Features of metastable states in liquid-vapor phase transitions

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The current state of the physics of metastable liquid systems is reviewed. The experimental data and results of theoretical calculations of the properties of liquids in the metastable region near the *binodal*, including the critical point, are discussed. A classification of metastable states is presented. The criteria for the possible depth of intrusion into the metastable region are discussed, and their relation to the Ginzburg criterion known in the theory of critical phenomena is studied. Especial attention is paid to the problem of the equation of state. A comparative analysis is performed of the equations of state in the metastable region, both far from the critical point and in its close vicinity. The results are discussed of studies devoted to investigating metastable systems (liquids and liquid crystals) near the *spinodal*. The problem is discussed of the appearance and development of fractal structures in the metastable region.

1. INTRODUCTION

The study of the physical properties of substances in a metastable state pertains to the general problem of phase transformations and is one of the most important and pressing problems in modern physics. Metastable states arise in first-order phase transitions, examples of which are such widespread phenomena as evaporation, condensation, or crystallization. Examples of processes of another nature in which metastable states can be realized are phase transitions in nuclear matter and in a quark-gluon plasma, the inflational expansion of the Universe at the early stages of its evolution, and the condensation and decomposition of an electron-hole liquid in semiconductors. Metastable states arise in biological and chemically reacting systems far from the state of thermodynamic equilibrium near the threshold of self-organization. In dynamic systems described by Lorentz-type models, metastable chaotic states are also formed for certain values of the parameters of the model. It has been recently found that metastable states have an important role in the onset of high-temperature superconductivity in compounds of the 1-2-3 type, where the problem of labile oxygen is important.

One of the fundamental properties of metastable states is their finite lifetime. The decay of metastable states is caused by the fluctuational formation and growth of nuclei of a competing phase. Thus the thermophysical properties, stability, and lifetime of metastable states are closely connected with the nature of the fluctuation processes that lead to development of the new phase.

In recent years interest has grown considerably in studying the nature of metastable states and first-order phase transitions. In many ways this has happened owing to the overall progress that was achieved during the 70s in the physics of second-order phase transitions. The latter science, based on the fundamental ideas of scale invariance and the renormalization group, and also on the results of a large number of precision experiments, attained, following the studies of A. Z. Patashinskiĭ and V. L. Pokrovskiĭ, and of C. T. R. Wilson, a state of "respectability" (in the expression of K. Domb). This appeared to mark the logical culmination of the hundred-year cycle of development of this science. The ideas and methods that have proved themselves so well in creating the fluctuation theory of second-order phase transitions are being used ever more intensively now for studying the features of first-order phase transitions and the nature of metastable states that arise here.

Up to now a very considerable experimental and theoretical material has been amassed on studies of superheated and supercooled liquids, metastable polymeric and liquid-crystalline systems, and also metallic alloys and amorphous alloys.

The aim of this review is to discuss the properties of liquids in the metastable region in the liquid-vapor phase transition. This article studies the criteria of stability of metastable states and their relationship to the Ginzburg criterion known in the theory of critical phenomena. The possibility is discussed of using the equation of state to describe the thermophysical properties of liquids in different parts of the metastable region. Near the binodal, where the symmetry of the metastable liquid is analogous to the symmetry of a stable liquid, one can extrapolate the equation of state from the homogeneous liquid phase into the metastable region. In the vicinity of the spinodal, where the symmetry of the system is determined by fluctuations of the order parameter that are strongly correlated at great distances, the features of the thermodynamic quantities are described by using the pseudocritical indices. In closing we discuss the fractal nature of the nuclei of the new phase being formed.

2. DEVELOPMENT OF IDEAS ON THE NATURE OF METASTABLE STATES OF MATTER

The beginning of the experimental studies of the very possibility of existence of materials in a metastable state goes back to the latter half of the 17th Century, when the experiments of Ch. Huygens and R. Boyle first demonstrated that water and mercury can be converted into a metastable state having a negative pressure.[1] This happened even before the publication of I. Newton's "Principia" (1687), and also long before the rise in physics of ideas of the equation of state of condensed matter. Apparently this is the explanation of

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the fact that, although the results of the very first experiments of Huygens and Boyle were still known as late as 1805 by T. Young and P.-S. Laplace, however, they were forgotten for a rather prolonged time. The rediscovery of the possible existence of negative pressures in liquids then occurred several times, beginning in 1846 (F. Donni), and later owing to the studies of O. Reynolds published in 1882. Only after the publication of the equation of state of van der Waals in 1873 was the possibility opened for interpreting negative pressures in connection with the appearance of metastable states of the liquid phase. The term "metastable" was proposed by W. Ostwald in 1893 as a generalization for the states described by the van der Waals isotherm that lie outside the region of absolute stability.

The first experimental studies of metastable superheated liquids pertain to the 70s of the 18th Century, when the very possibility of superheating a liquid was demonstrated.[2] Already at that time it was shown that carefully degassed water at normal pressure can be brought to a temperature greater than 200 °C without boiling. The statement was even expressed that a completely pure liquid containing no dissolved gases cannot boil at all. The modern stage of the experimental study of the properties of superheated liquids begins with the studies of K. L. Wismer published in 1922.[3] However, even before this work, studies were begun on nucleation phenomena in a supersaturated vapor by using the Wilson chamber.[4,5] These studies, which were substantially refined later, were the foundation of an entire experimental field on the study of nucleation that has developed until the present.[6–9] As regards the development of the theory on the nature of metastable states, as the science of phase transitions in materials has become established, this problem has entered the "jurisdiction" of the physics of first-order phase transitions, the foundations of which were laid in the classical studies of J. W. Gibbs, M. Vollmer, F. Becker, W. Döring, Ya. I. Frenkel', and Ya. B. Zel'dovich,[10–14] and also in the studies of many other investigators. We should note that a complete microscopical theory of first-order phase transitions (analogous, e.g., to the corresponding theory of second-order phase transitions and critical phenomena) has not yet been created up to now.[15]

From the standpoint of theory, metastable states are understood to be certain transitions or intermediate states of matter that precede the appearance of a stable phase. Initially the thermodynamic stability of metastable states was studied within the framework of the van der Waals–Maxwell theory[16,17] for the liquid-vapor phase transition. There are a number of equivalent thermodynamic theories that contain the possibility of describing metastable states in systems of another physical nature (e.g., the Bragg–Williams theory[18] for binary alloys). These, just like other analogous theories, have used the concept of the self-consistent field (SCF), which acts on the molecules or atoms of the system. A general approach to thermodynamic phase transitions within the framework of the SCF theory was developed by L. D. Landau.[19] One of the important results of Landau's theory of phase transitions was the possibility of deriving equations for the line of phase equilibrium (coexistence curve, or binodal), and also for the spinodal.

Statistical physics lacks at present a consistent theory of metastable states possessing the same level of rigor as the Gibbs theory of equilibrium statistical ensembles. The fundamental difficulty here involves the fact that the methods of equilibrium statistical thermodynamics must be applied to phenomena that occur outside the region of complete thermodynamic stability, i.e., to phenomena that are in essence dynamic and non-equilibrium. What we have said pertains directly to the process of formation of a new phase.

Definite progress has been attained along the path of development of quasithermodynamic approximations.[8–12] By using the Einstein formula to calculate the probability of spontaneous formation of nuclei of spherical form with definite values of the radius and surface tension coefficient, together with kinetic estimates for the number of colliding molecules of the metastable phase with drop nuclei of the new stable phase, it was possible to solve successfully a number of problems of the physics of metastable states involving processes of evaporation, condensation, and crystallization. This includes important problems on the magnitude of the energy barrier of formation of spherical nuclei of critical dimension and on the rate of growth of the new phase.[8–12]

At the same time we should note that up to now a number of new methods has been developed for solving problems in the physics of metastable states. These methods are based to a substantial degree on the fundamental ideas of statistical thermodynamics and physical kinetics. We should include among them first of all:

–the derivation by Ya. I. Frenkel' and Ya. B. Zel'dovich of a kinetic equation of the Fokker–Planck–Kolmogorov type for the distribution function of the nuclei with respect to dimensions;[13-14]

–the creation by E. M. Lifshits and V. V. Slëzov of a theory of coalescence of nuclei, i.e., of the process of growth of large nuclei owing to disappearance of small nuclei in the late stage of phase transformation;[20,21]

–the application in the studies of F. M. Kuni and his associates of the idea of a hierarchy of characteristic times for correct solution of the Zel'dovich–Frenkel' equation for the different stages of the nucleation process;[22–24]

–the obtaining of a set of rigorous results based on the methods of introduction of contracted statistical ensembles pertaining to the problem of substantiating the statistical mechanics of metastable systems;[25–27]

–use of Monte Carlo methods and molecular dynamics for computer simulation of metastable states and studying the kinetics of first-order phase transitions.[28–32]

However, along with this we should note that taking account of the effects involving the presence of fluctuations of the order parameter correlated at large distances and times is essential not only near the critical point, but also in the neighborhood of the spinodal.[33–44]

It has been experimentally established[45,46] that, as one approaches points of the spinodal in a metastable system, response functions increase, such as the isothermal compressibility (susceptibility), the isobaric heat capacity, and the coefficient of thermal expansion. Such a behavior of the thermodynamic quantities in the metastable region is analogous to critical phenomena and indicates that, for correct description of the properties of metastable states lying near a spinodal, one must also use the methods of scaling and renormalization groups, besides the classical approach based on the Landau SCF theory.

In connection with what we have said above, the question of how far the analogy extends between critical phenom-

ena and phenomena near a spinodal is highly essential for a correct description of processes throughout the metastable region of a material. In particular, the problem of calculating the so-called pseudocritical indices that characterize the features of the physical properties of a material near a spinodal, but far from the critical point, acquires a fundamental significance.[47–55] Another question, no less important, is to establish the conditions under which a transition (crossover) occurs from pseudocritical behavior of the system to critical behavior, which corresponds to transition in the metastable region from the neighborhood of the spinodal to the critical point. Such a crossover was first studied in Refs. 54 and 55 for a metastable fluid within the framework of the SCF theory.

Evidently one of the questions of principle in the physics of metastable states is the question of the magnitude of the neighborhood of the binodal in which one can actually observe metastable states and study their properties. It was shown[53] that the magnitude of the energy barrier for formation of nuclei, which determines the depth of possible incursion into the region of metastable states is associated with the Ginzburg number—a factor that takes account of the nonlocal and nonlinear interaction of the fluctuations of the order parameter.[19,34] For systems in which the Ginzburg number is small (the phase transitions in such systems are described by the SCF theory), one should expect a real possibility of reaching the close vicinity of the spinodal under real experimental conditions. We should include among objects of this type primarily systems having a large radius of interparticle interaction: certain binary alloys and nematic liquid crystals.

Among the typical experimental methods of observing deeply metastable states and studying their properties, we shall point out first of all the methods of light scattering and slow-neutron scattering, and also ultrasound absorption.[37,38,40,57] The methods of computer simulation of three-dimensional Ising systems with a large number of closest neighbors also play an important role.[31,57,58] These experiments have observed the fast approach to zero of the reciprocal susceptibility as the spinodal is approached that is predicted by theory. Here the lifetimes of the metastable states near the spinodal prove to be greater as the number of closest neighbors for each lattice node increases, i.e., as the system being studied approaches that described by the SCF theory.

As regards metastable states lying near the line of phase equilibrium (the binodal), they can be rather fully studied within the framework of the theory already mentioned above of the type of the Becker–Döring and Frenkel'–Zel'dovich theories. However, in studying the features of the relaxation of metastable states near the spinodal, great difficulties arise. In this situation, on the one hand, one must take account of the features of the response function caused by the interaction of the fluctuations of the order parameter, and on the other hand—the complex nonlinear process that occurs on this same background of appearance and growth of large-scale heterophase fluctuations, i.e., nuclei of the new phase.

