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Atmospheric Ice Nucleation by Glassy Organic Compounds: A Review

Anastasia Salameh and Vangelis Daskalakis*

Cyprus University of Technology

***Corresponding author:** Vangelis Daskalakis,Department of Environmental Science and Technology, Cyprus University of Technology; Tel: +357-25002458; E mail: evangelos.daskalakis@cut.ac.cy

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Abstract

Aerosol particles play a vital role in atmospheric processes and the climate as they facilitate the formation of clouds and precipitation. Secondary organic aerosols (SOA) represent a significant subclass of atmospheric compounds, and recent research revealed that they could exist in a semi-solid or glassy state at low temperatures and relative humidity conditions. Glassy organic compounds influence ice nucleation, ice growth, chemical reactions and water uptake of aerosols have an effect on the pathway of activation of cloud droplets and ice crystals. There are no proposed mechanisms at the atomic level to describe ice nucleation on glassy organic aerosol. The present paper reviews existing knowledge and identify mechanisms regarding glassy organics in atmospheric aerosols and their implications for atmospheric processes that affect climate modeling.

Keywords: Ice Nucleation, Glassy Organics, Secondary organic aerosols, Climate.

Introduction

Why do we study glassy organics in the atmosphere? In the following sections, we will answer this question, and we will follow the literature in search of proposed methodologies to study glassy organics. Ice nucleation by glassy organic aerosol compounds remains poorly understood and unquantified. In this review, heterogeneous ice nucleation under cirrus conditions is evaluated. Glassy aerosols impeding homogeneous freezing can nucleate ice heterogeneously [1]. These mechanisms require rather low tropospheric temperatures so that mainly cirrus formation would be affected [2]. Glass aerosol particles may clarify the phenomena of abnormal supersaturations observed at the tropopause, although there is an ongoing discussion as to the accuracy of humidity measurements at low temperatures and pressures. Below −70°C, cubic ice nucleates in preference to hexagonal ice, thereby enhancing the dehydration caused by cirrus clouds [3]. First, we define the framework where such events occur (atmosphere), we present the raw material (aerosols and composition) and then we refer to the actual processes taking place (ice nucleation, cloud formation, transition of organics to glassy state, ice nucleation enhancement by glassy organics).

Earth’s Atmosphere

Earth’s atmosphere is a thin, shallow spherical shell of a mixture of gases held in place by the gravity [2]. The key role of the atmosphere is to maintain life by absorbing solar ultraviolet radiation, warming the surface through heat retention and moderating temperature extremes throughout the diurnal cycle. It is thickest near the surface and thins out with height until it eventually merges with space. The atmosphere is a combination of nitrogen (78.08%), oxygen (20.95%), argon (0.93%), carbon dioxide (0.039%) and mini traces of other gases like ozone and methane. Furthermore, it has an abundance amount of water vapour in the whole atmosphere [4]. Earth’s atmosphere is divided into five layers: the troposphere, the stratosphere, the mesosphere, the thermosphere and the exosphere. The troposphere is the most important atmospheric layer for the study of ice nucleation as it is the site of all-weather on Earth.

The troposphere

The troposphere is between an inversion layer (tropopause), which parts the troposphere from the stratosphere and the surface of the Earth. The troposphere extends upward 20 km in the tropics, 17 km in the mid-latitudes and 7 km in the polar regions in winter. In the upper troposphere, water vapour can deposit directly onto the solid particle. The troposphere contains approximately 75% of the atmosphere’s mass and 99% of its water vapour and aerosols [4]. Temperature and water vapour decrease rapidly with altitude in the troposphere where the tropopause acts as an inversion layer, where the air temperature stops to decline with height and remains constant [4]. Air pressure and density also decrease with altitude as the atmosphere is nearly in hydrostatic equilibrium.

The change in pressure with height can be equated to the density by the hydrostatic equation

$$dp / dz \approx -\rho g$$

where ρ is the air density (at the Earth’s surface) and g = 9.8 ms^{-2} is the gravitational constant while the temperature can be described by the adiabatic law

$$dT / dz \approx -(RT / c_p) dlnp / dz)$$

where R and c_p are the gas constant and specific heat of the air respectively. Therefore, upward motion can be described as cooling, and downward motion as warming. At higher altitudes of the troposphere, where the temperature is below 273.16 K, an upward movement reduces the temperature to the ice–vapour phase boundary, where the vapour pressure is equal to the vapour pressure over a flat surface of the hexagonal ice.

