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# Nucleation in superheated liquid argon–krypton solutions

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We report nucleation-rate measurements in metastable liquid argon–krypton solutions at pressures of 1.0 and 1.6 MPa over a wide temperature and concentration range. These measurements were performed with the use of a superheated liquid lifetime measurement method. The experimental results are compared with the homogeneous nucleation theory data both using a macroscopic (capillary) approach and taking into account the dependence of critical bubble surface tension on interface curvature. The size effect in nucleation is considered in the framework of the Van-der-Waals, Cahn–Hilliard method. The experimental data indicate that the homogeneous nucleation theory quantitatively describes the kinetics of a first order phase transition in binary solutions of simple liquids if the size effect is taken into account and nucleation rates are  $J \geq 10^6 \text{ m}^{-3} \text{ sec}^{-1}$ . At  $J \leq 10^6 \text{ m}^{-3} \text{ sec}^{-1}$  there is initiated nucleation. A diffusion spinodal of a solution is approximated. The attainable superheating temperature data are presented. © 1997 American Institute of Physics. [S0021-9606(97)50511-3]

## I. INTRODUCTION

A phase transition of the first kind presupposes the existence of metastable states and begins with the formation and growth of nuclei of a new phase. In “pure” systems in the absence of external actions initiating a phase transition nuclei form at the expense of fluctuations (homogeneous nucleation). The emergence of a new-phase fragment in a homogeneous metastable system is connected with the formation of a phase boundary and accompanied by an increase of the excessive free energy  $\Delta G$ . The competition of the surface and volume members entering into a free energy with opposite signs results in the existence of a finite maximum  $\Delta G = W_*$ . The fragments corresponding to the maximum  $\Delta G$  are critical nuclei, and the quantity  $W_*$  is the work of their formation. At each moment the overwhelming majority of fragments has precritical sizes  $R < R_*$ . Their existence is energetically unprofitable, and they resolve. However, due to fluctuations some of the fragments may grow to sizes exceeding the critical one and then their further growth is thermodynamically irreversible.

The discussed notions form the basis of the classical nucleation theory formulated by Volmer,<sup>1</sup> Doring,<sup>2</sup> Zeldovich,<sup>3</sup> and Frenkel.<sup>4</sup> For one-component systems the theory defines the nucleation rate  $J$ , i.e. the number of viable fragments of new phase forming per unit volume in a unit of time.

Distinct from a one-component system, to characterize new-phase fragments in a binary system it is necessary to have at least two parameters: the radius of a new-phase fragment  $R$  and its composition  $x''$ , or the number of molecules of the first  $n_1''$  and the second  $n_2''$  components in the fragment. Binary nucleation is the process of fluctuation overcoming of the activation barrier in the variable  $n_1'', n_2''$  was first considered by Reiss<sup>5</sup> and Nesis and Frenkel.<sup>6</sup> In Ref. 5 it was

assumed that the direction of the two-dimensional vector of a nuclei flow in the vicinity of the activation-barrier pass ridge point was determined only by the relief of the surface  $\Delta G(n_1'', n_2'')$ . Later papers by Stauffer,<sup>7</sup> Shi and Seinfeld,<sup>8</sup> and Melikhov *et al.*<sup>9</sup> took into account the dependence of the direction of the descent from the ridge on all the physical parameters of the problem.

All the mentioned approaches postulated the Boltzmann distribution for precritical fragments. The possibility of an abnormal binary nucleation regime, when the equilibrium of precritical fragments is violated, and the flow of nuclei bypasses the saddle point of the ridge, was discussed, for example, in Refs. 8 and 10.

When losing stability for finite disturbances connected with the formation of a new phase a metastable system retains a reductive reaction to infinitesimal continuous changes of the state parameters. The relation

$$\left( \frac{\partial \Delta \mu}{\partial x} \right)_{p,T} = 0 \quad (1)$$

is fulfilled at the boundary of the essential phase instability, the solution spinodal. Here  $\Delta \mu = \mu_1 - \mu_2$ , and  $\mu$  is the chemical potential.

A superheated liquid is a particular case of the metastable phase state and the most convenient object for a check of the homogeneous nucleation theory.<sup>11</sup> In this paper we present the results of an experimental investigation of the fluctuation boiling-up kinetics of superheated argon–krypton solutions. The good wettability of solid materials by liquefied gases, the small content in them of dissolved gases and solid suspended particles, makes it possible to realize the homogeneous mechanism of nucleation at comparatively small velocities of intrusion into the metastable region. Experiments were made at pressures up to 1.6 MPa in a wide interval of concentrations and temperatures under changes of

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nucleation rate from  $10^4$  to  $10^8 \text{ m}^{-3} \text{ sec}^{-1}$ . Information about the attainable superheats of pure solution components was obtained by us earlier.<sup>12–14</sup>

The plan of the paper is the following. In the second part of the paper we examine the thermodynamics of a new-phase formation and the kinetics of fluctuation boiling-up of a superheated binary solution. The third part is devoted to the experimental procedure and the results of experimental investigations. In the fourth part one can find a comparison of the experimental data with the homogeneous nucleation theory and a discussion of different approaches to the calculation of the nucleation work and the kinetic coefficient.

## II. BINARY NUCLEATION THEORY

### A. Critical nucleus and the work of its formation

According to Gibbs,<sup>15</sup> in a superheated binary solution the work  $W$  of formation of a vapor bubble of radius  $R$  under conditions of constancy of the external pressure  $p'$  and the temperature  $T$  is determined by the variation of the thermodynamic potential

$$W = \Delta G = 4\pi R^2 \sigma + \frac{4}{3}\pi R^3 (p' - p'') + \sum_i n_i'' (\mu_i'' - \mu_i'), \quad (2)$$

where  $\sigma$  is the surface tension at the solution–vapor bubble boundary. The quantities with one prime pertain to the liquid, and with two primes to the vapor. The surface of tension has been taken as a dividing surface.

The critical size bubble is in mechanical

$$p''_* - p' = 2\sigma/R_* \quad (3)$$

and substantial

$$\mu_i''(p'', T, x''_*) = \mu_i'(p', T, x'), \quad (i = 1, 2) \quad (4)$$

equilibrium with a superheated liquid. The critical bubble formation work is

$$W_* = \Delta G_* = 4\pi R_*^2 \sigma/3. \quad (5)$$

We shall consider the vapor in the bubble an ideal gas. Expanding  $\Delta G(n''_1, n''_2)$  in the vicinity of point  $n''_{1*}, n''_{2*}$  in a power series and restricting ourselves to the quadratic in  $n''_1 - n''_{1*}, n''_2 - n''_{2*}$  terms, we get

$$\Delta G(n''_1, n''_2) = \Delta G_* + \sum_{i,j} G_{ij}^* (n''_i - n''_{i*})(n''_j - n''_{j*}), \quad (6)$$

where

$$G_{ij}^* = -\frac{4\pi\sigma R_*^2}{9n''_*^2} - \frac{kT}{2n''_*} \left( -\frac{n''_{1*}}{n''_{2*}} \right)^{i+j-3} \quad (7)$$

and  $n'' = n''_1 + n''_2$ . The determinant of the quadratic form (6) is

$$\det \Delta G = G_{11}^* G_{22}^* - G_{12}^{*2} = -\frac{2}{9} \frac{\pi k T \sigma R_*^2}{n''_* n''_{1*} n''_{2*}}. \quad (8)$$

At  $\det G < 0$  the matrix  $G_{ij}^*$  has one positive and one negative eigenvalue. It means that a surface of double curvature

corresponds to the function  $\Delta G(n''_1, n''_2)$  in the region of metastable states, and the point with coordinates  $n''_{1*}, n''_{2*}$  is the saddle point of this surface.

