4. G. A. Ostroumov, Interaction of Electrical and Hydrodynamic Fields [in Russian], Moscow (1979).
5. I. P. Vershchagin, V. I. Levitov, G. Z. Mirzabekyan, and M. I. Pashin, Fundamentals of Electrodynamics of Dispersed Systems [in Russian], Moscow (1974).
6. R. I. Nigmatulin, Dynamics of Multiphase Media, Parts 1 and 2 [in Russian], Moscow (1987).
7. S. Sou, Hydrodynamics of Multiphase Systems [in Russian], Moscow (1971).
8. M. K. Bologa, O. V. Motorin, F. M. Sazhin, and G. V. Sekrieru, Elektron. Obrab. Mater., No. 6, 41-47 (1987).
9. F. M. Sazhin, M. K. Bologa, and V. M. Rudenko, Elektron. Obrab. Mater., No. 6, 56-60 (1983).
10. F. M. Sazhin, M. K. Bologa, V. M. Rudenko, and G. V. Sekrieru, Elektron. Obrab. Mater., No. 5, 62-67 (1984).
11. M. K. Bologa, F. M. Sazhin, I. K. Savin, and Yu. N. Gordeev, Heat-Mass Transport, International Forum, Minsk, May 24-27. Reports, Sect. 6-7, Minsk (1988), pp. 44-61.

BEHAVIOR OF LIQUID THERMODYNAMIC STABILITY UNDER SUPERHEATING AND SUPERCOOLING

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It is noted that evaluation by van der Waals equation of the asymptotic (T → 0 K) spinodal tensile stress of liquids is close in order of magnitude to the ideal strength of solids and the limiting pressure on the extension of the fusion line of various substances.

1. Equilibrium coexistence of phases on a planar phase boundary is determined by equality of temperatures, pressures, and chemical potentials μ within the phases. For slow (quasistatic) processes phase transition produces no marked deviation of the system from equilibrium conditions. But for sufficiently rapid change in external parameters such deviations may become significant. This is especially true of the initial stage of phase transition. This stage includes the appearance of metastability of the original phase, nucleation, and growth of the new phase. A number of questions arising here were considered in a previous study [1]. The thermodynamic factor in the expression for nucleation rate is very sensitive to difference in the chemical potentials of the phases and the value of the interphase surface tension. With deeper penetration into the metastable state range, the height of the activation barrier for nucleus formation decreases rapidly. Development within the system of an intense flux J of fluctuation nuclei of the new phase is of almost a threshold character [1]. This may be treated as loss of stability of the medium with respect to heterophase local fluctuations. The onset of such instability is not necessarily accompanied by reduction in stability of the metastable system relative to homophase changes in density and entropy. The response of the isotropic system to small local perturbations in pressure and temperature is characterized by the isothermal compressibility $\beta_T = -(1/v)(\partial v/\partial P)_T$ and the isobaric specific heat $c_p = T(\partial s/\partial T)_P$. For stability the conditions of [2] must be satisfied: $\beta_T > 0$, $c_p > 0$ or $(\partial P/\partial v)_T < 0$ and $(\partial T/\partial s)_P > 0$.

The boundary of thermodynamic stability (spinodal) is defined by the equations

$$\left(\frac{\partial P}{\partial v}\right)_T = 0, \quad \left(\frac{\partial T}{\partial s}\right)_P = 0. \tag{1}$$

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In the future we will use the first of these, which refers to the limit of mechanical stability. Beyond that state are unstable states for which system reaction leads to intensification of small disturbances, i.e., there $(\partial P/\partial v)_T > 0$. In two- and multicomponent systems instability may set in relative to composition fluctuations (component concentrations, x). This occurs when $(\partial \mu/\partial x)_{P,T} < 0$.

A more general approach to stability of the state of multiparticle systems permits analysis of response to perturbations of various wavelengths. If we consider a molecular scale, then Eq. (1) corresponds to the longwave limit.

