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Sectional modeling of nanoparticle size and charge distributions in dusty plasmas

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Abstract

Sectional models of the dynamics of aerosol populations are well established in the aerosol literature but have received relatively less attention in numerical models of dusty plasmas, where most modeling studies have assumed the existence of monodisperse dust particles. In the case of plasmas in which nanoparticles nucleate and grow, significant polydispersity can exist in particle size distributions, and stochastic charging can cause particles of given size to have a broad distribution of charge states. Sectional models, while computationally expensive, are well suited to treating such distributions. This paper presents an overview of sectional modeling of nanodusty plasmas, and presents examples of simulation results that reveal important qualitative features of the spatiotemporal evolution of such plasmas, many of which could not be revealed by models that consider only monodisperse dust particles and average particle charge. These features include the emergence of bimodal particle populations consisting of very small neutral particles and larger negatively charged particles, the effects of size and charge distributions on coagulation, spreading and structure of the particle cloud, and the dynamics of dusty plasma afterglows.

(Some figures may appear in colour only in the online journal)

1. Introduction

Most numerical models of nonthermal dusty plasmas assume that the population of dust particles is monodisperse. This includes models of plasmas that contain dust particles in the micrometer-size range [1–5] as well as plasmas where particles are in the nanoscale range [6–9]. In view of the challenges involved in modeling dusty plasmas [10], which involve a large number of interacting physical and chemical phenomena, the assumption of monodispersity would seem, in many cases, to be reasonable, and is attractive given the large reduction in computational expense that it affords. Moreover, a monodisperse model clearly addresses questions such as how particles of given size are spatially distributed, how much charge they carry on average, what forces they experience, and so forth. Thus a numerical simulation using a monodisperse model can be regarded as a well controlled numerical experiment whose results are relatively straightforward to interpret.

However, while monodisperse models may be an obvious choice for plasmas with dust particles in the micrometer-size range, they have several shortcomings for plasmas containing nanoparticles, or so-called ‘nanodusty plasmas’ [11]. Micrometer-size dust particles can typically be treated as either pre-existing or externally injected into the plasma, with sizes that are fixed. On the other hand, nanodusty plasmas are typically chemically reacting, dust particles form by gas-phase nucleation, and particles grow by vapor deposition on their surfaces and/or by coagulation. Several of these processes may cause the aerosol to deviate from monodispersity. Nucleation may occur not as an instantaneous pulse but over a finite time, meaning that different particles nucleate and begin growing at different times. Spatial inhomogeneities in chemical species concentrations may cause particle surface growth at different locations to occur at different rates. Also, coagulation can broaden size distributions.

Adding to the complexity introduced by polydispersity in nanodusty plasmas, stochastic charging causes particles of given size to have a distribution in terms of the number of charges on each particle. This may be of relatively little consequence for dusty plasmas with particles in the micrometer-size range, where each particle may carry thousands of elementary (negative) charges, particles typically reach an equilibrium charge distribution, and an average charge...
per particle is adequate to describe most qualitative features of the system. However, in nanodusty plasmas, distributions of per-particle charge can be crucially important, especially considering the strong effect of particle charge states on particle transport and on coagulation. This is especially obvious for the early times following nucleation, when particles are at most a few nanometers in diameter. At this size particles are unlikely to carry more than one or two charges, meaning that for a given particle discrete charging events cause fluctuations among negative, neutral and positive charge states. Moreover, particularly in the early stages following nucleation, nanoparticle concentrations can be comparable to or even exceed the density of electrons in the pristine plasma. Under such circumstances, a substantial fraction of the nanoparticles may be neutral or even positively charged, in spite of the much greater mobility of electrons compared with ions. As particles grow, particle charge distributions can be expected to depend not only on particle size but also on plasma properties such as the local densities of ions and electrons, and electron temperature.

If plasma properties are fixed, then dust particles of given size acquire an equilibrium charge distribution [12]. However, because of the dynamic, strongly coupled nature of nanodusty plasmas, plasma properties may change significantly on time scales that are short relative to the time required for particles to reach such an equilibrium, thereby necessitating a finite-rate charging model. For example, in the simulations presented herein, particle charging frequencies equal $\sim 10^{7} - 10^{9} \text{ s}^{-1}$, so that attaining an equilibrium charge distribution requires times on the order of milliseconds. However, in many cases the change in density profiles of electrons and ions over millisecond time scales is large enough that the particle charge distribution deviates significantly from equilibrium.

In summary, even if one assumes that all dust particles are spherical and have uniform chemical composition, a correct description of nanodusty plasmas requires one to consider distribution functions for both particle size and particle charge, i.e. bivariate distributions.

One approach that appears well suited for handling simultaneous particle size and charge distributions is to use a sectional representation for the particle size distribution. In this approach, the continuous particle size distribution is divided into a number of bins, or sections, of finite width, and a separate population balance equation is written for each section. Since charge is a discrete quantity, such an approach lends itself naturally to also treating size-dependent charge distributions. Sectional methods are widely used in aerosol modeling, and have been used by a number of researchers to model bivariate distributions, where the second variable (in addition to particle size) is, for example, particle chemical composition [13–15], agglomerate structure [16–21], or charge [22–25].