A rigorous calculation of the pressure and the composition of a critical bubble on the basis of Equations (3)–(5) requires a knowledge of the equation of state of a substance and the surface tension of critical bubbles, as a function of the temperature and their radii. Since the latter dependence is usually not known, the homogeneous nucleation theory assumes  $\sigma = \sigma_s$ , where  $\sigma_s$  is the surface tension at a plane interface. This macroscopic or capillary approximation limits the applicability of the Gibbs method in the nucleation theory by small superheats. The limitations mentioned above are lifted if for calculating the critical bubble formation work use is made of the Cahn–Hilliard approach<sup>16</sup> based on the Van-der-Waals capillarity theory.<sup>17</sup>

The nonequilibrium Helmholtz free energy functional of the binary inhomogeneous system that contains a fragment of a new phase and a metastable solution is written as<sup>16,17</sup>

$$F[\rho_1, \rho_2] = \int \left( f_0 + \sum_{i,j} \kappa_{ij} \nabla \rho_i \nabla \rho_j \right) d\mathbf{r}. \quad (9)$$

Here  $f_0$  is the free energy per unit volume of the homogeneous system,  $\rho_i$  is the local density of the  $i$ -th component,  $\nabla \rho_i$  is the gradient of the local density, and  $\kappa_{ij}$  is the matrix of influence parameters depending in the general case on the temperature and density and determined by the character of intermolecular interaction in the system.

A homogeneous metastable phase is stable with respect to infinitesimal perturbations. Therefore the second addendum (a quadratic form) in (9) is a positive definite,

$$\kappa_{11} > 0, \quad \det \kappa_{ij} = \kappa_{11}\kappa_{22} - \kappa_{12}^2 > 0. \quad (10)$$

In an isolated isothermal system the equilibrium density distribution in a critical bubble is found from the condition of equality to zero of the first variation of the grand potential  $\Omega$ , i.e.

$$\delta \Omega[\rho_1, \rho_2] = 0, \quad (11)$$

where

$$\Omega[\rho_1, \rho_2] = F[\rho_1, \rho_2] - \sum_i \mu_i \int \rho_i d\mathbf{r}. \quad (12)$$

Assuming that vapor bubbles are spherical, from (9), (11), and (12) we have

$$\begin{aligned} \mu_i = \mu_{0i} - 2 \sum_j \kappa_{ij} \left( \frac{d^2 \rho_j}{dr^2} + \frac{2}{r} \frac{d\rho_j}{dr} \right) \\ + \sum_{j,k} \left( \frac{\partial \kappa_{jk}}{\partial \rho_i} \right) \frac{d\rho_j}{dr} \frac{d\rho_k}{dr}. \end{aligned} \quad (13)$$

Here  $\mu_{0i} = \partial f_0 / \partial \rho_i$  is the chemical potential of the  $i$ -th component in a homogeneous system of density  $\rho_i$ . It can be shown<sup>18</sup> that in an isotropic system the solution of the system of equations (13) with boundary conditions  $\rho_i \rightarrow \rho_{0i}$ , if

$r \rightarrow \infty$  and  $d\rho_i/dr \rightarrow 0$ , if  $r \rightarrow 0$  or  $r \rightarrow \infty$ , correspond to the functional saddle point (12). In this case the critical nucleus formation work is

$$W_* = \min \max \Omega[\rho_1, \rho_2]. \quad (14)$$

The use of the Van-der-Waals, Cahn–Hilliard approach in the determination of the work of formation of a new phase requires knowledge of the equation of state of a binary solution and the matrix of influence parameters  $\kappa_{ij}$ .

## B. Nucleation rate

A bubble growth in a superheated binary solution is described in homogeneous nucleation theory as an activation overcoming a potential barrier on the two-dimensional surface of the free energy  $\Delta G$  in the variables  $n_1''$ ,  $n_2''$ . The nucleation kinetic equation determining the distribution function of new-phase fragments  $P$  by  $n_1''$ ,  $n_2''$  at the moment  $t$  has the following form<sup>8</sup>

$$\frac{\partial P(n_1'', n_2'', t)}{\partial t} = -\frac{\partial j_1}{\partial n_1''} - \frac{\partial j_2}{\partial n_2''}, \quad (15)$$

where

$$j_i = -D_{ii} P_e \frac{\partial(P/P_e)}{\partial n_i''} \quad (16)$$

is the flow of bubbles in the  $i$ -th direction of the plane  $n_1''$ ,  $n_2''$ . The generalized bubble-diffusion coefficient  $D_{ii}$  characterizes the probability of transition of molecules of the  $i$ -th component from one phase into another, connected with the diffusion, the heat transfer, etc. If the velocity of evaporation of molecules into a bubble is a determining factor of bubble growth, then

$$D_{ii} = 4\pi R^2 p_i'' (2\pi m_i kT)^{-1/2}. \quad (17)$$

Here  $p_i''$  and  $m_i$  are the partial pressure and the mass of a molecule of the  $i$ -th component. In this approximation the superheated solution boiling-up theory and the supersaturated vapor mixture condensation one are identical completely. For the equilibrium distribution function  $P_e$  in Relation (16) one observes fulfillment of the principle of detailed equilibrium between the transitions of bubbles of neighbouring classes (in a stable region  $P_e$  has the meaning of the real equilibrium distribution function of bubbles emerging in a fluctuation way). According to the thermodynamic theory of fluctuations

$$P_e = C \exp(-W/kT), \quad (18)$$

where  $C$  is the proportionality coefficient.

In a stationary case  $\partial P/\partial t = 0$ , and the resulting flow of nuclei on the plane  $n_1''$ ,  $n_2''$  does not depend on bubble size and is equal to the number of supercritical nuclei forming in a unit volume in a unit time, i.e., to the nucleation rate  $J$ . The main difficulty in solving the problem of binary nucleation is connected with the fact that the variables  $n_1''$  and  $n_2''$  are separated neither in distribution (18) nor in kinetic equation (15). As is shown in Refs. 5 and 7–9 by a successive transforma-

tion of the variables Equation (15) can be reduced to the Zeldovich–Frenkel one-dimensional nucleation equation,<sup>3,4</sup> the solution of which has the form

$$J = CB \exp(-W_*/kT) = CDz \exp(-W_*/kT). \quad (19)$$

Here  $D$  is the coefficient of the bubble generalized diffusion, and  $z$  is a nonequilibrium factor similar to the Zeldovich factor in an one-component system.

