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Statistical thermodynamics of formation of a new phase. II. Theory of boiling of volatile liquids

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The fluctuating growth of a vapor-filled macroscopic bubble in a moderately superheated or decompressed volatile liquid is treated as two-dimensional diffusion of a germ of a new phase in the space of its variables, viz., the volume v and the pressure p of the vapor in it. The relief of the free energy of a s "liquid + bubble with vapor" over the (v, p) plane is investigated in the vicinity of the labile equilibrium of the system, and the two-dimensional equilibrium distribution function of the germs with respect to their variables is determined. The nondiagonal diffusion tensor in (v, p) space near the saddle point is also calculated. A two dimensional stationary equation of the Kramers-Zel'dovich type of the kinetics of formation of a new phase is solved and an expression is obtained for the probability of homogeneous nucleation at arbitrary viscosity and volatility of the liquid far from its critical point. Various limiting cases are considered.

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1. INTRODUCTION

The analysis of the kinetics of formation of a new phase[1–8] has led to the development of a new method of describing the kinetics of a first-order phase transition in which the growth of a macroscopic germ of a new phase is treated as diffusion over the germ-size axis. The difference between the equation of the kinetics of new-phase formation (the Fokker-Planck equation) and the ordinary diffusion equation lies in the fact that the germ-size axis is not homogeneous: a certain force field is superimposed on it and is governed by the "supersaturation" of the investigated system. A natural macroscopic model of the kinetics of new-phase formation is therefore diffusion in the field of external forces.

The task of determining the rate of formation of the new phase in this approach breaks up into two stages: (a) determination of the coefficient of diffusion of the germ over the size axis as a function of the germ size; (b) determination and investigation of the "potential relief" on this axis, the relief being specified by the position of the system on the Van-der-Waals diagram in its metastable region. We make use here essentially of the fact, first pointed out by Gibbs, that the potential relief on the size axis is a potential barrier that separates the quasi-single-phase region of the size axis from the two-phase region. It is the diffusion flux from one region to the other which determines the kinetics of new-phase formation. Both stages of the solution of the nucleation problem become much more complicated if a single variable no longer suffices for a macroscopic description of the new-phase germ. This is the situation with a boiling volatile liquid, where two parameters characterize the macroscopic bubble, its volume v and the vapor pressure p in it. This can also be the case for non-isothermal condensations (where the parameters are v and the temperature Θ), as well in some other problems.

Stage (a) is made complicated by the fact that if we have several variables the diffusion coefficient D is in the general case a nondiagonal tensor. In stage (b), before we seek the flux of the germs from the quasi-one-dimensional region to the two-phase region it is necessary first to investigate the potential relief on the plane of the two variables, but it is impossible to state beforehand how this relief separates the quasi-one-dimensional region on the plane of the germ variables from the two-phase region.

We consider in this paper the boiling of a volatile liquid, regarded as the process of diffusion of a germ bubble in the space of its two variables v and p. The analysis is based on a method proposed by a number of workers,[5,7,8] and on an approach developed by one of us,[9] which makes it possible to calculate accurately the bubble equilibrium distribution function. Just as in[9], the analysis is restricted to moderate decompression or superheating of the liquid, corresponding to a high potential barrier between the quasi-single-phase and the two-phase regions.

We consider first the physical formulation of the problem. We isolate in a large liquid volume W with rigid adiabatic walls a small part (having volume V) bounded by a semi-permeable shell with pores of a size that prevents passage of near-critical bubbles. The volume V must satisfy here the relation

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

where v_c is the volume of the critical bubble. The problem is to calculate the probability ν [sec^{-1}] of formation of one transcritical vapor-filled bubble in the volume V per unit time under the condition that the "medium" $W - V$ is in a single-phase state. The probability of simultaneous existence of several near-critical bubbles in the volume V will be neglected.

2. ANALYSIS OF THE RELIEF OF THE SADDLE

The dynamics of the variation of the state of a real bubble in a volatile liquid is quite complicated. For example, apart from the fact that this bubble is not in thermodynamic equilibrium with the surrounding liquid and that there is no mechanical equilibrium between the external pressure, the capillary pressure, and the vapor pressure in the bubble, we must consider also the inhomogeneities of the pressure p and of the temperature Θ inside the bubble, the variation of the temperature on the bubble boundary with changing number of molecules in the bubble, the ambiguities in the variation of the bubble shape at constant volume, and others.

We assume the macroscopic bubble to be spherical. The temperature effects on the bubble boundary, which are accounted for by introducing a correction in the diffusion coefficient,[10] will not be considered here. As to the inhomogeneities of p and Θ in the bubble, we shall neglect both, assuming that the characteristic times of establishment of hydrodynamic and thermodynamic equilibrium inside the bubble are much shorter than the times of variation of the bubble dimensions and of the number of vapor molecules in it. Therefore the pressure p at any instant of time will be connected with the number N of molecules in the bubble by the equation of state of an ideal gas

$$pv = N_v\Theta. \tag{2}$$

The use of this equation means, besides the statements made above, that we assume that $\delta \equiv \rho_v/\rho_l \ll 1$, where ρ_v and ρ_l are the vapor and liquid densities in cm^{-3}. The temperature Θ [ergs] will be assumed to remain constant in the course of the nucleation, by virtue of the condition (1) and the large heat capacity of the liquid.

We 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) which is the reason for the appearance of the second variable p of the bubble.

The free energy of a spherical bubble of volume v containing N_v vapor molecules and situated in a liquid with temperature Θ at a pressure P is equal to the minimum work required for its formation:

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

Taking into consideration the condition for 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 (3) into

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

where p_c is the saturated-vapor pressure in the critical bubble. Going over to the dimensionless variables $x = v/v_c$, $y = p/p_c$, $\Psi = F_{vp}/\Theta$ and expanding $\Psi(x, y)$ near the point (1, 1) (see Fig. 1) corresponding to the state of labile equilibrium of a "liquid + bubble with vapor" system in the volume V in powers of $\Delta x = x - 1$, $\Delta y = y - 1$ up to second order inclusive, we obtain

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

where

$$\hat{A} = \begin{pmatrix} \left.\dfrac{\partial^2\Psi}{\partial x^2}\right|_c & \left.\dfrac{\partial^2\Psi}{\partial x\,\partial y}\right|_c \\ \left.\dfrac{\partial^2\Psi}{\partial y\,\partial x}\right|_c & \left.\dfrac{\partial^2\Psi}{\partial y^2}\right|_c \end{pmatrix} = \begin{pmatrix} -2\sigma s_c/9\Theta & 0 \\ 0 & N_v^c \end{pmatrix} = \begin{pmatrix} 1/R_x & 0 \\ 0 & 1/R_y \end{pmatrix}$$

is the matrix of the second derivatives of $\Psi(x, y)$ at the saddle point; $\Delta \mathbf{r} = (\Delta x, \Delta y)$ is the radius vector drawn to an arbitrary point from the saddle point; Ψ_c is the dimensionless work of formation of the critical germ;