Atmospheric Aerosols

Atmospheric aerosols are the topic of some fundamental research questions because of their effects on Earth's atmosphere, global climate, and public health [5]. Atmospheric aerosols play a vital role on Earth's climate by directly scattering and absorbing solar and terrestrial radiation [6-8]. As a direct effect, the aerosols absorb and scatter sunlight directly back into space while indirectly in the lower atmosphere, aerosols can modify the size of cloud particles, changing how the clouds reflect and absorb sunlight[6]. Atmospheric aerosols also affect climate through their influence on the formation of clouds and participating in many atmospheric chemical reactions [2].

The key characteristics required for a full characterization of an aerosol are particle size distribution, the total number of particles, the total mass of suspended particulate matter, particle density, particle shape, particle phase and chemical composition [2]. A fundamental property is particle size. Aerosol diameters can range from less than a nanometer to tens of micrometres. Their size and composition define many properties such as phase, volatility, hygroscopicity, chemical reactivity, light scattering and absorption and cloud nucleating activity. These properties affect the transport and lifetimes of chemicals in the atmosphere, visibility, the hydrologic cycle, cloud formation, climate, and environmental and human health [8].

Atmospheric aerosol particles are an internal mixture of organic/inorganic compounds, composed of complex solid and liquid particles of different chemical composition as they originate from various sources [9].

The main categories of aerosols that influence Earth's climate are:

a) Volcanic aerosols formed in the stratosphere after major volcanic eruptions. After the eruption, sulphur dioxide gas is transformed to sulfuric acid droplets in the stratosphere throughout weeks. Desert dust aerosol particles, which are microscopic particles coming from the desert. They are comparatively big for atmospheric aerosols and usually, fall of the atmosphere after a short flight by intense dust storms.

b) Anthropogenic aerosols are coming from human activities. They mainly contain sulphates produced by biomass burning and can survive in the atmosphere for about 3-5 days. Since the industrial revolution, the concentration of human-made sulphate aerosols in the atmosphere has full-grown and nowadays is outweighing the naturally produced sulphate aerosols. The sulphate aerosols absorb sunlight and reflect it, thereby cutting the amount of sunlight reaching the Earth's surface they also enter clouds causing the number of cloud droplets to increase while making the droplet sizes smaller.

Organic aerosols

Earth's atmosphere contains a variety of organic compounds, and aerosol mass contains ~20–50% of organics at continental mid-latitudes and 90% in tropical forested areas [10,11]. The organic compounds differ by orders of magnitude regarding fundamental properties such as volatility, reactivity and tendency to form cloud droplets [12]. Organic aerosols form from the oxidation of volatile organic compounds [10,13,14]. After their formation, they undergo further chemical processing by reactive trace gases such as ozone, ammonia, hydroxyl and nitrate radical [15-18]. Influencing in this way chemical and particle size distribution and hence affecting the aerosol characteristics like gas-particle partitioning, hygroscopicity, viscosity, radiative properties and toxicity [19].

Cloud formation by organic aerosols can be prompted through many different pathways depending on ambient conditions and composition. At high temperature and high humidity, liquid organic particles can act as cloud condensation nuclei (CCN). At low temperature, they facilitate the formation of ice crystals. As seen in Figure 1 the particle phase state determines the active ice nucleation pathway: glassy solids can nucleate ice in the deposition mode, partially deliquesced particles with core-shell morphologies may act as IN in the immersion mode and liquid particles nucleate ice homogeneously, at a significantly higher ice supersaturation.

Compared to IN such as dust, soot and biological particles, glassy organic particles require temperatures below ~ 230 K to nucleate ice heterogeneously [20]. This restriction confines their atmospheric activity range to the upper troposphere–lower stratosphere region.

