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Hyperbolic metamaterials based on graphene sheets with different values of chemical potentials

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In this paper possibility of creating a medium based on graphene-dielectric structures with the hyperbolic shape wave number dispersion is considered for the case when two types of graphene sheets with different chemical potentials periodically alternate. Using the Bloch theorem and the transfer matrix method, dispersion relations for the light wave numbers are derived for the layered structure and the possibility is demonstrated to manipulate the light propagation. The optical conductivity of graphene sheets is known to be frequency dependent and in the present scrutiny it is estimated via Kubo formula which simultaneously accounts for both the inter band and the intraband transitions of electrons. To apply the transfer matrix method we routinely express the amplitudes of the incident and reflected radiation at the input to the layered structure in terms of the amplitudes of electromagnetic waves at the output. The transmission spectrum of the layered dielectric medium which is sliced by two types of graphene sheets with different chemical potentials have a staircase behavior. It is demonstrated that the jump points in the transmission spectrum are simply controlled by adjusting the values of chemical potentials of graphene sheets.

Key words: hyperbolic metamaterials, graphene, dispersion of electromagnetic waves, transmission, absorption PACS number(s): 78.20.-e; 78.20.Bh; 78.20.Ci; DOI: by publisher

Introduction

With the rapid development of nanotechnology it has become possible to create entirely new materials with a variety of unusual physical properties. These certainly include photonic crystals [1], metamaterials [2,3], and a number of other man-made materials. Among them a special place is occupied by the so-called hyperbolic materials, i.e. nano composites fabricated by the creation of a periodic structure of alternating layers of metal and dielectric media or by deposition of metal nanorods on a dielectric substrate [4]. A distinctive feature of nanocomposite materials is that their dielectric constant is described by the diagonal tensor whose components have different signs in a certain range of frequencies. In this case, it is conventional to speak of the hyperbolic "meta" material, in which, for instance, a phenomenon of negative light refraction is usually observed. Functionality of hyperbolic metamaterials is vastly confirmed by a large number of publications on the observation of various optical effects. In particular, it was demonstrated that metamaterials can help in

overcoming the diffraction limit, in creating optical resonators and biosensors, as well as in observing nonlinear effects at rather low intensity of electromagnetic fields [4,5].

Graphene, due to its unique optical properties, is a more promising material for creating hyperbolic metamaterials than conventional metals. This statement is based on the fact that it is possible to control the light transmission through a layered structure by changing its chemical potential [7]. Electrodynamic properties of a graphene, a two-dimensional lattice of carbon atoms, are characterized by its surface conductivity, which can be phenomenologically defined within the Kubo formalism [7-8].

Surface conductivity and permittivity of a graphene

Graphene is the first known truly twodimensional crystal. Unlike earlier attempts to create two-dimensional conductive layers, for example, two-dimensional electron gas, from semiconductors by controlling the width of the forbidden band, electrons in graphene are much more localized in the plane.

The variety of chemical and physical properties is due to the crystal structure and π -electrons of the carbon atoms that make up graphene. Wide study of the material in universities and research laboratories is primarily due to its availability and ease of its preparation using mechanical splitting of graphite crystals. The material, which showed its unique properties like high electrical and thermal conductivities, rather high mechanical strength etc., is interesting not only for researches, but also for engineers. The motion of free electrons in graphene can be described using the Dirac equation, since charge carriers in graphene have a linear dispersion law near the Dirac points [9]. In the absence of an external static magnetic field and under neglect of the spatial dispersion, the surface conductivity is determined as a scalar function of frequency ω , the chemical potential μ (which depends on a voltage applied and/or on the chemical doping), phenomenological scattering rate Γ (or the corresponding relaxation time $\tau = 1/(2\Gamma)$), and the temperature *T* :

$$\sigma_{g}(\omega,\mu_{c},\Gamma,\Gamma) = -\frac{ie^{2}(\omega+i2\Gamma)}{\pi\hbar^{2}} \left[\frac{1}{(\omega+i2\Gamma)^{2}} \int_{0}^{\infty} \varepsilon \left(\frac{\partial f_{d}(\varepsilon)}{\partial \varepsilon} - \frac{\partial f_{d}(-\varepsilon)}{\partial \varepsilon} \right) d\varepsilon - \int_{0}^{\infty} \left(\frac{f_{d}(-\varepsilon) - f_{d}(\varepsilon)}{(\omega+i2\Gamma)^{2} - 4(\varepsilon/\hbar)^{2}} \right) d\varepsilon \right].$$
(1)

Here ε is the energy, \hbar denotes the Planck's constant, *e* designates the elementary charge, k_B stands for the Boltzmann constant, and $f_d(\varepsilon) = \left(\exp(\varepsilon - |\mu_c|/k_BT) + 1\right)^{-1}$ is the distribution function in the Fermi-Dirac statistics.

The surface conductivity $\sigma_g(\omega, \mu_c, \Gamma, T)$ of graphene consists of two main contributions, namely the intraband σ_{intra} and the interband σ_{inter} conductivities, respectively. The former can be written in the following analytic form:

$$\sigma_{\text{int}ra}(\omega,\mu_c,\Gamma,T) = i \frac{e^2 k_B T}{\pi \hbar^2 (i2\Gamma + \omega)} \left[\frac{\mu_c}{k_B T} + 2\ln\left(\exp\left(-\frac{\mu_c}{k_B T}\right) + 1\right) \right],\tag{2}$$

whereas the second one reads as

$$\sigma_{\text{inter}}(\omega,\mu_c,\Gamma,T) = \frac{ie^2}{4\pi\hbar^2} \text{Log}\left[\frac{2\mu - (\omega + i2\Gamma)\hbar}{2\mu + (\omega + i2\Gamma)\hbar}\right] \quad (3)$$

A standard 2D graphene sheet is an optically anisotropic material whose diagonal permittivity tensor is written as follows:

$$\varepsilon_g = \begin{pmatrix} \varepsilon_{g\parallel} & 0 & 0\\ 0 & \varepsilon_{g\parallel} & 0\\ 0 & 0 & \varepsilon_{g\perp} \end{pmatrix}.$$
 (4)

Here $\varepsilon_{g\perp} = 1$ and $\varepsilon_{g\parallel} = 1 + i\sigma_g/\varepsilon_0 \omega d$, d denotes the thickness of the graphene sheet, ε_0 signifies vacuum permittivity.

Transfer matrix of graphene-dielectric layered structure

A photonic crystal is a solid structure with periodically varying dielectric permittivity or inhomogeneity, whose period is comparable with the wavelength of light.

Photonic crystals, thanks to a periodic change in the refractive index, make it possible to obtain allowed and forbidden bands for photon energies, analogous to semiconductor materials in which allowed and forbidden bands are observed for the energy of charge carriers. In practice, this means that if а photon with energy (wavelength/frequency) falls on a photonic crystal, which corresponds to the forbidden band of a given photonic crystal, then it can not propagate in a photonic crystal and is fully reflected back. Conversely, this means that if a photon that has energy (wavelength/ frequency) that falls on a photonic crystal corresponds to the allowed band of a given photonic crystal, then it can propagate in a photonic crystal. In other words, the photonic crystal serves as an optical filter that separates electromagnetic waves of various frequencies.

Of interest herein is the 1D photonic structure of dielectric layers, which are separated by the graphene sheets, as shown in Figure 1. The idea of the following consideration is that the graphene sheets have different chemical potentials. During the calculation the incidence of the p-polarized plane wave (TM-wave with the components $E = (E_x, 0, E_z)$ and $H = (0, H_y, 0)$). We essentially focus on the wave propagating along the Z-axis.

It is well known that the wavenumber dispersion of the photonic structure with the same graphene sheet has following form:

$$k_z^2 = \varepsilon_d k_0^2 - \frac{\varepsilon_d}{\varepsilon_g} k_t^2, \qquad (5)$$

where ε_d is simply the permittivity of the dielectric layer. It can be seen that, depending on the sign of $\varepsilon_{g\parallel}$, the two modes of the wave propagation are possible: the elliptic modeand the hyperbolic one.Figs. 2a and 2b show the real and imaginary parts of the surface conductivity and permittivity of the graphene. It is clearly seen that for the graphene layer at room temperatures and at the fixed value of the chemical potential μ =0.5 eV the real part of the permittivity remains negative in the frequency range higher than 220 Thz. The change in the value of the chemical potential µ shifts the negative region to higher frequencies. In this work we will consider one interesting case when the photonic structure consists of the two types of the periodically repeated graphene sheets with different values of the chemical potential (see Fig. 1).



Figure 1 – Layout of the layers of the periodic structure based on the dielectric and the graphene

The transfer-matrix method is widely used in optics to describe how the electromagnetic waves propagate through a stratified medium.

The light reflection due to a single interface between two physically different media is subject to the Fresnel formulas. The situation is not so simple if there are many interfaces because the reflected waves are partially transmitted as well and again partially reflected. Depending on the wavelength and the exact length of the light path, those reflections interfere, either destructively or constructively. The most difficult problem seen in this case is that the overall reflection of a layered structure is a result of an infinite number of reflections at various interfaces.

To avoid such difficulties the transfer matrix method was put forward by exploiting the insight that in view of Maxwell's equations simple continuity conditions can be derived for the electric field at interfaces between two media of distinct physical properties. Thus, the transfer matrix method makes it possible to formally relate the amplitudes of the incident and reflected electromagnetic waves at the input to the layered structure with the amplitudes at the output by means of the matrix M which is obtained by multiplying: the transition matrix D through the interface, and the transmission matrix in the dielectric medium P_d :

$$\begin{bmatrix} E_1^+\\ E_1^- \end{bmatrix} = M \begin{bmatrix} E_{n+1}^+\\ E_{n+1}^- \end{bmatrix},$$
(6)

$$M_{TM} = D \cdot P_d = \frac{1}{2} \begin{bmatrix} (1 + \eta_{TM} + \zeta_{TM}) & (1 - \eta_{TM} - \zeta_{TM}) \\ (1 - \eta_{TM} + \zeta_{TM}) & (1 + \eta_{TM} - \zeta_{TM}) \end{bmatrix} \begin{bmatrix} e^{-ik_z d} & 0 \\ 0 & e^{ik_z d} \end{bmatrix}.$$
 (7)

Here $\zeta_{TM} = \sigma(\omega, \mu, \Gamma)k_z / \varepsilon_d \varepsilon_0 \omega$ stands for the so-called wave impedance, $\sigma(\omega, \mu, \Gamma)$ denotes the conductivity of the graphene determined by the Kubo formula above and $\eta_{TM} = \varepsilon_{d1}k_{z2} / \varepsilon_{d2}k_{z1}$ is the ratio of the wavenumbers at the adjacent layers of the dielectric media. The latter is equal to 1 of the dielectric medium is the same throughout the metamaterial sample.

Let us consider the simple case when the two graphene sheets are separated by the dielectric layer. Assuming each graphene sheet has the distinct chemical potentials, the transfer matrix of the single unit cell gives rise to the following matrix product:

$$M = D_{2 \to 2}(\sigma_1) P(d) D_{2 \to 2}(\sigma_2) P(d)$$
(8)

To find the dispersion relation we employ the Bloch theory, which advocates that wave is weakened due to passing through each layer of the dielectric according to:

$$E_{n+1}^{+} = E_{n}^{+} e^{-\alpha d}, \qquad (9)$$

$$E_{n+1}^{-} = E_n^{-} e^{-\alpha d}.$$
 (10)

Solving equations (9) - (10) together with relation (6), the following homogeneous linear equation is obtained in the matrix form

$$\begin{pmatrix} M_{11} - e^{\alpha d} & M_{12} \\ M_{21} & M_{22} - e^{\alpha d} \end{pmatrix} \begin{pmatrix} E_{n+1}^+ \\ E_{n+1}^- \end{pmatrix} = 0,$$
(11)

whose nonzero solution only exists if the determinant of the matrix turns zero

$$M_{11}M_{22} + e^{2\alpha d} -$$

-($M_{11} + M_{22}$) $e^{\alpha d} - M_{12}M_{21} = 0.$ (12)

Here α is the Bloch wavenumber and *d* designates the thickness of the dielectric layer located in between the graphene sheets.

Recalling that the condition $M_{11}M_{22} - M_{12}M_{21} = 1$ must always be satisfied for a periodic structure, expression (12) is simplified to the following form:

$$\cosh(\alpha d) = (M_{11} + M_{22})/2.$$
(13)

It is well understood that expression (13) imposes strong restriction on the wavenumbers of electromagnetics waves and is called the dispersion relation.

If α is considered to be a complex number $\alpha = \kappa + iq$ we can easily write the following equation which corresponds to the undamping wave in the periodic structure and strictly determines its bandwidth

$$\cos(qd) = \cos^{2}(dk_{z}) - \frac{i kz \cos(dk_{z}) \sin(dk_{z})}{\varepsilon_{0} \varepsilon_{d} \omega} (\sigma_{1} + \sigma_{2}) - \sin^{2}(dk_{z}) - \frac{kz^{2} \sigma_{1} \sigma_{2} \sin^{2}(dk_{z})}{2\varepsilon_{0}^{2} \varepsilon_{d}^{2} \omega^{2}}.$$
⁽¹⁴⁾

The dispersion relation (14) describes the law of propagation of the p-polarized wave in the periodic photon structure of the two types of the graphene layers with the different values of the chemical potential such that they have different conductivities σ_1 and σ_2 . It should be noted that in the subwave regime, at which $k_z d \square$ 1 and $\beta d \square$ 1, expression (14) turns into the dispersion relation obtained on the basis of the effective medium model (5):

$$k_{z}^{2} = \frac{q^{2}}{4 + \frac{2i}{d\varepsilon_{0}\varepsilon_{d}\omega} (\sigma(\mu_{1}) + \sigma(\mu_{2}))}$$
(15)

Taking into account that $k_z = \sqrt{\varepsilon_d k_0^2 - k_\perp^2}$ and $k_\perp^2 = k_x^2 + k_y^2$, the dispersion relation can be rewritten as:

$$\frac{k_x^2 + k_y^2}{\varepsilon_d} + \frac{q^2}{4\varepsilon_d + \frac{2i}{d\varepsilon_0\omega} (\sigma(\mu_1) + \sigma(\mu_2))} = 1$$
(16)

The analysis of this dispersion relation suggests that the elliptical regime switches to the hyperbolic one when the wavelength varies in a certain range of optical spectra.

Figure 3 shows the dependence of k_z on the transverse component of the wave number k_{\perp} ,

normalized to k_0 . For numerical calculations the permittivity is taken to be $\varepsilon_d = 2$ and the width of the dielectric layer is assumed to be d = 80 nm. It is clearly envisaged from this figure that for the fixed values of the chemical potentials $\mu_1 = 0.4$ eV and $\mu_2 = 0.8$ eV the dependence $k_z(k_{\perp})$ remains purely elliptic right above the frequency $\omega = 1.23 \cdot 10^{15}$ Hz, see Figure 3b. If the frequency is lowered beyond this critical value the elliptic character of the dispersion goes over to the hyperbolic one, as evidenced by Figure 3a. It has to be mentioned that under ordinary experimental conditions the variation of the chemical potential can be practically realized either by the doping of graphene or by applying an external electric field [10].



Figure 2 – The real and imaginary parts of the surface conductivity and the permittivity of the graphene layers



a) $\omega = 1.18 \cdot 10^{15}$ Hz T = 300 K, $\Gamma = 0.043$ eV, $\mu_1 = 0.4$, $\mu_2 = 0.8$

b) $\omega = 1.23 \cdot 10^{15} \text{ Hz}$ T = 300 K, $\Gamma = 0.043 \text{ eV}$, $\mu_1 = 0.4$, $\mu_2 = 0.8$

Figure 3 – The real and imaginary parts of the surface conductivity and the permittivity of the graphene layers

Spectral characteristics of multilayer graphene-dielectric structures

A numerical study of the dependence of the transmittance of light on frequency in the periodic photonic structure with the different graphene sheets indicates the existence of the two regions where the transmitted light undertakes jumps. Transmission for a one stack or unit is illustrated in Figure 4 (cf. Fig.1). It is evident from this figure that the value of the chemical potential determines the region of the jump in the transmission spectrum of the light wave. Because the graphene sheets have two different values of the chemical potential μ_1 and μ_2 the transmission spectrum have a staircase behavior.

Figure 5 shows the transmission and absorbance spectra for different numbers of stacks. The thickness of dielectric layer in this case is d=80 nm and permittivity $\varepsilon = 2$. It follows from the figure that increasing the number of stacks leads to a stronger absorptions of light at the second jumped point.

For the dielectric layer of the width d=2000 nm the spectral dependence of transmission gives the

similar result which is shown in Figure 6excluding the well pronounced interference pattern.



Figure 4 – The transmittance of the photonic structure consisting the two graphene sheets with the different values of the chemical potentials

Figure 7 shows the comparative reflection spectra of the layered structure for several layers at the thicknesses d = 80 nm and d = 2000 nm of the dielectric layer. In contrast to the transmission and reflection spectra, the spectral dependence of the reflection coefficient does not exhibit a sharp change.



Figure – 5 Transmission (a) and absorbance (b) spectra of the graphene-dielectric layered structure with different number of stacks



Figure – 6 Transmission (a) and absorbance (b) spectra of the graphene-dielectric layered structure with different number of stacks



Figure – 7 Reflections spectra of the graphene-dielectric layered structure with different number of stacks

Conclusions

In this paper we have investigated of the optical characteristics of the photonic structure with the two types of the graphene sheets which are separated by the dielectric medium. The frequency dependent optical conductivity of the graphene sheet is calculated via Kubo formula which takes into account both the interband and the intraband transitions of electrons.

It has been discovered that for the fixed values of the chemical potentials $\mu_1 = 0.4$ eV and $\mu_2 = 0.8$ eV the dispersion relation $k_z(k_{\perp})$ is purely elliptic right above the frequency $\omega = 1.23 \cdot 10^{15}$ Hz, whereas for lower frequencies the hyperbolic dispersion persists. The latter regime is known to be responsible for the appearance of the forbidden photon energies which is the characteristic feature of the photonic crystals designed to filter the incoming electromagnetic radiation.

It has been found that for a dielectric layers of width d=2000 nm the interference pattern occur in contrast to the case of d=80 nm. This can be evidently understood by recalling the fact that the frequencies and the wavelengths of interest herein all correspond to the optical spectrum.

It has to be inferred that when the frequency of the incoming electromagnetic wave lies in the frequency range, strictly corresponding to the forbidden bands of the photonic crystal, the wave itself is totally reflected, whereas the transmitted wave at the output of the sample reaches its minimal intensity. In view of the results obtained, it is straightforward to conclude that owing to its unusual optical properties the graphene proves to be a more promising material for fabricating new generation of the hyperbolic metamaterials than conventional metallic structures. The latter speculation entirely stems from the experimental insight that the light passing through a layered

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structure is willingly manipulated by an appropriate variation of the chemical potential of the graphene sheets.

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Ion drift in parent gas for cesium, rubidium, and mercury

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The results of Monte Carlo calculations of the ion drift characteristics in a constant and homogeneous electric field are presented for the values of the applied intensity in the range $1 \le I / N \le 1000$ Td for cesium, rubidium and mercury. The results of molecular dynamics simulation are used together with the Monte Carlo method for calculation of collisional characteristics. The drift velocity, mean kinetic energy, longitudinal and transverse diffusion coefficients, mean free path, and the fraction of collisions with backward scattering are calculated. It is shown that the introduction of dimensionless units makes it possible to reduce the characteristics for different gases to universal curves. And the Bhatnagar, Gross, and Krook collision integral for the problem of ion drift in an own gas leads to significant errors. Also, an unexpected and nontrivial fact about the collisions with backward scattering is obtained and conclusions provided. It is found that using the BGK collision integral foe deseviling of ion drift an own gas leads to significant errors. There are some discussions regarding the large difference between present calculations and data of the BGK theory.

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Introduction

The flow of ions in a constant homogeneous electric field is usually characterized by the drift velocity, the values of the average energies of ions, with coefficients of mobility and diffusion in the longitudinal and transverse directions. The velocity of the ion drift in a gas under the action of a constant homogeneous electric field is given by the relation

$$W = \mu E, \tag{1}$$

where the coefficient of ion mobility $\mu(E, N, T)$ generally depends on both the field strength and gas parameters (temperature *T*, pressure p = NT, composition). A large number of experimental studies have been devoted to the determination of the diffusion coefficients and the mobility of ions in gases, and it can be assumed that in weak and moderately strong fields (E / N < 1000 Td) the ion mobility is known with a very high accuracy <1% [1-4].

In the handbooks, experimental and calculated data are usually presented only the drift velocity, but other kinetic characteristics of the ion drift are necessary for analyzing the properties of the gas discharge. For example, to determine the ion Debye radius, it is necessary to know the average ion energy, taking into account their heating in an electric field. Many characteristics of a gas discharge are determined from the ionic distribution of velocities, and knowledge of the ion velocity distribution function is often sufficient.

In [5], a modeling technique used to calculate the ion drift characteristics in a gas is described. The results of calculations of the characteristics of ion drift in a constant and homogeneous electric field at $1 \le N \le 1000$ for all noble gases. In this paper, which is a continuation of [6, 7], the results of molecular dynamics calculations are presented together with the Monte Carlo procedure for collision simulation. The characteristics of ion drift in a constant and homogeneous electric field at $1 \le N \le 1000$ Td for cesium, rubidium and mercury are calculated.

Theory

In Table. 1 - 3 shows the flow characteristics of singly charged rubidium, cesium and mercury ions during their drift in a constant and homogeneous electric field in their own gas at atom temperature 300 K and atomic density 2.69 $*10^{19}$ cm⁻³. In addition to the drift velocity, the tables show: the effective temperature of the ions, which is related to the

average kinetic energy of the ions by the ratio $\langle \varepsilon \rangle = \frac{1}{2}m\langle v^2 \rangle = \frac{3}{2}T_{eff}$; temperature of ions along the field T_{\parallel} and across the field T_{\perp} , so the average energy of the ion is equal to $\langle \varepsilon \rangle = \frac{1}{2}mW^2 + \frac{1}{2}T_{\parallel} + T_{\perp}$;

the diffusion coefficients in the direction along and across the field, the mean free path, and the fraction of collisions with backward scattering with respect to the total number of collisions. The exact values of the various characteristics at intermediate points can be obtained by interpolation.

Table 1 – Characteristics of the cesium ion flow during their drift in a constant and homogeneous electric field in their own gas at 300 K and atomic density 2.69 10^{19} /cm³.

E/N, Td	W, km/s	$T_{e\!f\!f}$, K	T_{\Box} , K	T_{\perp} , K	$D_l \ { m cm}^{2/{ m s}}$	D_t cm ² /s	т.f.p. нм	BS / (BS+Iso)
1	0.0006	300.2	300.3	300.2	0.0056	0.0056	3.8	0.093
2	0.0012	300.2	300.3	300.2	0.0056	0.0056	3.8	0.093
5	0.0031	300.3	300.4	300.2	0.0056	0.0056	3.8	0.093
10	0.0062	300.4	300.7	300.3	0.0056	0.0056	3.8	0.093
20	0.0124	301.1	302.3	300.5	0.0056	0.0056	3.8	0.094
50	0.0310	306.1	313.7	302.2	0.0056	0.0056	3.8	0.095
100	0.0613	323.1	353.4	308.0	0.0057	0.0056	3.9	0.098
200	0.119	384.3	496.7	328.0	0.0060	0.0058	4.2	0.11
500	0.259	676.7	1199	415.3	0.0068	0.0063	5.4	0.16
1000	0.431	1259	2649	563.8	0.0078	0.0068	6.9	0.24

Table 2 – Characteristics of the rubidium ion flow during their drift in a constant and homogeneous electric field in their own gas at 300 K and the density of atoms $2.69 \ 10^{19} \text{cm}^3$.

