Thermodynamics and Kinetics of Vapor Bubbles Nucleation in One-Component Liquids

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ABSTRACT: The multivariable theory of nucleation (*J. Chem. Phys.* **2006**, *124*, 124512) is applied to the problem of vapor bubbles formation in pure liquids. The presented self-consistent macroscopic theory of this process employs thermodynamics (classical, statistical, and linear nonequilibrium), hydrodynamics, and interfacial kinetics. As a result of thermodynamic study of the problem, the work of formation of a bubble is obtained and parameters of the critical bubble are determined. The variables V (the bubble volume), ρ (the vapor density), and T (the vapor temperature) are shown to be natural for the given task. An equation for the dependence of surface tension on bubble state parameters is obtained. An algorithm of writing the equations of motion of a bubble in the space $\{V, \rho, T\}$—equations for $\dot{V}$, $\dot{\rho}$, and $\dot{T}$—is offered. This algorithm ensures symmetry of the matrix of kinetic coefficients. The equation for $\dot{T}$ written on the basis of this algorithm is shown to represent the first law of thermodynamics for a bubble. The negative eigenvalue of the motion equations which alongside with the work of the critical bubble formation determines the stationary nucleation rate of bubbles is obtained. Various kinetic limits are considered. One of the kinetic constraints leads to the fact that the nucleation cannot occur in the whole metastable region; it occurs only in some subregion of the latter. Zeldovich's theory of cavitation is shown to be a limiting case of the theory presented. The limiting effects of various kinetic processes on the nucleation rate of bubbles are shown analytically. These are the inertial motion of a liquid as well as the processes of particles exchange and heat exchange between a bubble and surrounding liquid. The nucleation rate is shown to be determined by the slowest kinetic process at positive and moderately negative pressures in a liquid. The limiting effects of the processes of evaporation-condensation and heat exchange vanish at high negative pressures.

$$W = (\mu - \mu_0)(N + \overline{N}) + (T - T_0)(S + \overline{S}) - (P - P_0)V + \sigma A$$

$$\dot{T} = -\frac{P_*}{C_V^*}\dot{V} + \lambda_{\rho\rho}\frac{kT_0}{c_V\rho_*}\widetilde{q}(\rho - \rho_*) - \frac{3\alpha}{c_V\rho_*R_*}(T - T_0)$$

$$I = N_b\sqrt{\frac{kT_0}{2\pi}|h_{11}^{-1}|}|\kappa_1|e^{-\frac{W_*}{kT_0}}$$

1. INTRODUCTION

The kinetics of bubbles nucleation in a metastable liquid[1−9] (or the kinetics of boiling up) is one of the classical problems of the nucleation theory; its studying starts with the work of Döring and Volmer.[1] An important milestone in the development of the theory of bubbles formation is the classical work of Zeldovich[2] in which the one-dimensional theory of cavitation in a liquid at high negative pressures is suggested (the presence of vapor in a bubble is neglected). A significant idea to use the macroscopic equations of motion of a nucleus in the space of its parameters for determining the kinetic coefficients of the nucleation theory (diffusivities in the Fokker−Planck equation) is offered in this paper. Hydrodynamic equations are employed for this purpose. Thereby, it becomes possible to determine the limiting effects of various processes on nucleation: viscosity, heat conductivity, and diffusion. The importance of this approach is obvious not only for cavitation but also for other problems of nucleation, so it is universal. The use of this approach makes the nucleation theory consistent; i.e., it becomes fully *macroscopic*. The nucleation rate is determined only by macroscopic parameters of the mother phase both thermodynamic and hydrodynamic (the coefficients of viscosity, heat conductivity, and diffusion) which can be measured.

At the same time, the approach which can be called "miscellaneous" is more common now in the nucleation theory. Macroscopic (thermodynamic) study is used for getting the work of nucleus formation, whereas the kinetic coefficients are obtained from microscopic consideration. Namely, kinetic processes on the interface are considered and the probabilities of forward and backward elementary processes are calculated. Historically, the nucleation theory began to develop just by this way. However, this approach is limited; it is not applicable to all tasks and does not take into account properly the kinetic properties of the mother phase.

Returning to the boiling up of a superheated liquid at positive and negative pressures, it is clear that a multivariable theory of nucleation[10−14] is necessary to investigate this process in detail, i.e., to clarify the effects of the kinetic processes mentioned above on nucleation. The multivariable theory of nucleation of vapor bubbles presented in the given report uses the maximum number of variables, three, differently from earlier one-[2,4] and two-variable[5] theories. This number would be equal to two according to the Gibbs phase rule if either the number of vapor particles or vapor density was constant; however, these are not the cases. As a consequence, all the limiting effects in this problem are taken into account properly: the inertial motion of a liquid, the evaporation−condensation processes, and the heat exchange between a bubble and surrounding liquid. The importance of thermal processes in calculating the nucleation rate of bubbles was noted in ref 4. The Einstein−Smoluchowski approach[14] is employed in the presented theory; i.e., the case of

sufficiently viscous liquids is considered. However, the criterion of applicability of this approach involves the bubble critical size;[9] hence, it can be satisfied in a certain region of metastability for "not very viscous" liquids also.

The paper is organized as follows. A detailed thermodynamic consideration of the problem is carried out in section 2. The work of vapor bubble formation is obtained here. Further, parameters of the critical bubble and the most convenient variables for the given problem are determined. The dependence of surface tension on bubble state parameters is also considered, and an equation for this dependence is obtained (an analogue of the Gibbs adsorption equation in the equilibrium theory). Section 3 focuses on the kinetic part of the problem, just getting the equations of motion of a bubble in the space of its variables. For this purpose, the algorithm of writing these equations is formulated and employed. Using these equations as well as the bubble formation work, the stationary nucleation rate of bubbles is calculated. Various kinetic limits are considered in section 4. The limiting effects of different kinetic processes on the nucleation rate of bubbles are shown here.

2. THERMODYNAMICS OF NUCLEATION

2.1. Model and General Equation for the Work.

We consider a vapor bubble in a liquid. The bubble volume V is negligibly small in comparison with the volume V_0 of a liquid, so the bubble formation does not change the thermodynamic state parameters of the latter—the pressure P_0 and the temperature T_0. Hereafter, the quantities relating to a liquid will be provided by the subscript 0, the quantities relating to a nucleus will be used without index, and the critical nucleus parameters will be denoted by an asterisk. In view of smallness of the bubble size, we can assume that the characteristic times of relaxation processes inside a bubble are sufficiently small (in comparison with other characteristic times of the problem), so the thermodynamic equilibrium takes place here at any time. The ambient phase (liquid) is in the state of metastable equilibrium. In other words, each of the coexisting phases is equilibrium, but there is no equilibrium between them; such equilibrium takes place only for the bubble of critical size. Nevertheless, considering near-critical bubbles, we can assume the deviations from the equilibrium of the whole system "nucleus + ambient phase" small and apply the classical thermodynamic approach to such a quasiequilibrium system.

The main goal of thermodynamic consideration is to determine the work of nucleus formation. For this purpose, the expression for the minimum work W done by a system (thermostat) on its subsystem[15,16] has to be employed:

$$W = \Delta E - T_0 \Delta S + P_0 \Delta V \tag{1}$$

The changes of energy, ΔE, entropy, ΔS, and volume, ΔV, of the subsystem relate in our case to the region of inhomogeneity in the mother phase which is associated with a nucleus. Since the state of the ambient phase does not change under nucleus formation, these quantities can be attributed to the *whole* system also. This general expression for W is a consequence of the first and second laws of thermodynamics. It is employed in ref 15 for studying fluctuations. A nucleus is also a fluctuation but a heterophase one.[17] Thus, there exists the interface, as distinct from the case of a homophase fluctuation.

The work W determines the change ΔS_{tot} of the entropy of a system upon a fluctuation[15] or nucleus formation:

$$\Delta S_{tot} = S_2 - S_1 = \Delta S = -\frac{W}{T_0} \tag{2}$$

where S_1 is the entropy of the system without a nucleus (the initial state) and S_2 is the entropy of the system "nucleus + ambient phase".

According to Einstein's formula, the probability of a fluctuation is proportional to $\exp(S_2/k)$ or, equivalently, to $\exp(\Delta S/k)$, where k is the Boltzmann constant. Therefore, the work, eq 1, determines the equilibrium distribution function of nuclei

$$f_{eq}(\{x_i\}) = C_{eq} e^{-W(\{x_i\})/kT_0} \tag{3}$$

where $\{x_i\}$ is the set of variables describing a nucleus. In ref 13, the normalizing constant C_{eq} has been determined for multivariable nucleation processes including binary nucleation.

The well-known conditions of equilibrium in thermodynamics are obtained from the condition of entropy maximum[15,16] $dS = 0$. However, this equation is only the necessary condition of an extremum, but not sufficient one. There is the state with $dS = 0$ which does not correspond to the maximum entropy. This is the case of nucleation, just the state "critical nucleus + ambient phase". Considering deviations from this state (denoted by an asterisk), let us transform eq 2 as follows:

$$\Delta S = S_2 - S_1 = -\frac{W_* + \Delta W}{T_0} = S_2^* - S_1 - \frac{\Delta W}{T_0}$$

from where

$$S_2 - S_2^* = -\frac{\Delta W}{T_0} = -\frac{W - W_*}{T_0} \tag{4}$$

The equilibrium condition, $dS_2 = 0$, leads, in view of eq 4, to

$$dW = 0 \tag{5}$$

It will be shown below that this equation determines the parameters of the critical nucleus.

The second differential d^2W shows the type of an extremum. In the case of a usual (homophase) fluctuation, we have $d^2W < 0$ which corresponds to the maximum of entropy for state 1 (without a fluctuation or a nucleus); this is the stable equilibrium state. If we consider deviations from the state "critical nucleus + ambient phase", the quadratic form d^2W is not of a definite sign, so it represents the saddle surface in the space $\{x_i\}$; the mentioned state itself corresponds to the saddle point[10−13] of W. Thus, the equilibrium of the critical nucleus with ambient phase is unstable; one of the variables $\{x_i\}$ (relating to the nucleus size) is unstable.

2.2. Energy of the System "Nucleus + Ambient Phase" and Equations for Surface Tension.

From the two approaches to the description of interface phenomena—the finite-thickness layer method[18] and Gibbs' method[19]—the latter is used here in considering the thermodynamics of the heterogeneous system "nucleus + ambient phase" near the saddle point. The superficial (or excessive) quantities[19] relating to the interface between a nucleus and ambient phase are denoted by the subscript Σ; these are the energy E_Σ, the entropy S_Σ, and the number of particles N_Σ. The energy of the initial homogeneous system (without a nucleus) consisting of N_{tot} particles and having the volume V_1 is[18]

$$E_1 = T_0 S_1 - P_0 V_1 + \mu_0 N_{tot} \tag{6}$$

where μ_0 is the chemical potential of the homogeneous (bulk) ambient phase and S_1 is the entropy of the mentioned state 1.

The energy of the system "nucleus + ambient phase" can be represented as the sum of three parts: the energy of the bulk phase in the nucleus, $E = TS - PV + \mu N$, the energy of the ambient bulk phase, $E_0 = T_0 S_0 - P_0 V_0 + \mu_0 N_0$, and the superficial energy E_Σ:

$$E_2 = (TS - PV + \mu N) + (T_0 S_0 - P_0 V_0 + \mu_0 N_0) + E_\Sigma \tag{7}$$

where μ, P, T, S, and N are, respectively, the chemical potential, the pressure, the temperature, the entropy, and the particle number of the nucleus bulk phase (vapor in a bubble); the same quantities with the subscript 0 have the same meaning for the ambient bulk phase.

