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Stochastic theory of diffusional planar-atomic clustering and its application to dislocation loops

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Atomic clustering into circular planar disks is an important process responsible for interstitial-loop formation in the bulk of irradiated materials, and the evolution of atomic planes during thin-film growth. We develop a stochastic theory for the formation of planar-atomic clusters by atomic diffusion. The theory accounts for the transient coupling between master equations representing small-size atomic clusters and a Fokker-Planck (FP) equation for larger ones. The FP equation is solved self-consistently, together with the master equations by the moments method. Equations for the rates of change of atomic species and for the nucleation rate of atomic clusters are simultaneously solved with appropriate equations for the average size and various moments of the distribution function. An application of the theory is given by comparing the results of calculations with experimental data on interstitial-loop formation in ion-irradiated nickel.

I. INTRODUCTION AND BACKGROUND

Atomic clustering in solids, which are in nonequilibrium thermodynamic conditions, has been described by rate equations, in analogy to formulations used in chemical kinetics, as far back as the early 1950's. The work of Damask and Dienes[1] is an example of early theoretical models of atomic clustering. Their approach, which is an extension of Chandrasekhar's theory of colloid coagulation,[2] has been successful in explaining various aspects of defect annealing. Theoretical efforts have been concerned with either the nucleation phase of clustering[3-5] or the growth regime.[6-9] Only recently have theories been advanced to treat nucleation and growth of atomic clusters as inseparable parts of an evolution process.

Early efforts in this area have investigated atomic-clustering processes using systems of nonlinear ordinary differential equations. These systems represent conservation equations for hierarchies of atomic clusters of increasing size.[10-17] Theoretical implications of system boundedness, global conservation, and boundary and initial conditions were largely unexplored. Solution of the ensuing system of clustering equations is analytically not possible, and mathematical and numerical approximations are therefore necessary. For example, grouping methods, where a group of equations are assigned the same reaction rate, have been introduced by Kiritani[13] and Hayns.[14] Solution of a large system with global atomic conservation to determine the necessary number of equations has been developed by Ghoniem.[18] It is shown in this work that additional equations must be included as a function of time and that the number of equations for an accurate solution can be prohibitively large. In the study of multistate kinetic transitions, the hierarchy of master equations (or rate equations) can be transformed to an equivalent parabolic partial differential equation.[19] The resulting continuum equation is of the Fokker-Planck (FP) type, and it describes a process of particle diffusion in a general drift field. This approach was used to model vacancy and interstitial atomic clustering by Sprague, Russell, and Choi,[20] Wolfer, Mansur, and Sprague,[21] and also by Hall.[22] The mathematical properties of the continuum equation have led to some controversy over the validity of the representation for small-size clusters. The truncation of the Taylor series at the second derivative may be invalid for $\Delta x / x \simeq O(1)$ and $\Delta K / K \simeq O(1)$, where x is the cluster size and K is a generic rate constant. Therefore, a hybrid method was successfully developed by Ghoniem and Sharafat.[23] In this method, the details of small-size clustering are conserved by rate equations, and the behavior of large-size clusters is described by the FP equation. The hybrid method was also discussed for helium effects on nucleation by Trinkaus and Ullmaier.[24]

Approximate solutions for the distribution function of a kinetic system, obtained by replacing the master equation with a parabolic partial differential equation in the distribution function itself, is rooted in statistical physics. Rayleigh,[25] and somewhat later Einstein,[26] were the first to use this technique. The procedure was then developed in greater generality by Fokker[27] and Planck.[28]

Problems with the mathematical approximation to the discrete master equation are well known in the statistical-mechanics literature.[29-33] Kramers[29] and Moyal[30] observed that it would be wrong to assume that a valid next approximation to the FP equation can be formed by truncating the higher-order terms in the Taylor-series expansion. Van Kampen[31] and Gurol[32] have studied the problem of correcting the FP approximation using the system-size expansion method. The second approximation in the expansion yields the FP equation, while successive corrections add to the coefficients in the FP equation in addition to adding higher-derivative terms. The FP equation becomes an exact equivalent to the master equation only if the transition probabilities are Gaussian.[33]

The approach followed thus far for analyzing microstructure evolution is based on a deterministic, causal description provided by rate-theory conservation equations. However the existence of a large number of interacting entities, on the order of 10^{30} atoms in a typical engineering solid, implies that the degrees of freedom of the system are much larger than what can be represented by rate equations. Such a situation naturally leads to fluctuations around a reference state. The existence of these fluctuations can be important in two respects. First, fluctuations around a critical state can determine the extent of nucleation of embryonic clusters. Second, as the clustering system evolves, fluctuations determine the dispersion or spread around the average state.

Recent efforts by Gurol,[32] Clement and Wood,[34] Trinkaus,[35] and by Kitajima and co-workers[36–39] have considered an interpretation to atomic clustering within the framework of statistical mechanics. In this regard, the conventional rate equations describing concentrations of various cluster sizes are replaced by probability-density equations. Invoking the assumptions of a Markovian-Gaussian process for the transition probabilities, it can be shown that the FP equation is a valid representation of the probability-density function. Kitajima[38] has in fact used this procedure, which was established within the past 20 years for other problems involving fluctuations.[19,33] In this paper, we develop and solve equations representing the evolution of the probability density of planar-atomic clusters. We consider atomic agglomeration in two-dimensional (2D) planar disks as a result of single-atom diffusional transport. Once agglomeration starts, the atomic cluster is considered to be immobile. The description is an extension of the author's earlier hybrid method,[23] where discrete master equations can accurately describe the transient nucleation process, and an FP equation is used to represent larger sizes. Instead of the conventional Taylor-series expansion,[21] we present a description of fluctuations within the framework of statistical mechanics.[19,35] In this approach, it is possible to include the collisional and diffusional effects of cascades. Chou and Ghoniem[40,41] have studied both effects using the Monte Carlo method, and reasonable estimates of the influence of cascade-induced fluctuations are calculated. Section II is devoted to development of master and FP equations describing system evolution. We will not consider coalescence of atomic disks caused by their migration, as in the case of loops in irradiated bcc materials or surface clusters during thin-film growth. This is followed in Sec. III by a derivation of a coupled set of equations for the moments of the system distribution function. The method is then applied in Sec. IV to the results of experiments on the evolution of interstitial loops during irradiation with heavy ions. Limitations of the method are finally discussed in Sec. V.

