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Statistical Thermodynamics of the Formation of a New Phase in the Boiling Up of Volatile Liquids

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The fluctuation growth of a macroscopic bubble containing a vapor in a moderately superheated or tensile-stressed volatile liquid is treated as the two-dimensional diffusion of a nucleus of a new phase in the space of variables made up of its volume v and the pressure of the vapor in it p. The shape of the free energy surface of the system "liquid plus bubble with vapor" in the plane $(v; p)$ in the neighborhood of the labile equilibrium of the system is examined, and a two-dimensional nucleus distribution function given with respect to its variables is derived. Close to the pass in the surface a nondiagonal diffusion tensor in the space (v, p) is also calculated. A two-dimensional stationary equation of the kinetics of the formation of a new phase of Kramers type is solved, and an expression is derived for the probability of homogeneous nucleation for an arbitrary viscosity and volatility of a liquid far from its critical point. Various limiting cases are examined.

KEY WORDS: Nucleation; boiling-up.

1. INTRODUCTION

Consideration of the thermodynamics and kinetics of the formation of a new phase$^{(1-8)}$ resulted in the development of a general method for the description of a first-order phase transition, where the growth of macroscopic nuclei of the new phase is interpreted in terms of diffusion along the nucleus size axis. In this case, a certain field of generalized forces due to the "supersaturation" of the system under examination is superimposed on the size axis. The problem of finding the formation rate of the new phase consists in determining the diffusion flow through a potential barrier separating the quasi-single-phase region of the size axis from the two-phase region.

If the use of one variable proves to be insufficient for the macroscopic

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characterization of a new-phase nucleus, the solution of the nucleation problem is considerably complicated. Two variables were used for the first time for the description of the first-order phase transition in Ref. 9 in order to study the phase transition in binary systems, where two parameters of a nucleus naturally arise: its size and composition. Subsequently, a similar approach to examining heteromolecular condensation was generalized for multicomponent systems.(10) The two-parameter approach proved to be useful in the theory of nonisothermal nucleation,(11) where, in order to take into account the effect of the release of latent heat in a condensing droplet, it was characterized by its size and temperature.

In Ref. 12, an attempt was made to develop nucleation theory in a more general way, from the point of view of the multiparameter description of a new-phase nucleus and of determining the preexponential factor. In this study, the nucleation process is interpreted as the decomposition of the metastable state of a supersaturated system through thermal activation of a localized unstable fluctuation (for example, of a near-critical droplet).

This approach(13) was applied to the description of the condensation of a supersaturated vapor in the vicinity of the critical point. The multiparameter approach to nucleation theory was used in a similar way in Ref. 14, where condensation theory was generalized for the case of many coordinates of a nucleus, starting from the description of dense gases by means of the basic kinetic equation. The authors have applied the formalism developed in Ref. 14 mainly to describing condensation in the vicinity of the critical point, as well as to describing the condensation of a mixture of gases.(15)

In the present study,[2] we shall consider the boiling up of a viscous, volatile liquid in terms of the diffusion of a vapor-containing bubble nucleus in the space of two variables: its volume v and the pressure of vapor in it p.

Considered from the point of view of the multiparameter description of the new-phase nucleus, the present study is cognate with the studies of Refs. 9–15. However, let us note two essential differences of the former from the latter.

First, from the very beginning we have posed as our object, not the description of the most general boiling-up scheme, but the development of the theory of the boiling up of a liquid having arbitrary volatility and viscosity at moderate "supersaturations" of the system. Though this problem seems to be simpler, it proves to be fairly complicated, especially in the case where we attempt to develop a strict theory. Let us note the following in this connection: although there is a great number of papers dealing with the boiling up of liquids (see, for example, the references in Refs. 16 and 17), few theoretical investigations concern the very process of formation (but not of

[2] See also Ref. 28.

the supercritical growth!) of nucleus bubbles, inasmuch as most studies dealing with the boiling up of liquids are characterized by a purely engineering approach. As we limit ourselves to the case of moderate superheatings and/or tensions of the liquid, we shall deal with a macroscopic bubble nucleus possessing a distinct vapor–liquid boundary.

Second, in distinction to Refs. 12 and 14, the calculations of the boiling-up rate are based on an original method for the calculation of the preexponential factor of an equilibrium bubble distribution function,(18) based on taking into consideration the grand Gibbs ensemble of all possible states of the volume of liquid in which nucleation takes place.

Let us consider the physical background of the problem. In a large volume of liquid W having rigid adiabatic walls, let us separate off a small part, say volume V, by using a semipermeable partition having pores of such size that near-critical bubbles cannot pass through them. The volume V must satisfy the relationship

$$v_c \ll V \ll W \tag{1}$$

where v_c is the critical bubble volume.

The problem involves calculating the probability ν [sec^{-1}] of the formation of one hypercritical vapor-containing bubble in volume V per unit time under the condition of a single-phase state of "medium" $W - V$. In this case, we will neglect the probability of the simultaneous existence of several near-critical bubbles in volume V.

2. ANALYSIS OF THE SHAPE OF THE FREE ENERGY SURFACE

The dynamics of a change in the state of a real bubble in a volatile liquid is fairly complex. Both thermodynamic equilibrium with the surrounding liquid as well as mechanical equilibrium with the external pressure may be absent in a bubble. In addition, inside the bubble there exist inhomogeneities of pressure p and temperature θ, and there are variations in temperature at the bubble boundaries due to variations in the number of molecules in it, and uncertain changes in its form for given v, etc.

The macroscopic bubble will be considered to be spherical. Also, we shall not consider the temperature effects at the bubble boundaries, which may be taken into account by a correction to the diffusion coefficient.(19) As regards inhomogeneities of p and θ in the bubble, we will neglect them both, because we assume that the characteristic times for establishing the hydrostatic and the thermodynamic equilibria inside the bubble are much shorter than the characteristic times of changes in the bubble size and in the number of the molecules of vapor in it. Therefore, at any moment of time, the pressure p will be related to the number of molecules N_v in the bubble by the ideal-gas equation of state:

$$pv = N_v\theta \tag{2}$$

The use of this equation means that we consider $\delta \equiv \rho_v/\rho_l \ll 1$, where ρ_v and ρ_l are the vapor and liquid densities [cm^{-3}], respectively. According to condition (1) and in view of the large heat capacity of the liquid, the temperature θ [ergs] will be considered as constant during the nucleation process.

Let us emphasize that it is precisely the difference between the pressure p and the saturated vapor pressure in a bubble of given curvature (i.e., the absence of thermodynamic equilibrium) that is responsible for the appearance of the second bubble variable: p.

The free energy of a spherical bubble of volume v containing N_v molecules of vapor, in a liquid raised to a temperature θ under a pressure P is equal to the minimum work of its formation:

$$F_{vp} = v(P - p) + \sigma s + N_v[\mu_v(p, \theta) - \mu_l(P, \theta)] \tag{3}$$

Taking into account the condition of the thermodynamic equilibrium of the critical bubble with the surrounding liquid $\mu_v(p_c, \theta) = \mu_l(P, \theta)$ and the expression $\mu_v(p, \theta) = \mu_v(p_c, \theta) + \theta \ln(p/p_c)$ we transform Eq. (3),

$$F_{vp} = v(P - p) + \sigma s + N_v\theta \ln(p/p_c) \tag{4}$$

where p_c is the saturated vapor pressure in the critical bubble.

Passing over to dimensionless variables $x \equiv v/v_c$, $y \equiv p/p_c$, and $\Psi \equiv F_{vp}/\theta$ and expanding Ψ close to the point (1, 1), corresponding to the labile equilibrium of the system "liquid plus bubble with vapor" in volume V, in a power series in $\Delta x = x - 1$ and $\Delta y = y - 1$ up to the second order inclusively, we obtain

$$\begin{aligned}\Psi(x, y) &= \Psi_c + \tfrac{1}{2}(\Delta\mathbf{r}'\, \hat{A}\, \Delta\mathbf{r})\\ &= \Psi_c + \tfrac{1}{2}(\Delta x,\ \Delta y)\begin{pmatrix} 1/R_x & 0 \\ 0 & 1/R_y \end{pmatrix}\begin{pmatrix} \Delta x \\ \Delta y \end{pmatrix} = \Psi_c + \frac{(\Delta x)^2}{2R_x} + \frac{(\Delta y)^2}{2R_y}\end{aligned} \tag{5}$$

where

$$\hat{A} = \begin{pmatrix} \partial^2\Psi/\partial x^2|_c & \partial^2\Psi/\partial x\,\partial y|_c \\ \partial^2\Psi/\partial y\,\partial x|_c & \partial^2\Psi/\partial y^2|_c \end{pmatrix} = \begin{pmatrix} -2\sigma s_c/9\theta & 0 \\ 0 & N_v^c \end{pmatrix} = \begin{pmatrix} 1/R_x & 0 \\ 0 & 1/R_y \end{pmatrix} \tag{5a}$$

is the matrix of second derivatives $\Psi(x, y)$ at the pass point. Here $(\Delta\mathbf{r}) = (\Delta x, \Delta y)$ is the radius vector of an arbitrary point, which is drawn from the pass point; Ψ_c is the dimensionless work of critical nucleus formation; R_x and R_y are the main radii of curvature of the surface $\Psi(x, y)$ at point (1, 1); σ is the surface tension [g sec^{-2}]; s is the critical bubble surface area [cm^2]; and $N_v{}^c$ is the equilibrium number of molecules of vapor in the bubble. In this case, the first derivatives $\partial\Psi/\partial x|_c$ and $\partial\Psi/\partial y|_c$ are both equal to zero due to the thermodynamic and mechanical equilibrium conditions, respectively. The absence of a crossed square term in Eq. (5) is attributable to the fact that $\overline{\Delta x\,\Delta y} = 0$, i.e., that the fluctuations of the variables x and y are statistically independent, at least close to the pass.

