



HAL
open science

The formation and transport phenomena of nanometre-sized particles in a dc plasma

Lisa Wörner, Eva Kovacevic, Johannes Berndt, Hubertus M. Thomas, Markus
H. Thoma, Laifa Boufendi, Gregor Morfill

► **To cite this version:**

Lisa Wörner, Eva Kovacevic, Johannes Berndt, Hubertus M. Thomas, Markus H. Thoma, et al.. The formation and transport phenomena of nanometre-sized particles in a dc plasma. *New Journal of Physics*, 2012, 14, pp.023024. 10.1088/1367-2630/14/2/023024 . hal-00690916

HAL Id: hal-00690916

<https://hal.science/hal-00690916>

Submitted on 25 Apr 2012

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

The formation and transport phenomena of nanometre-sized particles in a dc plasma

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2012 New J. Phys. 14 023024

(<http://iopscience.iop.org/1367-2630/14/2/023024>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 194.167.30.129

The article was downloaded on 24/04/2012 at 16:24

Please note that [terms and conditions apply](#).

The formation and transport phenomena of nanometre-sized particles in a dc plasma

L Wörner^{1,2,3}, E Kovacevic², J Berndt², H M Thomas¹,
M H Thoma¹, L Boufendi² and G E Morfill¹

¹ MPE, Giessenbachstrasse, 85748 Garching bei München, Germany

² GREMI, 14 rue d'Issoudun, 45067 Orléans Cedex 2, France

E-mail: woerner@mpe.mpg.de

New Journal of Physics **14** (2012) 023024 (10pp)

Received 10 October 2011

Published 13 February 2012

Online at <http://www.njp.org/>

doi:10.1088/1367-2630/14/2/023024

Abstract. The growth of nanoparticles in low-temperature plasmas is often accompanied by the formation of complex particle patterns and intricate transport processes. This paper deals with the formation and growth of nanoparticles operated in a mixture of argon and acetylene. The experiments are performed in a cylindrical dc discharge, the so-called PK-4 facility that shall be launched to the International Space Station (ISS) in 2014. The experiments show that the particles are formed in a localized region close to the anode and are transported as still localized dust structures ('dust bullets') along the glass tube. The formation of new particles triggers an oscillatory process that is characterized by the periodic appearance and subsequent removal of dust particles. The frequency of this process, as well as the size of the particles within each 'dust bullet', can be controlled by means of the neutral gas flow. This behaviour can be understood by analysing the size-dependent forces acting on the growing particles.

³ Author to whom any correspondence should be addressed.

Contents

1. Introduction	2
2. Experimental setup	3
3. Experimental results and discussion	4
4. Summary	9
Acknowledgments	9
References	10

1. Introduction

The production of nanoparticles by means of (low-temperature) plasmas has become an important topic for both fundamental research and plasma technology. Nanoparticles can be observed in astrophysical environments [1, 2], in the ionosphere [3], in fusion devices [4, 5] and now increasingly in different kinds of plasma-based technological processes [6]. The formation and growth of nanometre-sized particles has been observed in various types of gas discharges such as, for example, radio-frequency (RF) [7, 8], microwave [9] and arc discharges [10]. Depending on the discharge type, operation conditions and so on, particle formation can be triggered either by the reactive gas component (e.g. CF_4 [11], C_2H_2 [12, 13], SiH_4 [14, 15] and CH_4 [16]) or by precursors obtained, for example, through the sputtering of electrode material [17, 18]. Independent of the details of the growth process, the occurrence of nanometre- or micrometre-sized dust particles can have a tremendous influence on the discharge characteristics [19–21]. One of the most fundamental consequences concerns the electron density. Micrometre-sized particles which are embedded in a plasma can collect up to several thousand elementary charges, a process that can lead to a significant reduction of the electron density [22]. The negative charging of the particles is also responsible for their confinement in the positive plasma potential. The spatial distribution of the particles inside a discharge results from the interaction of the various forces acting on the particle (e.g. gravity, electric force and ion drag force). Since these forces depend strongly on the particle radius, the generation and growth of nanometre-sized particles are very often accompanied by intricate time-dependent transport processes (of the particles) and the formation of complex spatial particle patterns. The study of these processes is interesting not only from a fundamental point of view but also for technological processes where it is important either to avoid the contamination of specific areas of the discharge or to control the targeted deposition of nanometre-sized particles. This paper deals with the formation and transport of nanometre-sized particles in a dc discharge, more specifically the so-called PK-4 facility [23, 24]. PK-4 is the successor of PKE-Nefedov [25] and PK-3 plus [26], both setups used on board the International Space Station (ISS). PK-4 laboratory setups (see below) exist at the Max-Planck-Institute for Extraterrestrial Physics (Garching, Germany), at the Joint Institute for High Temperatures (Moscow, Russia) and at GREMI (Orleans, France). In addition, there is a setup used under microgravity in parabolic flight experiments [27]. The PK-4 facility for the ISS supported by the European Space Agency is under construction and shall be launched in 2014. In contrast to its precursors PKE-Nefedov and PK-3 Plus, which are based on RF discharges in cubic plasma chambers, PK-4 will focus on the liquid state and flow phenomena of complex plasmas. In addition, particle growth experiments, which have been performed mostly in RF discharges so far, can also be done