The thermodynamic stability limit is not reached by a quasistatic path, but the position of the spinodal on the phase diagram can be found asymptotically, extrapolating to zero the elasticity $-(\partial P/\partial v)_T$ or the inverse isothermal compressibility β_T, for example, along isochors or isotherms. Another approach is simultaneous solution of the condition $(\partial P/\partial v)_T = 0$ and the equation of state. It is also convenient to use the following property of the spinodal. On the plane T, P the spinodal acts as the envelope of an adjacent family of isochors [3, 4]. At the point of attachment of the isochors to the spinodal the former have a common tangent, i.e.,

$$\frac{dP}{dT_{\text{sp}}} = \left(\frac{\partial P}{\partial T}\right)_v. \tag{2}$$

The adiabats have a similar property:

$$\frac{dP}{dT_{\text{sp}}} = \left(\frac{\partial P}{\partial T}\right)_s.$$

For a model van der Waals fluid the isochors are rectilinear in the plane T, P. This simplifies demonstrating the properties of Eq. (2). In the dimensionless coordinates $\tau = T/T_{cr}$, $\pi = P/P_{cr}$, $\varphi = v/v_{cr}$, we have

$$d\pi/d\tau_{\text{sp}} = (\partial\pi/\partial\tau)_\varphi = (1/Z_{\text{cr}})(\varphi - 1/3)^{-1},$$

where $Z_{cr} = P_{cr}v_{cr}/RT_{cr} = 3/8$ is the critical coefficient.

In view of the rectilinear nature of the isochors, the angular coefficient $(\partial\pi/\partial\tau)_\varphi$ of each one is constant and equal to the value at the point of attachment of the isochors to the spinodal. The spinodal is divided into liquid $(1/3 \le \varphi < 1)$ and gaseous $(1 < \varphi < \infty)$ branches and encompasses the entire volume range accessible to the van der Waals equation $(1/3 \le \varphi < \infty)$. With respect to temperature, the spinodal occupies the segment from $\tau = 0$ to $\tau = 1$, and with respect to pressure from $\pi = -27$ (for the gaseous branch from $\pi = 0$) to $\pi = 1$.

2. In the future we will be especially interested in the form of the liquid spinodal and the limiting stress values $\sigma = -P$ as $T \to 0$ for volume extension deformation. The negative pressure region refers to metastable liquid states, since it lies below the equilibrium pressure $P_s(T)$ of the liquid—vapor and its extension to limitingly low temperatures.

The spinodal forms the natural limit of liquid strength with regard to volume extension. Such an approach is an alternative to kinetic treatment of the process of spontaneous nucleation and subsequent growth of vapor (cavitation) bubbles. With decrease in the characteristic time for decay of the homogeneous system the kinetic limit approaches the spinodal [3], found from the real equation of state. Estimates by homogeneous nucleation theory have been found to correspond to experiment for many substances [3, 5] at pressures from atmospheric to near-critical and at quite small values of the product $t_{ex}V$, where t_{ex} is the characteristic time of the experiment and V is the volume of the metastable system.

Table 1 shows estimated temperatures of intense homogeneous nucleus formation T_* and the spinodal T_{sp} of argon at the triple point pressure. For T_* we take the condition $J(T_*) \simeq 10^5\ \text{sec}^{-1}\cdot\text{cm}^{-3}$. To calculate T_* for supercooled liquid argon a value of surface tension on the boundary with the crystalline nucleus of 5 mJ/m^2 was used. For the superheated crystal the value of T_* was not calculated. The second line of the table is of principal significance. Although as an argon-type liquid supercools the probability of appearance of a crystalline nucleus increases, the stability of the liquid to homophase density perturbations does not decrease, but even increases [6]. Apparently there is no spinodal for supercooled states of normal liquids. For water, [7] assumed a common spinodal for

