The Ginzburg criterion and the equation of state of metastable liquids

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The physical properties of metastable liquid systems in various parts of the metastable region are investigated. The role of the Ginzburg criterion in determining possible penetration depths into the metastable region is analyzed. The problem of the equation of state of metastable liquids and of the possibility of reliable extrapolation of the isotherm from the stable to the metastable region is considered. Problems of the fractal nature of the new-phase seeds are discussed for various penetration depths into the metastable region.

1. INTRODUCTION

The study of the physical properties of materials existing in the metastable state near first-order phase-transition points has in recent years aroused growing interest.[1-3] This has to do in large measure with the overall progress towards understanding the nature of phase transitions. At the same time, on the theoretical plane it has not been first-order phase transitions and metastable states, but rather continuous phase transitions (second-order phase transitions) that have received the most attention. The application of fundamental ideas that lie at the basis of scaling and the renormalization group has permitted the development and realization of analytical and numerical methods of arriving at a consistent account of fluctuation effects due to the interaction of fluctuations of the characteristic order parameter of the investigated system which are correlated over large distances and times.

Fluctuation effects prove to be important also far from the critical points in the case of deep penetration into the region of metastable states. In fact, as the boundary of thermodynamic stability of the homogeneous phase states (the spinodal) is approached the response functions of the system (the isothermal compressibility, the isobaric heat capacity, the thermal expansion coefficient, etc.) grow. A consistent description of the metastable states near the spinodal requires first that those peculiarities of the response functions which are due to strongly interacting homophase fluctuations of the order parameter be taken into account and second that the complex nonlinear process of generation and growth of large-scale heterophase fluctuations, taking place against this background, also be taken into account. It is specifically the coalescence of the nuclei of the new phase (droplets, bubbles) in the process of coalescence and coagulation that leads in the final stages of their growth to the appearance of macroscopic, thermodynamically stable formations.

It is natural that in the near vicinity of the first-order phase transition line (the phase-coexistence curve of the phases or the binodal) there exists a region quite far removed from the critical point and from the spinodal where fluctuation effects, which are characteristic of continuous phase transitions, do not play a noticeable role. The phase diagram of the metastable system (for definiteness, the liquid–vapor system) shown in Fig. 1 illustrates the schematic arrangement of those regions where fluctuation effects do not play a decisive role (region 1) and those in which an account of the fluctuations is of fundamental importance (region 2). Region 3 is transitional (crossover) from fluctuational to nonfluctuational behavior of the metastable system.

In this paper we present a study of the physical properties of metastable systems for various penetration depths into the region of metastable states. A criterion for the fluctuational (or nonfluctuational) description of the metastable region is obtained, which in a certain sense is an analog of the well-known Ginzburg–Levanyuk criterion of the applicability of self-consistent field theory to the description of second-order phase transitions and critical phenomena. We also analyze the problem of the equation of state of metastable matter. Knowledge of such an equation of state and the physical properties connected with it is needed to analyze the available experimental data on the thermodynamic properties of metastable states.[2,3] In particular, this is important for the study of metastable liquids, and also for those systems in which it is possible to achieve a quasi-equilibrium penetration depth into the metastable region (polymers, liquid crystals, etc.). Questions are also discussed which are associated with the fractal nature of the nuclei (seeds) of the new phase which form in the various regions of the phase diagram.

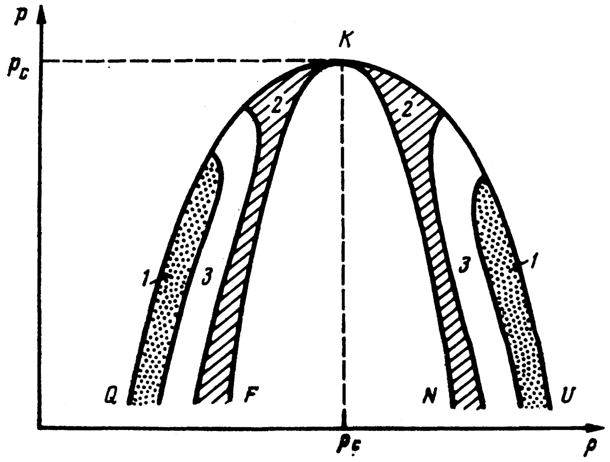

FIG. 1. Coexistence curve (binodal) *QKU* and spinodal *FKN* of the system liquid–vapor in the coordinates density (ρ) and pressure (p); *K* is the critical point, ρ_c and p_c are the critical values of the density and pressure.

