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Seebeck effect in electrolytes

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We study Seebeck effect in liquid electrolytes, starting from its simple neutral analog—thermodiffusion (so-called Ludwig-Soret or Soret effect). It is observed that when two or more subsystems of mobile particles are subjected to the temperature gradient, various types of them respond to it differently. In the case when these fractions, with different mobility parameters (Soret coefficients), are oppositely charged (a case typical for electrolytes), the nonhomogeneous internal electric field is generated. The latter field prevents these fractions from space separation and determines the intensity of the appearing Seebeck effect.

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I. INTRODUCTION

The variety of thermoelectric phenomena (the effects of Seebeck, Peltier, and Thompson) take place in a conducting media in presence of a gradient of temperature ∇T and an electric field $\mathbf{E}$. To characterize them quantitatively one can use the standard linear response theory approximation [1–4] and write the appearing electric current as the expansion over these perturbations:

$$j_i^{(e)} = \sigma_{ik} E_k + \beta_{ik} \nabla_k T, \qquad (1)$$

where β_{lk} and σ_{ik} are conductivity and thermoelectric tensors. The simplest effect is the Seebeck one (ES), and it is observed in conditions when the external circuit is broken (the current in the system does not flow, $\mathbf{j}^{(e)} = 0$). The ES consists of the appearance of nonzero electric field related to the gradient of temperature in a conductor due to the condition of absence of current:

$$E_i = -\sigma_{il}^{-1} \beta_{lk} \nabla_k T = S_{ik} \nabla_k T. \qquad (2)$$

As it is seen, in frameworks of the linear theory Seebeck coefficient S_{ik} is expressed in terms of tensors β_{lk} and σ_{ik}. More sophisticated Peltier and Thompson effects are observed in conditions when $\nabla T \neq 0$ and $j \neq 0$.

Being natural for the infinite media Eqs. (1) and (2) fail to describe self-consistently the realistic experimental situation when the system has finite sizes. Indeed, from Eq. (2) follows $\nabla \cdot \mathbf{E} = 0$. Thus it corresponds to the Poisson equation in absence of charges and allows the solution

$$\nabla T = \text{const}, \quad E_i = S_{ik} \nabla_k T = \text{const}, \qquad (3)$$

which does not assume the appearance of the density inhomogeneity, i.e., is valid for $n_i = \text{const}$ (n_i is the ion concentration). At the same time it is evident that any thermoelectric effect should be accompanied by the formation of the domains where $\nabla n_i \neq 0$ correspondingto variation of the distribution function along the temperature gradient direction.

In this paper we consider ES in liquid electrolyte, when the boundary conditions for the case $\nabla n_i \neq 0$ can be explicitly written down. To do this we will start from its simple neutral analog—thermodiffusion (so-called Ludwig-Soret, or Soret, effect [5]). It is observed when a mixture of two or more types of mobile particles is subjected to the temperature gradient and different types of particles respond to it differently. Specifically, we consider the neutral solution, where the existence of ∇T results in a break of homogeneity of neutral particles distribution $n_0(\mathbf{r})$ and the appearance of gradient of their concentration $\nabla n_0 \neq 0$. Some time ago this problem was carefully studied for superfluid solutions of He_4 (see Ref. [6]).

Seebeck effect can be considered as the variety of Soret effect for the solution of easily dissociated particles. The latter usually break up into charged parts with the different degrees of thermal flow drug. The account for Coulomb interaction on the process of thermodiffusion of charged particles modifies the character of stationary Soret effect even in the linear regime. We will show that the conditions of linearity are very subtle and can be easily violated. It is why we devote special attention to the analysis of the nonlinear version of the problem. We stress the formal analogy between the effect of Seebeck and sedimentation of the asymmetric electrolytes [7–10], and also discuss the series of known examples where the specifics of the diffusion in electric field are important.

II. NEUTRAL THERMAL DIFFUSION (SORET EFFECT)

We start our discussion from the definition of the neutral mass flow, which occurs in the system where the chemical potential (concentration) and temperature gradients take place. We will assume them as sufficiently small. In this case the mass flow density $\mathbf{j}^{(m)}$, in complete analogy with Eq. (1), can be expanded over the gradients [4,11,12],

$$j_i^{(m)} = -\alpha_{ik} \nabla_k \mu(\mathbf{r},T) - \eta_{ik} \nabla_k T.$$

The first term, proportional to the chemical potential gradient $\mu(\mathbf{r},T)$, describes the diffusion contribution to the mass flow, the second one, proportional to the gradient of temperature, has the force origin. The expansion coefficients α_{ik} and η_{ik}

determine the values of diffusion ($\mathcal{D}_{ik}$) and thermodiffusion ($k_T\mathcal{D}_{ik}$) coefficients:

$$\mathcal{D}_{ik} = \frac{\alpha_{ik}}{\rho}\left(\frac{\partial\mu}{\partial n_0}\right)_{P,T}, \tag{4}$$

$$k_T\mathcal{D}_{ik} = -\frac{\alpha_{ik}T}{\rho}\left(\frac{\partial\mu}{\partial T}\right)_{n_0,P} + \eta_{ik}. \tag{5}$$

The dimensionless parameter k_T is called thermodiffusion ratio. We note that in case of charged particles tensor η_{ik} is directly related to the thermoelectric tensor: $\eta_{ik} = \beta_{ik}/q$, where q is the value of particle charge.

