NUMERICAL SIMULATION OF NANOPARTICLES COAGULATION IN RF-DISCHARGE

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This paper presents the simulation results of nanoscale dust particles coagulation in capacitive radio-frequency discharge of low pressure in argon. Simulations carried out under the self-consistent kinetic model that takes into account the stochastic nature of the process of dust particles charging and their coagulation using general dynamic equations for aerosols. We analyze the distribution of dust particles by size and charge at different distances from the electrodes. It is shown that a significant number of dust particles of opposite charges present in sheaths, which improves the process of their coagulation, compared with the central region inter-electrode gap. It is shown that the presence of dust particles increases the concentration of electrons in the discharge, as well as increases the average electric potential drop in sheaths.

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INTRODUCTION

Low temperature plasmas containing dust particles are widely studied for fundamental research as well as technological applications [1]. Plasmas present exciting opportunities for nanoparticle synthesis. In particular, for the creation of dust particles having the desired properties are used radiofrequency discharges. Such dust particles could find applications in medicine, materials science, in the production of nanostructured materials if the formation, growth and transport of theirs in plasmas can be controlled. In order to control the morphology, composition and transport of the particles in the above mentioned and other existent and future technological applications a better understanding of the particle formation mechanisms and their influence on plasma is needed.

Radiofrequency discharges with dust particles investigated in the framework of the hydrodynamic model [2], as well as using the method of particles in cells [3, 4]. In these studies, it was assumed that the size of the dust particles was constant in time and uniform in space. 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’. In the latter case, the coagulation can broaden size distributions and the discharge chamber contains particles of different sizes and charges. 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.

The coagulation of dust particles in rf discharges has been studied in [5, 6]. In these reports, densities and charge distributions are calculated in the frame of one-dimensional hydrodynamic model, in addition the influence of particle charging on coagulation frequency not taken into account. It should also be noted, hydrodynamic model is not applicable to describe the discharge at low gas pressures.

In this paper, we model the rf discharge with dust nanoparticles in argon gas at low pressures ($p<1 Torr$) using PIC/MCC method [7], taking into account the coagulation of dust particles.

1. MODEL AND SIMULATION METHOD

A one-dimensional RF discharge is considered between two plane electrodes separated by a gap which is filled with Ar. Dust particles of a given radius $r_d = 1\,nm$ are distributed uniformly at initial time in the inter-electrode gap. In our model, the dust particles are assumed unmovable. Simulations have been carried out with dust densities $n_d = 5\cdot 10^{13} ... 5\cdot 10^{14}\ m^{-3}$, the rf frequency and the amplitude of rf power were set $\nu_{rf} = 103{,}56\,MHz$ and $V_{rf} = 150\,V$. In the frame of Monte-Carlo method, we take in account elastic collisions of electrons and ions with atoms, an ionization and excitation of atoms by electrons, the charge exchange between ions and atoms.

Nanoparticles in the plasma are charged because of collisions with electrons and ions. The electron and ion currents collected by a dust particle in the nanometer regime can be described by the orbital-motion-limited (OML) probe theory. A particle with radius r_d which carries a charge $Z_k = k\cdot e$ (with e the elementary charge and k an integer) is charged to a surface potential of $\Phi_k = Z_k / 4\pi\varepsilon_0 r_d$, with ε_0 the vacuum dielectric constant. Using OML theory, expressions for the frequency with which a particle with charge Z_k is hit by electrons and ions, respectively, can be derived

$$\nu_{e,i}^k = n_{e,i} S v_{e,i} \exp\left(-\frac{q_{e,i}\Phi_k}{k_B T_{e,i}} \right), \quad q_{e,i}\Phi_k \ge 0$$

$$V_{e,i}^k = n_{e,i} S v_{e,i} \left(1 - \frac{q_{e,i}\Phi_k}{k_B T_{e,i}} \right), \quad q_{e,i}\Phi_k < 0.$$

$S = 4\pi r_d^2$ is the particle surface area, $v_{e,i} = \left(k_B T_{e,i} / 2\pi m_{e,i} \right)^{1/2}$, $n_{e,i}$ stands for the electron and ion densities, $m_{e,i}$ and $T_{e,i}$ are the mass and temperature of electrons and ions, respectively, and

$q_{e,i} = \mp e$ is the respective charge, k_B is Boltzmann constant.