II. NUCLEATION AND FOKKER-PLANCK EQUATIONS

We focus here on the formation of interstitial loops for several reasons: (1) Nucleation of loops is a very fast process and the critical cluster size is on the order of two to three interstitial atoms;[18] (2) a 1D FP equation is sufficient for the description of evolution, which allows for tractable presentations of analytical solutions; (3) well-quantified experimental measurements exist[15] where the present theory can be used to test the effects of various approximations.

The evolution of interstitial-atom clusters starts with conventional rate equations for the conservation of radiation-produced point defects: vacancies and interstitial atoms. The concentrations of vacancies C_v and interstitials C_i are given by[17]

$$\frac{dC_v}{dt} = \epsilon P - \alpha C_v C_i - \lambda_v C_v \ , \tag{1}$$

$$\frac{dC_i}{dt} = \epsilon P + K_v^{2i}(2) C_v C_{2i} + 2\delta C_{2i} - K_i^{i}(1) C_i^2 - \alpha C_v C_i - K_i^{2i}(2) C_i C_{2i} - \lambda_i C_i \ , \tag{2}$$

where P is the production rate of point defects, ϵ is the fraction of point defects surviving instantaneous recombination within the cascade, α is their subsequent mutual recombination rate, $K_a^b(x)$ is a general reaction rate between a mobile species (a) and an immobile species (b) containing x atoms, and δ is the di-interstitial dissociation rate. The parameters λ_i and λ_v represent effective loss rates to homogeneous microstructural sinks and are given by

$$\lambda_v = \left[\sum_j D_v k_{v,j}^2 + \sum_{x=x^*}^{X} K_v^l(x) C_l(x) \right] , \tag{3}$$

and

$$\lambda_i = \left[\sum_j D_i k_{i,j}^2 + \sum_{x=x^*}^{X} K_i^l(x) C_l(x) \right] , \tag{4}$$

where D_v and D_i are diffusion coefficients, $k_{v,j}^2$ and $k_{i,j}^2$ are sink strengths of type j as in conventional rate theory,[7] and $C_l(x)$ is the concentration of interstitial loops containing x atoms. The first summation is over all sink types, and the second is carried over the loop distribution function up to a maximum size X. Details of expressions for the various reaction rates have been previously reported[10–14,17] and will not be repeated here. It is to be noted here that trapping of self-interstitial atoms can be readily included by a modification of the interstitial diffusion coefficient,[15,42] where a trap binding energy is introduced.

The formation of di-interstitial atomic clusters can also be adequately described by the homogeneous rate theory,[17] which results in the following equation:

$$\frac{dC_{2i}}{dt} = K_i^i(1) C_i^2 - K_i^{2i}(2) C_i C_{2i} - \delta C_{2i} - \lambda_{2i} C_{2i} - 2K_{2i}^{2i}(2) C_{2i}^2 \ , \tag{5}$$

where the di-interstitial cluster was also assumed to be mobile. The absorption rate constant at sinks λ_{2i} is given by an expression similar to Eq. (4).

The clustering of large-size interstitial loops can, in principle, be described by an expanded set of master equations. However, it was shown previously by several authors[13–18] that if the di-interstitial binding energy is large (≥ 1 eV), the backward reaction rates become very small. We will use this idea to simplify the clustering problem by single atomic steps. First Eq. (5) is written as

$$\frac{dC_{2i}}{dt}=J_1-J_2 , \tag{6}$$

where J_1 is a current representing the net rate of transformation of single interstitial atoms to a di-interstitial cluster, and J_2 is for the net rate of transformation to triclusters or tetraclusters, i.e.,

$$J_1=K_i^i(1)C_i^2-\delta C_{2i}-\lambda_{2i}C_{2i} , \tag{7}$$

and

$$J_2=K_i^{2i}(2)C_iC_{2i}+2K_{2i}^{2i}(2)C_{2i}^2 . \tag{8}$$

The rate constants δ and λ_{2i} are not strongly dependent on x, and Eq. (6) can be replaced by an equivalent equation describing diatomic cluster nucleation:

$$\frac{\partial C^*}{\partial t}\simeq\frac{\partial}{\partial x}J^* . \tag{9}$$

In Eq. (9), the concentration of critical nuclei $C^*=C_{2i}$, and the nucleation current J^* is approximated by J_2. The equation provides a simple means for calculating the nucleation current, which, in turn, supplies one of the necessary boundary conditions for the FP equation, representing the size distribution of planar-atomic clusters.

For sizes above the di-interstitial critical nucleus size (i.e., $x\geq 3$), the master equation describing the rate of change of the concentration $C(x)$ or equivalently the probability density is given by[17]

$$\begin{aligned}\frac{\partial C(x)}{\partial t}=&(\alpha C_i+\gamma)K(x-1)C(x-1)\\&+\beta C_vK(x+1)C(x+1)\\&-(\alpha C_i+\gamma+\beta C_v)K(x)C(x) ,\end{aligned} \tag{10}$$

where the reaction rate has now been separated into a time-dependent component and a size-dependent component. αC_i represents the rate of interstitial-atom impingement while $K(x-1)$ is the corresponding combinatorial factor that is size dependent. γ is the vacancy thermal emission rate, which is nearly independent of x for $x\geq 3$, and βC_v is the rate of vacancy impingement. Following the conventional methods,[25–39] we expand the cluster concentration C and the combinatorial numbers K around x, and truncate the Taylor series after second order. This results in the familiar FP equation:

