kappa \)-Köhler theory (Guo...
et al., 2015; Petters and Kreidenweis, 2007):

\[ ALW_{\text{org}} = V_{\text{org}} k_{\text{org}} \frac{a_w}{1-a_w} \]

where \( V_{\text{org}} \) is the volume concentration of organics with a typical density of 1.4 g/cm\(^3\) (Cerully et al., 2015), \( k_{\text{org}} \) is the hygroscopicity parameter of the organics, \( a_w \) represents the water activity, which is assumed to have the same value as RH. In this study, we used a fixed \( k_{\text{org}} \) of 0.06 to evaluate \( ALW_{\text{org}} \), which was the average value of the overall \( k_{\text{org}} \) in the consideration of POA and SOA contributions in the total non-refractory organics \((k_{\text{POA}} = 0 \text{ and } k_{\text{SOA}} = 0.1)\) (Wu et al., 2016; Gunthe et al., 2011). However, it should be noted that \( k_{\text{org}} \) has been found to exhibit a positive linear relationship with the aerosol oxidation degree, which varied among species (Chang et al., 2010; Duplissy et al., 2011). \( f_{44} \), the fraction of m/z 44 fragment signal to total organic signal, is widely used to represent the atmospheric aging process of OA species (Ng et al., 2010; Canagaratna et al., 2015). Real-time \( k_{\text{org}} \) was calculated by the parametrization of \( k_{\text{org}} = 1.04 \times f_{44} - 0.02 \), as reported by Kuang et al. (2020) for the North China Plain (NCP). The predicted real-time \( k_{\text{org}} \) ranged from 0.13 to 0.24, which was consistent with the variation range reported for winter Beijing (0.06-0.3) (Li et al., 2019; Jin et al., 2020).

For fixed \( k_{\text{org}} \), the contribution of organics to ALW was \(~12\%\) on average during the observation. However, considering the variation of real-time \( f_{44} \), organics were capable to provide more than 30\% and 20\% of the total ALW mass on average during clean and polluted days, respectively (Figure S3 and Text S2).

For a given internal mixture, the overall particle hygroscopicity \((k_{\text{total}})\) was calculated by a simple mixing rule by weighting the hygroscopicity parameters of the components by their volume fractions in the mixture (Petters and Kreidenweis, 2007):

\[ k_{\text{total}} = k_{\text{inorg}} \cdot \text{frac}_{\text{inorg}} + k_{\text{org}} \cdot \text{frac}_{\text{org}}, \]

Where \( \text{frac}_{\text{inorg}} \) and \( \text{frac}_{\text{org}} \) are the inorganics and organics volume fractions in NR-PM\(_1\), respectively. Considering the variability in the composition of inorganics and organics,
the hygroscopicity parameters of inorganics ($k_{\text{inorg}}$) was weighted by volume fractions. The main form of inorganic species (NH$_4$NO$_3$ and (NH$_4$)$_2$SO$_4$) in the urban atmosphere was considered due to the lower abundance of chloride in NR-PM$_1$. The volume fraction of each inorganic species was calculated based on the ion-pairing scheme as described in Gysel et al. (2007) with their gravimetric density (1720 kg m$^{-3}$ for NH$_4$NO$_3$ and 1769 kg m$^{-3}$ for (NH$_4$)$_2$SO$_4$) (Wu et al., 2016). The hygroscopicity parameters of NH$_4$NO$_3$ and (NH$_4$)$_2$SO$_4$ are 0.58 and 0.48, respectively following previous studies (Wu et al., 2016; Jin et al., 2020; Petters and Kreidenweis, 2007). For hygroscopicity parameters of organics ($k_{\text{org}}$), real-time $k_{\text{org}}$ were used as above, which effectively captured the characteristics of the investigated area in our study.