E/N, Td	W, km/s	$T_{e\!f\!f}$, K	T_{\Box} , K	T_{\perp} , K	$D_l m cm^{2/s}$	$D_t \ { m cm}^2/{ m s}$	m.f.p. nm	BS / (BS+Iso)
1	0.00041	300.2	300.4	300.2	0.0038	0.0038	3.3	0.11
2	0.00084	300.2	300.4	300.2	0.0038	0.0038	3.3	0.11
5	0.00212	300.2	300.4	300.2	0.0038	0.0038	3.3	0.11
10	0.0043	300.4	300.5	300.3	0.0038	0.0038	3.3	0.11
20	0.0085	300.9	301.7	300.5	0.0038	0.0038	3.3	0.11
50	0.0213	304.5	310.3	301.7	0.0039	0.0038	3.3	0.11
100	0.0423	317.2	340.0	305.8	0.0039	0.0038	3.4	0.12
200	0.0822	363.5	449.2	320.6	0.0040	0.0039	3.6	0.13
500	0.183	594.3	1006	388.5	0.0045	0.0042	4.5	0.17
1000	0.307	1070	2192	508.6	0.0051	0.0044	5.6	0.24

E/N, Td	W, km/s	T _{eff} , K	$T_{_{\square}}$, K	$egin{array}{c} T_{ot} \ , \ \mathbf{K} \end{array}$	D_l cm ² /s	D_t cm ² /s	m.f.p. nm	BS / (BS+Iso)
1	0.0006	300.2	300.3	300.1	0.0055	0.0055	8.0	0.36
2	0.0012	300.2	300.3	300.1	0.0055	0.0055	8.0	0.36
5	0.0032	300.3	300.5	300.2	0.0055	0.0055	8.0	0.36
10	0.0063	300.7	301.5	300.3	0.0055	0.0055	8.0	0.36
20	0.0127	302.4	305.6	300.7	0.0055	0.0055	8.0	0.36
50	0.0313	313.4	333.5	303.3	0.0056	0.0055	8.2	0.37
100	0.061	348.4	422.7	311.3	0.0057	0.0055	8.6	0.38
200	0.113	457.8	704.6	334.4	0.0062	0.0054	9.6	0.41
500	0.243	969.3	2046	430.8	0.0099	0.0058	12.7	0.48
1000	0.441	2457	5937	716.4	0.0257	0.0085	18.3	0.53

Table 3 – Characteristics of the mercury ion flow during their drift in a constant and homogeneous electric field in their own gas at 300 K and atomic density $2.69 \ 10^{19}$ /cm³.

The numerical data given above make it possible to obtain a fairly complete picture of the character of ion drift. We note some features of ion velocity distributions:

1) Analysis of the distribution functions shows that when ion drift, in conditions typical for gasdischarge plasma conditions, there is an appreciable heating of the ions not only in the longitudinal direction, but also in the transverse direction. This is due to close collisions, when besides recharging, scattering also occurs at an arbitrary direction in the center-of-mass system;

2) Even at a sufficiently high reduced electric field strength an ion flow does not form supersonic flux, in which the velocity of thermal, chaotic motion would be less than the velocity of the directed motion - the drift velocity. As already noted, due to the fact that with increasing field strength simultaneously with the increase of drift velocity there is an increase in the dispersion of the distribution function of the ion velocity (i.e., the longitudinal and transverse temperatures);

3) In the velocity distribution of ions there is a large anisotropy (and a large difference between the longitudinal and transverse temperatures T_{\parallel} and T_{\perp}). Therefore, the diffusion fluxes along and across the field can vary greatly in magnitude;

4) From the analysis of ion velocity distribution functions, from the analysis of other characteristics of the ion flux it follows that velocity module distribution, as well as the velocity projections, has significant differences from the corresponding Maxwellian distributions. Moreover, there is a difference not only in the tails of the distribution functions, but also in the central part. Accordingly, the distribution function of ion velocity during their drift in their own gas cannot be described by a Gaussian curve (shifted Maxwell distribution function).

In this connection, calculations were made with the determination of the fraction of collisions with backward scattering with respect to the total number of collisions, depending on the reduced field strength (naturally, the number of collisions does not include collisions with scattering at small angles due to divergence of the corresponding collision integral). The results of the calculations showed that there is an unexpected fact - although the cross sections with charge exchange are the largest, collisions with scattering back are only 15 - 45 percent. This takes place not only for the ions considered here for cesium, rubidium and mercury, but also for noble gases [7].

An analysis of the results of calculations shows that even in a strong field collisions with backward scattering are not dominant. But it is generally accepted that there is a decisive influence of collisions with the transfer of a charge, and often, when considering ion drift, only collisions with charge exchange are taken into account.

To take into account the effect of collisions on the velocity distribution of ions, the model collision integral of Bhatnagar, Gross, and Krook (integral BGK) is often used [6, 8-11]. However, the ion flow characteristics given in the calculations show a large deviation from the equilibrium distribution and a significant effect of collisions with isotropic scattering. In this connection, let us consider, as an example, the result of using BGK of the collision integral for analyzing the characteristics of the ion flux, taking into account only collisions with resonant charge exchange [7, 8].

The characteristics of the ion flux can be determined by solving the Boltzmann kinetic equation for the ion distribution function $f(\mathbf{v})$:

$$\frac{\partial f}{\partial t} + \mathbf{v}\nabla f + \frac{eE}{m}\frac{\partial f}{\partial \mathbf{v}} = I_{st}(f), \qquad (2)$$

where e - charge, m - ion mass, $I_{st}(f) - collision integral.$

In a weakly ionized plasma, it is often possible to neglect elastic collisions of ions with atoms, electrons, and ions. Since in the case of collisions of ions with the atoms of the proper gas, the cross section for the resonant charge exchange of an ion is usually greatest, then we consider the kinetic equation (2) in the spatially homogeneous case with a constant electric field, taking into account only the resonant charge exchange of ions:

$$\frac{eE}{m}\frac{\partial f}{\partial u} = \int [f(\mathbf{v}')\varphi(\mathbf{v}) - f(\mathbf{v})\varphi(\mathbf{v}')] |\mathbf{v} - \mathbf{v}'|\sigma_{res}n_a d\mathbf{v}', (3)$$

where u - component of velocity along the direction of the electric field, σ_{res} - the cross section of resonant charge exchange, n_a - atomic density, The distribution functions of ions and atoms are normalized to unity: $\int f(v)dv = \int \varphi(v)dv = 1$. Equation (3) describes the process of ion transport, which is a relay character – this model was suggested by L. A. Sena [8, 12]. According to this model, the ion velocity after the collision is equal to the velocity of the atom with which it collided. This model does not take into account the change in the velocity of the atom during the collision.

Let us consider the model of ion motion in the case of the fulfillment of two conditions:

1) The drift velocity W considerably exceeds the thermal velocity of the atoms $W >> V_T = (T_i / m)^{1/2}$;

2) There are only collisions of one type-with a resonant charge exchange of ions on the atoms of the own gas.

When these conditions are met, we can neglect the thermal motion of the atoms and assume that the ions move uniformly accelerated in a constant electric field E > 0, stopping after each collision event. The condition $W >> V_T$ can be satisfied with good accuracy either in the case of a high electric field strength or at a low gas temperature.

In neglecting the thermal energy of the atoms and taking into account only collisions with charge exchange, the Boltzmann kinetic equation has the form [7, 8, 12]:

$$\frac{eE}{m}\frac{\partial f}{\partial u} = -f\frac{u}{\lambda_{st}}, \ f(u<0) = 0, \qquad (4)$$
$$f(0) = c_1 \quad .$$

If the cross section of resonant charge exchange depends on the velocity, then the ion distribution function has the form:

$$f(u) = c_1 \Theta(u) \exp\left(-\frac{m}{eE} \int_0^u n_a \sigma_{res}(u') u' du'\right), \quad (5)$$

where $\Theta(u)$ - Heaviside function, c_1 – the constant, determined from the normalization condition.

If the cross section of resonant charge exchange and the mean free path of the ion $\lambda_{st} = 1/\sigma_0 n_a$ do not depend on the velocity, then the solution of (4) has the form

$$f(u) = \Theta(u) \left(\frac{2m}{\pi T_E}\right)^{1/2} \exp\left(-\frac{mu^2}{2T_E}\right), \qquad (6)$$

where $T_E \equiv eE\lambda_{st}$. The distribution (6) is half the Maxwell distribution with a temperature equal to the energy recruited by the ion at the mean free path. Consequently, the average kinetic energy of the ions, due to the motion in the direction of the field, is $\frac{1}{2}m(u^2) = \frac{1}{2}T = \frac{1}{2}eE\lambda$. The ion flux density for

is
$$\frac{1}{2}m\langle u^2 \rangle = \frac{1}{2}T_E = \frac{1}{2}eE\lambda_{st}$$
. The ion flux density for

this distribution is $J_i = n_i (2eE\lambda_{st} / \pi m)^{1/2}$, the average ion velocity (drift velocity) is $W = (2eE\lambda_{st} / \pi m)^{1/2} = (2T_E / \pi m)^{1/2}$.

Collisions with charge exchange play the most important role, but collisions of other types have a significant effect on the characteristics of ion velocity distribution. In addition to collisions with recharging, an important role can be played by polarization and gas-kinetic collisions. In the case of such collisions, the ion does not stop, but dissipates at the fixed center in the center-of-mass system of the atom-ion. A good approximation of this type of collision is the model of hard spheres, i.e. isotropic scattering. Without consideration of these collisions, heating of the ions in the transverse direction can not be taken into account. By analogy with the hydrodynamic approximation, it is often assumed that the drift of ions in a strong field is described by the shifted distribution function of Maxwell:

$$f_0(\bar{\mathbf{v}}) = \left(\frac{m}{2\pi T_i}\right)^{3/2} \exp\left(-\frac{m[(u-W)^2 + v^2 + w^2]}{2T_i}\right).$$
(7)

This distribution has two parameters - the drift velocity W and the ion temperature T_i , which determines the thermal dispersion of the ion velocities $V_i = (T_i / m)^{1/2}$, here the direction of the field and drift coincides with the x axis.

To take into account the impact of collisions, the model collision integral of Bhatnagar, Gross, and Kruk (BGK integral) is often used [7-9]:

$$I_{st} = \frac{\varphi - f}{\tau_0},\tag{8}$$

which describes the relaxation of the ion distribution function *f* to the equilibrium distribution function of atoms φ with a characteristic relaxation time $\tau_0 =$ const. The BGK integral qualitatively correctly describes the process of plasma relaxation to equilibrium in the case of a slight deviation from it. But it is inapplicable if the collision frequency of ions with atoms depends on their relative velocity, or the deviation from equilibrium is large. The ion transport equation in the spatially homogeneous case has the form: $V_E \partial f / \partial u = \varphi(u) - f(u)$, where $V_E = eE\tau_0 / m$. Its solution has the form:

$$f_E(u) = \frac{1}{V_E} \int_{-\infty}^{u} \varphi(u') \exp\left(-\frac{u-u'}{V_E}\right) du'.$$
(9)

In the case of a subthermal flow velocity, when the drift velocity $W \le (T/m)^{1/2}$, and the Maxwellian distribution of atoms $\varphi(u) = (m/2\pi T_0)^{1/2} \exp(-mu^2/2T_0)$, the solution (2) with the collision integral (8) has the form

$$f(u) = \varphi(u)(1 + uV_E / V_T^2)$$
. (10)

This distribution coincides with the expansion of the shifted Maxwellian distribution (7) at $V_E = W \ll V_T = (T/m)^{1/2}$. As expected, in the case of a small deviation from equilibrium, the use of the model integral BGK gives a reasonable result. In the case of a high ion flow rate $W \gg V_T = \sqrt{T_0/m}$ and a Maxwellian distribution of atoms, the distribution (9) has the asymptotics:

$$f(u) = \frac{\Theta(u)}{V_E} \exp\left(-\frac{u}{V_E}\right).$$
(11)

This distribution describes the uniformly accelerated motion of ions in a constant electric field E > 0, which stop after each collision event, the probability of which does not depend on the velocities of the ion and the atom. This unnatural hybrid model (taking the properties of polarization and resonant collisions) is a consequence of the structure of the integral BGK for large fields, when $W >> (T/m)^{1/2}$. It does not take into account the difference of the ion velocity from zero after the collision.

If we neglect the thermal motion of the atoms in comparison with the flow velocity and represent the distribution function of atoms in the form $\varphi(u) = \delta(u)$, then the particle profit in the BGK integral has the form $I_{BGK}^+ = \varphi / \tau_0$, the decrease is $I_{BGK}^- = f / \tau_0$. For collisions with a resonant predissection at a constant cross section, the profit and loss of the particles has, respectively, a form $I_{res}^+ = \varphi / \tau_0$, a decrease - $I_{res}^- = \sigma_0 n_a u f$. Consequently, the BGK integral even incorrectly conveys the nature of the particle loss at a qualitative level, this explains the radical difference between the distribution (11) and the physically reasonable distributions (6) and (7).

For polarization collisions characterized by a constant mean free path, the particle loss in the BGK integral can be reduced to the form $I_{pol}^- = f / \tau_0$. But the profit of particles in the collision integral depends on the entire distribution

function and can in no way be approximated by the quantity $I_{BGK}^+ = \varphi / \tau_0$. This means that, regardless of the form of the distribution function $f(\mathbf{v})$, the

The BGK integral does not allow to take into account the following factors:

1) for collisions characterized by a constant cross section (charge exchange, gas-kinetic), it does not take into account the dependence of the collision probability on the velocity;

2) for collisions characterized by a constant mean free path (polarization collisions), he does not take into account the difference between the ion velocity after the scattering event from zero.

These factors are decisive at a drift velocity comparable to the thermal velocity of the atoms. Consequently, the BGK integral is inapplicable for the problem of determining the characteristics of the ion drift in its own gas.

Let us compare the results of calculating the drift velocity of cesium, rubidium and mercury ions

$$\overline{V_T} = \frac{1}{\pi^{1/2} (1 + F^{1/2} + F)} \cdot$$
(12)

Results and discussions

In Figure 1 shows the results of calculating the drift velocity of an ion in its own gas, depending on the electric field strength for cesium, rubidium and mercury. In Figure 2 shows the same results, but the drift velocity is normalized to the value of the thermal velocity (the velocity of an ion with an energy equal to the temperature of the atoms), and the field is normalized by the value of the characteristic "heating field": $F = E / E_T$. The magnitude of the heating field is determined in such a way that an energy equal to the temperature of the atoms is accumulated on the mean free path.



Figure 1 – Results of calculating the drift velocity of an ion in its own gas as a function of the electric field strength in dimensionless units. The drift velocity is normalized to the value of the thermal velocity (the velocity of an ion with an energy equal to the temperature of the atoms), the field is normalized to the value of the characteristic "heating field", in which an energy equal to the temperature of the atoms is accumulated on the mean free path. The shaded curve is the solution of the Boltzmann equation with the BGK collision integral (11).



Figure 2 – Results of calculating the drift velocity of an ion in its own gas as a function of the electric field strength in dimensionless units. The drift velocity is normalized to the value of the thermal velocity (the velocity of an ion with an energy equal to the temperature of the atoms), the field is normalized to the value of the characteristic "heating field", in which an energy equal to the temperature of the atoms is accumulated on the mean free path. The shaded curve is the solution of the Boltzmann equation with the BGK collision integral (11)

Conslusions

The above graphs make the following conclusions:

1) The introduction of dimensionless units makes it possible to reduce the characteristics for different gases to universal curves;

2) The BGK collision integral for the problem of ion drift in an own gas leads to significant errors, which does not allow even describing real processes at a qualitative level (see, for example [7-9]);

3) There is an unexpected and nontrivial fact: although cross sections with charge exchange are the largest, collisions with backward scattering make up only 15-45 percent for noble gases at 300 K (for this reason see [16], where an attempt was made to approximate collisions in the form of a sum of collisions with isotropic scattering and backscattering).

The analysis showed that such a large difference in the calculations and the BGK theory is due to the fact that even in a strong field, collisions with backward scattering are not dominant. The results of the calculations demonstrate that the approach to the analysis of ion drift based on the BGK collision integral [10] is accompanied by large errors. These features of ion drift play an important role when considering the properties of cryogenic discharges and in a mixture of gases [5, 13-15]. The above numerical data explain the results of the analysis of ion-atom collisions [16] and significantly supplement the reference data [1-4].

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Space-charge wave in a dusty plasma column containing collisional streaming ions

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In this work, we have obtained the dispersion relation for the space-charge wave propagating in a dusty plasma column containing collisional streaming ions by using the fluid equations and the Poisson equation which lead to a Bessel equation. The growth rate of the space-charge and the geometric and collisional effects on the growth rate have been investigated. It is shown that the space-charge wave can be excited for a large axial wave number. The growth rate of excitation increases as the order of the roots of the Bessel function increases. It is also found that the growth rate decreases with an increase of the radius of column as well as with an increase of the collision frequency. In addition, it is found that the disturbance of wave can be damped only for small wave numbers and the ion collision plays a significant role in the physical properties of the space-charge wave.

Key words: Space-charge wave; Dust plasma PACS: 36.40.Gk

Introduction

The effects of radial boundaries of plasma columns on plasma waves have been investigated previously [1-5]. A decade ago, the behavior that the radial boundary leads to a frequency cutoff in the dust-acoustic wave dispersion relation was reported [6, 7]. Recently, the plasma waves in a radially bounded system such as a column plasma were reported to account for the Landau damping of dustacoustic space-charge waves, diffusion effects on the dissipation of waves in a turbulent plasma column, wake potential effects on the propagation of dust ion-acoustic waves, etc. [8-10]. The dispersion relations for plasma wave in a radially bounded collisional dusty plasma also have drawn much interests since they explain the boundary effects for the streaming charged particles in an electric field and the dissipative ion-dust streaming instability [3, 11]. The streaming instability plays an important astrophysical role various plasmas and in environments since it is connected to various physical dynamic phenomena including the heating mechanism in plasma systems [12-17]. For instances, the effects of non-Maxwellian ion-dust streaming instability, the effects of cyclotron motion in a positron-electron pair plasma, dust-dust two streaming instability in dust clouds, etc. have been recently reported [18-20]. In this work, we are motivated to study the excitation and dissipation of

the plasma waves in a column dusty plasma containing the collision-dominated streaming ions. To the best of our knowledge, the boundary effects on the excitation and dissipation of the plasma wave in a collisional two-stream dusty plasma in a column has not been reported yet. Since the ion stream is collision dominated, the susceptibility of the ion must contain the appropriate collision frequency [13, 21]. Then the fluid equations for each charged particle species and the Poisson's equation will construct a closed system to yield a Bessel equation whose solution is finite at the origin and null at the boundary of the column dusty plasma. Then, we obtain the new results on the dispersion relation for the space-charge wave propagating in a column dusty plasma containing collision-dominated ion flow. The growth rate of the space-charge wave is also derived and the geometric and collisional effects on the growth rate are investigated.

Numerical Simulation

Our duty plasma is uniform, bounded by a column, and contains electrons, singly charged ions, and negatively charged dust grains of the charge state Z_d so that the dust charge is denoted as $q_d = -Z_d e$. In the equilibrium, the quasineutrality condition yields, $n_{e0} + Z_d n_{d0} - n_{i0} = 0$, where n_{j0} is the equilibrium density of the plasma species j (= e, I, d for electrons, ions, and dust grains,

respectively). The plasma has a cylindrical geometry with coordinates (r, θ, z) and is azimuthally symmetric so that there is no θ -dependence. We shall consider that the curl of electric field will be vanished, i.e., the perturbation is electrostatic. Under these conditions, plasma motions on the $r - \theta$ plane can be ignored and the wave propagation in the *z*-axis is important. The system is then described using the continuity, momentum, and Poisson's equations for each charged particle species given by

$$\frac{\partial n_j}{\partial t} + \nabla \cdot (n_j \mathbf{v}_j) = 0, \qquad (1)$$

$$m_{j}n_{j}\left(\frac{\partial \mathbf{v}_{j}}{\partial t} + \mathbf{v}_{j} \cdot \nabla \mathbf{v}_{j}\right) = -\nabla P_{j} - q_{j}n_{j}\nabla \varphi, \qquad (2)$$

and $\nabla^2 \varphi = -4\pi \sum_{j=e,i,d} q_j n_j$, respectively. Here,

the symbols n_j , v_j , P_j , q_j , and φ denote the density, velocity, pressure, and electrostatic potential, respectively. We linearize the above equations by letting $n_j = n_{j0} + n_{j1}$, $v_j = v_{j0} + v_{j1}$, and $\varphi = \varphi_1$ where the quantity with subscript 0 denotes the equilibrium quantity and the quantity with subscript 1 denotes the small deviation from its equilibrium values. We let $\varphi_0 = 0$. In a cylindrical coordinate system, the perturbed quantities n_{j1} , v_{j1} , and φ_1 are assumed to vary as [22, 23]:

$$n_{j1}(\mathbf{r},t) = \overline{n}_{j1}(r)e^{i(k_z z - \omega t) - i\xi\theta}, \qquad (3)$$

$$\mathbf{v}_{j1}(\mathbf{r},t) = \overline{\mathbf{v}}_{j1}(r)e^{i(k_z z - \omega t) - i\xi\theta}, \qquad (4)$$

$$\varphi_{1}(\mathbf{r},t) = \overline{\varphi}_{1}(r)e^{i(k_{z}z - \omega t) - i\xi\theta}, \qquad (5)$$

where $\overline{n}_{j1}(r)$, $\overline{\mathbf{v}}_{j1}(r)$, and $\overline{\varphi}(r)$ are the amplitudes of perturbation in the transverse direction and k_z is the propagation wave number along the axial zdirection of the column, k_r is the transverse wave number, and ξ is the separation constant for the azimuthal angle θ . For the azimuthally symmetric system, we have the following form of the differential equation for the transverse potential $\overline{\varphi}_1(r)$ [23] by linearizing Eqs. (1) and (2) with Poisson's equation,

$$\frac{d^2\overline{\varphi}_1(r)}{dr^2} + \frac{1}{r}\frac{d\overline{\varphi}_1(r)}{dr} + \beta^2\overline{\varphi}_1(r) = 0, \qquad (6)$$

where the separation parameter β^2 is given by the plasma dielectric function $\varepsilon_l(\omega, k_z)$ in the form $\beta^2 / k_z^2 = -\varepsilon_{\ell}(\omega, k_z)$. In Eq. (6), the solution can be written as $\overline{\varphi}_1(r) = d_1 J_0(\beta r) + d_2 N_0(\beta r)$ where $J_0(\beta r)$ is the zeroth-order Bessel function of the first kind and $N_0(\beta r)$ is the zeroth-order Neumann function, with constant coefficients d_1 and d_2 . The boundary condition at r = R requires that the transverse potential must be zero, i.e., $\overline{\varphi}_{1}(R) = 0$, where R is the radius of the column. At the origin, we must have finite potential, i.e., $c_2 = 0$. Therefore, at r = R, we just have $J_0(\beta R) = 0$ and the separation parameter β is determined by $\beta R = \alpha_{0n}$, where α_{0n} are the *n*th-roots of $J_0(\beta R) = 0$, i.e, $\alpha_{01} =$ 2.4048, $\alpha_{02} = 5.5201$, $\alpha_{03} = 8.6537$, etc. We now consider a cold ion stream in a cold dusty plasma where the streaming ions are collision dominated, whereas the electrons and dusty particles are stationary. Here, we assume that the collision dominant ions are flowing in the z-direction. The longitudinal dielectric permittivity for a cold plasma with streaming ion reads [13]:

$$\varepsilon_{\ell}(\omega, k_{z}) = 1 - \omega_{pe}^{2} / \omega^{2} + i\omega_{pi}^{2} / \left[v(\omega - k_{z}u_{i}) \right] - \omega_{pd}^{2} / \omega^{2},$$

where $\omega_{pj} = (4\pi n_j q_j^2 / m_j)^{1/2}$ is the plasma frequency of species *j*. After some mathematical manipulations, we obtain

$$\omega(k_z) \approx \omega_{pe} \left(1 - \frac{\alpha_{0n}^2}{k_z^2 R^2} \right)^{1/2} - \frac{i\omega_{pi}^2 \omega_{pe}}{2\nu \left(\omega_{pe} - k_z u \right)} \left(1 - \frac{\alpha_{0n}^2}{k_z^2 R^2} \right)^{-1/2},$$
(7)

where we assume for simplicity $\omega \approx \omega_{pe}$ and $\omega >> \omega_{pd}$ provided that $\alpha_{0n}/k_z R < 1$. Here, for $k_z > \omega_{pe}/u_i$, the instability of the wave occurs. Therefore, the system can be unstable in spite of the collisional dissipation. We also find that the wave frequency for a column plasma is always smaller than that for a bulk plasma due to the geometric effect of the bounded plasma. However, the growth rate for a column plasma is larger than that for a bulk plasma due to the geometric effect of the bounded plasma. However, the growth rate for a column plasma is larger than that for a bulk plasma. In addition, the range of wave number for propagation is suppressed by the finite radius of the column. For the numerical analysis, we would

$$\overline{\gamma}(\overline{k}_z) = \frac{\overline{\omega}_{pi}^2}{2\overline{\nu}\left(1 - \overline{k}_z\right)} \left(1 - \frac{\alpha_{0n}^2}{k_z^2 R^2}\right)^{-1/2}, \quad (8)$$

where other scaled quantities are defined by $\overline{\omega}_{pi} \equiv \omega_{pi} / \omega_{pe}$, $\overline{v} \equiv v / \omega_{pe}$, $\overline{k_z} \equiv k_z u_i / \omega_{pe}$ and $\overline{R} \equiv R \omega_{pe} / u_i$. Therefore, the instability of the wave occurs when the scaled axial wave number is greater than unity. However, the wave will be damped for $\alpha_{0n} / \overline{R} < \overline{k_z} < 1$. Hence, we have found that the unstable mode of the space-charge wave would be caused by the coupling between the electron plasma wave and the positive dissipation due to the collision-dominated streaming ions. In addition, the damping mode would be caused by the coupling between the negative dissipation.