$$\frac{\partial C}{\partial t}+\nabla\cdot\mathbf{J}=0 , \tag{11}$$

where the operator $\nabla=\partial/\partial x$ in this case, and current $\mathbf{J}$ is given by the 1D component

$$\mathbf{J}=J_x=\mathcal{F}C-\frac{\partial}{\partial x}(\mathcal{D}C) , \tag{12}$$

where the drift coefficient $\mathcal{F}$, and the dispersion coefficient $\mathcal{D}$ can be expressed as

$$\mathcal{F}=g_1K(x) , \tag{13}$$

and

$$\mathcal{D}=\mathcal{D}_s=g_2K(x) , \tag{14}$$

and g_1 and g_2 are mainly functions of the temperature and displacement rate, given by

$$g_1=\frac{4}{3}\left[\frac{3}{\pi}\right]^{1/4}(\alpha ZC_i+\gamma-\beta C_v) , \tag{15}$$

$$g_2=\frac{2}{3}\left[\frac{3}{\pi}\right]^{1/4}(\alpha ZC_i+\gamma+\beta C_v) , \tag{16}$$

and Z is a constant bias factor for dislocation loops, ensuring that $g_1\geq 0$ at a quasisteady state, and $K(x)$ is a size-dependent combinatorial factor.[17] Equations (13) and (14) are based on mixed diffusion- and surface-reaction-controlled kinetics, where the combinatorial number $K(x)$ is proportional to the number of atoms around the loop perimeter $x^{1/2}$ and a size-dependent function (see Ref. 17).

The previously outlined approach for the derivation of the FP equation is based upon the master equation for single-step transitions. However, the effects of large-scale transitions of a more general stochastic nature can be described by the methods of statistical mechanics, with the Smoluchowsky-Chapman-Kolmogorov (SCK) equation for a Markovian process as a starting point,[33,38] i.e.,

$$C(x,t)=\int C(x_0,0)\psi(x,t;x_0,0)dx_0 , \tag{17}$$

where the transition probabilities, ψ in this case, need not be exactly known. An integro-differential equation can be formulated for ψ, from which various moments are calculated. The FP equation [Eq. (11)] is shown[19,33,37] to be an approximation to the SCK equation [Eq. (17)] for Markovian-Gaussian stochastic processes. The drift and dispersion functions can be defined in a more general sense as[19]

$$\mathcal{F}_j(x)=\frac{\langle\Delta x(x)\rangle}{\Delta t_j} , \tag{18}$$

and

$$\mathcal{D}_j(x)=\frac{\langle[\Delta x(x)]^2\rangle-[\langle\Delta x(x)\rangle]^2}{2\Delta t_j} , \tag{19}$$

where the interval Δt_j is a characteristic correlation time for a statistically independent stochastic process j. The notation $\langle\ \rangle$ is used to indicate time averaging of a size fluctuation Δx over a time interval Δt_j.

There are three different stochastic processes that influence the evolution of interstitial loops: single atomic transitions, transitions caused by the diffusion of defects contained in a cascade, and transitions caused by direct cascade collisions. The overall drift and diffusion coefficients can be expressed as the sum of the respective values of the statistically independent processes. Using the subscript s for the first process, CD for the second, and CC for the third, we have

$$\mathcal{F}=\mathcal{F}_s+\mathcal{F}_{\mathrm{CD}}+\mathcal{F}_{\mathrm{CC}}\simeq\mathcal{F}_s \ , \tag{20}$$

and

$$\mathcal{D}=\mathcal{D}_s+\mathcal{D}_{\mathrm{CD}}+\mathcal{D}_{\mathrm{CC}} \ . \tag{21}$$

The expressions for single-step transitions are already given in Eqs. (13) and (14), while those for cascade collisions $\mathcal{D}_{\mathrm{CC}}$ and diffusion $\mathcal{D}_{\mathrm{CD}}$ can be estimated in a manner similar to the work of Kitajima.[36,38] We now proceed to describe our application of the moments method to the solution of the general FP equation for loop evolution.

III. MOMENTS METHOD FOR THE SOLUTION OF THE FOKKER-PLANCK EQUATION

The moments method has been successfully used for the approximate determination of distribution functions, when described by partial or integro-differential equations, as in the work of Sigmund[43] and in that of Clement and Wood.[44] Equations (11) and (12) can be put in the form

$$\frac{\partial C}{\partial t}=-\frac{\partial}{\partial x}(\mathcal{F}C)+\frac{\partial^2}{\partial x^2}(\mathcal{D}C) \ . \tag{22}$$

The zeroth moment of Eq. (22) gives

$$\frac{dN}{dt}=J^* \ , \tag{23}$$

where

$$N=\int_{x^*}^{\infty} C\,dx$$

and is readily obtained by the direct integration of Eq. (23). N is the total density of atomic clusters, regardless of their size. The upper bound has been approximated as ∞ for mathematical simplicity. Solution to the second-order parabolic partial differential Eq. (22) is possible, provided the following boundary and initial conditions are satisfied:

$$\begin{gathered} C(\infty,t)=0 \ , \\ C(x^*,t)=C_{2i}(t)\equiv C^* \ , \\ \text{or} \\ J(x^*,t)=J^* \ , \\ \text{and} \\ C(x,0)=0 \ , \quad x>x^* \ . \end{gathered} \tag{24}$$

The average size $\langle x \rangle$ is obtained as follows:

$$\langle x \rangle N=\int_{x^*}^{\infty} xC\,dx \ .$$

Taking time derivatives, we obtain

$$\frac{d}{dt}\langle x \rangle=\langle \mathcal{F}(x)\rangle-(\langle x \rangle-x^*)\frac{d}{dt}\ln N+\frac{\mathcal{D}^*C^*}{N} \ , \tag{25}$$

where $\langle \mathcal{F}\rangle$ is the average value of the drift function $\mathcal{F}$ over the size distribution function C. The quantities with an asterisk are evaluated at the critical size. The second and third terms of Eq. (25) give the effects of nucleation on the average size. Here the symbol $\langle\ \rangle$ is used for averages over the distribution function, i.e.,

$$\langle \eta(x)\rangle=\int_0^{\infty}\eta(x)C(x)dx \ ,$$

and $\eta(x)$ is any arbitrary function of x.

