

Experimental study of liquid argon in the metastable state

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Specific-volume measurements with deep penetration into the region of metastable (superheated) states have been made for a simple liquid for the first time. It is shown that both the first and second derivatives of the thermodynamic potentials vary smoothly, exhibiting no singularities when the system crosses the liquid-gas phase equilibrium line without macroscopic phase separation. The experimental data are approximated by an equation of state, which is then used to find the thermodynamic stability limit (spinodal curve) for liquid argon, defined as the curve on which the isothermal compressibility becomes infinite.

INTRODUCTION

First order phase transitions arise because of the competition between at least two different phase states of a system consisting of a large number of molecules. While each of the phases maintains its internal stability with respect to continuous variations, the relative stability of the phases "changes sign" at the line of intersection of the two thermodynamic-potential surfaces. This line (for a simple system it is a curve on the temperature-pressure plane) determines the equilibrium of fairly extended competing phases and is the line of a quasistatic phase transition. Each of the surfaces extends smoothly into the region of metastable states, the phase equilibrium line (binodal) being in no way distinguished on it. In this sense a first order phase transition is "unexpected" as far as the behavior of the initial phase is concerned.

However, the idea of two thermodynamic-potential surfaces is not always a justified simplification. For example, the presence of a critical point in the liquid-vapor system of a pure substance presupposes a single surface in the region above the critical point. Moreover, it is not entirely clear how to reconcile the "unexpectedness" of the phase transition with its description in terms of a Gibbs ensemble in the thermodynamic limit ($N \rightarrow \infty$, $V \rightarrow \infty$, $N/V = n = \text{const}$), where only a very small part of the accessible phase volume corresponds to the metastable states of the system. In this case the phase transition occurs so close to the equilibrium line where the phases coexist as to preclude any penetration into the metastable region.

Figure 1 illustrates the behavior of the isotherms in the vicinity of a liquid-gas phase transition. The sections BL and MC correspond to homogeneous metastable states of the liquid and vapor.¹⁾ The points L and M lie on the curve bounding the region in which the phase is essentially unstable, i.e., on the curve on which the isothermal compressibility becomes infinite.

In finite systems with limited observation time and in the absence of "seeding," a spontaneous first order phase transition begins from the metastable state of the initial phase. The smaller the system and the shorter the characteristic time of the experiment, the higher the degree of supersaturation required for the beginning of the phase transition. The process takes place via the formation of nuclei of the new phase as a result of fluctuations and the subsequent growth of these nuclei. An earlier paper^[1] was devoted to an experimental study of the kinetics of fluctuation nucleation in superheated liquid argon.

Here we report the results of a study of specific volumes $v = 1/\rho$ in metastable argon. We were able to trace the behavior of a finite system deep into the metastable region and to confirm the absence of any singularities on the isochores or isotherms where they cross the phase equilibrium line. Earlier papers reporting investigations conducted in our laboratory^[2-4] were concerned with liquids having complex molecules.

EXPERIMENTAL TECHNIQUE AND RESULTS

Figure 2 is a simplified diagram of the chamber used for the P-v-T measurement. The investigated liquid is contained in the glass piezometer 2 (volume $V_p \sim 1.5 \text{ cm}^3$), which in turn is mounted in the thermostated aluminum block 1. The temperature of the block is automatically held constant within $\pm 0.01^\circ$ or better. The temperature is measured by a standard platinum resistance thermometer 8 ($R_0 = 9.9402 \Omega$) used with a class 0.002 type R-348 potentiometer.

The piezometer 2 communicates via a glass-Kovar junction and a capillary tube (volume $V_{\text{cap}} \sim 2.7 \times 10^{-3} \text{ cm}^3$) with the capacitance type pressure transducer 3, which is used as a null indicator. The metallic diaphragm 4 and the copper plate 5, which is insulated from the body of the transducer by mica and Teflon, are responsible for the capacitance $C_t \sim 90 \text{ pF}$ of the transducer. The transducer is connected in the tank circuit of the LC oscillator 7, whose frequency ($\sim 10 \text{ MHz}$) is measured with a Ch3-33 electronic digital frequency meter. The sensitivity of the capacitance transducer in the investigated range of temperatures and pressures is $\Delta P/\Delta f \sim 10^{-5} \text{ bar/Hz}$. The upper cavity of the transducer, which is filled with the working liquid, has a volume of $V_t \sim 0.16 \text{ cm}^3$. The transducer 3 is mounted in the massive copper cup 6, and its temperature is held constant during the measurements at $93.0 \pm 0.1^\circ \text{K}$.

