The influence of surface charge on dust agglomeration growth in the mesosphere

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Background: It is assumed that meteoric smoke particles (MSP) are the main dust component in the mesosphere. MSP are small condensates that form in the diffusing meteor and are transported in the atmosphere where they grow by condensation. A second dust component consists of ice particles that form during summer months at mid and high latitude. These Polar Mesospheric Cloud (PMC) particles are composed of water ice and possibly include a fraction of the smaller MSP. The growth of particles is an important consideration toward a better understanding of the role of dust, ice and refractory particles in the upper mesosphere and lower thermosphere (MLT, ~ 60 - 130 km).

Method: We investigate the effect of surface charge on the aggregation and growth of particles in the MLT region. We apply a model of the electrostatic interaction between particles of dielectric materials (Bichoutskaia et al. 2010) that includes like-charge attraction. This occurs due to the mutual polarisation of surface charge densities leading to regions of negative and positive surface densities close to the point of contact between the particles (Stace et al. 2011). This general model allows the investigation of interactions between particles of different size, charge and composition. We simulate the interactions for particles of the same charge and pairs of neutral and charged particles under different collision conditions in the MLT. We consider particles of sizes > 0.5 nm and different material compositions resulting in different refractive indices.

Result: We apply the model to collisions between sub-nm refractory particles and 20 nm sized ice particles and find that like-charge attraction when both particles carry a negative charge can lead to coalescence when the ice particles carry just one or two free electrons. For larger numbers of charge, the collision velocities required to achieve coalescence are beyond 1000 m/s. The size of the refractory particle has to be smaller than roughly 2 nm. We assumed that the refractory particles consist of either metal oxide or silicate and find similar results for both materials.

Assumptions and energy barriers

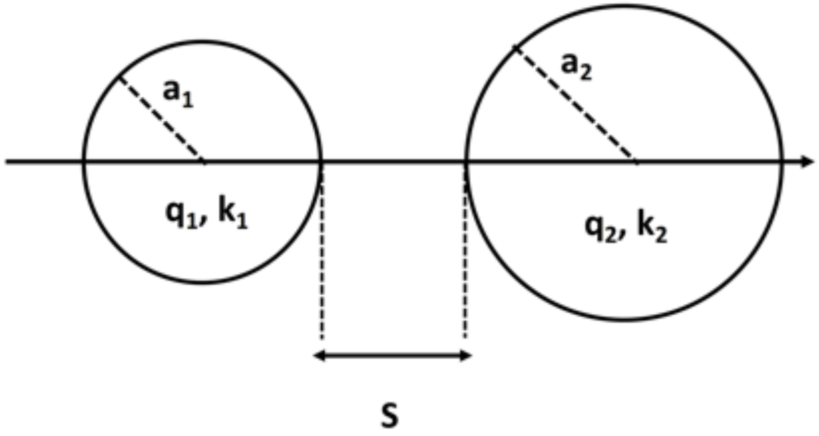


Figure 1a: Consider two interacting dissimilar spheres at a surface-to-surface separation s. The dielectric constants, permanent charges, and the radii for spheres 1 and 2 are denoted as k_1, q_1, a_1 and k_2, q_2, a_2, respectively.

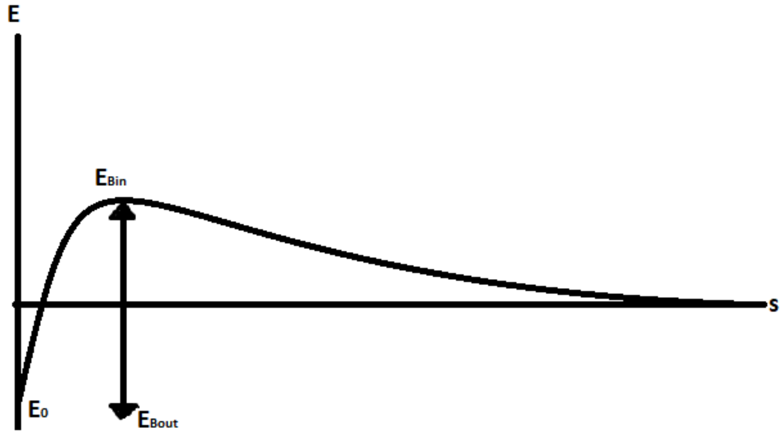


Figure 1b: Sketch of the energy profile between the particles as function of separation s. E_0 is the energy between the two spheres at zero separation, E_{Bin} energy barrier for collision, B_{Bout} limit for sticking.

