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The kinetics of first-order phase transitions. Non-stationary many-parameter nucleation

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We consider the Brownian motion of a bubble in the multi-dimensional space of its parameters when the external pressure of the cavitating fluid depends on time. We construct for the distribution function, the flux, and the nucleation rate expressions which are asymptotically exact as far as the magnitude of the nucleation barrier is concerned. We study the structure of the non-stationary "source" of hypercritical bubbles in the limiting cases of large and small viscosity of the fluid.

INTRODUCTION

According to Zel'dovich[1] one can treat the process of a fluctuative formation of nuclei of a new phase (the so-called nucleation) as a Brownian motion of the nuclei along the axis of their sizes. One can naturally generalize the problem to a multi-dimensional case when description of the thermodynamic state of the nucleus calls for an additional set of parameters which characterize the deviation from the quasi-equilibrium values of the temperature,[2] pressure,[3] shape,[4] chemical composition,[5] and so on, of the nucleus. One calls such a nucleation a multi-parameter one and one describes it by a Fokker-Planck type equation[1)] in the space of the bubble parameters $\mathbf{q}$[6]

$$\frac{\partial f}{\partial t}=-\frac{\partial}{\partial \mathbf{q}}\mathbf{j},\quad \mathbf{j}=-N\mathbf{D}\frac{\partial}{\partial \mathbf{q}}\frac{f}{N}. \tag{1}$$

Here f is a "kinetic" distribution function, $\mathbf{j}$ the flux density, $\mathbf{D}$ the diffusion tensor, and N the equilibrium distribution function which is connected with the minimum work required $W(\mathbf{q})$ to form the nucleus:

$$N(\mathbf{q})\sim\exp\{-W/T\}.$$

The potential contour $W(\mathbf{q})$ has a saddle point corresponding to a critical nucleus with parameters $\mathbf{q}_*$. The value $W(\mathbf{q}_*)\equiv W_*$ determines the height of the activation barrier which limits the kinetics of the nucleation process.

The region of large dimensions in Eq. (I.1) is a sink, and only current distributions which differ from equilibrium ones are possible. When the state of the initial phase is time-independent a stationary non-equilibrium distribution is established in the system[6] and the rate of nucleation is determined by the total flux which is constant along the size axis. The region of applicability of the stationary solution is, however, necessarily restricted as the lifetime of the metastable state is finite. Changing the external conditions and depleting the initial phase through the formation of nuclei affects first of all the quantity W_*/T which is most sensitive to the values of the thermodynamic parameters of the system (in a comparatively narrow range of parameters, corresponding to the instability region, W_* changes from ∞ to 0). It may turn out that the most important non-stationarity in the initial stage of the nucleation, when the biggest nuclei, which are responsible for the subsequent removal of the metastability and for the peculiarities of the way the system changes to an asymptotic regime,[7] are formed.

In the present paper we consider cavitation in a viscous fluid when the external pressure depends on the time; in a stationary version the process was studied in Ref. 1 "single-parametrically" and in Refs. 8 and 3 "multi-parametrically." It turns out that the non-stationarity affects in an essential manner the rate of formation of bubbles, and under well defined conditions also their properties (pressure). The results obtained may turn out to be useful also for an analysis of other physical situations where the role of the non-stationarity of the nucleation process is actively discussed—when metastable states are quenched,[9] when the electron-hole liquid condenses,[10] and so on. We note that earlier a non-stationary analysis was carried out only from the point of view of studying relaxation to a stationary distribution (see the reviews in Refs. 9 and 11), and the situation when the level of metastability of the initial phase changed so rapidly that the stationary approximation turned out to be inapplicable was not studied.

1. NON-STATIONARY DISTRIBUTION FUNCTION

The formation of a bubble of volume v and vapor pressure p in a liquid of pressure P requires a minimum work[8]

$$W=v(P-p)+\sigma s+pv\ln(p/p_*). \tag{1.1}$$

Here σ is the surface-tension coefficient, s the surface area of the bubble, p_* the pressure in a bubble of critical dimensions (we shall in what follows denote all quantities corresponding to a critical nucleus by an asterisk). In dimensionless variables $u_0=v/v_*$, $u_1=p/p_*$ Eq. (1.1) takes the form

$$W=W_*\{3u_0^{2/3}-2u_0+2u_0b^{-1}(u_1\ln u_1-u_1+1)\}, \tag{1.2}$$

where $b=1-P/p_*$. The initial equation (I.1) for the unknown function $w=f/N$ takes in the variables $\mathbf{u}=(u_0,u_1)$ the form

$$\left(\frac{\partial}{\partial t}+\mathbf{s}\frac{\partial}{\partial \mathbf{u}}\right)w-w\left(\frac{\partial}{\partial t}+\mathbf{s}\frac{\partial}{\partial \mathbf{u}}\right)\frac{W}{T}=\frac{\partial}{\partial \mathbf{u}}\mathbf{D}\frac{\partial w}{\partial \mathbf{u}}-\frac{1}{T}\frac{\partial W}{\partial \mathbf{u}}\mathbf{D}\frac{\partial w}{\partial \mathbf{u}}. \tag{1.3}$$