The entropy, S_2, and the volume, V_2, of the mentioned system are

$$S_2 = S + S_0 + S_\Sigma, \qquad V_2 = V + V_0 \tag{8}$$

from where

$$\Delta S = S_2 - S_1 = S + S_0 + S_\Sigma - S_1,$$
$$\Delta V = V_2 - V_1 = V + V_0 - V_1 \tag{9}$$

Also

$$N + N_0 + N_\Sigma = N_{tot} \tag{10}$$

Calculating the difference $\Delta E = E_2 - E_1$, we use the equations $S_0 - S_1 = \Delta S - S - S_\Sigma$, $V_0 - V_1 = \Delta V - V$, and $N_0 - N_{tot} = -N - N_\Sigma$ which follows from eqs 9 and 10. Substituting ΔE into eq 1, we find the following expression for the work:

$$W = (\mu - \mu_0)N + (T - T_0)S - (P - P_0)V + E_\Sigma - T_0 S_\Sigma - \mu_0 N_\Sigma \tag{11}$$

The following step is to get an expression for E_Σ. To this end, we have to extend properly the expression for the energy of a two-phase system "nucleus + ambient phase" being in equilibrium[18]

$$E_2 = T_0 S_2 - PV - P_0 V_0 + \sigma A + \mu_0 N_{tot} \tag{12}$$

to a nonequilibrium (the mentioned above quasiequilibrium) case. Here, σ is the surface tension and A is the nucleus surface area; $T = T_0$ and $\mu = \mu_0$ in view of equilibrium.

The superficial entropy S_Σ, as an additive quantity, can be represented as the sum of two parts

$$S_\Sigma = \overline{S} + \overline{S}_0 \tag{13}$$

where $\overline{S}$ and $\overline{S}_0$ are the contributions to S_Σ from the new and ambient phases, respectively. The same is true for N_Σ:

$$N_\Sigma = \overline{N} + \overline{N}_0 \tag{14}$$

Thus, the direct generalization of eq 12 looks as

$$E_2 = T(S + \overline{S}) + T_0(S_0 + \overline{S}_0) - PV - P_0 V_0 + \sigma A + \mu(N + \overline{N}) + \mu_0(N_0 + \overline{N}_0) \tag{15a}$$

or

$$E_2 = \{T(S + \overline{S}) - PV + \mu(N + \overline{N}) + \sigma A\} + \{T_0(S_0 + \overline{S}_0) - P_0 V_0 + \mu_0(N_0 + \overline{N}_0)\}$$
$$\equiv E + E_0 \tag{15b}$$

The separation of S_Σ into two parts, eq 13, solves the problem of what temperature corresponds to S_Σ in the equation for E_2. Each of the parts, $\overline{S}$ and $\overline{S}_0$, enters in eqs 15 with its own temperature, T and T_0, respectively. The similar problem with N_Σ and chemical potentials is solved by the separation yielded by eq 14. So, eq 15 is fully symmetric with respect to both of the phases and seems a logical extension of eq 12 to the quasiequilibrium case. It is seen that the energy E_2 naturally splits into two parts: the nucleus energy E and the ambient phase energy E_0. The quantities $(S + \overline{S})$ and $(N + \overline{N})$ are the *true* values of the nucleus entropy and number of particles, and $(S_0 + \overline{S}_0)$ and $(N_0 + \overline{N}_0)$ are the true values of the ambient phase entropy and number of particles.

The desired quantity E_Σ is determined now by comparison of eqs 7 and 15:

$$E_\Sigma = T\overline{S} + T_0 \overline{S}_0 + \sigma A + \mu \overline{N} + \mu_0 \overline{N}_0 \tag{16}$$

or, in equivalent form,

$$E_\Sigma = E_\Sigma^{(eq)} + (T - T_0)\overline{S} + (\mu - \mu_0)\overline{N} \tag{17a}$$

$$E_\Sigma^{(eq)} = T_0 S_\Sigma + \sigma A + \mu_0 N_\Sigma \tag{17b}$$

where the equation for $E_\Sigma^{(eq)}$ has the same form as for the equilibrium value of E_Σ in Gibbs' method.[18,19]

As is known, eq 17b together with the equation

$$dE_\Sigma = T_0 dS_\Sigma + \sigma dA + \mu_0 dN_\Sigma \tag{18}$$

lead to the Gibbs adsorption equation[18,19]

$$A d\sigma = -S_\Sigma dT_0 - N_\Sigma d\mu_0 \tag{19}$$

The generalized adsorption equation for the quasiequilibrium case is derived from eqs 17 and the following one:

$$dE_\Sigma = T_0 dS_\Sigma + \sigma dA + \mu_0 dN_\Sigma + (T - T_0)d\overline{S} + (\mu - \mu_0)d\overline{N} \tag{20}$$

It has the form

$$A d\sigma = -S_\Sigma dT_0 - N_\Sigma d\mu_0 - \overline{S}d(T - T_0) - \overline{N}d(\mu - \mu_0) \tag{21}$$

In equilibrium, $T = T_0$ and $\mu = \mu_0$, it converts to eq 19, as it must.

The properties of an interface have to depend on the properties of coexisting phases, so the surface tension is a function of thermodynamic parameters of both of these phases. If these phases are in equilibrium, their thermodynamic parameters are not independent—they are connected with each other via the conditions of equilibrium. Thus, the surface tension in this case is a function of thermodynamic parameters of one of the phases: $\sigma = \sigma_{eq}(P_*, T_*) = \sigma_{eq}(P_0, T_0)$; the equalities $T_* = T_0$ and $P_* = P_*(P_0, T_0)$ at the equilibrium point are shown below. In a nonequilibrium case, the surface tension depends on the new-phase parameters also: $\sigma = \sigma(P, T; P_0, T_0)$. Equation 21 serves for determining such dependence (it should be noted that the finite-thickness layer method[18] is more convenient for this purpose). One of the assumptions of our

model is the ambient phase parameters do not change upon the nucleus formation and further evolution, i.e., T_0 = const, P_0 = const, and hence $\mu_0(P_0, T_0)$ = const. Therefore, eq 21 is simplified and takes the form

$$(A d\sigma)_{T_0,\mu_0} = -\bar{S} dT - \bar{N} d\mu \tag{22}$$

This equation determines the dependence $\sigma(P, T)$ of the surface tension on the nucleus parameters. Generally, this dependence has the form

$$\sigma(P, T) = \sigma_{eq}(P_0, T_0) + \bar{\sigma}(P, T) \tag{23}$$

which can be also regarded as an expansion of $\sigma(P, T)$ into a series in the vicinity of the equilibrium point (the saddle point):

$$A_*\bar{\sigma}(P, T) = -\bar{N}_* v(P - P_*) - (\bar{S}_* - \bar{N}_* s)(T - T_0) + \ldots \tag{24}$$

where $v = \partial\mu/\partial P = V/N$ and $s = -\partial\mu/\partial T$ are the volume and the entropy per one particle in a nucleus.

Adding the Gibbs–Dugem equation for a bulk phase

$$-S dT - N d\mu + V dP = 0 \tag{25}$$

to eq 22, we obtain one more representation of the latter:

$$(A d\sigma)_{T_0,\mu_0} = -(S + \bar{S}) dT + V dP - (N + \bar{N}) d\mu \tag{26}$$

2.3. Work near the Equilibrium Point. Substituting eqs 17 into eq 11, we obtain

$$W = (\mu - \mu_0)(N + \bar{N}) + (T - T_0)(S + \bar{S}) - (P - P_0)V + \sigma A \tag{27a}$$

or

$$W = \Delta G + (T - T_0)(S + \bar{S}) - (P - P_0)V + \sigma A$$
$$= \Delta\tilde{G} + (T - T_0)(S + \bar{S}) \tag{27b}$$

where $\Delta G = G_2 - G_1 = (\mu - \mu_0)(N + \bar{N})$, $G_2 = \mu(N + \bar{N}) + \mu_0(N_0 + \bar{N}_0)$, and $G_1 = \mu_0 N_{tot} = \mu_0(N + \bar{N} + N_0 + \bar{N}_0)$; $\Delta\tilde{G} = \tilde{G}_2 - G_1$, $\tilde{G}_2 = -(P - P_0)V + \sigma A + \mu(N + \bar{N}) + \mu_0(N_0 + \bar{N}_0)$. G_2 is the Gibbs free energy of the system "nucleus + ambient phase" according to the rigorous thermodynamic definition of this quantity for an equilibrium heterogeneous system[18] and extension to a nonequilibrium case. $\tilde{G}_2$ is the thermodynamic potential defined for the system "nucleus + ambient phase" similarly to the Gibbs free energy of a homogeneous system;[18] the pressure–volume term is chosen in this definition as $P_0(V + V_0)$.

The minimum work W done by a system on a body (with the temperature T and the pressure P) located in it is equal to the change in the Gibbs free energy of the body, ΔG, only if $T = T_0$ and $P = P_0$.[15] In our case, a part of the system itself (the selected amount of substance) plays the role of the "body". Obviously, the condition $P = P_0$ is never satisfied in nucleation phenomena. Therefore, the potential $\tilde{G}$ is employed when nucleation is considered in isothermal isobaric conditions.[18] It is seen from eq 27b that $W = \Delta\tilde{G}$ only if $T = T_0$. Thus, the method of thermodynamic potentials leads to certain difficulties in determining the work. For this reason, eq 1 for W is used here as the most general one.

Calculating the differential of W at constant T_0 and P_0, we employ eqs 22 and 25. As a result, one obtains

$$(dW)_{T_0,P_0} = (\mu - \mu_0) d(N + \bar{N}) + (T - T_0) d(S + \bar{S}) - (P - P_0) dV + \sigma dA \tag{28}$$

The condition of equilibrium, eq 5, leads to the well-known equations

$$T_* = T_0 \tag{29a}$$

$$\mu_* = \mu_0 \tag{29b}$$

$$P_* - P_0 = \frac{2\sigma}{R_*} \equiv P_L^* \tag{29c}$$

where R is the nucleus radius; P_L^* is the Laplace pressure for the critical nucleus.

Therefore, the dependence of surface tension on the nucleus state parameters does not change the classical conditions of equilibrium, as it must from the physical point of view.

Equations 29 determine the parameters of the critical nucleus: the temperature, the vapor pressure or the density, and the critical radius. As is known,[15,16] the Kelvin equation connecting the pressure P_* of a saturated vapor in a bubble with the critical radius R_* follows from eqs 29b and 29c and has the form

$$P_* = P_\infty(T_0) e^{-2v_0\sigma/kT_0 R_*}, \qquad P_\infty(T_0) = C e^{-q/kT_0} \tag{30}$$

where $P_\infty(T_0)$ is the pressure of a saturated vapor at the plane interface, v_0 is the volume per one molecule in a liquid, q is the heat of evaporation per one molecule, and C is the constant. Equations 30 and 29c are combined into a transcendental equation for the critical radius:

$$P_0 + \frac{2\sigma}{R_*} = P_\infty(T_0) e^{-2v_0\sigma/kT_0 R_*} \tag{31}$$

Substitution of eqs 29 into eqs 27 leads to the well-known Gibbs equation for the critical work

$$W_* = \frac{1}{3}\sigma A_* \tag{32}$$

A further step is to get the second differential of the work. The following relations are employed below:

$$S = sN, \quad V = vN, \quad A = gV^{2/3}, \quad g = 3^{2/3}(4\pi)^{1/3} \tag{33}$$

and

$$[\sigma d^2 A - (P - P_0) d^2 V]_* = -\frac{2}{9} g\sigma V_*^{-4/3} (dV)^2 \tag{34}$$

Calculating the differential of eq 28 at the equilibrium point (i.e., with account for eqs 29a and 29b) and at constant T_0, P_0, we obtain

$$(d^2 W)_{T_0,P_0} = d\mu d(N + \bar{N}) + dT d(S + \bar{S}) - dP dV + d\sigma dA + (\sigma d^2 A - (P - P_0) d^2 V) \tag{35}$$

In view of the equations $d\mu = -s dT + v dP$, $dS = s dN + N ds$, and $dV = v dN + N dv$, eq 35 is transformed as follows:

$$(d^2 W)_{T_0,P_0} = N(dT ds - dP dv) + (\sigma d^2 A - (P - P_0) d^2 V) + [d\mu d\bar{N} + dT d\bar{S} + d\sigma dA] \tag{36}$$

Let us assume that the expression in square brackets in this equation is equal to zero and consider the meaning of this approximation. Thus, differentiating eq 22, we have

$$d\mu d\bar{N} + dTd\bar{S} + d\sigma dA = -Ad^2\sigma - \bar{S}d^2T - \bar{N}d^2\mu = 0 \tag{37}$$

from where

$$(Ad^2\sigma)_{T_0,P_0} = -\bar{S}d^2T - \bar{N}d^2\mu \tag{38}$$

and

$$d\sigma = -\frac{d\bar{S}}{dA}dT - \frac{d\bar{N}}{dA}d\mu \tag{39}$$

Comparing eqs 39 and 22, we find that the considered approximation means

$$\frac{d\bar{S}}{dA} = \frac{\bar{S}}{A} \quad \text{and} \quad \frac{d\bar{N}}{dA} = \frac{\bar{N}}{A} \tag{40a}$$

i.e.,

$$\bar{S} = C_{\bar{S}}A, \quad \bar{N} = C_{\bar{N}}A \tag{40b}$$

where $C_{\bar{N}}$ and $C_{\bar{S}}$ are the constants.

