Void nucleation at elevated temperatures under cascade-damage irradiation

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The effects on void nucleation of fluctuations respectively due to the randomness of point-defect migratory jumps, the random generation of free point defects in discrete packages, and the fluctuating rate of vacancy emission from voids are considered. It was found that effects of the cascade-induced fluctuations are significant only at sufficiently high total sink strength. At lower sink strengths and elevated temperatures, the fluctuation in the rate of vacancy emission is the dominant factor. Application of the present theory to the void nucleation in annealed pure copper neutron-irradiated at elevated temperatures with doses of 10^{-4}–10^{-2} NRT dpa showed reasonable agreement between theory and experiment. This application also predicts correctly the temporal development of large-scale spatial heterogeneous microstructure during the void nucleation stage. Comparison between calculated and experimental void nucleation rates in neutron-irradiated molybdenum at temperatures where vacancy emission from voids is negligible showed reasonable agreement as well. It was clearly demonstrated that the athermal shrinkage of relatively large voids experimentally observable in molybdenum at such temperatures may be easily explained in the framework of the present theory.

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I. INTRODUCTION

The conventional approach to modeling void nucleation under irradiation is based on the classical description of the formation of small precipitates in a supersaturated solution. In this approach, small thermally unstable new-phase embryos are continuously formed and redissolved in the supersaturated solution, and can grow beyond the critical size via stochastic fluctuations.[1–7] Beyond the critical size, nuclei of the new phase become thermally stable, and on average can grow directly from the supersaturated solution, without the help of the stochastic fluctuations.

In most studies of void nucleation only statistical fluctuations produced by random point-defect jumps are taken into account, and the dislocation bias is the only driving force for the evolution of the damage microstructure.[4,5] Under cascade damage irradiation, however, point defects are produced in the form of small mobile or immobile vacancy and interstitial clusters.[8–12] Recognition of this fact has led to the introduction of production bias[13,14] as an alternative driving force for the microstructure evolution at elevated temperatures. An additional effect of cascade damage is the fluctuations in the point-defect fluxes received by the void embryos, caused by the random (in time and space) production of point defects in packets during cascade irradiation.[15,16] It has been shown that the effects of the two types of fluctuations are additive, and the relative importance of the cascade-induced fluctuations increases with the increase of the total sink strength and the sink absorption radius. In the nucleation of interstitial loops from immobile clusters, cascade-induced fluctuations have been found to have a dominating effect, and their inclusion in the theory is crucial in explaining the observed loop densities.[16] In this regard, the role of such fluctuations in void nucleation remains to be investigated.

In another aspect, the contribution of vacancy emission to the stochastic variations of the void size is conventionally treated in a way similar to the contribution to the *average* void growth rate, i.e., it is assumed to be proportional to the void radius.[1,3–5,7] However, it is physically obvious that the emission itself should be proportional to the void surface area. The issue of the correct treatment of fluctuations due to vacancy emission had been discussed in Ref. 17, and corresponding statistical characteristics of the fluctuations in the rate of emission from the new-phase embryo had been obtained in Ref. 18, but have not been applied to void nucleation theories. The effect of these fluctuations on the rate of void nucleation under irradiation is also included in the present investigation. The role of gas pressure in the evolution of a void embryo is beyond our present scope.

II. FORMULATION OF THE KINETIC EQUATION

As a void embryo, we consider a small immobile three-dimensional (i.e., uncollapsed) vacancy cluster. Within the mean-field theory and a spherical approximation for the voids, the number n_V of vacancies in the voids is governed by the following conventional equation:

$$\frac{dn_V}{dt}=\frac{3n_V^{1/3}}{a^2}[D_\nu C_\nu-D_iC_i-D_\nu C_s^e(n_V)], \tag{1}$$

where D_j and C_j ($j=i,\nu$) are the diffusion coefficient and the concentration of point defects, respectively, $a=(3\Omega/4\pi)^{1/3}$, and Ω is the atomic volume. The mean equilibrium concentration $C_s^e(n_V)$ of vacancies in the neighborhood of a void of radius $R_c(n_V)=an_V^{1/3}$ can be written as

$$C_s^e(n_V)=C_\infty\exp\left(\frac{2\gamma_s\Omega}{kTR_c}\right)\approx C_\infty\left(1+\frac{2\gamma_s\Omega}{kTR_c}\right). \tag{2}$$

Here C_∞ is the equilibrium vacancy concentration, γ_s is the surface tension coefficient, k is the Boltzmann constant, and T is the absolute temperature. We note that the approximation in Eq. (2) is only valid for sufficiently large void sizes.

From Eqs. (1) and (2), a void will grow when it receives a net vacancy flux ($D_\nu C_\nu>D_iC_i$), if it exceeds the critical size, with the critical radius R_{cr} given by

$$R_{cr}=\frac{\beta}{\ln[1+(D_\nu C_\nu-D_iC_i-D_\nu C_\infty)/D_\nu C_\infty]}\approx\frac{\beta D_\nu C_\infty}{D_\nu C_\nu-D_iC_i-D_\nu C_\infty}, \tag{3}$$

where $\beta=2\gamma_s\Omega/kT$.

In this regard, small void embryos with a subcritical size are thermally unstable and will immediately start shrinking upon creation. To consider the growth of an individual void embryo, one has to go beyond the mean-field theory and consider the effects of stochastic fluctuations in the point-defect fluxes.

The general kinetic equation for the microstructure evolution under cascade-damage irradiation, including the full statistical effects, has been derived in Ref. 16. Adopting the simplest approximation, which still keeps the effect of fluctuations, this equation takes the form of the Fokker-Planck equation:[16]

$$\frac{\partial P_V(n,t|n_0,t_0)}{\partial t}=-\frac{\partial}{\partial n}\left\{V(n)-\frac{\partial}{\partial n}D(n)\right\}P_V, \tag{4}$$

where $P_V(n,t|n_0,t_0)$ is the probability density that a void with an initial size of n_0 vacancies at time t_0 will have a size of n vacancies at a later time t, and $V(n)$ is the drift velocity equal to the right-hand side of Eq. (1). By definition of P_V, the initial condition of Eq. (4) may be written as

$$P_V(n,0|n_0,t_0)=\delta(n-n_0). \tag{5}$$

The diffusivity in Eq. (4) governs the "diffusive spread" of P_V due to stochastic fluctuations in the point-defect fluxes received by the void, including vacancy emission from the void. It depends on the average point-defect fluxes and the cascade properties, with expressions derived previously:[15,16,18]

$$D(n)=D^s(n)+D^c(n)+D^e(n), \tag{6}$$

where

$$D^s(n)=\frac{3n^{1/3}}{2a^2}\{D_\nu[C_\nu-C_s^e(n)]+D_iC_i\}, \tag{7}$$

$$D^c(n)=\frac{3n^{2/3}}{4a}\left[\frac{G_\nu\langle N_{d\nu}^2\rangle}{k_\nu N_{d\nu}}+\frac{G_i\langle N_{di}^2\rangle}{k_iN_{di}}\right], \tag{8}$$

$$D^e(n)=\frac{9D_\nu C_s^e(n)n^{2/3}}{2a^2}. \tag{9}$$

where G_j is the effective generation rate of free point defects, N_{dj} and $\langle N_{dj}^2\rangle$ are the average number and the average square number of free point defects generated in a single cascade, respectively, and k_j^2 is the total sink strength for point defects of the type j. In Eqs. (7) to (9), the superscripts s, c, and e refer to the stochastic fluctuations due to the random migratory jumps, random cascade initiation, and random vacancy emission, respectively. Note also that D^e is proportional to the void surface area,[17,18] instead of to the void radius, as usually assumed in most other studies. The dependence of D^e on the void size was discussed in detail in Ref. 17.

