On Nature of the Dielectric Response of Liquid Water (Review)
Airat A. Khamzin
Kazan Federal University, https://kpfu.ru/
Kazan 420008, Russian Federation
E-mail: airat.khamzin1976@gmail.com
Received 23 April, 2021, peer-reviewed 03 May, 2021, accepted 10 May, 2021

Abstract: The article presents a brief review of the currently popular interpretations of the microscopic nature of the dielectric relaxation of water in the liquid phase in the giga- and terahertz frequency ranges. The main emphasis is on models that allow for analytical consideration.

Keywords: hydrogen bonds, water, dielectric relaxation, conductivity, orientation and ionic defects, Debye relaxation, Raman spectroscopy, fractons

PACS: 77.22.Gm; 77.22.Ch; 63.50.+x

For citation: Airat Khamzin. On Nature of the Dielectric Response of Liquid Water (Review). RENSIT, 2021, 13(2):119-128. DOI: 10.17725/rensit.2021.13.119.

Contents
1. INTRODUCTION (119)
2. THE MAIN RELAXATION PROCESS OF WATER (120)
3. NON-DEBYE RELAXATION BEHAVIOR OF WATER (124)
4. CONCLUSION (126)
REFERENCES (127)

1. INTRODUCTION
The necessity to study the structure and properties of water is due to its unique role in animate and inanimate nature, science and technology, modern technologies. In a liquid state, water has many anomalous properties that distinguish it from other simple liquids [1]. Many of these properties are not fully understood. Among them, dielectric properties also play a significant role. In particular, the dielectric loss, which is determined by the imaginary part $\epsilon''$ of the complex dielectric permittivity (CDP) and quantitatively gives the field energy loss due to absorption by the sample. Understanding the processes that regulate dielectric loss is an urgent challenge not only for everyday applications such as microwave cooking, airport body scanners, or the biological effects of mobile phone radiation, but also for lesser known but nonetheless important effects, such as, for example, attenuation of electromagnetic waves in fog or clouds, affecting communications and radar devices.

Now, the methods of broadband dielectric spectroscopy and far infrared spectroscopy allow to measure dielectric spectra in a wide frequency range [2]. Fig. 1 shows the spectrum of dielectric losses of water at a temperature 20°C up to 17 THz [3-6]. The main peak of dielectric losses at about 20 GHz obeys Debye's law up to several tens of gigahertz with a characteristic relaxation time $\tau_D \approx 9.3$ ps at room temperature [7], which represents the collective reorientation dynamics of water [8-10]. In the frequency range 0.1-2 THz, a deviation from the Debye

![Fig. 1. Dielectric spectrum of water at temperature 293 K.](image-url)
behavior is observed, which manifests itself in the form of an “excess wing” and indicates the contribution of a faster dynamic process with a characteristic relaxation time $\tau_f \approx 1 \text{ ps}$ [11]. Data up to 1 THz can be fitted by the sum of the two Debye functions, where the second relaxation is superimposed on the dominant process around 20 GHz [11-12]. At even higher frequencies, several vibration-related processes are detected, which can be approximated by Lorentz functions. A discussion of these processes is beyond the scope of this paper.

Until now, there is no clear understanding of the microscopic nature of both the relaxation process around 20 GHz and the supposed second faster relaxation process. Early papers suggested several scenarios that explained the second process. One of them is the so-called "structural" scenario, which is based on the two-fraction model of water [11-13], where water is represented as a mixture of two fractions: a small fraction of weakly bound or not at all hydrogen-bonded water molecules, and a fraction with molecules, hard connected by hydrogen bonds. A fast dynamic process is caused by the rotation of weakly bound water molecules or inelastic collisions of molecules. This scenario is confirmed by two experimental facts: the relaxation time $\tau_f$ is small and is approximately equal to the collision time of molecules in the gas phase, the ratio of the amplitudes of the main and fast processes approximately coincides with the fraction of molecules forming no more than two hydrogen bonds. This scenario contradicts the data of coordination analysis [14], infrared [15] and Raman spectroscopy [16], which indicate a smooth distribution of fractions from undercoordinated, with two hydrogen bonds, to supercoordinated ones, with five hydrogen bonds. Therefore, the separation of water into two separate fractions is questionable. Another, so-called “dynamic” scenario [17], assumes the existence of another type of molecular motion in the THz range, where non-Debye behavior is observed. This scenario is based on the fact that the relaxation peak in the Raman spectrum of water is in the same frequency range as the non-Debye behavior in the spectrum of dielectric losses [18]. Therefore, vibrations of the network of hydrogen bonds are an additional molecular motion in the dynamic scenario.

