Proton Electrodynamic in Liquid Water

A. A. Volkov¹*, V. G. Artemov³, A. V. Pronin¹,²

¹ A. M. Prokhorov Institute of General Physics, RAS, 119991 Moscow, Russia
² Dresden High Magnetic Field Laboratory, HZ Dresden-Rossendorf, 01314 Dresden, Germany
(Dated: December 12, 2012)

The dielectric spectrum of liquid water, $10^4 - 10^{11}$ Hz, is interpreted in terms of diffusion of charges, formed as a result of self-ionization of H2O molecules. This approach explains the Debye relaxation and the dc conductivity as two manifestations of this diffusion. The Debye relaxation is due to the charge diffusion with a fast recombination rate, $1/\tau_2$, while the dc conductivity is a manifestation of the diffusion with a much slower recombination rate, $1/\tau_1$. Applying a simple model based on Brownian-like diffusion, we find $\tau_2 \approx 10^{-11}$ s and $\tau_1 \approx 10^{-6}$ s, and the concentrations of the charge carriers, involved in each of the two processes, $N_2 \approx 5 \times 10^{26}$ m$^{-3}$ and $N_1 \approx 10^{14}$ m$^{-3}$. Further, we relate $N_2$ and $N_1$ to the total concentration of $\text{H}_3\text{O}^+ - \text{OH}^-$ pairs and to the pH index, respectively, and find the lifetime of a single water molecule, $\tau_0 \approx 10^{-9}$ s. Finally, we show that the high permittivity of water results mostly from flickering of separated charges, rather than from reorientations of intact molecular dipoles.

PACS numbers: 77.22.-d, 66.10.Ed

INTRODUCTION

Electrical properties of water are of high importance in many vital, environmental, and technological processes [1–4]. They have been under intensive investigation for many decades [3–5]. It has long been recognized that at room temperature, water is a good insulator with negligible electronic conductivity and a dielectric constant $\varepsilon \approx 80$. Potentiometric measurements reveal an appreciable proton conductivity, $\sigma_{dc} = 5.5 \times 10^{-6}$ Ω$^{-1}$m$^{-1}$ at room temperature [7]. This value is associated with the pH index, which is a key indicator of activity of protons in chemical reactions [4, 6]. Normally, pH = 7; this water is regarded as neutral with the “free”-proton concentration of $6 \times 10^{19}$ m$^{-3}$. It is believed that under normal conditions, a given H$_2$O molecule will on average dissociate in roughly $10^4$ seconds (11 hours) [10, 11].

The origin of the high static dielectric constant of water is commonly explained by the orientational motion of the molecular dipoles, which is referenced as the Debye relaxation [5]. The relaxation is particularly evident in the frequency spectrum of dielectric permittivity, $\varepsilon''(\omega) = \varepsilon'(\omega) + i\varepsilon''(\omega)$, as a strong anomaly near a characteristic frequency $\nu_0 = \omega_0/2\pi$; $\nu_0 \approx 20$ GHz at room temperature.

Room-temperature dielectric spectra of water, re-plotted from the data of Refs. [4, 6], are shown in Fig. 1. The $\varepsilon''(\omega)$ spectrum is dominated by an absorption peak, accompanied by a step-like frequency dispersion in $\varepsilon'(\omega)$. The step connects the high-frequency dielectric constant, $\varepsilon_\infty = 5$, with the low-frequency (static) constant, $\varepsilon(0) = 80$. Let us note, that $\varepsilon'(\omega)$ and $\varepsilon''(\omega)$ are connected by the Kramers-Kronig relations, thus the high value of the static permittivity, $\varepsilon(0)$, is due to a large integral intensity of the Debye absorption band in $\varepsilon''(\omega)$.

