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# Theory of gas bubble nucleation in supersaturated solution of vacancies, interstitials and gas atoms

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## Abstract

A general form of the kinetic coefficients of the Fokker–Planck equation describing gas bubble nucleation in supersaturated solution of vacancies, interstitials and gas atoms is obtained. No assumptions concerning the detailed balance are used to describe the absorption and desorption of point defects and gas atoms at the bubble surface. This allows us to investigate limits of the usual formalisms of the gas bubble nucleation in irradiated materials. The ‘hard sphere’ equation of state is applied to describe the gas in the bubble. High densities of the gas atoms collected in the nucleated bubbles considerably decrease the critical bubble size and its nucleation barrier. The nucleation rate of the gas bubbles is obtained and its temperature dependence is investigated in detail. It is shown that an increase of the gas atom concentration results in decrease of the temperature of the nucleation rate maximum. © 1999 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

Radiation swelling and high temperature radiation embrittlement of structural materials result from formation and evolution of the vacancy void and gas bubble ensemble. Decay of three component supersaturated solid solution of vacancies, interstitials and gas atoms formed in the material by irradiation results in appearance of small gas–vacancy clusters. Transformation of these clusters to gas bubbles increasing irreversible their volume results from the cluster size fluctuations and is similar to the first order phase transition. Initial stage of this evolution (nucleation of gas bubbles) defines the void density at the developed stages and influences the kinetics of radiation swelling.

The nucleation kinetics of the gas bubbles are investigated using the rate equation and nucleation theory formalisms [1–5]. Because probabilities of absorption and evaporation of point defects and gas atoms from the

bubble determine the kinetics of the gas bubble formation the obtained results depend crucially on model assumptions used to describe the probabilities. The best way is an investigation of the microscopic kinetics of point defects and gas atoms at the bubble surface, but usually semiphenomenological models are used to obtain these probabilities. For example, to calculate these probabilities the authors of Refs. [2,3] used the distribution function  $f_0$  of the bubbles maintaining the detailed balance in the bubble size space (i.e. resulted from zero bubble current in any point of this space). However, in multi-component systems only specific forms of the absorption and evaporation probabilities result in the detailed balance [6,7]. In the case of the gas bubble nucleation the detailed balance may be achieved due only to additional assumptions concerning the microscopic kinetics of point defects and gas atoms at the bubble surface kinetics. It was shown in Ref. [8] that even for two component nucleation in supersaturated solution of vacancies and gas atoms the forms of the absorption and desorption probabilities used in Refs. [2,3] cannot result in the detailed balance in the gas bubble ensemble. The problem becomes much more

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complicated when interstitials are also introduced into the nucleation kinetics [2,3].

In the present paper we use no assumptions concerning the detailed balance to describe the absorption and desorption of point defects and gas atoms at the bubble surface. This allows us to investigate the influence of parameters of the material and irradiation on the limits of the usually used formalisms of the gas bubble nucleation. It should be noted that when the diffusion mobility of the dissolved gas is low (helium) the multi-component problem of the helium bubble formation can be successfully reduced to the one component one [9] but in this paper we especially investigate multi-component systems to describe the gas bubble formation in the general case.

The ‘hard spheres’ equation of state [10] is used to describe the gas in the bubble. It is shown that high densities of gas atoms which is realized in the nucleated bubbles considerably decrease the critical bubble size and its nucleation barrier. The nucleation rate of the gas bubbles is obtained and its temperature dependence is investigated in detail. It is shown that an increase of the gas atom concentration results in decrease of the temperature of the maximum of the nucleation rate.

## 2. Governing equations

We shall characterize a small spherical gas bubbles by numbers of the gas atoms ( $x$ ) and vacancies ( $n$ ) which form the bubble volume

$$V = \omega_g x + \omega n. \quad (1)$$

Here  $\omega_g$  is an increase of the bubble volume due to absorption of a gas atom dissolved in the matrix and  $\omega$  is the atomic volume.

To describe the nucleation kinetics we introduce the distribution function  $f(x, n)$  so that  $f(x, n; t) dx dn$  represents the volume density of the bubbles having dimensions  $x-x+dx$  and  $n-n+dn$  at time  $t$ . When the bubble growth results from absorption and desorption of single vacancies, interstitials and gas atoms at the bubble surface, an evolution of the distribution function is described by the Fokker–Planck equation [7]:

$$\frac{\partial f}{\partial t} = -\frac{\partial J_x}{\partial x} - \frac{\partial J_n}{\partial n}, \quad (2)$$

$$J_z = A_z f - \frac{\partial}{\partial x_z} (B_z f). \quad (3)$$

Here  $z = x, n$ . In Eq. (3) the kinetic coefficients  $A_z$  and  $B_z$  are, respectively, the ‘hydrodynamic’ rate and ‘diffusion’ coefficient of the bubbles in the dimensions space. These coefficients depend on the probabilities of absorption ( $P_x$ ) and desorption ( $Q_x$ ) of  $\alpha$ -type defects at the bubble

surface per unit time ( $\alpha = x, v, i$ , where  $v$  and  $i$  denote vacancy and interstitial, respectively):

$$A_x = P_x - Q_x; \quad B_x = (P_x + Q_x)/2, \quad (4)$$

$$A_n = A_n^v - A_n^i = (P_v - Q_v) - (P_i - Q_i), \quad (5)$$

$$B_n = B_n^v + B_n^i = (P_v + Q_v)/2 + (P_i + Q_i)/2. \quad (6)$$

Eqs. (2) and (3) should be supplied by initial and boundary conditions which will be formulated below.

