A general theory for the formation of a new phase. Static cavitation in a nonvolatile liquid

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The rate of formation of cavities in a nonvolatile liquid subjected to negative pressure is calculated. The pressure is assumed to be sufficiently moderate, so that the critical bubble (hole) can be treated macroscopically. If this condition is satisfied one may apply the Zel'dovich saddle-point method. However, in distinction from that method, the present paper makes use of a construction of a Gibbs grand canonical ensemble, which allows one to avoid the ambiguities that appear in the calculation of the microscopic initial stage of formation of the hole and yields a more accurate value of the kinetic (preexponential) factor. A more accurate value of the work required to form a critical hole, the value which occurs in the exponent, is obtained by taking into account the dependence of the surface tension of the hole on the curvature of the surface. For this purpose we use an expansion of the surface tension in powers of the curvature of the surface of the hole. Since the surface tension occurs in the exponent of the expression for the probability or rate of cavitation, it is necessary to retain the expansion terms which are linear or quadratic in the curvature, whereas the correction factors to the cavitation rate, due to higher-order terms tend to unity as the expansion of the liquid decreases, in contradistinction from the first terms. It is important that for large expansions, and hence for small curvatures of the surface of the critical hole, the series for the surface tension diverges.

Since the time of Volmer the probability of nucleation—i.e., the formation of a viable germ of a new phase—has traditionally been computed by considering a Markov chain of events leading from the molecular level to the macroscopic, i.e., critical germ. However, in the general case this path requires information about properties of aggregates or complexes of molecules, starting with dimers, which is not accessible to us, and even if this information were available, its use would require overcoming tremendous computational difficulties. It is true that by using the method of steepest descent one can avoid this difficulty for the special case where the number of monomeric molecules is many times larger than the number of molecular complexes. In this case one can express the number of "equilibrium" critical germs in terms of the number of molecules[1] so that after a substitution into the Kramers-Fokker-Planck equation one can find the "flux of germs" in the space of their sizes[2]. However, this simplification is not applicable in the case of dense vapors, when the number of polymeric complexes is sufficiently large.

Moreover, as a matter of principle, the introduction into the computation of the equilibrium distribution of germs with respect to their sizes is objectionable in a system of infinitely large volume, where not only is there no equilibrium, but there occur essentially nonequilibrium processes of avalanche-like growth of postcritical germs.

To these difficulties is added in the case of cavitation or boiling a difficulty of principle, related to the indeterminacy of the number and even of the concept itself of germ-holes of molecular size and the fact that the initial stage of their growth is unknown. Therefore the Zel'dovich formula[2] for the number of approximately critical holes in an expanded nonvolatile liquid contains in fact an undetermined pre-exponential factor of the dimension of length.

Yu. Kagan[3] has attempted to construct the theory of boiling of an overheated liquid of arbitrary volatility and at the same time he has criticized the paper of Zel'dovich. As we shall see below (cf. footnote [2)]), Kagan's results are valid only for a liquid of high vapor pressure. For a nonvolatile liquid his formulas are not applicable. Thus, so far there is no general theory of boiling of liquids.

I have proposed[4] an essentially new approach to the calculation of the nucleation rate, based on the use of the Gibbs grand canonical ensemble and the Kramers-Fokker-Planck equation, which makes it unnecessary to calculate the initial stages of nucleation, at least for small supersaturations. An important advantage of this general statistical method is the fact that since the initial stage of the kinetics of nucleation is excluded from consideration, this method can be applied in a stereotype and universal manner to any cases of nucleation. In the present paper we apply it to the calculation of the probability of cavitation, assuming for simplicity that the liquid is nonvolatile or weakly volatile; in the sequel we shall generalize this theory to the case of boiling and the formation of gas bubbles under decompression.

Consider the behavior of an expanded (pressure $P < 0$) liquid in a big box of volume W with rigid walls which do not transfer heat. For this purpose we construct a Gibbs grand canonical ensemble, where as system with variable number of molecules we take a volume V separated inside the volume W with adiabatic rigid walls containing the liquid; the volume V satisfies the inequalities

$$v^c \ll V \ll W, \tag{1}$$

where v^c is the volume of a critical germ. We separate the volume by means of a porous shell, with pores of a size preventing near-critical and postcritical germs from passing. The volume $W-V$ plays the role of

thermostat and molecule reservoir which determines the temperature and the chemical potential up to the time when a bubble is formed inside it as a result of nucleation, which will reduce the expansion, leading to a state which is close to the two-phase bubble-liquid equilibrium.