The formation of fluctuation clusters in the metastable region, just like the growth of the new phase near the spinodal, is an example of processes characterized by the appearance of structures of fractal nature. The study of fractals has penetrated rather deeply into physics as a whole, while the language of fractal geometry has proved very convenient and useful for solving many problems in the physics of phase transitions.[59] The analysis conducted in Ref. 60 of the dimensionalities and codimensionalities of the structures formed in the metastable region shows that the appearance of compact spherical nuclei is improbable, since the structure of the nuclei that arise near the spinodal is typically fractal. The description of the merger of fractal clusters in the process of phase transformation is related in nontrivial fashion with the ideas of transversality of the intersection of manifolds and with catastrophe theory.[61]

Another, no less important aspect in the study of metastable states and the properties of materials outside the region of complete thermodynamic stability is the need to know the equation of state of the metastable system being studied. Review papers have been devoted to the problem of the equation of state in the metastable region[9,26] (see also Refs. 62 and 63). Here it is essential (primarily from the standpoint of experimental studies) that the corresponding equation of state enables a rather exact calculation of the fundamental thermodynamic functions of the metastable material.

3. CLASSIFICATION OF METASTABLE STATES

Let us examine the diagram of state of a one-component system that undergoes a liquid-gas phase transition in the coordinates p (pressure) and ρ (number density) (Fig. 1). The metastable states in this diagram correspond to the region between the binodal AKB and the spinodal CKD, at the points of which $(\partial p/\partial \rho)_T = 0$, where T is the temperature. The region to the left of $\rho = \rho_c$ (ρ_c is the critical density) corresponds to supersaturated vapor, while the region to the right of $\rho = \rho_c$ corresponds to superheated liquid. The curve CKD bounds the region of thermodynamically absolutely unstable states: $(\partial p/\partial \rho)_T < 0$. Separation of the system into two phases occurs in this region by the mechanism of spinodal decomposition, which is an essentially nonlinear nonequilibrium process. To analyze the stability of the system with respect to fluctuations of the volume V, let us study the function

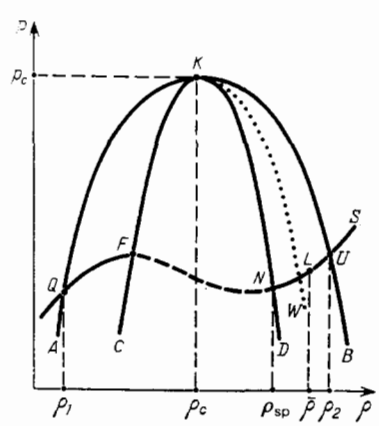

FIG. 1. Isotherm $SULNFQ$ of a liquid-gas system corresponding to a temperature $T < T_c$, in the coordinates density (ρ) as a function of pressure (p); T_c, p_c, and ρ_c are the critical values of the temperature, pressure, and density, K is the critical point, AKB is the coexistence curve (binodal), CKD is the spinodal, ρ_1 is the density of the gas at the binodal, ρ_2 is the density of the liquid at the binodal, and ρ is the observed density in the metastable state, ρ_{sp} is the density at the spinodal on the side of the liquid branch of the isotherm.

$$f(V) = f(V, N, p, T)$$
$$= \Xi^{-1}(p, T, N) \exp[-pV(k_B T)^{-1}] Z(V, T, N), \quad (3.1)$$

Here $\Xi(p,T,N)$ is the partition function of the isobaric-isothermal ensemble, k_B is the Boltzmann constant, $Z(V,T,N)$ is the partition function of the canonical ensemble, and N is the number of molecules in the system. We note that V is a possible value of the volume of the system, the observed mean value of the volume is $\langle V \rangle = -k_B T(\partial \ln \Xi/\partial P)_{T,N}$, and $\langle(\Delta V)^2\rangle = \langle(V - \langle V\rangle)^2\rangle = -k_B T(\partial \ln \langle V\rangle/\partial P)_{T,N}$.[64]

The function $f(V)$ is the probability density of finding a system of N molecules at the temperature T and pressure p in a state of volume V. The schematic form of $f(V)$ is shown in Fig. 2. Since $Z(V, T, N) = \exp(-F(V, T, N)/k_B T$, where $F(V, T, N)$ is the free energy, then, upon assuming the volume fluctuations to be small $\langle(\Delta V)^2\rangle^{1/2}/\langle V\rangle \ll 1$, we expand the argument of the exponential $-(pV + F(V, T, N)/k_B T$ in (3.1) in powers of ΔV up to second-order terms. Consequently we obtain

$$f(V) \sim \exp[-N(\Delta V)^2(2k_B T\rho\chi)^{-1}], \quad (3.2)$$

where χ is the isothermal compressibility. The form of the function $f(V)$ from (3.2) shows that the approximation of small fluctuations in a smooth region of variation of the thermodynamic variables is justified, since the half-width D of the $f(V)$ curve (in units of ΔV) is

$$D \approx \frac{2{,}36\,(k_B T\rho\chi)^{1/2}}{N^{1/2}}$$
$$= O\left(\frac{1}{N^{1/2}}\right) = o(1). \quad (3.3)$$

This implies that states with $V = \langle V\rangle$ for $N \gg 1$ are most probable, while the possible fluctuations are vanishingly small.

It will be more convenient below in characterizing the different regions of the diagram of state to plot the relationship of $-\ln f(V) = F(V, T, N) + pV$ to V instead of $f(V)$. We note that $-\ln f(V)$ does not coincide with the thermodynamic Gibbs potential G, since we have

$$G(p, T, N) = F(\langle V(p, T, N)\rangle, T, N) + p\langle V(p, T, N)\rangle.$$

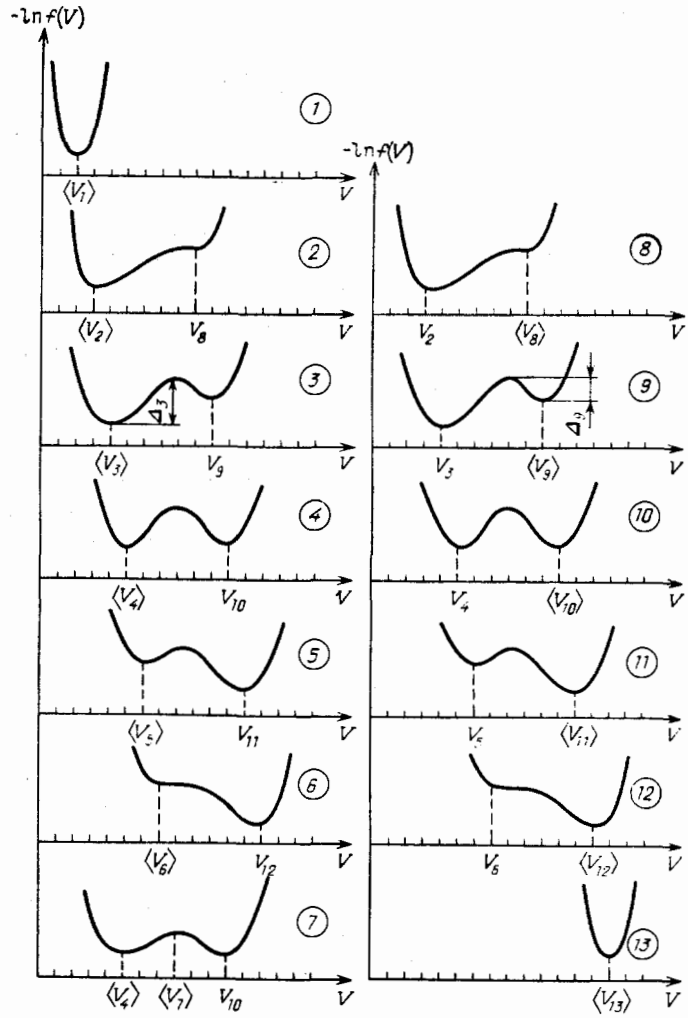

FIG. 3. (See explanation in text.)

A set of $-\ln f(V)$ dependences is shown schematically in Fig. 3, while the corresponding points of the $p - \rho$ diagram are shown in Fig. 4.

Diagrams *5* and *9* of Fig. 3 correspond to a metastable state (the corresponding points are *5* and *9* in Fig. 4). Diagram *7* of Fig. 3 (point *7* in Fig. 4) corresponds to an abso-

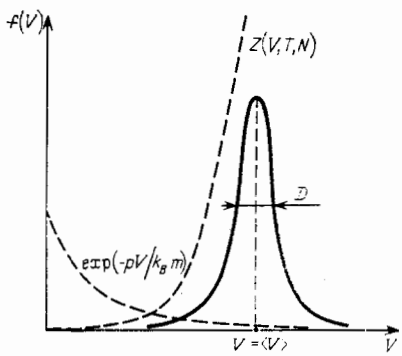

FIG. 2. (See explanation in text.)

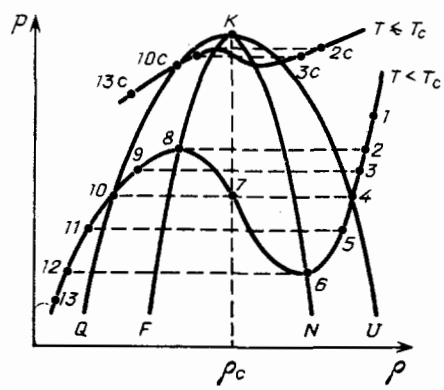

FIG. 4. Phase diagram of metastable states corresponding to the cases shown in Fig. 3.

lutely unstable state. The stable states (e.g., diagrams *2* and *3* of Fig. 3) contain in the partition function Ξ (p, T, N) information on the extrema of the function $-\ln f(V)$ (or as is the same, on the second maxima of $f(V)$) lying at the points $V = V_8$ and $V = V_9$. However, in view of (3.3), the statistical weight of the metastable states far from the critical point is very small, since they are not realized in phase space owing to the large value of the energy barrier Δ_3. In the case in which one observes a metastable state (diagram *9* of Fig. 3), the magnitude of barrier Δ_9 can differ, depending on the position of point *9*; if it is close to the binodal (while diagram *9* of Fig. 3 resembles diagram *10* more than diagram *8* of Fig. 3), then the barrier diminishes, and in the limit we have $\Delta_9 \to \Delta_8 = 0$.

As we approach the critical point, the extrema of the function $-\ln f(V)$ approach one another, whereby the magnitude of the energy barrier between the metastable and stable states decreases. Actually, one can easily show that in this case we have

$$|[\ln f(V)|_{V=V_{\max}} - \ln f(V)|_{V=V_{\min}}]|(k_B T)^{-1} \to O\left(\left|\frac{V_{\min} - V_{\max}}{V_{\min}}\right|\right). \quad (3.4)$$

Here $V_{\min}$ and $V_{\max}$ are the values of the volume corresponding to the minimum and maximum of the function $-\ln f(V)$. Then at the points $2c$ and $3c$ (see Fig. 4) the system already "senses" the existence of the extrema of the function $f(V)$, since, at large values of the isothermal compressibility, D becomes of the order of unity, even for a macroscopic value of the fluctuating volume V.

Thus the physical properties of metastable states depend substantially on the magnitude of the contribution of the fluctuation effects of different types to the thermodynamic potentials of the system under study. Thus, for metastable states in the close vicinity of a critical point, the decisive contribution is that of the fluctuations of the characteristic order parameter $(\rho - \rho_c)$ that are strongly correlated at great distances. On the other hand, far from the critical point, but near the spinodal, under certain conditions the homophase fluctuations of the order parameter $(\rho - \rho_{sp})$ that are associated with the closeness of the metastable states to the stability boundary prove to be essential. In the region close to the binodal and far from the critical point, the fluctuational contributions to the thermodynamic quantities are not decisive.[65] In line with what we have presented above, in studying processes that occur in the metastable region, it is convenient to divide this region into the parts shown in Fig. 5.

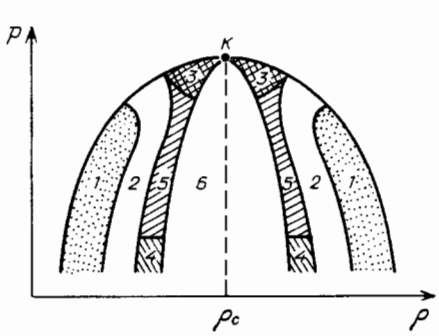

FIG. 5. Classification of metastable states (see explanation in text).

Part 1–nonfluctuational region.

Part 2–transitional (crossover) region from nonfluctuational to fluctuational.

Parts 3–5–fluctuational regions with different types of fluctuations.

Part 3–region of critical fluctuations.

Part 4–region of homophase fluctuations involving the closeness to the stability boundary (pseudocritical region).

Part 5–transition (crossover) region from pseudocritical to critical behavior.