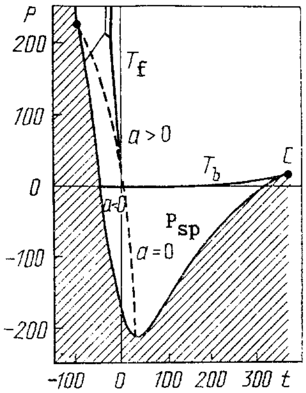

Fig. 1. Spinodal of water P_{sp} proposed in [7] and unstable state region (shaded): T_b) liquid—vapor equilibrium line; C) critical point; P, MPa; t, °C.

TABLE 1. Temperature of Intense Nucleation T_* and Spinodal T_{sp} for Metastable Phases of Argon at Triple Point Pressure (P_{tr} = 0.069 MPa, T_{tr} = 83.8 K)

Characteristic temperature, K	Liquid		Superheated crystal	Supersaturated vapor
	superheating	supercooling		
T_*	130	74	—	70
T_{sp}	136	—	105	64

superheated and supercooled liquid. The turning of the spinodal at approximately P = −200 MPa shown in Fig. 1 is related to the anomalous change in density of water. The estimate of T_{sp} for the superheated crystal was taken from [8], and was obtained by molecular dynamic modeling of argon.

With temperature reduction below τ = 0.7, the liquid strength achievable in experiment proves to be significantly below the theoretical strength estimated using kinetic calculations, or by the pressure on the spinodal. For water at T = 291 K (τ = 0.45) the burst pressure under the record conditions of [9] comprised P_B = −27.0 MPa, while by homogeneous nucleation theory P_* = −138 MPa, and the point on the water spinodal at T = 291 K corresponds to a pressure P_{sp} = −262 MPa. We will present the corresponding pressures for argon at T = 85 K (τ = 0.56): P_B = −1.2 MPa [10], P_* = −19 MPa, P_{sp} = −32 MPa.

Briggs [9] observed a reduction in water strength by a factor of several times upon approach to the crystallization temperature. A similar effect, but not as strongly expressed, was also noted by him in benzol, aniline, and acetic acid. Apparently this is due to impurities, which encourage boiling (cavitation). There are many studies of cavitation in water and they lead to the conclusion of heterogeneous nucleus formation.

Water has a specific volume anomaly not far from the fusion line. For isobaric temperature increase the sign of the thermal expansion coefficient $\alpha = (1/v)(\partial v/\partial T)_P$ changes. The line of maximum density α = 0 in the plane T, P has a negative slope, $(\partial P/\partial T)_{\alpha=0} < 0$, and has been found for both positive and negative pressure [11, 7]. From the relationship $(\partial P/\partial T)_v = -(\partial P/\partial v)_T(\partial v/\partial T)_P$ is can easily be seen that the derivatives $(\partial P/\partial T)_v$ and $(\partial v/\partial T)_P$ are of identical sign in the stability region, so that upon transition through the line α = 0 the angular coefficient of the isochor $(\partial P/\partial T)_v$ changes sign. This property is maintained upon approach of the line α = 0 to the spinodal. Considering that in the plane T, P the spinodal serves as the envelope of isochors, we arrive at the conclusion that at the point where the line α = 0 meets the spinodal the direction of the latter must change, as shown in Fig. 1. Without considering in detail the reconstruction of [7] for the boundary of unstable states, shown in Fig. 1, we will call attention to the significant reduction in maximum tensile stress to be expected in water in this case as compared to monotonic extension of the spinodal. [The asymptotic value of P_{sp} (T → 0) for water from the van der Waals equation comprises −597.2 MPa.]