We shall therefore consider only such states of the volume $W-V$ which are close to the state of metastable equilibrium of the expanded liquid when it does not contain near-critical and postcritical germ-bubbles. For moderate expansions such states of the volume $W-V$ can last for a long time and are practically indistinguishable from states of true thermodynamic equilibrium.

The probabilities of various states of the reservoir $W-V$ belonging to the metastable "single-phase" region will then satisfy the classical equation (cf., e.g.,[5])

$$w = C \exp\{S(E', N')/k\}, \qquad (2)$$

where k is the Boltzmann constant, S is the entropy of the reservoir, considered as a function of the energy E' and the particle number N' and C is a factor which is constant for a given reservoir, and is the same, independent of the state in which the volume V is. At the same time the probability w will be <u>proportional</u> to the probability of those states of the volume $\overline{V}$ which are characterized by the number of molecules and the energy of the n-th quantum state E coexisting with the given state of the reservoir. Therefore we may consider in the sequel that w is proportional to the probabilities of the different states of the volume V. As we shall see, the coefficient C will cancel in the following calculations of the nucleation probability, and therefore there is no need to worry about the normalization.

The volume V may be in one of the following classes (subensembles) of states:

Class 1. The volume V is filled with liquid in a state close to the metastable equilibrium, under the pressure P and contains no bubbles (holes) of near-critical or postcritical size. The state of the volume is characterized by the number N of molecules.

Class 2. The volume V contains a near-critical germ. We assume the vapor pressure inside the germ equal to zero, but for convenience we call it a bubble and representative of the second phase. The state of the volume V is described, in addition to the number of molecules of liquid, also by the size of the bubble.

Class 3. A postcritical bubble was formed in the volume V, which with probability nearing certitude leads to an emptying of the volume V of liquid without substantially affecting the expansion of the liquid in the volume $W-V$ as long as the latter is sufficiently large. The surface of the liquid will be in the pores of the shell, forming concave menisci, remaining in equilibrium owing to the capillary pressure, provided the walls of the pores are wetted by the liquid (or it will be on the exits of the pores in agreement with the conditions of applicability of the Cantor formula). Attaining this state our system of volume W will remain in it for a very long time, oscillating around the state of two-phase equilibrium, before returning into one of the classes 1 or 2 as a result of a large, and therefore very rare, fluctuation. In the sequel we shall not be interested in the class 3, since it is our purpose to compute the probability of transition from the class 1 through

class 2 into class 3, but not the stability of the latter. However, one must take into account the presence of the class 3 in order that the constructed Gibbs ensemble be in statistical equilibrium.

Thus, we restrict our attention to the consideration of states of the volume V which belong to the classes 1 and 2. If the ratio V/v^C is not too large states of the class 1 will be realized most of the time, states which correspond to a metastable equilibrium, and consequently to a relative minimum of the free energy. Compared to these states the states of class 2 corresponding to a maximum of the free energy will be realized relatively rarely, with a relatively small probability. This probability η will be the smaller the smaller the volume V and the larger the volume v^C of the germ, and consequently the work necessary to produce it. One may thus consider as negligible the probability for the simultaneous formation of several near-critical bubbles.

It is now necessary to introduce some clarification into the formal definition of the lower and upper limits on the size of near-critical bubbles. In order to characterize the size of a bubble in this region we shall surround it mentally by a sphere safely containing a germ of near-critical size and having volume V^l equal to the upper limit on the sizes of near-critical bubbles.

The size of the germ can be characterized by the number N_2 of molecules which are inside the sphere V^l. The volume of the germ cavity, v, can be expressed in terms of N_2 through the relation

$$v = V_2{}^l - N_2/c = (N_3 - N_2)/c, \qquad (3)$$

where c is the number of molecules per unit volume of the liquid, N_3 is the number of molecules which completely fill the volume V_2^l. Since N_3 is much smaller than the total number N of molecules in the volume V, one may neglect the influence of the density fluctuations on the quantities N_3, v for given N_2, whereas when one considers the probabilities of various values N of the number of molecules in the volume V (or in the volume $V - V_2 = V_1$) one must, of course, take them into account.