Dielectric constants are K_{ice} =100, low frequency dielectric constant of ice, K_{MgO} = 9.7, $K_{IronOxide}$ =14.2, $K_{Alumina}$ = 9.8, K_{Silica}= 3.9, K_{Lime} = 2; for surrounding medium K_m=1 (medium is unpolarizable) is reasonable for low-pressure mesosphere.

Force as function of distance

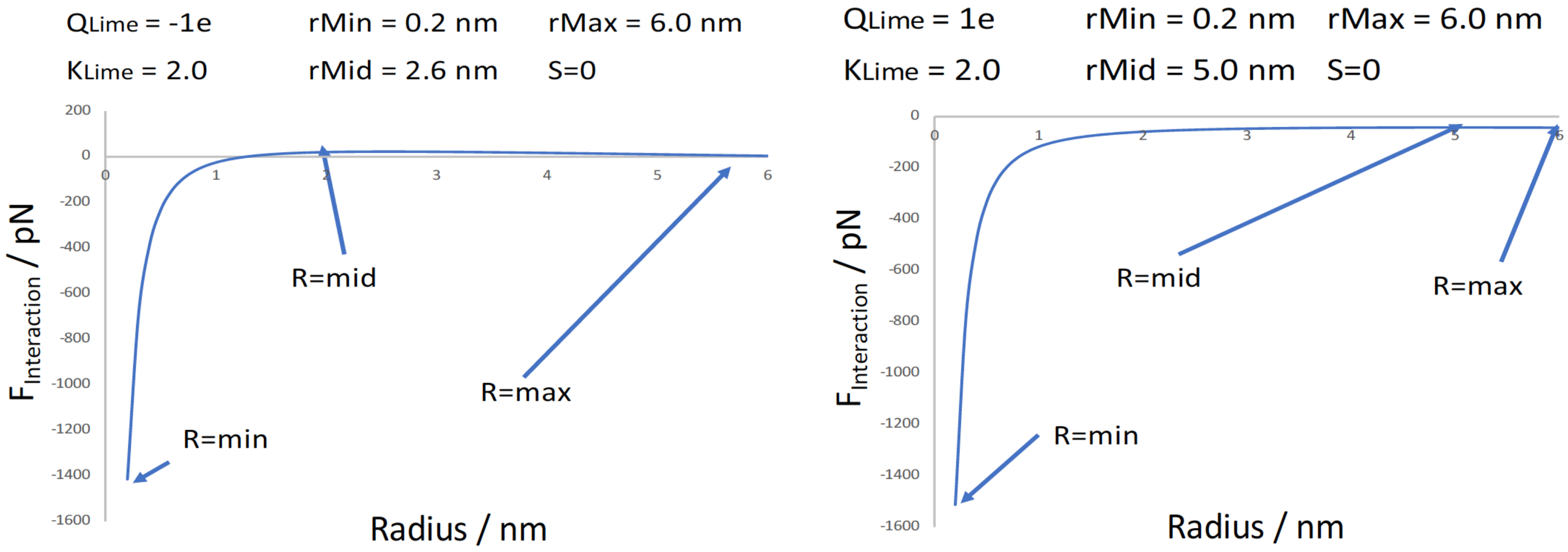
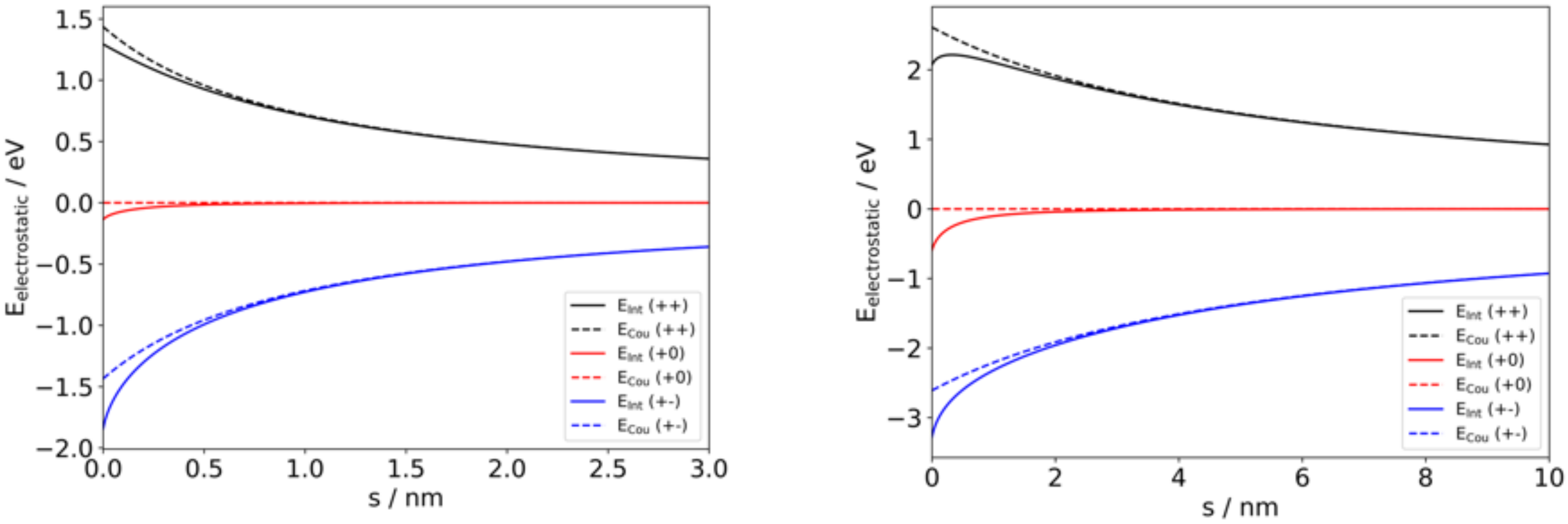