Compressed helium was used to produce and regulate

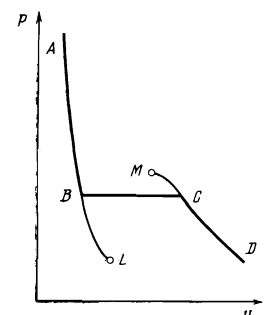


FIG. 1. Isotherm in the region of the liquid-gas phase transition (below the critical temperature). Sections BL and MC correspond to metastable states.

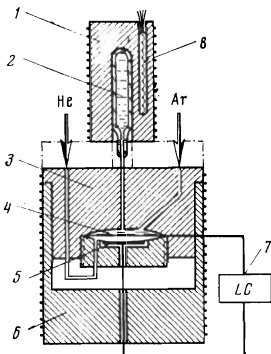


FIG. 2

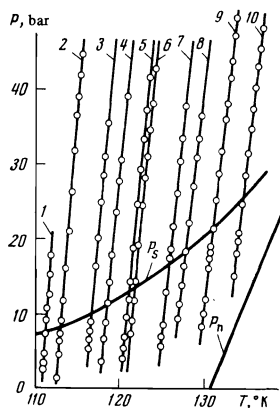


FIG. 3

FIG. 2. Simplified diagram of the chamber for P-v-T measurements.
 FIG. 3. Quasiisochores of liquid argon with penetration into the region of metastable states: 1) $\rho_S = 1.2314$ g/cm³, 2) 1.2104, 3) 1.1796, 4) 1.1648, 5) 1.1443, 6) 1.1398, 7) 1.0992, 8) 1.0826, 9) 1.0484, 10) 1.0082. P_S is the saturation line, and P_N is the spontaneous efferescence limit ($J_1 = 10^2$ cm⁻³ sec⁻¹).

the pressure in the system, the pressure being transmitted from the helium to the investigated liquid through the diaphragm 4. In the stable region, the pressure was measured with an MP-60 piston gauge, and in the metastable region, with a spring gauge. The assembled chamber was sealed in a thin walled stainless steel air tight jacket and placed in a Dewar vessel. The system was cooled with liquid nitrogen boiling at atmospheric pressure; the nitrogen level in the Dewar vessel was regulated. Argon (certified purity 99.99%) was admitted to the previously evacuated and cooled chamber through a thin walled stainless steel capillary.

In the experiment we measured the pressure as a function of temperature along quasiisochores, i.e., with a constant volume of liquid in the piezometer-transducer system. After the desired temperature had been established in the thermostat block 1, the pressure corresponding to the null position of the transducer diaphragm was determined. In the stable region, the pressure on the quasiisochore was measured both on lowering the temperature, and on raising it. As the system penetrated into the metastable region, the pressure fell smoothly beyond the phase equilibrium line. The time required for equalization of the pressure on the liquid was ~ 40 sec, whereas the thermal relaxation time for the liquid in the piezometer was $\sim 15-20$ sec.

We made only relative measurements. To normalize our results we used the data of [5] on the density of liquid argon on the saturation line $\rho_S(T)$; according to [6], these data, together with those of [7,8], provide the basis for the international tables of the thermodynamic properties of argon now under preparation. The unknown density can be determined from the condition that the mass be constant on the quasiisochore, using the formula

$$\rho(P, T) = \rho_s + \frac{V_t + 0.5V_{cap}}{V_p + 0.5V_{cap}} [\rho(P_s, T_t) - \rho(P, T_t)] = \rho_s + \delta\rho. \quad (1)$$

