

A COMBINED DISSOCIATIVE AND KICK-OUT DIFFUSION MODEL WITH CHARGE EFFECTS, PART I: IN-DIFFUSION

By

J.R. KING

School of Mathematical Sciences, University of Nottingham

and

M.G. MEERE*

Department of Mathematical Physics, National University of Ireland, Galway

[Received 19 May 1999. Read 30 November 2000. Published 30 August 2002.]

ABSTRACT

In this paper we propose a new model for impurity diffusion in compound semiconductors. The model incorporates both the kick-out and the dissociative mechanism, as well as charge effects; the resulting system includes as limit cases many models that have previously appeared in the literature. An initial–boundary value problem that models surface source in-diffusion conditions is then considered. The model is studied using a combination of asymptotic and numerical techniques. In particular, the transition from dissociative to kick-out behaviour is analysed, with some noteworthy features of the solutions being highlighted in a number of regimes, including a novel class of moving boundary problems.

1. Introduction

1.1. *The model*

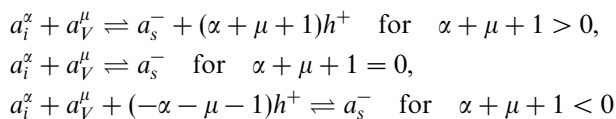
In this paper we propose and study a model for the diffusion of impurities in compound semiconductors. This paper is the first of a pair, in-diffusion boundary and initial conditions being studied here, with out-diffusion conditions being considered in the second part (J.R. King and M.G. Meere, in this volume, pp 79–105, hereafter ‘Part II’). The model consists of a combined dissociative and kick-out diffusion mechanism with charge effects; a charge neutral version of the model is discussed in King and Meere [3]. While the dissociative and kick-out models with charge effects have been discussed separately a number of times (see, for example, Tuck [9], Yu *et al.* [12] and references therein), we believe the current paper to be the first to formulate and analyse a model for their combined effect. There is good evidence that a rather complex combination of diffusion mechanisms may underpin the behaviour of many impurity/semiconductor systems, and it is hoped that the model presented here is flexible enough to describe a wide range of them. In many cases it is unclear *a priori* which of the mechanisms is dominant, and, by pursuing an asymptotic analysis in which their contributions to the diffusion process are allowed to vary, we aim to identify features of the diffused profiles by which such

*Corresponding author, e-mail: martin.meere@nuigalway.ie

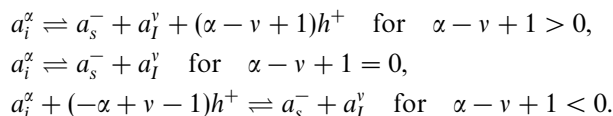
matters could be assessed experimentally. The analysis of out-diffusion in Part II provides a complementary set of such indicators. A particular result of the analysis is that in many cases the differences in observed behaviour between the mechanisms may be somewhat subtle, and we indicate features that should be identified if such differences are to be discerned in experimental profiles.

We now give a brief description of the combined mechanism. In this model it is assumed that an impurity atom can exist in either an interstitial state or a substitutional state. Moreover, it is assumed that the diffusivity of the impurity in the substitutional state is negligible, so that the impurity can move through the crystal lattice only in its interstitial form. An impurity atom can switch from substitutional to interstitial either by leaving the lattice site to become interstitial, leaving behind a vacancy, or by being knocked onto an interstitial site by an interstitial host atom (a self-interstitial). The reverse processes are also allowed. In the pure dissociative mechanism a substitutional impurity atom diffuses by first occupying an interstitial site, diffusing interstitially, and then returning to the substitutional state by occupying a vacant lattice site. In the pure kick-out mechanism a substitutional impurity atom can diffuse by first being knocked onto an interstitial site by a self-interstitial, diffusing interstitially, and then returning to the substitutional state by knocking a host atom onto an interstitial site. In the combined mechanism an impurity atom can change between substitutional and interstitial states by either of these mechanisms. The diffusion mechanisms are illustrated schematically in Fig. 1.

We denote by a_i^α , a_s^- , a_V^μ , a_I^v and h^+ an interstitial impurity atom, a substitutional impurity atom, a vacancy, a self-interstitial and a hole, respectively. Here, we have denoted by α the charge on the interstitial impurity atoms, by μ the charge on the vacancies and by v the charge on the self-interstitials. The substitutional impurity atoms are fixed to be singly negatively charged (the corresponding model for singly positively charged impurity atoms is mathematically identical). We can now represent the dissociative mechanism by



and the kick-out mechanism by



For brevity we initially take $\alpha + \mu + 1 > 0$ and $\alpha - v + 1 > 0$; the appropriate formulation for the other cases should then be clear. We note that in any case the holes in each of the reactions could be replaced by electrons on the other side of the reaction (or by appropriate combinations of the two); since the model with which we work (see (1.6) below) involves reaction equilibrium, such changes have no influence on the results. Our eventual assumptions of reaction equilibrium also

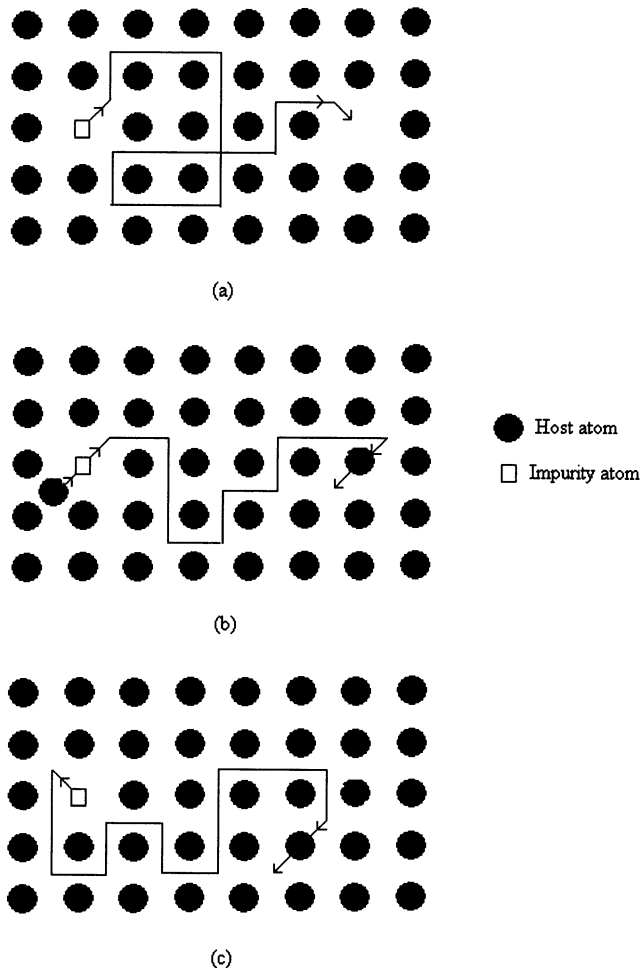
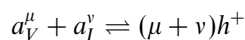


FIG. 1—(a) The dissociative mechanism. A substitutional impurity atom becomes interstitial by occupying a vacant interstitial site. It then diffuses interstitially before occupying a vacant lattice site. (b) The kick-out mechanism. A substitutional impurity atom becomes interstitial by knocking a host atom onto an interstitial site. It then diffuses interstitially before returning to the substitutional state by knocking a host atom into an interstitial site. (c) One example of how an impurity atom can diffuse via the combined mechanism. A substitutional impurity atom becomes interstitial by occupying a vacant interstitial site. It then diffuses interstitially before returning to the substitutional state by forcing a host atom into an interstitial site.

mean that it is not necessary to account separately for the reaction



(if $\mu + \nu \geq 0$), in which a self-interstitial annihilates a vacancy (or an I-V pair is created); equilibrium of the kick-out and dissociative reactions, together with

the principle of detailed balance, ensure that this reaction is necessarily also in equilibrium (cf. [3]).

If we denote by $s(x, t)$, $i(x, t)$, $V(x, t)$, $I(x, t)$ and $p(x, t)$ the concentrations of substitutional impurity, interstitial impurity, vacancies, self-interstitials and holes, respectively, at distance x into the crystal and at positive time t the governing system of partial differential equations is

$$\begin{aligned}
 \frac{\partial s}{\partial t} &= -k_{dL}s p^{\alpha+\mu+1} + k_{dR}iV - k_{kL}sIp^{\alpha-\nu+1} + k_{kR}i, \\
 \frac{\partial i}{\partial t} &= k_{dL}s p^{\alpha+\mu+1} - k_{dR}iV + k_{kL}sIp^{\alpha-\nu+1} - k_{kR}i + D_i \frac{\partial}{\partial x} \left(\frac{\partial i}{\partial x} - \alpha \frac{i}{p} \frac{\partial p}{\partial x} \right), \\
 \frac{\partial V}{\partial t} &= k_{dL}s p^{\alpha+\mu+1} - k_{dR}iV + D_V \frac{\partial}{\partial x} \left(\frac{\partial V}{\partial x} - \mu \frac{V}{p} \frac{\partial p}{\partial x} \right), \\
 \frac{\partial I}{\partial t} &= -k_{dL}sIp^{\alpha-\nu+1} + k_{kR}i + D_I \frac{\partial}{\partial x} \left(\frac{\partial I}{\partial x} - \nu \frac{I}{p} \frac{\partial p}{\partial x} \right), \\
 p &= \frac{1}{2} \left(s - \alpha i - \mu V - \nu I + \sqrt{(s - \alpha i - \mu V - \nu I)^2 + 4n_i^2} \right). \tag{1.1}
 \end{aligned}$$

Here k_{dL} , k_{dR} are the reaction constants for the dissociative mechanism, k_{kL} , k_{kR} are those for the kick-out mechanism, and n_i is the intrinsic carrier concentration. We note two combinations that we use in the subsequent analysis, namely

$$\begin{aligned}
 \frac{\partial}{\partial t}(s + i) &= D_i \frac{\partial}{\partial x} \left(\frac{\partial i}{\partial x} - \alpha \frac{i}{p} \frac{\partial p}{\partial x} \right), \\
 \frac{\partial}{\partial t}(V - I + s) &= D_V \frac{\partial}{\partial x} \left(\frac{\partial V}{\partial x} - \mu \frac{V}{p} \frac{\partial p}{\partial x} \right) - D_I \frac{\partial}{\partial x} \left(\frac{\partial I}{\partial x} - \nu \frac{I}{p} \frac{\partial p}{\partial x} \right), \tag{1.2}
 \end{aligned}$$

the first of which expresses conservation of impurity and the second conservation of host (semiconductor) atoms, whose concentration is given by $L - V - s + I$, where the constant L denotes the density of lattice sites.

The $\partial p/\partial x$ terms appearing in equations (1.1)₂, (1.1)₃ and (1.1)₄ are sometimes referred to as drift terms and are due to the electric field produced by the charge carriers. We briefly indicate the derivation of the drift term appearing in equation (1.1)₂. The usual form for such a term is (see, for example, [7])

$$\frac{\partial}{\partial x} \left(\alpha \mu_i i \frac{\partial \psi}{\partial x} \right), \tag{1.3}$$

where μ_i is the mobility of the interstitial impurity atoms and ψ is the electrostatic potential. The mobility μ_i and the interstitial diffusivity D_i are related by Einstein's relationship

$$\mu_i = qD_i/\kappa T,$$

where q is the electron charge, κ is Boltzmann's constant and T is the temperature.

It is assumed that the holes follow a Boltzmann distribution, so that

$$p = n_i \exp(-q\psi/\kappa T).$$

If we use these last three equations, the quoted form for the drift term easily follows, the derivations for the other such terms being similar.