Figure 2: The attracting force between lime particles colliding with a 10 nm ice particle with QIce = -20e for different sizes of lime particle. For **negatively charged lime particles shown on the left** the force is attracting for small sizes r < 1 nm.; rMid denotes the particle radius of maximum repelling force, here it is 6 nm, Rmax is the maximum distance that we considered. **Positively charged lime particles (on the right) are always attracted.** (Lime is used as example for material with low dielectric constant, i.e. low polarizabilty). (Note, that typical charge of the ice particles is expected less than 20 electrons.)

Example: interaction energies between iron oxide particles



Same sizes

$a_1 = a_2 = 0.5$ nm

$q_1 = +1$ e; $q_2 = -1$ e/0/+1 e

$k_i = 14.2$

Different sizes

$a_1 = 0.5$ nm; $a_2 = 5.0$ nm

$q_1 = +1$ e; $q_2 = -10$ e/0/+10 e

$k_i = 14.2$

Figure 3: The Interaction energy between iron oxide particles with different charges.

Energy barriers for particles with opposite and same charge polarity

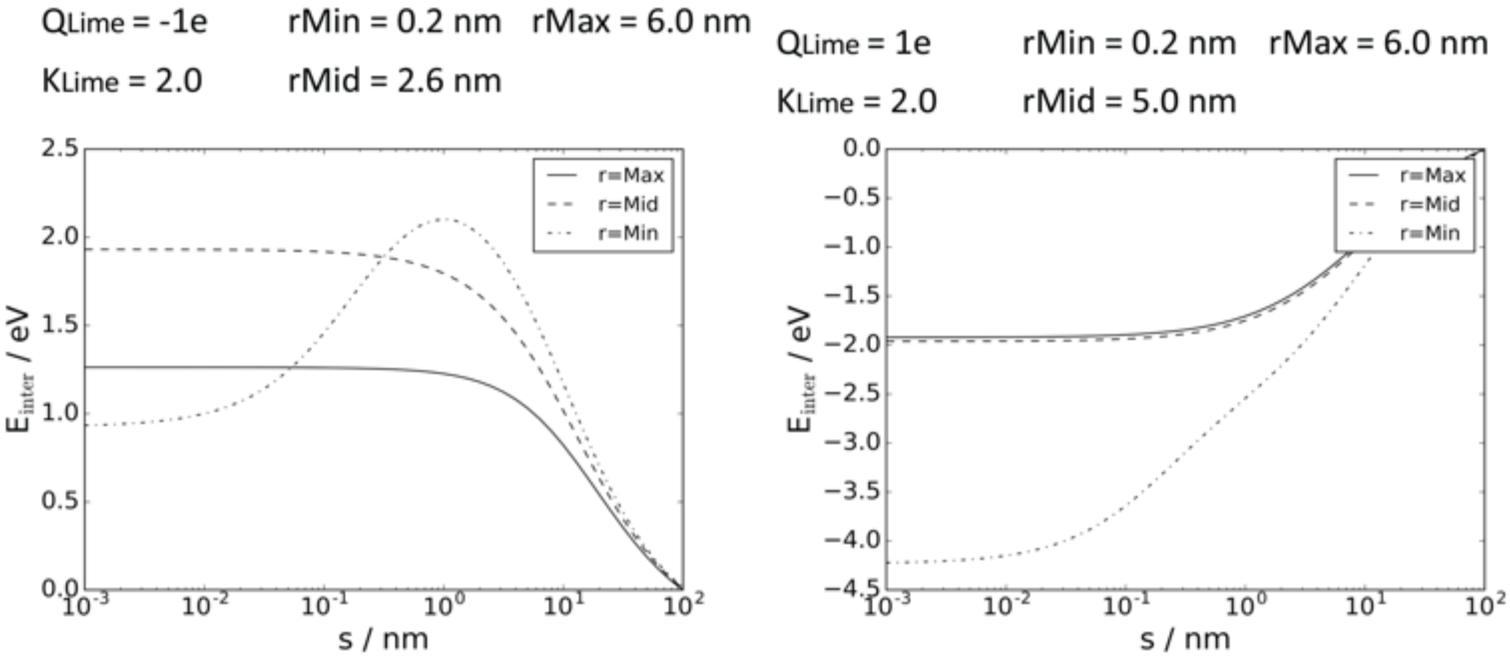


Figure 4: Shown is interaction energy for particles with opposite and same charge polarity. The plot is for a negatively charged lime particle, right side for a positively charged lime particle. The ice is negatively charged as above. Consider RMin: if the kinetic energy of the lime particle relative to the ice particle is larger than the barrier (about 2.2. eV), then the particles can achieve contact, s < 0.001 nm where the binding energy is – 1.2 eV. To leave again the lime particle needs to overcome the reverse barrier of 3.4 eV. With kinetic energy in the interval 2.2 eV < E_kin < 3.4 eV the lime **particles can stick to the ice particles with same charge polarity.** Particles of opposite charge have negative mutual energy shown on the right for comparison.