The authors of [12] proposed that other liquids as well, even those not having a density anomaly in the state range studied, may have one below the triple point. Then the situation becomes similar to that of water, and the reduction in maximum tensile stress as compared to results of conventional calculations is explained. In [12] (and two subse-

TABLE 2. Values of σ_{max} Characterizing Ideal Strength of Solids and Spinodal Stresses of Liquids $27P_{cr}$ from van der Waals Equation as T → 0 K

Material	σ_{max}, GPa			$27P_{cr}$,	P_θ,
	[13]	[14]	filamentary crystal	GPa	
Ar	0,254			0,131	0,211
Na	0,85	1,67		0,692	1,20
Zn			0,98	6,64	6,0
Sn			1,23	4,9	5,7
Pb		7,2		4,3	3,2
Al	2,62		2,27	2,24	7,0
Bi			0,59	3,5	
Cd			2,80	4,0	4,5
Ag	19,7	18,9	1,73	3,1	9,2
Cu	33	29	4,4	4,6	13,4
Ge		10,7	4,3	1,2	
Fe	48		13,1	11,4	
Ni	25		2,9	13,2	17
NaCl	2,95		1,10	0,94	1,67
KCl	2,66			0,59	0,69

quent studies) a thermodynamic analysis of system properties near the spinodal minimum was carried out. But it is difficult to agree with the authors' assumption that materials with such behavior are not rare exceptions. A more realistic path is to seek the cause of the divergence not in rotation of the spinodal, but in a shift of the cavitation boundary due to the heterogeneous character of nucleus formation in experiments on liquids under tension.

3. The absence of any direct experimental method for determination of a liquid spinodal at large negative pressure makes it desirable to resort to indirect estimates. One such is based on the following considerations. For similar densities of an ideal crystal and a supercooled liquid their volume strengths are of the same order of magnitude. Such behavior has been seen in comparisons of the crystalline and vitreous states of various materials.

Theoretical calculations of the ideal strength of crystals have been undertaken from various positions [13]. Modern estimates rely on calculating the potential energy of the deformed crystal using the potential of two-particle atomic interaction and introduction of elastic constants into the calculation. In essence, a thermodynamic approximation is constructed. The system stability limit is found for a specified type of deformation — extension, shear, with attachment to crystallographic axes. The majority of ideal strength calculations show $\sigma_{max} \approx 0.1E$ and $\tau_{max} \approx 0.1G$, where E is Young's modulus and G is the shear modulus. The strength of real specimens is usually two orders of magnitude lower than the ideal. This is due to various defects (microfissures, dislocations, etc.). A similar pattern of strength reduction has been observed for amorphous solid materials and glasses. We note that reduction of the cavitation threshold in liquids, discussed above, should be considered within this class of phenomena.

The thermodynamic stability limit (spinodal) in the sense of the condition $(\partial P/\partial v)_T = 0$ corresponds to the ideal strength of a fluid relative to volume extension $\sigma_{max} \approx -P_{sp}(T)$. If we are concerned only with the order of magnitude of the ideal strength we need not distinguish between volume and uniaxial extension. Comparison of independently determined values of σ_{max} and $-P_{sp}$ will permit us to judge the agreement of the results. Such a comparison (with assumption of the same order of magnitude for the ideal strengths of crystal and liquid) is presented in Table 2 for a number of substances. The second column gives calculated values of σ_{max} obtained by various authors. Citations are given in [13]. The third column shows results of σ_{max} calculations [14] at 0 K using the Morse potential. Experimental values of strength in filamentary crystals [15, 13] are in the fourth column. The limiting (T → 0 K) tensile stress corresponding to the spinodal is taken from the van der Waals equation $P_{sp}(0) = 27\ P_{sp}$. Values of the critical pressure for the metals are from [16], and for sodium and potassium chloride from [17]. From the table one can see that the quantities σ_{max} and $27\ P_{cr}$ are of the same order of magnitude. The filamentary crystal strengths are at room temperature. In this case, σ_{max} should be compared to the quantity $-P_{sp}$ (T = 293 K). For high-temperature metals the relative shift $\delta P_{sp} = (P_{sp}(0)$ −

$P_{sp}(293))/P_{sp}(0)$ is not large. It can be estimated by using the approximation $P_{cr} - P_{sp} = a(T_{cr} - T_{sp})^{1,3}$. For copper, taking $P_{sp}(0) = -27\ P_{cr}$, we obtain $\delta P_{sp} \simeq 0.06$. Such a correction can be neglected in view of the approximate character of all values in the table.