The expression (1.1)₅ for the holes follows from the electron-hole equilibrium equation, $np = n_i^2$ (where n is the electron concentration), together with the assumption that the semiconductor is charge neutral, so that

$$p + \alpha i + \mu V + \nu I = n + s. \quad (1.4)$$

We simplify the governing equations considerably by assuming that both the dissociative and the kick-out reaction are in equilibrium. Mathematically, this means that the reaction constants k_{dL} , k_{dR} and k_{kL} , k_{kR} appearing in (1.1)₃ and (1.1)₄ are sufficiently large that we can assume, to leading order, that

$$k_{dL}Sp^{\alpha+\mu+1} = k_{dR}iV, \quad k_{kL}SIp^{\alpha-\nu+1} = k_{kR}i. \quad (1.5)$$

Although we have in (1.1) described cases with $\alpha + \mu + 1 > 0$, $\alpha - \nu + 1 > 0$, it is easily seen that the reduced model (1.2), (1.5), in which reaction equilibria hold, is valid without these constraints.

We can now present the complete system of equations that is analysed in this pair of papers, namely

$$\begin{aligned} k_{dL}Sp^{\alpha+\mu+1} &= k_{dR}iV, \quad k_{kL}SIp^{\alpha-\nu+1} = k_{kR}i, \\ \frac{\partial}{\partial t}(s+i) &= D_i \frac{\partial}{\partial x} \left(\frac{\partial i}{\partial x} - \alpha \frac{i}{p} \frac{\partial p}{\partial x} \right), \\ \frac{\partial}{\partial t}(V-I+s) &= D_V \frac{\partial}{\partial x} \left(\frac{\partial V}{\partial x} - \mu \frac{V}{p} \frac{\partial p}{\partial x} \right) - D_I \frac{\partial}{\partial x} \left(\frac{\partial I}{\partial x} - \nu \frac{I}{p} \frac{\partial p}{\partial x} \right), \\ p &= \frac{1}{2} \left(s - \alpha i - \mu V - \nu I + \sqrt{(s - \alpha i - \mu V - \nu I)^2 + 4n_i^2} \right). \end{aligned} \quad (1.6)$$

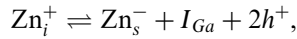
The mathematical problem is completed by specifying boundary and initial conditions, and these are discussed in Section 1.3.

1.2. *Experimental evidence*

In view of the large number of parameters appearing in the governing system, it is not possible to give an exhaustive study of all possible charge values. We restrict our attention instead to cases that are believed to be most physically relevant. Two sets of charge values are considered in this paper, for which we adopt the terminology: (I) neutral defects, in which case $\mu = \nu = 0$, $\alpha = 1$; (II) charged defects, in which case $\mu = 0$, $\nu = 2$, $\alpha = 1$. These values are motivated by existing experimental data and past modelling work on the diffusion of impurities in III-V semiconductors.

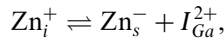
Zinc is one of the principal p-type dopants used in gallium arsenide, and much of the analysis in this paper is appropriate to the Zn/GaAs system. It is now thought that charged defects play an important role in the behaviour of this system.

However, in the original kick-out model for Zn/GaAs proposed by Gosele and Morehead [2], the self-interstitials were assumed to be neutral. The form of the kick-out mechanism adopted was



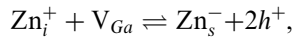
where Zn_i^+ is an interstitial zinc donor, Zn_s^- is a substitutional zinc acceptor and I_{Ga} is a neutral gallium self-interstitial; this corresponds to (I) above. They found that aspects of the behaviour of the Zn/GaAs system that could not be explained using the dissociative mechanism could then be satisfactorily explained within the context of the kick-out model.

Under p-type doping conditions, the earlier work of Winteler [10] had already indicated that doubly positively charged self-interstitials (as in (II) above) could play an important role in the diffusion mechanism. The appropriate form for the kick-out reaction is then



and this model was extensively studied by Yu *et al.* [12], who showed that it consistently explained many aspects of the diffusion behaviour. More recent work, Bosker *et al.* [1], suggests that triply charged self-interstitials (I_{Ga}^{3+}), as well as doubly charged self-interstitials, are involved in the kick-out reaction; an analysis of a model of this kind can be found in [4]. It should be noted that charged self-interstitials are also believed to be involved in the diffusion of many other species, including Cr and Be in GaAs; see [11], [12].

For the dissociative model and the Zn/GaAs system, there has been much less speculation about the value of the charge on the defects (that is, the vacancies), with most authors taking the vacancies to be neutral, as in (I) above, and representing the mechanism by



where V_{Ga} is a gallium vacancy.

One purpose of the present study is to evaluate the effect that the charged self-interstitials have on the diffusion process, by making comparison with the corresponding model with the neutral defects. This necessitates analysing both neutral defect and charged defect models, as represented respectively by (I) and (II). Even in the neutral defect case, earlier models for both the dissociative and the kick-out mechanism have frequently been in error because drift terms (notably (1.3)) have often been omitted. These terms can have a strong influence on the diffusion behaviour, and their omission changes the model fundamentally. Moreover, as we will see, the two representative cases (I) and (II) discussed here exhibit significantly different behaviour, indicating that fairly subtle features of the modelling can have a substantial effect on the results.

The diffusion behaviour of impurities in compound semiconductors is complex. The charge and type of the dominant defects can depend on the diffusion conditions and the crystal type. For example, under intrinsic conditions and for n-type crystals, triply negatively charged vacancies play an important role in the diffusion behaviour. The analysis presented in this paper is appropriate to extrinsic conditions and for

a p-type dopant, in which case the concentrations of negatively charged defects are negligible (owing to the Fermi-level effect). The corresponding results for extrinsic n-type diffusion (when concentrations of positively charged defects are negligible) can readily be deduced, however (essentially by replacing p 's by n 's in what follows). For a recent review of the role of point defects in impurity diffusion in GaAs, see Tan [8].

1.3. Boundary and initial conditions; non-dimensionalisation

For in-diffusion, the appropriate boundary and initial conditions are

$$\begin{aligned} i &= i^*, \quad V = V^* && \text{on } x = 0, \\ i &\rightarrow 0, \quad V \rightarrow V^* && \text{as } x \rightarrow +\infty, \\ i &= 0, \quad V = V^* && \text{at } t = 0, \end{aligned}$$

where V^* is the equilibrium vacancy concentration and i^* is the (constant) interstitial concentration provided by the surface source. The appropriate non-dimensionalisation depends, to some extent, on whether we are considering the neutral or the charged defect case. We begin by considering the former (case (I)) and define three positive constants s^* , I^* and p^* via the relations

$$\begin{aligned} k_{dL}s^*p^{*2} &= k_{dR}i^*V^*, \quad k_{kL}s^*I^*p^{*2} = k_{kR}i^*, \\ p^* &= \frac{1}{2} \left(s^* - i^* + \sqrt{(s^* - i^*)^2 + 4n_i^2} \right); \end{aligned}$$

throughout this paper s^* and p^* will denote the surface concentrations of s and p . We now non-dimensionalise the equations by writing

$$\begin{aligned} \bar{s} &= \frac{s}{s^*}, \quad \bar{i} = \frac{i}{i^*}, \quad \bar{V} = \frac{V}{V^*}, \quad \bar{I} = \frac{I}{I^*}, \\ \bar{p} &= \frac{p}{p^*}, \quad \bar{t} = \frac{t}{T}, \quad \bar{x} = \frac{x}{\sqrt{D_i T}}, \end{aligned} \tag{1.7}$$

where T is a representative time-scale, such as the duration of the diffusion. If we drop the overbars, the non-dimensional equations are

$$\begin{aligned} sp^2 &= iV, \quad sIp^2 = i, \\ \frac{\partial}{\partial t}(s + \lambda i) &= \lambda \frac{\partial}{\partial x} \left(\frac{\partial i}{\partial x} - \frac{i}{p} \frac{\partial p}{\partial x} \right), \\ \frac{\partial}{\partial t}(\delta V - \varepsilon I + s) &= \beta \delta \frac{\partial^2 V}{\partial x^2} - \gamma \varepsilon \frac{\partial^2 I}{\partial x^2}, \\ p &= \frac{s - \lambda i + \sqrt{(s - \lambda i)^2 + 4\varpi^2}}{1 - \lambda + \sqrt{(1 - \lambda)^2 + 4\varpi^2}}, \end{aligned} \tag{1.8}$$

subject to

$$\begin{aligned} i &= 1, \quad V = 1 && \text{on } x = 0, \\ i &\rightarrow 0, \quad V \rightarrow 1 && \text{as } x \rightarrow +\infty, \\ i &= 0, \quad V = 1 && \text{at } t = 0, \end{aligned} \tag{1.9}$$

where

$$\lambda = \frac{i^*}{s^*}, \delta = \frac{V^*}{s^*}, \varepsilon = \frac{I^*}{s^*}, \beta = \frac{D_V}{D_i}, \gamma = \frac{D_I}{D_i}, \varpi = \frac{n_i}{s^*}. \quad (1.10)$$

Note that it is clear from (1.7) that $s = I = p = 1$ on $x = 0$, and $s = 0, I = 1$ and $p = \theta_1$ at $t = 0$ and at $x = +\infty$, where

$$\theta_1 = \frac{2\varpi}{1 - \lambda + \sqrt{(1 - \lambda)^2 + 4\varpi^2}}$$

is in practice an extremely small (though non-vanishing) quantity.

The non-dimensionalisation needs to be modified when the self-interstitials are doubly charged (case (II)). If we denote by I^* the intrinsic equilibrium concentration of doubly charged self-interstitials, then at the semiconductor surface we take the concentration of these self-interstitials to be $I_s^* = I^*(p^*/n_i)^2$, this being an assumption of surface defect equilibrium. The three quantities s^*, I^* and p^* are now defined by

$$\begin{aligned} k_{dL}s^*p^{*2} &= k_{dR}I^*V^*, \quad k_{kL}s^*I^*(p^*/n_i)^2 = k_{kR}I^*, \\ p^* &= \frac{1}{2} \left(s^* - i^* - 2I^*(p^*/n_i)^2 + \sqrt{s^* - i^* - 2I^*(p^*/n_i)^2 + 4n_i^2} \right). \end{aligned}$$

The non-dimensionalisation is again given by (1.7), except that now the self-interstitials are scaled by I_s^* . On dropping overbars, we obtain the non-dimensional equations

$$\begin{aligned} sp^2 &= iV, \quad sI = i, \\ \frac{\partial}{\partial t}(s + \lambda i) &= \lambda \frac{\partial}{\partial x} \left(\frac{\partial i}{\partial x} - \frac{i}{p} \frac{\partial p}{\partial x} \right), \\ \frac{\partial}{\partial t}(\delta V - \varepsilon I + s) &= \beta \delta \frac{\partial^2 V}{\partial x^2} - \gamma \varepsilon \frac{\partial}{\partial x} \left(\frac{\partial I}{\partial x} - \frac{2I}{p} \frac{\partial p}{\partial x} \right), \\ p &= \frac{s - \lambda i - 2\varepsilon I + \sqrt{(s - \lambda i - 2\varepsilon I)^2 + 4\varpi^2}}{1 - \lambda - 2\varepsilon + \sqrt{(1 - \lambda - 2\varepsilon)^2 + 4\varpi^2}}, \end{aligned} \quad (1.11)$$

and these are again to be solved subject to (1.9). The dimensionless parameters are again given by (1.10), except that now $\varepsilon = I_s^*/s^*$. From (1.11) and (1.9) it is clear that $s = I = p = 1$ on $x = 0$. The behaviour at $t = 0$ and at $x = +\infty$ is slightly more complicated in the framework of this model. Since $IV = p^2$, then (using $V = 1, s = i = 0$) the dimensionless version of the charge neutrality condition (1.4) implies that at $t = 0$ and at $x = +\infty$ the value of p is determined by the positive root of the cubic

$$\frac{2I_s^*}{p^*} p^3 + p^2 - \left(\frac{n_i}{p^*} \right)^2 = 0; \quad (1.12)$$

defining this root to be θ_2 , we have at $t = 0$ and at $x = +\infty$ that $s = 0, I = \theta_2^2$ and

$p = \theta_2$, where (1.12) can be rewritten as

$$\frac{4\varepsilon}{1 - \lambda - 2\varepsilon + \sqrt{(1 - \lambda - 2\varepsilon)^2 + 4\varpi^2}}\theta_2^3 + \theta_2^2 - \frac{4\varpi^2}{\left(1 - \lambda - 2\varepsilon + \sqrt{(1 - \lambda - 2\varepsilon)^2 + 4\varpi^2}\right)^2} = 0. \quad (1.13)$$

In practice, the first term of (1.13) is negligible (since $\varepsilon, \varpi \ll 1$), so that

$$\theta_2 \sim \frac{2\varpi}{1 - \lambda - 2\varepsilon + \sqrt{(1 - \lambda - 2\varepsilon)^2 + 4\varpi^2}}; \quad (1.14)$$

this approximation is used for the numerical solutions.

