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Peculiarities of first-order phase transitions in the presence of an electric field

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In this study, we developed a variational approach for thermodynamic systems with nondistributed parameters in the presence of the external electrostatic field. Using the obtained general relations, we analyzed some characteristic features of the first-order phase transitions in the presence of electric field. We determined the range of the thermodynamic parameters where both phases are stable (hysteresis), and the range of the parameters whereby both phases are metastable. In the range where both phases are metastable, we considered kinetics of formation of a new phase and determined the dependencies of the concentrations of phases in the region of their metastability on the amplitude of the external electric field. The obtained results imply the feasibility to control phase composition in the system by varying the amplitude of the external electrostatic field.

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I. INTRODUCTION

Effect of the external electric field upon the dynamics of phase transitions and chemical reactions is of interest both from a purely theoretical point of view and in view of various technological applications (see, e.g., Ref. [1], and references therein). In contrast to a field theory [2], the electrodynamics of continuous media is a system of phenomenological approaches [3–5]. In spite of the variety of approaches suggested in the literature, the approach based upon the variational principal is one of the most consistent. In Ref. [6], we employed this approach for the analysis of the first-order phase transitions in the presence of electric field, which are accompanied by formation of the nuclei with decreasing sizes. In this study, we generalized this approach to account for the dependence of the system response to the external electric field upon the entropy of the system.

Another problem, which is considered in this investigation, is kinetics of phase formation in the domain where both phases are metastable. Although the existence of this domain was established before (see Refs. [7,8]), variation of concentrations of phases with time was not addressed before. Solution of the latter problem allowed us to determine the dependence of the equilibrium concentration of phases upon the amplitude of the external electric field. Thus, we demonstrated the feasibility to change concentrations of phases in the system by varying the amplitude of the external electric field.

This paper is organized as follows. In Sec. II, we described a variational approach for the description of thermodynamic system with nondistributed parameters. In Sec. III using the general relations obtained in Sec. II, we analyzed some characteristic features of the first-order phase transitions in the presence of electric field. Here, we determined the range of temperatures and pressures whereby both phases are metastable, considered the kinetics of formation of a new phase in this range of temperatures and pressures, and determined the dependencies of concentrations of phases in the region of their simultaneous metastability on the amplitude of the applied electric field.

II. CONDITIONS FOR PHASE EQUILIBRIUM IN THE PRESENCE OF EXTERNAL FIELD

Consider a system consisting of K components which are characterized by a set of parameters $\{N_i, v_i, s_i\}$, where N_i is a number of particles, v_i is a specific volume, and s_i is a specific entropy per one particle. The equation of state of the ith component reads $\varepsilon_i = \varepsilon_i^0(v_i, s_i)$, where ε_i is the energy of a component i per one particle. Energy associated with an external loading per unit volume is denoted by $\overline{\varepsilon_L}$. In the framework of a thermodynamic approach, energy of the system in the presence of the external loading can be written as follows:

$$E = \sum_{i=1}^{K} N_i[\varepsilon_i^0(v_i, s_i) + v_i \overline{\varepsilon_L}(\{v_i\}, \{s_i\}, \{\lambda\})], \tag{1}$$

where $\{\lambda\}$ is a set of parameters that characterize the external loading.

Let us assume that the energy of the system is minimum at a given magnitude of the total entropy

$$S = \sum_{i=1}^{K} s_i N_i .$$

The latter requirement is equivalent to the minimization of a function $F = E - TS$. The multiplier T is determined from a given total entropy and it is equal to the temperature of the system. A condition for extremum

$$\left.\frac{\partial F}{\partial s_i}\right|_{N_1, v_i, s_{j\neq i}} = 0 \tag{2}$$

yields a system of K equations

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$$N_i\left[\left(\frac{\partial \varepsilon_i^0}{\partial s_i}+v_i\frac{\partial \overline{\varepsilon_L}}{\partial s_i}\right)-T\right]=0,\quad i=1,\ldots,K. \tag{3}$$

Since N_i in Eq. (3) is arbitrary, the expression in square brackets must vanish. Thus, one arrives at K equations that determine the values of entropies s_i as functions of parameters $\{v_i\},T,\{\lambda\}$.

