

# The velocity of sound and the thermodynamic stability of liquid argon

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(Submitted 9 March 1978)

Zh. Eksp. Teor. Fiz. 75, 1007-1016 (September, 1978)

The velocity of sound is measured in liquid argon with a deep descent into the range of metastable (superheated) states. The variation of the thermodynamic properties of the metastable argon is described by using the results of the present investigation and those of previous works [V. G. Baidakov et al., Sov. Phys. JETP 38, 557 (1974) and 40, 335 (1975)]. The indistinguishability of the transition of a homogeneous system through the phase equilibrium line for the second and third derivatives of the thermodynamic potential is confirmed. The boundary of appreciable instability (spinodal) of superheated argon, which corresponds to the usual definitions of the spinodal, is approximated, as is the boundary of the stronger instability (adiabatic spinodal). However, it cannot be stated definitely that the boundaries do not coincide.

PACS numbers: 64.70.Fx, 65.50.+m, 62.60.+v

## STATEMENT OF THE PROBLEM

In first-order phase transitions that take place rapidly, departures of the system from the conditions of phase equilibrium are observed. One of the coexisting phases turns out to be in a metastable state. For example, in intense boiling, a liquid is significantly superheated relative to the saturation temperature  $T_s(p)$ . In recent years, fast phase transitions have been widely used in the laboratory and in engineering practice (obtaining metastable alloys, metallic glasses, the action of a powerful laser radiation on material, and so on). This has stimulated the investigation of the boundaries of stability of aggregate states and the character of processes with participation of metastable and labile phases.

We study here superheating of liquid argon. Results were given previously of an investigation of the kinetics of fluctuation boiling<sup>[1]</sup> and data of  $p, v, T$  measurements that included a significant descent into the region of the metastable states,<sup>[2]</sup> and the equation of state was discussed. For a broader study of the thermodynamic behavior of superheated argon, it is necessary to have data on the heat capacity  $C_v$  or the sound velocity

$$W = v(-\partial p / \partial v)_s = (\beta_s / v)^{-1/2}, \quad (1)$$

where  $\beta_s$  is the adiabatic compressibility. Then we can determine other properties with the help of well-known thermodynamic relations. We pause to consider the measurements of the sound velocity, since experiments<sup>[3]</sup> with metastable xenon have turned out to be encouraging.

An important problem of this research is the obtaining of information on the stability of the liquid behind the line of equilibrium coexistence with the vapor. This line (binodal) corresponds to the boundary of absolute stability of the phase. The incompletely stable (metastable) states are characterized by a finite lifetime. In a "pure" system, the inverse mean lifetime  $\bar{\tau}^{-1} = J$  determines the stationary current of viable seeds of the competing phase (vapor). Its dependence on the parameters of the liquid state ( $p, T$ ) is well described<sup>[1,4]</sup> by the theory of homogeneous nucleation<sup>[5,6]</sup> over a wide range of values of  $J$ . If  $\bar{\tau}$  is regarded as the time of appearance of the instability, then the radius of the critical seed  $r_*$  has the

meaning of the minimum "instability length" for discontinuous local changes, corresponding to a first order phase transition. On the binodal, we have  $\bar{\tau} \rightarrow \infty, r_* \rightarrow \infty$ . The free energy barrier  $\Delta F_*$  which the system must overcome in fluctuating fashion for initiation of the phase transition, increases rapidly with increase in  $r_*$ ,  $\Delta F_* = (4/3)\pi r_*^2 \sigma$ , where  $\sigma$  is the surface tension. This leads to the result that the spontaneous phase transition does not begin at weak supersaturations and all the properties are continued smoothly into the metastable region.

A stability of another type is characterized by the response of a homogeneous system to a continuous (homophase) change of state. A stable system should possess a restoring reaction to such perturbations. For this case it follows from the requirement<sup>[7]</sup> of positive definiteness of the second variation of the internal energy  $u$  that

$$D = u_{rr}u_{ss} - u_{rs}^2 > 0, \quad (2)$$

$$u_{rr} = \left(\frac{\partial^2 u}{\partial v^2}\right)_s = -\left(\frac{\partial p}{\partial v}\right)_s > 0, \quad u_{ss} = \left(\frac{\partial^2 u}{\partial s^2}\right)_v = \left(\frac{\partial T}{\partial s}\right)_v = \frac{T}{C_v} > 0. \quad (3)$$