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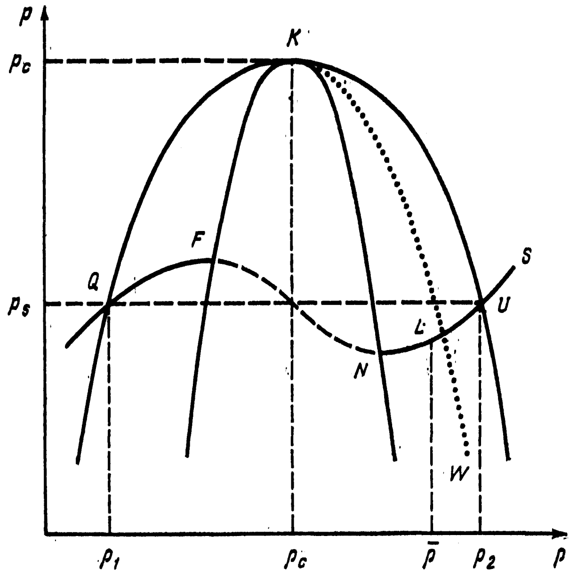

FIG. 2. The isotherms *SULNFQ* corresponding to a temperature $T < T_c$ in the coordinates density (ρ) and pressure (p); *K* is the critical point; *QKU* is the binodal; *FKN* is the spinodal; ρ_1 is the density of the gas on the binodal; ρ_2 is the density of the liquid on the binodal at the temperature *T*; $\bar{\rho}$ is the observed density in the metastable state; p_s is the pressure on the binodal; and T_c, p_c, and ρ_c are the critical values of the temperature, pressure, and density.

2. THE GINZBURG CRITERION AND METASTABLE SYSTEMS

Let us consider metastable states in a one-component liquid system at fixed temperature. The corresponding notation is shown in Fig. 2. As the system moves along a noncritical isotherm, e.g., *SULNFQ*, at a subcritical temperature ($T < T_c$), it turns out that on the segment *UN* the system is in the region of metastable states. In this region (*U* is the binodal point) thermodynamic stability with respect to the fluctuational formation of new-phase nuclei (bubbles of vapor) having a volume greater than the volume of the critical nucleus breaks down.

So that at some point *L* of the metastable region the system will still retain its thermodynamic stability, it is necessary that the inequality

$$R_{min}/k_B T > X,$$

be satisfied, where $R_{\min}$ is the minimum work necessary for the formation of a new-phase nucleus of critical dimension, and *X* is a dimensionless quantity $\gtrsim 10^2$. In the case of the formation of liquid droplets in the metastable supercooling of vapor one commonly takes $X = 60$ (Ref. 4). In fact, the frequency or rate of nucleation *J* is proportional to the probability $w \sim \exp(-R_{\min}/k_B T)$ of formation[5] of the new-phase nucleus, and in the superheating of a liquid we have

$$J = \rho_2 K \exp(-R_{min}/k_B T),$$

where $\rho_2 \sim 10^{28}$ m^{-3}, and the kinetic factor $K \sim 10^{10}$ sec (Ref. 3). Then for $R_{\min} > 10^2 k_B T$ the quantity *J* becomes vanishingly small. As the system continues to move along the isotherm in the direction of the spinodal point (the point *N* in Fig. 2) the quantity $R_{\min}$ decreases and, consequently, the stability condition is violated.

Obviously, the equality $R_{\min} = X k_B T$ determines the maximum permissible heating of the liquid (the physical spinodal)— the dotted curve *KW* in Fig. 2. To the right of the curve *KW* in the metastable region near the binodal, where

$$\frac{R_{min}}{k_B TX} \gg 1 \qquad (1)$$

is found the region where density fluctuations are not important for the description of the thermodynamic properties of the system, and to the left of the curve *KW*, where

$$\frac{R_{min}}{k_B TX} \ll 1 \qquad (2)$$

is found the fluctuation region. In the intermediate region, in the vicinity of the curve *KW* itself, there takes place a crossover in the behavior of the system from the classical nucleation regime to the spinodal nucleation regime. In this region strongly developed fluctuations of the order parameter play a decisive role.

Let us consider the region corresponding to inequality (1). In this case the characteristic dimension of the critical nuclei exceeds the correlation radius of the density fluctuations. Correspondingly, actual nuclei in the system are almost spherical in shape. In fact, the critical profiles which form as a consequence of the density fluctuations, do not have a spherical shape at the moment of formation; however, the spherical harmonics with nonzero indices vanish quickly, so that the critical profile acquires a spherical shape.[6,7]