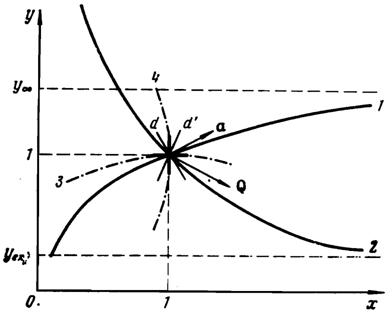

FIG. 1. Projection of the dimensionless free-energy surface $\Psi(x, y)$ of the system near the saddle on the plane (x, z) of the dimensionless variables of the germ. The cross marks the principal axes of the saddle; d and d' are its linear generators; 1 and 2 are the respective phase- and mechanical-equilibrium lines of the germ, while 3 and 4 are the line of the energywise most favorable growth of the germ and the watershed between the quasi-single-phase and two-phase regions of the (x, y) plane; a and Q are the steepest-descent directions of n_{xy}/φ_{xy} and of the flux of germs at the saddle point.

R_x and R_y are the principal curvature radii of the $\Psi(x, y)$ surface at the point (1, 1); σ[g/sec^2] is the surface tension, s_c [cm^2] is the area of the critical-bubble surface; N_v^c is the equilibrium number of vapor molecules in the bubble. The first derivatives $(\partial\Psi/\partial x)_c$, $(\partial\Psi/\partial y)_c$ are equal to zero here because the respective conditions of chemical and mechanical equilibrium are satisfied here. The absence of a quadratic cross term in (5) follows from 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 near the saddle point.

It is seen from (5) that the principal curvature radii R_x and R_y are of opposite sign, i.e., that the labile-equilibrium point (1, 1) of the system is always a hyperbolic point of the surface. In this case the relief (4) of the free energy of the bubble can be approximated in the vicinity of the saddle point by the surface of a hyperbolic paraboloid. This saddle-shaped free-energy surface of the system lies inside the first quadrant of the (x, y) plane parallel to the coordinate axes. The saddle point is the point of intersection of the phase-equilibrium line 1 and the mechanical-equilibrium line 2 (see the figure). These lines are expressed in the coordinates x and y by the respective equations

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

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

where $y_\infty = p_\infty/p_c$, $y_{ext} = P/p_c$; p_∞ is the saturated-vapor pressure over a flat surface; P is the external pressure on the liquid,

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

is the ratio of the capillary pressure to the vapor pressure p_c in the critical bubble; R_c is the radius of the critical germ bubble. Since R_c and p_c decrease with increasing decompression or superheat of the liquid, the parameter $b = 2\sigma/R_c p_c$ can serve as a measure of the supersaturation of a volatile liquid relative to the boiling process.

In the region between 1 and 2 lies the energywise most favored trajectory 3 of the fluctuation variation of the macroscopic subcritical germ, a trajectory joining the vicinity of the origin with the saddle point. It constitutes the bottom of a trough going through the saddle; this bottom is, from the point of view of the theory of surfaces,[11] one of the two surface-curvature lines (i.e., lines such that at each of their points the tangent is directed along the principal direction of the surface) passing through the saddle point. Using the differential equation of these curvature lines[11]

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

where

$$p = \frac{\partial\Psi}{\partial x}, \quad q = \frac{\partial\Psi}{\partial y}, \quad r = \frac{\partial^2\Psi}{\partial x^2}, \quad s = \frac{\partial^2\Psi}{\partial x\,\partial y}, \quad t = \frac{\partial^2\Psi}{\partial y^2}, \tag{9a}$$

in conjunction with the condition $(dy/dx)_c = 0$, we can extend the trough-bottom line to the interior of the region of small germs so long as the macroscopic expression (4) for the free energy of the bubble holds in this region. The second curvature line (4), which passes through the saddle point and staisfies the condition $(dy/dx)_c = \infty$, is the line of the crest that separates the quasi-line-phase and two-phase regions of the (x, y) plane.

In the general case of a viscous and volatile liquid, the fluctuation growth of the subcritical bubbles is connected neither with the phase-equilibrium line 1 nor with the mechanical-equilibrium line 2, and not even with the energywise most favored trajectory 3. The reason is that, besides the physical liquid volatility and supersaturation parameters with which all these three lines are connected, the nucleation problem involves also a viscosity parameter, which influences the nucleation process not via the potential relief in germ-size space, but through the nondiagonal tensor of diffusion in this space. The most probable germ-growth parameter is therefore obtained for the vector flux **Q** as a function of the variables x and y. By way of an example that illustrates how strongly the viscosity of the liquid alters the most probable germ growth trajectory, we consider the case of an ideal inertialess liquid. In this case, at all pressure fluctuations, the volume of the bubble assumes instantaneously a value such that the bubble is in mechanical equilibrium. It follows therefore from physical considerations that in this limiting case the most probable trajectory for the germs is the mechanical-equilibrium line 2. We note that the Döring's hypothesis[4] that all the subcritical germs are in mechanical equilibrium is precisely equivalent to replacing an arbitrary liquid by the limiting case of an ideal inertialess liquid.

It turns out, however, that not at all values of supersaturation and volatility of the liquid is the equilibrium of the bubble stable. To elucidate this question, we consider the condition for the stability of the mechanical equilibrium of a near-critical bubble.

Since the volume changes in an ideal inertialess liquid much more rapidly than the number of vapor molecules in the bubble, it follows that the equation of state (2) can be written in the coordinates x and y in the form $xy=1$. Calculating at the saddle point the derivatives dy/dx of the equation of state and of the mechanical-equilibrium equation (7), we find that the mechanical equilibrium of a near-critical bubble is stable at $b<3$ and unstable at $b>3$.

Thus, in an ideal inertialess liquid, the most probable trajectory of the fluctuation growth of a subcritical germ coincides with the mechanical-equilibrium line only at $b<3$. If $b>3$ the most probable trajectory no longer coincides with the line 2 and its determination calls for an analysis of the general expression for the vector flux **Q**. It was Dörings assumption[4] that at $b>3$ the growth of the germs is also connected with the condition of their mechanical equilibrium which led to the incorrect conclusion that the nucleation rate tends to infinity as $b\to 3$ and that the final formulas of[4] are discontinuous when b goes through 3.