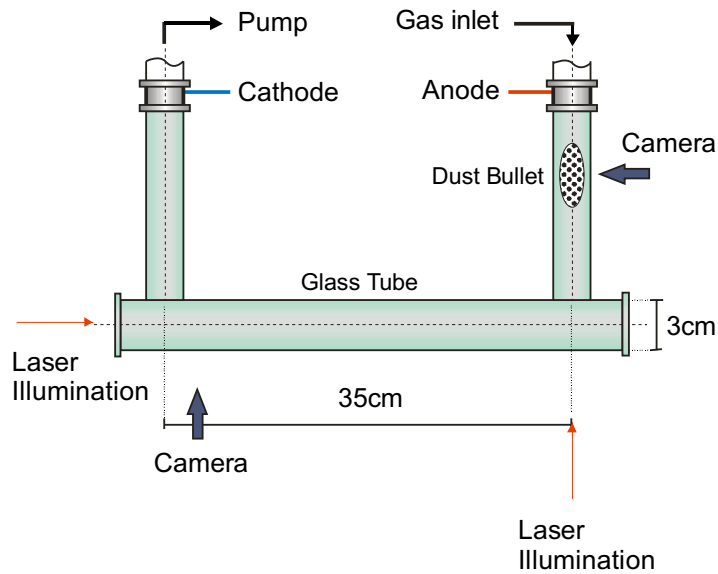


Figure 1. Scheme of the PK-4 chamber [23] (the gravity vector is perpendicular to the drawing plane).

with PK-4. This will enable the observation of particle formation also in microgravity conditions, as was done earlier in PKE-Nevedov [28]. In order to understand the mechanisms and behaviour of the discharge during growth, ground-based experiments are necessary before taking the experiment to space.

In this paper, we concentrate on the formation of nanoparticles obtained from a mixture of argon and acetylene performed with the PK-4 setup at GREMI and report on the first observations of particle growth within the PK-4 plasma chamber.

2. Experimental setup

Figure 1 shows a sketch of the experimental setup. The plasma chamber in this system (PK-4) consists of a U-shaped glass cylinder, with an inner diameter of 3 cm and an overall length of 74.4 cm. Each side arm has a length of about 19.7 cm. The electrodes are installed in the side arms at both ends of the cylinder. The discharge in our experiments is operated at pressures between 40 and 100 Pa and dc currents of up to 3 mA (corresponding to voltages of the order of 2 kV).

All the experiments presented in this paper were performed with a continuous gas flow. The gas was always introduced through the anode and pumped out through the cathode. The introduced gas mixture consisted of argon and acetylene (2.2%). A butterfly valve installed between the pumping system and the glass cylinder was used to control the pressure inside the glass tube (for a given gas flow ranging between 1 and 10 sccm). To observe the formation of dust particles and the behaviour of the plasma, laser light scattering experiments and optical emission spectroscopy were performed. The setup included LDM 405 diode laser from Oxxius (405 nm), an Avaspec 3648 spectrometer from Avantes and a Pike F0320B charge-coupled device camera from Allied Vision.