In the case of new-phase nuclei of spherical shape the expression for $R_{\min}$ is written as follows:[3,5]

$$R_{min} = 16\pi\sigma^3\bar{\rho}^2 / [3(p_s - \bar{p})^2(\bar{\rho} - \rho_1)^2], \qquad (3)$$

where p_s is the pressure on the binodal, $\bar{p} = p(\bar{\rho}, T)$, and σ is the coefficient of surface tension. We introduce the dimensionless temperature $t = T/T_c$, density $R = \bar{\rho}/\rho_c$, pressure difference $\Delta p = (p_s - p)/p_c$, density difference $\Delta\rho = (\rho_2 - \rho_1)/\rho$, and parameter $\varepsilon = (\rho_2 - \bar{\rho})/(\rho_2 - \rho_1)$, which defines the penetration depth into the region of metastable states along the isotherm. Criterion (1) can then be rewritten in the form

$$\frac{3X}{16\pi} \frac{(\Delta\rho)^2(\Delta p)^2 t v_c z p_c^3}{\sigma^3 R^2} \ll 1 + O(\varepsilon), \qquad (4)$$

where $z = k_B T_c / p_c v_c$ is the compressibility factor and v_c is the critical volume per molecule.

Inequality (4) is the Ginzburg criterion, which defines the boundary of the nonfluctuation region. To prove this, let us first consider thermodynamic states far from the critical point, where the density of the saturated vapor is small (i.e., $\rho_1 \ll \rho_2$). Then[8]

$$\sigma = \frac{\pi}{8} \bar{\rho}^2 \int_0^\infty \varphi'(r) g(r) r^4 \, dr, \qquad (5)$$

where $g(r)$ is the radial distribution of the liquid phase and $\varphi(r)$ is the potential of pairwise intermolecular interaction. Choosing $\varphi(r)$ to be in the form of the three-dimensional Kac potential

$$\varphi(r) = \begin{cases} \infty, & r < D, \\ -\dfrac{a}{4\pi}\gamma^3 e^{-\gamma r}, & r > D, \end{cases} \qquad (6)$$

where D is the diameter of the rigid core of the model molecule $\gamma^{-1} = R_0$ is the radius of action of the attraction forces between the molecules, and $a\gamma^3/4\pi$ is the interaction constant, we obtain

$$\sigma = \frac{\bar{\rho}^2 a R_0}{32}\left[\int_{\gamma D}^{\infty} g(xR_0)e^{-x}x^4\,dx - \frac{4\pi k_B T D^3}{a}\frac{D}{R_0}\right]. \qquad (7)$$

For an approximate estimate of the magnitude of the terms in brackets in expression (7), one can set $g(xR_0) \approx 1$, which is valid for large values of R_0. We then have

$$\int_{\gamma D}^{\infty} g(xR_0)e^{-x}x^4\,dx = 24 + O(D/R_0).$$

Let us now approximately estimate the coefficient of D/R_0 in the second term. If we use the van der Waals equation for this purpose (the intermolecular potential (6) leads to an equation of state of such type for $R_0 \to \infty$), then

$$4\pi k_B T D^3/a = 16t/9,$$

i.e., a quantity of the order of unity far from the critical point.

Thus, for $D/R_0 \lesssim 1$ the main contribution to the coefficient of surface tension σ comes from the first term in brackets in expression (7). Within the framework of this approximation the coefficient in front of the brackets in expression (7) is equal to

$$a\bar{\rho}^2 R_0/32 = 3p_c R^2 R_0/32.$$

We then have the following estimate for the surface-tension coefficient σ

$$\sigma \approx \frac{9}{4} p_c R^2 R_0. \qquad (8)$$

Let us calculate σ for argon with the help of this expression. For argon near the triple point $R^2 \approx 7.2$ and $p_c \approx 4.9$ MPa. If we take as R_0 the value of the amplitude of the correlation radius,[9] then $R_0 \approx 1.6 \cdot 10^{-10}$ m and it then follows that $\sigma \approx 12.7 \cdot 10^{-3}$ N/m, while experiment gives $\sigma \approx 13.4 \cdot 10^{-3}$ N/m. If $R_0 \approx 3.4 \cdot 10^{-10}$ m, which approximately corresponds to the position of the first maximum of the radial distribution function, then $\sigma \approx 27 \cdot 10^{-3}$ N/m. These estimates confirm the validity of the obtained relations for σ. Substituting expression (8) into inequality (4), in the approximation $\varepsilon \ll 1$ and $\rho_1 \ll \rho_2$ we obtain a criterion for the nonfluctuation region in the form

$$\frac{4Xzv_c(\Delta p)^2(\Delta\rho)^2 t}{243\pi R_0^3 R^8} \ll 1 + O(\varepsilon). \qquad (9)$$

Note that experimentally obtainable maximum values of ε are of the order of 10^{-2}.