Since small clusters consisting of two or three vacancies are mobile,[19,20] a void embryo shrinking below the minimum size $n_{\nu0}$ is not a void anymore. To reflect this situation, we write down the left boundary condition for the kinetic equation (4) in the form

$$P_V(n=n_{\nu0},t|n_0,t_0)=0. \tag{10}$$

Assuming that the probability for a sufficiently large supercritical void to become subcritical is negligible, the right boundary condition can be written as[1,3,6]

$$P_V(n=n_m\gg n_{cr},t|n_0,t_0)=0. \tag{11}$$

With this boundary condition, the probability $P_m(t)$ for a subcritical void to become supercritical during the time period (t_0,t) can be calculated from the integral:

$$P_m(t)=-\left[\frac{\partial}{\partial n}\int_{t_0}^{t}D(n)P_V(n,t|n_0,t_0)dt\right]_{n=n_m}. \tag{12}$$

From the Fokker-Planck equation (4), the initial condition (5) and the boundary conditions (10) and (11), we can also write the following conservation law:

$$P_0(t\to\infty)+P_m(t\to\infty)=1, \tag{13}$$

where $P_0(t)$ is the probability for the void nucleus to shrink below the minimum size $n_{\nu0}$, i.e.,

$$P_0(t)=\left[\frac{\partial}{\partial n}\int_{t_0}^{t}D(n)P_V(n,t|n_0,t_0)dt\right]_{n=n_{\nu0}}. \tag{14}$$

Equation (13) has a simple physical meaning: a small void nucleus either shrinks away or becomes supercritical and grows during its evolution.

The probability $P_m\equiv P_m(t\to\infty)$ for a void embryo to eventually attain a supercritical size is given by

$$P_m=\int_{n_{\nu0}}^{n_0}\frac{dn'}{D(n')\varphi(n')}\Bigg/\int_{n_{\nu0}}^{n_m}\frac{dn'}{D(n')\varphi(n')}. \tag{15}$$

Here $\varphi(n)$ is the stationary solution of Eq. (4) with zero flux in the space of void sizes (see the Appendix for the derivation).

If the void growth rate does not depend on the vacancy emission from voids, Eq. (15) reduces to

$$P_m(n_0)=\int_{n_{\nu0}}^{n_0}f(n)dn\Bigg/\int_{n_{\nu0}}^{\infty}f(n)dn, \tag{16}$$

where

$$f(n)=\exp\left\{-\frac{3\alpha_s^2}{2\alpha_c^3}\left(\frac{\alpha_c}{\alpha_s}n^{1/3}-1\right)^2 -\frac{3\alpha_s^2}{\alpha_c^3}\ln\left(\frac{\alpha_c}{\alpha_s}n^{1/3}+1\right)\right\}, \quad (17)$$

$$\alpha_s=\frac{D_\nu C_\nu+D_iC_i}{2(D_\nu C_\nu-D_iC_i)}, \quad (18)$$

$$\alpha_c=\frac{a}{4(D_\nu C_\nu-D_iC_i)}\left[\frac{G_\nu\langle N_{d\nu}^2\rangle}{k_\nu N_{d\nu}}+\frac{G_i\langle N_{di}^2\rangle}{k_iN_{di}}\right]. \quad (19)$$

Here α_s represents effects coming from the random point-defect jumps, and α_c, from the random cascade initiation.

In the limit $\alpha_c\rightarrow 0$, $P_m(n_0)$ in Eq. (16) is approximated by

$$P_m(n_0)=1-\exp[-(n_0-n_{\nu 0})/\alpha_s]. \quad (20)$$

In the other limit $\alpha_s\rightarrow 0$,

$$P_m(n_0)=1-\frac{(3/2\alpha_c)^{1/2}n_0^{1/3}\exp(-3n_0^{2/3}/2\alpha_c)+\sqrt{\pi}Q(\sqrt{3/\alpha_c}n_0^{1/3})}{(3/2\alpha_c)^{1/2}n_{\nu 0}^{1/3}\exp(-3n_{\nu 0}^{2/3}/2\alpha_c)+\sqrt{\pi}Q(\sqrt{3/\alpha_c}n_{\nu 0}^{1/3})}, \quad (21)$$

where

$$Q(x)=\frac{1}{\sqrt{2\pi}}\int_x^\infty \exp(-x^2/2)dx. \quad (22)$$

According to Eqs. (16), (20), and (21), even when void embryos are growing on the average, independent of their sizes, not all them will survive during the further evolution. Physical implications of this result will be considered in Sec. III.

When the vacancy emission from voids is not negligible, expression (15) for the probability of void nucleation can be calculated approximately as [see Eq. (A14) in the Appendix]

$$P_m\cong\sqrt{\frac{\beta}{2\pi a^3 n_{\rm cr}}\frac{(D_\nu C_\nu-D_iC_i)}{D(n_{\rm cr})}} \times\exp\left[\int_{n_0}^{n_{\rm cr}}V(n)/D(n)dn\right](n_0-n_{\nu 0}). \quad (23)$$

At this juncture, we would like to point out that D^e in Eq. (9) used in the present work is proportional to the surface area of the void, as is natural to expect in the case of emission. In most of the existing works in this area,[3–5] however, the contribution of the vacancy emission to the diffusion term $D(n)$ in the kinetic equation (4) is treated like the emission contribution to the average void growth rate, i.e., it is assumed to be proportional to the void radius instead. The consequence of the two different assumptions can be seen immediately, when the cascade-induced fluctuations is neglected for simplicity. In this case, the corresponding total diffusion coefficient becomes

$$D^s(n)+D^e_{\rm conv}(n)=\frac{3n^{1/3}}{2a^2}\{D_\nu[C_\nu+C_s^e(n)]+D_iC_i\}. \quad (24)$$

Compared to the corresponding quantity in the present work, the term proportional to $n^{2/3}$ is absent.

Referring to Eq. (23) and recalling that $V(n)$ is negative at $n<n_{\rm cr}$, it is clear that the fluctuations in the vacancy emission rate results in the higher void nucleation probability compared to that given by the conventional approach, unless

$$\frac{D^e(n_{\rm cr})}{(3n_{\rm cr}^{1/3}/2a^2)\{D_\nu[C_\nu+C_s^e(n_{\rm cr})]+D_iC_i\}}<1. \quad (25)$$

By the definition of critical void size, the right-hand side of inequality (25) is equal to $3(n_{\rm cr})^{1/3}(D_\nu C_\nu-D_iC_i)/2D_\nu C_\nu$. Furthermore, if ϵ_i is the fraction of interstitials produced in cascades in the form of immobile clusters, then, assuming that production bias is the main driving force for void growth at elevated temperatures,[13] the ratio $(D_\nu C_\nu-D_iC_i)/D_\nu C_\nu$ can be estimated as ϵ_i, and the last inequality is only satisfied when $n_{\rm cr}^{1/3}<2/(3\epsilon_i)$. Thus, the conventional theory always underpredicts the survival probability of the void nucleus, down to a critical void size as small as $n_{\rm cr}\approx 20$ [$\epsilon_i\cong 0.25$ to 0.4 (Ref. 12)].