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Here the vector

$$s=\partial u/\partial t|_{v,p=\text{const}}=(-u_0\,\partial\ln v_*/\partial t,\qquad -u_1\,\partial\ln p_*/\partial t)$$

is due to the non-stationarity of the external conditions. We assume that the non-stationarity is caused by the fact that the pressure P depends on the time. As the pressure in the critical bubble is close to the standard vapor pressure of a plane surface (the difference is small in a parameter equal to the ratio of the vapor and the liquid densities[11]) we can put $\partial \ln p_*/\partial t = 0$ in the expression for s with sufficient accuracy. With the same accuracy

$$\left(\frac{\partial}{\partial t}+s\frac{\partial}{\partial \mathbf{u}}\right)\frac{W}{T}=-\gamma u_0, \tag{1.4}$$

where

$$\gamma=-\frac{\partial}{\partial t}\frac{W_*}{T}\approx-\frac{2}{3}\frac{W_*}{T}\frac{\partial\ln v_*}{\partial t}$$

is the rate of change of the height of the activation barrier.

The boundary conditions for Eq. (1.3) are determined from the requirement that the kinetic and equilibrium distribution functions for bubbles of extremely small size be the same[1] and that the total number of nuclei in the system be bounded

$$w(u_0=0)=1,\qquad w(u_0\to\infty)=0. \tag{1.5}$$

We study Eq. (1.3) for large values of the activation barrier height W_*/T. The time-derivative $(\partial/\partial t + s\partial/\partial u)w$ in Eq. (1.3) does not contain a large parameter. The stationarity of the boundary conditions (1.5) enables us to state that for not too fast a change in the external conditions (we shall establish the criterion below) an intermediate quasistationary regime is realized in the region $u_0 \lesssim 1$ and is determined by the equation

$$\gamma u_0 w=\frac{\partial}{\partial \mathbf{u}}\mathbf{D}\frac{\partial w}{\partial \mathbf{u}}-\frac{1}{T}\frac{\partial W}{\partial \mathbf{u}}\mathbf{D}\frac{\partial w}{\partial \mathbf{u}}. \tag{1.6}$$

The difference between the nucleation regime considered and a stationary one can be very important and is characterized by the quantity γ which is retained in the last equation as the derivative of the large quantity W_*/T.

We solve Eq. (1.6) by the method of matched asymptotic expansions.[12]

Far from the saddle point $\mathbf{u}_* = (1, 1)$ the derivative $\partial W/\partial \mathbf{u}$ is not small and we can neglect in (1.6) the diffusion term $(\partial/\partial \mathbf{u})\mathbf{D}(\partial w/\partial \mathbf{u})$:

$$\gamma u_0 w=\dot{\mathbf{u}}\partial w/\partial \mathbf{u}. \tag{1.7}$$

Here $\dot{\mathbf{u}}$ is the velocity of the macroscopic (neglecting fluctuations) motion of the nucleus in configuration space and is connected with the tensor $\mathbf{D}$ through the Einstein relations $\dot{\mathbf{u}} = -T^{-1}\mathbf{D}\partial W/\partial \mathbf{u}$. We introduce the length interval dl and the velocity $|\dot{u}|$ along the trajectory

$$dl^2=d\mathbf{u}\mathbf{D}^{-1}d\mathbf{u},\qquad |\dot{\mathbf{u}}|^2=\dot{\mathbf{u}}\mathbf{D}^{-1}\dot{\mathbf{u}} \tag{1.8}$$

(a similar metrization enables us in the simplest possible way to match the "interior" and "exterior" solutions). Using the first of the boundary conditions (1.6) we have

$$w(\mathbf{u})=\exp\left\{\gamma\int_0^{l(\mathbf{u})}dl\,u_0/(-|\dot{\mathbf{u}}|)\right\}, \tag{1.9}$$

where the integration is along the decay trajectory while the length $l = \int dl$ is reckoned from the point where it intersects the u_1 axis.

