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Laser-induced particle formation and coalescence in a methane discharge

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Laser-induced formation of submicrometer dust particles and the subsequent coalescence phenomena in a low-pressure methane radio-frequency plasma have been analyzed. Six distinct phases can be distinguished: (a) nanoparticle synthesis by laser interaction with the plasma species, (b) particle conglomeration and the formation of ordered Coulomb lattices at the plasma–sheath region above the powered electrode, (c) coalescence of grains within the Coulomb lattice and formation of submillimeter strings, (d) condensation of the strings in the discharge and the formation of V-shaped structures, (e) condensation of the V structures into a single network of several centimeters in diameter suspended in the plasma, (f) deposition of the network on the electrode and its subsequent growth on the surface. Large carbon structures as well as nanoparticles have been analyzed in situ by He–Ne laser light scattering and laser ablation and ex situ by an optical and a scanning electron microscope, and by micro-Raman spectroscopy. © 1999 American Vacuum Society. [S0734-2101(99)01106-9]

I. INTRODUCTION

Formation of macroscopic grains under low-pressure conditions is a phenomenon that attracts much attention in plasma physics, astrophysics and surface processing technology. Large particles are readily formed in many rarefied media, in which active gases are present. Examples of chemistries are numerous: fluorocarbon or SF₆ etching plasmas used for fabrication of semiconductor elements, silane plasmas used for deposition of amorphous silicon in solar cell technology and various sputtering discharges.¹ A separate category is particle formation induced by high-power lasers.²–⁴ Much effort has been invested in the clarification of the particle growth mechanisms and particle behavior in the plasma. Plasma-produced macroscopic grains have been investigated from different perspectives, either as dangerous pollutants of the surface in plasma processing, or as interesting mesoscopic objects with unique properties, different from the bulk solid state properties.⁵ Nowadays, small grains find many applications in catalysis, ceramic industry and various coating technologies. They have been also found to improve the quality of solar cells.⁶ Therefore, a relatively new development in the dusty plasma research concentrates on fabrication and handling of special particles, and tailoring their properties by means of low-pressure plasmas.⁷ On the fundamental side, particle interactions in ionized gases are extensively studied⁵,⁸. Charging of the macroscopic grains and their levitation as a result of Coulomb interactions is a hot topic in astrophysics, in relation to the rings of Saturn and the Mars atmosphere.⁹ In many laboratory discharges one can observe levitating particle suspensions kept in a stable form by Coulomb interactions. Morfill and Meltzer have performed experiments by transferring the laboratory reactors into space, in order to simulate the nongravitation conditions relevant for astrophysical research on dust particles.⁷

In this article we report on particle growth in a low-pressure, radio-frequency methane discharge. The system is normally used for diamondlike or nanocrystalline diamond deposition. Under standard conditions for diamond deposition no particle formation is observed. Hayashi and Tachibana have shown that particles can grow in methane plasmas from small externally introduced seeds.¹⁰ When the particles reach a critical size on the order of a micrometer and a critical density dependent on the plasma parameters, they arrange themselves in regular patterns, called Coulomb crystals. In this work we report on particle formation initialized by a pulsed laser, resulting in the formation of nanoparticles. The laserproduced nanoparticles are the precursors for larger structures, which cluster and form Coulomb crystals, similar to the ones described by Hayashi and Tachibana.¹⁰ However, growth and conglomeration does not stop at the stage of a Coulomb crystal. Under our conditions the particles form millimeter size chains, which further coalesce. Eventually, the whole particle cloud can appear as a single frozen structure, as large as few centimeters in diameter. This structure floats in the plasma due to electrostatic interactions. Laser-induced particle formation, growth and coalescence will be discussed below, after a brief introduction to particle dynamics in a plasma and a description of the experimental setup.

