Chapter 11

Molecular Corridors, Volatility and Particle Phase State in Secondary Organic Aerosols

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Secondary organic aerosols (SOA) derived from the multigenerational oxidation of gaseous precursors are major components in atmospheric aerosols. Chemical evolution of SOA from a variety of volatile organic compounds (VOC) adheres to characteristic “molecular corridors” with an inverse correlation between volatility and molar mass. Parameterizations were developed to predict the saturation mass concentration of organic compounds containing oxygen, nitrogen, and sulfur from the elemental composition that can be measured by soft-ionization high-resolution mass spectrometry. The chemical nature of organic compounds observed in field measurements and laboratory experiments was characterized by mapping them into molecular corridors. SOA can occur in amorphous solid or semi-solid phase states depending on chemical composition, relative humidity (RH), and temperature. The phase transition between amorphous solid and semi-solid states occurs at the glass transition temperature ($T_g$). A method was developed to estimate $T_g$ of pure compounds containing carbon, hydrogen, and oxygen atoms based on their elemental composition. Viscosity can be predicted using the $T_g$-scaled Arrhenius plot of fragility by accounting for hygroscopic growth of SOA and applying the Gordon-Taylor mixing rule. Applying this method in an air quality model, recent global simulations have shown that SOA particles should be mostly liquid or semi-solid in the planetary boundary layer and glassy solid in the middle and upper troposphere.
Introduction

 Organic aerosols are major components of atmospheric fine particulate matter \((1, 2)\). They are introduced into the atmosphere either by being directly emitted by primary sources such as fossil fuel combustion and biomass burning, or being formed through secondary processes such as multigenerational oxidation of gaseous precursors. The evolution of secondary organic aerosols (SOA) is a complex process involving both chemical reactions and mass transport in the gas and particle phases; this complexity makes interpretation of field measurements and laboratory experiments as well as accurate representation of OA evolution in chemical transport models challenging \((3–5)\). Here we introduce a model framework, referred as “molecular corridors”, which can help to constrain and describe the properties of SOA compounds and their formation pathways and kinetics. This framework can also be applied in air quality and climate models \((6)\).

Current two-dimensional (2D) frameworks proposed for efficient representation of SOA properties and the associated multiphase processes were built based on various SOA properties, including volatility, number of carbon and oxygen atoms in a molecule, mean carbon oxidation state, atomic O:C or H:C ratios, polarity, solubility, or the equilibrium partitioning coefficient \((2, 7–16)\). Among current 2-D frameworks, the volatility basis set (VBS) approach has been extensively applied in chemical transport models and significantly improves predictions of SOA concentrations \((17–20)\).

In the VBS method, the total organic mass is classified into volatility bins and their distribution between gas and particle phases is calculated according to absorptive equilibrium partitioning, which implicitly assumes gas-phase formation of semi-volatile organic compounds as the limiting step of SOA formation \((7, 10, 21)\). However, other processes can also be the dominant rate-limiting steps in SOA formation. Shiraiwa et al. \((2014)\) found that SOA from a variety of biogenic and anthropogenic precursors can be represented well by the concept of molecular corridors with a tight inverse correlation between molar mass \(M\) and volatility of SOA oxidation products. Molecular corridors can help to constrain chemical and physical properties as well as reaction rates and pathways with characteristic kinetic regimes of reaction-, diffusion-, or accommodation-limited multiphase chemical kinetics involved in SOA evolution \((6)\).

The saturation vapor pressure or pure compound saturation mass concentration \((C_0)\) is a critical thermodynamic property describing the equilibrium gas-particle partitioning of organic compounds \((21–25)\). Multiplying \(C_0\) with an activity coefficient \((\gamma)\) gives the effective saturation mass concentration \((C^*)\) that includes the effect of non-ideal thermodynamic mixing \((10, 26)\). The term volatility often refers to \(C^*\) and can also be used for \(C_0\) under the assumption of ideal thermodynamic mixing. According to their volatility, organic compounds can be classified as volatile organic compounds (VOC), intermediate volatility OC (IVOC), semi-volatile OC (SVOC), low-volatile OC (LVOC), and extremely low-volatile OC (ELVOC) \((27, 28)\). Quantitative estimates of the volatility of ambient OA are uncertain, especially for compounds with low volatility. Large discrepancies often exist in volatility distributions measured by different
techniques (29–33). Current computational methods to estimate vapor pressure utilizes a functional group contribution approach that needs the information of molecular structure (34–40). In terms of ambient SOA, chemical composition is complex and molecular specificity is often unknown (16). An alternative way to assess vapor pressures of individual SOA constituents is based on their elemental composition, which can be measured by soft-ionization high-resolution mass spectrometry (HRMS) (10, 41).

In addition to volatility, viscosity is another important physical property of SOA. SOA phase state can be liquid (low dynamic viscosity $\eta; \eta < 10^2$ Pa s), semi-solid (highly viscous ‘liquid’; $10^2 \leq \eta \leq 10^{12}$ Pa s), or solid (crystalline or glass; $\eta > 10^{12}$ Pa s), depending on particle composition and ambient conditions (42–47). Particle-phase water can act as a plasticizer to decrease viscosity (48–50). SOA particles containing high molar mass compounds tend to have higher viscosity (43, 51, 52). The relationship between viscosity and O:C is more complex (47). Increasing the oxidation degree, on one hand can generally lead to the increase of glass transition temperature ($T_g$) and thus increase viscosity (43); on the other hand aerosol hygroscopicity can be enhanced at the same time (53) and thus result in liquefying particles (43, 50, 54). SOA formation conditions can also affect the particle phase state (55, 56). The viscous behavior may also arise from highly ordered three-dimensional self-assembly of surface-active species (57). A mayonnaise effect on viscosity shows that structuring caused by the mixing of liquids or the addition of solutes to a solvent could increase the viscosity dramatically (58). A number of experimental approaches have been developed to infer particle viscosity, i.e., particle rebound (44, 47, 59), poke flow (60), bead mobility (61), aerosol optical tweezers (62, 63), fluorescence lifetime imaging (64), light scattering (65), dimer relaxation (66, 67) and atomic force microscopy (68). These methods are complementary in their capabilities accessing different viscosity ranges, particle sizes and compositions, and requiring different sample volumes (69).

