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Thermodynamics of phase equilibrium in nonuniform fields

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We obtain conditions of phase equilibrium of a substance in a nonuniform potential field of forces. If the force per mass unit is phase dependent, the field may induce a shift of phase equilibrium. In this case, chemical potentials of the substance do not coincide at the phase boundary with equal temperatures and pressures for each phase. The equality condition at the phase boundary in the presence of the field for the full chemical potentials of the phases, including the additional field component, can be reduced to the equality condition of the chemical potentials under different pressures for each phase. Thus the field-induced phase equilibrium becomes impossible for a given geometry, and the system has to change its phase abruptly when one of the phases reaches its spinodal state. An example of such a transition is the case of a liquid current-carrying conductor in its own magnetic field rapidly turning to a dispersion state (drops in vapor). Similar phenomena can occur at the final stage of electrical explosion of conductors. We also show that for a liquid dielectric in a nonuniform external electric field the thermodynamical equilibrium state is liquid with vapor bubbles, the latter being localized into the domain of the higher value of the field. [S1063-651X(97)05510-4]

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I. INTRODUCTION

As is known, strong external fields penetrating inside a body radically affect its thermodynamical properties. Examples of general thermodynamical relations for the matter-field system are given in the monographs [1,2]. An elegant sample of the application of these relations is provided in [3], where the problem of the condensation of an electrically charged drop is considered. At the same time the question of strong field influence on the thermodynamics of phase equilibrium is not quite clear, though the issue is practically important in connection with the research of substance compression in a setup that uses pinch effect, electrical explosion of conductors, and a number of other applied problems.

Recently a number of works were published (see, for example, [4–6]) in which the expected effects of dealing with the shift of the phase equilibrium in a high density current-carrying conductor in the presence of an azimuthal magnetic field were discussed. Nevertheless the self-consistent solution of the problem of external field influence on the thermodynamics of phase equilibrium is absent.

In the present study we consider the effect of a nonuniform potential field of forces on thermodynamics of phase equilibrium. Assume the substance is uniform on the distances on the order of the correlation fluctuation density radius. The appropriate restriction on the force value will be given below.

First we consider a single-phase state. The expression for the full thermodynamical potential of the matter-field system is written as a functional of substance density and field of forces. Minimization of this functional leads to two conditions. The first one is the constancy of the full chemical potential throughout the system. The second one is the condition of the mechanical equilibrium of the matter-field system, in which the pressure gradient is balanced by the external force. As is shown, the field not only leads to the formation of a pressure profile but it also creates an additional component in the full matter-field chemical potential that depends on the external force work. The thermodynamical relations and the equation of state without the field are valid for both local values of substance chemical potential and the density-pressure dependence at every point.

We also produce the corresponding functional for a two-phase system. Its minimization gives conditions of the phase equilibrium. They reduce to equality of the full chemical potentials of phases at the phase boundary. The part of the potential associated with the external field work is added to or subtracted from the substance chemical potential. If the forces acting per mass unit for each phase differ then these field potentials differ too. It means that the substance chemical potentials at the phase boundary with identical temperatures and pressures are not equal to each other. The equality of the full chemical potentials of the phases can be presented as the equality of the substance chemical potentials of the phases with different pressures. For example, the shift of phase equilibrium arises when either a current-carrying liquid conductor is in its own magnetic field or a liquid dielectric is an electrical field. However, in a field of gravitation this effect is absent.

The possibility of the equality of the substance chemical potentials with identical temperatures and different pressures is analyzed below qualitatively and also on the basis of the van der Waals equation. As shown for fields caused by forces of compression in the substance, densities and pressures of the coexisting phases in the presence of the field are higher than those without it. Under thermodynamical equilibrium, the phase with lower density is in the state that without field is metastable (supersaturated vapor). In the case of fields creating forces of expansion in the matter, densities and pressures of the phases at the phase boundary are lower than those without the field. Moreover, the phase with higher density is in the state which corresponds to the metastable

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liquid branch of states (superheated liquid). In both cases, there are limiting values of the potential of the volume density forces when one of the phases reaches its spinodal point. The phase equilibrium in a given geometry and field is made impossible and the system has to change its state. So we have a field-induced phase transition.

When a high density current-carrying conductor is in its own magnetic field, the only possible state after transition is a dispersion mixture of liquid drops in vapor. We estimate the drop size and expansion speed of this mixture. We assume that such a transition can be the direct reason for the sharp increase of the conductor radius and the resistance at the final stage of electrical explosion of conductors taking place in so-called fast regimes [7–9].

The phase equilibrium of a liquid dielectric in the presence of a nonuniform electrical external field has also been given consideration. In this case there is vapor bubble formation in the domain of higher values of the electrical field.

II. PRELIMINARY REMARKS

Consider a substance at constant temperature in a volume V in the presence of some nonuniform potential field of forces $\mathbf{f}(\mathbf{r})$. Here $\mathbf{f}(\mathbf{r})$ is the force per unit volume or the volume density of the force, $\mathbf{r}$ is the position. The force on the element of volume evidently is equal to $\mathbf{f}dV$.

As is known, the matter will be at rest in a constant field of forces if

$$\nabla P=\mathbf{f}, \tag{1}$$

where P is the pressure of substance. The force per unit volume is balanced by the pressure gradient. The field of forces can be presented as the gradient of a scalar function. The pressure of the substance in equilibrium with the field of forces equals the potential of the field of volume density forces taken with inverse sign. Our observations for the fields that have the potential of the volume density of forces follow.

Direct integration of Eq. (1) gives the pressure distribution throughout the system,

$$P(\mathbf{r})+\Pi(\mathbf{r})=P^{I}, \tag{2}$$

where P^I is the substance pressure at the zero field point, and $\Pi(\mathbf{r})$ is the potential of the volume density forces which is determined from the expression

$$\Pi(\mathbf{r})=-\int_0^{\mathbf{r}}\mathbf{f}\cdot d\mathbf{u}. \tag{3}$$

Generally, to find the pressure distribution one should use the equation of state and integrate it taking into account that the force $\mathbf{f}$ can depend on the substance state.