The initial development by Seinfeld and co-workers of sectional representations of particle size distributions in neutral aerosols was motivated mainly by the problem of modeling the evolution of an aerosol undergoing coagulation [13,26]. The sectional approach was subsequently extended to treat the evolution of aerosols undergoing simultaneous nucleation, coagulation and surface growth, as well as particle transport [27]. Coagulation coefficients (effectively, rate constants) for coagulation between particles of dissimilar sizes are larger—and as the size dissimilarity increases, they become much larger—than for coagulation of same-sized particles. While Coulombic repulsion between unipolar negatively charged particles may in most cases make coagulation insignificant for dusty plasmas containing micrometer-size particles, a number of studies have indicated that coagulation is important in nanodusty plasmas [11,24,28–34]. And, unlike the case in neutral aerosols, the charge states of particles are obviously of crucial importance for coagulation rates. Coagulation is suppressed by unipolar charging but can be strongly enhanced by bipolar charging, and coagulation between charged and neutral particles can be enhanced by image potentials [11]. Thus polydispersity in both particle size and charge can have major effects on coagulation, potentially leading to large errors in models that neglect these effects.

Several researchers have used sectional models for particle size distributions in nanodusty plasmas. All of these studies involved conditions typical of RF silane (or silane diluted in noble gas) plasmas with pressures in the $\sim 100 \text{ mTorr}$ range. These plasmas are of considerable industrial interest, are known to be prone to gas-phase nucleation, and have been the most studied experimentally of any nanodusty plasma system.

Kortshagen and Bhandarkar [24] used a 0D sectional model to study coagulation in dusty plasmas, with self-consistent coupling to a simple plasma model. They calculated charge distributions within each section, and accounted for the effects of particle size and charge on coagulation coefficients. Kim et al [35,36] used a 0D discrete-sectional model, in which particles above a certain size were treated with a sectional model, with smaller sizes treated in terms of their discrete number of monomers [37–39], the chemical substance of the monomers here being unspecified. They assumed that particles of each size class had a Gaussian charge distribution. Then, for each of the positive, negative and neutral charge fractions, they calculated an average charge, and used that to calculate the Coulombic enhancement of coagulation coefficients.

Bhandarkar et al [40] used a 0D sectional model to calculate particle nucleation and growth in RF capacitive silane plasmas. They modeled nucleation with a detailed chemistry model for clustering of silicon hydrides. The nucleation rate thus calculated served as a source term to the sectional model. A surface chemistry model was used to calculate particle surface growth. The chemistry and aerosol models were self-consistently coupled to a 0D plasma model to determine electron and ion densities. The discrete charge distribution for each size section was calculated, as was the effect of particle charge on coagulation.

De Bleecker et al [41] also used a sectional model to simulate an RF discharge in silane. Their model was 1D and self-consistently coupled to a plasma fluid model, including solution of Poisson’s equation for the electric field. Nucleation was calculated using a modified version of the detailed chemistry mechanism in [40]. Particle charge distributions were not calculated. Instead an average particle charge was determined for each section based on the calculated
floating potential for particles of that size. Coagulation was modeled, though the effect of particle charge on coagulation was neglected. Particle surface growth was not included. Results were presented in terms of spatial distributions of various quantities for particles of specific sizes, though without any indication of size distribution or time dependence.

Warthesen and Girshick [42] used a 1D sectional model to model a dusty argon plasma containing silicon nanoparticles. The aerosol model was self-consistently coupled to a plasma fluid model, including solution of Poisson’s equation for the electric field. Chemistry was not modeled. Rather, profiles of particle nucleation and surface growth rates were treated as input parameters. Charge distributions were calculated within each section, and the effect of particle charge on coagulation was considered. The spatiotemporal evolution of the system was calculated as particles grew to several tens of nanometers in diameter. For conditions of their simulations, Warthesen and Girshick [42] found coagulation to be insignificant, i.e. there was no discernible difference in the results if coagulation was turned ‘on’ or ‘off’. The reason for this is that coagulation between negatively charged nanoparticles is strongly suppressed by Coulomb repulsion, positively charged nanoparticles were predicted to exist only in very small concentrations, and time scales for coagulation involving neutral nanoparticles were long relative to their loss to the walls by diffusion in the low-pressure plasma.

In an extension of the model in [42], Ravi and Girshick [11] included the effect on coagulation of image potentials that are induced in neutral particles that are in close proximity to charged particles. Accounting for this effect, and running simulations for the same conditions as in [42], coagulation was now found to be significant. However, only a particular type of coagulation was seen to be important: coagulation between very small (~1 or 2 nm in diameter) neutral particles and larger, negatively charged particles, which are electrostatically trapped in the plasma, allowing them time to grow.