The left side of inequality (9) is the product of different kinds of factors. The factor

$$(\Delta p)^2(\Delta\rho)^2 t/R^8$$

is the quantity that determines the position of the system in the thermodynamic plane. The factor

$$4Xzv_c/(243\pi R_0^3)$$

depends only on the individual molecular properties of the investigated system. The compressibility factor for a large number of materials is equal on average to 3.7. For a large number of liquids (carbonic acid, ethane, ethylene, methane, benzene, water, argon, etc.) $v_c \approx (4\text{–}5)v_0$, where $v_0 = 4\pi r_0^3/3$ is the volume occupied by one molecular and r_0 is the corresponding radius of the molecule. Taking the above-presented estimates into account, inequality (9) can be rewritten as

$$10z\,\mathrm{Gi}^{1/2}\frac{(\Delta p)^2(\Delta\rho)^2 t}{R^8} \ll 1 + O(\varepsilon), \qquad (10)$$

where

$$\mathrm{Gi} = (r_0/R_0)^6$$

is the Ginzburg number.[10]

Thus the applicability of theories of the metastable state in which fluctuation effects are not taken into account is determined both by the properties of the molecular parameters of the materials ($\mathrm{Gi} \ll 1$) and by the parameters that characterize the thermodynamic state of the system. If the system moves into the region of metastable states along the isotherm, then the factor which determines the behavior of the system is the magnitude of the isothermal compressibility χ in light of the singular character of its dependence on the density with approach to the spinodal.

It is interesting to note that the van der Waals model corresponds to the case $\gamma \to 0$ (or $R_0 \to \infty$), wherefore $\mathrm{Gi} = 0$ and the behavior of the system over the entire metastable region all the way to the spinodal is described by the mean-field theory. For real systems the closer the Ginzburg number is to zero, the better this theory works. Such a situation corresponds to far-range attraction forces between the molecules, which is the case for large values of the dipole moment of the molecules, as, for example, in the case of liquid crystals, where $\mathrm{Gi} \approx 0.2$.[11]

Let us obtain order-of-magnitude estimates of the quantities on the left-hand side of inequality (10) in the case of water. Far from the critical point for the isotherm with $T = 433$ K we have $\rho_1/\rho_2 \approx 0.025$. Then upon penetrating into the metastable region from the liquid branch of the isotherm $p_s = 0.62$ MPa and for $\bar{p} = 0.1$ MPa we obtain $(\Delta\rho)^2 \approx 0.6 \cdot 10^{-3}$, $\Delta\rho^2/R^8 \sim 10^{-3}$, $t \sim 1$, and $z = 4.35$. Inequality (10) takes here the form

$$10^{-9}\,\mathrm{Gi} \ll 1.$$

If we allow for the fact that for water $r_0 \sim R_0$, then it is clear that in the pressure interval $0.1 \leqslant p \leqslant 0.62$ MPa isothermal compression of water at $T = 433$ K can be described by standard methods of thermodynamic perturbation theory not allowing for fluctuational corrections to the thermodynamic quantities and their derivatives.

Note that the derivation of criterion (10) does not depend on whether we consider a superheated liquid or a supercooled (supersaturated) vapor. However, it is of interest that criterion (10) is not symmetric with respect to these two terms if we carry out the corresponding numerical estimates. It turns out that the values of the quantity R^{-8} for the liquid branch of the isotherm is a few orders of magnitude smaller than in the case of the gaseous branch of the isotherm. In fact, taking water as an example, we have

$(R_l/R_g)^8 \sim (\rho_2/\rho_1)^8 \sim 10^{20}$ at $T = 433$ K, $(R_l/R_g)^8 \sim 10^{12}$ at $T = 533$ K, and $(R_l/R_g)^8 \sim 10^9$ at $T = 573$ K, where R_g and R_l are the values of R on the gaseous and the liquid branch of the isotherm, respectively. The values of the thermodynamic quantities used to make the estimates were chosen near the binodal. Thus, whereas in the case of the superheated liquid inequality (10) is satisfied with room to spare, in the case of the supercooled vapor it can hold only at insignificant penetration depths (which corresponds to small Δp or $\bar{p}/p_s$ near unity). Consequently, in considering the equation of state of the supercooled vapor it is necessary to take into account the decisive role played by the fluctuational corrections immediately after the transition through the binodal.

In considering metastable states near the critical point we will make use of universal relations that follow from the theory of scale invariance. Thus, for the coefficient of surface tension the relation

$$\sigma=\sigma_0\tau^{2\nu}, \tag{11}$$

is valid, where σ_0 is the amplitude of the coefficient of surface tension, $\tau = (T_c - T)/T_c$, ν is the critical exponent of the correlation radius R_c. Since the coexistence curve is characterized by the equality

$$\tau=x_0(\Delta\tilde{\rho})^{1/\beta},$$

where $\Delta\tilde{\rho} = (\rho - \rho_c)/\rho_c$, β is the index of the coexistence curve, and x_0 is the corresponding amplitude,

$$\sigma=\sigma_0 x_0^{2\nu}(\Delta\tilde{\rho})^{2\nu/\beta},$$

and $R_{\min}$ is written as

$$R_{\min}=\frac{16\pi\sigma_0^3 x_0^{6\nu}(\Delta\tilde{\rho})^{6\nu/\beta}\bar{\rho}^2}{3(p_s-\bar{p})^2(\bar{\rho}-\rho_1)^2}. \tag{12}$$