The rth central moment M_r is given by

$$M_rN=\int_{x^*}^{\infty}(x-\langle x \rangle)^r C(x,t)dx \ . \tag{26}$$

Taking the time derivatives of both sides of Eq. (26) and using the initial and boundary conditions, we obtain

$$\begin{aligned} \frac{dM_r}{dt}&=r\langle \mathcal{F}(x-\langle x \rangle)^{r-1}\rangle+r(r-1)\langle \mathcal{D}(x-\langle x \rangle)^{r-2}\rangle \\ &\quad+r\frac{\mathcal{D}^*C^*}{N}(x^*-\langle x \rangle)^{r-1} \\ &\quad+\frac{d}{dt}(\ln N)[(x^*-\langle x \rangle)^r-M_r]-rM_{r-1}\frac{d}{dt}\langle x \rangle \ . \end{aligned} \tag{27}$$

Substituting for $d\langle x \rangle/dt$, a general equation for the rth moment can be derived:

$$\begin{aligned} \frac{dM_r}{dt}&=r[\langle \mathcal{F}(x-\langle x \rangle)^{r-1}\rangle-M_{r-1}\langle \mathcal{F}\rangle]+r\frac{\mathcal{D}^*C^*}{N}[(x^*-\langle x \rangle]^{r-1}-M_{r-1}] \\ &\quad+\frac{d}{dt}(\ln N)[(x^*-\langle x \rangle)^r-M_r-rM_{r-1}(x^*-\langle x \rangle)]+r(r-1)\langle \mathcal{D}(x-\langle x \rangle)^{r-2}\rangle \ . \end{aligned} \tag{28}$$

Now let us define the nucleation functions ξ_r, the distortion functions Φ_r, and the dispersion functions Ψ_r as,

$$\begin{aligned} \xi_1&=\frac{\mathcal{D}^*C^*}{N}-(\langle x \rangle-x^*)\frac{d}{dt}\ln N \ , \\ \xi_r&=r\frac{\mathcal{D}^*C^*}{N}[(x^*-\langle x \rangle)^{r-1}-M_{r-1}]+\frac{d}{dt}(\ln N)[(x^*-\langle x \rangle)^r-M_r-rM_{r-1}(x^*-\langle x \rangle)] \ , \\ \Phi_r&=r[\langle \mathcal{F}(x-\langle x \rangle)^{r-1}\rangle-M_{r-1}\langle \mathcal{F}\rangle] \ , \\ \Psi_r&=r(r-1)\langle \mathcal{D}(x-\langle x \rangle)^{r-2}\rangle \ . \end{aligned} \tag{29}$$

The complete system of moment equations can now be described as,

$$\frac{d}{dt}\langle x \rangle = \langle \mathcal{F} \rangle + \xi_1 ,$$
$$\frac{dM_r}{dt} = \Psi_r + \Phi_r + \xi_r , \quad r = 2,3,\ldots,\infty . \tag{30}$$

Since the distribution function is not known *a priori*, averaging of functions can only be made in an approximate way. For an arbitrary function of x, the average value over the distribution function is given by,

$$\begin{aligned}\langle \eta(x) \rangle &= \frac{1}{N}\int_{x^*}^{\infty} \eta C \, dx \\ &= \frac{1}{N}\int_{x^*}^{\infty} \left[\eta(\langle x \rangle) + \frac{(x-\langle x \rangle)}{1!}\eta'(\langle x \rangle) + \frac{(x-\langle x \rangle)^2}{2!}\eta''(\langle x \rangle) + \cdots \right] C \, dx , \\ \langle \eta(x) \rangle &= \eta(\langle x \rangle) + \sum_{k=2}^{\infty} \frac{M_k}{k!}\frac{d^k \eta(\langle x \rangle)}{dx^k} .\end{aligned} \tag{31}$$

The dispersion function Ψ_r is given by averaging the product of the diffusion coefficient and the quantity $(x - \langle x \rangle)^{r-2}$ over the distribution function. Thus

$$\Psi_r = r(r-1) \left[\mathcal{D}(\langle x \rangle - \langle x \rangle)^{r-2} + \sum_{k=2}^{\infty} \frac{M_k}{k!}\frac{d^k}{dx^k}[\mathcal{D}(x - \langle x \rangle)^{r-2}] \bigg|_{\langle x \rangle} \right] . \tag{32}$$

The function Ψ_r takes different forms, depending on the value of r. For $r = 2$, we obtain

$$\Psi_2 = 2\langle \mathcal{D}(x - \langle x \rangle)^0 \rangle = 2\langle \mathcal{D} \rangle = 2 \left[\mathcal{D}(\langle x \rangle) + \sum_{k=2}^{\infty} \frac{M_k}{k!}\frac{d^k \mathcal{D}}{dx^k} \bigg|_{\langle x \rangle} \right] . \tag{33}$$

Now, since $\mathcal{D} = g_2 K(x) x^{1/2}$, we obtain for $K(x) = 1$,

$$\Psi_2 = 2 \left[\mathcal{D} + \frac{g_2}{2} \sum_{k=2}^{\infty} \frac{M_k}{k!}(-1)^{k-1} \frac{1 \times 3 \times 5 \cdots \times (2k-3)}{2^{k-1}} \langle x \rangle^{-(2k-1)/2} \right] . \tag{34}$$

