Particle nucleation and growth in dusty plasmas: On the importance of charged-neutral interactions

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Steven L. Girshick

AFFILIATIONS
Department of Mechanical Engineering, University of Minnesota, 111 Church St. SE, Minneapolis, Minnesota 55455

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Electronic mail: slg@umn.edu

ABSTRACT

Particle nucleation and growth in gases involves nucleation via growth of small molecular or ionic clusters, growth by vapor deposition on nanoparticle surfaces, and coagulation due to collisions between nanoparticles. Under typical conditions that apply in low-pressure nonthermal plasmas, all three of these phenomena are dominated by interactions between negatively charged bodies (anion clusters or nanoparticles) and neutral ones (molecules or nanoparticles), with collision rates enhanced by the dipole or image potential induced in the neutral collision partner. The current understanding of these phenomena is reviewed, with a focus on silane-containing plasmas in which silicon nanoparticles nucleate and grow.

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I. INTRODUCTION

The key phenomena involved in the formation of condensed-phase particles in a gas that does not contain pre-existing particles can be described in terms of particle nucleation and particle growth. Particle growth occurs by either or both of two mechanisms: single particle growth by vapor deposition on particle surfaces, and coagulation, in which two nanoparticles collide and stick. Understanding the formation of nanoparticles in plasmas thus requires the understanding of these three phenomena—nucleation, particle surface growth, and coagulation—in the special context of conditions that exist in plasmas, which differ in important respects from ordinary neutral gases.

In this paper, we argue that in low-pressure nonthermal dusty plasmas, under conditions that most commonly exist, all three of these phenomena are dominated by interactions between negatively charged bodies and neutral ones. By “bodies” we mean molecules or nanoparticles not free electrons, even though free electrons are typically primary drivers of the chemistry and other important phenomena in nonthermal plasmas. Nucleation is typically dominated by reactions between anion clusters and neutral molecules, particle surface growth is typically dominated by heterogeneous reactions involving negatively charged nanoparticles and neutral molecules, and coagulation is typically dominated by collisions of negatively charged nanoparticles with neutral nanoparticles. (We use the term “molecule” here to encompass monatomic and polyatomic species as well as radicals.) This implies that collisions that dominate particle nucleation and growth in nonthermal plasmas—whether the collision partners are molecules, clusters, nanoparticles, or various two-body combinations of these—are all governed by the fact that a charged body induces an electric dipole in a neutral collision partner, and the existence of this dipole affects collision rates, which pose an upper bound on reaction or coagulation rates. If this hypothesis is correct, then it is interesting to note that for all three phenomena—homogeneous ion-molecule reactions, heterogeneous reactions of neutral molecules on the surfaces of charged nanoparticles, and coagulation of charged nanoparticles with neutral ones—knowledge of key mechanisms and rate coefficients still involves considerable uncertainty.

In the following, we focus on low-pressure silane-containing plasmas in which silicon nanoparticles nucleate and grow, as this particular chemistry is probably the most studied, both experimentally and numerically, in terms of particle formation in nonthermal plasmas.
sequence of chemical reactions. In the case of gases such as silane or hydrocarbons, cluster growth can be expected to proceed mainly by chemical reactions.

Studies in the 1990s by Hollenstein and co-workers used quadrupole mass spectrometry to measure the abundances of SiH$_m$ clusters in low-pressure capacitively coupled radio frequency (RF) silane plasmas.2–6 As seen in Fig. 1, they observed Si$_n$H$_m$ anions up to large sizes.6 In contrast, they found that the abundances of Si$_n$H$_m$ cations and neutrals decayed much more rapidly with cluster size.

