

## Critical Electric-Field Strength for Anisotropic Spinodal Decomposition of Water

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**Abstract**—Threshold values of an electric field for anisotropic spinodal decomposition of water in a supercritical region at  $T = 670$  K and at a low temperature of about 350 K have been calculated. This threshold depends on the second derivative of the dielectric permittivity with respect to density. The dependence of the permittivity of medium on its density was determined by studying fluctuations of the polarization vector in a broad range of densities at the given temperatures. Time series of fluctuations of the polarization vector of ensembles of water molecules were constructed by the method of molecular dynamics.

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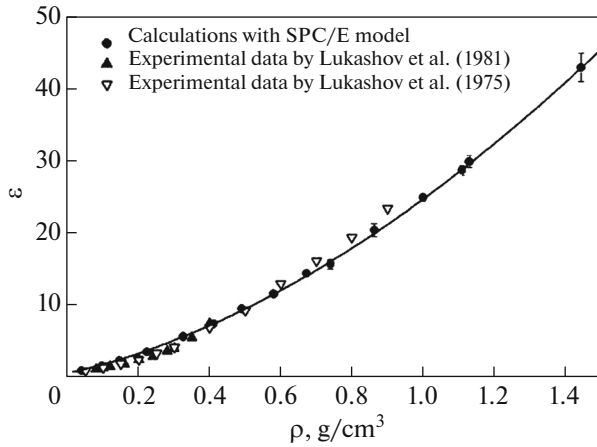
Under the action of an extremely strong electric field, the thermodynamic state of a dielectric fluid (dense gas) may become unstable, which results in a phase transition with the formation of a gas phase in the liquid (or liquid in the vapor). It has been established [1] that a shift of the temperature and pressure of the critical point of a dielectric fluid in an electric field is proportional to the square of the electric field and the second derivative of the permittivity of medium with respect to its density. In addition, the entire spinodal exhibits a shift, which implies that stable states situated close to a binodal can fall into the region of metastable states or even in a region of instability. Previously, we have demonstrated [2] that the decay into liquid and gas phases in a strong electric field has an anisotropic character, whereby elongated vapor channels oriented along the field lines are formed in the liquid. The increment of instability was calculated, which turned out to depend on the second derivative of the permittivity of medium with respect to its density. This phenomenon can explain, in particular, how the electric breakdown of a dielectric liquid can lead within very short time ( $\sim 1$  ns) to the formation and ultrafast propagation of streamers in which the density of substance is several orders of magnitude lower than that of the liquid phase. Accordingly, the electric strength of the substance in these channels is several orders of magnitude lower than that of the liquid, which leads to the development of partial discharges and formation of streamers in the dielectric liquid.

To estimate the minimum critical field in which the anisotropic decomposition takes place, it is necessary

to know the dielectric permittivity of the substance as a function of its density,  $\epsilon(\rho)$ , in a rather broad range at a constant temperature. Very few measurements of this dependence are available in the literature (see, e.g., review [3]). The present work was aimed at (i) finding  $\epsilon(\rho)$  based on the microscopic description of an ensemble of model water molecules and (ii) determining critical electric fields for the anisotropic spinodal decomposition of water [1]. For this purpose, the permittivity of water have been calculated at a supercritical temperature of  $T = 670$  K and at two values of temperature below critical,  $T = 350$  and  $300$  K.

The permittivity of water was calculated based on the analysis of fluctuations of the polarization vector [4]. The values of polarization vector at various moments of time were determined from simulations of the evolution of ensembles of  $\sim 5000$  water molecules by the method of molecular dynamics (MD) using LAMMPS program package [5]. The initial state of the ensemble of water molecules was generated with the aid of Moltemplate software [6]. MD simulations were performed for  $N-V-T$  ensemble under boundary conditions of mirror reflection upon preliminary thermalization. Model calculations were carried out on the cluster of the Information-Computation Center at Novosibirsk State University [7], which significantly reduced the time of calculations.