The series is convergent for large values of $\langle x \rangle$. This can be seen by an examination of the radius of convergence of the series for large k. However, this cannot be made self-consistently without complete knowledge of the distribution function. If the distribution function is assumed to be nearly Gaussian, the series can be shown to be monotonically decreasing, and hence convergent, for evolution times approximately greater than $2\tau\sqrt{k}/\Delta Z$. τ is a characteristic growth time for the average loop; $\tau \cong 2/g_1$ is the time required for addition of one atom to the average-size loop; and $\Delta Z \cong Z - 1$. This is inherently a short transient time, and convergence is fast for longer time scales. It is interesting to note that convergence for a higher-order moment M_k is guaranteed past time scales proportional to $\sqrt{k}$. An approximation to Ψ_2 can be obtained by truncating the series at its lowest limit, i.e., $k = 2$,

$$\Psi_2 \approx 2 \left[\mathcal{D}(\langle x \rangle) + \frac{g_2}{2}(-1)\frac{M_2}{M}\langle x \rangle^{-3/2} \right] = 2g_2 \langle x \rangle^{1/2} \left[1 - \left[\frac{\sqrt{M_2}}{2\langle x \rangle} \right]^2 \right] . \tag{35}$$

The distortion function ϕ_r is given by

$$\begin{aligned}\phi_r &= r \left[\mathcal{F}(\langle x \rangle)(\langle x \rangle - \langle x \rangle)^{r-1} + \sum_{k=2}^{\infty} \frac{M_k}{k!}\frac{d^k}{dx^k}[\mathcal{F}(x - \langle x \rangle)^{r-1}] \bigg|_{\langle x \rangle} - M_{r-1}\langle \mathcal{F} \rangle \right] \\ &= r \left[\delta(r-1)\mathcal{F}(\langle x \rangle) + \sum_{k=2}^{\infty} \frac{M_k}{k!}\frac{d^k}{dx^k}[\mathcal{F}(x - \langle x \rangle)^{r-1}] \bigg|_{\langle x \rangle} - M_{r-1} \left[\mathcal{F}(\langle x \rangle) + \sum_{k=2}^{\infty} \frac{M_k}{k!}\frac{d^k}{dx^k}(\mathcal{F}) \bigg|_{\langle x \rangle} \right] \right] .\end{aligned} \tag{36}$$

Similar to the dispersion function, for $r = 2$, we obtain $\phi_2 = 2[\langle \mathcal{F}(x - \langle x \rangle) \rangle - M_1 \langle \mathcal{F} \rangle]$, but $M_1 = \langle x - \langle x \rangle \rangle = 0$ and

$$\langle \mathcal{F}(x - \langle x \rangle) \rangle = \mathcal{F}(x - \langle x \rangle)|_{\langle x \rangle} + \sum_{k=2}^{\infty} \frac{M_k}{k!}\frac{d^k}{dx^k}[\mathcal{F}(x - \langle x \rangle)] . \tag{37}$$

Using similar arguments to those given in Eq. (34), and as an approximation, we truncate the series at $k = 2$ to obtain

$$\phi_2 \approx \frac{M_2}{2}[\mathcal{F}+(x-\langle x\rangle)\mathcal{F}']' = \frac{M_2}{2}[2\mathcal{F}'+(x-\langle x\rangle)\mathcal{F}''] = 2M_2\mathcal{F}' = g_1 M_2\langle x\rangle^{-3/2} . \tag{38}$$

Now, let $\lambda \equiv [(M_2)^{1/2}/2\langle x\rangle]^2$.

Approximate equations for the average value of x and the second moment are then given by

$$\frac{d\langle x\rangle}{dt} \approx \xi_1 + g_1\langle x\rangle^{1/2}\left[1-\frac{\lambda}{2}\right] , \tag{39}$$

and

$$\frac{dM_2}{dt} \approx \xi_2 + 2g_2\langle x\rangle^{1/2}\left[1-\lambda\left[1-\frac{2g_1}{g_2}\right]\right] . \tag{40}$$

Integration of the set of Eq. (30) can, in principle, describe the distribution function by defining any desired number of moments. Representation of the distribution function from the knowledge of the various moments is not unique, however. To accomplish this task, we will use the cummulant functions κ_n where

$$\kappa_1 = \langle x\rangle , \quad \kappa_2 = M_2 , \quad \kappa_3 = M_3 , \quad \kappa_4 = M_4 - 3M_2^2 , \quad \ldots ;$$

the coefficients of skewness and excess, $G_1 = \kappa_3/\kappa_2^{3/2}$, $G_2 = \kappa_4/\kappa_2^2, \ldots$; and the normal or Gaussian function $Z(y) = (1/\sqrt{2\pi})e^{-y^2/2}$, $y = [(x-\langle x\rangle)/\sqrt{M_2}]$.

The distribution function $C(x,t)$ can now be found as[45]

$$C(x,t) = N\left[Z(y) - \left[\frac{G_1}{6}Z^{(3)}(y)\right] + \left[\frac{G_2}{24}Z^{(4)}(y) + \frac{G_1^2}{72}Z^{(6)}(y)\right] - \left[\frac{G_3}{120}Z^{(5)}(y) + \frac{G_1G_2}{144}Z^{(7)}(y) + \frac{G_1^3}{1296}Z^{(9)}(y)\right]\right.$$
$$\left. - \left[\frac{G_4}{720}Z^{(6)}(y) + \frac{G_2^2}{1152}Z^{(8)}(y) + \frac{G_1G_2}{720}Z^{(8)}(y) + \frac{G_1^2G_2}{1728}Z^{(10)}(y) + \frac{G_1^4}{31\,104}Z^{(12)}(y)\right] + \cdots\right] . \tag{41}$$

Here $Z^{(m)}$ represents the mth derivative of Z. Equation (41) can be simplified, knowing that the normal function Z satisfies the differential equation

$$Z^{(m+2)}(y) + yZ^{(m+1)}(y) + (m+1)Z^{(m)}(y) = 0 ,$$

and hence the recurrence relation,

$$Z^{(m)}(y) = (-1)^m H(y,m)Z(y) ,$$

holds. The functions $H(y,m)$ are the Hermite polynomials

$$H_0 = 1 , \quad H_1(y) = y , \quad H_2(y) = y^2 - 1 , \quad H_3(y) = y^3 - 3y , \quad \ldots .$$