From Eq. (5a) it appears that the main radii of curvature R_x and R_y have different signs—that is, the labile equilibrium point (1, 1) of the system is always a hyperbolic point of the surface. In that case, the shape (4) of the surface of the bubble free energy in the neighborhood of the pass may be approximated by the surface of a hyperbolic paraboloid ("saddle").

This saddle-type pass of the system free energy surface lies inside the first quadrant of the surface (x, y), parallel to the coordinate axes. The pass point is the intersection point of the thermodynamic equilibrium line (I) with the mechanical equilibrium line (II) (see Fig. 1), the lines being defined in (x, y) coordinates by the expressions.

$$y = y_\infty \exp(-\rho_v{}^c b/\rho_l x^{1/3}) \tag{6}$$

and

$$y = y_{\text{ext}} + b/x^{1/3} \tag{7}$$

where $y_\infty \equiv p_\infty/p_c$, $y_{\text{ext}} \equiv P/p_c$, p_∞ is the saturated vapor pressure over the flat surface, P is the external pressure applied to the liquid, and

$$b \equiv 2\sigma/p_c r_c = 1 - P/p_c \tag{8}$$

is the ratio of the capillary pressure and vapor pressure p_c in the critical bubble. For an increase in the tensile stretching and superheating of the liquid, the values of r_c and p_c decrease. Hence, the parameter $b = 2\sigma/p_c r_c$ may be used as a measure of the "supersaturation" of the volatile liquid relative to the boiling-up process.

In this region lies the thermodynamically most advantageous path (III) of the fluctuation growth of the nucleus, the path connecting the neighborhood of the origins of the coordinates with the pass point. It represents the "bottom of a trough" running through the pass. From the point of view of the theory of surfaces,$^{(20)}$ that bottom is defined by one of the two lines of curvature of the surface (i.e., lines that have tangents at all points oriented parallel to the surface main directions) passing through the pass point.

The differential equation of those lines of curvature is$^{(20)}$

$$[pqt - (1 + q^2)s]\left(\frac{dy}{dx}\right)^2 + [(1 + p^2)t - (1 + q^2)u]\frac{dy}{dx} + (1 + p^2)s - pqu = 0 \tag{9}$$

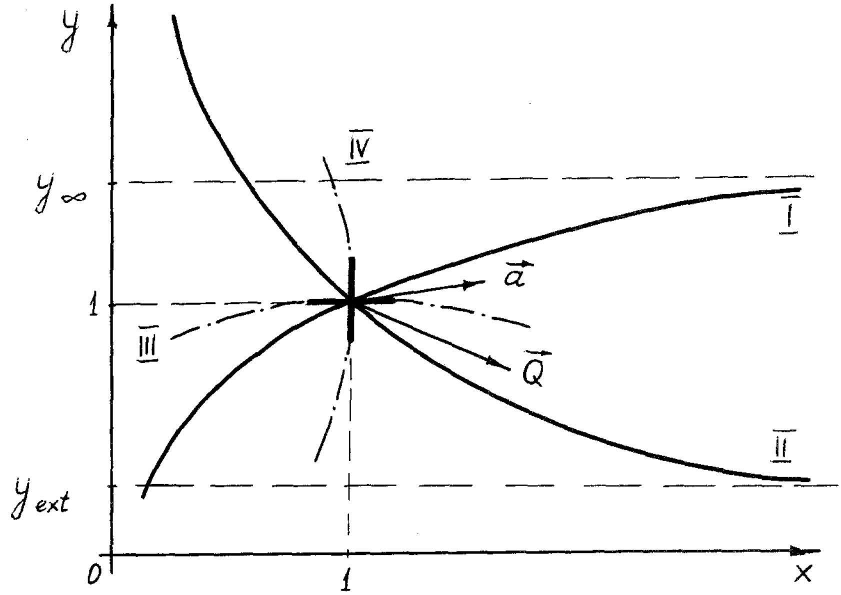

Fig. 1. Projection of the dimensionless free energy surface $\Psi(x, y)$ of the system in the neighborhood of the pass onto the plane of dimensionless variables (x, y). The cross indicates the main axes of the saddle-shaped pass; I and II are the nucleus phase and mechanical equilibrium lines, respectively; III is the nucleus growth line which is the most advantageous from the energy point of view, and IV is the "watershed" between the quasimonophase and the two-phase regions of the plane (x, y). a and Q are the directions of steepest descent n_{xy}/φ_{xy} and of the nucleus flux at the pass point, respectively.

where

$$p \equiv \frac{\partial \Psi}{\partial x}, \qquad q \equiv \frac{\partial \Psi}{\partial y}, \qquad u \equiv \frac{\partial^2 \Psi}{\partial x^2}, \qquad s \equiv \frac{\partial^2 \Psi}{\partial x \, \partial y}, \qquad t \equiv \frac{\partial^2 \Psi}{\partial y^2} \tag{9a}$$

in combination with the condition $dy/dx|_c = 0$ allows the trough bottom line to be prolonged inside the region of small nuclei until the macroscopic expression (4) of the bubble free energy keeps its validity in it. The second curvature line (IV), passing through the pass point and satisfying the condition $dy/dx|_c = \infty$, is the line of a ridge forming a "watershed" between the quasi-single-phase and the two-phase regions of the plane (x, y).

In the general case of a viscous and volatile liquid, the fluctuation growth of subcritical bubbles is not connected with the thermodynamic equilibrium line I, the mechanical equilibrium line II, or even with the trajectory III which is the most advantageous from energy considerations.

This is attributable to the following fact: besides the physical parameters of the volatility and the supersaturation of the liquid, to which all three aforesaid lines are connected, the nucleation process is also controlled by the viscosity. The viscosity influences the nucleation process, not through the shape of the potential in the space (x, y), but through a nondiagonal diffusion tensor. Therefore, we shall be able to find the most probable nucleus growth trajectory only when, after having solved the two-dimensional diffusion equation, we have derived an expression for the vector flux **Q** as a function of x and y. Let us consider the case of an ideal, inertialess liquid as an example to illustrate how essentially the viscosity of the liquid changes the most probable nucleus growth trajectory.

In this case, for any pressure fluctuation, the bubble volume is "adjusted instantaneously" in such a manner that the bubble is in mechanical equilibrium. Consequently, on the basis of physical considerations it follows that in the given limiting case, the mechanical equilibrium line II is the most probable nucleus trajectory. Döring(4) adopted for the totality of subcritical nuclei a hypothesis of mechanical equilibrium. This means replacing the examination of an arbitrary liquid by that of an ideal, inertialess liquid.

However, it turns out that the mechanical equilibrium of a bubble is not stable at all the values of supersaturation and volatility of a liquid. To clarify this question, we use the stability condition of the mechanical equilibrium of a near-critical bubble.

In an ideal, inertialess liquid a volume change occurs much more rapidly than does a variation in the number of vapor molecules in a bubble. Hence, the state equation (2) in (x, y) coordinates may be written in the following manner: $xy = 1$. On calculating at the pass point the derivative dy/dx from the state equation and the mechanical equilibrium equation (7), we obtain that the mechanical equilibrium of the near-critical bubble is stable at $b < 3$ and unstable at $b > 3$.

Thus, in the ideal, inertialess liquid the most probable trajectory of the fluctuation growth of a subcritical nucleus coincides with the mechanical equilibrium line at $b < 3$. Now, at $b > 3$, the most probable trajectory does not coincide with the line II, and its determination requires an analysis of the general expression for the vector flux **Q**.