Possible kinetic pathways for polymerization of Si$_n$H$_m$ anions were considered in a number of studies.3,5,7 This work led to the conclusion that the dominant path to cluster growth in silane-containing plasmas likely consists of reactions between anion clusters and neutral silicon hydride molecules or radicals, where the neutral contributes one or more Si atoms to the growing anion cluster.8–14

The qualitative physical arguments to support such a picture are straightforward. As electrons are much more mobile than heavy species, walls that bound plasmas are typically charged to negative potentials relative to the bulk plasma. The resulting electric field confines anions and negatively charged nanoparticles to the bulk plasma, while neutral species, cations, and neutral or positively charged nanoparticles are free to diffuse from the bulk plasma toward the walls. Hence, anion clusters have time to undergo polymerization reactions that grow them to large sizes, whereas neutrals and cations do not have time to grow to large sizes because they are rapidly lost by diffusion, particularly at the small sizes where diffusivities are highest and under the low-pressure conditions that prevail in most nonthermal dusty plasmas.14,15 However, due to mutual Coulomb repulsion, anions are unlikely to grow by collisions with other anions, and anion–cation collisions, which have a large cross section but lead to mutual neutralization, have been ruled out as a major contributor to cluster growth in studies that have considered them.14,15 Thus, the rates of anion–neutral reactions are key determinants in the rates of cluster growth, i.e., of nucleation.

The collision rate of ions and molecules is given by the Langevin theory and is based on the effect of the dipole induced in the neutral molecule by the ionic collision partner. For the case of nonpolar molecules such as SiH$_4$, the rate constant $k_i$ for ion-neutral collisions given by the Langevin theory can be written as

$$k_i = e \sqrt{\frac{\pi \alpha}{\epsilon_0 m_r}}$$

where $e$ is the elementary charge, $\alpha$ is the polarizability of the neutral molecule, $\epsilon_0$ is the permittivity of free space, and $m_r$ is the reduced mass of the collision pair. The Langevin rate constant poses an upper bound on the reaction rate for any given ion-neutral reaction. Thus, reactions of the type

$$\text{Si}_n\text{H}_m^- + \text{SiH}_p \rightarrow \text{Si}_{n+1}\text{H}_{m+p-2}^- + \text{H}_2$$

are expected to dominate cluster growth, with $m$ equaling either $2n$ or $2n+1.15,17$

Elimination of H$_2$ helps to stabilize the Si–H product cluster and is consistent with the experimental observation that as clusters grow, their Si:H ratio increases.16 Note that reversibility of this reaction may be important, as hydrogen dilution is known to suppress nucleation in silane pyrolysis,16,17 and the reverse reaction is itself an anion-neutral reaction.

The main candidates for neutral growth species SiH$_p$ in Eq. (2) are generally believed to be SiH$_n$, which is often by far the most abundant Si-containing species in the plasma but is relatively unreactive, and SiH$_3$, which is typically the most abundant Si-containing radical and is quite reactive. The Langevin collision rate for both of these species with SiH$_3$ $^-(n = 1, m = 3)$ is about $10^{-20}$ cm$^3$ s$^{-1}$, and the actual reaction rate constant with neutral SiH$_3$ as the collision partner is believed to be close to this value.11 However, with SiH$_4$ as a collision partner, the actual reaction rate constant is estimated as $4 \times 10^{-12}$ cm$^3$ s$^{-1}$, much lower than the Langevin rate constant by a factor of $\sim$300–1000, much lower than with neutral SiH$_3$ as a collision partner.10,12 More recently, Bao et al.19 performed high-level quantum chemistry calculations to analyze reactions of SiH$_4$ with either Si$_2$H$_4^-$ or Si$_2$H$_5^-$ and proposed that these reactions involve a three-step mechanism, with large energy barriers to reaction transition states resulting in much lower overall rate constants than suggested by those earlier estimates. On the other hand, it has been suggested that vibrationally
excited SiH$_4$, being much more reactive than the ground state, could be a key growth species.\(^8\)