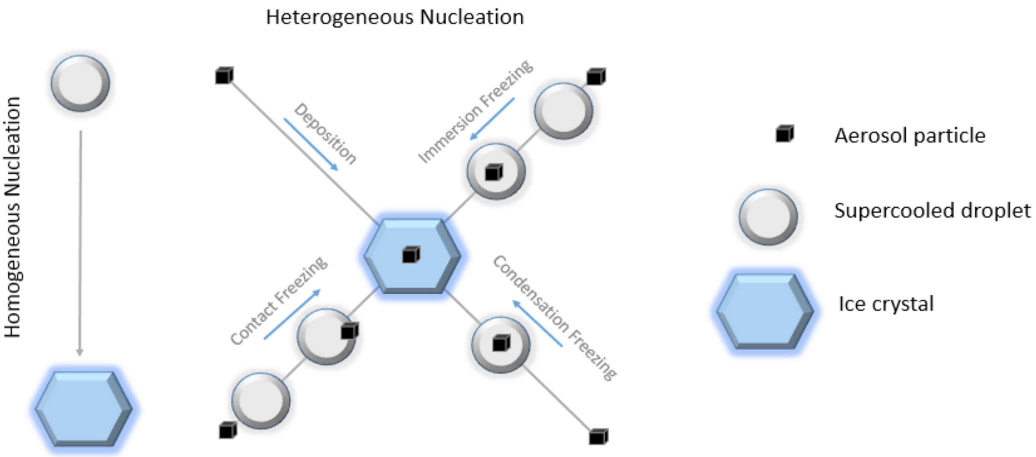

Figure 1: Ice nucleation modes

Numerous studies have signified that organic aerosol plays an important role in the direct and indirect aerosol forcing [21-26].

Atmospheric organic aerosol particles come from a variety of sources and formation processes classified as being primary or secondary. Primary organic aerosol (POA) are emitted directly from the source while secondary organic aerosol (SOA) are formed in the atmosphere from gas-phase precursors which may have been emitted from natural sources or formed in the atmosphere by chemical reactions.

Primary organic aerosol (POA): Primary organic aerosols (POAs) are directly emitted by mechanical processes directly into the atmosphere as a liquid or solid particles or as semi-volatile vapours. They have larger particles (diameter > 2.5 mm). Their main sources are: natural and anthropogenic biomass burning (e.g. domestic heating, forest fires, slashing and burning), fossil-fuel combustion (domestic, industrial, traffic), biological materials (microorganisms, pollen, spores, etc.), sea spray, and spray from other surface waters with dissolved organic compounds[5,27].

Secondary organic aerosol (SOA): Secondary Organic Aerosols (SOAs) are typically formed in the atmosphere via gas-to-particle conversion of volatile compounds such as sulphates, nitrates and some organics [27,28]. Once released they develop by condensation of molecules from the gas phase or by the collision of their particles (coagulation), which leads to the evolution of larger but fewer aerosol particles of mixed chemical composition [2]. These particles are then removed by cloud droplets and wet deposition, leading to the formation of new particles by nucleation [2]. There are three main pathways for SOA formation. The first pathway is the new particle formation where semi-volatile organic compounds (SVOCs) forms by gas-phase reactions and participates in the nucleation and growth of new aerosol particles. The second pathway is the gas–particle partitioning where SVOCs form by gas- phase reactions and uptake by preexisting aerosol or cloud particles. Lastly, the third pathway is the heterogeneous or multiphase reactions where low-volatility (LVOCs) or non-volatile organic compounds (NVOCs) forms by chemical reaction of VOCs at the surface or in the bulk of aerosol or cloud particles [5,29].

The formation, transformation and removal pathways of SOAs are of high importance affecting the public health and the environment [11,30].

Ice Nucleation in the Atmosphere

Clouds form by nucleation when water molecules condense by cloud condensation nuclei (CCN). In clouds warmer than −37 °C, liquid water is in a supercooled state, and IN can prompt droplets to freeze. Ice nucleation processes including aerosols are key to the formation and properties of cirrus, and mixed-phase clouds, and thereby can impact both the atmospheric radiative energy distribution and precipitation processes. Ice in clouds is formed either by homogeneous freezing of water and solution droplets at temperatures below -35°C or by heterogeneous ice nucleation processes produced by insoluble aerosol particles which nucleate ice under conditions of supercooling between 0 and -35°C or ice supersaturation at temperatures below 0°C. Although homogeneous freezing is significant for the formation of cirrus clouds, heterogeneous freezing is the main process by which mixed-phase clouds form.

Classical Nucleation Theory (CNT)

Ice nucleation is described by the classical nucleation theory (CNT) [8,31]. CNT was born in the 1930s, and it is attributed to the work of Volmer and Weber [32-35]. While qualitatively correct, CNT is not proficient enough to predict atmospheric particle nucleation on a quantitative scale because of its inadequacy to describe the properties of clusters that consists few molecules.

