SPONTANEOUS NUCLEATION OF BUBBLES IN A GAS-SATURATED MELT UNDER INSTANTANEOUS DECOMPRESSION

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Based on the kinetic theory of phase transitions, the problem of spontaneous nucleation of gas bubbles in a gas-saturated melt under instantaneous decompression is considered. The total number of nucleation centers formed in the process and their size distribution function are found.
Key words: *decompression, spontaneous nucleation, diffusion, volcanic eruption.*

Introduction. According to Henry's law, the gas dissolved in a liquid undergoing decompression becomes supersaturated, which results in spontaneous origination of gas bubbles in the liquid. Despite of considerable efforts undertaken in studying this phenomenon, there is no theory adequately predicting the final number of bubbles formed in the process and their mean size. Therefore, in most studies, the nucleation of bubbles is assumed to be instantaneous, while the total number of bubbles is determined either from experimental data or from rather rough estimates [1].

In the present work, we consider the problem of the nucleation kinetics of bubbles in a gas-saturated liquid undergoing instantaneous decompression with allowance for the decrease in the gas-supersaturation level, which results in nucleation cessation. The model allows one to find the total number of formed bubbles and their size distribution function. As a gas-saturated liquid, we consider a magmatic melt with dissolved water; investigation into the degassing process of this substance is of considerable significance in modeling explosive volcanic eruptions [2].

Problem Formulation and Analytical Solution. We consider a volume of a gas-saturated melt that undergoes instantaneous decompression at the initial time. As was noted above, decompression results in spontaneous nucleation of gas bubbles. As the bubbles grow in size, a diffusion zone where the nucleation of other bubbles is suppressed is formed around them. A typical pattern of the process is illustrated in Fig. 1. The general probabilistic solution of a similar problem of the crystallization kinetics of an undercooled melt was found by A. N. Kolmogorov [3]. From the condition that new nucleation centers can appear only in the uncrystallized region, the time evolution of the crystallized-mass fraction and of the total number of formed crystallization centers was obtained for a fixed nucleation frequency and a fixed number of centers being formed. Modifying this solution to the case of degassing kinetics and using the analogy between the crystallite volume and the diffusion-zone volume around an individual bubble, we have

$$X_D(t) = 1 - \exp\Big(-\int\limits_0^t J(t')\, v_D(t - t')\, dt'\Big), \tag{1}$$

where X_D is the total volume of all diffusion zones around the bubbles in a unit volume of the melt, J is the nucleation frequency, and v_D is the volume of the diffusion zone around an individual bubble, which will be defined below. Then, the total number N_{b} of bubbles formed in a unit volume during the time t is

$$N_{\mathrm{b}}(t) = \int\limits_0^t J(t')\,(1 - X_D(t'))\, dt'. \tag{2}$$
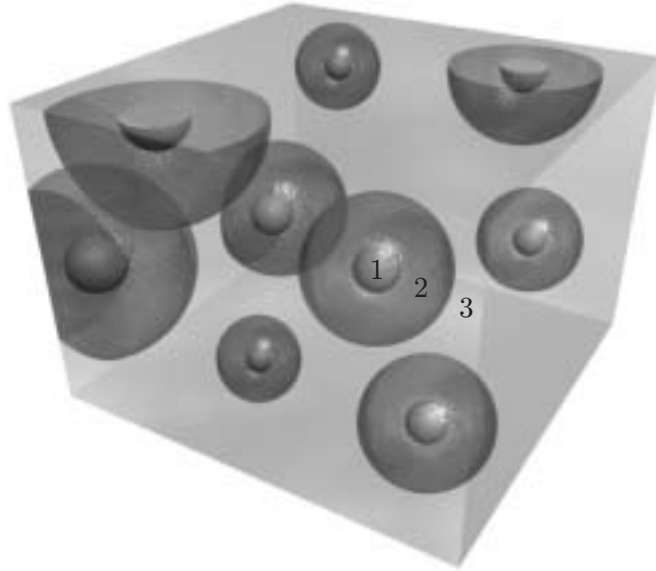

Fig. 1. Schematic representation of the bubble nucleation process in a gas-saturated melt under decompression: 1) bubble; 2) diffusion layer; 3) nucleation region.