The stability conditions (2) and (3) are equivalent to the conditions

$$-\left(\frac{\partial p}{\partial v}\right)_r = (v\beta_r)^{-1} > 0, \quad \left(\frac{\partial T}{\partial s}\right)_p = \frac{T}{C_p} > 0, \quad (4)$$

where  $\beta_r$  is the isothermal compressibility. On the stability boundary (spinodal)  $D = 0$ . For unstable conditions  $D < 0$ . The condition  $D = 0$  does not require the vanishing of the adiabatic derivatives  $u_{ss}$  or  $u_{rr}$ . If we assume that  $u_{ss}$  or  $u_{rr}$  vanish simultaneously with  $D$ , then this will mean the vanishing of all the elements of the determinant  $D$ .<sup>[4]</sup> Such a case is a special one. We assume that the inequalities (3) are conserved on the spinodal.<sup>[1]</sup> We then obtain the usually employed definition of the spinodal:

$$\left(\frac{\partial p}{\partial v}\right)_r = 0, \quad \left(\frac{\partial T}{\partial s}\right)_p = 0. \quad (5)$$

Specifying the two variables  $x$  and  $y$  (for example,  $v, T$ ) as independent is sufficient for a simple, homogeneous and single-component system; any equilibrium property  $z$  ( $z = p, s, F$  and so on) can be represented as a surface that depends on  $x$  and  $y$ . On such a surface, the binodal and the spinodal are represented by space curves with complicated mutual orientation. The description of the

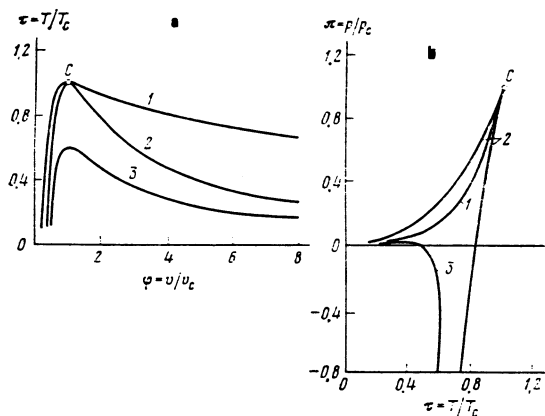


FIG. 1. Binodal (1), spinodal (2) and adiabatic spinodal (3) according to Van der Waal's equation in the coordinates: a)  $\tau - \varphi$ . b)  $\pi - \tau$ ; C is the critical point.

nonequilibrium states is complicated since it contains one or several additional parameters (for example, a stabilizing external field).<sup>[10,11]</sup> Upon implicit introduction of these parameters, we shall assume that the considered surface encompasses also the region of labile homogeneous states. We can then define one more stability boundary by the conditions

$$\left(\frac{\partial p}{\partial v}\right)_s = 0, \quad C_s = 0 \quad (6)$$

—the adiabatic spinodal. It is important for the qualitative analysis of the kinetics of the spinodal decay of a one-component system.<sup>[9,12]</sup>

We consider the surface  $p = p(T, v)$ , smooth and continuous over the entire region of fluid states. Figure 1 shows the mutual orientation of the binodal—1, the spinodal—2 and the adiabatic spinodal—3 invarious projections, according to the Van der Waals equation in the relative coordinates  $\tau = T/T_c$ ,  $\varphi = v/v_c$ ,  $\pi = p/p_c$ .

We must now take the next step—attempt to construct the adiabatic spinodal from experimental data for a material in a metastable region, and to elucidate the behavior of the thermodynamic properties near the phase stability boundary.

### MEASUREMENT OF THE SOUND VELOCITY

The velocity of propagation of sound in liquid argon (certified purity 99.998%) with a deep descent into the metastable region, was measured in the temperature range  $T = 115-140$  K. Two diverse pulse methods were used: the method of direct measurement of the time of flight of the ultrasonic signal through the investigated material and the sing-around method.<sup>[13]</sup> The liquid was heated in a glass acoustic cell 1 ( $V \sim 1.5$  cm<sup>3</sup>; see Fig. 2), which for elimination of easily activated boiling centers was carefully washed and degassed before filling. The cell was thermostatted ( $\pm 0.007$  K) in a copper block 11. the temperature was measured by a standard platinum resistance thermometer 9 ( $R_0 = 10.0013$  ohm) in the system with a potentiometer P-363/2. The pressure in the system was produced by compression of the helium and was measured by two standard spring manometers of the class 0.16. The investigated liquid was separated from