Another point to note is that when void growth is driven by the dislocation bias, as in most existing calculations, the corresponding critical void size $n_{\rm cr}^{1/3}$ should be smaller than $2Z/[3(Z-1)]$, where Z is the dislocation bias for interstitials. Compared to the case of void swelling driven by production bias, the conventional theory of void nucleation based on dislocation bias would significantly underestimate the nucleation rate at significantly larger void critical sizes.

A. The case of large critical size

In the case of sufficiently large critical void size, we may use the approximation in Eq. (2) for the equilibrium concentration of vacancies in the neighborhood of the void. Then, the integral in Eq. (23) can be evaluated analytically to give

$$P_m \cong \sqrt{\frac{\beta}{6\pi R_{\rm cr} n_{\rm cr}} \frac{(D_v C_v - D_i C_i)}{D_i C_i (1 + d n_{\rm cr}^{1/3})}} (n_0 - n_{v0}) \times \exp\left\{ -3\frac{\nu}{d}\left[\frac{(n_{\rm cr}^{2/3} + n_0^{2/3})}{2} - n_{\rm cr}^{1/3} n_0^{1/3} + \frac{n_{\rm cr}^{1/3} - n_0^{1/3}}{d} - \frac{1 + d n_{\rm cr}^{1/3}}{d^2} \ln\left(\frac{1 + d n_{\rm cr}^{1/3}}{1 + d n_0^{1/3}} \right) \right] \right\}, \quad (26)$$

where

$$\nu = \frac{3 n_{\rm cr}^{1/3} (D_v C_v - D_i C_i)[1 - \exp(-\beta/R_{\rm cr})]}{a^2 D^s(n_{\rm cr})} = \frac{(D_v C_v - D_i C_i)[1 - \exp(-\beta/R_{\rm cr})]}{D_i C_i} \quad (27)$$

and

$$d = d^c + d^e, \quad (28)$$

with

$$d^c = \frac{D^c(n_{\rm cr})}{n_{\rm cr}^{1/3} D^s(n_{\rm cr})} = \frac{a G_i}{4 D_i C_i} \left[\frac{G_v \langle N_{dv}^2 \rangle}{G_i N_{dv} k_v} + \frac{\langle N_{di}^2 \rangle}{N_{di} k_i} \right], \quad (29)$$

$$d^e = \frac{D^e(n_{\rm cr})}{n_{\rm cr}^{1/3} D^s(n_{\rm cr})} = \frac{3 D_v C_s^e(n_{\rm cr})}{2 D_i C_i} = \frac{3(D_v C_v - D_i C_i)}{2 D_i C_i}. \quad (30)$$

It can be easily shown that in the limit $d \to 0$, Eq. (26) reduces to

$$P_m \cong \sqrt{\frac{\beta}{6\pi R_{\rm cr} n_{\rm cr}} \frac{(D_v C_v - D_i C_i)}{D_i C_i}} (n_0 - n_{v0}) \times \exp\left\{ -\frac{\nu n_{\rm cr}}{2} \left[1 - 3\left(\frac{n_0}{n_{\rm cr}} \right)^{2/3} + \frac{2 n_0}{n_{\rm cr}} \right] \right\}. \quad (31)$$

Similar to Eq. (25), the ratio $(D_v C_v - D_i C_i)/D_i C_i$ can be estimated as $\epsilon_i/(1-\epsilon_i) = 1/3$ to 2/3. Therefore, the value of the parameter d^e is on the order of 0.5 to 1. In Fig. 1, the probability P_m according to Eq. (26) is plotted as a function of critical void size for different values of the ratio d and parameter ν. Note that for a relatively low total sink strength ($k_j^2 < 10^{15}\ \mathrm{m}^{-2}$), d^c can be neglected ($d^c < 1.5 \times 10^{-1}$, $N_{dj} \cong 50$), and in this case the value of d is dominated by the vacancy emission term d^e.

The foregoing results can be used to further compare the conventional treatment of fluctuations in vacancy emission with the present one. There is no term proportional to $n^{2/3}$ in the diffusion coefficient Eq. (24). This is equivalent to setting the value of d in Eq. (26) to zero, yielding an expression for P_m having the same form as Eq. (31), but with

$$\nu = \frac{(D_v C_v - D_i C_i)[1 - \exp(-\beta/R_{\rm cr})]}{D_v C_v}. \quad (32)$$

Taking into account that at elevated temperatures $D_i C_i / D_v C_v \cong 1 - \epsilon_i \cong 0.6$ in the evaluation of the parameter ν in Fig. 1, and comparing the curves for $d=0$ with those for $d \neq 0$, it can be seen that the conventional treatment of vacancy emission contribution to the diffusion coefficient $D(n)$ underestimates the survival probability of the void embryo by several orders of magnitude.

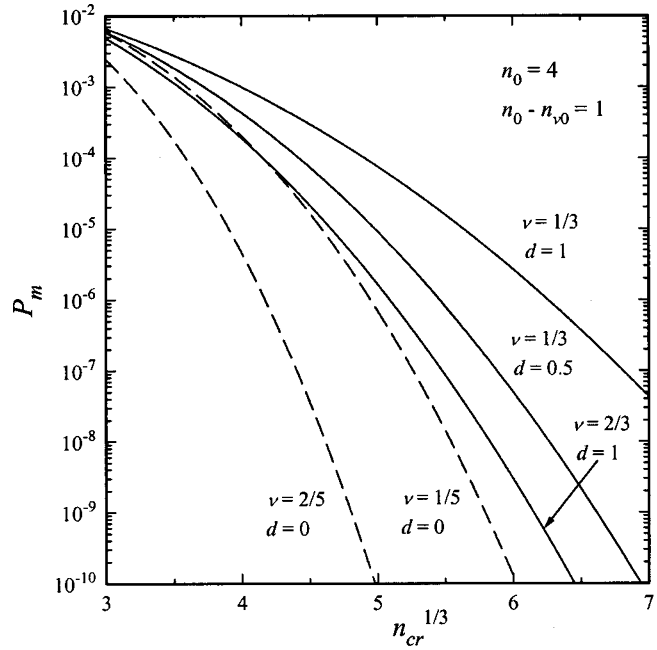

FIG. 1. Probability for small void nucleus to become supercritical calculated with Eq. (26) as a function of void critical size at different values of parameters ν and d. Dashed lines correspond to the probability given by Eq. (31).

