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Diffusion-Controlled Reaction Kinetics*

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The theory of diffusion-controlled correlated reaction kinetics is developed for the radiation boundary condition (RBC) at the reaction surface. Limited only by the assumptions of purely radial spatial dependence, of a spherical reaction surface, and of continuum diffusion, these results comprise a complete solution for these kinetics. The limiting solutions are obtained for the case of the Smoluchowski boundary condition (SBC) at the reaction surface; numerical solutions are presented, as are the analytic forms of certain limiting cases. The initial recovery for the RBC is linear in time, whereas for the SBC it is well known to be proportional to the square root of time. The discussion is presented in the context of radiation damage in solids, although the results are applicable to other fast-kinetics systems, e.g., radiation and photophysics, chemistry, and biology.

I. INTRODUCTION

The treatment of diffusion-controlled reaction kinetics goes back to Smoluchowski.[1] He showed that in a system of randomly dispersed reacting species (in his case, molecules coagulating to form colloidal particles), there is an initial fast process arising from the fact that in the uniform distribution of reacting species some are very close to each other and can react with very little diffusional motions. This fast process is enhanced when the reacting species are not uniformly distributed with respect to each other but have an initial spatial correlation between reacting species. While correlated reaction kinetics is a special case of diffusion-controlled processes, it nonetheless occurs widely, since often the physical phenomena which create the reacting species produce them with a spatial correlation, and a major motivation for studying this kinetics is the elucidation of these phenomena. For example, when energetic collisions dissociate molecules or create free radicals, ion-hole pairs, electron-hole pairs, vacancy-interstitial pairs, etc., the kinetics describing the recombination (and other fate of the species) must perforce reflect the initial correlation of the particles arising from the production process. Thus such kinetics occur in many areas of physics, chemistry, biology, etc., in particular, the radiation and photosubfields. We will discuss the problem in terms of the radiation-damage example, e.g., lattice vacancy-interstitial (Frenkel) pairs; it is here that the theory has advanced furthest and received its most thorough application and testing.

Briefly, in radiation-damage experiments an energetic collision displaces a lattice atom, creating an interstitial atom and leaving behind a vacancy. The dynamics of the displacement process is generally such that the interstitial is close to the vacancy. Several regimes can be distinguished. First, the displaced interstitial can stop its outward motion at such a small distance from the vacancy that they strongly interact and immediate recombination occurs; the collision has heated the lattice, but no Frenkel pair results. Second, the interstitial may stop beyond this spontaneous-recombination volume but still come to rest in a site where it interacts statically with the vacancy; at a sufficiently low temperature the interstitial will be frozen in its site—a bound Frenkel pair exists and is termed a "close pair"; when the interstitial, say, is thermally stimulated to jump, the interaction impels the interstitial to return to its vacancy with very high probability. Third, the interstitial may come to rest beyond the close-pair volume; when the interstitial subsequently moves, it undergoes a random walk oblivious of the near presence of its own vacancy. This is precisely the regime of correlated reaction kinetics: The interstitial still has a significant probability of encountering the capture volume of its own vacancy (correlated recombination), simply because of the spatial correlation, but the interstitial also may "escape" the correlation and undergo uncorrelated recombination or other processes.

These concepts were introduced into radiation-damage literature by Fletcher and Brown,[2] who obtained approximate analytic expressions for the various stages and an outline of the more complete treatment. They considered both a continuum diffusional treatment and the numerical treatment of diffusion in a discrete lattice[3-8] by difference equations. Waite[9-15] developed the continuum theory into a mathematically sophisticated comprehensive form. He considered two boundary conditions at the recombination surface: (i) the Smoluchowski boundary condition (SBC)—the concentration of the diffusing species (interstitial) is set to zero at the boundary at the initiation of diffusion and remains zero throughout the problem; and (ii) the radiation boundary condition (RBC)—the gradient of the concentration is proportional to the concentration. The SBC leads to simpler mathematics and gives solutions which seem quantitatively applicable to experiments.[16-39] The RBC is more general, since it contains the SBC as a special case, and, physically speaking, allows for (fractional) reflection of the interstitial from the vacancy capture volume. That partial reflection can occur experimentally is implied in the Wertheim[33-39] model for defects in semiconductors and of course by the accommodation coefficient in precipitation.

Waite obtained solutions of diffusion-controlled kinetics for the SBC for the case of a uniform initial distribution of reacting species and for the case of an initially correlated distribution; he also obtained the solution for the RBC for a uniform distribution. We present the solution for the RBC for an initially correlated distribution.

In Sec. II we review the elements of the Waite formulation. In Sec. III we obtain separately the solutions for the correlated recovery and for the uncorrelated recovery; in Sec. IV we obtain the full solution for both correlated and uncorrelated recovery. Section V contains the concluding discussion.

II. ELEMENTS OF WAITE FORMALISM

The probability of finding an interstitial at a given position in the irradiated crystal will depend, in general, on the locations of the vacancies in its proximity. Hence the rate of change of defect concentration will depend in an average way on the joint probability that an interstitial is in an element of volume at some position and that a vacancy is in another element of volume at some other position at the same time. More precisely, the quantity of interest in the Waite theory[9,10] is the probability that the ith vacancy is in dV_i at $\vec{r}_i$ at time t *and* the jth interstitial is in dV_j at $\vec{r}_j$ at time t, which is denoted as

$$\rho_{ij}(\vec{r}_i,\ \vec{r}_j;\ t)\, dV_i\, dV_j\ . \qquad (2.1)$$

The functions ρ_{ij} are probability densities in the six-dimensional hyperspace spanned by the set of ordered pairs $(\vec{r}_i, \vec{r}_j)$. In a given elemental hypervolume $dV_i dV_j$, the time rate of change of ρ_{ij} is due, in part, to the next flux of probability current through the bounding hypersurface and, in part, to the probable rate of recombination of the ith vacancy with all interstitials in dV_i and of the jth interstitial with all vacancies in dV_j. As Waite demonstrates, the ρ_{ij} then satisfy

$$D_V \nabla_i^2 \rho_{ij} + D_I \nabla_j^2 \rho_{ij} + f_{ij}(t)\rho_{ij} = \partial_t \rho_{ij}\ , \qquad (2.2)$$

where the $f_{ij}(t)$ act as time-dependent chemical rate-of-reaction coefficients; D_V and D_I are the vacancy and interstitial diffusion constants.

The Frenkel pairs produced in electron irradiation in the MeV energy range are randomly distributed throughout the sample, which we otherwise assume to be homogeneous. The spatial dependence of the ρ_{ij} can thus be completely described by the coordinates

$$\vec{r} = \vec{r}_j - \vec{r}_i\ . \qquad (2.3)$$

We will assume without loss of generality that the interstitial is the migrating species. Letting $D = D_I$ and employing (2.3), we write (2.2) as

$$D\nabla^2 \rho_{ij}(\vec{r},\ t) + f_{ij}(t)\rho_{ij}(\vec{r},\ t) = \partial_t \rho_{ij}(\vec{r},\ t)\ . \qquad (2.4)$$

An additional assumption made in the Waite calculation is that there is spherical symmetry about each vacancy; i.e., the capture surface is a sphere and the distribution function is a function of radius only. While this hypothesis is of dubious validity,[7] the gross features of the recovery process may not be very sensitive to the symmetries of the damaged material, and we shall take spherical symmetry as approximate. If the recombination surface is a sphere of radius r_0, then with Waite we can write

$$f_{ij}(t) = -4\pi r_0^2 D\left(\frac{N_V^0}{C_V} \sum_{k\neq j}^{N_I^0} (\partial_r \rho_{ik})_{r_0} + \frac{N_I^0}{C_I} \sum_{m\neq i}^{N_V^0} (\partial_r \rho_{mj})_{r_0}\right) \qquad (2.5)$$

and

$$\frac{dC_I}{dt} = \frac{dC_V}{dt} = -4\pi r_0^2 D \sum_{i=1}^{N_V^0} \sum_{j=1}^{N_I^0} (\partial_r \rho_{ij})_{r_0}\ , \qquad (2.6)$$

where C_I and C_V are the macroscopic concentrations of interstitials and vacancies, respectively, and N_I^0 and N_V^0 are the corresponding initial numbers. Equation (2.6) indicates the precise manner in which the defect concentration is related to the joint probability functions. Of course, to evaluate (2.6) it is necessary to solve (2.4); the system given by (2.4) and (2.5) forms a set of coupled equations which, from a mathematical point of view, may present a formidable problem. We will return to this point later.