Consider the case $\mathbf{j}^{(m)} = 0$ in conditions when $\nabla_k T \neq 0$. In such situation

$$\nabla_i\mu(\mathbf{r},T) = -\alpha_{il}^{-1}\eta_{lk}\nabla_k T, \tag{6}$$

which means that the stationary nonhomogeneous distribution of particles appears in solution as the response to the temperature gradient applied. Indeed, the chemical potential for particles can be assumed here in Boltzmann form,

$$\mu_0(\mathbf{r},T) = T\ln n_0(\mathbf{r},T), \tag{7}$$

and substituting this expression to Eq. (6) one finds

$$\frac{\nabla_i n_0(\mathbf{r},T)}{n_0(\mathbf{r},T)} = -\Xi_{ik}\frac{\nabla_k T(\mathbf{r})}{T(\mathbf{r})} \tag{8}$$

with the dimensionless coefficient of the Soret effect,

$$\Xi_{ik} = \alpha_{il}^{-1}\eta_{lk}. \tag{9}$$

Passing from Eq. (6) to Eq. (8) we omitted the terms of the order of $O[(\Delta T/T)^2]$, where ΔT is a small temperature difference between the boundaries of the system which generates the gradient ∇T.

Experimental study of Soret effect involves the measurement of the stationary concentration gradient under conditions when $\nabla T = \text{const}$. The coefficient α_{ik} is supposed to be known from independent measurements, hence Eq. (9) allows us to determine the coefficient η_{lk}. Note that, apart from direct measurement, the value of Ξ_{ik} can be also obtained from the independent studies of the relaxation process when the diffusion part adjusts the stationary distribution Eq. (8) (see Ref. [5]).

Let us discuss the conditions of observability of the linear Soret effect in more detail. We consider a liquid poured in cuvette of the length L; the axis x we direct along the cuvette. Temperature increases from the value $T(0)$ at the left border of the cuvette ($x = 0$) to $T(L)$ at its right border. In the assumption of constant and small temperature gradient

$$T'_x = \frac{T(L) - T(0)}{T(0)} \ll 1$$

one can easily find from Eq. (8) distributions of the particles' concentration and temperature

$$n_0(x) = n(0)\exp\left(-\Xi\frac{T'_x\cdot x}{T(0)}\right), \tag{10}$$

$$T(x) = T(0)\left(1 + \frac{T'_x\cdot x}{T(0)}\right) \tag{11}$$

(we assume low enough particles concentration). One can see that the characteristic length

$$l_{\mathrm{S}} = \frac{1}{\Xi}\frac{T(0)}{T'_x} \tag{12}$$

appears in the problem. The Soret effect can be considered as linear when $L \ll l_{\mathrm{S}}$ and it is nonlinear in the opposite case. The condition of linearity can be easily satisfied just decreasing the gradient T'_x in conditions when a cuvette length is fixed. The smallness of the Soret constant Ξ also favors the linearity of the Soret effect. On the other hand, the opposite limit $l_{\mathrm{S}} \ll L$ becomes essential for such applications as isotope separation, centrifugal sedimentation of different solutions in order to get mass stratification of components, etc. [7–10]. Two different Soret distributions of neutral particle concentrations with different Soret length along the cuvette length in the presence of the linear temperature distribution are shown in Fig. 1. When both Soret lengths $l_{\mathrm{S}1}$ and $l_{\mathrm{S}2}$ are smaller to the cuvette length L, the distributions are localized in the cold domain of the cuvette. The degree of their localization is different (it is determined by the value of corresponding Soret length) which can work toward their separation in the case when some repulsive forces occur.

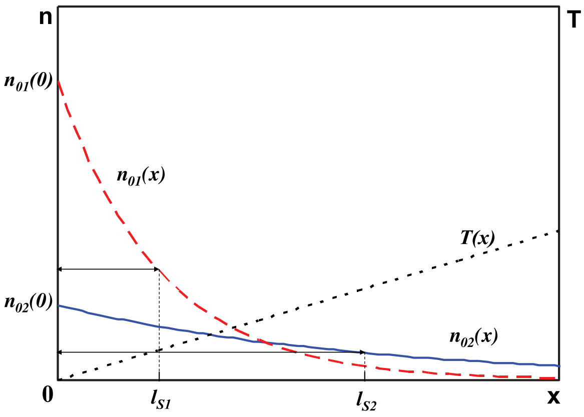

FIG. 1. (Color online) Qualitative presentation of Soret distributions $n_0(x)$ for two different kinds of neutral particle subsystems along the length of the cuvette ($0 < x < L$) in the presence of temperature gradient. Solid line corresponds to the distribution $n_{01}(x)$ with Soret length $l_{s1} < L$. Dashed line demonstrates the distribution function $n_{02}(x)$ with Soret length $l_{S2} < L (l_{S2} > l_{S1})$.