Thus, the near-critical state of the volume V is characterized by the numbers N and N_2, of which the latter is the number of molecules in the subsystem V_2. One may also characterize the state by means of the numbers N_1 and N_2, where N_1 is the number of molecules in the volume V_1.

For the remaining computations by means of the method of steepest descent it is necessary that there exist an interval of germ sizes characterized by numbers N_2^m and N_2^l of such a width that owing to the validity of the conditions $N_2^m \ll N_2^C \ll N_2^l$ the kinetics of the nucleation will be controlled by the stage in which the germ passes through this interval. On the other hand, this interval must be sufficiently narrow, encompassing states so close to the critical germ states, that the existence in the volume V of two or more germs with sizes within this interval be excluded. Both requirements can be satisfied at the same time if v^C is sufficiently large. The corresponding values $N_2 = N_2^l$ and $N_2 = N_2^m = 0$ will be considered as characterizing the lower and upper bounds on the sizes of near-critical bubbles. The second limit, N_2^m, has been set equal to zero for simplicity, by appropriate choice of the value of the volume of the sphere V_2^l.

In view of the second condition, i.e., the sufficient

narrowness of the interval of sizes of near-critical germs, one may consider in this interval a uniquely determined function $\varphi(N_2)$ describing the distribution of states in the Gibbs ensemble constructed by us, with respect to the sizes of the near-critical germs in the volume V. The function $\varphi(N_2)$ will be proportional to the distribution of near-critical germs with respect to the sizes N_2.

Let us now consider the probability distribution of different states of the volume V, when the statistical equilibrium distribution of the ensemble is violated by removing the states of class 3 as they appear, and replacing them with states of class 1. The nucleation probability is determined from the formula

$$v = Q/g_1, \qquad (4)$$

where Q is the flux of states of the volume V, in the statistical approach chosen by us. For a stationary process, when the distribution of states does not depend on time, this flux is constant for all states of the ensemble. In the region of states of class 2 (near-critical) this flux coincides with the flux of germs in the space of their sizes N_2.

In Eq. (4), g_1 is the total probability for states of class 1, referring to the metastable state of the expanded liquid in the absence of near- and postcritical bubbles. The heterophase fluctuations related to the formation of microcavities in the expanded liquid can be enhanced, which is taken into account in the following calculations of g_1, since they contain the thermodynamic parameters of supersaturated vapor: its chemical potential and its derivatives, depending on the density fluctuations through the mean density of the liquid.

Thus, both the flux of states and the probability of states of the ensemble of class 1 near the metastable equilibrium can be computed on the basis of one and the same Gibbs grand canonical ensemble. This removes the necessity to consider and compute the initial microscopic stage of formation of the critical bubble, the character of which is not known even qualitatively.

Restricting ourselves to the cases of moderate expansion of the liquid, and consequently of a high potential barrier for nucleation, we can compute Q by means of the saddle point method, when the flux of states coincides with the flux of germs. For this purpose we follow Zel'dovich[2] and use the Kramers equation for states of class 2 (near-critical states) for a stationary process:

$$\frac{\partial}{\partial N_2}\left\{ D\varphi \frac{\partial}{\partial N_2}\left(\frac{n}{\varphi}\right)\right\} = 0, \quad Q = D\varphi \frac{\partial}{\partial N_2}\left(\frac{n}{\varphi}\right), \qquad (5)$$

where $n(N_2)$ is the distribution of states of class 2 of the volume V with respect to the bubble size, corresponding to a stationary nucleation process, D is a generalized diffusion coefficient of states of the volume V in the space of numbers of molecules N_2. One must integrate the equations (5) with the boundary conditions

$$n(N_2)/\varphi(N_2) = 1 \text{ for } N_2 = N_2', \qquad (6)$$

$$n(N_2)/\varphi(N_2) = 0 \text{ for } N_2 = 0. \qquad (6')$$

Integrating (5), we obtain

$$Q = \frac{1}{J}, \quad J = \int_0^{N_2''} \frac{dN_2}{D\varphi(N_2)}. \qquad (7)$$