Döring(4) connected the growth of nuclei with mechanical equilibrium condition at $b > 3$. Hence, the incorrect conclusion was drawn that the nucleation rate tends to infinity at $b \to 3$; and that there is no continuity of the formulas in Ref. 4 when b passes through 3.

Taking into account Eq. (2), we find that the mean curvature $H(x, y)$ of the surface (5) has the form

$$H(x, y) = \frac{1}{2}\left(\frac{1}{R_x} + \frac{1}{R_y}\right) = \frac{1}{2}\left(N_v^c - \frac{2\sigma s_c}{9\theta}\right) = \frac{N_v^c}{2}\left(1 - \frac{b}{3}\right) \qquad (10)$$

where

$$b/3 = -R_y/R_x = 2\sigma/3r_c p_c \qquad (11)$$

Considering $H(x, y)$, we find that the dimensionless parameter b is the ratio of the main curvature radii of the pass, which characterizes the "pass width." As the superheating or tensile stress of the volatile liquid increases, that is, upon going from $b \ll 3$, $H \gg 0$, $|R_x| \gg R_y$ to $b \gg 3$, $H \ll 0$, $|R_x| \ll R_y$, the pass changes from wide into narrow. Thus, in the two-dimensional approach, it is easy to see that the transition of the mean curvature of the surface through the zero point causes no break in the continuity of the matrix $\hat{A}$ [see Eq. (5a)] or the matrix $\hat{D}$ [see Eq. (B17)], the specification of which completely defines the nucleation process. Let us examine the two-dimensional distribution function φ_{xy}, which, as is shown in Appendix A, has the form

$$\varphi_{xy} = g_0 N_V N_l^c N_v^c \exp[-\Psi(x, y)] \tag{12}$$

where Ψ is given in Eq. (5), $N_V = V\rho_l$, $N_v^c = v_c\rho_v^c$, $N_l^c = v_c\rho_l$, and g_0 is the total probability that volume V does not contain bubbles.

Substituting Eq. (5) into Eq. (12), we see that close to the pass, the variables in φ_{xy} are separated:

$$\varphi_{xy} = \varphi_x \varphi_y \tag{13}$$

$$\varphi_x = g_0 N_V N_l^c \exp\left[-\Psi_c + \frac{\sigma s_c}{9\theta}(\Delta x)^2\right] \tag{13a}$$

$$\varphi_y = N_v^c \exp[-\tfrac{1}{2}N_v^c(\Delta y)^2] \tag{13b}$$

The function φ_x describes the equilibrium distribution of nuclei along the bottom of the trough running through the pass. That function is similar to the ordinary distribution function introduced by Zeldovich$^{(8)}$ in the one-dimensional nucleation problem. The function φ_y, describing the equilibrium distribution of bubbles according to the pressure in them—that is, in the trough cross section—requires, according to fluctuation theory,$^{(21)}$ ordinary normalization

$$\int_{-\infty}^{+\infty} \varphi_y \, d(\Delta y) = 1$$

Consequently, instead of Eq. (13b), a correctly normalized transverse distribution function will have to be written:

$$\varphi_y = \left(\frac{N_v^c}{2\pi}\right)^{1/2} \exp[-\tfrac{1}{2}N_v^c(\Delta y)^2] \tag{13c}$$

the presence of which is one of the peculiar features of the two-dimensional nucleation problem. Then, using Eq. (13c), we obtain instead of Eq. (12)

$$\varphi_{xy} = g_0 V v_c \rho_l^2 (N_v^c/2\pi)^{1/2} \exp[-\Psi(x, y)] \tag{13d}$$

3. CALCULATION OF THE NUCLEATION PROBABILITY

In Section 1 we considered a volume V of liquid which, in the nucleation process, may be found in different states differing from one another in energy E, the number of molecules N in V, the volume of a nucleus bubble, and the pressure in it.

The totality of all possible states—single phase and two phase—of the volume V represents the Gibbs grand ensemble. In that case, the volume $W - V$ plays the role of a single-phase thermostat and a reservoir of molecules having a given chemical potential.

From the point of view of statistical physics, the nucleation process is determined by the flux **Q** of the states of the volume V per unit time, which is directed from metastable, quasi-single-phase states of the volume V (which, in view of the absence of a macrobubble, is characterized by two variables only: E and N) to its two-phase states containing a supercritical bubble (which are characterized by, besides the aforementioned two variables, two variables pertaining to the bubble).

Let us note that, in view of inequality (1), the formation and growth of a bubble in V changes but slightly the fluctuations of such thermodynamic characteristics of volume V as its energy E and the total number of molecules N. Thus, these variables form an almost invariable "background" on which the process of the nucleus fluctuation growth develops.

In order to get rid of the "background" of variables E and N, we pass over from the four-dimensional space of states of the volume V to the two-dimensional space of variables v and p. Each point of this space is a "trace" of the space of variables E and N and possesses almost the same statistical weight g_0. Summing up the quasi-single-phase states with respect to E and N, we obtain the total probability g_0 of the states of the volume V in which there is no macroscopic nucleus present (see Appendix A).

Integrating the flux **Q** flowing through the pass over its cross section, we find the total flux I directed from the heterophase fluctuation region to the two-phase region of the plane (v, p). Dividing the total flux I by g_o, we obtain

$$\nu = I/g_0 \tag{14}$$

where ν is the nucleation probability per unit time in volume V containing no macrobubbles in its metastable state.

To calculate **Q**, it will be necessary to solve a two-dimensional bubble diffusion equation in the space of dimensionless variables (x, y) exhibiting a potential shape Ψ_{xy}. In the neighborhood of the pass, the two-dimensional equation of the nucleation kinetics may be written as an equation of the continuity of flux **Q**, which is similar to that suggested by Zeldovich(8) for the one-dimensional case[3]:

$$\partial n/\partial t = \operatorname{div} \mathbf{Q} \tag{15}$$

$$\mathbf{Q} = \varphi_{xy}\hat{D}\ \operatorname{grad}(n/\varphi_{xy}) \tag{15a}$$

where $\varphi_{xy} \equiv \varphi(x, y)$ is the equilibrium nucleus distribution density with respect to the variables (x, y); $n \equiv n(x, y)$ is the nucleus distribution density in the nucleation process; and $\hat{D}$ is the "generalized diffusion" tensor, whose calculation is given in Appendix B. Considering only one nucleus in volume V, we normalize n by the condition that $\int_0^\infty n\,dx\,dy = 1$. Already when considering the potential shape (4), we have assumed that the external pressure P and the temperature of the liquid θ are constant. In other words, we assume that no variation in tensile stress or in the superheating of the liquid occurs in the nucleation process. Hence, we assume the nucleation process is steady $(\partial n_{xy}/\partial t) = 0$, where n_{xy} is the steady-state nucleus distribution density). For that purpose, we resort to a boundary condition that removes from the states ensemble of the volume V the states with a grown bubble and replace them by quasi-single-phase states. The boundary conditions to Eq. (15) are given in the following manner. At point 0 having coordinates $x = 0$, $y = 0$, where a source of nucleus bubbles is located, following Ref. 8, we prescribe a boundary condition

$$n_{xy}/\varphi_{xy} = 1 \tag{16}$$

Of course, from the physical point of view we prescribe such a condition, not at the very point 0, but at points that, on the one hand, are so remote from the point 0 that a bubble formed can be treated macroscopically, while, on the other hand, their distance to the point 0 can be neglected as compared with the distance to the pass point.

The boundary condition

$$n_{xy}/\varphi_{xy} = 0 \tag{16a}$$

where y is an arbitrary value, $x = x^* \gg x_c$, removes states with supercritical bubbles from the states ensemble.

We suppose that practically the entire drop n_{xy}/φ_{xy} from one to zero occurs in the neighborhood of the pass. Therefore, we define the gradient n_{xy}/φ_{xy}, similar to the one-dimensional case, in the form

$$\operatorname{grad}(n_{xy}/\varphi_{xy}) = C\mathbf{a}\exp[\tfrac{1}{2}\lambda(\mathbf{a}\cdot\Delta\mathrm{r})^2] \tag{17}$$

which determines the solution sought for Eq. (15), corresponding to a curve going from the origin of the coordinates through the pass. Here **a** is an

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[3] The method of solving Eqs. (15) and (15a) was suggested by V. N. Likhachev.

unknown vector indicating the direction of most rapid descent n_{xy}/φ_{xy}; $\Delta\mathbf{r} = (\Delta x, \Delta y)$ is the radius vector of an arbitrary point, as drawn from the pass point; and λ is an unknown number determining the rapidity of descent n_{xy}/φ_{xy} ($\lambda \leqslant 0$).