In the saddle-point region, where the velocity is close to zero and Eq. (1.9) cannot be applied, we change to the "interior" variable

$$\mathbf{x}=(\mathbf{u}-\mathbf{u}_*)(W_*/T)^{1/2}.$$

In the main order in $(W_*/T)^{1/2}$ Eq. (1.6) takes the form

$$\gamma w=\frac{\partial}{\partial \mathbf{x}}\mathbf{D}\frac{\partial w}{\partial \mathbf{x}}-\mathbf{x}\mathbf{V}\mathbf{D}\frac{\partial w}{\partial \mathbf{x}}, \tag{1.10}$$

where the tensor

$$\mathbf{V}=\frac{1}{T}\frac{\partial}{\partial \mathbf{x}}\frac{\partial}{\partial \mathbf{x}}W$$

describes the shape of the saddle.

The explicit form of the tensors $\mathbf{D}$ and $\mathbf{V}$ is given in Section 3; here we shall use the following properties: the tensor $\mathbf{V}$ is symmetric and contains exactly one negative eigenvalue, the tensor $\mathbf{D}$ is symmetric and is positive-definite. Upon a non-degenerate change of variables $\mathbf{x} = \mathbf{A}\mathbf{y}$, the contravariant tensor $\mathbf{D}$ and the covariant tensor $\mathbf{V}$ transform differently:

$$\mathbf{D}_y=\mathbf{A}^{-1}\mathbf{D}_x\tilde{\mathbf{A}}^{-1},\qquad \mathbf{V}_y=\tilde{\mathbf{A}}V_x\mathbf{A}$$

($\tilde{\mathbf{A}}$ is the transpose of the matrix $\mathbf{A}$). To find the simultaneous diagonalizing transformation of $\mathbf{A}$ we change to the covariant tensor $\mathbf{D}^{-1}$ which, like $\mathbf{D}$, is symmetric and positive-definite. After diagonalization, the matrices of the tensors $\mathbf{D}$ and $\mathbf{V}$ take the form

$$\mathbf{D}_y=\mathbf{I},\qquad \mathbf{V}_y=\operatorname{diag}\{\lambda_0,\lambda_1,\ldots,\lambda_d\}, \tag{1.11}$$

where d is the dimensionality of the space of stable variables ($d = 1$). Among the diagonal elements $\lambda_0,\ldots,\lambda_d$ there is exactly one (λ_0) which is negative ("law of the inertia of quadratic forms"[13]) and they are determined as the roots of the characteristic equation

$$\operatorname{Det}(\mathbf{V}-\lambda\mathbf{D}^{-1})=0. \tag{1.12}$$

In the new variables Eq. (1.10) has the form

$$\sum_{i=0}^{d}\left(\frac{\partial^2}{\partial y_i^2}-\lambda_i y_i\frac{\partial}{\partial y_i}\right)w=\gamma w. \tag{1.13}$$

In the main approximation in W_*/T the solution depends solely on the unstable variable y_0; this is confirmed when we match up with the exterior solution (1.9), and (1.13) reduces to an ordinary differential equation

$$\frac{d^2w}{dy_0^2}-\lambda_0 y_0\frac{dw}{dy_0}-w\gamma=0 \tag{1.14}$$

(a similar equation was considered in Ref. 14). The possibility of separating the variables means that we have in fact a single-parameter nucleation in the regime considered; this is, in particular, demonstrated by the formal agreement of the stationary solution of an equation such as (I.1) with Zel'dovich's one-dimensional solution.

The solution of Eq. (1.14), which decreases as $y_0 \to \infty$, has the form[2)]

$$w(y)=\frac{B(\gamma)}{\pi^{1/2}}\int_{\zeta}^{\infty}(\xi-\zeta)^{\gamma/|\lambda_0|}e^{-\xi^2}d\xi,\qquad \zeta=y_0\left(\frac{|\lambda_0|}{2}\right)^{1/2}. \tag{1.15}$$

The coefficient $B(\gamma)$ is determined from the condition that the asymptotic form of the interior solution (1.15) as $y_0 \to \infty$ be the same as the exterior solution (1.9) as $\mathbf{u} \to \mathbf{u}_*$.

We consider the asymptotic behavior of the exterior solution. In the variables $\mathbf{u}$ the width of the saddle is small as $(W_*/T)^{-1/2}$ and one can consider the single trajectory which passes through the saddle point. On this trajectory (1.9) has the asymptotic form

$$w(\mathbf{u}\to\mathbf{u}_*)=\{l_*^{-1}C(l_*-l)\}^{\gamma/|\lambda_0|}, \tag{1.16}$$

$$C=\exp\left\{\int_0^{l_*}dl(\mathbf{u})\{-u_0|\lambda_0|/|\dot{\mathbf{u}}|-1/(l-l_*)\}\right\}. \tag{1.17}$$

The integration in (1.17) is along the decay trajectory of the critical nucleus.