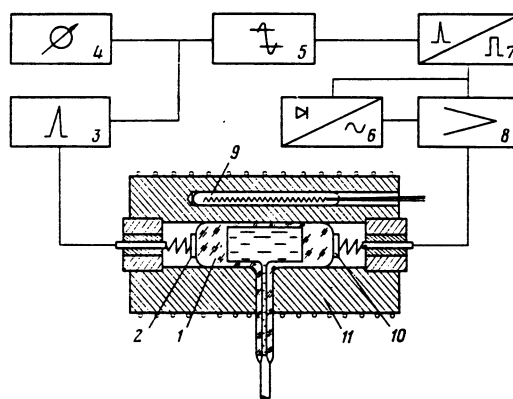


FIG. 2. Block diagram of the setup for measurement of the sound velocity in superheated liquids: 1—acoustic cell, 2—piezoelectric radiator, 3—blocking oscillator, 4—frequency meter, 5—limiter, 6—system of automatic volume control, 7—differential amplifier, 8—amplifier, 9—platinum resistance thermometer, 10—piezo-receiver, 11—thermostating block.

the gas by a metallic siphon bellows, extending outside the block with the cell. The temperature of the cavity of the bellows was maintained close to the normal boiling temperature of argon ( $T \sim 87$  K). The transition to the metastable state of the liquid in the cell was brought about by a smooth decrease in the pressure behind the phase equilibrium line.

In the sing-around method, individual video pulses, generated by the synchronized blocking generator 3, are fed to the transmitting piezoceramic radiator 2. The natural frequency of the electroacoustic transducers was  $\sim 2.5$  MHz. The signal was amplified after passing through the investigated liquid. The automatic gain control system 6 assures a constant amplitude at the output of the receiver-amplifier circuit. After the differentiating amplifier 7 and the limiter 5, the electric pulses travel by two paths—to the frequency meter 4 and to a repeat triggering of the blocking generator 3. Thus the time of flight of the ultrasonic signal through the investigated material determines the repetition frequency  $f$ , which is then measured experimentally. We then have for the sound velocity

$$W = lf / (1 - t_d), \quad (7)$$

where  $l$  is the acoustic path length in the liquid,  $t_d = f^{-1} - t_p$  is the delay of the signal in the process of passage through the electronic circuit and the walls of the cell. The quantity  $l$  was determined with the help of an optical measuring instrument ( $\pm 0.005$  mm). The delay time  $t_d$  was found from the known value of the sound velocity  $W_s$  on the saturation line.<sup>[14,15]</sup> The accuracy of these data in the temperature range  $T = 85-145$  K was  $\sim 0.15\%$  and in the critical region  $\sim 0.7\%$ . The results of our measurements have error of not more than 0.2–0.3%. The data of the two series of measurements, completed by the sing-around method and the method of direct measurement of the time of flight of the ultrasonic signal through the studied liquid, agree within the limits of  $\sim 0.1\%$ .

Figure 3 shows a group of isotherms of the sound velocity. The portions of the isotherms to the left of the line  $W_s$  refer to the superheated liquid. The descent into

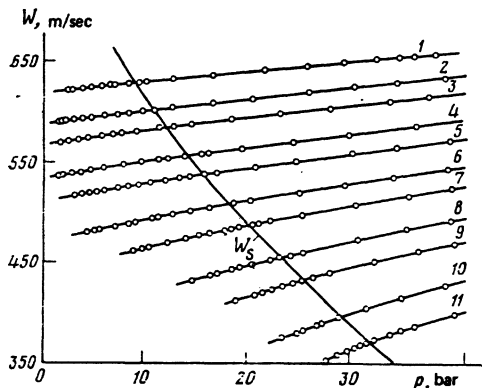


FIG. 3. Sound velocity in liquid argon along the isotherms: 1— $T=115$ , 2—118, 3—120, 4—123, 5—125, 6—128, 7—130; 8—133, 9—135, 10—138, 11—140 K;  $W_s$  is the sound velocity on the saturation line.

the metastable region reached 14 bar. At a pressure of 1.55 bar, the superheating  $\Delta T = T - t_s$  amounted to 31.5 K (the boundary of spontaneous boiling  $J_1 = 10^2$ ;  $\text{cm}^{-3}\text{-sec}^{-1}$  corresponds to  $\Delta T = 39.5$  K (Ref. 1)). As is seen from the drawing, a transition through the phase equilibrium line without disruption of the homogeneity of the sample is not noted on the sound velocity isotherm, which indicates the smoothness of the continuation of the second and third derivatives of the thermodynamic potential from the stable region to the metastable.