Understanding the phase state of organic particles is important in many aspects related to SOA formation mechanisms and associated air quality, climate and health effects. The semisolid or solid phase states can limit the diffusion of condensable gas-phase molecules from the surface into the particle bulk and disturb the equilibrium in gas–particle partitioning (54, 70–76). Current aerosol models generally use either a thermodynamic partitioning approach (assuming instant equilibrium between semi-volatile oxidation products and the particle phase) (7, 17–22) or a kinetic approach (accounting for the size dependence of condensation) (77–84). Global aerosol microphysics models show that applying a kinetic approach rather than a thermodynamic approach in biogenic SOA formation could enhance the global mean first aerosol indirect effect by 24 % (82). The direct radiative effect due to biogenic SOA is less sensitive to the way gas–particle partitioning is treated (82). The particle phase state also affects ice nucleation (IN) processes: liquid particles can freeze homogeneously, whereas (semi-)solid particles can form ice crystals heterogeneously via deposition nucleation or via immersion freezing on partially liquefied particles that undergo a kinetic transition from glassy to liquid (69, 85–91). The rates of heterogeneous reactions and photochemistry are also dependent on ambient particle viscosity.
(69, 92–95), as molecular motion can be hindered in a highly viscous matrix (96–98). Phase state also plays an important role in particle size distribution (71, 80, 99, 100). Low bulk diffusivity inside viscous semi-solid SOA can affect the growth of the smallest particles, i.e. those in the nucleation mode (71, 101). Low-temperature oxidation in a glassy solid state contributes to an increase of cloud droplet number concentrations (102). Phase state also affects the life-time of reactive pesticides (103) and estimations of aerosol acidity (104). Most of the current regional and global aerosol models treat particles as liquid droplets considering no particle phase diffusion limitations (54, 105, 106). Chamber experiments probing mixing timescales of SOA particles derived by oxidation of various precursors such as isoprene, terpene, and toluene have observed strong kinetic limitations at low RH, but not at moderate and high RH (107, 108). Gorkowski et al. (2017) did not observe significant diffusion limitations for glycerol and squalene in α-pinene SOA (109). Quasi-equilibrium versus kinetically-limited or non-equilibrium SOA growth is an open issue which is subject to further investigations.

Here we outline the molecular corridor approach to constrain chemical and physical properties of SOA, parameterizations to predict the saturation mass concentration and the glass transition temperature, and their application in a chemistry climate model to present a global picture of atmospheric SOA phase state.

**Molecular Corridor**

Figure 1 shows two-dimensional maps of molar mass (\(M\)) plotted against saturation mass concentration for pure organic compounds (\(C_0\)) for identified SOA compounds formed from oxidation of dodecane, α-pinene and isoprene (6). These compounds, detected in laboratory experiments and the related references, were summarized in Shiraiwa et al. (2014) (6). Values of \(C_0\) were estimated using the EVAPORATION model (36). The markers in Figure 1 are color-coded with atomic O:C ratio. Generally, volatility decreases and molar mass increases with chemical aging of SOA both in the gas and particle phases. Molar mass of oxidation products tightly correlates with volatility with a high coefficient of determination (\(R^2\)). The 95% prediction intervals (dashed lines in Figure 1) can be regarded as molecular corridors within which additional unidentified oxidation products are likely to fall. The negative slope of the fit lines corresponds to the increase in molar mass required to decrease volatility by one order of magnitude, -d\(M/d\log C_0\). It increases from ~15 g mol\(^{-1}\) for isoprene to ~25 g mol\(^{-1}\) for dodecane, depending on the molecular size of the SOA precursor and the O:C ratio of the reaction products (6). Figure 1(d) shows the ensemble of molecular corridors with a total of 909 identified oxidation products from seven different SOA precursors (dodecane, cyclododecane, hexylcyclohexane, α-pinene, limonene, isoprene, and glyoxal) (6). They are constrained by two boundary lines corresponding to the volatility of linear alkanes \(C_nH_{2n+1}\) and sugar alcohols \(C_nH_{2n+2}O_n\). These lines illustrate the regular dependence of volatility

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on the molar mass of organic compounds; the different slopes of 30 g mol\(^{-1}\) for \(\text{C}_n\text{H}_{2n+2}\) and 12 g mol\(^{-1}\) for \(\text{C}_n\text{H}_{2n+2}\text{O}_n\) reflect that the decrease of volatility with increasing molar mass is stronger for polar compounds.

**Figure 1.** Molar mass vs. volatility (saturation mass concentration of pure compounds, \(C_0\)) at 298 K for oxidation products of (a) dodecane at low NO condition, (b) \(\alpha\)-pinene and (c) isoprene. The open and solid markers correspond to the gas- and particle-phase products, respectively, color-coded by atomic O:C ratio. With a linear regression analysis, the coefficient of determination \((R^2)\), fitted lines (dotted lines) and their slopes \((m)\), and prediction intervals with 95% confidence (dashed lines) are shown. (d) Ensemble of molecular corridors. The dotted lines represent linear alkanes \(\text{C}_n\text{H}_{2n+2}\) (purple with O:C = 0) and sugar alcohols \(\text{C}_n\text{H}_{2n+2}\text{O}_n\) (red with O:C = 1). Chemical structures of some representative products are shown. Adapted from reference (6). Copyright 2014, Copernicus Publications.