The total energy and the number of particles in the volume W are constant, so that the energy and the particle number of the heat reservoir depend on the energy and the particle number of the volume V. As a result of this the probability of different quantum states of the volume V equals

$$w_{nN} = C \exp \{ S \, (E' - \Delta E, \, N' - \Delta N)/k \}, \qquad (8)$$

where S is the entropy of the "medium" corresponding to a state of the volume V which contains N particles and the n-th quantum state of energy E_{nN} is realized; $\Delta E = E - \bar{E}_0$, $\Delta N = N - N_0$. Here $\bar{E}_0$ is the average energy corresponding to the particle number N_0 in the volume V. In (8) E' and N' are average values of the energy and particle number of the reservoir (thermostat) $W - V$ in an equilibrium state with the state of the volume V, of average energy $\bar{E}_0$ and number N_0 from which we count ΔE and ΔN. The factor C does not depend on the particular state of class 1 or 2 in which the subsystem V, separated from W, is, and consequently it is independent of the values of N_0 and $\bar{E}_0$. In particular, C retains its value even when a near-critical or postcritical germ appears in the volume V (cf. infra).

Expanding the entropy S of the system in powers of ΔE and ΔN, we obtain

$$w_{nN} = C \exp\left\{\frac{1}{k} S(E', N')\right\} \exp\left\{\frac{\mu'}{\theta}\Delta N - \frac{E_{nN} - \bar{E}_0}{\theta}\right\}, \qquad (8')$$

where μ' is the chemical potential of the molecules of the "medium" in the metastable equilibrium state (this chemical potential is, of course, equal to the chemical potential μ of the molecules in the volume V in the same state, i.e., $\mu' = \mu_0$). Summing w_{nN} first with respect to n and expressing $\bar{E}_0$ in terms of F_0 by means of the relation $\bar{E}_0 = F_0 + TS_0(\bar{E}_0, N_0)$, we obtain

$$g_1 = A' \sum_N \exp\left[\frac{\mu\Delta N - \Delta F_N}{\theta}\right], \qquad (9)$$

where

$$A' = C \exp(S^*/k), \quad S^* = S(E', N') + S_0(\bar{E}_0, N_0); \qquad (10)$$

S^* is the entropy of the liquid in the whole box of volume W, $\Delta F_N = F_N - F_0$ is the increment of the free energy of the volume V (compared to that of the metastable state F_0).

We now calculate the flux in Eq. (7), for which it suffices to consider the values of $\varphi(N_2)$ in the vicinity of $N_2 = N_2^c$, where $1/\varphi(N_2)$ has a sharp maximum. We note that to various "two-phase" (near-critical) states of the volume V corresponds the probability distribution

$$w_{nN_1N_2} = C \exp[S \, (E'^c - \Delta E, \, N'^c - \Delta N_1 - \Delta N_2)/k], \qquad (11)$$

where $\Delta N_1 = N_1 = N_1^c$ is the change in the number of molecules in the volume $V - V_2$ compared to the critical state (which represents, as is well known, an unstable equilibrium state); $\Delta N_2 = N_2 - N_2^c$ is the change of the number of molecules in the volume V_2; $\Delta E = E_{nN_1N_2} - \bar{E}_0^c$ is the change of the energy of the volume V compared to its average value in the critical state. As above, S in (11) is the entropy of the "medium" $W - V$; $E_{nN_1N_2}$ is the energy of the n-th quantum state of the volume V for given N_1, N_2. Expanding S near the point of unstable equilibrium into a double series with respect to ΔE and $\Delta N = (\Delta N_1 + \Delta N_2)$, we obtain

$$w_{nN_1N_2} = C \exp\left\{\frac{1}{k} S(E'^c, N'^c)\right\} \exp\left[\frac{\mu^c}{\theta}\Delta N - \frac{E_{nN_1N_2} - \bar{E}_0^c}{\theta}\right]. \qquad (12)$$