The similarity between the Soret effect and the phenomenon of sedimentation is noteworthy. Indeed, in the specific case of the latter—gravitational differentiation—the equilibrium of the system of particles in the gravitational field can be formally written as (we assume here a low particles concentration)

$$\nabla[\mu_0(x) + U(x)] = 0,\ \mu_0 = T\ln n_0,\ U(x) = mgx, \tag{13}$$

with m the mass of particle. These conditions evidently are completely analogous to Eqs. (6) and (12), which describe the above-discussed Soret effect. Mapping Eqs. (13) on the latter leads to the expression for sedimentation length,

$$l_{\mathrm{m}} = T/mg. \tag{14}$$

Below we will use this analogy discussing the actual limits of both problems.

III. THERMODIFFUSION OF CHARGED PARTICLES (SEEBECK EFFECT)

A. Clarification of the basic equations

We will discuss now the process of a mass flow at the same conditions as in previous section but in the case of charged particles. In this situation the nonhomogeneity of their distribution should be accompanied by the appearance of some electric field. Indeed, as it is well known [2], in doped semiconductors, where the distribution of immobilized charged donors is homogeneous, any deviation of the electron density distribution from homogeneity results in the appearance of the electric field preventing further charge separation. This effect is less pronounced in the electrolytes [4,11,13–21] since all charged components there are mobile. The relative shift between oppositely charged subsystems of a strong electrolyte appears only in the case when these subsystems react differently to the applied gradient of temperature. Such situation can happen when ions of different subsystems have different diffusion or thermodiffusion coefficients. Even more delicate is the situation in weak electrolyte, where charged particles are diluted in neutral liquid. Here the homogeneities of charged and neutral subsystems are perturbed differently due to the Soret effect, but these perturbations should be adjusted in view of the possibility of molecule dissociation. For simplicity, we will limit our considerations below by the case of a strong electrolyte only.

The starting equations, declaring the absence of a mass flow for each component of a strong electrolyte, are determined by Eq. (6):

$$\alpha_+ \nabla\mu_+ + \eta_+ \nabla T = 0, \tag{15}$$

$$\alpha_- \nabla\mu_- + \eta_- \nabla T = 0 \tag{16}$$

(subscript "±" indicates positive and negative components). In the special case

$$\alpha_+/\eta_+ = \alpha_-/\eta_- \tag{17}$$

Eqs. (15) and (16) give $\nabla\mu_+ = \nabla\mu_-$, i.e., the application of the temperature gradient does not result in charge separation, no intrinsic electric field appears.

Of course, Eq. (17) generally speaking is not fulfilled and creation of a temperature gradient leads to the appearance of local concentrations difference $(n_+ - n_-)$, i.e., to generation of the internal electric field in cuvette:

$$E = -\nabla\varphi \propto (n_+ - n_-).$$

Accounting for this field in Eqs. (15) and (16) can be done by means of replacement of chemical potentials $\mu_\pm$ by corresponding electrochemical potentials $\mu_\pm \pm e\varphi$ (e is the absolute value of the electron charge):

$$\alpha_+ \nabla\mu_+ + \alpha_+ e\nabla\varphi + \eta_+ \nabla T = 0, \tag{18}$$

$$\alpha_- \nabla\mu_- - \alpha_- e\nabla\varphi + \eta_- \nabla T = 0. \tag{19}$$

Subtracting and summing Eqs. (18) and (19) one finds

$$(\eta_+ - \eta_-)\nabla T + (\alpha_+ + \alpha_-)e\nabla\varphi + (\alpha_+ \nabla\mu_+ - \alpha_- \nabla\mu_-) = 0, \tag{20}$$

$$(\eta_+ + \eta_-)\nabla T + (\alpha_+ - \alpha_-)e\nabla\varphi + (\alpha_+ \nabla\mu_+ + \alpha_- \nabla\mu_-) = 0. \tag{21}$$

Equations (20) and (21) constitute the basis for the consistent description of Seebeck effect, i.e., the appearance of the electric field $E = -\nabla\varphi$ as the response to the applied gradient of temperature ∇T.

It is noteworthy that in the literature devoted to thermoelectric effects in semiconductors [2] and electrolytes [11,13–18] a simplified version of Eqs. (20) and (21),

$$(\alpha_+ + \alpha_-)e\nabla\varphi + (\eta_+ - \eta_-)\nabla T \simeq 0, \tag{22}$$

ignoring the term $(\alpha_+ \nabla\mu_+ - \alpha_- \nabla\mu_-)$, is used. Equation (22), being equivalent to Eq. (2), allows us to find the Seebeck coefficient

$$S^{(\nabla T)} = \frac{1}{e}\frac{(\eta_+ - \eta_-)}{(\alpha_+ + \alpha_-)} = \frac{1}{e^2}\frac{(\beta_+ - \beta_-)}{(\alpha_+ + \alpha_-)} \tag{23}$$

without addressing the Poisson equation (we recall that $\eta_\pm = \beta_\pm/|e|$). Nevertheless, this approach does not provide us with the answers to paradoxes mentioned in the Introduction.