The properties of water were described using SPC/E molecule model [8]. Electrostatic interactions were taken into account by placing three point electric charges at the centers of hydrogen and oxygen atoms,  $-0.84$  elementary units (EU) for oxygen and  $+0.42$  EU for hydrogen. The distance between hydrogen and



**Fig. 1.** Plot of permittivity  $\epsilon$  vs. density  $\rho$  of water on the isotherm  $T = 670$  K: (circles) results of calculations; (curve) approximation by Eq. (1); (triangles) experimental data of Lukashov et al. (taken from review [3]).

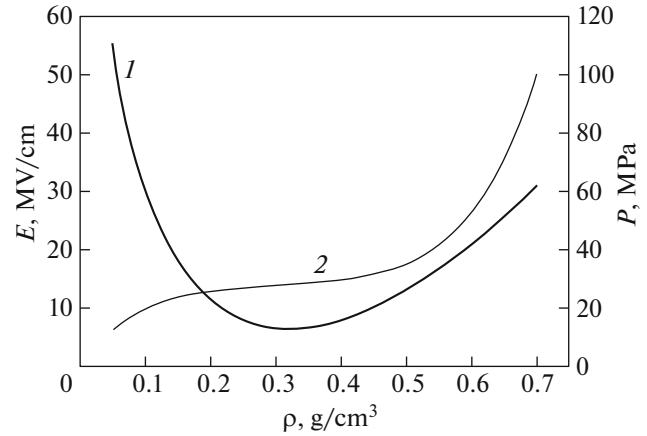
oxygen atoms was fixed at 0.1 nm, and the angle between O–H bonds was fixed at  $109.47^\circ$ . According to [9], this model most adequately describes the curves of liquid–vapor coexistence at a temperature of 300 K and above in comparison to other models (TIP4P, TIP5P, Dang–Chang). This circumstance is substantial for descriptions of the evolution of two-phase media and phase transitions.

The current states of all water molecules in the ensemble were recorded at equal time intervals corresponding to a physical time of 5 ps. Then, the current value of the dipole moment of the ensemble was determined for the corresponding distribution of electric charges. The obtained time series were used to calculate the permittivity of water by the following formula [4]:

$$\epsilon = 1 + \frac{\langle \langle \mathbf{M}^2 \rangle \rangle - \langle \mathbf{M} \rangle^2}{3\epsilon_0 V k T},$$

where  $\mathbf{M}$  is the dipole moment of the ensemble,  $V$  is the ensemble volume,  $T$  is the absolute temperature,  $k$  is the Boltzmann constant, and  $\epsilon_0$  is the dielectric constant.

Calculations of the permittivity of water were performed for its densities ranging from 0.039 to 1.44 g/cm<sup>3</sup> at  $T = 670$  K. This temperature falls in the supercritical domain on the phase diagram (the critical point corresponds to 647 K), which allowed  $\epsilon$  values to be determined in a very broad range of densities for the region of parameters containing no phase transitions. As is known,  $\epsilon$  variations slowly decrease with increasing number of elements in the time series of  $\mathbf{M}$ . For this reason, data were accumulated for large periods of time ( $\sim 10$  ns), while the states of molecular ensemble were recorded every 5 ps. The obtained values of permittivity at  $T = 670$  K well agree with the experimental data [3] (Fig. 1).



**Fig. 2.** Plots of (1) critical field  $E$  vs. density  $\rho$  for anisotropic spinodal decomposition of water and (2) isotherm of pressure at  $T = 670$  K.

Approximate dependences of permittivity  $\epsilon$  on the density of water at  $T = 670$  K were constructed for  $\rho$  values varying from 0.039 to 1.44 g/cm<sup>3</sup>. The  $\epsilon(\rho)$  curve in this interval is well approximated by the following relation:

$$\epsilon = 1 + 11.25\rho + 14.05\rho^2 - 0.98\rho^3, \quad (1)$$

where the density is expressed in units of g/cm<sup>3</sup>.