According to Refs. 5 and 7–9

$$B = \lambda(-2\pi \det \Delta G)^{-1/2}, \quad (20)$$

where  $\lambda$  is the positive root of the quadratic equation

$$\lambda^2 + (D_{11}G_{11}^* + D_{22}G_{22}^*)\lambda + D_{11}D_{22}(G_{11}^*G_{22}^* - G_{12}^{*2}) = 0. \quad (21)$$

The nonequilibrium factor is determined as

$$z = -\frac{G_{11}^* \cos^2 \phi + 2G_{12}^* \cos \phi \sin \phi + G_{22}^* \sin^2 \phi}{\sqrt{-2\pi \det \Delta G}}, \quad (22)$$

where  $\phi$  is the angle between the axis  $n_1''$  and the direction of the nuclei flow through the saddle point. In the Reiss<sup>5</sup> theory this angle depends only on the configuration of the surface of the thermodynamic potential in the region of the saddle point, and  $\tan \phi$  is the positive root of the equation

$$G_{12}^* \tan^2 \phi + (G_{11}^* - G_{22}^*) \tan \phi - G_{12}^* = 0. \quad (23)$$

In the theories of Stauffer,<sup>7</sup> Shi and Seinfeld,<sup>8</sup> and Melikhov *et al.*<sup>9</sup> the value of  $\phi$  also depends on the dynamics of the bubble growth. The tangent of the angle  $\phi$  is determined by the equation

$$D_{11}G_{12}^* \tan^2 \phi + (D_{11}G_{11}^* - D_{22}G_{22}^*) \tan \phi - D_{22}G_{12}^* = 0. \quad (24)$$

The effective generalized diffusion coefficient for all the theories considered here is

$$D = D_{11}D_{22}/(D_{11} \sin^2 \phi + D_{22} \cos^2 \phi). \quad (25)$$

The coefficient of proportionality  $C$  in the equilibrium distribution function by the data of Melikhov *et al.*<sup>9</sup> is inversely proportional to the volume per one molecule of a nucleus, i.e.,  $C = \rho''$ . According to Refs. 5, 7 and 8 the value  $C = \rho_1' + \rho_2'$  is the total number of molecules in a unit volume of the metastable phase.

An approach to the problem of nucleation in a multicomponent system that differs from those considered above has been suggested by Wu.<sup>19</sup> The author proceeds from a most general determination of the stationary nucleation rate  $J = \lim_{t \rightarrow \infty} dY/dt$  ( $Y$  is the number of nuclei forming in the time  $t$ ), which assumes a variety of ways of bubble transition through the potential barrier. An expression for the kinetic coefficient  $B$ , different from the results<sup>7–9</sup> by the factor  $\beta < 1$ , where

$$\beta = \frac{1}{2} \left\{ \operatorname{erf} \left[ \sqrt{\frac{|\lambda_1|}{2D_{11}kT}} \frac{n''_{1*}}{\sin \phi} \right] + \operatorname{erf} \left[ \sqrt{\frac{|\lambda_1|}{2D_{22}kT}} \frac{n''_{2*}}{\cos \phi} \right] \right\}, \quad (26)$$

and  $\lambda_1$  is the negative root of Equation (21), has been obtained for a binary system in the regime of a free-molecular growth of bubbles and a square-law form of the potential barrier.

Away from the line of critical points the first component in  $G_{12}^*$  [see Eq. (7)] is approximately an order of magnitude smaller than the second one. Neglecting it, from Eq. (23) we have

$$\tan \phi = n''_{2*}/n''_{1*} = x''_*/(1-x''_*). \quad (27)$$

In this case the tangent to the trajectory of the nucleus motion in the plane  $n''_1, n''_2$  coincides with the line of the constant concentration value in a bubble, and

$$B = \sqrt{2\sigma/(\pi m_{12})} \sqrt{n''_{1*} x''_*}, \quad (28)$$

where  $m_{12} = ((1-x''_*)\sqrt{m_1} + x''_*\sqrt{m_2})^2$ . Expression (28) differs from that obtained in the paper by Danilov, Sinitsyn, and Skripov<sup>20</sup> by the factor  $\sqrt{n''_{1*} x''_*}$ . At  $x''_* \rightarrow 0$  or  $x''_* \rightarrow 1$  this factor makes the kinetic coefficient vanish, while the first cofactor in (28) turns into the well-known Döring–Volmer expression for a one-component system. In the general case the expression for the kinetic coefficient (20) does not reduce to the corresponding expression for  $B$  in a one-component system.

### III. EXPERIMENT

#### A. Apparatus and methods of measurements

The nucleation rate in superheated liquid argon–krypton solutions was determined by the lifetime measuring method.<sup>11,12,21</sup> The solution under investigation filled glass tube 3 and metallic bellows 7 (Fig. 1). In the experiment part of the liquid solution with the volume  $V \approx 70 \text{ mm}^3$  thermostated ( $\pm 0.002 \text{ K}$ ) in copper block 1 was superheated. The temperature in the block was measured with a platinum resistance thermometer 2. The error in determining the temperature of the solution under investigation with allowance for the inhomogeneity of the temperature field in the block was  $\pm 0.02 \text{ K}$ . The pressure was created with compressed helium and transferred to the solution through bellows 7. The bellows chamber and low-temperature valve 6 were thermostated ( $\pm 0.05 \text{ K}$ ) in block 8 at a temperature close to the temperature of the solution normal boiling. The measuring device was placed in vacuum jacket 4 fixed in Dewar vessel 5. Cooling was realized with liquid nitrogen.

An experiment began with preparing a gas mixture of the required concentration. The purity of initial components was 99.993% (Ar) and 99.997% (Kr). The mixture was condensed into the measuring device. Differences in the temperatures of blocks 1 and 8 resulted in the origination of a concentration gradient throughout the height of the measuring device. To define the solution concentration in a super-

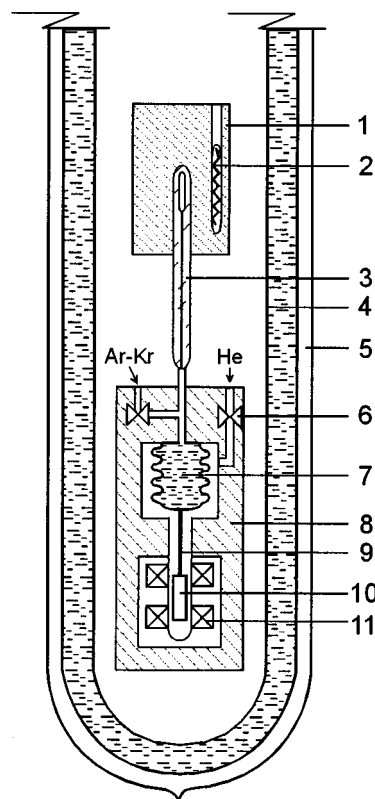


FIG. 1. Schematic of experimental apparatus.

heated volume before the beginning and after completion of an experiment the solution saturation pressure was measured. For this purpose at experiment temperature  $T$  (the temperature in block 1) the pressure in the solution was decreased below the saturation pressure. The liquid solution in the upper part of tube 3 turned into a gaseous state. Then the pressure gradually increased and with the help of a system of detection of changes in the volume of the solution under investigation the pressure was recorded at the moment of the solution transition from a gaseous into a liquid state [the saturation pressure  $p_s(T)$ ]. The system of detection of changes in the volume consists of rod 9 attached to bellows 7 and ending with core 10 made of a ferromagnetic material. The displacement of the core results in a change of the reactance of coil 11 connected in the bridge circuit. The error in determining the saturation pressure was  $\pm 0.01 \text{ MPa}$ . In calculating the concentration use was made of the data on the phase equilibrium of an argon–krypton system by Schouten, Deerenberg and Trappeniers.<sup>22</sup> The error in determining the concentration is  $\pm 0.5\%$ .