B. The case of small critical size

Under irradiation, the vacancy concentration is usually much higher than the corresponding equilibrium value, i.e., the condition $\beta/R_{\rm cr} < 1$ is not fulfilled, and the approximate expression for the equilibrium concentration $C_s^e(n)$ in Eq. (2) is no longer valid. However, recognizing the dominant role of vacancy emission from the void embryos during void nucleation, instead of using the series expansion of the exponential function in Eq. (2), we may alternatively approximate the integral in Eq. (23) according to

$$\int_{n_0}^{n_{\rm cr}} V(n)/D(n)\,dn = \frac{3}{a^2} \int_{n_0}^{n_{\rm cr}} \frac{n^{1/3} D_v (C_s^e(R_{\rm cr}) - C_s^e(n))\,dn}{D^e(n)[1 + D^s(n)/D^e(n) + D^s(n)/D^e(n)]} \cong \frac{2}{3[1 + 1/(d^e n_{\rm cr}^{1/3}) + d^c/d^e]} \times \int_{n_0}^{n_{\rm cr}} n^{-1/3} \{\exp[\beta/R_{\rm cr} - \beta/R(n)] - 1\}\,dn. \quad (33)$$

The last integral in Eq. (33) can be expressed in terms of the exponential integral function $E_1(x)$:

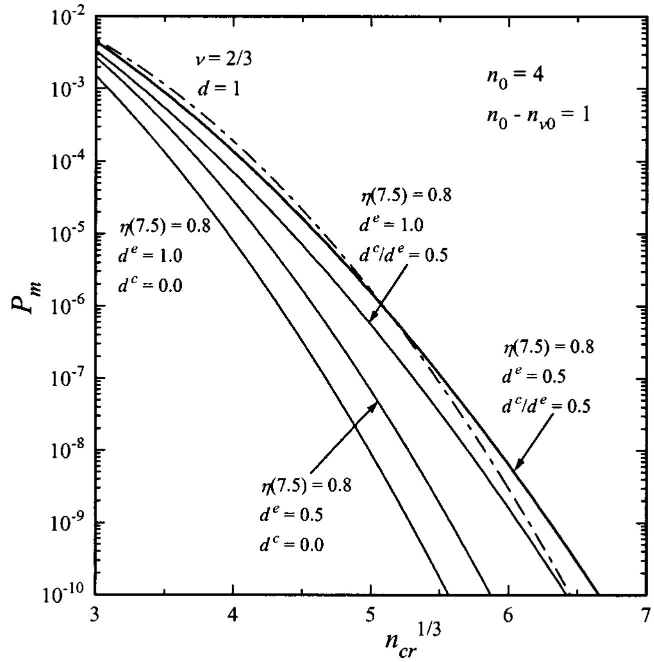

FIG. 2. The same as Fig. 1, but the probability P_m calculated with expression (37). The probability P_m calculated according to Eq. (26) is also shown (dashed line) for comparison.

$$\frac{2}{3}\int_{n_0}^{n_{\rm cr}} n^{-1/3}\{\exp[\beta/R_{\rm cr}-\beta/R(n)]-1\}dn$$

$$=-\eta(\beta/R_{\rm cr})n_{\rm cr}^{2/3}+n_0^{2/3}\{1-\exp[\beta/R_{\rm cr}-\beta/R_0]\}$$

$$+\eta(\beta/R_0)n_0^{2/3}\exp[\beta/R_{\rm cr}-\beta/R_0], \tag{34}$$

where

$$\eta(x)=x[1-x\exp(x)E_1(x)], \tag{35}$$

$$E_1(x)=\int_x^\infty \frac{\exp(-t)}{t}dt. \tag{36}$$

Noting that $\eta(x)<1$ $[x>1$ (Ref. 21)] and $\beta/R_0 \gg 1$, the probability P_m can be written as

$$P_m \cong \sqrt{\frac{\beta}{6\pi R_{\rm cr}n_{\rm cr}}\frac{(D_\nu C_\nu - D_i C_i)}{D_i C_i(1+dn_{\rm cr}^{1/3})}}(n_0-n_{\nu 0})$$

$$\times\exp\left[-\frac{\eta(\beta/R_{\rm cr})n_{\rm cr}^{2/3}-n_0^{2/3}}{1+1/(d^e n_{\rm cr}^{1/3})+d^c/d^e}\right]. \tag{37}$$

When $x>1$, the approximate expression for the function $\eta(x)$ can be presented in the form[21]

$$\eta(x)\cong\frac{(b_1-a_1)+(b_2-a_2)/x}{1+b_1/x+b_2/x^2}. \tag{38}$$

Here a_i and b_i ($i=1,2$) are some positive constants, such that $b_1-a_1\approx 1$. Within the interval $x\in[2,10]$, the function $\eta(x)$ takes on values between 0.55 and 0.84. A plot of P_m calculated using Eq. (37) is shown in Fig. 2. Compared with Fig. 1, the values can be seen to be significantly smaller than that obtained from Eq. (26). This is because, when $\beta/R>1$, the average rate of vacancy emission from voids is significantly underestimated by the approximate expression for the equilibrium concentration $C_s^e(R)$. As a result, the void survival probability is substantially overestimated. Note also that when the total sink strength is sufficiently high ($k^2\cong 5\times 10^{15}$ m^{-2}), the parameter d^c is no longer negligible. In this case, fluctuations in the void growth rate due to the random cascade initiation can substantially increase the survival probability of the void embryo and hence the nucleation rate (see Fig. 2). In the following section we compare the theoretical results with experimental observations.

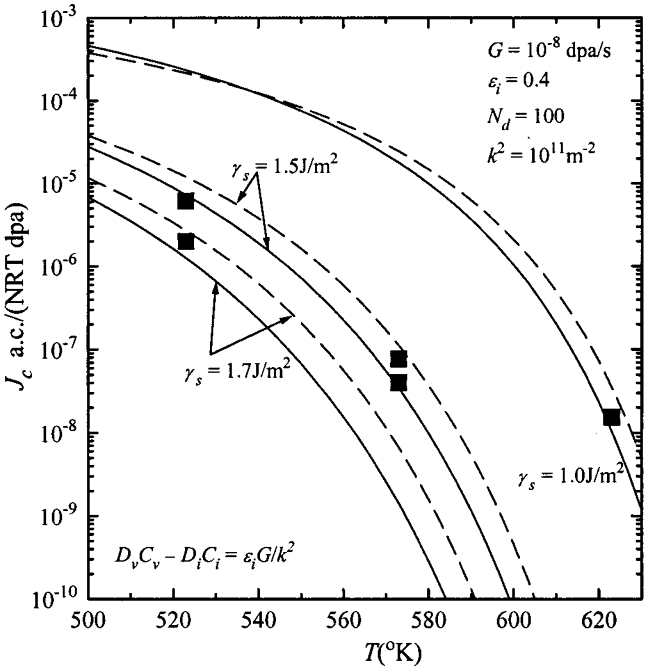

FIG. 3. Rates of void nucleation in annealed copper at different values of void surface energies. Corresponding nucleation probability P_m is calculated with expression (37). Parameter d^e is equal to 1.0 (solid lines) and 0.5 (dashed lines). Experimental points are obtained from Refs. 22–24 by dividing the experimental values of void concentration by the corresponding irradiation doses.

III. RESULTS

A small immobile three-dimensional vacancy cluster can be formed directly in a collision cascade or through the agglomeration of several single vacancies present in a solid solution. Such vacancy clusters can also appear as a result of evolution of larger vacancy loops, which are initially generated due to the cascade collapse and further shrinks under irradiation conditions because of its thermal instability or the preferential absorption of mobile interstitials. Thus, if the formation of small void nuclei through the consecutive agglomeration of single vacancies can be neglected, the rate J_c of void nucleation under cascade damage irradiation is equal to the probability P_m multiplied by the average rate of cascade production:

TABLE I. Material parameters for copper.