II. PARTICLE BEHAVIOR IN LOW-PRESSURE PLASMAS

The growth of particles in a low-pressure discharge is efficient due to their long residence times. The particles immersed in the plasma acquire a negative charge, and therefore remain trapped in the positive plasma glow. Negative charging of floating objects in an ionized medium is a common phenomenon, caused by the difference in mobility be-

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between electrons and positive ions. A simple way to estimate the charge is described in the Appendix in this article. For an isolated spherical particle the charge is proportional to the particle radius. Under typical low-pressure plasma conditions the theory predicts about one elementary charge per 1 nm of the particle radius. Charge measurements for submicrometer size grains show that this is a reasonable estimate. However, this macroscopic approach to charging is valid for particles that are large enough to be treated as solid state objects. For nanometer size particles one has to consider charging in terms of molecular interactions, taking into account effective cross sections for electron and ion capture. Small grains carry very little charge, and this charge has a stochastic character, so trapping efficiency of nanoparticles was under discussion.

At a certain particle density, the average distance between particles will be on the order or smaller than the Debye length in the plasma. This enables electrostatic interactions between the particles, which leads to formation of ordered structures. The so-called Coulomb crystals are dense suspensions of negatively charged nuclei immersed in a positively charged background of ions. These lattices behave in many aspects as metal crystals. Formation of Coulomb crystals results in the depletion of the local electron density. In extreme cases, this can lead to (local) extinction of the electric field and consequently the collapse of the particle suspension. Generally, the average charge on a particle within a Coulomb lattice is somewhat lower than estimated for an isolated particle [see Eq. (A2) in the Appendix].

A very interesting feature of particles in the plasma is their tendency to coalesce. This means that they overcome the Coulomb repulsion and form large conglomerates. Clustering of particles is a commonly known effect in silane deposition plasmas. However, in this case coalescence was observed only for nanometer size particles, which can carry at most a few elementary charges. Theoretical studies revealed that the charge of nanoparticles fluctuates on a time scale comparable with the particle collision frequency. This implies that the charge can even enhance the coalescence, as there are both positively and negatively charged nanoparticles present in the plasma. However, for larger particles, which carry a permanent negative charge, such a mechanism cannot explain the coalescence. The time scale for charge fluctuations is inversely proportional to the particle size, and much shorter than the particle collision frequency. Thus, the particles sustain their stationary negative charge during coalescence, and they must have sufficient initial kinetic energy to overcome the Coulomb barrier at the distance of closest approach \((2a, \text{where } a \text{ is the particle radius})\):

\[
E = \frac{1}{2} m v^2 = (4 \pi \varepsilon_0)^{-1} (Ze)^2 / 2a.
\]

Some estimates can be made for a 1 \(\mu\)m carbon particle (density: \(2.3 \times 10^3\) kg/m\(^3\), carrying 1000 elementary charges. The potential barrier a particle has to pass is 0.7 V, and the corresponding initial particle velocity is 0.15a m/s, where \(a\) is the particle radius in micrometers. Particles accumulate in the transition region between the plasma and the sheath, where potential variations of a few volts occur. Therefore, such particle energies and velocities can be expected as a result of interactions of the particles with the electric field and they are readily observed experimentally. Coalescence of submicrometer particles is thus enhanced by the electric field and its fluctuations.

Various forces acting on a particle and determining its position in the plasma are described in detail elsewhere. Here we shall consider a typical geometry with a discharge generated above a planar powered electrode. During plasma operation the most important force is due to Coulomb interactions. The electric field \(E\) in the plasma sheath region exerts a force \(F_e = ZeE\), which prevents particles from falling on the electrode and keeps them trapped in the positive plasma glow. On the other hand, gravitation force \((F_g = mg)\) pushes them toward the electrode. Other forces are due to momentum transfer from the plasma species: the neutral drag force acting in the direction of the gas flow, the thermophoretic force acting in the direction opposite to temperature gradients and the ion drag force acting in the direction of the positive ion flow. The latter force pushes the particles towards the electrode. As a result of various forces, the particles remain suspended at the plasma boundary region above the powered electrode. In principle, they can move freely in the direction parallel to the electrode, but generally there are small radial fields due to surface defects on the electrode, resulting in local potential traps and some radial particle confinement.

