

## Heterogeneous ion-induced nucleation in thermal dusty plasmas

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

2011 J. Phys. D: Appl. Phys. 44 215201

(<http://iopscience.iop.org/0022-3727/44/21/215201>)

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

Download details:

IP Address: 188.163.80.93

The article was downloaded on 05/05/2011 at 07:53

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

# Heterogeneous ion-induced nucleation in thermal dusty plasmas

V I Vishnyakov, S A Kiro and A A Ennan

Physical-Chemical Institute for Environmental and Human Protection, National Academy of Sciences of Ukraine, 3, Preobrazhenskaya str., Odessa 65082, Ukraine

E-mail: [eksvar@ukr.net](mailto:eksvar@ukr.net)

Received 25 December 2010, in final form 21 March 2011

Published 4 May 2011

Online at [stacks.iop.org/JPhysD/44/215201](http://stacks.iop.org/JPhysD/44/215201)

## Abstract

Heterogeneous ion-induced nucleation in thermal dusty plasmas such as welding fumes or combustion plasmas containing metals and metal oxide vapours is considered. The influence of nucleus charging as a result of the interphase interaction on the nucleation free energy is determined. It is shown that the environment enrichment by electrons results in the formation of nuclei at lower values of supersaturation than without electrons. The nucleus equilibrium and the critical radii dependences on the plasma temperature and dusty plasma contents are demonstrated.

## 1. Introduction

A low-temperature thermal plasma is a gas at atmospheric or higher pressure and at temperatures of 1000–3000 K. Ionization in a thermal plasma occurs due to collisions between gas particles; therefore, such a plasma is strongly collisional unlike a low-pressure gas-discharge plasma. It usually contains easily ionizable atoms of alkali metals as a natural impurity or in the form of specific additional agents, which are the basic suppliers of free electrons and singly charged positive ions [1]. Examples of thermal collisional plasmas are the combustion plasma, which is formed in flames [2, 3], and the condensation zone welding fumes [4]. Both kinds of plasmas represent ionized gas containing atoms of metals and/or molecules of metal oxides. This gas is similar to the supercooled vapour, which is ready to condensate; therefore, as a result of volume condensation, such a plasma contains either solid or liquid particles (dust).

Such a plasma is interesting because of its technological application, in particular in the technology of synthesis of nano-sized oxide particles with the required properties in a plasma environment. Thus, a new technology can be developed to obtain new materials. New materials are not the only issue, as refining, conservation of materials and new processes are also targeted; the particles are used in various forms such as powders, composite materials, suspensions and films [5]. Flexible ceramics is an example of such new materials that can be used to make crucibles for melting metals, gas turbines, liners for jet and rocket motor tubes,

resistance furnaces and ultra-high-frequency furnaces [6]. Another application of nano-sized particles is the production of fuel cells. Solid oxide fuel cells differ from other fuel cell technologies, because they are composed of all-solid-state materials, and as a result can operate at temperatures significantly higher than any other category of fuel cells [7].

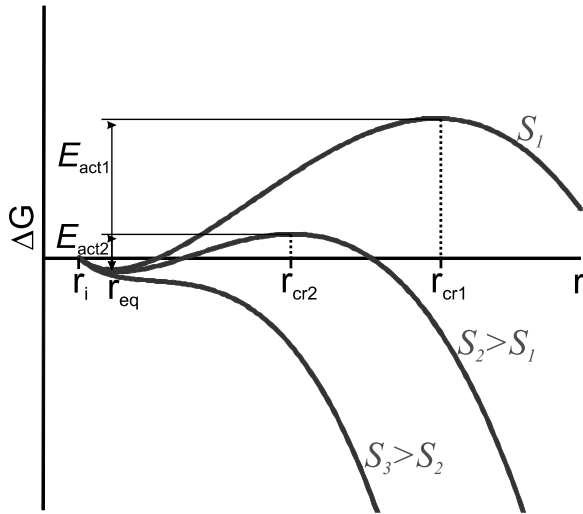
The nano-sized particles are formed in the plasma as a result of vapour-phase condensation. There are two kinds of nucleation in the plasma: homogeneous nucleation (as a result of fluctuations) and heterogeneous nucleation on some wettable nuclei [8–11]. In the case of homogeneous nucleation, the change in Gibbs free energy of casual nucleus formation is equal, according to classical nucleation theory [12–14]:

$$\Delta G = 4\pi r_n^2 \gamma - \frac{4}{3}\pi r_n^3 \frac{\rho}{m_M} k_B T \ln S, \quad (1)$$

where  $r_n$  is the radius of the nucleus;  $\gamma$  is the surface free energy per unit area, or surface tension;  $\rho$  is the density of the nucleus substance;  $m_M$  is the molecular mass;  $T$  is the temperature in kelvin;  $k_B$  is the Boltzmann constant and  $S$  is the vapour supersaturation, equal to the ratio of the pressure of condensed substance vapour  $P$  to the pressure of saturated vapour:

$$S = \frac{P}{P_{\text{sat}}}, \quad P_{\text{sat}} = \alpha \exp\left(\frac{-\beta}{T}\right),$$

where  $\alpha$  and  $\beta$  are constants that characterize the condensed substance.



**Figure 1.** Typical dependences of the Gibbs free energy change on the nucleus radius during heterogeneous nucleation for different values of supersaturation  $S$ .