The charge distribution of particles of a given radius r_d is described by the fraction of particles F_k carrying a charge $k \cdot e$. It is normalized by $\sum_k F_k = 1$. The rate equation for a charge state k can then be written as

$$\frac{dF_k}{dt} = \nu_e^{k+1} F_{k+1} - \nu_e^k F_k - \nu_i^k F_k + \nu_i^{k-1} F_{k-1}.$$

It is assumed that the charging of particles is much faster than coagulation so the charge distribution can be considered in steady state [8]. This assumption enables the use of recursive relations for the charge distribution

$$F_{k+1} = \frac{\nu_i^k}{\nu_e^{k+1}} F_k \ .$$

In the present paper, we will focus on the growth of nanoparticles due to coagulation. Similar to [9], we suppose that the typically coagulation of particles in a low-pressure plasma is identical to the coagulation in a bipolar aerosol. Since the charging time is much shorter than the typically coagulation time of particles we separate the problems of charging and coagulation from each other.

The volume distribution function of dust particles $n(v)$ is described by the general dynamic equation [9]

$$\frac{\partial n(v)}{\partial t} = \frac{1}{2}\int_0^v \beta(v', v-v') n(v') n(v-v') dv' -$$

$$\int_0^\infty \beta(v, v') n(v) n(v') dv',$$

where v is the volume of the dust particle, $n(v)\,\mathrm{d}v$ denotes the particle number density in a volume range $[v, v+dv]$. Coefficient $\beta(v, v')$ is the frequency for coagulation between two particles with a volume v and v'. According to [10], $\beta(v, v')$ is given

$$\beta(v, v') = \alpha(v, v') \left(\frac{3}{4\pi}\right)^{1/6} \left(\frac{6k_B T}{\rho_p}\right)^{1/2} \left(\frac{1}{v} + \frac{1}{v'}\right)^{1/2} \times$$

$$\left(v^{1/3} + v'^{1/3}\right)^2,$$

where v and v' are the volumes of the particles interacting, ρ_p is the density of the particles, and T is the temperature of the particles. $\alpha(\mathrm{v}, \mathrm{v}')$ is a coefficient which describes that the effective cross section for coagulation depends on the charge of both particles

$$\alpha(v, v') = \sum_{k=-\infty}^{\infty} \sum_{k'=-\infty}^{\infty} F_k(\mathrm{v}) F_{k'}(\mathrm{v}')\, \mathrm{Q}(\mathrm{k}, \mathrm{k}', \mathrm{v}, \mathrm{v}')$$

with

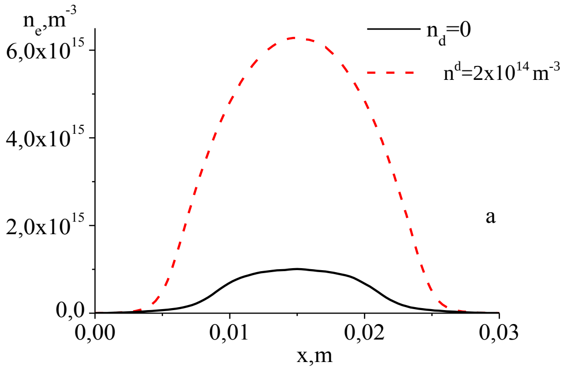
$$Q(k, k', v, v') = \exp\left(-\frac{kk'e^2}{4\pi\varepsilon_0 R_s k_B T}\right), \quad kk' > 0$$

$$= 1 - \frac{kk'e^2}{4\pi\varepsilon_0 R_s k_B T}, \quad kk' \le 0.$$

2. RESULTS AND DISCUSSION

We here present selected results of radio-frequency discharge numerical simulation. The plasma process parameters are as follows: electrode spacing is $0.03\,m$, gas pressure is $0.1\,Torr$, and pulse frequency is $13.56\,MHz$. Initially, neutral nanoparticles having a radius of 1 nm are uniformly arranged in the interelectrode gap with density $n_d = 2 \cdot 10^{14}\, m^{-3}$. Subsequently, the dust particles are charged in the plasma and have an influence on the discharge parameters.

Fig. 1,a shows spatial distributions of electron density averaged over the period of the discharge for case without dust particles (solid line) and for case with dust density $n_d = 2 \cdot 10^{14}\, m^{-3}$ (dash line).