3 Results and Discussion

3.1 Chemical Composition and Phase State of Sub-micrometer Particles

Figure 1 shows the time series of meteorological parameters, chemical composition of NR-PM$_1$, gas pollutants, and particle rebound fraction from December 16, 2020, to January 10, 2021. The average mass concentration of NR-PM$_1$ was 15.8±16.8 μg m$^{-3}$ during the measurement period. During clean periods (NR-PM$_1$ < 20 μg m$^{-3}$), organics dominated the aerosol composition, accounting for ~45% of NR-PM$_1$ mass. Nitrate, sulfate, and ammonium contributed 20%, 16%, and 16% to total NR-PM$_1$ on average, respectively (Figure S4). However, several pollution episodes occurred with rapid growth in NR-PM$_1$ and ALW mass concentration with higher concentrations of NO$_x$ and SO$_2$, as marked by yellow shadow in Figure 1. These four polluted episodes typically started with ambient RH below 40% and higher O$_3$ levels (> 30 ppb) and mounted up with stagnant meteorological conditions bringing high RH (> 60% RH) and low surface wind speed (< 3 m/s). This meteorological pattern is commonly observed over the NCP during haze episodes (Sun et al., 2015; Sun et al., 2013). During these polluted episodes, nitrate increased rapidly accounting for an average of 33% of the total NR-PM$_1$ mass. ALW was minor during clean days, but increased up to 26% in
PM$_1$ during severe polluted episodes with NR-PM$_1 > 80$ μg m$^{-3}$ (Figure S5). The mass concentrations of POA and SOA both increased during these polluted episodes as shown in Figure 1d. Moreover, the mass contribution of SOA to total OA showed an upward trend in particulate mass, indicating the important contribution of secondary formation during haze formation (Figure S6).

As shown in Figure 1f, particle rebound fraction, $f$, varied with ambient RH from 1.0 to ~0.0 during the observation, indicating that particles possessed phase transition from non-liquid to liquid state. Similar patterns of particle-phase transition were found for several polluted episodes. Taking P4 as an example, $f$ remained stable at 0.8 with RH = ~20% during the initial period of stagnant conditions, but gradually dropped to ~0.1 along with the increasing RH and NR-PM$_1$ during the subsequent haze formation. In addition, we collected several PM$_{2.5}$ filter samples to characterize the bulk-phase viscosity during clean and polluted days based on poke-and-flow experiment, as described in our previous study (Song et al., 2022) and Text S3 (indicated by black and red frames in Figure 1f). As shown in Figure S7, the viscosity was proved to be higher than ~10$^8$ Pa s with a mean value of $f > 0.8$ during clean days, indicating that particles existed in a solid or semi-solid state. However, the viscosity was lower than ~10$^2$ Pa s with an average $f < 0.2$ under higher RH conditions during polluted days, indicating the liquid state. It should be noted that the viscosity measurement captured the bulk-phase viscosity for water soluble components in PM$_{2.5}$ filter samples, but the online measurement of $f$ depicted 300 nm particles representative of accumulation mode particles, which normally contributed the majority fraction of PM$_1$. While the differences in chemical composition between PM$_{2.5}$ filter samples and 300 nm particles may introduce uncertainties when comparing the phase state of the targeted aerosols, the viscosity results showed good agreement with the average variation of $f$ during the corresponding period. Further validation is still necessary to compare the two different techniques and will be displayed in our further study. To directly indicate the phase transition from the perspective of viscosity, RH-dependent $f$ was measured for these...
filter samples with known bulk-phase viscosity (Figure S8 and Text S4). As expected, the decreasing $f$ from $>0.8$ to $0$ covered the transition range from $\sim 10^8$ Pa s to $\sim 10^2$ Pa s, which indicated the consistent behavior of particle rebound and measured bulk-phase viscosity for the investigated aerosols.