B. V. Deryagin

Summing with respect to n for fixed values of ΔN_1 and ΔN_2 we obtain

$$\sum_n w_{nN_1N_2} = A^c \exp\left(\frac{\mu^c \Delta N - \Delta F_{N_1N_2}}{\Theta}\right), \qquad (13)$$

$$A^c = C \exp\{S^{**}/k\}, \qquad (14)$$

where μ^c is the chemical potential of the molecules of the medium and

$$S^{**} = S(E^c, N^c) + S_0(E_0{}^c, N_1{}^c, N_2{}^c)$$

is the total entropy of the volumes $W-V$ and V in the unstable "critical" equilibrium state;

$$\Delta F_{N_1N_2} = F_{N_1N_2} - F_{N_1{}^cN_2{}^c} \qquad (15)$$

is the increment of the free energy of the liquid in the volume V when the molecule numbers N_1 and N_2 change respectively by $\Delta N_1 = N_1 - N_1^C$ and $\Delta N_2 = N_2 - N_2^C$. By analogy with the thermodynamics of solutions we set

$$F_{N_1N_2} = F_N + F_s + \Theta \ln(1/N), \qquad (16)$$

where the first term expresses the volume free energy of $N = N_1 + N_2$ particles, and the second term is the contribution to the free energy depending on the presence of the bubble, whereas the third term in the right-hand side expresses a contribution to the free energy depending on the mobility of the bubble, or on the mixing entropy. Here

$$F_s = \sigma s + Pv, \qquad (17)$$

where σ is the surface tension, P is the pressure of the liquid, s is the area of the surface, v is the volume of the bubble. Since $s \sim (N_3 - N_2)^{2/3}$, $v \sim N_3 - N_2$, we have

$$(\partial s/\partial N_2)^c = 2s^c/3(N_3 - N_2{}^c), \quad (\partial^2 s/\partial N_2{}^2)^c = -2s^c/9(N_3 - N_2{}^c)^2,$$

$$(\partial v/\partial N_2)^c = -v^c/(N_3 - N_2{}^c), \quad (\partial^2 v/\partial N_2{}^2)^c = 0. \qquad (18)$$

Considering further $F_{N_1N_2}$ as a function of the two variables N and N_2, we obtain

$$(\partial F_{N_1N_2}/\partial N_2)^c = -2\sigma s^c/3(N_3 - N_2{}^c) - Pv^c/(N_3 - N_2{}^c), \qquad (19)$$

$$(\partial^2 F_{N_1N_2}/\partial N_2{}^2)^c = -2\sigma s^c/9(N_3 - N_2{}^c)^2. \qquad (20)$$

Expanding $\Delta F_{N_1N_2}$ in (13) into a series of powers of ΔN_2 we obtain

$$\varphi(N_2) = \sum_{nN} w_{nN_1N_2} = \sum_N A^c \exp\left[\frac{\mu^c \Delta N - \Delta F_N}{\Theta}\right.$$

$$\left. - \Delta\left(\ln\frac{1}{N}\right) + \frac{2\sigma s^c/3 + Pv^c}{\Theta(N_3 - N_2{}^c)}\Delta N_2 + \frac{\sigma s^c(\Delta N_2)^2}{9(N_3 - N_2{}^c)\Theta}\right]. \qquad (21)$$

Owing to its smallness one may neglect the term $\Delta \ln(1/N)$. The coefficient of ΔN_2 vanishes due to the condition of unstable equilibrium

$$-P = 2\sigma s^c/3v^c = 2\sigma/R^c, \qquad (22)$$

where R^C is the radius of the bubble. Therefore we can write

$$\varphi(N_2) \approx A^c \sum_N \exp\left\{\frac{\mu^c \Delta N - \Delta F_N}{\Theta}\right\} \exp\left[\frac{\sigma s^c(\Delta N_2)^2}{9(N_3 - N_2{}^c)^2\Theta}\right]. \qquad (23)$$

The summation over N differs from the analogous summation in Eq. (9) only in that it refers to the volume $V - v^c$, rather than V, which is inconsequential in view of the condition $v^C \ll V$. Therefore, comparing (23) with (9) we obtain

$$\varphi(N_2) = \frac{A^c}{A'} g_1 \exp\left\{\frac{\sigma s^c(\Delta N_2)^2}{9(N_3 - N_2{}^c)^2\Theta}\right\}. \qquad (24)$$

