WATER AS A NANOSTRUCTURED MATERIAL

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Abstract

A nanostructured disordered ice *Ih* fraction in a water environment is theoretically investigated. The disordered ice fraction is taken into account as a nanocomposite consisting of a substance and a vacuum. The pattern of interaction between electrical charges considerably changes and thus leads to the formation of stable ice clusters that are consolidated by bound charges.

1. Introduction

Since ancient times, water has been one of the main resources of the mankind [1]. At the same time, the physical and biological properties of water should be the subject of further intensive scientific researches. There are a number of properties that are still poorly understood by modern science. Some of them refer to issues related to the existence of properties of "activated" water [2–5].

Paper [6] describes the method of obtaining nanostructured thin films based on vanadium. It was shown in [7] that these films exhibit specific physical and biophysical properties. Particularly, the effect of electrochemical transformation (activation) of distillated water during interaction with a thin nanostructured film (thickness of ~10 nm), which is a process similar to the contactless transformation of water in the high-frequency microwave range, was described [3].

Numerous experiments and theoretical investigations [4, 5] proved that water is not a homogeneous amorphous medium even in a standard environment. Together with the fraction which is usually identified as "ordinary water" H_2O, it contains a fraction which will be referred to as "liquid ice". At the microscopic level, it is similar to ice; however, it probably exhibits an amorphous disordered pattern (Figs. 8.7 in [4]).

We shall do our best to prove that, in liquid ice, the pattern of interaction between electric charges substantially changes; this effect leads to the existence of stable liquid ice clusters in the volume of ordinary water clusters having a special structure that is responsible for unusual physical and biophysical properties of the activated water containing these clusters.

The liquid ice medium in the form a system of structured elements of hydrogen and oxygen atoms dipped into a vacuum and arranged in a disordered amorphous system was considered. The average size of this element is a = 0.7 nm. Comparison of the thicknesses of ice

and water reveals that a portion of vacuum (intrinsic molar volume) in the liquid ice system is not smaller than $c \approx 0.09$. (916.7 vs. 999.8 kg/m^3 at $T = 0$°C). At the same time, in ordinary water, a portion of vacuum (c_W) can be assessed only indirectly on the basis of either theoretical or experimental data. For instance, it can be estimated on the magnitude of the parameter *b* from the van der Waals equation. However, these data are several times overvalued.

We believe that we should take into account the values of $c_W \approx 0.01 << c$ for water [8]. This estimate does not include the areas of empty spaces between the water molecules that cannot be reached by any experimental techniques. In our further evaluations, we consider that ordinary water, which incorporates these areas of empty spaces (unlike liquid ice), represents a nearly homogeneous medium.

In the conclusion of this section, we can note that all our last interpretations about space that cannot be reached by experimental techniques have respect only to physical particles of water (atoms). These conceptions involve electric fields for which the water volume is an ordinary nanocomposite of two dielectric media (vacuum and matter).

2. Results and discussion

2.1. Modified Coulomb law

We should take into account the space dispersion phenomenon in the systems including ice, while interpreting the processes involving electromagnetic waves [9]. In this section, we shall make use of a phenomenological approach based on the use of longitudinal dielectric function ε*(r)* of an inhomogeneous medium and try to make some conclusions on the basis of this approach. Equations (1)–(3) represent a reduced system of Maxwell's equations [10, 11] for an electric field that is constant in time and variable in space for a nonmagnetic medium with a spatial dispersion:

$$div(\vec{D}(\vec{r})) = \rho(\vec{r}), \tag{1}$$

$$rot(\vec{E}(\vec{r})) = 0, \tag{2}$$

$$\vec{D}(\vec{r}) = \varepsilon_0 \int d^3r' \varepsilon(\vec{r} - \vec{r}')\vec{E}(\vec{r}'), \tag{3}$$

where ρ(*r*) is the density of the external charges (free charges), $\vec{D}(\vec{r})$ is the induction, and $\vec{E}(\vec{r})$ is the electric field intensity. For simplicity, we shall assume that this description is appropriate if the characteristic length of the medium *L* is considered to be greater than or of the same order as structural elements $a \approx 0.7nm$. The longitudinal permittivity function is defined as

$$\varepsilon(\vec{r}) = \frac{1}{(2\pi)^{3/2}} \int d^3k \tilde{\varepsilon}(\vec{k}) \exp(i\vec{k}\vec{r}), \tag{4}$$

and the Fourier transform thereof is determined as follows:

$$\tilde{\varepsilon}(k) = (1/2\pi)^{3/2} \left[{\varepsilon_{eff}}^{-1} + \eta^{-1} k^2 / (k^2 - h^2) \right]^{-1}, \tag{5}$$

while regarding wave vector *h* of the ultrashort mode [12, 13] and dimensionless constants $\varepsilon_{eff} = \tilde{\varepsilon}(k \to 0)$ and η which depend on the type of the material as known magnitudes. The ultrashort modes can also be referred to as "dark modes" in accordance with the terminology used in [14].