1.4. Overview of the paper

The analysis in this paper becomes quite involved, with a number of different asymptotic limits needing to be considered. We therefore give a brief description here of the layout of the remainder of the paper. As already indicated, we are considering two sets of equations, each being subjected to boundary and initial conditions appropriate to in-diffusion. The systems are given by (1.8) and (1.11) and are both subject to the boundary and initial conditions (1.9). Motivated by the small values that ε and δ each typically has in practice, we consider for each of these problems three subcases, namely (i) the dissociative model, $\varepsilon = 0, \delta \rightarrow 0$; (ii) the kick-out model, $\delta = 0, \varepsilon \rightarrow 0$; (iii) transition scalings.

We should note that the solutions to the problems considered in this paper are self-similar, with

$$s = s(x/\sqrt{t}), \quad i = i(x/\sqrt{t}), \quad V = V(x/\sqrt{t}), \quad I = I(x/\sqrt{t}), \quad p = p(x/\sqrt{t}),$$

so they could be rewritten as boundary value problems for coupled systems of ordinary differential equations. However, this reformulation is not of much value in the present context, and we retain the systems in their original form; this has the benefit of making the extension of the results to more general initial-boundary value problems relatively straightforward.

2. Numerical methods

While our main focus will be on asymptotic solutions, we start by briefly describing the procedures we use to obtain complementary numerical solutions. Given our emphasis on the modelling and the asymptotic results, the numerical procedures we adopt are simple-minded but robust. Whenever we introduce a subscripted equation number in what follows, we are referring to all of the equations appearing on that line; for example, (1.8)₁ means $sp^2 = iV, sIp^2 = i$.

The method is a time-stepping procedure on a uniform mesh, with finite difference approximations being used for the derivatives. We use forward difference approximations for the first derivatives in both x and t (with the time-step chosen

to be sufficiently small that numerical stability is ensured) and central difference approximations for the second derivatives in x . For example, for the term

$$\frac{\partial}{\partial x} \left(\frac{i}{p} \frac{\partial p}{\partial x} \right) = \frac{i}{p} \frac{\partial^2 p}{\partial x^2} + \frac{1}{p} \frac{\partial i}{\partial x} \frac{\partial p}{\partial x} - \frac{i}{p^2} \left(\frac{\partial p}{\partial x} \right)^2,$$

we use a central difference approximation for $\partial^2 p / \partial x^2$ and forward difference approximations for both $\partial i / \partial x$ and $\partial p / \partial x$. It should be noted that using forward difference approximations for $\partial i / \partial x$ corresponds to upwinding, since the coefficient of $\partial i / \partial x$ when brought to the left-hand side of (1.11)₂ is the negative quantity $\lambda \partial(\ln p) / \partial x$. In the case of the neutral defect model, it is clear from (1.8)₂ and (1.8)₃ that we have time-stepping procedures for updating $s + \lambda i$ and $\delta V - \varepsilon I + s$. If we use these, together with the three algebraic equations (1.8)₁ and (1.8)₄, it would then, in principle, be possible to obtain the updated values for all five species s, i, p, I, V . However, this approach requires the numerical solution of algebraic equations at each point and for each time-step, which is undesirable from a computational point of view. We choose instead to use the following, simpler procedure.

Equations (1.8)₁ arose from assuming both the dissociative and the kick-out reaction to be in equilibrium. Had we not made this assumption, we would have obtained an equation for s of the dimensionless form

$$k_1 \frac{\partial s}{\partial t} = -sp^2 + iV + k_2(-sIp^2 + i), \quad (2.1)$$

where k_1, k_2 are dimensionless parameters with $k_1 \ll 1$ in practice. However, retaining the k_1 term in (2.1), we can use it in our numerical procedure to update the values for s at each time-step. In the numerical computations, we used the value $k_1 = 0.0001$; the value of k_2 is unimportant and was often taken to be zero in the numerical calculations. We now have time-stepping procedures for $s + \lambda i$, $\delta V - \varepsilon I + s$ and s , and so, if we use these, together with the relation $IV = 1$ and (1.8)₄, it is straightforward to obtain the updates for all five species, with no numerical solution of algebraic equations required.

The procedure for the charged defect model is similar but with an added complication. The stepping procedures for $s + \lambda i$, $\delta V - \varepsilon I + s$ and s follow as before, but the resulting algebraic relations now need to be solved numerically. We avoid this difficulty by retaining expression (1.8)₄ for the holes (as opposed to using (1.11)₄). The εI terms can in fact make a leading order contribution to the expression for the holes in the limit $\varepsilon \rightarrow 0^+$, as the forthcoming asymptotic analysis will reveal, so this simplification does involve some loss of accuracy. However, it does not affect the structure of the asymptotic solution as $\varepsilon \rightarrow 0^+$, and so the numerical profiles have the correct qualitative (and in most cases quantitative) form. In particular, the εI terms do not make a leading order contribution to p near the right edge of the support for s (see below), which is where much of the interesting behaviour is observed. In [12] both the λi and the εI terms are neglected in the expression for p , but the subsequent numerical calculations for that kick-out model still have the correct qualitative appearance.

As will shortly become clear, within the asymptotics many of the reduced prob-

lems cannot be solved analytically, so the numerical solutions play an important complementary role in illustrating the solution behaviour, as well as in providing validation for the asymptotics. In turn, the asymptotic analysis is helpful in guiding the choice of parameter values in the numerical studies and in providing a considerable amount of both qualitative and quantitative information about the differences in behaviour between the various mechanisms.

3. The neutral defect case

In this section we consider the model in which both the self-interstitial and the vacancy defects are neutral, the appropriate non-dimensional equations being given by (1.8). We present some asymptotic and numerical solutions and describe the transition from pure dissociative to pure kick-out behaviour.

The appropriate boundary and initial conditions are now given by (1.9). Before considering the various limit cases, we first simplify the expression for the holes p given by (1.8)₄. The quantity $\varpi = n_i/s^*$ is extremely small in practice, and so we neglect it in the asymptotic analysis and therefore set $\theta_1 = 0$. We assume that $\lambda < 1$ (which is the case in practice), and then, for the boundary and initial conditions with which we are concerned, we have $s \geq \lambda i$ and our expression for p simplifies to

$$p = \frac{s - \lambda i}{1 - \lambda}. \quad (3.1)$$

The subsections below consider the dissociative, kick-out and combined models. The kick-out and dissociative models have been individually discussed elsewhere; see [5] and [6]. However, it is instructive to outline both of these cases briefly before considering the combined model.

3.1. Dissociative model

Setting $\varepsilon = 0$ in (1.8), we obtain

$$\begin{aligned} sp^2 &= iV, \quad p = (s - \lambda i)/(1 - \lambda), \\ \frac{\partial}{\partial t}(s + \lambda i) &= \lambda \frac{\partial}{\partial x} \left(\frac{\partial i}{\partial x} - \frac{i}{p} \frac{\partial p}{\partial x} \right), \\ \frac{\partial}{\partial t}(\delta V + s) &= \beta \delta \frac{\partial^2 V}{\partial x^2}, \\ i &= 1, \quad V = 1 \quad \text{on} \quad x = 0, \\ i &\rightarrow 0, \quad V \rightarrow 1 \quad \text{as} \quad x \rightarrow +\infty, \\ i &= 0, \quad V = 1 \quad \text{at} \quad t = 0. \end{aligned} \quad (3.2)$$

Note now that I has decoupled from the problem, being given by $I = 1/V$. A numerical solution of the in-diffusion problem for the dissociative model is plotted in Fig. 2; the plateau in the substitutional profile and the substantial depletion of vacancies (due to vacancies being occupied by impurity) are particularly noteworthy. The asymptotic structure in the limit $\delta \rightarrow 0$ for this model is discussed in [5]; this behaviour can be reproduced from results given below by setting $\sigma = 0$ in the results of case (C).

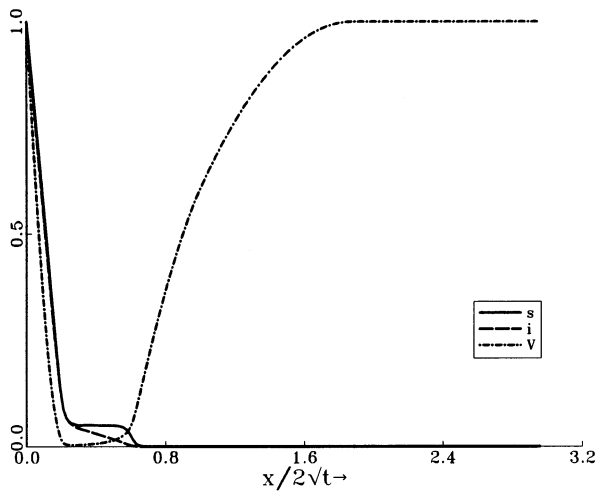


FIG. 2—Numerical solution of the dissociative model with parameter values $\delta = 0.03$, $\lambda = 0.4$, $\beta = \gamma = 1$ and $\varpi = 0.0001$.

3.2. Kick-out model

If we set $\delta = 0$ in (1.8), the system reduces to (cf. [6])

$$\begin{aligned}
 i &= sIp^2, \quad p = (s - \lambda i)/(1 - \lambda), \\
 \frac{\partial}{\partial t}(s + \lambda i) &= \lambda \frac{\partial}{\partial x} \left(\frac{\partial i}{\partial x} - \frac{i}{p} \frac{\partial p}{\partial x} \right), \\
 \frac{\partial}{\partial t}(\varepsilon I - s) &= \gamma \varepsilon \frac{\partial^2 I}{\partial x^2},
 \end{aligned} \tag{3.3}$$

which are to be solved subject to

$$\begin{aligned}
 i &= 1, \quad I = 1 \quad \text{on} \quad x = 0, \\
 i &\rightarrow 0, \quad I \rightarrow 1 \quad \text{as} \quad x \rightarrow +\infty, \\
 i &= 1, \quad I = 1 \quad \text{at} \quad t = 0,
 \end{aligned} \tag{3.4}$$

and where V has now decoupled from the problem (with $V = 1/I$). A numerical solution for the in-diffusion problem of the kick-out model is displayed in Fig. 3. The vacancies are again significantly undersaturated (with a corresponding increase of self-interstitials, these being generated by the impurity through the kick-out process); the plateau in the substitutionals is absent, however.

3.3. Transition scalings

We need to consider three distinct scalings, namely (A) $\varepsilon = O(\delta)$, (B) $\varepsilon = O(\delta^{3/2})$ and (C) $\varepsilon = O(\delta^3)$, in order to track the full transition between the purely dissociative and purely kick-out models just described. Case (A) is largely kick-out-dominated, with case (C) being largely dissociative; some pertinent numerical solutions for the

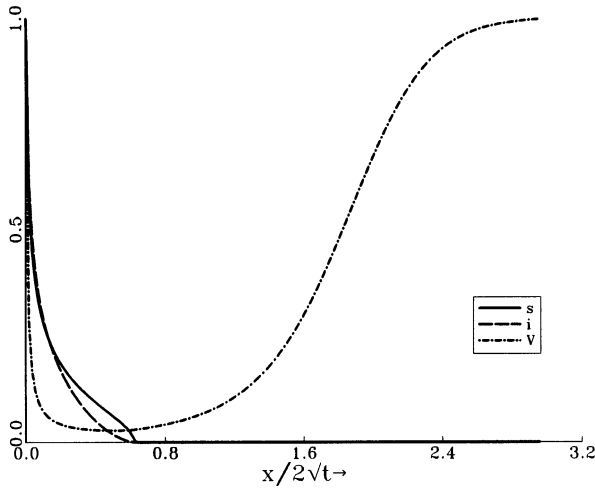


FIG. 3—Numerical solution of the kick-out model with parameter values $\varepsilon = 0.001$, $\lambda = 0.4$, $\gamma = 1$ and $\varpi = 0.0001$.

substitutionals, impurity interstitials and vacancies can be found in Fig. 4. In Fig. 5 we plot the corresponding numerical solutions for the self-interstitials, from which it is clear that the self-interstitial concentrations can be very greatly enhanced by the impurity diffusion.