Because of the principle of additivity, i.e., assumption that energy associated with the external loading appears as an additional term in the expression for the total energy E (see, e.g., Ref. [3]), the exact solution of Eq. (3) exceeds the thermodynamic accuracy. Indeed, let $s_i=s_i(v,T,\overline{\varepsilon_L})$ be the exact solution of Eq. (3). Since s_i depends on $\overline{\varepsilon_L}$ nonlinearly, a function $F(\{v_i\},T,\overline{\varepsilon_L})$ is also a nonlinear function with respect to the external loading. In order to preserve an additivity principle in all thermodynamic representations, it is necessary to neglect nonlinear terms with respect to the external loading. However, in order to simplify notations, hereafter we use a general expression while the nonlinear terms with respect to the external loading are neglected only in the final formulas.

Equation (3) is solved by iterations with respect to the external loading $\overline{\varepsilon_L}$. Let $s_i^0(v,T)$ be an equation of state for the entropy of the ith component, and $s_i=s_i^0(v_i,T)$ is a solution of Eq. (3) for $\overline{\varepsilon_L}=0$. After substituting this value of $s_i=s_i^0(v_i,T)$ into the term associated with the external loading, Eq. (3) yields

$$T(s_i,\sigma_i)+T_i^L=T, \tag{4}$$

where $T_i^L=v_i\,\partial\overline{\varepsilon_L}/\partial s_i|_{s_i=s_i^0(v_i,T)}$ and $T(s_i,v_i)$ is a state function, $T(s_i,v_i)=\partial\varepsilon_i^0(s_i,v_i)/\partial s_i$. Thus, if $s_i=s_i^0(v_i,T)$ is a solution of Eq. (3) for $\overline{\varepsilon_L}=0$, then a new solution of Eqs. (3) and (4) can be written as follows:

$$s_i^1=s_i^0(v_i,T-T_i^L). \tag{5}$$

Only the first term in the expansion of formula (5) in power series of parameter T_i^L has a physical meaning in the framework of thermodynamic accuracy:

$$s_i^1=s_i^0(v_i,T)-\frac{c_i}{T}T_i^L, \tag{6}$$

where $c_i/T=\partial s_i^0/\partial T$. Note that Eq. (4) describes the electrocalorific effect (see, e.g., Ref. [3]), Chap. 2, Sec. 12). Substituting the values s_i^1 given by Eq. (5) into expression for the function $F=E-TS$ yields

$$F=\sum_{i=1}^{K}N_i[\varepsilon_i^0(v_i,s_i^0(v_i,T-T_i^L))+v_i\overline{\varepsilon_L}(v_i,s_i^0(v_i,T),\{\lambda\})$$
$$-Ts_i^0(v_i,T-T_i^L)].$$

Since in the final formulas we retain only the first iteration with respect to the external loading, in the second term of the latter expression we substituted as an argument $s_i=s_i^0(v_i,T)$.

In the framework of thermodynamic accuracy, this expression can be rewritten as

$$F=\sum_{i=1}^{K}N_i[f_i^0(v_i,T-T_i^L)+f_i^L]. \tag{7}$$

Here, $f_i^0(v_i,T)$ is a free energy of an unloaded system per one particle:

$$f_i^0(v_i,\tilde{T})=\varepsilon_i^0(s_i(v_i,\tilde{T}),\tilde{T})-\tilde{T}s_i^0(v_i,\tilde{T}),\quad \tilde{T}=T-T_i^L, \tag{8}$$

and

$$f_i^L(v_i,T)=v_i\overline{\varepsilon_L}-T_i^Ls_i^0(v_i,T). \tag{9}$$

Equation (7) describes the effect of renormalization of temperature in the presence of electric field. The effective temperature of a subsystem (component i) differs from the temperature of the thermostat. This effect is similar to the effect described in Ref. [3] whereby a thermodynamic pressure in a subsystem in the presence of the external loading (e.g., electric field) is different from the external pressure.