The Debye relaxation in water, investigated experimentally and theoretically in many details [4, 4, 12, 13], is surprisingly well described by a simple relaxation formula:

$$\varepsilon'(\omega) = \varepsilon_\infty + \frac{\Delta\varepsilon_D}{1 + \omega^2\tau_D^2}, \varepsilon''(\omega) = \omega\tau\frac{\Delta\varepsilon_D}{1 + \omega^2\tau_D^2}. \quad (1)$$

Here $\tau_D$ is the temperature-dependent relaxation time and $\Delta\varepsilon_D = \varepsilon(0) - \varepsilon_\infty$ is the contribution of the dielectric relaxation to the static dielectric constant.

For a long time, the Debye’s idea about the orientational motion of water molecules has been exploited as the main microscopic mechanism responsible for the static permittivity. Basically since its introduction, it has been acknowledged, that the Debye model is oversimplified [5]. Therefore, the model is being permanently modified. The present-day models involve the dynamics of protons and large molecular clusters [5, 10]. Important is that in all these models, the geometry of the water molecule is a substantial input parameter.

Here, we propose an interpretation of the dielectric spectrum of water alternative to the Debye’s approach. We argue that considering exclusively the diffusive motion of protons in water is sufficient for quantitative description of its dielectric spectrum at frequencies lower than $10^{11}$ Hz.

REMARKS ON EXISTING EXPERIMENTAL DATA

Due to the reasons, which will become apparent in the course of the article, our analysis is performed in terms of complex dynamical conductivity, rather than the dielectric function. The complex conductivity, $\sigma^* = \sigma' - i\sigma''$, is defined as:

$$\sigma'(\omega) = \frac{1}{\omega}\frac{d\varepsilon''(\omega)}{d\ln\omega}, \sigma''(\omega) = \frac{\varepsilon'(\omega)}{\omega}.$$

Here, $\omega$ is the angular frequency, $\varepsilon''(\omega)$ is the loss factor, $\varepsilon'(\omega)$ is the real part of the complex dielectric function, and $\sigma''(\omega)$ is the imaginary part of the complex conductivity.
Re(σ*) + iIm(σ*), is related to the dielectric constant via: 
\[ \varepsilon'(\omega) = \varepsilon_0 + i\sigma^*(\omega)/\varepsilon_0\varepsilon_\omega, \]
where \( \varepsilon_0 \) is the free-space permittivity \cite{24}. Thus, the real part of conductivity, \( \sigma(\omega) \equiv \sigma \), is merely the imaginary part of permittivity multiplied by frequency: \( \sigma(\omega) = \omega\varepsilon_0\varepsilon''(\omega) \).

The room-temperature \( \sigma(\omega) \) spectrum of water is presented in the main frame of Fig. 1 (left-hand scale). In order to be specific, we use the data from Refs. \[5, 7\], for the dielectric constant, \( \Delta\varepsilon_D \), the relaxation time, \( \tau_D \), and the dc conductivity, \( \sigma_{\text{dc}} \). The values of these parameters for 25°C are listed in Table 1.

The most important, for further consideration, features of the conductivity spectrum are the two well-distinguished plateaus, \( \sigma_1 \) and \( \sigma_2 \), situated at \( 10^6 - 10^7 \) and \( 10^{10} - 10^{14} \) Hz, respectively. The plateaus are connected by a section, where \( \sigma(\omega) \propto \omega^s \) with \( s = 2 \). At frequencies around the lower-frequency plateau, the available experimental data differ from each other. On the one hand, there are spectroscopic indications of a frequency-dependent conductivity in this range \cite{5} (thin black line in Fig. 1). On the other hand, in electrochemistry the conductivity below \( 10^7 \) Hz is considered frequency-independent and equal to its dc value \cite{5} (dashed line in Fig. 1). Noteworthily, in the common conductometry measurements, the working frequency is usually not even mentioned \cite{21}. Hereafter, we take \( \sigma_{\text{dc}} \) as the lower-frequency plateau value. Taking the data from Ref. \[5\] instead, would only lead to minor quantitative corrections.