The asymptotic form of the interior solution (1.15) is

$$w(y_0\to-\infty)=B(\gamma)\{|y_0|(|\lambda_0|/2)^{1/2}\}^{\gamma/|\lambda_0|}. \tag{1.18}$$

We note that expressions (1.8) for the line element dl and the velocity $|\dot{\mathbf{u}}|$ along the decay trajectory are invariant and, in particular, can be written in the variables $\mathbf{y}$, for which $\mathbf{D}=\mathbf{I}$. Hence it follows that when one approaches the saddle point along the unstable direction $dl \to dy_0$ we have $-|\mathbf{u}| \to |\lambda_0|y_0$. From a comparison of (1.16) and (1.18) we find

$$B(\gamma)=\{l_*^{-1}C(2/|\lambda_0|)^{1/2}\}^{\gamma/|\lambda_0|}. \tag{1.19}$$

The thermodynamic state of the nucleus on the saddle trajectory of the decay is uniquely determined by its volume v. This means that we can eliminate the stable variables and represent the results in an effectively one-dimensional form[3)]

For sizes close to the critical one we have

$$v-v_*=v_*(W_*/T)^{-1/2}A_{00}y_0,$$

where A_{00} is a component of the transforming matrix $\mathbf{A}$. In the $\mathbf{y}$-representation the tensor $\mathbf{V}$ is diagonal and $\lambda_0 = T^{-1}\partial^2 W/\partial y_0^2$ or, using the preceding equation,

$$\lambda_0=A_{00}{}^2\frac{v_*^2}{W_*}\frac{\partial^2 W_{\text{eff}}}{\partial v^2}\bigg|_*, \tag{1.20}$$

where $W_{\text{eff}}(v)$ is the work done to form a nucleus with parameters corresponding to the decay trajectory; one can use the condition $\lambda_0 = d\dot{v}/dv|_*$ to eliminate the quantity A_{00}.

When considering the decay trajectory one-dimensionally it is natural to parametrize not the length l but the quantity $u_0 = v/v_*$. Under the formal substitution $l \to u_0$, $-|\dot{\mathbf{u}}| = \dot{u}_0$, (1.17) determines the constant $\tilde{C}$ and Eq. (1.15) for the distribution function takes the form

$$w=\left\{-\frac{v_*^2}{2\tilde{C}^2T}\frac{\partial^2 W_{\text{eff}}}{\partial v^2}\bigg|_*\right\}^{-n/2}\pi^{-1/2}\int_{\zeta}^{\infty}(\xi-\zeta)^n e^{-\xi^2}d\xi,$$

$$\zeta=(v-v_*)\left(-\frac{1}{2T}\frac{\partial^2 W_{\text{eff}}}{\partial v^2}\bigg|_*\right)^{1/2}, \tag{1.21}$$

where $n=\gamma/(\partial\dot{v}/\partial v)_*$ characterizes the level of non-stationarity of the nucleation process. From the condition that one can neglect the non-stationary term $\partial w/\partial t$ it follows that the solution is applicable when

$$-1<n\ll 2W_*/T\ln(W_*/\tilde{C}^2T),$$

i.e., in an asymptotically wide range (see Appendix). The allowable sizes are limited by the possibility of linearizing the coefficients in (1.6): $|v-v_*|\ll v_*$. For n-values within the above-mentioned range the quasi-stationary distribution extends over a large range of size, but consideration of nuclei with $v-v_* \ll v_*$ turns out to be sufficient to determine the nucleation rate. In the stationary limit $n=0$, Eq. (1.21) changes to the solution[1] $w=\frac{1}{2}\operatorname{erfc}(\zeta)$.

The presence of the large parameter

$$(v_*^2/T)\partial^2 W_{\text{eff}}/\partial v^2|_*\sim W_*/T$$

in (1.21) leads to a significant difference from the stationary solution even when $|n|\sim 1$. The initial stage of the nucleation corresponds to $n>0$ and the final stage to $n<0$, when the height of the barrier increases and the nuclei which were formed earlier with sizes which turn out to be subcritical decay. (this corresponds to a maximum in (1.21)—the flux changes sign in the circumcritical region).