Many early generation gas-phase oxidation products of alkanes as well as dimers or oligomers with low O:C ratio (LOC) fall close to the \(\text{C}_n\text{H}_{2n+2}\) line, which we designate as the LOC corridor \((-dM/d\log C_0 \geq 25\) g mol\(^{-1}\), blue shaded area). Aqueous-phase reaction and autoxidation products with high O:C ratio (HOC), e.g. isoprene and glyoxal oxidation products, tend to fall into a corridor near the \(\text{C}_n\text{H}_{2n+2}\text{O}_n\) line, designated as the HOC corridor \((-dM/d\log C_0 \leq 15\) g mol\(^{-1}\), red shaded area). The area in between is characterized by intermediate O:C ratios and accordingly designated as IOC corridor \((-dM/d\log C_0 \approx 20\) g mol\(^{-1}\)), which, for example, can be occupied by oxidation products of terpene such as \(\alpha\)-pinene and limonene.
The three main reaction types of SOA evolution are functionalization, oligomerization, and fragmentation, which can also be represented in Figure 1(d). Single-step functionalization usually leads to a small increase in molar mass, corresponding to one order of decrease in volatility (6). Particle-phase dimerization and oligomerization involving two or more molecules usually leads to the formation of compounds with low volatility and high molar mass lying in the upper left area in the 2D space. The formation of such particle-phase products is likely limited by reaction or diffusion in the particle bulk or by gas-to-particle mass transfer when the reactions are sufficiently fast, such as those catalyzed by acid (4, 70, 110–116). Fragmentation, on the other hand, can lead to a substantial decrease of molar mass and increase in volatility (117–121). As a result, simple gas-phase oxidation products are confined to the lower right area in the 2D space.

Because molar mass and O:C ratio also correlate with the glass transition temperature of organic compounds (43), presenting identified SOA products in a molecular corridor encapsulates fundamental aspects of SOA formation and aging: volatility, molar mass, O:C ratio, and phase state. The clustering of identified reaction products in molecular corridors may facilitate estimation of the relative importance of gas- vs. particle-phase routes to SOA formation. For example, Vogel et al. (2016) studied the new particle formation and the particle growth during a field campaign conducted at a rural mountain top station in central Germany. They found that the compounds of the smaller m/z (mass-to-charge ratio) mode were less present in the particle phase during nucleation while they became important during particle growth. Vogel et al. (2016) explained the above phenomenon applying the relationship between molar mass and volatility indicated by the molecular corridor (122). Pye et al. (2017) used the molecular corridor to constrain SOA species in the CMAQ (Community Multiscale Air Quality) model (Figure 2). Historically, in CMAQ v5.1 and prior, the number of carbons, saturation mass concentration, and the organic matter to organic carbon ratios (OM/OC) were set independently, which could lead to some apparent contradictions (123, 124). CMAQ v5.2 relates C0, molar mass, and OM/OC, updating molar mass as a function of pure species C0 and OM/OC (123). The updates can lead to 5–8% decrease in OC concentrations across the southeast US (123). Based on data from over 30 000 organic compounds, Li et al. (2016) showed that almost all of those 30 000 organics covering a wide variety of functional groups were located into the molecular corridor bounded by the two lines representing linear alkanes and sugar alcohols, except some compounds with branched structures or with O:C ratios higher than 1 (41). In the following sections the molecular corridor refers to the 2-D space bounded by molar mass and volatility of linear alkanes and alcohols.

Volatility Estimation

Parameterization

Following Donahue et al. (2011) in which C0 is estimated as a function of numbers of carbon and oxygen for compounds containing oxygen (10), we
broadened their parameterization to \( \log_{10} C_0 = f(n_C, n_O, n_N, n_S) \) to be applicable to the N and S-containing compounds:

\[
\log_{10} C_0 = (n_C^0 - n_C)b_C - n_O b_O - 2 \frac{n_C n_O}{n_C + n_O} b_{CO} - n_N b_N - n_S b_S
\]

where \( n_C^0 \) is the reference carbon number; \( n_C, n_O, n_N, \) and \( n_S \) denote the numbers of carbon, oxygen, nitrogen, and sulfur atoms, respectively; \( b_C, b_O, b_N, \) and \( b_S \) denote the contribution of each atom to \( \log_{10} C_0 \), respectively, and \( b_{CO} \) is the carbon-oxygen nonideality \( (4I) \). Table 1 showed the values of \( n_C^0 \) and \( b \) for each chemical composition class (CH, CHO, CHN, CHON, CHOS, and CHONS) at 298 K \( (4I) \).

![Molecular corridor representation of SOA species in CMAQ (Community Multiscale Air Quality) Model. The arrows start at the old molecular weights assumed in CMAQ v5.1 and end at the new molecular weights in CMAQ v5.2. Reprinted from reference (123). Copyright 2017, Copernicus Publications.](image)

Table 1. Composition Classes and the \( n_C^0 \) and \( b \) Values for Saturation Mass Concentration Parameterizations \( (4I) \).