Knowing $\varphi(N_2)$ we find J from (5). Since $1/\varphi(N_2)$ has a sharp maximum at the point $\Delta N_2 = 0$ we write by means of the saddle point method

$$J = \frac{A'}{A^cD^cg_1}\int_{-\infty}^{+\infty}\exp\left[-\frac{\sigma s^c}{9(N_3 - N_2{}^c)^2}\frac{(\Delta N_2)^2}{\Theta}\right]d(\Delta N_2).$$

Carrying out the integration, we obtain

$$Q = \frac{1}{J} = \frac{A^cDg_1}{A'(N_3 - N_2{}^c)}\left(\frac{\sigma s^c}{9\pi\Theta}\right)^{1/2}. \qquad (25)$$

Finally, from (6), (11) and (25), taking into account the expressions (10) and (14), we obtain the required probability of formation of a germ in the volume V:

$$v = \frac{D^c}{N_3 - N_2{}^c}\left(\frac{\sigma s^c}{9\pi\Theta}\right)^{1/2}e^{\Delta S/k}, \qquad (26)$$

where $\Delta S = S^{**} - S^*$ is the increment of the entropy of the whole system (the whole volume W) in the transition from the metastable state into the unstable (critical) one. Since the system is isolated and its energy and volume are constant, the increment in entropy equals the increment in thermodynamical (Gibbs) potential of the system, divided by the absolute temperature at which the germ formation occurs. One may, however, neglect the variation of such an intensive quantity like the temperature in view of the large heat capacity of the volume W and the smallness of the heat of formation of a bubble of critical size. We have assumed from the very beginning that the nucleation takes place isothermally, and that the volume $W-V$ serves as a thermostat.

At the same time the term $\Theta \ln(1/N)$ which takes into account the "mixing" entropy of the bubble and the liquid[1] must be taken into account. As a result we find that the increment of thermodynamic potential exceeds the work of formation of a critical bubble, U, by the amount $\Theta \ln(1/N)$ (taking into account that the volume V is separated from the volume $W-V$ of the "thermostat" by a barrier which is impenetrable for germs of bubbles). We have

$$v = \frac{N_1D^c}{3(N_3 - N_2{}^c)}\left(\frac{\sigma s^c}{\pi\Theta}\right)^{1/2}e^{-U/\Theta}. \qquad (26')$$

It is now necessary to determine the generalized diffusion coefficient D. For this we use the Einstein equation

$$D = (\Theta/\Psi)dN_2/dt, \qquad (27)$$

where $\Psi = -d\Phi/dN_2$ is the "force" producing the "motion" with velocity dN_2/dt, Φ is the "potential" of that force, which in this case coincides with the R-dependent terms in the expression for the free energy of the volume V in (17):

$$\Phi = \sigma s + Pv. \qquad (28)$$

We relate the diffusion coefficient D in the space of particle numbers N_2 to the diffusion coefficient D_R in the space of bubble radii R, by means of the obvious formula

$$D = \Theta\frac{dN_2/dt}{-d\Phi/dN_2} = \Theta\frac{dR/dt}{-d\Phi/dR}\left(\frac{dN_2}{dR}\right)^2 = D_R\left(\frac{dN_2}{dR}\right)^2. \qquad (29)$$

Here

$$N_3 - N_2 = \tfrac{4}{3}\pi R^3c, \quad (dN_2/dR)^2 = 16\pi^2 R^4c^2, \qquad (30)$$

where c is the number of molecules per unit volume.

The calculation of D_R can now be carried out by solving the Navier-Stokes equation and the continuity equation:

$$\frac{\partial u}{\partial t} + (u\nabla)u = -\frac{1}{\rho}\nabla P + \frac{\eta}{\rho}\Delta u, \quad \frac{\partial\rho}{\partial t} + \rho\nabla u = 0 \qquad (31)$$