Let us require now that the total energy of the system is minimum for a given volume of the system $V=\Sigma_{i=1}^{K}v_iN_i$. The latter requirement can be written using a function $\Phi=F+pV$, where p is a Lagrange multiplier. A condition $\partial\Phi/\partial V=0$ yields a system of K equations

$$N_i\left[\left(\frac{\partial f_i^0}{\partial v_i}+\frac{\partial f_i^L}{\partial v_i}\right)+p\right]=0. \tag{10}$$

Equation (10) can be considered as a condition for mechanical equilibrium between the subsystems, while Eq. (3) is a condition for thermal equilibrium. Using Eqs. (7) and (8), we find that

$$\frac{\partial f_i^0}{\partial v_i}=-p(v_i,T-T_i^L)+\frac{\partial f_i^0}{\partial T_i^L}\frac{\partial T_i^L}{\partial v_i}, \tag{11}$$

$$\frac{\partial f_i^L}{\partial v_i}=\overline{\varepsilon_L}+v_i\frac{\partial\overline{\varepsilon_L}}{\partial v_i}-T_i^L\frac{\partial s_i^0}{\partial v_i}-s_i^0\frac{\partial T_i^L}{\partial v_i}, \tag{12}$$

where $p(v_i,\tilde{T})$ is an equation of state of the ith component. Now we employ the same procedure as was used for transition from energy E to function F. Assume that $v_i=v_i^0(p,T)$ is a solution of Eq. (10) for $\overline{\varepsilon_L}\equiv 0$, and solve Eq. (10) by iterations, i.e., substitute $v_i^0(p,T)$ into all terms containing $\overline{\varepsilon_L}$ and its derivatives [see Eqs. (11) and (12)].

Then, if $v_i=v_i^0(p,T)$ is a solution of Eq. (10) for $\overline{\varepsilon_L}\equiv 0$, the new solution of Eq. (10) v_i^1 can be written as

$$v_i^1=v_i^0(p-p_i^L,T-T_i^L), \tag{13}$$

where $p_i^L=-(\partial f_0/\partial T_i^L\,\partial T_i^L/\partial v_i+\partial f_i^L/\partial v_i)|_{v_i=v_0(p,T)}$.

Substituting the equilibrium value (13) into function Φ and keeping only terms with the thermodynamic accuracy yield

$$\Phi=\sum_{i=1}^{K} N_i[f_i^0(v_i^1,T-T_i^L)+v_i^0\overline{\varepsilon_L}-T_i^L s_i^0(v_i^0,T)+pv_i^1].$$

Introducing the chemical potential

$$\mu_i(p,\tilde{T})=f_i^0(v_i(p,\tilde{T}),\tilde{T})+pv_i(p,\tilde{T}), \tag{14}$$

we can rewrite formula for Φ as follows:

$$\Phi=\sum_{i=1}^{K} N_i[\mu_i^0(p-p_i^L,T-T_i^L)+\mu_i^L], \tag{15}$$

where $\mu_i^L=f_i^L+p_i^L v_i^0(p,T)$.

Finally, a condition for chemical equilibrium is determined from the requirement for the minimum of a function

$$A=\Phi-\mu\sum_{i=1}^{K} N_i$$

with respect to parameters N_i:

$$\mu_i^0(p-p_i^L,T-T_i^L)+\mu_i^L=\mu_k^0(p-p_k^L,T-T_k^L)+\mu_k^L. \tag{16}$$

Expanding Eq. (16) in power series of the parameters of the external loading, we find that

$$\mu_i^0(p,T)-\mu_k^0(p,T)=v_i p_i^L-v_k p_k^L+\mu_k^L-\mu_i^L-s_i T_i^L+s_k T_k^L, \tag{17}$$

where $v_i(p,T)$ and $s_i(p,T)$ are specific volume and entropy per one particle, respectively.