After preparing a solution of the required concentration  $x'$  the initial pressure  $p_1 > p_s(T, x')$  was created in the measuring system. The penetration into the metastable region was realized by an abrupt pressure decrease below the saturation pressure. To reduce both the effect of cooling a liquid solution and the hydraulic oscillations in the measuring system the liquid was brought to a metastable state in two stages. At first the pressure was decreased to the value  $p_2$ ,

which is 0.3–0.5 MPa less than the saturation pressure  $p_s(T, x')$ . The probability of boiling-up of a solution at pressure  $p_2$  is sufficiently small. The solution was kept at this pressure  $p_2$  for approximately 20 sec, after which its final release to the value  $p'$  was realized. The error of the maintenance of the pressure  $p'$  was  $\pm 0.005$  MPa. At the moment of the final pressure release a chronometer was started up. It recorded the time of  $\tau$  the stay of the solution in the given metastable state before its boiling-up (the lifetime of a superheated solution). The moment of boiling-up was recorded by a water hammer in the measuring system. After the boiling-up of a solution the initial pressure  $p_1$  was created in the bellows chamber and the measurement process was reiterated. Up to  $N=100$  values of  $\tau$  was measured at every given  $p'$  and  $x'$ , and the mean lifetime  $\bar{\tau} = \sum_i \tau_i / N$  was determined. In processing the results of the experiments allowances were made for the corrections for the liquid cooling in the process of pressure release, and the delay time  $\tau_0$  caused by the sluggishness of the pressure-release system was subtracted from the measured value of  $\bar{\tau}$ . For our setup  $\tau_0$  is equal to 0.5 sec.

The time  $\tau$  measured in the experiment is determined by the time  $\tau_w$  of waiting for a viable nucleus in the system and the time of its growth  $\tau_g$  ( $\tau = \tau_w + \tau_g$ ). In the investigated area of the parameters of a state we have  $\tau_g \approx 10^{-3}$  sec.<sup>11</sup> The characteristic times  $\tau$  in our experiments are more than 0.1 sec. The relationship  $\tau \gg \tau_g$  makes it possible to believe that  $\tau \approx \tau_w$  and to deduce the nucleation rate  $J$  from the equation  $J = 1/(\bar{\tau}V)$ .

## B. Statistical laws of nucleation

The classical homogeneous nucleation theory regards the evolution of fragments of a new phase as a continuous Markovian process described by the Fokker–Planck equation. As for the emergence of a spontaneous nucleus in the metastable phase, it is a random event of the discrete type and represents a discontinuous Markovian process. The probability  $P(R, R_0, \tau)$  that the size of the fragment of a new phase at the moment  $\tau$  will be equal to  $R$ , if at  $\tau=0$  it was equal to  $R_0$ , in the region  $R_0 < R < R_*$  obeys the one-dimensional Fokker–Planck equation. A solution of the latter can be represented in the form

$$P(R, R_0, \tau) = \sum_i a_i w_i(\tau) P_i(R), \quad (29)$$

where the coefficients  $a_i$  are determined by the initial distribution  $P(0, R_0, 0)$  and  $P_i(R)$  is an eigenfunction of the equation

$$\frac{d}{dR} \left( P_i + \frac{dP_i}{dR} \right) = \varepsilon_i P_i \quad (30)$$

with the eigenvalue  $\varepsilon_i$ . For the function  $w_i(\tau)$  we have

$$\frac{dw_i}{d\tau} = -\varepsilon_i w_i. \quad (31)$$

In the region of weak metastability, where the probability of emergence of a critical nucleus is small, the equilibrium dis-

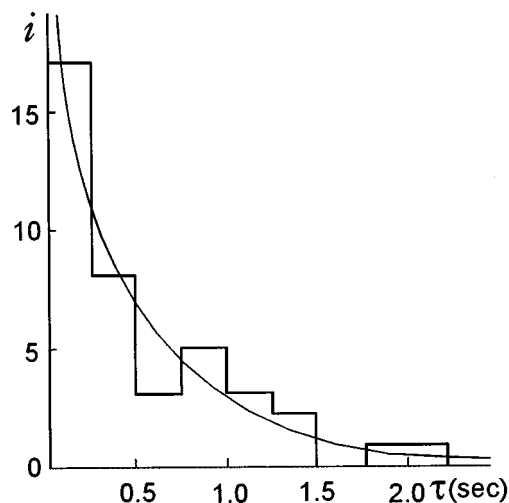


FIG. 2. The histogram of experiments.  $x'=0.428$ ;  $p=1.6$  MPa;  $T=154.47$  K;  $N=40$ ;  $\bar{\tau}=0.52$  sec. The smooth curve has been calculated from Eq. (34).

tribution of fragments in size is set rapidly. This means that in expansion (29) the term with  $i=0$  is dominant and for all  $i>0$  the eigenvalues  $\varepsilon_i > \varepsilon_0$ . Then from (29)–(31) we obtain

$$P(R, R_0, \tau) \approx \exp(-\varepsilon_0 \tau) P_0(R). \quad (32)$$

We are interested in the probability of formation of a critical nucleus (solution boiling-up) over the time interval  $\tau$ ,  $\tau + \Delta\tau$ , which is found by multiplication of two probabilities: the probability  $w_0(\tau)$  and the probability  $1 - w_0(\Delta\tau)$  of the emergence of a critical nucleus during the succeeding small time interval  $\Delta\tau$ . At first approximation for  $w_0(\tau)$  we have

$$w_0(\tau) = \exp(-\varepsilon_0 \tau) \int_0^R P_0(R) dR \approx \exp(-\varepsilon_0 \tau). \quad (33)$$

Expanding (33) into a series and restricting ourselves to the first term of the expansion we get  $1 - w_0(\Delta\tau) = \varepsilon_0 \Delta\tau$ . Thus, for the average number of events of liquid boiling-up in the interval  $\tau$ ,  $\tau + \Delta\tau$  in a series of  $N$  experiments one can write

$$i = N \varepsilon_0 \Delta\tau \exp(-\varepsilon_0 \tau). \quad (34)$$

Equation (34) describes the Poisson process. According to (34) the mean time of waiting for a critical nucleus is  $\bar{\tau} = \varepsilon_0^{-1}$ . The dispersion of the random quantity  $\tau$  in this case coincides with its average value, i.e.  $\sigma_\tau = \bar{\tau}$ .

In experiments with Ar–Kr solutions, as well as with pure liquids,<sup>11,21</sup> in the whole investigated range of  $p'$ ,  $T$ ,  $x'$  one can observe the proximity of the quantities  $\bar{\tau}$  and  $\sigma_\tau$ . The Poisson character of the boiling-up of a superheated solution is also corroborated by the histograms of experiments (Fig. 2), which are in good agreement with distribution (34).