(A) $\varepsilon = O(\delta)$

We write $\varepsilon = c\delta$ where $c = O(1)$, and in the limit $\delta \rightarrow 0$ the application of the method of matched asymptotic expansions requires the separate analysis of two regions, as follows.

(i) Boundary layer, $x = O(\delta^{2/3})$

If we write $x = \delta^{2/3}\hat{x}$, the appropriate scalings are

$$s \sim \hat{s}_0(\hat{x}, t), \quad i \sim \hat{i}_0(\hat{x}, t), \quad p \sim \hat{p}_0(\hat{x}, t), \quad I \sim \hat{I}_0(\hat{x}, t), \quad V \sim \hat{V}_0(\hat{x}, t),$$

giving the leading order equations

$$\begin{aligned} \hat{i}_0 &= \hat{s}_0 \hat{I}_0 \hat{p}_0^2, \quad \hat{I}_0 \hat{V}_0 = 1, \quad \hat{p}_0 = (\hat{s}_0 - \lambda \hat{i}_0)/(1 - \lambda), \\ \frac{\partial}{\partial \hat{x}} \left(\frac{\partial \hat{i}_0}{\partial \hat{x}} - \frac{\hat{i}_0}{\hat{p}_0} \frac{\partial \hat{p}_0}{\partial \hat{x}} \right) &= 0, \quad \frac{\partial^2}{\partial \hat{x}^2} (\beta \hat{V}_0 - \gamma c \hat{I}_0) = 0. \end{aligned} \tag{3.5}$$

Integrating the second-last of these equations and imposing

$$\frac{\partial \hat{i}_0}{\partial \hat{x}} - \frac{\hat{i}_0}{\hat{p}_0} \frac{\partial \hat{p}_0}{\partial \hat{x}} \rightarrow 0 \quad \text{as} \quad \hat{x} \rightarrow +\infty$$

(which is required for matching), as well as the boundary conditions $\hat{i}_0 = \hat{s}_0 = 1$ on

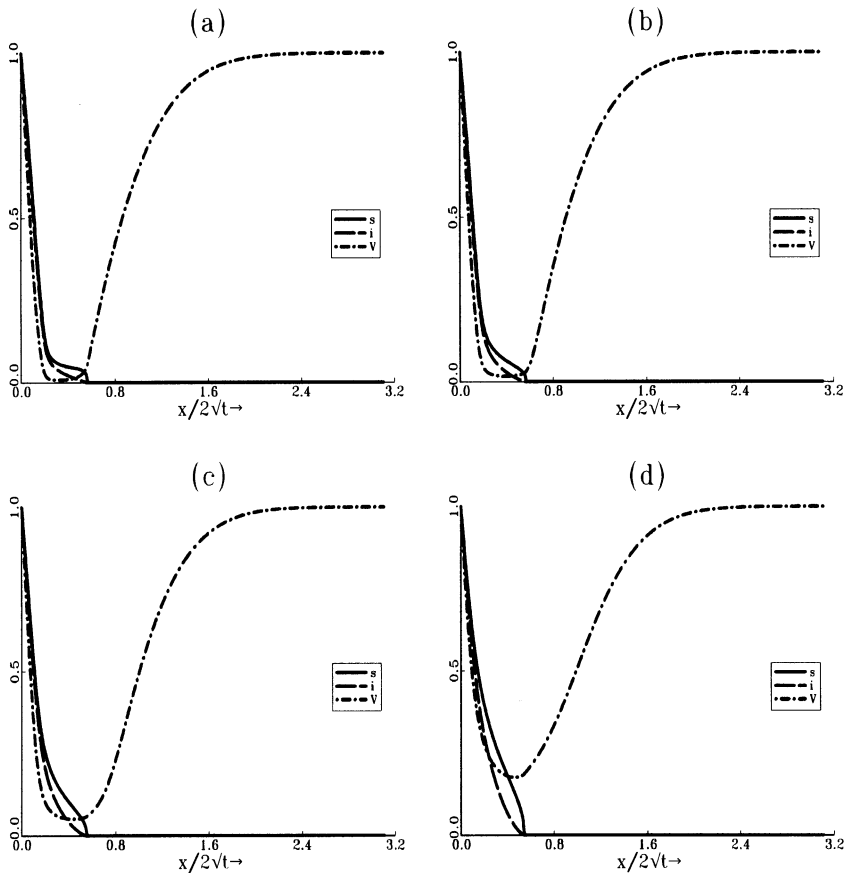


FIG. 4—Numerical solutions for the in-diffusion problem of the defect neutral model. The parameter values are $\beta = 1$, $\gamma = 1$, $\lambda = 0.4$, $\delta = 0.03$, $\varpi = 0.0001$ and (a) $\epsilon = 0.00001$, (b) $\epsilon = 0.0001$, (c) $\epsilon = 0.001$ and (d) $\epsilon = 0.01$. The progression is from dissociative to kick-out domination.

$\hat{x} = 0$, we obtain $\hat{p}_0 = \hat{i}_0 = \hat{s}_0$, $\hat{I}_0 = 1/\hat{s}_0^2$. Integrating the last of (3.5), we obtain

$$\beta \hat{V}_0 - \gamma c \hat{I}_0 = \beta - \gamma c - \gamma c J(t) \hat{x},$$

where $J(t)$ is defined by

$$J(t) \equiv \lim_{x \rightarrow 0} \left(\frac{\partial \tilde{I}_0}{\partial x} \right), \quad (3.6)$$

the leading order outer problem for $\tilde{I}_0(x, t)$ being described below. Recalling that $\hat{I}_0 \hat{V}_0 = 1$, we can then solve for \hat{I}_0 to obtain

$$\hat{I}_0 = \frac{1}{2} \left\{ J(t) \hat{x} + 1 - \frac{\beta}{\gamma c} + \sqrt{\left(J(t) \hat{x} + 1 - \frac{\beta}{\gamma c} \right)^2 + \frac{4\beta}{\gamma c}} \right\}, \quad (3.7)$$

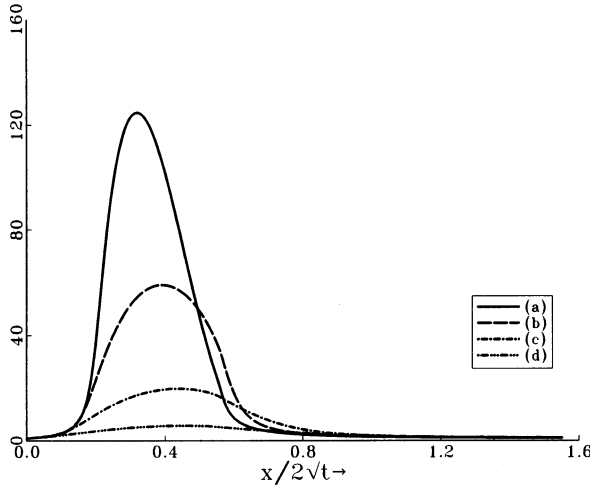


FIG. 5—Numerically calculated self-interstitial profiles for the neutral defect model, illustrating self-interstitial supersaturation. The relevant parameter values are given in the caption to Fig. 4.

and expressions for the remaining species follow immediately. Hence, in particular, the substitutional impurity profile in this region can be characterised by the algebraic decay

$$\hat{s}_0 \sim 1/(J(t)\hat{x})^{1/2} \quad \text{as } \hat{x} \rightarrow +\infty. \tag{3.8}$$

The only leading order contribution of dissociative terms in this regime is in the β terms in (3.7). Their effect can perhaps be discerned in the rather different shapes in the substitutional profiles at high concentrations between Fig. 4(d) and the pure kick-out case in Fig. 3; both of these exhibit at intermediate concentrations the type of concave profile expected from (3.8).

(ii) Outer region, $x = O(1)$

In $x = O(1)$ we write

$$s \sim \delta^{1/3} \tilde{s}_0(x, t), \quad i \sim \delta^{1/3} \tilde{i}_0(x, t), \quad p \sim \delta^{1/3} \tilde{p}_0(x, t), \quad I \sim \delta^{-2/3} \tilde{I}_0(x, t), \quad V \sim \delta^{2/3} \tilde{V}_0(x, t) \tag{3.9}$$

to give the leading order equations

$$\begin{aligned} \tilde{i}_0 &= \tilde{s}_0 \tilde{I}_0 \tilde{p}_0^2, \quad \tilde{p}_0 = (\tilde{s}_0 - \lambda \tilde{i}_0)/(1 - \lambda), \quad \tilde{I}_0 \tilde{V}_0 = 1, \\ \frac{\partial}{\partial t} (\tilde{s}_0 + \lambda \tilde{i}_0) &= \lambda \frac{\partial}{\partial x} \left(\frac{\partial \tilde{i}_0}{\partial x} - \frac{\tilde{i}_0}{\tilde{p}_0} \frac{\partial \tilde{p}_0}{\partial x} \right), \\ \frac{\partial}{\partial t} (c \tilde{I}_0 - \tilde{s}_0) &= \gamma c \frac{\partial^2 \tilde{I}_0}{\partial x^2}, \end{aligned} \tag{3.10}$$

so that we have recovered the full kick-out balance at leading order. We accordingly make no attempt to solve these equations, simply noting that $\tilde{I}_0 \sim J(t)x$ as $x \rightarrow 0$

where $J(t)$ is determined by solving the outer problem (3.10) subject to

$$\begin{aligned}\tilde{i}_0 &\sim 1/(J(t)x)^{1/2}, \quad \tilde{I}_0 \sim J(t)x \quad \text{as } x \rightarrow 0, \\ \tilde{i}_0 &\rightarrow 0, \quad \tilde{I}_0 \rightarrow 0 \quad \text{as } x \rightarrow +\infty, \\ \tilde{i}_0 &= 0, \quad \tilde{I}_0 = 0 \quad \text{at } t = 0.\end{aligned}\tag{3.11}$$

This is identical to the outer problem for the pure kick-out mechanism (see [6]).

The solutions for \tilde{s}_0 , \tilde{i}_0 and \tilde{p}_0 are compactly supported, and we can use a local analysis near the edge of support $x = q_0(t)$ (which is determined as part of the solution to (3.10)–(3.11)) to show that

$$\tilde{I}_0 \sim A, \quad \tilde{s}_0 \sim (1-\lambda)(\dot{q}_0/\lambda A)^{1/2}(q_0-x)^{1/2}, \quad \tilde{p}_0 \sim \tilde{s}_0/(1-\lambda), \quad \tilde{i}_0 \sim A\tilde{s}_0^3/(1-\lambda)^2\tag{3.12}$$

as $x \rightarrow q_0^-$, where A is a constant that must also be determined as part of the solution. In fact, the solutions s , i and p to the full problem ((1.8)₁–(1.8)₃ and (3.1)) are also compactly supported, and if we denote by $q(t; \delta)$ the right edge of their support, then $q(t; \delta) \sim q_0(t)$ as $\delta \rightarrow 0$. For $x > q(t; \delta)$ we have

$$s = i = p = 0,$$

so that this region is of limited interest and full details will not be given. We simply note that in $x > q(t; \delta)$ the vacancies and self-interstitials exactly satisfy

$$IV = 1, \quad \frac{\partial V}{\partial t} - c \frac{\partial I}{\partial t} = \beta \frac{\partial^2 V}{\partial x^2} - \gamma c \frac{\partial^2 I}{\partial x^2};$$

in the current case we have from (3.12) that $I \sim \delta^{-2/3}A$ on $x = q_0(t)$.