Examination of the average curvature $H(x,y)$ of the surface (5), given when account is taken of (2) by

$$\begin{aligned}H(x,y)&={}^1/_2(1/R_x+1/R_y)\\&={}^1/_2(N_v^c-2\sigma s_c/9\Theta)={}^1/_2N_v^c(1-b/3),\end{aligned}\tag{10}$$

where

$${}^1/_3b=-R_y/R_x=2\sigma/R_cp_c,\tag{11}$$

shows that the dimensionless parameter $\frac{1}{3}b$ is the ratio of the principal curvature radii of the saddle and characterizes the "width of the saddle." As the superheat or decompression of the volatile liquid increases, i.e., on 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 saddle changes from wide to narrow.

Thus, it is easily seen that in the two-dimensional approach the passage of the average curvature of the surface (5) through zero produces no discontinuity whatever either in the matrix A (see (5)) or in the matrix $\hat{D}$ (see (II.12) of Appendix II), which specify completely the nucleation process. We shall return to this question in Sec. 4.

We investigate the two-dimensional equilibrium distribution function given, as shown in Appendix I, by

$$\varphi_{xy}=g_0N_VN_l^cN_v^c\exp\{-\Psi(x,y)\},\tag{12}$$

where $\Psi(x,y)$ is defined in (5), $N_V=V\rho_l$, $N_l^c=v_c\rho_l$, $N_v^c=v_c\rho_v^c$, g_0 is the total probability that the volume V contains no macrobubbles. Substituting (5) in (12) we see that near the saddle the variables separate in φ_{xy}:

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

$$\varphi_x=g_0N_VN_l^c\exp\{-\Psi_c+\sigma s_c(\Delta x)^2/9\Theta\},\tag{13a}$$

$$\varphi_y=N_v^c\exp\{-{}^1/_2N_v^c(\Delta y)^2\}.\tag{13b}$$

The function φ_x, which describes the equilibrium distributions of the germs along the trough that leads through the saddle, is similar to the usual equilibrium distribution function introduced by Zel'dovich[8] in the one-dimensional nucleation problem. The function φ_y, which describes the equilibrium distribution of the bubbles with respect to the pressure inside them, i.e., in the cross section of the trough, calls in accordance with fluctuation theory[12] for the natural normalization:

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

Consequently, it is necessary to write in place of (13b) the correctly normalized transverse distribution function

$$\varphi_y=(N_v^c/2\pi)^{1/2}\exp\{-{}^1/_2N_v^c(\Delta y)^2\},\tag{13c}$$

the presence of which is one of the distinguishing features of the two-dimensional nucleation problem. Then, using (13c), we obtain in place of (12)

$$\varphi_{xy}=g_0V\rho_l^2v_c(N_v^c/2\pi)^{1/2}\exp\{-\Psi(x,y)\}.\tag{13d}$$

3. CALCULATION OF THE NUCLEATION PROBABILITY

The liquid volume V introduced in Sec. 1 can have in the course of the nucleation various states that differ from one another in the energy E, in the number N of the molecules in V, in the volume of the nucleated bubble, and in the pressure in it. The aggregate of all possible (single-phase and two-phase) states of the volume V is a grand Gibbs ensemble. The volume $W-V$ plays the role here of a single-phase thermostat and a reservoir of molecules with a specified 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, directed from the metastable quasi-single-phase states of the volume V (which, by virtue of the absence of a macro-bubble, are characterized by two variables, E and N), to its two-phase states, which contain a transcritical bubble with vapor (the later states are additionally characterized by two more variables pertaining to the bubble).

We note that by virtue of inequality (1) the production and growth of the bubble in V affects only insignificantly the fluctuations of such thermodynamic characteristics of the volume V as its energy E and the total number of molecules. These variables form thus a constant background against which the fluctuation growth of the germ evolves. To get rid of the background of the variables E and N, we change over from the four-dimensional space of the states of the volume V to the two-dimensional space of the variables v and p, in which each point is the trace of the space of the variables E and N and has, by virtue of the foregoing, practically the same statistical weight g_0. Summing the quasi-single-phase states over E and N, we obtain the total probability g_0 of V-volume states in which there is no macroscopic germ (see Appendix I).

Integrating the flux **Q** through the saddle over its cross section we obtain the total flux I from the region of the heterophase fluctuations into the two-phase region of the (v,p) plane. Dividing the total flux I by g_0 we get

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

where ν is the probability of nucleation per unit time in the volume V that contains no macrobubbles in the metastable state.

To calculate $\mathbf{Q}$ we must solve the two-dimensional equation of the diffusion of vapor-filled bubbles in the space of the dimensionless variables $(x, y) = (v/v_c,\ p/p_c)$ that has a potential relief

$$\Psi_{xy} = F_{vp}/\Theta.$$

In the vicinity of the saddle, the two-dimensional nucleation-kinetics equation can be written in the form of a continuity equation for the flux $\mathbf{Q}$, similar to the equation proposed by Kramers[6] and Zel'dovich[8] for the one-dimensional case[1]:

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

$$\mathbf{Q} = \varphi_{xy} \hat{D} \operatorname{grad} \frac{n}{\varphi_{xy}}, \tag{15a}$$

where $\varphi_{xy} \equiv \varphi(x, y)$ is the equilibrium distribution density of the germs relative to the variables x and y; $n \equiv n(x, y)$ is the distribution density of the germs in the nucleation process; D is the generalized diffusion tensor and is calculated in Appendix II. Considering only a single germ in the volume V, we normalize thereby $n(x, y)$ by the condition

$$\int_0^\infty n\, dx\, dy = 1.$$

The external pressure P and the liquid temperature Θ have been assumed constant already in the discussion of the potential relief. In other words, it is assumed that no change in the decompression or the superheat takes place in the course of the nucleation, i.e., the nucleation process is stationary ($\partial n_{xy}/\partial t = 0$, where n_{xy} is the stationary distribution density of the germs). To this end we shall remove from the ensemble of the states of the volume V, by using suitable boundary conditions, the states with grown bubbles and replace them by quasi-single-phase states.

The boundary conditions for Eq. (15) are formulated in the following manner: At the point O with coordinates $x = 0$ and $y = 0$, where the source of the germ bubbles is located in our problem,[8] we set the boundary condition

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

Of course, we set this condition not at the point O itself, but in those points in its vicinity which, first, are themselves far enough from the point O to be able to treat the produced bubble macroscopically, and second, have nevertheless distances close enough to the point O to be negligible in comparison with the distance to the saddle point.