Among the studies discussed above, only the recent work of Girshick and co-workers [11, 42] used an aerosol sectional model, calculated discrete particle charge distributions, and was self-consistently coupled to a plasma model to calculate the evolution in both space (1D) and time of a nanodusty plasma. Even though that work neglected chemistry, it was still computationally expensive. For example, the simulations presented below, which use a similar model as in [11, 42], required approximately 50 h of cpu time per second of plasma time, using 12 parallel processors on an Intel 6-core Xeon X5670 2.93 GHZ machine with 24 GB RAM. Note that the code used here is far from being optimized from the viewpoint of numerical efficiency, and greater than order-of-magnitude improvements may be possible by approaches such as domain decomposition based on grouping of particle size sections into size regimes dominated by different physical phenomena. Nevertheless, even with such improvements, the computational expense of using a sectional method will still be considerably greater than for a monodisperse model. The situation is exacerbated by the fact that fixed-sectional models, which are numerically exact in their treatment of coagulation, suffer from numerical diffusion in treating surface growth, which causes an artificial broadening of the size distribution [27]. Reducing numerical diffusion requires increasing the number $M$ of sections, which increases computational cost roughly as $M^2$. Various modified sectional schemes have been proposed to mitigate numerical diffusion [18, 27]. The computational expense of sectional models, and need for parallelization, has been the subject of detailed analysis in studies of sooting flames (e.g. [43, 44]), which have in common with nanodusty plasmas that the formation of nanoparticles and the behavior of the gas phase are strongly coupled.

The main purpose of this paper is to show why this extra computational expense is in many cases warranted. After giving an overview of the sectional method, we present several examples from numerical simulations, with results selected to illustrate important qualitative features of the spatiotemporal evolution of a nanodusty plasma, many of which would not be revealed without accounting for the polydisperse nature of nanoparticle size and charge distributions. Compared with the earlier work of Girshick and co-workers [11, 42] the example simulations presented here involve different conditions (e.g. they include gas flow, and examine a case of plasma afterglow), take advantage of a number of numerical enhancements, and run to longer plasma times, thereby allowing consideration of phenomena affecting particles up to a few hundred nanometers in diameter. Unlike the earlier work, we here show and discuss particle charge distributions. However, these simulations are presented merely as examples, the goal being not to explore these particular simulations in depth, but to emphasize key features that justify the use of a numerical approach that can accurately account for the polydisperse nature of particle size and charge distributions.

2. Sectional modeling of particle size and charge distributions

We here give a brief overview of sectional modeling of particle size and charge distributions, focusing on those aspects that are particularly germane to nanodusty plasmas. For more general and detailed discussion, the reader is referred to [26, 27].

Let the population of aerosol particles be classified into $M$ sections that are evenly spaced by the logarithm of particle volume $v_p$, i.e. the sections are evenly spaced with respect to a variable $u$ defined by

$$u = \ln v_p,$$

and let $u_{j-1}$ and $u_j$ denote the boundaries of the $j$th section. This relation implies that the particle volume at the boundary of each section can be written

$$v_{p,j} = a v_{p,j-1},$$

where $a$ is a constant factor.

If $q(u)$ represents any size-dependent property of an aerosol (e.g. particle mass, volume, surface area or diameter), then the average value of $q(u)$ in the $j$th section can be written

$$\bar{q}_j = \frac{\int_{u_{j-1}}^{u_j} q(u) n(u) \, du}{\int_{u_{j-1}}^{u_j} n(u) \, du},$$

where $n(u)$ is the number density.
where $n(u)$ is the particle size distribution function. The integral in the denominator represents the total number density $N_j$ of particles in section $j$. Making the approximation that $n(u)$ is constant over each section, one obtains

$$\tilde{q}_j = \int_{u_j}^{u_{j+1}} n(u) \, du / u_j - u_{j-1}. \quad (4)$$

Let each section be divided into a range of discrete particle charge states. Then the population balance equation for the number density of particles $N_{j,k}$ that lie in the $j$th section and $k$th charge state can be written

$$\frac{dN_{j,k}}{dt} + \nabla \Gamma_{j,k} = \left[ \frac{dN_{j,k}}{dt} \right]_{\text{nuc}} + \left[ \frac{dN_{j,k}}{dt} \right]_{\text{coag}} + \left[ \frac{dN_{j,k}}{dt} \right]_{\text{growth}} + \left[ \frac{dN_{j,k}}{dt} \right]_{\text{charging}}, \quad (5)$$

where $\Gamma_{j,k}$ is the local spatial flux of $(j, k)$ particles due to transport, and the terms on the right-hand side represent the rate of increase in $N_{j,k}$ due, respectively, to nucleation, coagulation, surface growth and particle charging. This equation can be considered as the sectional form of the aerosol general dynamic equation, for the case where particle charge distributions are considered.

In a plasma, the particle flux term on the left-hand side of equation (5) includes contributions from terms representing electrostatic forces, neutral gas drag, ion drag, diffusion, gravity, thermophoresis (in the case of nonuniform gas temperature), gravity, and potentially others. A detailed discussion of these can be found in [42].