Results and Discussions

Figure 1 shows the scaled growth rate $\overline{\gamma}$ (> 0) of the space-charge wave in a column filled with the collision-dominated streaming ions as a function of the scaled axial wave number for various values of the root of the zero-the order Bessel function. In this figure, we have found that the space-charge wave can have unstable growing modes for large axial wave numbers. As shown in this figure, the scaled growth rate of the space-charge wave increases with an increase of the order of roots of the Bessel function. However, it is found that the influence of harmonic-order on the scaled growth rate decreases with increasing scaled axial wave number. Hence, we have found that the harmonic-order effect on the scaled growth rate decreases with an increase of the streaming velocity.

Figure 2 shows the scaled growth rate $\overline{\gamma}(>0)$ of the space-charge wave as a function of the scaled axial wave number for various values the scaled radius of the plasma column. From this figure, it is found that $\overline{\gamma}$ decreases with an increase of \overline{R} . It is also understood that $\overline{\gamma}$ decreases with an increase of the electron plasma frequency. In

addition, it is found that the influence of radial-size on $\overline{\gamma}$ decreases with increasing scaled axial wave number. Figure 3 shows the scaled damping rate $\overline{\gamma}$ (< 0) of the space-charge wave as a function of the scaled axial wave number for various values the scaled radius of the plasma column. From this figure, it is found that the space-charge wave can be damped for small axial wave numbers. As it is seen, the damping domain increases with an increase of the scaled radius of the plasma column. Hence, we have found that the ion collision plays a crucial role in the physical characteristics of the space-charge wave. These result would be useful for understanding the propagation of the space-charge wave in a dusty plasma column.



Figure 1 – The scaled growth rates $\overline{\gamma}$ are drawn as a function of the scaled wave number $\overline{k_z}$ for various roots of the Bessel function. The solid, dashed, and dotted lines are plotted for the roots $\alpha_{01} = 2.4048$, $\alpha_{02} = 5.5201$, and $\alpha_{03} = 8.6537$, respectively, for $\overline{\nu} = 1 \times 10^{-4}$ and $\overline{R} = 1$



Figure 2 – The scaled growth rates $\overline{\gamma}$ are drawn as a function of the scaled wave number $\overline{k_z}$ for various roots of the Bessel function. The solid, dashed, and dotted lines are plotted for the roots $\overline{R} = 1$, $\overline{R} = 2$, and $\overline{R} = 10$, respectively, for $\overline{\nu} = 1 \times 10^{-4}$ and $\alpha_{o1} = 2.4048$.



Figure 3 – The scaled damping rates $\overline{\gamma}$ are drawn as a function of the scaled wave number $\overline{k_z}$ for various roots of the Bessel function. The solid, dashed, and dotted lines are plotted for the roots $\alpha_{01} = 2.4048$, $\alpha_{02} = 5.5201$, and $\alpha_{03} = 8.6537$, respectively, for $\overline{\nu} = 1 \times 10^{-4}$ and $\overline{R} = 1$.

Conclusions

The new results on the dispersion relation have been obtained for the space-charge wave propagating in a dusty plasma column with collisional streaming ions. It is has been also derived the growth rate of the space-charge wave. The geometric and collisional effects on the growth rate have been investigated. Obtained results show that the unstable mode of the space-charge wave would be caused by the coupling between the electron plasma wave and the positive dissipation due to the collision-dominated streaming ions. In addition, the damping mode would be caused by the coupling between the electron plasma wave and the negative dissipation. The space-charge wave can have unstable growing modes for large axial wave numbers. Influence of harmonic-order on the scaled growth rate decreases with increasing scaled axial wave number. And the harmonic-order effect on the scaled growth rate decreases with an increase of the streaming velocity. The space-charge wave can be damped for small axial wave numbers. Damping domain increases with an increase of the scaled radius of the plasma column. It is shown that the ion collision plays a crucial role in the physical characteristics of the space-charge wave.

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Fundamental frequencies in the Schwarzschild Spacetime

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We consider the Keplerian, radial and vertical fundamental frequencies in the Schwarzschild spacetime to study the so-called kilohertz quasi-periodic oscillations from low-mass X-ray binary systems. We show that, within the Relativistic Precession Model, the interpretation of observed kilohertz quasi-periodic oscillations in terms of the fundamental frequencies of test particles in the Schwarzschild spacetime, allows one to infer the total mass M of the central object, the internal R_{in} and external R_{ex} radii of accretion disks, and innermost stable circular orbits r_{ISCO} for test particles in a low-mass X-ray binary system. By constructing the relation between the upper and lower frequencies and exploiting the quasi-periodic oscillation data of the Z and Atoll sources we perform the nonlinear model fit procedure and estimate the mass of the central object. Knowing the value of the mass we calculate the internal R_{in} and external R_{ex} radii of accretion disks and show that they are larger than r_{ISCO} , what was expected.

Key words: quasi-periodic oscillations, compact objects, neutron stars, X-ray binaries, accretion disks. PACS numbers: 04.20.-q, 95.30.Sf, 04.40.Dg, 97.10.Gz, 97.60.Jd, 97.80.Jp

Introduction

According to the models studying and explaining the physical properties and origin of the quasi-periodic oscillations (OPOs) discovered in low-mass X-ray binary (LMXRB) systems, the QPOs data could provide independent information about the mass of the central compact object (a white dwarf, neutron star and black hole), hence give some clues about the structure of accretion disks [1-2]. Moreover it is believed that the QPO data might allow one to test the effects of General Relativity (GR) in the strong field regime [3].

There are several models attempting to explain the QPOs in the literature [4-12]. In all of these models the key point is the assumption that the QPOs originate in the orbits around the compact object onto which the matter accretes. In this paper we will refer to the model that assumes that the QPOs are caused by the fundamental (epicyclic) frequencies associated with the orbital motion of the matter in the accretion disc, such as the Relativistic Precession Model (RPM) [13]. The RPM has been put forward in a series of papers [14-16]. It explains the QPOs as a direct manifestation of modes of relativistic epicyclic motion of test particles at various radii r in the inner parts of the accretion disk. The model identifies the lower (periastron precession f_{per}) and upper (Keplerian f_K) frequencies. In the past years, the RPM has been considered among the candidates to explain the twin-peak QPOs in several LMXBs, and the related constraints on the sources have been discussed [17-18].

For test particles in circular orbits, the epicyclic frequency is the frequency of radial and polar motions due to a small perturbation in the orbit. For example, consider the motion of a particle in the field of a compact star in a circular orbit. If the motion of this particle is slightly perturbed in the radial direction, its orbit will still be circular with small oscillations. The epicyclic frequency is the frequency of these oscillations [19].

The properties of congruencies of nearly circular geodesic orbits in a static and spherically symmetric spacetime such as the Schwarzschild metric are studied because of their fundamental role in the theory of accretion disks around compact objects with strong gravity. The radial epicyclic frequency and vertical epicyclic frequency are the most important characteristics of these orbits.

Analytic formulas for the frequencies in the Schwarzschild, Kerr and Hartle-Thorne metrics have been published many times by several authors [19-20] and are well known. In this paper we consider the frequencies for the Schwarzschild metric in the equatorial plane, and we perform an analysis of a mass estimate carried out in Ref [15]. We show that good fits can be reached leading to an inference of the model parameters; the mass, external and internal radii of the accretion disk. From this we can obtain the innermost stable circular orbit radius since it depends only on the mass in the case of the Schwarzschild metric.

The Schwarzschild Spacetime

In Einstein's theory of general relativity, the Schwarzschild metric is the solution to the gravitational field equations that describes the exterior gravitational field of mass M, based on the assumptions that the electric charge, angular momentum, and other parameters of the source are zero. The Schwarzschild solution was the first exact solution of the Einstein field equations other than the trivial flat space solution.

In (*ct*, *r*, θ , ϕ) coordinates with signature (+, -, -, -) the Schwarzschild line element has the form

$$ds^{2} = \left(1 - \frac{r_{g}}{r}\right)c^{2}dt^{2} - \left(1 - \frac{r_{g}}{r}\right)^{-1}dr^{2} - \frac{r^{2}\left(d\theta^{2} + \sin^{2}\theta d\phi^{2}\right)}{(1)}$$

where $r_g = 2GM / c^2$ is the Schwarzschild radius, *M* is the mass of the source, *c* is the speed of light in vacuum and *G* is the gravitational constant [21-22].

The fundamental (epicyclic) frequencies.

For the Schwarzschild spacetime in the equatorial plane $\theta = \pi / 2$ the Keplerian frequency for test particles in circular orbits is defined as

$$f_{K} = \frac{1}{2\pi} \sqrt{\frac{GM}{r^{3}}}$$
(2)

The radial and vertical frequencies of oscillations are given by

$$f_r = \frac{1}{2\pi} \sqrt{\frac{GM}{r^3} \left(1 - \frac{6GM}{c^2 r}\right)}$$
(3)

$$f_{\theta} = \frac{1}{2\pi} \sqrt{\frac{GM}{r^3}}$$
(4)

As one can see the Keplerian and vertical frequencies are equivalent to each other [19]. However in more complex spacetimes they differ. In the RPM the upper frequency is defined as the Keplerian frequency $f_U = f_K$ and the lower frequency is defined as the periastron frequency i.e. $f_L = f_{per} = f_K - f_r$. To perform the non-linear model fit it is convenient to express the lower frequency as a function of the upper frequency $f_L(f_U)$

$$f_{L} = f_{U} \left(1 - \sqrt{1 - \frac{6(2\pi f_{U} GM)^{2/3}}{c^{2}}} \right)$$
(5)

One may call this expression as the fitting function and here only the mass of the central compact object is a free parameter. The lower and upper frequencies are provided through observations. Knowing the QPO data with their error bars and performing a non-linear model fit procedure one can easily infer the mass with its error bars.

The non-linear model fit routine is based on the least-squares techniques. When there are explicit errors in the data, we use the inverse of the squared errors as fitting weights and form the corresponding chi-squared function of the model parameters. The best-fit parameters are those which minimize this function. In general for a non-linear fit there may be various local minima and therefore an iterative Levenberg-Marquardt algorithm, which starts from an initial guess of the parameter vector, is needed.

The innermost stable circular orbits.

Let us consider the motion of a particle in a centrally symmetric gravitational field of a central massive body. As in every centrally symmetric gravitational field, the motion occurs in a single "plane" passing through the origin; we choose the equatorial plane with $\theta = \pi/2$, for the sake of simplicity.

The radius of the innermost stable circular orbits is defined as

$$r_{ISCO} = 3r_g = \frac{6GM}{c^2} \tag{6}$$

 r_{ISCO} is considered to be the closest radius around a black hole where one can still have stable circular orbits for test particles [23]. Hence we use it here as a reference to make sure that the inner radius of the accretion disk is larger than r_{ISCO} .

Results and discussions

Formula (5) is the fitting function that we exploit to infer masses for Z (Cir X-1, GX 5-1, GX 17+2) and Atoll (4U1608-52, 4U1728-34) sources. The QPOs data with error bars have been taken from [18, 24–27] and references therein.



Figure 1 – Left panel: the lower frequency (f_L) is shown as a function of the upper frequency (f_U) for low mass X-ray binary system Cir X-1. Right panel: schematic illustration of the accretion disk around central compact object of Cir X-1. Green dashed circle indicates the radius (in kilometers) of the innermost stable circular orbit ($r_{ISCO} = 6GM/c^2$), the inner black circle shows the inner radius, whereas the outer black circle represents the outer edge of the accretion disk.



Figure 2 – Low mass X-ray binary system GX 5-1. The legend is the same as in Fig.1.



Figure 3 – Low mass X-ray binary system GX 17+2. The legend is the same as in Fig.1.



Figure 4 – Low mass X-ray binary system 4U1608-52. The legend is the same as in Fig.1.



Figure 5 – Low mass X-ray binary system is 4U1728-34. The legend is the same as in Fig.1.

On left panel of Figures 1-5 we have constructed the lower frequency versus the upper frequency using the fitting function and inferring the mass for Z (Cir X-1, GX 5-1, GX 17+2) and Atoll (4U1608-52, 4U1728-34) sources. In addition on right panel of Figs. 1-5 we show schematic representations of the structure of the accretion disks with their internal R_{in} and external R_{ex} radii (in kilometers). The width of the disks varies for all sources. One can show that the r_{ISCO} is always less than R_{in} and R_{ex} . The results are summarized in Table 1. In Fig. 6 we show the mass-radius relations of Lattimer and Prakash [28] constructed for static neutron stars with various equations of state. All stable configurations are inside the white region. If nuclear physics is correct, a measurement of M and R provides the internal composition of the neutron star i.e. one can rule out non-physical equations of state. Some masses are known with 99.9% accuracy! Up to now observational constraints for the mass-radius relations of neutron stars favor stiff equations of state where one gets masses larger than

two solar mass. Additional observational data are needed to determine whether the equation of state is stiff or super-stiff [29].

In Table 1 we show the main results of this paper. Using formula (6) we have found radius of innermost stable circular orbits r_{ISCO} for test particles in the gravitational field of compact objects. Internal R_{in} and external R_{ex} radii of the accretion disks have been inferred from using the lowest and highest values of the Keplerian frequencies from the QPO data. If one assumes that the central object in the LMXBs is a neutron star (NS), then knowing mass M of the sources one can show the range for the radius R of neutron stars approximately using the Lattimer and Prakash diagram. If one assumes a black hole (BH) as a central compact object in the LMXBs, then using

the Schwarzschild radius one can find the event horizon radius.



Figure 6 – The mass-radius relation for different equation of states for neutron stars [28].

Sources	$M(M_{\odot})$	risco (km)	R_{in} (km)	R_{ex} (km)	Central object	<i>R</i> (km)
Cir V1	2.22	10.6	52.7	122.2	BH	6.6
	2.23	19.0	52.7	155.5	NS	10.2-15
GX 5-1	2.16	19.0	26.4	66.7	BH	6.4
					NS	9.5-15
GX 17+2	2.02	17.8	22.0	20.2	BH	6
				29.5	NS	9-15
4U1608-52	1.96	17.3	20.6	30.8	BH	5.8
					NS	8.8-15
4U1728-34	1.74	15.3	19.4	25.0	BH	5.1
				23.9	NS	8.5-15

Table 1 - Main characteristics of the compact objects and accretion disks

Conclusions

In this paper we studied the quasi-periodic oscillation from the low-mass X-ray binary systems. To explain the quasi-periodic oscillations in our work we exploited the relativistic precession model, because it is one of the simplest models, that involves the minimum set of free parameters.

In light of the relativistic precession model, we presented a detailed analysis. We considered the kilohertz quasi-periodic oscillations in the field of a static central object. Using analytic formulas for fundamental frequencies in the Schwarzschild spacetime we interpret the kilohertz quasi-periodic oscillations of low-mass X-ray binaries of the Atoll and Z sources.

Particularly we perform analyses for Z and Atoll sources Cir X1, GX 5-1, GX 17+2, 4U1608-52, 4U1728-34. We show that the quasi-periodic oscillations data can provide information on the

parameters, namely, the mass and radius of compact objects in low-mass X-ray binaries.

Furthermore, we calculated the external and internal radii of the accretion disk and the innermost stable circular orbit radius. Unfortunately, from observations it is hard to obtain precise values of LMXB masses. Nevertheless, the approach used in this work can be considered as an alternative approach inferring the mass of the compact object.

One can state that the value for the radius of the central compact object is realistic, because it is less than the radius of the innermost stable circular orbits r_{ISCO} and, in turn, r_{ISCO} itself is less than inner and outer radii of the accretion disk. We assumed that our compact object is a non-rotating body; it could be either a neutron star or a black hole, but not a white dwarf since its mass exceeds the Chandrasekhar mass limit. The mass values suggest these LMXBs harbor neutron stars but not black holes, unless the neutron star critical mass for gravitational collapse is very small. However, the

observation of two solar mass neutron star in PSR J0348+0432 [30] puts this value as a firm lower limit to the mass of black holes form from stellar gravitational collapse.

In order to have further confirmation of the nature of the compact object as a neutron star or a black hole one should consider a more general solution for the Einstein field equations taking into account the mass M, the angular momentum J and the quadrupole moment Q. It is well-known that for a rotating black hole we have the relation between the angular momentum and quadrupole moment $Q=J^2/M$ and for a rotating neutron star we have always this relation $Q>J^2/M$. After inferring the values of M, J and Q, and comparing the relationship for Q and J one can determine that the

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compact object is a neutron star or a black hole for sure. The first attempt in this direction is taken in Refs. [31-32]. If a neutron star nature for these objects is confirmed, these calculations will serve in addition to confirm or reject whether some of them are indeed more massive than PSR J0348+0432 as Table 1 suggests. However this issue is out of the scope of the current work. It will be considered in our future works.

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UDC 539

Schwinger effect for non-Abelian gauge bosons

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We investigate the Schwinger effect for the gauge bosons in an unbroken non-Abelian gauge theory (*e.g.* the gluons of QCD). For the simplicity the SU(2) non-Abelian gauge theory is considered. We consider both constant "color electric" fields and "color magnetic" fields as backgrounds. As in the Abelian Schwinger effect we find there is production of "gluons" for the color electric field, but no particle production for the color magnetic field case. Since the non-Abelian gauge bosons are massless there is no exponential suppression of particle production due to the mass of the electron/positron that one finds in the Abelian Schwinger effect. Despite the lack of an exponential suppression of the gluons, we find that the critical field strength is even larger in the non-Abelian case as compared to the Abelian case. The calculations for gluon production from a uniform chromoelectric field are made. This is the result of the confinement phenomenon on QCD.

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Introduction

The Schwinger effect [1, 2] is the creation of electron-positron pairs from a uniform electric field. The energy to create the pairs comes from energy of the electric field. Since the rest mass energy of the electron is large relative to the electric field energy density that one can achieve in the laboratory the Schwinger effect has not been observed experimentally in the form in which it was first calculated – a uniform background electric field producing electron-positron pairs. The reason for this is the probability per unit volume per unit time of creating e^+e^- pairs is given by

$$\frac{\text{prob}_{e^+e^-}}{\text{Vol}\times time} \propto e^2 E_{EM}^2 \exp\left(-\frac{\pi m^2}{eE_{EM}}\right), \qquad (1)$$

where *e* and *m* are the charge and mass of the electron/positron, E_{EM} is the magnitude of the uniform electric field and *c* and \hbar have been set to 1. Since the electron/positron have a finite rest mass the exponential will suppress e^+e^- production unless $\frac{\pi m^2}{eE_{EM}} \sim 1$. If one takes $\frac{\pi m^2}{eE_{EM}} = 1$, restores factors of *c* and \hbar then one finds the this uniform electric field magnitude is enormous $-E_{EM} = 1.4 \times 10^{14} \frac{dyne}{esu}$ or $E_{EM} = 4.2 \times 10^{18} \frac{N}{c}$ – well beyond the present

ability to create in a laboratory. If electron/positrons were lighter, or massless, one would more readily be able to observe the electromagnetic Schwinger effect.

While the electron/positron mass is non-zero there is a system where a charged particle is massless and thus the Schwinger effect should not have the exponential suppression found in the electromagnetic case. The is the case of gluons in quantum chromodynamics (QCD). Gluons are massless and carry color charge due to the non-Abelian nature of QCD. Thus we want to investigate the QCD version of the Schwinger effect whereby a constant background color "electric" field creates gluons. Of course due to color confinement one can not really make a constant color field over a macroscopic distance. However within QCD bound systems one might think of the quantum chromodynamic flux tubes that are postulated to bind quarks together into mesons/baryons as giving a uniform color electric and color magnetic fields inside the tubes.

In this work we consider, for simplicity, the SU(2) non-Abelian gauge theory. This has almost all of the features of larger non-Abelian groups like SU(3) but the details of the calculations are simpler and more transparent. Often in this work we will mention "gluons" or QCD which technically refer to the strong SU(3) gauge group, but we mean by this the SU(2) toy model of the true SU(3) interaction.

Brief review of electric Schwinger effect

In this section we will give a very brief overview of Schwinger's method for calculating pair production in the case of Abelian electromagnetic fields. In the following section we will use this background to address pair production in a non-Abelian color electric and color magnetic fields. In addition to the original articles on the Schwinger effect [1, 2] there are many good discussion of this method in the literature. A very small sample of these are found in references [3, 4, 5, 6]. We will follow most closely the pedagogical article [3].