## 3. Kinetic coefficients

### 3.1. Probabilities of absorption and desorption

The probability of desorption  $Q_x$  depends on the equilibrium concentration of  $\alpha$ -type defects in the layer of thickness  $l$  at the bubble surface and on the height of the barrier for their diffusion jump into the matrix [8] (see Fig. 1):

$$Q_x(R; x, n) = \frac{4\pi R^2 l \zeta}{\omega \lambda_\alpha^2} D_\alpha \exp(-\varepsilon_\alpha/T) C_{\text{eq},\alpha}(R; x, n). \quad (7)$$

Here, temperature  $T$  is measured in the energy units;  $D_\alpha = v_\alpha \lambda_\alpha^2 \exp(-\Phi_{\alpha\text{m}}/T)$  is the diffusion coefficient of  $\alpha$ -defects [11];  $v_\alpha$  is the attempt frequency for an  $\alpha$ -defect (below we assume  $v_\alpha = v$ , where  $v$  is the frequency of atomic oscillations in the matrix);  $\Phi_{\alpha\text{m}}$  is the free enthalpy barrier for the diffusion of  $\alpha$ -defects in the matrix;  $\lambda_\alpha$  is the diffusion jump length of an  $\alpha$ -defect in the

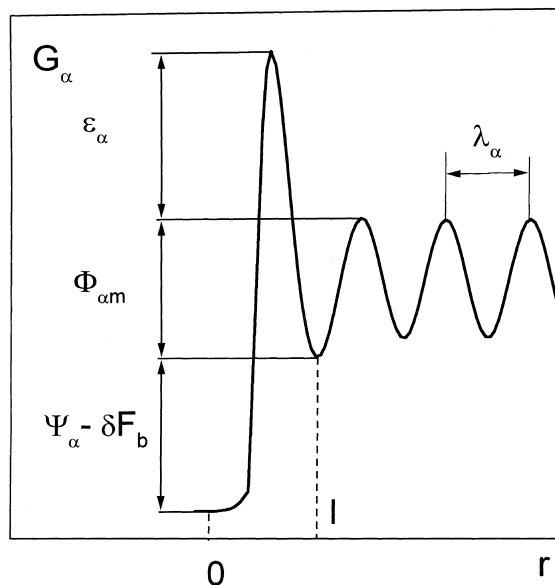


Fig. 1. The Gibbs free enthalpy of the system containing the gas bubble of size  $(x, n)$  and an  $\alpha$ -type defect via positions of this defect from the bubble surface. ( $\delta F = (\partial F_b / \partial x_\alpha) + (\partial F_s / \partial x_\alpha)$ ).

matrix;  $\varepsilon_\alpha$  is an additional diffusion barrier resulting from a possible matrix distortion near the bubble surface;  $\xi$  and  $\zeta \leq 1$  take into account a number of evaporation sites in the surface layer and correlation effects between diffusion jump directions, respectively.

The concentration  $C_{\text{eq},\alpha}(R; x, n)$  of the  $\alpha$ -defects which are in equilibrium with the curved surface of the gas bubble can be defined from the equality of their chemical potentials in the surface layer and matrix (see Refs. [8,12] and Fig. 1):

$$C_{\text{eq},\alpha}(R; x, n) = \exp \left\{ -\frac{\Psi_\alpha - [(\partial F_b / \partial x_\alpha) + (\partial F_s / \partial x_\alpha)]}{T} \right\}, \quad (8)$$

where  $\Psi_\alpha$  is the free enthalpy of dissolution of  $\alpha$ -objects from a flat surface into the matrix;  $F_b(R; x, n)$  and  $F_s(R; x, n)$  are Gibbs free energies of gas atoms in the bubble and the bubble surface, respectively. In this paper we neglect a bubble volume relaxation resulting from an influence of the gas pressure and curved bubble surface to the elastic matrix.

The absorption probability  $P_\alpha$  depends on a number of the  $\alpha$ -kind defects in a matrix layer neighboring to that at the bubble surface and a frequency of their jumps into the bubble:

$$P_\alpha = \frac{4\pi R^2 l \xi}{\omega \lambda_\alpha^2} D_\alpha \exp(-\varepsilon_\alpha / T) c_\alpha(R; x, n), \quad (9)$$

where  $c_\alpha(R; x, n)$  is the local atomic concentration of  $\alpha$ -defects in the matrix near the bubble surface. Note that we neglect a small difference between locations of the surface layer and its neighbor in the matrix.

### 3.2. Diffusion problem for an isolated bubble

A difference between the absorption and desorption probabilities of  $\alpha$ -defects at the bubble surface coincides with the diffusion current of these types of defects into the bubble and depends on the local concentration  $c_\alpha(R; x, n)$  near the surface (see Eq. (9)).

In a dilute ensemble of bubbles the concentration  $c_\alpha(R; x, n)$  can be obtained from the solution of the steady-state diffusion problem for an isolated spherical bubble [8] because the time scale of accommodation of the  $\alpha$ -object concentrations to the bubble is much shorter than that for the evolution of the bubble itself.

$$\nabla^2 c_\alpha = 0,$$

$$c_\alpha |_{r \gg R} = c_{\alpha\infty}, \quad (10)$$

$$(4\pi R^2 / \omega) D_\alpha \nabla c_\alpha |_{r=R} = P_\alpha - Q_\alpha,$$

where  $r$  is the radial distance from the bubble center and  $c_{\alpha\infty}$  is the concentration of  $\alpha$ -defects far from the bubble.

Solving Eq. (10) we obtain the concentration of  $\alpha$ -defects at the bubble surface:

$$c_\alpha(R; x, n) = c_{\alpha\infty} + \frac{R l \xi \exp(-\varepsilon_\alpha / T)}{\lambda_\alpha^2 + R l \xi \exp(-\varepsilon_\alpha / T)} \times [C_{\text{eq},\alpha}(R; x, n) - c_{\alpha\infty}]. \quad (11)$$

1. In the diffusion controlled case, when  $(\lambda_\alpha^2 / R l) \ll \xi \exp(-\varepsilon_\alpha / T)$ , we define from Eq. (11)

$$c_\alpha(R) \approx C_{\text{eq},\alpha}(R). \quad (12)$$

In this case diffusion profiles of  $\alpha$ -defects exist in the vicinity of the bubble.