III. PHASE TRANSITION IN THE PRESENCE OF THE EXTERNAL ELECTRIC FIELD

Using the approach outlined in the preceding section, consider a first-order phase transition in the presence of the external electric field. Although this problem was a subject of many experimental and theoretical studies (see, e.g., Refs. [1,9,10]), some aspects of the problem were not analyzed before in spite of their significance for elucidating the problem. The principal effect of the electric field upon the first-order phase transition is the splitting of the phase equilibrium curve whereby the equilibrium curves for the direct and for the inverse phase transitions do not coincide. The latter effect occurs because a work of formation of a nucleus of a new phase depends upon the electrodynamic parameters of the nucleus and of the host medium. In the following, we denote parameters of a nucleus by the subscript 0 and parameters of the host medium by the subscript 1. Energy of the system comprised an embedded nucleus and a host medium in the external electric field can be written in the form given by Eq. (1). To this end, we determine the change of the energy of the electric field (see Ref. [3], Chap. 2, Sec. 11):

$$W_e=\int(\vec{E}\cdot\vec{D}-\vec{E}_0\cdot\vec{D}_0)d\vec{r},$$

where $\vec{E}_0,\vec{D}_0$ and $\vec{E},\vec{D}$ are the strengths of the electric field and induction before and after formation of the nucleus, respectively. In the case of a spherical nucleus, we arrive at the following formula for W_e (see, e.g., Ref. [3], Chap. 2, Sec. 12 and Ref. [9]):

$$W_e=\overline{\varepsilon_f}v_1N_1,$$

where

$$\overline{\varepsilon_f}=\frac{\beta_0-\beta_1}{8\pi}\frac{3\beta_0E_0^2}{\beta_1+2\beta_0}. \tag{18}$$

Here, β_0 and β_1 are dielectric permittivities of the external (host) and internal (nucleus) phases, respectively, which relate electric induction with the strength of electric field, $\vec{D}=\beta\vec{E}$. The value $\overline{\varepsilon_L}$ in Eq. (1) can be written as $\overline{\varepsilon_L}=\overline{\varepsilon_f}$.

Let us neglect the dependence of the dielectric permittivities β_0 and β_1 upon the entropies and specific volumes of the external and internal phases. According to Eq. (4) $T_i^L=0$, and according to Eq. (9) $f_i^L=v_i\overline{\varepsilon_f}$. Using Eqs. (12) and (13), we find that $p_i^L=-\overline{\varepsilon_f}\delta_{il}$, where δ_{mn} is a Kronecker's delta. Thus,

$$\mu_i^L=f_i^L+p_i^L v_i=0. \tag{19}$$

In order to determine the size of a critical nucleus, we must take into account the surface tension. The equation for determining the radius of a critical nucleus r_1 can be derived using Eqs. (17) and (19) and taking into account that the radius of a critical nucleus is an additional variational parameter in the problem [12]:

$$\mu_1^0(p,T)-\mu_0^0(p,T)=-v_1\left(\overline{\varepsilon_f}+\frac{2\alpha}{r_1}\right), \tag{20}$$

where α is a coefficient of surface tension.

Formulas (19) and (20) were often used in the literature (see, e.g., Refs. [7–10]) for the analysis of the phase transitions. Equations (18) and (19) show that the main effect of the electric field on phase transitions is related to that ε_f changes sign depending on the magnitude of the dielectric permittivity of the internal phase. The similar situation occurs in the case of phase transitions in current-carrying conductors. In Refs. [10,11] using equations of the same type as Eqs. (18)–(20), we demonstrated the existence of the thermodynamic domain where both phases are metastable. In this domain for a given value of pressure, there exists a temperature interval $\Delta T(p)$ where the sizes of the critical nucleus for the direct and inverse phase transitions assume positive values simultaneously. A case of electrostatic field is associated with some differences. The latter is the reason that in this study, we performed a complete analysis of the problem. Apart from the temperature range $\Delta T(p)$ where for a given pressure both phases are metastable, we also considered the range $\Delta p(T)$ of pressures where for a given temperature both phases are metastable. If the difference between the specific volumes of both phases is small, the latter range can be quite large $\Delta p(T) \gg \overline{\varepsilon_f^-}$. In conclusion, we considered also kinetics of phase transition in the domain of coexistence of both phases.