The relative contributions to anion cluster growth of SiH$_3$, SiH$_4$, and vibrationally excited SiH$_4$ were estimated in a chemical kinetic model by De Bleecker et al.,\(^17\) as shown in Fig. 2. In this work, each of these neutral species was assigned a different rate constant for Eq. (2), but it was assumed that these rate constants were independent of the value of $n$, up to $n = 11$, the maximum anion cluster size considered in the model. Noting the considerable uncertainties in the rate constant for clustering with ground state SiH$_4$, they varied its rate constant from $10^{-10}$ to $10^{-12}$ cm$^3$ s$^{-1}$, roughly corresponding to the range spanning from 10 times lower than the Langevin rate constant, as assumed by Bhandarkar et al.,\(^13\) to $\sim 1000$ times lower than the Langevin value, corresponding to the lowest value given in the compilation by Perrin et al.\(^12\) For their assumed conditions, De Bleecker et al.\(^17\) found that, at the lower end of this range, the relative contributions to cluster growth were fairly evenly divided between ground state SiH$_4$ (38%), vibrationally excited SiH$_4$ (36%), and SiH$_3$ (25%), while at the upper end ground-state SiH$_4$ provided nearly 100% of growth.

These relative contributions depend on plasma conditions. In particular, the relative abundances of SiH$_3$ and SiH$_4$ depend on conditions such as applied power (equivalently, voltage) and the input silane partial pressure, which affect the degree of silane dissociation. For example, in the kinetic modeling of Gallagher et al.,\(^11\) the SiH$_3$-to-SiH$_4$ abundance ratio equaled $\sim 10^{-2}$; in De Bleecker et al.,\(^17\) $\sim 10^{-3}$; and in Agarwal and Girshick,\(^21\) $\sim 10^{-4}$.

While these results indicate that caution is required in drawing general conclusions regarding cluster growth pathways from calculations performed for a particular set of conditions, one can conclude that ground-state SiH$_4$ is likely an important nucleation species even under conditions where radical concentrations are relatively high. Therefore, uncertainties in the rate constant for SiH$_4$ reacting with cluster anions pose an important open question in quantitative modeling of nucleation in low-pressure silane-containing plasmas.

### III. PARTICLE SURFACE GROWTH

When clusters grow large enough to be considered condensed-phase “nanoparticles,” they can continue to grow by accretion of mass due to physical or chemical vapor deposition on their surfaces. Just as with macroscopic surfaces that bound the plasma, the higher mobility of electrons compared to heavy species causes nanoparticles to be predominantly negatively charged. A dynamic equilibrium between the fluxes of electrons and positive ions to the nanoparticle surface results in a multielectron fluctuating charge. This is in contrast to anions, whose single electron is attached due to positive electron affinity. Very small particles, at most a few nanometers in diameter, can hold only one or two electrons.\(^22\) As these particles experience discrete charging events, at any time some fraction can be neutral or even positively charged. However, once particles are large enough to hold more than one or two electrons, they can be considered stably negative, as they are then unlikely to be neutralized. Being electrostatically trapped in the plasma, they can grow by vapor deposition on their surfaces, which allows them to accumulate even more negative charge.

Particles that are only 1 or 2 nm in diameter are effectively large clusters, and the situation for particle surface growth can be expected to be qualitatively similar to that for nucleation discussed in Sec. II. Larger nanoparticles, however, can be treated in some sense as small chunks of the condensed phase. In the case of silicon and most other inorganic materials that nucleate in dusty plasmas, the condensed-phase nanoparticles are expected to be solid, though whether they are amorphous or crystalline, as well as the chemical composition of the surface—for example, in the case of silicon, whether and to what extent the surface is hydrogenated—can affect heterogeneous surface chemistry.

In the few models of particle surface growth in dusty plasmas that have been reported,\(^17,22\) the approach has been to use a sticking coefficient formalism, with values of sticking coefficients taken from the literature of film growth on macroscopic surfaces. For example, Fig. 3 shows results of a study of reaction and sticking probabilities of SiH$_3$ during plasma deposition of either amorphous (a-Si:H) or microcrystalline ($\mu$-c-Si:H) hydrogenated silicon films, where “sticking” denotes the subset of reactions that adds a silicon atom to the film.\(^23\)