### COMPRESSIBILITY, HEAT CAPACITY OF THE SUPERHEATED LIQUID

The results of ultrasonic and  $p, v, T$  measurements of the superheated liquid enable us to determine the total complex of its thermodynamic properties. Corresponding calculations were made by us for liquid argon in the temperature range from 90 K to close to critical, and at pressures from 500 bar to the boundary of the thermodynamical stability phase. The location of the spinodal of the heating liquid argon on the  $p, v, T$  surface was previously determined<sup>[2]</sup> from results of density measurements.

We consider the behavior of the second derivatives of the thermodynamic potential in the metastable region: the isothermal and adiabatic compressibilities, the isochoric and isobaric heat capacities. For the heat capacities we have

$$C_p = \frac{T\alpha_p^2 v}{\beta_T - \beta_p}, \quad (8)$$

$$C_v = C_p \frac{\beta_p}{\beta_T}, \quad (9)$$

where  $\alpha = v^{-1}(\partial v / \partial T)_p$  is the coefficient of thermal expansion.

Reduction of the data of the sound velocity, together with the results of  $p, v, T$  measurements, has shown that, throughout the entire range of temperature and pressures studied, the dependences of the adiabatic modulus of the liquid— $(\partial p / \partial v)$  on the temperature along the isochores and of the sound velocity  $W$  on the densities along the isotherms are close to linear. Upon increase in the pressure range to 100 bar and in temperatures from 85 to

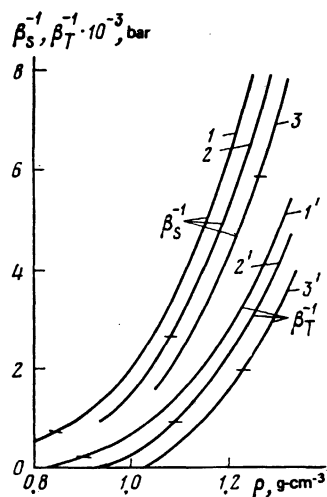


FIG. 4. Reciprocal isothermal and adiabatic compressibilities: 1, 1'— $T=145$ , 2, 2'—130, 3, 3'—110 K. The primes indicate the values of  $\beta_S^{-1}$  and  $\beta_T^{-1}$  on the saturation line.

145 K, the departure from linearity is  $\sim 0.5\%$ . All the thermodynamic properties of the metastable argon were calculated in these approximations.

The isothermal and adiabatic compressibilities characterize the reaction of the system to external mechanical action. With approach to the boundary curve (Fig. 4) and descent to the metastable region, the stability of the liquid decreases; this is expressed in a decrease in the quantities  $\beta_T^{-1}$  and  $\beta_S^{-1}$ . By virtue of the inequality  $\beta_T > \beta_S$ , which follows from the theory of thermodynamic stability, the liquid is always more stable relative to the isentropic mechanical perturbations than to isothermal ones. The primes in Fig. 4 indicate the values of  $\beta_S^{-1}$  and  $\beta_T^{-1}$  on the line of equilibrium coexistence of the phases. At atmospheric pressure, the adiabatic modulus of the liquid on the boundary of spontaneous boiling ( $T = 130.5$  K) is only 29% less than its value on the boundary curve; the isothermal modulus is smaller by 36%. We note that the depth of the encroachment into the metastable region at this temperature,  $p_s - p$ , amounts to  $\sim 19.7$  bar. The point of the spinodal lies even deeper, approximately 45 bar from the saturation line.

