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Anisotropic Spinodal Decomposition of a Polar Dielectric in a Strong Electric Field: Molecular Dynamics Simulation

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Abstract—The evolution of a one-component, initially single-phase, dielectric medium that represents a two-dimensional system of dipole molecules has been studied by the molecular dynamics method after the application of a uniform electric field. It is shown that the initially homogeneous medium under the action of the applied field can separate into two phases, liquid and gaseous. In the two-dimensional model system, these phases appear as bands extended along the field direction.

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As is known, substances characterized by a nonlinear dependence of the permittivity on the density exhibit a change in the critical temperature under the action of an applied electric field [1]. In the presence of a field, the equation of spinodal takes the following form [2, 3]:

$$\left(\frac{\partial P}{\partial \rho}\right)_T = \frac{E^2\rho}{8\pi}\left(\frac{\partial^2 \varepsilon}{\partial \rho^2}\right)_T, \qquad (1)$$

where P is the pressure, ρ is the density, ε is the permittivity, and E is the local electric field strength in the medium. It follows from Eq. (1) that a single-phase system in the stable state near the curve of coexisting phases can loose the stability with respect to density perturbations and separate into liquid and vapor phases upon the application of a sufficiently strong electric field.

An analogous phenomenon of phase separation in the electric field was observed in binary mixtures of liquid dielectrics. In a uniform field, the mixtures of some liquids separate into components provided that $E^2(\partial^2\varepsilon/\partial\phi^2)_T > 0$, where ϕ is the fraction of one of the system components [4]. In nonuniform fields, experiments showed evidence for the separation of components according to a different mechanism, according to which a dielectric with greater ε was pulled into the region of stronger field [5].

Using the thermodynamic methods, Vorob'ev et al. [6] showed that the electric field must influence the dimensions of nuclei of a new phase representing liquid drops in a supersaturated vapor and vapor bubbles in an overheated liquid. However, the analysis in [6] was restricted to spherically symmetric nuclei of the new phase, although this assumption is not always valid.

Previously, electrohydrodynamic flows in liquid dielectrics were simulated [2, 3] using the method of lattice Boltzmann equations. It was established that an anisotropic spinodal decomposition could take place in extremely strong electric fields (E ~ 10–100 MV/cm), where a vapor phase in the liquid separates in the form of channels extended along the electric field, and it was suggested [2, 3] that the anisotropic spinodal decomposition is probably the main mechanism of the formation of primary channels of fast streamers in initially homogeneous liquid.

Within the framework of a model of continuous medium, the interphase boundary is either considered as a negligibly thin surface or smeared within several periods of the computational lattice (in numerical methods). In the latter case, the boundary thickness is significantly greater than that of a physically thin interfacial layer. For this reason, the phase transition kinetics cannot be studied in detail. At the same time, it is the interphase boundary that plays a decisive role in the initial stages of phase transitions. In this context, the most adequate approach consists in simulating processes in a condensed medium by the method of molecular dynamics (MD) [7, 8].

In the present investigation, the MD method was applied to an ensemble of dipole molecules in an electric field. The aim was to study the evolution of this one-component, initially single-phase dielectric medium, and trace its separation into phases after application of an extremely strong electric field. The molecules were modeled by round particles bearing $+q$ and $-q$ charges,

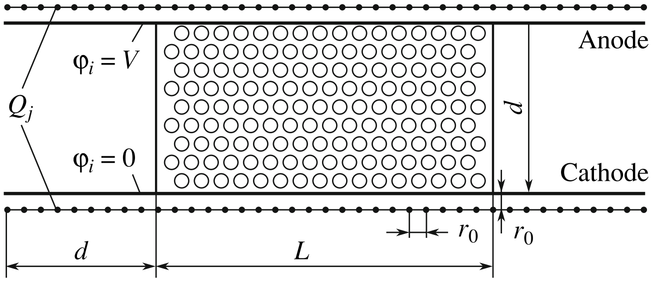

Fig. 1. Schematic diagram showing the geometry of electrodes, the MD domain, and the arrangement of effective charges Q_j (see text for explanations).

which were fixed symmetrically with respect to the center. In order to simplify calculations, the MD simulation was performed for a two-dimensional (2D) model. The pair interaction between particles was described by the Lennard-Jones potential as

$$U_S = 4e_0\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right], \tag{2}$$

where e_0 and $\sigma = 1.782r_0$ are the parameters, and r_0 is the characteristic radius of molecules, which amounts to half of the distance corresponding to the minimum of potential (2). The moment of inertia of a molecule was defined as $I = mr_0^2/2$, where m is the molecular mass, and the distance between charges in the molecule was assumed to be r_0.