Further analysis is performed using Eq. (20) in order to determine the size of the critical nucleus r_- for a phase transition $+ \rightarrow -$ and r_+ for a phase transition $- \rightarrow +$. Hereafter, the subscripts $+$ and $-$ denote a high temperature and a low temperature phase, respectively. Using Eq. (20) in the vicinity of temperature $T = T_0(p)$ for a given pressure p, we find that for a phase transition $+ \rightarrow -$ (phase $-$ is considered to be the internal phase)

$$r_-(T) = -\frac{2\alpha v_-^0}{\lambda_0 \frac{\Delta T}{T_0} + v_-^0 \overline{\varepsilon_f^-}}, \quad \Delta T = T - T_0, \tag{21}$$

where v_-^0 is a specific volume of a low temperature phase at the phase equilibrium curve $T = T_0(p)$, $\lambda_0 = T_0(s_+^0 - s_-^0) > 0$, s_+^0 and s_-^0 are specific entropies of the high temperature and low temperature phases, respectively, and

$$\overline{\varepsilon_f^-} = \beta_+ \frac{1-\kappa}{8\pi} \frac{3}{\kappa+2} E_0^2, \quad \kappa = \frac{\beta_-}{\beta_+}. \tag{22}$$

Consider now a phase transition $- \rightarrow +$, assuming that phase $+$ is the internal phase. In this case,

$$r_+(T) = \frac{2\alpha v_+^0}{\lambda_0 \frac{\Delta T}{T_0} - v_+^0 \overline{\varepsilon_f^+}}, \tag{23}$$

where v_+^0 is a specific volume of the high temperature phase and

$$\overline{\varepsilon_f^+} = \beta_+ \frac{\kappa-1}{8\pi} \frac{3\kappa}{1+2\kappa} E_0^2. \tag{24}$$

Formula (21) allows us to determine a temperature T_- such that at temperatures $T > T_-$, the nuclei of the low temperature phase $(-)$ are not formed,

$$\frac{T_- - T_0}{T_0} = -\frac{v_- \overline{\varepsilon_f^-}}{\lambda_0}, \tag{25}$$

while formula (23) allows us to determine a temperature T_+ such that at temperatures $T < T_+$, nuclei of the high temperature phase $(+)$ are not formed,

$$\frac{T_+ - T_0}{T_0} = \frac{v_+ \overline{\varepsilon_f^+}}{\lambda_0}. \tag{26}$$

Define a parameter

$$\gamma = \frac{T_- - T_0}{T_+ - T_0} = \frac{1+2\kappa}{(\kappa+2)\kappa} \frac{v_-}{v_+} > 0. \tag{27}$$

Equation (27) implies that the curves $T_-(p)$ and $T_+(p)$ are shifted in the same direction with respect to the curve $T_0(p)$ since the differences $T_- - T_0$ and $T_+ - T_0$ have the same sign. As follows from Eqs. (21)–(24), when $\kappa > 1$ the curves $T_-(p)$ and $T_+(p)$ are shifted towards higher temperatures, and when $\kappa < 1$ these curves are shifted towards lower temperatures. If $T_-(p) < T_+(p)$, then in the temperature range

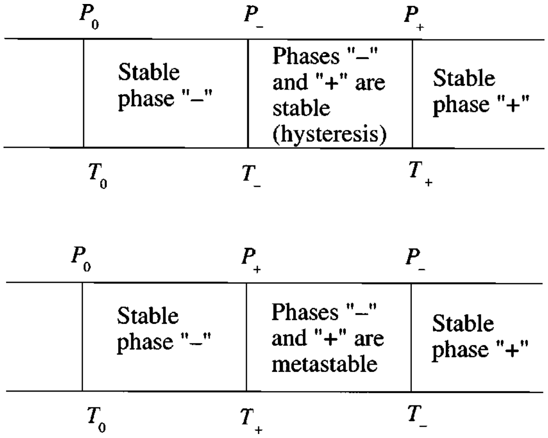

FIG. 1. Locations of domains of stability and metastability of phases for different values of parameter γ $(\kappa > 1)$.

$$T_-(p) < T < T_+(p), \tag{28}$$

the nuclei of the new phase are not formed. The latter conclusion is a direct consequence of the definition of $T_-(p)$ and $T_+(p)$. In the temperatures range determined by Eq. (28), both phases are stable, i.e., it is a range of a hysteresis.