Using the boundary conditions (16)–(16a), we find the constant C:

$$C = (-\lambda/2\pi)^{1/2} \tag{18}$$

Substituting Eqs. (5), (13d), (17), and (18) into Eq. (15a), we obtain the flux of nuclei

$$Q = \frac{g_0 V v_c \rho_l^2}{2\pi}(-\lambda N_v^c)^{1/2} \exp\left[-\Psi_c - \frac{\Delta\mathbf{r}' \hat{A}\,\Delta\mathbf{r}}{2} + \frac{\lambda(\mathbf{a}\,\Delta\mathbf{r})^2}{2}\right]\hat{D}a \tag{19}$$

Due to the non-diagonal tensor $\hat{D}$, in the general case the direction of that flux does not coincide with the direction of the most rapid descent n_{xy}/φ_{xy} or with the main axes of the pass, or with lines I and II (see Fig. 1).

If $\mathbf{r}$-dependent formulas for $\hat{A}$ and $\hat{D}$ are derived, then expression (19) allows a vector field $\mathbf{Q}$ to be built on the plane (x, y) and the problem of the most probable trajectory of the nucleus fluctuation growth to be solved completely.

Then, from the condition of the steady-state nucleation process, we derive an equation for $\mathbf{a}$ and λ:

$$-(\Delta\mathbf{r}\,\hat{A}\hat{D}\mathbf{a}) + \lambda(\Delta\mathbf{r}\,\mathbf{a})(\mathbf{a}\hat{D}\mathbf{a}) = 0$$

or

$$\hat{A}\hat{D}\mathbf{a} = \lambda\mathbf{a}(\mathbf{a}\hat{D}\mathbf{a}) \tag{20}$$

Equation (20) is split up into a characteristic equation

$$\hat{A}\hat{D}\mathbf{a} = \lambda\mathbf{a} \tag{21}$$

for determining the proper eigenvalues λ and the proper eigenvectors $\mathbf{a}$ of matrix $\hat{A}\hat{D}$, and a condition for normalizing the proper eigenvector $\mathbf{a}$:

$$(\mathbf{a}\hat{D}\mathbf{a}) = 1 \tag{21a}$$

Rewriting Eq. (21) at the pass point by using Eqs. (15) and (B17), we obtain

$$\hat{A}\hat{D}\mathbf{a} = \begin{bmatrix} D_x^c/R_x & (D_x^c/R_x)(\delta - \omega)/\omega \\ (D_x^c/R_y)(\delta - \omega)/\omega & (D_x^c/R_y)(1 + \omega)/\omega \end{bmatrix} \cdot \mathbf{a} = \lambda\mathbf{a} \tag{22}$$

where $D_x^c \equiv 3\theta/4v_c\eta$, $\delta \equiv \rho_v^c/\rho_l$ and $\omega \equiv p_c r_c/\beta v_t \eta$ are dimensionless parameters; η is the viscosity of the liquid [g cm^{-1} sec^{-1}]; β is the dimensionless condensation coefficient; and $v_t = (8\theta/\pi m)^{1/2}$ is the mean thermal velocity of the vapor molecules [cm sec^{-1}]. Thus, we obtain a linear system

$$D_x^c \frac{2\sigma s_c}{9\theta} x_a + D_x^c \frac{2\sigma s_c}{9\theta} \frac{\delta - \omega}{\omega} y_a = -\lambda x_a$$

$$D_x^c N_v^c \frac{\delta - \omega}{\omega} x_a + D_x^c N_v^c \frac{1 + \omega}{\omega} y_a = \lambda y_a$$

On solving this system, we obtain an expression for the negative root of Eq. (22),

$$\lambda = -\frac{3\beta v_t}{8r_c} \{[(1 - \chi + \omega)^2 + 4\chi]^{1/2} - (1 - \chi + \omega)\} \tag{23}$$

where $\chi \equiv b\omega/3 = 2\sigma/3\beta v_t \eta$ is a dimensionless parameter. For $\omega \lesssim \delta^2$ the problem is markedly complicated because of the necessity of taking into account the inertia terms in Eq. (B5), and this lies outside the scope of the present paper.

The proper eigenvector $\mathbf{a} = (x_a, y_a)$ corresponding to the given root λ has the form

$$\mathbf{a} = \kappa\left(1, \frac{\omega}{\omega - \delta}\left[1 + \frac{2r_c\eta}{\sigma}\lambda\right]\right) \tag{24}$$

In (x, y)-coordinates the pass point (1, 1) is invariable for all the physical values of the parameters r_c, η, and p_c; still, the direction a indicating the steepest descent n_{xy}/φ_{xy} depends, via λ, on all the physical parameters of the problem (see Fig. 1). In the limiting case of a nonvolatile liquid ($p_c \to 0$, $\omega \to 0$), we have $\lambda \to -\sigma/2r_c\eta$ and $\mathbf{a} \to \kappa(1, 0)$, coinciding with the x axis. In the case of $(2r_c\eta/\sigma)\lambda \to \infty$, $\mathbf{a}$ becomes antiparallel to the y axis.

On the basis of the normalizing condition (21a),

$$\kappa^2\left(1, \frac{\omega}{\omega - \delta}\left[1 + \frac{2r_c\eta}{\sigma}\lambda\right]\right) \times \begin{pmatrix} D_x^c & D_x^c \frac{\delta - \omega}{\omega} \\ D_x^c \frac{\delta - \omega}{\omega} & D_x^c \frac{1 + \omega}{\omega} \end{pmatrix} \begin{pmatrix} 1 \\ \frac{\omega}{\omega - \delta}\left[1 + \frac{2r_c\eta}{\sigma}\lambda\right] \end{pmatrix} = 1$$

we find the value of κ, which is equal to

$$\kappa = \frac{1}{(D_x^c G)^{1/2}}, \qquad G \equiv \frac{\omega(1 + \omega)}{(\omega - \delta)^2}\left(1 + \frac{2r_c\eta\lambda}{\sigma}\right)^2 - \frac{4r_c\eta\lambda}{\sigma} - 1 > 0 \tag{25}$$

From Eqs. (24) and (25), we find the modulus **a**, which is equal to

$$a = \left\{ \frac{1}{D_x{}^c G} \left[1 + \frac{\omega^2}{(\omega - \delta)^2} \left(1 + \frac{2r_c\eta\lambda}{\sigma} \right)^2 \right] \right\}^{1/2} \tag{26}$$

To find the nucleation probability v in the volume V per unit time requires integrating **Q** along the axis passing through the pass point and perpendicular to the vector $\mathbf{Q} \sim \hat{D}_c\mathbf{a}$ and dividing the result, according to Eq. (14), by g_0.

Yet, since $\operatorname{div} \mathbf{Q} = 0$, the integration result does not depend on the direction of the axis chosen. It would be more convenient to integrate **Q** along the axis perpendicular to vector **a**. Then $\Delta\mathbf{r} \equiv \Delta z \cdot \mathbf{n}_0$ and $(\mathbf{an}_0) = 0$, where

$$\mathbf{n}_0 = \tilde{\kappa}\left(\frac{\omega}{\delta - \omega} \left[1 + \frac{2r_c\eta\lambda}{\sigma} \right], 1 \right) \tag{27}$$

is the unit vector which is perpendicular to **a**. From the condition $n_0 = 1$, we find

$$\tilde{\kappa} = \left\{ 1 + \frac{\omega^2}{(\delta - \omega)^2} \left[1 + \frac{2r_c\eta\lambda}{\sigma} \right]^2 \right\}^{-1/2} \tag{28}$$

Taking into account Eqs. (14), (19), and (21a), we obtain

$$\begin{aligned} v &= \frac{1}{g_0} \int_{-\infty}^{\infty} \mathrm{Q}_n \, \mathrm{d}(\Delta \mathrm{z}) = \frac{1}{g_0} \int_{-\infty}^{\infty} \frac{(\mathbf{aQ})}{a} \, d(\Delta z) \\ &= \frac{V v_c \rho_l{}^2}{2\pi a} (-\lambda N_v{}^c)^{1/2} \exp(-\Psi_c) \\ &\quad \times \int_{-\infty}^{\infty} \exp\left\{ -\frac{(\Delta z)^2}{2} (\mathbf{n}_0{}' \hat{A} \mathbf{n}_0) + \lambda \, \Delta z (\mathbf{an}_0)^2 \right\} (\mathbf{a}\hat{D}\mathbf{a}) \, d(\Delta z) \\ &= \frac{V v_c \rho_l{}^2}{a} \left[\frac{-\lambda N_v{}^c}{2\pi(\mathbf{n}_0{}' \hat{A} \mathbf{n}_0)} \right]^{1/2} \exp(-\Psi_c) \end{aligned} \tag{29}$$

where

$$\mathbf{n}_0{}' \hat{A} \mathbf{n}_0 = \tilde{\kappa}^2 N_v{}^c \left[1 - \frac{\omega^2}{(\omega - \delta)^2} \frac{b}{3} \left(1 + \frac{2r_c\eta\lambda}{\sigma} \right)^2 \right] > 0 \tag{30}$$

at any values of r_c, η, p_c.