The size and morphology of the particles was investigated *ex situ* by means of a scanning electron microscope (SEM). Particles collected in PK-4 are shown in figure 2. The shape and

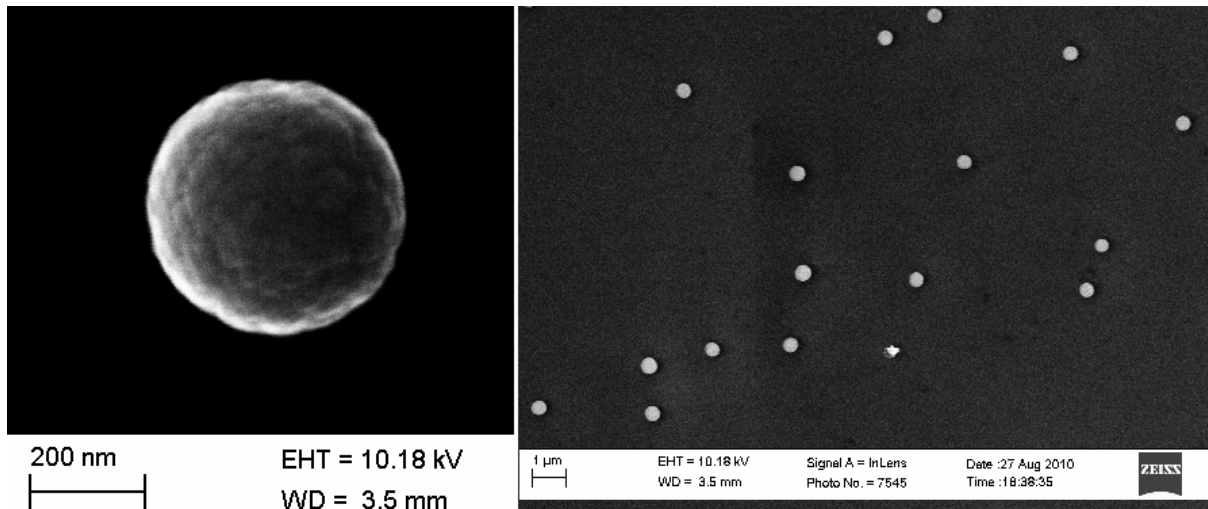


Figure 2. Hydrogenated carbonaceous particles collected in PK-4. On the left-hand side is a picture taken by zooming in on the uniformly distributed particles shown on the right-hand side. These particles were collected after 1 min of plasma at 80 Pa, 3 mA and 1 sccm.

surface structure of the particles resemble those of particles grown in RF discharges and show the cauliflower structure typical of such particles [2]. The similarity of both types of particles has also been proven by means of near edge x-ray absorption fine structure spectroscopy, which reveals a chemical composition typical of hydrogenated carbonaceous plasma polymers [13].

3. Experimental results and discussion

The experiments presented here were performed at 40, 60, 80 and 100 Pa. At 40 Pa the formation of dust particles was difficult to trigger and was only observed for high powers. Systematic laser light scattering measurements show that the particles can be detected independent of the parameters, at first always near the anode. The nanometre-sized particles are then transported along the glass tube until they finally reach the cathode. Figure 3 shows the intensity of the scattered laser light (measured near the anode in the side arm of the discharge—see figure 1) as a function of time.

The measurements reveal an oscillatory behaviour of the scattered laser light, indicating periodic appearance and disappearance of dust particles in the observed plasma volume. The whole process is illustrated in figure 4.

The initial growth of particles near the anode leads to the formation of elongated compact clouds of particles (‘dust bullets’) which travel along the discharge tube. Each ‘dust bullet’ passing the observation point corresponds to an oscillation in the intensity of the scattered laser light. This process resembles the growth oscillations observed in several RF discharges [7].

Generally, the spatial distribution of particles in a discharge results from the interplay between the various forces acting on the particles. Since these forces—such as the electric force F_e (proportional to the particle radius r), the ion drag force F_I (approximately proportional to r^2), the neutral drag force F_N (proportional to r^2), the thermophoretical force F_{Th} (proportional to r^2) and the gravitational force F_G (proportional to particle volume, i.e. proportional