The value of the response of the system to thermal perturbation is determined by its heat capacity, and the stability is characterized by the reciprocal value of  $C$ . The isochores of the coefficient of thermal stability  $T/C_p$ ,

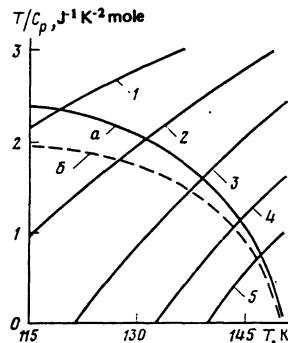


FIG. 5. Coefficient of thermal stability  $T/C_p$  of liquid argon along the isochores: 1— $v=0.8$ , 2—0.95, 3—1.05, 4—1.15, 5—1.25  $\text{cm}^3\text{g}^{-1}$ ; a—boundary curve, b—line of achievable superheating ( $J=10 \text{ cm}^{-3}\text{sec}^{-1}$ )

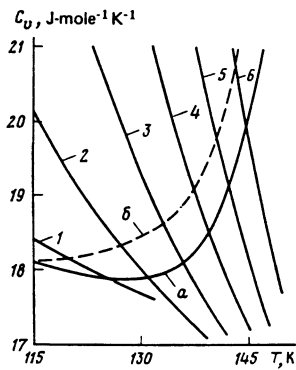


FIG. 6. Isochores of the heat capacity  $C_V$ : 1— $\nu=0.9$ , 2—0.95, 3—1.0, 4—1.05, 5—1.10, 6—1.15  $\text{cm}^3 \text{g}^{-1}$ ; a—boundary curve, b—line of achievable superheating ( $J=10 \text{ cm}^3 \text{sec}^{-1}$ ).

are given in Fig. 5. The descent into the metastable region (the left lower corner) is accompanied by a decrease in the stability of the liquid. Figure 5 also shows the values of  $T/C_p$  on the saturation curve and the superheating that is achieved. In the entire range of temperatures investigated, the values of  $C_p$  on the boundary of spontaneous boiling are about 20% higher than on the binodal. The use of various methods of extrapolation of the adiabatic compressibility into the metastable region leads to values of the isobaric heat capacity that agree with one another within limits of 2–3% (an exception is the immediate vicinity of the spinodal and the critical point). The error in the calculation of the heat capacity from ultrasonic data and  $p, v, T$  measurements was 3–5%.

The behavior of the isochore heat capacity is more complicated. As the liquid density decreases,  $C_V$  on the isotherm falls off, passes through a minimum, and then increases monotonically. At  $T \geq 125 \text{ K}$ , the minima in the isotherms of  $C_V$  are located in the stable region, at lower temperatures, in the metastable region. According to the thermodynamic relation

$$\left(\frac{\partial^2 p}{\partial T^2}\right)_v = \frac{1}{T} \left(\frac{\partial C_V}{\partial v}\right)_T \quad (10)$$

the isochores of the pressure change the sign of their curvature at the extremal points of  $C_V$ . In the high temperature region, the isochores of the liquid are convex to the pressure axis ( $(\partial^2 p / \partial T^2)_v < 0$ ). Near the boundary curve and in the metastable region, the negative curvature changes to positive ( $(\partial^2 p / \partial T^2)_v > 0$ ). This latter means that at the point of encounter of the isochore with the spinodal, these lines have opposite signs of curvature.

The isochores of the heat capacity  $C_V$  are shown in Fig. 6. With drop off in the metastable region (the region of states above the line a)  $C_V$  increases, however, not so significantly as, for example, the isobaric heat capacity. With approach to the critical point, both the value of  $C_V$  and the value of the derivative  $\partial C_V / \partial T$  increase. The dependence of  $C_V$  on the temperature is close to linear in the stable and metastable regions.

## BOUNDARIES OF STABILITY OF THE HOMOGENEOUS PHASE

Any phase in the region of its stable existence is stable relative to arbitrary changes in the internal parameters

TABLE I. Thermodynamic properties of liquid argon on the lines of achievable superheating ( $J_1 = 10 \text{ cm}^3 \text{sec}^{-1}$ ) and the boundary curve (in parentheses) ( $T_c = 150.65 \text{ K}$ ,  $p_c = 48.98 \text{ bar}$ ,  $v_c = 1.867 \text{ cm}^3 \text{gm}^{-1}$ ).

