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THERMODYNAMIC INSTABILITY OF COMPOUND AND FORMATION OF NANOSIZED PARTICLES NEARBY THE CRITICAL POINT OF PHASE GENERATING MEDIA

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An analysis is presented for the possibility of metal dispersion, driven by the development of thermodynamic instabilities of its physical state in the vicinity of the critical point in an electrical explosion of conductors (EEC). A new geometrical configuration of conductors, arranged in a thin-walled cylindrical shell on a rigid dielectric cylinder with axially guided, internal return current is proposed. This constrains the part played by instabilities of non-thermodynamic origin and provides the required power density distributed uniformly in the conductor. For metals of the aluminum and copper type, the rates of heating have been estimated, which ensure homogeneous vaporization as the key factor governing the mechanism of liquid metal dispersion during the development of thermodynamic instabilities in the material. Directions in which magnetohydrodynamic (MHD) modeling of high-power electrical discharge in EEC should be pursued in the development of optimal regimes for energy injection into the conductor are outlined. Processes governing condensation of explosion products in an aqueous environment in the case of the particles being electrically charged and involved in chemical interaction with supercritical fluids have been analyzed. The method of synthesis proposed will eventually permit the production of oxide nanoparticles which differ from nanoparticles of the same oxides synthesized in electrical discharge in air and other oxygen-containing gas media, as well as in hydrothermal synthesis employed in its classical methodological implementation.

Keywords: thermodynamic instability, critical state, phase explosion, metal dispersion, nanoparticles, oxides, electrical explosion of conductors, supercritical fluid.

Contents

1. Introduction

Nanoparticles can form by condensation or deposition from a matrix medium in close to thermodynamically equilibrium conditions, or by dispersion from consolidated material in nonequilibrium thermodynamic processes driven by the application of powerful external energy fluxes. The latter method increases substantially the energy contained in the nanoparticles, which can account for their unique catalytic, sorption and other properties, as well as for the observed threshold phenomena. Of particular interest for the field of dispersion are extremely fast (close to non-equilibrium) thermodynamic processes involved in high rate phase transitions of a material through the sequence of “solid—liquid—gaseous” aggregate states, including transitions through the critical point. It is the only extremum in the equilibrium curves of the phase diagram, which belong simultaneously to the liquid and vapor. Approaching it is accompanied by substantial growth of density fluctuations in microvolumes of the material compared with the regions where metastable states exist, adjoining the curves describing equilibrium of two phases. For strong enough energy influxes, density fluctuations can become self-organized to the extent where material can lose its thermodynamic stability, being replaced by assembly of dissipative microstructures. They can serve as pre-nuclei for the subsequent formation of dispersed particles during the disruption of the starting consolidated materials, and transfer a part of the energy to the material of the environmental medium. This predetermines the possibility, in principle, of producing particles of an extremely small size, down to a few nanometers, to be compared with the results obtained by application of other well-known mechanisms of dispersion, e.g., mechanical or thermal action, for example, impact crushing of a solid, its melting and breakup of the liquid into drops, vaporization and subsequent deposition from the vapor phase.

Because the size and number of particles depend on the rates of influx and dissipation of energy in the material under dispersion and its environment, methods providing high power of the incoming energy fluxes become particularly important. They should be adequate to the conditions required and the mechanisms involved in development of thermodynamic instability in the material in question, as well as to its characteristic dissipation channels and of the material of the environment. Under laboratory conditions, such means for energy input into a material can be provided by high-power pulsed lasers, charged particle beams and heavy-current electrical discharges. Heavy current electrical discharges offer certain advantages in their potential to generate the desired energy density of particle beams in volumes larger than those obtainable with lasers and corpuscular beams. Electric discharges providing a high density for the discharge current, $J > 10^6$ A/cm^2, in a material with metallic electrical conductivity in the initial state have acquired the name “electric explosion”. A number of researchers, including the authors of the present paper, believe the electric explosion of conductors to rank among the most energy-efficient methods for the preparation of nanosized powders of metals and of their chemical compounds.

Although electrical explosions have been known for more than 200 years [1,2], systematic studies of them have been undertaken already for about fifty years at various research centers [3-54]. Despite this study, a number of points still remain to be clarified. First, this bears on the conditions and mechanisms driving the instabilities of material, which culminate in destruction of the conductor and formation of nanoparticles, allowing for the interrelation among the processes that are at work both in the metal proper and in its environment [34,45,46,52,55,56].

The present work offers an analysis of these points, drawing from the available literature data, as well as from our original research.

2. Conditions and the characteristic pattern of development of instabilities of material in an electric explosion of conductors

In the case of the comparatively slow Joule heating of a metal by electric current, the most significant factors involved in destruction of a wire conductor in the process of variation of its physical state are the forces of surface tension and waist and convective MHD instabilities [4-7,9,15,17,18,20,21,30,32,33,41]. One more possible factor is development of the barocapillary instability [57], which arises in the intense vaporization of material from the surface of the molten metal and turbulization of vapor jets, destroying this surface. Such an instability can be amplified by the positive feedback coupling of the vapor recoil reaction with the depth of piercing of the molten metal surface. Each of these processes has its characteristic time scale. Indeed, the time of action of capillary forces is on the order of $t_k = (\rho_{liq} r^3/\sigma)^{0.5}$, $t_c = \mu_0 r^2/\rho_e$, and the time taken up by development of magnetodynamic instabilities of the neck type $-t_m = (2\pi\rho_{liq} r^2/H_0^2)^{0.5}$ [9,15,33,58,59]. Here, ρ_{liq} – is the density of the metal in its liquid state, r is the conductor radius, σ is the surface tension coefficient, μ_0 is the magnetic constant, ρ_e is the electrical resistivity of the metal, $H_0 = I/r$, and I is the current through the conductor. When a metal is subjected to heating by current for a time longer than the characteristic relaxation time of a material required to reach the equilibrium thermodynamic state (estimates [60-62] yield for it $1-10$ ns far from the critical point), the processes involved in the development of the above instabilities may be considered as being in thermodynamic equilibrium. The effect of each of them becomes manifest when their characteristic metal heating time scales become equal. It can be estimated in terms of the specific current action integral $t = h/I^2$, where $h = \int_0^t I^2 dt$ – is the integral value of the current action required to heat the metal within the range over which the corresponding process extends. The relative part played by each of these instabilities can vary depending on the particular effect of the environment (rarefied gas or a dense liquid) in which the electric explosion of the conductor takes place. The actual size of the particles formed may depend on the uniformity of the heating (current density), level of the energy input, radius of the wire, its initial microstructure, characteristics of the environment (density, chemical activity, electric strength). On the whole, however, the characteristic size of the "drops" formed during the development of such instabilities turns out to be on the order of the diameter of the wire to be exploded (a few hundred to thousands of nanometers) [5,31–33,50,63,64].

Particles of substantially smaller dimensions (down to a few nanometers) can be prepared by noticeably increasing the power input into the conductor. Under the conditions providing fast enough Joule heating in a time shorter than the characteristic time required for relaxation to the equilibrium thermodynamic state, the part played by the above instabilities becomes of secondary importance, with the mechanism of dispersion stemming from violation of thermodynamic stability of the state of material becoming dominant [35,38,44,49,55,56,65,66]. In the course of intense heating, the temperature of the molten metal can rise above the boiling point at a given pressure above its surface, culminating in a transition of the system into the region of metastable biphasic state, with a fast approach to the line of the highest possible overheating (spinodal) with increasing heating rate (Fig. 1).

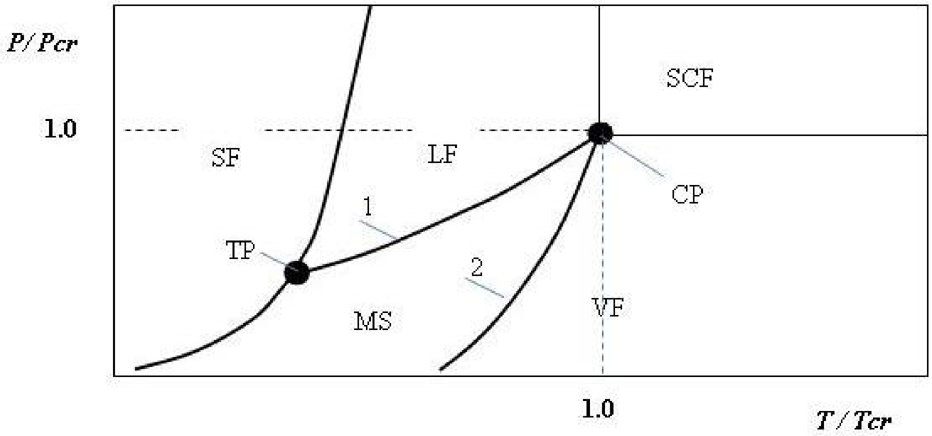

FIG. 1. Typical diagram of the phase state of a material: 1 - binodal (liquid-vapor phase equilibrium curve, or saturation line), 2 - spinodal (curve of maximum possible liquid phase overheating). Notes: SF - Solid Phase; LF - Liquid Phase; VF - Vapor (Gas) Phase; MS - Metastable Sate; SCF - Supercritical Fluid; TP - Triple Point; CP - Critical Point

This brings about reduction of the time the system spends in this state, uncertainty in the thermodynamic parameters and, as a consequence, tendency to spontaneous relaxation to the equilibrium boundary (bimodal) of the metastable region through "explosive" boiling-up of the metal paralleled by a sharp growth in homogeneous vapor bubble formation. The mechanisms governing such a relaxation depend on the properties of the material and conditions of its heating, of which the most important is the specific power of energy input into the material and the pressure (density) of the environmental medium. For instance, for water and organic liquids the critical size of a vapor nucleus whose probability of further growth is higher than that of collapse, just as the magnitude of the Gibbs free energy needed for its formation, in overheating turns out to be lower than those on the bimodal under conditions of thermodynamic equilibrium. Indeed, with overheating increased by only 1 K, the average time taken by a critical nucleus to form may drop by three to four orders of magnitude, with the rate of growth of a vapor bubble of above critical size exhibiting fast rise [35,38,50]. Intense nucleation involving the formation of multiple vapor bubbles in a heavily overheated liquid close to the spinodal initiates "explosive" boiling-up ("phase explosion"), with eventual breakup into a mixture of vapor and droplets [35,38,56].

The possibility of using phase explosion of a liquid metal for preparation of metal powders has been a subject of intense discussion in literature, but without a comprehensive analysis of the dependence of the particle size obtained for particular energy input conditions and the properties of the environmental medium. Significantly, Joule heating of a metal conductor by current gives rise to a number of specific effects, complicating the mechanism of explosive boiling. This comes from the need to consider the effect exerted by the electric and magnetic fields on the work of critical vapor nucleus formation and the frequency (rate) of homogeneous formation of vapor bubble nuclei. Another specific feature of Joule heating of conductors was found to be the nonuniformity of the pressure field inside the metal initiated by the appearance of the magnetic component, a factor which complicates markedly the overall calculation of the process [33,48,56].

3. A possible scenario of development of a phase explosion in a liquid metal and of formation of nanosized particles of a new phase

As previously mentioned, in the case of comparatively slow Joule heating with a not too close approach to the critical temperature of the metal, $T < (0.8-0.9)T_c$, and in the case of a low-density, chemically-inert environmental medium (rarefied gas), the electric explosion of a conductor may acquire the pattern of explosive decomposition of a molten and boiling-up metal, as a result of development of the above-mentioned instabilities of non-thermodynamic origin. The characteristic size of the "droplets" formed in such an explosion turns out to be $10^2 - 10^3$ nm, depending on the working conditions, i.e. on the order of the diameter of the wire to be exploded.

