



**HAL**  
open science

## Two stage Seebeck effect in charged colloidal suspensions

I. Chikina, Sawako Nakamae, V. Shikin, A. Varlamov

► **To cite this version:**

I. Chikina, Sawako Nakamae, V. Shikin, A. Varlamov. Two stage Seebeck effect in charged colloidal suspensions. 2020. cea-02977768

**HAL Id: cea-02977768**

**<https://cea.hal.science/cea-02977768>**

Preprint submitted on 26 Oct 2020

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

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

# Two stage Seebeck effect in charged colloidal suspensions

I. Chikina,<sup>1</sup> Sawako Nakamae,<sup>2</sup> V. Shikin,<sup>3</sup> and A. Varlamov<sup>4</sup>

<sup>1</sup>LIONS, NIMBE, CEA, CNRS, Université Paris-Saclay, CEA Saclay, 91191 Gif-sur-Yvette, France

<sup>2</sup>Service de physique de l'état condensé, SPEC, CEA, CNRS,

Université Paris-Saclay, CEA Saclay, 91191 Gif-sur-Yvette, France

<sup>3</sup>ISSP, RAS, Chernogolovka, Moscow District, 142432 Russia

<sup>4</sup>CNR-SPIN, c/o DICII-Università di Roma Tor Vergata, Via del Politecnico, 1, 00133 Roma, Italy

(Dated: October 20, 2020)

We discuss the peculiarities of the Seebeck effect in stabilized electrolytes containing the colloidal particles. Its unusual feature is the two stage character, with the linear increase of differential thermopower as the function of colloidal particles concentration  $n_{\odot}$  during the first stage and dramatic drop of it at small  $n_{\odot}$  during the second one (steady state) [2]. We show that the properties of the initial state are governed by the thermo-diffusion flows of the mobile ions of the stabilizing electrolyte medium itself and how the colloidal particles participate in formation of the electric field in the bulk of suspension. In its turn the specifics of the steady state in thermoelectric effect we attribute to considerable displacements of the massive colloidal particles in process of their slow thermal diffusion and break down of their electroneutrality in the vicinity of electrodes

PACS numbers: 82.45.Gj, 65.20.-w, 44.35.+c

## I. INTRODUCTION

In recent years, liquid thermoelectric materials are emerging as a cheaper alternative with semiconductor based solid counterpart for low-grade waste heat recovery technologies. A breakthrough to the enhancement of the thermo-electric efficiency of thermo-electrochemical cell has been achieved using ionic liquids [1]. And more recently, the dispersion of charged colloidal particles (magnetic nanoparticle) was also found to increase the Seebeck coefficient of the host electrolyte. Incorporation of the nano- and micro-meter sized colloidal particles can dramatically change the transport properties of such systems. For example, in Ref. [2] a novel use of charged colloidal solution was proposed to improve the Seebeck coefficient of aqueous thermo-electrochemical cell. The authors study transport properties of the charged colloidal suspensions of iron oxide nanoparticles (maghemite) dispersed in aqueous medium and report the values of the order of  $1 - 1.5mV/K$  for the Seebeck coefficient. The inclusion of Tetrabutyl ammonium as counterions, lead to an enhancement of the fluids initial Seebeck coefficient by 15% (at nanoparticle concentration 1%). The authors of Ref. [3] also indicate on high values of Seebeck coefficient ( $\approx 2mV/K$ ) for many electrolyte-electrode combinations, what is much higher than existing prediction.

The charged colloidal suspensions of iron oxide nanoparticles (maghemite) dispersed in aqueous medium was used by the authors of Ref. [2]. Point in fact, that when 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 such that they acquire surface ions

(e.g., hydroxyl groups, citrate, *etc.* [4–6]) resulting in accumulation by them of very large structural charge  $eZ$  ( $|Z| \gg 10$ ). Its sign can be both positive and negative, depending on the surface group type. Such procedure is called stabilization and obtained suspension is considered stabilized.