In the general case, the nucleation frequency J is the sum of the homogeneous-nucleation frequency J_{hom} and the heterogeneous-nucleation frequency J_{het}, which have the following form in the classical kinetic theory of phase transitions:

$$J_{\mathrm{hom}} = J^*_{\mathrm{hom}} \exp\left(-\frac{W_*}{k_{\mathrm{B}}T}\right), \qquad J_{\mathrm{het}} = \sum_{i=1}^{N_{\mathrm{het}}} J^*_{\mathrm{het},i} \exp\left(-\frac{W_*\psi(\varphi_i)}{k_{\mathrm{B}}T}\right). \tag{3}$$

Here k_{B} is the Boltzmann constant, T is the melt temperature, $J^*_{\mathrm{hom}} = (2n^2_{\mathrm{gas}}v_{\mathrm{g}}D/d)(\sigma/(k_{\mathrm{B}}T))^{1/2}$ is the preexponent [5], σ is the surface tension at the melt–gas interface, n_{gas} is the number of potential nucleation centers that can be formed in a unit volume of the melt, assumed to be equal to the total number of gas molecules in the melt, D is the diffusivity of the gas in the melt, v_{gas} is the volume of the gas molecule, d is the mean distance between the neighboring gas molecules in the melt, $\psi(\varphi_i) = (1/4)(1 + \cos\varphi_i)^2(2 - \cos\varphi_i)$, φ_i is the equilibrium wetting angle of the surface of the ith foreign particle, N_{het} is the number of foreign particles in a unit volume of the melt, $W_* = 16\pi\sigma^3/(3\Delta P^2)$ is the work spent on forming a critical nucleus in the homogeneous process, and $\Delta P = P_{\mathrm{sut}} - P_f$ is the difference between the saturation pressure P_{sut} and the current pressure P_f. The pressure difference ΔP can be expressed in terms of melt supersaturation $C - C_f$ with the use of Henry's law, which has the form $C(P) = K_{\mathrm{H}}\sqrt{P_{\mathrm{sut}}}$ (C is the equilibrium mass concentration and K_{H} is Henry's constant) for water dissolved in a magmatic melt [4]. The preexponent for heterogeneously nucleated bubbles has the same form as in the homogeneous case, except for the replacement of n_{gas} by the number n_i of potential nucleation centers (molecules) on the surface of the ith foreign particle.

It follows from (3) that the heterogeneous-nucleation frequency depends on supersaturation more weakly than the homogeneous-nucleation frequency does. Therefore, the prevailing process for $\Delta P \gtrsim \{8\pi(1 - \psi(\varphi))\sigma^3 /[3k_{\mathrm{B}}T\ln(n_{\mathrm{gas}}/(nN_{\mathrm{het}}))]\}^{1/2}$ is homogeneous nucleation. In deriving the latter formula, it was assumed, for simplicity, that the melt contains foreign particles of one type.

Generally speaking, the *a priori* description of heterogeneous nucleation is difficult because the process depends on many factors whose role still remains poorly understood. For this reason, we restrict ourselves to the qualitative description of the process. Prior to considering heterogeneous nucleation, let us study the case of purely homogeneous nucleation.

To find the thickness of the diffusion layer formed around an individual growing bubble, we use the solution obtained in [6], where it was shown that the bubble growth is a diffusion-controlled process for Peclet numbers $\mathrm{Pe} = \Delta P R^2_{\mathrm{b}}/(\eta D) \gg 1$; for $\mathrm{Pe} \ll 1$, this process is governed by viscous stresses (R_{b} is the bubble radius and η is the melt viscosity). The quasi-stationary solution of the problem is [6]

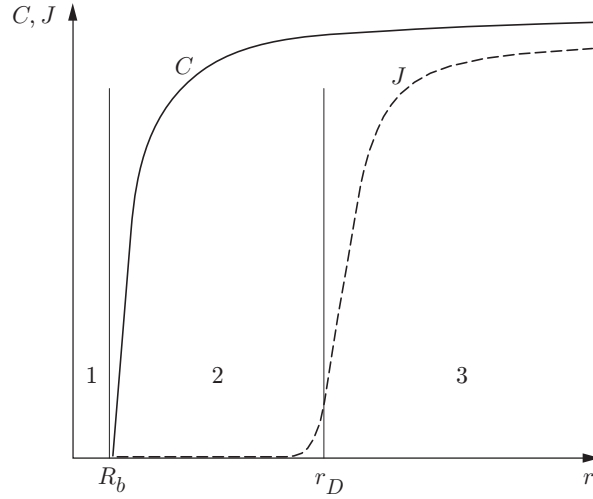$$C(r) = C_i - (C_i - C_f)R_{\mathrm{b}}/r. \tag{4}$$

Fig. 2. Gas concentration and nucleation frequency as functions of r (notation the same as in Fig. 1).