The nucleus, at homogeneous nucleation, is the liquid droplet that grows if its size exceeds some critical value, since the free energy decrease corresponds to the growth in this case only. The value of the critical radius  $R_0$  for droplet is defined by the Kelvin equation,

$$R_0 = \frac{2m_M\gamma}{\rho k_B T \ln S}. \quad (2)$$

The change in Gibbs free energy (1) at the heterogeneous ion-induced nucleation depends on the electrostatic energy [15, 16],

$$\Delta U = \frac{e^2}{2} \left( \frac{1}{\varepsilon} - 1 \right) \left( \frac{1}{r_i} - \frac{1}{r_n} \right), \quad (3)$$

where  $\varepsilon$  is the nucleus dielectric constant,  $r_i$  is the single-charged ion radius and  $r_n$  is the nucleus radius.

In this case the nucleation regime at the expense of fluctuations is still valid, i.e. the droplets with radius  $r_{cr}$  (to which the maximum of  $\Delta G(r)$  corresponds) appears. Moreover, smaller equilibrium nuclei with radius  $r_{eq}$  are formed on the ions. The minimum of  $\Delta G(r)$  corresponds to this nucleus (figure 1; it is taken into account that  $\Delta G$  at the point  $r = r_i$  falls to zero because the plasma already contains the ions and their formation requires no additional energy [10]). It is worth noting that the equilibrium nucleus cannot grow at small values of supersaturation  $S$ , as their growth results in an increase in Gibbs free energy. There is a necessity for some activation energy  $E_{act}$  for nucleus growth. The activation energy decreases monotonically as the vapour supersaturation increases [10].

During nuclei formation in the plasma, the dust–gas interaction results in the charging of dust grains and nuclei, as well as in changes in plasma ionization degree [17]. Thus, the metal (metal oxide) vapour condensation in a thermal plasma is not described by classical nucleation theory, where the ionized environment saturated by electrons is not considered. The

nuclei exchange electrons with the plasma. There is electron flux on the nucleus surface as a result of sporadic collisions; plus there is a flux of thermionic emission from the high-temperature nucleus, which is opposite to the former one. As a result, the nucleus gets a charge resulting in an electric field, which maintains the dynamic balance of fluxes on the nucleus surface. It should be noted that the mean free path of the electrons and ions is much less compared with the screening length in the thermal plasma, therefore the dust charging occurs in the drift-diffusion regime [18].

In [3, 19] homogeneous nucleation in a plasma consisting of dust grains and electrons is considered, and the influence of nucleus–plasma electron exchange on the nucleation is demonstrated. The same processes are observed during heterogeneous nucleation in an ionized gas containing dust components, but equilibrium nuclei formation on ions is added. This paper deals with the heterogeneous ion-induced nucleation in a thermal strongly collisional dusty plasma and special attention is paid to the nuclei–plasma electron exchange.

## 2. Nucleus electric energy

The classical theory of heterogeneous ion-induced nucleation suggests that the equilibrium nucleus formation on an ion results in a change in the ion’s electric field through the dielectric constant change (see (3)). It is supposed that the nucleus particle is an uncharged dielectric one with the exception of its own ion charge. Equation (3) is not suitable for a charged nucleus.

The electric energy of spherical vacuum volume with radius  $r_n$  containing the single-charged ion with radius  $r_i$  at the centre is equal to

$$U_i = \frac{1}{8\pi} \int_{r_i}^{r_n} \left( \frac{e}{r^2} \right)^2 4\pi r^2 dr = \frac{e^2}{2} \left( \frac{1}{r_i} - \frac{1}{r_n} \right). \quad (4)$$

According to classical theory, it is assumed that, during nucleation, this spherical volume is filled with a substance with dielectric constant  $\varepsilon$ , therefore, the energy change is reduced to equation (3). But, if the nucleus gets some additional charge  $eZ$ , the energy (4) must change. For the dielectric nuclei, it may be regarded as the volume-charged sphere with the total charge number  $Z_n = Z + 1$ . It is a simplified consideration of course; in more detail the charge distribution into the nucleus can be considered separately for each substance. In our simplified case, the charged sphere energy is added to the actual ion energy,

$$U_{sph} = \frac{3}{5} \frac{e^2 Z_n^2}{\varepsilon r_n},$$

and the total electric energy of the nucleus with dielectric constant  $\varepsilon$  is

$$U_n = \frac{3}{5} \frac{e^2 Z_n^2}{\varepsilon r_n} + \frac{e^2}{2\varepsilon} \left( \frac{1}{r_i} - \frac{1}{r_n} \right).$$

The change in electric energy to be considered in the change in Gibbs free energy (1) is described as follows:

$$\Delta U_Z = \frac{e^2(\varepsilon - 1)}{2\varepsilon} \left[ \frac{6}{5} \frac{Z_n^2}{(\varepsilon - 1)r_n} + \frac{1}{r_n} - \frac{1}{r_i} \right]. \quad (5)$$

Such an energy change is true in the case where the metal oxide vapours are condensed. However, the condensation of metal vapours is possible as well. In this case, the substance of the nucleus is a conductor, i.e. all the charge is concentrated on the nucleus surface and the total electric energy is

$$U_n = \frac{e^2 Z_n^2}{2r_n},$$

and the energy change is described by the following equation:

$$\Delta U_Z = \frac{e^2}{2} \left[ \frac{Z_n^2 + 1}{r_n} - \frac{1}{r_i} \right]. \quad (6)$$