The nucleation rate is a source term to the first particle size section, and does not appear in the population balance for any other section. Thus one can write

$$\left[ \frac{dN_{j,k}}{dt} \right]_{\text{nuc}} = \delta_{j,1} J_k, \quad (6)$$

where $\delta_{j,1}$ is the Kronecker delta function and $J_k$ is the nucleation rate of particles of charge $k$.

Coagulation of nanoparticles in a plasma is affected by both the sizes and the charge states of the interacting particles. For detailed treatment of the implementation of coagulation in a sectional model, the reader is referred to [13,26,27]. We here focus on expressions for the coagulation coefficient that are appropriate for nanodusty plasmas.

Coagulation conserves total particle mass (equivalently, particle volume, if one assumes spherical particles of uniform mass density) and charge. Consider coagulation between two particles of size-charge classes denoted as 1 and 2. Assuming that all collisions between particles result in their sticking to form a new particle, the coagulation rate can be written

$$R_{\text{coag},1,2} = f(z_1, z_2, r_1, r_2) \beta_{1,2} n_1 n_2, \quad (7)$$

where $n_1$ and $n_2$ are the number densities of particles of the two size-charge classes, $\beta_{1,2}$ is the ordinary Brownian coagulation coefficient, and $f(z_1, z_2, r_1, r_2)$ is a factor that accounts for the effects of charge on particle collision rates, $z$ being particle charge and $r$ particle radius.

Nanoparticles in low-pressure plasmas lie generally in the free-molecule regime, where the dust particle Knudsen number $Kn \gg 1$, i.e. where the radius of the nanoparticle is much smaller than the mean free path for molecular collisions in the gas. The Brownian coagulation coefficient in the free molecule regime is identical to the rate coefficient for bimolecular collisions among species that have Maxwell–Boltzmann velocity distributions. Conventionally recast in terms of particle volume, assuming that particles are spherical, the Brownian coagulation coefficient can be written

$$\beta_{1,2} = \left( \frac{3}{4\pi} \right) \frac{k_BT}{\rho_p} \frac{1}{\nu_1} + \frac{1}{\nu_2} \left( \nu_1^{1/3} + \nu_2^{1/3} \right)^2, \quad (8)$$

where $k_B$ is the Boltzmann constant, $\rho_p$ is the particle mass density, $T$ is the temperature, and $\nu_1, \nu_2$ are the volumes of the two coagulating particles.

For the factor $f$ in equation (7), one must distinguish among four cases: coagulation between neutral particles; coagulation between charged particles of opposite sign; coagulation between charged particles of same sign; and coagulation between neutral and charged particles. The approach followed in [11], and in the simulations below, considers the effect of the image potential induced in a neutral particle that interacts with a charged particle, but neglects the effect of van der Waals interactions on neutral–neutral coagulation. If one further assumes that coagulation between particles whose charge is of the same sign is completely suppressed, the resulting expression for $f$ can be written as follows:

$$f(z_1, z_2, r_1, r_2) = \begin{cases} 1 & \text{if } z_1 = z_2 = 0 \\ 1 - \frac{z_1 z_2^2}{4\pi \varepsilon_0 (r_1 + r_2)^3} k_BT & \text{if } z_1 z_2 < 0 \\ 0 & \text{if } z_1 z_2 > 0 \\ E_{\text{image}} & \text{if } z_1 \neq 0, z_2 = 0 \end{cases}, \quad (9)$$

where $e$ is the elementary charge and $\varepsilon_0$ is the permittivity of free space.

The term $E_{\text{image}}$, which represents the enhancement in coagulation rate due to the image potential induced in a neutral particle undergoing interaction with a charged particle, is given by Huang et al. [45] for the free-molecule regime as follows:

$$E_{\text{image}} = \left. \frac{1}{2} \int_0^1 \frac{1}{x^2} \left( \frac{d\Phi}{dx} \right) \exp \left( \frac{x}{2} \frac{d\Phi}{dx} - \Phi \right) \, dx + \exp \left( \frac{1}{2} \frac{d\Phi}{dx} \right)_{x=1} - \Phi(1) \right|_{x=1}, \quad (10)$$

where $\Phi(x)$ is the inter-particle potential and $x$ is the dimensionless distance between the particle centers,

$$x = \frac{r_1 + r_2}{r}, \quad (11)$$

$r$ being the physical distance between the particle centers. The expression for $\Phi(x)$ derived by Huang et al. [45] is rather lengthy. In the case of a nanodusty plasma, coagulation between neutral and charged particles is dominated by coagulation between very small neutral particles and larger
charged particles [11]. In this case the expression for the inter-particle potential can be approximated by the following set of relations:
\[
\Phi(x) = \frac{a M x^2}{2(1 - bx^2)},
\]
where
\[
M = \frac{e^2}{4 \pi \varepsilon_0 k_B T (r_1 + r_2)},
\]
\[
d = \frac{\varepsilon - 1}{\varepsilon + 1} \left[ 1 - \frac{r_1}{r_1 + r_2} \right],
\]
and
\[
b = \left( \frac{\varepsilon - 1}{\varepsilon + 1} \right)^2 \left( \frac{r_1}{r_1 + r_2} \right) \left( 1 - \frac{r_1}{r_1 + r_2} \right),
\]
\(
\varepsilon\) being the dielectric constant of the particles.