With this choice of $\tilde{\varepsilon}(k)$ in (5), we must obey be the equality

$$\tilde{\varepsilon}(h_i) \equiv 0\,, \tag{6}$$

In fact, taking into account (2), we obtain the relationship

$$\vec{E}(\vec{r}) = -grad(\Phi(\vec{r}))\,, \tag{7}$$

which is afterwards substituted in (1). After having rewritten (1-3) in the form of (4) for Fourier transforms and on the basis of (5), we obtain

$$\varepsilon_0 \tilde{\Phi}(k) = \tilde{\rho}(k)\left[\varepsilon_{eff}{}^{-1}/k^2 + \eta^{-1}/(k^2 - h^2)\right]. \tag{8}$$

It follows from (8) that at $k = h$, a nontrivial solution for potential $\tilde{\varphi}(k) \neq 0$ of the electric field is possible even at zero values of $\tilde{\rho}(k) \equiv 0$ and this is a factual definition of ultra short mode *h*. The ε_{eff} magnitude can be determined employing the methods used in [15, 16]. As in our case, both components (the medium and the vacuum) penetrate the liquid ice medium without breaking down into isolated parts, we shall consider in our further estimations that

$$\varepsilon_{eff} = \varepsilon(1-c) + c\,, \tag{9}$$

where the magnitude of $\varepsilon \approx 90$ is almost equal to the relative dielectric constant of ice. The addition relationship

$$\eta^{-1} = \left[\varepsilon^{-1}(1-c) + c\right] - \varepsilon_{eff}^{-1} \tag{10}$$

makes it possible to obey the following condition: in the liquid ice medium, the Coulomb's law at utmost small distances, which are much smaller than the *a* magnitude, does not change in comparison with the ordinary ($G(r)_{r\to a} \to const/r$). Assuming that

$$\rho(\vec{r}) = \delta(\vec{r} - \vec{r}')\,, \tag{11}$$

we shall obtain the equation of the Green's function for system ($\delta(r)$–delta function). The Green's function for potential $G(\vec{r} - \vec{r}')$ is in fact an altered Coulomb law for the nanostructured medium

$$G(\vec{r} - \vec{r}') = \frac{1}{4\pi\varepsilon_0}\left[\frac{1}{\varepsilon_{eff}\,|\vec{r} - \vec{r}'|} + \frac{\cos(h\,|\vec{r} - \vec{r}'|)}{\eta\,|\vec{r} - \vec{r}'|}\right]. \tag{12}$$

To obtain the numerical value of *h*, it is necessary to carry out a separate investigation. The ordinary Coulomb law excludes the existence of mechanically stable states for any configurations and signs of electrical charges [17]. However, if the modified Coulomb law (12) is obeyed, a stable mechanical configuration is possible even for two classical particles regardless of the sign of their charges (see Fig. 1).

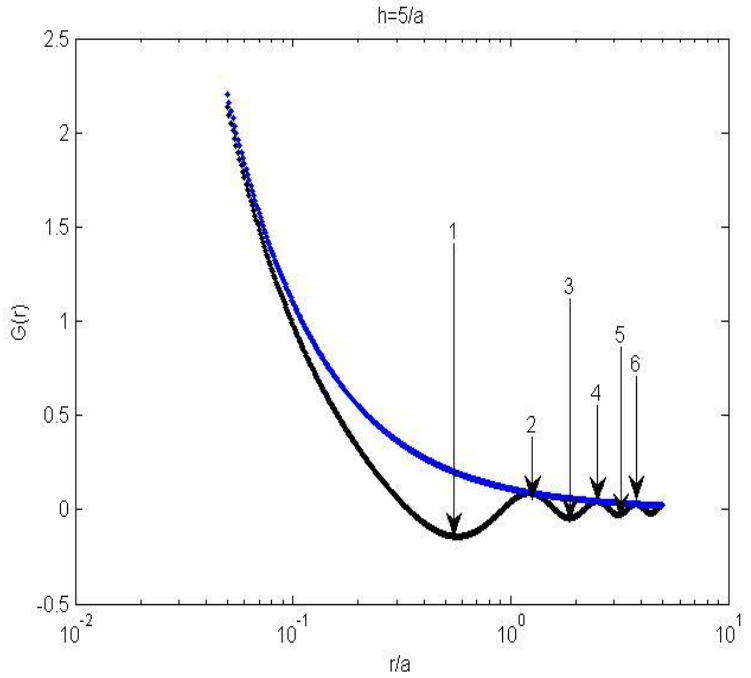


Fig. 1. Usual Coulomb law (blue) versus modified Coulomb law (black) for the potential of point charge. Arrows 1, 3, and 5 show equilibrium points for charges with the same sign. Arrows 2, 4, and 6 show equilibrium points for charges of different signs