2. For the reaction controlled case, when  $(\lambda_\alpha^2 / R l) \gg \xi \exp(-\varepsilon_\alpha / T)$ , a concentration ‘step’ is realized near the bubble surface

$$c_\alpha(R) \approx c_{\alpha\infty}. \quad (13)$$

### 3.3. Kinetic coefficients

Using Eqs. (4), (5), (7), (9) and (11) and neglecting the equilibrium concentration of interstitials at the bubble surface ( $C_{\text{eq},i}(R) = 0$ ) we obtain the general forms of the kinetic coefficients describing the gas bubbles kinetics:

$$A_x = \frac{4\pi R^2 l \xi}{\omega} \frac{D_x \exp(-\varepsilon_x / T)}{\lambda_x^2 + R l \xi \exp(-\varepsilon_x / T)} [c_{x\infty} - C_{\text{eq},x}(R; x, n)]. \quad (14)$$

$$A_n = \frac{4\pi R^2 l \xi}{\omega} \left\{ \frac{D_v \exp(-\varepsilon_v / T)}{\lambda_v^2 + R l \xi \exp(-\varepsilon_v / T)} [c_{v\infty} - C_{\text{eq},v}(R)] - \frac{D_i \exp(-\varepsilon_i / T)}{\lambda_i^2 + R l \xi \exp(-\varepsilon_i / T)} c_{i\infty} \right\}. \quad (15)$$

Below we assume for simplicity  $\lambda_i \approx \lambda_v$  and  $\varepsilon_v \approx \varepsilon_i$ .

The dimension space  $(x, n)$  of the gas bubble can be separated into growth and nucleation regions by the ridge of the saddle-like potential surface of the ‘hydrodynamic’ rate  $\vec{A} = (A_x, A_n)$ , when the components of this rate  $A_x$  and  $A_n$  alternate their signs [3]. It is clear from Eq. (15) that the coefficient  $A_n$  alternates its sign in the dimension space only when

$$\frac{D_i c_{i\infty}}{D_v c_{v\infty}} < 1. \quad (16)$$

In this paper we investigate only the case (16) when the general three component nucleation problem is reduced to the two component one for the gas atom–vacancy clusters.

### 4. Critical size region

Being determined from the conditions  $A_x(x_c, n_c) = 0$  and  $A_n(x_c, n_c) = 0$ , the critical bubble size  $(x_c, n_c)$  is a saddle point of the system of ‘hydrodynamic’ growth rates of bubbles:

$$\begin{aligned} dx/dt &= A_x(x, n), \\ dn/dt &= A_n(x, n). \end{aligned} \quad (17)$$

In the vicinity of the critical size the gas bubbles penetrate into the growth region due only to the ‘diffusion’ coefficients  $B_z$  in the Eqs. (2) and (3). Small values of the parameters  $|A_z/B_z| \ll 1$  in this region result from small supersaturation of gas atoms near the surface of bubbles in the vicinity of the critical size (critical region) (see Eq. (14)):

$$\left| \frac{c_{x\infty} - C_{\text{eq},x}(R; x, n)}{c_{x\infty}} \right| \ll 1, \quad (18)$$

and small value of the parameter (see Eq. (15)):

$$\left| \frac{D_i c_{i\infty}}{D_v c_{v\infty}} - \frac{c_{v\infty} - C_{\text{eq},v}(R; x, n)}{c_{v\infty}} \right| \ll 1. \quad (19)$$

Introducing a function

$$\begin{aligned} Y(x, n) &= -x\Psi_x - n\Psi_v - xT \ln c_{x\infty} \\ &\quad - nT \ln \left[ c_{v\infty} \left( 1 - \frac{D_i c_{i\infty}}{D_v c_{v\infty}} \right) \right] + F_b + F_s. \end{aligned} \quad (20)$$

Eqs. (14) and (15) can be transformed in the critical region to the following form:

$$A_x = -\frac{4\pi R^2 l \xi}{\omega \lambda_x^2} D_x c_{x\infty} \frac{\lambda_x^2 \exp(-\varepsilon_x/T)}{\lambda_x^2 + R l \xi \exp(-\varepsilon_x/T)} \frac{\partial Y(x, n)}{T \partial x}, \quad (21)$$

$$\begin{aligned} A_n &= -\frac{4\pi R^2 l \xi}{\omega \lambda_v^2} D_v c_{v\infty} \left( 1 - \frac{D_i c_{i\infty}}{D_v c_{v\infty}} \right) \frac{\lambda_v^2 \exp(-\varepsilon_v/T)}{\lambda_v^2 + R l \xi \exp(-\varepsilon_v/T)} \\ &\quad \times \frac{\partial Y(x, n)}{T \partial n}. \end{aligned} \quad (22)$$

In the same region the ‘diffusion’ coefficients  $B_z$  have the following forms:

$$B_x = \frac{4\pi R^2 l \xi}{\omega \lambda_x^2} D_x \exp(-\varepsilon_x/T) c_{x\infty}, \quad (23)$$

$$\begin{aligned} B_n &= \frac{4\pi R^2 l \xi}{\omega \lambda_v^2} D_v \exp(-\varepsilon_v/T) c_{v\infty} \\ &\quad \times \left[ 1 + \frac{D_i \exp(-\varepsilon_i/T) c_{i\infty} \lambda_v^2}{D_v \exp(-\varepsilon_v/T) c_{v\infty} \lambda_i^2} \right]. \end{aligned} \quad (24)$$

