

Microscopic simulations of laboratory and interstellar ice structure and chemistry

Robin T. Garrod¹  and Aspen R. Clements²

¹Depts. of Astronomy & Chemistry, University of Virginia, USA
email: rgarrod@virginia.edu

²Dept. of Chemistry, University of Virginia, USA

Abstract. We describe recent simulations of interstellar and laboratory ices using the 3-D, off-lattice microscopic Monte Carlo kinetics model *MIMICK*. The simulations indicate that interstellar ices are capable of achieving porous structures, dependent on physical conditions. In some cases, such structures may be filled as they are formed, by mobile/volatile species such as H₂ that become trapped in those structures. Simulations of laboratory water-ice deposition using *MIMICK* suggest that an additional non-thermal diffusion mechanism is required to reproduce the high degree of porosity achieved for experimental ices at temperatures less than ~80 K. This mechanism is related to the deposition process itself. Simulations of temperature-programmed desorption of mixed molecular ices are ongoing. The interstellar models have also recently been developed to incorporate a full gas-phase chemistry, coupled with the grain-surface chemistry.

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1. Introduction

Interstellar ices, formed on the surfaces of microscopic dust grains (canonical size 0.1 μm), consist mostly of water, with substantial quantities of CO, CO₂, NH₃, CH₃OH and CH₄. The production of these species depends largely on the accretion and surface thermal diffusion of atoms and simple molecules originating in the gas phase. Laboratory experiments on water deposition at low temperatures (~10–100 K) indicate that such ices may achieve significant porosities (up to ~50%); however, there have been no reliable interstellar detections of the O-H dangling bond mode of water that is thought to indicate porosity, although this feature may not be a good tracer in interstellar ices (e.g. [Bossa *et al.* 2014](#)). Importantly, the timescales and formation mechanisms in the lab differ from conditions prevalent in the interstellar medium. In order to understand the physical/porous structure and chemistry of interstellar ices, the formation of both laboratory and interstellar ices must be simulated using the same chemical kinetics methods.

2. Simulations of laboratory water deposition

The *MIMICK* chemical kinetics model simulates the formation of ices based on locally-calculated rates of diffusion between surface binding sites. The positions of atoms and molecules correspond to surface potential minima, which are re-calculated when surface processes alter the local environment. The choice of which process occurs at any moment (diffusion, desorption, accretion, or where appropriate, reaction) is determined by a Monte Carlo algorithm. Atoms/molecules are deposited on randomized trajectories.

Using a periodic boundary-condition implementation of the model ([Clements *et al.* 2018](#)), we simulate laboratory deposition of pure water, at a rate of 10^{13} molecules cm^{-2}

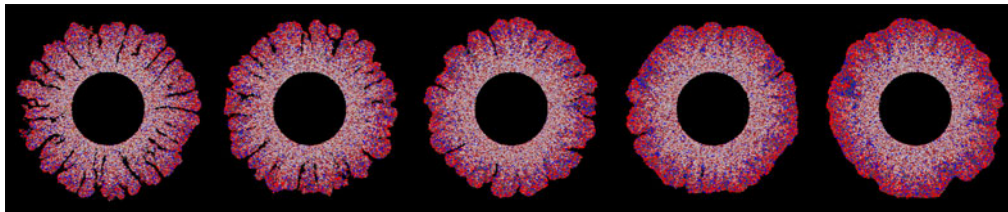


Figure 1. Cross-sections of simulated interstellar ice mantles formed at $T_{\text{dust}}=8, 9, 10, 11, 12$ K (left-right). Each atom/molecule in the ice is shown in the image; color indicates atom type.

s^{-1} . At lower surface temperatures, laboratory measurements indicate that the ice density is lower, indicating more porosity (Brown *et al.* 1996; Bossa *et al.* 2014). Initially, the *MIMICK* model was used to simulate the deposition experiments assuming a purely thermal diffusion mechanism for water molecules. The high-temperature (>80 K) simulations match the experiments of Brown *et al.* (1996) well, but thermal diffusion alone is not sufficiently fast at lower temperatures, resulting in excessive porosity.

Further modeling work by Clements *et al.* (2018) introduced an additional, non-thermal diffusion mechanism, in which the energy gained by the deposited particle as it enters the surface potential is available for immediate diffusion of the incoming particle, before it gradually thermalizes with the surface. An average of 1–2 initial non-thermal hops by each deposited H_2O molecule is sufficient to reproduce the experimental behavior.

3. Temperature programmed desorption simulations

Using a well-parameterized model of the porous structure of laboratory-deposited ice, we have begun simulations of the temperature-programmed desorption of CO from amorphous water ice. Preliminary models have been run to simulate all of the stages of a TPD experiment: firstly, a porous water ice is produced, as described above; then, CO is deposited onto that surface; as the temperature is ramped linearly, starting at 11 K, the CO diffuses into the pores; the water pores re-arrange and some CO is trapped; by ~ 130 K, the pores are completely lost, with a small amount of CO still trapped.

4. Interstellar simulations

The interstellar grain-surface chemistry simulations, based on the preliminary models of Garrod (2013), use a fully 3-D representation of a dust grain. In these models (Garrod, *in prep.*), which include H, O, C, and N atoms and molecules, ~ 1 million ice molecules are formed/deposited under various dust temperatures and gas densities. The ices and their porous structures are formed through chemical reactions, rather than direct deposition. Porosity is determined by the relative rates of deposition and diffusion of H atoms versus the other species (e.g. O) from which the ices are formed. Higher temperatures allow greater diffusion of O, and thus lower water porosity (see Fig. 1).

A fully-operational gas-grain version of the interstellar model has now also been constructed, using a complete gas-phase chemical network (Deselm & Garrod, *in prep.*).

References

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