The change in free energy  $\Delta G$  results from the electric energy change in the form of equation (5) or equation (6) as well as a result of the nucleus–plasma electron exchange. As a result of thermionic emission, the charge and energy are transferred by electrons to the gas phase, thus reducing the free energy  $\Delta G$ . At the same time, there is electron backflow to the nucleus surface, which increases the free energy  $\Delta G$ . The balance of these fluxes determines the displacement of  $\Delta G$ . It was demonstrated [19] that the electron exchange results in a nucleus energy change and can be described in the following form:

$$\Delta U_{ex} = -Z_n \left( W_n + \frac{3}{2} k_B T \right). \quad (7)$$

Further, one should keep in mind that the surface tension depends on the nucleus curvature [20, 21]

$$\gamma(r) = \gamma_0 \frac{r_n}{r_n + 2\delta}, \quad (8)$$

where  $\gamma_0$  is the surface tension of the corresponding planar surface and  $\delta$  is the Tolman length [22].

Moreover, the nucleus charge leads to the double electrical layer formation on its surface and to the surface tension  $\gamma$  change, which can be considered by the Lippmann equation [23],

$$\frac{d\gamma}{dV_b} = -\frac{Z_n}{4\pi r_n^2}, \quad (9)$$

where  $V_b$  is the potential barrier on the plasma–nucleus boundary.

Therefore, it is necessary to define the nucleus charge and the potential barrier on the plasma–nucleus boundary. The system under consideration is a thermal dusty plasma containing electrons, ions, dust grains and neutral gas at atmospheric pressure. The values of components' temperatures are close to each other and the whole system may be considered isothermal. A thermal plasma without ions, i.e. a dust–electron plasma is considered in [24, 25] where the theory of neutralized charges is proposed. This theory describes a system consisting of dust grains and electrons emitted by these grains only. Most of the dust grains are

charged positively in such a system, and the total charge of the dust grains  $eZ$  is the sum  $eZ = e\tilde{Z} + eZ_0$ , where the charge part  $eZ_0$  together with some part of electrons with number density  $n_0$  (unperturbed number density) forms the neutralized background, and  $Z_0 = n_0/n_d$ , where  $n_d$  is the dust number density. Another visible part of charge  $e\tilde{Z}$  forms the potential barrier  $V_b$  at the dust grain surface with respect to the neutralized background and is defined by the ratio of the surface electron number density to the unperturbed number density:

$$V_b = k_B T \ln \left( \frac{n_{es}}{n_0} \right), \quad (10)$$

where the surface electron number density is described by the Richardson equation

$$n_{es} = v_e \exp \left( \frac{-W_d}{k_B T} \right), \quad (11)$$

where  $W_d$  is the electronic work function from the dust, and  $v_e = 2(m_e k_B T / 2\pi \hbar^2)^{3/2}$  is the effective density of the electron states. While considering the nucleus, it is necessary to take into account the work function change for the smaller particles. According to [26], it is possible to use the following expression for nucleus:

$$W_n \cong W_d + \frac{0.39e^2}{r_n}, \quad (12)$$

where the subscript 'd' is used for the dust and 'n' for the nuclei particles.

The visible charge of the particle is described by the following expression [24]:

$$\tilde{Z}_x = \frac{\sqrt{2} k_B T (\lambda_D + r_x) r_x}{\text{sgn}(V_b) e^2 \lambda_D} \left[ \exp \left( \frac{V_b}{k_B T} \right) - \frac{V_b}{k_B T} - 1 \right]^{1/2}, \quad (13)$$

where  $\lambda_D = (k_B T / 4\pi e^2 n_0)^{1/2}$  is the screening length;  $r_x$  is the radius of the particle; for dust grain  $x = d$  and for nucleus  $x = n$ .

In addition to the electrons emitted by the dust grains it is necessary to consider the electrons formed through gas ionization. In this case, some electrons are screened by the positive ions with an average number density of  $n_i$ . Therefore, the charge number of the neutralized background,

$$Z_0 = \frac{n_0 - n_i}{n_d}, \quad (14)$$

and equations (13) and (14) describe the total charge of the grain or nucleus.

The total charge of the dust with the electron and ion number densities defines the neutrality of the plasma  $Zn_d = n_e - n_i$ . The average electron number density  $n_e$  and unperturbed number density  $n_0$  are related by the following equation [24]:

$$n_e = n_0 \exp \left( \frac{e\varphi_0}{k_B T} \right), \quad (15)$$

where  $\varphi_0$  is the potential of the neutralized background. The potential of the neutralized background (or bulk plasma potential) is the reference point for the potential barrier  $V_b$ ,

but in the complex plasma (with ions) it also describes the non-equilibrium ionization of the plasma [17] as a result of interphase interaction (see equation (22) below).

It is necessary to define this potential. The Coulomb energy per electron can be defined as  $e^2/R_e$  [27], where  $R_e = (3/4\pi n_e)^{1/3}$  is the half of the average distance between the electrons. Accordingly, the Coulomb energy per ion is  $e^2/R_i$ , where  $R_i = (3/4\pi n_i)^{1/3}$ ; and the Coulomb energy of the neutralized charge per dust grain is  $(eZ_0)^2/R_W$ , where  $R_W = (3/4\pi n_d)^{1/3}$  is the Wigner–Seitz radius [18]. Then, taking into account that  $n_e/n_d$  electrons and  $n_i/n_d$  ions are needed per dust grain, it is possible to define the potential of the neutralized background,

$$\varphi_0 = \frac{3}{2} \frac{e}{n_d} (Z_0^2 n_d^{4/3} - n_e^{4/3} + n_i^{4/3}). \quad (16)$$

Here we assumed that  $(4\pi/3)^{1/3} \cong 3/2$ .