To begin the vacuum to vacuum transition amplitude is given very generally by the expression

$$amp(vac \rightarrow vac) \rightarrow \int [d\phi] \exp(i \int d^4x L(\phi, \partial_\mu \phi)),$$
 (2)

where ϕ is some generic field, $\int [d\phi]$ is a path integral over different field configurations, and $L(\phi, \partial_{\mu}\phi)$ is the Lagrange density for the field ϕ . The Lagrange density will lead to an equation of motion for the field $\phi(x)$ in terms of some operator $O\phi$. The field $\phi(x)$ can be expanded as $\phi(x) =$ $\sum_{n} a_n \chi_n(x)$ where $\chi_n(x)$ are eigenstates of the equation of motion given by

$$0\chi_n(x) = \lambda_n \chi_n(x), \tag{3}$$

with λ_n being the eigenvalues. In terms of the operator O the vacuum to vacuum amplitude is $amp(vac \rightarrow vac) \sim \frac{const.}{deto}$ where the determinant of the operator can be written in terms the eigenvalues as $detO = \prod_n \lambda_n$. Using all this we can write out the results as

$$\frac{1}{det0} = \exp[-\ln(det0)] =$$
$$= \exp[-\ln\prod_n \lambda_n] =$$
(4)
$$= \exp\left[-\sum \ln\lambda_n\right] = \exp[-tr\ln(0)].$$

Next we use the representation of the logarithm
as
$$\ln \lambda_n = -\int_0^\infty \frac{\exp(-\lambda_n s)}{s} ds$$
 to write the middle
expression in(4) as

 \sum_{n}

$$tr(\ln 0) = -\sum_{n} \int_{0}^{\infty} \frac{\exp(-\lambda_{n}s)}{s} ds \equiv \zeta.$$
 (5)

Finally the vacuum to vacuum amplitude from (2) becomes

 $amp(vac \rightarrow vac) \propto \exp[-\zeta].$ (6)

If ζ has a real part (*i.e.* $\gamma = Re(\zeta)$) then one can square the amplitude to get the probability for pair production as

$$prob_{pair} = (1 - \exp[-2\gamma]). \tag{7}$$

This is the basic procedure which we will apply to the pair production of gluons in uniform color electric and color magnetic fields. However before moving on to this we give a few more details about the pair production of scalar particles of mass m and charge e in a uniform electric field. For a uniform electric field in the z-direction $E = E_0 \hat{z}$ the vector potential can be of the form $A(t) = -E_0 t \hat{z}$ or $\phi(z) =$ $-E_0 z$. (In the QCD case we will find a similar situation for the QCD potentials). For the timedependent vector potential, $A(t) = -E_0 t \hat{z}$, the operator in footnote 1 becomes

$$0 = \partial_t^2 - (\partial_z - ieE_0t)^2 - \partial_x^2 - \partial_y^2 + m^2.$$
(8)

The eigenvalues connected with (8) are

$$\lambda_n = eE_0(2n+1) + p_x^2 + p_y^2 + m^2, n = 0, 1, 2...$$
(9)

Using this eigenvalues in (5) and performing the sum of the different pieces of λ_n yields

$$\zeta = -iL^3 T \frac{eE_{EM}}{16\pi^2} \int_0^\infty \frac{ds}{s^2} \frac{\exp[-m^2 s]}{\sin(eE_{EM}s)},$$
 (10)

where *L* and *T* are the spatial and temporal size to "cube" inside which the system is quantized. The factor of *i* comes from doing a rotation to imaginary time and back (*i.e.* $t \rightarrow iT$). This time rotation also

involves the change $E_{EM} \rightarrow iE_{EM}$. We will use the same procedure when we carry out the QCD version of this calculation. In order to have particle production ζ needs to have a real part which will occur if the integral in (10) has an imaginary part. The integral in (10) does have imaginary parts coming

from the contour integrations involving the poles in the integrand at $s_n = n\pi/eE_{EM}$. (The $1/s^2$ divergence in the integrand in (10) leads to an infinite imaginary part which is removed via renormalization [7]). Taking semi-circular deviations around each of the poles s_n leads to a real part of ζ given by

$$\gamma = Re(\zeta) = L^3 T \frac{e^2 E_{EM}^2}{16\pi^3} \sum_{n=1}^{\infty} \frac{(-1)^{n+1}}{n^2} \exp\left(-\frac{\pi n m^2}{e E_{EM}}\right) \approx L^3 T \frac{e^2 E_{EM}^2}{16\pi^3} \exp\left(-\frac{\pi m^2}{e E_{EM}}\right).$$
(11)

Due to the exponential term the main contribution comes from n = 1 term in the sum. The result in (11) can be used to obtain the result in (1) by inserting it into (7) and dividing by (Vol \times time)

$$\frac{\operatorname{prob}_{e^+e^-}}{\operatorname{Vol\times time}} = \frac{1}{\operatorname{Vol\times time}} \left(1 - e^{-2\gamma}\right) \approx \frac{e^2 E_{EM}^2}{8\pi^3 \hbar^2 c} \exp\left(-\frac{\pi m^2 c^3}{e E_{EM} \hbar}\right) = \frac{\alpha_{EM} E_{EM}^2}{8\pi^3 \hbar} \exp\left(-\frac{\pi m^2 c^3}{e E_{EM} \hbar}\right),\tag{12}$$

where we have restored factors of \hbar and c and then written the result in terms of the fine structure constant $\alpha_{EM} = \frac{e^2}{\hbar c} \approx \frac{1}{137}$. We want to use (12) to determine $prob_{e^+e^-}$ when the electric field is at the critical value $E_{EM} \approx 1.4 \times 10^{14} \frac{dyne}{esu}$. To do this we need some way to characterize what a "natural" value is for the volume and time in the denominator of (12). For the volume we take it to be the cube of the reduced Compton wave length of the electron $Vol = (\frac{\hbar}{mc})^3 \approx 5.7 \times 10^{-32} cm^3$. For the time we take the reduced Compton time $time = \frac{\hbar}{mc^2} \approx 1.3 \times 10^{-21} sec$. Putting all these values together in (12) yields

$$prob_{e^+e^-} \approx 0.015$$
 . (13)

In the next section we will calculate the equivalent result to equation (12) but for gluons produced from uniform chromoelectric fields and uniform chromomagnetic fields. We will set the probability of gluon production (*i.e.* prob_{gg}) to the same value as that of e^+e^- production from (13) for the critical electric field, E_{EM} . In this way we will arrive at the critical chromoelectric/chromomagnetic field strength to produce gluons. The initial expectation might be that the critical color field strength might be smaller since gluons are massless so there will be no exponential suppression as occurs due to the rest mass of the electron for the QED case.

Schwinger effect for uniform color electric field and uniform color magnetic field

To calculate the production rate for gluons from uniform chromoelectric and chromomagnetic fields we follow reference [8] and place gluon field excitations in a fixed background field. For the two background fields we take a uniform chromoelectric field and uniform chromomagnetic field. These calculations are rather involved and we put the details in appendix 1 for the uniform chromoelectric field and Appendix 2 for the uniform chromomagnetic field. The result for the production rate for gluons in a uniform chromoelectric field is given by equation (42) as

$$\gamma \approx 0.00187 \times L^3 T \frac{g^2 E_0^2}{16\pi^3}.$$
 (14)

Using this result from (14) in (7) we obtain the probability for SU(2) gluon creation per unit volume and unit time

$$\frac{\text{prob}_{gg}}{\text{Vol} \times \text{time}} = \frac{1}{\text{Vol} \times \text{time}} (1 - e^{-2\gamma}) \approx$$
$$\approx \frac{0.00187g^2 E_0^2}{8\pi^3 \hbar^2 c} = \frac{0.00187\alpha_{QCD} E_0^2}{8\pi^3 \hbar}.$$
(15)

In the last step we have restored factors of \hbar and c and introduced the QCD fine structure constant $\alpha_{QCD} = \frac{g^2}{\hbar c}$. We will take $\alpha_{QCD} \approx 1$ so that we are in non-perturbative regime. For the present case we take

the distance scale to be 10^{-12} cm. This is one order of magnitude larger than the typical strong interaction bound state size of 1*fermi*. Thus is the volume factor in (15) we have $Vol = 10^{-36}$ cm³ and for the time factor we take time $= \frac{10^{-12}}{3 \times 10^{10}} = 3.3 \times 10^{-23}$ sec. Finally we take the value for the probability of gluon production, prob_{gg} at the critical chromoelectric field magnitude to be the same as that for the electromagnetic case as given in (13) namely $\text{prob}_{gg} \approx 0.015$, using these assumptions in (15) we can calculate the value of the critical chromoelectric field magnitude as

$$E_0 \approx 2.5 \times 10^{17} \frac{\text{dyne}}{\text{esu}}.$$
 (16)

This is then three orders of magnitude larger than the E&M critical field value of $E_{EM} \approx 1.4 \times$ $10^{14} \frac{dyne}{esu}$. Thus although gluons are massless (and thus there is no exponential suppression factor as in the electromagnetic case due to the mass of the electron) this does not lower the critical chromoelectric field value, and in fact we find the critical field value for QCD is three orders of magnitude larger than in the *E*&*M* case. This, at first sight, surprising result arises from the fact that QCD has a confinement scale in the range of 1fermi = 10^{-13} cm. This distance is smaller than the Compton wave length of the electron which we used to set the volume and time in the electromagnetic case as $Vol = \left(\frac{\hbar}{mc}\right)^3 \approx 5.7 \times 10^{-32} \text{ cm}^3 \text{ and time} = \frac{\hbar}{mc^2} \approx$ 1.3×10^{-21} sec respectively. In the QCD case we overestimated the distance scale as 10 times larger than 1fermi = 10^{-13} cm and also used this to obtain the characteristic time for the QCD case. Even though we (slightly) overestimated the QCD distance and time scales (which would by (15) would be favorable toward to decreasing the critical QCD field strength) we nevertheless found that the critical QCD field strength was larger than the critical *E*&*M* critical field strength. Even if we had used (without justification) the electron Compton wave length and associated Compton time in (15) this would give a QCD critical field strength of $E_0 \sim 10^{14} \frac{dyne}{esu}$ *i.e.* the same as for E&M. Thus the masslessness of the gluons does not lead to a lower critical field strength relative to what is found in the canonical Schwinger mechanism case.

Conclusions

We presented the Schwinger effect for SU(2) gluons. We did this since gluons being massless we expect this effect to be more important than standard Schwinger effect which is exponentially suppressed due to electron/positron rest mass. The calculation details for gluon production from a uniform chromoelectric field and from a uniform chromomagnetic field are found in Appendix A and B respectively. As in the electromagnetic case a chromoelectric field will produce gluons while the chromomagnetic field does not.

gluon The motivation for investigating production, as opposed to the production of quarks, was that since gluons are massless there will not be an exponential suppression due to the mass of the quarks that one finds in the electromagnetic case due to the mass of the electron (i.e. the last exponential term in (1)). However, due to confinement the natural length scales and time scale for the QCD case were several orders of magnitude smaller than the similar scales for the electromagnetic case which were set to the reduced Compton length of the electron and the associated time. This in turn made the factor Vol \times time smaller for the OCD case as compared to the *E*&*M* case which in turn, given the expression for the probability for production per unit volume per unit time in (15) gave a larger magnitude for the chromoelectric field for producing gluons as compared to the magnitude of the electric field for producing electrons and positrons.

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Appendix I: Uniform Color Electric Field Calculation

To have a constant color electric field in the $\hat{z} = 3$ spatial direction and in the a = 3 color direction,

$$E^{a}_{\mu} \rightarrow E^{3}_{3} = F^{3}_{03} = \partial_{0}A^{3}_{3} - \partial_{3}A^{0}_{0} + g\varepsilon^{3bc}A^{b}_{3}A^{c}_{0} = E_{0}\hat{z}, \qquad (17)$$

there are two gauge choices one can make for the potential

$$(i)A^a_\mu = E_0 t \delta_{\mu 3} \delta^{a3}; \ (ii)A^a_\mu = -E_0 z \delta_{\mu 0} \delta^{a3}.$$
 (18)

For the calculation in this appendix we use the (*i*) form of the potential. Inserting form (*i*) from (18) into (17) does give $E_{\mu}^{a} \rightarrow E_{3}^{3} = \partial_{0}A_{3}^{3} = E_{0}\hat{z}$. We

now take the potential (*i*) from (18) as a background potential (*i.e.* $A_{\mu}^{(0)a}$) and we consider small variation A_{ν}^{a} around this background (the background nature of the potential is indicated by the superscript (0)). In this way the QCD action can be written as

$$F^{a}_{\mu\nu}F^{a\mu\nu} = \begin{bmatrix} \left(\partial_{\mu}A^{(0)a}_{\nu} - \partial_{\nu}A^{(0)a}_{\mu}\right) + \left(\partial_{\mu}A^{a}_{\nu} - \partial_{\nu}A^{a}_{\mu}\right) \\ + g\varepsilon^{abc} \left(A^{(0)b}_{\mu} + A^{b}_{\mu}\right) \left(A^{(0)c}_{\nu} + A^{c}_{\nu}\right) \end{bmatrix}^{2}.$$
(19)

We now run through the color indices a = 1,2,3and insert the explcit form of the background potential $A_{\mu}^{(0)3} = E_0 t \delta_{\mu 3}$. The only non-zero values of $\partial_{\mu}A_{\nu}^{(0)3} - \partial_{\nu}A_{\mu}^{(0)3} + g\varepsilon^{3bc}A_{\mu}^{(0)b}A_{\nu}^{(0)c}$ are when $\mu = 0$ and $\nu = 3$ or vice versa, each of which contribute a term of E_0 .

$$F_{\mu\nu}^{a}F^{a\mu\nu} = \left\{\partial_{\mu}A_{\nu}^{1} - \partial_{\nu}A_{\mu}^{1} + g\left[A_{\mu}^{2}(A_{\nu}^{3} + E_{0}t\delta_{\nu3}) - (A_{\mu}^{3} + t\delta_{\mu3})A_{\nu}^{2}\right]\right\}^{2} \\ + \left\{\partial_{\mu}A_{\nu}^{2} - \partial_{\nu}A_{\mu}^{2} + g\left[(A_{\mu}^{3} + E_{0}t\delta_{\mu3})A_{\nu}^{1} - A_{\mu}^{1}(A_{\nu}^{3} + E_{0}t\delta_{\nu3})\right]\right\}^{2} \\ + \left[\partial_{\mu}A_{\nu}^{3} - \partial_{\nu}A_{\mu}^{3} + g(A_{\mu}^{1}A_{\nu}^{2} - A_{\mu}^{2}A_{\nu}^{1})\right]^{2} \\ + 2E_{0}^{2} - 2E_{0}\left[\partial_{\mu}A_{\nu}^{3} - \partial_{\nu}A_{\mu}^{3} + g(A_{\mu}^{1}A_{\nu}^{2} - A_{\mu}^{2}A_{\nu}^{1})\right](\delta_{\mu3}\delta_{\nu0} - \delta_{\mu0}\delta_{\nu3})$$
(20)

We now expand the above expression to 2^{nd} order in the A^a_{μ} which gives

$$F_{\mu\nu}^{a}F^{a\mu\nu} \approx \approx \left[\partial_{\mu}A_{\nu}^{1} - \partial_{\nu}A_{\mu}^{1} - gE_{0}t\left(A_{\nu}^{2}\delta_{\mu3} - A_{\mu}^{2}\delta_{\nu3}\right)\right]^{2} + \left[\partial_{\mu}A_{\nu}^{2} - \partial_{\nu}A_{\mu}^{2} - gE_{0}t\left(A_{\mu}^{1}\delta_{\nu3} - A_{\nu}^{1}\delta_{\mu3}\right)\right]^{2} (21) + \left(\partial_{\mu}A_{\nu}^{3} - \partial_{\nu}A_{\mu}^{3}\right)^{2} + 2E_{0}^{2} - 4E_{0}\left[\partial_{3}A_{0}^{3} - \partial_{0}A_{3}^{3} + g\left(A_{3}^{1}A_{0}^{2} - A_{3}^{2}A_{0}^{1}\right)\right].$$

We now require that at spatial and temporal infinity the variation of the potential goes to zero $A_0^3(x_3 \to \pm \infty) = 0$ and $A_3^3(x_0 \to \pm \infty) = 0$. This

causes the source terms for A^3_{μ} in the last term to vanish by partial integration. Note that $(\partial_{\mu}A^3_{\nu} - \partial_{\nu}A^3_{\mu})^2$ is a free Lagrange density, so it is not of interest and can be dropped.

$$F^{a}_{\mu\nu}F^{a\mu\nu} = = \left[\partial_{\mu}A^{1}_{\nu} - \partial_{\nu}A^{1}_{\mu} - gE_{0}t\left(A^{2}_{\nu}\delta_{\mu3} - A^{2}_{\mu}\delta_{\nu3}\right)\right]^{2} + \left[\partial_{\mu}A^{2}_{\nu} - \partial_{\nu}A^{2}_{\mu} - gE_{0}t\left(A^{1}_{\mu}\delta_{\nu3} - A^{1}_{\nu}\delta_{\mu3}\right)\right]^{2} (22) + 2E^{2}_{0} - 4E_{0}g(A^{1}_{3}A^{2}_{0} - A^{2}_{3}A^{1}_{0}).$$

We now re-write this using complex potential forms as

$$F_{\mu\nu}^{a}F^{a\mu\nu} = \begin{bmatrix} \partial_{\mu}(A_{\nu}^{1} + iA_{\nu}^{2}) - \partial_{\nu}(A_{\mu}^{1} + iA_{\mu}^{2}) \\ -gE_{0}t[(A_{\nu}^{2} - iA_{\nu}^{1})\delta_{\mu3} - (A_{\mu}^{2} - iA_{\mu}^{1})\delta_{\nu3}] \end{bmatrix}^{2} + 2E_{0}^{2} - i2gE_{0}[(A_{3}^{1} + iA_{3}^{2})(A_{0}^{1} - iA_{0}^{2}) - (A_{0}^{1} + iA_{0}^{2})(A_{3}^{1} - iA_{3}^{2})].$$

$$(23)$$

We now replace A^1_{μ} and A^2_{μ} by defining the following complex potentials

$$W_{\mu} = \frac{1}{\sqrt{2}} \left(A_{\mu}^{1} + i A_{\mu}^{2} \right),$$

$$W_{\mu}^{\dagger} = \frac{1}{\sqrt{2}} \left(A_{\mu}^{1} - i A_{\mu}^{2} \right).$$
 (24)

In terms of these new, complex potentials $F^a_{\mu\nu}F^{a\mu\nu}$ becomes

$$F^{a}_{\mu\nu}F^{a\mu\nu} = \left|\sqrt{2}\,\partial_{\mu}W_{\nu} - \sqrt{2}\,\partial_{\nu}W_{\mu} - i\sqrt{2}gE_{0}tW_{\nu}\delta_{\mu3} + i\sqrt{2}gE_{0}tW_{\mu}\delta_{\nu3}\right|^{2} + 2E_{0}^{2} - -i2gE_{0}(2W_{3}^{\dagger}W_{0} - 2W_{0}^{\dagger}W_{3}).$$
(25)
This finally leads to the following Lagrange density for gluons in the background potential of a uniform color electric field

$$\mathcal{L} = -\frac{1}{4} F^{a}_{\mu\nu} F^{a\mu\nu}$$
(26)
$$= -\frac{1}{2} |(\partial_{\mu} - igE_{0}t\delta_{\mu3})W_{\nu} - (\partial_{\nu} - igE_{0}t\delta_{\nu3})W_{\mu}|^{2} -igE_{0}(W_{3}^{\dagger}W_{0} - 2W_{0}^{\dagger}W_{3}) - \frac{1}{2}E_{0}^{2}.$$

This Lagrange density leads to the following equation of motion

$$\begin{aligned} (\partial^{\mu} - igE_{0}t\delta^{\mu3}) [(\partial_{\mu} - igE_{0}t\delta_{\mu3})W_{\nu} \\ &- (\partial_{\nu} - igE_{0}t\delta_{\nu3})W_{\mu}] - \\ &- igE_{0}(\delta_{\nu3}W_{0} - \delta_{\nu0}W_{3}) = 0. \end{aligned}$$
(27)

Choosing the background gauge condition $(\partial^{\mu} - igE_0 t\delta^{\mu 3})W_{\mu} = 0$ simplifies (27) to

$$(\partial^{\mu} - igE_{0}t\delta^{\mu3})(\partial_{\mu} - igE_{0}t\delta_{\mu3})W_{\nu} = -2igE_{0}(W_{0}\delta_{\nu3} - W_{3}\delta_{\nu0}).$$
(28)

The above equation can be written in matrix form as

$$(\partial^{\mu} - igE_0 t\delta^{\mu 3})^2 W_{\nu} - 2gE_0 \begin{pmatrix} 0 & 0 & 0 & -i \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ i & 0 & 0 & 0 \end{pmatrix} W_{\mu} = 0.$$
⁽²⁹⁾

The four eigenvalues for this matrix are ± 1 and a double eigenvalue of zero. The zero eigenvalues are excluded by our chosen gauge condition so for now we consider just the eigenvalues ± 1 . Thus (29) becomes

$$[(\partial^{\mu} - igE_0 t\delta^{\mu 3})^2 W_{\nu} - 2gE_0(\pm 1)]W_{\nu} = 0.$$
 (30)

Recalling that we are using the metric signature (+, -, -, -) (30) can be expanded as

$$\left\{\frac{\partial^2}{\partial t^2} - \frac{\partial^2}{\partial x_1^2} - \frac{\partial^2}{\partial x_2^2} + \left(i\frac{\partial}{\partial x_3} + gE_0t\right)^2 \mp 2gE_0\right\}W_{\nu} = 0.$$
(31)

Next we Fourier transform (31) to $\widetilde{W}_{\nu}(t, k_1, k_2, k_3)$ with the result

$$\left\{\frac{\partial^2}{\partial t^2} + k_1^2 + k_2^2 + g^2 E_0^2 \left(\frac{k_3}{gE_0} + t\right)^2 \pm 2gE_0\right\} \widetilde{W}_{\nu} = 0.$$
(32)

Now making the substitution $t' = \frac{k_3}{gE_0} + t$ (for a rotation to imaginary time, $t' \to -i\tau$, $E_0 \to -iE_0$ we arrive at we arrive at

$$\left\{-\frac{\partial^2}{\partial\tau^2} + g^2 E_0^2 \tau'^2 + k_1^2 + k_2^2 \pm 2igE_0\right\} \widetilde{W}_{\nu} = 0.$$
(33)

The first two terms in (33) correspond to a harmonic oscillator with frequency $\omega = gE_0$, which has eigenvalues given by $-\frac{\partial}{\partial \tau^2} + g^2 E_0^2 \tau^2 \rightarrow 2\left(n + \frac{1}{2}\right)gE_0$. With this (33) becomes $\{(2n+1)gE_0 + k_1^2 + k_2^2 \pm igE_0\}\widetilde{W}_{\nu} = 0$. From this equation we can read of the eigenvalues as

$$\lambda_n = (2n+1)gE_0 + k_1^2 + k_2^2 \pm 2igE_0 \quad .(34)$$

Note that λ_n is a combination of discrete (*i.e.* $(2n + 1)gE_0$) and continuous (*i.e.* $k_1^2 + k_2^2$) parts. Substituting these eigenvalues from (34) into (5) we find that ζ becomes

$$\zeta = -\sum_{n} \int_{0}^{\infty} \frac{\mathrm{d}s}{s} \exp\{-\left[(2n+1)gE_{0} + k_{1}^{2} + k_{2}^{2} \pm 2igE_{0}\right]s\}$$
(35)

We take our system to be quantized in a cubical spatial volume with sides of length *L* and over a total

(imaginary) interaction time $\tau = -iT$ which then turns (35) into

$$\zeta = -L \int_{-\infty}^{\infty} \frac{dk_1}{(2\pi)} L \int_{-\infty}^{\infty} \frac{dk_2}{(2\pi)} L \int_{0}^{gE_0\tau} \frac{dk_3}{(2\pi)} \sum_{n=0}^{\infty} \int_{0}^{\infty} \frac{ds}{s} \exp\{-[(2n+1)gE_0 + k_1^2 + k_2^2 \pm 2igE_0]s\}.$$
 (36)

