# The Effect of Glassy Organics on Ice Nucleation: A Molecular Dynamics Study

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# Introduction/Motivation

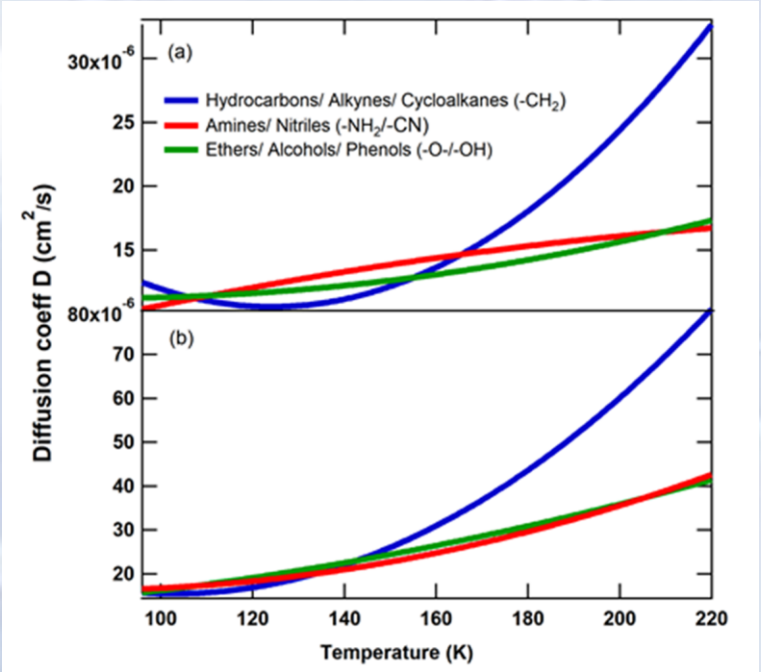
- Atmospheric OA particles can exist in a semi-solid or glassy state.
- The term glassy is used to describe an amorphous material that lacks the long-range molecular order of a crystal but behaves mechanically like a solid.
- The formation of glass depends strongly on the chemical and physical properties of a given substance and its mixing state.
- Aerosol particles present as glasses influence the atmospheric physical and chemical processes like ice nucleation, ice growth, water uptake, evaporation, diffusion, sorption and chemical ageing.
- Certain organic species can undergo this glass transition under atmospheric conditions, and those organic glasses can nucleate ice.
- By using computational methods like molecular dynamics (MD) simulations, valuable insight can be provided for the ability of glass atmospheric organic compounds to form ice nucleus.
- IN events are rare and demand long simulation times reaching at the μs time scale