Part 6–region of spinodal decomposition.

We note that the constants of the relaxation equation of the fluctuations of the characteristic order parameter $\eta = (\rho - \langle\rho\rangle)/\langle\rho\rangle$, $\partial_\eta/\partial t = -(a_1\eta + a_2\eta^2 + a_3\eta^3)$ satisfy the following relationships in the listed parts of the metastable region:

$$\begin{array}{ll} a_1 \gg (a_2;\ a_3) & \text{(part 1)} \\ (a_1 \sim a_2) \gg a_3 & \text{(part 2)} \\ (a_1 \sim a_2) \ll a_3 & \text{(part 3)} \\ a_1 \ll (a_2;\ a_3) & \text{(part 4)} \\ a_1 \ll a_2 \ll a_3 & \text{(part 5)} \end{array} \quad (3.5)$$

4. METASTABLE STATES NEAR THE BINODAL

4.1. Criteria of stability

The possible existence of metastable states that are stable with respect to fluctuations of the density and the entropy S leading to formation of a new phase during a time commensurate with the time of experimental observation involves the discontinuous character of a first-order phase transition, namely, $p|V_1 - V_2| \gg k_B T$, $|S_1 - S_2| \gg k_B$. Because of this, a phase transformation in a macroscopic region of the volume being studied initiated by spontaneous fluctuations is extremely improbable. For approximate estimates of this probability, let us study the isothermal fluctuations in a subsystem with the mean value of the volume V_0, when the probability distribution density of the fluctuation of the volume $\Delta V = V - V_0$ equals[19] $w_V \sim \exp[(\Delta V)^2(\partial p/\partial V)_T/2k_B T]$, or, upon taking account of the normalization conditions,

$$w_V = \left(\frac{p}{2\pi V_0 \chi^* k_B T}\right)^{1/2} \exp\left[-\frac{pV_0(\Delta v)^2}{2k_B T\chi^*}\right]. \quad (4.1)$$

Here we have $\chi^* = p\chi$, $\Delta v = \Delta V/V_0$, while ΔV is the change in volume in a fluctuation. Since in a first-order phase transition we usually have $\Delta V \sim V_0$, we can write the condition of discontinuity of the transition in the form $pV_0 \gg k_B T$. For estimates of the order of magnitude of w_V, we shall use as an example the experimental data for water (H_2O) from Ref. 9. Then, for $T = 300$ °C and $p = 0.1$ MPa, we have $\chi^* \sim 10^{-3}$, $pV_0(\Delta v)^2/2k_B T\chi^* \sim 10^{28}\ \mathrm{m}^{-3}\cdot V_0$. We obtain as the magnitude of the preexponential coefficient the estimate $(p/2\pi V_0\chi^* k_B T)^{1/2} \sim 10^{14}\ \mathrm{m}^{-1/2}\cdot V_0^{-1/2}$. The resulting estimate for the probability density of volume fluctuation in this sense acquires the form

$$w_V \approx 10^{14-(4.3\cdot 10^{26}\,\mathrm{M}^{-5})V_0\,\mathrm{M}^{-3/2}}\cdot V_0^{-1/2}. \tag{4.2}$$

That is, for macroscopic values of the volume V_0 this quantity is vanishingly small.

Thus, the fluctuational creation of a new phase can occur with appreciable probability only in rather small regions of the volume under study. However, in this case the term that becomes essential in the expression for the work of formation of a nucleus of the new phase becomes the one associated with the surface energy of the phase boundary. Thus nuclei with dimensions greater than the critical value ($R > R_0$) can grow further, while subcritical nuclei ($R < R_0$) disappear in time. In this regard, one can analyze the criteria of stability of a metastable phase within the framework of two approaches.

The first approach involves analyzing the probability w of formation of a nucleus of the new phase having compact form that is capable of further growth. Its volume is $V \sim R^d$, while the area of its surface is $A \sim R^{d-1}$, where R is the characteristic linear dimension of the nucleus, and d is the dimensionality of the space. In this case we have

$$w \sim \exp\left(-\frac{W_c}{k_B T}\right), \tag{4.3}$$

where W_c is the height of the activation barrier, which depends on the geometry of the surface of the nucleus being formed (the ratio $W_c/(k_B T) = G_c$ is sometimes called the Gibbs number). Thus, in the special case of spherical nuclei with $d = 3$, we have

$$\begin{aligned} W_c &= 16\pi\sigma^3\,[3\,(\bar{p} - p')^2]^{-1}, \\ R_c &= 2\sigma\,|\,\bar{p} - p'\,|^{-1}. \end{aligned} \tag{4.4}$$

Here σ is the surface-tension coefficient, and $\bar{p} - p'$ is the pressure difference between the point of observation and inside the nucleus. The corresponding change in the work of formation $\Delta\Phi$ of a nucleus as a function of its radius R is shown in Fig. 6. Equation (4.3) gives rise to an expression for the rate of nucleus formation in the steady-state case $J = nB\exp(-G)$, where B is the so-called kinetic coefficient (for a number of liquids $B \sim 10^{10}\ \mathrm{s}^{-1}$)[9], while $n \sim 10^{28}\ \mathrm{m}^{-3}$ is the number of molecules per unit volume of the liquid. Then the mean time of expectation of appearance of a viable nucleus of the new phase in the volume V is $\tau_0 = 1/JV$. If we choose $V \sim 10^{-6}\ \mathrm{m}^3$ and $\tau_0 \sim 1$ s, then one can write the criterion of stability of the metastable phase in this volume in the form $G_c \gtrsim 74$, or

$$16\pi\sigma^3\,[3k_B T\,(\bar{p} - p')^2]^{-1} \gg 1. \tag{4.5}$$

We should note that, in a number of studies devoted to problems of nucleation from a supersaturated vapor,[11,66] the inequality (4.5) corresponds to the criterion $G_0 = 60$, since in this case $n \sim 10^{25}\ \mathrm{m}^{-3}$.

We note that the kinetic coefficient has been estimated theoretically and its dependence of the thermophysical and molecular parameters of the system has been investigated in many studies devoted to problems of the kinetics of first-order phase transitions.[11–14,67,68]

The second approach to analyzing the criterion of stability of metastable states involves the treatment of the mean-square density fluctuations in an isobaric-isothermal ensemble[69]

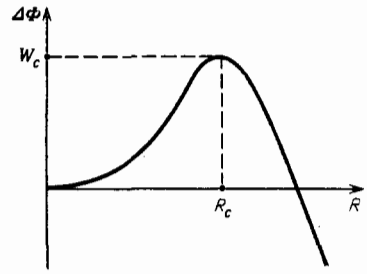

FIG. 6. Dependence of the work of formation of a spherical nucleus of the new phase $\Delta\Phi$ on its radius R.

$$\frac{\langle\Delta\rho^2\rangle}{\rho^2} = \frac{k_B T\chi}{V}. \tag{4.6}$$

Let us study the metastable states in a one-component liquid system at fixed temperature. The corresponding symbols are given in Fig. 1. As we move along a certain noncritical isotherm $SULNFQ$ at a temperature below the critical temperature ($T < T_c$), the system in the segment UN falls into the region of metastable states. In this region (U is a point of the binodal) thermodynamic stability breaks down with respect to fluctuational formation of nuclei of the new phase (bubbles of vapor) having a volume of the order of, or greater than, the volume v_c of a critical nucleus. In order that the system should still maintain thermodynamic stability at some point L of the metastable region, the inequality must be satisfied that

$$\langle\Delta\rho^2\rangle \ll (\bar{\rho} - \rho_1)^2.$$

Here $\langle\Delta\rho^2\rangle$ is the mean-square fluctuation of the density in a volume of the order of v_c calculated at the point L. Since we have $\langle\Delta\rho^2\rangle = \bar{\rho}^2 k_B T\chi/v_c$, evidently, for metastable states lying in the close vicinity of the binodal (where $v_c \to \infty$, while χ is not a singular quantity), the condition of thermodynamic stability is well satisfied. Upon further motion along the isotherm to a point of the spinodal (point N), we find $\chi \to \infty$, while v_c declines.[70] Therefore the condition of stability breaks down. Evidently the equation $k_B T\chi/v_c \approx [(\rho_1 - \bar{\rho})/\bar{\rho}]^2$ determines the boundary of the attainable superheating of the liquid (or the physical spinodal)—the dotted curve KW in Fig. 1. To the right of the curve KW in the metastable region near the binodal when

$$k_B T\chi\bar{\rho}^2\,[v_c\,(\bar{\rho} - \rho_1)^2]^{-1} \ll 1 \tag{4.7}$$

lies a region in which the density fluctuations are not essential in describing the thermodynamic properties of the system, while to the left of the curve KW, for which

$$k_B T\chi\bar{\rho}^2\,[v_c\,(\bar{\rho} - \rho_1)^2]^{-1} \gg 1, \tag{4.8}$$

lies the fluctuational region. In the intermediate region, in the vicinity of the curve KW itself, a crossover occurs in the behavior of the system from a regime of classical nucleation to a regime of spinodal nucleation, in which the decisive role is played by strongly developed fluctuations of the order parameter.

Let us study the region corresponding to the inequality (4.7). We shall introduce the dimensionless temperature $t = T/T_c$, the pressure $\Pi = p/p_c$, the density $R = \bar{\rho}/\rho_c$, the

compressibility $\chi^* = p\chi$, and the dimensionless parameter $\varepsilon = (\rho_2 - \bar{\rho})/(\rho_2 - \rho_1)$, which defines the depth of intrusion along the isotherm into the region of metastable states. Then we can rewrite the criterion (4.7) in the form

$$zv_c\chi^* tR^2 [v_c\Pi (\Delta\rho)^2(1 - \varepsilon)^2]^{-1} \ll 1. \quad (4.9)$$

Here $z = k_B T_c/p_c v_c$ is the compressibility factor, $\Delta\rho = (\rho_2 - \rho_1)/\rho_c$, while v_c is the critical volume per molecule (e.g., in the van der Waals theory v_c equals twelve times the volume of a single molecule). The inequality (4.9) amounts to the Ginzburg criterion, which defines the boundary of the nonfluctuational region for metastable states.

For proof, let us study the process of fluctuational formation of a spherical nucleus of the new phase (e.g., vapor bubbles). Here the radius of the critical nucleus in the approximation in which the quantities $|\bar{p} - p_s|$ and $|p' - p_s|$ are small (where p_s is the pressure at the binodal) is

$$R_c = 2\sigma\rho_2 [(p_s - \bar{p})(\rho_2 - \rho_1)]^{-1}. \quad (4.10)$$

If we study initially the thermodynamic states far from the critical point, for which the density of the saturated vapor is small (i.e., $\rho_1 \ll \rho_2$), then we have[71]

$$\sigma = \frac{\pi\bar{\rho}^2}{8} \int_0^\infty \varphi'(r)\, g(r)\, r^4\, dr. \quad (4.11)$$

Here $g(r)$ is the radial distribution function of the liquid phase, and $\varphi(r)$ is the pairwise intermolecular interaction potential. Upon choosing $\varphi(r)$ in the form of the three-dimensional Katz potential,

$$\varphi(r) = \infty, \quad r < D,$$
$$= -a\gamma^3 \frac{\exp(-\gamma r)}{4\pi}, \quad r > D, \quad (4.12)$$

where D is the diameter of the rigid core of the molecule, $\gamma^{-1} = R_0$ is the range of the attractive forces among the molecules, and $a\gamma^3/4\pi$ is the interaction constant, we obtain[60,69]

$$\sigma = \frac{\bar{\rho}^2 a R_0}{32} \left[\int_{\gamma D}^\infty g(xR_0) \exp(-x)\, x^4\, dx - \frac{4\pi k_B T D^3}{a} \frac{D}{R_0} \right]. \quad (4.13)$$

To make an approximate estimate of the magnitudes of the terms in the square brackets in Eq. (4.13), we can assume that $g(xR_0) \approx 1$, which is true for large values of R_0. Then the magnitude of the first term is $24 + O(D/R_0)$. For the second term we shall approximately estimate the coefficient of D/R_0. If we use for this purpose the van der Waals equation (the intermolecular potential of (4.12) leads to an equation of state of this type as $R_0 \to \infty$), then we have $4\pi k_B TD^3/a = 16t/9$. Thus, when $D/R_0 \lesssim 1$, the main contribution comes from the first term in square brackets in Eq. (4.13). Within the framework of this same approximation, the coefficient preceding the square brackets in (4.13) equals $a\bar{\rho}^2 R_0/32 = 3p_c R^2 R_0/32$.