The k_1 and k_2 integrations related to the momentum in the free directions and are simple Gaussian integrals, which give two factors of $\sqrt{\frac{\pi}{s}}$. The integration in the k_3 direction is related to the

momentum in the *z* direction which is the direction of the chromoelectric field. Thus as in [3] this integration is constrained to the range $0 < k_3 < gE_0\tau$. Performing the k_1, k_2, k_3 integrations gives

$$\zeta = -L^3 \tau \frac{gE_0}{8\pi^2} \sum_{n=0}^{\infty} \int_0^\infty \frac{\mathrm{d}s}{s^2} \exp\{-[(2n+1)gE_0 \pm 2igE_0]s\}.$$
(37)

We note that $\sum_{n=0}^{\infty} e^{-(2n+1)gE_0s} = \frac{1}{2} \frac{1}{\sinh(gE_0s)}$ which then transforms (37) into

$$\zeta = -L^3 \tau \frac{gE_0}{16\pi^2} \int_0^\infty \frac{\mathrm{d}s}{s^2} \frac{e^{\pm 2igE_0 s}}{\sinh(gE_0 s)} \ . \tag{38}$$

We now return to real time via the rotation $\tau \rightarrow iT$ which also involves changing the magnitude of the chromoelectric field as $E_0 \rightarrow iE_0$. This gives

$$\zeta = -iL^3 T \frac{gE_0}{16\pi^2} \int_0^\infty \frac{\mathrm{d}s}{s^2} \frac{e^{\mp 2gE_0 s}}{\sin(gE_0 s)} \ . \tag{39}$$

Equation (39) is now at the point in the

electromagnetic calculation given by equation (10), but now the exponential factor involving the electron mass (exp[$-m^2s$]) is replaced by an exponential suppression involving the field strength ($e^{\mp 2gE_0s}$). As before if ζ has a real part (*i.e.* if the integral in (39) has an imaginary contribution) there will be particle production. As in the case of the electromagnetic integral in (10) the integral in (39) does have an imaginary contribution coming from the poles of $\frac{1}{\sin(gE_0s)}$ which are located at $s_n = \frac{n\pi}{gE_0}$, where *n* is an integer. As before we ignore the singularity at s = 0. The integration contours are infinitesimal semicircular in the upper half plane and from (39) this gives

$$\gamma = \operatorname{Re}(\zeta) = -iL^{3}T \frac{gE_{0}}{16\pi^{2}} \sum_{n=1}^{\infty} \int_{s_{n}-\varepsilon}^{s_{n}+\varepsilon} \frac{\mathrm{d}s}{s^{2}} \frac{e^{\mp 2gE_{0}s}}{\sin(gE_{0}s)} = = -iL^{3}T \frac{gE_{0}}{16\pi^{2}} \sum_{n=1}^{\infty} \int_{s_{n}-\varepsilon}^{s_{n}+\varepsilon} \frac{\mathrm{d}s}{s^{2}} \frac{e^{\mp 2gE_{0}s}}{\cos(gE_{0}s_{n})gE_{0}(s-s_{n})}.$$
(40)

In the last step we have expanded $\sin(gE_0s)$ around the poles at s_n . From the Residue theorem, the poles of the integral in (40) give $-i\pi \times$ \sum Res(function), where the sum is over the residue of the integrand. The result is

$$\gamma = \operatorname{Re}(\zeta) = -L^{3}T \frac{1}{16\pi} \sum_{n=1}^{\infty} \frac{e^{\mp 2gE_{0}s_{n}}}{s_{n}^{2} \cos(gE_{0}s_{n})} = L^{3}T \frac{g^{2}E_{0}^{2}}{16\pi^{3}} \sum_{n=1}^{\infty} (-1)^{n+1} \frac{e^{\mp 2n\pi}}{n^{2}}, \quad (41)$$

where in the last step we have substitute in the poles $s_n = \frac{n\pi}{gE_0}$ and simplify. The $(-1)^{n+1}$ comes from $-\cos(n\pi)$. The $e^{+n\pi}$ choice in (41) leads to a divergent γ so we take the $e^{-n\pi}$ choice in (41) which leads to

$$\gamma = L^3 T \frac{g^2 E_0^2}{16\pi^3} \sum_{n=1}^{\infty} (-1)^{n+1} \frac{e^{-2n\pi}}{n^2} \approx$$
$$\approx 0.00187 \times L^3 T \frac{g^2 E_0^2}{16\pi^3}. \tag{42}$$

In the last step we have carried out the sum numerically with the result $\sum_{n=1}^{\infty} (-1)^{n+1} \frac{e^{-2n\pi}}{n^2} \approx$ 0.00187.

Calculations similar to the above were carried out in [9, 10, 11] for gluon production in a constant SU(3) color electric field. In these works the integration over the transverse momentum was not carried out, but if one does carry out the integration of the transverse momentum of the results in [9, 10, 11] one finds that our result for γ in (42) is consistent with these previous results. In particular there is no

mass suppression (as expected) and the production rate is proportional to $g^2 E_0^2$

Appendix II: Uniform Color Magnetic Field Calculation

In this appendix we show that, unlike the uniform color electric field of appendix I, a uniform color magnetic field does not produce gluons. This is similar to what occurs in the electromagnetic Schwinger effect – a uniform magnetic field does not produce electrons/positrons.

A constant color magnetic field in the $\hat{z} = 3$ spatial direction and in the a = 3 color direction.

$$B^{a}_{\mu} \to B^{3}_{3} = F^{3}_{12} = \partial_{1}A^{3}_{2} - \partial_{2}A^{3}_{1} + g\varepsilon^{3bc}A^{b}_{1}A^{c}_{2} = H_{0}\hat{z}, \qquad (43)$$

can be obtained by the potential

$$A^{a}_{\mu} = -H_0 x_1 \delta_{\mu 2} \delta^{a3}. \tag{44}$$

With the potential in (44) we perform a long calculation that is similar to the one for the constant color electric field, which leads to

$$(\partial^{\mu} - igH_0 x \delta^{\mu 2})^2 W_{\nu} - 2gH_0 \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & i & 0 \\ 0 & -i & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix} W_{\mu} = 0.$$
(45)

which is the color magnetic version of (29). Expanding (45) out we arrive at the color magnetic version (31) which leads to

$$\left[\frac{\partial^2}{\partial t^2} - \frac{\partial^2}{\partial x^2} - \frac{\partial^2}{\partial z^2} \mp 2gH_0 - \left(i\frac{\partial}{\partial y} + gH_0x\right)^2\right]W_{\nu} = 0.$$
(46)

Next we Fourier transform (46) to $\widetilde{W}_{\nu}(t, k_1, k_2, k_3)$ gives the color magnetic version of (32)

$$\left[-E^{2} + k_{3}^{2} \mp 2gH_{0} - \frac{\partial^{2}}{\partial x^{2}} + g^{2}H_{0}^{2}\left(x + \frac{k_{2}}{gH_{0}}\right)^{2}\right]\widetilde{W}_{\nu} = 0.$$
(47)

becomes

$$\left[-E^{2} + k_{3}^{2} \mp 2gH_{0} - \frac{\partial^{2}}{\partial\eta^{2}} + g^{2}H_{0}^{2}\eta^{2}\right]\widetilde{W}_{\nu} = 0.$$
(48)

The $-\frac{\partial^2}{\partial n^2} + g^2 H^2 \eta^2$ part of the above equation is the equation for a simple harmonic oscillator which

Making the change of variable $\eta = x + \frac{k_2}{gH_0}$ this has eignevalues $2\left(n + \frac{1}{2}\right)gH_0$. Substituting this eigenvalue into (48) leads to

$$\left[-E^{2} + k_{3}^{2} \mp 2gH_{0} + 2\left(n + \frac{1}{2}\right)gH_{0}\right]\widetilde{W}_{\nu} = 0.$$
(49)

We now rotate to imaginary time (Euclidean) as $t \rightarrow -i\tau$ and in conjunction with this we rotate the energy as $E \rightarrow = -iE$. This turns (49) into

$$\left[E^{2} + k_{3}^{2} \mp 2gH_{0} + 2\left(n + \frac{1}{2}\right)gH_{0}\right]\widetilde{W}_{\nu} = 0.$$
 (50)

The eigenvalues for the system can then be written out as

$$\lambda_n = E^2 + k_3^2 \mp 2gH_0 + 2\left(n + \frac{1}{2}\right)gH_0.$$
 (51)

Now substituting (51) into (5) yields ζ for this case as

$$\zeta = -\sum_{n} \int_{0}^{\infty} \frac{\mathrm{d}s}{s} \exp\{-[E^{2} + k_{3}^{2} + (2n+1)gH_{0} \mp 2gH_{0}]s\}.$$
(52)

Recalling that we are quantizing in a cube with sides length *L* and over a total (imaginary) interaction

time $\tau = -iT$ transforms (52) into

$$\zeta = -\tau \int_{-\infty}^{\infty} \frac{dE}{(2\pi)} L \int_{-\infty}^{\infty} \frac{dk_3}{(2\pi)} L^2 \frac{gH_0}{2\pi} \sum_{n=0}^{\infty} \int_0^{\infty} \frac{ds}{s} \exp\{-[E^2 + k_3^2 + (2n+1)gH_0 + 2gH_0]s\}.$$
 (53)

The *E* and k_3 integrations are simple Gaussian integrals that give two factors of $\sqrt{\frac{\pi}{s}}$. Thus (53) simplifies to

$$\zeta = -\tau L^3 \frac{gH_0}{8\pi^2} \sum_{n=0}^{\infty} \int_0^\infty \frac{\mathrm{d}s}{s^2} \exp\{-[(2n+1)gH_0 \mp 2gH_0]s\}.$$
(54)

We now use the geometric series $\sum_{n=0}^{\infty} e^{-(2n+1)gHs} = \frac{1}{2} \frac{1}{\sinh(gHs)} \text{ to write (54) as}$

$$\zeta = -\tau L^3 \frac{gH_0}{16\pi^2} \int_0^\infty \frac{\mathrm{d}s}{s^2} \frac{e^{\pm 2gH_0 s}}{\sinh(gH_0 s)} \ . \tag{55}$$

We now return to real time via the rotation $\tau \rightarrow iT$.

$$\zeta = -iTL^3 \frac{gH_0}{16\pi^2} \int_0^\infty \frac{\mathrm{d}s}{s^2} \frac{e^{\pm 2gH_0 s}}{\sinh(gH_0 s)} \ . \tag{56}$$

In contrast to the color electric case of the the previous appendix where the rotation back to real time, $\tau \rightarrow iT$, was accompanied by a rotation of the

electric field amplitude, $E_0 \rightarrow iE_0$, here the rotation back to real time does not lead to a change in the color magnetic field amplitude. In comparing (56) with (39) one finds that (56) does not have the series of poles at $s_n = n\pi/qE_0$ that are found in (39). Therefore the integral in (56) does not have any imaginary contributions coming from the residue theorem as was the case for the integral in (39). Thus from (56) the real part of ζ is zero so $Re(\zeta) = \gamma = 0$. Thus in the case of a uniform color magnetic field there is no particle production as is expected form the electromagnetic case where one finds that a constant magnetic field does not produce electron/positron pairs.

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Whittaker asymptotics of shell-model wave functions for excited states of ¹³C

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Halo and skin structure of $1/2^+$, $3/2^+$, $5/2^+$ excited states of ¹³C nucleus is under investigation. The modified radial functions have been constructed basing on the shell model functions. The matching procedure was performed while using the corresponding Whittaker exponential-like asymptotics. To find the matching radius via the oscillator parameter r_0 three options were examined related to the experimental and theoretical data on the mean square radii, and uncertainty relation. The renormalization of the modified functions shows the input of the asymptotic region near 15-20%. The most qualitative effect is the redistribution of the probability density both at short and long-range distances. The obtained functions are given as parametrization by Gauss basis. It is proposed to confirm the observed halo and skin states of ¹³C via the impulse distributions measured with different probing projectile like high-energy protons or α -particles. The most probable halo effect the 2S-state reveals due to the node behavior of the corresponding radial wave function.

Key words: halo nuclei, skin state, shell model, oscillator parameter, Whittaker function, matching radius. PACS: 24.10

Introduction

Currently, vast experimental material is assembled on the study the unusual properties of some atomic nuclei, known as the halo-states [1-5]. The defining feature of a halo was from the beginning understood to be a large spatial extension caused by neutrons tunneling out from a nuclear core. Nuclei may reveal not only well-developed *halo* states but also something intermediate between normal nuclei and halo nuclei, so called *skin*-states.

Halo effect research attractiveness that is quite enough reliably identify two main features of halo states as large root mean radius r_{ms} and narrow localized impulse distributions. These two characteristics, obviously, related to each other according the Heisenberg uncertainty relation $(\Delta x \Delta p \sim \hbar)$.

Despite the seeming simplicity and transparency of the question, both experimental and theoretical studies still face certain difficulties. First of all, it is ambiguity on rms radii data [6-7]. The difficulty lies in the fact that the lifetime of most neutron-rich isotopes is extremely short and is typically a few milliseconds. It is therefore to work with short-lived isotopes needed entirely new technique, compared with conventional ones. Recent advances are related to the collinear laser beams and anti-collinear technologies (CACLB) of the European Organization for Nuclear Research. Today, the installation ISOLDE at CERN synthesized radioactive isotopes up to Z = 10 in a collision energy of 1.4 GeV protons on uranium carbide target. Currently, it reports on the results of measurements of the charge and mass and radii for ^{7,9,10}Be isotopes by laser spectroscopy [8]. With great precision, it was found that ¹¹Be is a halo-nucleus with a radius of 7 *fm*, to compare ¹⁰Be isotope core radius is 2.5 *fm*. Experiments are planned to heavier isotopes, particularly for the carbon-oxygen group.

Theoretical models deal with the description of the nuclei with prominent α - cluster structure, which include the majority of *p*-shell nuclei, may be represented as a semi-phenomenological and microscopic. The first, are the cluster models and their various modifications [9]. To the second ones may refer the models such as the resonating group method (RGM), the method of K-harmonics, variational Monte Carlo (VMC), the method of fermion molecular dynamics (FMD), and others. It is believed that microscopic models not contain adjustable parameters. However, they are based on the nucleon-nucleon potentials, which, in turn, are fitted according to the elastic NN – scattering in a wide range of energies, so there are parameters a lot.

At the same time almost all the model approaches are based exactly on the data on the shell structure of atomic nuclei, as on the comparative, which are considered at the present time as the classic ones and obtained in the framework of the shell model (SM), which has only one oscillator parameter r_0 .

For the halo-states the radial functions that characterize the distribution of the probability density, can be divided into *internal* and *external* conventional parts. The first is a model-depending, and the second asymptotic one is model-independent. The last one determines the mean square r_{ms} size of the nuclear system, as well as so-called asymptotic normalization coefficient (ANC), which can be measured experimentally [10-11]. All models somehow have to "converge" in the section point, call it a matching radius r_m of these two areas. Thus, this is the main task to identify and substantiate the value of the r_m radius.

Present paper reports on the modification of oscillatory wave functions for low-lying 2s-, 2d-excited states with $J^{\pi} = 1/2^+$, $3/2^+$, $5/2^+$ of ¹³C nucleus. To construct the modified functions we have used the matching procedure of oscillatory wave functions with corresponding Whittaker functions.

In this context, the lower bound of the asymptotic region r_m is defined, and it allows to answer a question about a pronounced halo, skin- or normal structure of these states. The advantage of using the shell model is that almost all the calculations can be carried out analytically.

Modification procedure for the oscillator radial wave functions

We are basing on the fundamental postulate of nonrelativistic quantum mechanics telling that functions to be regarded as wave functions (WF) should be square integrated, continuous, unambiguous, and final.

Assume the potential in Schrodinger radial equation is defined in two space intervals $0 < r \le r_m$ and $r_m \le r < \infty$. Such a division is conventional, and depending on the properties of the treating microsystem may consist of more than two intervals. Let us restricted by one transition point.

The matching radius r_m we can find unambiguously from the continuity condition

$$\begin{cases} u_1(r_m) = u_2(r_m) & (a) \\ u'_1(r_m) = u'_2(r_m) & (b) \end{cases}$$
(1)

Here $u_1(r)$ is any model function that should be modified providing the correct extended asymptotic behavior by some appropriate analytical $u_2(r)$ function. As $u_1(r)$ the shell model radial oscillator WF have been used $u_1(r)=R_{n\ell}(r)$ for the state with main quantum number *n* and orbital momentum ℓ . For $u_2(r)$ various functions with exponential asymptotic at $r \rightarrow \infty$ may be used. Here we are taking $W_{0,\ell}(z)$ Whittaker functions [12] as $u_2(r)$

$$u_2(r) = C_{n\ell} \frac{\sqrt{2k_0}}{r} W_{0,\ell}(z) , \qquad (2)$$

where $z = 2k_0r$ – dimensionless variable, k_0 – wave number. Factor $C_{n\ell}$ is asymptotic normalization coefficient.

To operate with functions of one and the same dimension expression (2) should be rewritten as the following

 $u_2(r) = C_{n\ell} \omega_{0\ell}(r),$

$$\omega_{0,\ell}(r) = \frac{\sqrt{2k_0}}{2k_0} W_{0,\ell}(z) .$$
 (3)

Therefore, the continuity condition (1) may be represented as equation of type

$$\frac{R_{n\ell}'(r)}{R_{n\ell}(r)} = \frac{\omega_{0,\ell}'(r)}{\omega_{0,\ell}(r)},\tag{4}$$

and the corresponding real roots define the matching radius r_m . The solutions may be found analytically or numerically. To find asymptotic constant $C_{n\ell}$ equation (1a) is used

$$C_{n\ell} = \frac{R_{n\ell}(r_m)}{\omega_{0,\ell}(r_m)}.$$
(5)

Basing on the obtained values of r_m and $C_{n\ell}$, the modified radial channel functions are now defined as following

$$R_{n\ell}^{mod}(r) = \begin{cases} R_{n\ell}(r), & 0 < r \le r_m \\ C_{n\ell}\omega_{0,\ell}(r), & r_m \le r < \infty \end{cases}$$
(6)

The modified functions $R_{n\ell}^{mod}(r)$ should be normalized on to unit according the standard procedure

$$N^{2} \int_{0}^{\infty} \left(R_{n\ell}^{\text{mod}} \right)^{2} r^{2} dr = 1.$$
 (7)

This expression has the explicit form while taking definition (6) into account:

$$N^{2}\left[\int_{0}^{r_{m}} R_{n\ell}^{2} r^{2} dr + C_{n\ell}^{2} \int_{r_{m}}^{\infty} \omega_{0,\ell}^{2} r^{2} dr\right] = 1.$$
 (8)

To continue our notations let us introduce I_1 and I_2 for the first and second integrals in (8) respectively, then the normalizing constant N is

$$N = \frac{1}{\sqrt{I_1 + C_{n\ell}^2 I_2}}$$
(9)

Finally the normalized modified radial function is defined as $\tilde{R}_{n\ell}^{mod}(r)=N \cdot R_{n\ell}^{mod}(r)$, or taking into account (6) one arrives

$$\tilde{R}_{n\ell}^{mod}(r) = \begin{cases} N \cdot R_{n\ell}(r), & 0 < r \le r_m \\ N \cdot C_{n\ell} \omega_{0,\ell}(r), & r_m \le r < \infty. \end{cases}$$
(10)

It is formal to somewhat extent, but it makes obvious that all relations for obtaining of matching radius r_m and ANC $C_{n\ell}$ preserve.

To characterize the probability density in interior and exterior regions it is natural to introduce the corresponding weights

$$\begin{cases} P_{in} = N^2 \cdot I_1, & 0 < r \le r_m \\ P_{out} = N^2 \cdot C_{n\ell}^2 I_2, & r_m \le r < \infty, \end{cases}$$
(11)

there relative probabilities P_{in} and P_{out} will be given in %.

For completeness let us present the analytical expression for the Whittaker functions (3) obtained for the special case of zero Coulomb potential

$$W_{0,l}(z) = e^{-z/2} \sum_{n=0}^{l} z^{-n} \frac{(l+n)!}{(l-n)!n!}.$$
 (12)

Modified functions in space representation

Here we are giving the results of the calculations for the modified radial WF of the low-lying excited states $J^{\pi} = 1/2^+$, $3/2^+$ and $5/2^+$ of positive parity π with total momentum J in ¹³C nucleus corresponding to the $s^4 p^8 (2s-1d)^1$ configuration with ¹²C as a core and a valence neutron in 2s-1d shell. The choice of these states is due to the fact that they are the real candidates for the manifestation of skin or halo structure on grounds such as large rms radii r_{ms} , small binding energy of the valence neutron $\varepsilon = \hbar^2 k_0^2 / 2\mu$.

For the first excited state $J^{\pi} = 1/2^+$ with excitation energy $E_{exc}=3,089$ MeV oscillator $R_{2s}(r) = \frac{\sqrt{6}}{\pi^{1/4}} \cdot \frac{1}{r_0^{3/2}} \left(1 - \frac{2r^2}{3r_0^2}\right) e^{-\frac{r^2}{2r_0^2}}$ function was used.

For the other $J^{\pi} = 5/2^+$ and $3/2^+$ states with the excitation energies $E_{exc} = 3,854$ and 7,67 MeV

$$R_{2d}(r) = \frac{4}{\pi^{1/4}\sqrt{15}} \cdot \frac{r^2}{r_0^{7/2}} e^{-\frac{r^2}{2r_0^2}} \text{ radial function was}$$

employed.

Let us define how the appropriate parameters necessary for the modification procedure may be determined.

Method No1 consider the parameter k_0 to be known from the relation $\varepsilon = \hbar^2 k_0^2 / 2\mu$. Then using ρ_0 as the solution of equation (4) and relation $\rho_0 = k_0 r_m$, the matching radius r_m may be found. Finally the oscillator parameter we can obtain from $r_0 = 1 / k_0$.

Method No2 for the definition of oscillator parameter is basing on the known correlation for the 3D harmonic oscillator $\overline{r^2} = r_0^2 \cdot (n+3/2)$, using the rms value r_{ms} the oscillator parameter r_0 may be obtained. The matching radius r_m is coming from the relation $\rho_0 = r_m / r_0$.

We obtained the numerical values: $\rho_0 = 2,474556$ for R_{2s} matching function as well as $\rho_0 = 2,513260$ in case of R_{2d} . Table 1 is a summary of all obtained parameters with pointed above method in last column.

The resulting modified functions in space representation have been expanded by Gaussian basis. In case of $J^{\pi} = 1/2^+$ state the expansion coefficients are given in table 2 for the corresponding function of the form

$$\tilde{R}_{2s}^{mod}(r) = \sum_{i=1}^{15} B_i \cdot e^{-\beta_i \bar{r}^2} .$$
(13)

In case of $J^{\pi} = 5/2^+$ and $3/2^+$ states the corresponding expanded function is of the form

$$\tilde{R}_{2d}^{mod}(r) = r^2 \sum_{i=1}^{15} D_i \cdot e^{-\gamma_i \bar{r}^2} .$$
(14)

Corresponding expansion coefficients are given in tables 3 and 4.