For $\varepsilon = O(\delta)$ the behaviour in the outer region $x < q_0(t)$ is kick-out-dominated, but the dissociative effects influence the profiles near the surface through the β terms in (3.7); it is this feature that identifies $\varepsilon = O(\delta)$ as a pertinent scaling.

(iii) Discussion

The substitutional impurity is the most important species from the point of view of applications, partly since most of the impurity is usually in that form (it should be emphasised, however, that both ε and δ are typically much smaller than λ in practice). The substitutional profiles are also useful, as we shall see, in enabling us to distinguish between the various parameter regimes. In the present case the substitutionals drop rapidly (in a manner described by (3.8)) over a boundary layer, being $O(\delta^{1/3})$ in an outer region in which we have a full kick-out balance in the leading order equations. This contrasts strongly with the dissociative case, in which the outer substitutional profile is constant (see below). The substitutional profile in the outer region can be characterised as having compact support, approaching zero rather abruptly (as described by (3.12)). The type of behaviour just described is clearly apparent in Fig. 4(d), as well as in Fig. 3.

$$(B) \quad \varepsilon = O(\delta^{3/2})$$

(i) Outer region, $x = O(1)$

In this case it is more transparent to discuss the outer region first. We write $\varepsilon = \rho\delta^{3/2}$

where $\rho = O(1)$, and in the outer region $x = O(1)$ we pose

$$s \sim \delta^{1/2} \tilde{s}_0(x, t), \quad i \sim \delta^{1/2} \tilde{i}_0(x, t), \quad p \sim \delta^{1/2} \tilde{p}_0(x, t), \quad I \sim \delta^{-1} \tilde{I}_0(x, t), \quad V \sim \delta \tilde{V}_0(x, t),$$

to recover the leading order equations (3.10), except that in the last equation of (3.10) c is replaced by ρ . The boundary conditions are again given by (3.11), so the outer problem is identical to the previous case.

(ii) Surface region, $x = O(\delta^{1/2})$

We write $x = \delta^{1/2} \hat{x}$ and pose

$$s \sim \hat{s}_0(\hat{x}, t), \quad i \sim \hat{i}_0(\hat{x}, t), \quad p \sim \hat{p}_0(\hat{x}, t), \quad I \sim \hat{I}_0(\hat{x}, t), \quad V \sim \hat{V}_0(\hat{x}, t)$$

to obtain, in a similar way to before, the leading order equations

$$\hat{i}_0 = \hat{p}_0 = \hat{s}_0, \quad \hat{V}_0 = \hat{s}_0^2, \quad \hat{I}_0 = 1/\hat{s}_0^2 \quad (3.13)$$

with, for $\hat{x} < \hat{q}_0(t)$, a moving boundary problem for \hat{s}_0 and \hat{q}_0 , namely

$$\begin{aligned} \frac{\partial \hat{s}_0}{\partial t} &= 2\beta \frac{\partial}{\partial \hat{x}} \left(\hat{s}_0 \frac{\partial \hat{s}_0}{\partial \hat{x}} \right), \\ \hat{s}_0 &= 1 \quad \text{on} \quad \hat{x} = 0, \\ \hat{s}_0 &\rightarrow 0, \quad 2\beta \hat{s}_0 \frac{\partial \hat{s}_0}{\partial \hat{x}} \rightarrow -\gamma \rho J(t) \quad \text{as} \quad \hat{x} \rightarrow \hat{q}_0(t)^-, \\ \hat{q}_0 &= 0 \quad \text{at} \quad t = 0. \end{aligned} \quad (3.14)$$

The second condition in (3.14)₃ follows from matching into the transition layer described below, and it is this feature of (3.14) that identifies the scaling $\varepsilon = O(\delta^{3/2})$. The solution \hat{s}_0 is compactly supported, with $\hat{x} = \hat{q}_0(t)$ being determined as part of the solution.

(iii) Transition layer

This region is located at $\check{z} = O(1)$ where $\hat{x} = \hat{q}(t; \delta) + \delta^{1/4} \check{z}$, and in $\check{z} = O(1)$ we pose

$$s \sim \delta^{1/8} \check{s}_0(\check{z}, t), \quad i \sim \delta^{1/8} \check{i}_0(\check{z}, t), \quad p \sim \delta^{1/8} \check{p}_0(\check{z}, t), \quad I \sim \delta^{-1/4} \check{I}_0(\check{z}, t), \quad V \sim \delta^{1/4} \check{V}_0(\check{z}, t),$$

with $\hat{q}(t; 0) = \hat{q}_0(t)$, and obtain at leading order

$$\check{i}_0 = \check{s}_0 = \check{p}_0 = 1/\check{I}_0^{1/2}, \quad \check{V}_0 = 1/\check{I}_0;$$

and, since

$$\frac{\partial^2}{\partial \check{z}^2} (\beta \check{V}_0 - \gamma \rho \check{I}_0) = 0,$$

by a suitable choice of \hat{q} at $O(\delta^{1/4})$ we may take

$$\beta \check{V}_0 - \gamma \rho \check{I}_0 = -\gamma \rho J \check{z} \quad (3.15)$$

where we have matched as $\check{z} \rightarrow +\infty$ into the outer region, via (3.11). Hence

$$\check{I}_0 = \left(J\check{z} + \sqrt{J^2\check{z}^2 + 4\beta/\gamma\rho} \right) / 2, \quad (3.16)$$

so that

$$\check{s}_0 \sim (J\check{z})^{-1/2} \quad \text{as } \check{z} \rightarrow +\infty,$$

as is required to match into the outer (cf. (3.8)). Since $\check{V}_0 \sim \gamma\rho J(-\check{z})/\beta$ as $\check{z} \rightarrow -\infty$, matching gives the second condition of (3.14)₃. The expression (3.15) enables us to interpret physically this Stefan-like condition in (3.14). In the outer region we have a self-interstitial excess, causing diffusion of I 's towards the surface. Equation (3.15) states that for $\check{z} = O(1)$ this out-diffusion is balanced at leading order by in-diffusion of vacancies, in order to conserve numbers of host atoms. This depletion of V 's at the front $\hat{x} = \hat{q}_0$ causes impurity to convert from substitutional to interstitial, leading in (3.14) to a loss of substitutionals there.

(iv) Summary

While the outer solution is identical in form to that of case (A), it applies (for fixed $\delta \ll 1$) at much lower impurity concentrations. Moreover, the profile in the high concentration surface region drops abruptly as \hat{x} approaches \hat{q} (from (3.14) we have

$$\hat{s}_0 \sim (\gamma\rho J(\hat{q}_0 - \hat{x})/\beta)^{1/2} \quad \text{as } \hat{x} \rightarrow \hat{q}_0^-, \quad (3.17)$$

levelling off somewhat over region (iii). This may be contrasted with the smooth decay in case (A) represented by (3.8). The emergence of such features is apparent in the transition from (d) to (b) in Fig. 4, leading ultimately to the appearance of the substitutional plateau in (a).

(C) $\varepsilon = O(\delta^3)$

We write $\varepsilon = \sigma\delta^3$, where $\sigma = O(1)$. The behaviour can be viewed as dissociative-dominated, but the pure dissociative moving boundary problem (derived in [5]) is influenced by kick-out terms, as described below. In the limit $\delta \rightarrow 0$, the asymptotic structure is now as follows.

(i) Surface region, $x = O(\delta^{1/2})$

If we write $x = \delta^{1/2}\hat{x}$, the leading order equations in the boundary layer are, in the usual notation,

$$\hat{i}_0 = \hat{p}_0 = \hat{s}_0, \quad \hat{V}_0 = \hat{s}_0^2, \quad \hat{I}_0 = \hat{s}_0^{-2}$$

and

$$\begin{aligned} \frac{\partial \hat{s}_0}{\partial t} &= 2\beta \frac{\partial}{\partial \hat{x}} \left(\hat{s}_0 \frac{\partial \hat{s}_0}{\partial \hat{x}} \right), \\ \hat{s}_0 &= 1 \quad \text{on } \hat{x} = 0, \\ \hat{s}_0 &\rightarrow 0, \quad \frac{\partial \hat{s}_0}{\partial \hat{x}} \rightarrow -\frac{1}{2\beta} \frac{d\hat{q}_0}{dt} \quad \text{as } \hat{x} \rightarrow \hat{q}_0(t)^-, \\ \hat{q}_0 &= 0 \quad \text{at } t = 0. \end{aligned} \quad (3.18)$$

This problem is identical to that for the pure dissociative case [5] and corresponds to taking the limit $\rho \rightarrow 0$ in (3.14), the number of substitutionals \hat{s}_0 now being conserved at the front $\hat{x} = \hat{q}_0(t)$; the appearance of a front \hat{q}_0 now results from the degenerate nature of the effective diffusivity ($2\beta\hat{s}_0$).

(ii) Transition layer I

This is located at $\check{z} = O(1)$ where $\hat{x} = \hat{q}(t; \delta) + \delta^{1/2}\check{z}$, $\hat{q}(t; 0) = \hat{q}_0$ being the edge of the support to the solution for \hat{s}_0 . The appropriate scalings in $\check{z} = O(1)$ are

$$s \sim \delta^{1/2}\check{s}_0(\check{z}, t), \quad i \sim \delta^{1/2}\check{i}_0(\check{z}, t), \quad p \sim \delta^{1/2}\check{p}_0(\check{z}, t), \quad I \sim \delta^{-1}\check{I}_0(\check{z}, t), \quad V \sim \delta\check{V}_0(\check{z}, t),$$

giving, at leading order,

$$\check{i}_0 = \check{p}_0 = \check{s}_0, \quad \check{V}_0 = \check{s}_0^2, \quad \check{I}_0 = 1/\check{s}_0^2$$

and

$$-J\gamma\sigma - \frac{d\hat{q}_0}{dt}\check{s}_0 = 2 \left(\beta\check{s}_0 + \frac{\gamma\sigma}{\check{s}_0^3} \right) \frac{\partial\check{s}_0}{\partial\check{z}} \quad (3.19)$$

where $J(t)$ is defined below. This implies that

$$\check{s}_0 \sim (J\check{z})^{-1/2}, \quad \check{V}_0 \sim 1/(J\check{z}), \quad \check{I}_0 \sim J\check{z} \text{ as } \check{z} \rightarrow +\infty.$$

Equation (3.19) is separable, and integrating again yields the various concentration profiles across this region of rapid variation.

(iii) Moving boundary problem, $x = O(1)$

The moving boundary problem we now derive contains some of the most important aspects of the transition between dissociative and kick-out behaviour. For $x < q_0$, where q_0 is determined from the moving boundary problem below, we pose

$$s \sim \delta s_0(x, t), \quad i \sim \delta i_0(x, t), \quad p \sim \delta p_0(x, t), \quad I \sim \delta^{-2}I_0(x, t), \quad V \sim \delta^2V_0(x, t), \quad (3.20)$$

to yield (cf. (3.10)) the kick-out balance

$$\begin{aligned} i_0 &= s_0I_0p_0^2, \quad p_0 = (s_0 - \lambda i_0)/(1 - \lambda), \quad I_0V_0 = 1, \\ \frac{\partial}{\partial t}(s_0 + \lambda i_0) &= \lambda \frac{\partial}{\partial x} \left(\frac{\partial i_0}{\partial x} - \frac{i_0}{p_0} \frac{\partial p_0}{\partial x} \right), \\ \frac{\partial}{\partial t}(\sigma I_0 - s_0) &= \gamma\sigma \frac{\partial^2 I_0}{\partial x^2}; \end{aligned} \quad (3.21)$$

(3.21) is subject to

$$I_0 \sim J(t)x, \quad s_0, \quad i_0, \quad p_0 \sim (J(t)x)^{-1/2} \quad \text{as } x \rightarrow 0$$

where $J(t)$ is determined as part of the solution to the moving boundary problem formulated below.