Following a similar approach as in [27], the surface growth term in equation (5) can be written
\[
\frac{dN_{j}}{dt}_{\text{growth}} = \frac{B_j V_j}{v_{p,j}} + \frac{C_{j-1} V_{j-1}}{v_{p,j-1}} - \frac{C_j V_j}{v_{p,j}},
\]
where for simplicity we have assumed that surface growth does not affect particle charge and have dropped the subscript \(k\).

In equation (16), \(B_j\) and \(C_j\) are, respectively, intra- and intersectional growth coefficients (in units of s\(^{-1}\)), needed to account for the fact that growing particles can remain in the same size section or can grow into the next section; \(V_j\) is particle volume concentration (total volume of particles in section \(j\) per unit volume of gas); and \(v_{p,j}\) is the average particle volume in section \(j\), obtained as in equation (4).

The rate of volume addition to particles in section \(j\) can be written
\[
B_j V_j = N_i v_{m} A_{p,j} N_j,
\]
where \(N_i\) is the rate of particle growth in terms of molecules added per unit particle surface area, \(v_{m}\) is the molecular volume of the material added to the particle, and \(A_{p,j}\) is the average particle surface area in section \(j\), obtained as in equation (4). Note that \(N_i v_{m}\) represents the linear growth rate (nm s\(^{-1}\)) of particles due to surface growth. Evaluation of \(N_i\) requires a suitable sub-model, for example involving growth of particles by heterogeneous chemical reactions on their surfaces.

Finally, the intra- and intersectional growth coefficients are related by
\[
\dot{C}_j = B_j \frac{v_{p,j+1}}{v_{p,j+1}} - \frac{v_{p,j}}{v_{p,j}}.
\]

Assuming that all particle charging events change the particle charge by ±1 charge unit, the particle charging term in equation (5) can be written as
\[
\frac{dN_{j,k}}{dt}_{\text{charging}} = \nu_{j,k-1} N_{j,k-1} + \nu_{j,k+1} N_{j,k+1} - (\nu_{j,k} + \nu_{j,k}^\prime) N_{j,k},
\]
where \(\nu\) is charging frequency and superscripts ‘+’ and ‘−’ denote positive and negative charging, respectively. A suitable sub-model is required to calculate the charging frequencies, which in dusty plasmas can occur by processes such as electron and ion attachment, secondary electron emission, UV photodetachment, and electron detachment due to collisions with excited atoms or molecules [24].

3. Example numerical simulation results

We present selected results of a nanodusty plasma numerical simulation that uses a sectional model. These results are chosen to illustrate features of the system’s evolution that are predicted when one accounts for polydispersity in particle size and charge distributions, and that would be difficult to discover otherwise.

3.1. System modeled, and model description

The system modeled corresponds to the experiments of Agarwal et al [46], which involved a 13.56 MHz capacitive RF argon–silane (30 : 1) plasma at a pressure of 17 Pa, contained between parallel-plate electrodes with a 4 cm gap, the top electrode being powered, the bottom grounded. The applied voltage equals 55 V (amplitude), and the model accounts for a measured dc self-bias at the top electrode of −20 V. Gas flows through the top (showerhead) electrode with a velocity of 0.263 m s\(^{-1}\), corresponding to a flow rate of 31 sccm through an electrode with a diameter of 12 cm. The bottom electrode is solid, resulting in a stagnation flow velocity profile.

As chemistry is not modeled, the plasma is assumed to consist of pure argon, with Ar\(^+\) the only ion considered, and the nanoparticles are assumed to consist of pure silicon. While the computational domain covers the entire electrode gap, a chemically active zone is defined where either nucleation or particle surface growth can occur, reflecting in a qualitative way the competition between nucleation and surface growth for active species generated by plasma chemistry. This zone, whose extent changes with time, encompasses the plasma between the sheath boundaries, with the sheath boundaries defined as the location where the total negative charge lies 5% below the total positive charge. Within the chemically active zone, nucleation occurs whenever the local concentration of particle surface area lies below 1.8 × 10\(^6\) nm\(^2\) cm\(^{-3}\). Above this value nucleation is assumed to be quenched, and particle surface growth occurs instead. The nucleation rate is assumed to equal 10\(^{12}\) cm\(^{-3}\) s\(^{-1}\) and the surface growth rate is assumed to equal 12 nm s\(^{-1}\). The choices of these values are guided by the OMD modeling of Bhandarkar et al [40, 47], which included detailed chemistry, as well as by the fact that simulations using these values produce results for nanoparticle concentration and size that are roughly in accord with a body of experimental studies for similar conditions. Freshly nucleated particles are assumed to have a diameter of 0.75 nm, and to be electrically neutral. Particle charging is assumed to occur solely by electron and ion attachment, as described by orbital motion limited theory [48]. A maximum value of negative charge on a particle is imposed, which depends on particle size. This value is based on the expression for silicon particles developed by Gallagher [49], which considers the electron affinity of silicon and the mutual Coulomb repulsion of electrons.