In [19], these early ideas were revived. As a result of analyzing the data of dielectric and viscoelastic measurements, as well as data on light scattering, it was assumed that the fast process is the “true” structural relaxation of water, determined by the dynamics of single molecules. In contrast, the main dielectric peak is associated with a supramolecular structure similar to the Debye peak observed in monohydric alcohols. This work caused a heated discussion in subsequent numerous papers, as well as the advancement of new ideas about the origin of the main and the second, faster, processes. This article is devoted to a brief review of new interpretations of the microscopic nature of the dielectric response of liquid water that have appeared over the past five years.

2. THE MAIN RELAXATION PROCESS OF WATER

Historically, the first model of dielectric relaxation of water is the Debye model [20]. In this model, which is now considered erroneous, water molecules perform a Brownian small-angle rotational motion. Debye's model gives the following relaxation time equation: $\tau_D = 4\pi R^3 \eta / T$ (where $R$ – radius of molecules, $\eta$ - viscosity). This equation correctly describes the experimental data and gives the correct value for the radius of single water molecules $R = 1.44 \text{ Å}$. However, this equation is violated for water in the condensed state. The presence of a network of hydrogen bonds limits the rotation of water molecules and leads to the possibility of only jump-like rotations of the dipole moments of water molecules when hydrogen bonds are broken. To describe the intermittent reorientation of water molecules, the currently
most popular relaxation model “wait and switch” [21], according to which the reorientation of the water molecule occurs at a large angle only when it encounters a defect in the network of hydrogen bonds. In the waiting mode of the defect the relaxation in the liquid phase slows down compared to the gas phase. In water, we can distinguish two main types of defects: orientational (structural) and ionic. Hydrogen bond between water molecules leads to local tetrahedral ordering (see Fig. 2a). However, due to thermal fluctuations, the local ordering is distorted, which leads to the breaking of some hydrogen bonds and the formation of bifurcated bonds [22] (see Figs. 2b,c). The presence of such a defect (orientation defect) near a water molecule contributes to its reorientation (see Fig. 2b). Further migration of the orientational defect leads to a sequential reorientation of the remaining water molecules (see Fig. 2d). The migration of defects has an intermittent nature and is similar to the migration of orientation L-D Bjerrum defects in ice. [23-25]. Note that in water, orientation defects are formed in pairs (defect-antidefect) and are destroyed when meeting. In addition to orientation defects, the

Fig. 2. Orientation defects. a) The local tetrahedral ordering of water molecules without defects, b) the defect in the hydrogen bond network due to hydrogen bifurcation, c) the defect in the hydrogen bond network due to oxygen bifurcation, d) schematic representation of the migration of the orientation defect with a sequential change in the direction of the dipole moment of water molecules.

Fig. 3. The ionic defects H$_3$O$^+$ and OH$^-$ (a). Schematic representation of the generation and migration of ionic defects with a change in the direction of the dipole moments of water molecules (b).
formation of pairs of ionic defects \(\text{H}_3\text{O}^+\) and \(\text{OH}^-\) is possible in water (see Fig. 3). At a meeting of ionic defect the water molecule does not rotate as a whole, but rearranges the dipole moment due to the proton hopping along the hydrogen bond. Moreover, if on one side of the molecule a proton is received, then on the other side it is given away.

Orientation and ionic defects coexist in water, therefore the dielectric relaxation in water is determined by both mechanisms. In ice, due to the significant difference in the activation energies of ionic and orientational defects, it is possible that one mechanism dominates over another in a certain temperature range and, as a consequence, the presence of a dynamic crossover between them [24-28]. However, in liquid water, the activation energies of defects are approximately the same; therefore, it is difficult to distinguish them in dielectric measurements [22]. There is also no dynamic crossover in liquid water. Based on this fact, and also that dielectric relaxation does not react to pH changes [29], it is suggested that the orientational relaxation mechanism is dominant in liquid water [30].

