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I. Chikina,[1] V. Shikin,[2] and Andrey Varlamov[3]
[1] *IRAMIS, LIONS, UMR NIMBE 3299 CEA-CNRS, CEA-Saclay, F-91191 Gif-sur-Yvette Cedex, France*
[2] *ISSP, RAS, Chernogolovka, Moscow District, 142432 Russia*
[3] *CNR-SPIN, c/o DICII-Universitá di Roma Tor Vergata, Via del Politecnico, 1, 00133 Roma, Italy*
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We discuss the peculiarities of the Ohm law in dilute polyelectrolytes containing a relatively low concentration $n_\odot$ of the multiply-charged colloidal particles. It is demonstrated that in this conditions, the effective conductivity of polyelectrolyte is the linear function of $n_\odot$. This happens due to the change of electric field in the polyelectrolyte under the effect of colloidal particle polarization. Such mechanism gives grounds to propose the alternative scenario for the phenomenon observed experimentally.

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I. INTRODUCTION

In the Refs. [1, 2], among various observations, the authors report the effect of multiply-charged colloidal particles (with the effective charge $eZ \gg e$) on conductivity of the dilute polyelectrolytes. It turns out that the latter grows linearly with increase of the colloidal particles concentration. This finding seems to be non-trivial from different points of view, and in the first hand in the optics of the percolation theory (see, for example, [3]). Indeed, in accordance to the percolation theory the conductivity of a mixture between dielectric and conducting components, remains minute until the fraction of conducting phase approaches the percolation threshold. And only in vicinity of the latter the conductivity growths smoothly from the value of the dielectric component to that of metallic one.

Before discussing this contradiction, let us make an excursus into the physics of semiconductors. In the theory of semiconductors [3], the regions of weak and strong doping (i.e., introduction of charged impurities or structural defects with the purpose of changing the electrical properties of a semiconductor) are distinguished. In the low doping regime, the impurity concentration $n_\odot$ is so small that the distances between them significantly exceed the Debye length λ_0 and the bare radius of the colloidal particle R_0, i.e.

$$n_\odot \left(\lambda_0 + R_0\right)^3 \ll 1, R_0 \leq \lambda_0, \tag{1}$$

and the intrinsic charge carriers of semiconductor completely screen the electric fields produced by the charged impurities (see Fig. 1). In the strong doping regime, when the criterion (1) is violated, the fields produced by the dopants are screened only partially and their interaction becomes significant.

Returning to the case of the dilute colloidal polyelectrolytes one can identify $n_\odot$ with the concentration of the colloidal particles, while λ_0 is related to their characteristic size. The latter is determined by the known concentration n_0 of the counterions of the electrolyte hosting the charged colloidal particles.

The criterion (1) is in a reasonable agreement to the common concepts of the physics of dilute polyelectrolytes developed in Ref. [4, 5, 9] and known as DLVO formalism. Namely, if the colloidal particles are neutral, they can not exist stationary in dilute solution, coagulating due to the van der Waals forces acting between them. In order to prevent such coagulation processes, one can immerse individual colloidal particles in the electrolyte specific for each sort of them. The latter are called stabilizing electrolytes.

Being immersed (or synthesized within) an electrolyte solution, the nanoparticles acquire surface ions (e.g., hydroxyl groups, citrate, etc. [6–8]) resulting in a very large structural charge eZ ($|Z| \gg 10$). Its sign can be both positive and negative, depending on the surface group type. The latter in return, attracts counterions from the surrounding solvent creating an electrostatic shielding coat of the size λ_0 with an effective charge $-eZ$. In these conditions, nano-particles approaching between them to the distances $r \leq \lambda_0$ begin to repel each other without floculation [4, 5, 9]. The region of an essential interaction between them in terms of the criterion (1) corresponds to the condition

$$n_\odot^c \left(\lambda_0 + R_0\right)^3 \sim 1. \tag{2}$$

Coming back to the results of Ref. [1, 2] one can see that observation of the linear growth of the dilute colloidal polyelectrolytes conductivity σ as the function of the concentration $n_\odot$ is in the evident contradiction with the percolation theory [3]. Indeed, each massive multiply-charged colloidal particle is surrounded by the cloud of counter-ions screening its positive charge. Such formations, according to Ref. [3], should not affect on conductivity of the dilute solution until shells of the neighbor charged complexes will not overlap among themselves (see Eq. (2)). The results of Ref. [2] demonstrate the opposite: the conductivity of dilute colloidal

polyelectrolyte grows linearly with increase of concentration already in the range $n_\odot \ll n_\odot^c$, where there is not yet place for percolation effects.