The kinetic energy of each molecule consists of the energy of translational (E_T) and rotational (E_R) motions. The total potential energy can be written as follows:

$$U = U_S + U_D + U_E + U_B, \tag{3}$$

where U_S is the potential energy (2) that describes the symmetric part of the intermolecular interaction, U_D is the potential energy of the electric interaction related to the presence of a constant dipole moment in each molecule, U_E is the potential energy of a dipole in the electric field of electrodes, and $U_B = \kappa/r^{12}$ is the repulsive potential that ensures the elastic reflection of molecules from walls of the MD simulation domain.

It was also assumed that the intrinsic dipole moment of molecules is much greater than the induced moment, so that the additional polarization of molecules under the action of the applied electric field was ignored. Then, assuming that the potential energy of interaction $U_{\alpha\beta}$ between one of the charges (q_α) of dipole A and one of the charges (q_β) of dipole B is equal to zero when the distance between these dipoles is r_0, we obtain the following expression:

$$U_{\alpha\beta} = 2q_\alpha q_\beta(\ln r_{\alpha\beta} - \ln r_0). \tag{4}$$

In a 2D model, the potential energy of the electric interaction of two identical dipole molecules is as follows:

$$\begin{aligned} U_D &= U_{++} + U_{+-} + U_{-+} + U_{--} \\ &= 2q^2[\ln(r_{++}) - \ln(r_{+-}) - \ln(r_{-+}) + \ln(r_{--})]. \end{aligned} \tag{5}$$

In order to determine the moments acting upon a molecule, the electric forces were calculated for each pair of charges as $\mathbf{F}_{\alpha\beta} = -\nabla U_{\alpha\beta}$. The total moment $\mathbf{M}$ of all forces acting upon a given molecule was calculated with respect to the center of this molecule and with allowance for the charges on electrodes (external field). The positions $\mathbf{r}_i$, velocities $\mathbf{v}_i$, rotation angles φ_i, and angular velocities $\boldsymbol{\omega}_i$ of all molecules at each temporal step were calculated using the Verlet algorithm in a velocity form. The temporal step was constant for each calculation and selected so as to ensure total energy conservation over the entire calculation at a relative error below 10^{-3}.

The evolution of the ensemble of dipole molecules was simulated in a uniform electric field between two parallel electrodes (Fig. 1). The MD simulation domain represented a band of width d and length L confined between the upper (anode) and lower (cathode) electrodes. The electrostatic forces were calculated using the boundary element method [9, 10], according to which the surface distribution of electric charges on the electrodes is replaced by a certain distribution of effective charges immediately behind the boundaries of the MD domain, such that the field profile is approximated with a sufficiently good accuracy. It should be noted that these effective charges are not images of any real charges present in the MD domain. The electric field at any point in the computational domain at every moment of time represented a superposition of the total field of molecular charges and the field of effective charges replacing the electrodes.

In the present study, K effective point charges Q_j were arranged at a step of r_0 along two lines behind the anode and cathode, at a distance of r_0 from each electrode (Fig. 1). With this arrangement the electric field in the MD domain was uniform and the electrode surfaces were equipotential with a good precision. The values Q_j of the effective point charges were calculated so as to ensure that the potential at a finite number of reference points on the electrode surfaces was $\varphi_i = 0$ for the cathode and $\varphi_i = V$ for the anode. These reference points were situated on both electrodes at a constant step of r_0. For the given 2D model, the total potential φ_i created at the ith point of an electrode by the fields of $2N$ charges q_j of all molecules and K effective point charges Q_j, which are situated at distances $\tilde{r}_{ij}$ and r_{ij}, respectively, from this point, is as follows:

$$\varphi_i = \sum_{j=1}^{K} 2\ln(r_{ij})Q_j + \sum_{j=1}^{2N} 2\ln(\tilde{r}_{ij})q_j. \tag{6}$$