The proportionality of superficial quantities to the interface surface area is their natural property; the quantities $C_{\bar{S}}$ and $C_{\bar{N}}$ are the superficial densities of $\bar{S}$ and $\bar{N}$ similar to those introduced by Gibbs.[19] Starting from eq 40b, we come to eq 37. Thus, the given approximation seems to be physically plausible and the second differential at the equilibrium point has the form

$$(d^2W)_* = N_*[dTds - dPdv]_* - \frac{2}{9}g\sigma V_*^{-4/3}(dV)^2 \tag{41}$$

Here, as well as in eqs 29c–32, the surface tension σ has its equilibrium value $\sigma_* \equiv \sigma_{eq}$.

Thus, in the vicinity of the equilibrium point,[13]

$$W = W_* + \frac{1}{2}(d^2W)_*$$
$$= W_* + \frac{1}{2}\sum_{i,k} h_{ik}(x_i - x_i^*)(x_k - x_k^*) \tag{42}$$

2.4. Canonical Variables. Using eq 41, we can find the matrix **H** in eq 42 for different sets of variables $\{x_i\}$ describing a vapor bubble.

(1) $\{x_i\} = (V, \rho, T)$, $\rho = N/V$ is the density of the bulk vapor phase.

The familiar thermodynamic relation

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P \tag{43}$$

can be employed for the determination of $ds(\rho, T)$. Together with the equation of state of vapor,

$$P(\rho, T) = \rho kT \tag{44}$$

it yields $(\partial s/\partial\rho)_T = -k/\rho$, so

$$ds(\rho, T) = -\frac{k}{\rho}d\rho + \frac{c_V}{T}dT \tag{45}$$

where c_V is the heat capacity of vapor per one molecule at constant V. This equation also can be gotten from the equation for the entropy of an ideal gas[15] per one molecule:

$$s(\rho, T) = k\ln\frac{e}{\rho} + c_V\ln T + \text{const} \tag{46}$$

From the equation of state, eq 44,

$$dP(\rho, T) = kTd\rho + k\rho dT \tag{47}$$

Substituting eqs 45 and 47 into eq 41 and taking into account $dv = d(1/\rho) = -d\rho/\rho^2$, we obtain the matrix **H**:

$$\mathbf{H} = \begin{pmatrix} -\dfrac{2}{9}g\sigma V_*^{-4/3} & 0 & 0 \\ 0 & \dfrac{kT_0 V_*}{\rho_*} & 0 \\ 0 & 0 & \dfrac{c_V\rho_* V_*}{T_0} \end{pmatrix} \tag{48}$$

The matrix **H** has a canonical form in the variables (V, ρ, T), so these variables are canonical for the system considered. The variable V is a natural unstable variable for a bubble, the quadratic form $N_*[dTds - dPdv]_*$ is positive definite. The hypersurface represented by the quadratic form $H(\{x_i\})$ is a saddle one. Note that a similar expression, $[\Delta T\Delta S - \Delta P\Delta V]$, is employed in ref 15 for calculating the fluctuations of thermodynamic quantities. Hence, the fluctuations of stable variables for the critical nucleus are the same as in the theory of fluctuations.[15] They can be found from eq 48 according to the relation[13] $\langle(\Delta x_i)^2\rangle = kT_0/h_{ii}$. Thus, for the relative fluctuations of ρ and T, one obtains

$$\frac{\sqrt{\langle(\Delta\rho)^2\rangle}}{\rho_*} = \frac{1}{\sqrt{N_*}}, \qquad \frac{\sqrt{\langle(\Delta T)^2\rangle}}{T_0} = \sqrt{\frac{k}{c_V}}\frac{1}{\sqrt{N_*}} \tag{49}$$

From the physical point of view, the nucleation rate has not to depend on the choice of variables. Therefore, it is of interest to calculate the matrix **H** for other sets of variables.

(2) $\{x_i\} = (V, N, T)$

The following equations are employed:

$$ds(V, N, T) = \frac{k}{V}dV - \frac{k}{N}dN + \frac{c_V}{T}dT \tag{50a}$$

$$dP(V, N, T) = -\frac{NkT}{V^2}dV + \frac{kT}{V}dN + \frac{kN}{V}dT \tag{50b}$$

$$dv = \frac{dV}{N} - \frac{V}{N^2}dN \tag{50c}$$

As a result, eq 41 yields

$$\mathbf{H}_{(V,N,T)} = \begin{pmatrix} \left[\dfrac{N_*kT_0}{V_*^2} - \dfrac{2}{9}g\sigma V_*^{-4/3}\right] & -\dfrac{kT_0}{V_*} & 0 \\ -\dfrac{kT_0}{V_*} & \dfrac{kT_0}{N_*} & 0 \\ 0 & 0 & \dfrac{c_V N_*}{T_0} \end{pmatrix} \tag{51}$$

(3) $\{x_i\} = (V, P, T)$

The following equations are employed:

$$ds(P, T) = -\frac{k}{P}dP + \frac{c_P}{T}dT \tag{52a}$$

$$dv = \frac{k}{P}dT - \frac{kT}{P^2}dP \tag{52b}$$

the latter is obtained from the state equation in the form $v = kT/P$.

The matrix $\mathbf{H}_{(V,P,T)}$ is

$$\mathbf{H}_{(V,P,T)} = \begin{pmatrix} -\frac{2}{9}g\sigma V_*^{-4/3} & 0 & 0 \\ 0 & \frac{V_*}{P_*} & -\frac{V_*}{T_0} \\ 0 & -\frac{V_*}{T_0} & \frac{c_P P_* V_*}{kT_0^2} \end{pmatrix} \tag{53}$$

The set (V, P, T), as well as the set (V, ρ, T), contains one unstable (extensive) variable and two stable (intensive) variables. However, the matrix $\mathbf{H}_{(V,P,T)}$ is not canonical, differently from the matrix $\mathbf{H}$, since the variables P and T are not independent—P is the function of T according to the state equation 44.

The set (V, N, T) contains two extensive variables, V and N. Both of these variables are unstable. The transformation $N \rightarrow \rho = N/V$ retains only one unstable variable V; the variable ρ is stable. Here the similarity with binary nucleation[10] takes place, where a nucleus is described by the numbers n_1 and n_2 of monomers of both species. Both of these variables are physically equivalent; they are unstable. The transformation $(n_1, n_2) \rightarrow (n, c)$, where $n = n_1 + n_2$ and $c = n_2/n$, breaks this symmetry—the variable n is unstable, the variable c is stable.[13,20]

3. KINETICS OF NUCLEATION

3.1. Equations of Motion of a Nucleus and Symmetry of Kinetic Coefficients.
The equations of motion of a nucleus in the space $\{x_i\}$ in the vicinity of the saddle point have the form[13]

$$\dot{x}_i = -z_{ik}(x_k - x_k^*), \qquad \mathbf{Z} = \mathbf{DH}/kT \tag{54}$$

where $\mathbf{D}$ is the matrix of diffusivities in the Fokker–Planck equation; the summation over k is implied. The velocities $\dot{x}_i$ on definition (as they appear in the Fokker–Planck equation, $\dot{x}_i = \lim_{\Delta t \to 0}(\langle \Delta x_i \rangle_{\Delta t}/\Delta t)$) are macroscopic; i.e., $\dot{x}_i$ is the rate of change of the mean value[2] $\langle x_i \rangle$.

Our aim is to determine the negative eigenvalue κ_1 of the matrix $\mathbf{Z}$ which appears in the expression for the steady state nucleation rate.[11−13] The matrix $\mathbf{D}$ is shown[13,21,22] to be symmetric in nucleation processes, in accordance with Onsager's reciprocal relations. Hydrodynamic and phenomenological equations will be used here for deriving the matrix $\mathbf{Z}$. The question arises of whether they will provide symmetry of the matrix $\mathbf{D}$. To answer this question, let us consider at first a general algorithm of writing the motion eqs 54 which takes into account the symmetry conditions. Then, we shall consider how the given algorithm agrees with the use of hydrodynamic and phenomenological equations.

Let the variable x_1 be unstable (the volume V of a nucleus); the remaining variables x_i, $i > 1$, are stable. The incrementing δx_i of a stable variable, $i > 1$, in the elementary act consists of two parts—the regular one which is proportional to the

incrementing δx_1 of the unstable variable and the fluctuating one,[13,21,22] $\delta \tilde{x}_i$:

$$\delta x_i = a_i \delta x_1 + \delta \tilde{x}_i \tag{55}$$

In accordance with this fact, eq 54 for stable variables can be represented in the following form:

$$\dot{x}_i = a_i \dot{x}_1 + (\dot{x}_i)_{x_1}, \qquad i > 1 \tag{56}$$

where the addend $(\dot{x}_i)_{x_1}$ means that the derivative $\dot{x}_i$ is calculated at a constant value of x_1. Hence, $(\dot{x}_i)_{x_1}$ is proportional to stable variables only:

$$(\dot{x}_i)_{x_1} = -\lambda_{ik}(x_k - x_k^*), \qquad i, k > 1 \tag{57}$$

These equations are nothing but the familiar equations of linear nonequilibrium thermodynamics.[15]

As is evident from the foregoing thermodynamic treatment, the number of variables in our problem is equal to three; correspondingly, the system of eq 57 consists of two equations for two stable variables x_2 and x_3. Comparing eqs 56 and 57 with eq 54, it is easy to get expressions for a_i as well as relations between elements of the matrices $\mathbf{\Lambda}$ and $\mathbf{Z}$:

$$a_2 = \frac{z_{21}}{z_{11}}, \qquad a_3 = \frac{z_{31}}{z_{11}} \tag{58a}$$

$$\lambda_{22} = \frac{\overline{z}_{33}}{z_{11}}, \qquad \lambda_{23} = -\frac{\overline{z}_{32}}{z_{11}}, \qquad \lambda_{32} = -\frac{\overline{z}_{23}}{z_{11}},$$

$$\lambda_{33} = \frac{\overline{z}_{22}}{z_{11}} \tag{58b}$$

where the line denotes an algebraic adjunct to the corresponding matrix element. Equations 58b can be also presented in equivalent form as follows:

$$z_{22} = \lambda_{22} + a_2 z_{12}, \qquad z_{23} = \lambda_{23} + a_2 z_{13},$$

$$z_{32} = \lambda_{32} + a_3 z_{12}, \qquad z_{33} = \lambda_{33} + a_3 z_{13} \tag{58c}$$

As noted above, the matrix $\mathbf{D} = kT\,\mathbf{ZH}^{-1}$ has to be symmetric. The matrix $\mathbf{H}$ in our problem is canonical, eq 48. The conditions of symmetry of the matrix $\mathbf{D}$ yield the following relations:

$$a_2 z_{11} h_{11}^{-1} = z_{12} h_{22}^{-1} \tag{59a}$$

$$a_3 z_{11} h_{11}^{-1} = z_{13} h_{33}^{-1} \tag{59b}$$

$$z_{32} h_{22}^{-1} = z_{23} h_{33}^{-1} \tag{59c}$$

where h_{ii}^{-1} is an element of the matrix $\mathbf{H}^{-1}$; $h_{ii}^{-1} = 1/h_{ii}$ in our case.