### 3.2 Phase Transition Behavior of Sub-micrometer Particles

Figure 2a illustrates the frequency distribution of RH. $f$ as a function of RH were plotted in Figure 2b. During the observation, ambient RH was below 30% for more than half of the time with $f$ predominantly exceeding 0.8 under such conditions. When RH increased to $\sim 50$-60%, a majority of $f$ dropped to $<0.2$ along with the increasing NR-PM$_1$ mass. This means that particles went through a moisture-induced phase transition from non-liquid to liquid during haze formation when RH reached 60%, which aligned with our previous studies (Liu et al., 2017). Notably, some points with higher mass fraction of inorganics ($f_{\text{inorg}} > 0.7$) showed $f < 0.2$ at RH = 40-50%, indicating that particles with higher $f_{\text{inorg}}$ were already in a liquid state. Consequently, particles underwent phase transition with a relatively large RH range of 40-60%, exhibiting varying chemical compositions as marked by the red frame.

Particle-phase state is known to be sensitive to ALW by its unique plasticizer effect (Koop et al., 2011). In Figure 2d, $f$ as a function of ALW/NR-PM$_1$ were plotted to represent the relative water uptake of unit mass dry aerosols with corresponding particle rebound behaviors. Figure 2c displays the frequency distribution of three $f$ intervals in each ALW/NR-PM$_1$ bin. When ALW/NR-PM$_1 < 5\%$, the frequency of $f > 0.8$ was higher than 0.65, indicating that particles mostly stay in a more viscous non-liquid state with less water uptake capacity. When ALW/NR-PM$_1$ increased to 5-15\%, $f$ gradually decreased from 0.8 to 0.2, suggesting that the total water uptake gradually enhanced and lowered the viscosity to trigger the phase transition within this range. The non-liquid particles were dominant with the frequency of $f<0.2$ close to 0.8. When ALW/NR-PM$_1$ > 15\%, the frequency of $f<0.2$ dramatically increased from 0.2 to $\sim 0.8$, ...
reaching close to 1.0 at ALW/NR-PM$_1 > 25\%$ with higher particulate mass. This indicates that particles mostly convert to liquid as the mass fraction of ALW surpasses a certain threshold during haze formation. In general, a good correlation between ALW/NR-PM$_1$ and $f$ was observed. ALW/NR-PM$_1$, used as a mass-based hygroscopic growth factor (Chen et al., 2022; Liu et al., 2018), is suitable to quantify the moisture-induced phase transition capacity of atmospheric particles, and a value of 15\% can be the sudden change in the case of phase transition from non-liquid to liquid. It is suggested that caution should be exercised when using the above approach to characterize the phase state of targeted aerosols, as the measured $f$ was representative of accumulation mode particles that dominated the mass concentration of submicron particles (Seinfeld, 2006).

It is interesting to note that several points with ALW/NR-PM$_1 < 5\%$ and NR-PM$_1 > 30 \mu g/m^3$ exhibited lower rebound fraction ($f < 0.4$), which was attributed to the variation of RH background from high RH to low RH during the later stages of the haze episodes, as shown in Figure 2d and Figure S9. This suggests that liquid particles may not turn to be a more viscous semi-solid state in a brief period under dehydration process. There are two possible explanations for this phenomenon. Firstly, the presence of significant amounts of inorganic and organic compounds can alter the humidity conditions for deliquescence and efflorescence (Ushijima et al., 2021; Peckhaus et al., 2012). Secondly, these particles are likely become non-ideal mixing due to drying process that form core-shell structure (Shiraiwa et al., 2013; Ciobanu et al., 2009; Song et al., 2013). Studies have revealed that outer phase may form viscous organic shell to prevent water evaporation (Koop et al., 2011; Shiraiwa et al., 2013; Hodas et al., 2015), thus, the inner phase containing inorganics still keep liquid with residual water. However, it should be note that liquid-liquid phase separation was not optically detected under staged dehydration of filter-based Beijing PM$_{2.5}$ droplets by Song et al. (2022). Instead, they observed abrupt effloresced inorganics at ~30\% RH, which was much lower than (NH$_4$)$_2$SO$_4$ and NH$_4$NO$_3$ in pure form (Peng et al., 2022). This supports that
atmospheric particles are more likely to be metastable after liquification only if RH decreases to very low values.