The gravitation force has a stronger dependence on the particle size than the electric force \((a^3 \text{ vs } a)\). Therefore, at a given particle size the gravitation will balance the Coulomb force

\[
F_g = F_e.
\]

From the above the critical particle size can be evaluated. When the particle size exceeds this critical value, the electric field in the sheath will no longer be able to trap the particle, so eventually it will fall on the electrode. For spherical particles, the particle charge is proportional to the radius \(a\), and the mass equals \(4/3 \pi a^3 \rho\), where \(\rho\) is the material density. For carbon particles \(m = 9.6 \times 10^{-15} a^3\) kg, where \(a\) is in \(\mu\)m. The gravitation force balances the Coulomb force when the radius is \(a = 0.12 E^{1/2}\), with \(E\) in V/m. The typical potential gradient in the sheath is about \(10^3 - 10^5\) V/m. This implies that a spherical particle, or a spherically shaped structure with a radius larger than about 10–20 \(\mu\)m will fall on the electrode during plasma operation. This does not happen to string shaped conglomerates, as explained in the Appendix. The charge on a string consisting of \(N\) particles of radius \(a\) can be estimated by \(10^3 N \ln(4N)\) [see Eq. (A3)], and the mass is \(4/3 \pi a^3 \rho N = 9.6 \times 10^{-15} \rho^3 N\) (in kg). For a string consisting of 1 \(\mu\)m particles \((a = 1)\), the gravitation force exceeds the electric force for \(N\) larger than \(5 \times 10^6\). Of course, such long strings (10 m) are not realistic under laboratory conditions. In other words, a string of particles can remain floating in the plasma without collapsing under its own gravity. As a result, remarkably large string shaped
structures can be suspended in the plasma. Eventually these structures might collapse due to a disturbance in the electric field and local plasma extinction. Formation of very long particle strings and floating networks in the plasma, as well as their collapse during plasma instabilities, will be described in Sec. IV.

III. EXPERIMENTAL SETUP

Particle formation is studied in a low-pressure 13.56 MHz radio-frequency (rf) plasma. A schematic view of the setup is shown in Fig. 1. The rf power is applied to a water-cooled plate at the bottom of the reactor. Typically the output of the generator is 1 kV, 0.25 A. The actual rf electrode (20 cm in diameter) is elevated 10 cm above the bottom plate, to have optical access to the active plasma region through the viewing ports. The reactor walls act as a grounded electrode. A standard methane flow of 100 sccm is introduced at the top of the reactor, about 50 cm above the electrode, while the pump opening is at the bottom of the reactor, allowing free methane flow through the reactor. The pressure in the chamber is regulated by a throttle valve and the chamber is pumped by an Alcatel primary pump resulting in a background pressure of 200 mTorr. Particle formation is initialized by a Nd:YAG laser (Quanta system, handy YAG laser HYL 101, 5–6 ns pulse duration and wavelength 355 nm). The unfocused laser beam (6 mm in diameter) is guided through the reactor, parallel to and about 2 cm above the rf electrode. The maximum laser energy is 90 mJ per pulse and the repetition rate is 10 Hz, so the maximum average power density is about $3 \times 10^4$ W/m$^2$, while the maximum power density during the laser pulse is about $2 \times 10^{11}$ W/m$^2$. Apart from initializing particle synthesis, the Nd:YAG laser is simultaneously used as a diagnostic tool to monitor the presence of nanometer size particles. The detection method is based on the nonelastic interaction of a high power laser with the particles. Particles absorb the laser radiation and depend on their size, they can emit blackbody spectrum (large particles) or fluorescence spectrum (small particles). In both cases particle detection is possible by collecting the white light emission. For larger particles (>100 nm) a helium neon laser can be used to illuminate the particles and detect the light scattering signal. Submillimeter structures and larger are visualized using a tungsten ribbon lamp.