J^{π}	E_{exc} , MeV	r_{rms} , fm	r_m , fm	r_0, fm	No
1/2+	3,089	$5,04 \pm 0,75$	6,669	2,695	2
			8,604	3,477	1
5/2+	3,874	3,68±0,4	4,946	1,968	2
5/2			11,393	4,533	1
3/2+	7,67	-	7,218	2,872	1

Table 1 – Parameters of excited states $J^{\pi} = 1/2^+$, $5/2^+$, $3/2^+$ of ${}^{13}C$

Table 2 – Expansion coefficients for $1/2^+$ excited state of ${}^{13}C$ corresponding data of Table 1

i	$\mathcal{N} 2 \beta_i$	B_i	$№1$ $β_i$	B_i
1	0.995675768D-02	-0.214390442D-01	0.779153573D-02	-0.157705075D-01
2	0.336098351D-01	-0.189661409D+00	0.263009545D-01	-0.320160296D+00
3	0.599294538D-01	-0.190958104D+00	0.468970417D-01	0.188133220D+01
4	0.889974970D-01	0.464299511D+01	0.696438740D-01	-0.142428669D+02
5	0.121524851D+00	-0.323408024D+02	0.950977468D-01	0.577866466D+02
6	0.158690793D+00	0.104349783D+03	0.124181488D+00	-0.133732675D+03
7	0.202296685D+00	-0.185342008D+03	0.158304731D+00	0.201189391D+03
8	0.255142402D+00	0.204894845D+03	0.199658483D+00	-0.205576264D+03
9	0.321792941D+00	-0.147094874D+03	0.251815026D+00	0.144536068D+03
10	0.410216901D+00	0.688772842D+02	0.321010086D+00	-0.694744674D+02
11	0.535673529D+00	-0.205394784D+02	0.419184595D+00	0.222793718D+02
12	0.731454805D+00	0.368965561D+01	0.572390775D+00	-0.454905888D+01
13	0.108623797D+01	-0.359689964D+00	0.850021890D+00	0.545615092D+00
14	0.193686319D+01	0.155681470D-01	0.151566798D+01	-0.333966034D-01
15	0.653803936D+01	-0.195974076D-03	0.511626062D+01	0.835301964D-03

Table 3 – Expansion coefficients for $5/2^+$ excited state of ¹³C corresponding data of Table 1

i	$\mathcal{N} \mathfrak{2} \gamma_i D_i$		$\mathcal{N} \mathcal{I} \gamma_i D_i$	
1	0.934423119D-02	0.193301166D-04	0.507316101D-02	0.153278531D-04
2	0.282397165D-01	0.102243489D-02	0.171248624D-01	0.107571441D-02
3	0.477749532D-01	-0.839234710D-02	0.305352182D-01	-0.293365722D-02
4	0.684424019D-01	0.899360796D-01	0.453459496D-01	0.570832256D-01
5	0.908476504D-01	-0.425774826D+00	0.619192670D-01	-0.242640999D+00
6	0.115788434D+00	0.118540758D+01	0.808560348D-01	0.616231656D+00
7	0.144383322D+00	-0.156836386D+01	0.103074082D+00	-0.103888477D+01
8	0.178298554D+00	-0.991321547D-01	0.129999999D+00	0.120998646D+01
9	0.220180378D+00	0.411323404D+01	0.163959740D+00	-0.988919594D+00
10	0.274555699D+00	-0.670385983D+01	0.209013461D+00	0.567618348D+00
11	0.349930621D+00	0.537336858D+01	0.272936045D+00	-0.226320361D+00
12	0.464483627D+00	-0.243539615D+01	0.372690399D+00	0.613817482D-01
13	0.665419299D+00	0.632727569D+00	0.553459300D+00	-0.110395726D-01
14	0.112573289D+01	-0.935347961D-01	0.986869335D+00	0.132846869D-02
15	0.340214046D+01	0.112954444D-01	0.333125777D+01	-0.177390635D-03

i	$N \ge 1 \gamma_i$	D_i	i	γ_i	D_i
1	0.585738861D-02	0.118469219D-05	9	0.189305230D+00	0.107028918D+01
2	0.197720856D-01	0.309624471D-03	10	0.241323519D+00	-0.114006343D+01
3	0.352554628D-01	-0.523338692D-03	11	0.315127487D+00	0.713878510D+00
4	0.523556906D-01	0.195186077D-01	12	0.430302230D+00	-0.278365868D+00
5	0.714909714D-01	-0.737727901D-01	13	0.639015042D+00	0.682627507D-01
6	0.933550533D-01	0.212603276D+00	14	0.113942317D+01	-0.108208117D-01
7	0.119007646D+00	-0.110494484D+00	15	0.384621565D+01	0.184247221D-02
8	0.150095869D+00	-0.452967220D+00			

Table 4 –Expansion coefficients for 3/2⁺ excited state of ¹³C corresponding data of Table 1

Table 5 – Characteristics of radial modified wave functions $\tilde{R}_{2l}^{mod}(r)$

$J^{\pi}, \ ilde{R}^{mod}_{2l}(r)$	r_m , fm	$C_{2\ell}$	Ν	P _{out} , %
$1/2^+ \widetilde{p}^{mod}(r)$	6,669	0,278476	0,940277	24,9
$1/2$, K_{2s} (7)	8,604	0,181369	0,967572	20,1
$5/2^+ \widetilde{p}^{mod}(u)$	4,946	3,759468	0,979647	15,7
$5/2$, K_{2d} (7)	11,393	0,584071	0,958564	10,5
$3/2^+, \ \tilde{R}^{mod}_{2d}(r)$	7,218	0,584214	0,986567	10,8

Table 5 is a short summary on the general characteristics of the obtained modified radial functions $\tilde{R}_{2l}^{mod}(r)$. Let us pay attention to the probability of the localization of the valence neutron out of the mean square area of the core ¹²C given as P_{out} (%). Comparison of these values make it possible to conclude that $1/2^+$ state is the halo one, but states $5/2^+$ and $3/2^+$ are likely belong to the skin structure states.

Modified functions in impulse representation

Due to the Heisenberg uncertainty relation "coordinate-momentum" all modifications of the wave functions at large distances must, first of all reflected in the momentum distributions for small values q.

The corresponding analytical expressions for the oscillator and modified functions obtained on the base of (13) in impulse representation for the case $J^{\pi} = 1/2^{+}$ are:

$$R_{2s}(q) = r_0^{3/2} \frac{\sqrt{6}}{\pi^{1/4}} \cdot \left(1 - \frac{2q^2 r_0^2}{3}\right) e^{-\frac{q^2 r_0^2}{2}} \quad (15)$$

$$R_{2s}^{\text{mod}}(q) = \frac{\sqrt{\pi}}{4} \sum_{i=1}^{15} B_i \cdot \frac{1}{\beta_i^{3/2}} e^{-\frac{q^2}{4\beta_i}} .$$
 (16)

For excited states $5/2^+$ and $3/2^+$ the analogue expressions for the oscillator and modified functions on the base of (14) have been obtained

$$R_{2d}(q) = r_0^{3/2} \frac{4}{\pi^{1/4}\sqrt{15}} \cdot q^2 r_0^2 e^{-\frac{q^2 r_0^2}{2}}$$
(17)

$$R_{2d}^{\text{mod}}(q) = \frac{\sqrt{\pi}}{16} \sum_{i=1}^{15} D_i \cdot \frac{q^2}{\gamma_i^{7/2}} e^{-\frac{q^2}{4\gamma_i}} .$$
(18)

It is natural to discuss the probability density constructed as squared functions (15)-(18) $\rho_{2l}(q) = |R_{2l}(q)|^2$. The results of calculations are given in Figures 1 – 3.



Figure 1 – Impulse distributions for excited $1/2^+$ state of ${}^{13}C:(a)$ – linear scale; (b) – logarithmic scale. Set $N_2: \rho_{2s}^{mod}(q)$ – solid line, $\rho_{2s}(q)$ – dash-dot; set $N_2: \rho_{2s}^{mod}(q)$ – long dash, $\rho_{2s}(q)$ – dots



Figure 2 – Impulse distributions for excited 5/2⁺ state of ¹³C. Set No2: $\rho_{2d}^{\text{mod}}(q)$ – solid line, $\rho_{2d}(q)$ – dash; set No1: $\rho_{2d}(q)$ – dash-dot, $\rho_{2d}^{\text{mod}}(q)$ – dots



Figure 3 – Impulse distributions for excited $3/2^+$ state of ${}^{13}C$. $\rho_{2d}^{mod}(q)$ – solid line, $\rho_{2d}(q)$ – dash

As can be clearly seen from Figure 1, in fact, in the region of small momentum transfers $q \rightarrow 0$ momentum distributions obtained for all functions differ drastically. Thus, our assumption is that this characteristic is sensitive to the modifications of the asymptotic behavior is fully confirmed.

Figures 2 and 3 correspond the nodeless functions. They are exactly equal to zero at q = 0. Such momentum distributions are compared by a well-known characteristic of the width at half-of – height maximum Γ . It is for the Γ values can be seen how wide or narrow impulse distributions, and, consequently, to draw conclusions about the asymptotic behavior of the length of the asymptotic in the coordinate representation.

Conclusions

Sufficiently general method of the modification of radial functions for the improving of the asymptotic behavior is presented. The coming ambiguities appearing while defining the oscillator parameters have been examined. The modified functions are presented as convenient expansion by Gaussian basis. The different versions of the modifications N_21 and 2, as well as purely oscillator functions significantly distanced themselves in the momentum representation. To address the issue of choice of reliable functions it is necessary in the future to compare the obtained results with the available experimental data on elastic and inelastic form factors.

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Modeling the processes of combustion products formation in the coal-dust flame

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In this paper deals with development and application the numerical model for solution of processes at combustion chamber of the industrial boiler. The combustion chamber of the BKZ-75 boiler installed at Shakhtinskaya Thermal Power Plant (Karaganda, Kazakhstan) was chosen as the object of the research. As a result of computational experiments obtained distribution of concentrations of harmful substances: CO₂, CO, NO throughout the volume of the combustion chamber and on an output from it. In addition, the authors received a distribution of oxygen depending on the height of the combustion chamber. The minimum and maximum values of the investigated characteristics are established. The dynamics of the change in the characteristics of the heat and mass exchange process in the volume of the researched combustion products including harmful substances. The numerical model becomes a tool for investigation and design of combustion chambers with high-efficiency and reliable operation of boiler at thermal power plants. The results of this research has high practical importance, they allow studying heat exchange processes occurring in combustion in real geometry areas (combustion chambers of power plants).

Key words: combustion chamber, numerical modeling, temperature, coal, thermal power plant. PACS: 65.00

Introduction

Now the main share of energy is made due to burning or processing of natural raw materials coal, oil, gas, combustible slates, and peat. Any of modern ways of production and use of energy is to a greater or lesser extent connected with certain negative impacts on environment. In an energy drink, the main sources of pollution are thermal power plants energy production on which is followed first by pollution of atmospheric air [1-3].

The power system of Kazakhstan is presented mostly by thermal power stations more than 70 % of total amount of the electric power are generated. Thermal power stations work on solid fuel when pulverized coal combustion is predominant. Also natural gas and black oil can be used. Tendency of low grade coals usage to increase in domestic industry, it becomes especially important to develop and introduce new energy-saving technologies of solid fuel consumption and reduction in pollutant substance emissions. Applied technology of direct burning of low-grade coals in furnaces does not provide demanded reliability of working equipment and protection of environment from harmful combustion products due to approximately 50 % of pollutant emissions from stationary sources comes from thermal power enterprises and about 33 % are emitted by ferries and nonferrous metallurgy and mining [4-5]. Industrial implementation of any new technology is not possible without preliminary analysis of advantages and disadvantages suggested method. The rapid development in computer sciences gives the advance to computational techniques to be used for simulation of complex combustion processes in industrial furnaces. Products of combustion contain different harmful substances and the emission of these components grows in to a great problem. Industrial development causes an increase in hydrocarbonaceous fuels' consumption. These fuels contain harmful and poisonous components such as carbonic oxide (CO), nitric oxide (NO), sulphur dioxide, acid sulphate, lead combinations and different hydrocarbons etc. To decrease emissions of harmful substances various methods are applied, including special fire regimes (organization of combustion process), which suppresses the formation of harmful substances in flame and two-stage burning, when the burners work with low air surplus. In this way

numerical experiments became one of the most effective and suitable means for detail analysis and in-depth study of physical and chemical phenomena. In contrast to construction of an operating reduced model of the chamber, the three-dimensional modeling with the application of modern computer technology enables to carry out deep analysis of all chamber's parameters and save time and finances. At the same time, without additional inputs, it is possible to obtain the full set of characteristics of a convective heat and mass transfer process in reactive media, intervene flexibly in the process at any stage and reproduce separate technical solutions (the configuration of the fire chamber and assembly and construction burners), to model the formation of harmful dust and gaseous emissions and to investigate the influence of previous preparation of coal on its ignition and combustion stabilization.

About 50% of the consumed fuel are the share of production of heat and the electric power in Kazakhstan. The general power of the electro generating sources in the Republic of Kazakhstan makes more than 18 thousand MW, which about 87% of a basis make thermal power plant [6-7].

In this regard, researches in the field of progressive technologies on improvement of power stations on burning of coal-dust fuel and use of alternative methods of the organization of process of burning are the most actual for all power complex of the Republic of Kazakhstan now [8].

Numerical simulation

Computing experiments in this work were made on the basis on the solution of the three-dimensional equations of convective heat- and mass transfer taking into account distribution of heat, thermal radiation, chemical reactions and multiphase of the environment.

To describe the motion of three-dimensional reacting flows in the chamber uses a system of differential equations:

1. The continuity equation

$$\frac{\partial \rho}{\partial \tau} = -\frac{\partial}{\partial x_i} (\rho u_i). \tag{1}$$

2. The law of conservation of momentum (Navier-Stokes):

$$\frac{\partial}{\partial \tau} (\rho u_i) = -\frac{\partial}{\partial x_j} (\rho u_i u_j) + \frac{\partial}{\partial x_i} (\tau_{ij}) - \frac{\partial p}{\partial x_i} + \rho f_i,$$
(2)

where $\tau_{i,j}$ – viscous stress tensor, f_i – the external force;

3. The law of conservation of energy (the first law of thermodynamics):

$$\frac{\partial}{\partial t}(\rho h) = -\frac{\partial}{\partial x_i}(\rho u_i h) - \frac{\partial q_i^{res}}{\partial x_j} + \frac{\partial p}{\partial t} + u_i \frac{\partial p}{\partial x_i} + \tau_{ij} \frac{\partial u_j}{\partial x_i} + S_q,$$
(3)

where h – specific enthalpy, q_i^{res} associated with energy transfer by conduction and diffusion flux of matter, S_q – a source of energy due to chemical reactions and radiative heat transfer;

4. The conservation of components of the mixture:

Write the equation describing the concentration of a component mixture in the general form as follows:

$$\frac{\partial}{\partial t}(\rho c_n) + \frac{\partial}{\partial x_i}(\rho u_i c_n) =$$

$$= \frac{\partial}{\partial x_i} \left[\frac{\mu_{eff}}{\sigma_{c_{n,eff}}} \frac{\partial c_n}{\partial x_i} \right] + S_{c_n},$$
(4)

where S_c – the source term , taking into account the contribution of the chemical reactions in the change in the concentration of components .

The turbulent flow pattern is described by means of a two-equation k- ε turbulence model, where kturbulent kinetic energy, ε -turbulent energy dissipation [9-13]. A standard k- ε model of turbulence has been used to close off the system and model turbulent viscosity.

$$\frac{\partial(\overline{\rho}k)}{\partial t} = -\frac{\partial(\overline{\rho}\overline{u}_{j}k)}{\partial x_{j}} + \frac{\partial}{\partial x_{j}} \left[\frac{\mu_{eff}}{\sigma_{k}}\frac{\partial k}{\partial x_{j}}\right] + P - \overline{\rho}\varepsilon$$
(5)

Calculation of turbulent flows with chemical reactions is based on the knowledge of chemical kinetics and modeling methods of turbulent transfer processes [14].

Calculation domain is proposed according to power boiler BKZ-75 Shakhtinskaya thermal power station (Kazakhstan). The domain is depicted in figure 1, where dimensions and discretization of structured grid are shown.

The boiler of the BKZ - 75 – vertically water pipe, is manufactured by the Barnaul boiler plant, with a productivity of 75 t/hour (51,45 Gcal/h), temperature of superheated steam 440°C and pressure of superheated couple 39 kgfs/cm². Influence of volatiles essentially at an initial stage of burning fuel: the exit of volatiles is higher, the fuel ignites quicker and the more deeply it burns out. But the release of volatile substances must not exceed certain standards adopted in each region. Except the main components, which are formed because of burning organic fuel, emissions of combined heat and power plant contain dust particles of various structure, nitrogen oxides, oxides of metals, gaseous products of incomplete combustion of fuel [16-18].

To solve the problem of air pollution dust and gas emissions, it is necessary to develop the environmentally "clean" energy burning fuel. In this regard, the study of the concentration characteristics of harmful substances in the combustion products is an urgent task.



Figure 1 – Computational domain and finite volume discretization grid of the combustion chamber

Results and discussion

Figures 2-6 present the results of computational experiments investigating mass transfer characteristics and concentration of harmful dust and gas emissions in the combustion chamber of the boiler BKZ- 75 Shakhtinskaya CHP.

From all the nitrogen oxides in the flue assay device is viewed mainly nitrogen monoxide NO, which is formed largely from the combustion of coal. At relatively low temperatures, preferably nitrogen dioxide NO2 formation, but because of the low rate of its formation and the relatively short time of passage of the flue gases of the boiler, its content in the amount of nitrogen monoxide NO at the combustion chamber does not exceed $5 \div 10$ percent [19].

Figures 2-3 shows the distributions of concentrations of nitric oxide (NO) in different sections of the combustion chamber.

Figure 2 (a, b) show the distributions of concentrations of nitric oxide (NO) in different sections of the combustion chamber.

Analysis figures 2 (a, b) shows that a maximum area of nitric oxide, NO, is a region of high temperatures and intense eddy currents. For the study of the combustion chamber such area is in the area of the burners at the height of z = 4.0meter. Intensive mixing of fuel and oxidant produced by turbulent flow of injected fuel mixture near the burner, and the high temperature in the core of the flame (~ 1200°C), create favorable conditions for the formation of nitrogen oxides. In this area, the NO concentration reaches maximum values of 2201 mg / Nm³. As seen in figure 3, as the pulverized coal flame passage to the exit of the combustion chamber there is a uniform reduction in the concentration of NO, as this area contains less oxygen and a fuel component. Besides, the temperature is reduced and the height of the combustion chamber, thereby reducing the rate of formation of nitric oxide.

At the outlet from the combustion chamber average value of the nitrogen oxide NO concentration is 550 mg / Nm³. It meets standards of maximum concentration limit for furnace cameras of coppers of the thermal power plants working at coal-dust fuel.



Figure 2 – NO concentration distribution in cross sections: a) burners, b) at the outlet of the combustion chamber





Figures 4-5 show the distributions of concentrations of carbon monoxide (CO) in sections of the burners and the outlet of the combustion chamber [20].

The main result of the combustion process of carbon at high temperatures is a compound of oxygen with carbon pulverized coal to form carbon monoxide CO, carbon dioxide or CO_2 [21].

The special importance when burning coal-dust fuel is gained by reaction of oxidation of carbon to SO carbon monoxide. Because, further CO reacting with air oxygen, "burns down" to CO2, marking out thus the maximum value of energy, equal 571 kJ/mol.



Figure 4 - CO concentration distribution in cross sections: a) burners, b) at the outlet of the combustion chamber



Figure 5 – The distribution of the carbon monoxide concentration CO in height of the combustion chamber

The analysis of figures 4-5 shows that the maximum concentration of carbon monoxide CO takes in the central section of the region of the burners, because there are higher temperatures, there is a large concentration of carbon fuel and oxygen oxidizer. As a result, in the area of burner the concentration of CO takes the value equal to $4.7*10^{-3}$ kg / kg. At the outlet of the combustion chamber decreases the concentration of CO. It is associated with a reduced concentration of oxygen and carbon.

Figure 6 shows the distribution of the concentration of carbon dioxide CO_2 in sections of the burners and the outlet of the combustion chamber.



Figure $6 - CO_2$ concentration distribution in the cross sections: a) burners, b) at the outlet of the combustion chamber

Analysis of the figure 6 shows that the distribution of carbon dioxide CO2 is completely the opposite of the character of the distribution of oxide CO. It is evident that in the belt of burners at a height of 4 meters in the concentration of carbon dioxide CO2 is minimal and amounts to 0.07 kg / kg. Maximum CO₂ concentration is observed at the exit of the combustion chamber and has a value of 0.152 kg / kg.

Conclusions

We investigated the field of concentrations of combustion products CO, CO₂, NO during combustion of coal-dust flame. It is shown that in the region of the burner main reactions occur reaction with carbon form carbon monoxide. The distribution pattern of carbon monoxide CO ₂ does not match the field CO. It speaks about the differences in the formation of CO₂ and CO. The maximum concentration of CO at the burner takes a value equal to $4.7*10^{-3}$ kg / kg, and at the outlet of the combustion chamber, its average value of $4.40*10^{-4}$ kg / kg. In the zone of burners at a height of four meters concentration of carbon dioxide CO₂ is minimal and is 0.07 kg / kg, whereas the concentration of CO in the oxide in the area takes a

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It was found that intensive mixing of fuel and oxidizer, which is created by turbulent flow of injected fuel mixture near the burner, and the high temperature of the core of the torch, creating favorable conditions for the formation of nitrogen oxides. In this region, the concentration of nitrogen oxides NO reaches 2201 mg / Nm³, and the output of the combustion chamber, its average value is 550 mg / Nm³. The results will help power companies in Kazakhstan to solve important environmental problems and achieve cost-effective production of energy.

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Simulation of the aerodynamics and combustion of a turbulent pulverized-coal flame

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Using the three-dimensional modeling method, numerical experiments on flame combustion of pulverized-coal fuel have been performed. The results of a three-dimensional numerical simulation of flow aerodynamics, temperature and carbon oxides are presented. Studies have been carried out for a pulverized-angle flame of various dispersity. In the study of a wide range of modern problems of science and technology, numerical simulation of heat and mass transfer process is particularly important and has enormous practical application. Interaction of reacting flows is described by a complex system of nonlinear partial differential equations. Indispensable effective method of theoretical study of such flows is a numerical simulation. Recent results obtained in the course of this article allow solving the scientific and engineering issues, choosing the optimal option of the combustion process organization to increase its efficiency, minimize harmful gaseous and particulate emissions and reduce the negative impact on the environment. Addressing these issues is relevant in respect to the concept of energy safety of the country on the one side and the development of processes of "clean combustion" of fuel to meet strict standards of harmful substances emission into the atmosphere and economy use the equipment, on the other side.

Key words: simulation, coal combustion, aerodynamics, monodisperse flame, polydisperse flame, concentration fields. PACS number(s): 47.27, 47.70.Pq

Introduction

Numerical modeling is sufficiently accurate and inexpensive way to analyze complex processes that occur during combustion of the fuel in the combustion chambers of real power plants, and it allows to simultaneously consider the complex of processes that are almost impossible to do, conducting in situ experiments. Only the numerical carrying out computational modeling and experiments optimally solve scientific and project engineering tasks in this area (improvement, design of new boilers; burners upgrade; development of multistage fuel combustion systems, optimization of combustion processes and other) [1,2].

At the present stage of development of the energy industry, immediate consideration and resolution of environmental issues are required. Due to the fact, that for most countries the main sources of pollutant emissions into the atmosphere are companies operating in the burning of low-quality raw materials as well as with poorly equipped with flue gas cleaning systems, the problem of pollution of the Earth's atmosphere is an urgent. Environmentally hazardous emissions, which are products of coal combustion [3-5] reactions cause enormous damage to the earth's ecosystem. It is therefore necessary to carry out a detailed study of physical and chemical processes that occur during combustion of energy fuels and to solve the problem of environmentally "pure" making use of coal [6, 7].