The boundary condition

$$n_{xy}/\varphi_{xy} = 0, \quad x = x^* \gg x_c \quad (y \text{ is arbitrary}), \tag{16a}$$

removes from the ensemble of states of the volume V those states with grown bubbles.

We propose that practically the entire descent of n_{xy}/φ_{xy} from unity to zero occurs near the saddle. We therefore seek the gradient of n_{xy}/φ_{xy}, in analogy with the one-dimensional case, in the form

$$\nabla \frac{n_{xy}}{\varphi_{xy}} = C\mathbf{a} \exp\{{}^1/_2 \lambda \mathbf{a} \Delta \mathbf{r}\}, \tag{17}$$

which yields for Eq. (15) the required solution that goes from the origin through the saddle. Here $\mathbf{a}$ is an unknown vector that indicates the direction of the steepest descent of n_{xy}/φ_{xy}, $\Delta\mathbf{r} = (\Delta x,\ \Delta y)$ is the radius vector drawn from the saddle point to an arbitrary point, and λ is an unknown number that determines the speed of the descent of n_{xy}/φ_{xy} ($\lambda \leq 0$).

Using the boundary conditions (16) and (16a), obtain the constant C:

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

Substituting (5), (13d), (17), and (18) in (15a) we obtain for the germs a flux

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

whose direction does not agree, since the tensor $\hat{D}$ is not diagonal, with either the direction of the steepest descent of n/φ, or with the principal axes of the saddle, or even with the lines 1 and 2 (see the figure). If we find for $\hat{A}$ and $\hat{D}$ formulas that depend on $\mathbf{r}$, then expression (19) makes it possible to construct the vector field on the (x, y) plane and solve completely the problem of the most probable trajectory of the fluctuation growth of the germ.

We obtain next from the condition (15) of the stationary nucleation process 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) breaks up into the characteristic equation

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

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

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

Writing out (21) fully at the saddle point in the form

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

where $D_x^c = 3\Theta/4v_c\eta$, $\delta = \rho_v^c/\rho_l$, and $\omega = p_c R_c/\beta v_t \eta$ are dimensionless parameters, η [g-cm^{-1}-sec^{-1}] is the viscosity of the liquid, β is a dimensionless condensation coefficient, and v_t [cm-sec^{-1}] is the average thermal velocity of the vapor molecules, we obtain a system of linear equations

$$-D_x^c \frac{2\sigma s_c}{9\Theta} x_a + D_x^c \frac{2\sigma s_c}{9\Theta} y_a = \lambda x_a,$$

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

whose solution yields for the nonpositive root of (22) (this is the root of interest to us) the expression

$$\lambda=-D_x^c\{(H_d^2+K/\omega)^{1/2}-H_d\}=-\frac{3\beta v_t}{8R_c}\{[(1-\chi+\omega)^2+4\chi]^{1/2}-1+\chi-\omega\}, \tag{23}$$

where $H_d=H+1/2\omega R_y$ is the "dynamic" average curvature of the system free-energy surface (5), $K=1/R_xR_y$ is its Gaussian curvature, and $\chi=b\omega/3=2\sigma/3\beta v_t\eta$ is a dimensionless parameter.

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

$$\mathbf{a}=\varkappa(1, 1+2R_c\eta\lambda/\sigma). \tag{24}$$

Thus, although the saddle point (1, 1) does remain unchanged in terms of the coordinates x and y at all physical values of the parameters R_c, η, and p_c, the direction $\mathbf{a}$ of the steepest descent of n/φ depends via λ on all the physical parameters of the problem (see the figure). In the limiting case of a nonvolatile liquid ($p_c\to 0$, $\omega\to 0$) we have $\lambda\to-\sigma/2R_c\eta$ and $\mathbf{a}\to\varkappa(1,0)$, and coincides with the x axis. If $2R_c\eta\lambda/\sigma\to-\infty$, then $\mathbf{a}$ becomes antiparallel to the y axis.

From the normalization condition (21a)

$$\varkappa^2\left(1, 1+\frac{2R_c\eta\lambda}{\sigma}\right)\begin{pmatrix} D_x^c & -D_x^c \\ D_x^c\dfrac{\delta-\omega}{\omega} & D_x^c\dfrac{1+\omega}{\omega}\end{pmatrix}\begin{pmatrix}1\\ 1+\dfrac{2R_c\eta\lambda}{\sigma}\end{pmatrix}=1$$

we obtain for $\varkappa$ the value

$$\varkappa=(D_x^cG)^{-1/2},\qquad G=\frac{1+\omega}{\omega}\left(\frac{2R_c\eta\lambda}{\sigma}\right)^2+\frac{2+\delta}{\omega}\frac{2R_c\eta\lambda}{\sigma}+\frac{1+\delta}{\omega}. \tag{25}$$

From (24) and (25) we get the modulus of $\mathbf{a}$, namely

$$a=\left(\frac{1}{D_x^cG}\left[1+\left(1+\frac{2R_c\eta\lambda}{\sigma}\right)^2\right]\right)^{1/2}. \tag{26}$$

To find the nucleation probability ν in a volume V per unit time, we must integrate $\mathbf{Q}$ along the axis passing through the saddle point perpendicular to the vector $\mathbf{Q}\sim\hat{D}^c\mathbf{a}$, and divide the result according to (14) by g_0. But by virtue of $\operatorname{div}\mathbf{Q}=0$ the result of the integration does not depend on the direction of the chosen axis. It is more convenient to integrate $\mathbf{Q}$ along an axis perpendicular to the vector $\mathbf{a}$. Then $\Delta\mathbf{r}\equiv\Delta z\mathbf{n}_0$ and $\mathbf{a}\cdot\mathbf{n}_0=0$, where

$$\mathbf{n}_0=\tilde{\varkappa}(-1-2R_c\eta\lambda/\sigma, 1) \tag{27}$$

is a unit vector perpendicular to $\mathbf{a}$. From the condition $n_0=1$ we get

$$\tilde{\varkappa}=[1+(1+2R_c\eta\lambda/\sigma)^2]^{-1/2}. \tag{28}$$

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

$$\nu=\frac{1}{g_0}\int\limits_{-\infty}^{+\infty}Q_n\,d(\Delta z)=\frac{1}{g_0}\int\limits_{-\infty}^{+\infty}\frac{\mathbf{a}\mathbf{Q}}{a}d(\Delta z)$$
$$=\frac{Vv_c\rho_l^2}{2\pi a}(-\lambda N_v^c)^{1/2}\exp\{-\Psi_c\}\int\limits_{-\infty}^{+\infty}\exp\left\{-\frac{(\Delta z)^2}{2}(\mathbf{n}_0'\hat{A}\mathbf{n}_0)\right.$$
$$\left.+\lambda\Delta z\mathbf{a}\mathbf{n}_0\right\}(\mathbf{a}\hat{D}\mathbf{a})\,d(\Delta z)=\frac{Vv_c\rho_l^2}{a}\left(\frac{-\lambda N_v^c}{2\pi(\mathbf{n}_0'\hat{A}\mathbf{n}_0)}\right)^{1/2}\exp\{-\Psi_c\}, \tag{29}$$

where it can be shown that

$$\mathbf{n}_0'\hat{A}\mathbf{n}_0=\tilde{\varkappa}^2\left[N_v^c-\frac{2\sigma s_c}{9\Theta}\left(1+\frac{2R_c\eta\lambda}{\sigma}\right)^2\right]>0 \tag{30}$$

for all values of R_c, η, and p_c.