3.3 Effects of Phase Transition and ALW on SIA Formation during Haze Episodes

We investigated the $f$ and secondary aerosols during four polluted episodes (P1 to P4) under stagnant weather conditions with WS $< 3$ ms$^{-1}$. Sulfur and nitrogen oxidation ratios, SOR ($nSO_4/(nSO_4 + nSO_2)$) and NOR ($nNO_3/(nNO_3 + nNO_2)$), commonly used as indicators for secondary inorganic transformation (Li et al., 2017), are plotted as a function of $f$ in Figure 3a and 3b. We found that SOR (NOR) remained in a lower level with a mean value of $\sim 0.27$ (0.08) at $f > 0.2$ for non-liquid particles, but increased significantly to $\sim 0.8$ (0.35) with increasing ALW/NR-PM$_1$ at $f < 0.2$. This indicates that the secondary formation of SIA is facilitated to a certain degree through phase transition and the increasingly higher ALW mass. It should be noted that particles can be non-liquid during haze episodes with $f = 1.0$-0.2. Interestingly, SOR and NOR remained in lower levels and did not show notable increase between $f = 1.0$-0.8 and $f = 0.8$-0.2, until particles accomplished the phase transition at $f = 0.2$-0.0 (Figure 3c1 and 3c2). As a result, the median SOR (NOR) increased to higher levels with an increment of 48% (11%) via phase transition was observed along with the increase in ALW.

From the perspective of phase state, the increasing mass fraction of ALW reduces the viscosity and triggers the phase transition, which have important roles in the gas-particle mass transfer during haze formation. It is suggested that the secondary transformation of SIA is impeded by limited mass transfer between gas and particle phase when particles are not fully converted into liquid state. However, these limited factors disappear or the dominant formation pathway changes after phase transition. As reported in previous studies, ALW facilitates the secondary formation of sulfate and nitrate via the promotion of heterogeneous reactions (e.g. $SO_2$ heterogeneous oxidation, $N_2O_5$ hydrolysis), gas-particle partitioning of semi-volatile components or aqueous-phase reactions on wet aerosols (Chen et al., 2022; Cheng et al., 2016; Wang et al.,...
However, aqueous-phase oxidation of SO$_2$ may be constrained before phase transition due to the low diffusivity of multiple oxidants (e.g. O$_3$, H$_2$O$_2$, and NO$_2$) in the particles, and it may become the dominant formation pathway in liquid particles (Ravishankara, 1997; Liu et al., 2020). Additionally, the partitioning of nitrate into particles following Henry’s Law may also be facilitated by the increased ALW due to enhanced diffusivity of dissolved precursors in liquid particles. In Figure 3d, the mass fraction of SIA ($f_{\text{SIA/NR-PM}_1}$) is plotted as a function of $f$. The $f_{\text{SIA/NR-PM}_1}$, ALW mass concentration, and RH were grouped and averaged corresponding to $f$ bin width of 10%.

We found that $f_{\text{SIA/NR-PM}_1}$ remained stable at $f = 1.0-0.4$, but steadily increased from an average of ~0.50 to ~0.65 with elevated RH levels (>40%) and decreasing $f$ (from 0.4 to 0.0). This indicates that SIA formation was limited for non-liquid particles with higher viscosity under lower RH conditions. However, ALW was steadily enhanced by the increasing RH and started to trigger the phase transition, thereby facilitating the SOR and NOR to a larger extent. Therefore, $f_{\text{SIA/NR-PM}_1}$ apparently increased with the increase in ALW at $f = 0.2-0.0$. The presence of more ALW in liquid particles was expected to promote the SIA formation by acting as multiphase reaction vessels (Zheng et al., 2015; Wang et al., 2020a; Wang et al., 2020b).