Parameter	Value
Atomic volume, Ω	1.0×10^{-29} m^3
Vacancy migration energy[a]	0.8 eV
Vacancy formation energy[a]	1.2 eV
Vacancy diffusivity preexponential[a]	1.0×10^{-5} m^2/s
Surface free energy γ_s[b]	1.7 J/m^2
Melting temperature, T_m	1353 K

[a]Reference 26.
[b]Reference 24.

TABLE II. Material parameters for molybdenum.

Parameter	Value
Atomic volume, Ω	1.017×10^{-29} m^3
Vacancy migration energy	1.5 eV
Vacancy formation energy	3.0 eV
Vacancy diffusivity preexponential	3.0×10^{-6} m^2/s
Surface free energy γ_s	2.05 J/m^2
Melting temperature T_m	2898 K

$$J_c \cong \frac{G}{N_d} P_m , \tag{39}$$

where G is the effective generation rate of point defects in cluster and free form, and N_d is the average total number of point defects generated in a single cascade. The last equation together with the corresponding expression for the nucleation probability will be used in our further analysis.

A. Void nucleation in copper

In Fig. 3, we compare the experimental void nucleation rates with theoretical ones calculated with Eq. (37) for annealed pure copper with low dislocation density ($\sim 10^{11}$ m^{-2}) irradiated up to doses of 10^{-4}–10^{-2} NRT dpa.[22–24] The material parameters used for copper are listed in Table I. In this case, the ratio of $\beta/R_{\rm cr}$ ranges from 11.2 to 4.1 between 523 and 623 K. It can be seen from Fig. 3 that at 523 K there is good agreement between calculated and experimental values.

As it has previously been pointed out,[23] it is difficult for the conventional theory of void growth driven by the dislocation bias to explain the experimental void swelling rates (about 1% per NRT dpa) at such low dislocation densities, and the fact that the actual damage microstructure is not spatially homogeneous, but is heterogeneous and segregated.[22–24] The void and dislocation populations are almost completely separated, i.e., dislocation-dominated volumes generally contain no voids, and the regions between these volumes contain only voids and dislocations of very low density. On the other hand, development of spatially heterogeneous microstructure has been considered in Ref. 25 within the framework of a production bias model. It has been shown that at elevated temperatures in annealed pure copper with a low dislocation density, an initially homogeneous void distribution starts to become unstable and evolve spatially heterogeneously, when the void concentration approaches some temperature dependent critical value, which is less than or about equal to the experimental concentration. As the instability develops, voids grow in some regions and shrink in others. In regions where the void shrinkage takes place, the accumulation of interstitials in clusters and loops is favored. The present calculation shows that the spatially homogeneous rate of void nucleation in pure copper is indeed sufficiently high to bring the homogeneous ensemble of voids to the point of instability already at very low irradiation doses. More detailed study of the void nucleation in the presence of large-scale spatial heterogeneity of the damage microstructure will be considered in a separate publication.

In Fig. 3, there appears to be a large discrepancy between the experimental and theoretical void nucleation rates at higher temperatures, if the surface energy used in the calculation is the same as that in the low temperature case. In this regard, we note that the experimental void size distribution is bimodal at higher temperatures, with the position of the first peak weakly dependent on irradiation dose.[24] This feature indicates the presence of solute elements that stabilize voids against shrinkage and collapse into loops or stacking-fault tetrahedra. According to Ref. 24, the presence of oxygen in the copper sample under investigation may reduce the surface tension coefficient γ_s to below 1.0 J/m^2. With the reduced surface energy, the void-nucleation probability is much increased, and a good agreement between theoretical and experimental results can be reestablished (Fig. 3).

B. Void nucleation in molybdenum

In this section, we consider the opposite example in which vacancy emission is unimportant. A typical case can be found in molybdenum (material parameters listed in Table II) at temperatures below $0.35T_m \cong 1015$ K. The calculated critical void radius in this case can be seen to be very small and is only weakly dependent on the temperature [Fig. 4(a)]. This is consistent with the experimentally observed void concentration N_c of about 10^{23} m^{-3}, which is nearly temperature independent,[27,28] and which is one to three orders of magnitude higher than that normally observed in many other pure metals and steels. Although the time-average void swelling rate of molybdenum is very low,[28] vacancy emission is not a significant factor in their evolution at sufficiently low temperatures, even for very small voids [Fig. 4(b)].

When vacancy emission from void is negligible, we can use Eq. (16) for the void survival probability. Since voids are usually the dominant sink for point defects in Mo,[27–30] the parameter α_s can be approximately written as

$$\alpha_s = \frac{k_c^2(D_\nu C_\nu + D_i C_i)}{2dS/dt} \cong \left(\frac{dS}{dGt}\right)^{-1}. \tag{40}$$

When the void swelling rate $dS/d(Kt)$ varies between 10^{-4} and 3×10^{-4} per NRT dpa ($G/K \cong 0.3$), α_s takes on values between 1×10^3 to 3×10^3. Values of $P_m(n_0)$ from Eq. (16), where $n_0 = n_{\nu 0} + 1$ is the minimum number of vacancies in the void embryo, are plotted in Fig. 5. The dashed