B. Poisson equation and validity of the linear approximation in Seebeck problem

Equations (20) and (21) together with the Poison equation formally fully describe the problem of thermodiffusion of the oppositely charged particles accounting also for their Coulomb interaction. We start from discussion of the conditions required for applicability of the linearization procedure of this system. For the beginning we assume that such procedure is valid, and look for the solutions of Eqs. (20) and (21) in the form of

$$n_+(x) = n_0(x) + \delta n(x), \quad n_-(x) = n_0(x) - \delta n(x) \tag{24}$$

with $n_0(x)$ defined by Eq. (10). Using the relation (7) and substituting Eq. (24) to Eq. (21) one finds

$$\nabla\mu_0 \simeq -\frac{(\eta_+ + \eta_-)}{(\alpha_+ + \alpha_-)}\nabla T \tag{25}$$

[we omitted the term $\sim(\alpha_+ - \alpha_-)e\nabla\varphi$, which is of the second order of smallness]. It should be noted that the linearization of Eq. (25) is not yet required.

The next step is the linearization of Eq. (20) in δn, which gives

$$\begin{aligned}(\alpha_+ + \alpha_-)T\frac{\nabla\delta n}{n(0)} &= -(\eta_+ - \eta_-)\nabla T \\ &\quad -(\alpha_+ - \alpha_-)\nabla\mu_0 - (\alpha_+ + \alpha_-)e\nabla\varphi,\end{aligned} \tag{26}$$

with $\nabla\mu_0$ defined by Eq. (25) and $n(0)$ as the average value of the electrolyte concentration in equilibrium, when $T = \text{const}$ [see Eq. (10)].

Now one can solve the Poisson equation

$$\frac{d^2\varphi(x)}{dx^2} = \frac{4\pi e}{\epsilon}\delta n(x) \tag{27}$$

with δn taken from Eq. (26), ϵ as the solvent dielectric constant, and the boundary conditions corresponding to the total charge conservation. We will look for the solution of this nonhomogeneousequation in the form

$$\varphi(x) = \varphi_0(x) + \delta\varphi(x), \tag{28}$$

where the function $\varphi_0(x)$ satisfies Eq. (26) with $\delta n = 0$:

$$\begin{aligned}(\alpha_+ + \alpha_-)e\nabla\varphi_0 &= -(\eta_+ - \eta_-)\nabla T - (\alpha_+ - \alpha_-)\nabla\mu_0 \\ &= -\left[(\eta_+ - \eta_-) - \frac{\alpha_+ - \alpha_-}{\alpha_+ + \alpha_-}(\eta_+ + \eta_-)\right]\nabla T\end{aligned} \tag{29}$$

[we used here Eq. (25) relating explicitly the chemical potential and temperature gradients]. Correspondingly, the homogeneous field $E_0 = -\nabla\varphi_0$ occupies almost all the cuvette volume besides the boundary domains of the Debye length $[l_{\rm D} = (4\pi e^2 n_+/\epsilon T)^{1/2}]$ sizes. It should be noted that in these domains the charges, necessary for satisfaction of the particular correct boundary conditions $[E(0) = E(L) = 0]$ are concentrated. This means that the function $\delta\varphi(x)$ is localized close to the borders $x \lesssim l_{\rm D}$, $L - x \lesssim l_{\rm D}$ and in these domains it gradually reduces the total electric field from E_0 to zero. Considering the problem on semispace one can integrate Eq. (27) and get

$$\varphi_0'(0) + \delta\varphi'(0) = 0, \quad \delta\varphi(x \gg l_{\rm D}) \to 0. \tag{30}$$

It turns out that the solution $\delta\varphi(x)$ of Eqs. (27)–(30), different from zero only in the cuvette boundary domains, indeed exists. What concerns the electrostatic potential beyond these border regions is determined by the function $\varphi_0(x)$[see Eq. (29)], and namely this function determines the value of the Seebeck coefficient in this particular linear regime. In the limit $l_{\rm D} \ll L$ the solution of Eqs. (27)–(30) ceases to depend on the cuvette geometry.

