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Carbon Nanoparticles in the Radiation and Acoustic fields in the Vicinity of the Arc Discharge

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The paper considers a simple theoretical model of heating the nanoparticles, depending on their size and the parameters of the radiating arc and the surrounding gas. Heating of nanoparticles by the radiation can affect the process of synthesis. The degree of heating of the particle is determined by its geometry, which opens, apparently, additional possibilities for nonintrusive optical diagnostics. An effect of intensive ultrasound on the suspension of soot microparticles and nanoparticles in the inert gas, resulting in the coagulation of relatively large soot particles and leading to the improvement of the efficiency of production of nanoparticles, as has been observed in experiments, is also discussed. The effect of the particles charge on the possibility of coagulation is analyzed.

I. Introduction

The arc discharge between the graphite electrodes burning in the atmosphere of inert gases is one of the standard methods of nanoparticle synthesis [1-5]. Typically, in theoretical models, it is assumed (see., e.g. [2,3,5]) that the synthesis starts in the areas where the density of carbon atoms and the catalyst is still high, and the temperature of a buffer gas is reduced down to 1000-2000 K.

The arc is a very powerful light emission source, which is close to the blackbody. This radiation is scattered and partly absorbed by the nanoparticles. In the areas where a synthesis can occur theoretically, the radiation intensity of the arc is still quite high, and therefore, one should expect that the temperature of nanoparticles that absorb radiation may considerably exceed the local ambient gas temperature. The paper considers a simple theoretical model of heating the nanoparticles, depending on their size and the parameters of the radiating arc and the surrounding gas. This problem is of interest to diagnostics and modeling of the dynamics of the nanoparticles formation and their local size distribution.

In the peripheral region of arc burning in a high pressure inert gas, together with nanoparticles, a large number of microscopic soot particles is produced. Intensive soot generation significantly reduces the efficiency of the arc, as the technological process of production of fullerenes and other nanoparticles. Experimental studies have shown that exposure of intense ultrasound on the peripheral region of the arc leads to a noticeable increase in the efficiency of the synthesis of nanoparticles and to the reduction in the yield of soot (see., e.g. [6]). It is shown in this paper that the effect of ultrasound on the suspension of soot microparticles and nanoparticles in the inert gas results in the coagulation of soot particles, practically without affecting the nanoparticles. This effect contributes to the improvement of the efficiency of the nanoparticles generation, as has been observed in experiments [6].

Radiative heating of nanoparticles in the radiation field of the arc has been considered in the recent paper [7]. The dynamics of soot particles in an acoustic field, and the role of the acquired charge, is considered here for the first time.

II. Radiative Heating

A. Model and Assumptions

According to the numerical modeling [2,3], the arc plasma in a buffer helium, in which the synthesis of nanoparticles takes place, has a complex composition, which contains ions of C+, Ni+ Y+ and the corresponding

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neutral atoms and cluster molecules. However, the concentrations of these atoms and cluster molecules are very small and, therefore, we can assume that the collisional cooling of the nanoparticles is determined mainly by the collisions with atoms of the buffer gas. For simplicity of analysis, we assume that all nanoparticles are spherical. Also, we will restrict our consideration to the conditions where the ablation and vaporization of the particles can be neglected in accordance with the results presented in [8,9].

For a spherical particle with a diameter $D = 2a$, the absorption coefficient for coherent radiation in the Rayleigh approximation ($\lambda >> a$) [9,10] is

$$c_{abs} = \frac{\pi^2 D^3 E(m)}{\lambda} = \frac{\pi^2 D^3 E(m)\nu}{c}, \quad (1)$$

where $\nu = c/\lambda$ is the radiation frequency; $E(m)$ is the function of the complex refractive index m, $E(m) = -\mathrm{Im}\left(\frac{m^2-1}{m^2+2}\right)$ We use the broadband value $E(m) \approx 0.35$, which is close to the value estimated in [8] for soot particles, $E(m) \sim 0.32 - 0.4$.