To reduce the size of dispersed particles, one has to constrain the part played by the non-thermodynamic mechanisms involved in destruction of the metal in the course of varying the physical state of the exploding conductor, so as to ensure its transition to the region of the heaviest possible nonequilibrium metastable state with the maximum possible overheating and fast approach to the critical point through "explosive" boiling-up initiating homogenous vapor formation. This is favored by the magnetic field generated in the liquid metal by the current flowing through it. Its action increases the work and the time passing in waiting for the appearance of a vapor nucleus, which initiates the process of homogeneous vapor formation. After this, the size of the critical nucleus for the liquid (molten) metal will be larger, for the same overheating, than that for water and organic liquids. As a result, spontaneous nucleus formation of vapor bubbles in liquid metals is not reached even under intense overheatings, so that metals can be heated very close to the spinodal and, hence, to the critical temperature, before phase explosion occurs. Besides, a liquid metal may contain centers of heterogeneous boiling-up, which raise significantly the specific metal heating power needed to reach the limiting metastable state defined by the spinodal. It should be stressed, that as a result of the stabilizing action of electric current on the thermodynamic state of a liquid metal, spontaneous relaxation of metastable states may start for most metals only at temperatures $T \geqslant (0.8-0.9)T_c$, where T_c is the critical temperature of the metal.

It is the possibility of overheating a liquid metal close to the critical temperature at an adequately high energy input into the conductor that the proposed scenario of new phase formation rests. In these conditions, in the vicinity of the critical point fluctuations of the parameters of state of the material, primarily of the density and entropy, grow substantially, just as the radius of their interaction (correlation), by switching from the exponential law of decrease far from the critical point to the inverse proportionality law close to it [67]. The relation between the probability of system parameter fluctuations and the magnitude of the fluctuations themselves can be defined by the Einstein relation $W \sim \exp[-(\Delta T \Delta S + \Delta\mu \Delta N)/2T]$, which is essentially an outgrowth of the Boltzmann principle relating the probability of an arbitrary state of a system to its total entropy S_Π in the form $W \sim \exp(\Delta S_\Pi)$. Increase of density gradients (density fluctuations) in small volumes of an overheated liquid culminates in the loss of thermodynamic stability of the material and nucleation of vapor bubbles by fluctuations. The material takes on an opalescent, finely dispersed, light-scattering structure, which may be considered as a "gas of liquid drops" [68-70]. The characteristic size of these "drops" (correlation radius) increases, and the magnitude of the density gradients needed for fluctuation-based nucleation decreases as one approaches the critical point. Estimates based on various models of the critical state [50] suggest that for metals, the size of these drops can vary from a few to several tens of nanometers. At temperatures $T \approx (0.8 - 0.9)T_c$, defining the boundary at which the critical point still can be reached, the size of the liquid drops is on the order of $10 - 30$ nm. Realization of the corresponding conditions rests on the possibility of providing a high enough specific heating power combined with limiting metal expansion. Estimates of the heating power Q_V required to reach this goal yield $Q_V \geqslant 1$ TW/cm^3. Such power densities can provide electric current $J > 10^8$ A/cm^2 flowing through a wire with diameter $d = 0.1$ mm. These estimates were made under the assumption that metal expansion is limited by the local sound velocity and occurs along the bimodal, with the interpolation equation of the Van-der-Waals type used as the equation of state [33]. Additional possibilities for attaining optimum conditions of nanosized dispersion are considered below.

4. Specific features in modeling of local characteristics of phase-forming processes and media

The rich variety of the complex physical and physico-chemical processes involved in an electric explosion of metal conductors in a chemically active water medium accounts for the surprisingly large number of local characteristics required for evaluation of the conditions optimal for dispersion of a metal, a situation stemming from the development of thermodynamic instabilities showing up in its physical state in the vicinity of the critical point. This program is of considerable scientific and practical significance for the field of present-day nanotechnologies, including various aspects of development of adequate physical models, primarily in description of the variations in the state of material within a broad range of parameters, from the triple point to formation of supercritical fluids. The specific choice of the equations of state and of the dependence of transfer coefficients for dissipative processes on density and temperature contribute in more than one respect to the calculated characteristics of heating and subsequent explosion of an electric conductor.

4.1. Statistical modeling of critical phenomena in the close environment of the critical point. Scaling invariance

For more than 350 years, studies aimed at establishing the interrelation among the parameters of state of material, thousands of other publications on this subject have appeared, with many of them having gained recognition [71]. These studies were initiated by R. Boyle (1662) in experiments with gases. Kanjr (1822), M. Faraday (1823) and T. Endres (1869) extended them to the region of phase transitions, "liquid–vapor" critical point and supercritical fluids. Van der Waals (1873) provided theoretical generalization to the available experimental data with the use of an extended phenomenological model of an ideal gas by Clapeyron (1834), in which molecular attraction and repulsion at close distances were included in a simple form. Further systematization was provided by the physical theory of L. D. Landau (1964) in terms of the mean field approximation approach, which described supercritical phase transitions of the system as well [72]. No convenient equation for a physically adequate description of the state of matter over a sizable range of parameters, including phase transitions and the critical point, has, however, been derived, either in the context of the classical mean-field approach or with inclusion of fluctuation-induced deviations through introduction of small corrections into the expansion of free energy $F(T,V)$ in powers of $\nu = (V - V_c)/V_c$ and $\tau = \tau = (|\mathrm{T} - \mathrm{T_c}|)/\mathrm{T_c}$ relative to the critical point [73].

The idea of “scaling invariance (scaling)” involving the characterization of thermodynamic potentials through generalized homogeneous functions of nonintegral (fractional) order with respect to their fields was found to be universal enough for solution of this problem. It was advanced in the 1960’s, almost simultaneously, by Bakengem, Widm adanff Patashansky [74-79] for explanation of the experimentally revealed anomalous growth of large-scale fluctuations, as well as of the singular pattern of behavior followed by a number of thermodynamic functions close to the critical point. This idea was subsequently extended to cover description of attendant kinetic phenomena. Among them are the increase of the time of thermal relaxation, slowing down of the mutual diffusion of substances close to the critical points of the solutions, variation of the pattern of Brownian motion, decrease of the coefficients of thermal diffusivity close to the critical point of a pure liquid, the anomalously high absorption of ultrasonic vibrations, critical opalescence and others [68-70]. Significantly, kinetic phenomena occurring close to the critical point are assigned to the existence of a characteristic frequency, expressed in terms of the equilibrium radius of interaction of large-scale fluctuations (correlation radius).

The similarity of the critical phenomena observed in objects of different nature suggests the possibility of unified description of the interrelation of certain physical quantities (order parameters) in the vicinity of the critical point with a simple power function, for instance, reduced temperature $\tau = (T - T_c)/T_c$, or some other reduced parameters of similar type, $P_j(\tau) = B_j \tau^{-\delta j}$, where B_j is a numerical coefficient, and δ_j is the critical index of the quantity P_j. In particular, the asymptotic behavior of the susceptibility $\partial\rho/\partial P$, density $\Delta\rho = \rho - \rho_c$, correlation radius r_c (a quantity approaching in its sense the average size of a fluctuation), specific entropy S, heat capacity C_V, C_P and other parameters in pure liquids, concentration y and chemical potential μ in solutions are expressed with unified temperature dependences:

$$\partial\rho/\partial P, \partial x/\partial\mu \sim \tau^{-\gamma}; \quad C_V, C_P \sim \tau^{-\alpha}; \quad (\rho - \rho_c), (S - S_c), (x - x_c) \sim \tau^{-\beta}; \quad r_c \sim \tau^{-\nu}.$$

Numerical values of the critical indices α, β, γ, ν can be obtained only from experiment or from microscopic theory. The values of these indices, derived from experiment, or from analytical and numerical solutions for lattice-type models (Ising, Heisenberg, Berlin-Katz etc.) turn out to be invariant (equal or very close in magnitude) for phase transitions of different physical nature and are defined only by the dimension d of the space under consideration and the corresponding type of symmetry (order parameter) [68,80,81]. This versatility can be assigned to the cooperative nature of the critical phenomena, which stems from the properties of the totality of particles rather than from individual properties of each particle. The spatial scale of their interaction exceeds by far the average separation between particles. The size of density fluctuations grows as one approaches the critical point, up to hundreds and even thousands of Angstroms, to become comparable to light wavelength, and their amplitude reaching, by order of magnitude, the average values of the density proper. This accounts for the opalescent, finely dispersed structure of material observed in the critical region, which, as already mentioned, is usually referred to as “a gas of liquid droplets”.

The free Helmholtz energy can in this case be presented as consisting of components of the regular part and a non-analytical uniform function of its arguments. In such a system, it contains a term proportional to the number N of the “gas droplets” formed $F = F_0 + kT_c N = F_0 + 3kT_c V/4\pi r_c^3$, where F_0 is the regular part of free energy F, which does not depend on the closeness to the critical point; V is the volume of the material, and $4\pi r_c^3$ is the volume of droplet in three-dimensional space. Invoking the power-law dependence of the correlation radius r_c on temperature in the form $r_c \sim \tau^{-\nu}$, one can readily obtain an expression for the singular part of heat capacity at constant volume $C_V \sim (\partial^2 F/\partial T^2)_V \sim \tau^{3\nu-2} \sim \tau^{-\alpha}$. Now this expression yields a relation connecting the critical indices of the heat capacity and correlation radius in three-dimensional space, $3\nu = 2 - \alpha$. One can then employ the standard similarity relations to establish the relation connecting the two remaining indices $\alpha + 2\beta + \gamma = 2$, $\alpha + \beta(1 + \delta) = 2$, $d\nu = 2 - \alpha$; we see that in the general case, the number of independent critical indices is always two. The numerical values of these indices, derived theoretically by L. Onsager and C. Wilson [82–86] for the plane and three-dimensional Ising lattice and supported by numerous measurements [68], are $\alpha = 0.11$, $\beta = 0.325$, and $\gamma = 2 - \alpha - 2\beta = 1.24$, respectively.

Idealized model concepts of the scaling theory suggest that far from the critical point fluctuations are statistically independent, so that random variations of state at a given point of the sample do not affect other parts of the system. Significantly, at the critical point, the radius of correlation (of fluctuation interaction) becomes theoretically infinitely large, enveloping all of the material [68,79,87–90]. In real systems, however, their susceptibility to external perturbations of various physical origins (gravitational and electric fields, surface forces and shear stresses, nonideal nature of samples and presence of boundaries etc.) also grows $\sim \tau^{\gamma}$, as one approaches the critical point, so that even small perturbations $\Delta E \ll kT$ will be able to distort the pattern of a phase transition by $3 - 4$ orders of magnitude [68]. This not only significantly complicates measurements in an experimental study, but can, at an infinite growth of susceptibility of the system to external influence, culminate in noticeable suppression of critical fluctuations by an external factor. This may result in restoration in the system of the mean-field "classical" behavior with the corresponding set of critical indices close to the critical point, with the area in the immediate vicinity of it becoming again a region of the Van der Waals type. An analysis of this possibility is offered in Ref. [91]. It is shown that in the general case, the pattern of universal behavior for systems near the critical point may include both a transition from the "mean-field" classical behavior to that of the Ising type, whose position is defined by the Ginzburg criterion [92], and the appearance in its nearest environment of a reverse transition from the renormgroup to "mean-field" classical behavior. At the same time, as follows from the data presented by the same author, the transition in the reverse direction expected to occur far from the critical point in pure liquids is not observed experimentally [93]. Now, our own experimental data provided a basis for an analysis of the universal relations connecting critical indices and amplitudes. Consideration is also given to the "pseudospinodal hypothesis" concerning the possible existence of a "pseudospinodal", i.e., of a line, all points of which would possess the properties of a critical line, i.e., a line, on which the isothermal and adiabatic compressibilities, isochoric and isobaric heat capacities diverged simultaneously. It is shown that this possibility is provided only at one and the only "critical" point, which lies simultaneously at the bimodal, spinodal and critical isotherm.