# Methodology

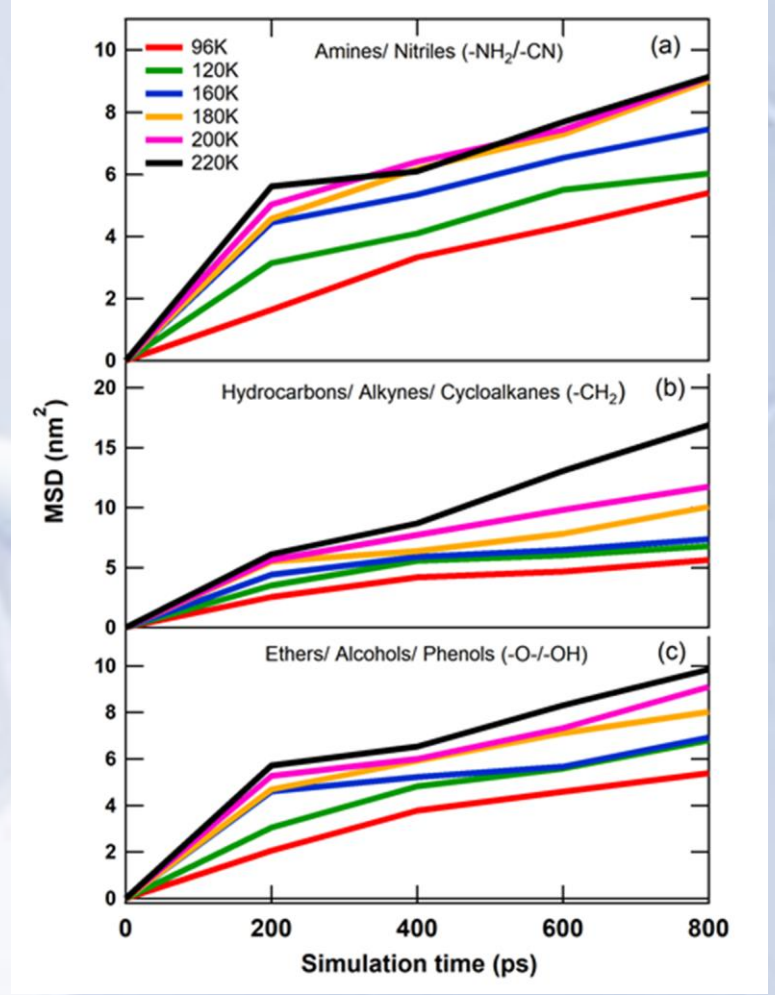
| Function Group | Molecular name | Molecular Formula |
|---|---|---|
| -O-/-OH (Oxygen-containing Compounds - Alcohols, Phenols) | Dimethyl Ether | $C_2H_6O$ |
| | Ethanol | $C_2H_6O$ |
| | Ethylene oxide | $C_2H_4O$ |
| | 1,2 - Dioxetane | $C_2H_4O_2$ |
| | Vinylhydroperoxide | $C_2H_4O_2$ |
| | PEG-06 | $C_{12}H_{26}O_7$ |
| $CH_2$- (Hydrocarbons - Alkyne, cycloalkanes) | Propyne | $C_3H_4$ |
| | Cyclopropene | $C_3H_4$ |
| $-NH_2$/-CN (Nitrogen-containing Compounds - Amines, Nitriles) | 3-aminopropyne | $C_3H_5N$ |
| | 1-Propyn-1-amine | $C_3H_5N$ |
| | Glycine | $C_2H_5NO_2$ |
| | Propanenitrile | $C_3H_5N$ |

- 12 organic species with different structures/functional groups
- Solvated in 1000 or 500 water molecules, [12.55 ] % of the total mass.
- Supercooling dynamics (from 220K to 96K) for 100ns per sample.
- Water Model TIP4P/2005 water
- OPLS-AA force field (FF)
- Gromacs 5.0.4 program package.
- Calculation  MSD, DC, Steinhardt local and AF
- Monitoring of the Ice Nucleation events by using the local Q4 and Q6 Steinhardt parameters
- Computational Simulations: Cy-Tera supercomputing facilities in the Cyprus Institute

