Vacancy Transients During Impurity Diffusion in Semiconductors

S. M. Hu* and M. S. Mock
IBM Components Division, East Fishkill Facility, Hopewell Junction, New York 12533
(Received 14 November 1969)

Vacancy transients associated with the diffusion of donor atoms in semiconductors are examined for a model of strong vacancy-impurity association. The causes for the vacancy transients are the drift of charged vacancies in the internal field and the shifting of the local thermal-equilibrium condition of vacancy concentration. The impurity is considered to diffuse into a semi-infinite solid with a constant surface concentration. Simultaneous equations of continuity for the impurity and the vacancy are obtained from phenomenological flux expressions, and their Boltzmann transforms are solved numerically. For the example studied, which is typical of donor diffusions in silicon, the maximum vacancy undersaturation was found to be 4.17×10^{-7}. An inequality estimation gives $\sigma \lesssim 8D_A(0)/D_v$, where σ is the vacancy supersaturation (negative in the present case), $D_A(0)$ is the impurity diffusivity at the surface, and D_v is the vacancy diffusivity. It is concluded that, during impurity diffusion, the departure of the vacancy concentration from its equilibrium value is entirely negligible for the model concerned. It is also pointed out that the cross coefficients of the phenomenological flux expressions are dependent on an atomistic model. For example, it is shown that if Seitz's chemical-pump model is assumed, then there will be significant vacancy nonequilibrium.

I. INTRODUCTION

In a diffusion which proceeds by means of a vacancy mechanism, the diffusivity of the diffusant is usually some function of the local vacancy concentration, the function being definitive for a specific atomistic model. Thermodynamical analyses of the equilibrium vacancy concentration as a function of the diffusant concentration in the semiconductor are available in the literature.[1,2] However, no quantitative study has been published on the possible departure of the vacancy concentration from its equilibrium value during the impurity diffusion. To study vacancy transients, one can proceed by constructing equations of continuity from the linear phenomenological equations

$$J_i=\sum_j L_{ij}X_j, \qquad (1)$$

where J_i is the flux of the ith component and X_j in the present paper is given by $-\partial\mu_j/\partial x$, μ_j being the chemical potential of the jth component. L_{ij}'s are the matrix elements of the phenomenological coefficients.

We consider $i, j=A, B, v$, representing, respectively, the impurity, the host lattice, and the lattice vacancy which form a ternary system. One problem hitherto has been how to obtain a self-consistent set of phenomenological coefficients, and the question of vacancy transients has remained rather academic. In a broader sense, this problem has recently been solved[2] for the ternary system A-B-v by establishing the relationship between the off-diagonal elements $L_{ij}(i\neq j)$ and the diagonal elements; and in a definitive sense, for the case where there is a strong association between the impurity atom and the vacancy. Historically, the problem of vacancy transients was first treated by Seitz[3] in connection with his explanation of the Kirkendall effect. His analysis leads to the following expression of vacancy flux:

$$J_v=(D_A-D_B)(\partial N_A/\partial x)-D_v\partial N_v/\partial x, \qquad (2)$$

where D is the diffusivity and N is the concentration, with subscripts denoting atomic species. Seitz called the first term in the right-hand side of Eq. (2) the chemical pump. The inadequacy of Seitz's analysis has been discussed in Ref. 2 and is the consequence of the existence of a correlation effect in both the impurity and the vacancy random walks. The kinetic origin of Eq. (2) assumes a probability N_AN_v (unnormalized), of which A is neighboring to v and an event of impurity jump occurs with a frequency ω_A. This implies that, after each impurity jump, the vacancy immediately randomizes itself into the bulk of the lattice, which is physically impossible. The tight-binding approximation treated in Ref. 2 represents the opposite extreme case, but, in contrast, is of probable physical existence. In fact, we may argue that this model is appropriate to the diffusion of donor impurities in semiconductor silicon,[4] which will be the subject of the present treatment.

Diffusion-induced vacancy transients arising from nonvanishing off-diagonal elements of the phenomenological coefficients may be called intrinsic. We may call extrinsic vacancy transients which are not part of a flux expression, and which come from a source term in the equation of continuity. The source may, for example,

* Presently on visiting assignment at the IBM Thomas J. Watson Research Center, Yorktown Heights, N. Y. The joint project was started while this author was at IBM East Fishkill Laboratory.

[1] R. L. Longini and R. F. Greene, Phys. Rev. **102**, 992 (1956).

[2] S. M. Hu, Phys. Rev. **180**, 773 (1969).

[3] F. Seitz, Phys. Rev. **74**, 1513 (1948); Acta Cryst. **3**, 355 (1958); Acta Met. **1**, 355 (1953); J. Phys. Soc. Japan **10**, 697 (1955).

[4] For example, impurity-vacancy complexes at low temperatures have been discussed by Mitsuji Hirata, Masako Hirata, H. Saito, and J. H. Crawford, Jr., J. Appl. Phys. **38**, 2433 (1967). One also expects complexes to exist at higher temperatures. One would also expect the tight binding between the impurity ion and the charged vacancy to arise partly from the Coulombic interaction. See also E. L. Elkin and G. D. Watkins, Phys. Rev. **174**, 881 (1968).

be the nonconservative motion of dislocations as discussed elsewhere.[5] The present discussion is restricted to intrinsic transients.