The aerosol sectional model in these simulations is self-consistently coupled to a plasma model, which solves population balance equations for electrons and ions, the electron energy equation under the assumption of a Maxwell–Boltzmann electron energy distribution, and Poisson’s
equation for the electric field. All of the forces acting on particles noted in the discussion of equation (5) are included, with the exception of thermophoresis, as the gas temperature here is assumed to have a uniform value of 300 K. For more detailed discussion of the numerical model, including discussion of time steps and solution procedure, the reader is referred to [11, 42].

In the simulations presented below, the sectional spacing factor \( a \) in equation (2) was set to 1.15, with the number of particle size sections and charge states calculated automatically adjusted to local conditions. The maximum number of size sections considered equalled 160, while the maximum numbers of negative and positive charge states considered equalled 100 and 10, respectively.

### 3.2. Simulation results

We here present selected simulation results for three times following the onset of particle nucleation: 0.05, 1 and 11 s. Additionally we show simulation results for a case where the applied RF voltage is switched off at 5 s, following which the system, now in an afterglow phase, is allowed to evolve for 100 ms.

#### 3.2.1. Case 1: \( t = 50 \text{ ms} \)

Figure 1 shows the calculated particle size distribution function, \( dN/d(\log(d_p)) \), across the electrode gap at 50 ms following the onset of nucleation. Here \( N \) is the particle concentration and \( d_p \) is the particle diameter. White contour lines indicate average particle charge. Particles at this early time are all smaller than 2 nm. Particles that become negatively charged by attaching an electron are pulled to the center of the plasma by the electric field, while neutral and positively charged particles diffuse toward the electrodes.

Figure 2(a) shows calculated density profiles of positive, negative and neutral nanoparticles, and figure 2(b) shows the corresponding density profiles of charge carried by the three types of charge carriers in the system (electrons, positive ions and nanoparticles). Particles at this time carry at most one charge. The simulation reveals the existence of different charge classes (positive, negative, neutral), each with their own distinct spatial profiles. Comparison of figures 2(a) and (b) shows the strong coupling between the aerosol and the plasma. Neutral nanoparticles, which are spread by diffusion over most of the discharge, with a concentration of \( \sim 10^9 \text{ cm}^{-3} \), do not directly affect the plasma. However, in the center of the discharge, where the negative nanoparticles are concentrated, these particles carry almost ten times as much negative charge as do free electrons, and the positive ions respond by adopting a profile in the center that mirrors that of the negative nanoparticles, maintaining quasi-neutrality.

#### 3.2.2. Case 2: \( t = 1 \text{ s} \)

One second following the onset of nucleation, the negatively charged and trapped nanoparticles have mostly grown to about 10–20 nm in diameter, as seen in figure 3, which shows profiles of particle size distribution and average particle charge across the electrode gap. The aerosol here is seen to be far from monodisperse. The development of separate nanoparticle populations already evident at \( t = 0.05 \text{ s} \) is now much more pronounced. Freshly nucleated particles diffuse toward the walls and fill the electrode gap, while negative particles, once they carry multiple charges, are unlikely to become neutralized, and thus are stably trapped and can grow.

As a consequence, the particle size distribution at the midplane of the discharge is now highly bimodal, as seen in figure 4(a), which shows the size distribution as a histogram, with each bar corresponding to one numerical particle size section. The calculated charge distributions of the two modes of this distribution are quite different, as shown in figure 4(b). The freshly nucleated particles (\( d_p = 0.75 \text{ nm} \)) have comparable numbers of neutral and singly charged states, as well as a non-negligible population of positive particles, while stochastic charging causes the \( \sim 15 \text{ nm} \) particles to exhibit a broad charge distribution.

Another interesting feature of the effect of polydispersity concerns the result that, if one considers the population of relatively large, negatively charged and trapped particles seen in figure 3, one sees that the larger the particle the farther it is pushed, on average, toward the bottom electrode. This result is attributable to the fact that the force on nanoparticles from both neutral drag and ion drag is proportional to \( d_p^2 \). However, ion drag is more complicated, as it also depends on particle charge. Since nanoparticles of given size have a distribution of charge states, they experience a corresponding distribution of forces due to ion drag as well as the electrostatic force. When a nanoparticle experiences a discrete charging event, it also experiences a corresponding change in net force that pushes it in one direction or the other. Thus polydispersity in both particle size and charge distributions causes the particle cloud to have a rich structure based on the effects of particle size and charge on the forces that transport nanoparticles.

#### 3.2.3. Case 3: \( t = 11 \text{ s} \)

At \( t = 11 \text{ s} \), most nanoparticles have grown to over 100 nm in diameter. Figure 5 shows the predicted growth
Figure 2. Simulation results at $t = 0.05$ s: (a) density profiles of positive, neutral and negative nanoparticles; (b) density profiles of electrons, ions and net negative charge carried by nanoparticles.