In the reaction controlled case, when  $(\lambda_x^2/Rl) \gg \xi \exp(-\varepsilon_x/T)$ , the kinetics coefficients  $A_x, A_n$  in the critical region are reduced to the following:

$$A_x^{(r)} = -\frac{4\pi R^2 l \xi}{\omega \lambda_x^2} D_x c_{x\infty} \exp(-\varepsilon_x/T) \frac{\partial Y(x, n)}{T \partial x}, \quad (25)$$

$$\begin{aligned} A_n^{(r)} &= -\frac{4\pi R^2 l \xi}{\omega \lambda_v^2} D_v c_{v\infty} \left( 1 - \frac{D_i c_{i\infty}}{D_v c_{v\infty}} \right) \exp(-\varepsilon_v/T) \\ &\quad \times \frac{\partial Y(x, n)}{T \partial n}. \end{aligned} \quad (26)$$

In the diffusion controlled case, when  $(\lambda_x^2/Rl) \ll \xi \exp(-\varepsilon_x/T)$ , we obtain in the critical region:

$$A_x^{(d)} = -\frac{4\pi R}{\omega} D_x c_{x\infty} \frac{\partial Y(x, n)}{T \partial x}, \quad (27)$$

$$A_n^{(d)} = -\frac{4\pi R}{\omega} D_v c_{v\infty} \left( 1 - \frac{D_i c_{i\infty}}{D_v c_{v\infty}} \right) \frac{\partial Y(x, n)}{T \partial n}. \quad (28)$$

## 5. Critical parameters of the $Y(x, n)$ surface

It will be shown below that the nucleation rate of the gas bubble (number of the gas bubbles penetrating into the growth region per second) depends crucially on the position of the saddle point  $(x_c, n_c)$  in the size space and the value and functional dependence of  $Y(x, n)$  in the vicinity of this point.

To calculate these parameters we neglect below both a relaxation of the bubble volume caused by the gas pressure and a small value of the relaxation free energy  $F_{\text{rel}} = -(3/8)(V/\mu)(p - 2\gamma/R)^2$  (where  $\mu$  is the shear modulus) resulted from elastic relaxation of the matrix [8,13].

High levels of the gas atom concentration in the matrix result in high density of the gas atoms in the bubble [13]. At such densities the ideal and van der Waals gas models [3,14] are hardly correct and we have to use the ‘hard spheres’ model which is valid both for low and high gas/liquid densities. In this model the state equation for the gas atoms has the following form [10]:

$$\frac{pV}{xT} = \frac{1 + 2\eta + 3\eta^2}{(1 - \eta)^2}, \quad (29)$$

here  $p$  is the gas pressure in the bubble;  $\eta = \omega_0 x/V$  is the packing density,  $\omega_0 = \pi d_0^3/6$  and  $d_0^3$  is the diameter of the gas atom.

The free energy of the monatomic gas consists of two parts [10]:

$$F_b(T, V, x) = F_b^{\text{id}}(T, V, x) + F_b^{\text{c}}(T, V, x) \quad (30)$$

Here  $F_b^{\text{id}}(T, V, x)$  is the free energy of the ideal gas:

$$F_b^{\text{id}}(T, V, x) = -xT \ln \left[ \frac{e\omega_0}{\eta} \left( \frac{mT}{2\pi\hbar^2} \right)^{3/2} \right], \quad (31)$$

where  $m$  is the mass of the gas atom,  $\hbar$  is the Planck constant, and  $F_b^{\text{c}}(T, V, x)$  is the configurational free energy resulting from interactions between gas atoms:

$$F_b^s(T, V, x) = xT \int_0^\eta \left( \frac{pV}{xT} - 1 \right) \frac{d\eta}{\eta} = xT \left[ \frac{6\eta}{1-\eta} + 2\ln(1-\eta) \right]. \quad (32)$$

Substituting Eqs. (31) and (32) into Eq. (30) we obtain

$$F_b(T, \eta, x) = xT \left\{ \frac{6\eta}{1-\eta} + \ln[\eta(1-\eta)^2] - \ln \left[ e\omega_0 \left( \frac{mT}{2\pi\hbar^2} \right)^{3/2} \right] \right\}. \quad (33)$$

Taking into account a spherical shape of the bubble and using Eq. (1), the free energy of the bubble surface is described by

$$F_s = 4\pi(3/4\pi)^{2/3} \gamma (\omega_g x + \omega n)^{2/3} = 4\pi(3/4\pi)^{2/3} \gamma (x\omega_0/\eta)^{2/3}, \quad (34)$$

where  $\gamma$  is the specific free energy of the bubble surface.

Substituting Eqs. (33) and (34) into Eq. (20) we obtain the number of gas atoms in the critical bubble  $x_c$  and their packing density  $\eta_c$  as a solution of the system  $\partial Y/\partial x = 0, \partial Y/\partial n = 0$ :

$$x_c^{1/3} = \frac{2(4\pi/3)^{1/3} \gamma \omega \eta_c^{1/3}}{\omega_0^{1/3} \left\{ T \ln \left[ c_{v\infty} (1 - D_i c_{i\infty} / D_v c_{v\infty}) / C_{eq,v}^0 \right] + p_c \omega \right\}}, \quad (35)$$

$$\chi(\eta_c) = \left\{ \ln \left( \frac{c_{x\infty}}{C_{eq,x}^0} \right) - \frac{\omega_x}{\omega} \ln \left[ \frac{c_{v\infty} (1 - D_i c_{i\infty} / D_v c_{v\infty})}{C_{eq,v}^0} \right] \right\} + \ln \left[ e\omega_0 \left( \frac{mT}{2\pi\hbar^2} \right)^{3/2} \right], \quad (36)$$

where

$$\chi(\eta_c) = \frac{6\eta_c}{1-\eta_c} + \ln[\eta_c(1-\eta_c)^2] + \frac{1+2\eta_c+3\eta_c^2}{(1-\eta_c)^2}, \quad (37)$$

$C_{eq,\beta}^0 = \exp(-\Psi_\beta/T)$  ( $\beta = x, v$ ),  $\eta_c$  is the packing density in the critical bubble,  $p_c = T(\eta_c/\omega_0)(1+2\eta_c+3\eta_c^2)/(1-\eta_c)^2$  is the gas pressure in the critical bubble.