**ARGUMENTS FOR OUR MODEL**

Being expressed in terms of \( \sigma(\omega) \), the Debye relaxation form (Eq. \[1\]) looks like:

\[ \sigma_D(\omega) = \omega^2\tau_D\varepsilon_0\frac{\Delta\varepsilon_D}{1 + \omega^2\tau_D^2}. \]  

At high frequencies, \( \sigma_D(\omega) \) is frequency-independent, corresponding to the second plateau of the experimental spectrum:

\[ \sigma_2 \approx \sigma_D(\omega \to \infty) = \Delta\varepsilon_D\varepsilon_0/\tau_D. \]

Surely, there is no physical difference between the representations in terms of \( \varepsilon'(\omega) \) and in terms of \( \sigma^*(\omega) \). However, we believe the conductivity representation gives a tip for a fresh look on the dielectric spectrum. Whereas the bell-shaped relaxation in \( \varepsilon''(\omega) \) is intuitively connected with the orientational motion of the H\(_2\)O molecules, the \( \sigma(\omega) \) curve of Fig. 1 hints to an alternative mechanism, namely, to the proton diffusion.

In fact, the \( \sigma(\omega) \) spectrum, given by Eq. \[2\] is consistent with acceleration-less motion of a charge \( q \) with mass \( m \) in a parabolic potential, \( \varphi(x) = kx^2/2 \). The equation of motion for this charge is: \( m\gamma x + kx = qE \), where \( k \) is the spring constant and \( \gamma \) is the relaxation rate. Then, the mobility is \( \mu = q/(m\gamma) \), the diffusion coefficient is \( D = k_BT\mu/q \), and finally the conductivity is:

\[ \sigma(\omega) = \varepsilon_0\frac{[q^2N(k_BT)/2\kappa^2]\omega^2}{1 + [(k_BT)^2/\kappa^2D^2]\omega^2}, \]

which coincides in spectrum shape with Eq. \[2\].

Noteworthily, the diffusion of particles, interacting with attractive centers, reveals such \( D(\omega) \), that gives rise to the same dispersion in conductivity as in our Eq. \[1\] \cite{21}.

The \( \sigma(\omega) \) spectrum, consisting of two plateaus and a \( \sigma \propto \omega^s \) section in-between of them, is typical for materials with high ionic conductivity, the superionics \cite{22}. The conductivity spectra of these materials have been studied in great details. Their common feature is a suppression of the dynamical conductivity at low frequencies due to localization of diffusing particles in the minima of lattice potential and/or due to interactions between the particles \cite{22, 23}.

**TABLE I**: Experimental data from Refs. \[5, 7\] used as input parameters in our model. All numbers are at room temperature.

| \( \Delta\varepsilon_D \) | \( \tau_D \equiv \tau_2 \) | \( \sigma_{\text{dc}}(\equiv \sigma_1) \) | \( \sigma_2 \approx \sigma_D(\omega \to \infty) \) |
|--------------------------|---------------------------|--------------------------|---------------------------|
| 73                       | \( 8.3 \times 10^{-12} \) s | 5.5 \times 10^{-6} \Omega^{-1} m^{-1} | 78 \Omega^{-1} m^{-1} |
We believe, that in regard to its proton conductivity, water gives all reasons to be compared with superionics. In accordance with the modern concept, protons, H\(^+\), and hydroxyl ions, OH\(^-\), are permanently generated (due to the self-ionization of H\(_2\)O molecules \([10, 11, 16, 17]\) and recombined in the volume of water.

Since free protons in water are not observed, they are considered to localize after their birth on neighboring neutral H\(_2\)O molecules (on femtosecond time scale). The excess proton converts the H\(_2\)O molecule into a charged complex H\(_3\)O\(^+\) with a positive charge \(q^+\), and leaves a “hole”, OH\(^-\), with a negative (twin) charge \(q^-\). Subsequently, by a relay-race manner the \(q^+\) and \(q^-\) charges wander diffusively over H\(_2\)O molecules until they meet each other and recombine to produce a neutral H\(_2\)O. The favorable-unfavorable molecular configurations for the proton exchange are stochastically formed by the thermal molecular motion \([15, 18]\).