A formal solution to (2.4) can readily be achieved by the substitution

$$\rho_{ij}(r,\ t) = \frac{w_{ij}(r,\ t)}{r} \exp \int_0^t f_{ij}\, dt'\ . \qquad (2.7)$$

The task then focuses on solving the simple one-dimensional diffusion equation

$$D\partial_r^2 w_{ij}(r,\ t) = \partial_t w_{ij}(r,\ t)\ , \qquad (2.8)$$

with appropriate boundary conditions. Since all of the spatial variation of ρ_{ij} is contained in w_{ij}/r, we designate w_{ij} as the *principle function*. In what follows, we concentrate mainly on developing expressions for principle functions compatible with a variety of boundary and initial conditions.

For the physical circumstances with which we are interested, the ith vacancy and ith interstitial will display a coupling due to spatial correlation. If the members of all the uncorrelated vacancy-interstitial pairs are related to one another in essentially the same manner (i.e., there are no distinguished pairs), there will exist two fundamentally different solutions to (2.8) reflecting spatial correlation or lack thereof. We need consider, therefore, only the two separate cases of Eq. (2.8), along with the associated boundary conditions, in which i is, and is not, equal to j. If we rewrite (2.6) in a trivial way as

$$\frac{dC_I}{dt}=\frac{dC_V}{dt}=-4\pi r_0^2 D\sum_i^{N_V^0}\left((\partial_r\rho_{ii})_{r_0}+\sum_{j\neq i}^{N_I^0}(\partial_r\rho_{ij})_{r_0}\right), \tag{2.9}$$

then, in view of the above argument, a distinction can be drawn between the two contributions to the rate-of-defect depletion on the right-hand side; the first term is due to correlated recovery, the second to uncorrelated recovery. The physical expectation is that the former will dominate during early annealing times, while the latter, because diffusion "washes out" the correlative aspects of the problem, should become the major term in the late stages of recovery.

The final point to be mentioned in this brief review of the Waite theory deals with the boundary condition imposed on solutions to (2.8) for radial separations equal to r_0. The SBC expresses the assumption that the vacancy and interstitial recombine spontaneously whenever they pass within the critical distance r_0 of each other, and requires that the probability of finding a vacancy-interstitial pair with spatial separation r_0 vanishes, i.e.,

$$\rho_{ij}(r_0,\ t)=0 \quad \text{for all } i,\ j \text{ and all } t\ . \tag{2.10}$$

Instead of demanding that recombination be inevitable at the critical approach, we may assume that it is only highly probable, and thus that there is a small but finite probability of escape from reaction. This circumstance can occur if, for instance, the recovery mechanism requires some activation energy, however small, and will certainly exist when the activation energy for recombination is comparable to or larger than activation energies for free diffusion. Waite has given boundary conditions appropriate to such a system called the *radiation boundary conditions* (RBC) in analogy with those of similar form in the problem of heat transfer.[40] Explicitly, we have

$$(\partial_r\rho_{ij})_{r_0}=\beta\rho_{ij}(r_0,\ t) \tag{2.11}$$

for all i and j, which for the principle function becomes

$$(\partial_r w_{ij})_{r_0}=\gamma w_{ij}(r_0,\ t) \tag{2.12}$$

for all i and j, where

$$\gamma=(\beta r_0+1)/r_0\ . \tag{2.13}$$

The RBC are more general than the SBC since the latter are obtainable from the former in the limit of infinite β.

III. PRINCIPLE FUNCTION

A. Correlated Recovery—Correlated Principle Function

In the previous section we indicated that the Waite model provides an analytical technique for describing the diffusion-limited regime of the recovery process. The rate of change of defect concentration given by (2.9) includes both the correlated and uncorrelated recovery contributions, though in low-temperature annealing of radiation damage in metals most of the diffusion-limited recovery (~70%) is due to correlated Frenkel pair annihilation.[17] Further, the correlated and uncorrelated processes are conceptually, as well as experimentally, separable for low defect concentrations. Hence we can begin our discussion with the investigation of the solutions to (2.8) for the case in which the vacancy-interstitial pairs are correlated via spatial proximity.

At the time of production, a given interstitial is assumed to be much closer, on the average, to the lattice site it has just vacated than to any other vacancy. It then commences to migrate through the lattice in a way much akin to a random walk. This jumping process is therefore Markovian and can be characterized by "loss of memory." As a consequence, it is probable that the interstitial will have lost its initial vacancy correlation before recombination if it has wandered a distance of the order of $(C_V^0)^{-1/3}$ (C_V^0 is the initial concentration of vacancies), that being the order of the average separation of radiation-produced vacancies; the subsequent recombination cannot be considered as part of the recovery due to correlated pairs.

If we concentrate solely on the depletion of correlated Frenkel pairs, we can approximate solutions to the full diffusion equation (2.4) without having to know the rate of loss of pairs due to competition, described by the $f_{ii}\rho_{ii}$ term, by utilizing the above argument. We assume that each vacancy is isolated with its correlated interstitial within a cell of volume $1/C_V^0$. If we replace this cell with an equivalent spherical volume $\frac{4}{3}\pi R^3$, then we can account for the loss of correlation as the interstitial passes out of the cell by requiring that the probability of finding a correlated pair separated by a distance R vanishes. This is the same as imposing the following boundary condition on Eq. (2.8):

$$w_{ii}(R,\ t)=0 \tag{3.1}$$

for all t. Thus, once the initial spatial distribution

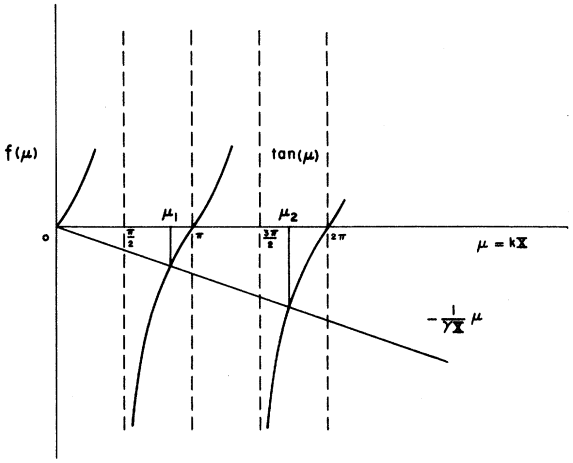

FIG. 1. Roots of $-\mu/\gamma X=\tan(\mu)$.

of correlated pairs is known, we can integrate (2.8), in principle at least, and consequently evaluate the empirically relevant relation (2.9).

