Density dependence of dielectric permittivity of water and estimation of the electric field for the breakdown inception

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Abstract. Density dependence of the dielectric permittivity for water was obtained using the molecular dynamics method for the supercritical region at $T = 670 \text{ K}$ in a broad range of density, and for $T = 300 \text{ K}$ and $T = 350 \text{ K}$ near the coexistence curve. Critical values of the electric field strength which make possible the spinodal decay “liquid-vapor” were calculated.

1. Introduction
The body force acting on a dielectric liquid in electric field is given by the Helmholtz formula [1]

$$
F = -\frac{\varepsilon_0 E^2}{2} \nabla \varepsilon + \frac{\varepsilon_0}{2} \nabla \left[ E^2 \rho \left( \frac{\partial \varepsilon}{\partial \rho} \right)_T \right].
$$

(1)

A phase transition with appearance of liquid and vapor phases is possible in fluids which are initially in a homogeneous liquid or gaseous state if the density dependence of the dielectric permittivity is nonlinear. If a single-phase system was in a stable state near the coexistence curve, it could become unstable to density fluctuation with following decay to liquid and vapor phases when a sufficiently strong electric field ($\sim 10 \text{ MV/cm}$ and higher under usual conditions) is applied. The reason of such instability is the shift of the spinodal curve to higher temperature in electric field.

The influence of electric field on mixtures of dielectric liquids is similar [2]. It was shown for several liquids that the critical temperature of demixing is proportional to the quantity $E^2 \left( \frac{\partial^2 \varepsilon}{\partial \phi^2} \right)_T$, where $\phi$ is the concentration of one of the components. If the condition $(\partial^2 \varepsilon / \partial \phi^2)_T > 0$ is satisfied, the electric field leads to the decay of a homogeneous mixture into a two-phase system.

The critical value of the electric field $E_0$ which enables the decay of a dielectric liquid was determined from the equation of the spinodal obtained in the work [3]

$$
\left( \frac{\partial \tilde{P}}{\partial \tilde{\rho}} \right)_T = \frac{\varepsilon_0 E_0^2 \tilde{\rho}}{2P_{cr} \left( \frac{\partial^2 \varepsilon}{\partial \tilde{\rho}^2} \right)_T},
$$

(2)

Here, $\tilde{P} = P / P_{cr}$, $\tilde{\rho} = \rho / \rho_{cr}$, and $\tilde{T} = T / T_{cr}$ are the reduced variables, where $P_{cr}$, $\rho_{cr}$, and $T_{cr}$ are the critical pressure, density, and temperature. Thus, the occurrence of the spinodal decay is defined by the dimensionless parameter $A = \varepsilon_0 E^2/(2P_{cr})$. In the same work, it was shown that the instability increment is
proportional to the second density derivative of the dielectric permittivity. The decay to liquid and vapor phases is anisotropic [3, 4], bubbles in liquid (and droplets in vapor) have elongated form and they are oriented along the electric field. The possibility of the spinodal decay was demonstrated by the molecular dynamics method in the work [5]. Authors of the work [6] showed that the characteristic time of the spinodal decay without the hydrodynamic stage, the formation of a nucleus of the new phase takes \( \sim 10^{-9} \) s or less.

Thus, the anisotropic spinodal decay discovered theoretically in [3] can explain the very fast (time of order of nanoseconds) appearance of vapor channels in a liquid during the electric breakdown of liquids. The substance inside channels has the electric strength which is lower than the one of the liquid itself by an order of magnitude. This leads to the development of discharge in channels and to the formation of streamers. Such mechanism of the inception of streamer channels can explain easily many phenomena observed experimentally at the breakdown of dielectric liquids, namely the ultra-fast propagation of streamer channels (velocity over 100 km/s), nearly cylindrical shape of channel segments, their branching, and the appearance of a sheaf of nonluminous channels with decreased density near a tip with following breakdown in one of the channels [7].

In order to estimate the critical electric field strength necessary for an anisotropic decay, one needs to know the density dependence of permittivity at the constant temperature in a sufficiently broad range of density. Such measurements are extremely rare [8]. Therefore, the development of a method to calculate the dependence \( \varepsilon(\rho) \) for a given liquid is important. In this paper, the calculations of the dielectric permittivity of water for the temperatures \( T = 670 \) K (above the critical one), \( T = 350 \) K, and \( T = 300 \) K in a broad range of density were performed. Based on the dependences obtained, the critical electric field for the streamer inception was estimated.

**2. Calculation of dielectric permittivity of water by the molecular dynamics method**

The algorithm was developed for calculation of the static dielectric permittivity of water in a broad range of temperature and density. The algorithm includes following stages: generation of the ensemble of water molecules with the prescribed density, molecular dynamic simulation of the evolution of the ensemble at the fixed temperature, recording the data on the coordinates of electric charges of oxygen and hydrogen in
consequent time intervals, calculation of the dipole moment $\mathbf{M}$, calculation of time averaged fluctuations of the dipole moment squared. Molecular dynamic calculations were performed using the freely distributed package LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator) [9].