CNT uses the capillarity approximation, which accepts that thermodynamic arguments can be used to compute the surface and bulk energy contributions to the free energy of critical particle formation [36].

Homogeneous classical nucleation theory: Gibbs free energy (ΔG_c) can be calculated for a cluster formation containing water molecules with CNT [37] and is the sum of the Gibbs energy needed for the formation of the ice-supercooled water interface, ΔG_S and the energy released by bond forming, ΔG_c.

$$\Delta G_c = \Delta G_S + \Delta G_B$$

The formation energy of a spherical cluster of n molecules of radius, r_n, is

$$\Delta G_c = 4\pi r_n^{\,2} \gamma_{sl}$$

where γ_{sl} is the interfacial tension between the ice-supercooled water interface. The Gibbs free energy for the bonding formation is calculated by

$$\Delta G_B = (\mu_s - \mu_l) n$$

where μ_s and μ_l are chemical potentials of the solid and liquid phase respectively. The chemical potentials can be formulated as

$$-(\mu_s - \mu_l) = kTlnS$$

where k is the Boltzmann constant, T is the temperature and S is the saturation of liquid water The number of molecules in the spherical cluster, n, is

$$n = \frac{4\pi r_n^{\,3}}{3v}$$

where, v is the molecular volume of water

$$\Delta G_C = 4\pi r_n^{\,2\,3}{}_{sl} - \frac{4\pi r_n^{\,3}}{3v} kTlnS$$

The radius of the critical cluster, r_c can be formulated as

$$r_c = \frac{2^{3}{}_{sl}}{kTlnS}$$

Moreover, the Gibbs energy of a new critically sized cluster, ΔG_{hom} can be extracted as:

$$\Delta G_{hom} = \frac{16\pi^{3}{}_{sl}^{\;3} v^2}{3\left(kTlnS\right)^2}$$

This expression underlines the dependence of the nucleation energy barrier on interfacial energy. In homogeneous nucleation, the metastable phase of ice nucleates in preference to the stable hexagonal phase [38] providing an explanation for the nucleation of liquid water droplets from the vapour phase.

The rate coefficient (J) is related to the Gibbs energy required to form a critical cluster in an Arrhenius form:

$$J = Aexp\left(-\frac{\Delta G_{hom}}{kT}\right)$$

Combine the two equations:

$$\ln J = \ln A - \frac{16\pi^{3}\,{}_{\mathrm{sl}}^{3}v^{2}}{3\left(kTlnS\right)^{2}}$$

Heterogeneous classical nucleation theory: The Arrhenius equation for homogeneous nucleation can be adjusted for the heterogeneous nucleation coefficient

$$J_{het}(T) = A_{het}\exp\left(-\frac{\Delta G^{*}\varphi}{kT}\right)$$

Where A_{het} is a pre-exponential factor and is the factor by which the presence of a solid surface reduces the height of the energy barrier relative to homogeneous nucleation. This factor is often expressed in terms of an ice nucleating efficiency parameter, m:

$$\varphi = \frac{(2+m)(1-m)^{2}}{4}$$

The heterogeneous nucleation rate expression is

$$\ln J = \ln A_{het} - \frac{16\pi^{3}\,{}_{\mathrm{sl}}^{3}v^{2}}{3\left(kTlnS\right)^{2}}\frac{(2+m)(1-m)^{2}}{4}$$

The above model has been used to parameterize experimental data [39] and has also been used to describe heterogeneous ice nucleation in atmospheric cloud models [20].

Atmospheric Ice Formation Processes

Homogeneous Ice Nucleation: Homogeneous ice nucleation is a stochastic process in which a stable ice germ is formed randomly through internal fluctuation [40]. The range of temperatures in which the homogeneous freezing occurs depends on a variety of factors e.g. the droplet size, the cooling rate and the purity of the water [41]. Throughout the nucleation process, before ice clusters become stable they have to reach a critical size. The possibility of developing a stable cluster is contingent on the liquid volume as in large water volumes, nucleation is expected to take place close to the melting point of ice, while in small droplets water is supercooled to ~236 K [42-44]. Ice nucleation in a closed system was first studied in 1952 by Turnbull [45]. Turnbull studied homogeneous nucleation with very small droplets to avoid heterogeneous nucleation. In general, the performance of experiments for studying homogeneous nucleation is very challenging as it is almost difficult to maintain condition with low enough impurities to avoid heterogeneous nucleation. However, recent techniques such as electrodynamic levitation and oil emulsion can limit heterogeneous nucleation centers allowing ice to form via homogeneous nucleation process [46].