For $x > q_0$ we have $s = i = p = 0$, and we write $V \sim V_0(x, t)$, $I \sim 1/V_0(x, t)$

to obtain

$$\frac{\partial V_0}{\partial t} = \beta \frac{\partial^2 V_0}{\partial x^2}$$

with $V_0 \rightarrow 1$ as $x \rightarrow +\infty$, $V_0 = 0$ at $x = q_0(t)$, and hence (in view of self-similarity)

$$V_0 = 1 - \frac{\operatorname{erfc}(x/2\sqrt{\beta t})}{\operatorname{erfc}(q_0/2\sqrt{\beta t})}. \quad (3.22)$$

The moving boundary conditions are determined by matching with the transition region (iv) discussed below. They are given by

$$i_0|_{q_0^-} = I_0|_{q_0^-} = 0, \quad \left(\lambda \frac{\partial i_0}{\partial x} + \dot{q}_0 s_0 \right) \Big|_{q_0^-} = 0, \quad \left(-\gamma \sigma \frac{\partial I_0}{\partial x} + \dot{q}_0 s_0 \right) \Big|_{q_0^-} = \beta \frac{\partial V_0}{\partial x} \Big|_{q_0^+}, \quad (3.23)$$

the first two of which are not independent. The final two of these conditions can be viewed, respectively, as expressions of conservation of impurity and of host atoms and can be inferred directly from (1.2). For example, equation (1.2)₁ in its dimensionless form (1.8)₂ implies that

$$\frac{d}{dt} \int_{q_-}^{q_+} (s + \lambda i) dx = \left[\lambda \left(\frac{\partial i}{\partial x} - \frac{i}{p} \frac{\partial p}{\partial x} \right) \right]_{q_-}^{q_+} + \dot{q}_+ (s + \lambda i)|_{q_+} - \dot{q}_- (s + \lambda i)|_{q_-},$$

for any $q_-(t)$, $q_+(t)$, whence the third condition of (3.23) follows via an appropriate limiting process in which

$$q_- \rightarrow q_0^-, \quad q_+ \rightarrow q_0^+.$$

The complete moving boundary problem can thus now be stated in $0 < x < q_0(t)$ as

$$\begin{aligned} i_0 &= s_0 I_0 p_0^2, \quad p_0 = (s_0 - \lambda i_0)/(1 - \lambda), \\ \frac{\partial}{\partial t} (s_0 + \lambda i_0) &= \lambda \frac{\partial}{\partial x} \left(\frac{\partial i_0}{\partial x} - \frac{i_0}{p_0} \frac{\partial p_0}{\partial x} \right), \\ \frac{\partial}{\partial t} (\sigma I_0 - s_0) &= \gamma \sigma \frac{\partial^2 I_0}{\partial x^2}, \\ i_0 \sim p_0, \quad I_0 &\rightarrow 0 \quad \text{as } x \rightarrow 0, \\ i_0 = 0, \quad s_0 = S, \quad \lambda \frac{\partial i_0}{\partial x} &= -\dot{q}_0 S, \quad \gamma \sigma \frac{\partial I_0}{\partial x} = \dot{q}_0 S - K(t) \quad \text{at } x = q_0, \\ q_0 = 0 \quad \text{at } t = 0, \end{aligned} \quad (3.24)$$

where

$$K(t) \equiv \beta \frac{\partial V_0}{\partial x} \Big|_{q_0^+} = \sqrt{\frac{\beta}{\pi t}} \frac{e^{-q_0^2/4\beta t}}{\operatorname{erfc}(q_0/\sqrt{2\beta t})} \quad (3.25)$$

and the constant S , as well as $q_0(t)$, is determined as part of the solution. Dissociative effects appear in (3.24) through $K(t)$, this balance identifying the scaling $\varepsilon = O(\delta^3)$.

(iv) Transition layer II

This region is at $z = O(1)$ where $x = q(t; \delta) + \delta z$ with $q(t; 0) = q_0(t)$, and the appropriate scalings are

$$s \sim \delta s_0^\dagger(z, t), \quad i \sim \delta^2 i_0^\dagger(z, t), \quad p \sim \delta s_0^\dagger(z, t)/(1 - \lambda), \quad I \sim \delta^{-1} I_0^\dagger(z, t), \quad V \sim \delta V_0^\dagger(z, t)$$

with

$$\begin{aligned} i_0^\dagger &= s_0^{\dagger 3} I_0^\dagger / (1 - \lambda)^2, \quad I_0^\dagger V_0^\dagger = 1, \\ -\dot{q}_0 s_0^\dagger &= \lambda \left(\frac{\partial i_0^\dagger}{\partial z} - \frac{i_0^\dagger}{s_0^\dagger} \frac{\partial s_0^\dagger}{\partial z} \right), \\ K - \dot{q}_0 s_0^\dagger &= \beta \frac{\partial V_0^\dagger}{\partial z} - \gamma \sigma \frac{\partial I_0^\dagger}{\partial z}, \end{aligned} \tag{3.26}$$

with $s_0^\dagger = i_0^\dagger = p_0^\dagger = 0$ for $z \geq 0$, so that the compactly supported nature of solutions manifests itself in this narrow layer (over which the impurity concentration drops rather abruptly, cf. Fig. 4(a)). Matching the outer region with (3.26) implies the final two conditions of (3.23).

(v) Discussion

The above analysis indicates the significant result that dissociative behaviour comes to dominate completely only for extremely small ε , namely $\varepsilon = o(\delta^3)$; this is borne out by Fig. 4. Comments similar to those under (B) (iv) again apply, although, in view of (3.18), expression (3.17) is replaced by

$$\hat{s}_0 \sim \frac{d\hat{q}_0}{dt} (\hat{q}_0 - \hat{x}) / 2\beta \quad \text{as } \hat{x} \rightarrow \hat{q}_0^-.$$

However, owing to the moving boundary conditions in (3.24), the outer solution is no longer of kick-out form in this regime. In the limit $\sigma \rightarrow 0$ (the pure dissociative model) it is easily seen from (3.24) that, to leading order, the substitutionals are constant and $O(\delta)$ in the outer region $x < q_0(t)$, in which $s \sim \delta S$. This plateau in the profile for the substitutionals is useful when diagnosing dissociative behaviour in experimental data; it is visible in Fig. 4(a) and is even more apparent in Fig. 2. The plateau gradually disappears as kick-out effects are increased (as illustrated by Fig. 4(b) and (c)).

4. The charged defect case

We now consider the solutions to (1.11) subject to (1.9) with ϖ and θ_2 set to zero, so that

$$p = (s - \lambda i - 2\varepsilon I) / (1 - \lambda - 2\varepsilon), \tag{4.1}$$

and address the dissociative and kick-out models and a single transition scaling; a noteworthy feature of this case is that only one such scaling is needed, with the resulting formulation having a number of novel features.

4.1. Dissociative model

Setting $\varepsilon = 0$ in the governing equations, we recover the same dissociative model as has previously been discussed; see Section 2.1.

4.2. Kick-out model

Setting $\delta = 0$ in the governing equations, we obtain the kick-out model, a numerical solution for this case being given in Fig. 6. We now briefly describe the behaviour of this model in the limit $\varepsilon \rightarrow 0$, as this has not been addressed elsewhere. V decouples from the problem, being given by $V = p^2/I$.

(i) Boundary layer, $x = O(\varepsilon^{1/2})$

We write $x = \varepsilon^{1/2}\hat{x}$. All concentrations are $O(1)$ in this layer, and, if we retain the previous notation, the leading order quantities satisfy (cf. (3.13))

$$\hat{i}_0 = \hat{p}_0 = \hat{s}_0, \quad \hat{I}_0 = 1. \quad (4.2)$$

The substitutional concentration is thus given by

$$\begin{aligned} \frac{\partial \hat{s}_0}{\partial t} &= 2\gamma \frac{\partial}{\partial \hat{x}} \left(\frac{1}{\hat{s}_0} \frac{\partial \hat{s}_0}{\partial \hat{x}} \right), \\ \hat{s}_0 &= 1 \quad \text{on} \quad \hat{x} = 0, \\ \hat{s}_0 &\rightarrow 0 \quad \text{as} \quad \hat{x} \rightarrow +\infty, \\ \hat{s}_0 &= 0 \quad \text{at} \quad t = 0, \end{aligned}$$

with

$$\hat{s}_0 \sim 4\gamma t / \hat{x}^2 \quad \text{as} \quad \hat{x} \rightarrow +\infty. \quad (4.3)$$

The corresponding similarity solution $\hat{s}_0(\hat{x}/t^{1/2})$ can be expressed analytically in terms of quadratures.

(ii) Outer region, $x = O(1)$

In view of (4.3), the appropriate scalings in $x = O(1)$ are

$$s \sim \varepsilon s_0(x, t), \quad i \sim \varepsilon i_0(x, t), \quad p \sim \varepsilon p_0(x, t), \quad I \sim I_0(x, t),$$

and we recover the full kick-out balance at leading order, giving

$$\begin{aligned} s_0 I_0 &= i_0, \quad p_0 = (s_0 - \lambda i_0 - 2I_0)/(1 - \lambda), \\ \frac{\partial}{\partial t}(s_0 + \lambda i_0) &= \lambda \frac{\partial}{\partial x} \left(\frac{\partial i_0}{\partial x} - \frac{i_0}{p_0} \frac{\partial p_0}{\partial x} \right), \\ \frac{\partial}{\partial t}(I_0 - s_0) &= \gamma \frac{\partial}{\partial x} \left(\frac{\partial I_0}{\partial x} - \frac{2I_0}{p_0} \frac{\partial p_0}{\partial x} \right). \end{aligned} \quad (4.4)$$

It should be emphasised that the balance here is such that the i_0, I_0 terms unavoidably appear in the expression for p_0 , so the complete neglect in [12] of the contribution of both charged impurity interstitials and self-interstitials to the charged neutrality

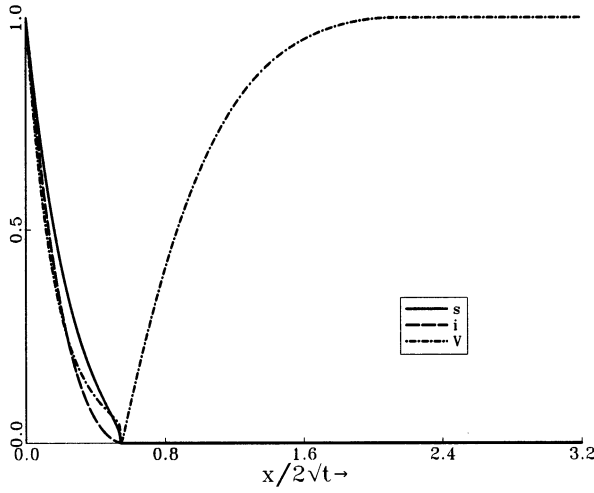


Fig. 6—Numerical solution of the kick-out model with charged defects and with parameter values $\varepsilon = 0.06$, $\lambda = 0.4$, $\gamma = 1$ and $\varpi = 0.0001$.

condition is open to criticism. The required solutions s_0, i_0, p_0 and I_0 to this problem are compactly supported (as are s, i, p and I for the full combined model with (4.1)), and we denote by $q_0(t)$ the edge of the support. We have that

$$s_0, i_0, p_0 \sim 4\gamma t/x^2, I_0 \rightarrow 1 \quad \text{as } x \rightarrow 0^+, \tag{4.5}$$

$$s_0 = I_0 = 0, \quad \frac{\partial i_0}{\partial x} - \frac{i_0}{p_0} \frac{\partial p_0}{\partial x} = 0, \quad \frac{\partial I_0}{\partial x} - \frac{2I_0}{p_0} \frac{\partial p_0}{\partial x} = 0 \quad \text{on } x = q_0(t), \tag{4.6}$$

and

$$s_0 = i_0 = p_0 = I_0 = 0 \quad \text{for } x > q_0(t). \tag{4.7}$$

Using a local analysis, we find that

$$s_0 \sim A(q_0 - x)^{\frac{1}{2}}, \quad i_0 \sim \frac{\dot{q}_0}{\lambda} A(q_0 - x)^{\frac{3}{2}}, \quad p_0 \sim \frac{A}{1 - \lambda} (q_0 - x)^{\frac{1}{2}}, \quad I_0 \sim \frac{\dot{q}_0}{\lambda} (q_0 - x) \tag{4.8}$$

as $x \rightarrow q_0^-$, where the quantity $A(t)$ needs to be determined as part of the solution. We note that it is not possible to impose the condition $V \rightarrow 1$ as $x \rightarrow +\infty$ in the framework of the pure kick-out model $\delta = 0$.