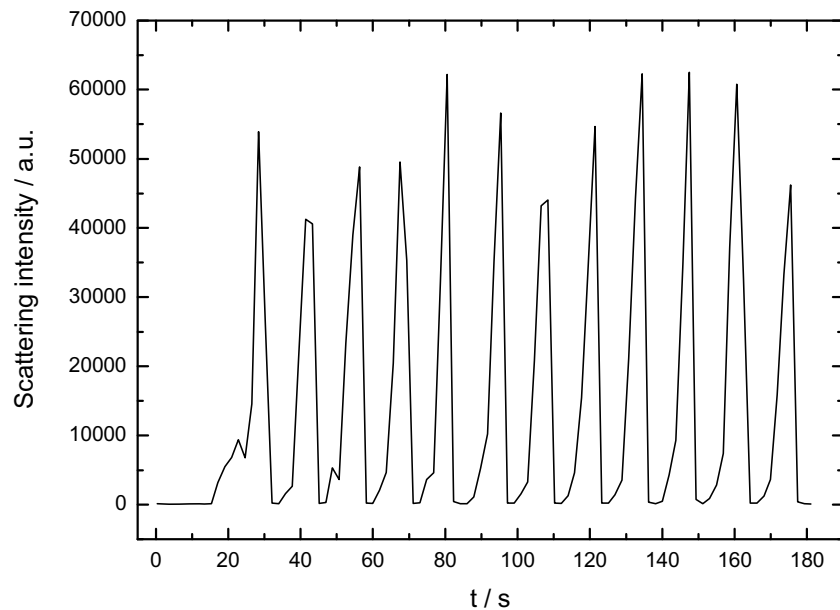


Figure 3. The time-dependent behaviour of the scattered laser light measured close to the anode. This measurement was performed at a pressure of 80 Pa, a dc current of 3 mA and a gas flow rate of 6 sccm.

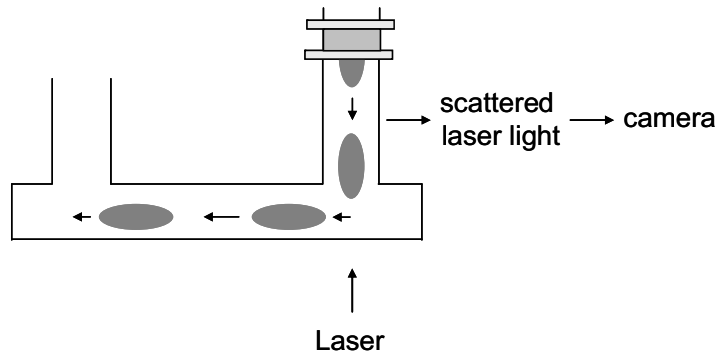


Figure 4. A sketch of the appearance and movement of the ‘dust bullets’ along the glass cylinder.

to r^3)—scale with different powers of the particle radius, the spatial distribution of the particles depends strongly on their size. In *reactive plasmas* where the particles can grow in size their spatial distribution is consequently subject to complex temporal changes. One example of such an interplay between particle size and the spatial distribution of the particles is the aforementioned ‘growth oscillations’ in reactive RF discharges: the negatively charged particles are confined in these discharges in the positive plasma potential as long as they are small enough. In the given setup this confinement is caused by the existence of a negative space charge close to the anode [29]. Once the particles reach a certain critical size, however, they are pushed out of the region of formation due to the action of the ion drag force, neutral drag or the gravity. The generation of new particles in the now particle-free centre triggers then a periodic process. The same mechanisms, i.e. the formation and subsequent growth of particles,