### 3.4 Effects of Phase Transition and ALW on SOA Formation during Haze Episodes

In Figure 4a and 4b, the ratio of SOA to POA (SOA/POA) is plotted as a function of $f$ during these four polluted episodes characterized by ALW/NR-PM$_1$ and $f_{44}$. For $f = 1.0-0.2$, particles possessed relatively lower SOA/POA values (1-2.5) with ALW/NR-PM$_1$ <15%, which was independent of NR-PM$_1$ mass concentrations. However, a noticeable increase in SOA/POA and elevated $f_{44}$ values were observed at $f = 0.2-0.0$, accompanied by increasing ALW/NR-PM$_1$ and NR-PM$_1$ mass. This indicates that more oxidized SOA was produced in liquid particles through the phase transition and the increasing mass fraction of ALW during haze formation. Interestingly, we observed that these liquid particles were primarily associated with polluted days during the nighttime (Figure S10). For these liquid particles, SOA/POA doubled to ~5.5 along with the increasing
compared to non-liquid particles, suggesting the important roles of phase transition and ALW in promoting the SOA formation through dark reactions during nighttime. From the perspective of phase state, phase transition was directly indicated by the decreasing $f$ during haze formation driving a large decrease in bulk phase viscosity from $>10^8$ Pa s to $<10^2$ Pa s as proved by viscosity measurement, which may enhance the gas-particle mass transfer. ALW reduces the viscosity and triggers the phase transition, thus facilitating the uptake of precursors and oxidants, and potentially altering the reaction pathway (Tillmann et al., 2010; Berkemeier et al., 2016; Li et al., 2018; Zhao et al., 2019).

For non-liquid particles, ALW facilitates the SOA formation via partition and heterogeneous uptake of water-soluble organics from gas phase into the particle phase, leading to a rapid increase in SOA along with ALW (Herrmann et al., 2015; Gkatzelis et al., 2021; Lim et al., 2010; El-Sayed et al., 2015). Subsequent aqueous-phase reactions may occur to form oligomers, organosulfates, and nitrogen-containing organics through radical or non-radical reactions (Surratt et al., 2007; Iinuma et al., 2007; Galloway et al., 2009; Lim et al., 2013; Wang et al., 2020c). However, these reactions may be limited in non-liquid particles by the lower diffusivity due to higher viscosity. In contrast, liquid particles provide unstrained mass transfer of necessary oxidants and precursors between gas and particle phase, which is favorable for aqueous-phase processing. It is well known that aqueous-phase processing can contribute more oxidized SOA (Xu et al., 2017; Ervens et al., 2011; Zheng et al., 2023). Recent field studies have demonstrated that oligomers or dicarboxylic acids were enriched in liquid particles from the reactive uptake of methylglyoxal during the severe haze episodes in Beijing (Zheng et al., 2021). These oxidation products formed through aqueous-phase reactions are typically more oxidized and less volatile than those formed through gas phase photochemistry (Ervens et al., 2011), which can be reserved in the particle phase and increased the SOA mass in total OA. Therefore, the significant growth of SOA/POA and $f_{44}$ after phase transition is attributed by the enhanced heterogeneous or aqueous-phase reactions in liquid.
particles with abundant ALW during the nighttime.

### 3.5 Positive Feedback Loops between ALW and Secondary Aerosol Formation Triggered by Phase Transition during Haze Episodes

In Figure 5a, the relationship between $k_{\text{total}}$ and RH is displayed. The $k_{\text{total}}$, ALW, and NR-PM$_1$ mass were grouped and averaged corresponding to an RH bin width of 10%.

