From molecules to dust grains: The role of alumina cluster seeds

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Abstract. Asymptotic Giant Branch (AGB) stars contribute a major part to the global dust budget in galaxies. Owing to their refractory nature alumina (stoichiometric formula Al_2O_3) is a promising candidate to be the first condensate emerging in the atmospheres of oxygen-rich AGB stars. Strong evidence for that is supplied by the presence of alumina in pristine meteorites and a broad spectral feature observed around ~ 13 μm. The emergence of a specific condensate depends on the thermal stability of the solid, the gas density and its composition. The evaluation of the condensates is based on macroscopic bulk properties. The growth and size distribution of dust grains is commonly described by Classical Nucleation Theory (CNT). We question the applicability of CNT in an expanding circumstellar envelope as CNT presumes thermodynamic equilibrium and requires, in practise, seed nuclei on which material can condense. However, nano-sized molecular clusters differ significantly from bulk analogues. Quantum effects of the clusters lead to non-crystalline structures, whose characteristics (energy, geometry) differ substantially, compared to the bulk material. Hence, a kinetic quantum-chemical treatment involving various transition states describes dust nucleation most accurately. However, such a treatment is prohibitive for systems with more than 10 atoms. We discuss the viability of chemical-kinetic routes towards the formation of the monomer (Al_2O_3) and the dimer (Al_4O_6) of alumina.

Keywords. nucleation, alumina, dust grains, AGB stars

1. Overview

Cosmic dust is crucial for the evolution of galaxies. It impacts the synthesis of complex organic molecules in molecular clouds, the wind-driving of evolved stars and the formation of celestial bodies (e.g. asteroids, planets) in protoplanetary discs Henning (2010). Asymptotic Giant Branch (AGB) stars represent a major contributor to the global dust budget in galaxies. The chemistry in the inner circumstellar envelopes of AGB stars (i.e. dust formation zone, $R = 1-10$ R$_*$) is primarily controlled by the carbon-to-oxygen (C/O) ratio. The CO molecule is triple bonded and very stable (dissociation energy of 11.1 eV) (see e.g. Gaydon (1947)). As a consequence the lesser abundant element (C or O) is predominantly locked up in the CO molecule limiting the formation of molecular species containing the lesser abundant element. The presence of the major molecules can be explained by thermodynamic equilibrium calculations.

However, this simple picture is challenged as carbon-bearing molecules (HCN, CS, CO_2) have been observed in O-rich AGB stars (Lindqvist *et al.* (1988); Decin *et al.* (2010a); Justtanont *et al.* (1998)) and oxygen-bearing species (H_2O, SiO) were found in C-rich AGB atmospheres (Decin *et al.* (2010b); Neufeld *et al.* (2011); Johansson *et al.* (1984)). Their presence can only be explained by processes deviating from chemical and thermal equilibrium. CO might be dissociated by shock-induced collisions (Gobrecht *et al.* (2016)), or by interstellar photons (Agúndez *et al.* (2010); Van de Sande *et al.* (2018)) releasing free C and O atoms to form other unexpected *exotic* molecular species.

In contrast to the exotic molecules, carbonaceous dust forms just in C/O>1 environments and oxygen-rich dust arises in regimes with C/O<1 only. In the latter case, metal oxides represent the majority of the solids as there are no stable, pure oxygen compounds larger than ozone (O_3). The main dust component in oxygen-rich AGB stars are silicates. Silicates are composed of at least three elements (Si, O and Mg) and are so called ternary oxides. Iron (Fe) might be incorporated in the Mg-rich silicate grains at a later stage and act as a thermostat for the grain (Woitke (2006)). In this case, the dust grains are quaternary oxides consisting of O, Si, Mg and Fe. Measurements on the vapor pressure of Mg-rich silicate grains as well as on pure silicon oxide (SiO) resulted in rather low condensation temperatures ($600-800$ K) for conditions prevailing in circumstellar envelopes (Wetzel *et al.* (2013)). ISO observations have shown that the silicate features around 10 μm and 18μm are absent for the low mass-loss rate stars W Hydrae and R Doradus (Decin *et al.* (2017)), but they are present in the high mass loss rate object IK Tau. Theses findings indicate that, albeit silicates represent the main component of oxygen-rich dust grains, they are not the first condensates to emerge in the outflows of O-rich AGB stars. The first condensate, or *seed* particle, initiating the nucleation process is supposed to have a high condensation temperature, made up from available and abundant elements and molecules, and sufficiently fast growing rates in circumstellar conditions. There are several metal oxides satisfying the above conditions: Titania (TiO_2), Magnesia (MgO), silicon monoxide (SiO) and alumina (Al_2O_3). In crystalline form, titania, or TiO_2, exist as anatase and rutile, both being highly refractory. However, the solar titanium abundance is rather low. Silicon monoxide (SiO) is fairly abundant in the envelopes of AGB stars, though its nucleation is rather unlikely to occur in circumstellar media (Goumans & Bromley (2012); Bromley *et al.* (2016)). On one hand, a homogeneous nucleation is hampered by slow kinetic reaction rates. On the other hand, Si starts to segregate and to form islands inside the most stable clusters for small cluster sizes $(SiO)_n$, $n \geq 10$. Gaseous MgO is hardly present in circumstellar environments (Turner & Steimle (1985)). Even if the MgO molecule is present, its nucleation rate turns out to be too small to form the seed nuclei for silicate dust formation (Köhler *et al.* (1997)). One reason are the *magic* cluster sizes (2, 4, 6, 9, 12 and 15 MgO units) with enhanced stability that hamper the formation of larger sized clusters. Alumina (stoichiometric formula Al_2O_3) does not exhibit the latter restrictions (sparse abundance, magic sizes, segregation) and is thus a promising seed particle candidate. Circumstellar alumina is observed as it shows a spectral emission feature around ~ 13 μm attributed to $Al-O$ stretching and bending modes (Posch *et al.* (1999); Sloan *et al.* (2003)). This feature has been seen in several oxygen-rich AGB sources (S Ori, R Cnc, GX Mon, W Hya, R Dor) close to the stellar surface at around $2-3$ R_* (Karovicova *et al.* (2013); Decin *et al.* (2017)).