<table>
<thead>
<tr>
<th>Classes</th>
<th>( n_C^0 )</th>
<th>( b_C )</th>
<th>( b_O )</th>
<th>( b_{CO} )</th>
<th>( b_N )</th>
<th>( b_S )</th>
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<tr>
<td>CH</td>
<td>23.80</td>
<td>0.4861</td>
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<td></td>
<td></td>
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<tr>
<td>CHO</td>
<td>22.66</td>
<td>0.4481</td>
<td>1.656</td>
<td>-0.7790</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CHN</td>
<td>24.59</td>
<td>0.4066</td>
<td></td>
<td></td>
<td>0.9619</td>
<td></td>
</tr>
<tr>
<td>CHON</td>
<td>24.13</td>
<td>0.3667</td>
<td>0.7732</td>
<td>-0.07790</td>
<td>1.114</td>
<td></td>
</tr>
<tr>
<td>CHOS</td>
<td>24.06</td>
<td>0.3637</td>
<td>1.327</td>
<td>-0.3988</td>
<td>0.7579</td>
<td></td>
</tr>
<tr>
<td>CHONS</td>
<td>28.50</td>
<td>0.3848</td>
<td>1.011</td>
<td>0.2921</td>
<td>1.053</td>
<td>1.316</td>
</tr>
</tbody>
</table>
The dataset used for deriving the above best-fit parameters is the National Cancer Institute (NCI) open database (http://cactus.nci.nih.gov/download/nci/), which contains 31,066 organic compounds. These compounds cover a molar mass from 41 to 1779 g mol\(^{-1}\). The Estimation Programs Interface (EPI) Suite software (version 4.1) is applied to estimate the saturation vapor pressure of each compound. The EPI Suite applies three separate methods, which use the normal boiling point to estimate vapor pressure. The estimation error of EPI Suite increases as the vapor pressure decreases, especially when the vapor pressure decreases below \(10^{-4}\) Pa (http://www.epa.gov/sab/pdf/sab-07-011.pdf). Comparing to the EPI Suite, the EVAPORATION model calculating the vapor pressure from molecular structure may give better estimations but this model does not cover all the compounds included in the NCI database, particularly some compounds containing heteroatoms (36).

For CHO compounds, when comparing to the EVAPORATION predictions, as shown in Figure 3a, both our parameterization and Donahue et al. (2011) give similar performance for compounds falling in IVOC and SVOC. For LVOC and ELVOC compounds, our estimates are generally higher than EVAPORATION predictions, while estimates of Donahue et al. (2011) tend to be lower. This may be partly because most estimation methods, including the EPI Suite, are constrained by databases heavily biased toward mono-functional compounds with vapor pressures in the range of \(-10^{3}–10^{5}\) Pa (10, 24, 125). Relatively large errors are also found for compounds with low volatility when comparing \(C_0\) estimated by our parameterization with the experimental data (Figure 3b). An accurate prediction of low vapor pressure is difficult due, in large part, to the limitation caused by measurement challenges. Measurements of vapor pressures could span orders of magnitude across different techniques, especially for low volatility compounds (16, 40, 126, 127). The effects of functionalization, phase states, and molecular structure need to be considered in future experimental studies (24, 25, 126, 128).

Despite some of the limitations as described above, our new estimation parameterization derived from a large dataset is sufficiently good to predict \(C_0\) for various structural organic classes (see Table S2 in Li et al. 2016). Since aerosol chemical composition is complex and often does not provide molecular structure specificity (16), estimations of \(C_0\) based on the elemental composition are well suited for the high-resolution mass spectra data as they provide an experimental distribution of molecular formulas in the SOA sample (129).

Application in Laboratory, Ambient, and Modeled Organic Aerosol

Li et al. (2016) compiled data sets with 9053 organic compounds detected in chamber experiments, and field and indoor measurements of OA formed from different sources. These large data sets were mapped into the molecular corridor applying Eq. (1). Figure 4 is an example of the molecular corridor constraining nitrogen or sulfur containing compounds found in ambient air. Among these species, nitroxy-organosulfates have the highest O:C ratio (> 0.9) and the lowest volatility falling into the ELVOC group with molar mass up to 400 g mol\(^{-1}\).
Organosulfates and organonitrates have an O:C ratio generally higher than 0.7, covering the range of IVOC to ELVOC with a broad molar mass range (100 – 600 g mol⁻¹) to occupy the high O:C corridor. Reduced sulfur compounds have a low O:C ratio (< 0.4) and are located close to the alkane line. Amine and N-heterocyclic alkaloid compounds found during new particle formation and biomass burning have the lowest O:C ratio and molar mass and the highest volatility (in VOC and IVOC groups), following the low O:C corridor.

Hatch et al. (2017) applied Eq. (1) estimating the volatility distribution of the non-methane organic gases (NMOGs) identified in laboratory biomass burning (BB) measurements, showing 6–11% of NMOGs were associated with intermediate-volatility organic compounds (Figure 5a), which historically had been unresolved in BB smoke measurements and should be considered in future updates of emission inventories (130). Applying Eq. (1), Koss et al. (2018) showed the volatility distribution of NMOGs can change considerably over the course of a fire. Species emitted from lower-temperature processes during the fire had a higher fraction of compounds with low volatility compared to the high-temperature processes (Figure 5b) (131). Considering freshly emitted BB organic aerosol (BBOA), Lin et al. (2016) investigated the molecular composition achieved during test burns of sawgrass, peat, ponderosa pine, and black spruce. The compounds in the fresh BBOA spanned a wide range of molecular weights, structures, and light absorption properties, and could be well constrained in the space characterized by molecular corridor (Figure 5c). It was estimated by Eq. (1) that many brown carbon (BrC) chromophores had low saturation mass concentration (<1 μg m⁻³) and were expected to be retained in the particle phase under atmospherically relevant conditions. Some BrC chromophores with higher saturation mass concentration were expected to evaporate from the particles (132).

