Attainable overheating of liquid argon

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The mean lifetimes $\bar{\tau}$ of liquid argon in the metastable (superheated) state are measured. The temperature dependence of $\bar{\tau}$ over several isobars on variation of $\bar{\tau}$ by three orders of magnitude is studied. The experiments are performed in a pure bubble chamber with a 0.042-cm^3 working volume. The experimental data are in satisfactory accordance with the Volmer–Zeldovich–Frenkel theory of fluctuation nucleation in which the "macroscopic" value of the surface tension σ is employed. The size of the critical bubbles ($2r_* \approx 10^{-6}$ cm) is estimated. The effect of γ radiation on the boiling kinetics of superheated argon is studied. An approximation is made of the boundary for thermodynamic stability of Ar corresponding to the condition $(\partial P/\partial v)_T = 0$.

In first-order phase transitions, the appearance of a new phase calls for activation. In the absence of a primer the nucleation occurs via thermal fluctuations. The presence of an activation barrier is due to the finite difference between the thermodynamic properties of the competing phases and the resultant existence of a surface free energy on their interface.

The phase-equilibrium conditions depend on the curvature of the interface. The smaller, for example, a spherical bubble of vapor, the deeper is the entry into the metastable region of the liquid that corresponds to equilibrium between the bubble and the liquid phase. For a single-component system the following relation holds true with good accuracy [1]:

$$P'' - P' = (P_s - P')(1 - v'/v''). \qquad (1)$$

The singly-primed quantities pertain here to the liquid, and the doubly-primed ones to the vapor; P_s is the saturation pressure in the case of a flat interface and a given temperature, and v is the specific volume. The condition (1) is obtained from the equality of the chemical potentials and denotes a weak dependence of the pressure in the equilibrium bubble on its radius r. When r changes under isothermal conditions, to retain equilibrium it is necessary to vary the pressure in the external phase (P′) in accordance with the Laplace formula

$$P'' - P' = 2\sigma/r, \qquad (2)$$

where σ is the surface tension on the phase boundary.

Conditions (1) and (2) correspond to an unstable phase equilibrium. The corresponding value $r = r_*$ determines the dimension of the critical nucleus. The work required to produce such a nucleus is equal, in the thermodynamic approximation, to the maximum excess free energy of the system upon appearance of the bubble:

$$W_* = \frac{1}{3} A_* \sigma = \frac{16}{3} \frac{\pi\sigma^3}{(P_s - P')^2 (1 - v'/v'')^2}, \qquad (3)$$

where A_* is the surface area of the critical bubble.

On the stable phase-equilibrium line, in the case of a flat interface, we have $r_* \to \infty$ and $W_* \to \infty$. In the region of the metastable states $W_* > 0$ retains a finite value, which decreases with increasing supersaturation of the initial phase, as can be seen from expression (3). We consider a superheated single-component liquid, but other cases of metastable states are described similarly. The suggestion that W_* be regarded as a measure of the stability of a homogeneous system relative to a discontinuous transition to another phase state dates back to Gibbs [2]. He also proposed that the work W_* vanishes at the limit of stability against continuous changes, or near this limit. The latter is obtained in such a way that $\sigma \to 0$ as $r \to 0$.

The questions as to the kinetics of production of a new phase as a result of thermal fluctuations and the limit of applicability of the macroscopic (thermodynamic) description of the nuclei are important in the problem of phase transitions. The Volmer-Zel'dovich-Frenkel theory [3-5] leads to the following expression for the frequency of the stationary process of nucleation per unit volume:

$$J_1 = N_1 B \exp(-W_* / kT), \qquad (4)$$

where N_1 is the density of the number of molecules in the metastable phase and $B \approx 10^{10}$ sec^{-1} is a kinetic coefficient that varies little with increase of supersaturation. The exponential factor in (4) ensures a very rapid temperature variation of the nucleus-formation frequency. Denoting W_*/kT by G, we get

$$\frac{d \ln J_1}{dT} \approx -\frac{dG}{dT} = G_T. \qquad (5)$$

The derivative G_T is close in value to 20. Correct determination of the kinetic coefficient B is a complicated problem, which has been considered most thoroughly by Kagan [6].

Until recently, the check on the theory reduced to fragmentary semiquantitative comparisons of the experimentally observed conditions for the spontaneous appearance of a new phase with the results expected from formula (4). To exclude accidental agreement (or disagreement) between theory and experiment, it is necessary to investigate the kinetics of the nucleation systematically at different pressures and to determine experimentally the temperature dependence of J_1, since it is directly connected with the derivative G_T. The results of the realization of such a program are described in a book by one of the authors [1] and indicates that the Volmer-Zel'dovich-Frenkel theory is a sufficiently good approximation.