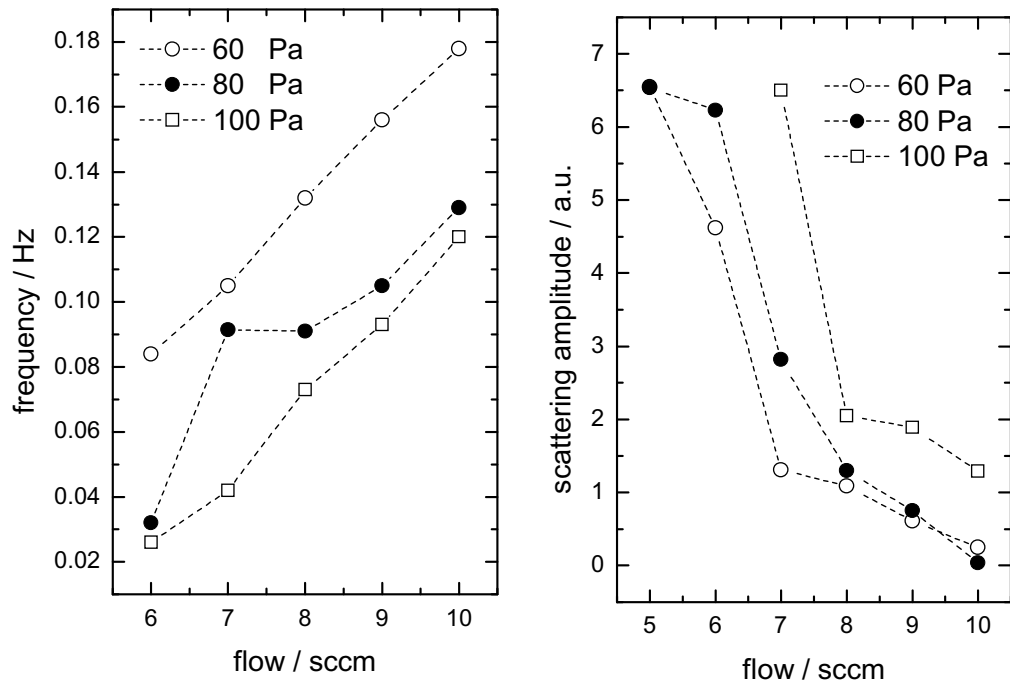


Figure 5. The frequency (left) and the amplitude (right) of the oscillation of the scattered laser light as a function of the gas flow. As the flow and thereby the frequency increase, the amplitude of the scattered light decreases, implying a decrease in particle size.

the development of dust-free regions and the generation of *new* particles in the dust-free regions, are also responsible for the periodic behaviour observed in figure 3. In the present case, the decisive factor is the neutral drag force which is introduced into the system by the continuous flow of gases streaming from the anode to the cathode. The importance of the neutral gas flow is shown in figure 5(a), which shows the frequency of the observed oscillations as a function of the gas flow. Figure 5(a) shows that the frequency increases (linearly) with increasing gas flow. In contrast to the frequency, the amplitude of the observed oscillation of the scattered laser light decreases with increasing flow rate (see figure 5(b)). Both phenomena can be explained qualitatively in the framework of the ‘growth oscillation model’ described above.

The dust particles which are initially formed close to the anode start to move towards the cathode when the sum of the ion drag force and the neutral drag force (which are both directed from the anode towards the cathode) exceeds the electric force (The ion drag force is proportional to r^2 only up to a logarithmic correction, which is negligible for small particles. Furthermore, it is typically an order of magnitude or more smaller than the electric and neutral drag forces [29].):

$$F_i + F_n = F_{el}. \quad (1)$$

Since

$$F_i \propto r^2 \quad F_n \propto r^2 V_g, \quad F_{el} \propto r \quad (2a-c)$$

equation (1) can be written as

$$(c_2 + c_3 V_g) r^2 > c_1 r, \quad (3)$$

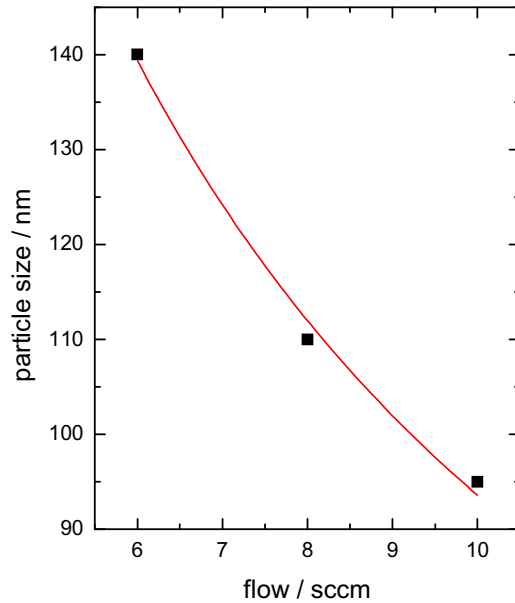


Figure 6. The size of the particles as derived from SEM pictures versus flow rate. The critical size of the particles decreases with the flow and thereby the neutral drag force increases. The experiments were conducted at 80 Pa and 3 mA.