Aqueous processing is an important pathway of SOA formation and traditionally considered to lower the volatility of organic compounds (133, 134). For example, Nie et al. (2017) used Eq.(1) and found that LVOC and ELVOC accounted for a large fraction of compounds found in water-soluble humic-like substances (HULIS) collected in a polluted megacity in eastern China (135). Romonosky et al. (2017) showed a complex effect of photooxidation on the volatility of dissolved SOA compounds. They prepared SOA particles formed from α-pinene and α-humulene oxidized with O₃, OH or NO₃ radicals in a smog chamber. The water-soluble compounds were extracted in water, then the resulting aqueous solutions were photolyzed. Eq. (1) was used to estimate the effect of photolysis on dissolved particle volatility (Figure 5d). It was found that the SOA compounds became more volatile on average during the photolysis, which could lead to a reduction of SOA loading (129). As atmospheric water could act as a reactant, product, or solvent in several ways, recent attention has focused on the role of relative humidity on chemical composition and mass yields of SOA as well as its associated climate effects (136–138). Hinks et al. (2018) used Eq. (1) to estimate the effect of RH on the volatility distributions of SOA formed from low-NOₓ toluene oxidation in the absence of seed particles. It was found that the compounds falling in the lower volatility bins were suppressed at high RH due to a significant reduction in the fraction of oligomers which however, did not occur under dry conditions (139). Budisulistiorini et al (2017) applied Eq.
in the CMAQ model to estimate the volatility of organosulfates during the simulation of aqueous-phase isoprene-epoxydiol (IEPOX) SOA formation (140).

Figure 3. (a) Saturation mass concentration ($C_0$) of CHO compounds predicted by Eq. (1) with the coefficients from Li et al. (2016) and Donahue et al. (2011) plotted against $C_0$ computed by the EVAPORATION model (36). The data comprise 704 SOA oxidation products from biogenic and anthropogenic precursors (6). (b) Comparison of $C_0$ predicted by Eq. (1) and experimental values taken from PHYSPROP Database in the EPI Suite. Adapted from reference (41). Copyright 2016, Copernicus Publications.

Figure 4. Molecular corridors of saturation mass concentration of pure compounds ($C_0$) vs. molar mass ($M$) for nitrogen or sulfur containing compounds collected from outdoor observations. The upper dashed line indicates the low O:C bound of the molecular corridor (linear alkanes $C_nH_{2n+2}$ with O:C=0), the lower dotted line indicates the high O:C bound (sugar alcohols $C_nH_{2n+2}O_n$ with O:C=1). The small markers represent individual compounds color-coded by O:C ratio. The larger symbols indicate surrogate compounds with the mean values of $M$, $C_0$, and O:C ratio. Reprinted from reference (41). Copyright 2016, Copernicus Publications.
Figure 5. Application of the molecular corridors of volatility (based on the parameterization of Li et al., 2016) vs. molar mass for various measurements: (a) non-methane organic gases (NMOGs) in laboratory biomass burning measurements (reprinted and adapted from reference (130). Copyright 2017, Copernicus Publications); (b) NMOGs from high- and low-temperature processes during burning of ponderosa pine (reprinted from reference (131). Copyright 2018, Copernicus Publications); (c) BBOA samples collected from burning of sawgrass ponderosa pine (adapted from reference (132). Copyright 2016, American Chemical Society); and (d) SOA compounds formed from α-pinene oxidized with O₃. (adapted from reference (129). Copyright 2017, American Chemical Society).

Glass Transition Temperature and Viscosity Estimation

Glass Transition Temperature of Organic Compounds

Shiraiwa et al. (2017) developed a parameterization for \( T_g \) estimation based on the molar mass and atomic O:C ratio of CH and CHO compounds with \( M < 450 \text{ g mol}^{-1} \) (90):

\[
T_g = A + BM + CM^2 + D (O:C) + E M (O:C) \quad (2.1)
\]
where $A = -21.57$ [K], $B = 1.51$ [K mol g$^{-1}$], $C = -1.7 \times 10^{-3}$ [K mol$^2$ g$^{-2}$], $D = 131.4$ [K] and $E = -0.25$ [K mol g$^{-1}$], respectively. These values were obtained by fitting the experimentally measured $T_g$ of 179 CH and CHO compounds with $M < 450$ g mol$^{-1}$ (43, 141).

The estimation of $T_g$ as a function of the molar mass and atomic O:C ratio is based on a strong dependence of $T_g$ on the molar mass and a relatively weak dependence on the atomic O:C ratio (Figure 6). However, application of Eq. (2.1) may provide unreasonable $T_g$ values for compounds with $M > 500$ g mol$^{-1}$ due to a lack of information on experimentally measured $T_g$ for high molar mass compounds. Recently, Rothfuss and Petters (2017) compiled an experimental dataset of $T_g$ for compounds with $M$ up to 1153 g mol$^{-1}$, providing an avenue to improve the $T_g$ parameterization (52). As shown in Figure 6, when $M$ increases above ~500 g mol$^{-1}$, the slope of $T_g$ decreases, making it challenging to extrapolate the formulation of Eq. (2.1) to higher $M$ values. When $M$ increases to ~1000 g mol$^{-1}$, the corresponding $T_g$ appears to level at around 420 K.

Figure 6. Characteristic relationships between molecular properties and the glass transition temperature ($T_g$) of organic compounds. (a) $T_g$ of organic compounds as measured (circles) and estimated with the Boyer-Kauzmann rule (squares) plotted against molar mass. The markers are color-coded by atomic O:C ratio. (b) Measured (circles) and estimated (squares) $T_g$ of organic compounds plotted against O:C ratio. The markers are color-coded by molar mass. (c) Predicted $T_g$ for CHO compounds using a parameterization (Eq. 2.2) developed in DeRieux et al. (2018) compared to measured (circles) and estimated $T_g$ by the Boyer-Kauzmann rule (squares). The solid line shows 1:1 line and the dashed and dotted lines show 68% (one standard deviation) confidence and prediction bands, respectively. Reprinted from reference (142). Copyright 2018, Copernicus Publications.