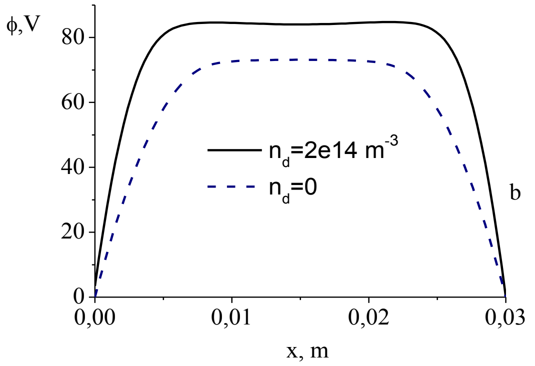


Fig. 1. Spatial distributions of electron density (a) and self-consistent electric potential (b), averaged over the discharge period

As can be seen, the electron density increases significantly in the present of dust particles at the same potential drop across the discharge gap. This is due to an increase in resistance of the discharge gap.

Fig. 1,b shows spatial distributions electric potential, averaged over the rf discharge period. Solid and dash lines correspond to the cases with dust particles and without dust particles, respectively. It is seen, that sheaths are formed near electrodes, which are characterized by a sharp change in potential. The potential drop in sheaths increases in the presence of dust particles.

Inhomogeneity of the plasma parameters in the discharge gap leads to a different charge distributions of dust particles at different points in space. This is confirmed figure 2, which shows the charge distribution of dust particles for different particle volumes V at the boundary of the sheath (a) and in the centre of the discharge gap (b). It is seen that the average charge of the smaller size of nanoparticles in the sheath is approximately equal to zero, since at this point the number of positive and negative particles of about the same. The increasing of particle volume due to coagulation increases the average charge in magnitude.

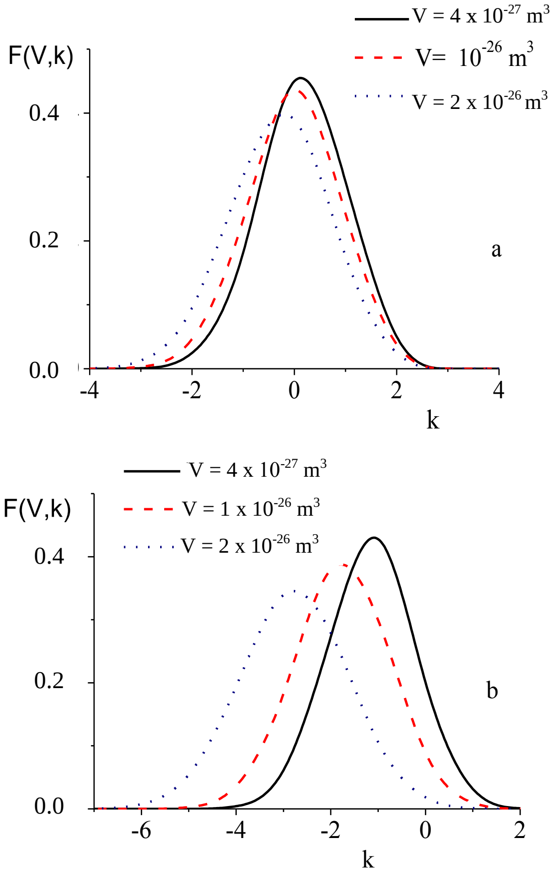


Fig. 2. Charge distributions of nanoparticles for different sizes (a – near the electrodes; b – in the center of the discharge gap)

However, we can observe an essential fraction of positively charged particles in these cases too. In the center of the discharge gap, the charge distribution significantly differs from one in the sheath. In this case, we can observe mainly negative dust particles.

Coagulation is a main reason of decrease in dust particle density as particles grow to larger size. Fig. 3 shows the densities of dust particles at various times after the ignition of the discharge. The presented dependences show that the minimum values of the concentration of dust particles are observed at the edges of sheaths. This can be explained by the fact that in this area the coagulation process is most effective. In the central part of inter-electrode gap coagulation frequency is lower that at the boundaries of sheaths. This is due to the presence in that area a significant amount of dust particles of the opposite sign. Near the electrodes (at $x = 0$ and at $x = 0.03\,m$) averaged over the period of the discharge the electron density is much less than the ions density. Consequently, nanoparticles are here mainly positive charged and their coagulation rate decreases. We concluded that interaction of positively and negatively charged particles is the main reason of enhance coagulation rate in comparison to the coagulation rate in the canter of discharge.