Here, $C(r)$ is the gas concentration in the melt as a function of the radial coordinate r with the origin at the bubble center, C_i and C_f are the equilibrium dissolved-gas concentrations under the initial pressure P_i and under the final pressure P_f, respectively (these concentrations are given by Henry's law), the time dependence of the bubble radius is $R_b(t) = \sqrt{D_{\text{eff}}t}$, where $D_{\text{eff}} = 2D\rho_m(C_i - C_f)/\rho_{\text{gas}}$ is the "effective" diffusivity, ρ_m is the melt density, $\rho_{\text{gas}} = M_{\text{gas}}P_f/(RT)$ is the gas density in the bubble (this density can be found from the equation of state for a perfect gas), and M_{gas} is the molecular weight of the gas.

Because of the low viscosity of heavily gas-saturated magmatic melts of interest [1], the above-given solution holds almost from the very beginning of bubble nucleation.

It follows from (4) that the dissolved-gas concentration decreases when approaching the growing bubble, i.e., a diffusion boundary layer is formed around the bubble (Fig. 2). Since the nucleation frequency strongly depends on supersaturation [see relation (3)], the bubbles can be assumed in the first approximation to nucleate outside the diffusion layer only (region 3 in Fig. 2), and the nucleation frequency in the diffusion zone can be assumed to equal the nucleation frequency at infinity. Indeed, nucleation of new bubbles in the diffusion layer, although possible, does not contribute appreciably to degassing because the nucleation frequency there is much lower then outside the diffusion zone.

In solving the problem posed, we consider only the growth mechanism of an isolated bubble. This can be made because, as follows from the reasoning described above, nucleation is observed until the diffusion layers of the neighboring bubbles start interacting with each other.

We determine the diffusion-layer thickness r_D from the condition $J(r_D)/J(r \to \infty) = 1/10$. Substituting expression (3) for the nucleation frequency into this relation and taking into account Eq. (4), we obtain $r_D(t) = æR_b(t)$, where $æ = 64\pi\sigma^3/(3k_B T(P_i - P_f)^2(1 + \sqrt{P_f/P_i})\ln 10)$. Since, in the problem of interest, $æ \gg 1$ (the diffusion-layer thickness is much greater than the bubble radius), the time evolution of the diffusion-zone volume around an individual bubble is described by the expression $v_D(t) = (4\pi/3)æ^3 R_b^3(t)$. Substituting the latter expression into (1) and (2), with due regard that, according to the accepted assumptions, the nucleation frequency outside the diffusion zone remains constant throughout the whole process and only the volume in which nucleation is possible is changed, we find the time dependence of the total number of bubbles formed in a unit volume of the melt:

$$N_b(t) = (J/D_{\text{eff}})^{3/5} [(8\pi/15)æ^3]^{-2/5} I\{[(8\pi/15)æ^3 J D_{\text{eff}}^{3/2}]^{2/5} t\}. \tag{5}$$

Here $I(\tau) = \int_0^\tau \exp(-\chi^{5/2}) d\chi$. It follows from Eq. (5) that the nucleation rate of bubbles rapidly decreases with time and finally vanishes. The reason is that, as the formed bubbles grow in size, the volume of the diffusion zone around them, where nucleation is suppressed, rapidly increases.

Let us estimate now the characteristic time of the nucleation process. Assuming that the nucleation rate of new centers dN_b/dt becomes negligibly low when the integrand exponent in the function $I(\tau)$ becomes equal to 100,

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we obtain $t_{\text{nucl}} \simeq 100^{2/5}[(8\pi/15)æ^3 J D_{\text{eff}}^{3/2}]^{-2/5}$. After this value of time, further degassing of the melt proceeds at the expense of already formed growing centers only. The characteristic nucleation time rapidly decreases with increasing supersaturation.

Let us find the total number of bubbles formed in the process. Taking into account that $I(\infty) \simeq 0.887$, we obtain

$$N_{\text{b}} = 0.887(J/D_{\text{eff}})^{3/5}[(8\pi/15)æ^3]^{-2/5}. \tag{6}$$

In fact, relation (6) describes the dependence of the total number of decompression-induced bubbles on the initial supersaturation of the melt.