Motivated by a good correlation between $T_g$ and volatility, another parameterization (Eq. 2.2) to estimate $T_g$ of CH and CHO compounds was developed using the number of carbon ($n_C$), hydrogen ($n_H$), and oxygen ($n_O$) atoms (142), similar to the formulation used to estimate the saturation mass concentration (Eq. 1) (Figure 6a). Eq. (2.2) can be applied to compounds with $M > 450$ g mol$^{-1}$.
\[ T_g = (n_C^0 + \ln(n_c)) \cdot b_C + \ln(n_H) \cdot b_H + \ln(n_C) \cdot \ln(n_H) \cdot b_{CH} + \ln(n_O) \cdot b_O + \ln(n_C) \cdot \ln(n_O) \cdot b_{CO} \]  

(2.2)

where \( n_C^0 \) is the reference carbon number, \( b_C, b_H \) and \( b_O \) denote the contribution of each atom to \( T_g \), and \( b_{CH} \) and \( b_{CO} \) are coefficients that reflect contributions from carbon-hydrogen and carbon-oxygen bonds, respectively. These values were obtained by fitting the measured \( T_g \) of 42 CH compounds and 258 CHO compounds included in Koop et al. (2011), Dette et al. (2014) and Rothfuss and Petters (2017). The best-fit parameters are summarized in Table 2. Because the evaluation dataset used to derive Eq. (2.2) contains CH compounds with \( M < 260 \text{ g mol}^{-1} \), the application of Eq. (2.2) to higher molar mass CH compounds requires further investigations.

Table 2. Composition Classes and the \( n_C^0 \) and \( b \) Values (K) for Glass Transition Temperature Parameterizations (142).

<table>
<thead>
<tr>
<th>Classes</th>
<th>( n_C^0 )</th>
<th>( b_C )</th>
<th>( b_H )</th>
<th>( b_{CH} )</th>
<th>( b_O )</th>
<th>( b_{CO} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH</td>
<td>1.96</td>
<td>61.99</td>
<td>-113.33</td>
<td>28.74</td>
<td></td>
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</tr>
<tr>
<td></td>
<td>(±1.81)</td>
<td>(±53.65)</td>
<td>(±44.47)</td>
<td>(±20.86)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CHO</td>
<td>12.13</td>
<td>10.95</td>
<td>-41.82</td>
<td>21.61</td>
<td>118.96</td>
<td>-24.38</td>
</tr>
<tr>
<td></td>
<td>(±2.66)</td>
<td>(±13.60)</td>
<td>(±14.78)</td>
<td>(±5.30)</td>
<td>(±9.72)</td>
<td>(±4.21)</td>
</tr>
</tbody>
</table>

Figure 6c shows that the \( T_g \) values predicted using Eq. (2.2) are in good agreement with the \( T_g \) values measured in experiments or estimated by the Boyer-Kauzmann rule as indicated by the high correlation coefficient of 0.95. The Boyer-Kauzmann rule applied \( T_g = g \cdot T_m \) where \( T_m \) is the melting temperature and \( g \) is adopted as 0.7 (43). \( T_g \) of individual compounds can be predicted by Eq. (2.2) to within ±21 K as indicated by the prediction band (dotted lines in Figure 6c); however, this uncertainty may be much smaller for multicomponent SOA mixtures under ideal mixing conditions as indicated in the confidence band (dashed lines, almost overlapping with the 1:1 line).

It is shown that Eq. (2.1) and Eq. (2.2) give similar performance for compounds with \( M < 450 \text{ g mol}^{-1} \) (142). Comparing with Eq. (2.1), Eq. (2.2) is more flexible to be potentially expanded to include compounds containing heteroatoms (e.g., nitrogen or sulfur), once substantial sets of experimental values of \( T_g \) for such compounds become available. Regarding the application in air quality and climate models, Eq. (2.1) can be applied in the volatility basis set (VBS)\(^7\) to predict the \( T_g \) of SOA particles (90). Eq. (2.2) is suitable for coupling with the statistical oxidation model (SOM) which characterizes the SOA evolution as a function of \( n_C \) and \( n_O \) (12, 143).
Glass Transition Temperature of SOA-Water Mixtures

SOA particles contain a number of organic compounds as well as a variable amount of liquid water. Estimations of $T_g$ for SOA-water mixtures can be made using the Gordon-Taylor equation, which has been validated for a wide range of mixtures of organics, polymer, and water \((42, 141, 144, 145)\). In Shiraiwa et al. (2017) \((90)\), $T_g$ of mixtures of SOA compounds under dry conditions ($T_{g,\text{org}}$) were calculated assuming the Gordon-Taylor constant ($k_{GT}$) of 1 \((141)\). Under humid conditions, the mass concentrations of water ($m_{H2O}$) absorbed by SOA particles can be estimated using the effective hygroscopicity parameter ($\kappa$) as \((146)\):

$$m_{H2O} = \frac{\kappa \rho_w m_{SOA}}{\rho_{SOA} (\alpha_w^{-1} - 1)}$$  \((3)\)

where $\rho_w$ and $\rho_{SOA}$ are the density of water and SOA particles, respectively. $m_{SOA}$ is the total mass concentrations of SOA, and $\alpha_w$ is the water activity calculated as $\alpha_w = RH/100$.

$T_g$ of organic - water mixtures can be simulated using the Gordon-Taylor equation \((43)\):

$$T_g(w_{org}) = \frac{(1-w_{org})T_{g,w} + \left(1-w_{org}\right)^{1/k_{GT}}w_{org}T_{g,\text{org}}}{(1-w_{org})^{1/k_{GT}}w_{org}}$$  \((4)\)

where $w_{org}$ is the mass fraction of organics in particles, equal to $m_{SOA} / (m_{SOA} + m_{H2O})$. $T_{g,w}$ is the glass transition temperature of pure water (136 K), and the Gordon-Taylor constant $k_{GT}$ is assumed as 2.5 (±1.0) \((43, 147)\).