# Diffusion Coefficient and Mean-square Displacement

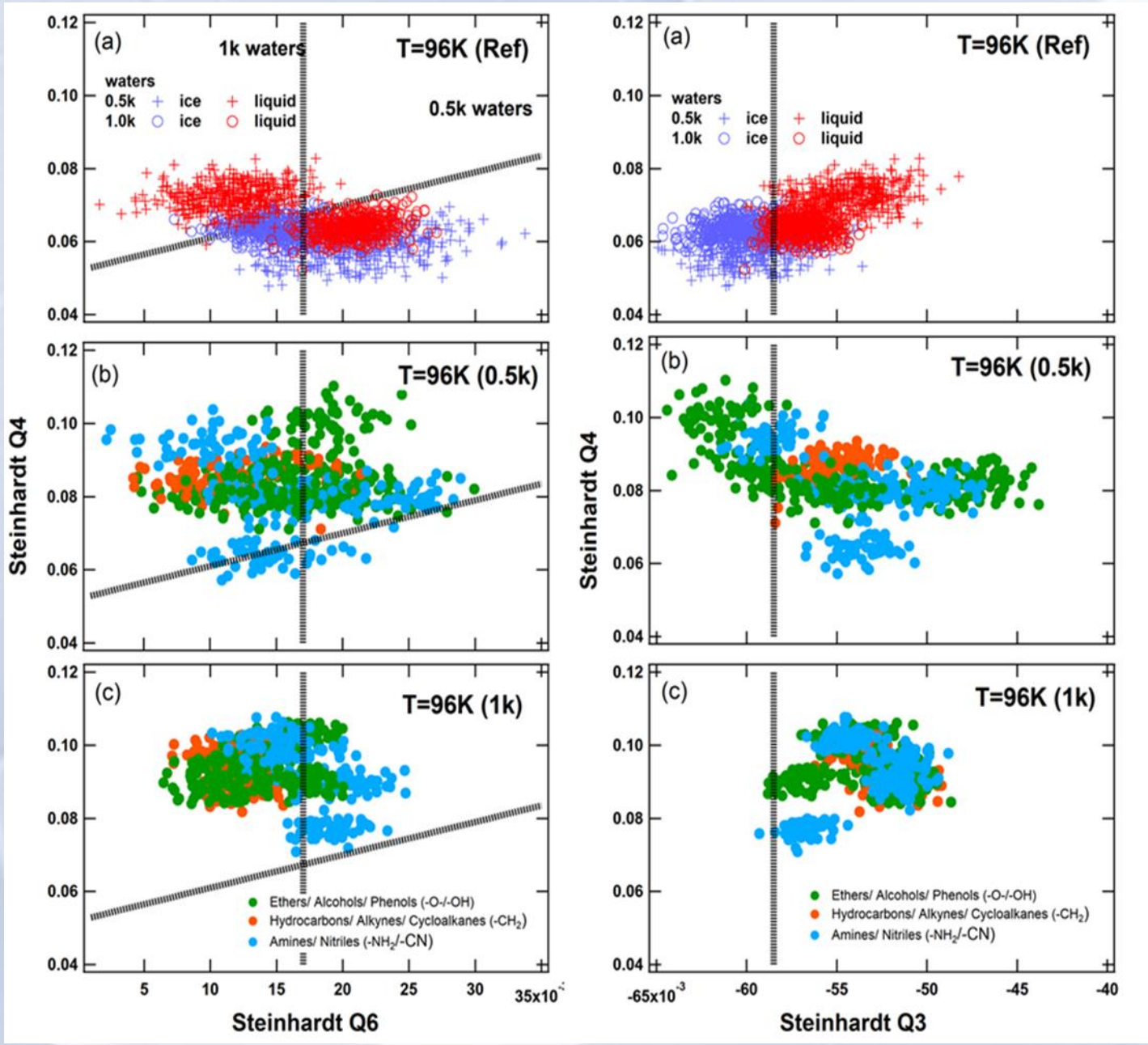



- Determine supercooling dynamic ⇨ MDS and DC calculation for all clusters at T from 220 down to 96 K.
- Reduction of water diffusivity ⇨result of delayed interactions with water ⇨ indication of a glassy phase ⇨ inhibition of the ability of droplets to act as ice nuclei.
- amine/ nitriles + ether/ alcohol/ phenols organic groups at 96 K is interact strongly with water, or are involved in a frozen amorphous state.
- MSD gradually increases ⇨ ordered structure
- 160 K - 96 K we obtain a “frozen” amorphous state.



# Steinhardt Order Parameters

- Q3, Q4 and Q6 are employed to monitor ice nucleation events and label each water molecule in the system as a liquid or solid
- Amines and nitriles (glycine) ⇨ form ice crystals matching the reference for ice inducing in this way ice nucleation.
- Most organic components do not promote ice nucleation.



# Conclusions

- Glass formation was observed in aqueous organic solutions of amines/nitriles (e.g. glycine) and ethers/ alcohols/ phenols
- Most organic components do not promote ice nucleation and organic-rich particles preferentially remain unfrozen.
- Influence aerosol-cold cloud microphysics and dynamics in different ways, even if nucleation is not observed for all the organics probed.
- MD simulations are of the utmost importance in unraveling the microscopic details of ice nucleation

**WHAT'S NEXT?**

- Parameterization of the nucleation activity in the presence of glassy organics, over a broad of temperature range
- The development of efficient enhanced sampling methods to target the limitations of the computational techniques currently employed to study crystal nucleation, enabling accurate simulations for organic systems