Considering the arc radiation as a blackbody radiation with a certain known emissivity $\zeta < 1$ and the Planck blackbody radiation spectral intensity

$$I(\nu) = \frac{2\pi h\nu^3}{c^2} \frac{1}{e^{h\nu/kT} - 1}, \quad (2)$$

where $I(\nu)d\nu$ is the radiant power per unit area of radiating surface in the frequency range from ν to $\nu + d\nu$, we find the total rate of absorption of the radiation energy by a spherical particle of the diameter D at a distance r from the boundary of the arc with the temperature T_{arc}

$$Q_{abs} = \zeta \int_0^\infty c_{abs} I(\nu, r) d\nu = \zeta \frac{4\pi^2 D^3 E(m)\sigma_{SB} k_B T_{arc}^5}{hc} \frac{r_0^2}{r^2}. \quad (3)$$

$\sigma_{SB} = \frac{2}{15}\frac{\pi^5 k_B^4}{h^3 c^2} \approx 5.670373 \cdot 10^{-8}$ W m^{-2} K^{-4} is the Stefan–Boltzmann constant. The formula (3) takes into account that in the experiment [4, 5, 2] and the computational models (e.g., [3]), the interelectrode gap is small (~ 2-3 mm), as compared to the distance from the arc $r > 1.5$ cm, wherein the gas temperature is reduced to a level where synthesis becomes possible. Therefore, it is natural to assume that the radiation intensity of the arc decreases with distance as $\propto 1/r^2$. For a typical arc discharge used for the synthesis of carbon nanoparticles, the emissivity is $\zeta \approx 0.8$ [4,5].

The heated particle is cooled by radiation with the radiative heat losses, determined by the expression [8,9]

$$Q_{rad} = 4\pi a^2 \int_0^\infty \varepsilon_\lambda \frac{2\pi h c^2 d\lambda'}{\lambda^5 \left[\exp(hc/\lambda' k_B T_p) - 1\right]}, \quad (4)$$

where $\varepsilon_\lambda = 8\pi a E(m)/\lambda$ is the emissivity of the particle. Integrating in (4) over the entire frequency spectrum, we find a convenient formula for the power of the radiation energy losses:

$$Q_{rad} = \frac{16\pi^2 D^3 E(m)\sigma_{SB} k_B T_p^5}{hc}. \quad (5)$$

The particle is also cooled in the collisions with the buffer gas atoms (conduction conductivity). The rate of heat loss in these collisions with the buffer gas atoms (conductive cooling) is Q_g, [9,10]:

$$Q_g = \frac{\pi a^2 \alpha_T p_g}{8T_g} \sqrt{\frac{R_m T_g}{2\pi\mu}} \left(\frac{\gamma+1}{\gamma-1}\right)(T_p - T_g). \quad (6)$$

For helium as a buffer gas: $\mu_{He} = 4$ g/mole; $\gamma = 1.66$; $R_m = 8.314$ J/mole K. α_T is the thermal accommodation coefficient of ambient gases with the surface of a particle. The exact value of the accommodation coefficient can be determined only by comparison of the theoretical calculations with the results of measurements. In this paper, we take $\alpha_T \approx 0.1$, given in [10,11] for the carbon nanoparticles in helium.

The heating of the particles to high temperatures is accompanied by the thermionic emission, which reduces the intensity of heating. In plasma, where the particles are negatively charged, taking into consideration the Schottky effect, the thermionic emission current is [12]

$$I_{e,T} = 4\pi a^2 A T_p^2 \exp[-(w_a - \Delta\phi)/k_B T_p], \qquad (7)$$

Where $A = 120$ A/cm^{2}K^2, $w_a = 4.7$ eV is the work function for the carbon nanoparticle; $\Delta\phi = \left(\frac{e|\varphi|}{4\pi\varepsilon_0 a}\right)^{1/2}$ is the reduction in the work function at the negative potential of the particle, $\varphi < 0$. However, in the non-ionized gas or, for typical conditions of weakly ionized plasma, at the distances of centimeters from the arc discharge when the electron current from the plasma on the particle is negligible as compared to the current thermionic emission, the particle loses electrons through the thermionic emission, acquiring a positive charge

$$q = \int_t I_{e,T} dt, \qquad (8)$$

and the potential

$$\varphi = q / C > 0, \qquad (9)$$

where $C = 4\pi\varepsilon_0 a$ is the capacity of the particle.

