About the mechanism of modification of melamine formaldehyde particles in dusty plasmas

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Abstract. The article presents the previously obtained results of the modification of spherical microparticles of melamine-formaldehyde injected as a dust component of complex plasma formed in stratified glow discharge in neon. Particular attention is paid to changing the particle size depending on the residence time in the plasma. A mechanism is proposed for heating particles by ion flow sustaining a stable charge of their surface. Calculations of the heat balance are presented, confirming the results obtained in the experiment.

1. Introduction
The investigation of the interaction of plasma with the surface is an extensive task associated with a number of problems [1–4]. For example, it is the confinement of plasma by the walls of chambers, the maintenance of the chemical composition of the plasma, the energy transfer and the breakdown of the operation of power plants [5]. Technological applications such as laser ablation, plasma etching and surface treatment with high-energy ions, as well as particle synthesis, are today elements of large-scale production. For relatively soft polymer films, fabric fibers, etc, surface treatment, even with low-energy ions, changes physical and chemical properties, such as adhesion, wetting, etc [6,7]. The use of dusty plasma for this problem allows for a comprehensive precision treatment of the surface of polymer microparticles suspended in the plasma [8–10].

In laboratory dusty plasma without the use of chemically active plasma media and without exposure to high-energy ions, a significant surface modification and degradation of the size of dust particles were found [11–15].

In the present paper, we rely on detailed experimental studies of the degradation of melamine-formaldehyde particles in dusty plasma and make quantitative estimates of the energy and momentum transfer to the surface of dust particles. Previously obtained results show that the modification of particles occurs under the action of a stream of ions; moreover, there are two stages of the process: slow, associated with the heating of particles, and relatively fast, at which the particles lose a significant part of their mass.
2. Experimental results and the idea of a modification mechanism

A modification of the size of spherical particles of melamine formaldehyde in dusty plasma created in a plasma-dust trap in a standing layer in a glow discharge was experimentally studied. The experimental conditions are as follows: neon; pressure \( p = 0.3 \) Torr; discharge current \( i = 0.2 \) mA; calibrated spherical particles with a diameter of \( 7.3 \pm 0.4 \) \( \mu \)m. By the method described in [16, 17], dust particles were injected into the glow discharge plasma, captured and removed from the discharge chamber after a fixed residence time in the plasma.

The extracted particles were examined using the SEM (scanning electron microscope) method. Figure 1 shows examples of obtained images of particles before being placed in the plasma and after a certain time in the plasma. Figure 2 shows the dependence of the diameter of the studied particles on the time of plasma exposure. We can see that the rate of resizing does not remain constant. The initial stage is visible until about 15 minutes, when the rate of size reduction is \((6.5 \pm 1.8) \times 10^{-4} \mu\text{m/s}\). Then the rate of size reduction increases to \((12.1 \pm 0.4) \times 10^{-4} \mu\text{m/s}\). At large times, of the order of 40 minutes or more, see, for example, [14], all particles are almost destroyed.

We assume that the material of the particles is knocked out when ions hit the surface. The energy required for the ejection of molecules is acquired by ions, accelerated by the field of each dust particle, in the process of maintaining its stationary charge. The first slow phase of the modification is associated with the heating of the particles. When the material of the particle is softened, the ions falling on its surface are able to effectively dislodge the material from the surface, while the particle size decreases faster. Next, we will conduct a numerical estimate of the process of heating the particles, and the energy of the ions reaching the surface of the particles.