4.3. Transition scaling

We need consider only one case, namely $\varepsilon = O(\delta)$ with $\delta \ll 1$, for which all of the details of the transition occur. Some numerical solutions of the substitutionals, impurity interstitials and vacancies can be found in Fig. 7, the corresponding profiles for the self-interstitials and self-interstitial supersaturations being given in Fig. 8. We write $\varepsilon = a\delta$, and, in the limit $\delta \rightarrow 0$, the asymptotic structure is as follows.

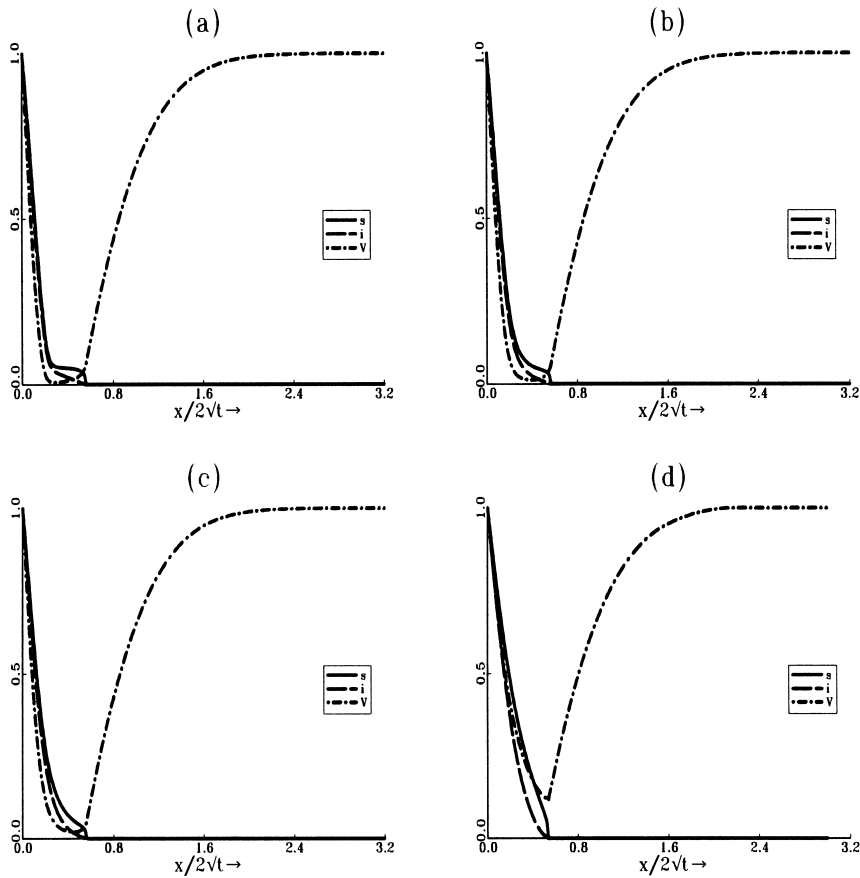


FIG. 7—Numerical solutions of the charged defect model with parameter values $\beta = \gamma = 1$, $\delta = 0.03$, $\varpi = 0.0001$ and (a) $a = 0.01$, (b) $a = 0.1$, (c) $a = 0.25$ and (d) $a = 2.0$. The progression is from dissociative to kick-out domination.

(i) Surface region, $x = O(\delta^{1/2})$

Writing $x = \delta^{1/2} \hat{x}$, we recover (4.2) with $\hat{V}_0 = \hat{s}_0^2$ and

$$\frac{\partial \hat{s}_0}{\partial t} = \frac{\partial}{\partial \hat{x}} \left(\left(2\beta \hat{s}_0 + \frac{2a\gamma}{\hat{s}_0} \right) \frac{\partial \hat{s}_0}{\partial \hat{x}} \right) \quad (4.9)$$

with

$$\hat{s}_0 = 1 \quad \text{on} \quad \hat{x} = 0, \quad \hat{s}_0 \sim 4\gamma a t / \hat{x}^2 \quad \text{as} \quad \hat{x} \rightarrow +\infty, \quad \hat{s}_0 = 0 \quad \text{at} \quad t = 0. \quad (4.10)$$

The different contributions of the two mechanisms can thus be conveniently assessed via the effective diffusivity in this surface region, as described by (4.9).

(ii) Outer region, $x = O(1)$

The leading order structure in the outer region is similar to the dissociative case,

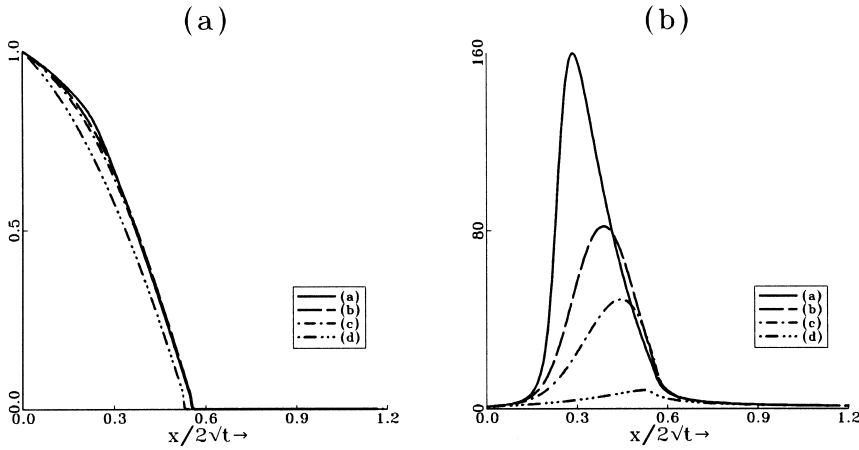


FIG. 8—Numerically calculated profiles of (a) self-interstitials and (b) self-interstitial saturations (I/p^2) for the charged defect model. The relevant parameter values are given in the caption to Fig. 7.

with a moving boundary that we again denote by q_0 . For $x < q_0$ the scalings are given by

$$s \sim \delta s_0(x, t), \quad i \sim \delta i_0(x, t), \quad p \sim \delta p_0(x, t), \quad I \sim I_0(x, t), \quad V \sim \delta^2 V_0^*(x, t),$$

giving

$$\begin{aligned} s_0 I_0 &= i_0, \quad p_0 = (s_0 - \lambda i_0 - 2aI_0)/(1 - \lambda), \quad I_0 V_0^* = p_0^2, \\ \frac{\partial}{\partial t}(s + \lambda i_0) &= \lambda \frac{\partial}{\partial x} \left(\frac{\partial i_0}{\partial x} - \frac{i_0}{p_0} \frac{\partial p_0}{\partial x} \right), \\ \frac{\partial}{\partial t}(aI_0 - s_0) &= \gamma a \frac{\partial}{\partial x} \left(\frac{\partial I_0}{\partial x} - \frac{2I_0}{p_0} \frac{\partial p_0}{\partial x} \right), \end{aligned} \quad (4.11)$$

with boundary conditions (cf. (4.5))

$$s_0, i_0, p_0 \sim 4\gamma t/x^2, \quad I_0 \rightarrow 1 \quad \text{as} \quad x \rightarrow 0^+.$$

We now need to formulate the moving boundary problem that determines $q_0(t)$. Interestingly, this can take two distinct forms, one closer to that of the kick-out model and the other to that of the dissociative model. In both cases we have in $x > q(t; \delta)$ that $s = i = p = I = 0$ with $V \sim V_0(x, t)$ and

$$\frac{\partial V_0}{\partial t} = \beta \frac{\partial^2 V_0}{\partial x^2},$$

with V_0 given by (3.22); however, the moving boundary conditions differ between the two cases, which are characterised according to whether $S > 0$ or $S = 0$, where

(as before)

$$S \equiv \lim_{x \rightarrow q_0^-} s_0.$$

(A) $S > 0$ ($a < a_c$)

The moving boundary conditions for (4.11) at $x = q_0^-$ are, cf. (3.23) or (3.24),

$$s_0 = S, \quad I_0 = 0, \quad \lambda \frac{\partial i_0}{\partial x} = -\dot{q}_0 S, \quad \gamma a \frac{\partial I_0}{\partial x} = \dot{q}_0 S - K, \quad (4.12)$$

where S is determined as part of the solution, with K (given by (3.25)) representing the flux of vacancies from the bulk into the moving boundary. Differentiating $i_0 = s_0 I_0$ with respect to x and evaluating at $x = q_0^-$, we obtain

$$\lambda S(\dot{q}_0 S - K) = -\gamma a \dot{q}_0 S, \quad (4.13)$$

so for the current case $S > 0$ we require that S and q_0 be related by

$$\dot{q}_0 \left(S + \frac{\gamma a}{\lambda} \right) = K. \quad (4.14)$$

This completes the specification of the moving boundary conditions in case (A).

The transition layer is at $z = O(1)$, where $x = q(t; \delta) + \delta z$, and in $z = O(1)$ we pose

$$q \sim q_0(t), \quad s \sim \delta s_0^\dagger(z, t), \quad i \sim \delta^2 i_0^\dagger(z, t), \quad p \sim \delta s_0^\dagger/(1 - \lambda), \quad I \sim \delta I_0^\dagger(z, t), \quad V \sim \delta V_0^\dagger(z, t)$$

to obtain (cf. (3.26))

$$i_0^\dagger V_0^\dagger = s_0^{\dagger 3}/(1 - \lambda)^2, \quad I_0^\dagger V_0^\dagger = s_0^{\dagger 2}/(1 - \lambda)^2, \quad (4.15)$$

$$-\dot{q}_0 s_0^\dagger = \lambda \left(\frac{\partial i_0^\dagger}{\partial z} - \frac{i_0^\dagger}{s_0^\dagger} \frac{\partial s_0^\dagger}{\partial z} \right), \quad (4.16)$$

$$K - \dot{q}_0 s_0^\dagger = \beta \frac{\partial V_0^\dagger}{\partial z} - \gamma a \left(\frac{\partial I_0^\dagger}{\partial z} - \frac{2I_0^\dagger}{s_0^\dagger} \frac{\partial s_0^\dagger}{\partial z} \right). \quad (4.17)$$

Taking the limit $a \rightarrow 0$ in (4.14), we have $K = \dot{q}_0 S$, and we recover results [5] for the dissociative model. We expect the above formulation to hold for sufficiently small $a = O(1)$, with S dropping as a increases (so that kick-out effects become more pronounced). We define $a = a_c$ to be the value of a at which S drops to zero, and from (4.14) it is clear that it satisfies

$$a_c = \frac{\lambda K(t; a_c)}{\gamma \dot{q}_0(t; a_c)},$$

where we have made the dependence of K and q_0 upon a explicit.