The transcritical state of matter can be employed as an initial approximation in describing its variations far from the critical point by introducing proper corrections to the asymptotic laws. In particular, in this way it becomes possible to describe the state of dense gases and liquids within a fairly large range of parameters, where, in contrast to solids and rarefied gases, straightforward calculation of thermodynamic quantities is impossible because of the uncertainties involved in particle interaction [68]. At the same time, despite numerous attempts undertaken in derivation of a scaling equation of state in physical variables which could be used to calculate the singular component of interest, these attempts have not thus far met with success. This possibility appeared with the use of a transition proposed by Josephson and Scoffield to a parametric form of equation in polar coordinates without direct expression through physical variables [94,95]. This transition is graphically interpreted in Fig. 2 [68].

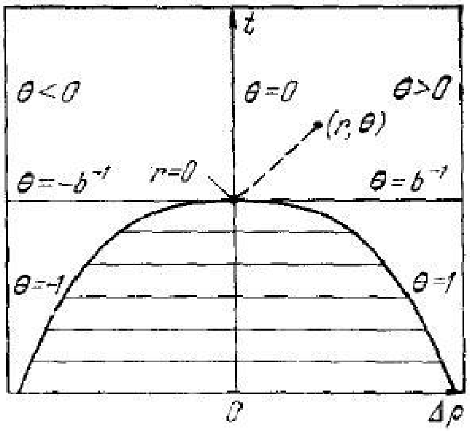

FIG. 2. Parametric presentation of the Sterling equation of state close to the critical point in polar coordinates

Its application turned out, however, to be inconvenient in approximation of experimental data and fairly difficult in the calculation of standard tables and matching with other equations of state, including those of the virial form, which adequately describe the behavior of various characteristics of material far from the critical point. Development of methods which could be employed in derivation of a unified scaling equation of state which would be free of the above shortcomings is still under way. Indeed, a nonparametric equation of state in the "density–temperature" physical variables has recently been obtained [96]:

$$F(\rho,T) = F_0(T) + RT_c f(\omega,t)\,|\Delta\rho|^{\delta+1} a_1(x) + RT\ln\rho + RT\omega\sum_{i=1}^{n_3}\sum_{j=0}^{j_3(i)} C_{ij}\tau_1^j(\Delta\rho)^i.$$

This equation satisfies the power laws of critical phenomena. It covers a broad range of parameters, including phase equilibrium lines (from the triple to the critical point), and metastable and single-phase regions, dense gas and liquids down to the solidification line in that number. Here, $\omega = \rho/\rho_c$ is the reduced density, δ is the critical index of the curve of the critical isotherm, $f(\omega,t) = \exp(-a\Delta\rho^2/\sqrt[5]{\omega})/T$ is the transition (crossover) function for a qualitatively correct description of the virial coefficients, $a(x)$ is a scaling function of the Helmholtz free energy in the form $a(x) = A_1(x+x_1)^{2-\alpha} + A_2(x+x_2)^{2-\alpha} + B_1(x+x_3)^{\gamma} + C$, whose parameters are calculated through the critical indices and the value of the scaling variable $x = \tau/|\Delta\rho|^{1/\beta}$ at the saturation line. As a measure of separation from the critical point, we can use here the isothermal compressibility $K_T = \rho^{-1}\left(\partial\rho/\partial p\right)_T$, assuming that it behaves similarly at the critical and non-critical isochores. The assumptions made here fit the phenomenological model of A. A. Migdal on the analyticity of the isoclinic line $H(m) = m + \varphi_3 m^3 + \varphi_5 m^5 + \ldots$, where $H = \Delta\mu[P_c V_c^2(\partial\rho/\partial\mu)]^{(\beta+\nu)/\nu}$, and $m = \Delta\rho[P_c V_c(\partial\rho/\partial\mu)]^{\beta/\nu}$ [97], as well as the hypothesis of J. Benedek on the functions $K_T(\rho,T)|_{\rho=\rho c} \sim K_T(\rho,T)|_{\rho\neq\rho c} \sim \tau^{-\gamma}$ following analogous behavior [98]. A comparison of the calculation results with data accumulated from a number of well-studied materials of technological significance, including cryogenic gases and liquids, as well as refrigerants of a variety of molecular structures (refrigerant R23, argon, perfluorpropane), suggests [96] that the scaling equation of state developed reproduces with a high accuracy the thermodynamic properties throughout the range of parameters specified above.

Because this approach has not yet enjoyed application in development of similar scaling equations of state for metals, the variations of their physical state in the course of a phase explosion are described by invoking semiempirical equations and models of transport coefficient calculations of various kinds. In the calculations presented below, we made use of wide range semi-empirical equations of state permitting description of the state of material in the condensed, gas, plasma and two-phase region of the phase diagram.

4.2. Phenomenological modeling of critical phenomena and thermodynamic stability of one- and two-phase systems in the mean-field approximation

If the linear dimensions of phases are large enough, one can neglect the curvature of their interface. In this case, thermodynamic equilibrium sets in when their temperatures, pressures and chemical potentials are equal [67,69]:

$$T' = T'' = T; \quad P' = P'' = P; \quad \mu'(T,P) = \mu''(T,P)$$

These equations define the interfaces for the regions of single-phase liquid and equilibrium two-phase (liquid–vapor) states of matter–the binodal.

For the Van der Waals type state equations, this system can be used to derive Maxwell's "equal areas" condition, which in the subcritical region of the diagram of state ($T < T_c$) is combined with the equation of state $P = P(T,\ \rho)$ to produce a system of equations for finding the equilibrium pressure $P_b(T)$ and densities of liquid $\rho_b'(T)$ and vapor $\rho_b''(T)$ at the binodal. Thermodynamic stability with respect to continuous variations of the parameters of state is defined here by the condition that the second variation of the internal energy of a thermodynamic system ε be a positive quantity. For this purpose it is necessary and sufficient that the following inequalities be met [67,99]:

$$D = \left(\frac{\partial^2 \varepsilon}{\partial s^2}\right)\left(\frac{\partial^2 \varepsilon}{\partial v^2}\right) - \left(\frac{\partial^2 \varepsilon}{\partial s \partial v}\right) > 0,$$

$$\frac{\partial^2 \varepsilon}{\partial s^2} = \left(\frac{\partial T}{\partial s}\right)_v = \frac{T}{C_p} > 0,$$

$$\frac{\partial^2 \varepsilon}{\partial v^2} = -\left(\frac{\partial P}{\partial s}\right)_s > 0$$

Here, C_P is the specific heat at constant pressure, and s and v are the specific entropy and specific volume, respectively. These expressions can be readily employed to derive other useful relations for isodynamic derivatives as well:

$$\left(\frac{\partial P}{\partial v}\right)_T = -\frac{1}{\beta_T v} = D\left(\frac{\partial T}{\partial s}\right)^{-1},$$

where β_T is the coefficient of isothermal compressibility.

To sum up, for stable states:

$$\left(\frac{\partial T}{\partial s}\right)_p > 0; \quad \left(\frac{\partial P}{\partial v}\right)_T = -\left(\beta_T v\right)^{-1}.$$

The inequality $D < 0$ defines the unstable state region for the homogeneous phase, in which any perturbations grow until it transfers to the equilibrium two-phase state. The equation $D = 0$ identifies the boundary of the phase state parameters stable with respect to their continuous variations, i.e., spinodal. For instance, for the Van der Waals model the equation for the spinodal in dimensionless variables reduced to the parameters of the critical point reads as:

$$4\,\theta\,\varphi^3 - 3\,\varphi^2 - 6\,\varphi - 1 = 0\,,$$

where $\theta = T/T_c$, $\pi = P/P_c$, $\varphi = \upsilon/\upsilon_c$ are dimensionless variables. Estimates can be conveniently obtained with the equation for spinodal derived in terms of the "hole" theory of liquids [100]:

$$\pi \cong 10\,\theta - 9$$

The coefficients of thermodynamic stability for the liquid phase at the spinodal pass through zero values:

$$\left(\frac{\partial P}{\partial \nu}\right)_T = 0, \quad \left(\frac{\partial \mu'}{\partial n}\right)_{(\nu,T)} = 0, \quad \left(\frac{\partial T}{\partial s}\right)_P = 0,$$

while the thermodynamic fluctuations related to them through the expressions:

$$\left(\frac{\partial P}{\partial \upsilon}\right)_T = -\frac{k\,T}{\langle \nu^2 \rangle}; \quad \left(\frac{\partial T}{\partial s}\right)_p = \frac{k\,T^3}{\langle \Delta h^2 \rangle},$$

grow sharply, a factor which may cause dispersion of the liquid.

In the supercritical region ($T > T_c$, $P > P_c$), the transition of material from the condensed to gaseous state takes place under continuous variation of its density within the temperature interval which corresponds to the region of thermodynamic hypostability of the state of material to development of fluctuations of its thermodynamic characteristics. The boundary of existence of a condensed phase in the supercritical region of the diagram of state (quasispinodal is the curve of supercritical liquid–vapor transitions) is defined by the points of extrema in the course of the thermodynamic stability coefficients of the condensed state [35,38,44,49,65,66]:

$$\left(\frac{\partial P}{\partial \upsilon}\right)_T < 0; \quad \left(\frac{\partial^2 P}{\partial \upsilon^2}\right)_T = 0; \quad \left(\frac{\partial \mu}{\partial n}\right)_{\upsilon,T} > 0; \quad \left(\frac{\partial^2 \mu}{\partial n^2}\right)_{\upsilon,T} = 0,$$

and is actually a continuation of the binodal into spinodals beyond the critical point. All branches of the binodal, spinodals and quasispinodal converge to the critical point. The coefficients of volumetric expansion and isothermal compressibility at the quasispinodal points pass through the final maxima. This opens the possibility of deriving the equation of quasispinodal from experimental data on the coefficients of volumetric expansion or isothermal compressibility in the supercritical region.

The spinodal–quasispinodal equation was calculated from available experimental data for mercury, whose physical properties were studied in considerable detail. These calculations resulted in the following equation:

$$\pi \cong 11.1\,\theta - 10.1$$

This equation draws upon the law of corresponding states and can apparently be extended to other metals as well. Thus, if one knows equations of state $P = P\,(T, \rho)$ and $\varepsilon = \varepsilon\,(T, \rho)$ or has experimental data on the physical characteristics of the material, it becomes possible to establish the boundary of thermodynamic stability of a material with the use of the above relation.

To disperse a material by subjecting it to thermodynamic instabilities, the heating conditions employed should provide the attainment of extreme metastable states, which in the subcritical region of the diagram of states, are defined by the spinodal, and in the supercritical region, by the quasispinodal. We analyze below the main factors which plague solution of this problem. In the conditions characteristic of "fast" EEW, when instabilities of other than thermodynamic nature play a limited part, these factors are surface vaporization and heterogeneous boiling.

4.3. Vaporization and dispersion of metal under high-power pulsed heating with a high-density current

Formation of a vapor nucleus in a liquid being limited by inertia and nonequilibrium processes, vaporization starts on the free surface of the liquid. Because the vapor forming in the process allows stronger compression that the liquid, the local velocity of displacement of the interphase cannot exceed the sound velocity at the corresponding point of the binodal. The time taken by a rarefaction wave to propagate to the center of the volume occupied by the liquid and back may be considered as a characteristic “sonic” time scale.

4.3.1. Vaporization wave in metals. If the heating conditions of a liquid are such that the latent heat of evaporation enters the liquid in a time longer than the “sonic” time, the system is in the regime of quasi-steady state evaporation from the surface. In this regime, the temperature at the interphase can be assumed to be determined by external pressure and to remain constant. In the case when the latent heat of evaporation is injected into the liquid during the “sonic” time, and the number of centers of heterogeneous boiling ready to operate is not large enough, the process dominating the mechanism of vaporization will be evaporation from the surface, whose temperature will grow in the course of liquid overheating.