Then unperturbed number density is defined by the following equation:

$$n_0 = n_e \exp \left[ \frac{3e^2}{2k_B T n_d} (n_e^{4/3} - n_i^{4/3} - Z_0^2 n_d^{4/3}) \right]. \quad (17)$$

Thus, the equations listed above are sufficient to describe the plasma environment.

From equation (8), taking into account (13) and assuming that  $r_n \ll \lambda_D$ , the amendment to the surface tension can be determined:

$$\gamma_Z = -\frac{Z_0 V_b}{4\pi r_n^2} - \frac{\sqrt{2}(k_B T)^2}{6\pi e^2 r_n} \left[ \exp \left( \frac{V_b}{k_B T} \right) - \frac{V_b}{k_B T} - 1 \right]^{3/2}. \quad (18)$$

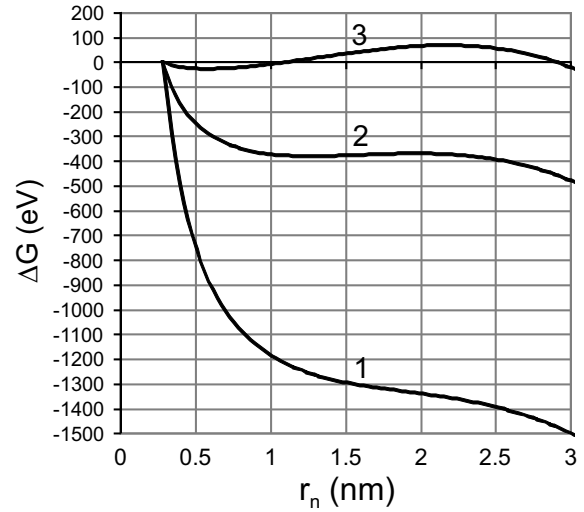
As a result, the change in Gibbs free energy during the heterogeneous ion-induced nucleation in an environment saturated with electrons is described by following expression:

$$\begin{aligned} \Delta G = & 4\pi r_n^2 \left( \gamma_0 \frac{r_n}{r_n + 2\delta} + \gamma_Z \right) - \frac{8}{3} \pi r_n^3 \frac{\gamma_0}{R_0} \\ & - Z_n \left( W_n + \frac{3}{2} k_B T \right) \\ & + \begin{cases} \frac{e^2}{2} \left( \frac{Z_n^2 + 1}{r_n} - \frac{1}{r_i} \right) \text{—for conductor} \\ \frac{e^2(\varepsilon - 1)}{2\varepsilon} \left[ \frac{6}{5} \frac{Z_n^2}{(\varepsilon - 1)r_n} + \frac{1}{r_n} - \frac{1}{r_i} \right] \text{—for dielectric.} \end{cases} \end{aligned} \quad (19)$$

Here, we assumed that  $\rho k_B T \ln(S)/m_M = 2\gamma_0/R_0$  is according to equation (2).

### 3. Influence of free electrons on heterogeneous nucleation

The case of heterogeneous ion-induced nucleation of the vapour of iron in a thermal dusty plasma is considered here. Let the plasma consist of a neutral buffer gas with an impurity of potassium atoms, iron vapour with supersaturation  $S = 2$  and monodisperse dust grains of iron with a radius of 10 nm, which are the result of previous condensation and growth. The system is isothermal with a kelvin temperature of  $T = 2000$  K.



**Figure 2.** Changes in Gibbs free energy at the heterogeneous nucleation of iron in the environment of dust grains at small number densities of ions:

curve 1,  $n_d = 10^7 \text{ cm}^{-3}$ ,  $n_e = 3.0 \times 10^8 \text{ cm}^{-3}$ ,  $Z_0 = 24$ ;

curve 2,  $n_d = 10^8 \text{ cm}^{-3}$ ,  $n_e = 1.5 \times 10^9 \text{ cm}^{-3}$ ,  $Z_0 = 13$ ;

curve 3,  $n_d = 10^9 \text{ cm}^{-3}$ ,  $n_e = 3.5 \times 10^9 \text{ cm}^{-3}$ ,  $Z_0 = 4$ .

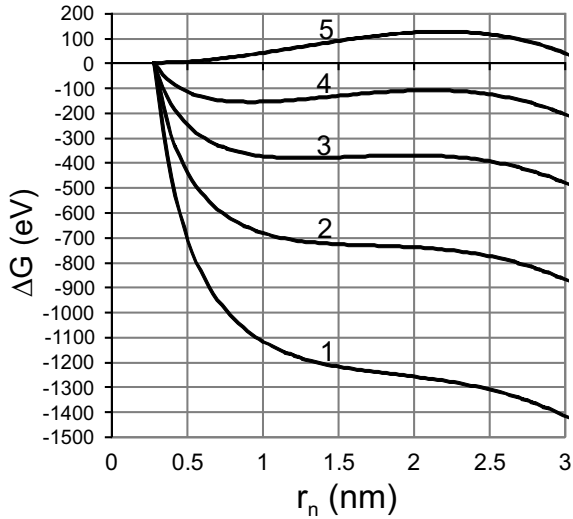
The number density of potassium ions  $n_i = 1 \text{ cm}^{-3}$ .