(B) $S = 0$ ($a > a_c$, $K < \gamma a \dot{q}_0/\lambda$)

This corresponds to taking the other root of (4.13). The conditions (4.12) on (4.11)

are now replaced by (cf. (4.6))

$$s_0 = 0, I_0 = 0, \frac{\partial i_0}{\partial x} - \frac{i_0}{p_0} \frac{\partial p_0}{\partial x} = 0, \gamma a \left(\frac{\partial I_0}{\partial x} - \frac{2I_0}{p_0} \frac{\partial p_0}{\partial x} \right) = -K \quad \text{as } x \rightarrow q_0^-. \quad (4.18)$$

These conditions imply local behaviour as $x \rightarrow q_0^-$ of the form

$$\begin{aligned} s_0 &\sim A(q_0 - x)^{\frac{1}{2}(1-\kappa)}, \quad i_0 \sim \frac{\dot{q}_0}{\lambda}(q_0 - x)^{\frac{1}{2}(3-\kappa)}, \\ p_0 &\sim \frac{A}{1-\lambda}(q_0 - x)^{\frac{1}{2}(1-\kappa)}, \quad I_0 \sim \frac{\dot{q}_0}{\lambda}(q_0 - x), \quad V_0^* \sim \frac{\lambda A^2}{(1-\lambda)^2 \dot{q}_0}(q_0 - x)^{-\kappa}, \end{aligned} \quad (4.19)$$

where $\kappa = \lambda K / \gamma a \dot{q}_0$ is a constant for the self-similar case treated here, with $0 < \kappa < 1$ for case (B) to apply, and $A(t)$ and $q_0(t)$ determined as part of the solution; if $\kappa > 1$, then (4.19) does not hold—we instead have case (A) with $S > 0$ in (4.14). For $a \rightarrow \infty$ we have $\kappa \rightarrow 0$ and we recover the kick-out result (4.8).

The transition region scalings are different in this case, namely (in view of (4.19)), $x = q(t; \delta) + \delta^{\frac{2}{1+\kappa}} z$ and

$$\begin{aligned} s &\sim \delta^{\frac{2}{1+\kappa}} s_0^\dagger(z, t), \quad i \sim \delta^{\frac{4}{1+\kappa}} i_0^\dagger(z, t), \quad p \sim \delta^{\frac{2}{1+\kappa}} s_0^\dagger / (1 - \lambda), \quad I \sim \delta^{\frac{2}{1+\kappa}} I_0^\dagger(z, t), \\ V &\sim \delta^{\frac{2}{1+\kappa}} V_0^\dagger(z, t), \end{aligned}$$

and we recover (4.15) and (4.16), but (4.17) is replaced by

$$K = \beta \frac{\partial V_0^\dagger}{\partial z} - \gamma a \left(\frac{\partial I_0^\dagger}{\partial z} - \frac{2I_0^\dagger}{s_0^\dagger} \frac{\partial s_0^\dagger}{\partial z} \right);$$

this system can be integrated explicitly, but we do not pursue details.

In Fig. 9 we plot numerical solutions of the substitutional profile for various a for a given set of the other parameter values. The transition from dissociative to kick-out behaviour is clear, and, if we use graphs such as these, it is possible to estimate the value of a_c .

4.4. Discussion

The pure dissociative case, with its characteristic substitutional plateau, is identical to that discussed in Section 3. Figure 6 illustrates the behaviour of the kick-out case, the vacancy depletion being much more pronounced than in Figure 3. This is to be expected from the asymptotics, the minimum vacancy concentration being $O(\varepsilon^{2/3})$ in case (I) and $O(\varepsilon^2)$ in case (II); the substitutional concentration in the outer region is $O(\varepsilon^{1/3})$ in case (I) and $O(\varepsilon)$ in case (II). The decay in the high concentration regime is again algebraic in the kick-out case, leading to a concave profile, but the relevant power law is significantly different from the neutral defect case (cf. (3.8) and (4.3)); this may provide a means to distinguish between the two cases experimentally. Unlike the neutral defect case, the two mechanisms interact at leading order in both surface and outer regions for the same transition scaling. In (4.9), if a decreases such that the dissociative (β) term comes to dominate, the degenerate nature of the

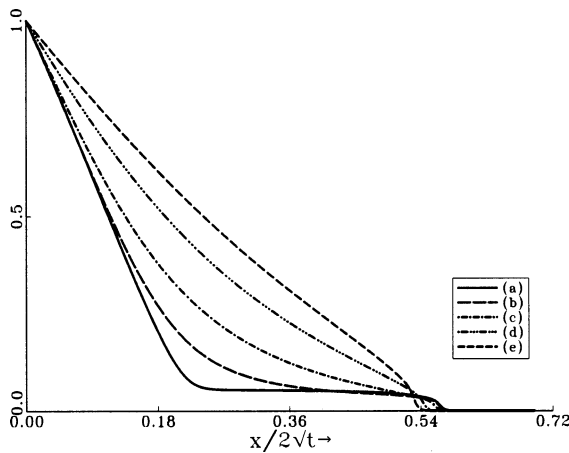


FIG. 9—Numerical solutions for the substitutional concentration of the charged defect model with various values of a . The parameter values are $\beta = \gamma = 1$, $\delta = 0.03$, $\varpi = 0.0001$, and a has values (a) 0.001, (b) 0.1, (c) 0.50, (d) 2.0 and (e) 5.0.

effective diffusivity $2\beta\hat{s}_0$ will result in a rather abrupt decrease in s , before levelling off into the plateau (as in Fig. 7(a)); however, even for moderate a , kick-out effects (which always dictate the behaviour of (4.9) as $\hat{x} \rightarrow +\infty$) will tend to dominate, as is apparent in Fig. 7(c) and (d). If $a < a_c$, then s drops rapidly to zero from a value δS over a narrow transition layer, this being apparent in Fig. 7(a) and (b), whereas, if $a > a_c$, s decays to zero much more steadily over the outer region (cf. Fig. 7(d)). Such comments indicate that rather complicated interactions between the two mechanisms can take place in case (II).

5. Conclusions

There are several aspects of the model studied in this paper that should be emphasised. Firstly, and as previously referred to in Section 1.2, drift terms have been included in the model. In many previous analyses, of the dissociative model in particular, these have been omitted, leading to significantly different behaviour from that predicted by the model discussed here. Consider, for example, the term

$$-\frac{\partial}{\partial x} \left(\frac{i}{p} \frac{\partial p}{\partial x} \right)$$

appearing in equation (3.2). Omitting this term for the in-diffusion problem for the dissociative model gives

$$i \sim \operatorname{erfc}(x/2\sqrt{t}) \quad \text{in } x = O(1)$$

as $\delta \rightarrow 0$, while the model (3.2), which includes the drift term, gives $i = O(\delta)$ in $x = O(1)$ as $\delta \rightarrow 0$, which is dramatically smaller.

Some discussion of the choice of charge values that we have used is given in Section 1.2 and will not be repeated here. Our results demonstrate that many aspects

of the diffusion behaviour displayed by the experimental results can be consistently explained using the present model in the parameter regimes we have studied; moreover, there are significant differences in behaviour between the two cases discussed. It should be emphasised that the asymptotic and numerical approaches developed here can readily be carried over to other choices of charge states.

The model considered in this paper contains five independent parameters (not including $\varpi = n_i/s^*$) in the dimensionless system. A complete study of all parameter regimes is clearly not feasible, and so we have focused instead on those that are usually of most importance from the point of view of applications. In particular, we have considered those cases in which $\delta = V^*/s^*$ and $\varepsilon = I^*/s^*$ or I_s^*/s^* are both small. This assumption is justified, since we are modelling semiconductor behaviour under extrinsic conditions, where the concentration of impurity greatly exceeds that of the defects. We have seen that, when both ε and δ are small, the behaviour is rather sensitive to their relative values. This reflects the fact that the diffusion behaviour is largely controlled by whether it is the vacancies or the self-interstitials that are the dominant defect species. This sensitivity is highlighted by noting that the dissociative model corresponds to $\varepsilon = 0$, $\delta \ll 1$, while the kick-out model is obtained when $\delta = 0$, $\varepsilon \ll 1$, typical impurity profiles for these limit cases being very different. In this paper both the dissociative and the kick-out model have been noted, as well as transition scalings corresponding to the (new) combined model. Clearly, a purely numerical approach to the problem is not straightforward, given the need to track the behaviour for ε and δ both small, with their relative values being of importance. However, we have analysed in full the transition from dissociative to kick-out behaviour, using asymptotic techniques that exploit the smallness of ε and δ , and this asymptotic analysis guided the numerical investigations.

The behaviour of the charged defect model when $\varepsilon = O(\delta)$, $\delta \rightarrow 0$ is quite unusual. It is found that the behaviour differs considerably according to whether $a < a_c$ or $a > a_c$, where a_c (which depends only on λ , β and γ) is a finite critical value of $a = \varepsilon/\delta$. We note that letting $a \rightarrow 0$ gives pure dissociative behaviour (a limit of the $a < a_c$ formulation), while letting $a \rightarrow \infty$ gives pure kick-out behaviour (a limit of the $a > a_c$ formulation). For $a < a_c$ the system clearly exhibits aspects of dissociative behaviour, while for $a > a_c$ kick-out behaviour is strongly featured. It is convenient to characterise the behaviour by considering the leading order substitutional concentration in the outer region. For $a < a_c$, as $x \rightarrow q_0^-(t)$ we have that

$$s \sim \delta S$$

where S is a non-zero constant. However, as $a \rightarrow a_c^-$, $S \rightarrow 0^+$ and for $a > a_c$, it is found that the substitutionals have the behaviour

$$s \sim B(1 - x/q_0)^{\frac{1}{2}(1-\kappa)}$$

as $x \rightarrow q_0^-$, where B is a constant and κ is defined above; we have $\kappa \rightarrow 1^-$ as $a \rightarrow a_c^+$, with the value of κ exhibited by a substitutional profile conveniently characterising the relative contributions of the dissociative and kick-out mechanisms. The value $a = a_c$ marks a rather abrupt transition in the diffusion behaviour,

whereby the nature of the competition between kick-out and dissociative effects changes significantly.

ACKNOWLEDGEMENTS

We are grateful to the British Council/Enterprise Ireland for the award of travel grants. MGM is also grateful to Forbairt for the award of a basic research grant. JRK gratefully acknowledges the support of the Leverhulme Trust.

REFERENCES

- [1] G. Bosker, N.A. Stolwijk, H.G. Hettwer, A. Rucki, W. Jager and U. Sodervall, Use of zinc diffusion into GaAs for determining properties of gallium interstitials, *Physical Review B* **52** (1995), 11927–31.
- [2] U. Gosele and F. Morehead, Diffusion of zinc in gallium arsenide: a new model, *Journal of Applied Physics* **52** (1981), 4617–19.
- [3] J.R. King and M.G. Meere, Asymptotic analysis of a combined dissociative and kick-out diffusion mechanism, *IMA Journal of Applied Mathematics* **56** (1996), 33–63.
- [4] J.R. King and M.G. Meere, The role of multiple charge states in zinc diffusion in gallium arsenide, *Mathematical Proceedings of the Royal Irish Academy* **101A** (1) (2001), 95–110.
- [5] M.G. Meere and J.R. King, The dissociative diffusion mechanism with charge effects I: one-dimensional in-diffusion, *The Quarterly Journal of Mechanics and Applied Mathematics* **54** (2001), 469–500.
- [6] M.G. Meere, An analysis of a kick-out diffusion mechanism with charge effects, *The Quarterly Journal of Mechanics and Applied Mathematics* **51** (1998), 515–41.
- [7] S.M. Sze, *Semiconductor devices. Physics and technology*, Wiley, New York, 1985.
- [8] T.Y. Tan, Point defects and diffusion mechanisms pertinent to the Ga sublattice of GaAs, *Materials Chemistry and Physics* **40** (1995), 245–52.
- [9] B. Tuck, *Atomic diffusion in III–V semiconductors*, Adam Hilger, Bristol–Philadelphia, 1988.
- [10] H.R. Winteler, Die Diffusion von Zink und Gallium in Galliumarsenid bei 1100°C, *Helvetica Physica Acta* **44** (1971), 451–86.
- [11] S. Yu, T.Y. Tan and U. Gosele, Diffusion mechanism of chromium in GaAs, *Journal of Applied Physics* **70** (1991), 4827–36.
- [12] S. Yu, T.Y. Tan and U. Gosele, Diffusion mechanism of zinc and beryllium in gallium arsenide, *Journal of Applied Physics* **69** (1991), 3547–65.