We shall restrict our consideration to the cases when the fields are not so intensive as to allow the nonuniformity to be essential at the distance on the order of the correlation density radius. In this case the equation of state obtained without field will be valid at every point. Let us find the requirement for the value of force associated with this assumption. The typical scale of the density variation in uniform matter is connected with its fluctuations

$$\sqrt{\langle\Delta\rho^2\rangle}=\rho\sqrt{kT\rho/-\rho(\partial P/\partial\rho)_T m}, \tag{4}$$

where $\langle\Delta\rho^2\rangle$ is the mean square of the density fluctuation, ρ is density, m is mass, and T is temperature. The typical density variation associated with the external force can be written as

$$\Delta\rho=\left(\frac{\partial\rho}{\partial P}\right)_T\Delta P=\left(\frac{\partial\rho}{\partial P}\right)_T f r_c, \tag{5}$$

where r_c is the correlation radius of density fluctuations. We can state that

$$r_c\sim r_0\sqrt{P/-\rho(\partial P/\partial\rho)_T}, \tag{6}$$

where $r_0\sim(m/\rho)^{1/3}$ is the mean interparticle distance. Requiring $\Delta\rho\ll\sqrt{\langle\Delta\rho^2\rangle}$, we obtain

$$-\rho\left(\frac{\partial P}{\partial\rho}\right)_T\left(\frac{\rho}{m}\right)^{1/3}\sqrt{\frac{kT\rho}{mP}}\gg f. \tag{7}$$

When inequality (7) is valid we may consider that gradient terms in the equation of state are of no significance.

Besides the chemical potential of the matter-field system μ^I in equilibrium must be constant throughout the system [1,2]. It means that its full differential is equal to zero,

$$\rho d\mu^I=\rho d\mu-\mathbf{f}\cdot d\mathbf{u}=0, \tag{8}$$

where μ is the chemical potential unit mass of the substance without field, and $d\mathbf{u}$ is the vector of infinitesimal displacement. The first term in Eq. (8) is the chemical potential change of the substance volume element. The second one is the infinitesimal work of the external force. The gradient terms are absent in Eq. (8) because the substance is uniform on the distance in the order of the correlation radius of density fluctuations. Integrating Eq. (10) by $\mathbf{u}$ from the point of the zero field, we obtain

$$\mu(\mathbf{r})+\varphi(\mathbf{r})=\mu^I, \tag{9}$$

where $\nu=1/\rho$ is the specific volume, μ^I is the substance chemical potential at the point $r=\mathbf{0}$ where the field is equal to zero, and the substance chemical potential coincides with the full chemical potential of the matter-field system. $\varphi(\mathbf{r})$ is the potential of the mass density forces which is equal to

$$\varphi(\mathbf{r})=-\int_0^{\mathbf{r}}\nu\mathbf{f}\cdot d\mathbf{u}. \tag{10}$$

It should be noted that the full chemical potential is determined with a precision of an arbitrary constant.

The line integral in Eq. (10) does not depend on the path of integration due to the potentiality of the force field. Change in the substance chemical potential is associated with the external field work per unit mass.

Replacing $\mathbf{f}\cdot d\mathbf{u}$ with dP from Eq. (1) in Eq. (10) we obtain the usual thermodynamical formula that connects the substance chemical potentials with different pressures.

$$\mu(P(r),T)=\mu(P^I,T)-\int_{P(r)}^{P^I}\nu\, dP. \tag{11}$$

It should be noted that the conditions of equilibrium (1) and (9) can be obtained from minimality condition of some functional. Consider the functional Ψ that is connected with a full thermodynamical potential of the system by the relation $\Psi = \Phi - \lambda m$, where m is the substance mass,

$$\Psi = \int_V \rho \, dV [\mu(\mathbf{r}) + \varphi(\mathbf{r}) - \lambda]. \tag{12}$$

The Ψ function has a minimum in the state of equilibrium if its first variation is equal to zero. If $\delta\mathbf{r}$ is the arbitrary displacement of substance element in Eq. (13), then the first variation equals zero, when

$$\frac{\delta\rho}{\delta\mathbf{r}} [\mu(\mathbf{r}) + \varphi(\mathbf{r}) - \lambda] + \rho \left[\frac{\delta\mu}{\delta\mathbf{r}} - \nu\mathbf{f} \right] = \mathbf{0}. \tag{13}$$

Terms in both square brackets in Eq. (13) must be equal to zero. The equality of the first term in the square brackets to zero gives the condition (9) with $\lambda = \mu^I$. The equality for the second term in the square brackets with $d\mu = \nu dP$ taken into account leads to the mechanical equilibrium condition of substance in the field (1).

Consider specific examples of fields and forces. The force can depend on the thermodynamical functions of matter. For example, in the case of a centrally symmetric field of gravity the force is given by

$$\mathbf{f} = -\gamma\rho \frac{m(r)}{r^3} \mathbf{r}, \tag{14}$$

where g is the gravity constant. The value

$$m(r) = 4\pi \int_0^r \rho r^2 dr \tag{15}$$

is the substance mass confined in a spherical volume of radius r.

As in [1] the force per unit volume in a liquid dielectric can be written

$$\mathbf{f} = \boldsymbol{\nabla} \left[\frac{E^2}{8\pi} \left(\rho \frac{\partial\varepsilon}{\partial\rho} \right)_T \right] - \frac{E^2}{8\pi} \boldsymbol{\nabla}\varepsilon, \tag{16}$$

where E is the strength of electric field and ε is the dielectric constant.

The force acting on a nonmagnetic current-carrying material in a magnetic field has the form

$$\mathbf{f} = \frac{1}{c} [\mathbf{j}, \mathbf{H}], \tag{17}$$

where c is the light speed, $\mathbf{j}$ is the current density, and $\mathbf{H}$ is the magnetic field strength.