2. FLUX OF NUCLEI AND RATE OF NUCLEATION

We turn to a multi-parameter consideration. On change of variables $\mathbf{x}=\mathbf{A}\mathbf{y}$ the flux density is transformed as $\mathbf{j}_x=\mathbf{A}\mathbf{j}_y$ and under a simultaneous diagonalization of the tensors $\mathbf{D}$ and $\mathbf{V}$ it takes in the vicinity of the saddle the simple form

$$\mathbf{j}_y=-N\frac{\partial w}{\partial \mathbf{y}}=-N\frac{\partial w}{\partial y_0}(1,0). \tag{2.1}$$

Integrating this expression over all stable variables we get the total flux in the y_0 direction

$$I_{y_0}=-\frac{\lambda_0}{2^{1/2}}N_*\frac{(2\pi)^{d/2}}{|\operatorname{Det}\mathbf{V}_y|^{1/2}}\frac{\partial w}{\partial \zeta}e^{\zeta^2}.$$

From the invariance of the divergence of the flux density $\mathbf{j}$ we have for the total flux I_v along the size axis

$$I_v=I_{y_0}\frac{\partial(q_0,\ldots,q_d)}{\partial(y_0,\ldots,y_d)},$$

where $\partial(q_0,\ldots,q_d)/\partial(y_0,\ldots,y_d)$ is the Jacobian of the transition. The quantity

$$N_*\frac{(2\pi)^{d/2}}{|\operatorname{Det}\mathbf{V}_y|^{1/2}}\frac{\partial(q_0,\ldots,q_d)}{\partial(y_0,\ldots,y_d)}$$

determines, accurate to a factor $(-T^{-1}\partial^2 W/\partial v^2)|_*)^{1/2}$

the equilibrium distribution function

$$N(v) = \int \prod_{i=1}^{d} dq_i N(\mathbf{q})$$

and using (1.21) we get from these expressions

$$I_v = I_{v,\mathrm{st}} \left\{ -\frac{v_*^2}{2T\tilde{C}^2} \frac{\partial^2 W_{\mathrm{eff}}}{\partial v^2} \Big|_* \right\}^{-n/2} 2\int_{\zeta}^{\infty} \xi(\xi-\zeta)^n e^{\zeta^2-\xi^2} d\xi. \tag{2.2}$$

Here $I_{v,\mathrm{st}}$ is the size-independent stationary flux value corresponding to Zel'dovich's formula

$$I_{v,\mathrm{st}} = \frac{1}{2\pi^{1/2}} \frac{\partial \dot{v}}{\partial v} \Big|_* \left\{ -\frac{1}{2T} \frac{\partial^2 W}{\partial v^2} \Big|_* \right\}^{-1/2} N(v_*). \tag{2.3}$$

The solution (2.2) is applicable for not too large sizes: $v - v_* \ll v_*$. However, even when

$$v - v_* \gg \{-(1/2T)\partial^2 W_{\mathrm{eff}}/\partial v^2|_*\}^{-1/2}$$

the "interior" variable ζ turns out to be large and (2.2) can be replaced by its asymptotic form

$$I_v = I_{v,\mathrm{st}} \tilde{C}^n \left\{ -\frac{v_*}{T} \frac{\partial^2 W_{\mathrm{eff}}}{\partial v^2} \Big|_* \right\}^{-n} (v-v_*)^{-n} \Gamma(n+1), \tag{2.4}$$

where $\Gamma(n+1)$ is a gamma function.

From a macroscopic point of view the region of subcritical sizes can be considered to be a "source" with characteristics which are the initial size of the nuclei which are formed v_0 and the nucleation rate J (the flux for $v = v_0$). These quantities can be found from the condition for matching the drift solution for the supercritical nuclei with the solution inside the source. It is clear that v_0 and $J(v_0)$ are then uniquely determined, since the flux in the macroscopic region $I(v) = I_{v_0}[t - \tau(v,v_0)]$ (τ is the time for a nucleus to grow to size v) is the only "observable," and the condition that it be independent of the choice of initial size is equivalent to the drift condition. One verifies easily that this means that the asymptotic expression (2.4) is applicable and must therefore be regarded as determining the non-stationary nucleation rate. In the region (A8) where the solution is applicable the nucleation rate decreases monotonically when the non-stationarity index n increases.

When finding the solution it is important to use the symmetry of the tensor **D**. The generalization to the case of an asymmtric tensor **D** (for instance, when the inertia of the fluid is taken into account[16]) does not involve in principle any difficulties. The expression (2.3) for the stationary nucleation rate remains then unchanged; in particular, one can show that if the nucleus moves without dissipation (completely antisymmetric tensor **D**[17]) Eq. (23) leads directly to the result of Eyring's theory, where the flux is independent of the form of the barrier top (in Ref. 1 it was proposed to obtain the corresponding result from an independent consideration).