The SPC/E was used to describe the molecule of water. The symmetric intermolecular interaction is described by the Lennard-Jones potential centered on the oxygen atom (potential parameter is 0.65 kJ/mol, equilibrium distance is 0.3166 nm). For the description of the Coulomb interaction, the positive charges of 0.42e are placed in the centers of hydrogen atoms, and the negative charge of 0.84e is placed in the center of oxygen atom. In our calculations, the bond lengths O-H and H-H were fixed as well as the angle H-O-H. According to [10], the SPC/E model describes the coexistence curve of vapor and liquid for water at the temperatures of 300 K and higher essentially better than several other models (TIP4P, TIP5P, Dang-Chang).

The ensemble of water molecules was placed in a parallelepiped region. The ensemble of 5000 molecules was simulated for the temperatures $T = 670$ K and $T = 300$ K, for the temperature $T = 350$ K the ensembles of 5000 and 5400 molecules were simulated. The periodic boundary conditions were used. At the initial stage, the ensemble was thermalized for 50000 time steps. The calculations were performed for a $N\cdot V\cdot T$ ensemble. The calculations of the dielectric permittivity of the ensemble of water molecules converge slowly, therefore calculations were performed for long time intervals of 50 ns ($5\cdot10^6$ time steps) and 100 ns ($10^7$ time steps). Calculations were performed using the HP BL2x220c G7 and HP BL2x220c G6 computer clusters of the Information and Computation Center of the Novosibirsk State University [11].

The values of the dielectric permittivity were calculated similar to the method proposed in [12] using the formula

$$\varepsilon - 1 = \frac{4\pi}{3kT} \left( \langle \mathbf{M}^2 \rangle - \langle \mathbf{M} \rangle^2 \right).$$

A typical time sequence of 20000 values of the fluctuations of the reduced dipole moment squared $\left(\langle \mathbf{M} - \langle \mathbf{M} \rangle \rangle / \mu \right)^2$ is shown in figure 1. Here $\mu$ is the module of the dipole moment of the water molecule. This sequence was calculated for the ensemble of 5400 water molecules in time intervals of 5 fs.

3. Calculation results

The calculations of static dielectric permittivity of water were performed in a supercritical region for the

![Figure 2](image.png)

**Figure 2.** Density dependence of the permittivity of water $\varepsilon$ along the isotherm $T = 670$ K. Triangles – the experimental data [8], circles – calculation results.
temperature $T = 670$ K in the density range from 0.03 to 1.4 g/cm$^3$ (figure 2). The density dependence of the permittivity $\varepsilon(\rho)$ obtained (figure 2) can be approximated by the formula

$$\varepsilon = 1 + 11.25\rho + 14.05\rho^2 - 0.983\rho^3. \quad (4)$$

The positive sign of the second derivative $\varepsilon''(\rho)$ in the range of density considered leads to the possibility of an anisotropic spinodal decay under the action of sufficiently high electric field.

![Figure 3](image3.png)

**Figure 3.** Dielectric permittivity of water at 300 K. Triangles are the data [13]. Circles are the result of calculations for an ensemble of 5000 water molecules (simulation time was 50 ns).

The positive sign of the second derivative $\varepsilon''(\rho)$ in the range of density considered leads to the possibility of an anisotropic spinodal decay under the action of sufficiently high electric field.

![Figure 4](image4.png)

**Figure 4.** Dielectric permittivity of water at 350 K. The dashed line is an approximation of $\varepsilon(\rho)$ by a fourth-degree polynomial.

At low temperatures, no dependence $\varepsilon(\rho)$ was obtained so far which would allow one to calculate reliably the value of second derivative $\left(\frac{d^2\varepsilon}{d\rho^2}\right)$. The dependence obtained looks non-monotonous, the
values of $\epsilon(\rho)$ change irregularly from low to high densities (figure 3). Probably, the potential interaction energy at low temperatures is so high that the correlations of the states of neighbor water molecules appear. In this case, the duration of the time sequence can be insufficient to exclude such “memory” effects.

Therefore, simulations at higher temperature of 350 K were carried out for ensembles of 5000 and 5400 water molecules for time intervals of 50 and 100 ns (figure 4). The shape of the simulation region was also changed. The rectangular region with a square base and the aspect ratio from 2.5 to 3.2 was used as well as a
nearly cubic region. The results were fitted with the polynomial of the forth order shown with the dashed line in the figure 4.

4. Estimations of the critical electric field strength
Using the data on the density dependence of the dielectric permittivity of water $\varepsilon(\rho)$, the calculation were performed of the critical electric field strength which enables the spinodal decay of the dielectric liquid. The critical fields for the supercritical region at $T = 1.035 T_{cr}$ (670 K) and the values of the reduced density from 0.1 to 3 are shown in figure 5. For the temperature $T = 0.541 T_{cr}$ (350 K), the critical fields are shown in figure 6. The real equation of state from [14] was used.

5. Conclusion
The density dependence of the dielectric permittivity for water was obtained using the molecular dynamics method for $T = 1.035 T_{cr}$ in a broad range of density, and for $T = 0.464 T_{cr}$ and $T = 0.541 T_{cr}$ near the coexistence curve. The critical values of the electric field strength were calculated which make possible the spinodal decay “liquid-vapor”. The results obtained are in agreement with the estimations of the electric field strength of the electric discharge inception based on the experimental data.

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