Detection of the blackbody or the fluorescence signal of the Nd:YAG laser and the scattered light of the He–Ne laser or the tungsten lamp is possible through a second optical port which is placed at 90° with respect to the first one, but about 10 cm higher. In this way a side/top view of the particle suspension in the discharge is obtained. In order to take in situ pictures of the conglomerates in the discharge a Canon camera with a telelens is used. An additional lens with a focal length of 25 cm is placed in front of the camera, such that the particles are in the focal plane of the lens, allowing a good focusing of the camera. The particles and the conglomerates are deposited on a silicon wafer, to be analyzed ex situ by an optical microscope, a scanning electron microscope (SEM), supplied with an energy dispersive x-ray (EDX) facility to study the particle composition, and by Raman spectroscopy.

IV. RESULTS AND DISCUSSION

A. Laser-assisted particle formation

Laser-assisted particle formation has been observed previously. It occurs during laser ablation of solid targets or it can be initiated in the gas phase. The latter case has been studied by Armand et al., who reported formation of fullerene clusters by irradiation of various hydrocarbon gases at atmospheric pressure with a CO$_2$ laser ($\lambda=10.6$ $\mu$m). In case of an infrared laser, particle formation occurred by nonresonant heating and pyrolysis of the gas. To our knowledge, laser-assisted particle formation in a low-pressure methane plasma has not been observed before. At reduced pressures, powder formation is unlikely to be initiated by heating the gas. However, absorption of UV photons by methane results in its efficient dissociation and creation of local high radical densities. As the applied photon energy of the Nd:YAG laser (3.5 eV) fits the dissociation energy of the C–H bond, dissociation of methane is probably a resonance-enhanced process. This explains the efficiency of particle formation at laser powers which are not high enough to cause nonresonant processes in a rarefied medium. Unlike in the neutral gas, particle formation in the plasma does not stop at the nanoparticle stage. As explained in Sec. III, the laser-produced small grains can be trapped in the plasma glow and serve as precursors for larger structures. In order to verify the effect of the laser irradiation on the initial particle formation, we have recorded the time needed to form the particles as a function of the power of the Nd:YAG laser. We monitor the presence of particles by observing He–Ne laser light scattering and the particle emission induced by the Nd:YAG laser. The emission of fluorescence/blackbody radiation offers a sensitive particle detection method, alternative to laser light scattering. Previous studies by Boufendi et al. showed that nanoparticles as small as 1 nm radius can be detected, subject to optimizing the optical detection sensitivity. The laser-induced emission becomes clearly visible as a white flash when the particle radius is about 20 nm. Laser light scattering becomes useful for the detection of particles larger than 100 nm. As we apply both techniques, some information about the time evolution of the particle size can be
In Fig. 2 the time delay between the beginning of the Nd:YAG laser operation (at 10 Hz) and the onset of the laser-induced fluorescence signal is plotted as a function of the laser power. It can be seen that laser-assisted particle formation is a threshold process. Below 0.35 W laser power no particle formation is observed, while above this threshold abundant particle formation occurs within 1 min of continuous laser operation. The initially formed particles cannot be visualized by light scattering using a He–Ne laser, indicating that they are relatively small (<100 nm). However, several tens of seconds after the appearance of the laser-induced fluorescence signal the He–Ne light scattering also becomes visible. This shows that once the nucleation of nanoparticles is accomplished, their further growth proceeds rapidly. It should be noted that He–Ne light scattering can never be observed even after several hours of plasma operation unless the Nd:YAG laser is operated too, and there is always a delay between the onset of the Nd:YAG laser and the laser-induced nanoparticle emission. This is proof that particle nucleation is a laser-assisted process. The density of nanoparticles continues to increase in time as long as the Nd:YAG laser is operated. Once the laser operation is stopped no new nanoparticles are formed, but the existing ones can grow and coalesce to form larger structures. The time constant for nanoparticle formation seems to be independent of the plasma power. At high plasma powers the plasma radiation is so intense that it interferes with the particle detection. Possibly the particle density is lower at high plasma powers, as it is known that particle trapping becomes increasingly difficult with increasing power, because of various instabilities. The methane flow has little impact on the particle formation kinetics. However, a minimum gas flow of about 30 sccm is necessary. This is most likely due to the small capacity of the pumps resulting in a high background pressure. Thus, at low flow rates the amount of methane in the discharge is insufficient. Concluding, the nucleation of nanoparticles seems to be the decisive step, determining further evolution of particles in the methane discharge. It is a threshold process, which requires sufficient laser energy and CH₄ content in the plasma. The time constant of nanoparticle nucleation is thus independent of plasma conditions and laser power (above threshold). Naturally, subsequent particle growth, density, and transport in the discharge are dependent on the plasma conditions, as in the further stages the trapping efficiency and the plasma chemistry are of importance.