## C. Results

The dependence of the mean lifetime of superheated liquid Ar–Kr solutions on the temperature and concentration has been traced in experiments at two pressures  $p' = 1.0$  and 1.6 MPa. The interval of the investigated values of the mean

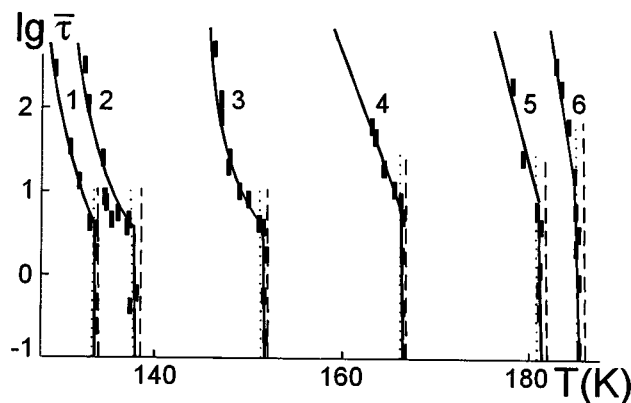


FIG. 3. Temperature dependencies of the mean lifetime of argon–krypton solution at  $p=1.0$  MPa for concentrations: (1)  $x' = 0$ ; (2) 0.109; (3) 0.428; (4) 0.708; (5) 0.938; (6) 1. Dashed lines represent calculations using Eqs. (5), (24) and  $\sigma = \sigma_s$ ; dotted lines, Eqs. (14), (24).

lifetime is from 0.1 to 1000 sec, which corresponds to the variation of the nucleation rate from  $10^4$  to  $10^8 \text{ m}^{-3} \text{ sec}^{-1}$ . Fig. 3 shows on a half-logarithmic scale temperature dependencies of the mean lifetime for several values of the concentration. The vertical size of the dots in the figure corresponds to the statistical error of determination of  $\bar{\tau}$ . The character of the temperature dependence of  $\bar{\tau}$  in solution is similar to pure liquids.<sup>12,14</sup> On all the lines of constant concentration on the achievement of a certain temperature (the boundary of spontaneous boiling) one can observe sections of an abrupt decrease of  $\bar{\tau}$ . We associate these sections of curves with homogeneous nucleation. Here with a temperature increase of 0.1 K the value of  $\log \bar{\tau}$  decreases by 0.6–1.2.

The bend of experimental curves at  $\bar{\tau} \approx 4\text{--}10$  sec is caused by heterogeneous nucleation and is initiated by ionizing radiation nucleation. The source of such radiation in experiments is cosmic rays and natural radiation background. Heat peaks, which appear during the deceleration of secondary electrons ( $\delta$ -electrons) in superheated liquid are the centers of its boiling-up. A ponderable argument in favor of the ionization hypothesis of bends of experimental curves is the result of experiments on measuring the lifetime of a superheated liquid in the field of  $\gamma$ -radiation (for argon the results of such experiments are presented in Ref. 12). The increase of intensity of ionizing radiation results in a shift of the gently sloping sections of curves into the region of smaller values of  $\bar{\tau}$  without violating the character of the dependence  $\bar{\tau}(T)$ . The effect of initiation in the series of condensed inert gases correlates with the radiation-stability and scintillation properties of a substance, which increases with increasing the atomic number of an element.<sup>23</sup> As a result, part of the energy of ionizing radiation is not transformed into thermal energy, but fluoresces. The bend of experimental curves in the case of krypton manifests itself at the initiation rate  $J_m \approx 1.5 \times 10^6 \text{ m}^{-3} \text{ sec}^{-1}$ , and in argon  $J_m \approx (2\text{--}3) \times 10^6 \text{ m}^{-3} \text{ sec}^{-1}$ . The increase of the krypton concentration in argon results in a monotonic decrease of  $J_m$  (Fig. 4). The de-

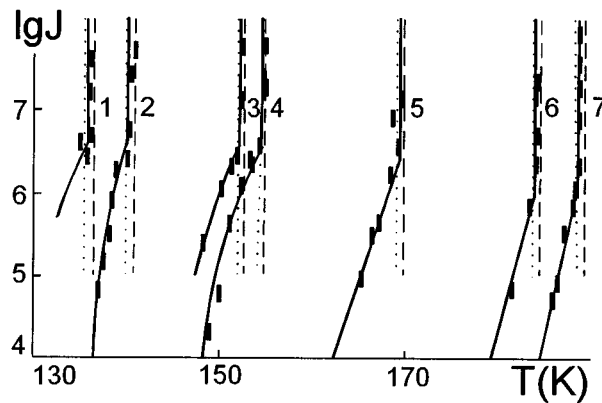


FIG. 4. Nucleation rate in superheated argon–krypton solution at  $p=1.6$  MPa for concentrations: (1)  $x' = 0$ ; (2) 0.109; (3) 0.382; (4) 0.428; (5) 0.708; (6) 0.938; (7) 1. Dashed and dotted lines are same as in Fig. 3.

tails of the process of transformation of the ionizing radiation energy into thermal energy, and then into the work of nucleation are not so far clear enough to calculate the probability of nucleation initiation by the molecular characteristics of a substance. Besides, at present one cannot be absolutely sure that the action of ionizing particles is the only reason for bends of experimental curves at large times of waiting for boiling-up. The similarity of the temperature and baric dependencies of  $\bar{\tau}$  obtained in natural conditions and in the presence of a  $\gamma$ -source is only indicative of the indubitable linkage between these phenomena. As shown in Ref. 24, the value of  $J_m$  changes in passing from glass to metallic measuring cells. The character of the dependence  $\bar{\tau}(T)$  at  $J < J_m$  is affected by easily activated boiling centers,<sup>25</sup> and ultrasonic fields.<sup>26</sup>

The temperature corresponding to the fixed nucleation-rate value is meant by the temperature of attainable superheating  $T_n$ . At  $J < J_m$  in processing the experimental data and determining the value of  $T_n$  an allowance was made for the correction for initiated nucleation. The error in determining  $T_n$  is  $\pm 0.2$  K.

#### IV. COMPARISON OF THEORY AND EXPERIMENT

To calculate by the formulae of the homogeneous nucleation theory it is necessary to know the solution equation of state and the surface tension at the vapor bubble–liquid boundary. Thermodynamic properties of pure argon and krypton satisfy the law of corresponding states with an error close to the experimental one. This makes it possible to write for them a unified reduced equation of state. We have chosen this equation in the form

$$\frac{p}{\rho k T} = 1 + \sum_{i=1}^n \sum_{j=1}^m b_{ij} \tilde{\rho}^i \tilde{T}^{-j}, \quad (35)$$

where  $\tilde{\rho} = \rho/\rho_c$ ,  $\tilde{T} = T/T_c$  and  $\rho_c$  and  $T_c$  are the density and the temperature at the critical point. The coefficients  $b_{ij}$  have been determined by the thermodynamic properties of argon and are presented in Ref. 27. Equation (35) describes the

liquid and vapor phases of a fluid, in the region of the liquid–gas phase transition has characteristic Van-der-Waals isotherms, and satisfies the Maxwell rule. Liquid and vapor spinodals calculated by this equation are in good agreement with the results of their approximation by experimental data.<sup>28,29</sup> It is assumed that the properties of an Ar–Kr solution coincide with those of a hypothetical pure fluid, whose critical parameters  $T_c$  and  $\rho_c$  are determined by the relations

$$T_c(x') = T_{c1}(1-x')^2 + 2T_{c12}x'(1-x') + T_{c2}x'^2, \quad (36)$$

$$\rho_c^{-1}(x') = \rho_{c1}^{-1}(1-x')^2 + 2\rho_{c12}^{-1}x'(1-x') + \rho_{c2}^{-1}x'^2, \quad (37)$$

where the parameters  $T_{c12}$  and  $\rho_{c12}^{-1}$  satisfy the rules of combining

$$T_{c12} = \zeta_T \sqrt{T_{c1}T_{c2}}, \quad \rho_{c12}^{-1} = \zeta_\rho [(\rho_{c1}^{-1/3} + \rho_{c2}^{-1/3})/2]^3. \quad (38)$$

The coefficients  $\zeta_T = 1.0012$  and  $\zeta_\rho = 1.017$  were determined by minimizing the root-mean-square deviation of the experimental data on saturation vapor pressure<sup>22</sup> and liquid-phase density<sup>30</sup> of an Ar–Kr solution from the data calculated by Eqs. (35)–(38).