It is clear from Fig. 2 and Eq. (36) that the large vacancy and low gas atom concentrations ( $c_{x\infty} \rightarrow 0$ ) result in negative values of  $\chi(\eta_c)$  which correspond to small packing density in the critical bubble ( $\eta_c \rightarrow 0, p_c \rightarrow 0$ ). For typical vacancy supersaturation and gas atom concentrations [1] the high densities ( $\eta_c \sim 0.3-0.45$ ) of the gas atoms are formed in the critical bubble (liquid state).

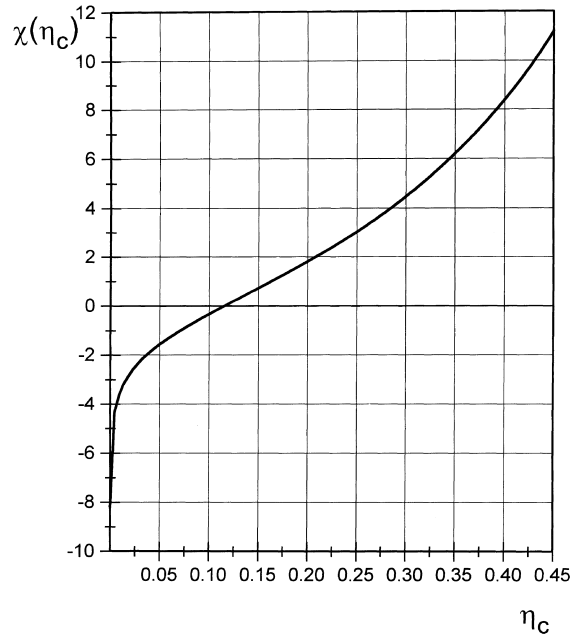


Fig. 2. The function  $\chi(\eta_c)$ .

We also can obtain the value of the  $Y_c = Y(x_c, n_c)$  in the critical point:

$$Y_c = \frac{16\pi}{3} \frac{\gamma^3 \omega^2}{\left\{ T \ln \left[ c_{v\infty} (1 - D_i c_{i\infty} / D_v c_{v\infty}) / C_{eq,v}^0 \right] + p_c \omega \right\}^2}. \quad (38)$$

In Figs. 3–6 we present the critical size  $x_c$  and  $Y_c$  for the different packing densities.

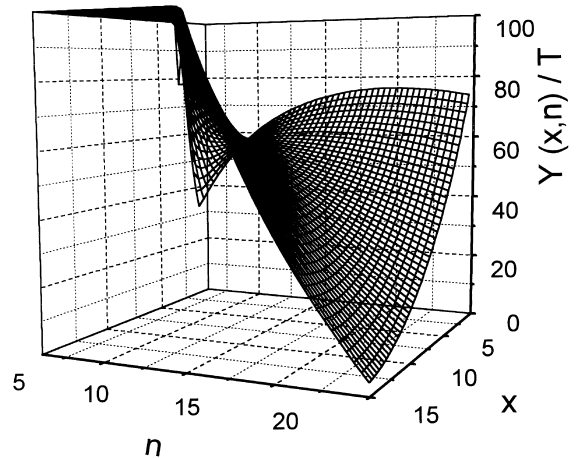


Fig. 3. Saddle form of the function  $Y(x, n)/T$  in the vicinity of the critical size ( $T = 800$  K,  $\gamma = 1500$  erg/cm<sup>2</sup>,  $c_{v\infty}/C_{eq,v}^0 = c_{x\infty}/C_{eq,x}^0 = 10^4$ ,  $D_i c_{i\infty} / D_v c_{v\infty} = 0.5$ ).