Figure 3. Particle size distribution and average particle charge at $t = 1$ s.

Profiles of particle size distribution and average negative charge per particle. The disappearance of the population of very small particles is due to the quenching of nucleation by the outward spread of the particle cloud. (While neutral drag and gravity both push particles toward the lower electrode, ion drag pushes particles out of the center of the discharge and toward both electrodes.) Thus the particle size distribution is no longer bimodal. Nevertheless, the size distribution is broad, with high concentrations of particles whose diameters range from roughly 100 nm to over 200 nm. This is a consequence of the broad range of nucleation and growth temporal trajectories experienced by the particles, related primarily to the different times at which particles nucleate and the highly nonuniform nature of coagulation in this system, discussed below.

An interesting feature of figure 5 is that, for the entire lower half of the discharge, the isocontours representing average particle charge are curved, and depart strongly from the horizontal. This implies that, for particles of given size, average particle charge depends sensitively on particle location. This behavior is explained by figure 6, which shows the density profiles of charge carried by electrons, ions and nanoparticles. Because the particles are pushed toward the lower sheath edge by neutral drag, ion drag, and, for these particle sizes, gravity, they deplete electrons in that region. The usual expectation that dust particles in a plasma will become negatively charged assumes that positive ions and electrons have comparable densities. In this case, however, because of the depletion of electrons by the particle cloud, the density of ions far exceeds that of electrons, and the nonuniform spatial distribution of the particle cloud causes the ratio of ions to electrons to vary strongly across the plasma. As particles of given size are transported from the center of the plasma toward the lower electrode, they experience progressively higher ratios of ion-to-electron attachment, and thus become, on average, less negatively charged.

The distortion of electron and ion density profiles caused by the particle cloud in turn affects particle charge distributions. Figure 7 shows calculated charge distributions at $t = 11$ s for 130 nm diameter particles at two different locations. At $x = 1.5$ cm, where $x$ is the distance from the lower electrode, the ion-to-electron density ratio equals 124, and the average charge on a 130 nm particle equals $-30.7$. Closer to the lower electrode, at $x = 0.6$ cm, the situation is rather different: the ion-to-electron density ratio equals 341, and the average charge on a 130 nm particle equals $-12.6$. At both locations, stochastic charging causes a distribution of charge states to exist. Indeed, a small fraction of the 130 nm particles located at $x = 0.6$ cm is neutral or positively charged.

Figure 8, which accounts for particles of all sizes, shows the predicted density profiles of negative, neutral and positive nanoparticles. Even though the fraction of non-negative particles at its peak equals only about $10^{-5}$, the existence of such large non-negative particles could have important
Figure 4. Nanoparticle size and charge distributions at midplane of discharge at $t = 1 \text{s}$: (a) particle size distribution function, with each bar of the histogram representing one numerical section; (b) charge distributions for the sections at the two modes of the size distribution, corresponding to diameters of 0.75 and 14.8 nm.

Figure 5. Particle size distribution and average particle charge at $t = 11 \text{s}$.

consequences. Since they are not trapped, they could diffuse to the lower electrode, with positive particles being accelerated across the sheath potential. Also, the non-negative particles could coagulate with the negative particles, forming yet larger particles, especially in the case of oppositely charged particles, with the coagulation rate enhanced by Coulomb attraction.

3.2.4. Case 4: afterglow, $t = 5.0–5.1 \text{s}$. Finally, we consider a simulation involving the same conditions, except that the applied RF voltage is turned off at $t = 5.0 \text{s}$, and the system is allowed to evolve in an afterglow phase for 100 ms, with the gas flow still on. Dusty plasma afterglows are of interest because the fate of nanoparticles when the plasma is turned off has important implications for particle contamination during semiconductor processing as well as for deliberate collection of nanoparticles for applications. In addition, afterglows are an intrinsic aspect of plasma pulsing, which is of increasing interest for control of plasma properties, and potentially of nanoparticle properties.

At $t = 5.0 \text{s}$, when the applied voltage is turned off, the profiles of particle size distribution and average particle charge are as shown in figure 9(a), while figure 9(b) shows the simulation results 100 ms later.

The behavior of the system during the afterglow is a consequence of the widely different time scales for particle charging by electron and ion attachment, electron energy relaxation, diffusion of electrons, ions and nanoparticles, neutral drag and coagulation, together with the spatially
inhomogeneous conditions that exist at the instant the applied voltage is switched off. Even in the absence of an applied electric field, the existence of charge carriers in the afterglow affects the system’s evolution via Poisson’s equation. Among the interesting features seen in comparing figures 9(a) and (b), one notes a rapid tendency toward both positive charging and particle growth. The former is a result of the much more rapid loss of electrons from the system compared with ions. Positive particle charging is particularly pronounced near the lower electrode, where at the instant the applied voltage is switched off the ion density far exceeds that of the electrons.