Different situation occurs when $T_+(p) < T_-(p)$. In this case, in the temperature range

$$T_+(p) < T < T_-(p), \tag{29}$$

both phases are metastable, so that $r_+(T)$ and $r_-(T)$ assume finite positive values. The latter conclusion can be verified as follows. Eliminating $\Delta T / T_0$ in formulas (21) and (23), we find that

$$\frac{2\alpha v_+}{r_+} + \frac{2\alpha v_-}{r_-} = -v_- \varepsilon_f^- \frac{\gamma-1}{\gamma} = v_+ \overline{\varepsilon_f^+} (\gamma - 1). \tag{30}$$

In the domain where both phases are metastable, $r_+(T)$ and $r_-(T)$ assume positive and finite values. Equation (30) implies that such a situation can occur only when its right-hand side is positive. Since for $\kappa > 1$, $\overline{\varepsilon_f^-} < 0$ and $\overline{\varepsilon_f^+} > 0$, Eq. (30) yields a condition for the metastability of both phases in the range $\kappa > 1$, $\gamma > 1$.

Similarly, it can be showed that in the range $\kappa < 1$, the condition for the metastability of both phases is $\gamma < 1$ with the only difference that $T_- < T_0$ and $T_+ < T_0$. In Figs. 1 and 2, we showed locations of different domains of stability of phases for $\kappa > 1$ and $\kappa < 1$ on the temperature axis. In Fig. 3, we showed locations of the domains of metastability of both phases on $v_-/v_+, \beta_-/\beta_+$ plane.

Above we considered different thermodynamic regions at the temperature axis for a given magnitude of pressure. Using a similar approach, we can analyze different thermodynamic regions at the pressure axis for a given magnitude of temperature. Thus, we obtained formulas for pressures p_-

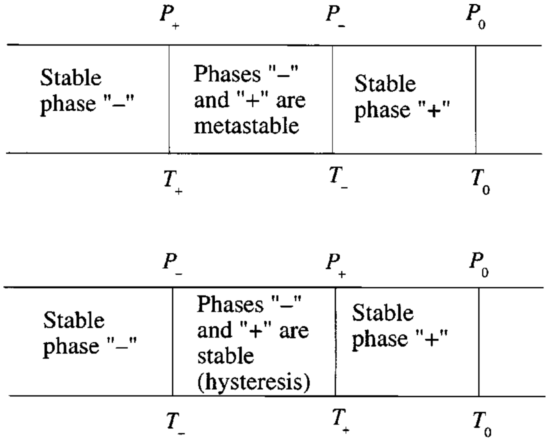

FIG. 2. Locations of domains of stability and metastability of phases for different values of parameter γ ($\kappa<1$).

and p_+, such that for $p>p_-$ a low pressure phase is not formed and for $p<p_+$ a high pressure phase is not formed:

$$p_- - p_0 = -\frac{\overline{\varepsilon_f^-}}{\Delta_-}, \quad p_+ - p_0 = \frac{\overline{\varepsilon_f^+}}{\Delta_+},$$

where $\overline{\varepsilon_f^-}$ is determined by Eq. (22), $\Delta_- = v_- - v_+/v_-$, $\Delta_+ = v_- - v_+/v_+$, $\overline{\varepsilon_f^+}$ is determined by Eq. (24), v_- and v_+ are specific volumes of low pressure and high pressure phases, respectively. Then, using considerations similar to those employed in the analysis of the temperatures range, we arrive at the thermodynamic domains of stability of phases shown in Figs. 1 and 2.