Here $\rho(P_S, T_t)$ and $\rho(P, T_t)$ are the densities of the liquid in the null indicating capacitance transducer at the pressures P_S and P , while V_p , V_t , and V_{cap} are the respective volumes of the piezometer, the upper cavity of the transducer, and the capillary joining them. Equation (1) was derived on the assumption that the temperature varies linearly along the capillary joining the piezometer

to the transducer; the error in determining the density resulting from this assumption does not exceed 0.01%. In processing the experimental data we corrected for the isothermal and isobaric changes in the volume of the piezometer. The mean error in determining the density was $\sim 0.05\%$ (without allowing for the error in the data on the saturation line used for normalizing). We made P-v-T measurements on liquid argon in the temperature range 110–138°K on ten quasiisochores. The penetration depth into the metastable region ranged from 5 to 11 bars. The results of the measurements are presented as a P-T plot in Fig. 3. The figure also shows the saturation line P_S and the spontaneous efferescence limit P_N for argon [1], at which the nucleation rate J_1 is 10^2 cm⁻³sec⁻¹. Over the entire investigated temperature range, the quasiisochores were nearly straight; they were also close to true isochores: the relative volume change $\Delta v/v$ on the experimental quasiisochores did not exceed 0.1%. As is evident from Fig. 3, none of the quasiisochores exhibits any peculiarity whatever at the point where it crosses the line on which macroscopic phases can coexist. Within the experimental accuracy, the derivative $(\partial P/\partial T)_v$ is continuous; this shows that both the first and second derivatives of the thermodynamic potential vary smoothly as the system crosses the phase equilibrium line into the metastable region without macroscopic phase separation. The results of our P-v-T measurements in the stable region agree (as regards density) within 0.15% (with allowance for the possible normalization error) with the results obtained by Street and Staveley [9], and by Sorokin and Blagoi [10].

EQUATION OF STATE AND THE THERMODYNAMIC STABILITY LIMIT

We constructed an empirical equation of state on the basis of the thermodynamic relation

$$\left(\frac{\partial^2 P}{\partial T^2}\right)_v = \frac{1}{T} \left(\frac{\partial C_v}{\partial v}\right)_T \quad (2)$$

with fitting to the saturation line, in order to approximate our P-v-T data. According to the calorimetric measurements of Gladun [11], the specific heat (C_v) isochores of liquid argon are linear near the limiting curve (except for a region contiguous to the critical point). Assuming that the C_v isochores are straight in the metastable region, too²⁾, we expressed Gladun's data [11] in the form

$$C_v(T, v) = A(v) + B(v)T. \quad (3)$$

Then after integrating (2) near the saturation line we obtain an equation of state of the form

$$P = P_s(v) + A'(v) \left[T \ln \frac{T}{T_s(v)} - (T - T_s(v)) \right] + \frac{B'(v)}{2} (T - T_s(v))^2, \quad (4)$$

where

$$P_s(v) = P_c(v) + \left(\frac{\partial P}{\partial T}\right)_c \Big|_s (T - T_s(v)). \quad (5)$$

The derivative $(\partial P/\partial T)_{v|s}$ was evaluated in the temperature range 110–138°K from our P-v-T measurements. The data of [9, 13] were used to evaluate $(\partial P/\partial T)_{v|s}$ in regions contiguous to the triple and critical points. The functions $A'(v)$, $B'(v)$, and $(\partial P/\partial T)_{v|s}$ have the forms

$$\begin{aligned} A'(v) &= 1.16454v - 0.95663, \\ B'(v) &= \frac{0.08938v^2 - 0.67676v + 0.45854}{(13.5163 - 3.57022v)^2}, \end{aligned} \quad (6)$$

$$\left(\frac{\partial P}{\partial T}\right)_{v|s} = 0.64901 \exp[-5.57790/v^8] + (0.57583v - 0.18977)^{-2}.$$

The quantities occurring in the equation of state have

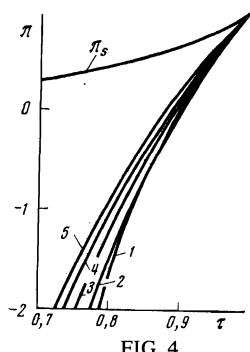


FIG. 4

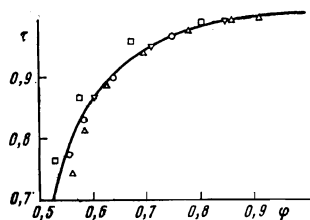


FIG. 5

FIG. 4. Spinodal curve for superheated liquid argon in reduced coordinates ($\pi = P/P_c$, $\tau = T/T_c$): 1—from the equation of state (4), 2—from Fürth's theory [15], 3—from the Pena-Lombardero hole theory [16], 4—from the theory significant structures [17], 5—from the McLellan hole theory [18]; π_s is the saturation line.