The rapid particle growth seen in figure 9 is due to coagulation. As particles rapidly lose their negative charge, coagulation becomes more important, particularly coagulation enhanced by Coulomb attraction between oppositely charged particles. The white contour lines in figure 9(b) show average particle charge, but if one considers that particles of given size have a broad distribution of charge states, it is evident that the aerosol here is basically bipolar. Even in regions and for particle sizes where the average particle charge is close to zero, most particles are charged. For example, figure 10 shows the charge distribution at 100 ms into the afterglow for 70 nm diameter nanoparticles located at \( x = 1.0 \) cm. The average particle charge in this case is close to zero (it equals +0.008), but in fact only 21% of these particles are neutral.

These features would be difficult to model correctly without accounting for particle size and charge distributions. This is particularly the case for the modeling of coagulation, which, as noted in the introduction, is believed to be important in nanodusty plasmas. To further illustrate this point, figure 11 shows calculated profiles of coagulation rate at several times corresponding to cases considered above. During the period when nucleation occurs, coagulation is overwhelmingly attributable to freshly nucleated, very small neutral particles that coagulate with larger, negatively charged particles, with coagulation rates enhanced by the image potential induced in the small neutral particles [11]. This phase applies to the curves at both \( t = 1 \) s and \( t = 5 \) s, though these curves are seen to be quite different from each other, because by \( t = 5 \) s the spreading particle cloud, pushed downward by neutral gas drag, has quenched nucleation except in the upper part of the discharge. Thus the coagulation rate at 5 s is highest at the upper edge of the particle cloud, adjacent to the region of fresh nucleation. The coagulation rate profile at \( t = 11 \) s is again quite different, and mirrors the profiles of non-negative particles seen at \( t = 11 \) s in figure 8. At this time fresh nucleation has long since been completely suppressed by the outward spread of the particle cloud, and coagulation here occurs between large particles, and primarily between oppositely charged particles, enhanced by Coulomb attraction. Finally, the coagulation rate profile for the 5.1 s (afterglow) case, which is responsible for the rapid particle growth near the lower electrode seen in figure 10, is also primarily due to coagulation between relatively large, oppositely charged particles.

4. Summary and conclusions

Nanodusty plasmas are characterized in many cases by dust particles that are polydisperse with respect to particle size and, for particles of given size, exhibit a distribution of particle charge states. The fact that particle size and charge are distributed over a range of values, rather than being monodisperse, has important consequences for the spatiotemporal evolution of a nanodusty plasma. Sectional representations of particle size distributions offer a means for numerical modeling of such plasmas.

In this work, an aerosol sectional model that is self-consistently coupled to a 1D plasma fluid model was used to conduct numerical simulations of a capacitively coupled RF argon plasma in which silicon nanoparticles nucleate and grow. Snapshots of particle size and charge distributions at several times are presented, together with corresponding plasma properties.
Figure 9. Behavior of the particle cloud in the afterglow: (a) particle size distribution and average particle charge at $t = 5\,\text{s}$, at which time the applied RF voltage is switched off; (b) corresponding profiles 100 ms later.

Figure 10. Charge distribution of 70 nm diameter nanoparticles located at $x = 1.0\,\text{cm}$, at $t = 5.1\,\text{s}$ (100 ms into the afterglow).

At very early times following the onset of nucleation, when particles are at most a few nanometers in diameter and contain at most one charge, stochastic charging produces the emergence of different particle populations: negatively charged particles, that are pulled to the center of the discharge by the electric field, and neutral particles (as well as a smaller population of positively charged particles), that diffuse toward bounding surfaces. At later times, as negative particles become multiply charged, they become stably trapped in the plasma and have time to grow. As long as fresh nucleation continues to occur, a strongly bimodal particle size distribution exists, and coagulation occurs mainly between very small neutral nanoparticles and larger, negatively charged particles. At still later times, as particles grow larger, forces on particles including neutral drag, ion drag and gravity cause the particle cloud to spread. These forces are size-dependent, resulting in a spatial classification of nanoparticles by their size. Moreover, both ion drag and the electrostatic force are charge-dependent, so that the existence of a broad charge distribution, for particles of given size, affects the detailed structure of the particle cloud. In turn, the spreading of the particle cloud strongly distorts the spatial profiles of electrons and ions. The ion-to-electron density ratio in the region of maximum particle charge concentration can become high enough to cause relatively large particles to become, on average, much less negatively charged, with a small fraction becoming neutral or even positively charged. These non-negative particles, not being electrostatically trapped, can deposit on nearby surfaces, and can coagulate with the negative particles.
Finally, the behavior of a dusty plasma afterglow is examined, where the applied RF voltage is switched off at a time when most particles are several tens of nanometers in diameter. Rapid loss of electrons causes particles to become more positively charged, and a bipolar charge distribution develops, allowing for rapid particle growth by coagulation among oppositely charged particles.

In conclusion, sectional modeling is a powerful tool which can facilitate discovery and insight into major qualitative aspects of the spatiotemporal evolution of nanodusty plasmas. While it is computationally expensive compared with monodisperse models, we anticipate that future reductions in the cost of massively parallel computing, together with greater attention to pertinent numerical and computational issues, will enable nanodusty plasma simulations of increasing sophistication and accuracy.

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