Let us find the size distribution function of the nuclei $f = (1/N_{\text{b}})\, dN_{\text{b}}/dR_{\text{b}}$ (apparently, this function is time-dependent because new bubbles appear in the melt while already formed bubbles grow in size):

$$f(R_{\text{b}}, t) = 2R_{\text{b}}\,(J/D_{\text{eff}})\, \exp\{-(8\pi/15)æ^3(J/D_{\text{eff}})(D_{\text{eff}}t - R_{\text{b}}^2)^{5/2}\}/N_{\text{b}}(t).$$

Note that the size distribution function is normalized to the total number of bubbles that emerged in the melt during the time t, i.e., $\int_0^{\sqrt{D_{\text{eff}}t}} f(R_{\text{b}}, t)\, dR_{\text{b}} = 1$. The integration here is performed to the size of the bubble originated at the very beginning of the process. Obviously, the final form of the size distribution function (after the nucleation is completed) remains unchanged; further diffusion-controlled growth of already formed bubbles just shifts the function to greater sizes. Knowing the size distribution function, one can readily find the time dependence of the mean bubble radius: $\bar{R}_{\text{b}}(t) = \int_0^{\sqrt{D_{\text{eff}}t}} R_{\text{b}} f(R_{\text{b}}, t)\, dR_{\text{b}}$.

The above-described considerations are also applicable to the case of heterogeneous nucleation; the only difference here is that the homogeneous-nucleation frequency is to be replaced everywhere by the heterogeneous-nucleation frequency for the ith foreign particle, followed by summation over all heterogeneous centers. In addition, a new parameter $æ_i = æ\,\psi(\varphi_i)$ should be introduced instead of $æ$. The latter relation is valid if foreign particles of one type are uniformly distributed throughout the volume, and the diffusion zones around the bubbles formed at foreign particles have a spherical shape. This approximation is fairly reasonable if foreign particles are small in size and not too active. The problem of the total gas emission on solid surfaces and coarse foreign particles requires an additional analysis and is not considered here.

It should be noted that the proposed approach can also be used in solving problems of degassing of supersaturated solutions, where supersaturation is caused by reasons other than decompression (e.g., segregation of the dissolved gas by a travelling crystallization front [7]). In particular, for different relations between the equilibrium dissolved-gas concentration and pressure in Henry's law, it suffices to properly recalculate the parameter $æ$.

Computation Results. We simulated degassing of heavily gas-saturated magmatic melts with an initial mass concentration of dissolved water greater than 3%. The problem parameters were as follows [6]: density $\rho_m = 2300$ kg/m^3, diffusivity $D = 2 \cdot 10^{-11}$ m^2/sec, Henry's constant $K_{\text{H}} = 4.33 \cdot 10^{-6}$ Pa$^{-1/2}$, and surface tension $\sigma = 0.076$ J/m^2. The melt temperature was assumed to be 1150 K.

Figure 3 shows the calculated number of bubbles formed in the process versus initial supersaturation. The solid curve refers to the case of homogeneous nucleation, which is manifested beginning from $\Delta P \gtrsim 80$ MPa. With increasing supersaturation, the number of decompression-induced bubbles increases. As was noted above, the exact description of this process is complicated because the expression for the heterogeneous-nucleation frequency includes parameters hard to obtain experimentally. The whole process can be better understood from the qualitative dependence represented by the dashed curve in Fig. 3. In the computations, the melt was assumed to contain one type of foreign particles 0.1 μm in size, the number of particles was 10^{12} m^{-3}, and the wetting angle was $\varphi = 3\pi/4$. Note, beginning from the supersaturation $\Delta P \approx 100$ MPa, homogeneous nucleation prevails over heterogeneous one. Figure 3 also shows the experimental data of [5]. In a wide range of ΔP, the calculated and measured values are in good agreement; a certain difference at high values of $\Delta P \approx 120$ MPa, is caused by the fact that the characteristic nucleation time in the case under consideration has the same order of magnitude as the duration of melt decompression in the experiment, whereas decompression in the proposed model is assumed to be instantaneous.
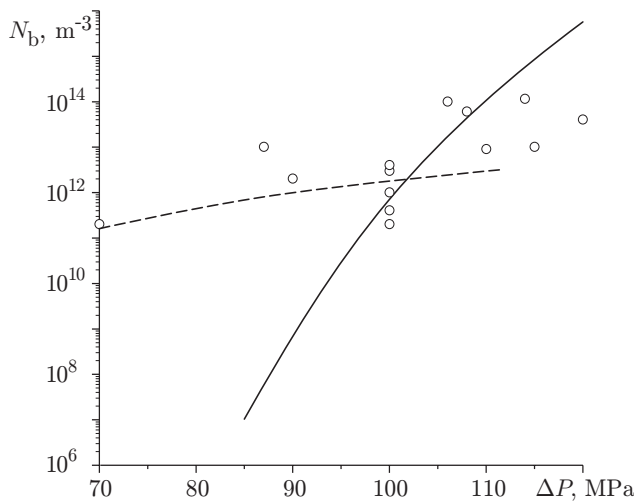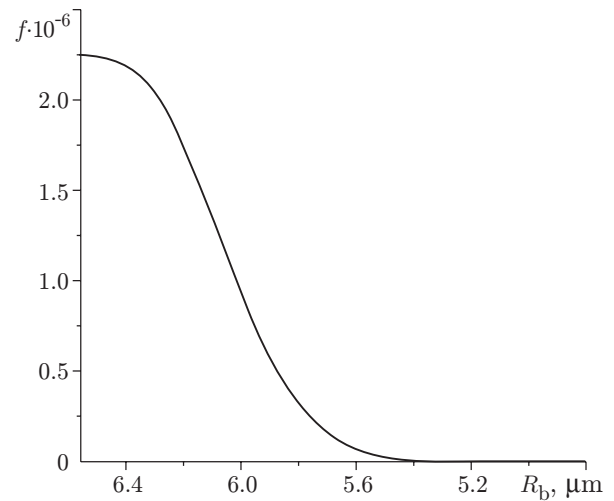
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Fig. 3