Utilizing the expression for the critical isotherm

$$(p-p_c)/p_c=D_0[(\rho-\rho_c)/\rho_c]^\delta,$$

where δ is the index of the critical isotherm and D_0 is the amplitude of the critical isotherm, we obtain the following expression for $R_{\min}$:

$$R_{\min}=\frac{16\pi\sigma_0^3 x_0^{6\nu}(\Delta\tilde{\rho})^{6\nu/\beta}R^2}{3p_c^2\delta^2 D_0^2\varepsilon^2(\Delta\tilde{\rho})^{2(\delta+1)}(1-\varepsilon)^2}. \tag{13}$$

Taking into account the universal relation between the critical amplitudes x_0 and D_0 (Ref. 9)

$$\xi_0^3=(0{,}83)^3\frac{x_0^{\beta(\delta+1)}k_B T_c}{D_0 p_c}, \tag{14}$$

where ξ_0 is the amplitude of the correlation radius, the equality relating the indices β, δ, and ν

$$6\nu/\beta=2(\delta+1),$$

and also the approximate equality $\Delta\rho \approx 2\Delta\bar{\rho}$, we arrive at the expression

$$R_{\min}=\frac{\pi R^2\xi_0^6 c k_B T_c}{3\varepsilon^2\delta^2(0{,}83)^6 v_c^2}, \tag{15}$$

where $c = \sigma_0^3 v_c^2/(k_B T_c)^3$ is a dimensionless quantity. According to the law of corresponding states,[12] c is a universal quantity for a class of liquids with similar intermolecular potentials. As a result, inequality (4) can be rewritten in the form

$$\frac{25X}{c}\mathrm{Gi}\frac{\varepsilon^2\delta^2}{R^2}\ll 1+O(\varepsilon), \tag{16}$$

where the Ginzburg number is equal to

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

We will give corresponding numerical estimates for water, taking into account known values of the critical exponent $\delta = 4.8$ and the amplitude $\sigma_0 \approx 0.2$ J/m^2 (Ref. 9). Inequality (16) can then be rewritten in the form

$$10^4\varepsilon^2\,\mathrm{Gi}\ll 1.$$

If in the estimate of the Ginzburg number we use the value $\xi_0 = 0.13$ nm from Ref. 9 and as r_0 the characteristic "radius" of the water molecule $r_0 \approx 0.29$ nm, then $\mathrm{Gi} \gtrsim 10^2$ and it is clear that not taking account of the fluctuations which lead to the formation of the new phase, we can achieve a description of the thermodynamic states in the metastable region near the critical point only for small values of the penetration depth. In this regard, it should be noted that near the critical point, in the description of the thermodynamic properties of the material, it is necessary to take into account the strongly developed, interacting density fluctuations, whose role in the behavior of the system becomes decisive even outside the metastable region.

It should be noted that near the critical point the criterion of penetration depth into the metastable region is asymmetric. The reason for this is the presence of asymmetric corrections to the equations of state of asymptotic scaling. In addition, in the asymmetric corrections to the scaling it is necessary to allow for the fact that the value of the correction terms depends on the sign of $\Delta\tilde{\rho}$.

3. THE EQUATION OF STATE IN THE NONFLUCTUATION REGION

In the nonfluctuation region on both sides of the coexistence curve the system possesses the same type of symmetry, wherefore the description of its thermodynamic properties can be based on the same approach for the metastable as for the stable states. In the investigation of the thermodynamic properties of the material in the vicinity of the spinodal points the appearance of a new type of symmetry, described by the renormalization group, is important.

Since in the nonfluctuation region the system possesses a definite symmetry with respect to simple variation of the scale of the spatial variables: $\mathbf{r}_i' = q\mathbf{r}_i$ (not averaging the order parameter over regions with dimensions of the order of the correlation radius), we will use this simple scaling transformation to construct a thermodynamic perturbation theory. If the scaling factor q is chosen to be of the form

$$q=(V/V_0)^{1/3}, \tag{17}$$

where V_0 is the initial (reference) value of the volume V, then for the configuration part of the sum of states the equality

$$Q(N,T,V)=q^{3N}Q_V(N,T,V_0), \tag{18}$$

is valid, where N is the number of molecules in the system and

$$Q_V(N,T,V_0)=\frac{1}{N!}\int\limits_{V_0}\ldots\int dr_1\ldots dr_N \times\exp\Big[-\sum_{i<j}\varphi(q|\mathbf{r}_i-\mathbf{r}_j|)/k_BT\Big] \tag{19}$$

is the configuration part of the sum of states of the system of N particles in volume V_0 with intermolecular interaction potential $\varphi(qr)$. Since the choice of the magnitude of q here satisfies Eq. (17), this means that the variation of the volume $\Delta V=(V_0-V)/V_0$ during the scale transformation enters into the potential function since $\Delta V=1-q^3$.