The quantitative and mechanistic comprehension of homogeneous nucleation of ice in water is a challenge [47]. It has been stated that some soluble organics obstruct homogeneous freezing [48,49] affecting the ice nucleation process [50]. Other observations revealed that some supercooled organic-aqueous solutions form glasses at low temperatures [28,51]. More recent studies, showcased ice crystallites in the atmosphere can form through homogeneous nucleation in pre-existing liquid aerosols [52]. The role of the glassy organic phase in enhancing homogeneous ice nucleation has been evaluated experimentally, and glassy aerosol particles may explain the high supersaturations observed at the tropical tropopause. We have to note, though, that there is an ongoing debate as to the accuracy of humidity measurements at low temperatures and pressures [2].

Heterogeneous Ice Nucleation: While ice formation proceeds via homogeneous ice nucleation pathway, heterogeneous ice nucleation is catalysed by a solid surface, such as an insoluble amorphous organic aerosol particle [31]. The formation of ice in nature takes place almost heterogeneously to the presence of particles.

Atmospheric aerosol particles both natural and anthropogenic which have the potential to act as IN are: mineral dust, soot, ash, primary biological aerosols, metallic particles, soluble inorganic crystalline particles and organic material. Conversely, the nucleation ability of each type differs depending on the atmospheric conditions. The capacity of a particle to act as an ice nucleus is summarised by Pruppacher and Klett in the following physical characteristics [31]:

Physical state: A solid substrate is required for ice embryo formation while particles that dissolve under wet conditions is not able to act as IN.

Particle size: Size is important for the efficiency of an IN, as smaller particles are soluble, it is not surprising that ice nucleation tends to occur on larger aerosols, specifically aerosols larger than 0.01 - 0.1 μm. The size of an IN depends on the chemical composition and the environment's supersaturation.

Hydrogen bonding: IN must have the ability to form hydrogen bonds with water as ice is connected by hydrogen bonds of specific polarity and strength. An effective IN would have similarbonding sites on its surface.

Crystallographic arrangement: The geometric arrangement of hydrogen bonding molecules on the surface of an IN must be in similar with the same geometry as that of an ice crystal lattice.

Active sites: Ice nucleation occurs on certain active sites due to specific physical properties. Active sites are surface defects (a step, crack, pore or cavity) or chemical impurities at a solid's surface.

The above characteristics provide a general outline for understanding what properties might make certain particles more efficient IN. However, they need to be reconsidered as they do not apply totally to hygroscopic solutions in a glassy state, atmospheric organic aerosol and secondary organic aerosol which have shown ice nucleation capability [38]. Considering this the best way of determining the effectiveness of ice nuclei must be by quantitative experimentation.

Heterogeneous ice nucleation according to the definition by the Committee on Nucleation and Atmospheric Aerosols [53], occurs by four different mechanisms referred as modes:

- **Deposition nucleation** is the formation of ice from water in supersaturated vapour environment

- **Condensation freezing**, where a liquid droplet acts as cloud condensation nucleus (CCN) at temperatures where quickly freezes.
- **Immersion freezing** generates when a particle immerses in the body of supercooled water.
- **Contact freezing** induces by a particle upon contact with the supercooled liquid water phase.

Some modes of heterogeneous nucleation may be more dominated, depending on the characteristics and concentration of the IN available, the humidity levels and temperature. Also, there is also a dependence on the physical and chemical properties of the surfaces of the ice nuclei that facilitates ice embryo formation.