In this case, the positive potential suppresses the thermionic current and is equal to:

$$I_{e,T} = 4\pi a^2 A T_p^2 \exp[-(w_a + \varphi)/kT_p]. \qquad (10)$$

The thermionic emission results in an additional cooling of the nanoparticles, because each “evaporating" electron carries away the energy $(w_a + \varphi)$. The corresponding power of heat loss is

$$Q_{TE} = -(|I_{e,T}|/e)(w_a + \varphi) \text{ [eV/s]}. \qquad (11)$$

The energy balance of the particle is determined by the equation:

$$M_p c_p \frac{dT_p}{dt} = Q_{abs} - Q_{TE} - Q_g - Q_{rad}. \qquad (12)$$

Here $M_p = \frac{4}{3}\pi\rho_p a^3$ is the mass of the particle.

The heat balance equation (12), together with (3), (5), (6), (8), (9) and (11) was solved for the initial conditions at t=0: $q = 0$, $\varphi = 0$; T_p=T_g.

B. Results and Discussion

As already mentioned, we consider spherical soot particles, assuming non temperature dependent value of density and heat capacity: $\rho_p = 2660$ kg/m^3; c_p=1900 J/kg/K [9], for the sake of simplicity. The calculations were performed for pressure $p = 68$ kPa, as in [3], and the two values of the background gas temperature: $T_g = 1000$ and 1500 K. We assumed that the equilibrium temperature at the center of an arc with a radius of $r_0 = 5$ mm was $T_{arc} = 7000$ K, which is close to the data obtained in the calculations [3] and the experimental works [4,5].

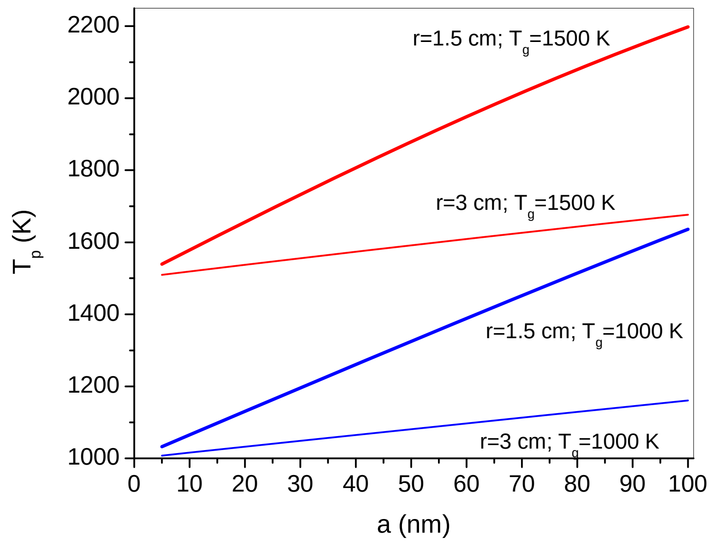

Figure 1. Stationary temperature of particles, depending on their radius for two positions of the particles *r* = 1.5 and 3 cm; and for two values of the buffer gas temperature T_g = 1000 and 1500 K.

The results presented in Fig. 1 show that in the radiation field of the arc, the temperature of the particles become very different from the background temperature, and depends on their sizes. The quasi equilibrium temperature of the particle is higher the closer this particle is to the arc. Thus, the particle temperature $T_p(r,a)$ is established for the time of the order of 10 microseconds. Fig. 2 shows an example of the calculation of the transitional regime for the particles of different sizes. In the presence of a convective flow of the buffer gas, the particles are not static and move with the flow. However, for the characteristic time for the establishment of a quasi-stationary temperature, the convective displacement of the particles is negligible, ~ 1 mm or less.