2. Nucleation descriptions

Top-down chemical prescriptions use a known macroscopic ensemble of atoms (e.g. a crystal structure) and interpolate the unknown properties and characteristics of smaller-sized systems like nanoparticles and molecular clusters. A prime example of a physio-chemical top-down approach is Classical Nucleation Theory (CNT). In CNT,
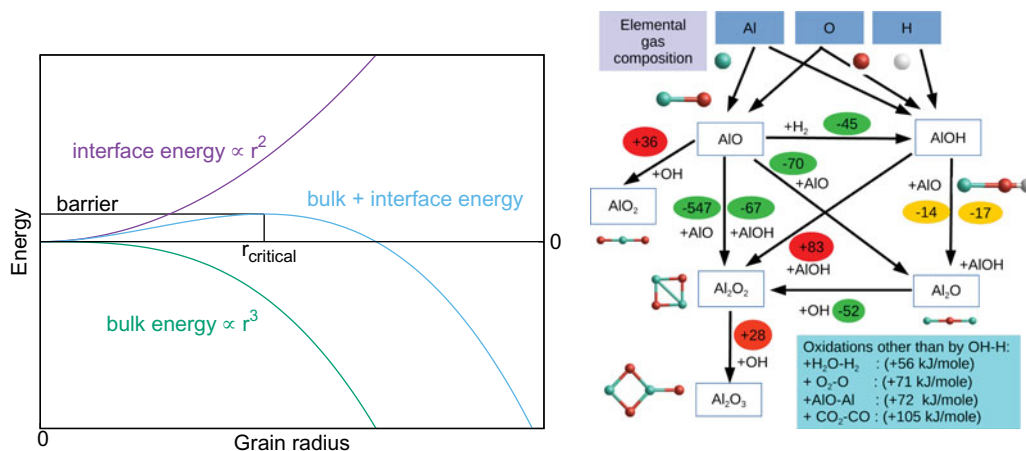
Figure 1. *left panel:* Schematic sketch of the top-down derived classical nucleation energy versus particle radius in blue. The bulk component is in green, and the interface component is in violet. *Right panel:* Bottom-up chemical reaction network describing the formation of alumina monomers (Al_2O_3). Al atoms are in turquoise, O atoms in red, and H atoms in white. Reaction enthalpies are given in kJ/mole and colored in red (endothermic), orange (slightly exothermic) and green (exothermic).

many generic properties of a particle with size N can be expressed as a sum of a bulk term and a surface interface) term. This is also true for the potential and free energies of the particles, i.e. $E_{pot} = E_{sur} + E_{bulk}$. An illustrative example is shown in the left panel of Figure 1.

The surface (interface) energy can be interpreted as a sort of surface tension. It is repulsive and scales with the particle size (or radius) as r^2. The volume (bulk) term is attractive and scales with the grain radius as r^3. The resulting curve considering both, bulk and interface, has a maximum for $r > 0$. The maximum is located at the so called critical radius r_{crit} and has an E_{crit} corresponding to an energy barrier. In the CNT regime, E_{crit} represents the energetic bottleneck of the nucleation process. Once this barrier is overcome (i.e. the dust particle has grown to a radius of r_{crit}), the subsequent nucleation is energetically favourable. However, it has been shown that the global minima structures of a variety of (sub-)nanosized clusters, including TiO_2 (Lamiel-Garcia *et al.* (2017)), SiO (Bromley *et al.* (2016)), MgO (Chen *et al.* (2014)), and Al_2O_3 (Li & Cheng (2012)), as well as SiC (Gobrecht *et al.* (2017)) do not exhibit bulk-like geometries. In contrast, potential and free energies, bond lengths and angles, atomic coordination, formal charges, deviate significantly from bulk-like analogues (bulk cuts). We conclude that CNT cannot be made to work for small clusters representing the basic building blocks of cosmic dust. We use a bottom-up approach starting with atoms, molecules and molecular clusters, and successively build up larger sized dust clusters and dust grains. We are convinced that the formation of condensates are describes more realistically using a bottom-up approach, as it mimics the onset of dust formation in expanding circumstellar shells. Hybrid approaches - using CNT with realistic free energies for the smallest clusters instead of extrapolated surface tensions - are computational less expensive alternatives to a full chemical-kinetic nucleation treatment (see e.g. Boulangier *et al.* (2019)). On the right hand side of Figure 1 we present part of the bottom-up chemical-kinetic network. The gas phase species AlO and AlOH can be easily formed from the atoms Al, O, and H, and they represent the most abundant species in oxygen-rich circumstellar shells (Tenenbaum & Ziurys (2010); Decin *et al.* (2017)). AlO and AlOH can be exothermically converted to Al_2O and Al_2O_2. However, the oxidation of Al_2O_2 to Al_2O_3 by OH and

H_2O are substantially hindered by large energy barriers. Hence, the nucleation is likely to proceed via different, less endothermic reaction channels that might involve heterogeneous species like aluminum silicates, or, that do not proceed via the alumina monomer.

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