We emphasize that volume density field of forces in an arbitrary magnetic field may not be potential. It will be potential if the following condition is valid:

$$\text{rot}\,\mathbf{f} = \frac{1}{c} \text{rot}[\mathbf{j}, \mathbf{H}] = \frac{1}{4\pi} \text{rot}[\text{rot}\,\mathbf{H}, \mathbf{H}] = 0. \tag{18}$$

The last expression leads to some restrictions of a magnetic field configuration.

III. PECULIARITIES OF THERMODYNAMIC EQUILIBRIUM OF CURRENT-CARRYING CONDUCTORS AND LIQUID DIELECTRICS

Depending on the sign of the work performed by the field force, we consider two cases. If $\mathbf{f} \cdot d\mathbf{u} < 0$, then the value $\Pi(\mathbf{r})$ is positive. The substance pressure is higher in domains where the field is lower. According to Eq. (9), the external field work is added to the substance chemical potential and the value $\mu^I > \mu$. We have such a situation for a cylindrical current-carrying conductor in its own magnetic field. The current creates an azimuthal magnetic field. The conductor is compressed by the ponderomotive force $f = -jH/c$. The zero field point is located at the axis of the conductor. In this case the distributions of the substance chemical potential and substance pressure have the form

$$\mu(P^I) = \mu(P(r)) + \frac{1}{c} \int_0^r \nu j H \, dr, \tag{19}$$

$$P^I = P(r) + \frac{1}{c} \int_0^r j H \, dr, \tag{20}$$

where μ^I and P^I are the values of the substance chemical potential and pressure at the axis of the conductor. The full chemical potential in this case is equal to the substance chemical potential at the conductor axis. It follows from Eqs. (19) and (20) that the values μ^I and P^I are maximal at the zero field point.

Let us give a graphical interpretation of the equilibrium conditions (19) and (20). The typical dependence of substance chemical potential on pressure under subcritical temperature is drawn in Figs. 1(a) and 1(b). Different parts of this dependence correspond to different states. The branch DS is gas, SE is supercooled gas, SA is liquid, FS is superheated liquid, FE corresponds to the absolutely unstable states. The point S is the point of phase equilibrium without the field at the planar interface. The corresponding values of the pressure and chemical potential are designated as P_s and μ_s.

The states of liquid conductor correspond to states lying at the liquid branch of this dependence. The straight line μ^I gives the full chemical potential value which is constant throughout the system. This line intersects the liquid branch SA at the point A with pressure P^I. This state corresponds to the zero field point which lies at the conductor axis. The point B corresponds to the state of the conductor at the distance r from the axis with the pressure $P = P^I - \Pi$ and with the chemical potential $\mu = \mu^I - \varphi$.

If $\mathbf{f} \cdot d\mathbf{u} > 0$, then the value $\Pi(\mathbf{r})$ is negative. The substance pressure is higher in domains where the field is higher too. The external field work is subtracted from the substance chemical potential, so that the value $\mu^I < \mu$. Such a situation can be realized, for example, in a liquid dielectric in the presence of an external electric field at a distance from electrodes. Consider a long cylindrical capacitor with external and inner radii equal to R and r_0. If the liquid dielectric is localized within the cylindrical capacitor, then the distribu-

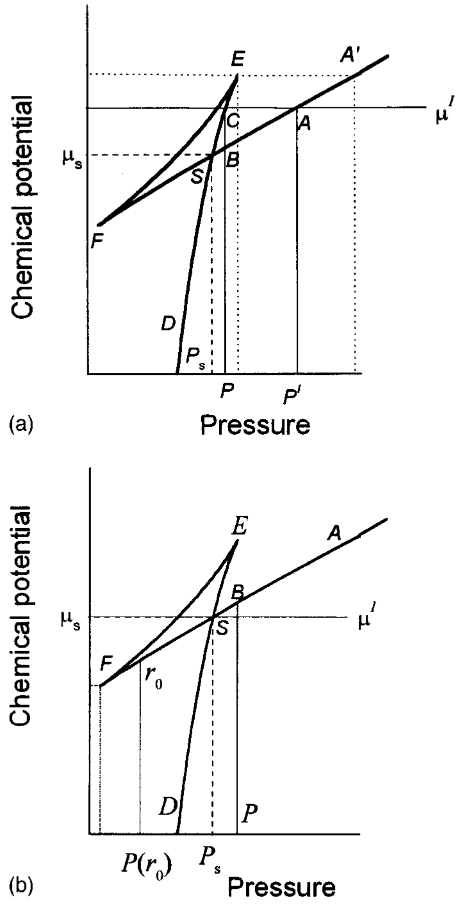

FIG. 1. (a) relates to the case of negative values of parameter Π, (b) to the positive values of this parameter. Substance chemical potential dependence on pressure at the constant temperature. The values of equilibrium pressure P_s and substance chemical potential μ_s are marked as dotted lines. The values of pressures and chemical potentials corresponding to the equilibrium in the presence of external field are marked as solid lines. The limit values of the pressure and the substance chemical potentials are marked as short dotted lines.

tions of the substance chemical potential and substance pressure at a distance from electrodes, following [2], are

$$\mu(P^I)=\mu(r)-\frac{E^2}{8\pi}\left(\frac{\partial\varepsilon}{\partial\rho}\right)_T, \tag{21}$$

$$P^I=P(r)-\frac{\rho E^2}{8\pi}\left(\frac{\partial\varepsilon}{\partial\rho}\right)_T, \tag{22}$$

Here μ^I and P^I are values of the substance chemical potential and pressure at the zero field point. It should be noted that near the electrodes the sign of force changes. There is a force at the boundary of a charged metallic body penetrating inside a dielectric liquid. This force moves apart the capacitor plates and expands the liquid. As a result, the pressure drop appears at the boundary between liquid and charged metallic body. This pressure drop can be written as [2,10]

$$P^I=P(r_0)+\frac{E^2(r_0)}{8\pi}\,\varepsilon(\varepsilon-1), \tag{23}$$

where $E(r_0)$ is the strength of the electric field at the surface of the inner electrode. The electrostriction force is equal to zero at this surface [10]. So the liquid pressure has a minimal value at the electrode surface due to the expansion of the liquid by electrical forces. As the volume element of liquid moves away from the electrode the electrostriction force first increases and then decreases. The latter is associated with a fall of the strength of the electric field as the point moves away from the electrode. So we have nonuniform pressure distribution throughout the liquid due to the presence of the electrical field. It is significant that the minimal value pressure of liquid can be realized via an electrode with a higher value of electric field strength. The zero field point can be located somewhere outside the capacitor. The dependence of the chemical potential on pressure for this case is shown in Fig. 1(b). The point r_0 corresponds to the liquid state at the surface of the electrode with the higher value of the electric field strength. The point B corresponds to the liquid state inside the capacitor at the point lying at a distance from the electrode. The zero field point $C=S$ coincides with the equilibrium one and the value of the substance chemical potential at this point is $\mu^I=\mu_s$.