(here ρ is the density of the liquid, η is the viscosity and u is its velocity) with the boundary condition

$$(P-2\eta\partial u/\partial r)\,|_{r=R}+2\sigma/R=0. \qquad (32)$$

In the quasistationary approximation the instantaneous velocity and pressure field has the form

$$u=R^2 u_0/r^2, \quad P=-P_0, \quad \nabla u=0.$$

Substituting these expressions into (32), we obtain

$$u_0=\frac{R}{4\eta}\left(P_0-\frac{2\sigma}{R}\right). \qquad (33)$$

Since $d\Phi/dR = r\pi R^2(P_0-2\sigma/R)$, we obtain

$$D_R=\Theta/16\pi\eta R. \qquad (34)$$

From Eqs. (29), (30) and (34) we derive

$$D^c=\pi\Theta(R^c)^3 c^2/\eta. \qquad (35)$$

Substituting this into the expression (26'), we obtain

$$\nu=\frac{VR^c c^2}{2\eta}\sqrt{\Theta\sigma}\,e^{-U/\Theta}. \qquad (36)$$

As it should be, the nucleation probability is proportional to the number of molecules and the volume of the medium. This was a direct consequence of taking into account the entropy term in the work of formation of the germ.[2]

On the other hand, since the work of formation of the critical germ, U, appears in the exponent of the exponential function, it is necessary to improve the Gibbs expression for $s\sigma/3$, by taking into account the curvature $1/R$ of the bubble. For this purpose we expand σ in Eq. (17) in a series in powers of $1/R$:

$$\sigma=\sigma_\infty(1+a/R+b/R^2+\ldots), \qquad (37)$$

where according to [6] a equals twice the distance δ between the tension surface and the equimolecular surface. According to Shcherbakov[7] a has the order of magnitude of the molecular diameter; the sign plus in front of a/R corresponds to a concave meniscus.

Starting from the (unstable) equilibrium condition $\partial F_s/\partial R=0$ and Eqs. (17) and (37), we obtain in place of the classical equation for the capillary pressure[7]

$$P=2\sigma/R^c+d\sigma/dR=-(2\sigma_\infty/R^c)(1+a/2R^c). \qquad (38)$$

For the work of formation of the "hole," which is equal to the change in thermodynamic potential of the system when cavitation sets in, we find (cf. also [8])

$$\Delta\Phi=s\sigma(R)+vP=-\frac{s\sigma_\infty}{3}\left(1+\frac{2a}{R}+\frac{b}{R^2}\right). \qquad (39)$$

In order to derive from here the expression for the work of formation of the critical bubble it is necessary to find its radius R^c from Eq. (38), which has a unique positive root, provided we know P. Omitting the computations we give the result of substitution of R^c into equation (39), neglecting terms with negative powers of R:

$$\Delta\Phi^c=\frac{16\pi\sigma_\infty^3}{3P^2}-a\frac{8\pi\sigma_\infty^2}{P}+\left(4\pi b+\frac{5\pi}{3}a^2\right)\sigma_\infty. \qquad (40)$$

Usually a more precise expression of the work of formation of the germ is considered necessary in nucleation theory for the case of small germs, when the curvature is large [7]. Indeed, only in this case the correction is not relatively small. Therefore, considering the opposite case of large R we have not introduced this correction so far; it would affect by little the factor in front of the exponential function.

However, in introducing corrections into the expression U/Θ in the exponent, consequently, into the computation of ν, the absolute rather than the relative magnitude of the corrections plays a role, and this absolute value does not decrease as R increases but rather increases. Moreover, generally speaking, the series (37) converges only asymptotically for large R[9], indicating another difficulty of principle in the construction of a theory of nucleation for large values of the supersaturation and the necessity to consider, so far, only moderate values of the supersaturation. Finally, we obtain for

$$\nu=\frac{Vc^2R}{2\eta}\sqrt{\Theta\sigma}\exp\left[-\frac{16\pi\sigma_\infty^3}{3\Theta P^2}+\frac{8\pi\sigma_\infty^2 a}{\Theta P}-\left(4b+\frac{5}{3}a^2\right)\frac{\pi\sigma_\infty}{\Theta}\right]. \qquad (41)$$

Taking into account the order of magnitude of a and b, the last correction term in the exponent can have the order of magnitude 10^2, which will change ν strongly. Even more will the probability of nucleation be changed on account of the first correction term, since under the same assumption of large values of R/a the ratio σ_∞/Pa is also large.