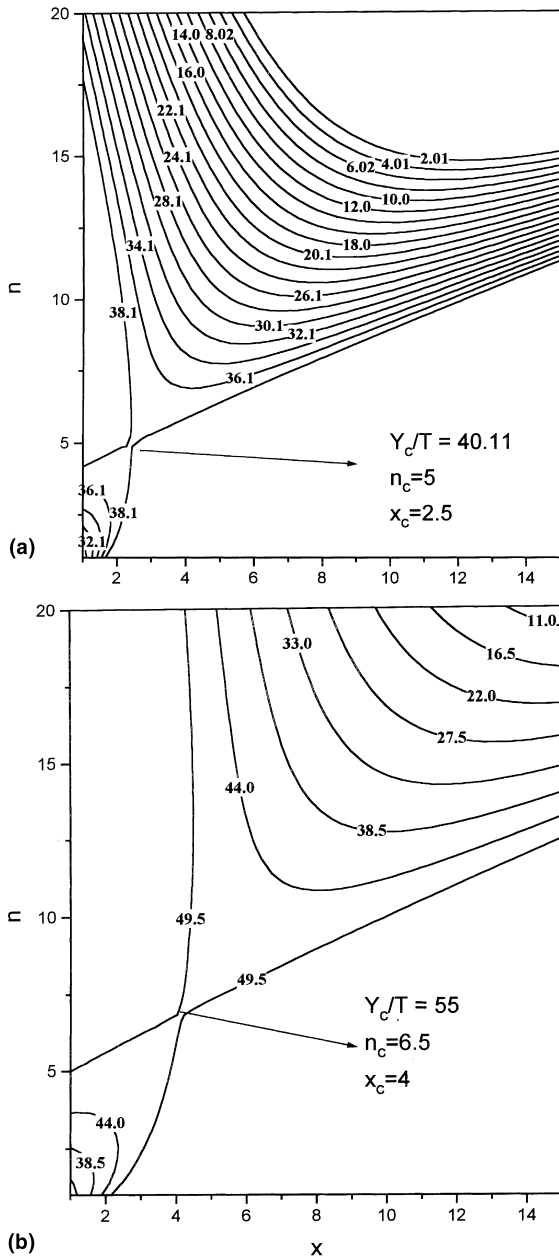


Fig. 4. Counter line plot of the surface  $Y(x, n)/T$ . Values of the critical size  $(x_c, n_c)$  and  $Y_c = Y(x_c, n_c)$ : (a)  $D_1c_{1\infty}/D_v c_{v\infty} = 0.3$ ; (b)  $D_1c_{1\infty}/D_v c_{v\infty} = 0.99$  ( $T = 800$  K,  $\gamma = 1500$  erg/cm<sup>2</sup>,  $c_{v\infty}/C_{eq,v}^0 = c_{x\infty}/C_{eq,x}^0 = 10^4$ ).

6. Steady-state nucleation rate

For the kinetic coefficients as well as the critical parameters (35)–(38) of the gas bubble ensemble the general analytical expressions (14), (15) and (21)–(28) involve only common restriction (16) to the effective

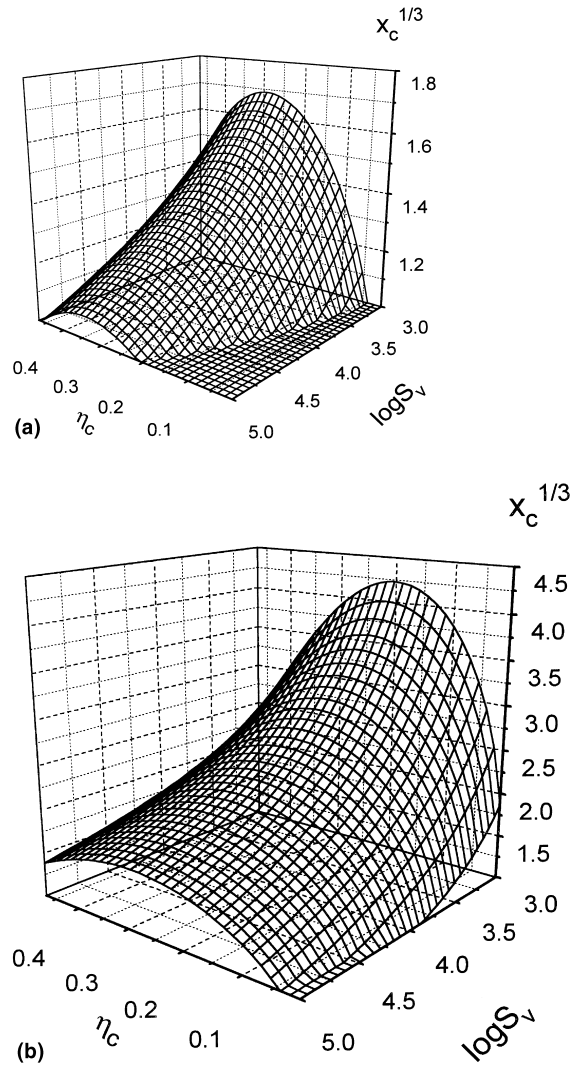


Fig. 5. The dependence of the critical size  $x_c^{1/3}$  on the packing density and vacancy supersaturation: (a)  $D_1c_{1\infty}/D_v c_{v\infty} = 0.1$ ; (b)  $D_1c_{1\infty}/D_v c_{v\infty} = 0.99$  ( $T = 800$  K,  $\gamma = 1500$  erg/cm<sup>2</sup>,  $c_{v\infty}/C_{eq,v}^0 = c_{x\infty}/C_{eq,x}^0 = 10^4$ ).

interstitial concentration. Below we shall describe the case when an analytical solution of the nucleation problem can be obtained that considerably restricts parameter values (e.g. the effective interstitial concentration) of the investigation system.

6.1. Potential conditions

Due to a fast development of the steady-state distribution of the bubbles in the nucleation region [7,15], we shall investigate below the steady-state nucleation problem. The distribution function  $\tilde{f}(x, n)$  which results in zero bubble current into the growth region usually

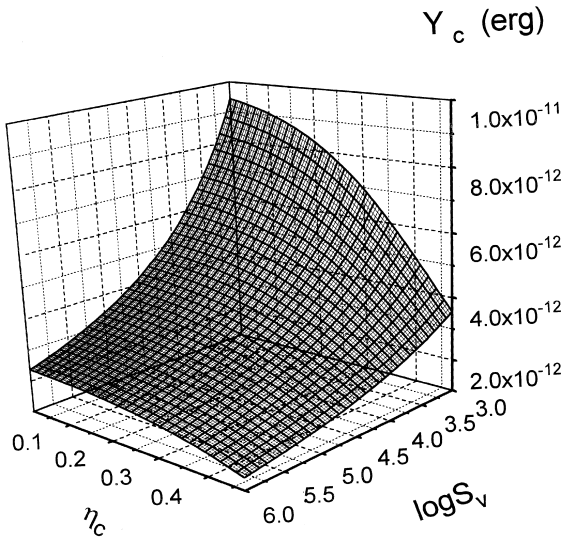


Fig. 6. The dependence of  $Y_c$  on the packing density and vacancy supersaturation ( $T = 800$  K,  $\gamma = 1500$  erg/cm<sup>2</sup>,  $c_{v\infty}/C_{eq,v}^0 = c_{x\infty}/C_{eq,x}^0 = 10^4$ ,  $D_i c_{i\infty}/D_v c_{v\infty} = 0.3$ ).

used to obtain the steady state solution of Eq. (2) [6,7]. In the one component system the analytical solution of the steady-state nucleation problem can be easily obtained because this function coincides with that ( $\tilde{f} = f_0(x)$ ) resulting in the detailed balance of the nuclei along the size axis and causing zero nuclei current in any point of this axis [16].