We are interested in more powerful regimes of liquid heating, in which the latent heat of vaporization is injected into the liquid phase in a time much shorter than the “sonic” time. In this case, the internal, not yet expanded regions of the liquid, will suffer overheating substantially above the temperature determined by the binodal at the corresponding local level of pressure. In these regions, conditions favoring the generation of homogeneous volume vaporization will become achievable. In the vicinity of vapor bubble formation, the liquid becomes strongly locally overheated, which initiates a still more intense growth of evaporation. This process may also become compounded by the formation of local electric arcs at the bubbles.

The “sonic” time can be estimated not from the real surface evaporation rate but rather from its maximum value, which is equal to the local sound velocity in the two-phase region at the binodal points [11-13,20,101]. Recalling that at the binodal the pressure $P_b(T)$ and density $\rho_b(T)$ of the liquid phase depend only on temperature, we obtain:

$$v_s = \sqrt{\left(\frac{\partial P}{\partial \rho}\right)_s} \cong \sqrt{\frac{T}{C_v\,\rho_b\,(T)}} \cdot \frac{dP_b}{dT}$$

In interpretation of the EEW experiments, this velocity was termed the velocity of “evaporation wave” in metals [11-13,20]. The dependences of the evaporation wave velocity calculated from this relation fit well enough the experimental results obtained in the initial region, but the discrepancy between the calculations and experiments was found to grow with increasing temperature. This does not come as a surprise, because the conditions in an overheated metal may become favorable for the onset of volume evaporation, a process developing with increasing overheating.

4.3.2. Volume boiling-up of a metal heated by a high-density current. Volume boiling-up of a liquid metal can be both heterogenic, i.e. develop on already available vaporization centers (structural inhomogeneities, charged particles and so on) and homogeneous, a process in which a water droplet nucleus is borne by thermodynamic density fluctuations.

In the regimes considered by us here, the necessary condition making possible spontaneous boiling-up of a liquid metal is metastability of its state, which can be reached by overheating the liquid above the temperature of its quasistationary boiling in the given ambient conditions. The appearance in the liquid of a "critical" vapor nucleus capable of growing as a center of volume vaporization is accompanied by overcoming a peculiar energy barrier. It can be correlated with the work spent in formation of this vapor nucleus in a given thermodynamic state of the liquid W_{cr}. This work accounts for the probability of spontaneous formation of a vapor nucleus in an overheated liquid and, eventually, for the frequency of homogeneous vaporization, i.e., the number of critical vapor nuclei per unit volume and per unit time [35,38,44,49,65,66]:

$$\frac{dN_{cr}}{dt} = B\left(T,P\right)\cdot\exp\left(-\frac{W_{cr}}{kT}\right)\cdot\exp\left(-\frac{\tau_p}{t}\right)$$

where τ_p is the relaxation time in establishment of steady-state regime of nucleus formation following instantaneous overheating of the liquid (estimates yield $\tau_p \leqslant 10\text{ns};$) $B\left(T,P\right) \cong 10^{23}\text{cm}^{-3}s^{-1}$ is a weakly temperature- and pressure-dependent function.

The work expended in formation of a viable vapor nucleus of volume υ_B of a metastable liquid is [35,38,44,48,49,56,65,66]:

$$W_{cr} = \alpha s + (P' - P'')v'' + W_B$$

where α is the surface tension coefficient; s is the surface area of the forming vapor nucleus; $P'P''$ are the pressures in the liquid and the vapor nucleus, and W_B is the work against the electromagnetic forces, with the dominant contribution to it coming from the work spent on the increase in the inductance of the system associated with formation in the liquid metal of a vapor void [48,56]:

$$W_B \cong \frac{\mu_0}{8\pi}\iint\left[J(r)J(r') - J_0(r)J_0(r')\right]\frac{dv'dv}{|r-r'|},$$

where J_0, J are the currents flowing through the conductor before and after formation of the vapor nucleus. The volume of the work spent in formation of the vapor void depends on its shape. This accounts for the possibility of generating critical nuclei of various shapes. The dimensions of the critical nucleus of a fixed shape correlates with the maximum value of W_{cr},while the actual shape of the nucleus is derived from the condition of minimum W_{cr}.

Close to the binodal, the work expended in formation of a critical vapor nucleus of a critical shape in an overheated liquid can be estimated from the relation [20,32]:

$$W_{cr} \cong \frac{16}{3}\pi\frac{a^3(v'')^2}{\Lambda_{vap}\varepsilon_T^2} + \frac{\pi^3}{4}\mu_0\frac{a^3(v')^3}{\Lambda_{vap}^3\varepsilon_T^3}J_0^2\xi(l_B^2 + R_0^2)\ln\left(\frac{\varepsilon_T\Lambda_{vap}R_0}{2av''}\right)$$

Here, $a = 2\alpha/(P'' - P')$ is the nucleus radius; R_0 is the characteristic size of the conductor cross section; $l_B \cong 2\sqrt{\tau/\left(\mu_0\ \sigma\right)}$ is the distance the magnetic field has passed by diffusion during the time τ the nucleus took to form (estimates yield $\tau \approx 0.1{-}1\ ns$); $\varepsilon_T = \left(T - T_b\right)/T_b$ is the relative overheating of the liquid metal; $\Lambda_{vap}\left(T\right), T_b$ are the latent heat of evaporation and temperature at the binodal, and coefficient $\xi = 2(\sigma' - \sigma'')/(2\sigma' + \sigma'')$, where σ', σ'' are the values of electric conductivity of the liquid metal and of the vapor Significantly, as a rule, $R_0 \gg l_B \gg a$.

Thus, Joule heating of a metal by electric current is characterized by an increase in the work expended in the formation of a critical vapor nucleus and of the time one spends in waiting for its appearance, compared with the case of other than Joule heating of liquid metal, for instance, with laser or beam energy injection. For small overheatings, $\varepsilon_T \to 0$, homogeneous creation of a viable nucleus is met with difficulties, $W_{cr} \to \infty$ Increasing the overheating brings about a sharp lowering of the activation barrier of W_{cr} and, hence, increase of the probability of homogeneous nucleus formation and of development of homogeneous boiling-up of the liquid metal. The lowest value of W_{cr} corresponds to the highest possible overheating of the condensed phase $\varepsilon_T = \varepsilon_T^{cr}$, which for the given outer conditions is determined by the temperature related to the spinodal, where the thermodynamic stability coefficients pass through zero values.

Estimates of the metal overheating needed for the onset of homogenous vaporization, $(dN/dt)_{cr} > 1\mathrm{cm}^{-3}\mathrm{s}^{-1}$, suggest that the frequency of spontaneous vapor generation grows strongly within a comparatively narrow temperature interval. For the first homogenous nucleus to appear, after which their number grows in an avalanche, the metal should be overheated close to the highest possible level, which corresponds to a very small environment of the critical point.

Reaching conditions favorable to homogeneous boiling-up of the liquid phase can be hindered by heterogeneous boiling developing on the already viable centers of vaporization, which starts at temperatures only slightly exceeding the temperature of quasi-stationary boiling. But if the specific power of heating of the liquid phase is high enough, it can be overheated if it contains artificial viable centers of boiling. This can be realized if we provide a specific energy input into the liquid which would exceed considerably the energy expended for heterogeneous boiling on the already available centers. This heating regime received the name "impact" regime. Its operating conditions are formulated by the relation [35,38]:

$$K = \frac{Q_v}{\Lambda_{vap}\varphi^{\frac{1}{k}}}\left(\frac{3}{4\pi}\frac{1}{\Omega_0}\frac{\rho'}{\rho''}\right)^{\frac{1}{3k}} \cdot \varepsilon_T^{\frac{1}{3k^{-1}}} \gg 1.$$

Here, Q_v is the specific power of the "impact" energy input, Ω_0 is the given concentration of heterogeneous boiling centers, and ρ', ρ'' are the densities of the liquid and vapor, respectively. The growth of the heterogeneous nucleus is approximated by a power-law form $r\,(t) \cong \varphi\,(t)\,t^k$, $\langle\varphi\rangle = \frac{1}{\tau^k}\int\limits_0^{\tau} \varphi\,(t)\,kt^{k-1}dt$, where $\Delta\tau$ is the time taken by a heterogeneous vapor nucleus to grow, and $< \varphi >$ is the value of function $\varphi(t)$ averaged over the temperature interval $T_b \leqslant T \leqslant T_{cr}$. The condition of "impact" heating can be presented in a more compact way with the relation:

$$\frac{\tau''}{\Delta\tau}\varepsilon_T^{\frac{1}{3k}} \gg 1,$$

where $\Delta\tau = \frac{\Lambda_{vap}\varepsilon_T}{Q_v}$, $\tau'' = \frac{1}{\varphi^{\frac{1}{k}}}\left(\frac{3}{4\pi}\frac{1}{\Omega_0}\frac{\rho'}{\rho''}\right)^{\frac{1}{3k}}$ is the time needed for boiling out of all of the liquid present on the heterogeneous centers. The law by which the nucleus radius grows in this case can be adequately approximated in terms of the thermal approach, in which the penetration of the liquid evaporation surface inside a nucleus is determined by the heat input:

$$r(t) \cong 2\sqrt{\frac{3}{\pi}\frac{b'}{\Lambda_{vap}\rho''}}(T - T_b)\sqrt{t},$$

where $b' = \sqrt{\rho'\lambda' C'}$, and λ' and C' are the heat conductivity and heat capacity of the liquid, respectively.

The above mechanism of metal boiling-up is realized at pressures $P < P_{cr}$ and within a specific range of metal heating power variation. The lower boundary of this range is defined by the criterion of homogeneous boiling-up, and its higher boundary, by the condition of steady-state homogeneous formation of vapor nuclei, $\tau_m > \tau_c \gg \tau_p$. Here τ_m is the maximum time during which heterogeneous boiling can be neglected, τ_c is the time in which ultimate overheating is reached at a given specific heating power, and τ_p is the time during which steady-state homogeneous formation of vapor nuclei in overheating liquid sets in.

4.3.3. Attainable overheating and heterogeneous boiling of liquid metals. The metallic state of a material is determined by the existence of free electrons; for normal metals there are not less than one of them per atom. At high enough temperatures ($T \geqslant 0.5$ eV, the concentration of charged particles close to the binodal becomes so high that they can become centers of heterogeneous volume vapor generation. Such a mechanism of vapor formation in metals with a low critical temperature ($T_{cr} \sim 1$ eV, e.g. aluminum, copper etc.) can become realized in isentropic conditions [102]. Under certain conditions specified below, heterogeneous vapor formation on charged particles can proceed in a high-power pulsed heating of a liquid metal as well.

The level of overheating of a liquid metal above which charged particles become centers of volume heterogeneous vapor formation can be estimated from the relation [102]

$$\varepsilon_T^c \cong \frac{3}{2\sqrt{2}} \frac{\alpha\,\omega}{\Lambda_{vap} k_B \zeta},$$

where α is surface tension, and the coefficient $\zeta = e^2/\sqrt[3]{16\pi\alpha}$. By substituting ε_T^c into the condition governing the onset of “impact” heating, we come to an estimate of the minimum rate of heating of a liquid metal $\dot{T}$, at which heterogeneous boiling of liquid metal on charged particles cannot already resist development of homogeneous volume evaporation initiated by fluctuations:

$$\dot{T} \gg \left(\frac{3}{4\pi}\frac{1}{\varphi\Omega_0}\right)^{-\frac{1}{3k}} \frac{\varepsilon_T^c}{T_b}.$$

Here, Ω_0 is the concentration of centers of heterogeneous boiling, which in the case under consideration coincides with that of charged particles.

The presence of charged particles close to the binodal shortens the time during which metastable states of the liquid metal persist up to their breakup into equilibrium two-phase states. Under the present conditions, it is primarily governed by the time a vapor nucleus takes to grow to equilibrium size, for which numerical estimates yield ~ 1 ns, with the time of metastable state decay $\sim 0.1 - 1$ ns. Significantly, the time the liquid metal spends in metastable states before the first vapor nucleus born in fluctuations appears extends to approximately $\tau \geqslant 1 - 10$ ns.