It has been pointed out previously that the Gordon-Taylor approach may fail if $T_g$ of each of the compounds are in very similar range or in the case of adduct or complex formation \((43, 67)\). Complex formation may occur in binary or ternary mixtures, where the two strongly interacting compounds occur at high mole fractions. However, adduct or complex formation is unlikely in multicomponent mixtures such as SOA with hundreds of compounds, which would favor a mean-field type Gordon-Taylor approach \((90)\).

**Viscosity Estimation**

When the glass transition temperature of SOA particles could be estimated, either the Vogel-Tammann-Fulcher (VTF) equation \((148)\) or the Williams-Landel-Ferry (WLF) equation \((149)\) can be used to predict the viscosity.
Angell (1991) shows a modified VTF equation as: \( \eta = \eta_\infty e^{T - T_0 / D} \), where \( \eta_\infty \) is viscosity at infinite temperature, e.g., 10\(^{-5}\) Pa s as suggested (150). \( D \) is called the fragility parameter, characterizing how rapidly the dynamics of a material slows down as \( T \) approaches \( T_g \). Smaller \( D \) values indicate that viscosity is sensitive to temperature change (fragile behavior); while larger \( D \) values indicate that viscosity is less sensitive to temperature change (strong or Arrhenius behavior). Typical \( D \) values for organic compounds are in the range of \( \sim 5–20 \) (151) and the value of 10 is used in the base simulations of Shiraiwa et al. (2017) (90). \( T_0 \) is the Vogel temperature, which is related to \( T_g \) through:

\[
T_0 = \frac{39.17 T_g}{D + 39.17},
\]

which was derived assuming \( \eta = 10^{12} \) Pa s at \( T = T_g \) (150, 152).

For viscosity estimations, both VTF and WLF equations are applied in the atmospheric community to predict the viscosity of SOA mixtures. Wang et al. (2015) applied the WLF equation to predict the viscosity of \( \alpha \)-pinene SOA assuming the \( T_g \) of \( \alpha \)-pinene SOA was 310 ± 15 K ranging from 295 to 328 K (153). Schill et al. (2013) applied the WLF equation to predict the viscosity of the mixture of 1,2,6-hexanetriol and 2,2,6,6-tetraakis (hydroxymethyl)cyclohexanol in their ice nucleation study (154). Maclean et al. (2017) used the WLF equation and the Gordon–Taylor equation to predict the viscosity of \( \alpha \)-pinene SOA (155). Rothfuss and Petters (2017) used an adapted VTF equation and the Gordon–Taylor mixing rule to model the viscosity of sucrose under a wide range of \( T \) and RH (67). Pratap et al. (2018) applied Eq. (2.1) and the VTF equation in a hybrid model accounting for the effects of temperature and relative humidity on the lifetime of biomass burning molecular markers (156).

Global Phase State Distribution

Shiraiwa et al. (2017) presented a global distribution of atmospheric SOA phase state using a global model EMAC (157) coupled with the organic aerosol module ORACLE (158). ORACLE uses the volatility basis set framework (7) for distributing SOA oxidation products into logarithmically spaced volatility bins (158). Once the values of molar mass and O:C ratio of oxidation products in different volatility bins are assigned based either on the molecular corridor approach (6, 41) or previous studies (159), \( T_g \) of dry SOA products in each volatility bin can be predicted using Eq. (2.1). \( T_g \) of SOA mixed with water due to hygroscopic growth at given RH is estimated using the Gordon-Taylor equation.

The SOA phase state can be inferred using the ratio of \( T_g \) and ambient temperature \( T \): \( T_g / T \geq 1 \) indicates an amorphous solid phase, and the threshold between semi-solid and liquid states is estimated at \( T_g / T \) of around 0.8 (90). Figure 7 shows that the annually average \( T_g / T \) ratio within the planetary boundary layer, indicates that SOA is mostly liquid in tropical and polar air with high relative humidity, semi-solid in the mid-latitudes, and solid over dry lands.
Figure 7. SOA Phase state in the global atmosphere. Modeled annual averages of the inverse ambient temperature (1/T) scaled by the glass transition temperature (T_g) of SOA (T_g/T) at the surface, 850 hPa and 500 hPa, respectively, for the years 2005-2009. T_g/T is an indicator of the particle phase state: T_g/T≥1, solid; ~0.8 < T_g/T < 1, semi-solid; T_g/T ≤ ~0.8, liquid. Adapted from reference (90).

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Ambient measurements of particle phase state are still scarce. For background conditions of the Amazonian tropical forest, a region dominated by isoprene-derived SOA and high RH, particles are mostly liquid while with the anthropogenic influence, they occur as a nonliquid phase (45, 46). Submicrometer particles in the highly polluted atmosphere of Beijing, China are reported to be in the liquid state during heavy haze episodes with RH often higher than 60% (160). At typical ambient RH and temperature, organic-dominated particles stay mostly liquid in the atmospheric conditions in the southeastern US, but they often turn semisolid when dried below ~50% RH in the sampling inlets (54). Organic particles collected in California, Mexico City and Chile may have higher viscosities and could occur in glassy states (161). Particles over the boreal forest in Finland have been shown to be amorphous solids at low RH (< ~30%) (44). Simulated results of SOA phase state in Shiraiwa et al. (2017) are consistent with those ambient measurements.

Figure 7 also shows transport of SOA particles to higher altitudes leads to more frequent occurrence of solid or semi-solid phases. At 850 hPa solid particles
prevail over most of the continents at low and mid latitudes, while particles remain semi-solid or liquid over the continents in the tropics and at high latitudes as well as over the oceans. After further uplifting to 500 hPa, almost all SOA particles are expected to undergo phase transition into a glassy solid state. The occurrence of viscous states at high altitudes with low temperature is consistent with recent chamber experiments, showing that α-pinene-derived SOA particles exist in a viscous state at low temperatures corresponding to the cirrus cloud region of the free troposphere (65).