IV. PHASE EQUILIBRIUM IN THE PRESENCE OF FIELD

Let us assume that the matter breaks down into two phases. Phase 1 occupies the inner volume V_1. Phase 2 occupies the external volume V_2. The location of the zero field point depends on the problem being considered. This point can at times be localized into the inner domain of phase 1 and at other times at the periphery domain of phase 2 or even outside volumes V_1 and V_2. The phase boundary is the surface $P(\mathbf{r}_1)$. The functional Ψ for the two-phase system has the form

$$\Psi=\int_{V_1}\rho_1 dV[\mu_1(\mathbf{r})+\varphi_1(\mathbf{r})-\lambda_1]+\int_{V_2}\rho_2 dV'[\mu_2(\mathbf{r}')+\varphi_2(\mathbf{r}')-\lambda_2]+\sigma S, \tag{24}$$

where σ is surface tension, S is interface. The value

$$\varphi_2(\mathbf{r}')=\varphi_2(\mathbf{r}_1)-\int_{\mathbf{r}_1}^{\mathbf{r}'}\nu_2\mathbf{f}_2\cdot d\mathbf{u} \tag{25}$$

is the potential at the point $\mathbf{r}'$ of phase 2. Minimization of the functional (24) with respect to $\delta\mathbf{r}$ and $\delta\mathbf{r}'$ leads to the conditions of equilibrium (1) and (10) for each phase. Moreover, the value λ_1 is equal to $\lambda_1=\mu_1(0)$. Since the full chemical potentials of each phase are constant, we write down the thermodynamical potential of the system

$$\Phi=m_1\mu_1(0)+m_2[\mu_2(\mathbf{r}_1)+\varphi_2(\mathbf{r}_1)]+\sigma S, \tag{26}$$

where m_1, m_2 are phase masses. When minimizing Eq. (20) with respect to m_1 provided there is constancy of the total mass of both phases ($dm_1=-dm_2$), we obtain the condition of equilibrium of the two-phase system in the form

$$\mu_2(\mathbf{r}_1)+\varphi_2(\mathbf{r}_1)=\mu_1(\mathbf{r}_1)+\varphi_1(\mathbf{r}_1)+\frac{\partial(\sigma S)}{\partial m_1}. \tag{27}$$

Assuming that σ does not depend on m_1, after usual transformations the surface term in Eq. (27) can be rewritten as

$$\sigma\left(\frac{\partial S}{\partial m_1}\right)=\sigma\nu_1\left(\frac{1}{R_1}+\frac{1}{R_2}\right), \tag{28}$$

where R_1 and R_2 are the main curvature radii of the interface at the point $\mathbf{r}_1$. Then the formula (26) can be presented as

$$\mu_2(T,P_2(\mathbf{r}_1))+\varphi_2(\mathbf{r}_1)=\mu_1(T,P_1(\mathbf{r}_1))+\varphi_1(r_1), \tag{29}$$

where $P_1(\mathbf{r}_1)$ and $P_2(\mathbf{r}_1)$ are substance pressures at the interface. Their difference causes surface effects and equals

$$P_1(\mathbf{r}_1)-P_2(\mathbf{r}_1)=\sigma\left(\frac{1}{R_1}+\frac{1}{R_2}\right). \tag{30}$$

The formula (29) is the condition of the phase equilibrium in the presence of the external field. If the external field is absent, then Eq. (29) turns into the usual equality of the phase chemical potentials with different pressures due to the curvature of the interface. In the presence of the field, the chemical potentials of the substance phases do not coincide at the phase boundary. The difference of these potentials can be written as

$$\Delta\mu(\mathbf{r}_1)=\varphi_1(\mathbf{r}_1)-\varphi_2(\mathbf{r}_1)=-\int_0^{\mathbf{r}_1}(\nu_1\mathbf{f}_1-\nu_2\mathbf{f}_2)\cdot d\mathbf{u}. \tag{31}$$

Generally the difference (31) is not equal to zero for an arbitrary field. It is equal to zero if the mass densities of the forces acting upon the phases are equal, i.e., $\nu_1\mathbf{f}_1=\nu_2\mathbf{f}_2$. The last equality is valid for a gravitational field. Therefore the gravitational field does not influence the phase equilibrium and we have the ordinary condition of phase equilibrium when the substance chemical potentials of the phases coincide at the phase boundary. At the same time, this difference may not be equal to zero either in an electrical field or in a magnetic field. In this case the field-induced shift of phase equilibrium parameters will occur.

The calculation of $\Delta\mu$ offers a special problem. It is convenient to present the substance chemical potential difference at the phase boundary as an equivalent change of phase 1 chemical potential

$$\int_0^{\mathbf{r}_1}(\nu_1\mathbf{f}_1-\nu_2\mathbf{f}_2)\cdot d\mathbf{u}=\int_{P_1}^{P_1+\tilde{\Pi}}\nu_1 dP. \tag{32}$$

This formula is the definition of the parameter $\tilde{\Pi}$. Using Eq. (32) we can rewrite the phase equilibrium condition (29) as

$$\mu_1(T,P+\Pi)=\mu_2(T,P)=\mu^I, \tag{33}$$

where $\Pi=P_1-P+\tilde{\Pi}$.