Ice Nucleation in Clouds

Clouds are aerosols containing small liquid droplets or ice crystals both containing of water. They are essential for the hydrological cycle as they are responsible for water transport and precipitation. Aside from this they reflect and scatter incoming solar radiation and absorb outgoing heat radiation from Earth playing a major role in Earth's weather and climate [54]. Every cloud droplet starts to grow when water vapour condenses on an airborne aerosol particle, called a cloud condensation nuclei (CCN). The increase in aerosols causes an increase in the droplet number concentration [55]. The quantity, morphology, size, and chemical composition, as well as the atmospheric conditions of the CCN, affect the number and size of cloud droplets, and therefore the dynamical and microphysical properties of clouds. Ice formation in clouds strongly controls their properties and plays a major role in precipitation formation [38]. When cloud particles evolve to an adequate size, they precipitate as hydrometeors. Hydrometeors is a concept used in precipitation measurement, and they are composed of liquid or solid water. The most important forms of precipitation include drizzle, rain, sleet, snow, graupel and hail [54].

Atmospheric clouds are classified according to their temperature or region into warm clouds (0°C), mixed-phase clouds (0°C to -35°C), cirrus clouds (below -35°C), polar stratospheric clouds (PSCs) and noctilucent clouds (NLCs). These clouds are affected by a variety of ice nucleation modes prompted by soluble and insoluble aerosol particles except the warm clouds which involve only the gaseous and liquid water phases. Ice crystals in clouds form through two main pathways: homogeneous freezing of liquid particles with temperatures below −36 °C and heterogeneous ice nucleation, activated by ice nuclei that retain surface properties favourable to lowering the energy barrier to crystallisation [56]. While homogeneous freezing is important for cirrus cloud formation, heterogeneous freezing is the dominant process by which mixed-phase clouds form. Heterogeneous ice nucleation requires the presence of ice nuclei (IN), as previously noted. Even though numerous attempts have been made by scientists to study the ice cloud formation mechanisms in the laboratory, there is a lack of information from field studies and when it comes to describing the results of ice nucleation experiments [20].

Cirrus clouds: Cirrus (classified as Ci) is a genus of atmospheric cloud characterised as thin, high, cold and wispy. Cirrus clouds name is derived from the Latin word cirrus, meaning a ringlet or curling alock of hair [57]. Cirrus clouds are the primary cloud category controlling Earth's radiation budget. They have a vital role in the warming effect of our planet as they absorb the outgoing longwave radiation [58]. Although their enormous significance and the vast research done in recent years to understand the microphysics behind their characteristics, their role in climate change remains unspecified due to the lack of parameterizations resulting to uncertainty in understanding the climate system. Cirrus clouds cover about 30% of Earth's surface, and specifically, in the tropics the can reach 60 – 70% [57,59-62].

The main physical properties that lead to cirrus cloud formation is decreased temperature and increased humidity. These properties can form be formed by the cooling of air containing aerosol particles when air rises and by very quick temperature fluctuations caused by gravity [63]. In-situ cirrus nucleates by soluble aerosol particles at higher humidities where ice can be nucleated homogeneously when soluble aerosol particles absorb water, dilute and freeze [64]. On the other hand, nucleation at lower humidities can lead to a considerable decrease of the cloud's ice particle concentration affecting in this way the radiative properties of the cloud [65]. Therefore, it is extremely imperative to identify which particles will act as heterogeneous IN.

Supercooled and Glassy Water

Liquid water becomes more compressible when cooled, and less viscous when compressed. The behaviour of glassy water is very complex. It can exist at temperatures below the glass transition temperature Tg (~ 130 K) and even though it is solid, its structure exhibits a disordered liquid-like arrangement [66]. Ice has more than eighteen polymorphs, most of these phases are stable within a given range of temperature and pressure (e.g. hexagonal ice, I_h) and other are metastable (e.g. cubic ice, I_c) [67]. Water also can form at two different glassy amorphous states (polymorphism), which areextensively studied. The first state is low-density amorphous ice (LDA) which has been known to exist since 1935 [68] and the second state is high-density amorphous ice (HDA), which was detected in 1984 [69].

Low-density amorphous ice (LDA)

Initially, LDA was produced by depositing water vapour onto a cold plate [68]or by rapidly cooling micrometre-sized droplets of liquid water [70]. Now it is agreed that LDA is amorphous and transforms to a highly viscous liquid upon heating to the known glass transition temperature of about 130 K[71].

High-density amorphous ice (HDA)

HDA was detected by compressing ice I_h below a temperature of 150 K [69]. The transformation from a crystalline phase to an amorphous phase is called amorphization [72]. When compressed further at low enough temperatures, HAD crystallises and becomes a high-density crystalline ice [73]. HDA has a similar structure to high-pressure liquid water, suggesting that HDA is a glassy form of high-pressure water [66]. LDA can be formed directly from HDA—and vice versa. This transition results in an unexpectedly large volume change when parameters as temperature or pressure decrease. The transformation between LDA and HDA is a first-order transition between two different metastable amorphous phases.