The diffusion paths of the separated charges, from their birth to recombination, are sketched in Fig. 2. The twin \(q^+\) and \(q^-\) charges are always in Coulomb field of each other. Therefore, in their majority they do not go far from the places of their birth (point 1 in Fig. 2). Instead, they recombine with their own twin partner in a close vicinity of their birth places the [area with characteristic size \(\ell\), point 2 in Fig. 2]. Sometimes, however, the “twins” fail to meet each other and recombine with “foreign” partners on a much larger distance \(L\) (points 3 and 4). Obviously, the most probable foreign partner is a partner from the first configuration sphere of the ionized molecules. Thus, effectively, there are two recombination processes for charges in water, faster and slower. We believe, that (similarly to superionics) the characteristic lifetimes of the two processes reveal themselves as characteristic knees in the conductivity spectrum.

**THE MODEL**

The model outlined above can be described by a set of equations. Let us designate the concentration, the average lifetime, and the mean free path of the charges, involved in the slow and in the fast processes, as \(N_1, \tau_1, L, N_2, \tau_2, \ell\), respectively. \(N_1\) and \(N_2\), can also be interpreted as the concentrations of the H\(_3\)O\(^+\)-OH\(^-\) pairs participating in the slow and fast processes. Similarly, \(\tau_1\) and \(\tau_2\) are the average life times of the H\(_3\)O\(^+\)-OH\(^-\) pairs, and \(L\) and \(\ell\) are their characteristic sizes.

The basic assumption we made is that the lower and upper conductivity plateaus in Fig. 1, \(\sigma_1\) and \(\sigma_2\), correspond to diffusion of long- and short-living charges, the latter (the fast) process giving rise to what is commonly referred as the Debye relaxation. Hence, the complete description of the \(\sigma(\omega)\) spectrum can be written as a sum of two terms:

\[
\sigma(\omega) = \sigma_1 \frac{\omega^2 \tau_1^2}{1 + \omega^2 \tau_1^2} + \sigma_2 \frac{\omega^2 \tau_2^2}{1 + \omega^2 \tau_2^2}.
\]

The conductivity at each, the lower and the upper, plateau is connected to the diffusion coefficient of charges, \(D\), by the Nernst-Einstein relation:

\[
\sigma_1 = 2CN_1D; \quad \sigma_2 = 2CN_2D,
\]

where \(C = q^2/k_BT\) and the coefficient 2 takes into account the occurrence of positive and negative charges.

Using the Einstein-Smoluchowski formula, we can also connect \(L, \tau_1, \ell,\) and \(\tau_2\) to the diffusion coefficient:

\[
D = \frac{\ell^2}{6\tau_2} = \frac{L^2}{6\tau_1}.
\]

Because both, slow and fast, processes span over all volume of water, for the unit volume one can write:

\[
1 = \frac{4\pi}{3}L^3N_1 = \frac{4\pi}{3}\ell^3N_2.
\]

Equations \(\text{[5]} - \text{[8]}\) constitute an equation set, the analytical solution of which gives the following result:

\[
N_2 = 3\left(4\pi\right)^2 \left(\frac{\sigma_1\sigma_2}{C}\right)^3; \quad \ell = \frac{C}{4\pi\tau_2\sigma_2}; \quad D = \frac{1}{6\tau_2} \left(\frac{C}{4\pi\sigma_2}\right)^2;
\]

\[
N_1 = N_2 \times \frac{\sigma_1}{\sigma_2}; \quad L = \ell \times \left(\frac{\sigma_2}{\sigma_1}\right)^{1/3}; \quad \tau_1 = \tau_2 \times \left(\frac{\sigma_2}{\sigma_1}\right)^{2/3}.
\]