where V_g is the velocity of the gas flow and c_1 , c_2 and c_3 are the proportionality factors in equations (2a–c). Relation (3) defines a critical radius

$$r_{\text{crit}} = \frac{c_1}{(c_2 + c_3 V_g)}. \quad (4)$$

Once the particle radius exceeds this value, inequality (1) is fulfilled. As the gas velocity is proportional to the gas flow Φ (in sccm), the critical radius can be written in the form

$$r_{\text{crit}} = \frac{c_1}{(c_2 + c_3 c_4 \Phi)}. \quad (5)$$

According to this equation the critical radius decreases with increasing flow rate, which is in agreement with the experimental results depicted in figure 5(b), i.e. the decrease of the scattered light with increasing flow rate. Particles collected from the ‘dust bullets’ confirm this result. Figure 6 shows the particles size (measured by means of electron microscopy) for three different flow rates: 6, 8 and 10 sccm. The measurement clearly shows that the particle size continuously decreases from 140 nm to about 90 nm.

If we assume a linear growth speed that is independent of the flow rate, we can write the time Δt that is necessary for the particles to reach this critical size as $\Delta t \propto r_{\text{crit}}$. The frequency of the observed oscillations is thus given by the relation

$$f \propto \frac{(c_2 + c_3 c_4 \Phi)}{c_1}, \quad (6)$$

which describes in accordance with the experimental results an oscillation frequency that increases with the flow rate. Equation (6) gives of course only a qualitative description of the whole process. (The assumption that the growth rate that is independent of the gas flow is of course a simplification. Moreover, one has to take into account that the growth rate is not linear for all times. Instead of $\Delta t \propto r_{\text{crit}}$ one could therefore use $\Delta t = k \cdot r_{\text{crit}} + \Delta t_{\text{add}}$. Here k is the

inverse growth rate during the linear growth phase and Δt_{add} accounts for the fact that there is a delay between the onset of the nucleation process and the beginning of the linear growth phase.)

At flow rates lower than the critical flow the behaviour of the dust formation cannot be explained by the model discussed. Instead of the periodic behaviour, two different observations were made. Below 3 sccm the particles stay in the vicinity of the place of their formation, i.e. they occupy the anode region and are not transported along the tube. This leads to continuous growth and measured particle sizes of up to $1 \mu\text{m}$ after 5 min of plasma on time. At these low flows an additional confinement, possibly introduced by a turbulent gas flow at the corner of the glass tube or the electric field from the negatively charged glass wall opposite to the anode (see figure 1), keeps the particles in place. If a higher flow rate is introduced, this additional confinement can be overcome and the particles formed are transported along the tube. Already at flow rates of 3 sccm this transport can be observed. But different from the periodic behaviour described above, at 3 and 4 sccm only a first growth cycle of particles that are formed and transported was observed. At both flow rates this first 'dust bullet' is not followed by any further ones. This might be caused by an insufficient amount of 'fresh' acetylene supplied by the inflowing gas so that only one generation of particles could be generated due to the initially higher gas density. After the ignition of the plasma the acetylene concentration starts to decrease due to the destruction of the acetylene molecule by electron impact dissociation (such as, e.g., in the reaction $\text{C}_2\text{H}_2 + \text{e}^- \rightarrow \text{C}_2\text{H} + \text{H} + \text{e}^-$) and due to subsequent reactions with radicals (e.g. with C_2H). Depending on the plasma parameters (electron density and electron temperature), the pumping speed and the amount of fresh gas that is introduced into the plasma chamber, the acetylene concentration stabilizes after a certain time on a level that is much smaller than that before the ignition of the discharge. If this level is too small it is not possible to produce enough new precursors (e.g. C_2H^- anions in reactions such as $\text{C}_2\text{H}_2 + \text{e}^- \rightarrow \text{C}_2\text{H}^- + \text{H}$) to restart the nucleation process again. And therefore only one generation of particles can be generated in this case. Different behaviours of the first growth cycle have been observed at all flow rates. Only in the first cycle is the emission of the plasma followed by the scattered light. During the following cycles a strong correlation between the emission of the plasma and the intensity of the scattered light occurs (see figure 7). At 5 sccm a transition towards periodic behaviour was observed. At this flow several cycles of formation occurred, while the intensity of both the scattered laser light and the plasma emission decreased rapidly. After a limited number of cycles have passed, no further growth was observed at 5 sccm. This non-periodic behaviour below the critical flow is not yet fully understood and will certainly be of interest for future study.