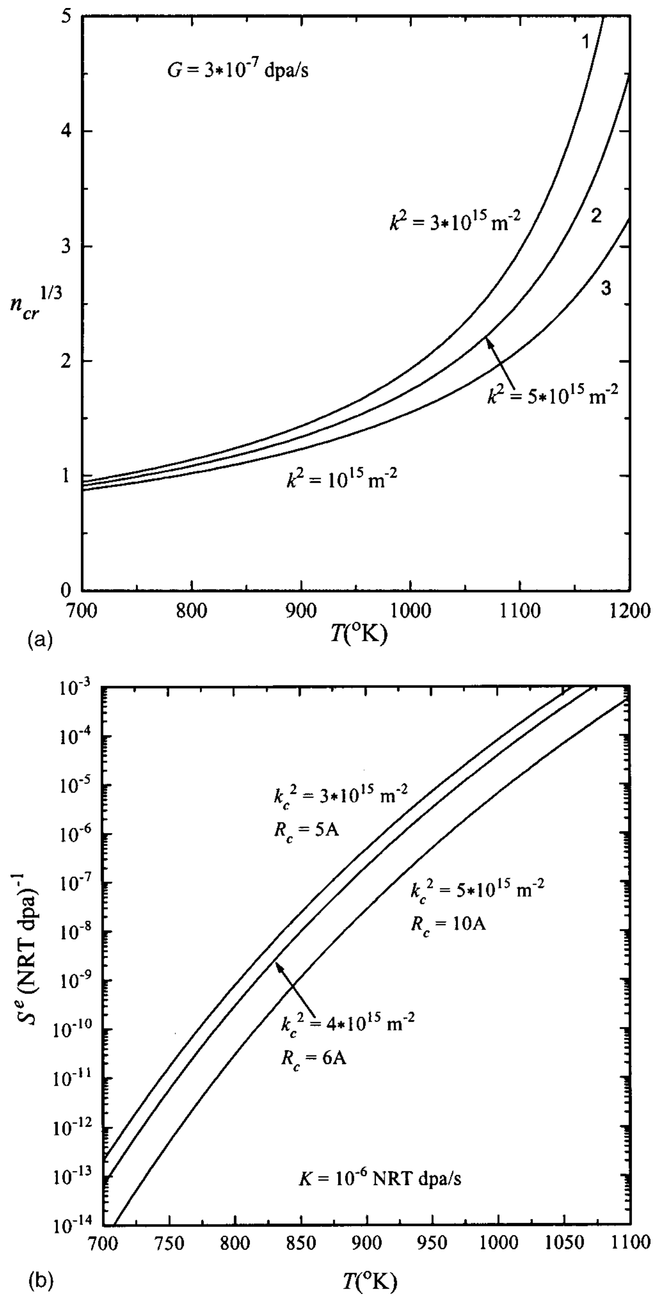

FIG. 4. (a) Void critical radius in molybdenum calculated as a function of temperature at different values of the total sink strength. Curve 1 is the critical radius when void growth is driven by the dislocation bias ($Z-1=0.07$), and curves 2 and 3 correspond to the void growth driven by the production bias ($\epsilon_i=0.4$). (b) Rate of vacancy emission from voids $[S^e=D_\nu k_c^2 C_s^e(R_c)/K]$ at different values of void average radius R_c and void sink strength k_c^2.

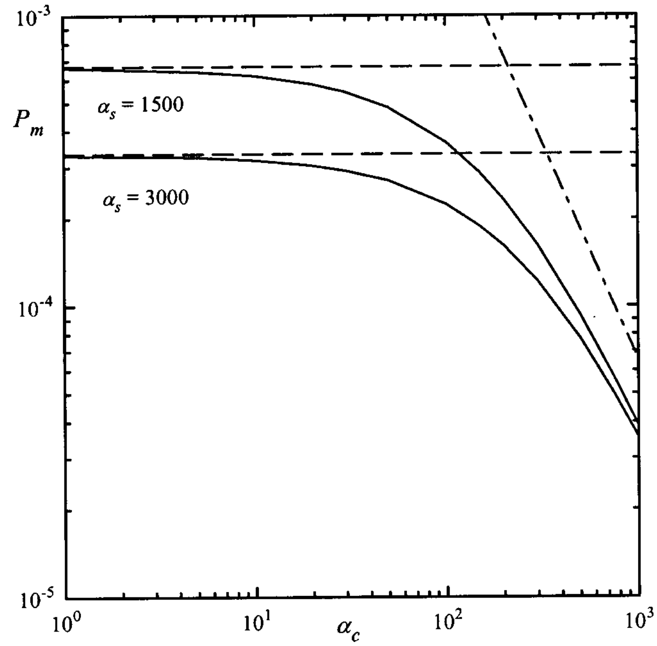

FIG. 5. Probability $P_m(n_{\nu 0}+1)$ of void nucleation in molybdenum as a function of parameter α_c at different values of parameter α_s. Dashed lines correspond to the probabilities given by Eqs. (41) (horizontal lines) and (42).

lines in the figure are the void nucleation probabilities in the two limiting cases, according to Eqs. (20) and (21), which are given, respectively, by

$$P_m(n_{\nu 0}+1)=1-\exp(-1/\alpha_s)\cong\frac{2(D_\nu C_\nu-D_iC_i)}{D_\nu C_\nu+D_iC_i}\cong\frac{dS}{dGt}, \tag{41}$$

$$P_m(n_{\nu 0}+1)=\frac{3}{\alpha_c}\left(\frac{3}{2\pi\alpha_c}\right)^{1/2}\cong\frac{3\alpha_s}{\alpha_c}\left(\frac{3}{2\pi\alpha_c}\right)^{1/2}\frac{dS}{dGt}. \tag{42}$$

Equations (41) and (42) give the same nucleation probability when

$$\frac{\alpha_c}{\alpha_s}=\frac{3}{(2\pi\alpha_s)^{1/3}}. \tag{43}$$

When the value of α_s falls in the range between 1×10^3 to 3×10^3, the above ratio is about 0.1. Since

$$\frac{\alpha_c}{\alpha_s}\cong\frac{ka}{4}\left[\frac{G_\nu\langle N_{d\nu}^2\rangle}{GN_{d\nu}}+\frac{G_i\langle N_{di}^2\rangle}{GN_{di}}\right], \tag{44}$$

this value of α_c/α_s corresponds to a value of the total sink strength $k^2\approx3\times10^{15}\ \mathrm{m}^{-2}$ ($N_{dj}\cong50$, $G_j/G\cong0.5$). When the void sink strength is much below this value, the rate of void nucleation is independent of α_c, and is determined by the average void growth rate. With the increase in the total sink strength, the nucleation rate starts to drop very fast as α_c/α_s increases, because the cascade-induced fluctuations significantly reduce the survival probability for the void embryos. As can be seen from Fig. 5, for temperatures at which vacancy emission from the voids is negligible, an irradiation dose of several NRT dpa is required to get the void density in Mo up to the order of $10^{23}\ \mathrm{m}^{-3}$. This is in agreement with the experimental observation.[28]

In this connection, the shrinkage of rather large voids with the positive average growth rate is of particular interest. While this kind of void shrinkage is not expected under the conventional theory of void swelling, it follows from our

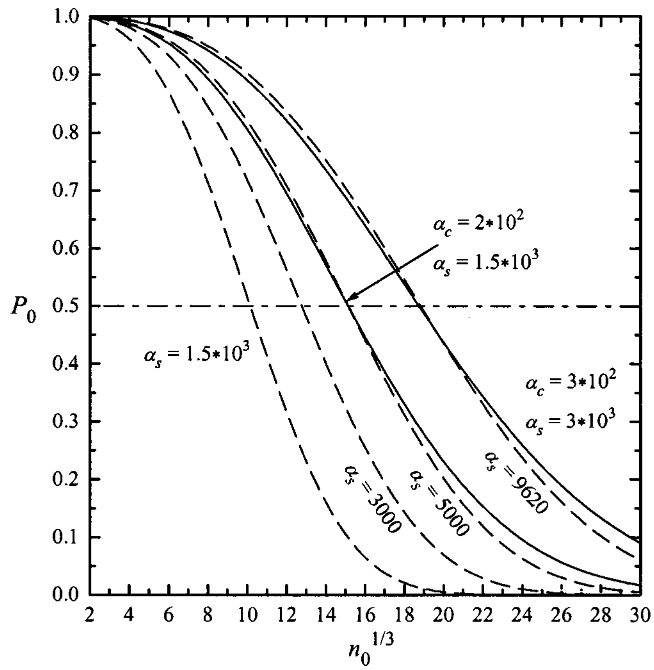

FIG. 6. Probability of void dissolution as a function of void size at different values of parameters α_s and α_c. Probability $P_0 = \exp[-(n_0 - n_{v0})/\alpha_s]$ is shown by the dashed lines.

consideration in Sec. II. The probability $P_0(n)$ for a void of the size n to completely dissolve is given by the conservation law (13) and Eq. (16). It is plotted as a function of void radius in Fig. 6, for different values of parameters α_s and α_c. It can be seen that even voids with a diameter as large as 5 nm may shrink away with a probability of more than 50%, even in the absence of vacancy emission. Thus, the thermal stability of a void, i.e., one with a positive average growth rate, is not sufficient to guarantee its survival in the course of its evolution. Only those voids for which $P_0(n)$ is substantially less than 1 will grow with time.