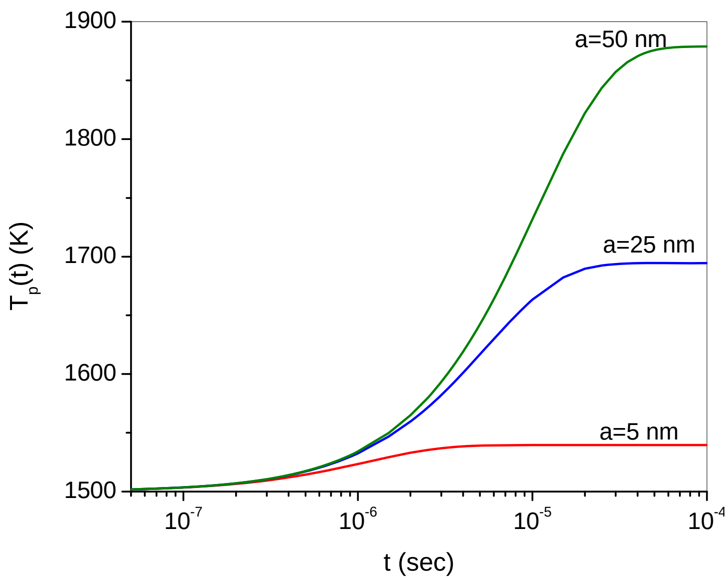

Figure 2. Establishment of a quasi-stationary temperature for the particles of different sizes: *a* = 5, 25 and 50 nm, at a distance of 1.5 cm from the arc axis.

Under our considered conditions, the the nanoparticles' temperatures are a function of their sizes, because electromagnetic energy absorption in the Rayleigh regime is volume dependent, and cooling (dominated by thermal conduction to the ambient gas) is area-dependent. Therefore, larger particles are heated to higher temperatures, than small particles.

An example of the contribution of various components of the heat balance at a steady-state regime, depending on the size of the particles at the distance of 1.5 cm from the center of the arc and the assumed background temperature T_g =1500 K, is shown in Fig. 3.

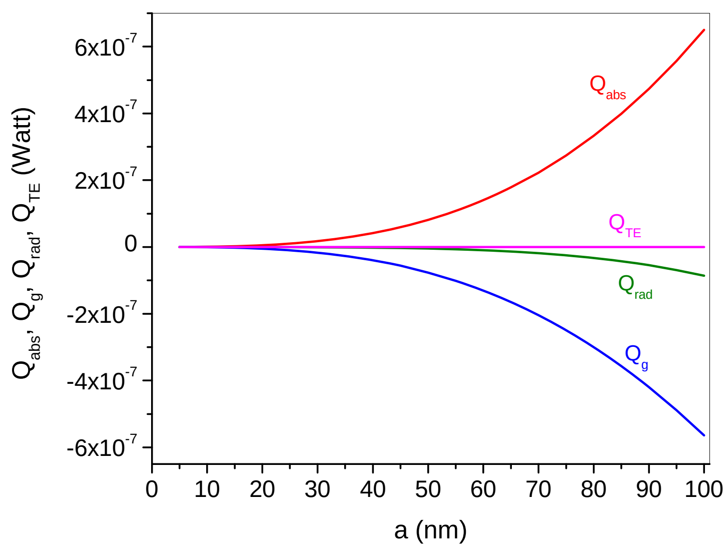

Figure 3. Quasi-stationary sources of heating and cooling of particles, depending on their radius, at a distance *r*=1.5 cm from the center of the arc and the background temperature T_g=1500 K.

Although we considered the impact of arc radiation on carbon nanoparticles, our results and conclusions may be applicable to other types of nanoparticles if the radiation absorption is in the Rayleigh regime.