Energy barriers for point charges and charge distribution on particles

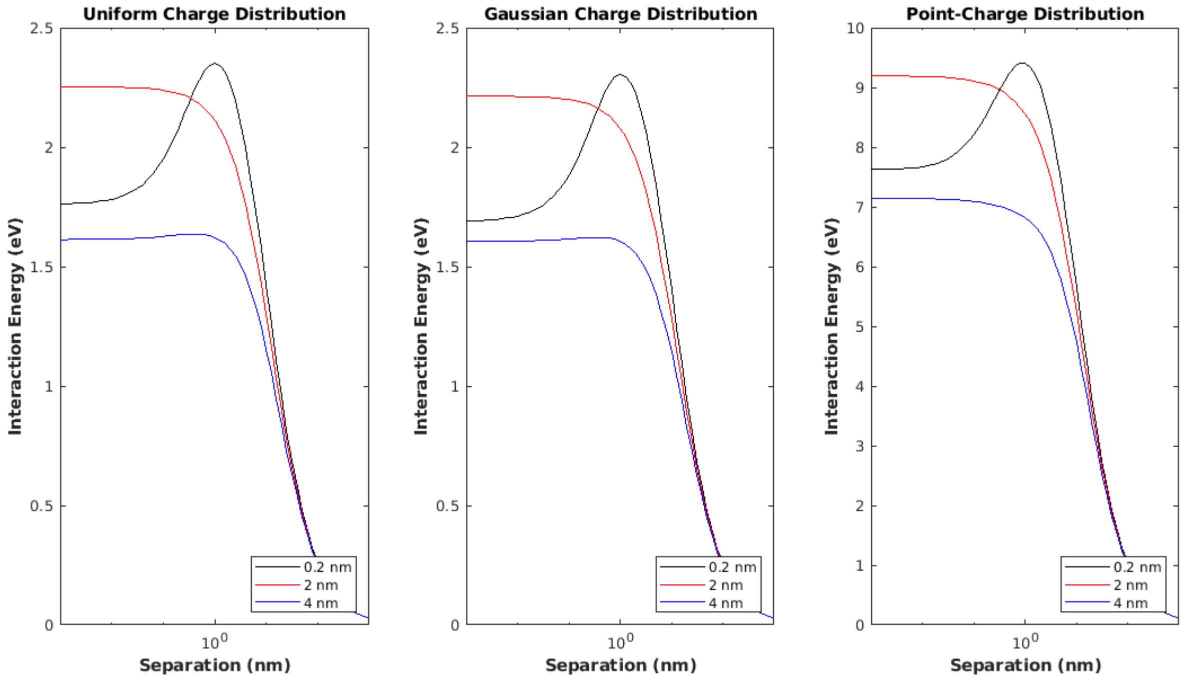


Figure 5: Interaction electrostatic energy between a MgO particle of -*e* charge and varying size (radius of 0.2 nm (black), 2 nm (red) and 4 nm (blue)) and **ice particle of -20*e* charge and 10 nm in radius** as a function of their separation. This figure indicates that the interaction of small MgO particles with large highly charged ice particle remains purely repulsive at all separation distances greater than 1 nm; however, the smallest particulates (*r* = 0.2 nm) can, in principle, form a metastable bound state with ice provided that after the collision they do not possess the kinetic energy sufficient to overcome the barrier and separate. Note that for a highly charged state of ice particle the uniform distribution of free charge might be more appropriate, and it predicts the barrier for separation of about 0.55 eV. The interactions of SiO_2 and FeO particles with ice show similar trend.

Energy barriers for point charges and charge distribution on particles