The dependences of change in Gibbs free energy (19) on the size of the iron nucleus are presented in figure 2. The number density of the potassium ions is so low ( $n_i = 1 \text{ cm}^{-3}$ ) that they do not influence the plasma neutralization, i.e. the saturation of the environment with electrons is defined by the thermionic emission from the dust grain surfaces only, and the neutrality condition is  $n_e \cong Z_d n_d$ , where  $Z_d$  is the average charge number of the dust. Since iron is a conductor, then  $\Delta U_Z$  is used in the form of equation (6).

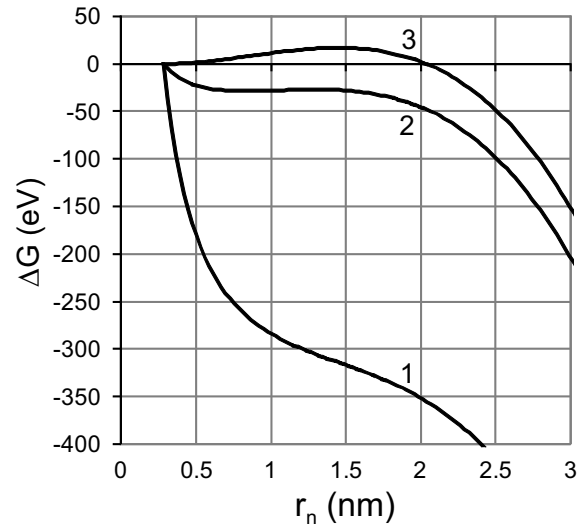
The free energy  $\Delta G$  decreases monotonically as the nucleus size grows when the number density of the dust grains is  $10^7 \text{ cm}^{-3}$ . Thus, barrier-less heterogeneous nucleation takes place, as the activation energy is equal to zero. The charge number of the neutralized background in this case is  $Z_0 = 24$ .

An increase in number density of the dust grains (for example, through nucleation and growth) results in the emergence of an equilibrium nucleus activation energy, and the neutralized charge  $Z_0$  decreases simultaneously. It is caused by the fact that the higher the number of dust grains participating in the neutralization of the volume charge of electrons the smaller is the charge needed per grain. Despite the fact that supersaturation is constant ( $S = 2$ ), the nucleation process occurs as if the supersaturation grows as the charge of neutralized background increases.

The saturation of plasma with potassium atoms leads to an increase in the electron number density due to collision ionization, thus the neutrality condition is  $n_e = Z_d n_d + n_i$ . It influences the nucleation in the same way as the increase in the number of dust grains (provided the gas collision ionization delivers the number of electrons comparable to the thermionic emission). The dependences of the change in Gibbs free energy (19) on the size of the iron nucleus are presented in figure 3 at a constant number density of dust grains  $n_d = 10^7 \text{ cm}^{-3}$  (which corresponds to curve 1 in figure 2) but at



**Figure 3.** Change in Gibbs free energy at the heterogeneous nucleation of iron in the environment of dust grains at large number densities of potassium ions:  
 curve 1,  $n_i = 2 \times 10^7 \text{ cm}^{-3}$ ,  $n_e = 3 \times 10^8 \text{ cm}^{-3}$ ,  $Z_0 = 23$ ;  
 curve 2,  $n_i = 2 \times 10^8 \text{ cm}^{-3}$ ,  $n_e = 4 \times 10^8 \text{ cm}^{-3}$ ,  $Z_0 = 18$ ;  
 curve 3,  $n_i = 5 \times 10^8 \text{ cm}^{-3}$ ,  $n_e = 6 \times 10^8 \text{ cm}^{-3}$ ,  $Z_0 = 13$ ;  
 curve 4,  $n_i = 2 \times 10^9 \text{ cm}^{-3}$ ,  $n_e = 2 \times 10^9 \text{ cm}^{-3}$ ,  $Z_0 = 9$ ;  
 curve 5,  $n_i = 2 \times 10^{10} \text{ cm}^{-3}$ ,  $n_e = 2 \times 10^{10} \text{ cm}^{-3}$ ,  $Z_0 = 0$ .  
 The number density of dust  $n_d = 10^7 \text{ cm}^{-3}$ .



**Figure 4.** Change in Gibbs free energy at the heterogeneous nucleation of silicon in the environment of dust grains of iron at high number densities of potassium ions:  
 curve 1,  $n_i = 2 \times 10^7 \text{ cm}^{-3}$ ,  $n_e = 3 \times 10^8 \text{ cm}^{-3}$ ,  $Z_0 = 23$ ;  
 curve 2,  $n_i = 2 \times 10^9 \text{ cm}^{-3}$ ,  $n_e = 2 \times 10^9 \text{ cm}^{-3}$ ,  $Z_0 = 9$ ;  
 curve 3,  $n_i = 2 \times 10^{10} \text{ cm}^{-3}$ ,  $n_e = 2 \times 10^{10} \text{ cm}^{-3}$ ,  $Z_0 = 0$ .  
 The number density of dust  $n_d = 10^7 \text{ cm}^{-3}$ .

variable number density of potassium ions. The values of temperature and supersaturation of the iron vapour are the same— $T = 2000 \text{ K}$ , and  $S = 2$ .