We can summarize this discussion by collecting the various parts of the problem we wish to solve. Let

$$x=r-r_0 \tag{3.2}$$

and

$$X=R-r_0 ; \tag{3.3}$$

then we must solve

$$D\partial_x^2 w_{ii}(x,\ t)=\partial_t w_{ii}(x,\ t) \tag{3.4}$$

on the interval $[0,\ X]$, with conditions

$$(\partial_x w_{ii})_{x=0}=\gamma w_{ii}(0,\ t)\ , \tag{3.5}$$

$$w_{ii}(X,\ t)=0\ , \tag{3.6}$$

and

$$w_{ii}(x,\ 0)=(x+r_0)\,g_{ii}(x)\ . \tag{3.7}$$

Equation (3.7) results from the initial probability density ρ_{ii}, which we have taken to be

$$\rho_{ii}(r,\ 0)=g_{ii}(r)\ , \tag{3.8}$$

where g_{ii} is as yet unspecified.

In the interest of simplicity we will develop solutions of (3.4) utilizing the method of separation of variables. The general solution for (3.4) can be expressed as

$$w_{ii}(x,\ t)=\sum_{n=1}^{\infty} a_n e^{-k_n^2 Dt}\xi_n(x)\ , \tag{3.9}$$

where the ξ_n's form a complete set of eigenfunctions of the separated spatial equation, which when normalized on $[0,\ X]$ are

$$\xi_n(x)=\frac{\sqrt{2}k_n[\cos(k_n x)+(\gamma/k_n)\sin(k_n x)]}{[X(\gamma^2+k_n^2)-(\gamma/2k_n)\sin(2k_n X)]^{1/2}}\ . \tag{3.10}$$

The k_n are the nonvanishing roots of the transcendental equation

$$k_n=-\gamma\tan(k_n X)\ . \tag{3.11}$$

Equation (3.11) results from the boundary conditions (3.5) and (3.6). In Fig. 1 we see how these roots vary as X is changed, as we will later do. We can evaluate the coefficients a_n by implementation of the initial condition (3.7), since

$$a_n=\int_0^X w_{ii}(x,\ 0)\xi_n(x)\,dx\ . \tag{3.12}$$

At this point it is obvious that no further progress can be obtained without detailed knowledge of how the interstitials are initially distributed about their corresponding vacancies.

The form of the vacancy-interstitial distribution function should be obtained from experiment, but there are indications that its exact nature is not of crucial importance to the gross features of the Waite analysis.[15] For an initial correlation between pair members to be meaningful, a spatial cutoff is necessary; in addition, as we will see in a moment, the positions of the maxima as well as the "width" of the distribution determine the fraction of correlated pairs which eventually recombine. Beyond this, little more can be said. Originally, Waite suggested the use of a Gaussian distribution function, and others have studied various exponential[14,15] and δ-function forms.[15] In this paper we use as an initial distribution a step function. Such a distribution is not proposed to mirror physical reality in any exact sense but serves as an illustrative example for which the analytic procedures are relatively simple. At the same time, it seems likely that any physically realistic distribution can be approximated by a sum of such step functions with the resultant calculation being a slight generalization of our results.

In what follows we assume that all the various Frenkel pairs are indistinguishable. Hence we shall assume that ρ_{ii} is a function of r and t which is independent of the index i. Then the precise functional expression of our initial distribution is

$$\rho_{ii}(r,\ 0)=\eta\Theta(r;\ R_1,\ R_2) \tag{3.13}$$

or, equivalently,

$$w_{ii}(x,\ 0)=(x+r_0)\eta\Theta(x;\ X_1,\ X_2)\ . \tag{3.14}$$

The function Θ is defined as follows:

$$\begin{aligned}\Theta(x;\ X_1,\ X_2)&=1\quad\text{if } X_1\le x\le X_2\\ &=0\quad\text{otherwise}\ ,\end{aligned} \tag{3.15}$$

where $0\le X_1\le X_2\le X$ and $X_k=R_k-r_0$. The constant η is a normalization coefficient which assures that initially

$$\iint_{\substack{\text{over total}\\ \text{volume of sample}}} \rho_{ii}\, dV_i\, dV_i' = 1 \; . \qquad (3.16)$$

We are now in the position to carry through the integration in (3.12).

First we calculate the coefficient η. The function ρ_{ii} has been defined in terms of the separation coordinates (2.3), while the integrations in (3.16) are over the position coordinates of the individual pair members. If we perform the coordinate transformations

$$\vec{r} = \vec{r}_i - \vec{r}_i' \; , \quad \vec{r}\,' = \tfrac{1}{2}(\vec{r}_i + \vec{r}_i') \; , \qquad (3.17)$$

then (3.16) can be shown to reduce to

$$4\pi V \eta \int \Theta(r;\; R_1,\; R_2) r^2 dr = 1 \; , \qquad (3.18)$$

where V is the sample volume. From this η is easily seen to be

$$\eta = 3/4\pi V(R_2^3 - R_1^3) \; . \qquad (3.19)$$

Returning to (3.12), we find

$$a_n = \frac{\sqrt{2}\, k_n \eta}{[X(\gamma^2 + k_n^2) - (\gamma^2/2k_n)\sin(2k_n X)]^{1/2}} \int_{X_1}^{X_2} (x + r_0)[\cos(k_n x) + (\gamma/k_n)\sin(k_n x)]\, dx$$

$$= \frac{3\sqrt{2}}{4\pi V(R_2^3 - R_1^3)[(\gamma^2 + k_n^2)(R - r_0) - (\gamma^2/2k_n)\sin(2k_n(R - r_0))]^{1/2}}$$

$$\times \{ r[\sin(k_n(r - r_0)) - (\gamma/k_n)\cos(k_n(r - r_0))] + (1/k_n)[\cos(k_n(r - r_0)) + (\gamma/k_n)\sin(k_n(r - r_0))]\} \Big|_{r=R_1}^{R_2} \; . \qquad (3.20)$$

Our ultimate goal is to evaluate the rate equation (2.9). For correlated recovery this becomes simply

$$\frac{dC}{dt} = -4\pi r_0^2 D \beta N^0 \rho_{ii}(r_0,\; t) \; , \qquad (3.21)$$

where $C = C_I = C_V$ and $N^0 = N_I = N_V$. In writing (3.21) we have used the assumptions that the ρ_{ij} vanish, that the ρ_{ii} are all identical, and that the boundary condition (2.11) is valid. Using (3.20) in conjunction with the solution (3.9) yields

$$\frac{dC}{dt} = -\frac{6D\beta r_0 C^0}{R_2^3 - R_1^3} \sum_{n=1}^{\infty} k_n^2 e^{-k_n^2 Dt} F_n \; , \qquad (3.22)$$

with

$$F_n = \frac{\{ r[\sin(k_n(r - r_0)) - (\gamma/k_n)\cos(k_n(r - r_0))] + (1/k_n)[\cos(k_n(r - r_0)) + (\gamma/k_n)\sin(k_n(r - r_0))]\} \big|_{R_1}^{R_2}}{k_n(R - r_0)(\gamma^2 + k_n^2) - (\gamma^2/2)\sin(2k_n(R - r_0))} \; ;$$

here C^0 is the initial defect concentration. We see that this rate equation is immediately integrable: If we let

$$\phi(t) = (C^0 - C)/C^0 \; , \qquad (3.23)$$

then

$$\phi(t) = \frac{6\beta r_0}{R_2^3 - R_1^3} \sum_{n=1}^{\infty} F_n (1 - e^{-k_n^2 Dt}) \; . \qquad (3.24)$$