$T, \text{ K}$	$p, \text{ bar}$	$v, \text{ cm}^3 \text{g}^{-1}$	$C_p, \text{ J}\cdot\text{mole}^{-1}\cdot\text{K}^{-1}$	$C_V, \text{ J}\cdot\text{mole}^{-1}\cdot\text{K}^{-1}$	$\beta T^{-10^4}, \text{ bar}^{-1}$	$\beta_s \cdot 10^4, \text{ bar}^{-1}$	$s, \text{ J}\cdot\text{g}^{-1}\cdot\text{H}^{-1}$
148	43.3 (43.85)	1.311 (1.232)	296 (251)	27.5 (25.5)	287 (232)	26.5 (23.5)	2.09 (2.078)
146	39.0 (40.52)	1.228 (1.204)	195 (163)	23.5 (21.7)	154 (116)	18.3 (15.7)	2.05 (2.041)
144	34.7 (37.38)	1.171 (1.144)	148 (123)	21.5 (20.0)	97.7 (72.7)	14.1 (11.8)	2.02 (2.012)
142	30.1 (34.44)	1.127 (1.095)	125 (102)	20.5 (19.1)	70.1 (50.0)	11.5 (9.40)	2.00 (1.986)
140	25.4 (31.65)	1.091 (1.061)	108 (89)	19.5 (18.6)	52.4 (36.8)	9.58 (7.75)	1.93 (1.961)
138	20.6 (29.08)	1.060 (1.030)	97 (80)	19.0 (18.3)	41.2 (28.7)	8.20 (6.56)	1.96 (1.937)
136	15.5 (26.65)	1.034 (1.003)	89 (74)	19.0 (18.1)	33.6 (23.0)	7.16 (5.66)	1.93 (1.914)
134	10.4 (24.33)	1.010 (0.979)	83 (69)	19.0 (18.0)	27.9 (19.0)	6.32 (4.96)	1.91 (1.893)
132	5.0 (22.23)	0.990 (0.958)	78 (65)	18.5 (17.9)	23.5 (16.0)	5.66 (4.40)	1.89 (1.868)
130	0.6 (20.23)	0.971 (0.938)	74 (62)	18.5 (17.9)	20.5 (13.8)	5.13 (3.94)	1.87 (1.846)

of both finite and infinitesimal size. Behind the spinodal the probability of spontaneous formation of a competing phase is determined by the value of the free energy barrier  $\Delta F_*$ , which the system must overcome to begin the phase transition. The value of  $\Delta F_*$  is a measure of the stability of the metastable system relative to finite perturbations, and falls off with superheating of the liquid. According to the theory of homogeneous nucleation<sup>[5,6]</sup> we have, for stationary flow of critical bubbles per unit time,

$$J_1 = N_1 B \exp(-\Delta F_*/kT), \quad (11)$$

where  $N_1$  is the number of molecules in a unit volume of the metastable phase, and  $B$  is the kinetic coefficient. Equation (11) at given  $J_1$  and  $p$  determines the temperature of achievable superheating. Experiments on the study of kinetics of spontaneous boiling of superheated liquid argon<sup>[1]</sup> have shown that we can assume the quantity  $\ln(N_1 B)$  to be constant to within a sufficient degree of accuracy,  $\sim 73$ , while on the line of achievable superheating,

$$p = p_c - \left(\frac{16\pi}{3(73 - \ln J_1)}\right)^{1/2} \sigma^{3/2} (kT)^{-3/2} (1 - \rho''/\rho')^{-1}. \quad (12)$$

The table lists the calculated thermodynamic properties of metastable liquid argon for  $J_1 = 10 \text{ cm}^3 \text{sec}^{-1}$ . The parentheses contain the values of the thermodynamic parameters on the saturation line. Two projections of the lines of achievable superheating are shown in Fig. 7. The region in which measurements of the sound velocity and density were carried out is shaded in Fig. 7a.

Thermal motion of large collections of particles is accompanied by local disruptions of the microhomogeneity. The second-order moments  $\langle(\rho - \langle\rho\rangle)^2\rangle$  and  $\langle(E - \langle E\rangle)^2\rangle$  are proportional to the compressibility and the heat capacity, respectively. Experiment shows (see the table) that  $\beta_T$  and  $C_p$  increase weakly along the line of achievable superheating in comparison with the saturation lines. For initiation of homogeneous nucleation, a decrease in the free energy barrier  $\Delta F_*$  is a more significant fact than an increase in the mean fluctuation level.