The growth of ion number density provokes the growth of electron density, and results in an increase in the activation energy of the equilibrium nuclei, which appears on the ions. As in the previous case, there is a neutralized background charge decrease. When the ion number density is very high so that the emitted electrons do not participate in plasma neutralization ( $n_e \cong n_i$ ), the charge of the neutralized background  $Z_0 = 0$  and the heterogeneous ion-induced nucleation can be described by classical theory (curve 5 in figure 3).

Thus, the mode of heterogeneous ion-induced nucleation in the dusty plasma changes as the electron number density changes, but the charge of the neutralized background  $Z_0$  is the parameter that describes the heterogeneous nucleation mode. It is caused by the fact that by varying the number density of both dust grains and potassium atoms one can obtain identical dependences  $\Delta G(r_n)$  for different values of electron number density, to which the identical value of  $Z_0$  corresponds. For example, curve 2 in figure 2 corresponds to the value  $n_e = 1.5 \times 10^9 \text{ cm}^{-3}$ , and  $Z_0 = 13$ . The same dependence  $\Delta G(r_n)$  corresponds to the value  $n_e = 6 \times 10^8 \text{ cm}^{-3}$ , and  $Z_0 = 13$  (curve 3 in figure 3). The electron number densities are different, but the values of  $Z_0$  are identical as well as the dependences  $\Delta G(r_n)$ .

In general, the nucleus should acquire some charge to reach an equilibrium with the plasma. The charge number influences the exchange energy of the nucleus  $U_{\text{ex}} \sim -Z_n$  and the change in electric energy  $U_Z \sim Z_n^2/r_n - 1/r_i$  (see equations (6) and (7)); the change in surface tension  $\gamma_Z$  is small. In most cases, the nucleus is charged positively, therefore  $U_{\text{ex}}$

reduces the free energy of nucleation while  $U_Z$  increases it, if  $Z_n \gg 1$ ; and the growth of  $\Delta G$  is inversely proportional to the nucleus radius  $r_n$ . It was determined that  $Z_n = \tilde{Z}_n + Z_0$ , and  $\tilde{Z}_n$  describes the relative charge of the individual nucleus, whereas  $Z_0$  characterizes all the dust components, i.e. it is the characteristic of interphase interaction in the dusty plasma. Therefore, the charge of the neutralized background is a suitable parameter to describe heterogeneous nucleation in an electronic environment.

The above fact concerns the nucleus of a conductive material. The behaviour  $\Delta G(r_n)$  in the case of a dielectric nucleus should be considered. Let the environment remain the same with the dust grains of iron and potassium ions at a temperature of  $T = 2000 \text{ K}$ , but the vapour of silicon with supersaturation  $S = 2$  is used as a condensed substance. The corresponding distributions  $\Delta G(r_n)$  are shown in figure 4.

In this case, all the tendencies stated above are the same. However, the influence of the electron environment is less than in the previous case. It is caused by the fact that the influence of charge decreases when the dielectric constant is introduced, i.e.  $U_Z \sim (Z_n^2/\epsilon r_n - 1/r_i)$ , and can be negative if the nucleus has a sufficiently big radius and  $\epsilon \gg 1$ .

#### 4. Nucleus radii

The Gibbs free energy  $\Delta G(r)$  (19) has the minimum value corresponding to the nucleus, which is in stable equilibrium with the vapour at nucleus radius  $r_{\text{eq}}$ . Thus,

$$\left(\frac{\partial \Delta G}{\partial r_n}\right)_{\text{eq}} = 0, \quad \left(\frac{\partial^2 \Delta G}{\partial r_n^2}\right)_{\text{eq}} > 0. \quad (20)$$

The maximum value  $\Delta G$  at the point  $r_{cr}$  corresponds to the unstable equilibrium of the nucleus with the vapour,

$$\left(\frac{\partial \Delta G}{\partial r_n}\right)_{cr} = 0, \quad \left(\frac{\partial^2 \Delta G}{\partial r_n^2}\right)_{cr} < 0. \quad (21)$$

Let us consider the dependences of radii  $r_{eq}$  and  $r_{cr}$  on the temperature, keeping the supersaturation  $S$  constant. The system consists of a buffer gas at atmospheric pressure, which contains potassium atoms with an initial number density  $n_A = 10^9 \text{ cm}^{-3}$  and iron dust, resulting from the previous condensation and growth, with size  $r_d = 10 \text{ nm}$  and number density  $n_d = 10^7 \text{ cm}^{-3}$ . As a result of collision ionization some ions are formed in the system. Their number density  $n_i(T)$  is determined by the modernized Saha equation [17, 28],

$$\frac{n_e n_i}{n_a} = K_S \exp\left(\frac{e\varphi_0}{k_B T}\right), \quad (22)$$

where  $n_e$ ,  $n_i$ ,  $n_a$  are the number densities of the electrons, ions and atoms;