Equation (3.24) gives the fraction of recombined correlated defects as a function of time, when a finite correlation volume is assumed and the RBC is employed. The initial density of defects is uniform for pair separations between R_1 and R_2, and is zero everywhere else. The corresponding solution for the SBC may be obtained by taking the limit of (3.24) as β approaches infinity. In this limit the transcendental equation (3.11) has the roots

$$k_n = n\pi/(R - r_0) \, , \quad n = 1,\; 2, \ldots \qquad (3.25)$$

and (3.24) becomes

$$\phi_S(t) = \frac{6 r_0 (R - r_0)}{R_2^3 - R_1^3} \sum_{n=1}^{\infty} \left\{ \left[-r \cos\left(n\pi \frac{r - r_0}{R - r_0} \right) + \frac{R - r_0}{n\pi} \sin\left(n\pi \frac{r - r_0}{R - r_0} \right) \right] \Bigg|_{R_1}^{R_2} \Bigg/ n^2\pi^2 \right\} (1 - e^{-n^2\pi^2 Dt/(R - r_0)^2}) . \qquad (3.26)$$

We may utilize the latter expression to illustrate the comment we made previously about the characteristics of the initial distribution determining the ultimate fraction of recovery. As is shown in the Appendix, the infinite time limit of (3.26) is

$$\phi_S(\infty) = \frac{-r_0}{R - r_0} + \tfrac{3}{2} r_0 \left(1 + \frac{r_0}{R - r_0} \right) \frac{R_1 + R_2}{R_1^2 + R_1 R_2 + R_2^2} \; . \qquad (3.27)$$

The inequality string

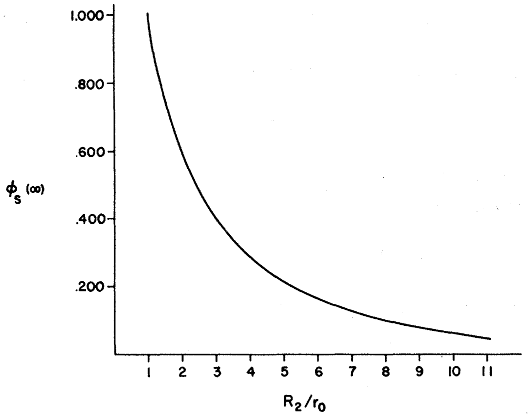

FIG. 2. Effect of the width of the initial pair separation distribution on the ultimate capture fraction. Here we have taken $R_1 = r_0$ and $R = 11r_0$.

$$r_0 \leq R_1 \leq R_2 \leq R$$

assures that

$$r_0 \frac{R_1 + R_2}{R_1^2 + R_1 R_2 + R_2^2} \leq \frac{2}{3} \ ,$$

from which it is clear that

$$\phi_S(\infty) \leq 1$$

as we expect. The equality obtains for the special case

$$r_0 = R_1 = R_2 \ ,$$

which is equivalent to a δ-function initial distribution located at r_0. This argument is in complete accord with the requirements of the SBC which declares that vacancy and interstitial combine spontaneously when separated by a distance r_0. We note that in any other case there is a finite probability of an interstitial escaping its vacancy, even in the limit of infinite dilution (i.e., even when correlation volume extends to infinity). Figures (2)-(4) further amplify how the annealed fraction depends on the width and position of the initial distribution. In Fig. 2 the effect of varying the width of the initial distribution is demonstrated. We fix R_1 to be r_0 in (3.27); $\phi_S(\infty)$ is then plotted as a function of R_2. We conclude that the broader the initial distribution, the less correlation exists, and the less correlated recovery can be expected. Next, we assume an initial δ-function distribution localized at R_i, and show the effect of centering of the distribution on the ultimate fraction of recombination. We see again that the more correlated the distribution, i.e., the closer R_i is to r_0, the greater will be $\phi_S(\infty)$. Finally, we select a δ-function distribution at $R_i = 1.5\, r_0$ and vary R to test the dependence of $\phi_S(\infty)$ on the range of correlation. As we expect, the fraction of correlated recovery is maximized by maximizing the range of correlation ($R \to \infty$).

Of possible interest is the solution of the correlated-recovery rate equation when the initial source has the form of a δ function. The δ function can be approximated by the Θ function defined in (3.15) when R_1 and R_2 are taken arbitrarily close to one another. Hence the desired result emerges directly from (3.24) when this approximation is invoked, namely,

$$\phi^\delta(t) = \lim_{R_1 \to R_2} \phi(t) \quad \text{as } R_1 \to R_2 \ . \tag{3.28}$$

If we let

$$R_1 = r_i \ , \quad R_2 = r_i + \epsilon \ ,$$

and allow ϵ to vanish, we have

$$\phi^\delta(t) = \frac{2\beta r_0}{r_i} \sum_{n=1}^{\infty} \frac{\cos(k_n(r_i - r_0)) + (\gamma/k_n)\sin(k_n(r_i - r_0))}{(R - r_0)(\gamma^2 + k_n^2) - (\gamma^2/2k_n)\sin(2k_n(R - r_0))}$$

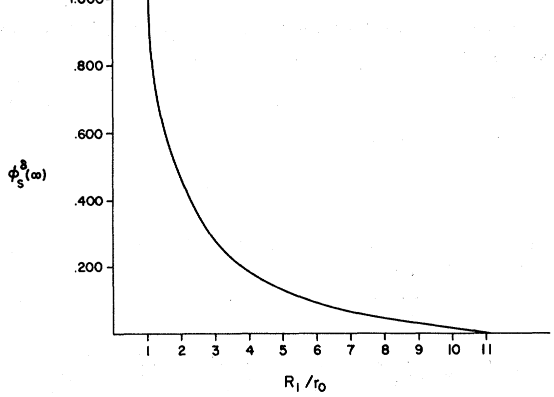

FIG. 3. Effect of the centering of the initial distribution on $\phi_s(\infty)$. Again, $R = 11r_0$, and the initial distribution is taken to be a δ function at R_i.

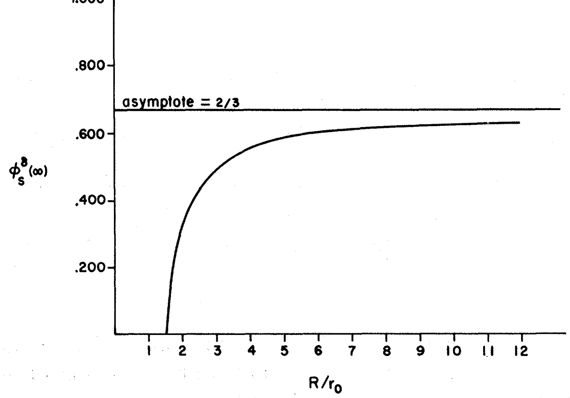

FIG. 4. Effect of the variation of the initial correlation volume on $\phi_s(\infty)$. The distribution is taken to be a δ function at $R_i = 1.5r_0$.

$$\times(1-e^{-k_n^2Dt}) \ . \qquad (3.29)$$

The corresponding Smoluchowski solution is

$$\phi_S^\delta(t)=\frac{2r_0}{r_i}\sum_{n=1}^{\infty}\frac{\sin[n\pi(r_i-r_0)/(R-r_0)]}{n\pi}$$

$$\times(1-e^{-n^2\pi^2Dt/(R-r_0)^2}) \ , \qquad (3.30)$$

which provides the asymptotic value

$$\phi_S^\delta(\infty)=\frac{r_0}{r_i}\left(\frac{R-r_i}{R-r_0}\right) \ . \qquad (3.31)$$

Of course, the same relationship is easily obtained as well from (3.27). The infinite-dilution limit of (3.31) is the well-known result r_0/r_i.