The similar matrix $\mathbf{D}_{st} = kT\mathbf{\Lambda H}_{st}^{-1}$ for the stable variables x_2 and x_3 is also symmetric according to Onsager's reciprocal relations; here

$$\mathbf{H}_{st}^{-1} = \begin{pmatrix} h_{22}^{-1} & 0 \\ 0 & h_{33}^{-1} \end{pmatrix} \tag{60}$$

From here

$$\lambda_{32} h_{22}^{-1} = \lambda_{23} h_{33}^{-1} \tag{61}$$

It is easy to show with the help of eqs 58c, 59a, and 59b that eqs 59c and 61 are identical.

Now the algorithm of writing eq 54 based on the conditions of symmetry of kinetic coefficients can be formulated.

(1) Equation 54 for $\dot{x}_1$ (the unstable variable derivative) is fully arbitrary; i.e., the matrix elements z_{11}, z_{12}, and z_{13} are arbitrary.

(2) Equation 57 for $\dot{x}_2$ is also arbitrary; i.e., the elements λ_{22} and λ_{23} are arbitrary.

(3) Only the summand proportional to $(x_3 - x_3^*)$, i.e., the element λ_{33}, is arbitrary in eq 57 for $\dot{x}_3$.

(4) The terms in eq 56 which are not arbitrary, just the coefficients a_2, a_3, and λ_{32}, are determined from the conditions of symmetry, eqs 59 and 61. Then, the remaining elements of the matrix $\mathbf{Z}$ are determined from eqs 58a and 58c.

Obviously, eq 54 written arbitrarily, in general, does not lead to a symmetric matrix $\mathbf{D}$. As an example, the nonsymmetric matrix $\mathbf{D}$ obtained in ref 5 can be presented. Only equations written in accordance with the given algorithm ensure symmetry of this matrix. After deriving the motion equations by this way, it is necessary to ascertain their physical meaning and to answer the question whether they are adequate to the considered process. Answers to these questions are given below by the example of the studied process of vapor bubbles formation.

Equations similar to eqs 59 and 61 as well as the algorithm of writing eq 54 take place in the case of arbitrary (noncanonical) matrix $\mathbf{H}$ also. However, they are not placed here for brevity.

3.2. Equations of Motion of a Vapor Bubble. Equations 54, 56, and 57 for a vapor bubble in the variables (V, ρ, T) have the following explicit forms:

$$
\begin{cases}
\dot{V} = -z_{VV}(V - V_*) - z_{V\rho}(\rho - \rho_*) \\
\qquad - z_{VT}(T - T_0) \\
\dot{\rho} = a_\rho \dot{V} + (\dot{\rho})_V \\
\dot{T} = a_T \dot{V} + (\dot{T})_V
\end{cases}
\tag{62a}
$$

$$
\begin{cases}
(\dot{\rho})_V = -\lambda_{\rho\rho}(\rho - \rho_*) - \lambda_{\rho T}(T - T_0) \\
(\dot{T})_V = -\lambda_{T\rho}(\rho - \rho_*) - \lambda_{TT}(T - T_0)
\end{cases}
\tag{62b}
$$

3.2.1. Equation for Bubble Volume. The dynamics of a spherical cavity in an inviscid and incompressible liquid is described by the Rayleigh equation[23]

$$
\rho_0\left[R\ddot{R} + \frac{3}{2}\dot{R}^2\right] = P_R - P_0
\tag{63}
$$

where R is the cavity radius, P_R is the pressure in a liquid at the cavity boundary (P_0 is the pressure far from the cavity), and ρ_0 is the mass density of a liquid.

Rederivation of this equation for a viscous liquid taking into account the viscosity terms both in the Navier–Stokes equation and boundary condition yields[4,5]

$$
\rho_0 R\ddot{R} + \frac{3}{2}\rho_0\dot{R}^2 + 4\eta_0\frac{\dot{R}}{R} = P - P_L - P_0
\tag{64}
$$

where η_0 is the viscosity of a liquid and P is the pressure of vapor in the bubble.

In terms of a volume, eq 64 has the form

$$
\ddot{V} = \frac{\dot{V}^2}{6V} - \frac{4\eta_0}{b\rho_0}\frac{\dot{V}}{V^{2/3}} + \frac{3}{b\rho_0}V^{1/3}\left(P - \frac{2\sigma}{\sqrt{b}\,V^{1/3}} - P_0\right),
$$
$$
b = (3/4\pi)^{2/3}
\tag{65}
$$

In this equation, we neglect by the term proportional to $\dot{V}^2$, since the motion equations are linear in the vicinity of the saddle point, and put $\ddot{V} = 0$, since the case of high viscosity is considered. As a result, we have the following equation:

$$
\dot{V} = 3\xi V\left(P - \frac{2\sigma}{\sqrt{b}\,V^{1/3}} - P_0\right), \qquad \xi \equiv 1/4\eta_0
\tag{66}
$$

Substituting here $P = \rho kT$ and expanding the right side near the saddle point up to linear terms in accordance with eq 54, we find

$$
z_{VV} = -\xi P_L^*, \qquad z_{V\rho} = -3\xi V_* kT_0,
$$
$$
z_{VT} = -3\xi k V_* \rho_* = -3\xi k N_*
\tag{67}
$$

3.2.2. Equation for Vapor Density. According to the definition of density, $\rho = N/V$, its derivative is

$$
\dot{\rho} = -\frac{\rho}{V}\dot{V} + \frac{1}{V}\dot{N}
\tag{68}
$$

The equation for $\dot{N}$[4,5]

$$
\dot{N} = \pi\beta u R^2[P_{eq}(T, R) - P]/kT = \pi\beta u R^2[\rho_{eq}(T, R) - \rho]
\tag{69}
$$

is the difference of fluxes of evaporation, $\sim P_{eq}$, and condensation, $\sim P$. The flux of evaporation is assumed to be the same as in the equilibrium state for given T and R ($P = P_{eq}(T, R)$), when both the fluxes are equal to each other in accordance with the detailed balancing principle;[13] $P_{eq}(T, R)$ is given by the Kelvin eq 30 with arbitrary T and R. Here $u = (8kT/\pi m)^{1/2}$ is the mean thermal velocity of vapor molecules, β is the condensation coefficient, and

$$
\rho_{eq}(T, R) = \frac{C}{kT}e^{-q/kT(1+(2v_0\sigma/qR))}
\tag{70}
$$

The first summand in eq 68 is proportional to $\dot{V}$, as in general equation 62a. In other words, eq 68 initially has the form of eq 62a. On the other hand, the form of the factor at $\dot{V}$ (the factor a_ρ) is dictated by one of the symmetry conditions, eq 59a (see point 4 of the algorithm):

$$
a_\rho = \frac{z_{V\rho}}{z_{VV}}\frac{h_{VV}}{h_{\rho\rho}}
\tag{71a}
$$

Substituting here expression 67 for z_{VV} and $z_{V\rho}$ as well as expressions for h_{VV} and $h_{\rho\rho}$, eq 48, we find

$$
a_\rho = -\frac{\rho_*}{V_*}
\tag{71b}
$$

which is in full agreement with eq 68 written near the saddle point.

Thus, the symmetry conditions do not change the natural form of the equation for $\dot{\rho}$. From eqs 68 and 62a,

$$
(\dot{\rho})_V = \frac{1}{V}(\dot{N})_V
\tag{72}
$$

Expanding $(\dot{N})_V$, eq 69, in ρ and T near the saddle point up to linear terms, we determine the elements $\lambda_{\rho\rho}$ and $\lambda_{\rho T}$ in the first of eqs 62b:

$$\lambda_{\rho\rho} = \frac{3}{4}\frac{\beta u(T_0)}{R_*}, \qquad \lambda_{\rho T} = -\lambda_{\rho\rho}\frac{\rho_*}{T_0}\tilde{q},$$

$$\tilde{q} \equiv \frac{q - kT_0 + 2v_0\sigma/R_*}{kT_0} \tag{73}$$

Thus, the desired equation for $\dot{\rho}$ is

$$\dot{\rho} = -\frac{\rho_*}{V_*}\dot{V} - \lambda_{\rho\rho}(\rho - \rho_*) + \lambda_{\rho\rho}\frac{\rho_*}{T_0}\tilde{q}(T - T_0) \tag{74}$$

with $\lambda_{\rho\rho}$ given by eq 73.

3.2.3. Equation for Vapor Temperature. According to the above algorithm, the coefficients a_T and $\lambda_{T\rho}$ in eqs 62a and 62b are determined from symmetry conditions 59b and 61:

$$a_T = \frac{z_{VT}}{z_{VV}}\frac{h_{VV}}{h_{TT}} = -\frac{kT_0}{c_V V_*} = -\frac{P_*}{C_V^*} \tag{75}$$

$$\lambda_{T\rho} = \lambda_{\rho T}\frac{h_{\rho\rho}}{h_{TT}} = -\lambda_{\rho\rho}\frac{kT_0}{c_V\rho_*}\tilde{q} \tag{76}$$

where $C_V^* = c_V N_*$ is the heat capacity of the critical bubble.

Therefore, the equation for $\dot{T}$ is

$$\dot{T} = -\frac{P_*}{C_V^*}\dot{V} - \frac{1}{C_V^*}\left[q - kT_0 + \frac{2v_0\sigma}{R_*}\right](\dot{N})_V$$
$$- \lambda_{TT}(T - T_0) \tag{77a}$$

or, in equivalent form,

$$dE = C_V^*dT + \left[q - kT_0 + \frac{2v_0\sigma}{R_*}\right]dN = -P_*dV + dQ \tag{77b}$$

where

$$dQ = -C_V^*\lambda_{TT}(T - T_0)dt = -4\pi R_*^2\alpha(T - T_0)dt \tag{77c}$$

is the heat received by the bubble from the ambient liquid ($Q > 0$, if $T < T_0$) in the time interval dt. The heat exchange occurs according to Newton's law

$$j = \alpha(T - T_0) \tag{78}$$

where j is the heat flux density and α is the coefficient of heat exchange between a vapor bubble and surrounding liquid.

The expression $\Delta\varepsilon = q - kT_0$ is the first law of thermodynamics for evaporating molecules (per one molecule): q is the heat of evaporation received from the liquid, $P_*(v - v_0) \approx P_*v = kT_0$ is the work done upon evaporation. The quantity $2v_0\sigma/R_* = \sigma\delta A_{(1)}$ is the work of the interface increase upon the evaporation of one molecule. The energy of an ideal gas is[15] $E = Nc_VT + N\varepsilon_0 = C_VT + \text{const}$. The constituent parts of a bubble are the vapor and the interface. The full change of the vapor bubble energy on the left side of eq 77b contains the contributions from both of these components: the change of the vapor energy due to the temperature change and the change of the bubble energy due to the addition of dN evaporated interfacial molecules to the vapor and due to the increase of the interface area. On the right side of eq 77b, we have the work done by the bubble during the change of its volume, dV, and the heat dQ received by the bubble from surrounding liquid.