The large structural charge attracts counterions from the surrounding solvent creating an electrostatic screening coat of the length  $\lambda_0$  with an effective charge  $-eZ$  (see Fig. 1). In these conditions, nano-particles approaching within the distances  $r \leq \lambda_0$  between them begin to repel each other preventing coagulation. Corresponding theory of stabilized electrolyte was developed in Refs. [7–9] and is often referred as the DLVO theory.

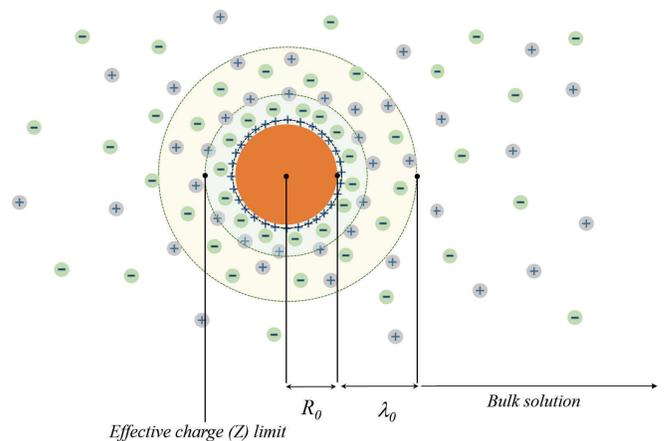


FIG. 1. The schematic presentation of the multiply-charged colloidal particle surrounded by the cloud of counter-ions.

A clear manifestation of stabilization phenomenon oc-

curs in such diluted solutions especially clearly in the region of concentrations where

$$n_{\odot} (\lambda_0 + R_0)^3 \ll 1, \quad (1)$$

where  $n_{\odot}$  is the density of colloidal particles and  $R_0$  is the bare radius of the colloidal particle. Important, that in conditions of Eq. (1) validity the stabilized DLVO solution is homogeneous.

In the case of thermocells considered here, with a temperature difference between two electrodes, the colloidal particles are dragged by the heat flow inducing a concentration gradient (Soret effect). The differences in transport coefficients of various charged components of the stabilized solution result in violation of the local electrical neutrality in the latter when the temperature gradient is applied. Namely this circumstance is the origin of the Seebeck effect occurring in the bulk of the stabilizing electrolyte. It is why the thermo-diffusion displacements of the colloidal particles can be observed only side by side with the Seebeck effect in stabilized colloidal suspension. One can call this phenomenon as the electrostatic potential difference induced by the Soret effect which is considered to be independent from the redox reactions of the solutes in the electrolyte. At the same time, the concentration of the colloidal particles, in accordance to the data of Ref. [2], considerably effects on the value of Seebeck coefficient. Discussion of the possible reasons of this nontrivial effect is the goal of presented work.

## II. THE PECULIARITIES OF THE SEEBECK EFFECT IN COLLOIDAL SOLUTION

When the temperature difference is imposed the two different kinds of the diffusion flows occur in a thermocell. First, these are the thermo-diffusion flows of the mobile ions of the stabilizing electrolyte, the second, much slower, is that one of the colloidal particles. The diffusion of positive and negative ions under the effect of temperature gradient occurs with different rates what results in the appearance of the charge separation and, as the consequence, formation of the internal electric field, i.e. Seebeck effect.

### A. Initial state of Seebeck effect in colloidal solution

In order to understand the effect of presence of the colloidal particles presence in solution on the strength of the Seebeck effect at the initial state let us assume that their concentration  $n_{\odot}$  remains homogeneous.

The electric current in the conducting media in presence of electric field and temperature gradient is described by the generic equation

$$\mathbf{j} = \sigma \mathbf{E} - \beta \nabla T. \quad (2)$$

Here  $\beta = -S\sigma$  and  $\sigma$  is electrical conductivity. For the further convenience we expressed the former in terms of conductivity and Seebeck coefficient (also called thermopower)  $S$ . Namely the Seebeck coefficient  $S$  determines the voltage appearing on the cell with broken circuit related to the applied temperature difference

$$V = \int_{T_1}^{T_2} S(T) dT \quad (3)$$

and it is this value which usually is measured in experiment (for example in Ref. [2]).