Then we have the following estimation formulas for the surface-tension coefficient σ and the radius R_c of a critical nucleus:

$$\sigma \approx \frac{9}{4} p_c R^2 R_0, \quad R_c = \frac{9R^2 R_0 p_c \rho_2}{2\rho_c (\rho_s - \bar{\rho})}. \quad (4.14)$$

Let us calculate σ for argon according to the expression that we have derived. Thus, near the triple point we have $R^2 \sim 7.2$, $p_c \approx 4.9$ MPa. If we choose as R_5 the value of the amplitude of the correlation radius,[72] then we have $R_0 \approx 1.6 \times 10^{-10}$ m, and then $\sigma \approx 12.7 \times 10^{-3}$ N/m, whereas experiment yields $\sigma = 13.4 \times 10^{-3}$ N/m. If $R_0 \approx 3.4 \times 10^{-10}$ m, which corresponds approximately to the position of the first maximum of the radial distribution function, then we have $\sigma \approx 27 \times 10^{-3}$ N/m. The presented estimates confirm the validity of the derived relationships for σ and R_c. Upon substituting (4.14) into the inequality (4.9) in the approximation $\varepsilon \ll 1$ and $\rho_1 \ll \rho_2$, we obtain the criterion for the nonfluctuational region in the form

$$zv_c (\Delta p)^3 \Delta\rho t\chi^* (10^2 R_0^3 R^7 \Pi)^{-1}, \quad (4.15)$$

where $\Delta p = (p_s - \bar{p})/p_c$. We note that the maximum values of ε actually attainable experimentally are of the order of 10^{-2}.

The left-hand side of the inequality (4.15) is the product of factors of differing natures. The cofactor $(\Delta p)^3 \Delta\rho \cdot t\chi^*/\Pi R^7$ amounts to a quantity that determines the position of the system in the thermodynamic plane. The cofactor $zv/10^2 R_0^3$ depends only on the individual molecular properties of the system being studied. The compressibility factor for a large number of substances is equal on the average to 3.7. For a large number of liquids (carbon dioxide, ethane, ethylene, methane, benzene, water, argon, etc.), we have $v_c \approx (4\text{–}5)v_0$, where $v_0 = (4/3)\pi r_0^3$ is the volume of one molecule, and r_0 is the corresponding radius of the molecule. When we take account of the estimates presented above, the inequality (4.15) is rewritten in the form

$$z^2 \cdot 10^{-2}\, \mathrm{Gi}\, [(\Delta p)^3 \chi^* \Delta\rho t (R^7 \Pi)^{-1}]^2 \ll 1 + O(\varepsilon), \quad (4.16)$$

where $\mathrm{Gi} = (r_0/R_0)^6$ is the Ginzburg number.[34]

Thus the applicability of the theories of the metastable state that take no account of fluctuational effects is determined by both the individuality of the molecular parameters of the material ($\mathrm{Gi} \ll 1$), and by the parameters characterizing the thermodynamic state of the system. If we move into the region of metastable states along an isotherm, then the factor determining the behavior of the system is the magnitude of the isothermal compressibility χ, owing to the singular character of its density dependence as we approach the spinodal.

Interestingly, the van der Waals model corresponds to $\gamma \to 0$ (or $R_0 \to \infty$). Then we have $\mathrm{Gi} = 0$, and the behavior of the system throughout the metastable region up to the spinodal is described by the mean-field theory. For real systems this theory will work all the better near the spinodal as the Ginzburg number approaches zero. Such a situation corresponds to long-range attractive forces between the molecules, as occurs for large values of the dipole moment of the molecules, as, e.g., in the case of liquid crystals, for which $\mathrm{Gi} = 0.2$.[35]

Let us make estimates of the orders of magnitude on the left-hand side of the inequality (4.16) in the case of water. Far from the critical point for the isotherm with $T = 433$ K we find $\rho_1/\rho_2 \approx 0.025$. Then as we enter the metastable re-

gion from the side of the liquid branch of the isotherm $p_s = 0.62$ MPa, for $p = 0.1$ MPa we have $\chi^* \sim 10^{-4}$, $(\Delta p)^3 \sim 10^{-4}$, $\Delta\rho/R^7 \sim 10^{-3}$, $t \sim 1$, $\Pi \sim 10^{-3}$, $z = 4.35$. Here the inequality (4.16) acquires the form $10^{-17}\,\mathrm{Gi} \ll 1$. If we take account of the fact that for water $r_0 \sim R_0$, then evidently, in the pressure range 0.1 MPa $< p <$ 0.62 MPa, the isothermal compression of water at $T = 433$ K can be described by the standard methods of thermodynamic perturbation theory without taking account of the fluctuational corrections to the thermodynamic quantities and their derivatives.

We note that the derivation of the criterion (4.16) does not depend on whether we are treating a superheated liquid or a supercooled (supersaturated) vapor. However, interestingly, the criterion (4.16) is not symmetrical with respect to these two cases when one performs the appropriate numerical estimates. It turns out that the values of the quantity $\omega = \chi^*/R^7$ for the liquid branch of the isotherm are smaller by several orders of magnitude than for the gas branch of the isotherm. Actually, if we choose water as the example, we have: at $T = 433$ K for the liquid $\omega_2 \sim 10^{-6}$, for the vapor $\omega_1 \sim 10^{14}$, and $\omega_1/\omega_2 \sim 10^{20}$; for $T = 533$ K we have $\omega_2 \sim 10^{-5}$, $\omega_1 \sim 10^9$, and $\omega_1/\omega_2 \sim 10^{14}$; at $T = 573$ K we have $\omega_2 \sim 10^{-5}$, $\omega_1 \sim 10^5$, and $\omega_1/\omega_2 \sim 10^9$. The values of the thermodynamic quantities for making the presented estimates were chosen near the binodal. Thus, while for the superheated liquid the inequality (4.16) is satisfied with much room to spare, for the supercooled vapor it can be satisfied only for slight depths of intrusion (which corresponds to the smallness of the quantity $(\Delta p)^3$ or the closeness to unity of the quantity $\bar{p}/p_s$). Thus, in studying the equation of state of a supercooled vapor one must take account of the decisive role of the fluctuational corrections immediately after passing through the binodal.

One can study the criteria of stability of metastable states near the critical point analogously to how this was done in Refs. 60 and 69. Upon using the universal expressions for σ, χ^*, and Δp following their theory of scale invariance, the universal relationships among the critical amplitudes,[72] as well as the law of corresponding states for σ,[73] we can write the criterion for the nonfluctuational region in the form

$$2{,}5 \cdot 10^3 \varepsilon^2 \delta^2 (cR^2)^{-1} \mathrm{Gi} \ll 1. \tag{4.17}$$

Here δ is the index of the critical isotherm, and c is a dimensionless quantity, which, according to the law of corresponding states,[73] is universal for a class of liquids having similar intermolecular potentials. In this case the Ginzburg number is

$$\mathrm{Gi} = \left(\frac{r_0}{\xi_0}\right)^6. \tag{4.18}$$

Here r_0 is defined in the same way as when remote from the critical point, while ξ_0 is the amplitude of the correlation radius R_{cor}:

$$R_{\mathrm{cor}} = \xi_0 \tau^{\nu}. \tag{4.19}$$

Here $\tau = (T_c - T)/T_c$, while ν is the critical index of the correlation radius.

The corresponding numerical estimates performed[60,69] for water allow us to write (4.17) in the form $10^6\varepsilon^2 \ll 1$. This implies that, without taking account of fluctuations leading to formation of the new phase, one can describe the thermodynamic states in the metastable region near the critical point only for small values of the depth of intrusion. In this regard we note that, near the critical point, in describing the thermodynamic properties of a substance, we must also take account of the strongly developed interacting density fluctuations.

4.2. Equation of state

At present the problem of the equation of state in the metastable region within the framework of statistical thermodynamics remains open. One cannot even say with all assurance that such an equation of state exists in the metastable region. This situation involves the finiteness of the lifetime of the metastable state, and as a consequence, the impossibility of formulating the ergodic hypothesis in valid fashion.[26] Actually, the mean (observable) value of the dynamic variable $\psi(\Gamma(t))$ with respect to the time t ($\Gamma(t)$ is the point of phase space) is

$$\bar{\psi} = \lim_{\tau_{\mathrm{H}} \to \infty} \tau_{\mathrm{H}}^{-1} \int_0^{\tau_{\mathrm{H}}} \psi(\Gamma(t))\, dt. \tag{4.20}$$

This is identifiable within the framework of the ergodic hypothesis with the mean over an ensemble having the distribution function $f(\Gamma)$

$$\langle\psi\rangle = \int f(\Gamma)\psi(\Gamma) d\Gamma, \tag{4.21}$$

and depends in the metastable region on the time of observation τ_{obs}. The adoption as a hypothesis of the equation $\bar{\psi} = \langle\psi\rangle$ is based on the idea that, as the time $\tau_{\mathrm{obs}} \to \infty$, the imaging point in phase space spends time in all regions of the phase volume allowed by the external conditions. How should we proceed if the lifetime of the metastable state, and hence also τ_{obs}, is a finite quantity? The natural conclusion suggests itself that, in calculating the integral in (4.21), one must exclude from the region of integration certain regions of the phase volume that correspond to states with fluctuations leading to formation of stable nuclei of the new phase. Such attempts have been made in Ref. 74. However, it is not known at present how to do this in correct fashion (as depending on the magnitude of τ_{obs}).

The situation in the equilibrium statistical mechanics of stable states is not so dramatic, since the existence of the thermodynamic limit associated with the equation of state

$$\lim_{\substack{N \to \infty \\ (N/V = \rho = \mathrm{const})}} F(T, V, N) N^{-1} = F_1(T, \rho), \tag{4.22}$$

where F is the free energy of the system of N particles in the volume V at the temperature T, has been proved rigorously under requirements on the intermolecular interaction potential that are not too severe. The proof of the existence of the limit in (4.22) that was given in Refs. 75 and 76 for stable states gave rise to a new branch of mathematical physics—mathematical statistical physics. Yet the problem of the corresponding proof (for metastable states) based on using the theory of statistical ensembles remains open (in this regard see the review of Ref. 26).

A number of studies along this line have been published in recent years.[32,77–79] However, the authors of these studies

had to sacrifice either the freedom of choice of the intermolecular interaction potential (essentially restricting the treatment to the case $r_0/R_0 = (\mathrm{Gi})^{1/6} \ll 1$), or to omit individual parts of phase space, which, as was noted in Ref. 80, were chosen rather arbitrarily.

In a certain sense this situation gives grounds for amazement, since already A. F. Andreev[65] proved that, although the passage of an isotherm through the binodal line is characterized by a singularity, it is so weak that it can hardly ever by detected experimentally.

It is clear from what we have presented above that the problem of the thermodynamic properties of metastable states as calculated within the framework of statistical mechanics remains open and constitutes the content of an incomplete chapter of mathematical statistical physics. The interest in this problem is also heated up by the results of machine experiments in an Ising model with a nonzero magnetic field.[79] It turns out that in this case metastable states are "observed" despite having $\mathrm{Gi} \sim 1$ and rather large lattice dimensions. Apparently this involves the fact that numerical methods realize a calculation of $\bar{\psi}$ by (4.20), rather than of $\langle\psi\rangle$ by (4.21).

The very fact of realization of metastable states and the reproducibility of the experimental results are evidence that the equation of state in the metastable region exists, despite the lack of justification for it within the contemporary framework of statistical mechanics. Without expecting an expansion of this framework, Refs. 9, 81–83 propose analytic parametrizations of the existing experimental thermophysical data, whose role is difficult to overestimate. The results of these pioneer studies are as yet of applied character. However, their use in the fields of science that "exploit" the equation of state (chemical thermodynamics, acoustics, physics of combustion and explosion, etc.) is of great significance. The situation here recalls the history of the equation of state of real gases and condensed systems in the stable region, which began in 1846 (the equation of state of Ritter[84]) and the contemporary state of affairs in the field of thermodynamics of nuclear material at high energy densities (the region of the "hadron matter–quark-gluon plasma" phase transition), where semiempirical equations of state are used to describe both the results of real and of "numerical" experiments in lattices.[85]

Upon taking account of the results of Ref. 65, we can apparently speak within the framework of statistical mechanics of deriving the equation of state in the region of small fluctuations, where the system weakly "senses" the existence of the competing phase. Let us study, following Refs. 60 and 69, one of the possible approaches to the problem of the equation of state for small intrusions into the metastable region corresponding to Part I (see Fig. 5).