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

$$\begin{gathered}\nu=V\rho_l^2R_c\left(\frac{3\beta v_t\Theta}{16\eta}\frac{MG}{L}\right)^{1/2}\exp\{-\Psi_c\};\\ M=[(1-\chi+\omega)^2+4\chi]^{1/2}-1+\chi-\omega,\\ G=\frac{1+\omega}{\omega}\left(1-\frac{M}{2\chi}\right)^2-\left(2-\frac{\delta}{\omega}\right)\left(1-\frac{M}{2\chi}\right)+1,\\ L=1-{}^1/_3b(1-M/2\chi)^2.\end{gathered} \tag{31}$$

Formula (31) is in fact the sought expression for the per-second probability of formation of a critical bubble with vapor in a volume V. This expression is valid for stationary volume boiling of a decompressed or superheated volatile liquid far from the critical point, in the entire range of variation of the viscosity and volatility of the liquid at not too large supersaturation of the system. The effect of the inertial properties of the liquid and of the heat relaxation on the interface between the bubble and the surface can be taken into account in the spirit of Kagan's work[10] by modifying the diffusion tensor $\hat{D}$ (see formula (22)) without changing the subsequent procedure of obtaining the final formula (31).

4. DISCUSSION OF RESULTS

The problem of the boiling of a volatile liquid involves three physical parameters whose values determine the state of the system: the radius R_c of the critical germ (it characterizes the supersaturation), the vapor pressure p_∞ over the flat liquid surface (it characterizes the volatility), and the viscosity η of the liquid. We neglect here the effect of the vapor density in the bubble on the surface tension σ. Representing (31) in the form

$$\begin{aligned}\nu&=V\rho_l^2\exp\left\{-\frac{\sigma s_c}{9\Theta}+\frac{1}{2}\ln\frac{MG}{L}\frac{3\beta v_t\Theta R_c^2}{16\eta}\right\}\\ &=V\rho_l^2\exp\{-f_1(R_c)+f_2(R_c, p_c, \eta)\},\end{aligned} \tag{32}$$

where

$$\frac{MG}{L}=M\left[\frac{1+\omega}{\omega}\left(1-\frac{M}{2\chi}\right)^2-\left(2-\frac{\delta}{\omega}\right)\left(1-\frac{M}{2\chi}\right)+1\right]\Big/\left[1-\frac{b}{3}\left(1-\frac{M}{2\chi}\right)^2\right] \tag{32a}$$

we see that by varying the viscosity and volatility of the liquid we can obtain $|f_2|>f_1$.

Thus, the criterion

$$\left|\ln\frac{MG}{L}\frac{3\beta v_t\Theta R_c^2}{16\eta}\right|>\frac{2\sigma s_c}{3\Theta} \tag{33}$$

determines the region of the values of R_c, p_c, and η where the pre-exponential factor has a stronger effect on ν than the work of formation of the critical germ. The limiting nucleation cases, which we shall now consider, identify several such regions. A detailed investigation of the criterion (33) is beyond the scope of the present paper.

In the course of solving our problem we have introduced in lieu of the three dimensional parameters R_c, p_∞, and η the three dimensionless parameters

$$\delta=\rho_v{}^c/\rho_l,\quad b=2\sigma/R_cp_c,\quad \chi=2\sigma/3\beta v_t\eta, \tag{34}$$

where

$$p_c=p_\infty \exp\{-2\sigma/\rho_l\Theta R_c\}.$$

Two of them are best combined into a dimensionless parameter ω:

$$\omega=3\chi/b=p_cR_c/\beta v_t\eta, \tag{35}$$

which contains all three dimensional parameters and is convenient for the investigation of the limiting cases of the problem. We shall consider various limiting values of the parameter ω, which enters the final formula (31) via the factor MG/L.

The limiting case $\omega\to 0$ corresponds to the following limiting values of the physical parameters: $\eta\to\infty$ or $R_c\to 0$, or else $p_c\to 0$. In the case of an infinitely viscous liquid we have $\lambda\to 0$, $D_x^c\to 0$ and $\nu\to 0$. The case of unlimited supersaturation of the system ($R_c\to 0$) cannot be considered in our scheme, since the latter is intended for small and moderate superheats and decompressions of the liquid.

As $p_c\to 0$ we go over to the analysis of a nonvolatile liquid, the cavitation in which was considered in[9]. An investigation of the relief (5) expressed in the coordinate v and p shows that one of the axes of the saddle drops to the v axis, and the trough leading through the saddle becomes infinitesimally narrow. The problem thus becomes one-dimensional, corresponding to a germ with a single variable, v. The expression (31) for the nucleation probability takes the limiting form

$$\nu=\frac{V\rho_l{}^2R_c}{2\eta}(\Theta\sigma)^{1/2}\exp(-\Psi_c), \tag{36}$$

which coincides with formula (36) of[9]. We note that Kagan's corresponding expression (34)[10] is equivalent in our notation to

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

i.e., it undervalues the result by a factor ρ_v^c/ρ_l and states erroneously that nucleation is impossible in a nonvolatile liquid.

The opposite limiting case $\omega\to\infty$ corresponds to the following limiting values of the physical parameters: $R_c\to\infty$ or $\eta\to\infty$. The case $R_c=\infty$ corresponds to eliminating the superheat or the decompression of the liquid. The work of formation of an infinitely large critical germ is then infinite, i.e., boiling of the liquid is impossible.2)

As $\eta\to 0$ we deal with the boiling of a nonviscous (ideal) volatile liquid. If we neglect in this limiting region the influence of the inertia of the liquid, then we obtain from (II.8) for an ideal liquid $\Delta y=-\frac{1}{3}b\Delta x$, i.e., a rigorous relation between the variables x and y, so that our problem becomes one-dimensional. This means physically that any finite fluctuation of the pressure in the bubble changes the volume instantaneously in such a way that the bubble remains in mechanical equilibrium. Thus, the bubble always remains on the mechanical equilibrium line (2) throughout its fluctuation growth, a fact ensured by the infinitely large D_x^c.