The modified Coulomb law (12) consists of two components. They are independent of one another; each of the components makes a contribution in the formation of the general electric field

$$\Phi(\mathrm{r}) = \Phi^{(0)}(r) + \Phi^{(h)}(r)\,. \tag{13}$$

The first component is usual modes corresponding to solutions k≡0 from (8). An equation in coordinate representation can be written for this mode as follows:

$$\Delta\Phi^{(0)}(r) = 0\,. \tag{14}$$

The second component is “dark” modes with wave vector k=h≠0. Another equation can be written for these “dark” modes:

$$\Delta\Phi^{(h)}(r) + h^2\Phi^{(h)}(r) = 0\,. \tag{15}$$

At the same time, each mode has its own dielectric constant ($\varepsilon_{\mathrm{eff}}$, η).

2.2. Evaluation of the h magnitude

Let us try to estimate the *h* magnitude making use of the results of the study of bidimensional periodical structures [12, 13]. Ultrashort modes have a form of one-dimensional structure; therefore, we shall make use of the idea of “channeling.” The gist of the matter is that, in three-dimensional crystals, the channeling of radiation, which is a directed movement of radiation along certain directions in crystalline structures, takes place [18]. Actually, in a three-dimensional system, modes of smaller dimension appear. Thus, under certain conditions, a three-dimensional crystal may behave as a two-dimensional pore system with cylindrical "channels" (or pores) along which the channeling process takes place. The quantity of directions (channels) along which channeling takes place depends on the type of crystalline structure. We shall

estimate the h magnitude for three-dimensional spatial structures assuming that a three-dimensional ultra short mode can be represented in the form of an ultrashort (dark) mode of the type [12, 13]. Then the wave vector of the ultrashort mode can be evaluated making use of formula (22) from [12] where a portion of the vacuum is determined from formula $c = \pi R_{por}/a^2$. Now, the formula for c still has parameters which can be similarly applied both for the case of a bidimensional porous system from [12, 13] and for a three-dimensional porous structure, which is of particular interested to us. It is evident that the h magnitude changes within large limits as a portion of vacuum in the system c changes from 0 to 1. More precise numerical estimates can be done on the basis of graphs from [12, 13]. We can see that there are several branches with different numerical values. From (22) of [12], it is believed that

$$h \approx 5/a. \tag{16}$$

For other branches, $h >> 1/a$. Conditions for validity of the conception of medium homogeneity for dielectric materials, such as ice and water, are broken in this case for characteristic sizes $L = 2\pi/h$.

The ordinary water included regions of empty space $c_w \approx 0.01 << c$; according to (16), $h >> 1/a$ at $L << a$. Therefore, in further calculations, we believe that dark modes are absent in ordinary water in contrast to liquid ice.

2.3. Properties of the cluster

Taking into account a spherical cluster of radius R (volume $V = 4\pi R^3/3$) from liquid ice surrounded by ordinary water. A spherically symmetrical electrical field in liquid ice is described as (13). Usual boundary conditions should be resolved for the general solution including the modes of both types (13–15) in a cluster border.

Since the system as a whole is electrically neutral, the solution of equation (14) is trivial in ordinary water at $r > R$ and it is $\Phi(r) \equiv 0$.

The electric field configuration inside the neutral and spherically symmetric cluster of liquid ice at $r < R$ will be foliated and spherically symmetric with $\approx 2\pi/h$-thick layers; it will be given by formula

$$\Phi(r) = \Phi_0[1-(J_{0.5}(rh)\sqrt{R})/(J_{0.5}(Rh)\sqrt{r})], \tag{17}$$

where $R = x/h$ ($x = \pi(0.5+N) + 1/(\pi(0.5+N)) + O(1/N^2)$ is a nonzero root of the equation $d[J_{0.5}(x)/\sqrt{x}]/dx = 0$, $N = 1,2,3...$). For convenience, we shall write out the average intensity of the squared electrical field in the cluster with an accuracy up to members on the order of $1/hR$:

$$< \vec{E}^2 >= \overline{E}^2 = \frac{1}{V}\int_V d^3r(\nabla\Phi)^2 = 3(\Phi_0 h)^2\left[1+O\left(\frac{1}{hR}\right)\right]. \tag{18}$$

The numerical value of Φ_0 can be estimated on the basis of simple consideration. Ice is a solid matter that exhibits piezoelectric properties. Liquid ice can be considered as an ordinary ice that has undergone a strong inhomogeneous deformation; therefore, the coefficient of relative deformation is on the order of $\overline{\xi} = 0.02$. The deformation transforms ice into a disordered state and simultaneously generates an electrical field (18). Since this deformation is accompanied by electrification, an average value of electrical field is as follows:

$$\overline{E} = \overline{\xi}K/\varepsilon\varepsilon_0 \ , \tag{19}$$

where K is the piezoelectric coefficient [19]. From (18) and (19), we obtain that

$$\Phi_0 = \frac{\bar{\xi} K}{\sqrt{3} h \varepsilon \varepsilon_0} = 8 \cdot 10^{-4} V < k_B T / e \,. \tag{20}$$

where $K = 0.5$ C/m^2, $\varepsilon = 100$.