In this study we investigated, for the first time, the kinetics of formation of viable nuclei of vapor in superheated liquid argon. The choice of the object of the investigation was dictated by the central position of simple liquids (particularly argon) in the theoretical treatment of problems of the liquid state and of phase transitions. A check on the nucleation theory also makes it possible to attempt to determine the lower limit of the thermodynamic description of small molecular systems, such as nuclei of a new phase. There is practically no other suitable approach for this purpose.

In the present paper we present the results of the measurements of the average lifetimes of superheated liquid argon. The installation operates on the pure bubble-chamber principle. A section through each working chamber is shown in Fig. 1. The investigated liquid is superheated in the upper part of a glass capillary 1, placed in a copper block 2. The volume V of the superheated zone was 42.4 and 17.1 mm^3 for the two capillaries used in the experiments. The capillary communicates with the chamber of bellows 4 and with low-temperature valve 6 through a Kovar-glass transition. The pressure in the system is produced by compressed nitrogen and is transferred to the investigated liquid through bellows 4. The substance is brought to a metastable state by rapidly decreasing the external pressure on the liquid through a system of electromagnetic valves. The bellows chamber and the low-temperature valve are inserted in a massive copper block 5. During the experiments, the temperature of the lower block 5 was kept close to the boiling temperature of argon at atmospheric pressure ($T_S = 87.3$°K). Argon (label purity 99.99%) is fed through valve 6 into a previously evacuated chamber, where it is liquefied and sealed. The chamber is placed in a hermetic jacket of thin stainless steel. The cooling is with liquid nitrogen that boils at atmospheric pressure in a Dewar flask. The nitrogen level is maintained automatically. For rapid cooling of the chamber to a specified temperature, the jacket is filled with helium, which is evacuated when the working temperature is reached. The temperatures of blocks 2 and 5 are maintained automatically with accuracies ±0.03° and ±0.07°, respectively. The temperature is measured with a standard platinum resistance thermometer 3 ($R_0 = 9.9402\ \Omega$) in conjunction with a potentiometer R-348 of class 0.002.

The experiment started with heating the liquid to the specified temperature T_{sup} at a pressure $P' > P_S(T_{\text{sup}})$. The pressure was then dropped to a lower value $P < P_S(T_{\text{sup}})$, and a frequency meter Ch3-33 was used to measure the time τ required for the liquid to boil. The instant of boiling was registered by the hydraulic shock in the system. The pickup was a system of relay contacts mounted on the bellows 4. When the pressure was dropped, the liquid expanded quasiadiabatically with decreasing temperature [1]. To decrease the effect of quasiadiabatic cooling, the liquid was brought to a metastable state in two stages. This decreased the correction for non-isothermy to 0.2°. The pressure P was maintained automatically. The accuracy with which the pressure was maintained was ±0.05 bar.

The production of a viable nucleus in a superheated liquid has a random character. At specified conditions, the distribution of the lifetimes τ obeys the Poisson exponential law with a probability density

$$\omega(\tau) = \lambda e^{-\lambda\tau}, \qquad (6)$$

where $\lambda = 1/\bar{\tau}$ and $\bar{\tau}$ is the average expectation time of the nucleus. The independence of the probability of the occurrence of an individual event, obeying the distribution law (6), of the time origin [7] is used to exclude the influence of the transient produced when the pressure is suddenly dropped [1]. An analysis of the histograms showing the distribution of the lifetimes τ has shown that the delay time for our installation was approximately 0.5 sec. The counting lead time τ', equal to 0.6 sec, was subtracted from all the measured times. Experiments in which $\tau < 0.6$ sec were discarded.

The random character of the boiling up of a superheated liquid is evidenced by the fact that the curve calculated from formula (5) fits well into the experimental histogram (Fig. 2). The proximity of the rms error of each individual measurement to τ also confirms the Poisson character of the boiling-up process.