Substituting Eqs. (23), (26), (28), and (30) into Eq. (29), we obtain an expression for the nucleation probability per unit time:

$$v = D_x{}^c \varphi_{xy}^c \left(\frac{MG}{2\omega L} \right)^{1/2} = V \rho_l{}^2 r_c \left(\frac{3\beta v_t \theta}{16\eta} \frac{MG}{L} \right)^{1/2} \exp(-\Psi_c) \tag{31}$$

where

$$M \equiv -\frac{8r_c\lambda}{3\beta v_t} = [(1-\chi+\omega)^2 + 4\chi]^{1/2} - (1-\chi+\omega) \geqslant 0$$

$$G \equiv \frac{\omega(1+\omega)}{(\omega-\delta)^2}\left(1 - \frac{M}{2\chi}\right)^2 + \frac{M}{\chi} - 1 > 0$$

$$L \equiv 1 - \frac{b}{3}\frac{\omega^2}{(\omega-\delta)^2}\left(1 - \frac{M}{2\chi}\right)^2 > 0$$

It is exactly formula (31) that defines the expression for the probability of the formation of a critical bubble in the volume V per second.

This expression is valid for the steady-state process of the homogeneous boiling up of a volatile liquid which is either under tension or superheated, far from the critical point, within the entire range of the viscosity and volatility of the liquid at not too great a supersaturation of the system. The influence of the inertial properties of the liquid and of the thermal relaxation at the "bubble–liquid" interface may be taken into account, following Ref. 19, by modifying the diffusion tensor $\hat{D}$ [see (22)] without changing the further procedure of deriving the final formula (31).

4. DISCUSSION OF THE RESULTS

The problem of the boiling up of a volatile liquid includes three physical parameters whose values determine the state of the system: the radius of a critical nucleus r_c, which is characteristic of the supersaturation of the system; the vapor pressure p_∞ over the flat surface of the liquid, which is characteristic of its volatility; and the viscosity of the liquid η. In this case, we disregard the influence of the vapor density on the surface tension σ. Writing Eq. (31) in the form

$$\begin{aligned} \nu &= V\rho_l^2 \exp\left[-\frac{\sigma s_c}{3\theta} + \frac{1}{2}\ln\left(\frac{MG}{L}\frac{3\beta v_t\theta r_c^2}{16\eta}\right)\right] \\ &= V\rho_l^2 \exp[-f_1(r_c) + f_2(r_c, p_c, \eta)] \end{aligned} \tag{32}$$

we see that $|f_2| > f_1$ if the viscosity and volatility of the liquid possess proper values. Thus, the criterion

$$\left|\ln\left(\frac{MG}{L}\frac{3\beta v_t\theta r_c^2}{16\eta}\right)\right| > \frac{2\sigma s_c}{3\theta} \tag{33}$$

determines the ranges of values r_c, p_c, and η where the preexponential factor influences the value ν more strongly than the work of critical nucleus formation. Several such ranges are revealed by considering the limiting cases of the nucleation problem, which are considered below. A thorough examination of the criterion (33) lies outside the scope of the present paper. In the process of solving the present problem, instead of three dimensional parameters r_c, p_∞, and η we have introduced three dimensionless parameters:

$$\delta \equiv \rho_v{}^c/\rho_l, \qquad b \equiv 2\sigma/r_c p_c, \qquad \chi \equiv 2\sigma/3\beta v_t \eta \tag{34}$$

where $p_c = p_\infty \exp(-2\sigma/\rho_l \theta r_c)$.

It is expedient to combine two of them into a dimensionless parameter ω:

$$\omega = 3\chi/b = p_c r_c/\beta v_t \eta \tag{35}$$

which contains all three dimensional parameters and facilitates the examination of the limiting cases of the problem. Let us examine various limiting values of the parameter ω, included in the final formula (31) through the factor MG/L.

To the limiting case $\omega \to 0$ there correspond the following limiting values of the physical parameters: $\eta \to \infty$, or $r_c \to 0$, or $p_c \to 0$. In the case of an infinitely viscous liquid $\lambda \to 0$, $D_x{}^c \to 0$, and $v \to 0$. The case of an infinitely high supersaturation of the system ($r_c \to 0$) cannot be examined within the scope of the present model, which is intended for small and moderate superheating and tensile stretching of the liquid.

For $p_c \to 0$, we pass over to the examination of a nonvolatile liquid. The process of cavitation in such a liquid was examined in Ref. 18. Examination of the shape (5) in coordinates (v, p) shows that one of the pass axes "rests" on the v axis, while the trough leading through the pass becomes infinitely narrow. Hence, the problem becomes one-dimensional, which corresponds to the setting value of one variable v of the nucleus. The expression (31) for the nucleation probability passes over into the limiting expression

$$\nu = (V\rho_l{}^2 r_c/2\eta)(\theta\sigma)^{1/2} \exp(-\Psi_c) \tag{36}$$

which coincides with formula (36) of Ref. 18.

Let us note that in terms of our symbols the corresponding expression (34) in Ref. 19 is equal to

$$\nu = \frac{\rho_v{}^c}{\rho_l} \frac{V\rho_l{}^2 r_c}{2\eta} (\theta\sigma)^{1/2} \exp(-\Psi_c)$$

that is, it underrates the result by a factor of $\rho_v{}^c/\rho_l$ and erroneously asserts the impossibility of nucleation in a nonvolatile liquid.

To the opposite limiting case $\omega \to \infty$ there correspond the following limiting values of the physical parameters: $r_c \to \infty$ or $\eta \to 0$. For the case $r_c \to \infty$ it is no longer a question of whether there is superheating of the liquid or an applied tension stress. In this case, the work of forming an infinitely great critical nucleus also will be infinitely great; i.e., the boiling up of the liquid becomes impossible.[4]

For $\eta \to 0$, we pass over to the examination of a nonviscous (ideal), volatile liquid. If the influence of the inertia of the liquid is disregarded in this region, then for the ideal liquid we obtain from (B8) the expression $\Delta y = -\frac{1}{3}b\,\Delta x$, i.e., a single-valued relationship of the variables x and y, which renders the problem one-dimensional.

From the physical point of view, this means that at any finite fluctuation of the pressure in the bubble its volume will instantaneously change in such a way that the bubble remains in mechanical equilibrium. Thus, in the process of its fluctuation growth the bubble always remains on the line (II) of mechanical equilibrium, which is guaranteed by an infinitely great value of $\hat{D}^c$. Taking into account the inertial properties of the liquid for $\eta \to 0$ destroys the rigid correlation between Δx and Δy, so that in the general case the nucleation problem remains two-dimensional for the ideal liquid, too. In this case, taking into account the inertia of the liquid will influence the probability of nucleation ν by changing the expression for $\hat{D}^c$ (see Appendix B).

To obtain quantitative results, we take into account (B7) and consider the region

$$\rho_l m\sigma/8\eta \ll \eta/r_c \ll p_c/\beta v_t \tag{37}$$

in which $\omega \gg 1$, but its value is not so great that the inertial properties of the liquid begin to exert their influence.

At $b/3 \gg 1$, which corresponds to a tension pressure $-P \gg 2p_c$, expression (31) reduces to the form

$$\nu = \frac{V\rho_l^2 r_c}{4\eta}(2\sigma - 3p_c r_c)\left(\frac{\theta}{\sigma}\right)^{1/2} \exp(-\Psi_c) \tag{38}$$

which passes over into expression (36) when we neglect $3/b$ as compared with 1. For $b/3 \ll 1$, which corresponds to positive and limited negative values of P, expression (31) becomes

$$\nu = \frac{\rho_l}{\rho_v^c}\frac{N_V\beta v_t}{2(1 - \frac{1}{3}b)}\left(\frac{\theta}{\sigma}\right)^{1/2} \exp(-\Psi_c) \tag{39}$$

On neglecting $b/3$, we find that this expression would differ from formula (36) in Ref. 19, by a factor ρ_l/ρ_v^c, if the temperature effects at the bubble interphase were not taken into account in that formula.

[4] It follows from (B7) that at $r_c \to \infty$ the influence of the inertia of the liquid on the value of the diffusion tensor will have to be taken into account.