3. CAVITATION IN A VISCOUS LIQUID

Neglecting effects connected with the thermal conductivity and with the inertia of the fluid, the equation for the rate of change of the radius R of a bubble has the form

$$\dot{R} = \frac{R}{4\eta}\left[p - \frac{2\sigma}{R} - P\right], \tag{3.1'}$$

where η is the viscosity of the fluid. To describe the rate of change in the number g of molecules in the drop we use the equation bubble

$$\dot{g} = 4\pi R^2 \alpha_c \beta_* (1 - p/p_*). \tag{3.1''}$$

Here α_c is the condensation coefficient and β_* the frequency of collisions of vapor molecules with a unit surface at a pressure p_*. Changing to a dimensionless time t': $dt' = dt\cdot 3bp_*/4\eta$ and to the variables $u_0 = v/v_*$, $u_1 = p/p_*$ we have

$$\dot{u}_0 = u_0 - u_0^{2/3} + u_0 b^{-1}(u_1 - 1), \tag{3.2'}$$

$$\dot{u}_1 = \theta(1-u_1)u_0^{-1/3} - u_1\dot{u}_0/u_0, \quad \theta = (1/2)\alpha_c \eta v_T/\sigma, \tag{3.2''}$$

where v_T is the average thermal velocity of the molecules.

The diffusion tensor and the potential contour tensor corresponding to (1.1) and (3.1) were evaluated in Ref. 3 and have in the foregoing variables the form

$$\mathbf{D}_u = \frac{T}{2W_*}\begin{pmatrix} 1 & -1 \\ -1 & 1+b\theta \end{pmatrix}, \quad \mathbf{V}_u = \frac{W_*}{T}\begin{pmatrix} -2/3 & 0 \\ 0 & 2/b \end{pmatrix}. \tag{3.3}$$

As is clear from the preceding consideration, the saddle trajectory plays the decisive role and its form $u_1 = u_1(u_0)$ is determined from (3.1) and (3.2) and from the condition $u_1(1) = 1$. It is impossible to determine analytically the shape of the trajectory for arbitrary θ. Below we consider the limiting cases as $\theta \to \infty$ and $\theta \to 0$ (the stationary solution is determined by the behavior of the trajectory solely close to the saddle point and can be obtained for any θ (Ref. 8).

As $\theta \to \infty$ (high viscosity) the pressure in the bubble remains close to equilibrium: $u_1 = 1 - (1/\theta)(u_0^{1/3} - 1)$. To determined the non-stationary nucleation rate (2.4) it is sufficient to evaluate the quantity $\tilde{C}$ (the width of the saddle differs little from the single-parameter one: $\partial^2 W_{\mathrm{eff}}/\partial u_{0_*}^2 = -\frac{2}{3}W_* + O(\theta^{-2})$). We determine the quantitiy $\tilde{C}$ accurate to $1/\theta$ ($u_0 \equiv u$)

$$\tilde{C} = \exp\left\{\int_0^1 du \left(\frac{u\,\partial\dot{u}/\partial u|_*}{\dot{u}} - \frac{1}{u-1}\right)\right\}$$

$$= \frac{1}{3}\exp\left\{\frac{11}{6} + \frac{1}{4\theta b}\right\}. \tag{3.4}$$

In the purely single-parameter situation[4)] $\tilde{C} = \frac{1}{3}e^{11/6} \approx 2.08$ and the expression for the non-stationary nucleation rate has the form

$$J = J_{\mathrm{st}}\left(0{,}32\frac{W_*}{T}\right)^{-n}\left(\frac{v_0 - v_*}{v_*}\right)^{-n}\Gamma(n+1), \quad -n = 3\frac{\partial}{\partial t'}\frac{W_*}{T}. \tag{3.5}$$

The situation as $\theta \to 0$ (low viscosity or small condensation coefficient) means that the number of molecules in the bubble changes very slowly. From the exhibit expressions (3.3) for the tensors **D** and **V** we find that when $\theta b \ll 1$ and $|b-3| \gg 9\theta$ we have

$$\lambda_0 = -\frac{\partial \dot{v}}{\partial v}\bigg| = \begin{cases} -\frac{1}{3}\left(1-\frac{3}{b}\right), & b>3 \quad (3.6') \\ -\theta\left(\frac{3}{b}-1\right)^{-1}, & b<3 \quad (3.6'') \end{cases}$$

From (3.6") and (2.3) it follows that the nucleation rate vanishes with θ for moderately expanded liquids ($b<3$), which is patently incorrect. Physically it is clear that for very slow evaporation the formation of practically empty cavities begins to play the decisive role,[1] and this does not correspond to the saddle trajectory where $p = p_*$.