If the characteristic times of volume evaporation are shorter than the “sonic” expansion time of a liquid metal, the above analysis suggests the following pattern for volume vapor formation in liquid metals. At heating rates $\dot{T} \leqslant 10^{10}$ K/s, liquid metal overheats insignificantly in the heterogeneous boiling initiated by charged particles. Therefore the conditions needed for the onset of homogeneous boiling-up are not met. To disperse a liquid metal in the conditions supporting homogeneous formation of vapor nuclei, the heating rate should be $\dot{T} \geqslant 10^{10}$ K/s.

5. EEC modeling based on similarity criteria

It is assumed that the EEW regimes most appropriate for the preparation of metal nanopowders are those providing current pause and maximum energy injected into the conductor by its beginning. Such regimes were defined in terms of the theory of dimensionalities and similarity (Kotov Yu.A., Azarkevich E.I., Sedoy V.S., Krivitskij E.V. et al.) [20,32,58,103]. The region of the initial conditions in which EEC develops in the regime with a current pause was identified by generalization of the available experimental data. One employed for this purpose the similarity criteria derived from an analysis of the dimensionalities of the physical parameters of the phenomenon and phenomenological ideas bearing on its mechanism. For wires of diameter d, the similarity criteria modeling EEC in the stages preceding firing of the discharge have the form:

$$\Pi_1 = \frac{R_0}{Z_0}, \quad \Pi_2 = \frac{C_0\,U_0^2}{d^4\,\varepsilon_0\,\sigma_0\,Z_0}, \quad \Pi_3 = \frac{v_0\sqrt{L_0\,C_0}}{d},$$

where ε_0 and σ_0 are the characteristic values of internal energy and electric conductivity of the metal, v_0 is the velocity of the rarefaction wave in the metal, and Z_0 is the wave resistance of the discharge circuit. In analysis of experiments performed with conductors prepared from the same metal, its characteristics ε_0, σ_0 and v_0 may be dropped, to transfer instead to the generalized variables:

$$\lambda = l\left(nd^2\sqrt{\frac{L_0}{C_0}}\right), \quad \varepsilon = \frac{C_0U_0^2}{n^2d^4\sqrt{L_0/C_0}}, \quad \nu = \frac{\sqrt{L_0C_0}}{d}.$$

These variables were employed in a quantitative description of the region of initial conditions in the electric explosion of copper wires in the regime with current pause. In particular, for the critical wire length we obtain:

$$\lambda_{cr} \approx A\left(10^{-6}\varepsilon\,\nu\right)^b,$$

where λ_{cr} is expressed in $(\mathrm{mm}^{-1}.\mathrm{Ohm})^{-1}$, ε – in $\mathrm{J/(Ohm.mm^4)}$; $\boldsymbol{v}$ – in mkc/mm; $A = (1,35 \pm 0,03)\cdot 10^3$; $b = 0,358 \pm 0,014$. For wires of critical length, the overvoltage coefficient can be found from the relation:

$$\frac{U_{max}}{U_0} \cong 0.45\left(10^{-6}\nu\right)^{-0.2}\exp\left[-0.011\left(10^{-6}\varepsilon\right)\nu\right].$$

Applying a similar approach to the problem of generalization of experimental results, it was demonstrated that EEW regimes developing in conditions without the current pause can be modeled with the use of the above similarity criteria Π_1, Π_2 and the criterion:

$$\Pi_4 = \frac{A_0\,l^3}{U_0^2\sqrt{L_0\,C_0}}.$$

Here, A_0 is a constant characterizing the properties of the medium in which an EEW is conducted; for an underwater EEC, for instance, $A_0 \approx 10^4$ Vcm^{-2}. The magnitude of overvoltage can be derived with the use of an approximate expression

$$\frac{U_{max}}{U_0} \cong 20\,\sqrt[4]{\Pi_2}\,\sqrt[3]{\Pi_4}.$$

While the criteria relations are certainly useful in practice, they are applicable only in the ranges of variation of the working conditions for which they were derived. In view of the area of applicability of any criterion relations being limited, one has to support activities in the field of engineering EEC research based on the theory of the related dominant processes.

6. MHD modeling of physical processes involved in an electric explosion in a metallic conductor

Complex numerical investigation of the main physical characteristics of dispersion draws from the modified model of magnetic radiation hydrodynamics applicable within a broad range of states (condensed, liquid, gaseous, plasma) [46, 104-162]. It encompasses the critical point and the metastable region, as well as transport coefficients for various kinds of processes involved in electric- and thermal conduction. In contrast to the conventional MHD model, this model takes into account the radiation component of energy exchange and describes magnetic field diffusion into a conductor, Joule heating, heat transport by electron and radiative heat conductivity, expansion and compression of the medium, including formation of shock waves. A possibility is provided for using various equations of state and of interpolation models for computation of transport coefficients. In a one-dimensional single-temperature approximation and in the case of cylindrical symmetry, this computational model is described by the following system of equations expressed in mass Lagrangian coordinates [33]:

$$\frac{dr}{dt} = u; \quad \frac{du}{dt} = -r\frac{\partial P}{\partial s} + F;$$

$$\frac{d}{dt}\left(\frac{1}{\rho}\right) = \frac{\partial}{\partial s}(ru);$$

$$\frac{d\varepsilon}{dt} = -P\frac{\partial}{\partial s}(ru) + Q_J - \frac{\partial W}{\partial s};$$

$$W = -\chi\rho r\frac{\partial T}{\partial s};$$

$$\frac{d}{dt}\left(\frac{B}{\rho r}\right) = \frac{\partial E}{\partial s}; \quad J = \frac{\rho}{\mu_0}\frac{\partial}{\partial s}(rB);$$

$$F = -JB; \quad J = \sigma E; \quad Q_J = \frac{\sigma E^2}{\rho}$$

Here, r is the radius (Eulerian spatial variable), s is the Lagrangean mass variable, u is the mass velocity, t is the time, ρ and T are the density and temperature of the material, E is the axial component of electric field strength, B is the azimuthal of magnetic field, J is the axial component of current density, Q_j is the specific power of Joulean heating, F is the Lorentz force; $P = P(T,\rho)$, $\varepsilon = \varepsilon(T,\rho)$ are the pressure and specific internal energy of the material, and $\sigma = \sigma(T,\rho)$; $\chi = \chi(T,\rho)$ are the electric conductance and heat conductivity of the material. One considers here two regions separated by a moving boundary $r(t)$. These are the regions occupied by the material of exploded conductor and by the medium in which the explosion takes place, accordingly.

The system of MHD equations is supplemented by the equations of the electric contour, which describe the variation of the current and voltage in components of the discharge circuit, with due account of their capacity, inductance and active resistance, as well as of the characteristics of the source and environmental medium:

$$\frac{d}{dt}[(L_0 + L_1)J] + U_1 + R_0 J = U_c, \quad \frac{dU_c}{dt} = -\frac{J}{C_0}.$$

Here, L_0 and R_0 are the intrinsic inductance and active resistance of the circuit, C_0 and U_0 are the capacity and charging voltage across the capacitor battery, L_V is the inductance of the conductor–return current lead, and U_1 is the voltage at the exploding conductor. To take into account the magnetic field in the environment, a variable inductance is included into the circuit substituting the circuit with the conductor. These equations are solved for the initial conditions $J(t = 0) = 0$, $U_c(t = 0) = U_0$, combined with the system of MHD equations.

Electric conductivities in single-phase regions are calculated with wide-range interpolation models [133-143, 149-162]. Significantly, these models describe in whatever approximation one chooses, the variation of the electric conductivity for a continuous variation of the density of material, from solid-state values to the levels characteristic of gases and the plasma. Thermal conductivity in single-phase regions was reduced from the Wiedemann–Franz law. In the region of two-phase states, determination of effective transport coefficients rests on the well-known model of the heterogeneous medium, which takes into account its phase composition and structure (mutual phase arrangement) [163]. The extensive characteristics of the material (specific volume, internal energy, enthalpy) in a two phase region are related to the corresponding characteristics of individual phases through the expressions:

$$\rho = g\rho_1 + (1-g)\,\rho_2; \quad \varepsilon = g\varepsilon_1 + (1-g)\,\varepsilon_2.$$

Here, g is the concentration of the first phase in the mixture, ρ_i, ε_i are the density and specific internal energy of phases at the coexistence boundary (binodal), which depend on one thermodynamic variable only, the temperature.

Numerical modeling (simulation) permits one, in particular, select a priori needed EEC regime by properly matching the initial working conditions (physical properties and dimensions of the conductor to be exploded, density of the environmental medium etc.), with the pulsed system of accumulation and transport of energy into the conductor. Its specific power and magnitude, combined with the homogeneity of distribution over the conductor cross section, are dominant factors in reaching the required physico-chemical properties of nanopowders as products of electrical explosion-based dispersion of a metal. Geometrical characteristics of the conductors to be exploded also markedly influence the possibility of developing instabilities, just as unfavorable effects of a dense environmental medium. In this regard, various conditions involved in electric explosion of conductors in the form of wires, plane plates and thin-walled cylindrical shells were modeled in rarefied gas and liquid water medium, with the temperature and density of the material being varied within a broad range of temperature and density of the material (from the condensed to plasma states), depending on the specific density of injected energy.

Calculations revealed that the part played by MHD “waist”-type instabilities in an electric explosion of a foil is insignificant. As for the uniformity of energy injection, however, it is impaired because of the nonuniform distribution of current density over the width of the foil as a result of edge effects. Edge effects can be eliminated by enclosing a plane foil into an envelope. It is these considerations that account for our having chosen the exploding conductor in the form of a thin-walled metallic shell encompassing a rigid dielectric cylinder, with the return current conductor in the form of a massive metallic rod extended along the cylinder axis (Fig. 3).

Such a configuration of the load has one more asset—indeed, it makes possible reducing to a minimum the inductance of the “load—return current” element of the electric circuit, an essential point in reaching high discharge current rise rates. In this case the load may be placed into a chamber, a reactor of an arbitrary shape and size. Preliminary estimates showed that a pulsed source of energy intended for experimental studies should generate current pulses with a leading edge < 10 ns and amplitude of up to 100 kA. For this purpose, one can use a high-voltage pulse generator, with pulse leading edges on the order of 1 ns and amplitudes of up to 200 kV, which was developed at the Ioffe FTI for an “Extreme-M” experimental facility. The basic diagram of the heavy-current electric discharge circuit developed for this facility, complete with the equivalent electric circuit and the corresponding diagram, which was employed in numerical studies of Z discharges, is displayed in Fig. 4. In the present work, the sharpening capacitance was not included, with the shortening switch S and circuit breaker with a steeply growing resistance $R_f(t)$ employed in physical and numerical electric circuit switching experiments.