Thus, eq 77a for the temperature is nothing but the *first law of thermodynamics* for a vapor bubble. The second summand in this equation is the change of the bubble temperature (cooling) due to the evaporation of molecules from its boundary.

From eq 77c,

$$\lambda_{TT} = \frac{4\pi R_*^2\alpha}{C_V^*} = \frac{3\alpha}{c_V\rho_*R_*} \tag{79}$$

Finally, the equation for $\dot{T}$ is

$$\dot{T} = -\frac{P_*}{C_V^*}\dot{V} + \lambda_{\rho\rho}\frac{kT_0}{c_V\rho_*}\tilde{q}(\rho - \rho_*) - \frac{3\alpha}{c_V\rho_*R_*}(T - T_0) \tag{80}$$

Therefore, the symmetry conditions for the kinetic coefficients not only do not impose some artificial restrictions on the motion equations, but they "help" us to write them correctly. Thereby, thermodynamics, hydrodynamics, and interfacial kinetics are combined into a self-consistent theory of nucleation. The question on the applicability of Onsager's reciprocal relations in the nucleation theory in view of the presence of an unstable variable was discussed in ref 13. These relations were shown to be a consequence of the detailed balancing principle. At the same time, the motion equation 54 involves this principle; they are obtained from the Fokker–Planck equation with the use of the equilibrium distribution function $f_{eq}(\{x_i\})$.[13] The derivation of the equations for $\dot{\rho}$ and $\dot{T}$ demonstrated here also shows that the reciprocal relations are a consequence of the fundamentals of kinetics (the detailed balancing principle) and thermodynamics (the first law). This conclusion supports and complements the result of ref 13. Thus, the reciprocal relations are validated in a phenomenological way, without resorting to a microscopic consideration.

3.3. Relaxation of Bubble Temperature. It is necessary to express the heat exchange coefficient α via thermal characteristics of the liquid which are more definite and experimentally measured. For this purpose, the thermal problem of the bubble temperature relaxation has to be considered (without regard for the processes of evaporation–condensation). When the bubble temperature T deviates from its equilibrium value T_0, it relaxes to the latter according to the equation of linear nonequilibrium thermodynamics[15]

$$\frac{dF(t)}{dt} = -\lambda_{TT}F(t), \qquad F(t) \equiv T(t) - T_0 \tag{81a}$$

from where

$$F(t) = F(0)e^{-\lambda_{TT}t} \tag{81b}$$

It should be recalled that, according to one of the model assumptions, relaxation processes inside the bubble occur sufficiently fast, so the temperature inside the bubble is uniform at any time.

Thus, the problem of the temperature distribution, $T(r, t)$, around the sphere of radius R and temperature $F(t)$ arises. Its solution is[23]

$$T(x, t) = \frac{Rx}{2(x + R)\sqrt{\pi\chi_0}}\int_0^t \frac{F(\tau)}{(t - \tau)^{3/2}}e^{-x^2/4\chi_0(t-\tau)}\,d\tau,$$

$$x \equiv r - R \tag{82}$$

where χ_0 is the thermal diffusivity of the liquid.

The heat flux density on the bubble boundary $r = R$ is

$$j(t) = -\theta_0 \frac{dT}{dx}\Big|_{x=0} = \theta_0 \left\{ \frac{F(t)}{R} + \frac{F(0)}{\sqrt{\pi \chi_0 t}} \right.$$

$$\left. + \frac{1}{\sqrt{\pi \chi_0}} \int_0^t \frac{dF}{d\tau} \frac{d\tau}{\sqrt{t-\tau}} \right\} \tag{83a}$$

or, with regard for eq 81b,

$$j(t) = \theta_0 \left\{ \frac{F(0)e^{-\lambda_{TT}t}}{R} + \frac{F(0)}{\sqrt{\pi \chi_0 t}} - \frac{2\sqrt{\lambda_{TT}}}{\sqrt{\pi \chi_0}} F(0)e^{-\lambda_{TT}t} \right.$$

$$\left. \int_0^{\sqrt{\lambda_{TT}t}} e^{y^2}\, dy \right\} \tag{83b}$$

where θ_0 is the heat conductivity coefficient of the liquid.

The total heat ΔQ_∞ transferred across the sphere $r = R$ is

$$\Delta Q_\infty = 4\pi R^2 \int_0^\infty j(\tau)\, d\tau = 4\pi R^2 \frac{\theta_0 F(0)}{R \lambda_{TT}} \tag{84a}$$

On the other hand, according to Newton's heat-exchange law,

$$\Delta Q_\infty = 4\pi R^2 \alpha \int_0^\infty F(\tau)\, d\tau = 4\pi R^2 \alpha \frac{F(0)}{\lambda_{TT}} \tag{84b}$$

From comparing these expressions, the desired relation is obtained:

$$\alpha = \frac{\theta_0}{R} \tag{85}$$

3.4. Nucleation Rate of Bubbles. The multivariable stationary nucleation rate calculated in ref 13 has the form

$$I = N_b \sqrt{\frac{kT_0}{2\pi}|h_{11}^{-1}|} |\kappa_1| e^{-W_*/kT_0} \tag{86}$$

where κ_1 is the negative eigenvalue of the matrix $\mathbf{Z} = \mathbf{DH}/kT$ corresponding to the system of eq 54 (note that the matrix $\mathbf{Z} = \mathbf{DH}$ is employed in ref 13, so κ_1 differs by the multiplier kT therein). N_b is the normalizing constant of the one-dimensional equilibrium distribution function. If a nucleus is described by the number of monomers forming it (e.g., a drop in a vapor), then N_b is the number of monomers of the parent phase in unit volume.[13] However, the determination of N_b for bubbles is a separate problem. Its solution can be obtained within the framework of the hole theory of liquids[17] in view of the analogy between holes in liquids and vacancies in solids.

The equilibrium number of vacancies or holes in a liquid at given T and P is[17]

$$N_h = N_1 e^{-w_h(P,T)/kT} \tag{87}$$

where $w_h(P, T)$ is the work of vacancy (the minimum-size hole in a liquid[17]) formation and $N_1 = 1/v_0$ is the number of atoms in a solid or monomers in a liquid in unit volume. Let ω_h be the volume of a vacancy or the minimum-size hole. The cluster of n vacancies or minimum-size holes has the volume $V = n\omega_h$, so the equilibrium distribution function of multivacancy complexes or bubbles is

$$f_{eq}(V) = \frac{N_h}{\omega_h} e^{-W(V)/kT} \tag{88}$$

where $W(V)$ is the work of formation of the bubble of volume V. The normalizing constant for bubbles, N_b, is obtained from eqs 87 and 88 as

$$N_b = \frac{1}{v_0 \omega_h} e^{-w_h(P_0, T_0)/kT_0} \tag{89}$$

This is only a simple reasoning designed to show how the normalizing factor for bubbles can be obtained within the classical nucleation theory (CNT). In fact, the problem of the preexponential factor in the equilibrium distribution of nuclei is deeper. Its detailed study based on the statistical mechanical approach is carried out in refs 24−28, where significant multipliers not appearing in CNT are obtained.

Having the equations for $\dot\rho$ and $\dot T$, we can get the remaining elements of the matrix $\mathbf{Z}$ according to eqs 58a and 58c:

$$\mathbf{Z} = \begin{pmatrix} z_{VV} & z_{V\rho} & z_{VT} \\ a_\rho z_{VV} & \lambda_{\rho\rho} + a_\rho z_{V\rho} & \lambda_{\rho T} + a_\rho z_{VT} \\ a_T z_{VV} & \lambda_{T\rho} + a_T z_{V\rho} & \lambda_{TT} + a_T z_{VT} \end{pmatrix} \tag{90a}$$

or, in more explicit form,

$$\mathbf{Z} = \begin{pmatrix} -\xi P_L^* & -3\xi V_* kT_0 & -3\xi k N_* \\ \xi P_L^* \dfrac{\rho_*}{V_*} & \lambda_{\rho\rho} + 3\xi P_* & \lambda_{\rho T} + 3\xi k \rho_*^2 \\ \xi P_L^* \dfrac{P_*}{C_V^*} & \lambda_{T\rho} + 3\xi \dfrac{(kT_0)^2}{c_V} & \lambda_{TT} + 3\xi \dfrac{k}{c_V} P_* \end{pmatrix} \tag{90b}$$

The determinant of $\mathbf{Z}$ is

$$\det \mathbf{Z} = z_{VV} \det \mathbf{\Lambda} \tag{91}$$

The cubic equation for eigenvalues of the matrix $\mathbf{Z}$ has the following form:

$$\kappa^3 - (Sp\mathbf{Z})\kappa^2 + B\kappa - \det \mathbf{Z} = 0 \tag{92}$$

where

$$B = \Delta_{V\rho} + \Delta_{VT} + \Delta_{\rho T}, \qquad \Delta_{V\rho} = \det \mathbf{Z}_{V\rho} = z_{VV}\lambda_{\rho\rho},$$

$$\Delta_{VT} = \det \mathbf{Z}_{VT} = z_{VV}\lambda_{TT}, \qquad \Delta_{\rho T} = \det \mathbf{Z}_{\rho T} \tag{93}$$

and

$$\mathbf{Z}_{V\rho} = \begin{pmatrix} z_{VV} & z_{V\rho} \\ a_\rho z_{VV} & \lambda_{\rho\rho} + a_\rho z_{V\rho} \end{pmatrix},$$

$$\mathbf{Z}_{VT} = \begin{pmatrix} z_{VV} & z_{VT} \\ a_T z_{VV} & \lambda_{TT} + a_T z_{VT} \end{pmatrix},$$

$$\mathbf{Z}_{\rho T} = \begin{pmatrix} \lambda_{\rho\rho} + a_\rho z_{V\rho} & \lambda_{\rho T} + a_\rho z_{VT} \\ \lambda_{T\rho} + a_T z_{V\rho} & \lambda_{TT} + a_T z_{VT} \end{pmatrix} \tag{94}$$

Employing the trigonometric form of solution of eq 92, the desired root is selected as

$$\kappa_1 = \frac{1}{3}\left\{ -2\sqrt{(Sp\mathbf{Z})^2 - 3B}\,\cos\left(\frac{\phi}{3} - \frac{\pi}{3}\right) + Sp\mathbf{Z} \right\} \tag{95}$$

where

$$\cos \phi = -\frac{U}{2\sqrt{-(Y/3)^3}},$$

$$U = -\frac{2}{27}(Sp\mathbf{Z})^3 + \frac{BSp\mathbf{Z}}{3} - \det \mathbf{Z},$$

$$Y = B - \frac{(Sp\mathbf{Z})^2}{3} \tag{96}$$

The calculation of κ_1 solves the problem of determining the stationary nucleation rate.

4. DISCUSSION. KINETIC LIMITS

4.1. Kinetic Region of Nucleation. Let us consider a consequence of the obvious physical condition $\det \mathbf{\Lambda} > 0$. From eqs 73 and 76, $\lambda_{\rho T}\lambda_{T\rho} = (k/c_V)\tilde{q}^2\lambda_{\rho\rho}^2$. Hence,

$$\det \mathbf{\Lambda} = \lambda_{\rho\rho}\lambda_{TT} - \lambda_{\rho T}\lambda_{T\rho} = \lambda_{\rho\rho}\left(\lambda_{TT} - \frac{k}{c_V}\tilde{q}^2\lambda_{\rho\rho}\right) > 0 \tag{97a}$$

i.e.,

$$\lambda_{TT} > \frac{k}{c_V}\tilde{q}^2\lambda_{\rho\rho} \tag{97b}$$

Substituting eq 79 for λ_{TT} and eq 73 for $\lambda_{\rho\rho}$, we obtain

$$\alpha > \tilde{q}^2 k\beta u_1\rho_*, \qquad u_1 = \sqrt{kT_0/2\pi m} \tag{97c}$$

Employing eq 85 for α, we find finally

$$\frac{R_*(T_0, P_0)\rho_*(T_0, R_*)}{\zeta(T_0)} < 1, \qquad \zeta(T_0) \equiv \frac{\theta_0}{\tilde{q}^2 k\beta u_1} \tag{98}$$

The quantity ζ weakly depending on temperature is a characteristic of the given liquid. The explicit dependences of R_* and ρ_* are indicated for further analysis of this inequality.