3. Numerical estimates

The process of maintaining a stationary charge of a solitary particle is described in terms of the OML (orbital motion limited) theory [8–10]. The number of ions falling on a surface area of a sphere \( 4\pi a^2 \) can be obtained from the expression for the ion current to probe

\[
I_i = e\sqrt{8\pi a^2 n_i v_{Ti}} [1 + eU/(kT_i)],
\]

where \( e \) is the ion charge; \( a \) is the radius of particle; \( n_i \) and \( v_{Ti} \) are the ion concentration and velocity; \( U \) is the absolute value of the potential of the particle relative to the plasma; \( kT_i \) is the ion thermal energy. Under typical experimental conditions (Ne gas, pressure 0.3 Torr, discharge current 2 mA), plasma characteristics will be as follows: plasma concentration \( n_i = 5 \times 10^8 \text{ cm}^{-3} \); electron temperature or average energy \( eU \) is about 10 eV. The number of ions entering the particle according to (1) is \( N = I_i/e = 10^{10} \text{ s}^{-1} \).
Figure 2. Dependence of the diameter of spherical microparticles on the residence time in the plasma of a glow discharge in neon. The experimental conditions: pressure $p = 0.3$ Torr, discharge current $i = 0.2$ mA, calibrated spherical particles with a diameter of $7.3 \pm 0.4$ µm.

The energy of one ion falling on the surface of a dust particle can be estimated from the ratio

$$mv_{is}^2/2 = eU,$$

where, $U$ is the absolute value of the potential of the particle relative to the plasma, and $v_{is}$ is the velocity of the ion on the surface of the particle. The ion velocity in contact with a particle is an order of magnitude greater than thermal $0.025$ eV. For neon $U$ is about $10$ V, the speed $v_{is}$ will be about $10^3$ m/s. Then each ion can transfer a particle energy of about $10$ eV. We note another possible channel for the transfer of particle energy; it is associated with the recombination of ions and electrons on its surface. The ionization energy for a neon ion is $21.6$ eV; however, the recombining atom can be in an excited state, retaining $16.6$ eV, it is up to $75\%$ of energy. As a process of energy transfer to the particle, we will consider both the transfer of kinetic energy from the ion and the recombination energy; in this case, we will estimate the energy from above. Thus, the dust particle in the plasma per unit of time receives energy $Q_1 = 7.7 \times 10^{-8}$ J. The heated particle is cooled through a neutral gas discharge due to heat conduction through the tube wall:

$$Q_2 = \kappa (dT/dr) S \Delta t,$$

where thermal conductivity of neon $\kappa = 10^{-2}$ J/(kg K) [18], $dT/dr$ is the temperature gradient, $S$ is the particle surface area. For a time $\Delta t = 1$ s heat $Q_2 = 7 \times 10^{-8}$ J is removed from the particle. Heating of the melamine-formaldehyde particle of $3.2 \times 10^{-13}$ kg to the melting temperature $350$ °C [19] and the melting itself occurs in the discharge at times up to $40$ minutes. The energy input per unit of time required for these processes is small compared with $Q_2$.

Based on the estimates made, it can be seen that the difference between $Q_1$ and $Q_2$ is close to zero, but it is possible that some of the heat is used to melt the particle. Elementary estimates cannot provide rigorous accuracy, but based on the experimental curve, it can be assumed that in $10$ minutes the particle softens, since the processes of its modification and size degradation
then begin to go with increased speed. Absolute accuracy cannot be expected from the given elementary estimates, but it can be assumed that, from the thermal balance of $Q_1 \approx Q_2$, in the experimental conditions, the heating of particles to the melting temperature may well occur. As a result, particles with an initial size of $d = 7.3 \, \mu m$ for a time of about 15 min are heated and softened, and since that time the processes of degradation are accelerated. It can be assumed that upon impact with an ion with an energy of 10 eV, molecules of melamine-formaldehyde resin with a binding energy of about 3 eV come off the surface [19].

4. Conclusion
Thus, elementary numerical estimates are consistent with the assumption of the mechanism of degradation of the size of dust particles of melamine-formaldehyde in a dusty plasma under the action of a stream of ions having a thermal energy of 0.025 eV, but acquiring a substantial speed in the process of maintaining a stationary charge of a dust particle.

Acknowledgments
This work is supported by the Russian Science Foundation (grant No. 18-12-00009). A part of the materials under study was obtained at the expense of the Saint-Petersburg State University (SPbSU) within the framework of the program of the development of material and technical basis of the SPbSU “Polymer particles in dusty plasmas”.

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