Since the electrolyte consists of two oppositely charged subsystems of positive and negative ions, its effective Seebeck coefficient is determined by the sum of the coefficients  $\beta_{\pm}$  of each ion subsystem divided by the total conductivity ( $\sigma_+ + \sigma_-$ ) of the solution:

$$S_{\text{tot}} = -\frac{\beta_+ + \beta_-}{\sigma_+ + \sigma_-} = \frac{S_- \sigma_- + S_+ \sigma_+}{\sigma_- + \sigma_+}. \quad (4)$$

The conductivity of electrolyte containing some low enough concentration (see condition (1)) of the colloidal particles was recently studied in Ref. [10], where the explicit expression for it was obtained:

$$\begin{aligned} \sigma_{\text{tot}}(n_{\odot}) &= \sigma_+(n_{\odot}) + \sigma_-(n_{\odot}), \\ \sigma_{\pm}(n_{\odot}) &= \sigma_{\pm}^{(0)} \left[ 1 + 4\pi n_{\odot} \left( \frac{\gamma_{\pm} - 1}{\gamma_{\pm} + 2} \right) (R_0 + \lambda_0)^3 \right], \end{aligned} \quad (5)$$

where  $\sigma_{\pm}^{(0)}$  are conductivities of the ion subsystems in absence of colloidal particles,  $\gamma_{\pm} = \sigma_{\odot}^{\pm} / \sigma_{\pm}^{(0)}$ ,  $\sigma_{\odot}^{\pm}$  is the effective conductivity of the screening coat of the colloidal particle for the ions of corresponding sign, while  $R_0$  and  $\lambda_0$  were introduced above. The effect of screened colloidal particles on the conductivity realizing by the positive ions, which can be drawn into the negatively charged screening coat, is positive:  $\gamma_+ > 1$ . Vice versa, the conductivity carried on by the negative ions is suppressed by presence of the colloidal particles, since the screening coats of the latter repulse the former, and corresponding  $\gamma_- < 1$ . It turns out that the effect of colloidal particles on the positive ions is dominant.

The conductivity growth as colloidal particles are introduced into the solution one can be understood as the facilitation of charge transfer in the media where some fraction of volume is occupied by these highly conducting objects. In result, at the same intensity of electric field  $E$  current increases, i.e. conductivity growths. The situation is different with the Seebeck coefficient  $S$ . It characterizes the voltage response of the media on the applied temperature gradient and there is no evident reasons to suppose the direct sensitivity of  $S_{\pm}$  to colloidal particles concentration.

In this assumption Eq. (4) acquires form

$$S_{\text{tot}}(n_{\odot}) = S_{\text{tot}}^{(0)} + \Delta S(n_{\odot}), \quad (6)$$

where

$$S_{\text{tot}}^{(0)} = \frac{S_-^{(0)}\sigma_-^{(0)} + S_+^{(0)}\sigma_+^{(0)}}{\sigma_-^{(0)} + \sigma_+^{(0)}}, \quad (7)$$

and

$$\Delta S_{\text{tot}}(n_{\odot}) = \frac{12\pi n_{\odot}(\gamma_+ - \gamma_-)(R_0 + \lambda_0)^3}{(\gamma_+ + 2)(\gamma_- + 2)} \cdot \frac{\sigma_-^{(0)}\sigma_+^{(0)}(S_+^{(0)} - S_-^{(0)})}{(\sigma_-^{(0)} + \sigma_+^{(0)})^2}. \quad (8)$$

The measured in experiment Ref. [2] change of the Seebeck coefficient as the function of colloidal particles concentration normalized on its value in absence of the latter takes form

$$\frac{\Delta S_{\text{tot}}(n_{\odot})}{S_{\text{tot}}^{(0)}} = 12\pi n_{\odot} \frac{(\gamma_+ - \gamma_-)(R_0 + \lambda_0)^3}{(\gamma_+ + 2)(\gamma_- + 2)} \cdot \frac{(S_+^{(0)} - S_-^{(0)})}{S_-^{(0)} \left(1 + \sigma_-^{(0)}/\sigma_+^{(0)}\right) + S_+^{(0)} \left(1 + \sigma_+^{(0)}/\sigma_-^{(0)}\right)}. \quad (9)$$