Based on the “wait and switch” model, a new theoretical model for describing the dielectric relaxation of liquid water was proposed in [31]. Let's briefly highlight its main provisions. Taking into account that the main mechanism of water relaxation is due to the migration of orientation and ionic defects along the network of hydrogen bonds, and using the relationship between the CDP and conductivity [24, 32] \(\varepsilon(\omega) = \varepsilon_\infty + \Delta\varepsilon/(1 + i\omega\tau)\), get

\[
\varepsilon(\omega) = \varepsilon_\infty + \frac{\Delta\varepsilon}{1 + [i\omega\tau_\infty]^{-1}}. \tag{1}
\]

Here \(\sigma_{or,\text{ion}}(\omega)\) is the complex conductivity of the orientation and ionic defects, respectively, which is related to the mean square deviation (MSD) of migrating defects by the relation

\[
\sigma_{\alpha \gamma}(\omega) = \alpha^2 (n_\alpha q_\alpha^2 / 6T) \hat{g}(\omega). \tag{2}
\]

where \(\hat{g}(s)\) is the Laplace image of the defect MSD, \(\Delta\varepsilon = \varepsilon_\infty - \varepsilon_\infty \) is the dielectric strength, \(\varepsilon_\infty\) is the static dielectric constant, \(\varepsilon_\infty = \varepsilon(\omega \to \infty)\). If we make a fairly obvious assumption that the orientation defects perform the normal diffusion motion, \(< r^2(t) >= 6D_or t \), \((D_{or})\) is the diffusion coefficient of orientation defects, then ionic defects in the presence of orientation defects, which will block proton hopping, already perform anomalous diffusion motion, \( < r^2(t) >= 6D_{ion} t^\alpha \). Performing Laplace transformation of MSD defects, \(\hat{g}_{or}(s) = 6D_{or} s^{-2}, \hat{g}_{ion}(s) = 6D_{ion} \Gamma(1 + \alpha) s^{-1-\alpha}\) we find from (1) the expression for the CDP of water

\[
\varepsilon(\omega) = \varepsilon_\infty + \frac{\Delta\varepsilon}{1 + [i\omega\tau_\infty]^{-1}}. \tag{3}
\]

Since, according to the experiment, the main peak of the dielectric loss of water has a Debye shape, the exponent \(\alpha \approx 1\), and from (3) we obtain the Debye expression for the CDP

\[
\varepsilon(\omega) = \varepsilon_\infty + \frac{\Delta\varepsilon}{1 + i\omega\tau_D}, \tag{4}
\]

with relaxation time

\[
\tau_D = (\tau_\infty^{-1} + \tau_\text{ion}^{-1}). \tag{5}
\]

A similar idea is developed in [33], where it is assumed that dielectric relaxation, both in ice and in liquid water, is entirely associated with the migration of only ionic defects. We will also briefly highlight the main provisions of the approach developed here. For the theoretical description of the dielectric relaxation of water, the author of [33] chooses the Langevin approach, which has already been applied earlier by other authors to describe the dielectric relaxation of ice. [28]. According to the model in [33], there are two types of correlations between ionic defects. The first type of correlations is the friction between the proton and the nearest environment. The second type of correlation...
NANOSYSTEMS

Fig. 4. Schematic representation of the model of paper [33]. White circles represent neutral water molecules, small circles represent excess protons (blue), proton holes (red). The large gray circle represents the hydration shell of water, and the large yellow circle represents the ion cloud of proton holes. Springs show electrostatic interactions between ions and neutral molecules (gray springs) and between ions and the center of the negative ion cloud (red spring).

is long-range electrostatic interaction between a positive H$_3$O$^+$ ion and a cloud of negatively charged OH$^-$ ions. Fig. 4 shows a schematic representation of the ionic model from [33]. Within the framework of this model, the system of equations for describing the dynamics of ionic defects has the form

\[ m\ddot{x} + m\gamma \dot{x} + \kappa_2 \int_0^1 M(t-t')\dot{x}(t')dt' + \kappa_1 (x - X) = f(t), \]

\[ M\ddot{X} + M\gamma \dot{X} - \kappa_1 (x - X) = F(t). \]