While this approach may be suitable for micrometer-sized particles in plasmas, there may be important differences between heterogeneous reactions on macroscopic surfaces and surface growth on nanoparticles, which are freely translating entities that carry various values of charge. Thus, surface growth on nanoparticles represents an intermediate case that lies between cluster growth via anion-neutral molecule reactions and coagulation between charged and neutral nanoparticles, discussed in Sec. IV. Although a neutral growth molecule is smaller (a few tenths of a
small nanoparticles in a plasma can be elevated considerably above the chemical structure of surface species, and which additionally can be treated as if they were stationary. 22,36 For example, in recent Monte Carlo charging simulations, Mamunuru et al. found that approximately 50% of 1-nm-diameter SiO2 particles are neutral under the plasma conditions they considered. 33 The positively charged nanoparticle fraction in these simulations was typically two or three orders of magnitude smaller than the neutral fraction, in which case the contribution of positively charged particles to coagulation may be relatively unimportant, in spite of the enhancement in coagulation rates due to the Coulomb attraction between oppositely charged particles. However, neutral particles, which may be abundant, can coagulate with each other as well as with charged particles.

In plasmas where fresh nucleation occurs concurrently with growth and electrostatic trapping of nanoparticles, a bimodal size distribution develops. 27,42 For example, from a self-consistent numerical simulation of a capacitively coupled parallel-plate RF argon-silane plasma by Agarwal and Girshick, 37 Fig. 4 shows the predicted particle size distribution at the midplane of the electrode gap, one second after the initiation of the discharge. The size distribution is seen to have a strongly bimodal character. Ravi and Girshick proposed that the dominant type of coagulation in plasmas undergoing nucleation involves coagulation of very small neutral nanoparticles with the population of larger, negatively charged nanoparticles. This type of coagulation could be strongly enhanced by two effects: first, the Brownian coagulation coefficient for coagulation between dissimilar-sized particles is greater than for same-sized particles; 22 and second, coagulation rates are enhanced by the image potential induced in a neutral particle that is in proximity to a charged particle. Note that coagulation of large particles with much smaller ones, termed "scavenging," tends to grow particles while not broadening the size distribution, unlike coagulation for the synthesis of nanocrystals, as the suppression of coagulation can result in the synthesis of nanoparticles that are nonagglomerated and monodisperse. 27,28 If nanoparticles grew only by surface reactions, and if the chemical composition of the plasma were spatially uniform, then the particles would all experience the same growth rate, and an initially monodisperse nanoparticle aerosol would remain monodisperse as the particles grew. On the other hand, coagulation of an initially monodisperse aerosol broadens particle size distributions. 29

However, nanoparticles in plasmas are not necessarily all negatively charged, especially if fresh nucleation continuously generates very small nanoparticles. The standard model of particle charging in plasmas, orbital-motion-limited (OML) theory, 25 does not account for the fact that the number of excess electrons a particle can hold is limited by electron tunneling, 22,31,32 which becomes particularly important for very small nanoparticles that can hold at most one or two electrons. For such particles, stochastic charging creates a charge distribution that may include a significant fraction that is neutral or even positively charged. Additionally, OML theory neglects several factors, including charge-exchange collisions of ions within the electric sheath around particles, 33,34 UV photo-emission, and secondary electron emission that can all shift the particle charge distribution toward less negative values. 35 Furthermore, the density of negative charge carried by particles can exceed the electron density, causing the electron density to become much smaller than the positive ion density, giving the plasma an electronegative character, and this too shifts the particle charge distribution in a positive direction. 31,36 For example, in recent Monte Carlo charging simulations, Mamunuru et al. found that approximately 50% of 1-nm-diameter SiO2 particles are neutral under the plasma conditions they considered. 33 The positively charged nanoparticle fraction in these simulations was typically two or three orders of magnitude smaller than the neutral fraction, in which case the contribution of positively charged particles to coagulation may be relatively unimportant, in spite of the enhancement in coagulation rates due to the Coulomb attraction between oppositely charged particles. However, neutral particles, which may be abundant, can coagulate with each other as well as with charged particles.