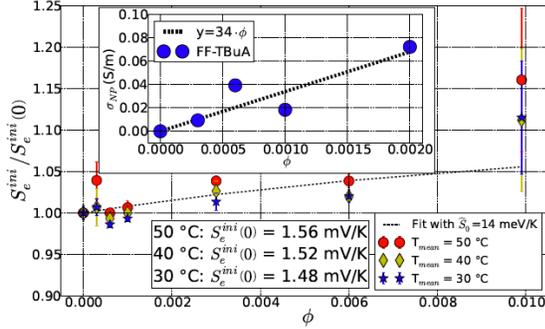


FIG. 2. Normalized initial state Seebeck coefficient and electrical conductivity (inset) as a function of nanoparticles concentration (taken from Ref. [2]).

It should be noted here that the thermogalvanic contribution to the overall temperature coefficient ( $\Delta V/\Delta T$ ) [11] is not taken into consideration. This is justified because this term is additive to  $S_{\text{tot}}^{(0)}$  and is independent of the nanoparticle concentration [2] and thus does not interfere with the  $\Delta S_{\text{tot}}^{(0)}$  in the Eq. (9). The obtained result convincingly demonstrates, that the Seebeck coefficient follows the linear growth of the colloidal particles concentration in the considered range (1) what corresponds to the experimental findings (see Fig. 2). This linear growth differs from that one of the colloidal solution conductivity  $\Delta\sigma_{\text{tot}}(n_{\odot})$  (see Eq. (5)) being proportional to

the difference  $S_+^{(0)} - S_-^{(0)}$  of the formal ion Seebeck coefficients in absence of colloidal particles. Such result is very natural: Seebeck effect always (in metals, in semiconductors) is related to the asymmetry of the charge carriers.

Hence, the direct measurements of  $\sigma_{\text{tot}}(0)$ ,  $S_{\text{tot}}^{(0)}$  and the values of the slopes in the dependencies of conductivity and Seebeck effect as the function of colloidal particles concentration, side by side with the independent knowledge of  $\gamma_{\pm}$  and  $R_0 + \lambda_0$  (according to Refs. [2, 10]  $\lambda_0 \approx 60\text{\AA}$ ,  $R_0 \approx 70\text{\AA}$ ) allow to determine the values  $\sigma_{\pm}^{(0)}$ .

## B. Steady state of Seebeck effect in colloidal solution

Application of the temperature difference across the thermocell results in charge separation among electrolyte ions. This happens first due to the difference of their coefficients  $\beta_{\pm}$ , second due to the difference of their diffusion coefficients [12]. The latter contribution to the Seebeck coefficient is specific for semiconductors and electrolytes and accounts for thermodiffusion of charged particles, which occurs in presence of temperature gradient. In result, at the initial state of the Seebeck effect, the accumulative layers of ions of opposite charges are formed in the vicinity of electrodes.

When the electrolyte contains some relatively small concentration of colloidal particles in process of time the measured value of Seebeck coefficient decreases. This decrease as the function of nano-particles concentration is drastic at the beginning, then Seebeck coefficient reaches the minimum, and finally, in accordance to Eq. (9), it linearly grows (see Fig. 3) [2].

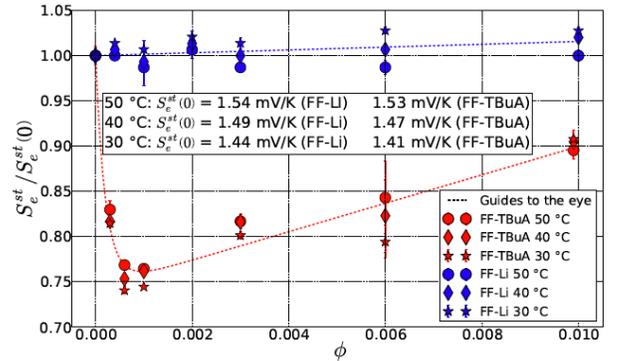


FIG. 3. Normalized steady state Seebeck coefficient as a function of nanoparticles concentration (taken from Ref. [2]).