**B. Conglomeration of small particles**

Typically the Nd:YAG laser is switched off after several minutes of operation. The particles grow and conglomerate in the discharge, but no new nanoparticle seeds are created. The particles are trapped in the positive plasma glow above the powered electrode, and their behavior during plasma operation will be described below. First, in Fig. 3 we present an overview of various stages of particle growth and conglomeration. Initially, nanoparticle precursors are spread evenly in the plasma glow in the radial direction, but in the course of growth and conglomeration they tend to accumulate in a small region of a few centimeters in diameter. After a few minutes of plasma operation, the nanoparticle precursors increase in size, until their radius is about 100 nm. These particles can be well visualized by He–Ne laser scattering. At
this stage the conglomeration processes start. There is a rapid transition from a suspension of small particles, spread evenly above the electrode and in the plasma glow, to larger conglomerates, confined in a smaller region above the rf electrode [Fig. 3(a)]. The size of the conglomerates and the individual grains is determined ex situ, by terminating the discharge operation and depositing the particles on the surface. Figure 4 shows a typical SEM micrograph of the particles collected just at the end of the conglomeration phase. The individual particles are spherical and monodisperse in size, but the conglomerates have a rather large size distribution. Size separation of conglomerates in the plasma is clearly visible. As a result of the balance of gravitation and electrostatic forces, large structures are situated closest to the electrode, while smaller conglomerates and loose particles float in the glow region of the discharge. At the end of the conglomeration phase, the local density of the clusters becomes high enough to cause interactions between them, and a Coulomb lattice is formed [Fig. 3(b)]. In Fig. 5(a) a photographe the lattice irradiated by a He–Ne laser is shown, and the individual particles/conglomerates can be distinguished.

C. Formation of strings

The Coulomb structure is partially immersed in the plasma sheath, where relatively strong electric fields are present. This causes oscillations and instabilities within the lattice. Typically, about 10 min after formation of the lattice, the Coulomb structure becomes unstable and larger conglomerates are formed. Because of the dipole interactions of the particles with the electric field in the sheath, the conglomerates have a string or rodlike shape. In this phase, the particle cloud is very similar to the floe and flow or the liquid phase of a Coulomb lattice. However, instead of individual particles being aligned vertically and moving slowly with respect to each other, in this case there are vertically aligned strings of particles at regular distances [Fig. 5(b)]. It is interesting to note that alignment of individual particles into strings occurs in a limited range of pressures. It is clear that the string formation requires the penetration of the electric field into the plasma. At higher pressures (about 1 mbar), when the thickness of the sheath is reduced, no strings are formed but particles conglomerate randomly. The resulting clusters are roughly spherical in shape, and they are not larger than 20 μm in diameter. Once they reach this size, they deposit on the electrode due to the gravitational force, as is shown in Fig. 6. The string-shaped particles, formed at lower pressures, remain floating in the plasma in spite of their large mass (see Appendix). Thus, under our conditions the formation of large floating networks, described below, is possible only at low pressures.