Methodology of investigation

For carrying out computational experiment the combustion chamber of the real power boiler BKZ-160 Almaty TPP-3 (Kazakhstan) was selected. The boiler BKZ-160 of drum-type furnace with dry slag removal has a calculated steam generating capacity 160 t/h at a pressure of 9.8 MPa and a temperature of the superheated steam 540 °C. The boiler has a U-shaped profile with a rectangular prism furnace. Combustion chamber volume is 790 m3. On the sides of the combustion chamber located four blocks direct flow slot burners (two burners in the block) which directed at a tangent to the circle with a diameter of one meter. Each burner has a fuel mixture channel and two secondary air channel, they

are located from above and from below the channel of air-fuel mixture, and divided lined piers. The top and bottom burners are also divided by a pier. In the center of burners is located oil-fired nozzle for lighting and lighting of the flame. The performance of each of the eight coal-fired burner fuels is 4 t/h.

Computational experiments on research heat and mass transfer processes have been carried out by the starting FLOREAN [8] software package, the geometry of the combustion chamber was created by a computer program «PREPROZ» (Figure 1b). The software package FLOREAN was created to solve problems in the field of burning solid fuel and was repeatedly tested in many modern studies [1-12]. During the numerical simulation of heat and mass transfer process, the control volume method has been applied. Combustion chamber of a power boiler BKZ-160 has been divided into control volumes; it is possible to obtain 217536 computational areas.



Figure 1 - a) Scheme of the furnace, b) General view of the camera, broken down into control volumes

Numerical simulation was carried out on the basis of solutions of the Navier-Stokes equations, equations of heat diffusion and diffusion of components of the reacting mixture and the reaction products based on thermal radiation and multiphase media, equations of state, and chemical kinetics equations defining the intensity of nonlinear energy and matter [8, 13-15].

For a qualitative description of combustion processes in a real three-dimensional physical and chemical system (combustion chamber of Thermal power plant) in the present work a numerical calculation of a turbulent pulverized coal flame was carried out taking into account the dispersion of coal. The percentage distribution of carbon particles in size: $d_p=10 \text{ mkm} - 10\%$; $d_p=30 \text{ mkm} - 20\%$; $d_p=60 \text{ mkm} - 40\%$; $d_p=100 \text{ mkm} - 20\%$; $d_p=120$

mkm - 10% corresponds to a polydisperse flame, $d_p=60 mkm - 100\%$ – is the averaged diameter, which corresponds to a monodisperse flame. Numerical calculation in the work was carried out for the two cases listed above.

Results of numerical simulation

Let us consider the profiles of aerodynamics combustion of a turbulent pulverized flame in different sections along the length of the flame. Figure 2 shows the distribution of the full-velocity vector in the longitudinal section of the furnace during combustion of a monodisperse and polydisperse flames. Obtained velocity fields allow us to visually analyze the aerodynamics of reacting flows in the combustion chamber. The fields of the full-velocity vector show the value of the flow velocity of the medium and its direction at each point.

In the Figure 2 the area of fuel and oxidizer is clearly visible: counter dust and gas streams from opposing tangential burners create a vortex in the central part on the location of burners and level of active burning zone. Clearly visible is the recirculation zone with reverse gas currents [15]. Part of the flow is directed down to the funnel, forming two symmetrical vortex in the area below the burner arrangement, it is typical both for burning of a monodisperse flame and for burning of a polydisperse flame. However, in a longitudinal section of the combustion chamber symmetry is broken relative to the vertical axis of the chamber when burning polydisperse flame (Figure 2b). It means that burning of dust and gas streams with different particle sizes affects to the character of the flow stream.

In cross-section chamber at a level between the lower and upper tiers of burners there is a clear picture of the current (Figure 3). The pulverized coal streams flowing into the chamber deviate from the direction of the burner axes (located tangentially) towards the adjacent walls, with which they make up a smaller angle. Fusing into the total flow, the jets create a volumetric vortex with a vertical axis of rotation, which, as it rises, untwists and then moves along the axis, as can be seen clearly in Figure 2.



Figure 2 – Field of a vector of full velocity in the longitudinal section of the combustion chamber (x = 3.16 m) for a) monodisperse flame; b) polydisperse flame

The central vortical motion of the pulverized coal stream leads to uniform heating of the combustion chamber walls, to a decrease in the slagging of the heat shields and heat losses, which prolongs the life of individual elements of the boiler plant, and also increases the heat removal surface, which speaks of the advantages of the furnaces with the tangential arrangement of the burners. The aerodynamics of flow in the combustion of monodispersed and polydispersed flames has some differences; however, if it is necessary to make quick estimates, in numerical simulation of the aerodynamic characteristics of the coal combustion process, one can use the model of burning a particle of averaged size, which in turn reduces the expenditure of computer time [1, 16-21].

Being the UNFCCC framework (the United Nations Framework Convention on Climate

Change) since 1995 and the Kyoto Protocol since 2009, Kazakhstan has a principled position and pursues a consistent policy in the field of preventing global climate change, in the field of reducing the carbon intensity of the economy and in the field increasing energy efficiency, creating conditions for the transition to technologies for environmentally "pure" burning of energy fuel [22]. In this connection, the study of the concentration characteristics of greenhouse gases is an urgent task. Figures 4, 5, 7 show a comparative analysis of carbon oxide concentration distributions for the case of a polydisperse and monodisperse flare.

Analyzing the Figure 4 it can be argued, the nature and pattern of carbon monoxide CO and carbon dioxide CO_2 are different from each other. Concentration of carbon oxide reaches area of the maximum values in a zone of active burning, unlike

carbon dioxide which concentration increases as it moves out of the combustion chamber.

Concentrations of poly- and monodisperse flames in the field of an arrangement of burners do not differ. The average value of the concentration of carbon monoxide for polydisperse flame in the first tier of burners (z=4,81m) is 0,184 $\cdot 10^{-2}$ kg/kg, for monodisperse is $0,185 \cdot 10^{-2}$ kg/kg, in the second tier (z = 5,79m) is $0,279 \cdot 10^{-2}$ kg/kg both for poly- and for monodisperse flames (Figure 4a). In the area of active burning the concentration of carbon monoxide CO reaches the maximum value, chemical processes of formation of carbon monoxide CO fade to output from the combustion chamber, for polydisperse flame at the exit of the combustion chamber the mean value is 1,35.10-4 kg/kg, for monodisperse is 0,61 10- 4 kg/kg (Figure 4a).



Figure 3 – Field of a vector of full velocity in the cross-section of the combustion chamber (z = 5.3m) for a) monodisperse flame; b) polydisperse flame



Figure 4– Comparison of the average values of concentration CO (A) μ CO₂ (B) for poly- and monodisperse flame on height of the combustion chamber



Figure 5 – Distribution of the carbon oxide concentrati on in the longitudinal section of the furnace combustion chamber (y = 3.7m) for a) monodisperse flame; b) polydisperse flame



Figure 6 – Comparison of average temperature values for poly- and monodisperse flames and a comparison with the field experiment [23]: A) on height of the combustion chamber B) zone of active burning C) at the outlet of the combustion chamber

Analyzing the distribution of CO concentration in the longitudinal sections of the combustion chamber (Figure 5), it can be said that in the active combustion zone, there is a clear difference in the formation of CO for a mono- and polydisperse flames, which indicates that the particle size has a significant effect on the formation of reaction products. The maximum values of carbon monoxide CO are explained by the intensive physico-chemical interaction between the fuel carbon and air oxygen, and with increased temperatures in this region (Figure 6).

Figure 6 shows the experimental points obtained directly from measurements at the termal power plant [23]. It is confirmed that the numerical simulation results are in good agreement with the results of a natural experiment. It is leading to the conclusion of the applicability of the proposed physical-mathematical model of combustion processes, used in the present work. It should also be noted that the experimental data obtained directly from TPP-3 lie closer to the temperature curve of the polydisperse flame, from which it can be argued that the polydisperse flame model is more sensitive and reflects a more real process of burning pulverized coal at Almaty TPP-3.

Analyzing Figures 4b, and 7 it can be said that as flow moves out of the combustion chamber CO₂ is restored from CO, this regularity is fair both for monodisperse, and for polydisperse flames. It is possible to determine value of concentration in any point of furnace by a color scale of the received figures which is not always possible to obtain during the field experiments on the thermal power plant. So the average values of carbon dioxide CO₂ in the longitudinal section of the combustion chamber (y =3,7m) for polydisperse flame is 0.155 kg/kg, for monodisperse flame is 0.158 kg/kg (Figure 7). At the exit of the combustion chamber average concentration of carbon dioxide for polydisperse flame is 0.1876 kg/kg, for monodisperse flame is 0.1895 kg/kg.



Figure 7 – Distribution of carbon dioxide concentration in a longitudinal section of the combustion chamber of the combustion (y = 3.7m) for a) monodisperse flame; b) polydisperse flame

Conclusions

In the present work, the calculation of aerodynamics, thermal and concentration characteristics of the combustion of mono- and polydisperse flames is performed; the results of the study can formulate the following conclusions:

1. A detailed picture of the structure of the flame is obtained, which includes a developed recirculation zone with return currents of the combustion products;

2. It is noted that the character of formation of the concentration fields CO and CO_2 is different. The maximum concentration of carbon monoxide reaches in the zone of active combustion, and the formation of carbon dioxide CO_2 increases as it moves towards the outlet from the furnace;

3. The results of computer simulation of temperature T, were compared with the results of

field experiments, the analysis of which confirms the correctness of the chosen model of numerical experiment.

In conclusion, we note that the nature of combustion of mono- and polydisperse dust has differences, i.e. The influence of fineness of grinding has a significant influence on the processes of heat and mass transfer in the combustion chamber of CHPP boilers. The combustion model of polydisperse dust more accurately reflects the actual combustion process, which confirms the comparison with the full-scale experiment. However, the application of this model requires large computer, time resources.

The results obtained in this study will give recommendations for optimizing the burning process of pulverized coal in order to reduce pollutant emissions and creations of power stations on 'pure' and an effective utilization of coal.

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Ternary cobalt-molybdenum-zirconium coatings: electrolytic deposition and functional properties

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Consistent patterns for electrodeposition of Co-Mo-Zr coatings from polyligand citrate-pyrophosphate bath were investigated. The effect of both current density amplitude and pulse on/off time on the quality, composition and surface morphology of the galvanic alloys were determined. It was established the coating Co-Mo-Zr enrichment by molybdenum with current density increasing up to $8 \text{ A} \cdot \text{dm}^{-2}$ as well as the rising of pulse time and pause duration promotes the content of molybdenum because of subsequent chemical reduction of its intermediate oxides by hydrogen ad-atoms. It was found that the content of the alloying metals in the coating Co-Mo-Zr depends on the current density and on/off times extremely and maximum Mo and Zr content corresponds to the current density interval 4–6 $\text{A} \cdot \text{dm}^{-2}$, on-/off-time 2–10 ms. It was shown that Co-Mo-Zr alloys exhibits the greatest level of catalytic properties as cathode material for hydrogen electrolytic production from acidic media which is not inferior a platinum electrode. The galvanic alloys Co-Mo-Zr with zirconium content 2–3 at.% demonstrate high catalytic properties in the carbon(II) oxide conversion. This confirms the efficiency of materials as catalysts for the gaseous wastes purification and gives the reason to recommend them as catalysts for hydrocarbon combustion.

Key words: cobalt ternary coatings, molybdenum, zirconium, citrate-pyrophosphate bath, catalytic properties, corrosion resistance, electrodeposition, hydrogen evolution reaction, pulse electrolysis PACS: 61.46.+w

Introduction

Energetic security of any country is based on the several factors, among which there are the network of national energy generating enterprises, developed industrial basis on the energy accumulating devices and energy sources production. Eco-friendly fuel cells (FC) are among the promising renewable energy sources, however, the high cost of the noble metal electrodes prevents their dissemination and widespread use [1, 2]. Development of the fuel cells and flow battery at various red-ox systems (RFB) needs to create effective catalytically active electrodes on the basis of transition metals [3, 4]. Among the most important requirements to electrode materials of FC and RFB are: chemical inactivity stability of the surface and to technological environment components; wide window of polarization potentials, in which electrode stays inactive; high selectivity and catalytic activity toward main electrode reactions; significant specific surface area. Even brief review gives an impression that electrode materials that are being used in these electrochemical systems are not optimized [5, 6]. For instance, one of the most widespread electrode material for FC and FRB is a number of carbon modifications - graphite, carbon fibers, porous and pressed carbon, carbon cloth, graphite with thermally or chemically modified surface, nickel foam, platinum or platinum titanium, oxides of platinum group metals, etc [7-10]. It is worth mentioning that in scientific literature for the last years there are too few publications on electrode materials on the basis of hi-tech materials, such as nanostructured and nanocrystalline materials based on the corrosion resistant amorphous metal alloys (metal glass), or nanostructured deposits by synergistic alloys [11–13]. The most efficient directions of catalytic materials synthesis by physicinorganic chemistry methods are electrochemical technologies that provide the opportunity to very flexibly control the component content, the rate of deposition, the state of the surface, by varying the electrolyte composition and polarization mode (static or pulse, reverse current or decrease of the potential) [14–16]. Utilization of the electrochemical methods favors the interactions in the chain "process parameters - composition and structure of the material - properties - functions application". Because of this it is possible to

fabricate the deposits of varied qualitative and quantitative composition and with desirable functional properties (synergistic or additive), such as microhardness, wear-, thermo-, chemical and corrosion resistance, catalytic activity, etc [17–20]. When synthesizing new and improving existing catalysts it is necessary to determine the factors influencing the catalytic activity and especially the nature of the catalyst, since electro-catalytic activity depends on chemical composition and state of the surface (amorphous, crystalline, grain size, etc.) [21–23].

It has previously been shown prospects of electrolytic binary cobalt alloys with molybdenum or tungsten to produce hydrogen by alkali electrolysis [24, 25] as well as to the oxidation of hydrocarbons [26, 27]. However, it is of interest to create catalytic materials based on ternary synergistic cobalt alloys with metals of differing affinity to oxygen and hydrogen and high corrosion resistance for use as catalysts, and electrode materials for fuel and flow batteries.

The aim of this work is to study the influence of the electrolysis parameters on the quality, composition, morphology, catalytic properties and corrosion resistance of ternary galvanic Co-Mo-Zr coatings.

Experimental

Coatings were deposited onto the substrates out of steel. Pretreatment of samples included grinding, degreasing in a solution of sodium carbonate at 50 °C, and washing, etching in a mixture of hydrochloric acid and sulfuric acid at a temperature of 20 °C and thoroughly washing in flowing water.

Deposits of cobalt with molybdenum and tungsten or zirconium were formed at temperatures of 25-50°C from a complex polyligand citratediphosphate bath. The coatings Co-Mo-Zr were deposited from electrolyte composition (M): cobalt sulfate 0.15, sodium molybdate 0.06, zirconium (IV) sulfate 0.05, sodium citrate 0.2, and potassium diphosphate 0.1. The pH value of electrolytes was adjusted within the range 8-9 by sodium hydroxide. Electrolytes were prepared from analytically pure reagents: CoSO₄·7H₂O, $Zr(SO_4)_2 \cdot 4H_2O$, $K_4P_2O_7$, $Na_2MoO_4 \cdot 2H_2O_1$ Na₃C₆H₅O₇·2H₂O dissolved in a small amount of distilled water following by solution mixture in a certain sequence, based on the ionic equilibrium study results [28].

The deposits were formed in pulsed mode with unipolar pulse current of amplitude 2–15 A·dm⁻² in the frequency f range of 19-910 Hz at a pulse duration $t_{on} = 2-50$ ms and pause time $t_{off} = 5-50$ ms, duty factor $q = (t_{on} + t_{of})/t_{on}$ was 2–26. Coplanar cobalt plates were used as anodes. The cathode-toanode area ratio was kept at 1:5. The pulse electrolysis was performed using pulse current supply unit (ZY-100 \pm 12). The electrode potentials were measured relative to an EVL-1M1 silver chloride reference electrode connected to the working cell via a salt bridge filled with saturated potassium chloride solution jellied with Ceylon gelatin. The potentials presented in the paper are given relative to the standard hydrogen electrode (SHE).

The electrodeposition current efficiency Ce (%) was determined from the weight and chemical composition of the deposited alloys and the charge passed using the electrochemical equivalent of the alloy. The thickness of the deposits was calculated from a sample actual weight increase after the electrolysis.

The chemical composition of the coatings was determined by energy dispersive X-ray spectroscopy on an Oxford INCA Energy 350 electron probe microanalysis integrated into the system of the SEM. The X-rays were excited by exposure of the samples to a beam of 15 keV electrons. The surface morphology of the deposits was studied with a Zeiss EVO 40XVP scanning electron microscope (SEM). Images were recorded by the registration of secondary electrons (SEs) via scanning with an electron beam; this mode made it possible to study the topography with a high resolution and contrast ratio. The surface roughness was evaluated by the contact method on $10 \times 10 \times 2$ mm samples with an NT-206 scanning probe AFM microscope (lateral and vertical resolutions 2 and 0.2 nm, respectively; 1024×1024 scanning matrix, CSC cantilever B as probe, probe tip radius 10 nm).

The structure of the deposits was examined by X-ray diffraction analysis using a diffractometer (DRON-2.0) in the emission of iron anode and CuK α radiation.

Corrosion tests of the deposits were carried out in a model media with 1 M sodium sulfate with the addition of sulfuric acid to pH 3 or potassium hydroxide to pH 11 and in 3% potassium chloride (pH 7). The corrosion current was determined by the polarization resistance technique using digital analysis of anodic and cathodic plots in Tafel coordinates within the range 200–300 mV from steady-state potential [29]. The potentiostat IPC-Pro controlled by PC was used for voltammetry measurements with scan rate 1 mV/sec⁻¹. Corrosion depth index k_h (mm per year) was converted from corrosion current:

$$k_h = (8.76k_e i_{cor})/\rho$$

where k_e – the electrochemical equivalent of alloy, kg/C⁻¹; i_{cor} – corrosion current density, A/m⁻²; ρ – density of the alloy, kg/m⁻³.

Electrochemical equivalent k_e and density ρ of the alloys were determined considering their quantitative composition [30].

Electro catalytic properties of covers were studied in model reaction of electrolytic hydrogen evolution from acidic and alkali media. The hydrogen current exchange density $i_{\rm H}^0$ is utilized as the criteria of electrochemical catalysis since this parameter is independent of the electrode potential. Experimentally $i_{\rm H}^0$ was determined at the point of intersection of the linear portion of the cathodic polarization dependence in Tafel coordinates at zero over potential [28]. The testing of catalytic properties was also carried out in the process of the carbon (II) oxide oxidation in a tubular flow reactor fabricated from quartz glass with the coaxially situated heating element. Initial mixture of CO (1 vol.%) and air was supplied to the reactor inlet at a rate of 0.025 dm³·min⁻¹. Reactor temperature was increased gradually from 20 to 420 °C. Content of CO in the final mixture was analyzed using the indicator-analyzer "Dozor" [26].

Theoretic aspects

It was shown in previous papers [28, 31] the necessity of using polyligand electrolyte for the codeposition of cobalt with molybdenum and zirconium because of the significant potential difference for alloying components. Citrate (Cit) and diphosphate ions that are indifferent to electrochemical oxidation and reduction in wide potential window and create coordination with many single and polyvalent ions are selected as ligands. The pH maintaining in the interval 8–9 is for stable diphosphate recommended $(pK[CoP_2O_7]^{2}=6.1)$ and citrate (pK[CoCit]=5.0)complexes since the strength of compounds depends on the ligands protonation. Moreover, in a weakly alkaline medium Mo (VI) is a mono-oxometalate ion MoO_4^2 [16, 31] and zirconium predominantly is ZrO^{2+} . These particles are involved in the formation of the heteronuclear complexes with cobalt discharging at the cathode by induced codeposition [32].

It was shown in previous studies [28] we can obtain ternary Co galvanic deposits and control their composition by changing the concentration ratio of salts of alloying metals and ligands in a bath, and electrolyte pH. We need to keep in mind that formation of heteronuclear complexes of cobalt with molybdenum and zirconium with citrate and diphosphate ligands and their subsequent reduction in the alloy may be competing as it was shown for iron ternary deposits [20].

Taking into account the considerable difference of alloying components' redox potentials (Table 1) and their step reduction conjugated with chemical reaction as it was shown in [16, 23, 31] preference is given to forming ternary coatings using pulse electrolysis mode. Thus, energy and time parameters of the electrolysis can be an effective instrument for control the composition and surface morphology, and hence the properties of ternary coatings especially catalytic activity and corrosion resistance.

Results and discussion

Increase the current density amplitude i of 2 to 4 $A \cdot dm^{-2}$ rises the Molybdenum content in the deposit Co-Mo-Zr up to $\omega(Mo)=24$ at.% (Figure 1 a) reaching the concentration plateau at 24-25 at.% at current densities of 4-8 A · dm⁻². Coating enrichment by this alloying component with increasing current density is entirely predictable since the reduction of molybdate is at least a complex multi-step process accompanied by chemical reduction of intermediate Molybdenum oxides with Hydrogen ad-atoms Had [23]. As we see from (Figure 1 b) the potential of the cathode at electrodeposition of the coatings Cobalt-Molybdenum-Zirconium is in the range – (2.0-2.8) V. Thus with increasing current density electrode potential shifts in the negative direction resulting in faster parallel reaction of Hydrogen reduction to form H_{ad} which are involved in a chemical step of intermediate Molvbdenum oxides reduction. Due to these processes the Molybdenum content in the deposits is increased. However, at current densities above 8 A dm⁻² reaction of Hydrogen evolution becomes the dominant as evidenced by the current efficiency (Figure 1 b)

whereby the molybdenum content in the alloy decreases.

The dependence of the Zirconium content in the ternary coatings from current amplitude i has an extreme character with a maximum $\omega(Zr)=3.6-3.7$ at% at current densities 4 A·dm⁻² (Figure 1 a). It should be stated that when the amplitude of the current is higher than of 4 dm⁻² there is a competitive deposition of Molybdenum and Zirconium in the coating, which is obviously due to the different mechanism of alloying metals reduction from polyligand electrolytes. Indeed, molybdenum reduction requires the transfer of 6 electrons accompanied by the removal of 4

coordinated oxygen atoms. Zirconium is likely included in the deposit in the form of oxygen compounds, which follows from the higher binding energy Zr–O [33-35] and confirmed by analysis of the composition of the surface layers.

A similar nonlinear relationship was observed for current efficiency of the ternary alloy Ce vs i (Fig 1 b): Ce increases by 20 % and reaches 63 % with rising current density from 5 to 8 $A \cdot dm^{-2}$; however further increase in i reduces the current efficiency up to 47 %. Such behavior may be attributed with acceleration of site Hydrogen evolution reaction at higher current amplitude.



Figure 1 – Pulse current density influence on the composition (a) and current efficiency (b) for Co-Mo-Zr coatings; ton/toff 2/10 ms; T 20–25 °C; pH 8; plated time 30 min

Time parameters of pulsed electrolysis (duration of pulse t_{on} and pause t_{off}) strongly affect the composition and current efficiency of multicomponent deposits. Thus, the minimum value t_{on} should be sufficient to achieve the potential of metals co-deposition in the alloy, and the maximum – to ensure quality coatings and efficiency of electrolysis.

It was found that with increasing pulse time of 0.5 to 2 ms at a constant current density $i=4 \text{ A} \cdot \text{dm}^{-2}$ and pause duration $t_{\text{off}}=10$ ms both Molybdenum and Zirconium content in the Co-Mo-Zr deposits grow (Figure 2 a). This is due to an increase in active current at the expense of a full signal handling, thereby achieving potential of alloying metals reduction in alloy. Increasing the pulse duration of more than 2 ms does not contribute to the growth of the above metals content in the

coating. Moreover, the zirconium content decreases with pulse duration exceeding 2 ms.