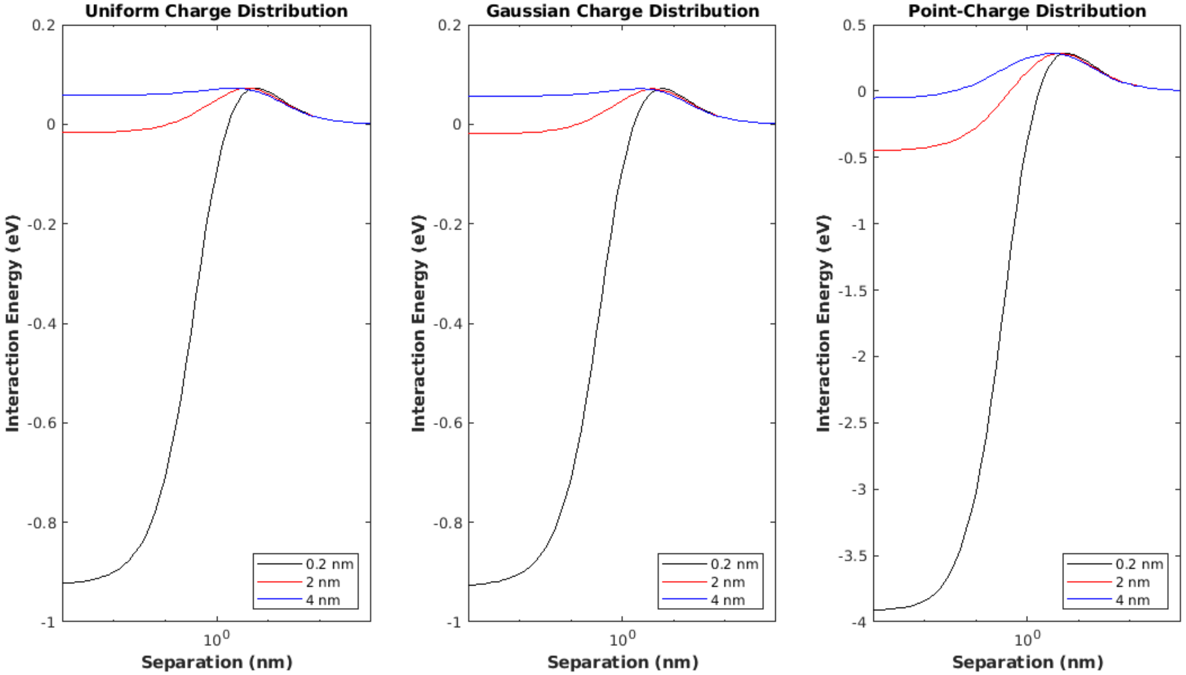


Figure 6: Interaction electrostatic energy between a MgO particle of -*e* charge and varying size (radius of 0.2 nm (black), 2 nm (red) and 4 nm (blue)) and **ice particle of -*e* charge and 10 nm in radius** as a function of their separation. Here, once again the interacting particles differ in size, with the ratio of particle radii varying from 2.5 to 50, but they carry the same amount of charge ($q = -e$). The interaction energy profile indicates the formation of a strong stable aggregate at separation distances below 1 nm**.** The Coulombs barrier is very low in this case and can be readily overcome in the considered conditions. As the approximation of a point free charge is the most appropriate in this case, we note the formation of a very strongly bound agglomerate with the binding energy reaching 4 eV. The critical radius of MgO particulate that leads to the emergence of a stable state is about 4 nm; this implies that for a MgO – ice pair of particles carrying the same charge the difference in their size should be at least 2.5.