4.3. The equation of state in the nonfluctuational region

In the nonfluctuational region the system on both sides of the coexistence curve possesses an identical type of symmetry. Therefore the description of its thermodynamic properties can be based on an identical approach, both for stable and for metastable states. In studying the thermodynamic properties of a substance in the vicinity of points of the spinodal, the appearance of a new symmetry type is essential, as described by the renormalization group. Since in the nonfluctuational region the system has a definite symmetry with respect to a simple change of scale of the spatial variables $\mathbf{r}_i' = q\mathbf{r}_i$ (without averaging the order parameter over regions of dimensions of the order of the correlation radius), we can use this simple scale transformation to construct a thermodynamic theory of the perturbations. If we choose the scale factor q in the form $q = (V/V_0)^{1/3}$, where V_0 is the initial (reference) value of the volume, then the configurational component of the partition function of the canonical ensemble equals $Q(N,T,V) = q^{3N} Q_V(N,T,V_0)$, where

$$Q_V(N, T, V_0) = (N!)^{-1} \int_{V_0} \ldots \int d\mathbf{r}_1 \ldots d\mathbf{r}_N \exp\left[-\sum_{i<j}^{N} \varphi(q|\mathbf{r}_i - \mathbf{r}_j|)(k_B T)^{-1}\right] \tag{4.23}$$

is the configurational component of the partition function of the system of N particles in the volume V, but with the intermolecular interaction potential $\varphi(qr)$. Since here the choice of the magnitude of q satisfies $q^3 = V/V_0$, this means that the change of volume $\Delta V = (V_0 - V)/V_0$ in the scale transformation enters into the potential function, since $\Delta V = 1 - q^3$. Thus one can construct a thermodynamic theory of the perturbations by using as the small parameter the dimensionless quantity ΔV.[86] Actually, if we turn to the experimental data in the metastable region,[9] then, e.g., for water in the pressure range of 10 MPa we have $\Delta V \sim 0.02$. In essence the smallness of the parameter ΔV over a broad pressure range is made possible by the smallness of the isothermal compressibility χ^*, since we have $\Delta V \approx \chi^*(p - p_0)p_0$ in the nonfluctuational region, while $\chi^* \sim 10^{-3}$ (in the case of water at $T = 400$ K–500 K).

The use in the theory of perturbations of the intermolecular potential (4.12) based on a simple scale transformation leads to an equation of state of the form in Refs. 87 and 88. The results of calculations based on this theory are given in Tables I–III.

We should especially note the possibility of describing the thermophysical properties of metastable heavy water on the isotherms using the values of the constants of the equation of state found in the stable region of ordinary water.

TABLE I. Water, isotherm $T = 260$ °C, $p_s = 4.694$ MPa.

$p_0 - p$, MPa (exp.)	V, 10^{-3} m³/kg (exp.)	$-(\partial p/\partial V)_T$, 10^3 Mpa·kg/m³ (exp)	$p_0 - p$, MPa (theory)	$-(\partial p/\partial V)_T$, 10^3 MPa·kg/m³ (theory)
6	1,2771	460,60	5,972	461,56
7	1,2793	451,84	6,979	453,47
8	1,2816	443,34	8,013	445,39
9	1,2838	435,16	8,984	437,30
9,9	1,2859	427,29	9,895	430,02

TABLE II. Water, isotherm $T = 300$ °C, $p_s = 8.592$ MPa.

$p_0 - p$, MPa (exp.)	V, 10^{-3} m^3/kg (exp.)	$-(\partial p/\partial V)_T$, 10^3 Mpa·kg/m^3(exp)	$p_0 - p$, MPa (theory)	$-(\partial p/\partial V)_T$, 10^3 MPa·kg/m^3(theory)
2	1,4068	216,72	2,010	216,26
3	1,4115	208,99	3,008	208,24
5	1,4214	193,28	4,996	192,22
6	1,4267	185,43	6,002	184,21
7	1,4322	177,21	7,005	176,20
8	1,4380	169,61	8,018	168,19
9	1,4440	161,43	9,022	160,19
9,9	1,4497	153,97	9,935	152,98

This possibility arises because the parameters of the equation of state involve the intermolecular interaction potential, have a quite concrete physical meaning, and hence, must be the same for H_2O and D_2O. The proposed equation of state differs by this property from the widely used empirical equations, whose constants are fixed to a number of reference points.

The possibility of smooth extrapolation of thermodynamic properties from the stable into the metastable region is confirmed in the experimental study of the equation of state for a number of other liquids.[83] In particular, it was shown that, upon passing through the saturation line, not only do the isotherms remain continuous (Fig. 7), but also the isochores (Fig. 8), the isobars, and the derivatives along them. The conclusion that the continuations of the (p, T) isochores are close to straight lines, which arose from the experimental data, is of interest. We note that these results agree with the conclusions of Ref. 65 that the singularity of the thermodynamic potential at the binodal is very weak and cannot be detected experimentally.

4.4. Metastable states near the critical point

Near the critical point in part 3 (see Fig. 5), where the spinodal approaches most closely to the region of stable states, the thermodynamic properties of metastable liquids must be determined with account taken of the presence of critical fluctuations, which play the decisive role in the behavior of the stable phase. The equation of state of the scaling theory of critical phenomena and its modifications satisfy these requirements.[89–97]

Let us discuss in greater detail the analysis of the so-called asymmetric equation of state,[92,97] which allows one to describe the thermodynamic properties of a substance not only in the broad neighborhood of the critical point in the one-phase region, but also in the region of metastable states including the spinodal. The equation for the spinodal is found in this case from the condition $[\partial(\Delta\mu/\partial(\Delta\rho)]_T = 0$, where $\Delta\mu = \mu - \mu(\rho_c, T)$ and $\Delta\rho = (\rho - \rho_c)/\rho_c$ are the deviations of the chemical potential and the density from their values on the critical isochore. A universal crossover function for the free energy was obtained on the basis of the asymmetric equation of state, which takes account of the fluctuation behavior when $\tau \ll \mathrm{Gi}$. The binodal and the spinodal here are described by identical universal equations

$$(\Delta\rho)_{\mathrm{B(S)}} = \pm B^{(0)}_{\mathrm{B(S)}}\tau^{\beta} \pm B^{(1)}_{\mathrm{B(S)}}\tau^{\beta+\Delta_1} + B^{(2)}_{\mathrm{B(S)}}\tau^{1-\alpha} + B^{(3)}_{\mathrm{B(S)}}\tau. \tag{4.24}$$

Here Δ_1 is the critical index of Wegner, the coefficient $B^{(i)}_{\mathrm{B}}$ corresponds to the binodal, and $B^{(i)}_{\mathrm{S}}$ to the spinodal. Here it was found that the ratio $B^{(0)}_{\mathrm{B}}/B^{(0)}_{\mathrm{S}}$ is a universal constant. On the spinodal we have $\chi^{-1} = 0$, while the heat capacity at constant volume C_V is always finite apart from the critical point:

$$\rho C_V T^{-1} = A^{(0)}_{\mathrm{B(S)}}\tau^{-\alpha} + A^{(1)}_{\mathrm{B(S)}}\tau^{\Delta_1-\alpha} + A^{(2)}_{\mathrm{B(S)}}\tau^{1-2\alpha-\beta} + A^{(4)}_{\mathrm{B(S)}}\tau + A^{(5)}_{\mathrm{B(S)}}. \tag{4.25}$$

TABLE III. Argon, isotherm $T = 125$ K, $p_s = 1.5812$ MPa.

$p_0 - p$, MPa (exp.)	V, 10^{-3} m^3/kg (exp.)	$-(\partial p/\partial V)_T$, 10^3 Mpa·kg/m^3 (exp)	$p_0 - p$, MPa (theory)	$-(\partial p/\partial V)_T$, 10^3 MPa·kg/m^3 (theory)
3	0,8972	112,58	2,985	111,39
3,5	0,9018	105,61	3,483	104,78
4	0,9066	99,37	3,971	99,16
4,4	0,911	93,82	4,393	92,87
5,5	0,924	79,00	5,503	78,31
7,5	0,955	49,86	7,493	51,85

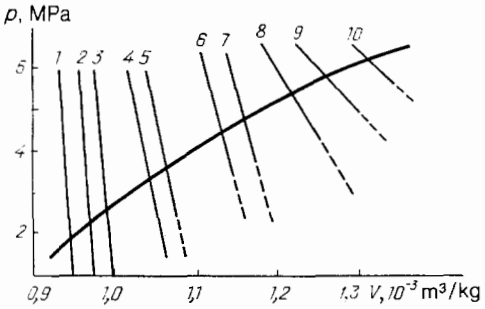

FIG. 7. Results of measuring the specific volume of carbon dioxide upon entry into the metastable region (from Ref. 83). Heavy line–binodal; thin lines–isotherms: (copy the rest from the legend in the original).

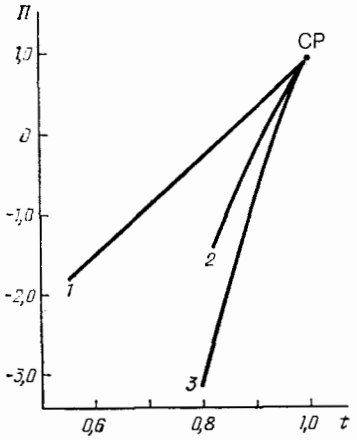

FIG. 9. Results of determining the spinodal[83] in the coordinates $t = T/T_c$ and $\Pi = p/p_c$. Extrapolation of the differences between the isobaric and isochoric heat capacities (curve 1–helium, curve 2–carbon dioxide, ethane, nitrogen); equation of state for the metastable region (curve 3–diethyl ether, *n*-hexane, argon); extrapolation of the compressibility (curve 2–argon); extrapolation of the isobaric heat capacity (curve 2–nitrogen).

In the region where $\tau \ll \mathrm{Gi}$, the critical indices and the ratio $B_B^{(0)}/B_S^{(0)}$ are equal: $\alpha = 0.11$, $\beta = 0.325$, $\Delta_1 = 0.5$, $B_B^{(0)}/B_S^{(0)} = 1.2$, while when $\mathrm{Gi} \ll \tau \ll 1$ we have $\alpha = 0$, $\beta = 0.5$, $\Delta_1 = 0$; $B_B^{(0)}/B_S^{(0)} = \sqrt{3}$.

The numerical calculations that have been performed for the binodal, the spinodal, and the quantities χ and C_V in the metastability region of ordinary water agree well with the experimental data.

We should stress that there are also rather well tested empirical methods for determining the spinodal based on extrapolating various thermal and caloric quantities. Figures 9 and 10 show the results of experimental determination of the spinodal by various methods (extrapolation of the difference between the heat capacities at constant pressure and constant volume, extrapolation of the compressibility, on the basis of the Fuert equation, and by other methods) in the reduced coordinates Π vs t and t vs Φ ($\Phi = V/V_c$).[83]

A number of studies (see, e.g., Refs. 97 and 98) have discovered and studied another line of singular points inside the two-phase region—points of reversal at which $C_V \to \infty$ (for $T < T_c$), while $\chi \to 0$ ($\chi^{-1} \to \infty$). Figure 11 shows the spinodal and the line of reversal for water[97] (the spinodal is calculated from the asymmetric scaling equation). As we see from Fig. 11, the reversal curve lies inside the spinodal, while the difference between them is insignificant, and for $\tau \lesssim 10^{-3}$ they practically merge. However, despite the closeness of these curves, the behavior of the thermodynamic quantities on them differs qualitatively.[97] Thus, on the spinodal the heat capacity at constant volume is finite, but infinite on the line of reversal, whereas the isothermal compressibility on the spinodal is infinite, while it equals zero on the line of reversal.