III. Effect of Ultrasound on the Mixture of Nanoparticles and Soot Microparticles

C. Neutral particles

There are experimental works in which the effect of ultrasound on the yield of fullerenes and nanoparticles formed in the vicinity of the arc with carbon electrodes burning in an inert gas, was studied, showing a simultaneous decrease in the output of soot particles (see., e.g., [6]). These results seem surprising, since acoustic effects on nanoparticles with a size much smaller than the mean free path of the atoms of a buffer gas in which ultrasound is maintained are not expected. However, in our opinion, these results have a simple explanation.

It is known that in the ultrasonic field acting on the gas with suspended microparticles it is possible for the particles to coagulate, i.e. form larger particles from smaller ones. The interaction of spherical particles in a gas in a sound wave is determined by the theory of Koenig [13]. The radial and tangential components of the Koenig force have the form [14]:

$$F_r = \frac{3}{4}\frac{\pi\rho a_1^3 a_2^3 u_0^2}{L^4}\left(3\cos 2\theta + 1\right), \tag{13}$$

$$F_\theta = \frac{3}{2}\frac{\pi\rho a_1^3 a_2^3 u_0^2}{L^4}\sin 2\theta \ . \tag{14}$$

Here u_0 is the amplitude of the the oscillatory velocity in the sound wave; ρ is the density of the medium; a_1, a_2 are the radii of the interacting spheres; L is the distance between the centers of the particles; θ is the angle between the center line and the wave vector of the acoustic wave. The amplitude of the oscillatory velocity in the sound wave is related to the ultrasound intensity I_s, its angular frequency, ω, and amplitude of the oscillations A_0 :

$$I_s = \tfrac{1}{2}\rho c_s \omega^2 A_0^2 = \tfrac{1}{2}\rho c_s u_0^2 \ , \tag{15}$$

where c_s is the speed of sound in the gas.

Depending on the angle θ, the particles can repel or attract each other. The maximum force of attraction (sometimes called the Bernoulli force) occurs when the line connecting the centers of the particles is perpendicular to the direction of propagation of the sound wave, that is, at $\theta = \pi/2$:

$$F_{r,m} = -\frac{3}{2}\frac{\pi\rho a_1^3 a_2^3 u_0^2}{L^4} \ . \tag{16}$$

The Koenig theory is valid for relatively large distances between the interacting particles, $L >> a_1 + a_2$. For smaller distances between the particles the perturbations of higher order should be taken into account. The corresponding correction has been received by Bjerknes [15,14]

$$\Delta F_r = -\frac{3}{4}\frac{\pi\rho a_1^3 a_2^3 (a_1^3 + a_2^3) u_0^2}{L^7}\left(3\cos^2\theta + 1\right). \tag{17}$$

If the particles are charged, the electrostatic interaction between them with the Coulomb force should be taken into account:

$$F_q = \frac{1}{4\pi\varepsilon_0}\frac{q_1 q_2}{L^2} \ . \tag{18}$$

In general, the equation of motion of spherical particles along a line connecting their centers is given by

$$m_{p_{1,2}}\frac{d^2 L}{dt^2} = (F_q + F_r + \Delta F_r) - F_{s_{1,2}} \ . \tag{19}$$

In a sufficiently dense gas when the particle size greatly exceeds the mean free path of the gas molecules, the retarding force $F_{s_{1,2}}$ acting on spherical particles is determined by the Stokes formula

$$F_{s_{1,2}} = -6\pi\eta a_{1,2}\frac{dL}{dt} \ , \tag{20}$$

where η is the dynamic viscosity of the buffer gas. In this case, the particles are moving with the instantaneous drift velocity, which is determined by the balance of forces acting on the particle:

$$\frac{dL}{dt} = (F_q + F_r + \Delta F_r)/6\pi\eta a \ . \tag{21}$$

The drift approximation is quite applicable to the sub-micron and micron-sized particles in helium at atmospheric pressure and relatively low temperatures < 3000 K, as, for example, at $p = 760$ Torr and $T = 298$ K, the mean free path $l_m \approx 0.2\ \mu$m .