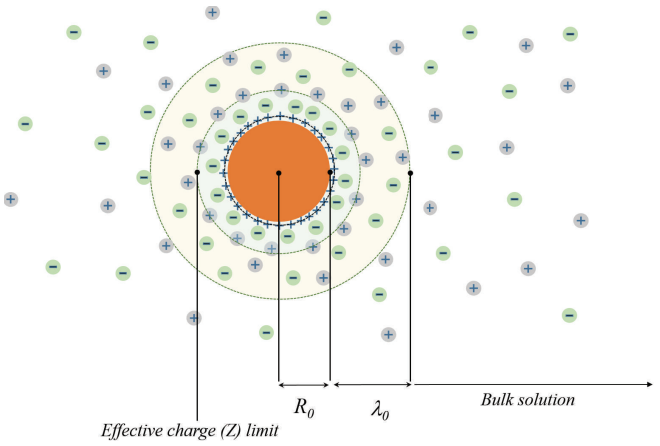

FIG. 1. The schematic presentation of the multiply-charged colloidal particle surrounded by the cloud of counter-ions.

This contradiction can be eliminated by noticing that presence of the multiply-charged colloidal particles has an effect not only on the value of conductivity of solution but also on the local value of the electric field:

$$j(n_\odot) = \sigma(n_\odot)E(n_\odot). \tag{3}$$

Important to note that the factors in Eq. (3) are affected by presence of the multiply-charged colloidal particles in different ways. While the conductivity of the electrolyte at low concentrations of multiply charged colloidal particles ($n_\odot \leq n_\odot^c$) remains almost unchanged, their effect on local electric field in this range of concentrations is essential. This happens due to polarization of the colloidal particles by an external electric field which, in accordance to the Le Chatelier's principle, results in the decrease of the effective value of the field. Consequently, the growth of conductivity [1, 2] as the function of concentration $n_\odot$ is observed in experiment. When the concentration of multiply charged colloidal particles reaches the percolation threshold ($n_\odot = n_\odot^c$) the role of factors in Eq. (3) is reversed. Here the subsystem of colloidal particles forms clusters and cannot be considered more as the gas of polarized highly conducting particles. Yet, namely in this range of concentrations, the new channel of percolation charge transfer is opened and the total conductivity of the electrolyte growth with further increase of $n_\odot$.

The state of art of transport phenomena in polyelectrolytes recently was reviewed in Ref. [1]. Focusing mainly on the results of the microscopic approach [10–12] the authors discuss in details mobility, diffusion coefficient, effective charge space distribution of the colloidal particles as the function of their concentration. Yet, in Ref. [1] there is no any information concerning the effect of clusters polarization on the charge transfer process in such complex systems. Namely this aspect of the problem is the subject of our work.

II. EFFECTIVE ELECTRIC FIELD IN BULK OF COLLOIDAL POLYELECTROLYTE

The colloidal polyelectrolyte presents itself a weakly conducting liquid with the small but finite fraction of relatively highly (due to $Z \gg 1$) conducting inclusions: colloidal particles. The collective polarization of these inclusions occurs when the external electric field E_0 is applied. This phenomenon is analogous to polarization of neutral atoms in gas. The only difference is that the neutral atoms reside in vacuum, while the charged conducting clusters of colloidal polyelectrolyte are immersed in a less, but still conducting, medium. Hence our goal is to account for this peculiarity and find the effective field which governs the charge transport in such complex system.

A. Electric field in absence of current

The space distribution of the effective electric field of the colloidal particle is determined by the Poisson equation (see [3, 5])

$$\Delta\varphi = \frac{4\pi}{\epsilon}\rho(r), \quad \rho(r) = |e|[n_+(r) - n_-(r)], \tag{4}$$

where ϵ is the dielectric permittivity of stabilizing electrolyte.