D. Formation of V structures

As the strings continue to grow by accumulating more particles, the string length becomes larger than the interstring distance. The vertical alignment becomes less efficient, and due to radial motions of the strings their ends make contact. This results in formation of V-shaped structures [Fig. 3(d)]. It is interesting to note that these structures always have the same orientation in the discharge. The connection point of the strings is pointed toward the powered electrode, while
E. Formation of the floating network

As the V structures increase in size and number, they also coagulate and finally form a structure of interconnected wires in the plasma [Fig. 3(e)]. Under our conditions this structure grows to about 2–4 cm in diameter, having a thickness of a few millimeters. This structure still floats freely at the plasma sheath boundary, as shown in Fig. 8, and continues to grow by capturing smaller structures still present in the plasma. This is a very stable phase that can last for over 1 h. In this time the floating network can remain stable at a single position or in the absence of strong radial gradients in the electrical field move around slowly ($\approx 1$ cm/s) above the rf electrode.

F. Deposition of the network on the surface

Eventually, the structure becomes so dense that it effectively shields the rf electrode from the plasma glow. This causes a large disturbance of the electric field and leads to a temporary collapse of the plasma sheath. As a result the floating network falls on the electrode [Fig. 3(f)]. Extinction of the electric field is a transient that lasts only a fraction of a second, just enough for the particles to pass through the sheath region. After the recovery of the electric field, a structure consisting of negatively charged particle strings is present on the electrode. Their free ends appear as whisks, aligned vertically to the electrode as a result of Coulomb repulsion from the surface. As in case of V structures, Coulomb repulsion also creates separation between the individual branches. A photograph of a deposited structure (Fig. 9) shows the whiskers stretched throughout the plasma sheath and reaching the glow. The structure keeps on growing by capturing particles and small conglomerates from the plasma. The presence of a negative charge on the whiskers can be easily demonstrated by varying the discharge power. Increasing the power results in an increase of the electric field in the sheath and the electron and ion density in the plasma. The effect of the Coulomb force on the whiskers can be easily evidenced, as the angle between the different branches becomes smaller when the discharge power is increased due to the increased Coulomb repulsion by the rf electrode. When the discharge power is further increased, the internal stress within the structure becomes too large and the whiskers break off till only a few vertical strings on the electrode are left. In Fig. 10 a typical ex situ SEM picture of the deposited structure is shown. The structure contains many long and connected strings. In comparison with the
structure of the floating network, the strings are longer and there are fewer interconnections. This is expected, as the strong fields of the sheath region will destroy any unstable link.

Figure 11 represents a SEM micrograph of the structure shown in Fig. 10. The deposition has taken place after about 1 h of plasma operation. In Fig. 11 it can be seen that the size of the individual grains within the whiskers is about 1 μm. As stated before, the coagulation of single particles into clusters and strings occurs when the particle size is on the order of 100 nm. Further growth of the grains is due to deposition of plasma species. This can be seen from the shape of the clustered particles: in Fig. 11 the grains are not longer spherical, as they were just after the first coagulation step (Fig. 4). Elemental analysis of the particle material by EDX shows that the grains consist of carbon. They are transparent in visible and infrared. The sample from Fig. 10 has been analyzed by Raman spectroscopy and the spectra of deposited particles and the surrounding film have been compared. A film is obtained on those regions of the substrate that are not shielded from the discharge by the floating network. It is interesting to note that directly below the floating network no film deposition is observed. Thus the network efficiently prevents depositing species formed in the discharge from reaching the substrate. The layer deposited on the substrate during plasma operation shows broad peaks of graphite (around 1590 cm\(^{-1}\), 100 cm\(^{-1}\) broad) and distorted graphite (around 1350 cm\(^{-1}\), 170 cm\(^{-1}\) broad). These features are also present in the particle spectrum. However, the particles also contain about 30 cm\(^{-1}\) broad peaks at 1450 cm\(^{-1}\) and at 1100 cm\(^{-1}\), which can be attributed to nanocrystalline diamond.\(^*\) Possibly, the laserproduced particle precursors are diamond-like, but they are coated by a graphite layer during plasma operation.