Examples of calculations for equal neutral microscopic soot particles in helium at $p = 760$ Torr, $T = 1000$ K for various particle sizes and intensities of ultrasound at $\theta = \pi / 2$ are shown in Fig. 4. It is assumed for definiteness that the initial concentration of particles is $n_p = 10^{15}$ m^{-3}. The dynamic viscosity of helium $\eta(T)$ was taken from [16].

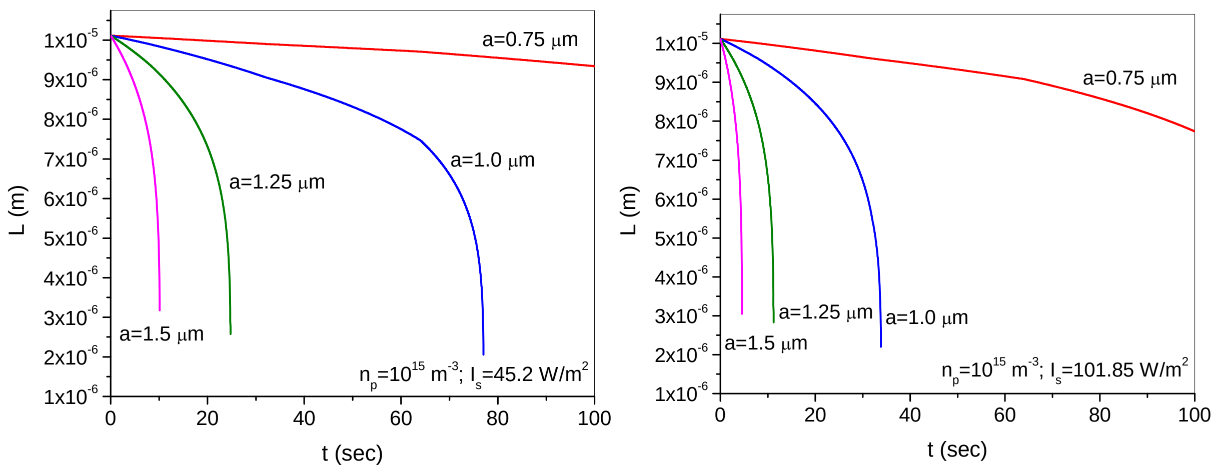

Figure 4. Distance between identical neutral microscopic soot particles in helium at $p = 760$ torr, $T = 1000$ K at $\theta = \pi / 2$ for various sizes of particles and ultrasound at intensities (a) $I_s = 45.2$ W/m^2 (u_0=1 m/s) and (b) $I_s = 101.85$ W/m^2 (u_0=1.5 m/s).

When approaching to a distance $L \approx a_1 + a_2$, the particles stick together under the influence of short-range van der Waals forces. For larger particles, the effect is stronger, and they will be brought together in a few seconds or even less. Thereafter, they fall out of the volume under the influence of gravity. (So, by the way, runs a standard method of ultrasonic cleaning of gases.) Thus, more fullerenes and nanoparticles remain in a volume to which ultrasound practically has no effect. These fullerenes have less chance to disappear by sticking to larger particles, as a result of Brownian motion, because of a significant decrease in the concentration of soot particles in the volume.

D. Charged particles

We have considered the case of neutral particles. In the plasma, or as a result of thermionic emission in the radiation field of the arc, particles are charged. In plasma, usually the particles acquire a negative charge, charging to the local floating potential. However, as a result of the thermionic emission, the particle loses electrons, i.e. it becomes positively charged. The Coulomb repulsion of the particles may be substantially greater than the Koenig force and the agglomeration of the microparticles occurs at increased ultrasound intensities or becomes completely impossible. Incidentally, charging of the agglomerates as a result of the thermionic emission caused by laser heating can lead to their disintegration in Laser Induced Incandescense (LII) experiments [17].