The concentrations of the screening counterions $n_\pm(r)$ is determined self-consistently via the value of local electrostatic potential

$$n_\pm(r) = n_0 \exp\left[e_\pm\varphi(r)/T\right], \tag{5}$$

$n_0 = n_0^+ = n_0^-$ is the counterions bare concentration, occuring due to the complete dissociation of the electrolyte which stabilizes the gas of colloidal particles.

In assumption $e\varphi(r) < T$ the Poisson equation can be linearized and takes form

$$\Delta\varphi = \varphi/\lambda_0^2, \quad \lambda_0^{-2} = \frac{8\pi e^2}{\epsilon T} n_0. \tag{6}$$

This equation should be solved accounting for the boundary conditions

$$r\varphi(r)_{|r\to R_0} \to Z|e|, \quad \varphi(r)_{|r\to\infty} \to 0, \tag{7}$$

what results in the standard screened Coulomb potential:

$$\varphi(r) = Ze\frac{\exp(-\frac{r}{\lambda_0})}{r}. \tag{8}$$

The values Z,R_0 and n_0 of the electrolyte, which stabilizes the colloidal solution can be determined by independent experiments (for example, by measurements of the electrophoretic forces, osmotic pressure, etc. [1]).

One should remember that even strongly diluted polyelectrolytes can undergo the transition to the state of Wigner crystal in the case of strongly charged colloidal particles ($Z \gg 1$). For description of this, observed experimentally [14–16], phenomenon the authors of [17] assumed that the interaction between two colloidal particles has the same form of Yukawa potential (8), yet with the renormalized effective charge $Z^* \ll Z$, explicitly depending on the colloidal particles density $n_\odot$. The value of Z^* is determined in the Wigner-Seitz model from the new boundary condition

$$\frac{\partial\varphi}{\partial r}|_{r\to n_\odot^{-1/3}} = 0$$

replacing that ones, valid for the isolated charged particle in the screening media (see Eq. (7)). For some range of the colloidal particles densities $n_\odot$ the conditions $Z \gg 1$ and $Z^* \ll 1$ can be satisfied simultaneously. The former characterizes the properties of the multiply-charged colloidal particles itself, while the latter is determined by strength of their interaction and $n_\odot$. In the range of densities $n_\odot$ satisfying Eq. (1) the effect of the effective charge Z^* on the Ohmic transport is negligible.

B. Electric field in presence of current

When a stationary current flows through the polyelectrolyte, an internal electric field $\vec{E}$ appears in it. In the approximation of a very diluted solution one can start consideration from the effect of presence of the isolated colloidal particle on flowing current. Namely, one should find the perturbation of the internal electric field which would provide the homogeneity of the transport current far from the colloidal particle. Corresponding problem recalls that one of the classic hydrodynamics: calculus of the associated mass of the particle moving in the ideal liquid [18].

We choose the center of spherical coordinates coinciding with the colloidal particle and direct the $z-$axis along the electric field $\vec{E_0}$. We assume that the conductivity of the electrolyte in absence of colloidal particles is σ_0. The highly charged colloidal particle we will model as the conducting solid sphere of the radius $R \simeq (R_0 + \lambda_0)$(see Fig 1) with conductivity $\sigma_\odot > \sigma_0$. Analysis of the charge transport in multi-phase systems (see [19]) is based on the requirements

$$div\vec{j} = 0, \quad \vec{j} = \sigma\vec{E}. \tag{9}$$

When the medium conductivity is invariable in space the constancy of current automatically means the homogeneity of the electric field. The situation changes when the system is inhomogeneous and $\sigma \neq const$. The continuity equation (9) in this case should be solved with the boundary conditions accounting for the current flow through the boundaries between domains of diverse conductivity. According to Ref. [19, 20] the tangential components of electric field intensity at the boundary must be continuous, while the normal ones provide the continuity of the charge transfer. Applying these rules to our simple model of the highly charged colloidal particle in the less conductive medium one can write

$$j_n^0 = J_n^\odot, \quad \text{or} \quad \sigma_0 E_0 = \sigma_\odot E_\odot. \tag{10}$$