Glassy Organics in the Atmosphere

The atmosphere has an abundance of organic aerosol particles [20]. Recent studies presented that glassy organic particles can act as IN at low-temperature cirrus conditions in the deposition mode or at slightly elevated temperatures in the immersion mode [29,74-79].

Glassy state defines an amorphous, highly viscous state with a dynamic viscosity (η) greater than 10^{12} pas and the mechanical properties of a solid [80]. The molecules of a glassy solids lack the long-range order that is characteristic of crystals. This characteristic form when a liquid is cooled to a temperature at which the molecules stop diffusing and its viscosity increases correspondingly, resulting in them being held in a "liquid-like" amorphous state [28]. The glassy state can occur by quench cooling, rapid drying of organic or aqueous solutions or vapour phase deposition at low temperatures [28].Glassy aerosol act as heterogeneous ice nuclei affecting the properties of ice clouds and cloud droplets [1] hence influencing ice nucleation and growth, chemical reactions and water uptake of aerosols [79] by altering processes like evapouration, reactivity and diffusion time scales [17]. Glassy aerosol particles when present at conditions advantageous to ice formation, they serve as heterogeneous IN through the immersion, contact and depositional freezing modes [81]. Simulations conducted by T Berkemeier, [82] showed that glassy states could persist for long that heterogeneous ice nucleation in the deposition and immersion mode can dominate over homogeneous ice nucleation.

Thermodynamically, a glassy state is a nonergodic metastable state, unable to rearrange to the ground state[28,79, 83].This phenomenon can set kinetic limitations to water transport to and from the particle during condensation and evaporation as it is likely to be inhibited by diffusion altering the possibility of SOA to act as ice nuclei (IN) or cloud condensation nuclei (CCN) and consecutively affect the formation number and properties of cloud droplets [1,79,80]. To characterise a glassy state, one has to look to a key property called dynamic viscosity η. An increase in the dynamic viscosity of molecular liquids leads to a decrease in macroscopic transport properties and molecular transport processes such as diffusion (D). The Stokes–Einstein equation gives the relation between D and η:

$$D = \frac{kT}{6\pi\eta r}$$

Where, k is the Boltzmann constant, T is the absolute temperature; η is the dynamic viscosity and r is the apparent radius of the molecule which is assumed to be spherical. Based on viscosity values, one can classify constituents into liquids ($<10^2$ Pa s), semi-solids (10^2–10^{12} Pa s) and solids ($>10^{12}$ Pa s). Amorphous substances with a viscosity larger than ($>10^{12}$ Pa s) classifies as glasses [80,83].

Ice nucleation on glassy organic aerosols demands a quantitative characterization, to improve our understanding of their role in the atmosphere. Recent studies indicated that glasses have the ability to influence numerous physical and chemical processes in the atmosphere and affect ice nucleation efficiency of aerosol particles Peter et al [84] recently proposed that a suppressed ice nucleation can explain high ice supersaturations. Further details for the transition of an aerosol to the glassy state are given below.

Glass transition

Glasses are amorphous substances that act like solids. Their chemical and physical properties play a fundamental role in forming a glass.Throughout the glass transition,there is no release of latent enthalpy. Thus, it is not a first-order phase transition. Glassy water (amorphous ice) can exist when the temperature drops below the glass transition temperature Tg (about 130 K at 1 bar). Although glassy water is solid, its structure exhibits a disordered liquid-like arrangement. Low-density amorphous ice (LDA) was discovered 60 years ago and the second kind of amorphous ice, high-density amorphous ice (HDA), was found in 1984 [66].

SOA particles can exhibit viscous semisolid or glassy state at low temperature and low humidity [29,78,85,86]. Evidence of this is provided by a number of literature based on field studies [87-89] and laboratory studies [1,81,90-93]. The organic particles that were examined and exhibited ice nucleation varies from simple sugars and acids [1,81,91-93], biomass burning compounds [81,91,93,94], aromatic volatile compounds [92] and aqueous particles [90]. In general, organic compounds can be used for assessing the glass forming properties of SOA using T_g data [28].