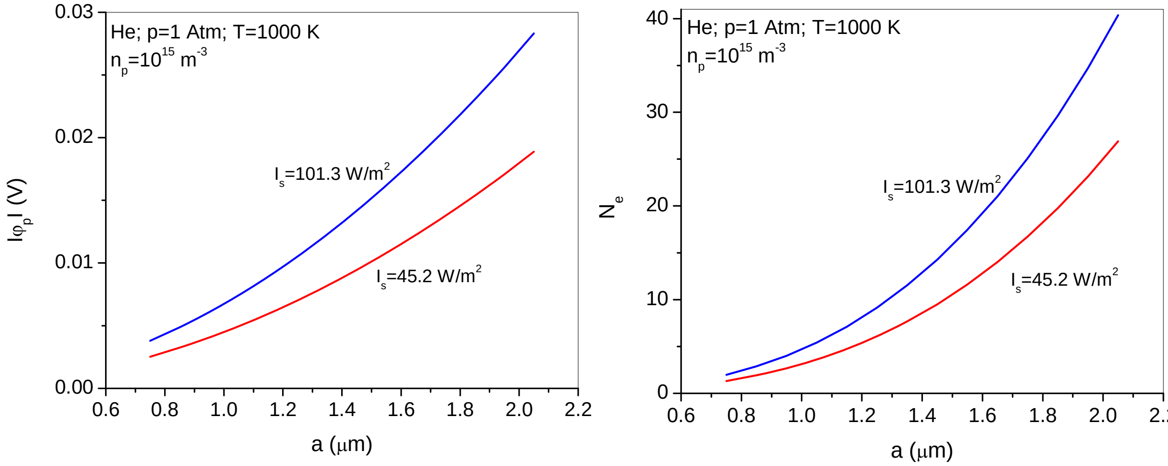

Figure 5. Critical values of the potential (a) and charge (b) for the coagulation of identical charged soot particles of different sizes in helium at $p = 760$ torr, $T = 1000$ K at $\theta = \pi/2$ and ultrasound intensities $I_s = 45.2$ W/m² and $I_s = 101.85$ W/m²

For simplicity, consider the background plasma of relatively low density, where the Debye length is greater than the average distance between the soot particles. For each ultrasound intensity and concentration of micro-particles of a certain size, there is a critical value of their charge (electrostatic potential), which still allows coagulation in an acoustic field. This limiting value of the potential can be determined when the absolute values of the Koenig attractive force (16) and Coulomb repulsive force (18) are equal. Charged particles approach each other by the action of the acoustic field, when

$$F_q \le |F_r| . \qquad (22)$$

For identical particles, regardless of the sign of the charge,

$$|q| \le |q_c| = \frac{\pi a^3 u_0}{L}(6\varepsilon_0 \rho)^{1/2} ,\ N_e = |q_c|/e \qquad (23)$$

where N_e is the corresponding number of electrons to be acquired (or lost) by the particle. Or, from the relation between the charge of the particle, its capacity and the potential (9), the coagulation is possible at

$$|\varphi| \le |\varphi_c| \le \frac{a^2 u_0}{2L}(3\rho/2\varepsilon_0)^{1/2} . \qquad (24)$$

The results of calculations with the estimated formulas (23),(24), presented in Fig.5, show that a very small charge acquired by the soot particles is sufficient to suppress the coagulation process. However, for the same conditions, with increasing ultrasound intensity, the coagulation again becomes possible.

IV. Conclusions

- The influence of arc discharge radiation with graphite electrodes on the synthesis of carbon nanoparticles in the helium buffer gas was analyzed.
- It is shown that the nanoparticles are heated by the black-body radiation of the arc and their temperatures significantly exceed the local temperature of the buffer gas.
- The heating of nanoparticles by the radiation can affect the process of synthesis.