Velocity range of coalescence

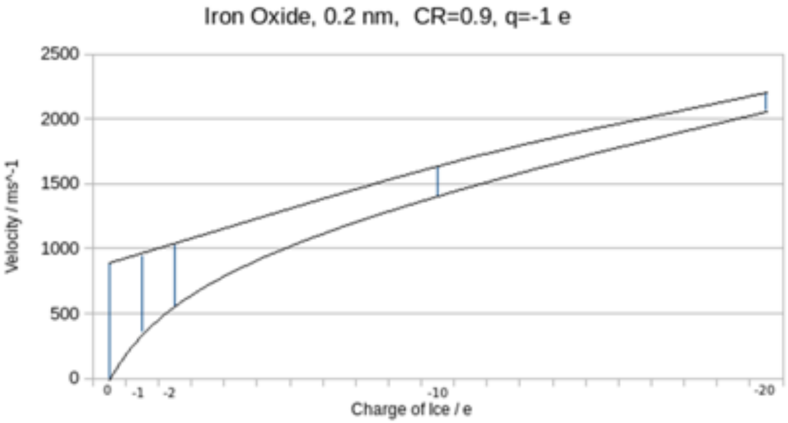


Figure 6a: Collision of negatively charged 0.2 nm iron oxide particles with 10 nm ice with varying charge, blue bar indicates range of velocities that lead to sticking coalescence.

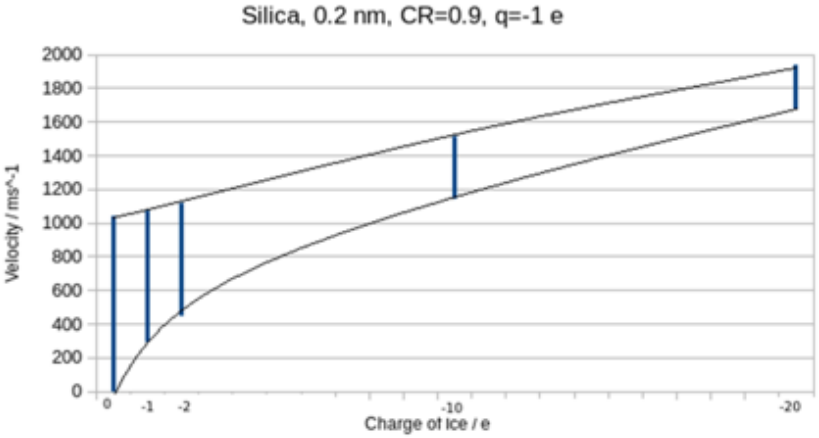


Figure 6b:2 Collision of negatively charged 0.2 nm silica particles with 30 nm ice with varying charge, blue bar indicates range of velocities that lead to sticking coalescence.

The figures above show examples for dust growth between like charged particles. We assume radii of 10 nm and 20 nm for the large ice particles and consider collisions with nanoparticles, the coefficient of restitution is assumed to be 0.9. When the smaller particles have sizes of 4 nm and larger, collision velocities must be very high to reach coalescence. We consider particles with 0.2 nm radius (at the limit of describing solid particles).

Discussion

We investigated the collisions between the metal oxides and larger ice particles. The collision velocity that leads to stable aggregation of nm-sized metal oxides with an ice particle of 10 nm radius is typically above 100 m/s which is at the upper limit for relative velocities that we expect from wind, turbulence and transport. For ice particles that carry a small amount of charge, the collision velocities for aggregation are in the range thermal velocities.

We will use this model to systematically study the growth rates of small meteoric smoke particles and water ice. The distribution of charge on the particles has an influence on the interaction. We will also compare different cases of charge distribution on the particles and expect this will have an influence on the growth rate. This model will also be used to investigate the growth of meteoric smoke particles under the conditions of meteors.

The properties of the water ice are an important parameter in this study. The temperature in the MLT region is variable and around 130 – 150 K when ice particles are present. According to phase diagram studies, at these temperatures ice particles are in a 'soft' state and may absorb some of the energy during a collision, and therefore have a lower coefficient of restitution. The assumed dielectric constant of ice affects the results, while they are not much influenced by the metal oxide assumed.

References

Bichoutskaia, E., (E. Besley), et al. J. Chem. Phys., 133(2), 024105 (2010).

Stace, A. J., et al. J. Colloid Interface Sci. 354(1), 417-420 (2011).

Acknowledgement

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