Here \(x, X\) are coordinates of the positive ion and the center of mass of the negative cloud in the coordinate system associated with water molecules, \(m, M\) are the mass of the positive ion and the effective mass of the negative cloud, respectively, \(\gamma, \Gamma\) are friction coefficients, \(\kappa_{1,2}\) are constants of electrostatic interaction between a positive ion and a negative cloud and the nearest neutral water molecules, respectively, \(f(t), F(t)\) are the Langevin's random forces, \(M(t) = <f(t)f(0)>/T_k\) is the memory function. Solution of the system of equations (6) using the Laplace transform and using the relation

\[ \hat{g}(s) = 6\hat{C}_\nu(s)/s^2, \]

where \(\hat{C}_\nu\) is the Laplace image of the velocity-velocity correlation function, gives the complex conductivity, the expression for which is conveniently represented in the form

\[ \sigma(\omega) = \frac{nq^2/m}{i\omega + \gamma + \omega_0^2 M(i\omega) + \Omega_0^2 \hat{M}(i\omega)}, \]

\[ \hat{M}(s) = \frac{s + \Gamma}{\Omega_0^2 (m/M) + s(s + \Gamma)}. \]

Here \(\omega_0 = \sqrt{\kappa_2/m}, \Omega_0 = \sqrt{\kappa_1/M}, \hat{M}(s)\) is the Laplace-image memory function \(\hat{M}(t)\). In [33], it is also assumed that the memory function has an exponential decay with a characteristic correlation time \(\tau_c\):

\[ M(t) = \exp(-t/\tau_c) = \hat{M}(s) = 1/(s + \tau_c^{-1}). \]

Note that at frequencies

\[ s < \Gamma: M_h(s) \approx 1/(s + \Omega_0^{-1}(m/M)) = M_h(t) = e^{-t/\tau_c}. \]

where \(\tau_c = \Gamma(M/m) + \Omega_0^2\). The expression for the conductivity (7) is used to obtain the expression for the CDP

\[ \epsilon(\omega) = \epsilon_\infty + \frac{\sigma(\omega)}{i\omega\epsilon_0} = \epsilon_\infty + \frac{nq^2/\epsilon_0 m}{i\omega(\omega + \gamma + \omega_0^2 M(i\omega) + \Omega_0^2 \hat{M}(i\omega))}. \]

Using the estimates of the model parameters for liquid water, which were obtained in [33] only from the analysis of the conductivity spectrum, \(M/m = 18, \gamma = 4.3\ \text{TГц}, \Gamma = 2.2\ \text{TГц}, \omega_0 = 4.4\ \text{TГц}, \Omega_0 = 31.4\ \text{TГц}, \tau_c^{-1} = 1.7\ \text{МГц}, \tau_{c1}^{-1} = 24.9\ \text{МГц}\), one can simplify the expression for CDP in the frequency range of the main peak (up to 0.1 THz). Indeed, in the frequency range of the main peak, we have

\[ \tau_c^{-1} << \omega << \gamma, \Gamma, \omega_0, \Omega_0, \tau_{c1}^{-1}, \]

as a result, expression (8) is reduced to the Debye form

\[ \epsilon(\omega) \approx \epsilon_\infty + \frac{nq^2/\epsilon_0 m}{1 + i\omega\tau_D}, \]

with a characteristic relaxation time

\[ \tau_D = (\gamma + \Omega_0^2 \tau_c)/\omega_0^2 \approx 2.3\ \text{ps}. \]

Note that this value is inconsistent with the observed relaxation time of 9.3 ps of the main relaxation, that seems to indicate the fact that the mechanism through ionic defects may be responsible for the second,
faster, process. The main problem of the model proposed in [33], as pointed out by many authors, is the inconsistency with the experimentally observed value of the fraction of ionic defects in liquid water, $10^{-7}$. The model also seems incompatible with modeling classical molecular dynamics, which satisfactorily reproduces the dielectric response of water, even if there are no charged defects in it. [34]. The discrepancy by the author [33] is explained by the fact that most ionic defects are short-lived and contribute only in the microwave frequency region, where their fraction can reach 1%. I would also like to note that the idea of the existence of two types of correlations of ionic defects in water is not new. So in papers [25-28] for hexagonal ice was performed the idea that in addition to anomalous diffusion motion along an inhomogeneous network of hydrogen bonds, there is a capture of ionic defects by traps formed by orientational defects. This type of correlations becomes significant at sufficiently low temperatures, when the motion of orientational defects is significantly slowed down.