When RH was below 30%, the averaged $k_{\text{total}}$ was ~0.35. However, it increased to 0.39 with higher ALW and NR-PM$_1$ mass at RH = 40-60%, and further rose to 0.43 with an average maximum ALW value of 56 μg/m$^3$ when RH reached 70-80%. This indicates that hygroscopic growth of particulate matter underwent two stages with increasing RH and NR-PM$_1$ mass, particularly at RH = 40-60% and RH > 70%. From the above discussion, we have demonstrated that the non-liquid to liquid phase transition was triggered by the increased ALW, with a transition RH threshold of 40-60% during haze episodes (as indicated by gradual color change in Figure 5a). Phase transition facilitated the formation of sulfate and nitrate aerosols, contributing higher proportion of SIA in total particles under higher RH conditions. Notably, this led to a continuous increase in the volume fraction of inorganics with increasing RH (Figure 5b). Besides, $k_{\text{inorg}}$ also slightly increased when RH reached 60% due to increased nitrate contribution in total SIA during haze episodes (Figure 5c and Figure S4). This may explain the first enhancement of $k_{\text{total}}$ at RH = 40-60%, which was mainly driven by the large increase in $\text{frac}_{\text{inorg}}$ favored by phase transition.

Furthermore, the increase in $k_{\text{total}}$, coupled with elevated RH levels, led to a greater abundance of ALW mass. Heterogeneous or aqueous-phase reactions were favored with increasing ALW, promoting the formation of more oxidized SOA in liquid particles. At RH > 70%, the significant increase in $k_{\text{org}}$ (~14%) compensated for the negative effect of decreased $\text{frac}_{\text{org}}$ on the total hygroscopicity contributed by organics ($k_{\text{org}}\text{frac}_{\text{org}}$), leading to a stable $k_{\text{org}}\text{frac}_{\text{org}}$ with increasing RH (Figure 5c and Figure S11). This, in turn, coordinated with the increased $\text{frac}_{\text{inorg}}$, resulting in the second enhancement of
As a result, phase transition accompanied by increasing ALW mass triggered a noticeable enhancement in $k_{\text{total}}$ with a mean value of 23% during haze episodes. The enhanced water uptake ability of aerosols is expected to contribute more ALW under elevated RH conditions, further facilitating the secondary aerosol formation and deteriorating air quality. These results indicate that the establishment of positive feedback loops between ALW and secondary aerosol formation was triggered by phase transition during haze episodes.

4. Conclusion and atmospheric implications

Our findings revealed that particles predominantly exist as semi-solid or solid during clean winter days with RH below 30%. However, non-liquid to liquid phase transition occurred when the ALW mass fraction surpassed 15% (dry mass) at transition RH thresholds ranging from 40% to 60%. Additionally, we observed a consistent pattern in the non-liquid to liquid phase transition during haze formation, as manifested by both particle-rebound fraction and bulk-phase viscosity measurements. Specifically, the decrease in $f$ from $>0.8$ to 0 corresponded to a viscosity transition ranging from $\sim 10^8$ Pa s to $\sim 10^2$ Pa s. During haze episodes, SOR and NOR rapidly increased through phase transition and increased ALW by 48% and 11%, respectively, resulting in noticeable increases in SIA. The presence of abundant ALW, favored by elevated RH and higher proportion of SIA, facilitates heterogeneous and aqueous processes in liquid particles, leading to a substantial increase in the formation of secondary organic aerosols and elevated aerosol oxidation. As a result, the overall hygroscopicity parameters exhibit a substantial enhancement with a mean value of 23%.

In our previous studies, we have revealed the positive feedback loops between ALW and anthropogenic SIA at elevated RH levels during haze formation (Wu et al., 2018; Wang et al., 2020b). The contribution of abundant ALW to SOA production has also been reported in various regions with active anthropogenic emissions, such as the Po Valley in Italy, southeastern U.S., and Beijing, China (Carlton and Turpin,
However, we observed that secondary transformation of SIA and SOA was significantly enhanced after phase transition with higher ALW mass during the observation. Our findings indicate that the secondary aerosol formation could be impeded on non-liquid particles due to limited mass transfer between gas and particle phase for relevant reaction components (Ravishankara, 1997; Shiraiwa et al., 2011; Abbatt et al., 2012; Ma et al., 2022), whereas it is facilitated in liquid particles. It is therefore recommended that non-liquid to liquid phase transition may be considered to be the kick-off for the positive feedback loops between ALW and secondary aerosol formation during haze events. This can be further supported by the case studies for varying polluted episodes, where episodes with phase transition generally exhibit higher secondary transformation rate of secondary aerosols compared to episodes without phase transition (Figure S12 and Text S5). This mechanism is expected to gain significance in other regions with abundant anthropogenic emissions and high background RH during haze formation.