In recent years, to describe the thermophysical properties of substances in the metastable region, a number of studies have employed the hypothesis of the pseudospinodal.[37,38,99,100] The essence of the hypothesis consists in the idea that, to describe the features of the metastable phase near the spinodal, one introduces new variables (instead of the variables generally adopted in the critical region $\tau = (T_c - T)/T_c$ and $\Delta\rho = |\rho - \rho_c|/\rho_c$), namely

$$\tau_s = |T - T_s(\rho)|\, T_s^{-1}(\rho), \quad \Delta\rho_s = |\rho - \rho_s(T)|\, \rho_s^{-1}(T), \quad (4.26)$$

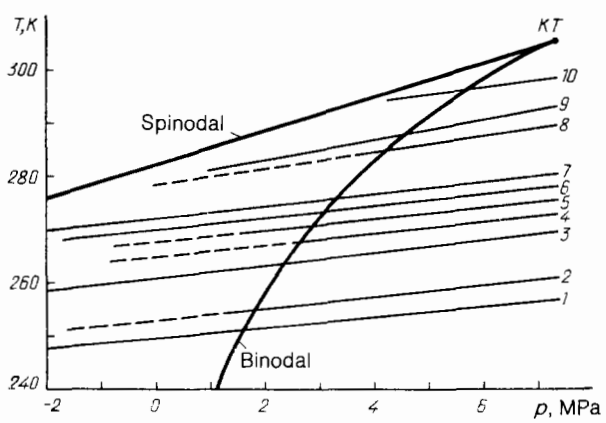

FIG. 8. Continuation of the isochores (thin lines) of carbon dioxide into the metastable region (from Ref. 83). CP–critical point. Values of the specific volumes in 10^{-3} m³/kg: (copy the rest from the legend in the original).

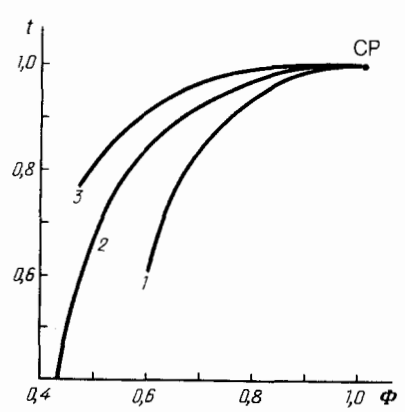

FIG. 10. Results of determining the spinodal[83] in the coordinates $\Phi = V/V_c$ and $t = T/T_c$. Explanation–see legend of Fig. 9.

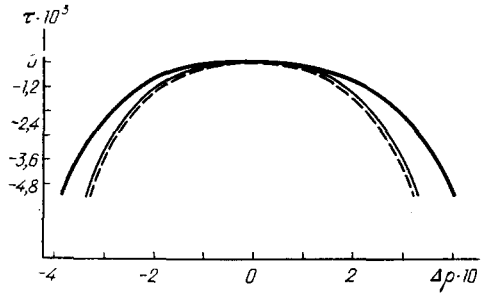

FIG. 11. Coexistence curve (heavy line), spinodal (thin line), and reversal line (dotted line) for water (from Ref. 97).

while the spinodal is defined as the line of singular behavior of the thermodynamic quantities. Here the character of their variation on the lines $\rho = \text{const}$ is the same as on the critical isochore with replacement of T_c by $T_s(\rho)$:

$$X - X_s = A_x \tau_s^{a_x}. \tag{4.27}$$

Here A_x and a_x are the corresponding amplitude and index of the quantity x. The $T_s(\rho)$ relationship is depicted by the pseudospinodal curve. The hypothesis of the pseudospinodal was the basis for creating a new field of computational-theoretical methods of studying the thermophysical properties of matter in the metastable region. Certain advances have been attained along this line at present, which have led to the development of economical and effective algorithms for machine methods of calculating the thermodynamic properties of technically important materials in the optimization of power plants, and have also enabled a considerable reduction in the expense of machine time for calculations of the thermophysical characteristics of working liquids.[96]

5. METASTABLE STATES NEAR THE BOUNDARY OF THERMODYNAMIC STABILITY (THE SPINODAL)

5.1. The SCF approximation

To describe the physical properties of metastable states lying near the spinodal, we shall employ an approach analogous to the theory of critical phenomena that is based on expanding the thermodynamic potential of the metastable system in a power series in the quantity $\eta = (V - V_{sp})/V_{sp}$. This expansion can be represented in the form

$$\Phi(p, T, \eta) = \Phi_0(T) + \frac{A\eta^2}{2} + \frac{B\eta^3}{3} + \frac{C\eta^4}{4} - V_{sp} h\eta. \tag{5.1}$$

Here $\Phi_0(T)$ is the regular part of the thermodynamic potential, A, B, and C are constants of the expansion, h is a quantity that plays the role of an external field, and V_{sp} is the volume at a point of the spinodal. We note that expansions analogous to (5.1) have been used in Refs. 49, 51, 58, and 101. Such expansions differ from those used in the theory of second-order phase transitions in the presence of a term cubic in η.

We obtain from the condition of equilibrium $(\partial\Phi/\partial\eta)_{p,T} = 0$ the following equation of state of the metastable substance:

$$A(T)\eta_0 + B(T)\eta_0^2 + C(T)\eta_0^3 - h = 0. \tag{5.2}$$

Here $\eta_0 \equiv \Delta V$ is the equilibrium value of the pseudocritical order parameter. When we choose the critical point (CP) as the reference point on the spinodal, η_0 goes over into the order parameter of the Landau theory.

The constants of the expansion in (5.2) can be determined by comparison with the corresponding expansion of the pressure $p(V,T)$ in a Taylor's series in powers of $(T - T_{sp})$ and $(V - V_{sp})$.

In the general case the value of the coefficients of the expansion depends on the choice of the point on the spinodal about which one performs the expansion. Thus, for two arbitrary points of reference ($i = 1,2$), the corresponding expansion of $p(V,T)$ will have the form

$$p = p_{sp,i} + D_i(T - T_{sp,i}) + A_i(T - T_{sp,i})(V - V_{sp,i}) + B_i(V - V_{sp,i})^2 + C_i(V - V_{sp,i})^3. \tag{5.3}$$

Upon setting $p = p_{sp,2}$, $T = T_{sp,2}$, $V = V_{sp,2}$, for $i = 1$ in (5.3), we obtain three equations interrelated by the coefficients of this expansion:[102] $C_1 = C_2 = C$; $A_1 = A_2 = A$, $D_2 = D_1 + (V_{sp,2} - V_{sp,1})A$, $B_2 = B_1 = 3C(V_{sp,2} - V_{sp,1})$ (Fig. 12). If we use the CP as the reference point on the spinodal, then (5.3) acquires the form

$$p = p_{sp} + [D_c + A'(V_{sp} - V_c)](T_{sp} - T_c) + A'(T - T_{sp})(V - V_{sp}) + 3C(V_{sp} - V_c)(V - V_{sp})^2 + C(V - V_{sp})^3. \tag{5.4}$$

In this expression the parameters D_c, A', C, and V_0 do not depend on the concrete choice of the reference point. If $V_{sp} \to V_c$, then (5.4) goes over into the expansion for the CP. It is important to note that the structure of the coefficient for $(V - V_{sp})^2$, which enables the possibility of a correct transition to the CP, is characteristic of those equations of state that correspond to the statistical approximation of the SCF. The form of the coefficient B in (5.3) for certain empirical equations of state is given in Table IV.

We note that, since the parameters in (5.4) do not depend on the reference point, then in principle we can determine them from experimental p-V-T measurements in the region of absolutely stable states near the CP.

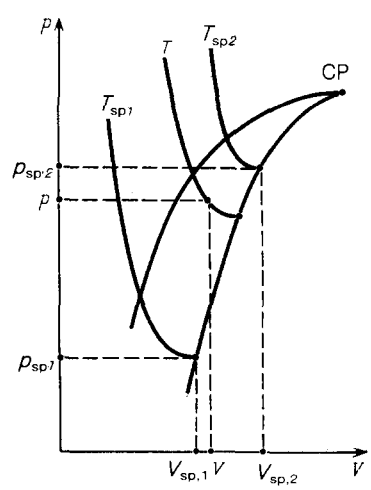

FIG. 12. $p = p(V,T)$– point in the metastable region: ($p_{sp,i}$, $V_{sp,i}$, $T_{sp,i}$)– reference point on the spinodal ($i = 1,2$). B–binodal, S–spinodal; CP–critical point; thin lines–isotherms.

TABLE IV.

Equation of state	Form of the coefficient B
van der Waals: $p=\frac{RT}{V-b}-\frac{a}{V^2}$	$-\frac{aV_c(V_{sp}-V_c)}{p_{sp}V_{sp}^2(V_{sp}-b)}$
Berthelot: $p=\frac{RT}{V-b}-\frac{a}{V^2T}$	$-\frac{aV_c(V_{sp}-V_c)}{p_{sp}V_{sp}^2T_{sp}(V_{sp}-b)}$
Dieterici: $p=\frac{RT}{V-b}\exp\left(-\frac{a}{RTV}\right)$	$-\frac{5aV_c(V_{sp}-V_c)}{9V_{sp}^{5/2}p_{sp}(V_{sp}-b)}$
Flory-Huggins: (5.18)	$\frac{x_{sp}+x_c-2x_{sp}x_c}{x_c^2x_{sp}^2N_A(1-x_{sp})^2}(x_{sp}-x_c)$

Upon comparing Eqs. (5.1) and (5.4) with one another, we obtain

$$h=p-p_{sp}=[D_c+A'(V_{sp}-V_c)](T-T_{sp}). \tag{5.5}$$

Upon going over to the CP, we have $h=h'=p-p_c-D_c(T-T_c)$, where $D_c=(\partial p/\partial T)V_c$ (see Ref. 19).

We can also easily find from (5.1) an expression for the metastable substance:

$$S=S_0-\frac{1}{2}A\eta_0^2-DV_{sp}\eta_0. \tag{5.6}$$

Here S_0 is the regular part of the entropy (independent of η). Equations (5.4) and (5.6) give a description of the entire thermodynamics of metastable states in the SCF approximation.

To determine the region of applicability of the discussed thermodynamic description of the properties of metastable states, it is expedient to study in the phase diagram the line of constant isothermal compressibility $V_{sp}^{-1}(\partial V/\partial p)_T=z^{-1}=\text{const}$.

In the Ornstein–Zernike theory (the approximation of a free field of fluctuations) we have $z^{-1}\sim R_c^2$. Therefore the quantity z can act as the parameter characterizing the "distance" to the spinodal in the thermodynamic plane. Upon using the CP as the reference point, one can derive from the equation of state (5.5) an expression for the line of constant compressibility of the form $T-T_c=(z/A)-(3C/A)(V-V_c)^2$, or in the variables p and V,

$$p-p_c=\frac{D_cz}{A}+z(V-V_c)-\frac{3CD_c}{A}(V-V_c)^2-2C(V-V_c)^3. \tag{5.5'}$$

If z^{-1} is larger than some critical value, then it becomes necessary to take account of fluctuation effects in describing the properties of metastable states. The spinodal corresponds to the condition $z=0$. Therefore, by starting with this criterion, one can separate the metastable region into several parts, depending on whether the fluctuation effects are essential or not in each of them (see Fig. 5).

5.2. Pseudocritical indices

By analogy with the theory of critical phenomena, where the concept exists of critical indices, Refs. 47, 50, 53–55, and 103 have introduced a system of pseudocritical indices, i.e., universal parameters that characterize the features of the physical properties of a metastable substance near the spinodal, and which depend only on the dimensionality of the system, the type of symmetry of the Hamiltonian, and the number of components of the order parameter. The pseudocritical indices α^*, β^*, γ^*, and ν^* are defined as the exponents in the following relationships in the approach to the limit ($T<T_c$) to the point on the spinodal along the line of constant field $h'=\text{const}\neq 0$:

$$C_{h'}\sim|\tau|^{-\alpha^*},\quad \Delta V\sim|\tau|^{\beta^*},\quad \chi\sim|\tau|^{-\gamma^*},\quad R_{cor}\sim|\tau|^{-\nu^*}. \tag{5.7}$$

Here we have $\tau=(T-T_{sp})/T_{sp}$, and $C^{-\nu^*}$ is the heat capacity at constant field h'. The approach to the limit along the line $h=0$ defines another system of pseudocritical indices, namely:

$$C_{h=0}\sim|\tau|^{-\alpha^*},\quad \Delta V\sim|\tau|^{-\beta^*},\quad \chi\sim|\tau|^{-\gamma^*},\quad R_{cor}\sim|\tau|^{-\nu^*}. \tag{5.8}$$

Here $C_{h=0}$ is the heat capacity for a field equal to zero ($h=0$).