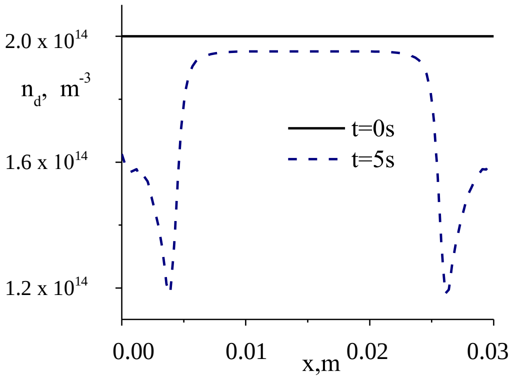


Fig. 3. Spatial distributions of dust density at different times after the ignition

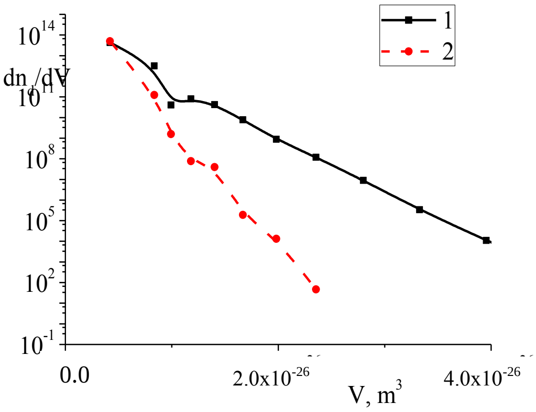


Fig. 4. Distributions of dust particles by volume at the sheath boundary (1) and at the center of the discharge gap (2)

Distributions of dust particles by volume are presented in Fig. 4. Solid line corresponds to the edge of the sheath and dash line corresponds to the centre of the discharge gap.

CONCLUSIONS

In this paper, particle-in cell (PIC) simulations with Monte-Carlo (MC) collisions have been performed to investigate the coagulation of nanoparticles in argon radiofrequency discharge and the their influence on the discharge. The analysis of the obtained simulation results indicates that the presence of dust particles in the discharge leads to increase the ionization rate of atoms, as well as to increase of electron and ion densities. It is obtained charge and volume distributions of nanoparticles at different points of interelectrode gap. It was shown that the coagulation of the nanoparticles is more effective in the sheath, since in this region there are dust particles of opposite charge.

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ЧИСЛЕННОЕ МОДЕЛИРОВАНИЕ КОАГУЛЯЦИИ НАНОЧАСТИЦ В РАДИОЧАСТОТНОМ РАЗРЯДЕ

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Представлены результаты компьютерного моделирования коагуляции наноразмерных пылевых частиц в ёмкостном радиочастотном разряде низкого давления в аргоне. Расчёты проведены в рамках самосогласованной кинетической модели, которая учитывает стохастическую природу процесса зарядки пылевых частиц, а также их коагуляцию при помощи общих динамических уравнений для аэрозолей. Анализируется распределение частиц по заряду и размеру на различных расстояниях от электродов. Показано, что на краях приэлектродных слоёв присутствует значительно большее количество пылевых частиц с противоположными зарядами, в сравнении с центральной областью межэлектродного промежутка, что значительно улучшает процесс их коагуляции. Проанализировано влияние пылевых частиц на параметры разрядной плазмы. Показано, что наличие пылевых частиц приводит к увеличению концентраций электронов в разряде, а также к увеличению скачков усреднённого электрического потенциала на приэлектродных слоях.

ЧИСЛОВЕ МОДЕЛЮВАННЯ КОАГУЛЯЦІЇ НАНОЧАСТИНОК В РАДІОЧАСТОТНОМУ РОЗРЯДІ

О.Ю. Кравченко, Ю.В. Ющишена

Представлені результати комп'ютерного моделювання коагуляції нанорозмірних пилових частинок в ємнісному радіочастотному розряді низького тиску в аргоні. Розрахунки проведені в рамках самоузгодженої кінетичної моделі, яка враховує стохастичну природу процесу зарядки пилових частинок, а також їх коагуляцію за допомогою загальних динамічних рівнянь для аерозолів. Аналізується розподіл пилових частинок по заряду та розміру на різних відстанях від електродів, а також вплив пилових частинок на властивості розряду. Показано, що в приелектродних шарах присутні значна кількість пилових частинок протилежних зарядів, в порівнянні з центральною областю міжелектродного проміжку, що значно прискорює процес їх коагуляції. Проаналізовано вплив пилових частинок на параметри розрядної плазми. Показано, що наявність пилових частинок приводить до збільшення концентрацій електронів в розряді, а також до збільшення стрибків усередненого електричного потенціалу на приелектродних шарах.