V. CONCLUSIONS

We observe particle formation and coalescence in a low-pressure methane discharge. This complex process is initiated by a high power pulsed laser. Formation of nanoparticles in a low-pressure discharge as a result of laser irradiation is most likely due to photodissociation of the parent gas. Locally, high radical densities are created and nucleation is enhanced. The nanoparticles acquire negative charge and remain trapped in the discharge, where they act as precursors for large structures. In the beginning, particles grow in the plasma until they reach a radius of about 100 nm. At this stage they start to form conglomerates. The evolution of the conglomerates depends on plasma conditions. Important factors are the Coulomb repulsion from the electrode and the gravitation. The former depends on the electric field in the plasma–sheath transition where the particles are trapped. At high pressures field penetration into the plasma is minor and particles coalesce into spherical clusters. These clusters fall on the electrode due to the gravitation force. At low pressures, when the electric fields penetrate deeper into the discharge, there is a relatively large transition region between the glow and the sheath. Particles present in this region form long strings, which are aligned in the field. Such strings do not fall on the electrode even when they reach high masses. As a result, submillimeter strings are formed, and at a later stage they join into a single network. This structure, as large as several centimeters in diameter, remains floating in the plasma until it collapses due to plasma instabilities.

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APPENDIX

A solid object immersed in an ionized medium is subject to charging. The charge is determined by the balance of the fluxes of electrons and positive ions toward the solid surface. In a stationary state these fluxes must be equal, but as electrons are much more mobile than positive ions, a negative charge on the surface is established, repelling electrons and attracting positive ions. In the orbital motion limited approach (OML) for an isolated particle the flux balance reads:

\[ \Phi_+ = \Phi_- \]

\[ \Phi_+ = n_+ \left( k T_+/2 \pi m_+ \right)^{1/2} \left( 1 \ eV/kT_+ \right) \]

\[ \Phi_- = n_- \left( k T_-/2 \pi m_- \right)^{1/2} \exp(eV/kT_-), \]

where \( n_{+,+}, m_{+,+} \) and \( T_{+,+} \) are electron and positive ion densities, masses and temperatures; \( V \) is the electric potential on the particle surface with respect to the potential of the plasma surrounding the particle, and depends on the particle geometry. For example, in case of spherical particles \( V = (4 \pi e_0)^{-1} Ze/a \), where \( Z \) is the number of elementary charges on the particle and \( a \) is the radius. The charge can be calculated by solving the flux balance numerically or introducing some approximations. Matsoukas and Russell\(^\text{19}\) found the following semiempirical formula for spherical particles:

\[ Ze = 4 \pi e_0 a V_p N / \ln(4N). \]  \( \text{(A3)} \)

The charge on a linear string of \( N \) particles is thus \( N \) times the charge on a single constituent of radius \( a \) [see Eq. (A2)], weighted by the factor \( \ln(4N) \). Alternatively \( N \) can be interpreted as the aspect ratio of a rod shaped particle of length \( L \) (\( N = L/2a \)). Thus the charge on a rod shaped particle of length \( L \) and radius \( a \) is

\[ Ze = 2 \pi e_0 V_p (2L/a). \]  \( \text{(A4)} \)

Knowledge of the dependence of particle charge on the particle size is essential, as the charge is responsible for particle trapping. The Coulomb force, proportional to \( Ze \), maintains the particles suspended, while the gravitation force, proportional to the particle mass, pushes them down toward the electrode. In the case of spherically shaped particles or particle conglomerates, the gravitation force increases as \( R^3 \), where \( R \) is the radius of the structure, while the electric force has a much weaker dependence (\( Ze \sim R \)). This means that as a spherical structure increases in size, the gravitation force will soon exceed the electric force and the object will collapse. For string-shaped conglomerates, however, the growth proceeds by capturing particles of radius \( a \). Thus, the characteristic size is the length of the string (\( 2Na \)). The Coulomb force increases with the string size as \( N/\ln(N) \), while the mass of the structure increases as \( N \). The Coulomb force has only slightly weaker size dependence than the gravitation force, so even large conglomerates will remain suspended in the plasma. The size estimates are discussed in Sec. II.