3. NON-DEBYE RELAXATION BEHAVIOR OF WATER

We proceed to discuss the nature of the non-Debye behavior of the dielectric response of liquid water in the frequency range 0.1-2 THz. Let us turn again to paper [31], where a new idea of the origin of the non-Debye behavior of the peak of dielectric losses in this frequency range was also proposed, which also caused many discussions in the literature. In [31], the authors analyzed the low-frequency Raman spectrum of water in [35], where the intensity of Raman scattering was measured at extremely low frequencies, up to 0.6 sm$^{-1}$. The frequency dependence of the intensity $I(v)$ of Raman light scattering, corrected by the Bose-Einstein factor of the level population, is shown in Fig. 5. The figure shows the presence of a wide relaxation peak just in the frequency range of non-Debye behavior, with a characteristic relaxation time $	au_R \approx 0.5$-1.5 ps. An analysis of the spectrum carried out in [31, 35] shows that the nature of this peak is associated with global oscillations of the network of hydrogen bonds. Therefore, in [31], it is concluded that the main reason for the non-Debye behavior of the dielectric loss spectrum is the oscillations of the network of hydrogen bonds. To take this effect into account, the concept of vibrational-diffusion motion of defects is adopted, according to which the motion of a defect is represented as a superposition of independent translational and oscillating motions: $\vec{r}(t) = \vec{R}(t) + \vec{u}(t)$. Then the MSD of the defect take the form

$$g(t) = \langle r^2(t) \rangle = \langle (\vec{R}(t) + \vec{u}(t))^2 \rangle = \langle \vec{R}^2(t) \rangle + \langle \vec{u}^2(t) \rangle.$$  

For the translational motion of defects, as discussed above, the normal diffusion law is adopted. To describe the oscillatory contribution to the MSD, it is assumed that the network of hydrogen bonds is a system of coupled harmonic oscillators with frequency $\omega$, then

$$\langle \vec{u}^2(t) \rangle = \frac{6T}{mn} \left(1 - \cos \omega t \right),$$

where $m$ is the mass of water molecule, $n$ is the concentration of water molecules. If we take into account that in reality in the network there

![Fig. 5. Frequency dependence of the imaginary part of the dielectric complex permittivity (left axis) and the normalized Raman intensity [35], corrected by the Bose-Einstein factor (right axis).](image-url)
is a dispersion of vibrational frequencies with a distribution density $\varphi(\omega)$, then
\[<u^2(t)> = \frac{6T}{mn} \int \varphi(\omega) \frac{(1-\cos \omega t)}{\omega^2} d\omega. \tag{12}\]

For a regular network of hydrogen bonds, the Debye frequency distribution law is satisfied:
\[\varphi(\omega) = 3\omega_D^2 / \omega^5, \quad \text{where } \omega_D \text{ is the Debye characteristic frequency (} \varphi(\omega > \omega_D) = 0). \]

However, in reality, the network has an irregular structure as a result of bond breaks, which can be approximated by fractal symmetry. Then, at frequencies $\omega_c < \omega < \omega_D$ in the system, there is a fracton spectrum with the density of states
\[\varphi(\omega) \approx \frac{\omega_D^2}{\omega^3}, \tag{13}\]
where $d_s$ is a spectral dimension of the hydrogen bond network ($1 \leq d_s \leq 4/3$), $n_f$ is a concentration of fractal fragments. Substituting (13) into (12) and performing the integration, we obtain
\[<u^2(t)> \approx \frac{6Td_n}{m\omega_D^{d_s}} \int \omega^{d_s-3}(1-\cos \omega t) d\omega \approx \frac{6Td_n}{m\omega_D^{d_s}} \cos(\pi d_s/2) \Gamma(d_s-2)t^{2-d_s}. \tag{14}\]

Performing the Laplace transformation of Eq. (14) for the MSD of defects and taking into account the relationship between the MSD and conductivity, we obtain an expression for the conductivity of defects taking into account the oscillations of the network of hydrogen bonds
\[\sigma(\omega) = -\omega \frac{nq^2}{6T} \hat{g}(i\omega) = \frac{i\omega}{T} \frac{nq^2}{2m\omega_D^{d_s}} \sin(\pi d_s/2) \frac{T\pi d_s \xi}{2m\omega_D^{d_s}} (i\omega)^{1/(2-d_s)}. \tag{15}\]