Note that the presence of cascade-induced fluctuations leads to a very substantial increase (several hundred %) in the probability of void shrinkage. Since the probability of shrinkage for smaller voids is substantially higher than that for the larger ones, a possible effect associated with the shrinkage may be identified as stochastic void coarsening. As shown in Ref. 31 stochastic void coarsening can also be interpreted as a nonequilibrium phase transition in the void ensemble induced purely by the stochastic fluctuations.

Experimental observation of the void coarsening effect has been reported in neutron-irradiated molybdenum at 450 °C, where the overall void number density drops from 2.8×10^{23} to 1.2×10^{23} m^{-3} during the medium-dose irradiation. This was observed to be due to a general reduction in the number of voids, mostly with diameters$\leqslant$3 nm ($n_0^{1/3} \leqslant 11.2$).[32] At the same time, larger voids continue to grow and maintain a positive swelling rate$\leqslant 2\times10^{-2}$% per NRT dpa. According to Fig. 4(b), vacancy emission from voids is not likely to have a significant role in the void shrinkage at such irradiation temperatures. On the other hand, voids of these sizes and concentration have a sink strength k_c^2 equal to 5.3×10^{15} m^{-2}, corresponding to a ratio of $\alpha_c/\alpha_s \cong 0.13$. It follows from Fig. 6 that the stochastic fluctuations in point-defect fluxes will lead to a reduction by 4–5 times in the number of voids having diameter$\cong$3 nm.

C. Comments on void lattice formation

We have shown in the foregoing that in the absence of vacancy emission from voids the survival probability of the void embryos depends exponentially on the void growth rate and the void size, which is directly related to the growth rate as well. Thus, when stochastic void coarsening takes place, the evolution of an individual void is very sensitive to the deviation of the local void growth rate from the spatial average. It was shown in Ref. 33 that when there is anisotropic transport of self-interstitial atoms by the crowdion mechanism, voids occupying spatial positions that form a regular lattice grow faster, on the average, than the randomly distributed voids. However, for the void lattice to form, randomly distributed voids have to disappear. This can be realized, for example, through the stochastic void coarsening. Indeed, since the void evolution in this case is sensitive to the spatial variations in the void growth rate, even a small fraction of interstitials moving as crowdions can significantly affect the spatial behavior of the void ensemble, resulting in the dissolution of randomly distributed voids with lower growth rates by stochastic fluctuations, and the nucleation and growth of voids forming a regular lattice. In this context it is interesting that a strong correlation is experimentally observable between the rate of void nucleation and void-lattice formation, i.e., a relatively high void density is required for the ordering to occur.[27,29,34] Initially these voids are randomly distributed in space, and void coarsening indeed takes place during the ordering process at later stages.[27,29,34] It is also worth mentioning that at higher temperatures, when vacancy emission from voids becomes important, void coarsening due to the vacancy emission has been shown capable of producing spatial ordering in a void ensemble.[35]

IV. SUMMARY AND CONCLUSION

Void nucleation essentially constitutes the growth of small void embryos to the critical void size, beyond which stable void growth can proceed. In this context, void nucleation can not occur within the mean-field theory, and can only take place via void growth due to the stochastic fluctuations of point-defect fluxes received by the void embryo. There are three sources of fluctuations of the point-defect fluxes: (1) from the statistical variation of jump directions, (2) from the random cascade initiation, and (3) from the random vacancy emission from the void. While the diffusion coefficient corresponding to fluctuations from type (1) is related to the sum of the average fluxes that are proportional to the void radius, those due to fluctuations of the other two types are proportional to the void surface area. At elevated temperatures and when the sink density is low, the fluctuation in the rate of vacancy emission from voids is the dominant factor that governs void nucleation. In this regard, the conventional assumption that fluctuations in the vacancy emission rate are linearly proportional to the void radius seriously underestimates the void nucleation rate. As for fluctuations of type

(2), their effect is important only when the total sink strength for point defects is high, e.g., $>10^{15}$ m^{-2}.

Application of the present approach to the void nucleation in annealed pure copper at elevated temperatures neutron-irradiated with doses 10^{-4}–10^{-2} NRT dpa showed reasonable agreement between theoretical and experimental results. This example also demonstrates that in such a case the spatially homogeneous void concentration can reach a sufficiently high level already at these small doses, so that the spatially homogeneous evolution of the damage microstructure becomes unstable, resulting in the development of large-scale spatial heterogeneity. The theory has also been applied to neutron-irradiated molybdenum at temperatures, where vacancy emission from voids is negligible. Comparison between experimental and calculated void nucleation rates also showed reasonable agreement.

It is also found that, in the regime of high nucleation rate and low average void growth rate, due to the increase of the total sink strength, caused by both void nucleation and growth, cascade-induced fluctuations may start dominating the void evolution. Under such circumstances, the majority of voids, particularly the smaller ones, will shrink away, while at the same time, the largest voids can still maintain their growth. The resulting void coarsening is not caused by vacancy emission from the voids, but by the stochastic fluctuations in the point-defect fluxes received by the void.

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APPENDIX: SOLUTION OF THE KINETIC EQUATION

Integrating Eq. (4) over time, with the initial condition (5), we obtain

$$-\delta(n-n_0)=-\frac{\partial}{\partial n}\left\{V(n)-\frac{\partial}{\partial n}D(n)\right\}P_V(n|n_0), \tag{A1}$$

where

$$P_V(n|n_0)=\int_{t_0}^{\infty}P_V(n,t|n_0,t_0)dt. \tag{A2}$$

As a result, the probability $P_m \equiv P_m(t\to\infty)$ for a void embryo to eventually attain the supercritical size is given by

$$P_m=-\left[\frac{\partial}{\partial n}D(n)P_V(n|n_0)\right]_{n=n_m}. \tag{A3}$$

The solution of Eq. (A1) with zero boundary conditions can be written as

$$P_V(n|n_0)=P_0\varphi(n)\int_{n_{\nu0}}^{n}\frac{dn'}{D(n')\varphi(n')} \qquad (n_{\nu0}\leqslant n<n_0), \tag{A4}$$

$$P_V(n|n_0)=P_m\varphi(n)\int_{n}^{n_m}\frac{dn'}{D(n')\varphi(n')} \qquad (n_0<n\leqslant n_m). \tag{A5}$$

Here

$$\varphi(n)=\frac{1}{D(n)}\exp\left\{\int_{n_{\nu0}}^{n}\frac{V(n')}{D(n')}dn'\right\} \tag{A6}$$

is the solution of the homogeneous first-order equation:

$$\left\{V(n)-\frac{\partial}{\partial n}D(n)\right\}\varphi(n)=0. \tag{A7}$$

Using the conservation law $P_0+P_m=1$ and that $P_V(n|n_0)$ must be a continuous function at $n=n_0$, and equating the right-hand sides of Eqs. (A4) and (A5), we have

$$P_m=\int_{n_{\nu0}}^{n_0}\frac{dn'}{D(n')\varphi(n')}\Bigg/\int_{n_{\nu0}}^{n_m}\frac{dn'}{D(n')\varphi(n')}. \tag{A8}$$