So we can see that formally the field influence shows itself as an additional displacement of phase 1 pressure on the value of $\tilde{\Pi}$. We emphasize that this is nothing more than a convenient form of the general condition (29) presentation. Moreover, the equality (33) corresponds to the choice of the phase 2 potential when $\varphi_2=0$ at the phase boundary. The difference of the chemical potentials of phases at the phase boundary is determined by Eq. (29). In this case the value of the phase 2 chemical potential at the phase boundary coincides with the value of the full chemical potential of the system. The latter is determined with the precision of an arbitrary constant.

Thus there is a shift of phase equilibrium parameters due to the presence of an external field described by Eqs. (29)–(33). (We emphasize that the free energy functional is used in [4] for the calculation of the work of new phase nucleus formation in the presence of a magnetic field. However, the magnetic field energy change connected with the nucleus formation for a particular size is only minimized. Such an approach does not give the necessary equilibrium conditions for the current-carrying conductor in its own magnetic field and leads to a number of erroneous conclusions.) There is a need to add Eqs. (28)–(32) to equations of state at the phase boundary and at the point phase 1 with the pressure $P+\Pi$.

$$P+\Pi=f(T,\nu_1), \quad P=f(T,\nu_2), \tag{34}$$

where ν_1 is the specific volume of phase 1 at the points with pressure $P+\Pi$. The system of equations (28)–(33) is determined by the substance densities at the phase boundary if the parameter Π is given.

We see from Eq. (33) that the field-induced phase equilibrium leads to the equality of phase chemical potentials with different pressures. Let us investigate the possibility of such equilibrium when parameter Π is given. Differentiating equality (33), we obtain

$$\frac{\partial\nu_2}{\partial\nu_1}=\frac{\nu_1\partial P_1/\partial\nu_1}{\nu_2\partial P_2/\partial\nu_2}. \tag{35}$$

The value of the derivative $\partial\nu_2/\partial\nu_1$ is equal to zero or infinity at the spinodal points where $\partial P/\partial\nu=0$. These values are not compatible with the mass conservation law. As a result, a two-phase system in the presence of an external field becomes unstable at the spinodal points and a field-induced phase transition may occur.

Now let us use the van der Waals equation to research a field-induced matter state in greater detail.

V. INVESTIGATION OF PHASE EQUILIBRIUM ON BASE VAN DER WAALS EQUATION

The field-induced phase equilibrium problem allows exact solution if the van der Waals equation is used. In reduced units, this equation is

$$P'=\frac{8T'}{3}\frac{1}{\nu'-1/3}-\frac{3}{\nu'^2}. \tag{36}$$

In Eq. (35) the values are $P'=P/P_c$, $T'=T/T_c$, $\nu'=\nu/\nu_c$, where P_c, T_c, ν_c are critical pressure, temperature, and specific volume. Below the primes will be omitted. Using Eq. (34), the temperature can be expressed as a function of the phase densities

$$T=\frac{1}{8}(\rho_1-\rho_2)(3-\rho_1)(3-\rho_2)\left[1-\frac{\Pi}{3(\rho_1^2-\rho_2^2)}\right]. \tag{37}$$

The pressure can be expressed as a function of the phase densities too. Then we obtain

$$P+\Pi=\rho_2\rho_1(3-\rho_2+\rho_1)-\frac{\Pi(3-\rho_2)\rho_1}{3(\rho_1-\rho_2)},\tag{38}$$

$$P=\rho_2\rho_1(3-\rho_2-\rho_1)-\frac{\Pi(3-\rho_1)\rho_2}{3(\rho_1-\rho_2)}.\tag{39}$$

The system (37)–(39) is determined by the temperature and pressures via the phase densities. The value Π is the parameter. In particular, if $\Pi=0$ and all densities are equal to unity, then the system (36)–(38) gives correct values of the critical temperature $T=1$ and pressure $P=1$. Equation (33) will be one more equation to add to the system (37)–(39). To obtain it, we write the free energy in van der Waals approach,

$$f=\frac{8T}{3}\ln\left(\frac{\varphi(T)}{\nu-1/3}\right)-\frac{3}{\nu},\tag{40}$$

where $\varphi(T)$ is a function of temperature. Using Eqs. (40), (36), and the thermodynamical relation $\mu=f+P\nu$, we can write the phase equilibrium condition (33) in the form

$$\frac{8T}{3}\ln\left(\frac{\nu_2-1}{\nu_1-1}\right)-(\rho_1-\rho_2)\left[6-\frac{8T}{(3-\rho_1)(3-\rho_2)}\right]=0.\tag{41}$$

Equations (36), (37), (39), and (40) permit us to find the densities, temperature, and pressure when the parameter Π has the same value.

First of all, we calculate the limit value of the parameter Π' allowing the equality of the phase chemical potentials with different pressures. Here one of the phases reaches its spinodal state where $(\partial P/\partial \nu)_T=0$. Using Eq. (35) to calculate this derivative we obtain that the temperature and pressure at the spinodal line have to satisfy the equations

$$P_{\mathrm{sp}}=\rho^2(3-2\rho),\quad T_{\mathrm{sp}}=\rho(3-\rho)^2/4.\tag{42}$$

Let us have $\Pi>0$. Setting temperature (37) equal to the temperature determined by the expression (41), we find the value

$$\Pi'=\frac{3(\rho_1-\rho_2)}{3-\rho_1}\,(\rho_1^2+\rho_1\rho_2+3\rho_2-3\rho_1-2\rho_2^2).\tag{43}$$

Substituting expression (43) in Eq. (37), from Eq. (41) we obtain the equation containing only the densities ρ_1 and ρ_2. Solving this equation numerically and using the expressions (37) and (43) we find the values T and Π'. The dependence Π' versus temperature is shown in Fig. 2. The value Π' tends to zero when the temperature is close to the critical point. This value grows when the temperature decreases.