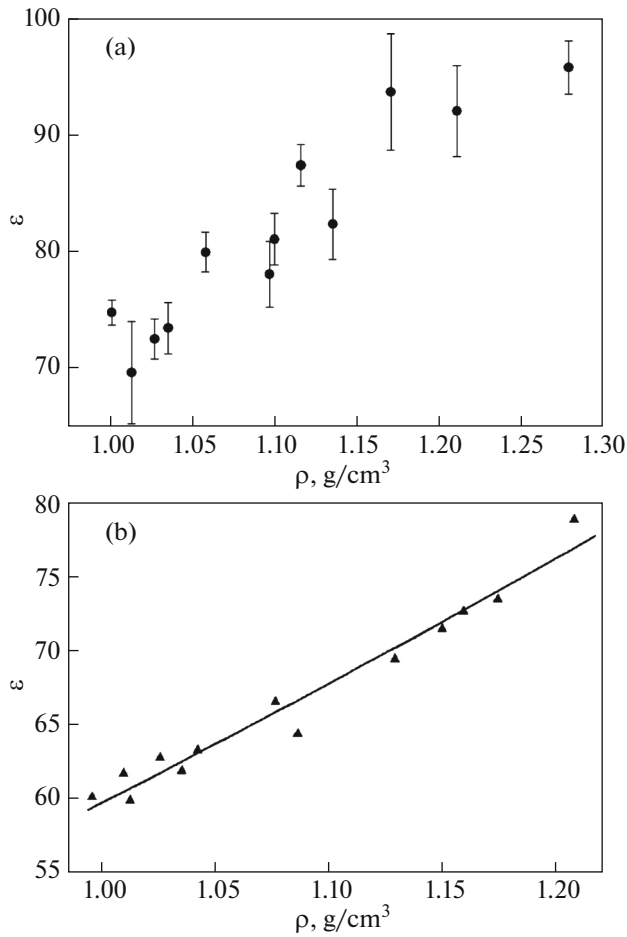
The critical value of an electric field for the anisotropic spinodal decomposition (field-initiated breakdown) of water can be calculated from the following relation [2]:

$$\left( \frac{\partial p}{\partial \rho} \right)_T = \frac{\epsilon_0 E_0^2 \rho}{2} \left( \frac{\partial^2 \epsilon}{\partial \rho^2} \right)_T.$$

The values of derivative  $(\partial p / \partial \rho)_T$  were determined using a real equation of state for water according to the IAPWS Industrial Formulation 1997 for the Thermodynamic Properties of Water and Steam [10]. The obtained estimations of critical field  $E_0$  for the anisotropic spinodal decomposition are presented in Fig. 2 (curve 1); curve 2 in this figure shows the pressure isotherm at  $T = 670$  K along which the  $E_0$  values were calculated.

At relatively low temperatures ( $T = 300$  and  $350$  K), the calculated values of permittivity exhibited significant scattering (Fig. 3a), which hindered obtaining a sufficiently smooth  $\epsilon(\rho)$  curve. At  $T = 350$  K, this difficulty was partly surmounted by increasing the calculation time to  $\sim 20$  ns. Figure 3b (triangles) presents the results of  $\epsilon(\rho)$  calculations at  $T = 350$  K for the model of water molecule with fixed O–H bond lengths. These data are well approximated by the following relation (Fig. 3, solid curve):

$$\epsilon = 1 + 31.36\rho + 22.54\rho^2, \quad (2)$$



**Fig. 3.** Plots of permittivity  $\epsilon$  vs. density  $\rho$  of water at sub-critical temperatures of (a)  $T = 300$  K and (b)  $T = 350$  K; the curve shows approximation of the calculated data (triangles) by Eq. (2).

where the density is expressed in units of  $\text{g}/\text{cm}^3$ . At this temperature, the critical field for water with a density of  $1 \text{ g}/\text{cm}^3$  is  $E = 23.9 \text{ MV}/\text{cm}$ . This value is close to estimations of the threshold field of pulsed electric

discharge initiation in water according to well-known experimental data.

In concluding, we have established dependences of the permittivity of water on its density at various temperatures and calculated the critical values of field strength necessary for the anisotropic spinodal decomposition of water, which makes it possible to estimate the electric strength of pure water.

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