In general, we will not be interested in restricting our attention solely to the correlated phase of the recovery. The complete process includes both correlated and uncorrelated aspects, as well as competition between them, and the principle function for correlated pairs, in the diffusional analysis, is defined over the entire spatial extent of the sample (assumed to be very large compared to r_0). To determine the appropriate principle function, we allow the correlation radius R to grow without bound in the expression for the principle function that we have already derived for the case of a finite correlation volume. Again, we point out that use of the RBC in (2.9) provides the simplification that we need know only the principle function for the spatial separation r_0, i.e., only $w_{ii}(r_0, t)$ (here, and in what follows, the functions w_{ij} and ρ_{ij} will be understood to be defined over the infinite medium). If we check Fig. 1, we see that as R becomes very large the roots of (3.11) become more and more like

$$k_n=n\pi/(R-r_0)+O(R^{-2}) \ .$$

At the same time only the large-n terms in the sum (3.9) will contribute, and if we define

$$\theta=n\pi/(R-r_0) \ ,$$

then we can write

$$w_{ii}(r_0,\ t)=\frac{6}{4\pi V(R_2^3-R_1^3)}\left(\int_{\theta=0}^{\infty}d\theta\,\frac{e^{-\theta^2Dt}\{(1-\gamma r)\cos(\theta(r-r_0))+(r\theta+\gamma/\theta)\sin(\theta(r-r_0))\}}{\theta^2+\gamma^2}\right)_{r=R_1}^{R_2} . \qquad (3.32)$$

Parts of this integral are tabulated in various places[41] and with a little effort the entire integral can be evaluated. The result is

$$w_{ii}(r_0,\ t)$$

$$=\frac{3}{4\pi\gamma V(R_2^3-R_1^3)}\left[(1-\gamma r)\,\mathrm{erfc}\left(\gamma(Dt)^{1/2}+\frac{r-r_0}{2(Dt)^{1/2}}\right)\right.$$

$$\left.\times e^{\gamma^2Dt+\gamma(r-r_0)}+\mathrm{erf}\left(\frac{r-r_0}{2(Dt)^{1/2}}\right)\right]_{r=R_1}^{R_2} . \qquad (3.33)$$

For a δ-function distribution located at r_i the procedure described in the preceding paragraph yields

$$w_{ii}^\delta(r_0,\ t)=\frac{1}{4\pi Vr_i}\left[\frac{e^{-(r_i-r_0)^2/4Dt}}{(\pi Dt)^{1/2}}-\gamma\,\mathrm{erfc}\left(\gamma(Dt)^{1/2}\right.\right.$$

$$\left.\left.+\frac{r_i-r_0}{2(Dt)^{1/2}}\right)e^{\gamma^2Dt+\gamma(r_i-r_0)}\right] . \qquad (3.34)$$

For the SBC it is necessary to evaluate the gradient of the probability density at r_0 for use in (2.9) rather than the function itself. It will be helpful, therefore, to be able to express the gradient of the principle function at the recombination radius r_0, since

$$(\partial_r\rho_{ii})_{r_0}=(\partial_r w_{ii})_{r_0}\,e^{\int_0^t f_{ii}dt'}/r_0 \qquad (3.35)$$

for the SBC. Using (2.12) in conjunction with (3.33) and (3.34), and allowing β to become infinitely large, we have

$$(\partial_r w_{ii,S})_{r_0}$$

$$=\frac{3}{4\pi V(R_2^3-R_1^3)}\left[\mathrm{erf}\left(\frac{r-r_0}{2(Dt)^{1/2}}\right)-\frac{re^{-(r-r_0)^2/4Dt}}{(\pi Dt)^{1/2}}\right]_{r=R_1}^{R_2}$$

$$(3.36)$$

and

$$(\partial_r w_{ii,S}^\delta)_{r_0}=\frac{r_i-r_0}{8Vr_i}\,\frac{e^{-(r_i-r_0)^2/4Dt}}{(\pi Dt)^{3/2}} \ . \qquad (3.37)$$

B. Uncorrelated Principle Function

We turn our attention now to the uncorrelated portion of the rate-of-reaction equation (2.9). As before, we assume there are no distinguished pairs so that the ρ_{ij} are index independent. These ρ_{ij} are defined for all $r\geq r_0$ and satisfy the general diffusion equation (2.4). We assume, as is appropriate for electron irradiation, at the time of production the uncorrelated pairs are distributed randomly throughout the sample medium and hence

$$\rho_{ij}(r,\ 0)=\text{const} \ . \qquad (3.38)$$

The normalization condition (3.16) shows that this constant must be the inverse square of the sample volume. In analogy to (3.13) we can write (3.38) as

$$\rho_{ij}(r,\ 0)=\lim_{\substack{R_1\to r_0\\ R_2\to\infty}}\eta\Theta(r;\ R_1,\ R_2) \ , \qquad (3.39)$$

where

$$\eta = V^{-2} . \tag{3.40}$$

The relevant principle functions for the uncorrelated recovery can be extracted by taking the same limit in our previously derived relations (3.33) and (3.36). Thus, we have

$$w_{ij}(r_0,\ t) = \{1 + \beta r_0 \operatorname{erfc}[\gamma(Dt)^{1/2}] e^{\gamma^2 Dt}\}/\gamma V^2 \tag{3.41}$$

and

$$(\partial_r w_{ij,s})_{r_0} = \frac{1 + r_0/(\pi Dt)^{1/2}}{V^2} . \tag{3.42}$$

IV. FULL DIFFUSIONAL ANALYSIS

Our main intent in this paper, as we have stated, is to present a treatment of the diffusion-controlled recovery of Frenkel defects produced by irradiation when a nonvanishing activation energy for recombination occurs. In particular, we are concerned with the extent to which diffusion and the presence of an activation energy influence the kinetics of the recovery process. The analytic developments of the preceding section enable us to pursue this program by providing us with the necessary information to evaluate the kinetic rate equation (2.9). If we again assume that all of the ρ_{ii} are identical, as are all of the ρ_{ij} $(i \neq j)$, and that the vacancy-interstitial defects are created and annihilated in pairs (i.e., $N_I = N_V = N$, $C_I = C_V = C$), then (2.9) is

$$\frac{dC}{dt} = -4\pi r_0 D\beta N^0 [w_{ii}(r_0,\ t) e^{\int_0^t f_{ii}\, dt'} + N^0 w_{ij}(r_0,\ t) e^{\int_0^t f_{ij}\, dt'}] , \tag{4.1}$$

for the RBC.[42] Equations (3.33) and (3.41) yield the appropriate principle functions, so that the explicit formulation of the right-hand side of (4.1) lacks only the clarification of the exponential factors.