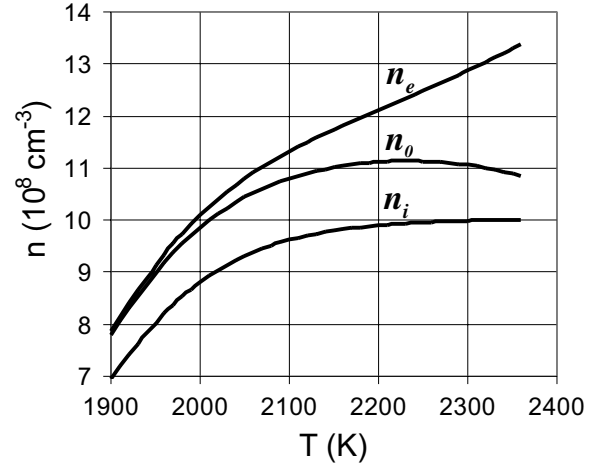
$$K_S = 2 \frac{g_i}{g_a} \left(\frac{m_e k_B T}{2\pi \hbar^2}\right)^{3/2} \exp\left(\frac{-I}{k_B T}\right)$$

is the Saha constant,  $m_e$  is the electron mass,  $\hbar$  is the Planck constant,  $g_i$  and  $g_a$  are the statistical weights of ions and atoms,  $I$  is the potential of ionization of atoms, and the bulk plasma potential (potential of neutralized background)  $\varphi_0$  describes the displacement of ionization balance as a result of interphase interaction.

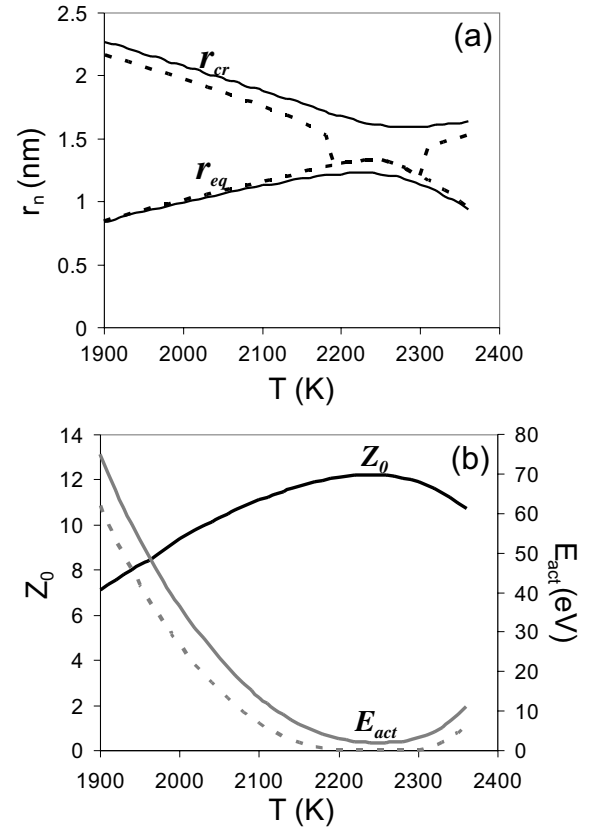
The electrons in the system are formed through both collision ionization and thermionic emission from the surface of the dust grains, and the number density of electrons is determined by the neutrality of the system:  $n_e = Z_d n_d + n_i$ . The average charge number of the dust component is equal to  $Z_d = Z_0 + \langle \tilde{Z}_d \rangle$ . As the monodisperse system of dust is considered,  $\langle \tilde{Z}_d \rangle = \tilde{Z}_d$  and it is defined by equation (13); the charge number of the neutralized background  $Z_0$  is defined by equation (14) as a function of the unperturbed number density  $n_0$  and the ion number density. The unperturbed number density, in its turn, is defined by equation (17) as a function of the neutralized background charge  $Z_0$ , and the number densities of electrons and ions. Thus, the calculation of the parameters of the environment where the nuclei are formed represents a self-consistent problem, the solution of which is shown in figure 5 as the temperature dependences of number densities.

Let us consider the condensation of iron vapour with supersaturation  $S = 2$  in the environment with the calculated parameters. The radii of nuclei  $r_{eq}$  and  $r_{cr}$  are defined by equations (20) and (21). The temperature dependences of these values are shown in figure 6(a). The temperature dependences of the charge number of the neutralized background  $Z_0$  and the activation energy  $E_{act}$  are shown in figure 6(b). All the dependences have an extremum within the temperature range of  $T \sim 2250 \text{ K}$ .

The existence of extremum is caused by the unperturbed number density dependence on the neutralized background charge. The unperturbed number density  $n_0$  depends linearly



**Figure 5.** Temperature dependences of the number densities of electrons  $n_e$ , ions  $n_i$  and unperturbed density  $n_0$ .



**Figure 6.** Temperature dependences of the radius of equilibrium nucleus  $r_{eq}$  and the radius of critical nucleus  $r_{cr}$  (a); the charge number of the neutralized background  $Z_0$  and the height activation barrier  $E_{act}$  (b) for supersaturation of iron vapour  $S = 2$  (full curves) and  $S = 2.05$  (broken curves).

on the average electron number density (15) which, according to the neutrality condition is proportional to the average charge  $n_e \sim Z_d = Z_0 + \tilde{Z}_d$ . At the same time,  $n_0$  exponentially depends on the bulk potential  $\varphi_0$  defined by the Coulomb energy of the dust (16) and, hence, is in quadratic relation to the neutralized charge  $\varphi_0 \sim Z_0^2$ . Therefore, the dependence of the unperturbed number density on the neutralized charge

has the following simplified form:

$$n_0 \sim Z_0 \exp(-Z_0^2),$$

which has a maximum.

The unperturbed number density depends on the temperature, therefore, there will always be such a temperature at which the dependence  $n_0(T)$  has a maximum value and, accordingly, the activation energy has a minimum value. Thus, in the thermal dusty plasma, there is a temperature at which the activation energy has a minimum value. It is worth noting that there are large temperature gradients in the condensation area in combustion plasmas and in condensation zone welding fumes. Therefore, it is expected that in such systems there will always be a space area where the heterogeneous nucleation occurs with a minimum activation energy.