Condition 98 is not satisfied a fortiori near the equilibrium curve $P_\infty(T_0)$, since $R_* \to \infty$ and $\rho_* \to \rho_\infty(T_0) = P_\infty(T_0)/kT_0$ here. If the pressure P_0 decreases at a fixed value of T_0, then R_* and ρ_* decrease also. Consequently, this inequality begins to be satisfied starting from some value of pressure $\tilde{P}_0(T_0)$.

The thermodynamic region of nucleation is the region under the equilibrium curve: $P_0 < P_\infty(T_0)$ (the metastable region). The inequality $P_0 < \tilde{P}_0(T_0)$ narrows the thermodynamic region of nucleation. In other words, the nucleation of bubbles can occur only in the region $P_0 < \tilde{P}_0(T_0)$, where $\tilde{P}_0(T_0)$ is implicitly given by the equation

$$\frac{R_*(T_0, \tilde{P}_0)\rho_*(T_0, R_*(T_0, \tilde{P}_0))}{\zeta(T_0)} = 1 \tag{99a}$$

together with eq 31 for $R_*(T_0, P_0)$. Combining both of these equations, we obtain one more representation of eq 99a:

$$\frac{\tilde{P}_0 R_*(T_0, \tilde{P}_0)}{kT_0\zeta(T_0) - 2\sigma} = 1 \tag{99b}$$

Since the region $P_0 < \tilde{P}_0(T_0)$ is obtained from the kinetic condition $\det \mathbf{\Lambda} > 0$, it can be called the kinetic region of nucleation. On the other hand, nucleation in the thermodynamic region does not occur near the equilibrium curve $P_\infty(T_0)$, since the critical radius is large here and the nucleation rate is practically equal to zero. The nucleation rate becomes appreciable at some distance from the equilibrium curve. If the

curve $\tilde{P}_0(T_0)$ lies sufficiently close to the curve $P_\infty(T_0)$, i.e., in the region of zero nucleation rate, then condition 98 does not impose any restriction on the nucleation process. Otherwise, if the curve $\tilde{P}_0(T_0)$ lies sufficiently deep in the metastable region, condition 98 can forbid the nucleation process at the given (T_0, P_0) even if it is allowed by thermodynamics (the work W_* yields an acceptable value of the exponential function in eq 86).

Inequalities 97b and 97c show the limiting character of the thermal process in the nucleation of bubbles: the heat exchange between a bubble and ambient liquid has to be sufficiently fast. The quantities R_* and ρ_* have to be sufficiently small for that, according to eqs 79 and 85.

As one of the limiting cases, a nonvolatile liquid, $P_\infty(T_0) \to 0$, is considered below. Hence, $P_* \to 0$ and $\rho_* \to 0$ also. For such liquids, condition 98 is always satisfied.

4.2. Limits in the Two-Variable (V, ρ)-Theory. Let us assume that the kinetic limit $\lambda_{TT} \to \infty$ occurs in our (V, ρ, T)-theory (it is considered below), so the theory becomes two-dimensional with the variables ρ and V. In this case, the equation for eigenvalues has the form

$$\kappa^2 - (Sp\mathbf{Z}_{V\rho})\kappa + \det \mathbf{Z}_{V\rho} = 0 \tag{100}$$

from where

$$\kappa_1 = \frac{1}{2}\{Sp\mathbf{Z}_{V\rho} - \sqrt{(Sp\mathbf{Z}_{V\rho})^2 - 4\det \mathbf{Z}_{V\rho}}\} \tag{101}$$

$$Sp\mathbf{Z}_{V\rho} = z_{VV} + \lambda_{\rho\rho} + a_\rho z_{V\rho} = -\xi P_L^* + \lambda_{\rho\rho} + 3\xi P_*$$

The following kinetic limits with respect to $\lambda_{\rho\rho}$ are possible.
(1) $\lambda_{\rho\rho} \gg \xi P_L^*, 3\xi P_*$
In this case,

$$(Sp\mathbf{Z}_{V\rho})^2 \gg |\det \mathbf{Z}_{V\rho}| = |z_{VV}|\lambda_{\rho\rho} \tag{102a}$$

and

$$Sp\mathbf{Z}_{V\rho} > 0 \tag{102b}$$

so eq 101 becomes

$$\kappa_1 = \frac{\det \mathbf{Z}_{V\rho}}{Sp\mathbf{Z}_{V\rho}} = \frac{z_{VV}\lambda_{\rho\rho}}{z_{VV} + \lambda_{\rho\rho} + 3\xi P_*} \tag{103}$$

from where, in view of condition 1,

$$\kappa_1 = z_{VV} = -\xi P_L^* = \kappa^{(1D)} \tag{104}$$

(2) $\lambda_{\rho\rho} \ll \xi P_L^*, 3\xi P_*; 3P_* - P_L^* > 0, (3P_* - P_L^*) \sim P_L^*, 3P_*$, so $\lambda_{\rho\rho} \ll \xi(3P_* - P_L^*)$.

Conditions 102a and 102b take place in this case also; hence, eq 103 is valid as before. Now it yields

$$\kappa_1 = -\lambda_{\rho\rho}\frac{P_L^*}{3P_* - P_L^*} \tag{105}$$

(3) $\lambda_{\rho\rho} \ll \xi P_L^*, 3\xi P_*; |3P_* - P_L^*| \ll P_L^*, 3P_*$, so $\lambda_{\rho\rho} \sim \xi|3P_* - P_L^*|$ and $|Sp\mathbf{Z}_{V\rho}| = O(\lambda_{\rho\rho})$.

In this case, we have $(Sp\mathbf{Z}_{V\rho})^2 \ll |\det \mathbf{Z}_{V\rho}|$ instead of condition 102a, and eq 101 yields

$$\kappa_1 = -\sqrt{|\det \mathbf{Z}_{V\rho}|} = -\sqrt{\lambda_{\rho\rho}\xi P_L^*} \tag{106}$$

independently of the sign of $Sp\mathbf{Z}_{V\rho}$.

(4) $\lambda_{\rho\rho} \ll \xi P_L^*, 3\xi P_*; 3P_* - P_L^* < 0, |3P_* - P_L^*| \sim P_L^*, 3P_*$, so $\lambda_{\rho\rho} \ll \xi|3P_* - P_L^*|$

In this case, condition 102a is satisfied again, but $Sp\mathbf{Z}_{V\rho} < 0$. Equation 101 yields

$$\kappa_1 = Sp\mathbf{Z}_{V\rho} = -\xi|3P_* - P_L^*| = -\xi|3P_0 + 2P_L^*| \tag{107}$$

where the equilibrium condition $P_* = P_0 + P_L^*$ is employed. The inequality $3P_* - P_L^* < 0$ means that $P_0 < -(2/3)P_L^*$. At high negative pressures P_0, $|P_0| \gg P_*$, the equilibrium condition looks as $P_0 = -P_L^*$, so eq 107 becomes as eq 104, the one-dimensional result again.

Case 1 corresponds to fast kinetics for the density ρ. In other words, the process of exchange by particles between a bubble and surrounding liquid (the evaporation−condensation process) is rapid. Any deviation of the density from its equilibrium value ρ_* relaxes rapidly, so always $\rho = \rho_*$. Correspondingly, the theory becomes one-dimensional which is confirmed by eq 104. The latter is the result of the one-dimensional theory.

Cases 2−4 correspond to slow kinetics for ρ. The pressure P_0 changes from case 2 to case 4 from positive or moderately negative to large negative values. Accordingly, $Sp\mathbf{Z}_{V\rho}$ changes from positive in case 2 to negative in case 4 values. Equations 105 and 106 show that the nucleation process in cases **2** and **3** is limited by the evaporation−condensation process which is the slowest in these cases; the quantity κ_1 is determined by the parameter $\lambda_{\rho\rho}$ of this process. Also, these equations show the significance of a multivariable theory. Namely, if a one-dimensional theory with $\kappa_1 = z_{VV}$ is used when case **2** takes place, a strongly overestimated value of the nucleation rate is obtained.

On the other hand, the inertial motion of the liquid determining the rate of the bubble volume change, $\dot{V}$, is the slowest process in case 1. Accordingly, κ_1 is determined by the parameter z_{VV} of this process, eq 104, as the limiting one in this case. Thus, the conclusion from these results is the nucleation rate is determined by the *slowest* kinetic process in a system.

As the negative pressure P_0 increases in absolute value, the limitation slackens: from linear with respect to $\lambda_{\rho\rho}$ in eq 105 it becomes square root in eq 106 and vanishes all together in eq 107.

4.3. Cavitation. Let us consider the limit of cavitation[2] in a nonvolatile liquid, or the formation of cavities at high negative pressures P_0. As noted above, $P_* \to 0$ and $\rho_* \to 0$ in this case; hence, $Sp\mathbf{Z}_{V\rho} = z_{VV} + \lambda_{\rho\rho}$ and eq 101 directly yields the one-dimensional result $\kappa_1 = z_{VV}$.

This one-dimensional result is obtained as the thermodynamic limit, $P_* \to 0$, within the kinetic theory. On the other hand, it can also be obtained as the purely thermodynamic limit according to the general theory of ref 13. From eq 48, the element $h_{\rho\rho}$ of the matrix $\mathbf{H}$ is equal to kT_0V_*/ρ_*, i.e., $(h_{\rho\rho}/kT_0) \to \infty$ at $\rho_* \to 0$. Accordingly, we have for the density variance $(\langle(\rho - \rho_*)^2\rangle)^{1/2} \to 0$. This means that a small value of density is equilibrium; the cavity in a nonvolatile liquid is equilibrium with respect to vapor density. In other words, the probability of deviation from ρ_* is negligibly small; always $\rho = \rho_*$, accordingly, the dimensionality of the theory decreases by unity and it becomes one-dimensional.[13] Recalling the expression for λ_{TT}, eq 79, we see that $\lambda_{TT} \to \infty$ at $\rho_* \to 0$; i.e., the condition specified in the beginning of section 4.2 is satisfied. In summary, the cavitation in a nonvolatile liquid within the (V, ρ, T)-theory is the limiting process to the one-dimensional (V)-theory. This limiting process is thermodynamic in ρ ($h_{\rho\rho}/kT_0 \to \infty$) and kinetic in T ($\lambda_{TT} \to \infty$).

Equation $\kappa_1 = z_{VV}$ regarded as a limiting case of eq 107 at $|P_0| \gg P_*$ can be interpreted as follows. At high negative pressures, nucleation occurs as cavitation in a nonvolatile liquid, despite the presence of vapor in a bubble; i.e., vapor does not affect the nucleation process.[2] Accordingly, the kinetic limitation vanishes in case 4 and a small value of $\lambda_{\rho\rho}$ is of no importance. The above-mentioned one-dimensional result $\kappa_1 = z_{VV}$ directly obtained from eq 101 in the case $P_* \to 0$ takes place at any $\lambda_{\rho\rho}$ value. Thus, thermodynamic conditions take precedence over kinetic ones in a nucleation process.[13] The conclusion about ref 2 following from the foregoing is the use of a one-dimensional theory therein is justified.