The matrix of the influence parameters  $\kappa_{ij}$ , the diagonal elements of which are concerned with the pure components has been determined from the experimental data on  $\sigma_s$ ; both of the pure components<sup>31–33</sup> and of solutions<sup>34</sup> neglect its density dependence and use the rule of combining  $\kappa_{12} = \zeta_\kappa \sqrt{\kappa_{11}\kappa_{22}}$  and the formula for the planar surface tension

$$\sigma_s = 2 \int_{-\infty}^{\infty} \sum_{i,j} \kappa_{ij} \left( \frac{\partial \rho_i}{\partial z} \right) \left( \frac{\partial \rho_j}{\partial z} \right) dz. \quad (39)$$

The value  $\zeta_\kappa \approx 1$  has been obtained in numerical calculations. According to (10), the case  $\zeta_\kappa = 1$  corresponds to the state of indifferent equilibrium ( $\det \kappa_{ij} = 0$ ). If we introduce a new variable  $\rho_a = \rho_1 \sqrt{\kappa_{11}/\kappa_{22}} + \rho_2$ , the system of differential equations (13) at  $\zeta_\kappa = 1$  will degenerate into one differential and one algebraic equations

$$\frac{d^2 \rho_a}{dr^2} + \frac{2}{r} \frac{d \rho_a}{dr} = \frac{\mu_2(\rho) - \mu_{02}}{2\kappa_{22}}, \quad (40)$$

$$\sqrt{\kappa_{22}}(\mu_1(\rho) - \mu_{01}) = \sqrt{\kappa_{11}}(\mu_2(\rho) - \mu_{02}). \quad (41)$$

At small supersaturations in a nucleus one can distinguish a homogeneous core and a transition layer, the thickness of which is small compared with the bubble size. With further penetration into a metastable region the homogeneity core becomes smaller, and the functions  $\rho_1(r)$ ,  $\rho_2(r)$  take a bell-like form. A shift in the distribution of  $\rho_1(r)$  with respect to  $\rho_2(r)$  means excess adsorption of the first component in the surface layer of a nucleus.

By solving the system of Eqs. (3)–(5) and (13) with respect to  $\sigma$  and  $R_*$  one can determine the dependence of the surface tension on the radius of curvature of the surface of tension. The results of such a calculation at a fixed temperature and several values of solution concentration are given in Fig. 5. Distinct from a one-component system, where  $\sigma$  is a monotonically function of  $R_*$ ,<sup>33,35</sup> for a solution with  $x' \approx 0.5$  the dependence  $\sigma(R_*)$  has a characteristic maxi-

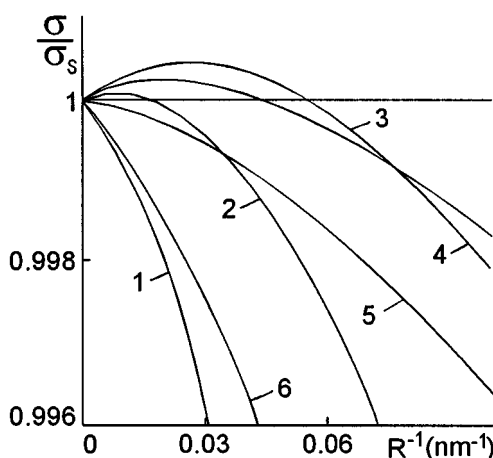


FIG. 5. The dependence of the reduced surface tension of critical bubbles on an interface curvature at  $T = 145$  K for concentrations: (1)  $x' = 0$ ; (2) 0.1; (3) 0.3; (4) 0.5; (5) 0.7; (6) 1.

mum. The value of  $\sigma_{\max}$  exceeds that of  $\sigma_s$  only by (0.5–0.7)%, which is close to the error of experimental  $\sigma_s$ -determining.

At steady temperature and concentration the dependence  $\sigma(R)$  is described by the equation<sup>15</sup>

$$\frac{1}{\sigma} \frac{d\sigma}{dR} = \frac{-2 \delta/R}{1 + 2 \delta/R}, \quad (42)$$

where

$$\delta = \sum_i \Gamma_i \left( \frac{\partial \mu_i}{\partial \rho} \right) / \sum_i (\rho_i'' - \rho_i') \left( \frac{\partial \mu_i}{\partial \rho} \right). \quad (43)$$

Here  $\Gamma_i$  is the absolute adsorption of the  $i$ -th component, which is connected with the distance  $\delta_i$  between the equimolecular dividing surface and the surface of tension by the relation  $\Gamma_i = \delta_i(\rho_i'' - \rho_i')$  at flat interface. The parameter  $\delta$  is a function of the temperature, concentration and curvature of the interface. In the case of surfaces of small curvature<sup>35</sup>

$$\delta = \delta_s + \alpha/R. \quad (44)$$

Here  $\delta_s$  is the value of  $\delta$  for a plane interface, and  $\alpha$  is a parameter which is a function of temperature and concentration. Substituting Eq. (44) into (42), the expansion of the obtained expression in powers of  $1/R$  and integration gives

$$\sigma = \sigma_s \left( 1 - \frac{2\delta_s}{R} + \frac{4\delta_s^2}{R^2} - \frac{\alpha}{R^2} \right). \quad (45)$$

At  $\alpha \rightarrow 0$  and neglect of the term square-law by  $\delta_s$ , Equation (45) transforms to the Tolman formula.<sup>36</sup> The sphere of action of formula (45) involves bubbles responsible for a liquid spontaneous boiling-up at nucleation rates  $J < 10^{15} \text{ m}^{-3} \text{ sec}^{-1}$ . The results of calculating the properties of such bubbles are given in Table I. The obtained data are compared with the results of macroscopic approximation.

In the region of nucleation rates, where the experiments have been carried out, the value of  $B$  depends only slightly on the temperature, pressure, and concentration. Different



TABLE I. Characteristic parameters of critical bubbles at pressure 1.0 MPa.

Parameter	$x'$		
	0	0.5	1.0
$T$ (K)	134	155	186
$p_s$ (MPa)	2.440	2.906	2.738
$W_*/kT$ , Eq. (5)	78.0	82.9	71.1
$W_*/kT$ , Eq. (14)	64.1	76.7	57.9
$\log J$ , Eqs. (5), (24)	5.5	4.1	8.3
$\log J$ , Eqs. (14), (24)	11.5	6.8	14.0
$\sigma_s$ (mN/m)	2.402	3.065	2.952
$\delta_s$ (nm)	0.035	−0.023	0.036
$\delta_{s,1}$ (nm)	0.035	−0.210	—
$\delta_{s,2}$ (nm)	—	0.182	0.036
$\sigma(R_*)$ (mN/m)	2.249	2.987	2.758
$R_*$ (nm)	3.55	3.62	3.59
$n''_*$	319	330	265
$n''_{2*}$	0	75	265
$\delta$ (nm)	0.207	0.095	0.219
$\delta_1$ (nm)	0.207	−0.067	—
$\delta_2$ (nm)	—	0.329	0.219

approaches to the determination of  $B$  yield values that are in agreement within one to one and a half order. At  $p=1.0$  MPa,  $T=155.0$  K,  $x'=0.5$ , the Reiss<sup>5</sup> theory gives  $B = 88.6 \times 10^{10} \text{ sec}^{-1}$ ; the theories by Stauffer,<sup>7</sup> Shi and Seinfeld,<sup>8</sup> and Melikhov *et al.*<sup>9</sup> produce  $B = 92.3 \times 10^{10} \text{ sec}^{-1}$ ; Wu,<sup>19</sup> gives  $4.63 \times 10^{10} \text{ sec}^{-1}$ ; Eq. (28) gives  $123.3 \times 10^{10} \text{ sec}^{-1}$ . Such uncertainty leads to the discrepancy in the temperature of the solution attainable superheat, which does not exceed  $\approx 0.15$  K. The normalization of the function of nuclei distribution suggested in Ref. 9 reduces the nucleation rate by approximately an order.