In conclusion, we consider kinetics of formation of two phases. Denote by x_+ and x_- the concentrations of a high temperature and a low temperature phase, respectively. We neglect fluctuations of concentrations and consider a linear domain where concentrations of both phases are far from depletion. Let p_+ and p_- be the probabilities of formation of phases (see Ref. [13], Chap. 12, Sec. 99). Since $x_+ + x_- = 1$ using the local approximation, we find that

$$\dot{x}_+ = p_+(1-x_+) - p_- x_+,$$

or

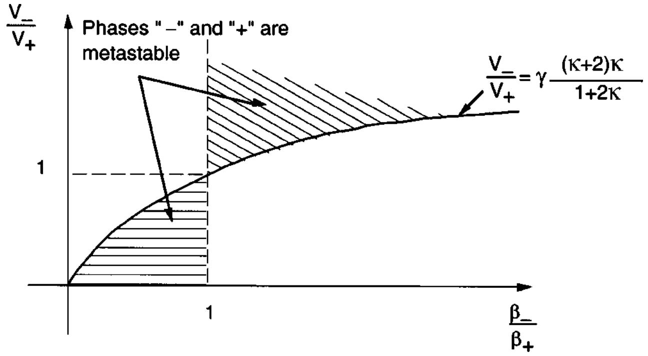

FIG. 3. Domains of metastability of both phases on v_-/v_+, β_-/β_+ plane.

$$x_+(t) = \frac{\varphi}{1+\varphi} + \exp(-\gamma t)\left(x_+(0) - \frac{\varphi}{1+\varphi}\right), \quad \varphi = \frac{p_+}{p_-},$$

$$x_-(t) = \frac{1}{1+\varphi} + \exp(-\gamma t)\left(x_-(0) - \frac{1}{1+\varphi}\right).$$

In the linear region where both phases are far from depletion, the probability of phase formation is determined by the critical radius (see Ref. [13], Chap. 12, Sec. 99), $p_\pm \propto \exp(-4\pi\alpha r_\pm^2/3kT)$, and

$$\varphi = \exp\left[-\frac{4\pi\alpha(r_+^2 - r_-^2)}{3kT}\right]. \tag{31}$$

Here, r_+ and r_- are the critical sizes of the nuclei in the domain of coexistence of phases which were determined above. Substituting these values into formula (31) yields the dependencies of phase concentrations x_+ and x_- upon the amplitude of the external electric field. Direct substitution of Eqs. (21)–(24) into Eq. (31) yields an expression which is too cumbersome for the direct analysis. In order to derive simple formulas for the dependencies of phase concentrations on the amplitude of the electric field, let us define the parameter

$$E_e^2 = \frac{\Delta T}{T_0} \frac{\lambda_0}{\tilde{V}(\kappa)}, \tag{32}$$

where $\tilde{V}(\kappa) = v_- v_+/(v_+ + v_-) \cdot (\kappa-1)/8\pi\beta_+ 3(\kappa^2+4\kappa+1)/(\kappa+2)/(1+2\kappa)$.

When the external electric field $E_0 = E_e$, at a given ΔT, $r_+(T) = r_-(T)$, i.e., $\varphi = 1$. Thus, formula (32) determines the magnitude of the external electric field E_e that renders concentrations of both phases equal. Note that Eq. (32) implies that when $\Delta T<0$, $\tilde{V}(\kappa)<0$ and $\kappa<1$. Thus, a domain where concentrations of both phases are equal is located in the region $\Delta T<0$ when $\kappa<1$, and in the region $\Delta T>0$ when $\kappa>1$. Consider a case with $\kappa<1$ and $\Delta T<0$. Hereafter, the amplitude of the external field is normalized by E_e so that $E_0^2 = x^2 E_e^2$. Using the latter relation and Eq. (32) rather than Eqs. (21) and (23), we arrive at the following formulas:

$$r_-(T) = \frac{r_0}{1-x^2 A}, \quad r_+(T) = \frac{r_0}{s\left(\frac{Ax^2}{\tau s} - 1\right)}, \tag{33}$$

where $r_0 = -2\alpha v_- T_0/(\lambda_0 \Delta T)$ is a radius of the critical nucleus of the low temperature phase without the external electric field and

$$s = v_-/v_+, \quad \tau = \frac{1+2\kappa}{\kappa(\kappa+2)}, \quad A = \frac{\tau(1+s)}{1+\tau}. \tag{34}$$