The two-variable (V,T)-theory can be considered in a similar way. It is obtained from the (V, ρ, T)-theory, when either a thermodynamic or kinetic limiting process with respect to ρ takes place. In this case, we use the matrix $\mathbf{Z}_{VT}$ instead of $\mathbf{Z}_{V\rho}$ and $Sp\mathbf{Z}_{VT} = z_{VV} + \lambda_{TT} + a_T z_{VT} = -\xi P_L^* + \lambda_{TT} + 3\xi(k/c_V)P_*$. However, now the situation differs from the (V, ρ)-theory considered.

At first, let us assume that the thermodynamic limiting process in ρ, $\rho_* \to 0$, takes place. As is shown above, $\lambda_{TT} \to \infty$ in this case, i.e., case 1 with respect to λ_{TT}, $\lambda_{TT} \gg \xi P_L^*$, $3\xi(k/c_V)P_*$ and, as a consequence, eq 104 for κ_1 take place. This is the case of cavitation in a nonvolatile liquid already discussed above. Thus, the cavitation is contained as a limiting case in both the (V, ρ)- and (V, T)-theories.

Hence, the cases of small values of λ_{TT} (cases 2−4 considered above) could occur in the two-variable (V, T)-theory only in the kinetic limiting process with respect to ρ, $\lambda_{\rho\rho} \to \infty$. However, this case cannot be realized in view of condition 97b which forbids the chain "$\lambda_{\rho\rho} \to \infty$, $\lambda_{TT} \to 0$". Though the elements $h_{\rho\rho}$ and h_{TT} are "symmetric" with respect to the replacement $\rho_* \leftrightarrow T_0$, kinetic condition 97b breaks this symmetry. Nevertheless, the case of small values of λ_{TT} can take place together with small values of $\lambda_{\rho\rho}$; it is studied below within the framework of the (V, ρ, T)-theory.

Note that the (V, T)-theory is also obtained if we artificially put $\rho = $ const $= \rho_c$ for all bubbles. In this case, the number of vapor particles is rigidly connected with the bubble volume by means of the state equation $PV = NkT$ in which $N/V = \rho_c$ (the case of ref 4). As follows from the foregoing, the limiting effect of evaporation−condensation (which is claimed in ref 4) cannot be revealed in this case. Moreover, as shown above, $\rho_c = \rho_*$ and the assumption of $\rho = \rho_*$ is valid only for $\rho_* \to 0$, when the (V, T)-theory converts to the one-variable (V)-theory of cavitation.

Therefore, the two-dimensional (V, T)-theory yields nothing new in addition to the (V, ρ)-theory. More precisely, it does not exist as such.

4.4. Kinetic Limits in the (V, ρ, T)-Theory. The explicit form of the quantities $\Delta_{\rho T}$ and B, eq 93, is

$$\Delta_{\rho T} = \det \mathbf{\Lambda} + (1 + 2\tilde{q})\left(3\xi\frac{k}{c_V}P_*\right)\lambda_{\rho\rho} + 3\xi P_* \lambda_{TT} \tag{108a}$$

$$B = z_{VV}(\lambda_{\rho\rho} + \lambda_{TT}) + \Delta_{\rho T} \tag{108b}$$

where $\det \mathbf{\Lambda}$ is given by eq 97a.

At first, let us consider the kinetic limit $\lambda_{TT} \to \infty$ employed above and show that it indeed leads to the two-variable (V, ρ)-theory. Physically, this limit means

(1) $\lambda_{TT} \gg \xi P_L^*$, $3\xi P_*$, $\lambda_{\rho\rho}$, $\tilde{q}^2\lambda_{\rho\rho}$

Conditions 102 of the (V, ρ)-theory are generalized in the given case as

$$(Sp\mathbf{Z})^2 \gg |B|, \qquad Sp\mathbf{Z} > 0 \tag{109}$$

Denote

$$\beta_1 = \frac{B}{(Sp\mathbf{Z})^2}, \qquad \beta_2 = \frac{\det \mathbf{Z}}{(Sp\mathbf{Z})^3}; \qquad |\beta_1| \ll 1,$$

$$|\beta_2| \sim \beta_1^2 \tag{110}$$

We have for case 1

$$Sp\mathbf{Z} = \lambda_{TT} + o(\lambda_{TT}),$$

$$\beta_1 = \frac{z_{VV} + \lambda_{\rho\rho} + 3\xi P_*}{\lambda_{TT}} = \frac{Sp\mathbf{Z}_{V\rho}}{\lambda_{TT}},$$

$$\beta_2 = \frac{z_{VV}\lambda_{\rho\rho}}{\lambda_{TT}^2} = \frac{\det \mathbf{Z}_{V\rho}}{\lambda_{TT}^2} \tag{111}$$

The quantities U, Y, and $\cos\phi$, eq 96, are transformed as follows

$$U = -\frac{2(Sp\mathbf{Z})^3}{27}\left\{1 - \frac{9}{2}\beta_1 + \frac{27}{2}\beta_2\right\}$$

$$Y = -\frac{(Sp\mathbf{Z})^2}{3}(1 - 3\beta_1)$$

$$\cos\phi = 1 - \frac{27}{8}\beta_1^2 + \frac{27}{2}\beta_2 \tag{112}$$

Using the identity

$$\cos\left(\frac{\phi}{3} - \frac{\pi}{3}\right) = \frac{1}{2}\cos\frac{\phi}{3} + \frac{\sqrt{3}}{2}\sin\frac{\phi}{3}$$

and smallness of ϕ, we obtain

$$\cos\left(\frac{\phi}{3} - \frac{\pi}{3}\right) = \frac{1}{2}\left(1 + \frac{\phi}{\sqrt{3}} - \frac{\phi^2}{18}\right) \tag{113}$$

Comparing the expansion $\cos\phi = 1 - \phi^2/2$ with eq 112, we find

$$\phi = 3\sqrt{3}\sqrt{\frac{\beta_1^2}{4} - \beta_2} \tag{114}$$

Expanding the root in eq 95 in small parameter β_1 and substituting eq 113 together with eq 114, we obtain up to linear in β_1 terms

$$\kappa_1 = (Sp\mathbf{Z})\frac{\beta_1 - \sqrt{\beta_1^2 - 4\beta_2}}{2}$$

$$= \frac{1}{2}\{Sp\mathbf{Z}_{V\rho} - \sqrt{(Sp\mathbf{Z}_{V\rho})^2 - 4\det \mathbf{Z}_{V\rho}}\} = \kappa_1^{(V,\rho)} \tag{115}$$

eqs 111 were used here.

Thus, eq 101 of the two-variable (V, ρ)-theory is obtained.

(2) $\lambda_{TT}, \lambda_{\rho\rho} \ll \xi P_L^*, 3\xi P_*, Sp\mathbf{Z} > 0$

In this case, conditions 109 are satisfied as before, so eq 115 for κ_1 takes place in which

$$Sp\mathbf{Z} = z_{VV} + 3\xi\left(1 + \frac{k}{c_V}\right)P_* + o(|z_{VV}|, 3\xi P_*) \tag{116}$$

and β_i are given by eq 110.

Now eq 115 yields

$$\kappa_1 = (Sp\mathbf{Z})\frac{\beta_1 - \sqrt{\beta_1^2 + 4|\beta_2|}}{2} = \vartheta\frac{B}{Sp\mathbf{Z}},$$

$$\vartheta = \frac{1}{2}\left\{1 \mp \sqrt{1 + \frac{4|\det \mathbf{Z}|Sp\mathbf{Z}}{B^2}}\right\} \tag{117}$$

where the upper and lower signs correspond to $B > 0$ and $B < 0$, respectively, and

$$\frac{B}{Sp\mathbf{Z}} = \frac{-P_L^*(\lambda_{\rho\rho} + \lambda_{TT}) + 3(1 + 2\bar{q})(k/c_V)P_*\lambda_{\rho\rho} + 3P_*\lambda_{TT}}{3(1 + k/c_V)P_* - P_L^*}$$

$$\sim \lambda_{\rho\rho}, \lambda_{TT} \tag{118}$$

If $|\det \mathbf{Z}|Sp\mathbf{Z}/B^2 \ll 1$, eq 117 is simplified as follows:

$$\kappa_1 = \begin{cases} \dfrac{z_{VV}\det\mathbf{\Lambda}}{B} & B > 0 \\[2ex] \dfrac{B}{Sp\mathbf{Z}} & B < 0 \end{cases} \tag{119}$$

Equations 117−119 generalize eq 105 of the (V, ρ)-theory.

(3) $\lambda_{TT}, \lambda_{\rho\rho} \ll \xi P_L^*, 3\xi P_*$; $(\lambda_{TT} + \lambda_{\rho\rho}) \sim \xi|-P_L^* + 3(1 + k/c_V)P_*|$, $|Sp\mathbf{Z}| = O(\lambda_{TT} + \lambda_{\rho\rho})$

In this case, $B < 0$ and $(Sp\mathbf{Z})^2 \ll |B|$. Denoting

$$\bar{\beta}_1 = \frac{(Sp\mathbf{Z})^2}{|B|} \ll 1, \qquad \bar{\beta}_2 = 9\frac{Sp\mathbf{Z}}{|B|^{1/2}} + 27\frac{\det \mathbf{Z}}{|B|^{3/2}},$$

$$\bar{\beta}_2 \sim \bar{\beta}_1^{1/2} \tag{120}$$

we find

$$U = -\frac{|B|^{3/2}(\bar{\beta}_2 + 2\bar{\beta}_1^{3/2})}{27}$$

$$Y = B\left(1 + \frac{1}{3}\bar{\beta}_1\right)$$

$$\cos\phi = \frac{1}{6\sqrt{3}}(\bar{\beta}_2 + O(\bar{\beta}_1^{3/2})) \tag{121}$$

The last equation implies $\phi = \pi/2 - \phi'$, where ϕ' is a small quantity, hence

$$\cos\left(\frac{\phi}{3} - \frac{\pi}{3}\right) = \frac{\sqrt{3}}{2}\left(1 - \frac{\phi'}{3\sqrt{3}} - O(\phi'^2)\right) \tag{122}$$

On the other hand, $\cos\phi = \sin\phi' = \phi'$, so ϕ' is determined by eq 121. Expanding the root in eq 95 in small parameter $\bar{\beta}_1$ and substituting eq 122, we find

$$\kappa_1 = -\sqrt{|B|}\{1 + O(\bar{\beta}_1^{1/2})\} \tag{123}$$

This equation generalizes eq 106 of the (V, ρ)-theory.

(4) $\lambda_{TT}, \lambda_{\rho\rho} \ll \xi P_L^*, 3\xi P_*$; $(Sp\mathbf{Z})^2 \gg |B|$ and $Sp\mathbf{Z} < 0$

We employ the same designations β_1 and β_2 as in case 1; now $\beta_2 > 0$. Instead of eq 112, we have

$$\cos\phi = -\left\{1 - \frac{27}{8}\beta_1^2 + \frac{27}{2}\beta_2\right\} \tag{124}$$

From here, $\phi = \pi - \phi'$, ϕ' is small, and $\cos\phi = -(1 - \phi'/2)$. Comparing with eq 124, we find ϕ' and

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$$\cos\left(\frac{\phi}{3} - \frac{\pi}{3}\right) = \cos\frac{\phi'}{3} = 1 - \frac{3}{2}\left(\frac{\beta_1^2}{4} - \beta_2\right) \tag{125}$$

Expanding the root in eq 95 in β_1 with regard for the condition $Sp\mathbf{Z} < 0$ as well as eq 125, we find

$$\kappa_1 = Sp\mathbf{Z}\{1 - \beta_1 + O(\beta_1^2)\} = -\xi|3(1 + k/c_V)P_* - P_L^*| \tag{126}$$

This equation generalizes eq 107 of the (V, ρ)-theory. At high negative pressures P_0, $|P_0| \gg P_*$, it also yields the one-dimensional eq 104.

