# **REALISTIC MODELLING OF THE NUCLEATION OF NANOSILICATE** DUST PARTICLES USING ATOMISTIC SIMULATIONS

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## Introduction

Dust grains comprise about 1% of the mass in the interstellar medium. These particles are generated in the latter stages of life of stars, and grow and evolve during this stage and are subsequently processed in the interstellar medium [1]. Dust grains are essential for astrochemical processes and through their protective interaction with the UV field assist and take part in formation of astronomical bodies (e.g. stars and planets). Current models for dust structure as well as experimental results seem to show that dust is formed from primary grains with sizes ranging from 10 to 50 nm, which later coalesce to form micron-sized particles [2][3].

Silicate dust is a major component in both interstellar and circumstellar environments. However, most of the detailed properties and processes in which this silicate grains are involved are unclear, as we lack detailed knowledge on how the size, structure and stoichiometry of this grains affect their physical and chemical properties. As a complimentary tool to laboratory experiments and observation we propose a powerful bottom-up atomistic simulation approach to clarify such questions.



Typical silicate dust grain size

nm

Fractal-like silicate particle aggregate formed from a vapour mixture. Primary particles are of the order of 10nm (taken from

## Atomistic Molecular Dynamics to simulate aggregation processes

The detailed theoretical investigation of individual silicate grains is too big for quantum mechanical based modelling methods, (10000s of atoms). Computational modelling studies thus typically assume that grains of between 10-100nm are featureless primary units and then simulate the aggregation of these units. Such an approach provides realistic looking dust aggregate morphologies at length scales of a few microns but loses all atomistic detail. As such, direct access to atomic level structure and the motion (e.g. vibrations responsible for IR spectra) are lost. Using, a reliable description of • interatomic interactions (i.e., force fields), classical molecular dynamics (MD) simulations can provide realistic models of systems ranging up to tens of thousands of atoms (~20nm). We have developed a code which uses MD to simulate the growth of dust up to 1000s of atoms size (10 nm) via molecular/atomic addition and use it to simulate the nucleation of magnesium silicate grains.



1.We select initial structure, temperature and final stoichiometry.



2.A monomer is randomly selected with a probability related with the stoichiometry. We assign it a velocity and velocity vector.

3. The simulation is divided in two steps: addition of monomer and cooldown. The later can be used to simulate non-equilibrium situations.

Temperature

time (ps)



4. Finally, we check for disconnected parts, which will be erased from simulation. The process is then repeated.

#### **Key Takeaway Points:**

- Nucleation is explicitly treated at the atomistic level
- Temperature (velocity), cool down time and stoichiometry can be set up by user to simulate different environments. (e.g. circumstellar, interstellar)
- Ability to track how properties change as the nucleation is taking place, (e.g. porosity, surface/volume ratio, or IR spectra).
- Direct calculation of IR spectra from atomic vibrations in realistically sized particles
- The method can be extended to other elements (e.g. Fe, Ti, C) as long as reasonable force-fields exist.

## **Proof of Concept: 4nm (=1500 atoms) olivine-like and pyroxene-like**

#### **Set-up:** Circumstellar environment (late AGB O-rich star)

 $T = 900K \rightarrow Used$  to determine velocity of incoming monomers. Initial Structures from global optimisation: 35 atoms olivine and 25 atoms for pyroxene. Each nucleation event will cool down in 1.25 ps. Nucleation + Cooldown = 2.25ps.

Pyroxene-type Mg<sub>312</sub>Si<sub>305</sub>O<sub>922</sub>



Incoming particles: SiO, Mg, O. Following model of heteroatomic nucleation [4] we use atomic oxygen used instead of water, as it appears that  $H_2$  is liberated after nucleation, giving effectively the addition of a single O atom on the cluster. ForceField: FFSiOH (Si,O)[5] and P2 (Mg) [6]

Olivine-type Mg<sub>436</sub>Si<sub>218</sub>O<sub>871</sub>







# Getting detail: Simulated IR evolution with size and stoichiometry

Preliminary results applying gaussian broadening to the directly calculated IR frequencies. Two regions are highlighted: 10 µm Si-O stretching (useful for mineral characterization) and 18µm O-Si-O bending, much broader and difficult to characterize.



#### Size dependency of IR peak positions

Peak positions at 10  $\mu$ m show the same behaviour as Enstatite (pyroxene family) and Forsterite (Olivine family) minerals for both bulk and grains, where forsterite peak is at slightly higher values than Enstatite.



#### Size dependency of IR peak intensities While pyroxene-like particles show a 0.34 ratio between $18\mu m$ and $10\mu m$ peaks, in olivine-like particles the ratio increases to ~0.72..We find a higher fluctuation in the ratio for olivine-like particles, where for the larger particles the ratio Idrops to 0.61. These values are consistent with current models of dust particles [7] where the ratio is expected to be between 0.3 and 0.7.









### **References:**

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## **Aknowledgments:**

- [1] Jones, Anthony P. "The mineralogy of cosmic dust: astromineralogy." European Journal of Mineralogy 19.6 (2007): 771-782.
- [2]Saunders, Russell W., and John MC Plane. "A photo-chemical method for the production of olivine nanoparticles as cosmic dust analogues." Icarus 212.1 (2011): 373-382.
- [3]L. J. Allamandola and S. A. Sandford in``Dust in the Universe'', Cambridge University Press, 1988.
- [4]MLA Goumans, T. P. M., and Stefan T. Bromley. "Efficient nucleation of stardust silicates via heteromolecular homogeneous condensation." Monthly Notices of the Royal Astronomical Society 420.4 (2012): 3344-3349.
- [5]Pedone, Alfonso, et al. "FFSiOH: a new force field for silica polymorphs and their hydroxylated surfaces based on periodic B3LYP calculations." Chemistry of Materials 20.7 (2008): 2522-2531.
- [6]Alfredsson, Maria, et al. "Crystal morphology and surface structures of orthorhombic MgSiO3 perovskite." Physics and chemistry of minerals 31.10 (2005): 671-682.
- [7]Henning, Thomas. "Cosmic silicates." Annual Review of Astronomy and Astrophysics 48 (2010): 21-46.