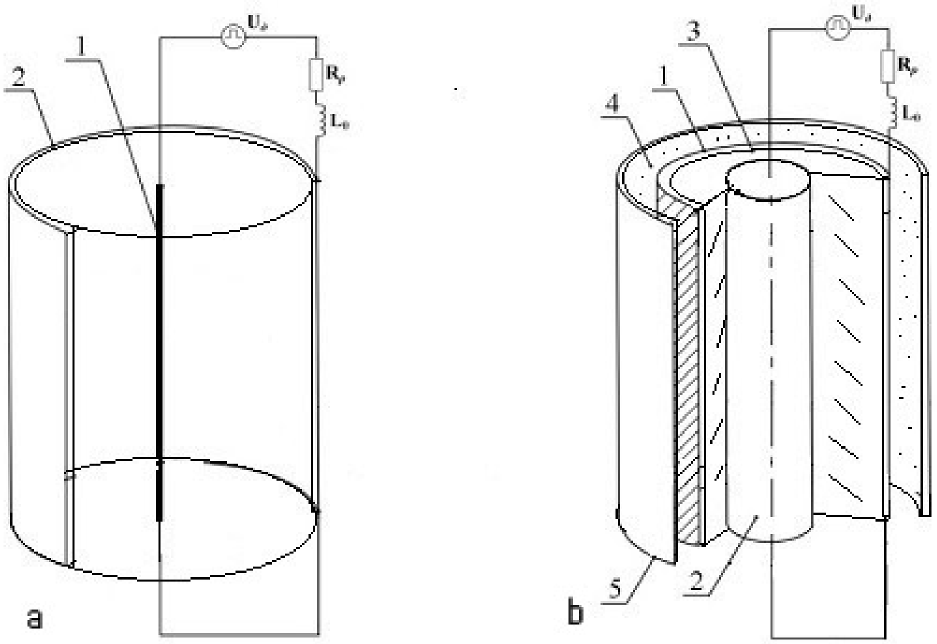

FIG. 3. Diagram of a typical arrangement of exploding conductor in the discharge chamber (a) and a version of its replacement with a thin-walled cylindrical shell mounted on a rigid dielectric cylinder, with a return current conductor – a massive metallic rod fixed on the cylinder axis (b). Notes: a: 1 - exploding conductor; 2 - return current conductor. b: 1 - exploding thin-walled metallic cylindrical shell; 2 - return current conductor; 3 - rigid dielectric cylinder; 4 - water medium; 5 - wall discharge chamber

MHD calculations of a thin-walled metallic shell suggest the possibility of building up the required EEW regime in a water medium, which would provide uniform energy injection into the metal and a current "pause".

Indeed, Fig. 5 demonstrates the behavior with time of the discharge current, voltage and energy injected into the conductor. We readily see that energy is injected into the material predominantly in the stage of the "explosion as such". Significantly, the main condition of matching of the conductor with the power supply is fulfilled, namely, the energy of the magnetic field stored in inductive elements of the electric circuit should be approximately equal to that of metal sublimation.

The data displayed in Fig. 6 show that conductor heating in the initial stage (stage of the conductor "waiting" for the explosion) preceding the stage of the explosion proper is uniform. The nonuniformity of Joule heating of the metal caused by the diffusion of electromagnetic field is seen to level off rapidly, with the distributions of current density and Joule heating over the shell cross section becoming practically uniform in the time which is shorter than the time the conductor is "waiting" for the beginning of the explosion proper, i.e., for the beginning of the discharge current fall-off [33].

Besides calculation of the transition process in the circuit, distribution of the electrostatic field in the apparatus in the vicinity of the load was studied. The distribution of the field in the regions where current and voltage are supplied to the load is shown in Fig. 7. The data obtained in the calculations were employed to determine the probability of breakdowns in the separating diaphragm when current is supplied to the operating inductive load.

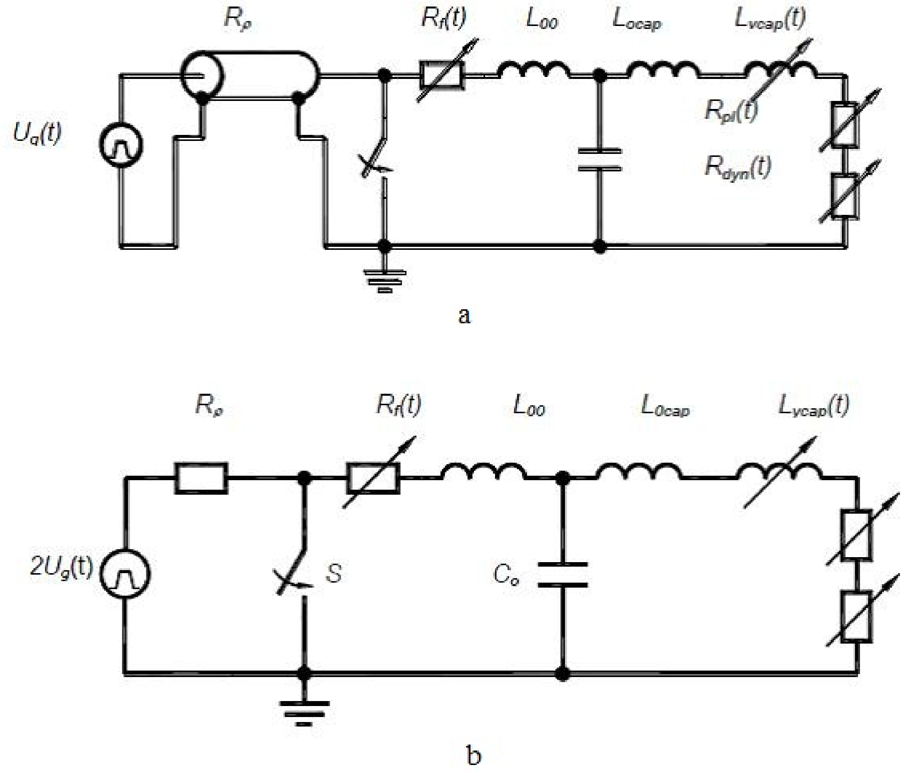

FIG. 4. Equivalent electric circuit (a) and the corresponding diagram (b) of the heavy-current electric discharge circuit which was employed in numerical studies of Z-discharges in the Extreme-M equipment

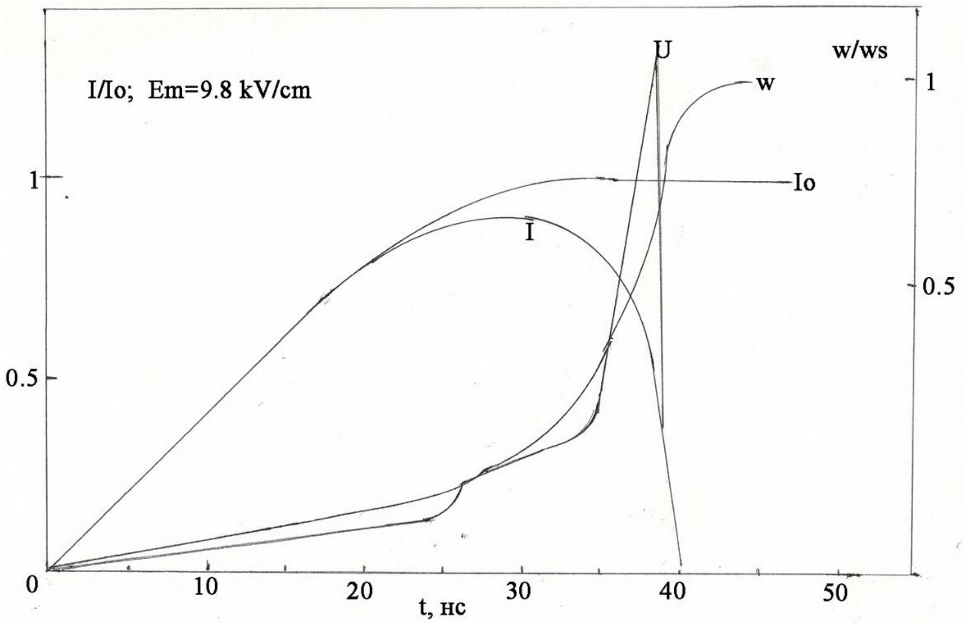

FIG. 5. Variation of discharge current, voltage and energy injected into the conductor of a thin-walled metallic shell during EEW in a water medium. Here I0 is the short circuit current, Em, Ws are the maximum values of voltage and energy

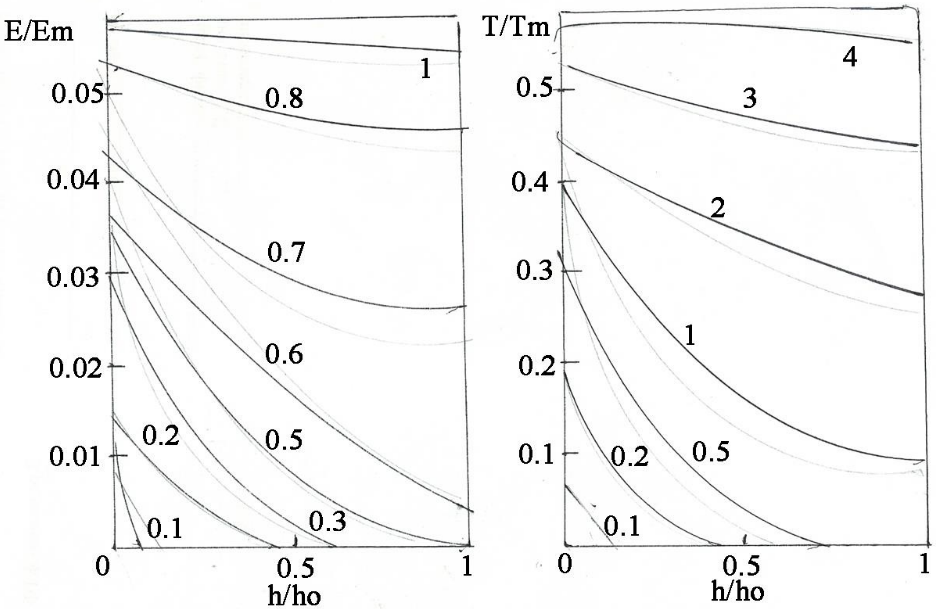

FIG. 6. Variation of the distributions of the relative electric field strength and of the temperature over the shell cross section in the course of Joule heating in the initial stage (conductor before explosion) preceding the stage of the explosion proper at different moments of time (ns)

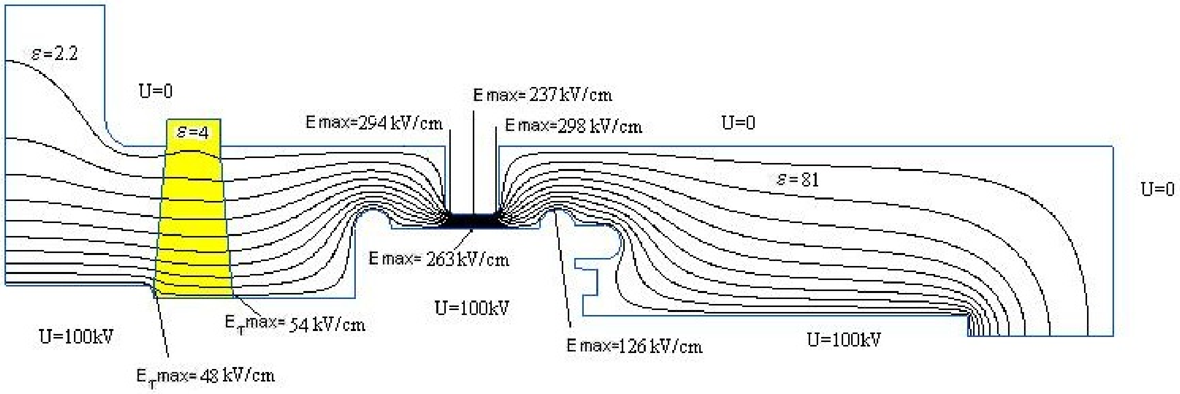

FIG. 7. Distribution of electrostatic field in the region of voltage supply to the load

Incidentally, approach to the critical point in metals is accompanied by a sharp drop of electrical conductivity resulting from free electron scattering from small-scale density fluctuations. For metals, however, whose critical temperature is comparable (in energy units) to the thermal ionization potential ($\sim$ 1 eV and higher) and which near the critical point can be actually a metallic plasma, electrical conductivity grows again with heating. Because ionization is one of the most energy-intensive processes (for aluminum, for instance, the melting heat is 10.8 kJ/mole, sublimation heat—327 kJ/mole, and the first ionization potential is already 577.6 kJ/mole [164]), under pulsed energy supply conditions, equilibrium among different energy dissipation channels does not set in. As a result, material can coexist simultaneously in different energy states. Also possible is repeated electric discharge, and, besides density, temperature, pressure and entropy fluctuations, variations of charge involving a local violation of electric quasi-neutrality of the plasma can form as well. The ambipolar electric field generated in these conditions should bring about a decrease of density fluctuations, in this way compressing, as it were, the material and raising its critical temperature, and preventing in this way the falloff of electrical conductivity. This could tentatively be assigned to free electrons leaving high-density regions for more rarefied regions of material with density fluctuations, as is the case of gaseous plasma supporting the characteristic phenomenon of double electric layer formation [33].