One of the reasons of its occurrence can be the com-

plex structure of the colloidal particles surrounded by their screening coatings. The process of thermodiffusion results in their slow drift whose direction depends sensitively on the ionic environment surrounding the colloidal particles. Let us recall, that in Ref. [10] the colloidal particle screening was considered in the spherically symmetrical situation by means of solution of the Poisson equation with the zero boundary conditions at infinity. Close to the electrode the Seebeck electric field in electrolyte is formed mainly due to the redistribution of ions and becomes non-homogeneous [13]. As the consequence, the colloidal complexes, acquiring induced dipole moment, get pulled into the domain of higher fields.

In the vicinity of the thermocell extremities the difference in electrostatic attraction of the charged counterions of the coat and the nucleos of the colloidal particle to the metallic electrode enters in play. Indeed, such attraction forces turn out to be very different for weakly charged counterions of the coating layer and strongly charged ( $Q = Ze$ ) core of the colloid. In result, the clusters lose their electro-neutrality and start to compensate the charge of ionic accumulative layer.

Let us evaluate the value of nanoparticles concentration corresponding to the minimum of Seebeck coefficient at Fig. 3. For this purpose to do this we recall some facts of electrostatics. The problem of a point charge interaction with the conducting plane, separating two semi-spaces with different dielectric constants  $\epsilon_1$  and  $\epsilon_2$ , can be reduced to that one of the charge interaction with the corresponding electrostatic image charge behind the plane (see Ref. [14]):

$$F_\epsilon(z) = \frac{Q^2(\epsilon_1 - \epsilon_2)}{4\epsilon_1(\epsilon_1 + \epsilon_2)z^2}. \quad (10)$$

Here the charge is supposed to be placed at the distance  $z$  from the plane in the semi-space with dielectric constant  $\epsilon_1$ .

When the semi-space is filled by electrolyte the electrostatic image force (10) is screened at the distances of the order of Debye length from the plane (Refs. [15, 16]):

$$F_{\text{WO}}(z) = F_\epsilon(z) \exp\left(-\frac{2z}{\lambda_0}\right). \quad (11)$$

with corresponding potential

$$U_{\text{WO}}(z) = -\int_z^\infty F_{\text{WO}}(x)dx = \frac{Q^2(\epsilon_1 - \epsilon_2)}{2\lambda_0\epsilon_1(\epsilon_1 + \epsilon_2)} \Gamma\left(-1, \frac{2z}{\lambda_0}\right),$$

whereas  $\Gamma(s, x)$  is the upper incomplete gamma function. In other words, a charged particle located in the electrolyte at distances exceeding the Debye length  $\lambda_0$  from the electrode interacts exponentially weakly with it. In the case under consideration we assume the dielectric constant of the metallic electrode  $\epsilon_2 \rightarrow \infty$ , while  $\epsilon_1 = \epsilon_{aq}$ . The corresponding electrostatic energy for the

the nucleos of the colloidal particle is

$$U_{\text{WO}}(z) = -\frac{Z^2 e^2}{2\lambda_0 \epsilon_{aq}} \Gamma\left(-1, \frac{2z}{\lambda_0}\right). \quad (12)$$

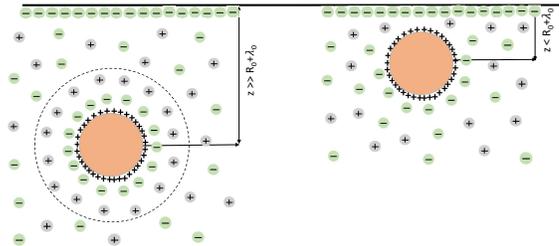


FIG. 4. Until the colloidal particle size exceeds the Debye length it keeps its integrity (a). When the colloidal particle approaches the charged electrode at the distances less than its size the cluster loses its electro-neutrality (b).