For the estimation of bulk diffusivity of water through a (semi-)solid matrix, the Stokes–Einstein equation is not applicable (63, 70, 72, 86, 162), but diffusivity can be estimated using a semi-empirical method of Berkemeier et al. (86) similar to the Vogel-Tammann-Fulcher (VTF) approach. The characteristic diffusion timescales of water molecules in SOA particles are predicted on the order of microseconds at the Earth’s surface and seconds at 850 hPa, and can range from several minutes to days at 500 hPa (90). Thus, the mixing timescales (τmix) can be longer than typical cloud activation time periods, potentially inhibiting full deliquescence and allowing the OA to serve as a substrate for ice nucleation (86, 89, 91).

The mixing timescales of organic molecules within the SOA matrix, which can be estimated using the Stokes-Einstein equation, are much longer than mixing timescales of water molecules. Recent research has shown that mixing times of organic molecules within SOA particles can be of the order of hours at room temperature and at low RH (55, 107, 112, 163–166). Our global simulations predict that τmix are shorter than minutes over oceans, tropics and high latitudes at the surface and 850 hPa, indicating that particles are homogeneously mixed and are likely to be in equilibrium between the gas and particulate phases. However, τmix are more than a day over dry regions at the surface, over most continental regions at 850 hPa, and over the entire globe at 500 hPa (90). Maclean et al. (2017) calculate that τmix are mostly < 1 h within the planetary boundary layer during both January and July when their parameterization uses experimental viscosity data of α-pinene SOA generated in the laboratory at mass concentrations of ~1000 μg m⁻³. However, the occurrences of τmix less than 1 h are significantly decreased when calculations use the experimental viscosity data of α-pinene SOA generated at a lower mass concentration of ~70 μg m⁻³ (155). These results suggest that viscosity measurements of SOA generated at atmospheric-relevant mass concentrations are needed (55). In addition, the Stokes–Einstein equation may underpredict diffusion coefficients in highly viscous SOA (95, 167–169).

The predicted global mixing timescales of organic molecules within the SOA matrix also have important implications for long-range transport of persistent organic pollutants and polycyclic aromatic hydrocarbons (90, 170, 171). Toxic compounds can be embedded within glassy SOA matrices with low bulk diffusivities and long mixing timescales (169), which can effectively shield them from chemical degradation by atmospheric photo-oxidants, facilitating efficient long-range transport in the atmosphere (113, 172). Recent experiments show that the sufficiently slow diffusion of reactant molecules in the semi-solid or solid physical states of organic aerosols can inhibit browning reactions in the atmosphere, thus may influence the atmospheric energy balance (173).
Conclusions and Outlook

A full characterization of the physical and chemical properties of SOA is desirable but challenging, given the complexity of SOA formation and the limitation of current analytical techniques. Based on molecular identification of SOA oxidation products, it was shown that the chemical evolution of SOA from a variety of VOC precursors adheres to characteristic “molecular corridors” with a tight inverse correlation between volatility and molar mass. The model framework of molecular corridors can provide insights into physical properties of SOA compounds, formation pathways, and kinetic regimes. Parameterizations predicting the saturation mass concentration and the glass transition temperature of SOA were developed based on molar mass, atomic O:C ratio or elemental composition. These parameterizations have been applied to laboratory and ambient organic aerosols to predict SOA volatility and viscosity and the predicted values are consistent with the observations. The utility of this approach for SOA components measured by soft-ionization high-resolution mass spectrometry to predict the bulk volatility and its evolution with aging needs further investigation (174, 175).

Several important aspects should be further explored in dedicated studies. A large fraction of inorganic species present in atmospheric particles can affect the partitioning of organic substances via non-ideal mixing and salt effects, which must be considered when simulating the phase state of ambient aerosols (72, 123, 176–187). Calculations indicate that comparing to a one-phase assumption, liquid–liquid phase separation can lead to either enhanced or reduced partitioning of organics to the particulate phase, depending on the overall composition of a system and the particle water content (72, 177, 188). When the phase separation occurs, the inorganic-rich and organic-rich phases may undergo glass transition at different temperatures (189). At ideal mixing conditions with one phase, the presence of inorganic salts (which often have lower $T_g$ compared to SOA compounds) would lead to lower viscosity (189). Changes in the activity coefficient, due to the interactions of organic compounds and inorganic salts in aerosols, result in changes of the particle volatility (10). In addition, phase separation would also affect the saturation mass concentration by including water and other inorganics in the absorbing phase (26, 188).

Other topics to be further explored include relating functional group analysis to volatility and viscosity parameterizations (51, 52, 62, 190), diel and seasonal variations of the phase state, the RH history of particles (191), dependence of phase state on particle size (192) and various anthropogenic and biogenic precursors, the impact of temperature-modulated particle phase on cloud condensation nuclei activity (102), the effects of extremely low volatile organic compounds (193, 194) and highly oxidized multifunctional organic compounds (HOM compounds) (195–198) as well as particle- and aqueous-phase chemistry (4, 199, 200). Considering the lifetime of atmospheric aerosols, laboratory measurements indicate that atmospheric chemical aging processes can increase the viscosity of particles, due to the formation of high molar mass compounds via oligomerization (64, 121). Experiments and simulations to track viscosity changes during the atmospheric processing of SOA are also subject to future
studies. Further development of advanced and detailed formalisms for the SOA lifecycle is required for better understanding and quantification of SOA effects on climate, air quality, and public health (90, 201).

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