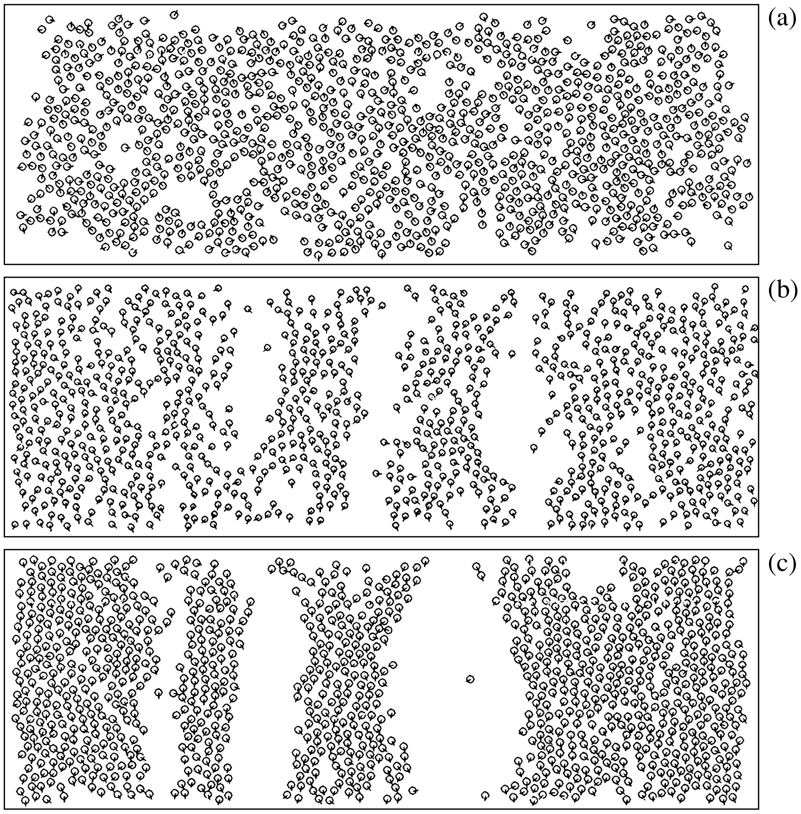

Fig. 2. Typical configurations of molecules in the space between electrodes (a) in the absence of an applied electric field at $T = 0.7$ and (b, c) in the state of an anisotropic phase separation caused by a strong electric field ($V = 30$) at $T = 0.7$ ($t = 70\,777$) and $T = 0.5$ ($t = 118\,360$), respectively.

For the existence of a unique solution of the system of equations (6) with respect to unknown charges Q_j, the number of reference points on the electrodes must be equal to the number K of effective charges. In the absence of a substance in the interelectrode gap, the field there is uniform. In this case, the relative error of calculations of the field in the central cross section of the MD domain was below 3×10^{-5}, while that at the domain ends was below 1%.

The lengths, masses, and energies were measured in the units of r_0, m and e_0. The MD simulations were performed in a region with dimensions 141×50, which contained $N = 1080$ molecules. Initially, the system was allowed to relax to the state of thermodynamic equilibrium for ~20000 temporal steps. As a result, the energies of translational and rotational motions acquired their mean values $\langle E_T \rangle$ and $\langle E_R \rangle$, respectively, such that $\langle E_T \rangle = 2\langle E_R \rangle$, in agreement with the number of degrees of freedom in the 2D case under consideration. The distribution of molecules with respect to their velocities became approximately Maxwellian with the corresponding dimensionless temperature T.

Figure 2a shows the typical configuration of molecules in the MD domain prior to the application of the electric field. According to estimations, the maximum heating of a dielectric due to the work performed by the electric field on changing the average dipole orientation (electrocaloric effect) during a nanosecond pulsed breakdown can reach several dozen kelvins, so that the temperature remains below critical. Then, it was assumed that the heating of the medium caused by the electric field switch-on took place and the subsequent simulation was carried out for the isothermal case.

At a relatively high temperature of $T = 0.7$, the initial equilibrium state corresponded to a dense gas (Fig. 2a). Under the action of the applied electric field, the dipole molecules acquired predominant orientation along the field lines. The dipole–dipole interaction led both to the formation of molecular chains extended along the field and to the aggregation of dipoles and their chains in the direction perpendicular to the field (Fig. 2b). As a result, regions of densification (liquid phase) separated by relatively rarefied spaces (vapor phase) appeared in the MD domain. With time, some regions of reduced density disappeared and new breaks appeared in some regions of high density. This dynamics is probably explained by the propagation of rarefaction and compression waves in the medium, which are formed under the action of electric forces. At a relatively low temperature of $T = 0.5$, where the initial state corresponded to a liquid, the effect of anisotropic phase separation was more clearly manifested (Fig. 2c). In this case, vapor channels appeared in the liquid phase in agreement with the results obtained previously [2, 3].

Evidently, the results of simulations in the 2D model system will also be qualitatively valid in the 3D case. It is of interest to compare the field strengths for which the phase separation was observed in the model system to the real local fields at which the breakdown of liquid dielectrics takes place. At $T = 0.7$, the minimum field strength between the electrodes, at which an anisotropic phase separation took place in our simulations corresponded to $\tilde{E} = Er_0/2q = 0.062$ (in dimensionless units of the 2D model). In experiments on a pulsed electric breakdown, local breakdown occurred at the values of the local electric field strength of $E = 20$ MV/cm [11], which corresponds to a dimensionless field strength of $\tilde{E} = El^3/p \sim 0.04$ for particles with a dipole moment of the molecule of water vapor $p = 6.1 \times 10^{-30}$ C m and a characteristic distance of $l = 10^{-10}$ m between charges. Thus, there is a quite satisfactory agreement between MD simulations and experiment, especially if we take into account the approximate character of the 2D model employed.

In conclusion, simulations using the MD method showed that, at a sufficiently high strength of the applied electric field, a homogeneous dielectric medium actually separates under the action of electric forces into an anisotropic two-phase system of vapor channels in a liquid phase or liquid filaments in a vapor phase.

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