Now one can find the conditions of applicability of this linearity. Indeed, in order to obtain the basic Eq. (29) we used expansions like

$$\nabla\mu_+ = T\frac{\nabla(n_0 + \delta n)}{n_0 + \delta n} \simeq \nabla\mu_0 + T\frac{\nabla\delta n}{n(0)}$$

[see Eq. (7)]. This requires to satisfy the condition of smallness of the exponent in $n_0(x)$ at any point of the cuvette, i.e.,

$$e\varphi_0(L) = e\varphi_0' L \ll T, \tag{31}$$

or, substituting in Eq. (31) Eqs. (25)–(29) one finds restriction on the gradient:

$$\nabla T \ll \left(\frac{T}{L}\right)\frac{(\alpha_+ + \alpha_-)^2}{\eta_+\eta_-\,|\alpha_+/\eta_+ - \alpha_-/\eta_-|}. \tag{32}$$

The estimations (31) and (32) confirm the intuitive ideas concerning the space scaleof the Seebeck effect. The latter can remain linear even in conditions when the Soret effect [see Eqs. (10)–(12)] takes off its linearity. The additional requirement $l_{\rm D} \ll L$ usually is fulfilled. This condition also clarifies the limits of applicability of Eqs. (2)–(22): only the homogeneous electric field (29) remains in the bulk of the cuvette (besides the border domains), the correction $\delta\varphi(x)$ here is negligible. Nevertheless, Eq. (29) itself, in contrast to Eq. (22), contains the term $(\alpha_+ - \alpha_-)\nabla\mu_0$.

The condition (32) generally speaking is restrictive enough, since the coefficients $\alpha_\pm$ contain additional smallness due to the presence of $\partial n/\partial\mu$ in it [see Eq. (4)]. Formally in accordance with Eq. (32) the linearity is not restricted at all when $\alpha_+/\eta_+ = -\alpha_-/\eta_-$, but, as we have seen above [see Eq. (17)], in this case the Seebeck effect is just absent. In the next subsection we will study what happens around this particular case.

Equations (27)–(30) present the main result of this work. Their accurate solution resolves the contradiction, mentioned in the Introduction, between the evident nonhomogeneity of a space charge distribution and the requirement $\nabla\cdot\mathbf{E} = \mathbf{0}$, necessary for validity of Eqs. (1)–(3). As the result, the ions' congestions are found in the cuvette boundary domains. It is the presence of these inhomogeneities that leads towards zero of the electric field intensity at the points $x = 0$ and $x = L$. In the well studied case of metals and degenerated semiconductors, where the validity of Eqs. (1)–(3) is undoubtful, these layers also exist but their thickness $l_{\rm D}$reaches interatomic distances. In these conditions, charges, corresponding to layers, can be considered as the surface ones and, in accordance with the Gauss theorem, they do not effect the homogeneity of the charge distribution in the bulk of conducting media. The electric field entering in Eqs. (1)–(3), can be considered in this case as uniform. Nevertheless, the latter statement is not universal. For example, the thermoelectric effect in a two-dimensional conducting system exists, but the charges distributed along the contour of the system affect the internal electric field in it.

Let us underline the important generalization of the theory of Seebeck effect in electrolytes achieved with respect to the standard theory Eq. (22) and formalized by Eq. (29). Looking at its second line one finds that in the Seebeck coefficient, side by side with the direct contribution $S^{(\nabla T)}$ [see Eq. (23)], induced by the difference of thermoelectric tensors of two ion subsystems $(\beta_+ - \beta_-)$, the additional term $S^{(\nabla\mu)}$ appears:

$$\begin{aligned}S^{(\rm tot)} &= S^{(\nabla T)} + S^{(\nabla\mu)} \\ &= \frac{1}{e^2}\frac{(\beta_+ - \beta_-)}{(\alpha_+ + \alpha_-)} - \frac{(\alpha_+ - \alpha_-)(\beta_+ + \beta_-)}{e^2\,(\alpha_+ + \alpha_-)^2}.\end{aligned} \tag{33}$$

Being proportional to $(\alpha_+ - \alpha_-)$, the contribution $S^{(\nabla\mu)}$ occurs due to the difference between the subsystems' diffusion coefficients [see Eq. (4)] and can be of the same order as $S^{(\nabla T)}$.

The standard definition (23) directly corresponds to Eq. (2) and is good for metals, but can be insufficient for semiconductors and electrolytes. The matter of fact is that $S^{(\nabla T)}$ accounts for thermodiffusion of charged particles in the Seebeck coefficient, which occurs in the presence of temperature gradient in all these systems. Yet, in semiconductors and electrolytes, where both subsystems of oppositely charged particles are mobile, in conditions of varying temperature, the gradient of concentration also appears. The latter leads to particle diffusion which generates the term $S^{(\nabla\mu)}$.

One can present Eq. (33) in a slightly different form:

$$S^{(\rm tot)} = \frac{1}{e^2}\frac{(\beta_+ - \beta_-)}{(\alpha_+ + \alpha_-)}\left[1 - \frac{(\alpha_+ - \alpha_-)(\beta_+ + \beta_-)}{(\alpha_+ + \alpha_-)\,(\beta_+ - \beta_-)}\right], \tag{34}$$

convenient for determination of the Seebeck coefficient sign. The latter can be manipulated due to the different temperature dependencies of the coefficients α_i and β_i. Indeed, the coefficients $\beta_i \propto T$ in view of their thermodiffusive nature. As for the coefficients α_i, they characterize the diffusion process [see Eq. (4)] and by means of the Einstein relation and the Stokes viscous law can be related to the viscosity of solution, which depends on temperature exponentially. Consequently, the sign of the square brackets in Eq. (34) can be reversed varying temperature in conditions of the same experiment. Such a possibility is absent from the framework of the simplified version of the Seebeck effect described by Eqs. (22) and (23).