For values $b/3$ near 1, the general formula (31) has to be applied, which, when $b/3$ passes through 1, remains continuous, without causing a nonphysical drop of the nucleation rate.

We have examined the limiting cases of the two-dimensional nucleation problem where, depending upon the numerical value of ω, one of the two parameters—the volatility or the viscosity of the liquid—is the determining one for the kinetics of formation of the new phase. Expression (35) for ω includes r_c, which is connected to the degree of supersaturation of the system. Hence, for any liquid the entire range of supersaturation of the system may be regarded as being made up of three regimes: volatile liquid ($\omega \gg 1$), when its viscosity may be neglected; viscous liquid ($\omega \ll 1$), when its volatility may be neglected; and an intermediate mode ($\omega \simeq 1$), when the liquid must be considered as being simultaneously viscous and volatile. Thus, in accordance with expression (35), in the case of strongly volatile liquids the intermediate mode is shifted to higher degrees of supersaturation, and in the case of strongly viscous liquids, to lower degrees of supersaturation.

It is a knowledge of the kinetic mode of the boiling up of a liquid that enables one to choose the desired form of preexponential factor. Otherwise, considerable errors are possible in the determination of the limit of superheating or tensile stressing of the liquid. Now, let us consider as an example the case of the boiling up of hexamethyldisiloxane (a liquid which is volatile and of low viscosity under ordinary conditions). If in this case the limit of the liquid tension is calculated by formula (39) corresponding to the limiting case of a low-viscosity volatile liquid, which would seem to be appropriate at first glance, then we obtain $P_{\text{lim}} \simeq -136$ atm. However, the calculation of ω shows that the liquid tension limit is attained at $\omega \ll 1$: this corresponds to the opposite limiting case of a very viscous nonvolatile liquid. Hence, the calculation ought to be performed by formula (36); this gives the liquid tension limit $P_{\text{lim}} \simeq -143$ atm, which differs from the aforementioned, incorrect value by about 5%.

In this case, the probability of nucleation at $P_{\text{lim}} \simeq -136$ atm varies from 3 sec^{-1} [according to formula (39)] to 8×10^{-4} sec^{-1} [according to formula (36)], that is, by four orders of magnitude. By the way, if the limit of the extension of liquid is calculated according to the correct mode ($\omega \ll 1$), but by the erroneous formula (36) of Ref. 19, it will be equal to -151 atm. Thus, the scatter among various erroneous values of the extension limit is about 10%.

The coefficient of evaporation β may also exert a substantial influence on the preexponential factor and, hence, the nucleation rate. For pure liquids, however, it usually varies but slightly and is close to unity (probably, under especially pure conditions, it may be close to 1 even for water). However, if liquid contains surfactants of the type of medium aliphatic alcohols, these, on being adsorbed on subcritical nuclei and forming a dense monolayer, can reduce β by many orders of magnitude. Thus, for example, cetyl alcohol (which exhibits a very low solubility in water) can reduce β to a value of the order of 10^{-5} by the formation of a monolayer on the water surface.(22,23)

In this case, a reduction in the preexponential factor may outweigh the growth of the exponent due to a decrease in the work of formation of the critical nucleus. That such an effect is real follows from the observation that adding a surfactant to toluene(24) prevents the evolution of the water dissolved in toluene as the temperature decreases.

5. CONCLUSIONS AND SUMMARY

A macroscopic examination of the kinetics of the boiling up of a volatile liquid suggests the necessity of characterizing the nucleus of a new phase, not by one, but by two variables—the volume v of a bubble and the pressure of vapor in it p.

In this case, the fluctuation growth of a vapor-containing bubble should be treated as the two-dimensional diffusion of a nucleus in the plane (v, p). Superimposed on this plane is the shape of the free energy surface of the system "liquid plus bubble with vapor," depending on the degree of superheating or that of the tensile stretching of the liquid, which are supposed in the present work to be not too high.

On examining the potential shape on the plane (v, p), it appears that the labile equilibrium point of the system is actually the top of a saddle-type pass leading from the region of heterophase fluctuations to the two-phase region. Differential equations have been derived for the watershed line between these two regions, and for the path of the fluctuation growth of a subcritical nucleus which is the most advantageous from energy considerations. The latter line is compared with the mechanical and the thermodynamic equilibrium lines of the nucleus. The influence of a variation in the mean curvature of the free energy surface at the pass point on the pass width and the probability of nucleation is considered. A two-dimensional nucleus distribution function with respect to its variables has been derived. We have also calculated a nondiagonal diffusion tensor in the space (v, p) close to the pass by using the joint approximate solution of the phenomenological equations of dynamics of variations in the bubble volume and in the number of molecules of vapor in it.

A two-dimensional equation of the kinetics of the formation of a new phase of the Kramers type is suggested to solve the problem of the boiling up of volatile liquids.

This equation has been solved for the steady-state case; and a general expression (31) has been derived for the probability of homogeneous nucleation in a given volume per unit time for any volatility and viscosity of a liquid far from its critical point, for not too great tensile stretching or superheating. Various limiting cases have been considered, and errors in the work of other authors have been corrected. A dimensionless parameter ω is introduced, allowing the entire range of superheating or tension of an arbitrary liquid to be subdivided into three regimes: the boiling up of a low-volatility viscous liquid; the boiling up of a low-viscosity, volatile liquid; and an intermediate mode.

A criterion (33) has been established allowing the regions of the values of viscosity, volatility, and degree of superheating or tensile stretching of the liquid to be determined in which the preexponential factor influences the probability of the boiling up of the liquid to a greater extent than the work of formation of the critical nucleus, which is included in the exponent.

APPENDIX A

In Section 3 it was pointed out that in the nucleation process each state of the volume V is characterized by four variables: the energy $E_{nN}(v, p)$ of the volume V, the number of molecules N in this volume, the volume of the bubble v, and the pressure of vapor p in the bubble. The last two variables have a physical sense only for states containing quasi-macroscopic nuclei of a new phase.

At small and moderate supersaturations of the system, the region of heterophase fluctuations and the two-phase region of the four-dimensional space (E, N, v, p) are divided by a high-energy "ridge." In such a case, in order to calculate the flux of states of V from the first region to the second one, there is no need to examine in detail the growth of the new-phase nucleus, including its microscopic stage. It is quite sufficient to examine, on the one hand, states close to the metastable equilibrium of the system, i.e., states of a homogeneous liquid being superheated or under tension, and, on the other hand, states close to the labile equilibrium of the system, containing a macroscopic, near-critical bubble.

We will consider that the near-metastable states correspond to values $v = p = 0$,[5] i.e., they are described by only two variables, E and N, in contrast to the near-labile states. The probability that such a near-labile state of the volume V is in the nth quantum state having energy E_{nN} and comprises N molecules of liquid (in the single-phase state of the surrounding medium $W - V$) is equal to(18)

$$w_{nN} = C \exp\{(1/k)S[E_0' - \Delta E, N_0' - \Delta N]\} \tag{A1}$$

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[5] The presence of microscopic nuclei influences the value of the chemical potential of the homogeneous liquid.

where C is the usual normalizing factor, which is constant for the given reservoir $W - V$, independent of the states of volume $V \ll W$; k is the Boltzmann constant; S is the entropy of the medium $W - V$ in the state corresponding to the given state of V; E_0' and N_0' are the energy and the number of molecules of volume $W - V$, respectively, in the state of equilibrium with the metastable state of volume V, which is characterized by E_0 and N_0; $\Delta E = E_{nN} - E_0$; $\Delta N = N - N_0$; the subscript zero characterizes the metastable state.

Expanding S in Eq. (A1) in a power series with respect to powers of ΔE and ΔN close to the metastable state, and then summing w_{nN} with respect to n and N, we find the total probability that the volume V has no macrobubbles, i.e., it is found near the point ($v = 0$; $p = 0$):

$$g_0 = \sum_{n,N} w_{nN} = A_0 \sum_{N} \exp \frac{\mu_l^0 \, \Delta N - \Delta F_N^0}{\theta} \tag{A2}$$

where $A_0 = C \exp[(1/k)S_0]$, and μ_l^0 is the chemical potential of the liquid in volume W at the metastable state of volume V; $\Delta F_N = F_N - F_N^0$ is the change in the free energy F_N of volume V as compared with its metastable state; S_0 is the full entropy of volume W when volume V is in the metastable state.

In considering the probability of near-labile states V, let us try to separate out an expression similar to Eq. (A2). This is necessary in order to find the change in the total probability of the states of volume V when it is passing over from the metastable state into the labile state.