The pseudocritical index δ^* is defined in the same way in both systems, i.e.,

$$\Delta p\sim|\Delta V|^{\delta^*},\quad T=\text{const},\quad T<T_c. \tag{5.9}$$

Here we have $\Delta p=|(p-p_{sp})/p_{sp}|$, where p_{sp} is the pressure on the spinodal that corresponds to the point at which the isotherm intersects the spinodal.

Naturally, the approach to the limit as the indices α^*, β^*, γ^*, and δ^* approach the corresponding critical indices occurs in the first system as $h'\to 0$, and in the second system as $h\to h'$, i.e., at the CP with $T<T_c$. The transition from δ^* to δ occurs as $T_{sp}\to T_c$, i.e., on the critical isotherm.

The fields h' and h are interrelated by the equation

$$h=h'-h_s'-A(V_{sp}-V_c)(T-T_{sp}). \tag{5.10}$$

Here h_s' is the value of h' on the spinodal. The lines of constant field h' and $h=0$ are shown schematically in Figs. 13 and 14.

The numerical values of the pseudocritical indices are determined within the framework of the SCF theory by comparing the thermodynamic relationships along the direc-

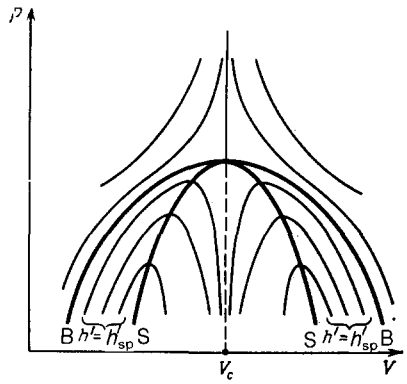

FIG. 13. pV diagram of a fluid with lines of constant field $h' = h'_{sp} \neq 0$. B–binodal, S–spinodal; the curves outside the binodal correspond to $T > T_c$.

tions being studied with (5.7), (5.8), and (5.9). Thus, for systems of the type of metastable fluids one can obtain[54,103] $\alpha^* = \beta^* = \gamma^* = 1/2$, $\delta^* = 2$, $\gamma^* = 1/4$. The same results were obtained in Refs. 50 and 53 for binary mixtures and in Ref. 47 for magnetic substances.

Pseudocritical indices determined according to (5.8) were found in Ref. 102: $\alpha^* = 1$, $\beta^* = 1$, $\gamma^* = 1$, $\delta^* = 2$, $\nu^* = 1/2$. These values coincide with those calculated in Ref. 52 along the line of constant chemical potential for supercooled metastable liquids, and also with the critical indices for a percolation problem on a Bethe lattice.[104]

It is also necessary to take account of the fluctuations of the pseudocritical order parameter near the spinodal, analogously to how this is done in a corresponding way in the theory of critical phenomena. A number of experimental studies (see, e.g., Refs. 37, 96, and 105) performed on simple liquids and binary mixtures have obtained "nonclassical" values of the pseudocritical indices. The experiments were performed along noncritical isochores. It turned out that $\gamma^* = 1.21$ and $\beta^* = 0.34$. These results indicate that taking account of fluctuational effects must prove very important for the numerical values of the pseudocritical indices. Moreover, the character of the singular behavior of the substance along the critical and noncritical isochores proves to be the same. In connection with what we have said above, the problem arises of calculating the corrections to the values of the pseudocritical indices as calculated in the SCF approximation. We can determine the region of applicability of this approximation by using the Ginzburg criterion. If the Ginzburg number $\mathrm{Gi} \ll |\tau| \ll 1$, then a region of applicability of the SCF theory always exists. By definition[34] we have

$$\mathrm{Gi} = \frac{\langle \Delta\eta^2 \rangle}{\eta^2} = \frac{\chi}{V\eta^2}. \tag{5.11}$$

Here $\langle \Delta\eta^2 \rangle$ is the mean-square fluctuation of the order parameter. Upon assuming that $V \sim R_{\mathrm{cor}}^d$ and taking account of the fact that $\chi \sim R_{\mathrm{cor}}^2$ in the Ornstein–Zernike approximation, we obtain

$$\mathrm{Gi} \sim |\tau|^{(d-6)/4} \tag{5.12}$$

for the system of pseudocritical indices defined by (5.7), and

$$\mathrm{Gi} \sim |\tau|^{(d-6)/2} \tag{5.13}$$

for the system of indices of (5.8). We see from (5.12) and (5.13) that, when $d > 6$, Gi is always small, and hence, the region of applicability of the SCF theory exists. When $d = 3$ the SCF theory (just as for the case of the CP) gives an adequate description of the metastable fluid when the intermolecular interaction in it is substantially long-range. In this case, since $\mathrm{Gi} \sim \xi_0^{-6}$, the smallness of Gi makes possible a large magnitude of the amplitude of the correlation radius ξ_0.

Let us turn to studying the fluctuational effects in a metastable fluid near the spinodal.

The theory of the spinodal singularities of thermophysical quantities was constructed under the assumption of thermodynamic stability of metastable states with respect to fluctuational variation of the order parameter $\delta\eta = \eta - \eta_0$, which can be treated as an external perturbation. In this regard it seems important to study the problem of the behavior of the relaxation time to the equilibrium state of the magnitude of $\delta\eta$ near the spinodal.

The response of a metastable system to an external perturbation differs, depending on the character of the perturbation and the properties of the metastable state itself. Large perturbations remove the metastable system from a state of local equilibrium, while leading to an irreversible process of phase separation. However, if the external perturbation is small enough, the metastable system can relax back to the state of local thermodynamic equilibrium. In this case the situation is that of relaxation about a state characterized by a relative minimum of the thermodynamic potential.

References 107 and 108 studied the relaxation of a nonconserved order parameter near the spinodal within the framework of the Landau–Khalatnikov theory. Expressions were obtained for the linear and nonlinear relaxation times near the spinodal. It turns out that the linear relaxation time is $t_l \sim 1|\tau|^{-y_l}$, where $y_l = 0.5$, while in the nonlinear case t_{nl} has a logarithmic divergence at the spinodal, i.e., $y_{nl} = 0$. The obtained values of y_l and y_{nl} agree with the known scaling equation $y_l - y_{nl} = \beta^*$. Here the dynamic critical index is $z = 2$ near the spinodal, just as for the CP in the analogous SCF approximation.

Yet if the order parameter is a conserved quantity, then all the characteristic relaxation times, just like the transport coefficients, acquire an identical form near the CP and near the spinodal in the case in which they are expressed in terms of R_{cor}. However, the corresponding dependence on the

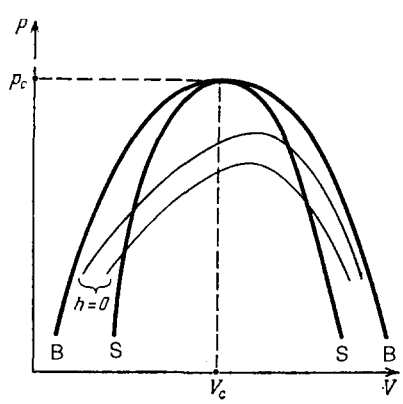

FIG. 14. pV diagram of a fluid with lines of constant field $h = 0$; B–binodal, S–spinodal.

variables τ and ΔV will differ for the CP and the spinodal. What we have said holds for optical and acoustic effects involving the singular behavior of the correlation radius.

5.3. Features of metastable states in binary mixtures and liquid crystals

5.3.1. Binary mixtures

Binary mixtures belong to the same universality class as one-component liquids. Therefore one can use the corresponding isomorphism to describe the thermodynamic properties of metastable binary liquids. For simplicity we shall assume that $p = \text{const}$. Then the expansion of the thermodynamic potential near the spinodal will have the form (5.1), with the difference that $\eta = x - x_{sp}$, where x is the mole fraction of one of the components, while the field is $H = \mu^* - \mu^*_{sp} - (\partial\mu^*/\partial T)_{x,sp}(T - T_{sp})$, where $\mu^* = \mu_2 - \mu_1$ is the difference in chemical potentials of the components of the mixture. We can go over to a description of the thermodynamics of metastable states in binary systems by making the substitutions in (5.1): $p \to \mu^*$, $h \to H$, $(V - V_{sp})/V_{sp} \to x - x_{sp}$.

An important case is that of polymer mixtures. Here, in the Flory–Huggins approximation,[109] the expression for the equilibrium thermodynamic Gibbs potential has the form

$$\Phi(x, v) = \frac{x \ln x}{N_A} + \frac{(1-x)\ln(1-x)}{N_B}. \qquad (5.14)$$

Here N_A and N_B are the lengths of the polymer chains of components A and B, and v is the Flory–Huggins parameter, which plays in this case the role of the temperature. Isomorphism with binary mixtures and one-component liquids is attained with the substitutions: $\tau \to (v - v_{sp})/v_{sp}$, $\eta_0 \to x - x_{sp}$, $H \to \mu^* - \mu^*_{sp} - (\partial\mu^*/\partial v)_{x,sp}(v - v_{sp})$.

5.3.2. Liquid crystals

In the phase transition from nematic liquid crystal (NLC) to isotropic liquid (IL), features are found experimentally that are typical of a first-order phase transition, namely: jumps in the density, the entropy, the enthalpy, etc.[110] At the same time, as one approaches the clearing temperature, one finds experimentally an anomalous increase in such quantities as the isothermal compressibility, the isobaric heat capacity, and the Kerr constant. These phenomena, which are called pretransitional effects, are usually characteristic of second-order phase transitions. The combination in the NLC-IL transition of such properties, seemingly completely mutually exclusive, can be explained by the closeness of the transition temperature T_c to the spinodal temperature (T^* or T^{**}) and by the influence of spinodal effects on the equilibrium states. The region of metastable states on the side of the nematic phase has the width $T^{**} - T_c \lesssim 0.3$ K, and on the side of the isotropic phase $T^* - T_c \sim 1$ K.[111] By analogy with the theory of critical phenomena, the pretransitional effects are described by power laws of the type $C_p = C_{p,per} + C_0[(T - T^{**})/T^{**}]^{-\alpha}$ and analogous relationships for the other quantities. However, the experimentally observed values of the "critical" indices α, β, etc., do not coincide with any of the known sets of values of indices of any universality class. Moreover, they do not satisfy the scaling identities.

A treatment of the pretransitional phenomena as being pseudocritical was presented in Ref. 112. The comparison of theory and experiment in this case is difficult, since experiments in liquid-crystalline systems are performed at $p = \text{const}$, which does not correspond to the conditions under which one finds the pseudocritical indices of this problem.

For an isobar one can obtain, e.g., $T - T^{**} \sim (V - V^{**})^{z_1}$, where $1 < z_1 < 3$, depending on the relationship between the parameters of the original expansion of the thermodynamic potential in powers of the quantity $\varphi = V - V^{**}$, which plays the role of the scalar pseudocritical order parameter. However, indices of the type of z are not universal and do not constitute critical indices. In the "isomorphous" case, in which $h_0 = p - p_0^* - (\partial p/\partial T)_{V_0^*}(T - T_0^*) = h^* \neq 0$, within the framework of the SCF approximation we have $\alpha^* = \beta^* = \gamma^* = 1/2$, $\delta^* = 2$, $\nu^* = 1/4$.[112]

As we have already noted, the NLC-IL phase transition is a first-order transition. For this reason it is natural to use the approaches of Refs. 113 and 114 to describe its features, which have been well tested in the theory of nucleation. The problem consists in describing the regimes of appearance and growth of nuclei of the nematic (or isomorphous) phase by using equations of the Zel'dovich type for an ensemble of drops. The experimentally established law of growth in time of the radius of nematic drops upon nucleation from a supercooled IL has the form $a(t) \sim t^{1/2}$.[113] Such behavior is known for other systems having a one-component order parameter, whereas it differs from the Lifshits-Slezov law ($a(t) \sim t^{1/3}$) established for coalescence processes.[20,21]

6. FRACTAL STRUCTURES IN THE METASTABLE REGION

Over the past decade the ideas of fractal geometry[115] have actively penetrated almost all fields of modern physics.[59,116,120] It has turned out that fractal nature is inherent in very many physical objects, both in the micro-[116–119] and in the macroworld, including the structure of galaxies in the Universe.[59,120] It is already clear now that the result of the penetration of fractals into physics was a radical change in the views on the nature of many phenomena such as, e.g., turbulence and chaos, the structure of disordered systems, the properties of materials, hardness, the nature of ball lightning,[116] etc. (for more details see Ref. 121).