In a two component system the distribution function  $f_0(x, n)$  of the detailed balance has to be obtained from the following two equations:

$$A_z f_0 - \partial(B_z f_0)/\partial z = 0, \quad z = x, n. \quad (39)$$

This system has a solution only when the ‘potential conditions’ are valid [6,7]:

$$\frac{\partial}{\partial x} \left( \frac{A_n - \partial B_n / \partial n}{B_n} \right) = \frac{\partial}{\partial n} \left( \frac{A_x - \partial B_x / \partial x}{B_x} \right). \quad (40)$$

In the reaction controlled case, when  $(\lambda_\alpha^2/RI) \gg \xi \exp(-\varepsilon_\alpha/T)$ , using Eqs. (23)–(26) we obtain:

$$\frac{\partial}{\partial x} \left( \frac{\partial B_n / \partial n}{B_n} \right) = \frac{\partial}{\partial n} \left( \frac{\partial B_x / \partial x}{B_x} \right) = \frac{\partial^2 Y(x, n)}{\partial x \partial n}, \quad (41)$$

$$\frac{\partial}{\partial x} \left( \frac{A_n^{(r)}}{B_n} \right) = \frac{1 - D_i c_{i\infty}/D_v c_{v\infty}}{1 + D_i c_{i\infty}/D_v c_{v\infty}} \times \frac{\partial}{\partial n} \left( \frac{A_x^{(r)}}{B_x} \right). \quad (42)$$

Comparing Eqs. (41), (42) and (40) one can see that the potential conditions are valid in the reaction controlled case only for more strong restriction than Eq. (16), namely small effective interstitial supersaturations

$$D_i c_{i\infty}/D_v c_{v\infty} \ll 1.$$

A solution of the steady-state nucleation problem in this case can be obtained by using the distribution function  $f_0^{(r)}(x, n)$  of the detailed balance ( $J_z(f_0^{(r)}) = 0$ ):

$$f_0^{(r)}(x, n) \propto \exp[-Y(x, n)/T]. \quad (43)$$

But taking into account Eq. (20) one can see that even in this case the function  $Y(x, n)$  coincides with the thermodynamical minimum work of the gas bubble creation only when the interstitial supersaturations vanishes ( $c_{i\infty} = 0$ ) (see also Refs. [2,3]).

Potential conditions (40) are not valid when the effective concentrations of the interstitials are high as well as in the diffusion controlled case, when  $(\lambda_\alpha^2/RI) \ll \xi \exp(-\varepsilon_\alpha/T)$ . In these cases it is not possible to define the distribution function  $f_0^{(d)}(x, n)$  which maintains the detailed balance. To obtain the distribution function resulting in zero total current of the bubble into the growth region in the diffusion controlled case one has to solve steady-state Eq. (2) with the general form (14) and (15) of the kinetic coefficients and boundary conditions corresponding to zero total current of bubbles into the growth region. This more general problem will be investigated elsewhere.

## 6.2. Steady-state nucleation rate

In the present paper we investigate the problem of the gas bubble nucleation for the simplest case i.e. the reaction controlled one with small effective interstitial supersaturations

$$(\lambda_\alpha^2/RI) \ll \xi \exp(-\varepsilon_\alpha/T),$$

$$D_i c_{i\infty}/D_v c_{v\infty} \ll 1 \quad (44)$$

In this case we can build the function  $f_0^{(r)}(x, n) = (N/R^2) \exp[-Y(x, n)/T]$  (where  $N$  is a normalization constant) which maintains the detailed balance and reduce the equations for the bubble currents in the dimension space to the following:

$$J_z/B_z f_0^{(r)} = -\partial(f/f_0^{(r)})/\partial z; z = x, n. \quad (45)$$

For a sharp saddle shape of the potential surface of the gas bubbles growth rate  $\vec{A} = (A_x, A_n)$  a fraction of the bubbles penetrating into the growth region far from the critical size region is negligible.

Moreover, we assume below that the nuclei penetrate into the growth region of the dimension space along the ‘ravine’ of the surface  $Y(x, n)$  [17]. Replacing in the vicinity of the saddle point  $(x_c, n_c)$  the variables  $(x, n)$  by  $(n = y, x = \kappa y)$ , where  $\kappa$  is the angle coefficient of projection of the ‘ravine’ of the surface  $Y(x, n)$  on to the  $(x, n)$ -plane, we reduce Eq. (45) to the single equation

$$\frac{\partial(f/f_0^{(r)})}{\partial y} = -\frac{B_n \kappa^2 + B_x J_n^{(r)}}{B_n B_x} \frac{J_n^{(r)}}{f_0^{(r)}}. \quad (46)$$

Solving Eq. (46) with boundary conditions  $(f/f_0^{(r)}) \rightarrow 0$  at  $y \rightarrow \infty$  and  $(f/f_0^{(r)}) \rightarrow 1$  at  $y \rightarrow 0$  we obtain the total steady state bubble current into the growth region (the nucleation rate)  $J$  in the following form:

$$\begin{aligned} J^{(r)} &= \sqrt{\left(J_n^{(r)}\right)^2 + \left(J_x^{(r)}\right)^2} \\ &= N \sqrt{\frac{\sigma}{\pi T} (1 + \kappa^2) \times \frac{\beta_n}{1 + \kappa^2 (\beta_n / \beta_x)} \times \exp(-Y_c/T)}. \end{aligned} \quad (47)$$

Here  $\sigma = |d^2 Y / 2 dy^2|$ ;  $\beta_x = (D_x c_{x\infty} / \lambda_x^2) \exp(-\varepsilon_x / T)$ ,  $\beta_v = (D_v c_{v\infty} / \lambda_v^2) (1 - D_i c_{i\infty} / D_v c_{v\infty}) \exp(-\varepsilon_v / T)$  and  $\eta_c \rightarrow 0 \Rightarrow \kappa \rightarrow 0$ ,  $\eta_c \rightarrow 0.47 \Rightarrow \kappa \rightarrow \omega \eta_c / [\omega_0 (1 - \omega_x \eta_c / \omega_0)]$ .