A similar procedure gives the following expression for the limit negative value Π' when the higher density phase reaches its spinodal state:

$$\Pi'=\frac{3(\rho_1-\rho_2)}{3-\rho_2}\,(2\rho_1^2+3\rho_2-\rho_2^2-\rho_1\rho_2-3\rho_1).\tag{44}$$

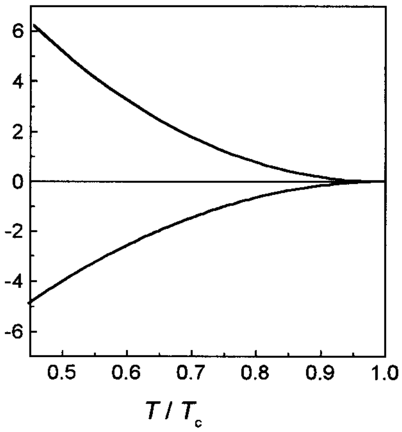

FIG. 2. Dependencies of the limit pressures Π' on reduced temperatures obtained on the basis of the van der Waals equation.

This dependence is also depicted in Fig. 2. The area between the limit positive and limit negative values of Π' determines the domain where the field-induced two-phase system may exist as stable.

The phase density (Fig. 3) and phase pressure (Fig. 4)

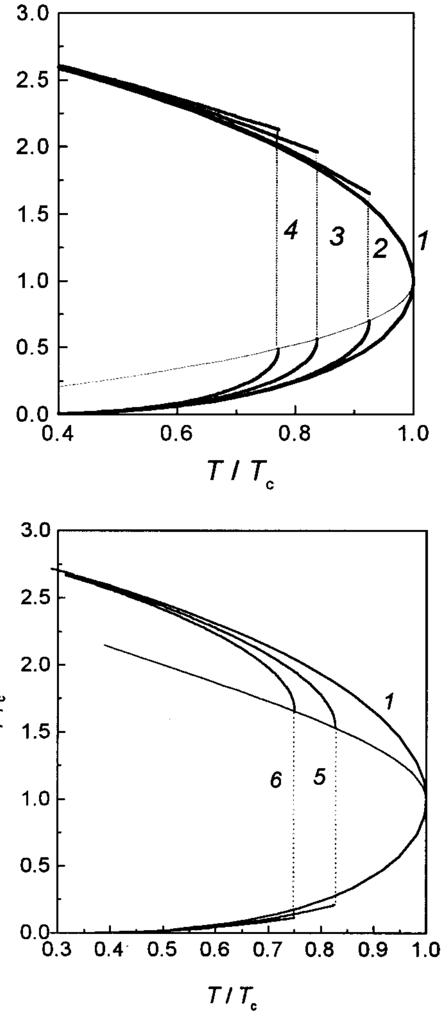

FIG. 3. Phase reduced density dependencies versus reduced temperature with the different values of the parameter Π: 1—$\Pi=0$; 2—0.1; 3—0.5; 4—1; 5—(−0.5); 6—(−1). The points at the limit temperature values are connected by short dotted lines.

dependencies in Figs. 3 and 4 correspond to fixed values of parameter $\Pi > 0$ (a) and $\Pi < 0$ (b). Curves 1 with $\Pi = 0$ correspond to the absence of field. Curves 2–4 correspond to increasing positive values of Π, curves 5 and 6 to increasing negative values of Π.

Two density curves are given for every value of Π. The lower one corresponds to the lower density phase at the phase boundary with pressure P, the upper one to the higher density phase at the point with pressure $P + \Pi$. The curves converge to curves for the case without field when the temperature becomes lower. For the positive values of Π the deviation of curves 2–4 from curve 1 takes place in the domain of higher densities as the temperature decreases. For negative values deviation takes place in the domain of lower densities. The deviates are the largest when the temperature reaches the value which corresponds to the liquid or gas in its spinodal state (see Figs. 3 and 4 for the spinodal lines). The field-induced phase equilibrium is impossible when the temperature exceeds this value. There is a limit temperature for every value of Π when the curves break. This limit temperature decreases when the absolute values of Π grow. The phase pressure curve corresponds to every value of Π in Fig. 4. As we can see from Fig. 4, the phase boundary pressures converge to pressure without the field when the temperature decreases. The curves break when the phase pressures reach the values corresponding to liquid or gas spinodal state.

Equality of the chemical potentials (32) can be presented as an equation $F(T,\Pi,\rho) = 0$. This equation gives a surface in the plane of variables T-Π (Fig. 5). The top part of this surface relates to the liquid state. The liquid state domain is limited by the liquid spinodal curve 2. The lower part of this surface relates to the gas state. It is restricted by the gas spinodal curve 3. The liquid and gas spinodals come together at the critical point (CP). The part of the surface between liquid 2 and gas 3 spinodals corresponds to unstable states. Projection of the liquid spinodal (curve CP$-G_2$) on the gas state surface restricts the domain of gas states which can be in equilibrium with liquid in the presence of the field. The same is true of the gas spinodal projection on the liquid state surface (curve CP$-L_1$). The plane curve 1 in this picture corresponds to the ordinary binodal without the field ($\Pi = 0$). In the presence of the field instead of the plane line we have the surface of field-induced two-phase states which is restricted by the liquid and gas spinodals and their projections.

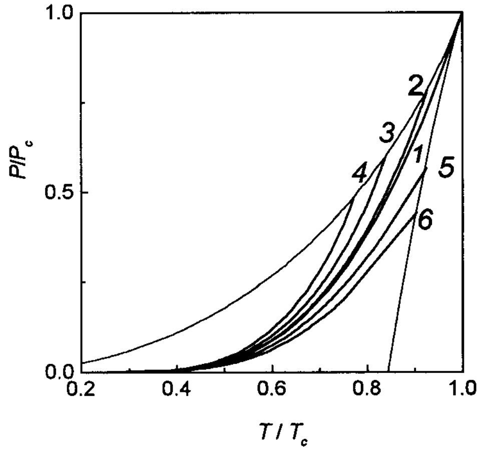

FIG. 4. Phase reduced pressure dependencies on reduced temperature with different values of the parameter Π: 1—$\Pi = 0$; 2—0.1; 3—0.5; 4—1; 5—(-0.5); 6—(-1).