Following Kendall and Stuart,[45] one can derive relationships between the cummulants and moments. When the transformation

$$z = y\sqrt{M_2} + \langle x\rangle \tag{42}$$

is substituted into Eq. (41) and the cummulants replaced by moments, we finally arrive at an approximation to the distribution function

$$C(x,t) \simeq \frac{N}{\sqrt{2\pi M_2}}\exp\left[-\frac{y^2}{2}\right]\left[1 + \frac{M_3}{6M_2^{3/2}}H_3(y) + \frac{1}{24}\left[\frac{M_4}{M_2^2} - 3\right]H_4(y) + \frac{1}{120}\left[\frac{M_5}{M_2^{5/2}} - 10\frac{M_3}{M_2^{3/2}}\right]H_5(y)\right.$$
$$\left. + \frac{1}{720}\left[\frac{M_6}{M_2^3} - 15\frac{M_4}{M_2^2} + 30\right]H_6(y)\right] . \tag{43}$$

Equation (43) is identical to the Edgeworth form of the type-A series, which differs from the Gram-Charlier series of type A by the term $\kappa_3^2 H_6(y)/72$.[45] Draper and Tierney[46] showed that the series given by Eq. (43) provides unimodal and positive probability densities for $G_1 \leq 0.25$. Thus the finite series is suitable for cases of moderate skewness, as expected on the basis of atomic-clustering physics.

IV. NUMERICAL RESULTS FOR A SIMPLIFIED EXAMPLE

An illustrative example of interstitial-loop evolution will be given in this section where comparison with experiments are made. It is instructive to show that, even though several complicating features are neglected, the solution gives qualitative agreements with experiments.

Hall and Potter[15] performed ion-irradiation experiments on Ni, Ni-Si, and Ni-Al alloys. A series of experiments on Ni–4 at. % Si were carried out, where 3.0-MeV Ni^{58+} ions were used to bombard samples at 465 °C. Their ion flux was 2.3×10^{11} $\mathrm{cm}^{-2}\,\mathrm{s}^{-1}$, which corresponded to a peak displacement damage rate of 3×10^{-4} dpa/s (1 dpa represents the radiation dose necessary to cause one displacement of each atom from its lattice site). A summary of their experimental observations is given in Table I.

A series of calculations was performed using Eqs. (1)–(5) for the concentrations of vacancies, self-interstitial atoms, and di-interstitials, respectively. Equation (23) was simultaneously integrated for the total loop density, and Eqs. (39) and (40) for the average loop size and the second moment of the distribution function. A PC-based computer program LOOP was developed by the author and written in Microsoft FORTRAN 77. The program, which can be directly obtained from the author, incorporates a modification of the GEAR package,[47] and uses an implicit Adam-Bashforth numerical integration method for stiff, coupled ordinary differential equations. A trapping model was adopted for interstitial-atom migration, where the effective migration energy E_i^{me} is written as $E_i^{\mathrm{me}} = E_i^m + E_i^t$, where E_i^m is the interstitial migration energy without traps and E_i^t is the binding energy of self-interstitials to atomic-size traps. A standard set of defect parameters has been used throughout the calculations. Only three parameters were treated as free variables, and those are the trapping energy E_i^t, the di-interstitial binding energy E_{2i}^B, and the loop-interstitial bias factor Z_i^l. The remainder of the defect parameters were treated as standard values commonly used in the literature on Ni. The standard set of parametric defect values are shown in Table II.

TABLE I. Hall-Potter experimental data[a] at 465 °C.

Dose (dpa)	Total loop density (loop/m^3)	Average loop diameter (nm)
0.05	4.78×10^{20}	5.6
0.11	4.84×10^{20}	11.5
0.35	4.97×10^{20}	30.2
0.67	4.87×10^{20}	34.1

[a] Reference 15.

TABLE II. Standard set of defect parameters

Defect parameter	Value
Vacancy migration energy E_v^m	1.28 eV
Vacancy formation energy E_v^f	1.6 eV
Cascade defect survival efficiency ϵ	0.3
Interstitial-atom vibration frequency ν_i	10^{13} s^{-1}
Vacancy vibration frequency ν_v	5×10^{13} s^{-1}
Initial dislocation density ρ	5×10^{14} m^{-2}
Dislocation-interstitial bias factor Z_i	1.01
Interstitial migration energy E_i^m	0.20 eV
Di-interstitial migration energy E_{2i}^m	0.80 eV
Trapping energy for self-interstitials E_i^t	0.35 eV
Di-interstitial binding energy E_{2i}^b	1.19 eV
Loop-interstitial bias factor Z_i^l	2.0

To compare with experimental data, the loop size distribution must be described as a function of the loop diameter D rather than its size x. Conservation of probability gives

$$C(x,t)dx = C(D,t)dD \ .$$

Hence

$$C(D,t) = C(x,t)\frac{dx}{dD} \ ,$$

since, for a circular atomic disk in an fcc material

$$\pi\frac{D^2}{4}\frac{a_0}{\sqrt{3}} = x\frac{a_0^3}{4} \ ,$$

where a_0 is the interatomic spacing. Thus

$$D = Kx^{1/2} \ ,$$

where

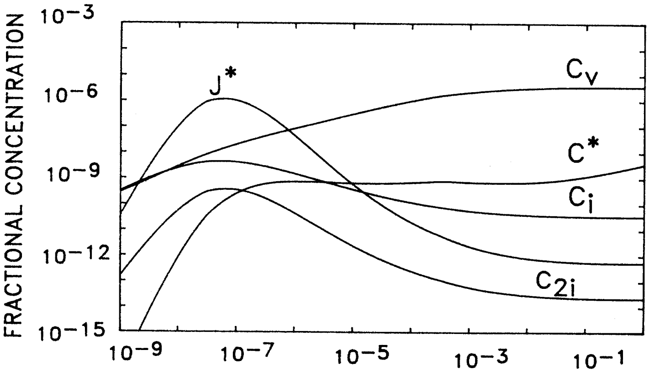

FIG. 1. Time dependence of vacancy C_v, interstitial C_i, di-interstitial C_{2i}, and critical nucleus C^* concentrations; also shown is the nucleation current $[J^*(at/at/s)]$ (dpa represents displacement per atom).