The formation of particles is usually accompanied by changes in the plasma parameters. This is demonstrated in figure 7, which shows the intensity of the scattered laser light and the emission from the plasma as a function of time. Figure 7 clearly shows that the intensity of the scattered laser light and the plasma emission oscillate in phase. As soon as the moving 'dust bullet' reaches the observation point the intensity of the plasma emission increases. The moving dust cloud is accompanied by a moving plasma region with enhanced emission (therefore it would be better to speak of a 'dusty plasma bullet' instead of simply a 'dust bullet'). This observation can be explained by the disturbance of the ionization loss balance (of electrons and ions) caused by the appearance of dust particles in the actual plasma volume. From a global point of view the electron temperature adjusts itself in a way to guarantee the balance between the loss of electrons and ions (due to diffusion) and their generation due to electron impact ionization. The formation of particles opens a new loss channel: ions and electrons impinging on the particles recombine there and form neutral atoms or molecules. To maintain the discharge

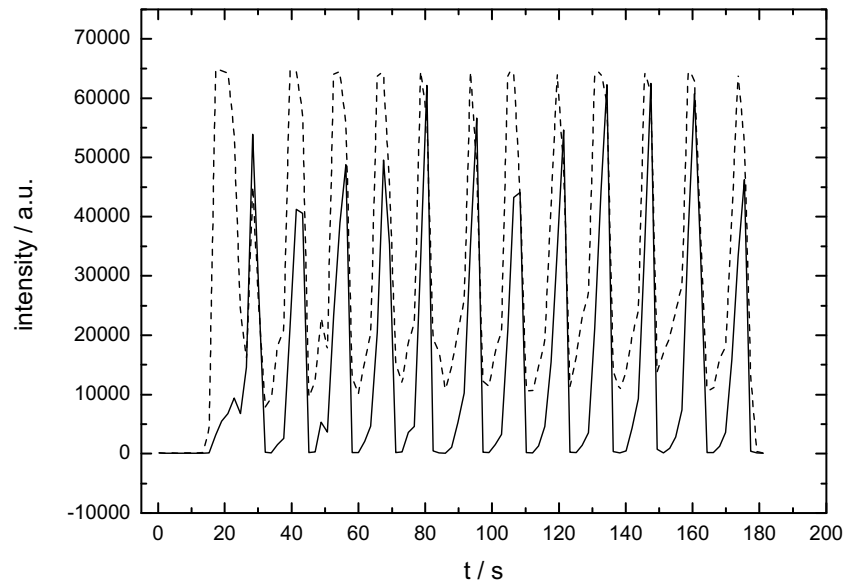


Figure 7. The correlation between the scattered laser light and an emission line of argon from the plasma (751 nm dashed).

these additional losses have to be compensated for by an increase of the ionization rate, i.e. by an increase of the electron temperature. The increase of the ionization rate is accompanied by an increase of the light emission from the plasma (see, e.g., [30, 31]).

4. Summary

The spatial distribution of particles in a (low-temperature) plasma, resulting from the interaction of the various forces acting on the particles, is a rather complex phenomenon. Particularly in reactive plasmas, where the particle size increases in time and where new particles can be generated, we have to deal with the formation of complex, time-dependent dust structures and with the occurrence of various transport processes. Particles initially formed in one region of the discharge are transported during their growth to other discharge regions, since the forces acting on the particles scale with different powers of the particle radius. The formation of new particles in the dust-free region can then trigger an oscillatory process that is characterized by the periodic appearance and disappearance of particles in specific regions of the discharge. In this paper, we have examined the formation and growth of particles in a dc glow discharge operated in a mixture of argon and acetylene. In this case, we observed the periodic appearance of ‘dusty plasma bullets’ that were travelling through the discharge. The experiments showed that the frequency of this process as well as the size of the particles within each ‘dusty plasma bullet’ can be controlled by means of the neutral gas flow.

Acknowledgments

This work was partially financed by the Deutsches Zentrum für Luft- und Raumfahrt (DLR) under grant number 50WM0804 and by the French National Research Agency under grant number ANR-09-BLAN-023-03. The work also received funding from the European

Community's Seventh Framework Programme (FP7/2007-2013) under grant agreement number 226716. The authors acknowledge the Helmholtz-Zentrum Berlin-Electron storage ring BESSY II staff for support during our activities, as well as Professor Dr Ch Wöll and Dr A Nefedov for access to the HESGM endstation. The authors also thank S Dozias, T Lecas and S Albrecht for their help with the experimental setup and their kind support.