The effective radius of the colloidal particle is the sum of the radius of charged nucleos and the thickness of the screening coat:  $R_0 + \lambda_0$ . Hence until its size exceeds the Debye length the colloidal particle keeps its integrity (see Figure 4a) and the potential energy of its nucleos interaction with the electrode is determined by Eq. (12). When the colloidal particle approaches the charged electrode at the distances less than its size it loses its electro-neutrality (see Figure 4b) and its consideration in the framework of Poisson equation with infinite boundary conditions [10] is no longer applicable. The detailed study of electrostatic interaction between a planar surface and a charged sphere immersed in the electrolyte media was performed in Ref. [17]. The author found corresponding energy  $U_{\text{HO}}$  of such interaction in the form

$$U_{\text{HO}}(z) = U_0 \exp\left(-\frac{z - R_0}{\lambda_0}\right). \quad (13)$$

Applying this consideration to the case of the colloidal particle core and matching Eqs. (12)-(13) at the distance  $z = R_0 + \lambda_0$  one can find the constant  $U_0$ :

$$U_0 \sim -\frac{Z^2 e^2}{\lambda_0 \epsilon_{aq}} \Gamma\left(-1, 2 + \frac{2R_0}{\lambda_0}\right).$$

Now one can estimate the maximal colloidal particles surface concentration  $N_{\odot}^{\text{max}}$  which can be localized in the vicinity of the electrode by means of the discussed above mechanism. Their attraction to the electrode, charged

due to the presence of excess ions with the surface concentration  $N_-$ , continue until the latter will not be compensated by the positive charges of the colloidal nuclei:

$$N_{\odot}^{max} = N_-/Z. \quad (14)$$

The value  $N_-$  can be found knowing the values of Seebeck coefficient at the end of Initial state  $S_{tot}$ , and the temperature gradient. Indeed, considering the thermocell with electrolyte as the parallel plate capacitor one can write:

$$E = \frac{4\pi e N_-}{\epsilon_{aq}},$$

$$N_{\odot} = n_{\odot} \left\{ \int_{R_0}^{R_0+\lambda_0} \left( \exp \left[ \frac{Z^2 e^2 \Gamma \left( -1, 2 + \frac{2R_0}{\lambda_0} \right)}{\lambda_0 k_B T \epsilon_{aq}} \exp \left( -\frac{z - R_0}{\lambda_0} \right) \right] - 1 \right) dz + \int_{R_0+\lambda_0}^{\infty} \left( \exp \left[ \frac{Z^2 e^2}{2\lambda_0 k_B T \epsilon_{aq}} \Gamma \left( -1, \frac{2z}{\lambda_0} \right) \right] - 1 \right) dz \right\}. \quad (16)$$

This equation relates the surface concentration of the colloidal particles  $N_{\odot}$  with their volume concentration  $n_{\odot}$ .

Using the asymptotic expressions for incomplete Gamma-function

$$\Gamma(-1, x) = \begin{cases} e^{-x}/x^2, & x \gg 1 \\ 1/x & x \ll 1 \end{cases}$$

and making sure that  $Z^2 e^2 \ll \lambda_0 k_B T \epsilon_{aq}$  ( the characteristic values of the parameters  $Z \approx 300, \epsilon_{aq} \approx 80, \lambda_0 \approx 60\text{\AA}, R_0 \approx 70\text{\AA}$ ) one can find analyzing the data of Ref. [2] with the help of Ref. [10]). Hence, the exponents in Eq. (16) can be expanded, what results in

$$N_{\odot} \sim n_{\odot} \frac{Z^2 e^2}{k_B T \epsilon_{aq}} \frac{e^{-2\left(1 + \frac{R_0}{\lambda_0}\right)}}{\left(1 + \frac{R_0}{\lambda_0}\right)^2}. \quad (17)$$

In order to estimate the values let us express Eq. (17) in terms of the Rydberg unit of energy  $Ry = e^2/a_B = 13.6\text{ eV}$  ( $a_B = 0.53\text{\AA}$  is the Bohr radius):

$$N_{\odot} \approx (n_{\odot} \lambda_0) \frac{Z^2 Ry}{2k_B T \epsilon_{aq}} \left( \frac{a_B}{\lambda_0} \right) \frac{e^{-2\left(1 + \frac{R_0}{\lambda_0}\right)}}{\left(1 + \frac{R_0}{\lambda_0}\right)^2} \sim 10^{-2} (n_{\odot} \lambda_0).$$