The insignificant increase in the iron vapour supersaturation to a value  $S = 2.05$  causes the activation barrier to disappear within the temperature range  $T = 2200\text{--}2300$  K (broken curves in figure 6(b)). Here, at the distribution  $\Delta G(r)$  the minimum and maximum result in the inflection point (broken curves in figure 6(a)). Further increase in  $S$  reduces the distribution  $\Delta G(r)$  to a monotonic function and equations (20) and (21) have no roots in this case.

The most interesting is the range of temperature values, where the activation energy is minimum, since the activation barrier depression increases the probability of growth of the equilibrium nucleus. As it follows from the analysis, in the same temperature range the charge number of the neutralized background  $Z_0$  accepts the maximum value. Such a correlation considerably simplifies the theoretical study of heterogeneous nucleation. The temperature range, where the neutralized background charge is a maximum, can be found through the definition of the parameters of the system where the nucleation occurs. There is a need for further analysis within this temperature range, because the minimum value of activation energy (i.e. the maximum probability of nucleus growth) is expected here.

## 5. Conclusion

An account of the charging of nuclei as a result of interphase electron exchange in a thermal dusty plasma (such as combustion plasmas and condensation zone welding fumes) helps in the determination of a new mechanism for heterogeneous ion-induced nucleation control, along with supersaturation change.

The neutralized background charge describing the free electron volume charge determines the heterogeneous nucleation in an electronic environment. The system is described by the classical nucleation theory, when the neutralized background charge  $Z_0 = 0$ . However, the increase in neutralized background charge produces the same result

as the increase in supersaturation. Therefore, equilibrium nuclei formation in the electronic environment at low values of supersaturation is possible, in contrast to the classical theory.

Control of the heterogeneous nucleation process by a change in supersaturation is possible through a change in substance quantity, as well as through a change in interphase interaction by changing the ion and dust number densities in the plasma. Thus, nano-sized particles with required properties could be obtained through heterogeneous nucleation in the plasma.

## References

- [1] Vishnyakov V I and Dragan G S 2006 *Phys. Rev. E* **73** 026403
- [2] Poletaev N I and Florko A V 2008 *Combust. Explos. Shock Waves* **44** 437
- [3] Doroshenko J A, Poletaev N I and Vishnyakov V I 2009 *Phys. Plasmas* **16** 094504
- [4] Kobayashi M, Maki S, Hashimoto Y and Suga T 1983 *Weld. J.* **62** 190-s
- [5] Borra J -P 2006 *J. Phys. D: Appl. Phys.* **39** R19
- [6] Laurvick C A and Singaraju B 2002 *Proc. 21st Digital Avionics Systems Conf. (Irvine, CA, October 2002)* vol 2 (Piscataway, NJ: IEEE) p 9A3-1
- [7] Singhal S C and Kendall K 2003 *High-Temperature Solid Oxide Fuel Cells* (New York: Elsevier)
- [8] Abraham F F 1974 *Homogeneous Nucleation Theory* (New York: Academic)
- [9] Mason B J 1971 *The Physics of Clouds* 2nd edn (Oxford University Press)
- [10] Kuni F M, Shchekin A K and Grinin A P 2001 *Phys. Usp.* **44** 331
- [11] Mokross B J 2003 *Mater. Phys. Mech.* **6** 13
- [12] Landau L D and Lifshitz E M 1976 *Statisticheskaya Fizika (Statistical Physics)* vol 1 (Moscow: Nauka) (Translated into English 1980 (Oxford: Pergamon))
- [13] Cacciuto A, Auer S and Frenkel D 2003 *J. Chem. Phys.* **119** 7467
- [14] Vehkamäki H 2006 *Classical Nucleation Theory in Multicomponent Systems* (Berlin: Springer)
- [15] Reist P C 1984 *Introduction to Aerosol Science* (New York: Macmillan Publishing)
- [16] Green H and Lane W 1964 *Particulate Clouds: Dusts, Smokes and Mists* 2nd edn (New York: Van Nostrand)
- [17] Vishnyakov V I 2005 *Phys. Plasmas* **12** 103502
- [18] Fortov V E, Khrapak A G, Khrapak S A, Molotkov V I and Petrov O F 2004 *Phys. Usp.* **174** 495
- [19] Vishnyakov V I 2008 *Phys. Rev. E* **78** 056406
- [20] Zhukhovitskii D I 2001 *Russ. J. Phys. Chem.* **75** 1043
- [21] Ono S and Kondo S 1960 *Molecular Theory of Surface Tension in Liquids* (Berlin: Springer)
- [22] Bahadur R and Ressel L M 2008 *Aerosol Sci. Technol.* **42** 369
- [23] Yeo L Y and Chang H -C 2005 *Mod. Phys. Lett. B* **19** 549
- [24] Vishnyakov V I and Dragan G S 2006 *Phys. Rev. E* **74** 036404
- [25] Vishnyakov V I, Dragan G S and Florko A V 2008 *J. Exp. Theor. Phys.* **106** 182
- [26] Smirnov B M 1997 *Phys. Usp.* **40** 1117
- [27] Ichimaru S 1982 *Rev. Mod. Phys.* **54** 1017
- [28] Vishnyakov V I 2006 *Phys. Plasmas* **13** 033507