Allowance for the influence of the inertia of the liquid as $\eta\to 0$ upsets the rigorous correlation between Δx and Δy, so that in the general case the nucleation problem remains two-dimensional also for an ideal liquid. Allowance for the inertia of the liquid affects the nucleation probability ν by altering the expression for $\hat{D}^c$ (see Appendix II). To obtain quantitative results we shall consider, taking (II.7) into account, 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 is not so large as to allow the inertia of the liquid to come into play at the very outset. If $b/3\gg 1$, which corresponds to a decompression $-P\gg 2p_c$, expression (31) reduces to

$$\nu=\frac{V\rho_l{}^2R_c}{4\eta}[2\sigma-3p_cR_c]\left(\frac{\Theta}{\sigma}\right)^{1/2}\exp(-\Psi_c), \tag{38}$$

which goes over into (36) if $3/b$ is neglected with unity.

At $b/3\ll 1$, which corresponds to positive and limited negative values of P, the expression (31) takes the form

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

If $b/3$ is neglected, this expression differs from Kagan's[10] formula (36), in which no account is taken of temperature effects on the bubble boundary, by a factor ρ_l/ρ_v^c, which corresponds to the correct choice of the pre-exponential factor of the equilibrium distribution functions.

At $b/3$ comparable with unity we must use the general formula (31), which remains continuous when $b/3$ goes through unity and does not lead to an unphysical decrease of the nucleation rate.

We have considered the limiting case of the two-dimensional nucleation problem, where, in accord with the numerical value of ω, one of the two parameters (volatility or viscosity of the liquid) is decisive in the kinetics of the formation of the new phase, but since expression (35) for ω contains the quantity R_c, which is connected with the degree of supersaturation of the system, it follows that for any liquid the entire system supersaturation range breaks up into three regimes: the volatile-liquid regime ($\omega\gg 1$), when viscosity can be neglected; the viscous-liquid regime ($\omega\ll 1$), when volatility can be neglected, and the intermediate regime ($\omega\approx 1$), when the liquid must be simultaneously regarded as liquid as well as volatile. According to (35), the intermediate regime for highly volatile liquids shifts towards larger saturations, and towards lower ones for highly viscous liquids.

APPENDIX I

As already mentioned in Sec 3, each state of the volume V is characterized in the nucleation process by four variables: the energy $E_{nN}(v,p)$, the volume V, the number N of molecules in it, the bubble volume v, and the vapor pressure p in the bubble; the last two variables are physically meaningful only for states with quasi-macroscopic germs of a new phase.

At small and moderate supersaturation of the system, when the region of the heterophase fluctuations and the two-phase region of the four-dimensional space (E, N, v, p) are separated by a high energy ridge, the calculation of the flux of the states of V from the first region to the second does not require a detailed examination of the growth of the germ of the new phase, including its microscopic stage. It is quite sufficient to consider, on the one hand, the states near the metastable equilbrium of the system, i.e., the states of a homogeneous superheated or decompressed liquid, and on the other, the states near the labile equilibrium of the system, which contain a macroscopic near-critical bubble.

Near-metastable states will be assumed to correspond to the values3) $v = p = 0$, i.e., they are described by only two variables, E and N, in contrast to the near-labile states. The probability of a near-metastable state of the volume V such that it is in an n-th quantum state with energy E_{nN} and contains N molecules of liquid (while the medium $W-V$ is in a single-phase state) is equal to

$$w_{nN}=C\exp\{k^{-1}S(E_0'-\Delta E,\ N_0'-\Delta N)\}, \tag{I.1}$$

where C is a normalization factor and is constant for the given reservoir $W-V$ regardless of the states of the volume $V \ll W$; k is Boltzmann's 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 number of molecules of the volume $W-V$ in the state of equilibrium with the metastable state of the volume V, characterized by E_0 and N_0; $\Delta E = E_{nN} - E_0$, $\Delta N = N - N_0$; the subscript zero labels metastable states.

Expanding S in (I.1) in powers of ΔE and ΔN about the metastable state and then summing w_{nN} over n and N, we obtain the total probability that the volume V has no macrobubbles, i.e., that it is at the point $(v=0,\ p=0)$

$$g_0=\sum_{n,N} w_{nN}=A_0\sum_N \exp\left\{\frac{\mu_l{}^0\Delta N-\Delta F_N{}^0}{\Theta}\right\}, \tag{I.2}$$

where

$$A_0=C\exp\{S_0/k\},$$

μ_l^0 is the chemical potential of the liquid in the volume W when the volume V is in a metastable state; $\Delta F_N^0 = F_N - F_N^0$ is the change of the free energy F_N of the volume V in comparison with its metastable state; S_0 is the total entropy of the volume W at the metastable state of V.

To consider the probability of the near-labile states of V, we shall attempt to separate an expression similar to (I.2), so as to determine the change of the total probability of the states of the volume V following the transition from the metastable to the labile state. According to[12], the probability $dw_{nN}(v,p)$ that the volume V in the n-th quantum state with energy $E_{nN}(v,p)$ contains N molecules of liquid as well as a bubble having a volume in the interval $(v, v+dv)$, in which the vapor pressure is in the interval $(p, p+dp)$, is

$$dw_{nN}(v,\ p)=C\exp\{k^{-1}S(E_c'-\Delta E_c,\ N_c'-\Delta N_c)\}\,dv\,dp, \tag{I.3}$$

where E_c' and N_c' are the energy and number of molecules of the medium $W-V$ in the state corresponding to the labile equilibrium of V; $\Delta E_c = E_{nN}(v,p) - E_c$ and $\Delta N_c = N - N_c$ is the change of the energy and of the number of molecules of the volume V in comparison with the state of the labile equilibrium, and c is an index that designates the labile-equilibrium state.