The mathematical complexity which arises from the nonlinearities involved in the f_{ij} terms [see Eq. (2.5)] can be simplified somewhat by assuming, along with Waite, that the concentration of vacancy-interstitial pairs become independent of pair separation for large separation distances. It can then be shown that ρ_{ij} condenses to

$$\rho_{ij}(r,\ t) = \frac{(C/C^0)^2 w_{ij}(r,\ t)}{r} . \tag{4.2}$$

This enables us to write

$$f_{ii}(t) = -8\pi r_0 D\beta (N^0/C^0)^2 C(t) w_{ij}(r_0,\ t) . \tag{4.3}$$

Since the absolute number of defects remaining at any given time is empirically less accessible than the number relative to that at time zero, we define the fraction of remaining pairs by

$$\Phi = (C^0 - C)/C^0 \tag{4.4}$$

(note that the symbol Φ refers to *all* vacancy-interstitial pairs, whereas the ϕ of Sec. III was restricted to correlated pairs), and rewrite (4.1), taking all of the above into account, as

$$\frac{d\Phi}{dz} = \left(2\pi r_0^3 z \frac{\beta r_0}{\beta r_0 + 1}\right) \left\{ \frac{3}{4\pi(R_2^3 - R_1^3)} \left[(1 - x(\beta r_0 + 1)) \operatorname{erfc}\left(\frac{\beta r_0 + 1}{2} z + \frac{x-1}{z}\right) e^{(\beta r_0 + 1)^2 z^2/4 + (\beta r_0 + 1)(x-1)} + \operatorname{erf}\left(\frac{x-1}{z}\right) \right]_{x = R_1/r_0}^{R_2/r_0} \epsilon(z) + C^0 \left[1 + \beta r_0 \operatorname{erfc}\left(\frac{\beta r_0 + 1}{2} z\right) e^{(\beta r_0 + 1)^2 z^2/4} \right] [1 - \Phi(z)]^2 \right\} , \tag{4.5}$$

where the following notation has been employed: z is a "reduced diffusion length," a dimensionless quantity defined as

$$z = (4Dt/r_0^2)^{1/2} . \tag{4.6}$$

The function $\epsilon(z)$ is the exponential incorporating (4.3),

$$\epsilon(z) = \exp\left\{ -4\pi r_0^3 C^0 \frac{\beta r_0}{\beta r_0 + 1} \int_0^z z'[1 - \Phi(z')] \times \left[1 + \beta r_0 \operatorname{erfc}\left(\frac{\beta r_0 + 1}{2} z'\right) e^{(\beta r_0 + 1)^2 z'^2/4} \right] dz' \right\} . \tag{4.7}$$

The first term on the right-hand side of (4.5) is the rate at which the recombination of correlated pairs contributes to the recovery process; the second term is due to the rate of uncorrelated pair recombination. Allowing β to be infinite in (4.5) produces the analogous rate equation in the SBC:

$$\frac{d\Phi_S}{dz} = (2\pi r_0^3 z) \left\{ \frac{3}{4\pi(R_2^3 - R_1^3)} \left[\operatorname{erf}\left(\frac{x-1}{z}\right) - \frac{2}{\sqrt{\pi}} \frac{x e^{-(x-1)^2/z^2}}{z} \right]_{x = R_1/r_0}^{R_2/r_0} \epsilon_S(z) + C^0 \left(1 + \frac{2}{z\sqrt{\pi}}\right) [1 - \Phi_S(z)]^2 \right\} . \tag{4.8}$$

Comparison of (4.5) and (4.8) reveals a clear mathematical difference in the early-time behavior of recovery for the two different boundary conditions. We consider both the dependence for $z \to 0$

and the small-z dependence. It is easily shown that

$$\lim_{z \to 0} \frac{d\Phi}{dz} = 0 \,, \tag{4.9a}$$

whereas

$$\lim_{z \to 0} \frac{d\Phi_S}{dz} = 4(\sqrt{\pi}) r_0^3 C^0 \quad \text{if } R_1 > r_0 \tag{4.9b}$$

$$= 4(\sqrt{\pi}) r_0^3 \left(C^0 + \frac{3}{4\pi(R_2^3 - R_1^3)} \right) \quad \text{if } R_1 = r_0 \,. \tag{4.9c}$$

A plot of experimentally derived values for the recovered fraction versus the square root of time will therefore be initially flat if the RBC is physically valid, or rise with finite slope, the value of which depends on the parameters r_0, C^0, and the placement of the initial distribution, if the SBC prevails. The difference between (4.9a) and (4.9b) or (4.9c) would seem at first glance to yield readily to such an empirical verification. As we have argued in Sec. III, however, correlation between vacancy-interstitial pairs makes reasonable sense only if $(C^0)^{-1} \gg \frac{4}{3}\pi r_0^3$. Hence in both the RBC and SBC cases the initial slope may be small. This limiting dependence carries over into the small-z dependence, however.

Consider the general distribution with $r_0 < R_1 < R_2$. For z arbitrarily close to zero, (4.5) may be expressed as

$$\frac{d\Phi}{dz} \approx \left(2\pi r_0^3 z \frac{\beta r_0}{\beta r_0 + 1} \right) \Bigg\{ \left(\frac{3}{4\pi(R_2^3 - R_1^3)} \right) \times \left(\frac{2[1 - x(\beta r_0 + 1)]}{z^2(\beta r_0 + 1) + 2(x - 1)} - \frac{1}{x - 1} \right) \frac{z e^{-(x-1)^2/z^2}}{\sqrt{\pi}} \Bigg|_{x = R_1/r_0}^{R_2/r_0} + C^0 \left[1 + \beta r_0 \operatorname{erfc}\left(\frac{\beta r_0 + 1}{2} z \right) e^{(\beta r_0 + 1)^2 z^2/4} \right] \Bigg\} \,. \tag{4.10}$$

At the onset the first part of the sum on the right-hand side will be much smaller than the second. This is because our distribution of correlated pairs has no such pair adjacent to r_0, while the uniform distribution of pairs in the sample means there is a small probability of uncorrelated interstitials being adjacent to r_0. During this period Φ grows in proportion with z^2 (linear in time) because of the annihilation of very close-lying *uncorrelated* pairs. Typically very little recovery occurs in this way. When z is such that

$$r_0 z \sim R_1 - r_0 \,, \tag{4.11}$$

then the first expression beings to contribute. Note that the amount of time associated with this z is necessary for the inner portion of the interstitial distribution to diffuse to the reaction radius r_0. If the interstitials are contained in a volume much smaller than the correlation volume $[(C^0)^{-1} \gg \frac{4}{3}\pi(R_2^3 - R_1^3)]$, then the correlated recovery term begins to dominate the right-hand side of the rate equation (4.10) after a short transition time. During this regime Φ *is still proportional to* z^2 but now the constant of proportionality is much larger. This may be *contrasted with the behavior of the* SBC *recovery equation* (4.8), which is well known to be initially such that Φ *is proportional to* z (i.e., to $\sqrt{t}$). Actually, with the distribution of interstitials chosen for this calculation, Eq. (4.8) reflects a scheme analogous to that outlined above: growth due to close-lying uncorrelated pairs, followed by growth due to correlated pairs after a time corresponding to (4.11); in both regimes, however, $\Phi_S \propto z$. Note that if β is sufficiently large, then it may be possible for

$$1 \gg z^2 \gg 2(x - 1)/(\beta r_0 + 1)$$

to be valid, and in this case the small-z dependence shows a transition from Φ proportional to z^2 to Φ proportional to z. We illustrate this by the results of numerical integration of (4.5) shown in Fig. 5. In this case the distribution is chosen so that the initial interstitial distribution is exactly at the capture radius ($R_1 = r_0$), so that the only delay in the recovery is due to the boundary condition, not to diffusional delay. We see that following an initial z^2 dependence there is a portion of the recovery which is linear in z, but which does not extrapolate to the origin. As β gets larger, the z^2 region gets smaller while the z region becomes more pronounced and extrapolates closer to the origin. In this way as $\beta \to \infty$ the transition from the RBC dependence ($\propto z^2$) to the SBC dependence ($\propto z$) takes place.

It can be shown that the correlated and uncorre-

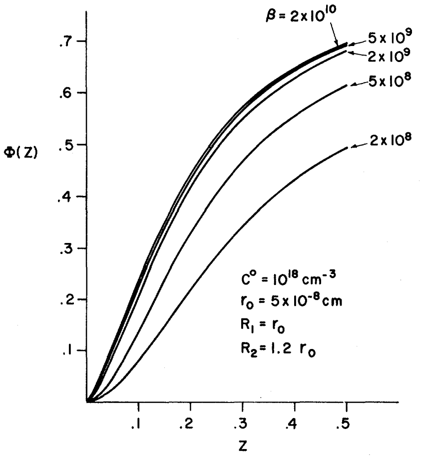

FIG. 5. Comparison of very-early-time solutions for different boundary conditions showing the progression from RBC-like (initially $\propto Z^2$) to SBC-like ($\propto Z$) as β increases.