The results of measurements of the dependence of the average lifetime of superheated argon are shown in a semilogarithmic scale in Fig. 3. The experiments were performed along 5 isobars. For the specified values of P and T, no fewer than 40–50 measurements of the time τ were made, and the average lifetime was taken to be the arithmetic mean. The experimental points are represented together with the indicated error in the determination of $\bar{\tau}$. The average lifetimes along isobar 1 were measured at a superheated volume V equal to 17.1 mm^3, whereas for the remaining isobars the superheated zone measured 42.4 mm^3. The isobar 1 shown in Fig. 3 has been recalculated to agree with the volume 42.4 mm^3. At an average lifetime $\bar{\tau} = 1$ sec, the superheat $T - T_S$ amounts to 37.5° (P = 1.9 bar). The dash-dot lines represent calculations by the formula

$$\bar{\tau} = 1 / J_1 V, \qquad (7)$$

where J_1 is the frequency of the spontaneous nucleus formation, calculated from the Doring-Volmer theory [3]. The dashed lines were obtained at J_1 taken from Kagan's theory [6]. Calculations by the theories of homogeneous

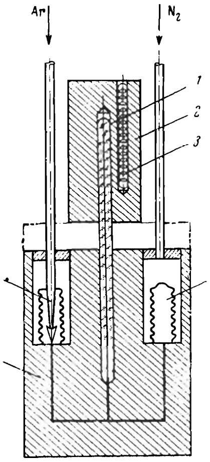

FIG. 1

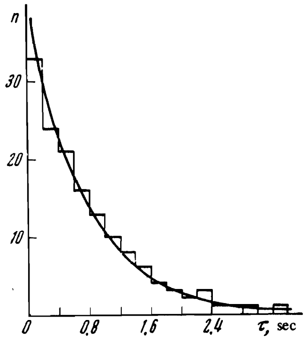

FIG. 2

FIG. 1. Section through working chamber.

FIG. 2. Histogram of experiments on the superheating of argon: $P = 14.0$ bar, $T = 135.3$°K, $T_S = 122.7$°K, $N = 1.47$, $\bar{\tau} = 0.75$ sec.

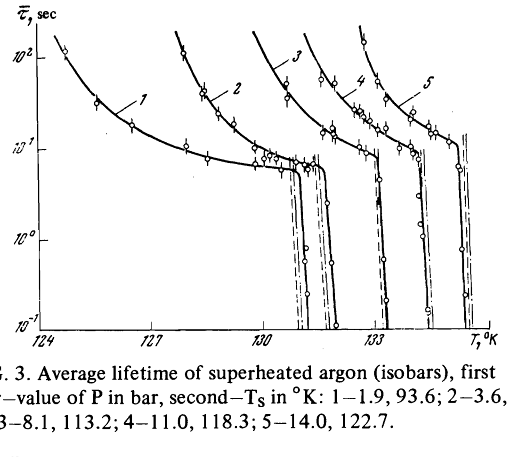

FIG. 3. Average lifetime of superheated argon (isobars), first number–value of P in bar, second–T_S in °K: 1–1.9, 93.6; 2–3.6, 101.3; 3–8.1, 113.2; 4–11.0, 118.3; 5–14.0, 122.7.

nucleation were carried out using the "macroscopic" surface tension σ_∞ for a flat interface [8]. Figure 3 demonstrates the good agreement (within 0.25°) between the experimental and theoretical superheats. Just as in the theory, a very strong dependence of the nucleus-formation frequency (average lifetime) on the depth of entry into the metastable region is observed at $\bar{\tau} \lesssim 8$–9 sec.

Experiments on the kinetics of nucleus formation in superheated liquids make it possible to determine the surface tension on the boundary between the liquid and the vapor nucleus of critical dimension from the experimentally obtained frequencies $J_1 = (\bar{\tau}V)^{-1}$, by using the theory of homogeneous nucleation. The results of the calculation of σ, r_*, and n_* for $J_1 = 10^2$ cm^{-3} sec^{-1} are given in the table. The radius of the critical nucleus was determined from formula (2), and the number n_* of molecules in the nucleus was determined from the saturated vapor density at the temperature of the experiment; B_1 and B_2 show calculations after Doring-Volmer and Kagan, respectively. The table shows good agreement between the calculated and measured values of the surface tension. This makes it possible to use a macroscopic description of the surface properties of new-phase nuclei in the theory of homogeneous nucleation. It should be noted that the discrepancy between the calculated values of σ and those measured for a flat interface σ_∞ [8] does not have a systematic character, unlike the case of hydrocarbons (where the calculated values are always lower than the measured ones) [1].

At $\bar{\tau} \gtrsim 9$ sec (Fig. 3), the isobars deviate from the theoretical lines. The appearance of a characteristic inflection is due to the initiating action of the background radiation and the natural radioactivity of the materials. The sensitivity of the superheated liquid to ionizing radiation was first observed by Glaser [9] and is widely used to register high-energy particles. We performed experiments to register the initiated boiling-up of superheated liquid argon. The investigated liquid was bombarded with γ rays (Co^{60} of activity 1 mg radium equivalent). The procedure for determining $\bar{\tau}$ was the same as without the bombardment. The experiments with the bombardment were carried out on the 3.6-bar isobar. Figure 4 shows the dependence of the average lifetime on the superheat under natural conditions and in the presence of a γ source. The similarity in the course of the curves confirms that the gently sloping sections on the isobars have the same cause, namely the action of ionizing radiation of different intensity. Just as under natural conditions, the distribution of the lifetimes τ under the influence of a γ-quantum source corresponds to the Poisson formula (6).