Thus, the same physical picture as in the two-variable (V, ρ)-theory takes place here, when the pressure P_0 changes from positive to high negative values in cases 2−4. At a positive or moderately negative pressure, the nucleation process is limited by slow kinetics of both kinds (the exchange by particles and the heat exchange), eqs 117 and 123. As the negative pressure increases in absolute value, the limitation slackens, eq 123, and vanishes at high values of pressure, eq 126.

5. CONCLUDING REMARKS

The "weak point" of the CNT under discussion for many years is the region of small sizes of a critical nucleus (which corresponds to high supersaturations). Therefore, the validity of the presented theory should be discussed in this context. First of all, the Kelvin formula, eq 30, is valid for a sufficiently large nucleus radius R_*. In ref 18, rigorous equations for the pressures of coexisting phases α and β being in equilibrium as functions of radius have been derived in the framework of the finite-thickness layer method. For a one-component system, they have the following form:

$$\left(\frac{dP^{(\alpha)}}{dR}\right)_T = -\frac{2\sigma v^{(\beta)}a}{R^2 v_{\alpha\beta}\left(a + \frac{2\omega}{R}\right)} \tag{127a}$$

$$\left(\frac{dP^{(\beta)}}{dR}\right)_T = -\frac{2\sigma v^{(\alpha)}a}{R^2 v_{\alpha\beta}\left(a + \frac{2\omega}{R}\right)} \tag{127b}$$

where $v_{\alpha\beta} = v^{(\beta)} - v^{(\alpha)}$, $a = A/N^{(\sigma)}$, $\omega = v_\beta^{(\sigma)} - v^{(\beta)}v_{\alpha\sigma}/v_{\alpha\beta}$, $v_{\alpha\sigma} = v^{(\sigma)} - v^{(\alpha)}$, $v_\beta^{(\sigma)} = V_\beta^{(\sigma)}/N^{(\sigma)}$, $v_\alpha^{(\sigma)} = V_\alpha^{(\sigma)}/N^{(\sigma)}$, $v_\alpha^{(\sigma)} + v_\beta^{(\sigma)} = v^{(\sigma)} = V^{(\sigma)}/N^{(\sigma)}$. The index σ relates to the surface layer, so $V^{(\sigma)}$ and $N^{(\sigma)}$ are, respectively, the volume and the particle number of this layer; the volume $V^{(\sigma)}$ consists of the two parts, $V_\alpha^{(\sigma)}$ and $V_\beta^{(\sigma)}$, separated by the dividing surface. Similar equations for the dependences of the equilibrium temperature, composition (in a multicomponent system), and surface tension on R have also been derived in ref 18.

In the case of a sufficiently large R, eqs 127 are simplified as follows:

$$\left(\frac{dP^{(\alpha)}}{dR}\right)_T \approx -\frac{2\sigma v^{(\beta)}}{R^2(v^{(\beta)} - v^{(\alpha)})} \tag{128a}$$

$$\left(\frac{dP^{(\beta)}}{dR}\right)_T \approx -\frac{2\sigma v^{(\alpha)}}{R^2(v^{(\beta)} - v^{(\alpha)})} \tag{128b}$$

The Kelvin formula for a liquid drop (α) in a vapor (β)

$$\ln\frac{P^{(\beta)}(R)}{P_\infty^{(\beta)}} = \frac{2\sigma v^{(\alpha)}}{RkT} \tag{129}$$

is obtained from eq 128b in view of $v^{(\alpha)} \ll v^{(\beta)}$ and $v^{(\beta)} = kT/P^{(\beta)}$. The Kelvin formula, eq 30, is obtained from eq 128a under the similar conditions $(\alpha \leftrightarrow \beta)$.

At sufficiently small values of R, when a nucleus almost consists of the surface layer (there is no bulk phase), the Kelvin formula is not valid. For this case, eqs 127 yield[18]

$$\left(\frac{dP^{(\alpha)}}{dR}\right)_T \approx -\frac{\sigma v^{(\beta)}a}{Rv^{(\alpha)}(v^{(\beta)} - v^{(\sigma)})} \tag{130a}$$

$$\left(\frac{dP^{(\beta)}}{dR}\right)_T \approx -\frac{\sigma a}{R(v^{(\beta)} - v^{(\sigma)})} \tag{130b}$$

The presence of $v^{(\sigma)}$ in these equations reflects the increasing role of surface effects at small sizes.

The limiting values of the pressures at $R \to 0$ obtained from eqs 127 as well as from the analysis of the limiting behavior of the quantities σ and ω/a have the following form:[18]

$$P^{(\alpha)} \approx P_c^{(\alpha)} - \frac{bv^{(\beta)}}{v_{\alpha\beta}}R^{1-m} \tag{131a}$$

$$P^{(\beta)} \approx P_c^{(\beta)} - \frac{bv^{(\alpha)}}{v_{\alpha\beta}}R^{1-m} \tag{131b}$$

where b and m are some constants, $m < 1$, and $P_c^{(\alpha)}$ and $P_c^{(\beta)}$ are the integration constants. It follows from these equations that the pressure in each of the phases tends to a finite limit at $R \to 0$, whereas Kelvin eq 129 yields infinity. Starting with some small radius comparable with the surface layer thickness, the curve of the true vapor pressure will drastically differ from the curve corresponding to the Kelvin formula. The quantities $P_c^{(\beta)}/P_\infty^{(\beta)}$ and $P_c^{(\beta)} - P_\infty^{(\beta)}$ characterize the theoretical limiting supersaturation of the (β)-phase.[18] Thus, eq 130b or eq 127b has to be employed for determining the critical drop radius at small sizes, instead of eq 129.

It should be noted that the nucleus radius R in the capillarity approximation is the radius of the dividing surface which is the surface of tension.[18,19] At the same time, the radius of the inhomogeneity in the mother phase which is associated with a nucleus is larger than R. Thus, the inhomogeneity does not vanish[18] at $R \to 0$ and this limit makes sense.

Returning to the theory presented, it should be noted that the limiting case of high negative pressures, $|P_0| \gg P_*(R)$, considered above just corresponds to small values of R_*. Hence, the dependence $P_*(R)$ does not play a role in eq 29c, and the equation for R_* is

$$\frac{2\sigma(R_*)}{R_*} = |P_0| \tag{132}$$

The equation for the isothermal dependence $\sigma(R)$ in a one-component system is[18]

$$\frac{1}{\sigma}\left(\frac{d\sigma}{dR}\right)_T = \frac{\frac{2\omega}{R^2}}{a + \frac{2\omega}{R}} \tag{133}$$

The surface-layer quantities in eq 132 (in view of eq 133) or some of their combinations may be regarded as fitting parameters of the theory; some estimates for them can be made also.

Thus, in the region of small sizes, the presented theory is also valid just because it becomes *one-dimensional* (as was shown above); i.e., the process looks like cavitation. Correspondingly, the form of the equation of state is not important in this case. The thermodynamic part of the problem reduces to determining the critical radius only, according to eq 132 instead of eq 31; the correction to the theory is only in that. This fact also reflects the increasing role of surface effects and the corresponding disappearance of bulk properties (to which an equation of state, a dependence $P_*(R)$, and the kinetic processes of evaporation–condensation and heat conductivity relate) from the theory at small sizes. Thus, the theory is consistent in the region of small sizes also.

As for the applicability of thermodynamic methods to small nuclei, the author of ref 18 thinks with arguments that as the thermodynamic approach generally as both the Gibbs method and the finite-thickness layer method are applicable to such small objects which are fully inhomogeneous and as if consist of the surface layer only. In other words, a method associated with the separation of two bulk phases and the dividing surface is *rigorous* regardless of the actual presence or absence of the interior bulk phase.[18] Indeed, the difference between the values of the extensive quantities of a nucleus (energy, entropy, and particle number) and the corresponding bulk values is compensated by the superficial quantities (in the Gibbs approach). The role of the superficial quantities increases with decreasing radius. For this reason, the quantities $\overline{N}$ and $\overline{S}$ in eq 27a for the work are not neglected in comparison with N and S and a more "soft" approximation, eq 37, is employed for them. At the same time, the distinction of the values of the intensive quantities of a nucleus (pressure, temperature, and composition) from their bulk values is given by the dependences of these quantities on radius, as shown above by the example of pressure.

In addition to thermodynamic constraints, the possible "kinetic" constraints on the nucleus size should be discussed also. Equations 54 and 86 are consequences of the Fokker–Planck (FP) equation. Though the equations of motion can also be postulated independently of the FP equation (they can be obtained from the mechanical equations of the macroscopic motion of a body in a medium with dissipation[14,15]), nevertheless, eq 86 is a solution of the FP equation.[13] The condition of applicability of the latter in our case is $(\langle(\Delta V)^2\rangle)^{1/2} \ll V_*$, where ΔV is the "Brownian jump" of the nucleus volume. The similar condition for a liquid drop consisting of N molecules looks more explicitly as $N_* \gg 1$. Also, the underlying condition[29] $W_* \gg kT$ has to be satisfied in deriving eq 86. Though all of these conditions are undetermined quantitatively, nevertheless, they imply that a nucleus cannot be arbitrarily small. However, in the early work of Becker and Döring,[30] the FP equation is not used for deriving the stationary nucleation rate. The process of the critical drop formation is considered as the chain of successive reactions of attachment and detachment of molecules which leads from one molecule to the critical drop via the clusters consisting of 2, 3, ..., $N_* - 1$ molecules. Further, the system of kinetic finite-difference equations is solved, so this method is not constrained by cluster sizes at all. The obtained formula for the stationary nucleation rate in general has a form similar to eq 86: the exponential function with some kinetic prefactor. Hence, one can assume that eq 86 is valid for small sizes also.

These assumptions can be verified with the help of molecular dynamics simulations,[31–33] so the works in this field are of great importance. In particular, the noteworthy result on the role of temperature fluctuations in the process of bubbles nucleation is reported in recent work.[31] The presented theory just takes into account thermal effects in this process. At the same time, works on molecular dynamics simulations require a robust nucleation-rate formula from CNT for the comparison of results. A simple formula of the one-dimensional theory[31] which is usually employed for the interpretation of experimental or molecular dynamics results from the perspective of CNT, generally speaking, is not suitable for this purpose, since neither kinetic properties of the mother phase nor thermodynamic properties of small nuclei are taken into account properly by it. Also, it does not take into account the prefactor corrections.[24–27] Hence, even if this formula sometimes gives an acceptable agreement with experimental results, this fact should be regarded as an accident, rather than a rule. It implies that given experimental conditions provide the fulfillment of either thermodynamic or kinetic limits, which leads to the one-dimensional result.

Therefore, CNT has to be further developed. Promising direction of its development is the multivariable approach, especially coupled with macroscopic kinetics. A "multivariable direction" within CNT starts with the classical work of Reiss[10] on binary nucleation, where basic notions of a multivariable theory such as the nuclei flux density and the free energy surface are defined and the scenario of a nucleation process is described. Later, a two-variable theory was applied to other problems of nucleation[5,6,21,22] including the nucleation of bubbles.[5,6] As is seen from the given report, the nucleation theory is multivariable in essence even in a one-component system; a multicomponent case only yields additional variables (composition). Thus, the employment of the one-dimensional theory anywhere as a limiting case should be justified. The use of the statistical mechanical approach[24–28] in the nucleation theory is very important for the verification of basic assumptions of CNT and getting corrections to it; also, this approach provides a basis for computer simulations.[28] Finally, thermodynamics at small nucleus sizes has to be more careful, as shown above. Thus, CNT has the potential to seriously improve its predictive capabilities both qualitative and quantitative.

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Notes
The authors declare no competing financial interest.

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