The data collected in Table 2 indicate in favor of a monotonic (van der Waals) extension of the spinodal into the region of high tensile stress.

4. Liquid and crystalline states not only exist at negative pressure, but may also coexist: the fusion line has a real continuation beyond the triple point. There both phases are metastable and thus have a finite lifetime. This does not hinder satisfaction of the phase equilibrium condition $\mu_\ell(P, T) = \mu_c(P, T)$. Continuation of the fusion line beyond the triple point was observed in [18] for both normal and heavy water.

Data on fusion of simple substances was generalized in [1, 19] using Simon's equation:

$$1+\frac{P}{P_0}=\left(\frac{T}{T_0}\right)^c.$$

Here $-P_0 = P_f(0)$ is the pressure on the extension of the fusion line as $T \to 0$. The exponent $c > 1$ has the sense of a thermodynamic similarity parameter. In the negative pressure region with decrease in temperature the fusion line approaches the spinodal of the liquid in tension. The asymptotic values $P_0 = -P_f(0)$ and $27\ P_{cr} = -P_{sp}(0)$ prove to be of the same order of magnitude. This is evident from comparison of the numbers in the last two columns of the table. Thus, the ideal strength of a crystal can be related not only to approach of the phase point to the spinodal, but also to crossing the extension of the fusion line. The relative closeness of the values $P_f(0)$ and $P_{sp}(0)$ is one more result in favor of the monotonic course of the liquid spinodal $P_{sp}(T)$ for deep intrusion ($\approx 27\ P_{cr}$) into the negative pressure region. This does not imply the impossibility of exceptions. If for water the density maximum on the isobars does not disappear at large extensions and the line $\alpha(T, P) = 0$ intersects the spinodal, as shown in Fig. 1, the spinodal should pass through a minimum. But its further course may not correspond to the figure. The experiments of [20] on crystallization of amorphous layers of water at T = 160-170 K and atmospheric pressure indicate a normal character for the phase transition – by means of nucleation and growth. If we take the spinodal form shown in Fig. 1, then at $T < 225$ K water is in a mechanically unstable state (beyond the spinodal), and this should affect its crystallization mechanism, including spinodal decay and related regularization of the structure.

Despite the very approximate nature of the van der Waals equation, its use in estimating the asymptotic ($T \to 0$) limiting tensile stress of a liquid $\sigma = -P_{sp}(0) = 27\ P_{cr}$ appears reasonable. This value is close in order of magnitude to the ideal strength of solids and the limiting pressure on the extension of the fusion line of various substances.

NOTATION

P, pressure; v, molar volume; T, temperature, K; t, temperature, °C; s, entropy; μ, chemical potential; J, nucleation rate (nucleus flux), $\sec^{-1}\cdot\mathrm{cm}^{-3}$; σ, tension. Subscripts: cr, sp, and f, values at thermodynamic critical point, on spinodal, and on fusion line.

LITERATURE CITED

1. V. P. Skripov, Inzh. Fiz. Zh., 53, No. 5, 920-826 (1987).
2. L. D. Landau and E. M. Lifshits, Statistical Mechanics, Part 1 [in Russian], Moscow (1976).
3. V. P. Skripov, Metastable Liquid [in Russian], Moscow (1972).
4. V. P. Skripov, Phase Transitions and Nonequilibrum Processes [in Russian], Sverdlovsk (1980), pp. 36-45.
5. V. P. Skripov, E. N. Sinitsyn, P. A. Pavlov, et al., Thermophysical Properties of Liquids in the Metastable State [in Russian], Moscow (1980).
6. V. P. Skripov, Equations of State of Gases and Liquids [in Russian], Moscow (1975), pp. 60-76.
7. S. J. Henderson and R. J. Speedy, J. Phys. Chem., 91, No. 11, 3062-3068 (1987).
8. V. G. Baidakov, A. E. Galashev, and V. P. Skripov, Fiz. Tverd. Tela, 22, No. 9, 2682-2687 (1980).
9. L. J. Briggs, J. Chem. Phys., 19, 970 (1951).