We can see that the value  $Y_c = Y(x_c, n_c)$  can be treated in this case as a nucleation barrier governing the nucleation kinetics of the gas bubbles.

### 6.3. Temperature dependence of the nucleation rate

Neglecting the preexponential term in Eq. (47) the temperature dependence of the nucleation rate is defined by

$$J \propto \exp[-(\Phi_{sm} + Y_c)/T], \quad (\beta_n / \beta_x) \ll 1 \quad (48)$$

It can be easily obtained from Eqs. (38) and (48) that the temperature dependence of the nucleation rate of the voids ( $p = 0, c_{i\infty} = 0$ ) has a maximum at the temperature [18]

$$T^* = T_0(1 + \tau), \quad (49)$$

here  $T_0$  is the temperature of the minimum of function  $[Y_c(p=0)]/T$  describing the nucleation of vacancy voids:

$$T_0 \simeq \Psi_v / 3 \left| \ln \left[ c_{v\infty} \left( 1 - \frac{D_i c_{i\infty}}{D_v c_{v\infty}} \right) \right] \right| \quad (50)$$

and

$$\tau = \left[ 2 + \frac{18\pi\gamma^3 \omega^2}{\Phi_{sm} \Psi_v^2} \right]^{-1}. \quad (51)$$

Gas atoms dissolved in the matrix result in an additional, temperature dependent term  $p_c \omega$  in the nucleation barrier  $Y_c(T)$ . That results in both the sharp increase of the gas bubble nucleation rate and the change of its temperature dependence in comparison to

those for the vacancy voids. Using Eqs. (35)–(38) we obtain the temperature  $T_0^x$  of the minimum of  $Y_c/T$  for gas bubbles:

$$\begin{aligned} T_0^x &= T_0 \left[ 1 - 2 \frac{\omega}{\omega_0} \eta_c(T_0^x) \frac{\Psi_x - (\omega_x/\omega) \Psi_v}{\Psi_v} \right] \\ &\times \left[ 1 - 2 \frac{\omega}{\omega_0} \eta_c(T_0^x) \left| \ln^{-1} \left[ c_{v\infty} \left( 1 - \frac{D_i c_{i\infty}}{D_v c_{v\infty}} \right) \right] \right| \right] \\ &\times \left[ \frac{1 - 2\eta_c^2(T_0^x)}{(1 - 2\eta_c(T_0^x))^2} \right]^{-1}. \end{aligned} \quad (52)$$

Taking into account that usually  $\Psi_x \gg \Psi_v$  (e.g. for helium atoms) and, in any case,  $\eta_c(T_0^x) > 0$ , we conclude that an increase of the packing density of the gas atoms in the bubble shifts the temperature maximum of the nucleation rate to low temperatures at the value:

$$\begin{aligned} \Delta T &= 2T_0 \frac{\omega}{\omega_0} \eta_c \left[ \frac{\Psi_x - (\omega_x/\omega) \Psi_v}{\Psi_v} - \frac{1 - 2\eta_c^2}{1 - \eta_c^2} \right. \\ &\times \left. \left| \ln^{-1} \left[ c_{v\infty} \left( 1 - \frac{D_i c_{i\infty}}{D_v c_{v\infty}} \right) \right] \right| \right] \quad (53) \end{aligned}$$

It was obtained in Ref. [1] that at the initial stage a position of the temperature of the maximum of radiation swelling moves down to the low temperatures when the helium concentration increases in the matrix (Fig. 8a of Ref. [1]). Assuming that at this stage the swelling increase results from the void density increase (see Fig. 3 of Ref. [1]) one achieves a qualitative agreement with our results concerning the shift of the maximum of the temperature dependence of the nucleation rate to low temperatures when the helium concentration increases.

## 7. Conclusions

1. Using no detailed balance assumptions, the general form of the kinetic coefficients of the Fokker–Planck equation describing gas bubble nucleation in three component supersaturated solution of vacancies, interstitials and gas atoms are obtained.
2. Based on the analysis of these coefficients we investigate conditions of both: (a) the reduction of the 3-component nucleation problem to the 2-component one for the gas bubble nucleation ( $D_i c_{i\infty} / D_v c_{v\infty} < 1$ ), and (b) the applicability of the distribution function, which maintains the detailed balance of the bubbles in the dimension space, to the calculation the nucleation rate of the bubbles (reaction controlled case  $(\lambda_x^2 / Rl) \gg \xi \exp(-\varepsilon_x / T)$  and small interstitial concentration  $D_i c_{i\infty} / D_v c_{v\infty} \ll 1$ ).
3. The ‘hard sphere’ model is used to describe the gas state in the bubbles. It is shown that the high packing density ( $\eta_c \sim 0.3\text{--}0.4$ ) of the gas atoms can be formed



in the nucleating bubbles. High gas density in the critical bubble decreases the barrier for the gas bubble nucleation in comparison to that for the vacancy voids.

4. An increase of the gas density in the critical bubble results in a shift of the position of the temperature maximum of the gas bubble nucleation rate to the lower temperatures.

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