C. Particular case

We have already mentioned above a special case described by the condition (17), when, in spite of the temperature gradient applied, no electric field is generated in the bulk of electrolyte. Let us address the consideration of Seebeck effect specifics in the system being close to this limit, namely when the parameter

$$\gamma = \left(\frac{\alpha_+}{\eta_+} - \frac{\alpha_-}{\eta_-}\right) \ll 1. \tag{35}$$

Equations (20) and (21) can be rewritten in the form

$$\begin{aligned} &\frac{\alpha_+}{\eta_+}(\nabla\mu_+ + e\nabla\varphi) + \nabla T = 0,\\ &\frac{\alpha_-}{\eta_-}(\nabla\mu_- - e\nabla\varphi) + \nabla T = 0. \end{aligned} \tag{36}$$

In the assumption that $\nabla\mu_+ \sim \nabla\mu_- = \nabla\mu_0(n_0)$ one finds for the sum and difference of the equations (36)

$$\gamma\nabla\mu_0 + 2e\nabla\varphi = 0, \tag{37}$$

$$\left(\frac{\alpha_+}{\eta_+} + \frac{\alpha_-}{\eta_-}\right)\nabla\mu_0 + \gamma e\nabla\varphi + 2\nabla T = 0. \tag{38}$$

The value of Seebeck coefficient directly follows from Eqs. (37); it is enough to substitute Eq. (25) in it. Recalling that $\eta = \beta/|e|$ one finds

$$S(\gamma \ll 1) = \frac{E}{\nabla T} = -\frac{\gamma}{2e^2}\frac{(\beta_+ - \beta_-)}{(\alpha_+ + \alpha_-)}. \tag{39}$$

One can see that the Seebeck coefficient turns zero linearly in γ, when $\gamma \to 0$, in agreement with Eqs. (17).

It is worth mentioning that Eq. (39) cannot be obtained from Eq. (33) just tending $\gamma \to 0$. The point is that the latter was derived in assumption of the temperature gradient smallness (32) and corresponding possibility of the chemical potential expansion [see Eq. (26)]. As regards result (39), it has been obtained without the need of such expansion, and it tells us what happens with the formula (39) beyond the limits of its applicability, when $\gamma \to 0$ and the condition (32) is broken.

Neglecting the second term in Eq. (38) (it is of the second order of smallness in $\gamma \ll 1$ with respect to the first one), one can find from Eqs. (37) and (38) the consistent definitions of the concentration and electric field in electrolyte. The distribution of concentration (38) turns out to be almost neutral and it is very close to Eq. (6).

The relation between electric field and concentration of the type (37) is *typical* for the problem of "ambipolar diffusion." Usually, the latter takes place in systems with quite different carrier mobilities. In the case of Seebeck effect for validity of Eq. (37) it is enough to satisfy the condition $\gamma \ll 1$. At the same time, each of subsystems can possess a noticeable Soret effect, such as $l_S \ll L$. As a result, the potential $\varphi(x)$ and concentration $n_0(x)$ distributions are essentially nonhomogeneous (and nonlinear in concentration) along the length of cuvette.

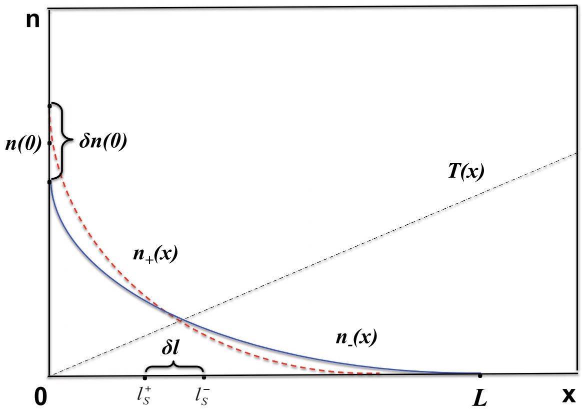

FIG. 2. (Color online) Coordinate dependency of the positive $n_+(x)$ and the negative ion $n_-(x)$ concentrations in conditions of a finite temperature gradient and $\gamma \ll 1$. The values $n(0) = [n_+(0) + n_-(0)]/2$ and $\delta n(0) = [n_+(0) - n_-(0)]$ are connected by the relation $\delta n(0)/n(0) \propto \gamma \ll 1$.

In order to illustrate the case $\gamma \ll 1$, in Fig. 2 we present the concentration distributions $n_+(x)$ and $n_-(x)$ side by side with their difference $\delta n(x) = n_+(x) - n_-(x)$. One can see that the uncompensated charges are localized in the domain restricted by the common Soret length $l_S \approx {l_S}^+ \approx {l_S}^-$ (${l_S}^- - {l_S}^+ \ll l_S$) for $\gamma \ll 1$. The Soret length l_S itself may considerably differ from the cuvette length (for instance, $l_S \ll L$). The opposite limit $\gamma > 1$ we will discuss in the next subsection.