According to Eq. (A6), the integral in the denominator of Eq. (A8) has the form

$$\int_{n_{\nu0}}^{n_m}\frac{dn'}{D(n')\varphi(n')}=\int_{n_{\nu0}}^{n_m}\exp[-\omega(n')]dn', \tag{A9}$$

with

$$\omega(n)=\int_{n_{\nu0}}^{n}V(n')/D(n')dn'. \tag{A10}$$

When the vacancy emission from voids cannot be neglected, the function $\omega(n)$ has a minimum at the critical void size ($n=n_{cr}\gg n_{\nu0}$). Expanding ω up to the second nonzero term in the vicinity of its minimum, we obtain the following approximation to integral (A9):

$$\int_{n_{\nu0}}^{n_m}\frac{dn'}{D(n')\varphi(n')}\cong\sqrt{\frac{2\pi}{\omega''(n_{cr})}}\exp[-\omega(n_{cr})]. \tag{A11}$$

Here $\omega''(n_{cr})$ is the second derivative of $\omega(n)$ at the critical size, given by

$$\omega''(n_{cr})=\frac{[dV(n)/dn]n_{cr}}{D(n_{cr})}=\frac{\beta}{a^3n_{cr}}\frac{D_\nu C_\nu-D_iC_i}{D(n_{cr})}>0. \tag{A12}$$

The last equality in Eq. (A12) follows directly from the definition of the critical void radius.

Assuming that the initial void embryo contains only a few vacancies more than the corresponding minimum value $n_{\nu0}$

[i.e., $(n_0 - n_{\nu 0}) \sim 1$], and noting that $\omega(n)$ is negative when $n < n_{\rm cr}$, the integral in the numerator of Eq. (A8) can be approximated by

$$\int_{n_{\nu 0}}^{n_0} \frac{dn'}{D(n')\varphi(n')} \cong \exp[-\omega(n_0)](n_0 - n_{\nu 0}). \quad \text{(A13)}$$

Within this approximation, we can write

$$P_m \cong \sqrt{\frac{\beta}{2\pi a^3 n_{\rm cr}} \frac{(D_\nu C_\nu - D_i C_i)}{D(n_{\rm cr})}} \exp\left[\int_{n_0}^{n_{\rm cr}} V(n)/D(n) dn \right] \times (n_0 - n_{\nu 0}). \quad \text{(A14)}$$

[1] Ya. B. Zeldovich, Zh. Eksp. Teor. Fiz. **12**, 525 (1942).
[2] Ya. I. Frenkel, *Kinetic Theory of Liquids* (Academy of Science of the USSR, Moscow, 1959).
[3] E. M. Lifshits and L. P. Pitaevsky, in *Theoretical Physics*, Vol. 10: *Physical Kinetics* (Nauka, Moscow 1979).
[4] J. L. Katz and H. Wiedersich, J. Chem. Phys. **55**, 1414 (1971).
[5] K. C. Russell, Acta Metall. **19**, 753 (1971); **26**, 1615 (1978).
[6] S. M. Antsupov and V. V. Slezov, Fiz. Tverd. Tela (Leningrad) **19**, 2932 (1977) [Sov. Phys. Solid State **19**, 2102 (1977)].
[7] Yu. V. Mikhailova and L. A. Maksimov, Zh. Eksp. Teor. Fiz. **59**, 1368 (1970) [Sov. Phys. JETP **32**, 747 (1971)].
[8] T. Diaz de la Rubia and M. W. Guinan, J. Nucl. Mater. **174**, 151 (1990).
[9] T. Diaz de la Rubia and M. W. Guinan, Phys. Rev. Lett. **66**, 2766 (1991).
[10] C. A. English, W. J. Phythian, and A. J. E. Foreman, J. Nucl. Mater. **174**, 135 (1990).
[11] A. J. E. Foreman, C. A. English, and W. J. Phythian, Philos. Mag. A **66**, 655 (1992).
[12] D. J. Bacon, F. Gao, and Yu. N. Osetsky, J. Nucl. Mater. **276**, 1 (2000).
[13] C. H. Woo and B. N. Singh, Phys. Status Solidi B **159**, 609 (1990); Philos. Mag. A **65**, 889 (1992).
[14] C. H. Woo, B. N. Singh, and A. A. Semenov, J. Nucl. Mater. **239**, 7 (1996).
[15] A. A. Semenov and C. H. Woo, J. Nucl. Mater. **233–237**, 1045 (1996).
[16] A. A. Semenov and C. H. Woo, Appl. Phys. A: Mater. Sci. Process. **69**, 445 (1999).
[17] S. M. Antsupov and V. V. Slezov, Fiz. Tverd. Tela (Leningrad) **19**, 3597 (1977) [Sov. Phys. Solid State **19**, 1718 (1977)].
[18] E. A. Koptelov and A. A. Semenov, Chem. Phys. **84**, 477 (1984).
[19] P. Ehrhart, K. H. Robrock, and H. R. Schober, *Basic Defects in Metals*, in *Physics of Radiation Damage in Crystals*, edited by R. A. Johnson and A. N. Orlov (Elsevier, Amsterdam, 1986).
[20] Yu. N. Osetsky, D. J. Bacon, A. Serra, B. N. Singh, and S. I. Golubov, J. Nucl. Mater. **276**, 65 (2000).
[21] *Handbook of Mathematical Functions*, edited by M. Abramowitz and I. A. Stegan (Dover, New York, 1965), p. 231.
[22] B. N. Singh, T. Leffers, and A. Horsewell, Philos. Mag. A **53**, 233 (1986).
[23] C. A. English, B. L. Eyre, and J. W. Muncie, Philos. Mag. A **56**, 453 (1987).
[24] NRT dpa: displacement per atom defined according to M. J. Norgett, M. T. Robinson, and I. M. Torrens, Nucl. Eng. Des. **33**, 50 (1976); ASTM standards E521-83 (1983).
[25] A. A. Semenov and C. H. Woo, Appl. Phys. A: Mater. Sci. Process. **74**, 639 (2002).
[26] H. E. Schaefer, in: *Proceedings of the 6th International Conference on Positron Annihilation, April, 1982*, edited by P. G. Coleman, S. C. Sharma, and L. M. Diana (North-Holland, Amsterdam, 1982), p. 369.
[27] K. Krishan, Radiat. Eff. **66**, 121 (1982).
[28] V. K. Sikka and J. Moteff, J. Nucl. Mater. **54**, 325 (1974).
[29] V. F. Zelensky, I. M. Nekludov, L. S. Ozhigov, *Some Problems in the Physics of Radiation Damage in Materials* (Naukova Dumka, Kiev, 1979).
[30] B. L. Eyre and A. E. Barlett, J. Nucl. Mater. **47**, 143 (1973).
[31] A. A. Semenov, C. H. Woo, and E. A. Koptelov, Appl. Phys. A: Mater. Sci. Process. **73**, 335 (2001).
[32] J. H. Evans, J. Nucl. Mater. **88**, 31 (1980).
[33] C. H. Woo and W. Frank, J. Nucl. Mater. **137**, 7 (1985).
[34] A. M. Stoneham, in *The Physics of Irradiation Produced Voids, Proc. Consult. Symp.*, Harwell Report No. AERE-R-7934, edited by R. S. Nelson (UK, Harwell, 1975), p. 319.
[35] E. A. Koptelov and A. A. Semenov, J. Nucl. Mater. **170**, 178 (1990).