For comparison we reproduce the formula for the probability of cavitation proposed by Zel'dovich[2]:

$$\nu^*=V\frac{2\sqrt{\Theta\sigma}}{\eta R^c d^2}\exp\left(-\frac{U}{\Theta}\right), \qquad (42)$$

where d is the diameter of the molecules of the liquid. Neglecting numerical factors and accordingly setting $c^2=d^{-6}$ we obtain $\nu^*/\nu=(d/R_C)^2$. Thus if we make abstraction of the computation of U, the Zel'dovich formula yields too low a probability of nucleation. In the other version indicated in Zel'dovich's paper

$$\nu^{**}=V\frac{2\sqrt{\Theta\sigma}}{\eta(R^c)^5}\exp\left(-\frac{U}{\Theta}\right)$$

an even greater lowering of the probability is obtained: $\nu^{**}/\nu=(d/R^C)^6$.

These differences are not surprising, since, not having the possibility of determing the normalization factor in the distribution of germs with respect to their sizes, Zel'dovich has introduced into the formula for the probability of nucleation factors of the dimension length on the basis of dimensional considerations, which in view of the presence of two linear quantities d and R^C in the problem makes the factor in front of the exponential dependent on the arbitrary function $f(R^C/d)$. In fact, the more precise form of the pre-exponential factor given here is practically much less essential than the more precise form of the work of formation of the germ (cf. also [10]).

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[1] It is obvious that the system liquid-bubbles can be considered as a solution sui generis of the bubbles in the liquid.

[2] In the general case of boiling of a liquid of arbitrary volatility it is necessary to take into account both the mutually independent flucuations of the radius of the bubble and of the number n of vapor molecules in it, which complicates the calculation of ν considerably. Therefore we cannot agree with Kagan's [3] discussion of the general case, taking into account as independent fluctuations only those of n. The correct result obtained by Kagan in the form of Eq. (36) is valid only for large n and (or) small viscosity η, when the independent fluctuations of R may be neglected. This neglect in the opposite limit of small n and

(or) large η has led Kagan to Eq. (34), from which the qualitatively unacceptable result follows that $\nu \to 0$ as $n \to 0$.

The introduction of a correction taking into account the small vapor pressure in the bubble will modify in our Eq. (36) only the work of formation of the critical bubble, U, on account of the change of R_c. If in Kagan's Eq. (34), refering to small n, one neglects the nonisothernal character, it is easy to see that this formula underestimates ν in the ratio ρ/c, where ρ is the concentration of vapor molecules. This is a result of not taking into account the fluctuations of size of the bubble.

We would like to add that introducing into equations (34) and (36) the factor N_0, Kagan refers to an article by Fürth and to the book of Ya. I. Frenkel', where this is justified only when applied to the process of condensation of vapors.

[1]Ya. I. Frenkel', Zh. Eksp. Teor. Fiz. **9**, 192, 952(1939); Kineticheskaya teoriya zhidkosteĭ (Kinetic Theory of Liquids) Izd. AN SSSR, 1945; Engl. Edition, Oxford U. Press, 1946.

[2]Ya. B. Zel'dovich, Zh. Eksp. Teor. Fiz. **12**, 525 (1942).

[3]Yu. Kagan, Zh. Fiz. Khimii **34**, 92 (1960).

[4]B. V. Deryagin, Dokl. Akad. Nauk SSSR **193**, 1096 (1970).

[5]L. D. Landau and E. M. Lifshitz, Statisticheskaya fizika, (Statistical Physics), Gostekhizdat, 1951, Sec. 35; Engl. Transl. Pergamon-Addison-Wesley, 1958.

[6]R. C. Tolman, J. Chem. Phys. **17**, 333 (1949); F. O. Koenig, J. Chem. Phys. **18**, 449 (1950). F. P. Buff, J. Chem. Phys. **19**, 1591 (1951). L. M. Shcherbakov, Kolloid. zh. **14**, 379 (1952).

[7]L. M. Sherbakov, in: Issledovaniya v oblasti poverkhnostnykh sil (Research in the Field of Surface Forces), vol. II, Nauka, 1967, p. 17.

[8]S. Ono and S. Kondo, Molecular theory of surface tention in liquids (Russian Transl.), IIL 1963.

[9]F. C. Goodrich, Trans. Farad. Soc. **64**, 3403 (1968); article in "Surface and Colloid Science," Vol. 1, N.Y., 1969.

[10]B. V. Deryagin and A. V. Prokhorov, Dokl. Akad. Nauk SSSR **207**, No. 6 (1972) [Sov. Phys. Doklady **17**, No. 12 (1973)].

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234