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of similar-size particles. In this case, the scavenged particles are effectively like large molecules in comparison to the much larger particles by which they are scavenged.

Huang et al. in 1991 developed an expression for the image potential and resulting coagulation enhancement factor for coagulation between charged and neutral aerosol particles, and their results have been utilized in several numerical studies of dusty plasmas undergoing coagulation. However, recent studies have pointed out deficiencies in the expression of Huang et al. Ouyang et al. compared several expressions in the literature for the enhancement factor due to image potentials for collisions between neutral nanoparticles and ions, with the ion assumed to be a point charge, and found that, over a wide range of neutral particle sizes, these expressions differed from each other by a factor of about two for particles in the free molecule regime.

Recently, Santos et al. argued that, whereas the theory of Huang et al. assumes a potential that is singular at the particle contact point, a more appropriate model for nanoparticles in plasmas would assume that charge is evenly distributed over the particle surface. Santos et al. used the multipolar coefficients potential (MCP) developed by Bichoutskaia et al. to conduct numerical simulations of the enhancement factor for coagulation between silicon nanoparticles over a range of particle sizes and charge states. Their results for the enhancement factor are strikingly different from the results obtained using the model of Huang et al.

Figure 5 shows results of the calculation of Santos et al. of the coagulation enhancement factor due to image potentials, for collisions between neutral particles that are 1–5 nm in diameter with charged particles having a range of sizes and number of charges. Solid white lines indicate the size-dependent average particle charge from OML theory for an assumed set of plasma conditions. As can be seen, the coagulation enhancement factor for the particles of average charge can reach ~100, and is highest when the charged particle, like the neutral particle, is smaller than about 10 nm in diameter.

For plasmas with a bimodal particle size distribution such as shown in Fig. 4, where all neutral particles can be assumed to lie in the small-particle mode (at most a few nanometers in diameter), these results imply, to the first order, that coagulation of particles is enhanced by two phenomena whose relative importance depends on whether the charged particle lies in the small-particle mode or the large-particle mode of the size distribution. Very small neutral particles can coagulate with other very small neutral particles, with very small charged particles, or with larger charged particles.
Coagulation of neutral particles with each other is not necessarily unimportant but is enhanced neither by size dissimilarity nor by image potential (neglecting van der Waals interactions). However, the enhancement of coagulation by image potentials is particularly important for coagulation of very small neutral particles with very small charged particles. Meanwhile, for coagulation of neutral particles with larger charged particles, coagulation enhancement by size dissimilarity is particularly important, while coagulation enhancement by image potentials appears to be relatively less important.

Santos et al. note that the numerical procedure they used to obtain the enhancement factors from the MCP is complicated and computationally time-consuming, so they also proposed a simplified analytical expression for the image potential that is 15–20 times faster to calculate but still produces results in reasonable agreement with the full calculations. Unfortunately, even this simplified expression appears to be difficult to implement within a self-consistent dusty plasma simulation, although one could envision a look-up table approach for the enhancement factor for particle pairs of various sizes and charge states.

We can conclude that treatment of coagulation in dusty plasmas is an area that is ripe for further study.

V. SUMMARY AND CONCLUSIONS

Particle nucleation and growth in low-pressure nonthermal dusty plasmas is dominated by interactions between charged bodies and neutral ones. Nucleation, which involves growth of small clusters, is often dominated by reactions between anions that are electrostatically trapped in the plasma and neutral molecules or radicals that contribute to cluster growth. Particle surface growth predominantly involves reactions of neutral molecules on the surfaces of negatively charged nanoparticles. Coagulation is dominated by collisions between very small neutral nanoparticles and charged nanoparticles, which may be very small or much larger. All three phenomena involve collisions that are affected by the fact that a charged ion or nanoparticle induces an electric dipole or image potential in a neutral molecule or nanoparticle. Considerable uncertainties currently exist with regard to quantitative understanding of all three of these phenomena, which constrains numerical models of particle nucleation and growth in plasmas.

REFERENCES