It is possible thus to construct a thermodynamic perturbation theory using as the small parameter the dimensionless quantity ΔV. Indeed, if we turn to the experimental data in the metastable region,[3] then, for example, for water in the pressure interval around 10 MPa $\Delta V\approx0.02$. In essence, the smallness of the parameter ΔV over a wide pressure interval is ensured by the smallness of the isothermal compressibility χ^* since ($\chi^*=p_0\chi$)

$$\Delta V\approx\chi^*\frac{(p-p_0)}{p_0}$$

in the nonfluctuation region and $\chi^*\sim10^{-3}$ (in the case of water for $T\approx400$–500 K).

In Refs. 13 and 14 a number of thermodynamic perturbation theories were constructed with the help of an expansion of the free energy in a functional Taylor's series in modified Mayer functions

$$\exp\{-[\varphi(qr)-\varphi(r)]/k_BT\}-1.$$

The use here of the Kac potential (6) as the intermolecular potential leads to an equation of state that is a generalization of the well-known isothermal Tate equation

$$p-p_0=(p-p_0)_T+\Delta VM(1+He^{\Delta V/A}), \tag{20}$$

where $(p-p_0)_T$ is the pressure difference corresponding to the Tate isothermal equation of state:

$$(p-p_0)_T=(e^{\Delta V/A}-1)(p_0+B), \tag{21}$$

and the constants A, B, M, and H are given by the following expressions

$$\begin{gathered}A=12\pi k_BT\exp(\gamma D)/a\gamma^4D,\\ B=\frac{2}{3}\pi\left(\frac{N}{V_0}\right)^2k_BTD^3g(r\to D+0)-p_0=p_0^*-p_0,\\ M=(B+p_0)(3+2C),\\ H=-(2+C)/(3+2C).\end{gathered} \tag{22}$$

Here p_0^* is the part of the pressure that is due to the repulsion forces between the molecules at $V=V_0$; $C=(1/3)\times[\partial\ln g(r)/\partial r]_{r-D+0}$, where $g(r)$ is the radial distribution function calculated also at $V=V_0$.

Since the numerical values of the quantities A, B, and C naturally depend in a major way on the choice of the intermolecular potential, it seems best to consider them on the isotherm as fitting parameters if we have in mind an investigation of the equation of state of a real rather than a model system. Let us compare the results of calculation according to Eq. (20) with experimental data[3] for ordinary water, heavy water, and argon. Note that for $\Delta V\ll1$ Eq. (20) changes over into Eq. (21), whose differential form

$$-\left(\frac{\partial p}{\partial V}\right)_T=\frac{p+B}{AV_0}$$

allows us to use the data of Ref. 3 on the isothermal compressibility.

First, from the experimental points from Ref. 3 in the region of stable states we find the parameters A and B. Since V_0 and p_0 were chosen near the binodal, $\Delta V\sim10^{-2}$, which presents the possibility of using the differential form of the

TABLE I.

V, 10^{-3} m^3/kg	p_0-p, MPa		$-(\partial p/\partial V)_T$, 10^3 MPa·kg/m^3	
	experiment	theory	experiment	theory
Water, isotherm T=260° C, p_s=4,694 MPa				
1,2771	6	5,972	460.60	461.56
1,2793	7	6,979	451.84	453,47
1.2816	8	8,013	443,34	445.39
1.2838	9	8.984	435.16	437,30
1.2859	9.9	9,895	427.29	430.02
Water, isotherm T=300° C, p_s=8,592 MPa				
1.4068	2	2,010	216.72	216.26
1.4115	3	3,008	208,99	208,24
1.4214	5	4,996	193.28	192,22
1.4267	6	6.002	185.43	184.21
1.4322	7	7,005	177,21	176.20
1.4380	8	8.018	169.61	168,19
1.4440	9	9,022	161,43	160.19
1.4497	9.9	9.935	153.97	152,98
Argon, isotherm T=125 K, p_s=1,5812 MPa				
0.8972	3	2,985	112,58	111,39
0.9018	3.5	3,483	105.61	104.78
0.9066	4	3,971	99.37	99.16
0.911	4.4	4.393	93.82	92.87
0.924	5.5	5.503	79,00	78,31
0,955	7.5	7.493	49,86	51.85

Tate equation and determining A and B from only two points. Further, as the need arises, the parameters M and H can be found from the data in the metastable region. Results are shown in Table I.