Returning to Eq. (14) and substituting in it Eq. (17) one finds

$$n_{\odot}^{max} = \frac{\epsilon_{aq}^2 S_{tot}}{2\pi e Z^3 a_B} \left( \frac{\Delta T}{\Delta L} \right) \left( \frac{k_B T}{Ry} \right) \cdot e^{2\left(1 + \frac{R_0}{\lambda_0}\right)} \left( 1 + \frac{R_0}{\lambda_0} \right)^2 \sim 10^{15} \text{ cm}^{-3}. \quad (18)$$

In the dimensionless units of Ref. [2] the maximal concentration of colloidal particles determined by Eq. (18)

where from

$$N_- = \frac{\epsilon_{aq}}{4\pi e} S_{tot} \left( \frac{\Delta T}{\Delta L} \right). \quad (15)$$

What concerns the value of the surface concentration of the colloidal particles  $N_{\odot}$  it can be found by comparison between the homogeneous distribution of the colloidal particles and that one in the presence of electrostatic potential of the electrode, determined by Eqs.(12)-(13):

corresponds to  $\phi^{min} \leq 0.001$  (see Fig. 3). Since we know that in these units  $\phi = 0.006 \rightarrow n_{\odot} \simeq 5.45 \cdot 10^{15} \text{ cm}^{-3}$ , it is easy to recalculate that the estimation (18)  $n_{\odot}^{max} \sim 10^{15} \text{ cm}^{-3} \rightarrow \phi^{min} \sim 0.01$ , which surprisingly well coincides to the experimental findings of Ref. [2] (see Fig. 3) considering the imperfect nature of metallic electrodes used in the *real* thermocells.

### III. DISCUSSION

In this work we have studied the nontrivial role of colloidal particles in formation of the Seebeck field in charged colloidal suspension. The reasons for the two-stage character of the Seebeck effect observed in stabilized colloidal electrolytes are discussed. It is shown that the ‘‘Initial state’’ is related to the phenomenon of thermal diffusion of the ions of the stabilizing electrolyte itself. The ensuing ‘‘Steady state’’ occurs when the thermodiffusion displacement of the colloidal particles becomes essential.

We demonstrate that, surprisingly, the neutral colloids affect on the Seebeck coefficient already in the ‘‘initial state’’. This happens due to their influence on the polyelectrolyte conductivity. As it was shown in Ref. [10] the presence in the bulk of stabilizing electrolyte of rarefied gas of colloids having a relatively large conductivity of the screening coats increases its effective conductivity. Accounting for this fact appears to explain the linear growth of the Seebeck coefficient as a function of the colloidal particles concentration observed in the experiment.

The observed sharp drop of the Seebeck coefficient when the small concentration of the colloidal particles is added to stabilizing electrolyte [2] is noteworthy. We propose the explanation of this feature basing on the spe-

cific behavior of colloidal particle in the vicinity of electrode. Approaching the latter colloid loses its neutrality, discharging the accumulative layer of ions formed during the Initial state. The decrease of the accumulative layer charge results in the drop of Seebeck signal. Our qualitative estimations give surprisingly good correspondence to experimental findings.

Finally, one can shed light on the discrepancy between the steady state establishment time lapse in the experiment ( $\tau_{exp} \sim 8$  hours) and the theoretical estimations counterpart by the authors of Ref. [2]. The latter,  $\tau_{theor} = (\Delta L)^2/D_{\odot} \sim 100$  hours is based on the entire length scale of the thermocell. In the model developed here, the formation of mirror charges occurs in the close vicinity of the electrode/electrolyte interfaces. Furthermore, we want to attract attention to the fact that, due to the inhomogeneity of the charge density distribution along the thermocell length, the electric field also becomes non-homogeneous [12], what results in polarization of the colloidal particles and acceleration of their motion with respect to a simple diffusion.