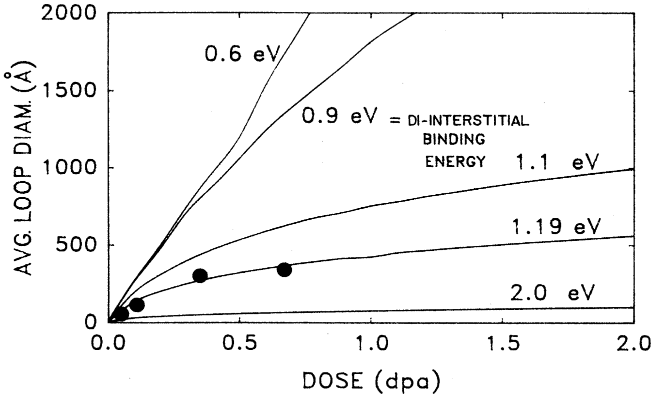

FIG. 2. Effect of di-interstitial binding energy on the average loop diameter (——, theory; ●, experiment; dpa represents displacement per atom).

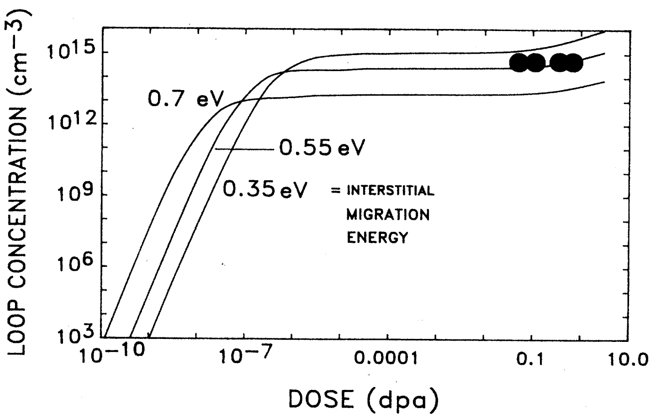

FIG. 4. Effect of the effective interstitial migration energy on the total loop concentration (——, theory; ●, experiment; dpa represents displacement per atom).

$$K=\frac{3^{1/4}}{\sqrt{\pi}}a_0 \ .$$

The distribution function $C(D,t)$ is now given by

$$C(D,t)=\frac{2}{K}x^{1/2}C(x,t) \ .$$

It is to be noted that the transformation from a number of atoms x to a circular disk with diameter D introduces another distortion to the distribution function.

The temporal dependencies of point-defect concentrations C_v and C_i, the di-interstitial concentration C_{2i}, the nucleation current J^*, and the density of critical clusters C^* are shown in Fig. 1. It is observed that quasistatic conditions are achieved within a short irradiation time (on the order of 0.001 dpa). This is in accordance with earlier calculations (e.g., Ref. 17). The bulk of interstitial-loop nucleation is achieved within this transient dose. Further irradiation results in a small amount of nucleation and in substantial development of the loop size distribution. This observation will be useful in further simplifications of the problem.

The effects of parametric variations in $E_i^{\rm me}$ and E_{2i}^b on the average size of dislocation loops and on the total loop density is shown in Figs. 2–4. An increase in the loop bias factor Z_i^l, results in an increase in the average loop diameter. On the contrary, the loop density is not sensitive to this factor. This is fortunate since measurements of the loop density can be used to determine defect parameters other than the bias factor, as discussed in Ref. 48. The effect of the di-interstitial binding energy on the average loop diameter is shown in Fig. 2. An increase in the E_{2i}^b will dramatically increase the loop density and reduce the average diameter. The value of 1.19 eV is shown to result in reasonable correlation with experimental data and is also consistent with our previous conclusions.[17] The effective interstitial migration energy shows an opposite dramatic influence on both the average diameter (Fig. 3) and the total density (Fig. 4). The interstitial-atom migration energy and the di-interstitial binding energy determine the probability of loop nucleation, and atomic conservation dictates the average loop size.

The distribution function of interstitial loops at 0.2, 1.0, and 1.8 dpa is shown in Fig. 5. In this calculation,

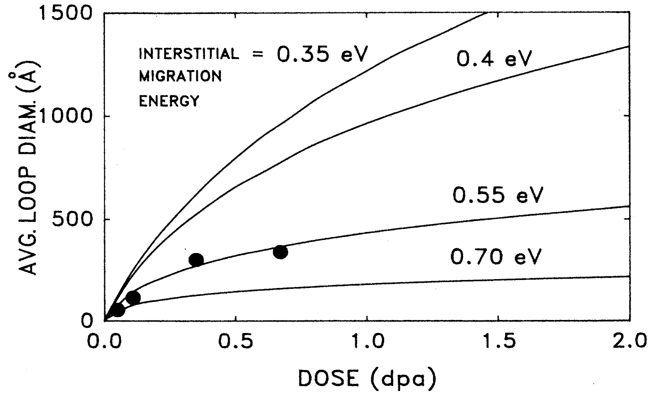

FIG. 3. Effect of the effective interstitial migration energy on the average loop diameter (——, theory; ●, experiment; dpa represents displacement per atom).