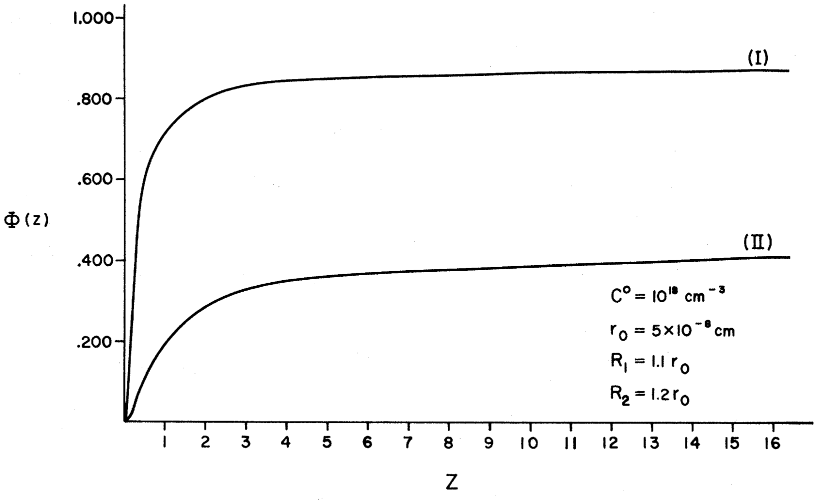

FIG. 6. Comparison of solutions for different boundary conditions: (I) for $\beta r_0 = 100$ (SBC-like), (II) for $\beta r_0 = 1$ (RBC). Both curves represent behavior in the relatively early-time regime.

lated terms in (4.5) contribute equally when

$$z^3 \sim (r_0^3 C^0)^{-1} , \qquad (4.12)$$

verifying that the length $\sim (C^0)^{-1/3}$ represents the average distance an interstitial must diffuse in order to lose the correlation it had with its vacated lattice site. Ultimately, as z becomes large compared to 1, the correlated term in (4.5) contributes negligibly and the late-time behavior is controlled by uncorrelated recovery. With $z \gg 1$, (4.5) becomes

$$\frac{d\Phi}{dz} \approx 2\pi r_0^3 C^0 z \frac{\beta r_0}{\beta r_0 + 1} (1-\Phi)^2 , \qquad (4.13)$$

so that

$$\Phi \to 1 - \left(\pi r_0^3 C^0 \frac{\beta r_0}{\beta r_0 + 1} z^2 \right)^{-1}$$

when

$$z \gg (r_0^3 C^0)^{-1} .$$

For the purposes of further illustration, we have numerically integrated (4.5) and displayed the results in Figs. 6–8. We set the interaction radius to be $r_0 = 5 \times 10^{-8}$ cm, and the initial correlated interstitial distribution was taken to be uniform in a thin spherical shell ranging from $R_1 = 1.1 r_0$ to $R_2 = 1.2 r_0$ about each vacancy, in all plots. In Figs. 6 and 7 we compare the theoretical annealing histories for a system in which the SBC is approximately valid with one in which there exist typical RCB parameters. In particular, curve I is SBC-like ($\beta r_0 = 100$), while curve II is RBC-like ($\beta r_0 = 1$). Figure 6 shows the early-time behavior of this annealing: Φ_{I} is seen to rise sharply from zero to its correlation asymptote of about 85%, while Φ_{II} rises much more leisurely and takes on a lower asymptote (~40%). For the first 50% or so Φ_{I} is almost linear (after a small z^2 region), agreeing with our expectation for Smoluchowski behavior; Φ_{II} is initially flat and has practically no linearity prior to the

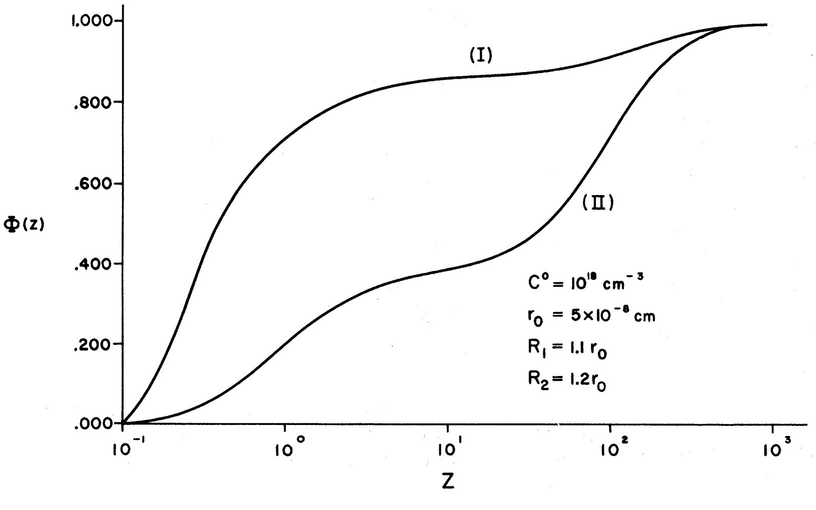

FIG. 7. Comparison of solutions for different boundary conditions over four decades in z: (I) for $\beta r_0 = 100$, (II) for $\beta r_0 = 1$.

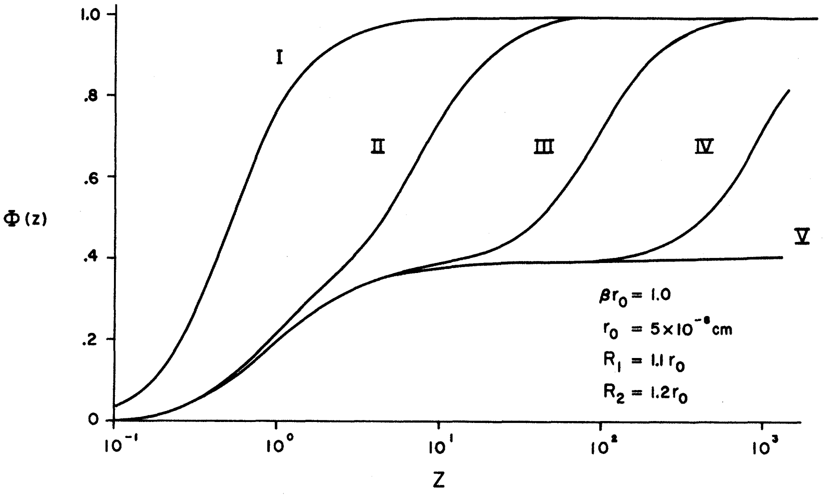

FIG. 8. Effect of the initial concentration on recovery. Curves I–V represent a family of theoretical recovery curves for different concentrations, all other parameters being fixed: $C_{\mathrm{I}}^0 = 10^{22}\ \mathrm{cm}^{-3}$, $C_{\mathrm{II}}^0 = 10^{20}\ \mathrm{cm}^{-3}$, $C_{\mathrm{III}}^0 = 10^{18}$, cm^{-3}, $C_{\mathrm{IV}}^0 = 10^{16}\ \mathrm{cm}^{-3}$, $C_{\mathrm{V}}^0 = 10^{14}\ \mathrm{cm}^{-3}$.

correlation limit. Figure 7 includes virtually all of the annealing history for these two systems. In each curve two distinct epochs can be differentiated corresponding to correlated and uncorrelated recovery. An obvious correlation asymptote is observed for Φ_{I}, while for Φ_{II} this characteristic is much less clear. The physical reason for this disparity resides in the fact that the RBC enhances the probability of the interstitial escaping its correlated vacancy, and hence diminishes the sense to which correlation can be ascribed to Frenkel pairs. As a consequence, uncorrelated recombination contributes all along II in higher proportion than along I.