Expanding S in (I.3) in powers of ΔE and ΔN about the labile equilibrium point and then summing $dw_{nN}(v,p)$ over n and N, we obtain, in analogy with[9], the probability $dw(v,p)$ that the vólume V contains a macroscopic bubble with a volume in the interval $(v,\ v+dv)$ with a vapor pressure in the interval $(p,\ p+dp)$:

$$\begin{gathered} dw(v,p)=\sum_{n,N} dw_{nN}(v,p)=A_c\rho_l\frac{v_c}{\Theta}\sum_N \exp\left\{\frac{\mu_l{}^c\Delta N_c-\Delta F_{Nvp}^{c}}{\Theta}\right\}dv\,dp;\\ A_c=C\exp\{S_c/k\}, \end{gathered} \tag{I.4}$$

where $\rho_l v_c/\Theta$ is the value of the Jacobian $\partial(N_l, N_v)/\partial(v,p)$ of the transition from the dimensionless space of the variables (N_l, N_v) to the dimensional space (v,p), where N_v is the number of vapor molecules in a bubble of volume v and with pressure p; N_l is the number of liquid molecules filling the bubble volume v at constant ρ_l; μ_l^c is the chemical potential of the liquid W when V is in the labile state; $\Delta F_{Nvp}^c = F_{Nvp} - F_{Nvp}^c$ is the change of the free energy of the "liquid + bubble with vapor" system in the volume V compared with the labile-equilibrium state; S_c is the total entropy of the volume W when V is in the labile state.

It is important to separate in the expression for F_{Nvp} the terms that do not depend on N and take them outside the sign of summation with respect to N. To this end, we treat the "liquid + bubble with vapor" as a sort of weak solution of bubbles in a liquid. The free energy of our system, according to thermodynamics of solutions is[12]

$$F_{Nvp}\approx F_N+F_{vp}-\Theta\ln N, \tag{I.5}$$

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

$$\Delta F_{Nvp}^{c}=\Delta F_N{}^c+\Delta F_{vp}{}^c-\Theta\ln(N/N_V), \tag{I.6}$$

where N_V is the number of liquid molecules in the volume $V-v_c$, the logarithmic term being neglected here because we are seeking $dw_{nN}(v,p)$ only in the vicinity of the labile equilibrium point.

Substituting (I.6) in (I.4) we obtain

$$dw(v,p)=f(v,p)\,dv\,dp\sum_{n,N}w_{nN}{}^{c}=$$

$$=\rho_l\frac{v_c}{\Theta}\exp\left\{-\frac{\Delta F_{vp}{}^{c}}{\Theta}\right\}dv\,dp\,A_c\sum_N\exp\left\{\frac{\mu_l{}^{c}\Delta N_c-\Delta F_N{}^{c}}{\Theta}\right\},\qquad\text{(I. 7)}$$

where

$$g_c=\sum_{n,N}w_{nN}{}^{c}=C\exp\left\{\frac{S_c}{k}\right\}\sum_N\exp\left\{\frac{\mu_l{}^{c}\Delta N_c-\Delta F_N{}^{c}}{\Theta}\right\}\qquad\text{(I. 8)}$$

is the total probability that the volume V has a macroscopic critical germ, and

$$f(v,p)=\rho_l\frac{v_c}{\Theta}\exp\left\{-\frac{\Delta F_{vp}{}^{c}}{\Theta}\right\}$$

is the probability density that the macroscopic germ in V has a volume and pressure in the respective intervals $(v,\ v+dv)$ and $(p,\ p+dp)$.

Thus, owing to (I. 5), the probability of formation in V of a given macrobubble can be represented as a product of the probability of formation in the volume V of a critical bubble in which the vapor pressure is saturated by the probability of the deviation of the critical bubble from the given values of v and p.

In comparing g_c with g_0 we shall neglect, in view of the inequality (1) and the invariance of the temperature and of the supersaturation of the system, the difference between $V-v$ and v, and will also assume that $\mu_l^c \approx \mu_l^0$. We shall also assume that the presence of the germ in the volume V produces practically no change in the fluctuations ΔN and ΔF_N of the number of molecules and of the free energy of the volume V. Then, substituting (I. 2) in (I. 8), we obtain

$$g_c\approx g_0\exp\{\Delta S/k\},\qquad\text{(I. 9)}$$

where $\Delta S=S_c-S_0$ is the increase of the entropy of the volume W when V goes from the metastable homogeneous-liquid state into the labile state of the "liquid +bubble" system, a state that serves as a thermodynamic characteristic of the process of new-phase formation.

Since the volume W is insulated, the entropy increment ΔS is equal to the change ΔF_{Nvp} of the free energy upon formation of the critical germ, divided by the absolute temperature T. Using (I. 5), we get

$$\Delta S/k=-\Delta F_{Nvp}/kT=-(F_N{}^{c}+F_{vp}{}^{c}-\Theta\ln N_v-F_N{}^{0})/\Theta\approx-F_{vp}{}^{c}/\Theta+\ln N_v\qquad\text{(I. 10)}$$

Substituting (I. 9) and (I. 10) in (I. 7), we get

$$dw(v,p)=\varphi(v,p)\,dv\,dp=g_0N_v\rho_l\frac{v_c}{\Theta}\exp\left\{-\frac{F_{vp}}{\Theta}\right\}dv\,dp.\qquad\text{(I. 11)}$$

Assuming that the onset of the macrogerm in V hardly changes the fluctuations of the number of particles and of the energy in the volume V, we arrive at the conclusion that the variables E and N, which characterize the states of the volume V together with v and p, are an almost constant background that accompanies the formation of the new phase in V. We can therefore go over from the four-dimensional space (E,N,v,p) to the two-dimensional space of the germ variables, each point (v,p) of which corresponds to a sum, over n and N, of all possible states (E,N,v,p) with fixed v and p. The probability density $\varphi(v,p)$ is then the equilibrium distribution function of the nucleating bubbles with respect to their variables v and p and is connected with the relief to the free energy F_{vp} of the system.

Changing to the dimensionless quantities $x=v/v_c$, $y=p/p_c$, $\Psi=F_{vp}/\Theta$, we obtain in (x,y) space

$$dw(x,y)=\varphi_{xy}dx\,dy=g_0N_vN_l{}^{c}N_v{}^{c}\exp\{-\Psi(x,y)\}dx\,dy;\qquad\text{(I. 12)}$$
$$N_l{}^{c}=v_c\rho_l,\quad N_v{}^{c}=v_c\rho_v{}^{c}.$$

APPENDIX II

In any diffusion problem, to find the diffusion tensor we must know the forces that act on the system, and the velocity with which the system moves under the influence of these forces. In Zel'dovich's formulation of the nucleation problem, the forces acting on the system are specified by the equilibrium distribution function φ_{xy} that determines the potential relief $\Psi(x,y)$ in the space of the germ variables

$$\mathbf{F}=\operatorname{grad}(\ln\varphi_{xy})=-\operatorname{grad}\Psi(x,y).\qquad\text{(II. 1)}$$