Solution of the system of Eqs. (9), (10) for the electrostatic potential in the vicinity of the colloidal particle ($r \geq R$) acquires the form:

$$\varphi(r,\theta) = -E_0 r\cos\theta + \left(\frac{\gamma-1}{\gamma+2}\right) E_0 \frac{R^3}{r^2}\cos\theta, \tag{11}$$

with $\gamma = \sigma_\odot/\sigma_0$. In the limit $\gamma \to 1$ the electric field remains unperturbed, $\vec{E} = -\nabla\varphi \to \vec{E}_0$. In the opposite case, $\gamma >> 1$, the dipole perturbation takes the form corresponding to the case of metallic inclusion of the radius R in the weakly conducting environment (Ref. [19]):

$$\varphi(r,\theta) = -E_0 r\cos\theta\left(1 - \frac{R^3}{r^3}\right). \tag{12}$$

One can see that in accordance to the intuitive expectations presence of an isolated colloidal particle in electrolyte leads to appearance of the local perturbation of the electric field of the dipole type $\nabla\varphi \propto r^{-3}$ with the value of the dipole moment of one colloidal particle

$$p_\odot = \left(\frac{\gamma-1}{\gamma+2}\right) R^3 E_0. \tag{13}$$

Returning to the initial problem of the rarefied gas of colloidal particles of the concentration $n_\odot$ in the electrolyte media one can introduce the effective dielectric permittivity $\epsilon_\odot$. It can be related to the dipole moment (13) by means of the Clausius–Mossotti relation (see Ref. [19]) and in terms of the material parameters of the problem is read as:

$$\epsilon_\odot = 1 + 4\pi\left(\frac{\gamma-1}{\gamma+2}\right) R^3 n_\odot. \tag{14}$$

One can try to make the model of colloidal particle more realistic assuming that the latter has the structure of thick-walled sphere: a "nut" with the conducting shell and the insulating core of the bare radius R_0. This intricacy leads to the change in the expression for the corresponding dipole momentum: instead of Eq. (13) it takes form (see Ref. [19])

$$\tilde{p}_{\odot}=\frac{(2\gamma+1)(\gamma-1)}{(2\gamma+1)(\gamma+2)-2(\gamma-1)^2 R_0^3/R^3}\left(R^3-R_0^3\right)E_0. \quad (15)$$

This formula contains two geometrical parameters: R and R_0. The latter should be determined from some independent measurements. The difference $R-R_0$ one can identify with the Debye length λ_0 or to consider it as the fitting parameter.

III. OHMIC TRANSPORT IN A WEAK COLLOIDAL POLYELECTROLYTE

Eq. (14) demonstrates that growth of the nanoparticles concentration $n_{\odot}$ leads to increase of the dielectric constant $\epsilon_{\odot}$, what, in its turn, results in the decrease of the effective electric field in electrolyte. The latter, in conditions of the fixed transport current, is perceived as the growth of conductivity with increase of the colloidal particles concentration:

$$\sigma(n_{\odot})=j\epsilon_{\odot}/E_0=\sigma_0\left[1+4\pi n_{\odot}\frac{p_{\odot}(E_0)}{E_0}\right]. \quad (16)$$

This expression can be already used for the experimental data processing.

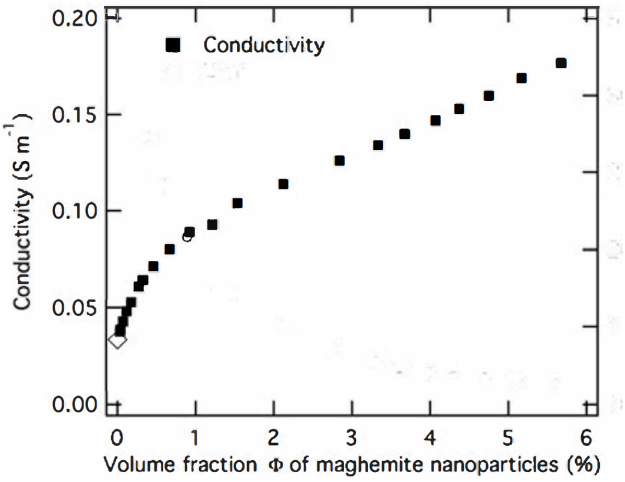

FIG. 2. Experimental values of electrical conductivity of water based polyelectrolyte solution as a function of colloidal concentrations. Measurements were performed on pH = 3.1 solutions containing maghemite nanoparticles with an average diameter of 12 nm. More detailed information on the colloidal solution preparation methods and the nature of other ions are found in Ref.[1, 2].