In Fig. 8 we fix β so that $\beta r_0 = 1$ and plot a family of curves generated by varying the initial defect concentration from a few percent to less than one part per billion. For the sample in which the heaviest damage was assumed (I), we see a very uniform curve corresponding to a single epoch. The conclusion to be drawn is that the copious initial supply of pairs caused correlation to be meaningless and the entirety of I is accountable in terms of uncorrelated recovery. A two-order-of-magnitude diminution of defect concentration in II results in observable correlative effects, manifest in a slight but noticeable change in curvature between $z = 1$ and $z = 10$. Smaller initial concentrations, and thus larger correlation volumes, yield (in III and IV) the two-regime behavior noted previously. The onset of uncorrelated recovery is more and more postponed on account of the increase in average time necessary for the interstitial to diffuse out of its region of correlation. In fact, so great is the correlation volume in V that, for the time scale plotted, no uncorrelated recovery is detectable.

V. SUMMARY

In this paper we have developed the theory of diffusion-controlled correlated reaction kinetics for the case of the RBC at the reaction surface, i.e., allowing partial reflection of the reacting species at this surface. The results are parametrized by a constant (β) which characterizes the degree of the reflection reaction at that surface. As such the results are quite general, containing as a limiting case the results for no reflection—the SBC. Within the confines of the relatively nonrestrictive assumptions made herein, the results constitute then *the complete solution for this type of kinetics*; the substantive assumptions are that the spatial character of the problem is purely radial with the reaction surface a sphere and that diffusion is treated in the continuum.

As with others before us, the results are not obtained in closed form but as a differential equation requiring numerical integration. Solutions were obtained which illustrated the major features of the problem. For example, depending upon the value of β, the RBC results do still exhibit the effects of correlated recovery, e.g., a portion of the recovery definably correlated and distinct from the uncorrelated, but, over-all, as reflection at the reaction surface becomes important, it tends to diminish correlated reaction and enhance uncorrelated reactions and interactions.

Where appropriate, we have obtained limiting cases of the functional dependence of the solution. For example, for small recovery times we find that the RBC results indicate an initial recovery proportional to time, whereas the well-known SBC result is proportional to the square root of time.

In the numerical examples here we have restricted our consideration to a constant value of β. Depending upon the physical origin of β this may be correct and will certainly be approximately correct where the reflection process is not the dominant rate-limiting process. For example, in the case of the vacancy interstitial in a solid we expect that the reaction surface for free interstitial migration may contain *within* it several metastable close-pair sites; capture of a freely migrating interstitial into these sites would give a very high probability of interstitial-vacancy recombination but would have a small, largely temperature-independent, reemission (reflection) probability. We should note here, however, that one possible origin of a reflection at the recombination surface is a possible barrier to recombination. In that case, thermal activation over the barrier would result in a temperature-dependent β. The equations we present in this paper are correct and applicable for $\beta(T)$, but comparison of theory to data becomes more involved. This is because, in general, experiments are not feasible over four decades of z or eight decades in time, so the experimenter accelerates the process by going to higher temperatures; for a constant β the kinetics simply scale through the temperature dependence of z; if $\beta = \beta(T)$, an additional complication arises, but we will defer illustration of this to a subsequent paper.

In this paper we have not treated experimental results, being content here to discuss the mathematics and general features of the problem. The SBC results, of course, have had their most extensive test in the low-temperature recovery of electron-irradiated copper; in a subsequent paper we will reconsider those data in the light of the results of this paper. The field of fast-reaction kinetics is rapidly developing, and we trust that this theory will stimulate experimentation which will elucidate further the radiation and photosubfields of physics, chemistry, and biology.

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APPENDIX

The infinite time limit of Eq. (3.26) requires us to consider sums of the form

$$S_1(x) = \sum_{n=1}^{\infty} \frac{\cos(nx)}{n^2} \qquad \text{(A1)}$$

and

$$S_2(x) = \sum_{n=1}^{\infty} \frac{\sin(nx)}{n^3} \qquad \text{(A2)}$$

before evaluation of $\phi_S(\infty)$ is possible. It is clear that

$$S_2(x) = \int_{x'=0}^{x} S_1(x')\, dx' \ , \qquad \text{(A3)}$$

so that the evaluation of S_1 suffices, in principle, to solve the problem. We note that

$$\frac{dS_1}{dx} = -\sum_{n=1}^{\infty} \frac{\sin(nx)}{n} \ . \qquad \text{(A4)}$$

This sum is tabulated[43] and results in

$$S_1(x) - S_1(0) = \tfrac{1}{2} \int_0^x (x' - \pi)\, dx' \qquad \text{(A5)}$$

or

$$S_1(x) = \tfrac{1}{6}\pi^2 - \tfrac{1}{2}\pi x + \tfrac{1}{4}x^2 \ . \qquad \text{(A6)}$$

From this it easily follows that

$$S_2(x) = \tfrac{1}{6}\pi^2 x - \tfrac{1}{4}\pi x^2 + \tfrac{1}{12}x^3 \ . \qquad \text{(A7)}$$

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Dilatometric and X-Ray Thermal Expansion in Noncubic Crystals. I. Role of Dislocation Climb[*]

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Comparison of macroscopic (dilatometric) and microscopic (x-ray) precision thermal-expansion measurements at elevated temperatures has been widely used to obtain the equilibrium concentration of vacancies in cubic crystals. For noncubic crystals these measurements must be made in more than one orientation (e.g., in axial crystals, along both the c and a axes). Such measurements give information not only on the equilibrium vacancy concentration, but also on the relative rates of climb of the various dislocations in the crystal, which act as sources and sinks for the vacancies. Quantitative expressions are obtained for the ratio Δ_c/Δ_a, where Δ is the difference between fractional macroscopic and microscopic linear expansions along the c or a direction in an axial crystal. Consideration is given to the two extreme cases of dislocation climb, viz., the diffusion limited and climb-rate limited cases. An important point is that the measurements, in general, will be sample dependent, so that the samples of different orientation must be taken from the same single crystal.

I. INTRODUCTION

The use of precision thermal-expansion measurements, both macroscopic (dilatometry) and microscopic (x-ray lattice parameters), for determining the equilibrium vacancy concentration in cubic crystals is well known.[1–8] It has been widely used to obtain the concentrations of vacancies in thermal equilibrium in fcc metals (e.g., Al, Ag, Au, and Pb) and more recently in bcc alkali metals (e.g., Na and Li). The extension of such measurements to noncubic (specifically, hexagonal) crystals was recently reported.[9,10] We shall see that such studies of noncubic crystals offer the opportunity to obtain information about the sources and sinks for the vacancies, which could not be obtained in the case of cubic crystals. The present paper explores the theory behind such measurements, while the following paper (paper II) will apply this theory to a detailed study of single crystals of cadmium.

The determination of point-defect concentrations from thermal-expansion measurements derives from the relation

$$V = Nv , \tag{1}$$

which relates the volume V of a specimen to the average volume v of a unit cell, where N is the number of unit cells. If N is unchanged on heating the crystal from temperature T_0 to temperature T, and if the volumes at T_0 are V_0 and v_0, and those at T are V and v, respectively, then $\delta V/V_0 = \delta v/v_0$, where

$$\delta V = V - V_0 ,$$