The magnitudes of parameters A, s, and τ are determined by the parameters of phases. Thus, Eqs. (32) and (33) determine the range of the external electric field E_0 where both phases are metastable. This range of the external electric field can be found from the conditions that the sizes of the critical nuclei of both phases are positive, i.e., $r_-(T)>0$ and $r_+(T)>0$. The latter conditions yield

$$1/A > E_0^2/E_e^2 > \tau s/A. \tag{35}$$

The existence of the range of the external electric field (35) requires the validity of the condition $\gamma=\tau s<1$, which was found before.

In the case $\Delta T>0$, the sizes of the critical nuclei are normalized by the size of the critical nucleus without the external electric field r_0, $r_0=2\alpha v_+T_0/(\lambda_0\Delta T)$ [compare with r_0 in Eq. (33)]. Then, using the same arguments allows us to determine a condition for the metastability of both phases $\kappa>1$, $\gamma=\tau s>1$, which was determined above.

Now we determine the dependence of the ratio of the concentrations of phases $\varphi=x_+(\infty)/x_-(\infty)$ in the vicinity of $\varphi=1$ upon the magnitude of the external electric field. Formulas for the sizes of the nuclei can be rewritten as follows:

$$r_-(T)=\frac{r_*}{1-\dfrac{(x^2-1)A}{1-A}}, \quad r_+(T)=\frac{r_*}{1+\dfrac{(x^2-1)A}{A-s\tau}}, \tag{36}$$

where r_* is a critical radius of the nuclei for $\varphi=1$:

$$r_*=\frac{r_0}{1-A}=\frac{r_0\tau}{A-\tau s}. \tag{37}$$

Note that a condition $r_*>0$, or $\tau s<A<1$, is a particular case of the Eq. (35) at $E=E_e$.

Using Eq. (33), we arrive at the following formula for the ratio of concentrations of two phases:

$$\ln(\varphi)=\frac{4\pi\alpha r_0^2}{3kT}\,\frac{[2\xi\tau+\xi^2(1-\tau)](1+\tau)}{(1-\xi)^2(\tau+\xi)^2(1-A)^2}, \tag{38}$$

where $\xi=(E_0^2-E_e^2)/E_e^2A/(1-A)$. Equation (38) determines the dependence of the ratio of concentrations of both phases on the magnitude of the applied electric field and parameters of the problem.

IV. DISCUSSION

In this study, we considered kinetics of phase formation in the domain of simultaneous metastability of both phases in the presence of the external electrostatic field. Although the existence of the domain of simultaneous metastability of both phases was demonstrated in the case of phase transitions in current-carrying conductors (see Refs. [7,8,11]), the kinetics of phase formation in this domain was not analyzed before.

The main result that was obtained in this study is that we demonstrated the feasibility to control concentrations of phases in the system by varying the amplitude of the external electrostatic field.

Concerning the experimental observation of the kinetics of phase formation in the external electrostatic field, it must be noted that the main obstacle for observation of the above discussed phenomena is the relatively small magnitude of electric field causing a breakdown. It is feasible to observe these effects when either a latent heat of phase transition is small or a difference of the specific volumes of two phases is small. One very essential factor which is not accounted for in this study is the mechanical instability of the nuclei with respect to their elongation into a spheroid shape and rupture into smaller fragments [14]. The latter instability occurs in the case of formation of droplets in a gaseous medium. On the other hand, in this study, we suggested a general approach with the end to determine the minimum requirements to the system where there exists a domain of simultaneous metastability of both phases. The existence of such a domain is of interest since in this domain, it is possible to change concentrations of phases by varying the amplitude of the external electric field.

These minimum requirements to the system imply that the response of the system to the external loading depends upon the phase state of the material and the work of nucleus formation depends upon the magnitude of the external loading. The similar situation occurs during phase transitions in current-carrying conductors, e.g., during surface melting [15].

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