Approximation of the conducting spheres

Substituting the dipole moment taken in the approximation of Eq. (13) in Eq. (16) one finds

$$\frac{\Delta\sigma_{\rm CP}(n_{\odot})}{\sigma_0}=\frac{\sigma(n_{\odot})-\sigma_0}{\sigma_0}=4\pi n_{\odot}\left(\frac{\gamma-1}{\gamma+2}\right)R^3, \quad (17)$$

where $\Delta\sigma_{\rm CP}$ is the excess conductivity due to the presence of colloidal particles. The left-hand-side of this equation can be extracted from the data presented in Fig. 2. Indeed, in the interval of the nanoparticles concentrations $0\le\phi\le 0.6\%$ the behavior of conductivity $\sigma(n_{\odot})$ is almost linear and $\sigma(n_{\odot})/\sigma_0-1=0.7$. In its turn the concentration $\varphi=0.6\%$ corresponds to $n_{\odot}^{(1)}=5.45\,.\,10^{15}cm^{-3}$.

For the further estimations will be crucial that the Eq. (17) is sensitive to the value of γ only when it is not very large. When $\gamma>>1$ (we will justify this limit below) the combination $(\gamma-1)/(\gamma+2)\to 1$ and it ceases to influence on the evaluations based on Eq. (17). This allows us to find in this limit

$$R_{exp}^{(1)}=2.17\,.\,10^{-6}cm,$$
$$n_{\odot}^{(1)}\left[R_{exp}^{(1)}\right]^3=0.055\ll 1. \quad (18)$$

One can see that these values, together with the nanoparticles concentration $n_{\odot}^{(1)}$, confirms validity of the assumed above approximation (1). The plausible reasons for the discovered considerable difference between $R_{exp}^{(1)}$ and the value of bare radius $R_0^{(1)}=6\,.\,10^{-7}cm$ given in Ref. [1] we will discuss below.

The above found conductivity correction $\Delta\sigma_{\rm CP}(n_{\odot})\propto n_{\odot}R^3$ (see Eq. (17)) caused by presence of nanoparticles in electrolyte can be confidently distinguished from the standard Onsager-Debye conductivity ($\sigma_{\rm OD}$) of the diluted 1:1 electrolyte [21–23]. Indeed, first of all the concentration dependencies of these conductivities are different: $\Delta\sigma_{\rm CP}(n_{\odot})\propto n_{\odot}$ while $\sigma_{\rm OD}(n_{\odot})\propto\sqrt{n_{\odot}}$.

Let us attract attention at the unusual dependence of the excess conductivity (17) on the nanoparticle size: $\Delta\sigma_{\rm CP}$ growths with increase of R. Usually, this dependence is supposed to be opposite (the larger radius of the sphere in Stokes viscous law, the lower its mobility, and hence, the conductivity).

One can analyze the available experimental data on conductivity of the stabilized diluted colloidal solution [1, 2] in the conditions described by Eq. (2). In accordance to Eq. (17) the excess conductivities for different sizes of nanoparticles in assumption of the same concentration should scale as $[R_0^{(1)}/R_0^{(2)}]^3$. Taking the value $R_0^{(1)}=6nm$ from [1] and $R_0^{(2)}=3.8nm$ from [2] one finds that the ratio

$$\frac{\Delta\sigma_{\rm CP}^{(1)}}{\sigma_0^{(1)}}/\frac{\Delta\sigma_{\rm CP}^{(2)}}{\sigma_0^{(2)}}=\left(\frac{6}{3.8}\right)^3\approx 4 \quad (19)$$

Experimental data for this value give even more striking difference:

$$\frac{\Delta\sigma^{(1)}_{\rm CP}}{\sigma^{(1)}_0}/\frac{\Delta\sigma^{(2)}_{\rm CP}}{\sigma^{(2)}_0}=\frac{0.7}{0.06}\approx 11.7. \qquad (20)$$