For water at $T = 260\,^\circ\mathrm{C}$, $V_0 = 1.2188\cdot 10^{-3}$ m^3/kg, and $p_0 = 10$ MPa, we obtain $A = 0.098$ and $B = 53.067$ MPa, with the mean relative error Δ in the extrapolation of the difference $p_0 - p$ with the help of the Tate equation into the metastable region equal to 0.2%. In the calculation of $(\partial p/\partial V)_T$ in the metastable region $\Delta = 0.4\%$. The same values of A and B in the same pressure interval were used to describe $p_0 - p$ in the metastable region of heavy water. Here $p_0 = 10$ MPa, $V_0 = 1.1449\cdot 10^{-3}$ m^3/kg, and $\Delta = 0.13\%$. For water at $T = 300\,^\circ\mathrm{C}$, $V_0 = 1.3978\cdot 10^{-3}$ m^3/kg, and $p_0 = 10$ MPa, we obtain $A = 0.089$, $B = 18.997$ MPa, $M = 9.121$ MPa, and $H = -1.195$. In the case of extrapolation of $p_0 - p$ into the metastable region with the help of Eq. (20) we have $\Delta = 0.2\%$, and in the calculation of $(\partial p/\partial V)_T$ with the help of the Tate equation we have $\Delta = 0.5\%$. These same values of the parameters A, B, M, and H lead to $\Delta = 0.15\%$ for the description of the quantity $p_0 - p$ in the metastable region of heavy water in the same pressure interval ($V_0 = 1.2694\cdot 10^{-3}$ m^3/kg and $p_0 = 10$ MPa). In the case of argon at $T = 125$ K, $V_0 = 0.8743\cdot 10^{-3}$ m^3/kg, and $p_0 = 4.5$ MPa, we obtain $A = 0.086$, $B = 6.919$ MPa, and $\Delta = 0.3\%$ for extrapolation of $p_0 - p$ and $\Delta = 1\%$ for extrapolation of $(\partial p/\partial V)_T$ with the help of the Tate equation.

Note that if we find A and B by using the entire set of points in Ref. 3 and not just two points in the stable region, then the magnitude of the errors Δ is substantially decreased. Thus, in the metastable region (in its nonfluctuational part) to describe the isothermal penetration we can use the Tate equation of state and its modification in the form of Eq. (20). It is interesting that even for an extremely unrealistic Kac intermolecular interaction potential the relation between the fitting constants M and H and the quantity C is satisfactorily maintained. Indeed, starting with Eq. (22),

$$C = \frac{1}{2}\left[\frac{M}{(B+p_0)} - 3\right]$$

and at $T = 300\,^\circ\mathrm{C}$ the quantity C is equal to $-4/3$ (as was noted in Ref. 14, $C<0$ and $|C|<1$). It follows then that $H = -2$, while experiment gives $H = -1.195$.

One should especially note the possibility of describing the thermophysical properties of metastable heavy water under isothermal conditions using values of the constants of the equation of state found in the stable region of ordinary water. This is possible because the parameters of Eq. (22) are determined by the potential of the intermolecular forces and, consequently, should be identical for H_2O and D_2O. The equation of state which we have proposed here differs in this property from empirical equations whose constants are bound to an entire set of reference points.

The results presented here, which testify to the possibility of extrapolating the isotherms from the stable to the metastable region, are found to be in agreement with the conclusions of Ref. 1 to the effect that the peculiarity of the thermodynamic potential on the binodal is very weak and is not detected experimentally.

In the fluctuation region near the critical point, where the condition of smallness of the quantity χ^* is not fulfilled, the Tate equation and its modified form are inapplicable. In this case it is necessary to use the asymmetric scaling equation of state (see Ref. 15 and 16).

4. ON THE FRACTAL NATURE OF THE NEW-PHASE NUCLEI

As was shown in Refs. 6 and 7, nuclei of spherical shape appear quite rapidly as a result of the temporal evolution of critical formations of quite arbitrary shape. Analysis of the results of numerical experiments on the formation of microclusters during the nucleation process[17] confirms that the clusters which obtain as a result of equilibrium fluctuations are nearly fractal in shape. The question of the interaction (coalescence) of such formations, which is very important for the refinement of the criteria of stability of the metastable state, remains open at the present time.