Fig. 4

Fig. 3. Number of bubbles formed due to decompression versus initial supersaturation: the solid and dashed curves refer to calculations for homogeneous and heterogeneous nucleation, respectively; the points show the experimental data of [5].

Fig. 4. Size distribution function of bubbles.

Figure 4 shows the size distribution function at the end of nucleation, $t_{\text{nucl}} = 0.002$ sec (the initial pressure was assumed to be 100 MPa, and the final one was assumed to equal the atmospheric value). The shape of the distribution function shows that nucleation primarily occurs at the initial stage of the process. The mean bubble radius by the end of nucleation reaches approximately 6 μm, whereas the simplest estimate [1] of the maximum possible bubble size that can be reached if the entire mass of the initially dissolved gas is converted into bubbles yield a value of 80 μm, i.e., the predominant fraction of the gas mass is released at the stage of diffusion-controlled growth of the bubbles ($t > t_{\text{nucl}}$). Hence, the assumption that nucleation of bubbles can be considered as an instantaneous process seems to be fairly reasonable.

Conclusions. The problem of spontaneous nucleation of bubbles in a gas-saturated magmatic melt under instantaneous decompression is considered. Based on the classical kinetic theory of phase transitions and on the modified total-conversion theory, the dependence of the total number of degassing-induced nucleation centers on the initial decompression-induced supersaturation is found. The characteristic nucleation time is estimated. The size distribution function of nuclei is obtained. The calculated results are in good agreement with experimental data reported by other authors.

REFERENCES

1. F. F. Chernov, "A model of magma solidification during explosive volcanic eruptions," *J. Appl. Mech. Tech. Phys.*, **44**, No. 5, 667–675 (2003).
2. O. E. Melnik and R. S. J. Sparks, "Nonlinear dynamics of lava dome extrusion," *Nature*, **402**, No. 4, 37–41 (1999).
3. A. N. Kolmogorov, "Statistical theory of metal crystallization," *Izv. Akad. Nauk SSSR, Ser. Mat.*, **3**, 355–359 (1937).
4. E. Stolper, "Water in silicate glasses: an infrared spectroscopic study," *Contrib. Mineral. Petrol.*, **81**, 1–17 (1982).
5. S. Hurwitz and O. Navon, "Bubble nucleation in rhyolitic melts: experiments at high pressure, temperature and water content," *Earth Planet. Sci. Lett.*, **122**, 267–280 (1994).
6. V. Lyakhovsky, S. Hurwitz, and O. Navon, "Bubble growth in rhyolitic melts: experimental and numerical investigation," *Bull. Volcanol.*, **58**, No. 1, 19–32 (1996).
7. A. I. Fedorchenko and A. A. Chernov, "Exact solution of the problem of gas segregation in the process of crystallization," *Int. J. Heat Mass Transfer*, **46**, No. 5, 915–919 (2003).