The direction of a flow of nuclei at the saddle point of the potential barrier  $\Delta G(n''_1, n''_2)$  with allowance made for both thermodynamic and kinetic factors [Eq. (24)] and in an approximation of concentration constancy in a bubble [Eq.

(27)] in the range from 15 to 20% coincides with the direction of the tangent to the trajectory of the nucleus motion on the plane  $n''_1, n''_2$  which is the most advantageous energetically [Eq. (23)]. An increase in the concentration of the second component in solution results in a turn of the saddle surface  $\Delta G(n''_1, n''_2)$ . If at small values of  $n''_2$  the “spillway” line is close to the axis  $n''_1$ , then at  $n''_1 \rightarrow 0$  it shifts to the axis  $n''_2$ .

In Table II and Figs. 3 and 4 experimental data on the temperature of attainable superheat of Ar–Kr solution are compared with the results of their calculation by the homogeneous nucleation theory in a macroscopic approximation and with allowance for the dependence  $\sigma(R_*)$ . The kinetic factor is determined according to the Stauffer,<sup>7</sup> Shi and Seinfeld,<sup>8</sup> and Melikhov *et al.*<sup>9</sup> theories by Eqs. (19), (22), (24), (25) and the proportionality coefficient  $C = \rho'_1 + \rho'_2$ , according to Refs. 5, 7, and 8. For pure Ar and Kr the calculations have been carried out by Eq. (19), where the kinetic factor  $B$  has been evaluated in the Doring–Volmer approximation.<sup>11</sup> In a macroscopic approximation  $T_n$ -discrepancies between the theory and experiments do not exceed 0.6 K. They are maximum for pure substances and minimum for solutions with  $x' \approx 0.5$  composition. Taking into account the dependence  $\sigma(R_*)$  in the critical bubble formation work improves the agreement between the theory and experiment for pure substances and weak solutions. The nonmonotonicity of the dependence  $\sigma(R_*)$  in solution in the vicinity of  $x' = 0.5$  composition bridges the gap between the values of  $\sigma$  for critical bubbles and  $\sigma_s$ . It shows up in decreasing the discrepancy between the values of the attainable superheat temperature calculated in a macroscopic approximation and experimental values.

Experimental temperature dependencies of the nucleation rate are also close to theoretical ones (Figs. 3 and 4). A shift of the temperature by 1 K results in a change of  $J$  by 6 to 12 orders. The derivative  $\partial \log J / \partial T$  increases with in-

TABLE II. The attainable superheat temperature of Ar–Kr solution,  $J = 10^7 \text{ m}^{-3} \text{ sec}^{-1}$ .

$x'$	$T_s$	$p_s$	$T_n$ (K)		
	(K)	(MPa)	Exp.	Theory <sup>a</sup>	Theory <sup>b</sup>
$p' = 1.0 \text{ MPa}$					
0.0	116.55	2.431	133.9	134.12	133.65
0.109	118.60	2.559	138.1	138.29	137.88
0.428	125.86	2.887	151.8	151.81	151.50
0.708	136.38	2.973	166.5	166.73	166.30
0.938	152.72	2.784	181.1	181.42	180.81
1.0	159.13	2.673	185.3	185.84	185.17
$p' = 1.6 \text{ MPa}$					
0.0	125.18	2.698	136.2	136.41	136.05
0.109	127.63	2.823	140.5	140.63	140.33
0.382	134.76	3.098	152.1	152.19	151.97
0.428	136.21	3.151	154.4	154.37	154.14
0.708	148.09	3.224	169.2	169.42	169.10
0.938	164.71	3.034	183.8	184.21	183.72
1.0	170.70	2.934	188.1	188.63	188.10

<sup>a</sup>Calculations with  $\sigma = \sigma_s$ , data from Ref. 34.

<sup>b</sup>Calculations with  $\sigma = \sigma(R_*)$ , data from this work.

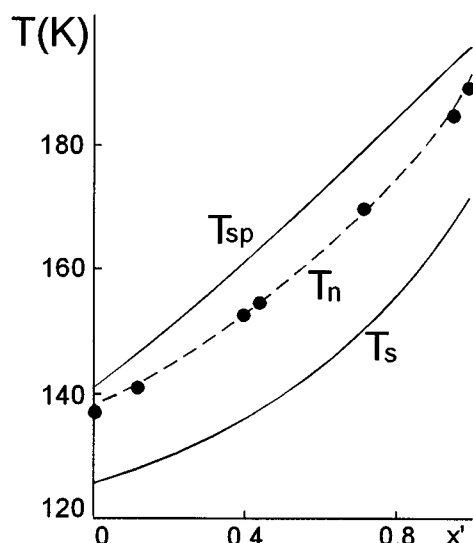


FIG. 6. The attainable superheat temperature of an argon–krypton solution at  $p = 1.6$  MPa. Circles are experimental data.  $T_n$  has been calculated using Eqs. (5), (24) and  $\sigma = \sigma_s$ ,  $J = 10^7 \text{ m}^{-3} \text{ sec}^{-1}$ .  $T_{sp}$ , Spinodal;  $T_s$ , Binodal of a liquid.

creasing pressure. Theory reproduces the concentration dependence of the attainable superheat temperature observed by experiment in a qualitatively correct way (see Fig. 6). At the pressure  $p = 1.0$  MPa and  $x' = 0.5$  the superheat achieved by experiment was  $\Delta T = T_n - T_s = 27.2$  K. The superheat  $\Delta T_{sp} = 36.2$  K corresponds to the diffusion spinodal at the same conditions. The spinodal has been calculated from Eq. (35) according to its definition (1).

According to (17), the value of  $D_{ii}$  is determined by the value of the partial pressure in the nucleus. Since  $p_i''$  is proportional to the concentration of the  $i$ -th component, there may arise a situation when the growth rate in one of the directions of the plane  $n_1''$ ,  $n_2''$  proves to be many orders of magnitude slower than in the other. In this case the line of the resulting flow of fragments of a new phase may bypass the saddle point.<sup>8,10</sup> Experimental data do not reveal any peculiarities in the nucleation kinetics in the vicinity of  $x' = 0$  and  $x' = 1$ . This confirms the justification of using the assumption of the equilibrium state of composition in a critical bubble and its interphase layer in the binary nucleation theory.

## V. CONCLUSION

A superheated liquid is the most convenient object for a check of the homogeneous nucleation theory. Distinct from a supercooled one, where the surface energy on the liquid–solid boundary is not known, the surface tension in a liquid–vapor system can be measured directly. During the investigation of nucleation in a supersaturated vapor it is much more difficult to ensure the isothermality of the process and to get rid of the initiating action of the vessel walls, and readily and easily activated nucleation centers.