7. Modeling of the physico-chemical processes involved in condensation of products of an electric explosion of metallic conductors in a water environment

Further development of fluctuations experienced by thermodynamic quantities of a metal as it approaches the critical point by the described scenario, which culminates in a phase explosion and condensation of its products in the environmental medium, may have some aspects essential for the formation of condensing nanosized particles and stemming from the properties both of this medium and of the explosion products proper. The above results of the numerical analysis stress the importance of imposing limits on the rate of metal expansion. It appears reasonable to invoke for this purpose high-power heating not of wires but rather of thin-walled tubular conductors immersed in a dense liquid medium. In contrast to a rarefied gas, a dense, in particular, an aqueous medium can intensify cooling of a melting and boiling-up metal of the conductor, thus inhibiting its expansion in the electric explosion. This medium, however, will experience itself the variations of the thermodynamic state up to development of supercritical fluids generated by fast local heating, shock wave propagation, collapse of cavitation bubbles and other similar phenomena described in considerable detail in the literature [50].

In these conditions, the process of metal vapor condensation reveals its specific features, which are associated not only with efficient cooling but with the presence of electric charge on the particles of explosion products as a result of thermal ionization of the metal close to the critical point, as well as with their interaction with supercritical water. The active $[(H_2O)n(\mathrm{Me})m]$ complexes formed in the process can transform into nuclei of the new phase – the metal oxide $\mathrm{Me}_m\mathrm{O}_n$. Formation of oxide nanoparticles in the supercritical fluid thus formed is supposedly governed by a chemical redox reaction accompanied by release of hydrogen $k(\mathrm{Me})+l(H_2O)= g(\mathrm{Me}_m\mathrm{O}_n)+l(H_2)$, where $k = gm$, $l = gn$. Such a reactor, with a proper choice of the metal to be exploded (Al, Ti, Zr etc.), can provide a highly productive synthesis of oxide nanoparticles. Incidentally, the method of synthesis described above is potentially capable of producing oxide nanoparticles differing from those of the same oxides but prepared by electrical explosion of metals in air or other oxygen-containing gas media, as was proposed in Refs. [43,65,159,165,166], or by hydrothermal synthesis in its classical methodological approach [167]. The oxide nanopowders formed in the above conditions can reveal, due to the reducing medium and the high-energy conditions characteristic of local-hydrothermal synthesis, in particular, a still higher level of catalytic, sorptive and other functional characteristics than, for instance, those obtained by the traditional hydrothermal method of their synthesis [168-172].

Evaluation of the necessary nucleus formation energy (the free Gibbs energy) and of the critical size of the nuclei corresponding to its maximum (Fig. 8), requires, in the conditions considered here, taking into account the contribution not only of the surface tension and of the difference between the "particle-environmental medium" chemical potentials but of the difference between their electric potentials as well.

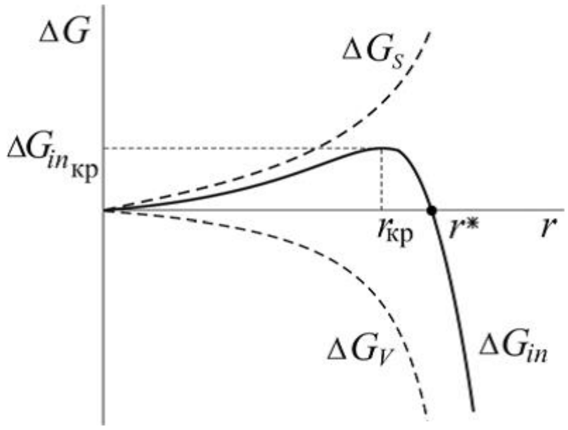

FIG. 8. Dependence of the Gibbs energy and of its components involved in formation of a nucleus on its radius

Spontaneous growth of a nucleus is known to be possible only under further decrease of the Gibbs free energy (Fig. 9). In the particular case of formation of a spherical nanoparticle and of absence in the system of spatial constraints described in Refs. [173,174], the Gibbs free energy can be conceived as a sum of its volume and surface components $\Delta G = -(4/3)\pi R^3 \Delta\mu / V_a + 4\pi R^2 \sigma(R)$. Here, $\Delta\mu > 0$ is the difference between the chemical (electrochemical) potentials of a nanoparticle and of the phase-forming medium, $V = (4/3)\pi R^3$ is the volume of the nucleus of a spherical nanoparticle, V_a is the molar volume of the material of the phase-forming medium, and $\sigma = \sigma(R)$ is surface tension. The critical size of the nucleus Rkp is found from the condition of maximum free energy $d(\Delta G)/dR = 0$. It is $Rkp = 2\sigma(\infty)V_a/\Delta\mu$ if one disregards the dependence of surface tension on particle size, and $Rkp = l_0[1 - 2\delta/l_0 + (2\delta/l_0 + 1)^{1/2}]$ – with its inclusion for small particle radii with the relation $\sigma(R) \approx \sigma(\infty)/(1 + 2\delta/R)$ where $l_0 = \sigma(\infty)V_a/\Delta\mu$, and δ is the "Tolman length" [175]. The critical Gibbs energy at the point of the maximum, derived for the case of formation of homogeneous condensation nuclei on the surface of the nuclei appearing spontaneously as a result of fluctuations of the density and concentrations of material in the system, disregarding the dependence of surface tension on particle size, makes up $\Delta Gkp = (4/3)\pi R^2 kp(\sigma - 2/3\sigma)$, or one third of the surface energy of a nucleus. The remaining two thirds are canceled by the chemical component of the excess energy generated in the phase transition. Incidentally, $\Delta\mu = 2\sigma(\infty)V_a/Rkp$.

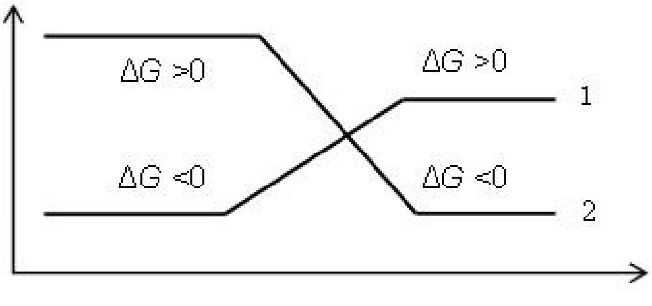

FIG. 9. Variation of the characteristics of thermodynamic processes plotted vs. size of the nanoformations: 1 - spontaneous design process is impossible, 2 - spontaneous design process is possible

The applicability of the general thermodynamic approach to estimation of the homogeneous formation of particles of small size is limited by the condition in which the specific surface energy $\sigma(R) \approx \sigma(\infty)/(1 + 2\delta/R)$ is higher by far than its RMS fluctuations $\langle\langle\Delta\sigma\rangle^2\rangle = (kT/8\pi R)(\delta\sigma/\partial R)_{P,S} = kT\delta\ \sigma(\infty)/[4\pi R(R + 2\delta)^2]$. This condition is met for $R \gg [kT\delta/\sigma(\infty)]^{1/3}$. Estimates suggest that at a low condensation temperature, the critical size of the nucleus can make up $Rkp = (5 \div 10) \cdot 10^{-10}$ m, which is the size of a few atoms. In this case, adding the next atom will change ΔG in a discrete way, which is incompatible with the principle of thermodynamic theory by which surface energy and the Gibbs free energy vary continuously. One has to transfer to the statistical theory of nucleus formation based on the parameters of interatomic interaction among individual atoms, with the specific features of their behavior governing the probabilities of growth and decay of clusters, in which the relative fluctuations of the number of atoms and energy follow the standard law $\sim N^{-1/2}$ [67]. At a high temperature, this condition of thermodynamic approach for nanosized particles is met.

Because in supercritical conditions the main factor responsible for homogeneous aggregation of particles associated with surface tension at the liquid—gas interface is inactive, supercritical water is capable of dissolving substances which are practically insoluble in standard conditions; some oxides also belong here [176-178]. Subsequently, when the solution reaches supersaturation, the solid crystalline phase of oxide nanoparticles of about the same size and with a fairly well developed surface is precipitated. The critical degree of supersaturation $\gamma = c/c_s$ can be evaluated by expressing the difference of the chemical potentials obtained above, $\Delta\mu = 2\sigma(\infty)V_a/Rkp$ of the critical nanoparticle nucleus and of the phase-forming medium, through the concentration c of the material in the supersaturated solution and its equilibrium solubility c_s relative to the crystalline phase. For an ideal solution we obtain $\ln\gamma = \ln(c/c_s) = \Delta\mu/RT = 2\sigma(\infty)V_a/Rkp\ RT$. The parameters of the solid nuclei forming in the liquid phase in a supercooled solution can likewise be derived from the above expression using the relation $\Delta\mu = \Delta H_\Pi - T\Delta S_\Pi = \Delta H_\Pi \Delta T/T_\Pi$ where $\Delta T = T_\Pi - T$s the supercooling, and ΔH_Π is the enthalpy of the process.

In a similar way, one can obtain quantitative estimates for heterogeneous condensation in formation of a new phase on the already available surfaces (walls of the vessel, particles of foreign substances acting as condensation nuclei). As follows from these estimates, the work expended for the formation of solid nuclei in heterogeneous condensation should be smaller than that spent in a homogeneous process by the same factor the volume of the bubble nucleus on the surface of a condensation nucleus is smaller than the volume of the sphere of the same curvature. The processes of adhesion and wetting, active in interaction between the new phase and a foreign surface lower the energy of formation of nuclei, and the stronger are the adhesion and wetting, the smaller is the degree of supersaturation that will initiate condensation. The appearance of a charge in a metastable system will likewise reduce the Gibbs energy of formation for nuclei. Therefore, nuclei carrying a charge form at lower degrees of supersaturation, primarily because surface tension decreases with increasing electric potential of the surface (as follows from Lippmann's relation, $d\sigma/d\phi = -q_s$, the effect being the stronger, the larger is the charge of the unit surface q_s).

The above estimates relate to a single nucleus only and disregard the entropy component of the energy involved in formation of a mass of nuclei. For low interface tensions, the entropy component can cancel out the surface energy and initiate spontaneous dispersion. Evaluation of the conditions governing formation of nuclei from materials residing in non-autonomous state in media with spatial limitations, in particular, those resulting from the presence of nanoparticles of another phase distributed in these media, becomes complicated significantly, by requiring inclusion of the structure, composition and properties of the latter. In the case of classically-shaped nuclei (cube, sphere, cylinder), one succeeds in deriving analytical expressions relating their geometrical characteristics to the size of the nucleus of the new phase [173,174].

By the theory of M. Volmer and Ya. I. Frenkel [100,179], the kinetics of condensation-based formation of a new phase are determined by the rates both of generation of condensation centers $I = A_1 \exp[-\Delta G_1/(RT)]$, and of the supply of the material to the new condensation centers $U = A_2 \exp[-E_\eta/(RT)]$. The first of them is proportional to the probability of generation of condensation centers in accordance with the Gibbs energy ΔG_1, and the second, proportional to the probability of their "survival", in accordance with the activation energy E_η of the transition of material from the original phase to the surface of the nucleus. The total rate is a product of these probabilities, and it can pass through an extremum, depending on the relative values of the energies ΔG_1, E_η, temperature T and coefficients of proportionality A_1, A_2.