The numerical values of these parameters, calculated using the experimental data of Table 1, are presented in Table 2. With these parameter values, Eq. \(\text{[5]}\) comprehensively describes both, the Debye relaxation and the dc conductivity (thick magenta line in Fig. 1).
we obtain:

\[ \Delta \varepsilon_D = \frac{q_+ q_-}{\varepsilon_0} \frac{2 N_2}{\varepsilon_0} \left( \frac{q \times \ell}{3kT} \right), \]

The polarizability (per unit volume) of these dipoles is \( N_2 \times p^2/3kT \). Thus, Eq. (12) shows that the diffusion of the charges to the average distance \( \ell \) is the reason for the step in the dielectric function, \( \Delta \varepsilon_D \), at frequencies around \( 1/2\pi \tau = 10^{10} \) Hz. The experimental value of this step, \( \Delta \varepsilon_D \approx 75 \), is automatically fulfilled in our model (through \( N_2 \) and \( \ell \)). This means that the dominant contribution (more than 90%) to the static dielectric constant (\( \varepsilon(0) \approx 80 \)) is provided by the restricted-distance currents of separated charges, rather than by orientational relaxation of intact \( \text{H}_2\text{O} \) dipoles.

Obviously, the orientational motion of the intact dipoles should also reveal itself in the dielectric spectrum. We believe, a good candidate for this is the Debye-like bands, found in the measurements at frequencies higher than \( 10^{11} \) Hz [27, 28]. These higher-frequency relaxation processes are also seen as the upturn of the experimental conductivity at the highest frequencies in Fig. 1.

The slow recombination process with the characteristic time \( \tau_1 \) also provides a contribution to the static dielectric constant. According to Eq. (3) this contribution is however very small, \( \Delta \varepsilon_1 \ll 1 \).

3. Diffusion coefficient. In our consideration, the diffusion coefficient, \( D = 1.2 \times 10^{-5} \text{ m}^2/\text{s} \) is related to the relay-race diffusion of charges (\( q^+ \) and \( q^- \)), not to diffusion of a tagged proton. In literature, however, this value (more accurately, \( 9.3 \times 10^{-9} \text{ m}^2/\text{s} \)) is commonly accepted as the diffusion coefficient of protons [9] and considered to be “anomalously” high. According to our findings, the real Brownian diffusion coefficient of a tagged proton, \( D^{H^+} \), is 100 times smaller: \( D^{H^+} = \left( a^2/6\tau_0 \right) \approx 10^{-10} \text{ m}^2/\text{s} \), where \( a = 2.5 \) Å is the distance between the \( \text{H}_2\text{O} \) molecule centers [17].

It is worth noting here, that if one substitutes the proton diffusion coefficient, \( D^{H^+} \), and the total proton concentration, \( 2N_0 \), into the Nernst-Einstein equation (Eq. 11), one gets the upper limit for the proton conductivity in water: \( \sigma = 4CN_0D^{H^+} = 74 \text{ } \Omega^{-1}\text{m}^{-1} \), that is precisely the value of the higher-frequency plateau in the \( \sigma(\omega) \) spectrum, \( \sigma_2 \).

4. dc conductivity and relevance to pH index. The found value for \( N_1 (3.8 \times 10^{19} \text{ m}^{-3}) \) is practically equal to the commonly accepted concentration of “free” protons (6 \( \times 10^{19} \text{ m}^{-3} \)), which provides \( \text{pH} = 7 \) in neutral water. This result shows that the common dc conductometric methods detect only those “survived” protons (of concentration \( N_1 \)), which are involved in the slow recombination process, while the short-living protons (concentration \( N_2 \)) are not detectable in these measurements. The occurrence of the short-living protons in water requires introducing a new, “fast”, dissociation constant, \( K_{W2} \), in addition to the common (“slow”) \( K_{W1} \), related to the pH index. Since both, long- and short-living, protons are chemically active, the conventional conception of the pH index could probably be revised in such a way that the fast \( K_{W2} \) is also taken into account.