Approximation of the conducting thick-walled spheres

Here it is necessary to notice that the value $R^{(1)}_{exp}$ obtained in the simple approximation of Eqs. (13), (16) and the measured in Ref. [1] bare radius of the colloidal particle R_0 form relatively small numerical parameter $[R_0/R^{(1)}_{exp}]^3\simeq 0.02$. It is why makes sense to improve the experimental data proceeding replacing the value $p_\odot$ in Eq. (16) by the two parametric expression (15). Tending $\gamma\to\infty$ in it one finds

$$\frac{\sigma(n_\odot)-\sigma_0}{\sigma_0}=4\pi n_\odot[R^{(1)}_{exp}]^3\left[1-\frac{3}{\gamma}-\frac{9}{2\gamma}\frac{R_0^3}{\left([R^{(1)}_{exp}]^3-R_0^3\right)}\right] \qquad (21)$$

From this expression it is clear that the approximation (17) is valid when $\gamma\gg 1$.

The parameter γ requires a special discussion. In the DLVO colloidal model it is assumed that some bare core exists which is able to cause the van der Waals forces between colloidal particles in dilute, non-stabilizing solution. What are the conducting properties of this core is not so essential. For example, one can suppose this bare core of the radius R_0 to be semiconductor possessing its intrinsic charge carriers which are confined in its volume. If the solvent possesses the stabilizing properties its own mobile charge carriers, counterions, have the same properties, as the intrinsic charge carriers of the bare core. The requirement of electrochemical potential constancy leads to the charge exchange between the bare core and the solvent. Such exchange results in the formation of the Debye shell (see Eqs. (4)-(8), where the concentration of counterions considerably exceeds that one in the solvent bulk. We assumed above that the value of corresponding conductivity $\sigma(n_\odot)$ considerably exceeds that one σ_0 of the electrolyte conductivity in absence of the nanoparticles. This assumption ($\gamma\gg 1$) breaks when the average value of electrochemical potential in the Debye shell $e\phi_\odot$, exceeds temperature. The authors of Ref. [24] state that in these conditions the Debye shell of the DLVO colloid can crystallize due to Coulomb forces and the latter becomes insulator with $\sigma(n_\odot)\lesssim\sigma_0$.

IV. CONCLUSIONS

The main result of this work consists of the proposition of alternative scenario explaining the linear growth of the polyelectrolyte conductivity versus the concentration of colloidal particles observed in Ref. [1, 2] in the conditions of the validity of Eq. (1). It drastically differs from the existing ideas of the transport in electrolytes resulting in the empirical Kohlrausch's law (see [23, 25])

$$\Delta\sigma\sim\sqrt{n_\odot}. \qquad (22)$$

The speculations justifying Eq. (22) were firstly proposed in so early papers as Ref. [21, 22] and the recent efforts to improve this mechanism were undertaken in the Ref. [26].

The fact of observation of the Ohmic transport in strong electrolyte (Ref. [1, 2]) denies the applicability of the Kohlrausch's law in the interval of very low concentration of the colloidal particles. Conversely, the mechanism proposed above, based on the analogy to percolation mechanism of conductivity occurring in doped semiconductors, allows to get an excellent agreement in the observed linear dependence. Moreover, it also provides very reasonable values of the microscopic parameters of the problem.

One can believe that the validity Kohlrausch's law is restored in the domain of higher concentrations and the crossover point between the two regimes (16) and (22) is determined by the condition (2), as it is shown in Fig. 2. One can find the pro-arguments for this statement also in the experimental curve shown in Fig. 2 of Ref. [1], where the regimes are changed in vicinity of the concentration $n^{(1)}_\odot=5.45\,.\,10^{15}cm^{-3}$.

The natural question arises: why such linear growth below the percolation threshold was never reported in measurements performed on semiconductors? The answer probably consists in the overwhelming supremacy of the colloidal particle dipole momentum in comparison to that one of the dopant in semiconductor.

It would be interesting to compare the values of effective charge Z extracted from the experiments on conductivity of Ref. [2] and the review article [1]. Unfortunately, this is not easy to do since analysis of the data for different Z results in very different values of R_0. It is why one cannot judge about the influence of the effective charge Z on the bare radius of the colloidal particle R_0.

The relative insensibility of the polyelectrolyte conductivity on the value of the parameter Z. is not extended on Seebeck coefficient. The measurements of Ref. [2] demonstrated existence in its kinetics of the two different phases: the initial and steady ones. The authors dealt with two types of colloids, one is almost electroneutral ($Z\geq 1.$), the other is supposed to have $Z\gg 1$.

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