D. Sedimentation in the system of charged particles

In order to demonstrate the specifics of Seebeck effect in nonlinear regime we will analyze the problem of sedimentation in electrolyte under the effect of gravitational force (gravitational differentiation). This problem is of interest for us for two reasons. First, as was mentioned above [see the discussion around Eq. (13)], the Seebeck effect and sedimentation are tightly connected. Second, the problem of nonlinear sedimentation arises in analysis of the experiments on charged particles separation in ultrafast centrifuges.

We assume that negative and positive ions with masses M and m respectively (which we suppose differ strongly: $m \ll M$) possess by charges $\mp e$. The ions concentration in the absence of gravitation is denoted as above, n_i. The size of the system L along the direction of gravitational field was chosen to be much larger than corresponding sedimentation lengths (14) for both subsystems of ions: $L_M = T/(Mg) \ll l_m = T/(mg) \ll L$. Without account for Coulomb forces the ions of each subsystem would be distributed in space in accordance with Boltzmann law [see Eqs. (10)–(14)].

The account for ion interaction leads to violation of the condition of local electroneutrality. As a result, in some domain there appears the internal electric field $E(x)$ (see Fig. 3), which

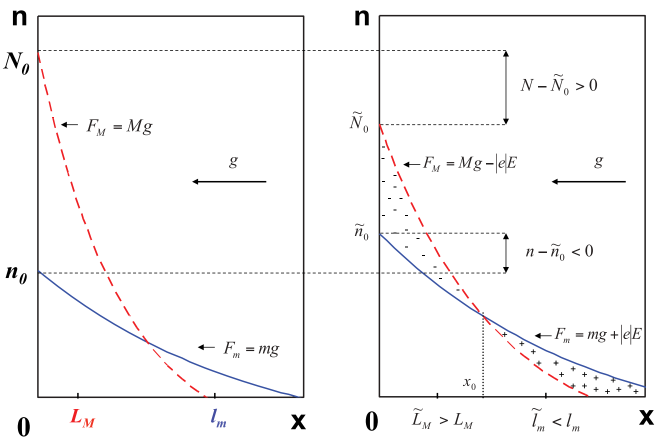

FIG. 3. (Color online) Boltzmann distributions for the concentrations of two different kinds of particles in electrolyte in presence of gravitation field: (a) without electric field; (b) in presence of additional electric field.

has to be taken into account side by side with gravitational forces. The effect of this electric field on sedimentation we evaluated neglecting its coordinate dependence. Below we will justify this assumption.

Corresponding sedimentation lengths are renormalized:

$$\tilde{l}_{\mathrm{m}}(E) = T/[mg + |e|E], \quad \tilde{L}_{\mathrm{M}}(E) = T/[Mg - |e|E]. \tag{40}$$

Consequently, distribution of the light particles

$$\tilde{n}(x) \propto \tilde{n}_0 \exp\left[-\frac{x}{\tilde{l}_m}\right] \tag{41}$$

shrinks, while that of heavy particles,

$$\tilde{N}(x) \propto \tilde{N}_0 \exp\left[-\frac{x}{\tilde{L}_M}\right], \tag{42}$$

stretches (see Fig. 3). The renormalized concentrations $\tilde{n}_0$ and $\tilde{N}_0$, accounting for the effect of electric field can be related to $n(0)$ and $N(0)$ due to conservation of the total number of particles:

$$\tilde{l}_{\mathrm{m}}\tilde{n}_0 = l_{\mathrm{m}} n(0), \quad n(0) = l_{\mathrm{m}}^{-1} \int_0^\infty n(x)dx = \frac{n_i L}{l_{\mathrm{m}}}, \tag{43}$$

$$\tilde{L}_{\mathrm{M}}\tilde{N}_0 = L_{\mathrm{M}} N(0), \; N(0) = L_{\mathrm{M}}^{-1} \int_0^\infty N(x)dx = \frac{n_i L}{L_{\mathrm{M}}}. \tag{44}$$

The supreme field E^*, determined by the condition $\tilde{l}_m(E^*) = \tilde{L}_M(E^*)$, restricts the limits of applicability of the model:

$$E^* = \frac{g}{2e}(M - m). \tag{45}$$

Determine the point x_0, where the distributions (41) and (42) intersect: $\tilde{n}(x_0) = \tilde{N}(x_0)$ (see Fig. 3). This is

$$x_0 = \tilde{L}_M \ln(\tilde{l}_m/\tilde{L}_M). \tag{46}$$

Charge separation can be modeled as the double layer with the surface charge density (see Fig. 3),

$$n_s = \int_0^{x_0} [\tilde{N}(x) - \tilde{n}(x)]dx \simeq n_i L(1 - \tilde{l}_m/\tilde{L}_M). \tag{47}$$