Function (16) at low frequencies transforms into the Debye law, and at high frequencies it exhibits an “excess wing” with a slope of $2-d_s$ on a double logarithmic scale. Fig. 6 shows the graphs of the imaginary part of the CDP (16) depending on the frequency for different values of the spectral dimension and the ratio $\theta = \tau_{osc}/\tau_{defect}$. It can be seen from the figure that the expression for the CDP indeed allows one to describe the non-Debye behavior above the frequency of the main peak. To obtain an excess wing at high frequencies and preserve the Debye behavior at low frequencies, it is only necessary to satisfy the condition: $\theta = \tau_{osc}/\tau_{defect} > 1$.

Fitting the experimental data for the dielectric spectrum of water at a temperature of 293 K using dependence (16), performed in [31], shows excellent agreement. As a result of the fitting, the following estimates were obtained for the model parameters: $\Delta \varepsilon = 75.3 \pm 1.4$, $\varepsilon_{\infty} = 1.7 \pm$
0.3, $\tau_{\text{defect}} = 12.4 \pm 0.2$ ps, $\tau_{\text{osc}} = 35 \pm 1$ ps, $d_s = 1.07 \pm 0.01$. The position of the maximum of the main relaxation peak with accounting excess wing is determined from the formula [31]

$$\tau_p \approx \tau_{\text{defect}} (1 + \theta^{d_s-2})^{-1} = 9.1 \text{ ps.} \quad (18)$$

This value is in excellent agreement with the experimental value at 293 K. In [37], a critical analysis of the literature on the absorption peak of liquid water and the “excess wing” in its high-frequency flank was carried out. Having performed large-scale modeling of molecular dynamics and fitting the dielectric spectrum of water with various models, the author of [37] came to the conclusion that the model of [31] describes the most adequately the dielectric response of water up to 2 THz.

Let us discuss two ideas about the microscopic nature of the dielectric relaxation of water in the sub-terahertz range, which appeared in the literature after the paper [31]. In [38], the authors measured the dielectric spectra of pure water and water mixed with LiCl in a wide range of frequencies and temperatures, which showed the similar spectral behavior. Unlike pure water, salt water solutions can be supercooled to low temperatures, close to the glass transition temperature. Undercooling shifts the main peak of dielectric losses to low frequencies faster than additional, faster processes, that makes it possible to better identify these processes. On cooling, in contrast to alcohols, in saline aqueous solutions a broadening of the main peak is observed, and the separation of relaxation processes (main slow and fast) does not occur. In aqueous solutions of LiCl, the main peak and the “excess wing” are species even for the lowest temperatures. This fact does not agree with the interpretation of [19], where the structural relaxation of water is attributed to a fast process in the terahertz range, as in monohydric alcohols. The shape of the spectrum and its temperature behavior in a LiCl solution are very similar to those observed in typical supercooled liquids [39-40]. As is known, in supercooled liquids, a sequence of dynamic processes manifests itself, namely, structural $\alpha$ relaxation, $\beta$ relaxation (in the form of an “excess wing”) and a “boson peak”. As a result, in [38], it is assumed that the non-Debye behavior in the spectrum of pure water is caused by a “boson peak” lying in the terahertz range, which causes excessive absorption at high frequencies. The nature of the "boson peak" is still not clear, but most researchers are inclined towards the phonon origin.

Another idea is proposed in [41]. The relaxation behavior of water from GHz to THz in [41] is interpreted within the framework of the coupling model (CM) [42], which defines the general rule of evolutionary dynamics of glass-forming liquids. At the highest frequencies (before vibrational modes), water molecules are caged. In caged molecules regime water dynamics manifests itself as nearly constant dielectric loss. This regime manifests itself in the form of flat valleys around 1-2 THz in the spectrum of water. With a decrease in frequency, the cage decays and a primitive relaxation begins (weakening of the coupling between molecules), which leads to a secondary $\beta$ relaxation of Johari-Goldstein, and then to a structural, almost exponential, $\alpha$ relaxation. These sequential processes, in the opinion of the author [41], explain the Debye main peak, the associated non-Debye behavior, and frequency dispersion at higher frequencies before reaching the vibrational contributions. Important arguments in support of this scenario obtain from neutron scattering experiments that demonstrate the existence of cage and its decay in the excess wing regime.