The velocities $\dot{x}=\dot{v}/v_c$ and $y=\dot{p}/p_c$ are obtained from the phenomenological equations of motion that describe the time dependence of the bubble radius (the bubble center is immobile):

$$\rho_lmR\ddot{R}+\frac{3}{2}\rho_lm\dot{R}^2=p-\frac{2\sigma}{R}-P-4\eta\frac{\dot{R}}{R},\qquad\text{(II. 2)}$$

where m is the molecule mass, and the dependence of the number of vapor molecules in the bubble on the time is

$$\dot{N}=\pi\beta v_tR^2(p_R-p)/\Theta\qquad\text{(II. 3)}$$

where $v_t=(8\Theta/\pi m)^{1/2}$, p_R is the pressure of the saturated vapor in a bubble of given curvature and is connected with the saturated-vapor pressure p_∞ over a flat surface by Kelvin's formula

$$p_R=p_\infty\exp\{-2\sigma/\rho_l\Theta R\}.\qquad\text{(II. 4)}$$

The calculation of the diffusion coefficients as functions of the arguments v and p require both an exact solution of Eqs. (II. 2) and (II. 3) and an exact calculation of the forces, using (II. 1) and (4). But the presence of a rather steep saddle in the problem allows us to replace this problem by the simpler one of calculating the diffusion coefficients in the vicinity of the saddle, near which the small forces F_x and F_y and the velocities $\dot{x}$ and $\dot{y}$ can be expanded in powers of Δx and Δy and only the linear terms retained:

$$F_x=-\frac{\partial\Psi}{\partial x}=-\frac{\Delta x}{R_x},\quad F_y=-\frac{\partial\Psi}{\partial y}=-\frac{\Delta y}{R_y}.\qquad\text{(II. 5)}$$

Neglecting in (II. 2) the term with $\dot{R}^2$ near the saddle and recognizing that $\ddot{R}=\dot{R}\,d\dot{R}/dR$, we get

$$\dot{R}=\left(p-\frac{2\sigma}{R}-P\right)\Big/\left(\frac{4\eta}{R}+\rho_lmR\frac{d\dot{R}}{dR}\right).\qquad\text{(II. 6)}$$

The criterion for neglecting the inertia term can be readily shown, with the aid of (II. 6), to be of the form[4]

$$\rho_l m\sigma R_c/8\eta^2 \ll 1, \qquad \text{(II. 7)}$$

from which it follows that at sufficiently small displacement of the system and low liquid viscosity we can disregard the effect of the inertial term.

We neglect next, for simplicity, the inertial term. We transform (II. 6) and (II. 3), with allowance for (II. 4), in the following manner:

$$\dot{R} = \frac{R_c}{4\eta}\left[p - p_c + p_c - P - \frac{2\sigma}{R_c} + \frac{2\sigma}{R_c} - \frac{2\sigma}{R}\right] = \frac{R_c}{4\eta}\Delta p + \frac{\sigma}{2R_c\eta}\Delta R,$$

$$\dot{N} = \frac{\pi\beta v_t R_c^2}{\Theta}(p_R - p_c + p_c - p) = \frac{2\pi\beta v_t \sigma \rho_v^c}{\rho_l \Theta}\Delta R - \frac{\pi\beta v_t R_c^2}{\Theta}\Delta p,$$

or else, changing to the coordinates x and y,

$$\dot{x} = \frac{3p_c}{4\eta}\left[\frac{b}{3}\Delta x + \Delta y\right], \qquad \text{(II. 8)}$$

$$\dot{y} = \frac{3\beta v_t}{4R_c}\left[\frac{b}{3}(\delta - \omega)\Delta x - (1 + \omega)\Delta y\right]. \qquad \text{(II. 9)}$$

To obtain the connection between the forces and the velocities, which defines the tensor $\hat{D}$, we reduce Eqs. (15) and (15a), assuming the tensor $\hat{D}$ and the forces to be functions that vary much more slowly than n_{xy} and grad n_{xy} in the vicinity of the saddle, to the form

$$\frac{\partial n_{xy}}{\partial t} = -(D_x^c F_x + D_{xy}^c F_y)\frac{\partial n_{xy}}{\partial x} - (D_y^c F_y + D_{yx}^c F_x)\frac{\partial n_{xy}}{\partial y} + D_x^c \frac{\partial^2 n_{xy}}{\partial x^2} + D_y^c \frac{\partial^2 n_{xy}}{\partial y^2} + (D_{xy}^c + D_{yx}^c)\frac{\partial^2 n_{xy}}{\partial x\,\partial y} \qquad \text{(II. 10)}$$

and, rewriting this equation of diffusion in an external field in the Fokker-Planck form

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

we obtain the system of equations

$$D_x^c F_x + D_{xy}^c F_y = \dot{x}, \quad D_y^c F_y + D_{yx}^c F_x = \dot{y}. \qquad \text{(II. 11)}$$

Substituting (II. 5), (II. 8), and (II. 9) in (II. 11), we write out the system of equations

$$D_x^c \frac{2\sigma s_c}{9\Theta}\Delta x - D_{xy}^c N_v^c \Delta y = \frac{b}{3}\frac{3p_c}{4\eta}\Delta x + \frac{3p_c}{4\eta}\Delta y,$$

$$D_{yx}^c \frac{2\sigma s_c}{9\Theta}\Delta x - D_y^c N_v^c \Delta y = \frac{b}{3}\frac{3\beta v_t}{4R_c}(\delta - \omega)\Delta x - \frac{3\beta v_t}{4R_c}(1 + \omega)\Delta y.$$

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

$$\hat{D}^c = \begin{pmatrix} D_x^c & -D_x^c \\ D_x^c \dfrac{\delta - \omega}{\omega} & D_x^c \dfrac{1 + \omega}{\omega} \end{pmatrix}, \quad D_x^c = \frac{3\Theta}{4v_c\eta}. \qquad \text{(II. 12)}$$

We see therefore that at $\omega \gg \delta$ the tensor $\hat{D}^c$ becomes symmetrical. The ratio of the viscosity, volatility, and superheat of the liquid, for which we can neglect the nondiagonal form of $\hat{D}^c$, can be determined from the criterion $\omega \ll 1$ and $\delta \ll 1$, which corresponds, for example, the low-volatility liquids or those with very low viscosity.

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[1] The method of solving (15) was proposed by V. N. Likhachev.

[2] As follows from (11.7), as $R_c \to \infty$ it is necessary to take into account the influence of the inertia of the liquid on the value of the diffusion tensor.

[3] The presence of microscopic germs is reflected in the value of chemical potential of the homogeneous liquid.

[4] A method for taking into account the inertial term in D is given in[10]. The criterion (II. 7) practically coincides with criterion (35) of that reference.

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