Analysis of the dimensionalities of the density fluctuations shows that the appearance of compact nuclei as a result of equilibrium fluctuations, although possible, is extremely improbable. Indeed, for the fluctuation of the number of particles in the volume V we have

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

whereas for the formation of a cluster of compact shape of dimensionality d with density $\rho_1 = \rho_2 - \rho_c \Delta\rho$ $(\Delta\rho \neq 0)$ it is necessary that $(\langle \Delta N^2\rangle)^{1/2} \propto L^d$, where L is the characteristic linear dimension of the fluctuating volume. In the nonfluctuation region χ is not a singular quantity and therefore

$$(\langle \Delta N^2\rangle)^{1/2} \propto L^{d/2}. \tag{23}$$

Thus, it is impossible for the fluctuation of the number of particles to lead to the formation of a compact cluster (manifold) of dimensionality d. Such a manifold in the space $\mathbf{R}^d$ does not look locally like a piece of this space; it does not even have the form of a piece of the space $\mathbf{R}^{d-1}$ (with the exception of the case $d = 2$). In the fluctuation region $\chi \propto R_c^{2-\eta}$, $R_c \to L$ and

$$(\langle \Delta N^2\rangle)^{1/2} \propto L^{(d+2-\eta)/2} = L^{d-\beta/\nu} = L^{d_f}, \tag{24}$$

where η is the critical index of the correlation function and d_f is the fractal dimensionality of the forming new-phase clusters.

Using known values of the critical indices υ and β, we can draw the following conclusions regarding the metastable states near the critical point. For $d = 4$ the dimensionality of the forming manifold ($\mathrm{Dim}(M) = d_f$) is equal to 3, whereas the codimensionality,[18] $\mathrm{Cod}(M) = d - \mathrm{Dim}(M)$, which characterizes the dimensionality of the boundary, is equal to 1. Thus, for $d = 4$ there appears as a result of the fluctuations a fractal "foam." For $d > 4$ the role of fluctuations leading to the formation of the new phase is insubstantial since in this case $\mathrm{Cod}(M) > 1$. For $d = 3$ more compact structures arise than for $d = 4$ since in this case $\mathrm{Dim}(M) = 17/7$ and $\mathrm{Cod}(M) = 4/7 < 1$. Finally, for $d = 2$ fluctuational formations can in fact already play the role of nuclei of the new phase since $\mathrm{Dim}(M) = 15/8 \approx 2$ and $\mathrm{Cod}(M) = 1/8$. It is interesting to observe that for the formation of a compact new-phase nucleus it is necessary that $\mathrm{Dim}(M) = d$ and $\mathrm{Cod}(M) = 0$ for any dimensionality of the enveloping space.

The latter circumstance underlines the importance of introducing the concept of codimensionality. Thus, the concept of transversality can also be formulated in the language of codimensionalities. Two submanifolds in $\mathbf{R}^d$ intersect transversly at a given point if they either do not intersect at all at this point or

$$\mathrm{Cod}(M_1)+\mathrm{Cod}(M_2)\leqslant d,\ \mathrm{Cod}(M_1\cap M_2)=\mathrm{Cod}(M_1)+\mathrm{Cod}(M_2). \tag{25}$$

For two arbitrarily chosen manifolds the probability that they intersect nontransversally is infinitesimally small.[18] Thus, if as a result of fluctuation in the number of particles in different volumes fractal manifolds (new-phase clusters) form in the system, then the situation in which they intersect tranversally is typical. The probability of their nontransversal intersection is equal to zero. Thus, near the critical point in the metastable region for $d = 3$ manifolds form with $2 < \mathrm{Dim}(M) < 3$ and intersect transversally with $\mathrm{Dim}(M_1 \cap M_2) \lesssim 2$ and $\mathrm{Cod}(M_1 \cap M_2) = 8/7$. In the case $d = 2$ we have $\mathrm{Dim}(M) = 15/8 \lesssim d$, and the transversal intersection of the forming clusters is a manifold of dimensionality $14/8 \lesssim d$, i.e., the coalescence of the clusters, leading to the growth of the new phase, is the most probable in this case.

The above analysis of the dimensionalities of the fluctuational manifolds shows that the question of the criteria of stability of the metastable state cannot be consistently resolved within the framework of an approach that uses the hypothesis of the formation of new-phase nuclei of compact shape. In connection with this, note should be taken of the results of numerical experiments according to which the structure of the clusters forming in the metastable region is nearly fractal.[17]

5. CONCLUSION

In the investigation of the behavior of matter in the region of metastable states a correct account of the fluctuational corrections of the thermodynamic properties of the investigated system is necessary. Far from the critical point the corrections associated with the instability of the system with respect to the fluctuation formation of the new phase play a decisive role. As the critical point is approached, the role of long-range density fluctuations grows. The condition that determines the importance of the fluctuational contribution to the thermodynamic quantity of interest for each concrete system is the Ginzburg criterion associated with the characteristics scales of the forces of attraction and repulsion between the molecules.

In the nonfluctuation region of superheated liquids the thermodynamic properties of the system are well described by the standard methods of the statistical mechanics of dense gases and liquids. The Tate isothermal equation of state and its modified form do not change their form upon passing through the binodal and make it possible to extrapolate the corresponding experimental dependence from the stable region into the metastable region all the way to the limit of superheating attainable in present-day experiments.

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