#### ACKNOWLEDGMENTS

This work is supported by European Union's Horizon 2020 research and innovation program under the grant agreement n 731976 (MAGENTA).

- 
- [1] M.F. Dupont and D.R. MacFarlane and J.M. Pringle, *Thermo-electrochemical cells for waste heat harvesting—Progress and perspectives*, *Chem. Commun.* **2017**, 53, 6288–6302.
- [2] Salez, Thomas J.; et al. *Can charged colloidal particles increase the thermoelectric energy conversion efficiency?* *Phys. Chem. Chem. Phys.* **2017**, 19, 9409-9416; DOI 10.1039/C7CP01023K.
- [3] André Luiz Sehnem, and Mathijs Janssen, *Determining single-ion Soret coefficients from the transient electrolyte Seebeck effect*, **2020** arXiv:2006.11081v1 19.
- [4] Riedl, J.C.; Akhavan Kazemi, M.A.; Cousin, F.; Dubois, E.; Fantini, S.; Lois, S.; Perzynski, R.; Peyre, V. *Colloidal Dispersions of Oxide Nanoparticles in Ionic Liquids : Elucidating the Key Parameters*. *ChemRxiv* **2019**; DOI 10.26434/chemrxiv.9817208.
- [5] Bacri, J.C.; Perzynski, R.; Salin, D.; Cabuil, V.; Massart, R. *Ionic ferrofluids: A crossing of chemistry and physics*. *J. Magnetism and Magnetic Materials*, **1990**, 85, 27-32; DOI 10.1016/0304-8853(90)90010-N.
- [6] Dubois, E. *Structural analogy between aqueous and oily magnetic fluids*. *J. Chem. Phys.* **1999**, 111, 7147-7160; DOI 10.1063/1.480007.
- [7] Derjaguin, B.V.; Landau, L.D. *Theory of the stability of strongly charged lyophobic sols and of the adhesion of strongly charged particles in solutions of electrolytes*. *Acta Physico Chemica URSS*, **1941**, 14, 633-662.
- [8] Verwey, E.; Overbeek, J. *Theory of the Stability of Lyophobic Colloids*. Elsevier, Amsterdam, **1948**; pp 131-136.
- [9] Landau, L.D.; Lifshitz, E.M. *Statistical Physics*. (Course of Theoretical Physics, Volume 5). 3rd Edition, Elsevier, Amsterdam, **2011**; pp 276-278.
- [10] Chikina, I., Shikin, V.B., Varlamov, A.A. *The Ohm law as alternative for the entropy origin nonlinearities in conductivity of dilute colloidal polyelectrolytes*. *Entropy*, **2020**, 22, 225 ; DOI 10.3390/e22020225
- [11] A. J. De Béthune, T. S. Licht, and N. Swendeman, *The Temperature Coefficients of Electrode Potentials: The Isothermal and Thermal Coefficients - The Standard Ionic Entropy of Electrochemical Transport of the Hydrogen Ion*, *Journal of The Electrochemical Society*, **1959**, 106, 616-624; DOI 10.1149/1.2427448
- [12] I.Chikina, V. Shikin, A.A.Varlamov, *Seebeck effect in electrolytes*, *Phys. Rev.* **2012**, E86, 011505.
- [13] I. Chikina, V. B. Shikin, and A. A. Varlamov, *Effect of boundary conditions on the character of ambipolar diffusion in electrolytes*, *Phys. Rev.* E92, 012310 (2015).
- [14] Landau, L.D.; Lifshitz, E.M. *Electrodynamics of Continuous Media*. (Course of Theoretical Physics, Volume 8). 2rd Edition, Pergamon Press, Oxford, **2011**; pp 276-278.
- [15] C.Wagner, *Phys Z.* 25, **1924**, 474.
- [16] L. Onsager, N.Samaras, *J.Chem.Phys.* **1934**, 2, 528
- [17] H. Ohshima, *Electrostatic Interaction between a Sphere and a Planar Surface: Generalization of Point-Charge/Surface Image Interaction to Particle/Surface Image Interaction*, *Journal of Colloid and Interface Science*, **1998**, 198, 42 .