To trace the transition between the various paths of nucleus formation we consider the motion of a bubble in the plane of the reduced variables $z_0 \sim u_0(1-1/b)^3$, $z_1 \sim u_1/(b-1)$ (see the figure). We shall characterize the trajectory by the parameter $\alpha = g/g_*$; the rate of change of α is small as θ is small. The line LM corresponds to mechanical equilibrium and on the section QL (Q is the point of tangency to the hyperbola $u_0 u_1 = \alpha_{cr} = \frac{4}{27}b^3/(b-1)^2$) the equilibrium is stable, but on the section QM it is unstable. The source region is bounded by the section EQ of the "critical" hyperbola and the line QM of unstable mechanical equilibrium. We consider the situation of the saddle point for $b \gtrless 3$.

When $b>3$ the saddle point turns out to lie on the line of unstable equilibrium (the point F in the figure). The decay of the critical nucleus proceeds along the "fast" line FH until it approaches the point H of stable equilibrium, after which a slow decay begins along the line HL of stable equilibrium. The quantity θ does not affect the rate of going through the saddle point [Eq. (3.6')] and its effect reduces to a decrease of the constant $\widetilde{C}$. This constant acquires a factor $\exp(-\frac{1}{2}\theta b^2)$ thanks to the slow section HL, as follows from the growth equations (3.2) at $b \gg 1$. For trajectories with smaller α the contribution from the slow section is smaller and is of the order $\exp(-\alpha^2/2\theta b^2)$. We compare the saddle trajectory FHL with the trajectory MO for the decay of an empty cavity ($\alpha = 0$). The height of the activation barrier at the point M is

$$\frac{W_M}{T} = \frac{W_*}{T}\left(1-\frac{1}{b}\right)^{-3} \approx \frac{W_*}{T} + \frac{3}{2}g_*, \qquad (3.7)$$

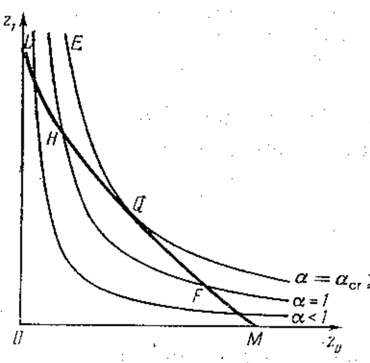

FIG. 1.

where g_* is the number of molecules in the critical bubble. One can therefore, taking (2.4) into account, estimate the ratio of the nucleation rates along the corresponding trajectories to be

$$J_F/J_M \sim \exp\left\{\frac{3}{2}g_* - \frac{n}{2\theta}\frac{1}{b^2}\right\} \qquad (3.8)$$

(we consider the initial stage of the nucleation where $n>0$). It is clear from this expression[5] that for any non-vanishing non-stationary index n and for sufficiently small θ the formation of empty cavities is decisive. The non-stationary nucleation rate can in that case be determined using Eq. (3.5), where the barrier height W_* is replaced by W_M in accordance with (3.7). When the level of non-stationarity decreases for fixed θ the role of trajectories with $\alpha > 0$ increases, and in the stationary limit the saddle trajectory remains decisive.

When $b<3$ the saddle point turns out to lie on the line of stable mechanical equilibrium (the point H in the figure). The critical nucleus decays along the slow trajectory HL; this leads to an increase of the non-stationary index n as $1/\theta$. The corresponding nucleation rate turns out to be negligibly small in the limit as $\theta \to 0$. More favorable is the fast surmounting of the higher barrier along the line FM. The relative contribution from those trajectories is taken into account similarly to the case $b>3$. The continuity of the obtained expressions when b passes through 3 follows from the merging of the point F and Q as $b \to 3$. In the stationary limit, as before, the saddle trajectory remains the decisive one provided θ does not turn out to be exponentially small [when the smallness of the quantity λ_0 of (3.6") compensates for the difference in the height of the activation barriers].

The non-stationary thus significantly redistributes the relative contributions of the different paths of nucleation, and this may turn out to be important also in the case when there are several saddle points in the potential contour $W(\mathbf{q})$.[5]

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APPENDIX. REGION OF APPLICABILITY OF THE SOLUTION

When changing to the quasi-stationary Eq. (1.6) we neglected the derivative $\partial w/\partial t|_{v=\text{const}}$. Rewriting the "exterior" solution (1.9) in one-dimensional form

$$w(u) = \exp\left\{\gamma \int_0^u du\, u/\dot{u}\right\}, \quad u = v/v_* \qquad (A1)$$

and using the equation $\partial \ln v_*/\partial t = -3\gamma T/2W_*$ we get

$$\frac{\partial w}{\partial t}\bigg|_{v=\text{const}} = w\left\{\frac{\partial \ln \gamma}{\partial t}\ln w + \frac{3}{2}\gamma^2\left(\frac{W_*}{T}\right)^{-1}\frac{u^2}{\dot{u}}\right\}. \qquad (A2)$$