Prolong pause of 5 to 10 ms at a constant current density and pulse duration (ton 2 ms) provides growth zirconium content in the alloy from 2.1 to 3.7 at.% which is followed by decreasing of $\omega(Zr)$ at larger current interruption (Figure 2 b). So the maximum concentration of Zirconium in the electrolytic alloy is reached under the ratio $t_{on}/t_{off} =$ 2/10 ms (duty factor q = 10, f = 85 Hz). At the same time, the content of molybdenum in Co-Mo-Zr deposits regularly increases from 16.0 to 24.0 at% with the duration of the pause due to more complete chemical reduction of intermediate oxides by H_{ad} (Figure 2 b). It also shows the different mechanism of Zirconium and Molybdenum reduction and confirms their competitive co-deposition in the ternary coating under studied conditions.



Figure 2 – Dependence of Co-Mo-Zr coating composition on the time of pulse t_{on} (a) (t_{off} 10 ms) and pause t_{off} (b) (t_{on} 2 ms); i=4 A·dm⁻²; T = 20–25 °C; pH 8; plated time 30 min

Current efficiency logically decreases of 60 to 36 % with increasing pulse time of 4 to 10 $A \cdot dm^{-2}$ due to the hydrogen evolution enhancement at a higher polarization. Prolong the pause positively influences the current efficiency of Cobalt-Molybdenum-Zirconium alloy as subsequent chemical reactions accompanying the alloying metals discharge are more fully but a larger current interruption reduces the efficiency of the process. Thus, current efficiency reaches 98 % when $t_{off} = 50$ ms and $t_{on} = 2$ ms.

Increasing the amplitude of the current changes the surface morphology and amplified internal stress that leads to fracture grid (Figure 3). The Figure 3 shows the surface becomes less smooth and more globular, and the crystallite sizes increase exactly due to the higher content of Molybdenum in the deposits. It should be emphasized sufficiently uniform distribution of the coating components on uneven relief, which may be attributed to a good dispersive capacity of the electrolyte. Increasing pulse time at a constant pause promotes the formation of spheroids on the surface but increasing tension in the coating and micro cracks become larger. Furthermore, some pores appear in coatings when the pulse time of 10 ms and the current density at $6-8 \text{ A} \cdot \text{dm}^{-2}$ (Figure 3 b, c), apparently due to hydrogen evolution.

The AFM analysis topography of the coatings Co-Mo-Zr show that their surface includes the parts of different morphology as one can see from Figure 4. The surface is characterized by globular structure with an average size of grains and crystallites 100-200 nm and singly located coneshaped (Figure 4 a) or semi-spheroid (Figure 4 c) hills with a base diameter of $1-3 \mu m$ and a height of 0.5-1.5 µm. As appears from 2D- and 3Dtopography maps of surface (Figure 4) the coneshaped hills are formed of the smaller spheroids. Such globular surface is caused by the presence of molybdenum in the deposits as it was shown in [20, 24] and we can see rather uniform distribution of alloying elements at picks and valleys (Figure 4 b, c) on the surface with a slight predominance of Mo and Zr at picks. As the current density increases the number of spheroids at the deposits surface is also increased but both their height and diameter are reduced (Figure 4 c).



Figure 3 – Morphology (x2000) and composition (at.%) of Co-Mo-Zr coatings deposited in pulse mode at current density. A · dm⁻²: 4 (a); 6 (b) and 8 (c); T = 20–25 °C; pH 8; plated time 30 min

The parameters of surface roughness $R_a=0.29$ and $R_q=0.38$ for ternary coatings deposited at current density 4 A·dm⁻² not differ from $R_a=0.29$ and $R_q=0.4$ for 6 A·dm⁻². According to the R_a and R_q the Co-Mo-Zr electrolytic coatings have a surface roughness class of 8–9. Such developed surface of globular structure as well as composition of material may be associated with high catalytic activity. A series of diffraction lines for α -Co on X-ray diffraction patterns for Co-MoZr deposits on steel substrates represent substitution solid solutions based on cobalt (Figure 5). No other phases including intermetallic compounds were not found in the coatings' structure even after a 3-hour annealing the coated sample on the air at a temperature of $600 \, ^\circ$ C. Furthermore, one can find a wide halo (full width at half maximum is about 5°) at angles $20 \sim 59 \, ^\circ$, which indicates an amorphous structure of above mentioned materials.



Figure 4 – 3D-. 2D-map and cross section of the surface Co-Mo-Zr between markers 1–2 deposited in pulse mode at current density 4 A·dm⁻² (a. b) and 6 A·dm⁻² (c); ton/toff = 2 / 10 ms; T = 25 °C; pH 8; plated time 30 min. Scan area AFM: a – 40x40 μm; b – 5.0x5.0 μm; c – 10x10 μm



Figure 5 – X-ray diffraction patterns for deposit Co-Mo-Zr. the composition is similar to Figure 3 a ($t_{on}/t_{off} = 2 / 10 \text{ ms}$)

Corrosion of cobalt based electrolytic coatings as it follows from the nature of alloying components predominantly with hydrogen proceeds depolarization in an acidic medium (Figure 6), and in neutral and alkaline under oxygen action. Corrosion potential of coatings alloyed with zirconium shifts in the negative direction in all environments (Figure 6, 7 Table 2) that agrees completely with the thermodynamic characteristics of zirconium. At the same time, the corrosion rate of a ternary alloy in the acidic and neutral chloridecontaining environment declines by almost an order of magnitude compared with the binary system (Table 2). It can be explained by an increased tendency to passivity of zirconium-containing material as can be seen from the corrosion plots (Figure 6) and the geometry of the anodic

polarization dependences (Figure 7). Also ternary alloy increases resistance to pitting corrosion initiated with chloride ions. The difference in corrosion rate of Co-Mo and Co-Mo-Cr coatings in an alkaline environment is not as great due to the acidic nature of passive oxides of molybdenum and zirconium which reacting with hydroxide ions. According to the calculated depth corrosion index k_h synthesized binary alloys with a molybdenum content not less than 10 at% and ternary ones with a zirconium content of at least 2 at.% belong to the group 1 – "very proof".

Results of testing the catalytic activity of Mo-Co and Co-Mo-Zr alloy coatings in the model reaction of hydrogen evolution from different media (Table 3) indicate the synergistic nature of the electrolytic alloys. The exchange current density of hydrogen on the surface of binary and ternary alloys is higher than this parameter on alloying components which can be attributed obviously with the change in the mechanism of the process. From the literature [34-36] it is known that the hydrogen evolution on cobalt occurs by Volmer-Heyrovsky mechanism (b = -0.1 V) with the limiting discharge stage (Volmer), which is described for the acidic medium by reaction

$$H_{3}O^{+} + e = H_{ad} + H_{2}O_{,}$$

and for neutral and alkaline

$$H_2O + e = H_{ad} + OH^-$$
.

Reducing of hydrogen on the metals subgroups of molybdenum and titanium is described by the same sequence of steps. However, the limiting stage



Figure 6 – Corrosion diagrams for coatings Co-Mo (1) and Co-Mo-Zr (2) in 1 M Na₂SO₄ (pH 3): cathodic plots (1. 2); anodic plots (1'. 2')

is electrochemical desorption (Heyrovsky step) occurring in an acid medium by reaction

$$H_3O^+ + H_{ad} + e = H_2 + H_2O$$
,

and in neutral and alkaline

$$H_2O + H_{ad} + e = H_2 + OH^{-}$$
.

As seen from the coefficient b = 0.03 (Table 3) hydrogen evolution both on the electrolytic Co-Mo alloy in an acidic medium and on Co-Mo-Zr coating in an alkali medium are limited by recombination stage

$$H_{ad} + H_{ad} = H_2,$$

i.e. flows through the Tafel mechanism. The same mechanism is typical for platinum, this is evidence of the high catalytic activity of the materials studied.

Thus, the combination of metals with different limiting stage of hydrogen evolution in the active layer allows obtaining a material with catalytic activity close to platinum metals.

Testing of the catalytic activity of the synthesized Co-Mo-Zr coatings was also performed in the model reaction of carbon (II) oxide conversion to carbon (IV) oxide. Quantitative characteristics of the oxidation are the carbon (II) oxide conversion degree X(CO) and ignition temperature T_i. The catalytic properties of galvanic alloys were compared to platinum which is the most effective catalyst. As one can see from the temperature dependencies (Figure 7, 1) at the platinum plate catalyst with $\omega(Pt)=100$ at.% the oxidation of CO begins at 190 °C, while 100 % conversion degree is achieved at 250 °C.



Figure 7 – Anodic polarization plots for coatings Co-Mo-Zr (1. 2) and Co-Mo (3. 4) in media: 1 M Na₂SO₄ pH 11 (1. 3); 3 % NaCl pH 7 (2. 4)


Figure 8 – Thermograms of CO conversion degree on Pt (1) and galvanic alloys Co-Mo-Zr of composition. wt .%: Co = 82.1. Mo = 17.1. Zr = 1.9 (2); Co = 83.0. Mo = 15.6. Zr = 1.4 (3); Co = 83.3. Mo = 15.8. Zr = 0.9 (4)

As can be seen from Figure 7, the thermograms of carbon (II) oxide conversion at the surface of catalyst coated with ternary alloys with various content of zirconium (dependences 2-4) have two sections with different slopes. In the first plot within the temperature interval 200-270 °C the kinetics of CO oxidation is not differ from the platinum plate catalyst with $\omega(Pt) = 100$ at.% although both the reaction initiation temperature T_{in} as well as temperature of 50 % conversion are higher than on platinum by 40–50 °C (Table 4). In the second plot at a temperature above 270 °C oxidation rate declines probably due to the formation of alloying metals oxides on the surface. The conversion degree rises by an average of 7-10% with increase the zirconium content in the coating by 1 at.% but the influence of zirconium weakens at the temperatures higher 350 °C. Evidence of high catalytic activity of materials is the fact that 99% conversion is achieved at temperatures of 375-380 °C. Catalytic properties of the synthesized systems are caused by cobalt ability to form nonstoichiometry oxides with different thermal resistance as well as by high affinity for oxygen of molybdenum and especially zirconium.

The above results are conclusive evidence not only of Co-Mo-Zr high catalytic activity but gives every reason to replace platinum catalysts at a cheaper galvanic alloys cobalt-molybdenumzirconium an added benefit of which is a metallic substrate.

1. Binary and ternary alloys of cobalt with molybdenum (zirconium) of different composition and morphology are obtained from polyligand citrate-pyrophosphate electrolyte in a pulsed mode by varying the current density and temperature. It is shown that at a current density of not more than $3 \text{ A} \cdot \text{dm}^{-2}$ coatings with micro-globular topography without stress and cracks are formed. Electrolytic alloys are solid solutions of zirconium and tungsten in cobalt in the wide range of alloying metals concentrations.

2. Chemical resistance of binary and ternary coatings based on cobalt is caused by the increased tendency to passivity and high resistance to pitting corrosion in the presence of molybdenum and zirconium, as well as the acid nature of their oxides. Binary coating with molybdenum content not less than 10 at % and ternary ones with zirconium content in terms of corrosion deep index are in a group "very proof" and can be recommended as protective for corrosive environments.

3. Electrolytic Co-Mo and Co-Mo-Zr alloys demonstrated synergism of catalytic activity for the hydrogen reduction from various media. It is shown that the combination of metals with different limiting stage of hydrogen evolution allows obtaining a material with catalytic activity close to platinum metals.

4. Electrolytic alloy Co-Mo-Zr with a Zr content of not less than 1.5 at% exhibits catalytic activity in the oxidation of carbon (II) oxide. This allows you to recommend the synthesized materials to replace platinum catalysts for improving the efficiency of the combustion of hydrocarbons and purification of gas emissions from toxic substances.

Conclusions

(i) Uniform ternary coatings Co-Mo-Zr of different composition can be produced in a pulsed mode from the polyligand citrate-pyrophosphate bath by varying the energetic and time electrolysis parameters.

(ii) The electro-catalytic activity of the Co-Mo-Zr alloys comparing with individual metals exhibits their synergetic nature. The greatest level of catalytic properties was obtained on synthesized alloys in acidic media for which the hydrogen exchange current density do not differ from the parameter for a platinum electrode.

(iii) The galvanic alloys Co-Mo-Zr with zirconium content 1.5–2.0 at.% exhibit high catalytic properties in the carbon oxide (II) oxidation. This confirms the efficiency of materials as catalysts for the gaseous wastes purification and gives the reason to recommend them as catalysts for hydrocarbon combustion.

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The percolation mechanism of conductivity in nanocomposite a-C:H<Ag+Ti> films

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The presented work is about percolation mechanism of electrical conductivity of composite a-C:H<Ag+Ti> films. The a-C:H<Ag+Ti> thin films were deposited onto quartz substrates by ion-plasma magnetron sputtering method. High purity argon (Ar) and methane (CH₄) gases mixture and combined target of polycrystalline graphite with the purity of 99.99%, silver (99.99%) and titanium (99.99%) were used to produce a-C:H<Ag+Ti> films. Resistance of the produced films has been measured using «two probe» method to obtain concentration dependence of electrical conductivity. Conductivity of a-C:H<Ag+Ti> films was described theoretically in two ways: using the classical theory of percolation and a general effective medium (GEM) theory. Staircase percolation can be seen from the experimental results. The first percolation threshold occurs at the concentration $x_c = 0.015$ and the second one - at $x_c = 0.07$. This could take place due to the fact that a-C:H<Ag+Ti> composite material consist of two different inclusions, silver and titanium dioxide nanoparticles. The percolation mechanism of a-C:H<Ag+Ti> film conductivity could be described by classical percolation theory and by effective medium model as well.

Key word: Amorphous carbon thin films, silver nanoparticles, nanocomposite, percolation, effective medium theory. PACS:61.00

Introduction

Composite materials based on the dielectric matrix with metal nanoparticles inclusions are of considerable interest in connection with possibility of their wide practical application in various fields of science and technology. A wide variety of functional properties of these composites allows using them, starting from energy sector (in solar cells) to targeted delivery of drugs in medicine [1-5].

Plasmon resonance absorption of electromagnetic radiation in the visible region of the spectrum on free surface electrons of metal nanoparticles takes place in nanocomposite materials based on the dielectric or semiconductor high-resistivity matrix and some metals nanoparticles in it [6]. Role of the matrix in such nanocomposite materials is to isolate the metal nanoparticles and preventing their agglomeration. Parameters of the resonance absorption are determined by dielectric permittivity of the matrix and by physical and chemical nature of the metal

[6,8]. This is shown in the studies of composite materials based on semiconductor matrices as SnO_2 [9], ZnO [10] and CdS [11, 12] and polymer matrices [13] with inclusions of silver and gold nanoparticles.

It is significant, that in such composite materials, under certain conditions, great surface amplification of Raman scattering of light (SERS effect) [14] is manifested, which allows to detect even individual molecules, and using silver nanoparticles, significantly enhance the antibacterial properties of coatings as well.

In modern nanomaterials science, amorphous diamond-like hydrogenated carbon films (a-C:H) have a special interest of researchers. This is due to a number of unique mechanical and electronic properties of these films. Taking into account high mechanical strength and reliability of the films, electronic devices made on the basis of these materials have extremely high speed, power, able to operate in a very wide temperature range and have high radiation resistance.

Diamond-like carbon materials containing metal nanoparticles represent а new class of nanostructured materials, called nanocomposites. In connection with this, development of nanomaterials with new properties based on diamond-like carbon modified by metal impurities media that significantly differ in nature by chemical interaction with carbon atoms and study of their structure and electronic properties is one of the most relevant and extremely important areas of research nanotechnology and nanomaterial science [15].

In addition, to optical effects of the a-C:H<Ag+Ti> film [16], there are unique electrical properties. In the a-C:H<Ag+Ti> films, a double

percolation transition with respect to conductivity is realized. Films with concentration of silver nanoparticles near the percolation threshold can be promising for creating highly sensitive small bending sensors [17, 18].

Experiment

Deposition of a-C:H<Ag+Ti> nanocomposite films was carried out in the vacuum chamber using ion-plasma magnetron sputtering of the combined target. Basic technological parameters of a-C:H <Ag+Ti> film production represented in the Table 1.

Table 1 - Basic technological parameters for a-C:H <Ag+Ti> film production

Working gas composition	The pressure in chamber P, Pa	Deposition temperature, °C	The distance from the target to the substrate, cm	Specific discharge power, W/cm	The magnetic field strength H, mlT
96% Ar + 4% CH ₄	0.8-1.0	100	3.5	3-4	~30

High purity argon (Ar) and methane (CH₄) gases mixture and combined target of polycrystalline graphite with the purity of 99.99%, silver (99.99%) and titanium (99.99%) were used to produce a-C:H<Ag+Ti> films. The a-C:H<Ag+Ti> films were deposited on a glass and quartz substrates.

Resistance of the produced films has been measured using «two probe» method to determine concentration dependence of electrical conductivity which represented on Figure 2. Note that conductivity of a-C:H<Ag+Ti> films at the maximum of Ag concentration remains much lower with respect to conductivity of polycrystalline graphite. This means that in these films there is no through-conduction channel over the regions of graphite-like carbon with sp²-hybridized bonds presented in diamond-like matrix with sp³hybridized bonds.

Simulation of the percolation conductivity processes in a-C:H<Ag+Ti> nanocomposite films

Conductivity of nanocomposite material can be described in two ways: using the classical theory of percolation (flow) and the model of a general effective medium.

Let us consider the main conclusions of percolation theory for conductivity analysis of the disordered structure, which is a set of conducting elements with concentration x and conductivity σ_M randomly distributed in a dielectric matrix with conductivity σ_D ($\sigma_D \ll \sigma_M$). According to percolation theory, conducting structure is a set of percolation clusters. For small values σ_M of x, all clusters are small. However, as we reach the percolation threshold, individual clusters merge, and their average size increases. At a certain concentration of x_c , the percolation cluster becomes infinite, i.e. there appears a path connecting remote to arbitrarily large distances the conducting regions inside the dielectric matrix and wholly passing through the conducting phase.

To the left of the percolation threshold x_c , at a sufficiently large distance from it, the total conductivity of the medium can be represented by [19]

$$\sigma_{\rm c} = \sigma_D (x_{cr} - x)^{-q}, \text{ for } x < x_c, \qquad (1)$$

where σ_D is conductivity of the matrix.

To the right of the percolation threshold, the concentration dependence of conductivity varies according to the law

$$\sigma_{\rm c} = \sigma_M (x - x_{cr})^t, \text{ for } x > x_c, \qquad (2)$$

where σ_M is the conductivity of the conducting phase.

Conductivity at the point of appearance of the infinite percolation cluster is described by

$$\sigma(x_{\rm c}) = \sigma_{\rm M} \left(\frac{\sigma_{\rm D}}{\sigma_{\rm M}} \right)^{\rm s}, \ x = x_{\rm c}, \ s > 0.$$
 (3)

The quantities q, t and s in (1-3) are called the critical indices of the conducting cluster.

The curve of theoretical dependence $\sigma(x)$ describing $\sigma(x)$ before and after the percolation threshold is shown in Figure 1. The transition curve (1) to (2) takes place in a small interval Δ in the vicinity of the x_c point. Relation (1) is satisfied if $\sigma(x) \ll \sigma(x_c)$ or $x_c - x \gg \Delta$, and relation (2) holds for $\sigma(x_c) \ll \sigma(x) \ll \sigma(x_M)$ or $x - x_c \gg \Delta$. The conducting cluster is also characterized by a correlation radius or a characteristic size *l*

$$l = l_o \left| \frac{x - x_c}{x_c} \right|^{-\nu},\tag{4}$$

where v is critical index, also called the critical index of the correlation radius, l_0 is the lattice period.



Figure 1– The theoretical dependence $\sigma(x)$ (solid line) [19]

Quantity *l* for $x < x_c$ is in the order of cluster size itself, and for $x > x_c$ in the order of nonconducting pores size in it.

The critical indices of the percolation theory q, t, s and v are related to each other by the relations

$$q = \frac{t}{s} - t, \qquad (5)$$

$$t = 1 + \nu (d - 2), \tag{6}$$

where *d* is dimension of space. For a threedimensional composite the classical values are: $t = (1.6 \div 2.0)$, $q \approx 1$, $s \approx 0.62$.

We note that index t plays a very important role, since, unlike the percolation threshold x_c , it does not depend on the type of the problem, but depends only on the dimensionality of the space. Therefore, in real systems, this index is primarily compared with the theory. On the other hand, the universality of critical indices of percolation theory just allows us to involve it for the analysis of heterogeneous disordered structures conductivity.

Figure 2 shows concentric dependence of conductivity of a-C:H <Ag+1.0 at.% Ti> films. In this figure, silver concentration x is represented as the volume fraction in the matrix of the films. The curves describing behavior of concentration dependence of conductivity up to (curves 1 and 2) and after (percolation curves 1 'and 2') are represented using expressions (1) and (2). It follows from this approach that concentration dependence experimental data of a-C:H<Ag+1.0 at.% Ti> films conductivity can be described by two percolation transitions (the so-called staicase percolation).

Note that there are inclusions of both Ag and TiO_2 nanoparticles in the matrix of the studied a-C:H<Ag+Ti> films, and several percolation transitions can occur in such nanocomposites.

Let us consider the concentration dependence of the a-C:H<Ag+Ti> films conductivity using the effective-medium model (General Effective Medium, GEM), which is used to describe concentration dependences of conductivity of composite materials [20]. The expression to determine the conductivity σ in the theory of general effective medium is written as follows [20]

$$\frac{x(\sigma_D^{\frac{1}{t}} - \sigma(x)^{\frac{1}{t}})}{\sigma_D^{\frac{1}{t}} + A\sigma(x)^{\frac{1}{t}}} = \frac{(1-x)(\sigma_M^{\frac{1}{t}} - \sigma(x)^{\frac{1}{t}})}{\sigma_M^{\frac{1}{t}} + A\sigma(x)^{\frac{1}{t}}} = 0,$$
(7)

$$A = \frac{1 - x_c}{x_c},\tag{8}$$

where the exponent is defined as $t = (1 - x_c)/(1 - l)$.

The results of a comparison of theoretical description of the percolation process according to the classical theory and general effective medium model with experimental values of concentration dependence of conductivity of a-C:H<Ag+1.0 at.% Ti> films are shown in Figure 2, curve 3.



Figure 2 – Theoretical (1 and 1 ', 2 and 2', 3 and 3 ') and experimental (x) dependence of conductivity of a-C:H<Ag+1.0 at.% Ti> nanocomposite films on Ag volume fraction

From the figure 2 it follows that classical theory of percolation and approach based on the general

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5. Jiongxin Lu, C. P. Wong. Recent Advances in High-k Nanocomposite Materials for Embedded Capacitor Applications // IEEE Transactions on effective medium model make it possible to describe the region of percolation transition before and after the percolation threshold in a-C:H<Ag+1.0 at.% Ti> nanocomposite films.

Conclusions

Conductivity of a-C:H<Ag+Ti> films at the maximum of Ag concentration remains much lower compared to conductivity of polycrystalline graphite. This means that in these films there is no through-conduction channel over the regions of graphite-like carbon with sp²-hybridized bonds presented in diamond-like matrix with sp³-hybridized bonds. From concentration dependence of conductivity we conclude that two percolation transition occur in the obtained a-C:H<Ag+Ti> composite material. These percolation mechanisms of film conductivity could be adequately described by the classical percolation and general effective medium theories.

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