The realized comparison of the phenomenological homogeneous nucleation theory and experiment with argon–krypton solutions supports the agreement between the physical Volmer–Kramers–Zeldovich model and the real process of creation of viable vapor bubbles, unless in detail, and then as a final result. With satisfactory agreement of the temperature and pressure dependence of a nucleation rate a systematic discrepancy is revealed between theory and experiment for the attainable superheat temperature. This discrepancy is maximum for pure liquids and minimum for solutions with  $x' \approx 0.5$ . The attainable superheat temperature is determined significantly by the surface tension of a nucleus. Taking into account the size dependence of the surface tension of critical bubbles makes it possible to fit the theoretical values of  $T_n$  to experimental ones over all the ranges of a concentration.

The kinetic coefficient  $B$  exerts essentially less influence on attainable superheat than  $\sigma$ . In the case of a superheated solution the factor  $B$  should be controlled by the rate of evaporation of molecules into a bubble, by viscosity and inertia of a liquid, by molecular diffusion in solution and by thermal processes at a bubble boundary. Upon comparison of the theory and experiment we believe that bubble growth in solution is determined by the kinetics of evaporation of molecules only. Very strong dependence of a nucleation rate on the exponential index in Eq. (19) leads to weak dependence of the attainable superheat temperature on  $B$ . For an one-component liquid the inclusion of all bubble growth controlling factors gives values of the kinetic coefficient, which are approximately one order less than under the assumption of a condensation–evaporation mechanism. This entails the discrepancy in  $T_n$ , which does not exceed  $\approx 0.1$  K.

Good agreement between theory and experiment attests that the equilibrium state of composition has time for forming in a critical bubble and its boundary and the resulting flow of nuclei goes through the saddle point of the barrier  $\Delta G(n_1'', n_2'')$ . Heterogeneous nucleation sources defy ordinary physical identification and statistical description. Considerably far from equilibrium states, the creation of a vapor phase usually has a spontaneous character with the low value of work  $W_*$ . This allows hope for the elaboration of effective models, in which the sections of experimental curves corresponding to the nucleation rates  $J < 10^6 \text{ m}^{-3} \text{ sec}^{-1}$  can be described too.

## ACKNOWLEDGMENTS

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<sup>1</sup>M. Volmer, *Kinetik der Phasenbildung* (Edwards Brothers, Inc., Ann Arbor, 1945).

<sup>2</sup>W. Döring, *Z. Phys. Chem. B* **36**, 371 (1937).

<sup>3</sup>Ya. B. Zeldovich, *Zh. Éksp. Teor. Fiz.* **12**, 525 (1942).

<sup>4</sup>J. I. Frenkel, *Kinetic Theory of Liquids* (Clarendon, Oxford, 1946).

<sup>5</sup>H. Reiss, *J. Chem. Phys.* **18**, 840 (1950).

- <sup>6</sup>E. I. Nesis and J. I. Frenkel, *Zh. Tekhn. Fiz.* **22**, 1500 (1952).
- <sup>7</sup>D. Stauffer, *J. Aerosol Sci.* **7**, 319 (1976).
- <sup>8</sup>G. Shi and J. H. Seinfeld, *J. Chem. Phys.* **93**, 9033 (1990).
- <sup>9</sup>A. A. Melikhov, V. B. Kurasov, Yu. Sh. Djikaev, and F. M. Kuni, *Zh. Tekhn. Fiz.* **61**, 27 (1991).
- <sup>10</sup>H. Trinkaus, *Phys. Rev. B* **27**, 7372 (1983).
- <sup>11</sup>V. P. Skripov, *Metastable Liquids* (Wiley, New York, 1974).
- <sup>12</sup>V. G. Baidakov, V. P. Skripov, and A. M. Kaverin, *Zh. Éksp. Teor. Fiz.* **65**, 1126 (1973) [*Sov. Phys. JETP* **38**, 557 (1974)].
- <sup>13</sup>V. P. Skripov, V. G. Baidakov, and A. M. Kaverin, *Physica A* **95**, 169 (1979).
- <sup>14</sup>A. M. Kaverin, V. G. Baidakov, and V. P. Skripov, *Inzh.-Fiz. Zh.* **38**, 680 (1980).
- <sup>15</sup>J. W. Gibbs, *Collected Works* (Yale University Press, New Haven, Connecticut, 1948), Vol. 1.
- <sup>16</sup>J. W. Cahn and J. E. Hilliard, *J. Chem. Phys.* **31**, 688 (1959).
- <sup>17</sup>J. D. Van der Waals and Ph. Kohnstamm, *Lehrbuch der Thermodynamik* (Maas and van Suchtelen, Leipzig, 1908).
- <sup>18</sup>J. S. Langer, *Ann. Phys.* **54**, 258 (1969).
- <sup>19</sup>D. T. Wu, *J. Chem. Phys.* **99**, 1990 (1993).
- <sup>20</sup>N. N. Danilov, E. N. Sinitsyn, and V. P. Skripov, in *Teplofizika Metastabilnykh Sistem* (Ural Division of Academy of Sciences of the USSR, Sverdlovsk, 1977), p. 28.
- <sup>21</sup>V. P. Skripov, E. N. Sinitsyn, P. A. Pavlov, G. V. Ermakov, G. N. Muratov, N. V. Bulanov, and V. G. Baidakov, *Thermophysical Properties of Liquids in the Metastable (Superheated) State* (Gordon and Breach, New York, 1988).
- <sup>22</sup>J. A. Schouten, A. Deerenberg, and N. J. Trappeniers, *Physica A* **81**, 151 (1975).
- <sup>23</sup>M. N. Medvedev, *Stsintillyatsionnye Detektory* (Atomizdat, Moskva, 1977).
- <sup>24</sup>A. M. Kaverin, V. G. Baidakov, V. P. Skripov, and A. N. Kat'yanov, *Zh. Tekhn. Fiz.* **55**, 1220 (1985).
- <sup>25</sup>V. G. Baydakov, *Fluid Mech. Sov. Res.* **16**, 62 (1987).
- <sup>26</sup>V. G. Baidakov, A. M. Kaverin, and V. P. Skripov, *Akust. Zh.* **27**, 697 (1981).
- <sup>27</sup>A. A. Vasserman and A. Ya. Krežerova, *Teplofiz. Vysok. Temp.* **16**, 1185 (1978).
- <sup>28</sup>V. G. Baidakov, *Sov. Tech. Rev. B Therm. Phys.* **5**, 1 (1994).
- <sup>29</sup>V. G. Baidakov, V. P. Skripov, and A. M. Kaverin, *Zh. Éksp. Teor. Fiz.* **67**, 676 (1974) [*Sov. Phys. JETP* **40**, 335 (1975)].
- <sup>30</sup>S. F. Barreiros, J. C. G. Calado, P. Clancy, M. Nunes da Ponte, and W. B. Streett, *J. Phys. Chem.* **86**, 1722 (1982).
- <sup>31</sup>V. G. Baidakov and V. P. Skripov, *Kolloid. Zh.* **44**, 409 (1982).
- <sup>32</sup>V. G. Baidakov, *Ukr. Fiz. Zh.* **27**, 1332 (1982).
- <sup>33</sup>V. G. Baidakov, *Mezhfaznaya Granitsa Prostykh Klassicheskikh i Kvantovykh Zhydkostei* (Nauka, Ekaterinburg, 1994).
- <sup>34</sup>C. D. Holcomb and J. A. Zollweg, *J. Phys. Chem.* **97**, 4797 (1993).
- <sup>35</sup>V. G. Baidakov and G. Sh. Boltachev, *Zh. Fiz. Khim.* **69**, 515 (1995).
- <sup>36</sup>R. C. Tolman, *J. Chem. Phys.* **17**, 333 (1949).