In Fig. 5, the temperatures of the maximum superheat of liquid argon T_{sup} ($J_1 = 10^2$ cm^{-3} sec^{-1}), obtained in a pure bubble chamber, are compared with the results of experiments in which T_{sup} was determined by the method of continuous heating ($J_1 = 10^3$–10^4 cm^{-3} sec^{-1})[10]. The two methods of determining the limit of spontaneous boiling-up lead to data that are in good agreement.

T, °K	P, bar	$r_* \cdot 10^7$, cm	n_*	σ, dyn/cm^{-1}		
				Calculation		Experiment [8]
				$B1$	$B2$	
131.2	1.9	3.3	260	2.84	2.86	2.78
131.9	3.6	3.3	270	2.70	2.72	2.65
133.3	8.1	3.6	400	2.38	2.41	2.38
134.4	11.0	3.7	510	2.16	2.19	2.17
135.4	14.0	4.0	650	1.94	1.96	2.02

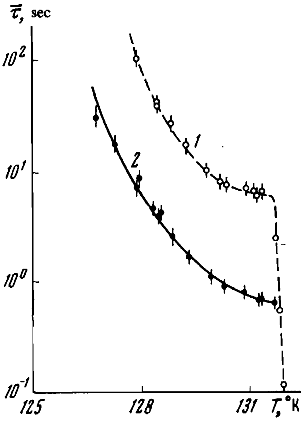

FIG. 4

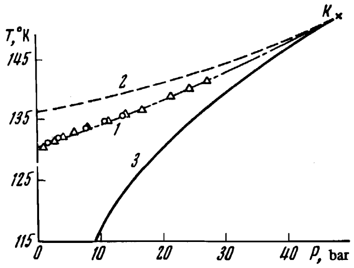

FIG. 5

FIG. 4. Temperature dependence of the average lifetime along the 3.6-bar isobar: 1—under natural conditions, 2—under the influence of radiation.

FIG. 5. Attainable superheat and spinodal of liquid argon: ○—bubble-chamber experiments ($J_1 = 10^2$ cm^{-3}sec^{-1}), △—experiments in glass capillaries under continuous heating [10] ($J_1 = 10^3 - 10^4$ cm^{-3} sec^{-1}). 1—Calculation by the homogeneous-nucleation theory, 2—spinodal; 3—saturation line, K—critical point.

In the study of the metastable states, the question arises as to the position of the stability limit—the spinodal. In thermodynamics, the spinodal of a homogeneous system is determined by the relations (see [11])

$$(\partial P / \partial v)_T = 0, \quad (\partial T / \partial S)_P = 0, \tag{8}$$

which makes it possible to determine the limits of essential instability if P, v, and T data are known in the entire region of homogeneous states, including the metastable states. The determination of the spinodal from the experimental data on P, v, and T calls inevitably for extrapolation of these data. As is well known [11], the spinodal plotted in P-T coordinates is the envelope of the family of isochors continued into the region of the metastable states. An experimental study of the behavior of isochors near the saturation line [12], both in the stable region and in the metastable region, for liquid n-hexane has shown them to be nearly straight lines. This property of the isochors was used by us to determine the spinodal of superheated liquid argon from the Verbeke and Jansoone data on P, v, and T [13]. The results of the calculations are shown in Fig. 5. At atmospheric pressure, the temperature corresponding to the loss of thermodynamic stability of the liquid is approximately 6° higher than the spontaneous boiling-up temperature obtained in bubble-chamber experiments, and 50% higher than the saturation temperature.

A more accurate determination of the spinodal calls for knowledge of the equation of state in the metastable region, and also for the use of data on the specific heat C_V in order to determine the curvature of the isochors. Work is continuing in this direction for argon. It should be noted that the spinodal obtained as the envelope of isochors agrees well (within 1°) with calculations in accordance with the model theories of the liquid state, such as the hole theory of Furth [14] and the multistructure theory of Eyring [15]. A "computer experiment" (Monte Carlo method) gives temperature values for the spinodal that are 3–4° higher than the aforementioned theories [10]. This may be due to the smallness of the system in the machine experiment for strongly correlated states near the stability limit.

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