FIG. 5. Spinodal curve for liquid argon projected onto the τ - φ plane ($\tau = T/T_c$, $\varphi = v/v_c$): curve—from the equation of state (4), \circ —from the theory of hyperchains [19], ∇ —from the Percus-Yevick theory [20], \triangle —from the Pena-Lombardero hole theory [16], \square —from the McLellan hole theory [18].

Spinodal curve and saturation line for liquid argon $v_c = 1.867 \text{ cm}^3/\text{g}$, $T_c = 150.86 \text{ K}$, $P_c = 48.98 \text{ bar}$

$v, \text{ cm}^3/\text{g}$	$T_c, \text{ K}$	$T_s, \text{ K}$	$P_{sp}, \text{ bar}$	$P_s, \text{ bar}$	$v, \text{ cm}^3/\text{g}$	$T_c, \text{ K}$	$T_s, \text{ K}$	$P_s, \text{ bar}$	$P_{sp}, \text{ bar}$
1.464	147.2	150	39.4	47.39	1.145	132.4	144	-16.3	37.36
1.358	144.6	149	31.2	45.58	1.099	127.7	142	-39.4	34.41
1.293	142.1	148	22.9	43.83	1.062	122.9	140	-65.1	31.64
1.245	139.6	147	13.6	42.14	1.047	115.6	137	-108.6	27.80
1.205	137.2	146	4.1	40.50	0.981	108.0	134	-160.0	24.32
1.173	134.7	145	-6.0	38.90	0.960	102.7	132	-200.9	22.19

the following dimensions:

$$[P] = \text{bar}, [T] = ^\circ\text{K}, [v] = \text{cm}^3/\text{g}.$$

The equation of state (4) describes our relative P - v - T measurements with a mean error of 0.06% and a maximum deviation of 0.09%, and it reproduces the data of [9, 10] at pressures up to 400 bars and temperatures in the range 85–145°K with high accuracy (within 0.2% or better for the densities).

The spinodal curve for superheated liquid argon, defined by the condition [14] $(\partial P/\partial v)_T = 0$, was calculated from the equation of state (4). The results of this calculation are presented in the table (T_{sp} and P_{sp} denote the temperature and pressure on the spinodal curve). The table also gives points on the saturation line (T_s and P_s). At atmospheric pressure, loss of thermodynamic stability takes place when the liquid is superheated by 49°; this is 5.4° higher than the degree of superheating that we attained in the bubble chamber [1].

In the statistical theory of liquids it is usually assumed that the system is homogeneous throughout the entire region in which the liquid and gas exist. The equation of state found in this approximation also describes the metastable regions. Structural models (hole models, cell theories, the theory of significant structures) lead to isotherms having the characteristic van der Waals shape in the phase transition region; the extrema on the isotherms correspond to the stability limits for the liquid and vapor. In theories based on partial distribution functions (the Percus-Yevick theory, the theory of hyperchains), the spinodal curve is defined by points at which the solution to the integral equations diverge. The

spinodal curve for superheated liquid argon given by the equation of state (4) is compared in Figs. 4 and 5 with the stability limits given by various statistical theories of the liquid state (the curves are plotted in reduced coordinates $\pi = P/P_c$, $\tau = T/T_c$, $\varphi = v/v_c$, where P_c , T_c , and v_c are the critical constants in the theory under consideration). As is evident from Fig. 4, structural models predict lower superheating on the spinodal curve than does Eq. (4). This is due to the approximate character of the models under consideration. The calculations based on Fürth's theory [15], in which the holes are treated as nuclei of the vapor phase, are in the best agreement with the approximation to the spinodal curve derived from the experimental data.

¹Sometimes the junctions between the horizontal section BC (Fig. 1) of the isotherm in the two-phase region and the inclined sections AB and CD in the single-phase region are incorrectly depicted as smooth rather than angular. If these junctions were smooth there could be no metastable states.

²Dahl and Moldover [12] have shown that the specific heat C_V of He^3 varies smoothly as the state of the system crosses the phase coexistence line without macroscopic phase separation.

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