In the region where (A1) is applicable the double inequality

$$\gamma u w \gg \frac{\partial}{\partial u}\left(D(u)\frac{\partial w}{\partial u}\right) \gg \frac{\partial w}{\partial t}\bigg|_{v=\text{const}} \qquad (A3)$$

must be satisfied. The diffusion coefficient $D(u_*)$ can be estimated at $(\gamma/n)(W_*/T)^{-1}$, whence it follows that as $u \to u_* = 1$

$$\partial/\partial u D \partial w/\partial u \sim n\gamma w (u-1)^{-2} (W_*/T)^{-1}$$

(we assume that $n \gg 1$). From this relation and the first part of the inequality (A3) we find that the solution (A1) is applicable when $1 - u \gg (W_*/nT)^{-1/2}$. Estimating the derivative $\partial \ln\gamma/\partial t$ in (A2) at $\gamma(W_*/T)^{-1}$ we find that the second part of inequality (A3) is satisfied under the very weak condition

$$n \ll W_*/T. \tag{A4}$$

In the above-critical region the "interior" solution (1.21) can be replaced by its asymptotic form

$$w \sim (W_*/T)^{-n/2} \tilde{C}^n \Gamma(n+1) e^{-\zeta^2} \zeta^{-n}, \qquad (2n)^{1/2} \ll \zeta \ll (W_*/T)^{1/2}. \tag{A5}$$

The derivative $\partial\zeta/\partial t|_v$ is determined as $\gamma(W_*/T)^{-1}[\zeta + (3W_*/T)^{1/2}/2]$ and, proceeding as before, we find

$$\frac{\partial w}{\partial t} \sim w\gamma \left(\frac{W_*}{T}\right)^{-1} \left\{\zeta \left(\frac{W_*}{T}\right)^{1/2} + n\left[\ln\left(\frac{W_*}{T}\right)^{1/2} - \ln \tilde{C} + \psi(n+1)\right]\right\}, \tag{A6}$$

where $\psi(n+1) = (d/dn)\ln\Gamma(n+1)$ is the digamma function. This expression must be small compared to γw, whence

$$n+1 \gg (W_*/T)^{-1}, \tag{A7}$$

$$n \ll 2(W_*/T)/\{\ln(W_*/T) - 2\ln \tilde{C}\}. \tag{A8}$$

Condition (A8) is a somewhat more stringent limitation than (A4) but the asymptotic range of applicability of the solution remains large.

We estimate for which reciprocal times ν of an action on the liquid (e.g., ν being the ultrasound frequency) the nonstationarity may turn out to be important ($n \gtrsim 1$). Changing to a dimensional time t we have at $b \gg 1$

$$-n = (4\eta/bp_*)\partial/\partial t(W_*/T).$$

Replacing $\partial/\partial t(W_*/T)$ by $\nu W_*/T$ and bp_* by $|P|$ we find from this equation that $n \gtrsim 1$ when

$$\nu \gtrsim |P|T/4\eta W_*. \tag{A9}$$

We did not consider in the present paper the effect of the inertia of the liquid, which may turn out to be important when the viscosity is small. The criterion for neglecting the inertia was established in Ref. 8:

$$|P| \gg \rho\sigma^2/\eta^2, \tag{A10}$$

where ρ is the density of the liquid. Combining (A9) and (A10) we find that the results can be used when

$$\nu \gg (W_*/T)^{-1}\rho\sigma^2/\eta^3. \tag{A11}$$

We note that for homogeneous nucleation $W_*/T \sim 10^1$ to 10^2.

[1)]To simplify the formulae we use matrix notation (no indices); vectors are denoted by lower case letters and second-rank tensors by capitals and they are assumed to be transformed to those variables in which the corresponding equation is expressed.

[2)]The integral in (1.15) can be expressed in terms of special functions, in particular, for integer $n = \gamma/|\lambda_0|$ it determines the so-called "repeated error function";[15] however, the representation (1.15) is more convenient for finding the asymptotic behavior as $\zeta \to \pm\infty$.

[3)]A. F. Andreev indicated the possibility of such a procedure.

[4)]If the diffusion coefficient has a power-law dependence on size, $D(u) \propto u^\nu$, we have for a macroscopic nucleus $\dot{u} \propto u^\nu(1 - u^{-1/3})$ and it follows from (3.4) that $\tilde{C} = \frac{1}{3}\exp\{\psi(7-3\nu) - \psi(1)\}$, where $\psi(\nu)$ is the digamma function (in the case considered $\nu = 1$).

[5)]On trajectories for which the slow section is sufficiently large it is impossible to establish the quasi-stationary regime considered; however, the nucleation rate along such trajectories is even smaller than the one obtained in the estimates and the conclusion reached below remains valid.

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