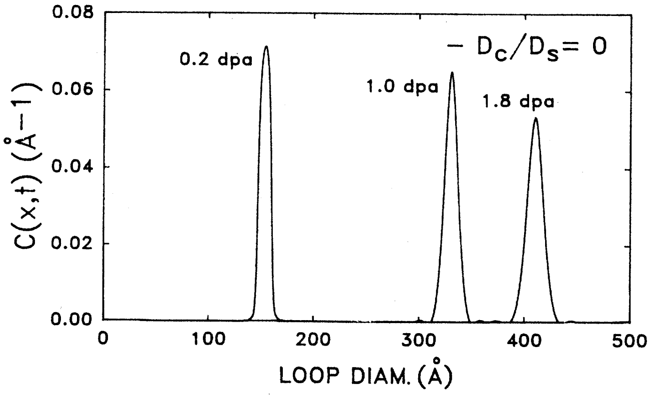

FIG. 5. Distribution function of interstitial loops at various displacement damage doses.

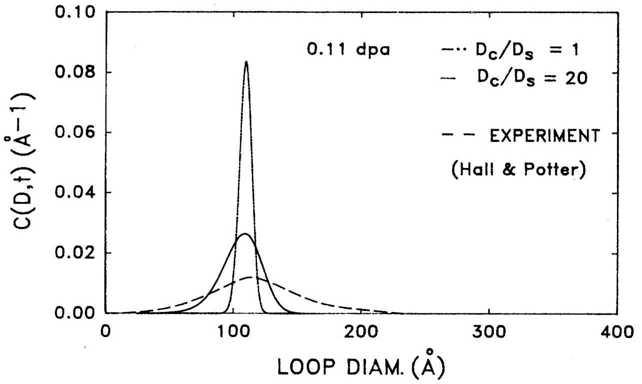

FIG. 6. Effects of cascades on the dispersion of the interstitial-loop distribution function (——, —··, theory; — — —, experiment).

only the effects of single-step transitions on the stochastic dispersion coefficient $\mathscr{D}$ are included. Comparison with the experimental data of Hall and Potter[15] shows that this may be an underestimation of the magnitude of stochastic fluctuations and that collision-cascade effects must be included.

In the following, we apply a simple model for estimating the effects of collision cascades on the dispersion coefficient and hence on the size distribution. Cascade-induced point-defect fluctuations and cascade re-solution were evaluated by Chou and Ghoniem in a series of papers.[40,41,49] In the absence of a detailed statistical treatment of the effects of such cascade-induced point-defect fluctuations on the dispersion coefficient, we will simply assume here that the cascade-induced dispersion coefficient $\mathscr{D}_{\text{CD}}+\mathscr{D}_{\text{CC}}$ is a multiple of the single-step transition dispersion coefficient. Figure 6 shows that the effects of cascades on the dispersion of the loop distribution function are significant and that the cascade-induced dispersion coefficient may be significantly larger than the single-step process coefficient. As is demonstrated in the figure, the experimental data show a much larger size dispersion than can be obtained by only single atomic transitions (i.e., small $\mathscr{D}_c$). In fact, the case $\mathscr{D}_c=0$ gives peak probability-density values which are almost an order of magnitude larger than the experimental values, as can be seen by comparing Figs. 5 and 6. As higher levels of cascade fluctuations are included (i.e., larger $\mathscr{D}_c$), the theoretical results come to close agreement with experimental observations. This behavior is an indication of the importance of the effects of cascades on the size distribution of interstitial loops.

V. CONCLUSIONS AND DISCUSSION

The nucleation phase of interstitial loops is shown to be very fast, and the transient period for loop formation is finished in about 0.001 dpa. The effects of three point-defect parameters on loop density and average size is studied by comparing theoretical calculations to experiments. As increase in the loop bias factor Z_i^l is found to increase the average loop size but has a very small effect on the total loop density. An increase in the di-interstitial binding energy E_{2i}^b increases the loop density and reduces the average diameter in a significant way. For nickel, a value of $E_{2i}^b=1.19$ eV reproduces available experimental data. The value of the effective self-interstitial migration energy has a dramatic effect on the total loop density and the loop average size. A value of $E_i^{\text{me}}=0.55$ eV shows consistency with experimental data. This is an indication that interstitial migration is hindered by atomic traps.

The distribution function of circular-planar atomic clusters, when displayed as a function of the loop diameter, is non-Gaussian. The deviation from Gaussian behavior is caused by several factors. First, the continuous nucleation of small-size clusters introduces a component of small-size clusters. Second, if the dispersion and drift functions are size dependent, higher-order additional terms are introduced as correlations to the Gaussian distribution function. Third, the assumption that the stochastic process of atomic additions to a cluster results in an instantaneous circular disk produces a transformation of the stochastic process from size space to diameter space. This transformation introduces another distortion to the distribution function.

The application of the theory to interstitial-loop formation reveals several simplifying features which are consistent with experiments. The high mobility of single interstitials and large binding energy of a di-interstitial cluster result in a rapid termination of the nucleation process, and hence nucleation-related distortions to the distribution function are nearly nonexistent. A consequence of cluster growth by diffusional accretion of single atoms or by addition of small numbers of multiple atoms from cascades is a distribution function that is nearly Gaussian in size space. Higher-order non-Gaussian corrections to the moments of the distribution function tend rapidly to zero for large $\langle x \rangle$ (or long times). This is a result of the growth law used for individual atomic clusters. Viewed from a different perspective, in the limit of large $\langle x \rangle$ and assuming no other growth mechanism to dominate (e.g., coalescence), the thermodynamic limit is attained where the ratio of the system variance to the average size tends to zero in accordance with the law of large numbers.[50]

Atomic agglomeration into interstitial loops under irradiation is affected by collision cascades. Comparisons of theoretical calculations and experiments indicate that the stochastic fluctuations in loop sizes caused by the net absorption of single interstitial atoms are not adequate to explain the wide dispersion in the distribution function. To be consistent with experimental observations additional fluctuations because of cascades must be included.

ACKNOWLEDGMENTS

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