10. J. W. Beams, Phys. Fluids, 2, No. 1, 1-4 (1959).
11. C. A. Angell and H. Kanno, Science (Washington), 193, No. 4258, 1121-1122 (1976).
12. P. G. Debenedetti and M. C. D'Antonio, J. Chem. Phys., 84, No. 6, 3339-3345 (1986).
13. N. Macmillan, Atomistics of Failure [Russian translation], Moscow (1987), pp. 35-103.
14. A. D. Izotov and V. B. Lazarev, Dokl. Akad. Nauk SSSR, 305, No. 5, 1155-1159 (1989).
15. G. V. Berezhkova, Filamentary Crystals [in Russian], Moscow (1969).
16. M. M. Martynyuk, Zh. Fiz. Khim., 57, No. 4, 810-821 (1983).
17. A. D. Kirshenbaum, J. A. Cahill, P. J. McGonigal, and A. V. Grosse, J. Inorg. Nucl. Chem., 57, No. 10, 1287-1298 (1962).
18. S. J. Henderson and R. J. Speedy, J. Phys. Chem., 91, No. 11, 3069-3072 (1987).
19. V. P. Skripov and M. Z. Faizullin, High Temp. High Pres., 18, 1-12 (1986).
20. N. M. Bogdanov, V. P. Koverda, and V. P. Skripov, Fiz. Khim. Stekl., 6, No. 4, 395-400 (1980).

CRITICAL BOILING HEAT TRANSFER: SPECIAL CASE OF SMOOTH EXCHANGE OF BUBBLE AND FILM BOILING REGIMES

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The author presents results of an unconventional analysis of critical heat transfer interpreted as boundaries of a transition boiling region with a smooth exchange of bubble and film boiling regimes. A stepwise exchange of these boiling regimes, i.e., critical heat transfer in the textbook sense, is examined as a special case. The influence of various parameters on the boundaries and the transition boiling zone is demonstrated.

For a better understanding of critical boiling heat transfer one should examine the question unconventionally. Then we shall see that one would not then consider critical boiling heat transfer as a sharp exchange of types of boiling. In the variation of wall temperature there is a smooth transition from pure bubble boiling to pure film boiling via a large boiling transition zone, extensive with respect to T_W, in which these two types interchange continuously, both in time and over the surface. Therefore, it would be more correct to speak of conditions (boundaries) for starting and stopping the transition boiling regime.

Then the usual concept of critical bubble boiling on a low thermal inertia surface as a breakdown as the heat input increases and as a stepwise transition to a remote region of film boiling can be considered as a special case of the usually smooth transition process.

As a special case of the general transition process it is also convenient to treat the hydrodynamic theories of critical bubble and film boiling, considering stepwise transitions from bubble boiling to film boiling and back as a consequence of perturbing the hydrodynamic stability of these processes. In critical bubble boiling heat transfer one considers conditions for stepwise separation of the liquid from the wall, and the creation of a complex vapor film, and in critical film boiling one considers conditions perturbing the vapor film and the establishment of bubble boiling over the entire surface.

In our opinion, it is much more general to study the mechanism and the physical processes of the transition boiling and the causes of its occurrence within the bubble and film boiling regimes.

In replacing bubble boiling by transition boiling with an increase of T_W an important matter will be the appearance and the comparatively long persistence of dry spots, i.e.,

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