The range of temperatures over which a glass transition occurs is called glass-transition temperature (T_g). It is lower than the melting temperature (Tm) of the crystalline state of the material. Glass transition is a second-order transition as the thermodynamic variables entropy (S), and enthalpy (H) shows continuity. Upon cooling H and S decreases in a stable liquid. If crystallisation occurs without supercooling, asudden drop in H and S can be observed at the melting point (T_m) while cooling the crystal to lower temperatures, H and S decrease in a continuous way. However, most liquids exhibit supercooling below T_m because a nucleation process is required as crystallisationis kinetically blocked and H and S decrease continuously even below T_m.

Nucleation can occur in a supercooled liquid suddenly and in this case H and S would decline unexpectedly to their crystal values at the nucleation temperature [79]. Upon cooling the viscosity of the liquid increases inhibiting nucleation [83] and in some case it can increase to a point where molecules are immobilised, preventing equilibration to the system's lowest energy state [79,83]. When this occurs a glass is formed, the phenomenon is called vitrification, and the corresponding temperature is the glass transition temperature, T_g[83]. The glass transition is characterised by a decrease of H and S,and thermodynamically is the isobaric heat capacity [$c_p=(\partial H/\partial T)_p$].

Because different experimental techniques respond differently to transition, the Tg value of a substance varies depending on how it is obtained. The most common way to determine Tg is calorimetry, a technique that is sensitive to the change in isobaric heat capacity associated with glass transition. The width of the calorimetric glass transition interval can be significant, leading to considerable differences in Tg values reported by different authors depending upon how they evaluated the heat capacity change.

Diffusion coefficients in glassy aerosol

To predict properties of SOA particles information on the diffusion rates of water is needed [95]. Information on the diffusion rates of water, oxidants, and organic molecules within SOAs are required to predict cloud condensation and ice nucleation [82,90,92,93,96-99] as well asgrowth rates and size distributions of these particles [15,16,100-108].The slow diffusion in the glassy phase may impact a particle's optical properties through its ability to take up water and activate as a CCN [38,97,109] as well as the ice nucleation capabilities of the particle [81,92-94]. Semi-solid aerosol undergoes diffusion-limited growth, which results in a different size distribution to that which would be produced by the quasi-equilibrium growth of liquid aerosol [110].

Methods for Future Studies

Due to the limited knowledge of glassy organic aerosol formation, composition, properties, and processes, real effects of glassy organic aerosol on climate are still far from being fully understood and quantified. Glassy organic aerosols effects on climate are indirect affecting water droplet and ice crystals formation, evaporation and deposition with a consequence to cloud formation and precipitation. Experiments to parameterize the nucleation activity in the presence of glassy organics, over a broad temperature range, are needed. This latter is important, given the fact that at least some water-soluble organic compounds show a strong temperature dependence of water activity for aqueous mixtures of constant composition [111]. Such improvements would reduce the model uncertainty in future modeling studies substantially.

Another type of uncertainty arises from uncertainty in heterogeneous ice nucleation onsets. Little is known about the exact microphysical mechanism by which amorphous organics compounds nucleate ice heterogeneously [90,91]. Reported ice nucleation onsets of glassy particles span wide ranges and are the most likely substance or substance class-specific [90,93]. Thus, further laboratory experiments are needed that reveal details on the ice nucleation mechanism, and that allow predictions of ice nucleation ability for a wide variety of substances.

Simulations in the context of Molecular Dynamics (MD) methodology [112] are affected by some insufficiencies, which obstruct a careful comparison with experimental nucleation rates and limit nucleation studies to systems. These weaknesses can be classified into two categories: (i) limitations correlated to the accuracy of the computational model used to represent the system and (ii) inadequacies due to the computational techniques used to simulate nucleation events. The Ab Initio Molecular Dynamics methodology appears promising [113] but highly expensive in computational resources.

Glassy state in SOA processes must be explored. Furthermore, as it may impact the set off of semi-volatile compounds, decrease the occurrence of heterogeneous chemical reactions, influence the ability of aerosol particles to put up water and act as ice nuclei and change the lifetime of the particles [29].

Further research is needed as there are no proposed mechanisms at the atomic level to describe ice nucleation on glassy organic aerosol. The investigation of the nucleation potential of organic compounds may reveal a common process by which ice is activated in all glassy organics that can serve as ice nuclei.

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