In accordance with Ref. 21, the probability $dw_{nN}(v, p)$ of such a state of V being in the nth quantum state with energy $E_{nN}(v, p)$, comprising N molecules of liquid, and having bubble volume and pressure within the ranges $(v, v + dv)$ and $(p, p + dp)$, respectively, is equal to

$$dw_{nN}(v, p) = C \exp[(1/k)S(E_c' - \Delta E_c, N_c' - \Delta N_c)] \, dv \, dp \tag{A3}$$

where C is the normalizing factor introduced earlier; S is the entropy of the medium $W - V$ in the state corresponding to the given state of volume V; E_c' and N_c' are the energy and the number of molecules of the medium $W - V$, respectively, in the state corresponding to the labile equilibrium state V; $\Delta E_c = E_{nN}(v, p) - E_c$ and $\Delta N_c = N - N_c$ are the variations in the energy and in the number of molecules of volume V as compared with the labile equilibrium state; c is the index characteristic of the labile equilibrium state.

By expanding S in Eq. (A3) with respect to powers of ΔE and ΔN close to the labile equilibrium state and then summing $dw_{nN}(v, p)$ over n and N, we obtain, as in Ref. 18, the probability $dw(v, p)$ that the volume V contains a macroscopic bubble having a volume within the range $(v, v + dv)$ with a vapor pressure within the range $(p, p + dp)$:

$$dw(v, p) = \sum_{n,N} dw_{nN}(v, p) = A_c \rho_l \frac{v_c}{\theta} \sum_N \exp \frac{\mu_l^c \, \Delta N_c - \Delta F^c_{Nvp}}{\theta} \, dv \, dp \quad \text{(A4)}$$

where $A_c = C \exp[(1/k)S_c]$, $\rho_l v_c/\theta$ is the value of the Jacobian $\partial(N_l, N_v)/\partial(v, p)$ of the transition from the dimensionless space of variables (N_l, N_v) to the dimension space (v, p), and N_v is the number of vapor molecules in a bubble having volume v with pressure p; N_l is the number of liquid molecules filling the bubble of volume v at a constant ρ_l; μ_l^c is the chemical potential of the liquid in W at the labile state of V; $\Delta F^c_{Nvp} = F_{Nvp} - F^c_{Nvp}$ is the change in the free energy of the system "liquid plus bubble with vapor" in volume V as compared with the labile equilibrium state; and S_c is the total entropy of volume W at the labile state of V.

In the expression for F_{Nvp}, it is important to separate out the terms that do not depend on N and remove them from the sum over N. For this purpose, we consider the system "liquid plus bubble with vapor" as a diluted solution of bubbles in a liquid. In accordance with the thermodynamics of solutions, the free energy of our system is equal to$^{(21)}$

$$F_{Nvp} \simeq F_N + F_{vp} + \theta \ln(1/N) \quad \text{(A5)}$$

where F_N is the bulk free energy of N molecules in volume $(V - v)$, F_{vp} is the free energy of a bubble characterized by v and p, and the third term takes into account the entropy of "mixing" the bubble and the liquid.

Then

$$\Delta F^c_{Nvp} = \Delta F_N^c + \Delta F^c_{vp} - \theta \ln(N/N_V^c) \quad \text{(A6)}$$

where N_V^c is the number of liquid molecules in volume $(V - v_c)$. In that case, the logarithmic term may be neglected in view of the fact that we try to determine ΔF^c_{Nvp} only in the neighborhood of the labile equilibrium point.

Substituting Eq. (A6) into Eq. (A4), we obtain

$$dw(v, p) = g_c \rho_t \frac{v_c}{\theta} \exp\left(-\frac{\Delta F^c_{vp}}{\theta} \right) dv \, dp \quad \text{(A7)}$$

where

$$g_c = \sum_{n,N} w^c_{nN} = C \exp \frac{S_c}{k} \sum_N \exp \frac{\mu_l^c \, \Delta N_c - \Delta F_N^c}{\theta} \quad \text{(A8)}$$

In comparing g_c with g_0, we shall, taking into account the inequality (1), as well as the fact that the temperature θ and the supersaturation of the system are invariable, neglect the difference between $V - v$ and V; we shall also assume $\mu_l^c \simeq \mu_l^0$. We also assume that the existence of a nucleus in volume V practically does not change the fluctuations of the number of molecules ΔN and of the free energy ΔF_N of volume V. Then, on substituting Eq. (A2) into Eq. (A8), we obtain

$$g_c \simeq g_o \exp(\Delta S/k) \qquad \text{(A9)}$$

where $\Delta S = S_c - S_0$ is the increase in the entropy of the volume that takes place when V passes over from the metastable state of the uniform liquid into the unstable state of the system "liquid plus bubble," which is the thermodynamic characteristic of the process of formation of the new phase.

With the volume W isolated, the increase in entropy ΔS is equal to the change in the system free energy ΔF_{Nvp} when the critical nucleus forms divided by the absolute temperature T.

Using Eq. (A5), we obtain

$$\frac{\Delta S}{k} = -\frac{\Delta F_{Nvp}}{\theta} = -\frac{F_N{}^c + F_{vp}^c + \theta \ln(1/N_V) - F_N{}^0}{\theta} \simeq -\frac{F_{vp}^c}{\theta} + \ln N_V \qquad \text{(A10)}$$

Substituting Eqs. (A9) and (A10) into Eq. (A7), we obtain

$$dw(v, p) = \varphi(v, p)\, dv\, dp = g_0 N_V \rho_l \frac{v_c}{\theta} \exp\left(-\frac{F_{vp}}{\theta}\right) dv\, dp \qquad \text{(A.11)}$$

We assume that the appearance of a macronucleus in V does not practically change the fluctuation of the number of particles nor that of the energy of volume V. Thus, we arrive at the conclusion that the variables E and N, which along with v and p are characteristic of the state of volume V, are almost an invariable "background" that accompanies the new-phase formation in V. Therefore, we may pass over from the four-dimensional space (E, N, v, p) to the two-dimensional space of the nucleus variables; each point (v, p) of that space corresponds to the sum taken over n and N of all possible states (E, N, v, p) having fixed v and p.

In that case, the probability density $\varphi(v, p)$ is an equilibrium bubble distribution function with respect to the variables v and p, which is connected to the shape of the free energy of the system.

Passing over to the dimensionless variables $x \equiv v/v_c$, $y \equiv p/p_c$, $\Psi \equiv F_{vp}/\theta$, we obtain in the space (x, y)

$$dw(x, y) = \varphi_{xy}\, dx\, dy = g_0 N_V N_l^c N_v^c \exp[-\Psi(x, y)]\, dx\, dy \qquad \text{(A12)}$$

where $N_l^c = v_c \rho_l$ and $N_v{}^c = v_c \rho_v{}^c$.

APPENDIX B

To find the diffusion tensor in any diffusion problem one must know the forces that are applied to the system, as well as the velocity at which it moves under the effect of those forces. Zeldovich gave such a formulation of the nucleation problem, in which the forces applied to the system are given by the equilibrium distribution function φ_{xy}, which determines the potential shape $\Psi(x, y)$ in the space (x, y):

$$\mathrm{F} = \mathrm{grad}(\ln \varphi_{xy}) = -\mathrm{grad}\, \Psi(x, y) \tag{B1}$$

The velocity $\dot{x} \equiv \dot{v}/v_c$ is found from a phenomenological equation of the radial motion of the surface of a growing bubble at rest, while $\dot{y} \equiv \dot{p}/p_c$ is found from an equation defining the vapor mass balance in the bubble. The surface of the bubble moves at a velocity $\dot{\mathbf{r}}$, while the liquid adjoining the surface moves at a rate $\mathbf{u}(\mathbf{r})$. The difference in the velocities causes a mass flow, $4\pi r^2 m\rho_l[\dot{\mathbf{r}} - \mathbf{u}(\mathbf{r})]$, which must be equal to the liquid evaporation rate in the bubble.

Thus, the mass balance written for the bubble surface yields(25)

$$\frac{d(mN_v)}{dt} = \frac{d}{dt}\left(\tfrac{4}{3}\pi r^3 m\rho_v\right) = 4\pi r^2 m\rho_l[\dot{r} - u(r)] \tag{B2}$$

whence, taking into account the continuity equation for a noncompressible liquid, it follows that

$$u = \left(\frac{r}{R}\right)^2 \left(\dot{r} - \frac{\dot{N}_v}{4\pi r^2 \rho_l}\right) \tag{B3}$$

where R is the radius vector of an arbitrary point of the liquid, drawn from the bubble center.

To derive the equation of motion of the bubble surface we use the Navier–Stokes equation. In the case of the spherical symmetry of the bubble, a noncompressible Newtonian liquid, and the absence of external mass forces, that equation reduces to the form(25)

$$m\rho_l \frac{\partial u}{\partial t} + \rho_l m u \frac{\partial u}{\partial r} = \frac{\partial p_{rr}}{\partial r} - 2\eta \frac{\partial^2 u}{\partial r^2} \tag{B4}$$

where p_{rr} is the radial component of the radial pressure.