Besides the kinetic characteristics, one can readily use in evaluation of the degree of thermodynamic non-equilibrium of the process involved and conditions of self-organization of dissipative structures, entropy-based indices characterizing internal instability of the conversion of energy, which should be assigned to the increasing part played by the entailed thermodynamic fluxes and forces. It was shown [180,181] that in two-phase media, fluctuations of their characteristics become energetically preferable to steady-state regimes, by supporting lower energy dissipation (gain of entropy) with the coefficient of thermodynamic nonstationarity $\varepsilon = \bar{S}_{nstat}/S_{stat} < 1$. Here, S_{stat} is the gain of entropy in a system with steady-state thermodynamic fluxes and forces, and S_{nstat} is its average value in nonstationary regimes with fluctuations of fluxes and forces.

8. Modeling of integral characteristics of the phase-forming media

In all cases of outwardly random formation of such two-phase macroscopically strongly-inhomogeneous media, they reveal elements of deterministic behavior (deterministic chaos [182] and fractal self-similarity [183]). They are actually consequences of nonlinear interaction among components of a dissipative system and become most prominent near a specific value of phase concentration called the percolation threshold [184].

One of such characteristic effects in the field of consideration is the sharp drop in the electric conductivity of metals caused by electrons scattering from small-scale density fluctuations as they approach the critical point. At the same time, in metals whose critical temperature is comparable to its first ionization potential and which close to the critical point represent, as it were, a metallic plasma, the electric conductivity again increases. In these conditions, electrodual phases, scattered chaotically in a randomly nonuniform medium, assemble into a cluster of a conduction chain (or of its antipode—an insulation chain). One can pass along it through the whole system, retaining or losing its electric conductivity, respectively, as shown in this particular case. Although these effects are governed only by the chain reaching the opposite boundaries of the system (percolation medium), the cluster itself will contain other chains as well, which adjoin this conducting "skeleton" while not maintaining the percolation of the system as a whole. Modeling of such phenomena in a randomly inhomogeneous system was analyzed, in particular, in Ref. [185].

8.1. Effective conductance of electro-dual media

If the characteristic dimension of averaging exceeds by far that of the inhomogeneity, some integral characteristics of the system, for instance, the effective electrical conductivity

σ_e, which relates volume-averaged fields $\langle E\rangle$ and currents $\langle j\rangle$ in the expression $\langle j\rangle = \sigma_e\langle E\rangle$, in the vicinity of the percolation threshold turn out not to depend on the specific geometry of phase arrangement in the system. Above the percolation threshold, the effective conductivity of the system will be determined only by the phase conductivities σ_1 and σ_2, concentration p of phase 1 and concentration $(1-p)$ of phase 2 in the form $\sigma_e = [\sigma_1\sigma_2/p(1-p)]^{1/2}$ [185], and below the percolation threshold the conductivity will be zero.

In the lattice model of the "percolation medium" [184,186,187] the phase conductances are identified as whole (conducting the electric current) or blocked (non-conducting) connections among the lattice sites, and phase concentrations, as the probabilities of the corresponding bonds being whole or blocked. The percolation threshold in the bond problem corresponds to the probability of connection of whole bonds into a cluster chain, which for the first time brings the conductivity of a system as a whole to a non-zero value, and the percolation threshold in a site problem, to the probability of blocking of all connections leaving a site and resulting in zero conductivity of the system. As follows from calculations, although the percolation threshold for the problem of connections for any lattice does not exceed that for the problem of sites for the same lattice, the thresholds themselves depend significantly on the type of the problem considered [184,188]. To that end, it turns out that the number of bonds per site, just as the average fraction of the volume occupied by unblocked sites around each lattice site, does not depend on the lattice proper. It is determined by the dimension of problem only, leaving 2 for two-dimensional lattices and 1.5 for the three-dimensional ones in the first case, as well as 0.45 for two-dimensional lattices and 0.15 for three-dimensional ones in the second case [184]. Another feature common for problems of all types is also the way in which these thresholds are approached by such parameters as the fraction of the lattice sites belonging to the cluster formed, the geometric size of the cluster (correlation radius) and the effective electrical conductivity of the system expressed in the form of power functions of a given phase concentration: $P_j(x) = B_j(x - x_c)^{\beta j}$ for $x > x_c$ and $P_j(x) = 0$ for $x < x_c$, where B_j is a numerical coefficient, and β_j is the critical index of the quantity P_j. Moreover, it turns out that the values of all critical indices are universal for all percolation problems; they do not depend on the specific choice of the model of the medium, and are determined by the dimension of space only. Indeed, for two-dimensional problems the universal critical index of correlation length is $\nu = 1.33$, while for three-dimensional ones $\nu = 0.8 - 0.9$, the index of electrical conductance for three-dimensional problems $t = 2\nu$, for two-dimensional ones $t = \upsilon$, and the mass ratio index for two-dimensional problems $\beta = 0.14$, while for three-dimensional ones – $\beta = 0.4$ [184].

8.2. Fractal characteristics of media with scaling invariance

This can be used as a basis for the determination of the fractal dimension of the conduction chain cluster formed. It is a specific characteristic of the self-organizing scaling symmetry (hierarchical self-similarity) in all space scales in which a system is considered, from the size of a few lattice cells to the characteristic size of fluctuations (correlation radius) encompassing the whole metastable region as one approaches the critical point (percolation threshold). Based upon the determination of fractal dimension as a power exponent D of non-Euclidian expression $\Phi \sim m^D$ relating the rate of variation of the number Φ of elements in the fractal and the variation of the scale m of their consideration [189], one can find the relation connecting the fractal dimension of a percolation cluster with the critical indices in the form $D = d - \beta/\nu$ The numerical values of the fractal dimension of the "percolation medium" is $D \approx 1.895$ for two-dimensional, and $D \approx 2.556$ for three-dimensional problems [188]. This is smaller than the topological (Euclidean) dimension of nested space and can be identified with versions intermediate between the dimensions of a line and an area, as well as between an area and a volume, so that the percolation skeleton reminds a lace cloth or a sponge in the first and second cases, respectively.

The above figures were taken from one of particular versions of numerical evaluation applied to such multifractal media. The Renji dimension serves as a general expression of their dimensions, used in the description of real dissipative objects [190] $D_{Rq} = \lim\limits_{\varepsilon \to 0} \lim\limits_{\tau \to 0} \lim\limits_{m \to \infty} \left[\frac{1}{1-q} \frac{\ln I_{Rq}(q,\varepsilon)}{\ln(1/\varepsilon)} \right]$. Here, $I_{Rq}(q,\varepsilon) = [\sum\limits_{i=1}^{M(\varepsilon)} p_i^q(\varepsilon)]$ is the generalized Renji entropy of order q; $M(\varepsilon)$ is the minimum number of "measuring" cubes with an edge ε required to cover the fractal in n-dimensional phase coordinate nesting space; p_i are the probabilities of contact of the i-th cube by the phase trajectory; and m is the number of points employed in calculation of the dimension. This relation yields, as particular cases for different q, the well-known relations for entropy of Kolmogorov-Sinay and of fractal dimension of Kolmogorov-Hausdorff ($q = 0$), entropy of Shannon and for the corresponding information dimension ($q = 1$), correlation entropy and correlation dimension ($q = 2$) [191]. The Renji dimension being a monotonically decreasing function of q, mapping of the fractal in the latter case for $q = 2$ requires the smallest dimension n of the nesting space, and it is this dimension that is used in evaluation of the fractal dimension of a percolation cluster as the most appropriate one for calculations.

Significantly, this fractal self-similarity for percolation clusters is met in the statistical meaning only. It reflects elements of deterministic behavior (deterministic chaos) in an externally chaotic formation of similar macroscopically inhomogeneous media as a product of nonlinear interaction of components of a strongly inhomogeneous dissipative thermodynamic system.

9. Conclusion

Dispersion of a metal driven by the development of thermodynamic instabilities of its physical state in the vicinity of the critical point is of a pure and applied research interest in the field of present-day nanotechnologies. This review offers an analysis of the possibility of employing the approach outlined here in obtaining oxide nanoparticles up to a few nanometers in size by electrical explosion of metallic conductors (EEC) in a chemically active dense aqueous medium.

Various physical models were invoked to show that this would require constraining the part played by non-thermodynamic mechanisms in destruction of a metal in the course of varying the physical state of the conductor being exploded, so as to mediate its transition close to the limit of the nonequilibrium metastable state with the maximum possible overheating and fast approach to the critical point through "explosive" boiling-up combined with generation of homogeneous vaporization.

Estimates suggest that the rate of Joule heating by electric current required for this purpose with a metal of the aluminum and copper type, performed with due account of counteracting factors, should be not less than $\dot{T} \geqslant 10^{11}$ K/s. This requirement is met for power densities generated in the material by injected energy in excess of $> 10^{10}$ W/cm^3 and supercritical temperatures ($T \geqslant T_{cr}$) reached in times $\tau < 100$ ns. Among the natural factors which plague reaching the highest possible metastable states of the melting metal and the onset of homogeneous vaporization are the evaporation wave propagating inside the overheating metal and formation of plasma in the vicinity of the critical point, which drives heterogeneous boiling on charged particles. To limit the part played by non-thermodynamic instabilities driven by surface tension forces, magnetohydrodynamic (MHD) instabilities of the waist and convective types, current skinning and development of barocapillary instability, it is proposed to employ a geometric configuration of electric explosion of conductors new for the problem considered here. It is the explosion of a thin-walled cylindrical shell positioned on a rigid dielectric cylinder, with the return current conductor stretched axially inside the shell. Significantly, the reactor being of a fairly arbitrary shape and size, the load can be placed into a water chamber.

Experimental studies prepared in accordance with the corresponding calculations require development of a pulsed source of energy which would provide a high rate of growth for the discharge current and a high power of electric discharge through the shell, $Q_V \geqslant 1$ TW/cm^3, by generating current pulses with the leading edge less than < 10 ns and amplitude of up to 100 kA. Present-day technology of accumulation and switching of energy offers adequate possibilities for injection of the required specific powers into a material.

Of a particular significance for realization of optimum regimes of energy input into a conductor is matching its physical properties and size with the characteristics of the energy source used. To solve this problem, one can conveniently use MHD calculations of EEC, which demonstrate the possibility of development of the desired EEC regime of a thin-walled metallic shell in a water medium, which would provide uniform power input into the metal and a current “pause”. These calculations involve equations of state, which take into account single-phase and equilibrium two-phase states of the material in mean-field approximation bounded by binodal branches. The fairly few attempts undertaken in investigation of EEC-based metastable states by MHD modeling and application of statistical approaches of the theory of macroscopic invariance to description of critical phenomena in the vicinity of the critical point of metals are still far from completion. At the same time, one succeeds in estimating within this framework some integral characteristics of such systems, of the type of their effective electrical conductivity and fractality. They show up as elements of deterministic behavior (deterministic chaos and fractal self-similarity) in all cases of outwardly chaotic formation of such two-phase, macroscopically strongly nonuniform media as a result of nonlinear interaction of components of a dissipative system.

The conclusive stage of nanoparticle formation in an electric explosion of metallic conductors in a water medium encompasses flying apart and condensation of its products. These processes are complicated by the presence on particles of an electric charge produced in thermal ionization of the metal near the critical point, as well as by their chemical interaction with the supercritical fluids forming as a result of fast local heating, shock wave propagation, collapse of cavitation bubbles and other similar phenomena. Because the main reason of homogeneous aggregation of particles, which is surface tension at the liquid—gas interface, is not realized in supercritical conditions, supercritical water is capable of dissolving substances practically insoluble under normal conditions, including some oxides. After the solution had reached subsequently supersaturation, a solid crystalline phase of oxide nanoparticles of about the same size and a fairly developed surface precipitates.

The method of synthesis considered here is potentially capable of producing oxide nanoparticles differing from nanoparticles of the same oxides but synthesized in electric explosion of metals in air or other oxygen-containing gaseous media, as well as in hydrothermal synthesis in its classical methodological form. The oxide nanopowders, formed in EEC of metals in water, can possess, in particular, due to the reducing medium employed and high-energy conditions mediating the locally hydrothermal synthesis in the supercritical fluid nanoreactor, a still higher level of catalytic, sorption and other functional characteristics.

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