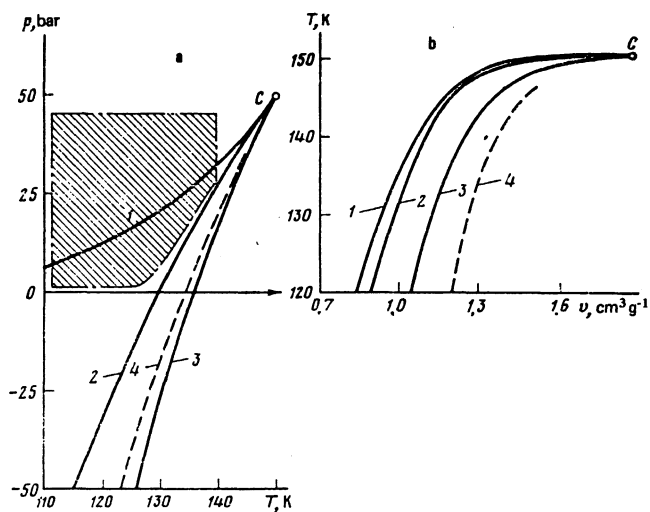


FIG. 7. Projection of the binodal 1, the line of achievable super-heating 2, the spinodal 3 and the adiabatic spinodal 4 of liquid argon in the coordinates  $p-T$  (a) and  $T-v$  (b); C is the critical point. The shaded region indicates the states in which the measurements of the  $p$ ,  $v$ ,  $T$  properties and the sound velocity were made.

The superheated liquid, manifesting an instability at distances  $\sim r_*$  after a time  $\sim \bar{\tau}$ , preserves the restoring reaction at infinitesimally small changes in the internal parameters. On the spinodal  $\beta_T \rightarrow \infty$  and  $C_p \rightarrow \infty$ ; consequently, the fluctuations of the density and energy on them increase catastrophically. Projections of the spinodal of liquid argon in the coordinates  $p-T$  and  $T-v$  are shown in Fig. 7. It is difficult in the experiment to proceed to the very boundary of the stability. The only exit of the spinodal into the region of stable states is the critical point.

We now consider two possibilities of the behavior of the system in the neighborhood of the spinodal. The thermodynamic theory of the spinodal is based on the admissibility of analytic continuation of the free energy along the corresponding departures of the temperature and the density. This is not valid if all the thermodynamic functions turn out to be nonanalytic relative to the external thermodynamic parameters. The spinodal in this case is a line of thermodynamically singular points, similar to the critical, and, simultaneously with (5) we should have  $\beta_s^{-1} = 0$ ,  $C_T^{-1} = 0$ .<sup>[16]</sup> Then the region of labile homogeneous states is not unattainable.

If the adiabatic coefficients of stability are different from zero on the spinodal, then there is a unique possibility of penetration into the region of lability for processes of isentropic expansion. This possibility exists through the route of nonstatic change in the parameters of state. This question was first discussed by Zel'dovich and Todes.<sup>[12]</sup> They assumed that the rate of decay of the homogeneous state in the labile region is limited by the heat exchange between the expanding and compressing elements of volume. The deeper the initial intrusion into the labile region, the higher the rate of decay. The transition through the spinodal in the case of preserva-

tion of the adiabatic stability is accompanied by a change in the sign of  $C_p$ . For labile states,  $C_p$  is negative. This leads to an exponentially increasing temperature differences, in the solution of the equation of thermal conduction. A substance in the labile state at  $(\partial d/\partial v)_T > 0$  and  $(\partial p/\partial v)_s < 0$  rapidly loses its spatial homogeneity. In relaxing, it takes on a "grainy" structure, initially without phase boundaries. As one penetrates into the labile region, states are achieved in which  $(\partial p/\partial v)_s = 0$ . Simultaneously,  $C_p$  vanishes. States satisfying the condition  $(\partial p/\partial v)_T > 0$  and  $(\partial p/\partial v)_s > 0$  should be assumed to be not only unstable, but also unattainable, since the usual estimate of the time of decay of a homogeneous phase  $\tau_p$ <sup>[12]</sup> at  $C_p = 0$  yields  $\tau_p = 0$ . The methods that we have used in the treatment of the experimental data on the sound velocity in the metastable region give finite values to  $\beta_s$  and  $C_v$  on the spinodal. The adiabatic modulus vanishes on the boundary of the thermodynamic stability, which is determined by the condition  $(\partial p/\partial v)_T = 0$ . The results of the approximation of the adiabatic spinodal of argon are given in Fig. 7.

Thus we have shown the possibility of the experimental determination of the thermodynamic properties of a material in the metastable region through the example of superheated liquid argon. However, the data for the spinodal (the behavior of  $C_v$ ,  $\beta_s$ ) cannot be regarded as reliably established, since there is still too great a region of the metastable states in which measurements have not been carried out.

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Translated by R. T. Beyer