The connection between fractals and the theory of second-order phase transitions and percolation theory is rather fully reflected in the reviews of Refs. 116 and 120. Some mathematical problems involved with the introduction of fractal (Hausdorf) dimensionalities are studied in Ref. 122. The properties of the objects called multifractals, which have recently attracted attention, are discussed in Ref. 123.

The nature of random (or stochastic[124,125]) fractals is directly manifested also in first-order phase transitions in the fluctuational structures of the nuclei (clusters) of the new phase, which are formed in the process of decay of metastable states. The character of the course of the phase transition substantially depends of how the nuclei of the new phase evolve in the process of their appearance and growth, how they interact with one another, and how stable (i.e., capable of further growth) the structures of the nuclei are. The language of the theory of singularities of differentiable maps

(catastrophe theory[61,126]) is very useful for analyzing this set of problems.

Let us study the fundamental features of the process of fluctuational formation of nuclei of a new phase. We have the following expression for the fluctuation of the number N of particles of the metastable phase in the volume V:

$$\langle(\Delta N)^2\rangle^{1/2} = V^{1/2}\rho\,(k_B T\chi)^{1/2}. \tag{6.1}$$

Here ρ is the mean density in the metastable state. Formation of a compact cluster of dimensionality d with density $\rho_1 = \rho_2 - \rho_c\Delta\rho$ ($\Delta\rho$ substantially different from zero; see Fig. 1) owing to fluctuation requires fulfillment of the condition $\langle(\Delta N)^2\rangle^{1/2} \sim L^d$, where L is the characteristic linear dimension of the fluctuating volume of the cluster being formed. In the nonfluctuational region (i.e., near the binodal of the system) the variation of the thermodynamic variables $\rho\,(k_B T\chi)^{1/2}$ is not singular. Hence we have

$$\langle(\Delta N)^2\rangle^{1/2} \sim L^{d/2}. \tag{6.2}$$

Equation (6.2) implies that one cannot create a compact cluster (manifold) of dimensionality d from particles fluctuating near the binodal. In the language of catastrophe theory one can say that in the case being discussed the structures formed fluctuationally in the space $\mathbb{R}^n$ will not look locally like a "piece" of this same space or of a space $\mathbb{R}^{d-1}$ (that is, they will not even be two-dimensional compact structures when $d = 3$). In order that such structures should actually be manifolds (i.e., compact clusters), as is implied by (6.2), they should have the dimensionality $\mathrm{Dim}(M) = d/2$, and a codimensionality $\mathrm{Cod}(M)$ equal also to $d/2$, since by definition $\mathrm{Cod}(M) = d - \mathrm{Dim}(M)$,[61] where the symbols $\mathrm{Cod}(M)$ and $\mathrm{Dim}(M)$ respectively correspond to the codimensionality of the manifold M being discussed and to its dimensionality. What we have said above implies that the mean-square density fluctuations in any volume on the nonfluctuational region of variation of the thermodynamic variables will not even lead to appearance of a compact "surface" (a manifold of dimensionality $d-2$) nor with any dimensionality of the enveloping space except $d = 2$. Yet even when $d = 2$, the formation of such a fractal "foam" does not lead to appearance of a compact nucleus of the new phase (a manifold with $d = 2$). Since the codimensionality characterizes the properties of the boundary between the regions of the enveloping and the inserted manifolds, then evidently in the nonfluctuational region the role of the corrections involving the effects of formation of the new phase increase with decreasing dimensionality of the enveloping space. When $d > 2$, we have $\mathrm{Cod}(M) > 1$, and the role of the fluctuational corrections is negligibly small throughout the metastable region.

As we approach the spinodal we have $\chi \to \infty$, so that the situation changes qualitatively. Since $\chi \sim R_{\mathrm{cor}}^{2-\eta}$, where η is the critical index of the correlation function, while $R_c \sim L$ at a point of the stability boundary, we have

$$\langle(\Delta N)^2\rangle^{1/2} \sim L^{(d+2-\eta)/2} = L^{d-\Delta_\rho}. \tag{6.3}$$

Here Δ_ρ is the scaling dimensionality of the fluctuating order parameter. Since $\Delta_\rho = \beta/\nu = d - d_f$, we have

$$\langle(\Delta N)^2\rangle^{1/2} \sim L^{d_f}, \tag{6.4}$$

TABLE V.

d	Dim (M)	Cod (M)
2	15/8	1/8
3	17/7	4/7
4	3	1
6	4	2
8	5	3

where d_f is the fractal dimension of the nucleus being formed of the new phase. The corresponding dimensionalities and codimensionalities of the fluctuational formations for different values at the critical point are given in Table V.

We see from the data of Table V that, even at $d = 4$, a fractal "foam" arises owing to fluctuations, since $\mathrm{Cod}(M) = 1$, more compact structures arise for $d = 3$, while for $d = 2$ the fluctuational formations already can actually play the role of nuclei of the new phase, since $15/8 \lesssim 2$. When $d = 4$, the role of the fluctuations that lead to formation of the new phase is inessential. If near the spinodal (far from the critical point) we use the results of self-consistent-field theory, then the corresponding dimensionalities and codimensionalities of the fluctuational formations will have the following values given in Table VI.

In the present case the boundary dimensionality is found between $d = 4$ and $d = 3$. Somewhere between these dimensionalities a fractal "foam" appears having a codimensionality equal to unity.

We can conveniently illustrate the physical meaning of the dimensionalities and codimensionalities of the fluctuations with the example of fluctuations of the number of particles in a cube of side L. If $\mathrm{Dim}(M) = 2$ and $\mathrm{Cod}(M) = 1$ for $d = 3$, then as a result of the fluctuations in the cube one of the faces moves (or, owing to the fluctuations, a layer of particles with $N \sim L^2$ grows or is lost). When $\mathrm{Dim}(M) = 1$ while $\mathrm{Cod}(M) = 2$, an edge fluctuates in the cube, while when $\mathrm{Dim}(M) = 0$ and $\mathrm{Cod}(M) = 3$, a vertex fluctuates. Interestingly, for formation of the new phase throughout the region of space, we must have $\mathrm{Dim}(M) = 3$, while $\mathrm{Cod}(M) = 0$!

From what we have presented above, it is clear that the concept of codimensionality of a manifold plays a more important role than the concept of dimensionality. In certain cases or models the dimensionality proves to be infinite, while the dimensionalities of the fluctuational manifolds that arise also prove to be infinite, but the codimensionality of the fluctuational formations can prove here to remain finite, while all its useful properties are conserved. Thus the concept fundamental in the theory of differentiable maps (catastrophe theory) of transversality can be formulated in the language of codimensionality. Then two submanifolds in

TABLE VI.

d	Dim (M)	Cod (M)
3	2,09	0,91
4	2,8	1,2
6	4	2
8	4,67	3,33

$\mathbb{R}^d$ intersect transversally at the given point if either we have $\mathrm{Dim}(M_1 \cap M_2) = \varnothing$, or

$$\mathrm{Cod}\,(M_1) + \mathrm{Cod}\,(M_2) \leqslant d, \quad \mathrm{Dim}\,(M_1 \cap M_2) = \mathrm{Dim}\,(M_1) + \mathrm{Dim}\,(M_2) - d. \tag{6.5}$$

According to the Bertini–Sarda and Toma theorems[126] the transversality of the intersection of two submanifolds is a stable property that is conserved upon small perturbations. For two manifolds taken randomly, the probability is infinitesimally small that they intersect nontransversally. Thus, if fractal manifolds (clusters) are formed in a system owing to fluctuations in the number of particles in different volumes, then the situation is typical that they intersect transversally. The probability of their nontransversal intersection equals zero.

In the nonfluctuational region the transversality of the intersection of two clusters implies that, if they intersect, they do so in a manifold, the measure of whose set equals zero, since $\mathrm{Dim}(M_1 \cap M_2) = (d/2) + (d/2) - d \equiv 0$. That is, growth of a new phase owing to merger of the clusters being formed does not occur. In this case the intersection of two fractal "hedgehogs" at individual points or the absence of intersection is typical.

Table V implies that we have $\mathrm{Dim}(M_1 \cap M_2) = 2$ at the critical point when $d \geqslant 4$. This implies the impossibility of merger of the clusters formed fluctuationally into a compact structure. Here the case $d = 4$ corresponds to the situation in which structures of the least degree of fractality are formed as a result of transversal intersection. When $d = 3$ clusters are formed with $3 < d_f \leqslant 2$, while they intersect transversally in a manifold with $\mathrm{Dim}(M_1 \cap M_2) \lesssim 2$. The case $d = 2$ is most interesting, since $\mathrm{Dim}(M) = 15/8 \leqslant d$, while transversal intersection occurs in a manifold of dimensionality $14/8 \leqslant d$. That is, in this case the merger of the clusters being formed to yield growth of the new phase is most probable of all.

Analysis of the dimensionalities and codimensionalities of the clusters that are formed in the vicinity of the spinodal in the case $d = 3$ shows that the growth of fluctuational clusters owing to their merger is less probable than in the vicinity of the critical point (see Table VI).[102]

The analysis that has been performed of the dimensionalities of the manifolds that arise upon fluctuation of the number of particles in the equilibrium case shows that the problem of the criteria of fluctuational stability of a phase in the metastable state cannot be solved systematically within the framework of an approach that employs the hypothesis of fluctuational creation of nuclei of the new phase having a compact form. In this regard we should note the results of machine experiments, according to which the structure of the clusters that are formed in the metastable region is close to fractal.

7. CONCLUSION

We have paid the major attention in this review to studying metastable states in liquid systems, for which, on the one hand, sufficient experimental material has already been accumulated, and on the other hand, substantial theoretical treatments exist. Since the studies of metastable states in liquids have already been conducted long ago, the experience acquired in this field can be successfully applied also to study metastable systems of another physical nature, the treatment of which lies outside the scope of our review. Among such systems we mention first of all the following: binary alloys, superconductors, layers adsorbed on a surface, polymer mixtures, gels, the electron-hole fluid in semiconductors, and chemically reacting systems. References to a series of studies that treat metastable states in the systems listed above are contained in the review of Ref. 127. In addition we should note that the '80s were characterized by a surge in scientific activity in the field of study of the thermodynamics of phase transformations and metastable states in nuclear matter and in the early Universe. A phase transition in superdense nuclear matter (the transition "hadron matter–quark-gluon plasma," which occurs at a temperature of the order of 200 MeV) was discussed recently in the review of Ref. 118. The possible role of metastable states in the evolution of the early Universe preceding confinement and primary nucleosynthesis (miniinflation and inflation in the hadronization stage) is studied in Refs. 128–133. It turns out that a possible supercooling of the quark-gluon plasma in the expansion of the Universe substantially determines the scenario of its hadronization. Here the rate of expansion involves the form of the equation of state in the metastable region, while the depth of intrusion is determined by a criterion analogous to the Ginzburg criterion discussed in this review.

This review also has not included a number of interesting problems that as yet have not been studied sufficiently. Thus it is not ruled out that, in the formation of a nucleus of the new phase in a metastable state, the structure of the phase boundary and its composition (in the case of solutions) substantially differ from the equilibrium case. Naturally, such a difference leads to a change in the surface-tension coefficient and to refinement of the criteria for depth of intrusion into the metastable region. The problems of the hydrodynamics of metastable liquids merit special treatment. Apparently, near the spinodal the hydrodynamic equations must be nonlocal and must take account of the effects of memory in the kinetic coefficients and susceptibilities. However, the literature contains little data on the viscosity, heat conductivity, and diffusion coefficients of superheated liquids. Such a situation does not offer possibilities for a comprehensive application in studying metastable states of the traditional methods of light scattering, acoustic relaxation, and slow-neutron scattering that are successfully applied to study the features of behavior of matter near the critical point. All these problems demand solution in the very near future.

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