4. CONCLUSION

In this article, we have presented an review of the main advances achieved in recent years in understanding the microscopic nature of the dielectric response of liquid water in the gigahertz and terahertz frequency ranges. Despite the seeming simplicity of water, the explanation of its dielectric properties seems to be a rather difficult problem for the scientific community.
If the understanding of microscopic processes in water in the GHz region has practically reached mutual agreement of specialists, then disagreements in the explanation of the dielectric behavior of water in the THz region still remain. The presence of disagreements will certainly stimulate the development of new ideas for explaining the non-Debye behavior of water in the terahertz range; therefore, in the near future, interest in studying the dielectric properties of water will not fade away.

Summarizing the ideas that were highlighted above, at present the most consistent with measurements obtained from a wide range of experimental methods for studying water, in our opinion, corresponds to the interpretation of the dielectric relaxation of water based on the model of migration of structural defects along the network of hydrogen bonds, which can be supplemented, as one of the versions, by the presence of the oscillatory dynamics of the network [31]. Taking into account the fluctuations of the hydrogen bond network does not contradict the ideas of the papers [38, 41].

REFERENCES
1. Ball P. Water – an enduring mystery. Nature, 2008, 452:291-292.
2. Ellison WJ. Permitivity of Pure Water, at Standard Atmospheric Pressure, over the Frequency Range 0–25THz and the Temperature Range. J. Phys. Chem. Ref. Data, 2007, 36:1-18.
3. Levy E, Puzenko A, Kaatze U, Ben Ishai P, and Feldman Y. Dielectric spectra broadening as the signature of dipole-matrix interaction. I. Water in nonionic solutions. J. Chem. Phys., 2012, 136:114502.
4. Ellison WJ, Lamkaouchi K and Moreau JM. Water: a dielectric reference. J. Mol. Liq., 1996, 68:171-279.
5. Ronne C, Thrane L, Astrand PO, Wallqvist A, Mikkelsen KV and Keiding SR. Investigation of the temperature dependence of dielectric relaxation in liquid water by THz reflection spectroscopy and molecular dynamics simulation. J. Chem. Phys., 1997, 107:5319-5331.
6. Mätzler C. Thermal microwave radiation: applications for remote sensing. London, Institution of Engineering and Technology Publ., 2006.
7. Kaatze U. Reference liquids for the calibration of dielectric sensors and measurement instruments. Meas. Sci. Technol., 2007, 18:967-976.
8. Sciortino F, Geiger A and Stanley HE. Network defects and molecular mobility in liquid water. J. Chem. Phys., 1992, 96:3857-3865.
9. Sciortino F, Geiger A and Stanley HE. Effect of defects on molecular mobility in liquid water. Nature, 1991, 354:218-221.
10. Kaatze U, Behrends R and Pottel R. Hydrogen network fluctuations and dielectric spectrometry of liquids. J. Non-Cryst. Solids, 2002, 305:19-28.
11. Buchner R, Barthel J and Stauber J. The dielectric relaxation of water between 0°C and 35°C. Chem. Phys. Lett., 1999, 306:57-63.
12. Yada H, Nagai M and Tanaka K. Origin of the fast relaxation component of water and heavy water revealed by terahertz time domain attenuated total reflection spectroscopy. Chem. Phys. Lett., 2008, 464:166-170.
13. Ronne C, Astrand PO and Keiding SR. THz Spectroscopy of Liquid H₂O and D₂O. Phys. Rev. Lett., 199, 82:2888-2891.
14. Malenkov GG, Tytik DL and Zheligovskaya EA. Hydrogen bonds in computer-simulated water. J. Mol. Liq., 1999, 82:27-38.
15. Brubach JB, Mermet A, Filabozzi A, Gerschel A and Roy P. Signatures of the hydrogen bonding in the infrared bands of water. J. Chem. Phys., 2005, 122:184509-1-7.
16. Chumaevskii NA, Rodnikova MN and Sirotkin DA. Raman spectra of light and heavy water in the O-H and O-D stretching vibrations region. J. Mol. Liq., 1999, 82:39-46.
17. Zasetsky AY. Dielectric relaxation in liquid water: two fractions or two dynamics? Phys. Rev. Lett., 2011, 107:117601-1-5.
18. Fukasawa T, Sato T, Watanabe J, Hama Y, Kunz W and Buchner R. Relation between Dielectric and Low-Frequency Raman Spectra of Hydrogen-Bond Liquids. Phys. Rev. Lett., 2005, 95:197802-1-4.
19. Hansen JS, Kisliuk A, Sokolov AP and Gainaru C. Identification of Structural Relaxation in the Dielectric Response of Water. Phys. Rev. Lett., 2016, 116:237601-1-5.
20. Debye P. Polar Molecules. Chemical Catalog Co., New York, 1929.
21. Sciortino F, Geiger A and Stanley HE. Nature,
22. Agmon N. Liquid Water: From Symmetry Distortions to Diffusive Motion. Acc. Chem. Res., 2012, 45:63-73.