The intensity of corresponding electric field, induced within the volume of this double layer, is related to n_s as $E \simeq 2\pi e n_s/\epsilon$. Substituting this expression to Eq. (47) one defines (with the accuracy $m \ll M$) the value of E in terms of E^* [see Eq. (45)]:

$$E = \frac{\zeta}{1+\zeta} E^*. \tag{48}$$

Here

$$\zeta = \frac{8\pi e^2 n_i L}{\epsilon g M} \tag{49}$$

is the characteristic "interaction constant." Evidently, $E \to 0$ when $\zeta \ll 1$ and formally $E \to E^*$ in the case of "strong interaction" ($\zeta \gg 1$). The explicit expressions for the renormalized lengths take the form ($m \ll M$)

$$\tilde{l}_{\mathrm{m}}(\zeta) = l_{\mathrm{m}} \frac{1}{1 + \frac{M}{2m}\frac{\zeta}{1+\zeta}}, \tag{50}$$

$$\tilde{L}_{\mathrm{M}}(\zeta) = L_{\mathrm{M}} \frac{1+\zeta}{1+\zeta/2}. \tag{51}$$

One can see that in the limit of strong interaction

$$\tilde{l}_{\mathrm{m}}(\zeta \gg 1) \to \tilde{L}_{\mathrm{M}}(\zeta \gg 1) = 2L_{\mathrm{M}} \tag{52}$$

which justifies the definition of the supreme field E^* (45).

The proposed evaluation, based on the model of plane capacitor and charged double layer, is applicable until $\tilde{l}_{\mathrm{m}} \gtrsim \tilde{L}_{\mathrm{M}}$, i.e., in the region of weak enough interactions ($\zeta \lesssim 1$). In the region of strong interactions ($\zeta \gtrsim 1$), the clouds of light and heavy ions overlap strongly and our simple model is no longer applicable. It is necessary to stress that the problem of sedimentation itself still makes sense here, but for such strong interactions its solution requires consistent definitions of distributions $\tilde{n}[x,\varphi(x,\tilde{n},\tilde{N})]$, $\tilde{N}[x,\varphi(x,\tilde{n},\tilde{N})]$, and $\varphi[x,\tilde{n}(x),\tilde{N}(x)]$.

Above discussion demonstrates the effect of Coulomb interaction of charged particles on their Boltzmann distributions and establishes the quantitative criterion (49) when such interaction becomes significant. It can considerably renormalize the localization lengths of Boltzmann distributions. We would like to point out that this approach remains valid for distributions under the effect of forces of various nature: gravitational, centripetal forces in centrifuge, image forces at the interface between different insulators.

The effect discussed is similar to the phenomenon of "ambipolar diffusion," well known in the cold plasma transport problems [22]. It is important to point out that information concerning the nonlinear effects, inherent to the problem, is contained in the general equations (20) and (21), but it cannot be described in the approximation (22).

It is worthwhile to mention that the space distributions of different components of electrolytes were studied experimentally [7–10]. For instance, the authors of Ref. [7] studied the ions and colloidal particles space distributions in initially symmetric electrolyte diluted by colloidal particles. They found deviation from the Boltzmann law, claimed as the new physical effect.

The characteristic sedimentation (or thermodiffusion) lengths can vary in wide limits. For example, the gravitational sedimentation length for molecules of the atmosphere is of the order of ten kilometers. The process of heavy isotopes separation in high-speed centrifuges at high temperatures takes place in the scale of one meter. In biophysical experiments on colloidal or polymer solutions the characteristic length reduces up to centimeters.

IV. CONCLUSIONS

Our analysis gives rise to several general conclusions on the issues outlined in the Introduction. First of all, the definition of a charged particles flow in the form of Eq. (1) indeed needs to be clarified. Namely, in situations when the temperature gradient is applied the diffusion component has to be taken into account. Only after this adjustment, such definition matches the standard thermal diffusion theory in the absence of electric field. Moreover, the account for diffusion terms enables one to provide the necessary boundary conditions for a common solution of the multicomponent continuity equation together with the corresponding Poisson equation. A particular example of such coexistence is given by Eqs. (24)–(29). The formal analogy between thermal diffusion transport and the problem of sedimentation of particles in solution in the presence of gravitational field is analyzed and used to demonstrate the specifics of nonlinear effects manifestation.

The above examples show that the description of the electrolyte charged fractions separation due to some forces of the nonelectrostatic origin must also take Coulomb interaction into account. In the simplest case when $l_S \gg L$ such interaction just renormalizes the observables [for example, the potential (29)]. Under the more rigid conditions $l_S \lesssim L$ (or $l_m \lesssim L$), the properties of neutral and charged systems turn out to be qualitatively different. The analysis of thermodiffusion or, close to it, the phenomenon of sedimentation in such systems is reduced to nonlinear scenarios. For one of such problems, sedimentation of asymmetric electrolyte, we proposed the self-consistent description.

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