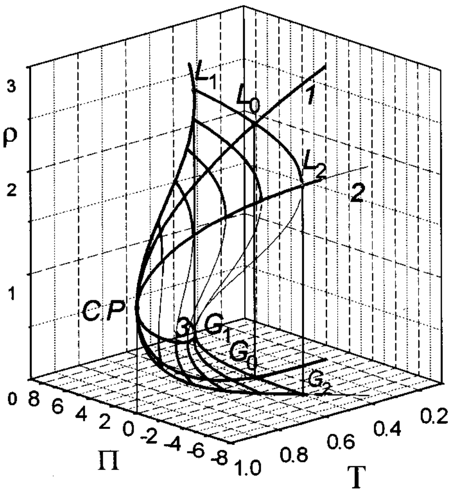

FIG. 5. Surface of reduced densities for field-induced two-phase states on reduced temperature and parameter Π. The upper part of this surface is related to liquid state, the lower one to the gas state. The space curves: (1) is the binodal in the absence of field ($\Pi = 0$), (2) is the gas spinodal, (3) is the liquid spinodal. CP is the critical point. Five curves with $T = \text{const}$ are also shown. The parts of these curves shown as thin lines are related to unstable states.

It should be noted that the liquid and gas spinodal curves form a critical line. This line is singular for substance thermodynamical functions just as an ordinary critical point is singular in the absence of the field [1]. The field-induced two-phase system becomes unstable when one of the phases reaches the critical line.

For every couple of values T-Π we can find the liquid ρ_1 and gas ρ_2 densities belonging to the upper and lower parts of the surface. These densities characterize the two-phase state with given values T-Π. The gas density ρ_2 belongs to the point at the phase boundary with the pressure P. The liquid density ρ_1 corresponds to the phase 1 state with the pressure $P + \Pi$. The five S-shaped curves $T = \text{const}$ are also shown in this picture. Consider, for example, the isotherm with $T = 0.5$. The top part of this curve $L_1 L_2$ is related to the liquid state, the lower part $G_1 G_2$ to the gas state; the states lying between points L_2 and G_1 are unstable. The points L_0 and G_0 determine the values of phase densities without field ($\Pi = 0$). The points L_1 and G_1 give the phase densities at the greatest possible positive value of parameter Π. The gas state G_1 in this case lies on the gas spinodal 3. The points L_2 and G_2 correspond to the limit possible two-phase state with the negative value of parameter Π. The point L_2 lies on the liquid spinodal in this case.

VI. PHASE EQUILIBRIUM IN LIQUID CURRENT-CARRYING CONDUCTOR AND LIQUID DIELECTRIC IN THE PRESENCE OF FIELD

Let us use the results obtained above to investigate a liquid-gas equilibrium for a liquid current-carrying conductor. We suggest that this conductor is surrounded by its own vapor and is in equilibrium with it under certain field parameters. Let the interface be a cylindrical surface. We neglect the effects induced by the curvature of the surface, so the phase pressures coincide at the interface. Besides, the magnetic field created by the current has practically no influence on the gas state. So the full chemical potential coincides with the chemical potential of the gas phase.

As before, it is very convenient to use $\mu(P)$ dependence [Fig. 1(a)]. The straight line $\mu^I = \text{const}$ giving the full chemical potential value intersects the liquid branch SA at the point A with pressure $P+\Pi$ corresponding to the zero field point. The intersection point C of this line with the gas branch SE determines the gas state at the phase boundary with pressure P. The point B corresponds to liquid state at this pressure. The phases can coexist along a planar interface at this pressure. The points B and C give the values of the liquid chemical potential μ_1 and gas chemical potential μ_2 at the phase boundary with the pressure P and with $\mu_1 - \mu_2 = \Delta\mu$.

The state of the substance changes in the following way. The liquid phase state changes along the AB branch till the value P at the phase boundary. There is the chemical potential jump at the point B to the value at the point C of the gas branch. The point C corresponds to gas state (the pressure changes due to the external field in the gas phase are negligible).

In the case being considered the liquid in the presence of the field is in equilibrium with the supersaturated vapor. (This conclusion differs from the one made by the authors of [4–6]. According to [4–6], the thermodynamical stability fails due to the attainment of the limit superheated state by the liquid phase. From what has been said, it might be assumed that this is impossible for the compressive forces.) The latter now becomes stable. So we see that in the presence of the field, metastable states may be stable.

Notice that the pressure at the conductor axis becomes higher if the magnetic field strength increases. Therefore the value of the full chemical potential μ^l increases too. As is seen from Fig. 1(a), there is the same limit value of the pressure and corresponding value of liquid chemical potential in which the equilibrium can still exist. This happens when the point C reaches gas spinodal state at the point E with the pressure P_{sp}. The dotted lines in Fig. 1(a) correspond to this situation. The equilibrium of the two-phase system in a given geometry is made impossible. The two-phase system has to change its state. In this case the transfer to a new state is accomplished by expansion of the conductor and formation of liquid drops. The final equilibrium state may be only a dispersion liquid-vapor system practically without current. The chemical potential and pressure of the liquid in this state will be equal to the chemical potential and pressure of the liquid at the phase boundary before decay, $P_{\text{sp}}(T)$.