Author contributions
X.X.Y.M. and Z.J.W. conceived the study. X.X.Y.M. conducted the experiments, analyzed the experimental data, and wrote the manuscript with contributions from Z.J.W., M.J.S., J.Y.L. and M.H. J.C.C. participated in the offline experiments and data analysis. Y.T.Q. and T.M.Z. participated in the field experiments and conducted the filter sampling.

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Competing interests
The authors declare that they have no conflict of interest.

Reference


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Figure 1. Time series of (a) wind speed (WS), wind direction (WD) and temperatures, (b) mass concentration of NR-PM$_1$ and ALW, (c) mass contribution of NR-PM$_1$, (d) mass concentrations of SOA and POA, (e) concentrations of gas pollutants (NO$_2$, NO, O$_3$, and SO$_2$), (f) rebound fraction and ambient RH during the field campaign. In panel (f), the black (red) frame with dashed line represents the non-liquid state (transition from non-liquid to liquid state) of bulk PM$_{2.5}$ droplets based on off-line viscosity measurement using poke-and-flow technique (Song et al., 2022).
Figure 2. The frequency distribution of ambient RH in each RH bin (a) and the frequency distribution of each $f$ interval in each ALW/NR-PM$_1$ bin (c). Rebound fraction $f$ as a function of ambient RH (b) and ALW/NR-PM$_1$ (d) during the observation. In panel (b) and (d), the scatter points are colored by $f_{\text{inorg}}$ in NR-PM$_1$ and the point size is scaled by NR-PM$_1$ mass concentration. The yellow and blue shadow represent the non-liquid and liquid phase, respectively.
Figure 3. SOR and NOR as a function of $f$ (a, b), relationship between SOR or NOR and three phase transition level (c1, c2), and the mass fraction of SIA in NR-PM$_1$ as a function of $f$ during haze episodes (d). Non-liquid particles are marked by yellow shadows and liquid particles are marked by blue shadows. In panel (a) and (b), the scatter points are colored by ALW/NR-PM$_1$ and the trend lines are obtained by sigmoid fitting. In panel (c1) and (c2), the box plots show 10th, 25th, median, 75th and 90th percentiles. In panel (d), RH is indicated by color, and ALW mass concentration is indicated by the size of the circle. The error bars show one standard deviation.
Figure 4. The relationship between SOA/POA and particle rebound fraction $f$ for phase transition (a) and oxidation degree (b) during haze episodes. Non-liquid particles are marked by yellow shadows and liquid particles are marked by blue shadows. The circles are colored by ALW/NR-PM$_1$ and $f_4$ to represent water uptake capacity and particle oxidation degree in panel (a) and panel (b), respectively. The sizes of the circles are scaled to NR-PM$_1$ mass concentrations. The black (red) frame with dashed line represent the off-line viscosity measurement results using poke-and-flow technique corresponding to Figure 1.
Figure 5. The overall hygroscopicity of particles (a), average volume fraction (b) and hygroscopicity (c) of inorganics and organics as a function of RH during haze episodes. $k_{\text{total}}$ was calculated using real-time $k_{\text{org}}$. Particles in different phase state condition, including non-liquid, phase transition from non-liquid to liquid, and liquid, are visually distinguished through a gradual color change from yellow to blue, which correlates with RH. In panel (a), the scatter points are colored by NR-PM$_1$ mass concentrations and averaged in each RH bin. Averaged ALW and NR-PM$_1$ mass concentrations are indicated by color and the size of the circle, respectively. The error bars show one standard deviation.