- The degree of heating of the particle is determined by the particle's geometry, and that opens additional possibilities for nonintrusive optical diagnostics.
- Coagulation of soot particles in the ultrasonic field is possible, resulting in a decrease in the concentration of soot particles and increase in production efficiency of fullerenes and nanoparticles.
- The threshold for the ultrasound intensity required for the coagulation depends on charge acquired by the soot particles, particle sizes and background gas parameters

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References

1. K. Ostrikov and A. B. Murphy, "Plasma-aided nanofabrication: where is the cutting edge?" *J. Phys. D: Appl. Phys.* **40**, 2223 (2007)

2. M. Keidar, A. Shashurin, J. Li, O. Volotskova, M. Kundrapu, and T. S. Zhuang, "Arc plasma synthesis of carbon nanostructures: where is the frontier?" *J. Phys. D: Appl. Phys*. **44**, 174006 (2011)

3. M. Kundrapu, M. Keidar, "Numerical simulation of carbon arc discharge for nanoparticle synthesis", *Phys. Plasmas* **19**, 073510 (2012)

4. J. Ng, Y. Raitses, "Self-organisation processes in the carbon arc for nanosynthesis", *J. Appl. Phys.* **117**, 063303 (2015)

5. A. G. Ostrogorsky, C. Marin, "Heat transfer during production of carbon nanotubes by the electric-arc process", *Heat Mass Transfer* **42**, 470–477 (2006)

6. G.N. Churilov, "Synthesis of Fullerenes and Other Nanomaterials in Arc Discharge, Synthesis of Fullerenes and Other Nanomaterials in Arc Discharge, Fullerenes", *Nanotubes and Carbon Nanostructures*, **16** ,5-6, 395-403 (2008)

7. M.N.Shneider, "Carbon nanoparticles in the radiation field of the stationary arc discharge", *Physics of Plasmas*, **22**, 073303 (2015)

8. C. F. Bohren and D. R. Huffman, Absorption and Scattering of Light by Small Particles (Wiley, New York, 1983)

9. F. Liu, K.J. Daun, D.R. Snelling, G.J. Smallwood, "Heat conduction from a spherical nano-particle: status of modeling heat conduction in laser-induced incandescence", *Appl. Phys. B: Lasers Opt*., **83**, 355 (2006)

10. K. J. Daun, G. J. Smallwood, F. Liu, "Investigation of Thermal Accommodation Coefficients in Time-Resolved Laser-Induced Incandescence", *J. of Heat Transfer*, 130, 121201-32008 (2008)

11. T. A. Sipkens, R. Mansmann, K. J. Daun, N. Petermann, J.T. Titantah, M. Karttunen, H. Wiggers, T. Dreier, C. Schulz, "In situ nanoparticle size measurements of gas-borne silicon nanoparticles by time-resolved laser-induced incandescence", *Appl. Phys. B* **116**, 623 (2014)

12. J. Orloff, Schottky emission. In: Handbook of Charged Particle Optics (2nd ed.) (CRC Press, 2008)

13. W. König, "Hydrodynamsch-akustische Üntersuchungen. Über die Kräfte zwischen zwei Kugeln in einer schwingenden Flüssigkeit und über die Entstehung der Kundtschen Staubfiguren", *Ann. Phys*. **42**, 4, 549 (1891).

14. N.L. Shirokova, Aerosol Coagulation, – in Sources of High-Intensity Ultrasound (Ultrasonic Technology) V.2 (Edited by L.D. Rozenberg), Springer, 477-536, 1973

15. C A Bjerknes, Hydrodynamische Fernkräfte , (Leipzig : Engelmann, 1915)

16. I.S. Grigoriev and I.S., E.Z. Meilikhov, Handbook of Physical Quantities (CRC, Boca Raton, FL, 1997)

17. J.M Mitrani, M.N. Shneider, B. Stratton, Y. Raitses, Modeling thermionic emission from laser-heated nanoparticles, Submitted to *Appl.Phys.Lett*. (2016)