The found parameters characterize a Brownian motion of thermally activated charges \( q^+ \) and \( q^- \) over the “sea” of neutral molecules, i.e. the drift currents. The mutual thermal motion of neutral \( \text{H}_2\text{O} \) molecules is not relevant for our consideration.

**CONSEQUENCES OF THE MODEL AND CONCLUSIONS**

1. Concentration of separated charges and life time of \( \text{H}_2\text{O} \) molecules. As one can see from Table 2, the concentration of short-living \( \text{H}_3\text{O}^+–\text{OH}^- \) pairs is huge, \( N_2 \approx 5 \times 10^{26} \text{ m}^{-3} \). Because \( N_2 > N_1 \), \( N_2 \) can be taken as the total concentration of the \( \text{H}_3\text{O}^+–\text{OH}^- \) pairs. Thus, roughly 1% of all \( \text{H}_2\text{O} \) molecules are ionized, the concentration of \( \text{H}_2\text{O} \) molecules being \( N_0 = 3 \times 10^{28} \text{ m}^{-3} \). The found charge concentration is by several orders of magnitude larger than the commonly accepted value for neutral water, \( 10^{-7} \) mole/liter = 6 \( \times 10^{19} \text{ m}^{-3} \). Figuratively, water constantly boils with \( \ell \)-sized \( \text{H}_3\text{O}^+–\text{OH}^- \) pairs, which have a life time of \( \tau_2 \approx 10 \text{ ps} \). This result agrees with what was reasoned in Ref. [10] based on molecular-dynamics stimulations.

Our value for the size of \( \text{H}_3\text{O}^+–\text{OH}^- \) pairs, \( \ell = 0.76 \text{ nm} \), correlates with the recent x-ray scattering results of Ref. [20], where density fluctuations in water were reportedly found on a comparable scale.

Because \( N_2 >> N_1 \), the life time of a neutral \( \text{H}_2\text{O} \) molecule in thermodynamic equilibrium, \( \tau_0 \), can be estimated from the following equation:

\[ \frac{N_2}{\tau_2} = \frac{N_0}{\tau_0}. \]

(11)

From here, we obtain \( \tau_0 \approx 1 \text{ ns} \), which is 14 orders of magnitude smaller than the “standard” \( 10^9 \) s.

2. Permittivity. The Debye relaxation time changes its meaning – it is now the average life time of the short-living separated charges (the \( \text{H}_3\text{O}^+–\text{OH}^- \) pairs). For the permittivity spectrum, by combining Eqs. (3) (5) and (6) we obtain:

\[ \Delta \varepsilon_D = \frac{\sigma \tau_2}{\varepsilon_0} = \frac{(q \times \ell)^2 N_2}{3kT}\frac{\varepsilon_0}{\varepsilon_0}, \]

i.e., the pairs of the separated charges can be considered as dipoles with the average dipole moment \( p = q \times \ell \).

**TABLE II: Room-temperature numerical values of the parameters obtained from our model (Eqs. 9–11).**

| \( N_1 \) | \( N_2 \) | \( D \) |
|---------|---------|---------|
| \( 3.8 \times 10^{19} \text{ m}^{-3} \) | \( 5.4 \times 10^{26} \text{ m}^{-3} \) | \( 1.2 \times 10^{-5} \text{ m}^2/\text{s} \) |

| \( L \) | \( \ell \) | \( \tau_1 \) |
|--------|-------|-------|
| 0.18 \( \mu \text{m} \) | 0.76 \( \text{nm} \) | \( 5 \times 10^{-7} \text{ s} \) |
Summarizing, we have found that the dielectric spectrum of liquid water at frequencies below $10^{11}$ Hz can be entirely understood in terms of proton diffusion, resulting from self-dissociation of H$_2$O molecules. No long-living geometric structures, created by the water molecules, are needed to be included in this consideration. We believe that many other physical properties of water are also determined mostly by the ability of H$_2$O molecules to dissociate rather than to form any sorts of geometric structures.