The chemical potentials of a drop and vapor which is in equilibrium with this drop are equal to each other and to the chemical potential of the liquid before decay. The pressure of the vapor can be found from the relation

$$\int_{P_1}^{P_{\text{sp}}} \nu_1 dP = \int_{P_s}^{P_G} \nu_2 dP. \tag{45}$$

From the expression (45) it follows that $P_G - P_s \approx (P_{\text{sp}} - P_s)\nu_1/\nu_2 \ll P_s$. The inequality is valid far from the critical point, where $\nu_1/\nu_2 \ll 1$. As a result $P_G \sim P_s$. The pressure difference between the liquid and the gas is compensated by the surface effects. The typical drop size can be found from the Laplace relation

$$a = \frac{2\sigma(T)}{P_{\text{sp}} - P_G}, \tag{46}$$

where $\sigma(T)$ is the surface tension. The drop numbers per unit of cylinder length are given by the expression

$$N = 2\pi r_1^2 \Big/ \frac{4\pi}{3} a^3. \tag{47}$$

The chemical potential difference between liquid and gas existing before transition is partially expended on the drop formation and partially converted into kinetic energy of the drops. Writing the corresponding energy balance, we obtain

$$2\pi r_l^2 \Delta\mu = N\left(4\pi r^2\sigma + \frac{4\pi\rho_1}{3} r^3 \frac{U^2}{2}\right), \tag{48}$$

where U is the expansion velocity. Knowing that $\Delta\mu \sim \Pi/\rho_1$ and using expressions (46), (47), we obtain from the expression (48) that

$$U = \sqrt{2[\Pi - 3(P_{\text{sp}} - P_s)/2]/\rho_1}. \tag{49}$$

The estimation on the basis of the van der Waals equation shows that $P_c - P_s \sim 0.2P_c$ at the range of temperatures $\sim (0.5–0.6)T_c$. Using this condition, we obtain that the values for the pressure drop are $\Pi \sim P_c \sim 8000$ atm and $\sigma \sim 100$ dyn/cm. These values are typical for such liquid metals as Al or Cu. From Eq. (46) we obtain that the typical drop size is $\sim 10^{-7}–10^{-6}$ cm, and from Eq. (48) we have that the typical velocity of expansion is equal to hundreds of meters per second. Orders of magnitude of these values correspond with those of experimental data [7,9].

Consider now a long cylindrical capacitor. This capacitor is filled with a dielectric liquid. As is seen from Fig. 1(b), a dielectric liquid in an electrical field cannot be in equilibrium with its own vapor along a planar interface due to the existing pressure drop between the points A and C. The phase coexistence is possible only when vapor bubbles are inside the liquid. Let us assume that the vapor nucleus is formed at a distance r from the axis. The electrical field has no influence on the gas state. Assume that $r \gg a$, where a is the characteristic transversal size of a nucleus. The minimum of the full thermodynamic potential of the two-phase system with $\mu = \text{const}$ and $T = \text{const}$ determines a minimal value for vapor bubble work formation. In long dielectric the minimum of the absolute value of the bubble formation work is attained for a thin long bubble of length $b \gg a$ oriented in the direction of the dielectric axis. Thus the bubble formation work per unit of length of the capacitor W is given by the expression

$$W = 2\pi\sigma a - \pi a^2[P_S - P(r)], \tag{50}$$

where P_S is gas pressure at the zero field point S. The critical dimension of a nucleus can be determined from the condition $\partial W/\partial a = 0$. The latter condition and formula (50) yield the equilibrium size of the bubble and the value of its minimal formation work, the latter being of the form

$$W = \pi \frac{\sigma^2}{(P_S - P)}. \tag{51}$$

This work will be minimal when the difference $P_S - P$ is maximal, i.e., at the surface of the inner electrode. Using expressions (22) and (23) we obtain the following expression for the minimal nucleus formation work in the presence of an electrical field:

$$W = \frac{8\pi^2\sigma^2}{E^2(r_0)\varepsilon(\varepsilon-1)}. \tag{52}$$

The size of the bubbles can be found from the relation

$$a = \frac{8\pi^2\sigma}{E^2(r_0)\varepsilon(\varepsilon-1)}. \tag{53}$$

From Eqs. (51) and (52) it follows that the work of the nucleus formation is minimal where the externally applied electric field is maximal. This is the general conclusion independent of a system geometry. So we obtain the explanation of the mechanism of vapor bubble formation near an electrode.

Let us compare the values of bubble size which follow from the expression (52) with ones from [12] obtained as a result of experimental investigation of prebreakdown phenomena in nitrobenzol. Using the values $\varepsilon = 36.4$ and $\sigma = 43.9$ dyn/cm for nitrobenzol and taking from [12] the characteristic value of electrical field strength near the electrode $E(r_0) = 5 \times 10^5$ V/cm, we obtain from Eq. (52) that the typical bubble size is equal to $a \sim 10^{-5}$ cm. This value correlates well with the data from [12].

It should be pointed out that the reasons for the violation of phase uniformity under pulse voltage and mechanisms of vapor bubble appearance up to now were obscure. It is well known that mechanisms of vapor bubble formation in dielectric liquid were the ''bottleneck'' in prebreakdown phenomena. There were a few previously suggested different hypotheses associated with the explanation of bubble formation near an electrode [11,12]. Now we can see that this effect is a result of the phase equilibrium shift due to the presence of an electrical field.

VII. CONCLUSION

The preceding analysis demonstrates that the conditions of phase equilibrium substantially change when external nonuniform fields lead to appearance of mass forces having different effect on the phases. A field-induced domain of stable states of a substance is extended up to corresponding spinodal curves. The domain of temperatures, pressures, and phase densities, corresponding to thermodynamic equilibrium of the two-phase system in the presence of a field, is extended too. There is a loss of stability of the two-phase system when one of the phases reaches its spinodal state. A configuration phase transition of the two-phase system into a dispersion state occurs in this case. The phase spinodal lines form the critical line of these transitions. The critical point belongs to the line in the absence of the field.

We also demonstrated the occurrence of several peculiar effects which accompany phase transitions in the presence of an external nonuniform field. The first of them is connected with the formation of the domain of instability of both phases in a current-carrying conductor leading to sharp expansion of the conductor and its transformation into a fine dispersion mixture of liquid drops in vapor. This mechanism can be the reason for electrical explosion of conductors, in the so-called fast regimes [7–9].

The second effect occurs in a liquid dielectric penetrated by an electrical field. The appearance of vapor bubbles in the domain of the high value of this field is caused by the change of the phase equilibrium conditions due to the field.

Many of the aspects of these problems have direct similarity to the problem of phase transition accompanied by melting processes, chemical reaction, and polymerization in the presence of the external field.

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