23. Podeszwa R and Buch V. Structure and dynamics of orientational defects in ice. Phys. Rev. Lett., 1999, 83:4870-4873.

24. Popov I, Puzenko A, Khamzin A, Feldman Y. The dynamic crossover in dielectric relaxation behavior of ice Ih. Phys. Chem. Chem. Phys., 2015, 17:1489-1497.

25. Popov I, Lunev I, Khamzin A, Greenbaum A, Gusev Y, Feldman Y. The low-temperature dynamic crossover in dielectric relaxation of ice Ih. Phys. Chem. Chem. Phys., 2017, 19:28610.

26. Khamzin AA, Nigmatullin RR. Multiple-trapping model of dielectric relaxation of the ice Ih. J. Chem. Phys., 2017, 147(20):204502.

27. Khamzin AA, Nasybullin AI. Trap-controlled proton hopping: interpretation of low-temperature dielectric relaxation of ice Ih. Phys. Chem. Chem. Phys., 2018, 20(35):23142-23150.

28. Christensen JH, Smith AJ, Reed RB and Elmore KL. Dielectric Properties of Phosphoric Acid Solutions at 25°C. J. Chem. Eng. Data, 1966, 11:60-63.

29. Laage D and Hynes JT. A molecular jump mechanism of water reorientation. Science, 2006, 311:832-835.

30. Popov I, Ben Ishai P, Khamzin A and Feldman Yu. The mechanism of the dielectric relaxation in water. Phys. Chem. Chem. Phys., 2016, 18:13941.

31. Khamzin AA, Popov II, Nigmatullin RR. Correction of the power law of ac conductivity in ion-conducting materials due to the electrode polarization effect. Phys. Rev. E, 2014, 89:032303-1-8.

32. Artemov VG. A unified mechanism for ice and water electrical conductivity from direct current to terahertz. Physical Chemistry Chemical Physics, 2019, 21(15):8067-8072.

33. Elton DS and Fernández-Serra M-V. Polar nanoregions in water: A study of the dielectric properties of TIP4P/2005, TIP4P/2005f and TTM3F. J. Chem. Phys., 2014, 140:124504.

34. Walrafen GE, Hokmabadi MS, Yang WH, Chu YC and Monosmith B. Collision-induced Raman scattering from water and aqueous solutions. J. Phys. Chem., 1989, 93:2909-2917.

35. Alexander S and Orbach R. Density of states on fractals: «fractons». J. Phys. Lett., 1982, 43:L625-L631.

36. Elton DC. The origin of the Debye relaxation in liquid water and fitting the high frequency excess response. Phys. Chem. Chem. Phys., 2017, 19:18739.

37. Lunkenheimer P, Emmert S, Gulich R, Köhler M, Wolf M, Schwab M and Loidl A. Electromagnetic-radiation absorption by water. Phys. Rev. E, 2017, 96:062607-1-10.

38. Lunkenheimer P and Loidl A. Dielectric spectroscopy of glassforming materials: α-relaxation and excess wing. Chem. Phys., 2002, 284:205-219.

39. Leheny RL and Nagel SR. High-frequency asymptotic shape of the primary relaxation in supercooled liquids. Europhys. Lett., 1997, 39:447-452.

40. Ngai KL. Interpretation of the GHz to THz dielectric relaxation dynamics of water in the framework of the Coupling Model. J. Mol. Liq., 2018, 253:113-118.

41. Capaccioli S, Paluch M, Prevosto D, Wang L-M, Ngai KL. Many-Body Nature of Relaxation Processes in Glass-Forming Systems. J. Phys. Chem. Lett., 2012, 3:735-743.