Substituting expression (B3) into this equation and integrating it over the radius between the bubble surface and infinity, we obtain

$$\begin{aligned} m\rho_l r\ddot{r} + \tfrac{3}{2} m\rho_l \dot{r}^2 - m\rho_l r^2 \frac{\ddot{M}_v}{M_r} + \frac{m\rho_l r^2}{2}\left(\frac{\dot{M}_v}{M_r}\right)^2 \\ = -P + p - \frac{2\sigma}{r} - 4\eta \frac{\dot{r}}{r} + 4\eta \frac{\dot{M}_v}{M_r} \end{aligned} \tag{B5}$$

Here $M_r = 3M_l = 4\pi r^3 \rho_l m$ is the effective mass of an expanding bubble, which has been introduced by analogy with Ref. 26, and which is equal to three times the mass M_l of liquid in the bubble volume; $M_v = mN_v$ is the mass of vapor in the bubble. Equation (B5) differs from the "generalized Rayleigh equation"(26) in that it includes terms describing a change in the mass of vapor M_v in the bubble with time.

Close to the pass point, the difference between the pressure of the vapor p in the bubble and that of the saturated vapor p_r in the bubble is small; thus, the rate of variation in the vapor mass in the bubble, calculated on the basis of the vapor mass balance for the bubble, may be represented in the form

$$\dot{M}_v = \frac{\pi\beta v_t r_c{}^2 m}{\theta}[p_r - p] \approx \frac{3\pi\beta v_t r_c p_c m}{\theta}\left(1 + \frac{b}{3}\frac{\rho_v{}^{\infty}}{\rho_l}\right)\Delta r - \frac{3\beta v_t}{4r_c}\Delta M_v \qquad \text{(B6)}$$

where p_r is related to the saturated vapor pressure over the flat surface p_∞ by Kelvin's formula:

$$p_r = p_\infty \exp(-2\sigma/\rho_l\theta r) \qquad \text{(B7)}$$

Since a fairly steep pass is present in the problem, the problem of calculating the diffusion tensor as a function of v and p can be replaced by the simpler problem of calculating it in the neighborhood of the pass, where small forces F_x and F_y and rates $\dot{x}$ and $\dot{y}$ may be regarded as linear with respect to Δx and Δy:

$$F_x = -\partial\Psi/\partial x = -\Delta x/R_x\,, \qquad F_y = -\partial\Psi/\partial y = -\Delta y/R_y \qquad \text{(B8)}$$

Neglecting terms in Eq. (B5) with $\dot{r}^2$ and $\dot{M}_v{}^2$ and taking into account that $\ddot{r} = \dot{r}\, d\dot{r}/dr$ and $\ddot{M}_v = \dot{M}_v\, d\dot{M}_v/dM_v$, we obtain

$$\left(\frac{4\eta}{r_c} + \rho_l m r_c \frac{d\dot{r}}{dr}\right)\dot{r} \simeq \Delta p + \frac{2\sigma}{r_c{}^2}\Delta r + \frac{4\eta\dot{M}_v}{M_r}\left(1 - \frac{3\beta v_t r_c \rho_l m}{16\eta}\right) \qquad \text{(B9)}$$

It is easy to show from Eq. (B5), that the criteria of smallness of the inertial terms are[6]

$$In_v = 3\beta v_t r_c \rho_l m/16\eta \ll 1 \qquad \text{(B10)}$$

$$In_l = \rho_l m \sigma r_c/8\eta^2 \ll 1 \qquad \text{(B11)}$$

The value

$$\chi = In_l/In_v = 2\sigma/3\beta v_t \eta \qquad \text{(B12)}$$

determines the relative importance of the inertial properties of liquid and gas.

From Eqs. (B10) and (B11) it follows that for a fairly low viscosity or superheating of the liquid, the inertial terms will have to be taken into account. To take into account the inertial terms, however, it is not enough to

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[6] The criterion (B11) practically coincides with a similar criterion (35) of Ref. 19.

introduce corrections to the generalized diffusion tensor $\hat{D}$ as was done in Ref. 19. The appropriate means of taking into account the inertia of the liquid for the case $In_l \gtrsim 1$ was carried out in Ref. 27.

For the sake of simplicity, we shall disregard the inertia term. Taking into account Eq. (B7), we transform Eqs. (B9) and (B6) in the following manner:

$$\dot{r} \approx \frac{\sigma}{2r_c\eta}\,\Delta r + \frac{r_c}{4\eta}\left(1 - \frac{\rho_v{}^c}{\rho_l\omega}\right)\Delta p, \qquad \dot{M}_v \approx \frac{2\pi\beta v_t m\sigma\rho_v{}^\infty}{\rho_l\theta}\,\Delta r - \frac{m\pi\beta v_t r_c{}^2}{\theta}\,\Delta p$$

or passing over to coordinates x and y, we obtain

$$\dot{x} \approx \frac{3p_c}{4\eta}\left(\frac{b}{3}\,\Delta x + \frac{\omega - \delta}{\omega}\,\Delta y\right) \tag{B13}$$

$$\dot{y} \approx \frac{3\beta v_t}{4r_c}\left[\frac{b}{3}(\delta - \omega)\,\Delta x - (1 + \omega)\,\Delta y\right] \tag{B14}$$

To derive the relationship between the forces and the velocities determining the tensor $\hat{D}$, we use Eqs. (15)–(15a); we consider the tensor $\hat{D}$ and the forces as functions that vary in the neighborhood of the pass much more slowly than do n_{xy} and grad n_{xy}. Thus, we reduce Eqs. (15)–(15a) to the following form:

$$\begin{aligned}\frac{\partial n_{xy}}{\partial t} &= -(D_x{}^cF_x + D^c_{xy}F_y)\frac{\partial n_{xy}}{\partial x} - (D_y{}^cF_y + D^c_{yx}F_x)\frac{\partial n_{xy}}{\partial y}\\ &\quad + D_x{}^c\frac{\partial^2 n_{xy}}{\partial x^2} + D_y{}^c\frac{\partial^2 n_{xy}}{\partial y^2} + (D^c_{xy} + D^c_{yx})\frac{\partial^2 n_{xy}}{\partial x\,\partial y}\end{aligned} \tag{B15}$$

On writing this diffusion equation in the external field in the form of a Fokker–Planck equation

$$\frac{\partial n_{xy}}{\partial t} = -\dot{x}\frac{\partial n_{xy}}{\partial x} - \dot{y}\frac{\partial n_{xy}}{\partial y} + D_x{}^c\frac{\partial^2 n_{xy}}{\partial x^2} + D_y{}^c\frac{\partial^2 n_{xy}}{\partial y^2} + (D^c_{xy} + D^c_{yx})\frac{\partial^2 n_{xy}}{\partial x\,\partial y}$$

we derive the following system of equations

$$D_x{}^cF_x + D^c_{xy}F_y = \dot{x}, \qquad D^c_{yx}F_x + D_y{}^cF_y = \dot{y} \tag{B16}$$

Substituting Eqs. (B8), (B13), and (B14) into Eq. (B16), we obtain the system of equations

$$D_x{}^c\,\frac{2\sigma s_c}{9\theta}\,\Delta x - D^c_{xy}N_v{}^c\,\Delta y = \frac{b}{3}\frac{3p_c}{4\eta}\,\Delta x + \frac{3p_c}{4\eta}\frac{\omega - \delta}{\omega}\,\Delta y$$

$$D^c_{yx}\,\frac{2\sigma s_c}{9\theta}\,\Delta x - D_y{}^cN_v{}^c\,\Delta y = \frac{b}{3}\frac{3\beta v_t}{4r_c}(\delta - \omega)\,\Delta x - \frac{3\beta v_t}{4r_c}(1 + \omega)\,\Delta y$$

Equating the coefficients at Δx and at Δy, we obtain the value of the diffusion tensor $\hat{D}$ at the pass point

$$\hat{D}^c = \begin{pmatrix} D_x^c & D_x^c(\delta - \omega)/\omega \\ D_x^c(\delta - \omega)/\omega & D_x^c(1 + \omega)/\omega \end{pmatrix} \tag{B17}$$

where

$$D_x^c = 3\theta/4v_c\eta$$

From the criteria $\omega \ll 1$ and $\delta \ll 1$ it is possible to determine the relationship of the viscosity, volatility, and the superheating of the liquid for which the nondiagonal form of $\hat{D}$ may be neglected. For example, low-volatility or very viscous liquids correspond to such a situation.

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