Equation (25) suggests that the depth of the potential well cluster is less than Boltzmann energy $k_B T$ and can serve as a small trap for ions of different types.

Let us consider the mechanical stability of liquid ice clusters under the influence of pressure exerted by ordinary water. The density of the electric energy of the cluster that restrains the external pressure of the surrounding ordinary water is

$$U_c = (\varepsilon_0 / 2V) \int_V d^3 r d^3 r' \vec{E}(\vec{r}) \varepsilon(\vec{r} - \vec{r}') \vec{E}(\vec{r}') \,. \tag{21}$$

We shall represent (5) in the form of two summands:

$$\tilde{\varepsilon}(k) = \tilde{\varepsilon}^{(1)} + \tilde{\varepsilon}^{(2)}(k) \,. \tag{22}$$

Then

$$U_c = U_c^{(1)} + U_c^{(2)} \,, \tag{23}$$

where

$$\tilde{\varepsilon}^{(1)} = \tilde{\varepsilon}(k \to \infty) = (1/2\pi)^{3/2} \left[\varepsilon_{eff}^{-1} + \eta^{-1} \right]^{-1} , \tag{24}$$

$$U_c^{(1)} = (2\pi)^{3/2} (\varepsilon_0 / 2V) \tilde{\varepsilon}^{(1)} \int_V d^3 r \vec{E}(\vec{r})^2 = (\varepsilon_0 / 2) \left[\varepsilon_{eff}^{-1} + \eta^{-1} \right]^{-1} (\Phi_0 h)^2 \left[1 + O(1/hR) \right] . \tag{25}$$

The second summand from (23) can be presented in the form of:

$$U_c^{(2)} = (\varepsilon_0 / 2V) \int d^3 k \, | \vec{\mathrm{H}}(\vec{k}) |^2 \, \tilde{\varepsilon}^{(2)}(\vec{k}) \,, \tag{26}$$

where

$$\begin{aligned} \tilde{\varepsilon}^{(2)}(k) &= \tilde{\varepsilon}(k) - \tilde{\varepsilon}(k \to \infty) = \\ &= (1/2\pi)^{3/2} \left[\varepsilon_{eff}^{-1} + \eta^{-1} \right]^{-1} \{ \left[\varepsilon_{eff}^{-1} + \eta^{-1} \right]^{-1} - 1 \} \frac{h^2}{k^2 - h^2 \left[\varepsilon_{eff}^{-1} + \eta^{-1} \right]^{-1}} \,, \end{aligned} \tag{27}$$

$$\begin{aligned} \vec{\mathrm{H}}(\vec{k}) &= \frac{1}{(2\pi)^{3/4}} \int_V d^3 r \exp(i\vec{k}\vec{r}) \nabla \Phi(\vec{r}) = \\ &= -2(2\pi)^{1/4} i\vec{k} \Phi_0 \left[\frac{\sin(kR)}{k^3} - \frac{\cos(kR)}{k^2} R \pm \frac{R}{2k \sin(hR)} \frac{\sin[(k \pm h)R]}{(k \pm h)} \right] . \end{aligned} \tag{28}$$

The dependence of electric energy density of the cluster on the radius and other parameters should be determined from formulas (21)–(28). It follows from (21)–(28) that, if the cluster radius is $R \approx 5a$, then

$$U_c / \varepsilon_0 (\Phi_0 h)^2 \approx -3 \cdot 10^2 \,. \tag{29}$$

We obtain from (25) that

$$| U_c | V \approx 3cpV \,, \tag{30}$$

where $p = 10^5$ Pa is the pressure of the ordinary water surrounding the cluster (1 atm at $T = 273$ K).

The right-hand side of (30) is equal to the work required for cluster elimination by squeezing external pressure. The left-hand side of Eq. (30) is equal to the potential electric energy of the cluster that provides its mechanical stability.

Thus, we can affirm that modified Coulomb law (12) provides the mechanical stability of the cluster due to electrical forces arisen between bounded charges. Estimates show that the resonance frequency of cluster vibrations can achieve the microwave frequency range [3].

3. Conclusions

The experimental and theoretical investigations suggest the following. Water can form stable nanoclusters of fraction *Ih* consolidated by bounded electric charges. Their existence can serve as the basis for the manifestation of unusual physical and biophysical properties of water.

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