We are grateful to S. D. Zakharov and G. M. Zhidomirov for useful discussions.

[1] G. W. Robinson, S. B. Zhu, S. Singh, and M. W. Evans, Water in Biology, Chemistry, and Physics: Experimental Overviews and Computational Methodologies, World Scientific Series in Cont. Chem. Phys., Vol. 9 (World Scientific, Singapore, 1996).
[2] S. W. Trimble, B. A. Stewart, and T. A. Howell, Encyclopedia of Water Science (Taylor & Francis, New York, 2008).
[3] D. S. Eisenberg and W. Kauffmann, The structure and properties of water (Oxford University Press, New York, 1969).
[4] Water, A Comprehensive Treatise, Vol. 1 – 7, ed. F. Franks (Plenum, New York, 1972 – 1982).
[5] A. von Hippel, Transactions on Electrical Insulation 23, 801 (1988).
[6] M. Chaplin, http://www.lsbu.ac.uk/water/index2.html
[7] T. S. Light, S. Licht, A. C. Bevilacqua, and K. R. Morash, Electrochemical and Solid-State Letters 8, E16 (2005).
[8] R. G. Bates, Determination of pH, Theory and Practice (John Wiley & Sons Inc., New York, 1973).
[9] J. O’M. Bockris and A. K. N. Reddy, Modern Electrochemistry (Kluwer Acad. Publishers, New York, 1998).
[10] P. L. Geissler, C. Dellago, D. Chandler, J. Hutter, and M. Parrinello, Science 291, 2121 (2001).
[11] H. J. Bakker and H.-K. Nienhuyst, Science 297, 587 (2002).
[12] R. Buchner, J. Barthel, and J. Stauber, Chem. Phys. Lett. 306, 57 (1999).
[13] N. Agmon, J. Phys. Chem. 100, 1072 (1996).
[14] V. I. Gaiduk and D. S. F. Crothers, Journal of Molecular Structure 798, 75 (2006).
[15] M. Sharma, R. Resta, and R. Car, Phys. Rev. Lett. 98, 247401 (2007).
[16] R. Bukowski, K. Szalewicz, G. C. Groenenboom, and A. van der Avoird, Science 315, 1249 (2007).
[17] N. Agmon, Chem. Phys. Lett. 319, 247 (2000).
[18] S. Walbran and A. A. Kornyshev, J. Chem. Phys. 114, 10039 (2001).
[19] A. A. Kornyshev, A. M. Kuznetsov, E. Spohr, J. Ulstrup, J. Phys. Chem. B 107, 3351 (2003).
[20] L. D. Landau, L. P. Pitaevskii, and E. M. Lifshitz, Electrodynamics of Continuous Media (Butterworth-Heinemann, Oxford, 1984).
[21] J. Stepisnik, I. Sersa, and A. Mohoric, arXiv:1010.1175v1 (2010).
[22] Physics of Superionic Conductors, ed. M. B. Salomon (Springer, Berlin 1979).
[23] W. Dieterich, P. Fulde, and I. Peschel, Advances in Physics 29, 527 (1980).
[24] J. C. Dyre and T. B. Schrøder, Rev. Mod. Phys. 72, 873 (2000).
[25] A. A. Volkov, G. V. Kozlov, S. P. Lebedev, and A. C. Rakitin, Fizika Tverdogo Tela 32, 329 (1990).
[26] C. Huang et al., PNAS 106, 15214 (2009).
[27] C. Rønne, L. Thrane, P.-O. Åstrand, A. Wallqvist, K. V. Mikkelsen, and S. R. Keiding, J. Chem. Phys. 107, 5319 (1997).
[28] U. Møller, D. G. Cooke, K. Tanaka, and P. U. Jepsen, J. Opt. Soc. Am. B 26, A113 (2009).