References

- [1] Pendleton Y J and Allamandola L J 2002 *Astrophys. J. Suppl.* **138** 75
- [2] Kovačević E, Stefanović I, Berndt J, Pendleton Y and Winter J 2005 *Astrophys. J.* **623** 242
- [3] Rao N N, Shukla P K and Yu M Y 1990 *Planet. Space Sci.* **38** 543
- [4] Winter J 1998 *Plasma Phys. Control. Fusion* **40** 1
- [5] Winter J 2004 *Plasma Phys. Control. Fusion* **46** B583
- [6] Ostrikov K, Cvelbar U and Murphy A B 2011 *J. Phys. D: Appl. Phys.* **44** 174001
- [7] Berndt J, Kovacevic E, Stefanovic I, Stepanovic O, Hong S H, Boufendi L and Winter J 2009 *Contrib. Plasma Phys.* **49** 107
- [8] Kortshagen U 2009 *J. Phys. D: Appl. Phys.* **42** 113001
- [9] Aggadi N, Arnas C, Bénédic F, Dominique C, Duten X, Silva F, Hassouni K and Gruen D M 2006 *Diamond Relat. Mater.* **15** 908–12
- [10] Ugarte D 1992 *Chem. Phys. Lett.* **198** 6596–602
- [11] Anderson H M, Radovanov S, Mock J-L and Resnick P L 1994 *Plasma Sources Sci. Technol.* **3** 302
- [12] Berndt J, Kovacevic E and Boufendi L 2009 *J. Appl. Phys.* **106** 063309
- [13] Kovacevic E, Berndt J, Stefanovic I, Becker H W, Godde C, Strunskus Th and Boufendi L 2009 *J. Appl. Phys.* **105** 104910
- [14] Hollenstein C, Dorier J L, Dutta J, Sansonnens L and Howling A A 1998 *Plasma Sources Sci. Technol.* **3** 278
- [15] Boufendi L and Bouchoule A 1994 *Plasma Sources Sci. Technol.* **3** 262
- [16] Nagai T, Feng Z, Kono A and Shoji F 2008 *Phys. Plasmas* **15** 050702
- [17] Michau A, Lombardi G, Arnas C, Colina Delacqua L, Redolfi M, Bonnin X and Hassouni K 2010 *Plasma Sources Sci. Technol.* **19** 034023
- [18] Samarian A A and James B W 2001 *Phys. Lett. A* **287** 125
- [19] Stefanović I, Kovačević E, Berndt J and Winter J 2003 *New J. Phys.* **5** 39
- [20] Perrin P, Molinas-Mata P and Belenguer P 1994 *J. Phys. D: Appl. Phys.* **27** 2499
- [21] Boufendi L, Gaudin J, Huet S, Viera G and Dudemaine M 2001 *Appl. Phys. Lett.* **79** 4301
- [22] Denysenko I, Berndt J, Kovačević E, Stefanović I, Selenin V N and Winter J 2006 *Phys. Plasmas* **13** 073507–1
- [23] Fortov V *et al* 2005 *Plasma Phys. Control. Fusion* **47** B537–B549
- [24] Thoma M H *et al* 2007 *IEEE Trans. Plasma Sci.* **35** 255
- [25] Nefedov A P *et al* 2003 *New J. Phys.* **5** 33
- [26] Thomas H M *et al* 2008 *New J. Phys.* **10** 033036
- [27] Thoma M H, Höfner H, Kretschmer M, Ratynskaia S, Morfill G E, Usachev A, Zobnin A, Petrov O and Fortov V 2006 *Microgravity Sci. Technol.* **XVIII** 3/4
- [28] Mikikian M, Boufendi L, Bouchoule A, Thomas H M, Morfill G E, Nefedov A P, Fortov V E and the PKE-Nefedov team 2003 *New J. Phys.* **5** 19
- [29] Raizer Y P 1991 *Gas Discharge Physics* (Berlin: Springer) p 211
- [30] Yaroshenko V *et al* 2005 *Phys. Plasmas* **12** 093503
- [31] Schweigert I V, Alexandrov A L, Ariskin D A, Peeters F M, Stefanovic I, Kovacevic E, Berndt J and Winter J 2008 *Phys. Rev. E* **78** 026410