II. DIFFUSION EQUATIONS

Following Ref. 2, we can write a set of linearly independent flux expressions for the ternary system A-B-v as follows:

$$J_A=-D_A^*\frac{N_A}{N_v^*}\left(1+\frac{N_A}{N_B}\right)\left(1+\frac{\partial\ln\gamma_A}{\partial\ln N_A}\right)\frac{\partial N_A}{\partial x}, \tag{3}$$

$$J_V=-D_v^*\frac{N_v}{N_s}\left(1+\frac{\partial\ln\gamma_A}{\partial\ln N_A}+\frac{N_S}{N_A}\frac{\partial\ln\gamma_v}{\partial\ln N_A}\right)\frac{\partial N_A}{\partial x}-D_v^*\frac{\partial N_v}{\partial x}, \tag{4}$$

where γ denotes the activity coefficient, the asterisk denotes equilibrium under intrinsic conditions, and N_S denotes the concentration of lattice sites. More specifically, we consider the impurity A to be a donor and B the semiconductor silicon. Making the approximations of local charge neutrality and of nondegeneracy, one has[2]

$$\begin{aligned}-\frac{\partial\ln\gamma_v}{\partial\ln N_A}&\cong\frac{\partial\ln\gamma_A}{\partial\ln N_A}\\&\cong\frac{\partial}{\partial\ln N_A}\left(\frac{E_F-E_F^*}{kT}\right)\\&\cong\left[1+\left(\frac{2n_i}{N_A}\right)^2\right]^{-1/2},\end{aligned} \tag{5}$$

where n_i is the intrinsic carrier concentration at the diffusion temperature and E_F is the Fermi energy. The term $[1+(2n_i/N_A)^2]^{-1/2}$ approaches unity for $N_A\gg 2n_i$, and reduces to $N_A/2n_i$ for $N_A\ll 2n_i$. Thus, the third term in the parentheses of Eq. (4) becomes $-N_S/N_A$ for large N_A and $-N_S/2n_i$ for small N_A. Since, under realistic conditions, $N_S\gg N_A$ and $N_S\gg 2n_i$, this term dominates the quantity in the parentheses in Eq. (4). Equation (4) may, thus, be approximated by

$$J_v=-D_v^*\frac{N_v}{N_A}\frac{\partial\ln\gamma_i}{\partial\ln N_A}\frac{\partial N_A}{\partial x}-D_v^*\frac{\partial N_v}{\partial x}. \tag{6}$$

The first term in the right-hand side of Eq. (6) can be easily identified (if one so prefers to the thermodynamical concept) with the drift of negatively charged vacancies in the internal field due to $N_A(x)$. Since $\partial\ln\gamma_v/\partial\ln N_A$ and $\partial N_A/\partial x$ have the same sign, the field-drift vacancy flux will be opposite to the direction of J_A. However, due to a very large D_v^* and the gradual decrease of $|\partial N_A/\partial x|$ with time in the region of small x, one should expect the term $D_v^*\partial N_v/\partial x$ to dominate and the vacancy flux direction in the region of small x to reverse. Quantitative results aside, the conclusion to be reached later in this paper will not be affected by the assumptions of local charge neutrality and nondegeneracy. Using Eq. (5), one can write the equations of continuity for N_A and N_v from Eqs. (3) and (6) as follows:

$$\frac{\partial N_A}{\partial t}=D_A^*\frac{\partial}{\partial x}\left\{\frac{N_v}{N_v^*}\left[1+\frac{N_A}{(N_A^2+4n_i^2)^{1/2}}\right]\frac{\partial N_A}{\partial x}\right\}, \tag{7}$$

$$\frac{\partial N_v}{\partial t}=D_v^*\frac{\partial}{\partial x}\left[\frac{\partial N_v}{\partial x}-\frac{N_v}{(N_A^2+4n_i^2)^{1/2}}\frac{\partial N_A}{\partial x}\right]. \tag{8}$$

We consider the case defined by the following initial and boundary conditions:

$$N_A(x,0)=0,\quad N_A(0,t)=N_{A,0},\quad N_A(\infty,t)=0, \tag{9}$$

$$N_v(x,0)=N_v^*,\quad N_v(0,t)=N_v^e,\quad N_v(\infty,t)=N_v^*, \tag{10}$$

where N_v^e is the equilibrium vacancy concentration, $N_v^e=\gamma_v^{-1}N_v^*$, and is a function of N_A. Under the assumptions leading to Eq. (5), the equilibrium vacancy concentration at the surface can be expressed as

$$\begin{aligned}N_v(0,t)&=N_v^e(N_{A,0})\\&=N_v^*[N_A/2n_i+(1+N_A^2/4n_i^2)]^{1/2}.\end{aligned} \tag{11}$$

We introduce two dimensionless variables θ and σ, defined by

$$\theta=N_A/2n_i+(1+N_A^2/4n_i^2)^{1/2},\quad N_v=N_v^*\theta(1+\sigma). \tag{12}$$

From Eqs. (11) and (12), one sees that σ is an explicit expression for the departure of the vacancy concentration from its equilibrium value; i.e., $\sigma=(N_v/N_v^e-1)$. The purpose of introducing σ is to effect an accurate solution in anticipation of a very small deviation of the vacancy concentration from equilibrium. In terms of these variables, Eqs. (7) and (10) become

$$\frac{\partial}{\partial t}(\theta-\theta^{-1})=D_A^*\frac{\partial}{\partial x}\left((1+\sigma)\frac{\partial\theta^2}{\partial x}\right), \tag{13}$$

$$\frac{\partial}{\partial t}[\theta(1+\sigma)]=D_v^*\frac{\partial}{\partial x}\left(\theta\frac{\partial\sigma}{\partial x}\right), \tag{14}$$

$$\begin{aligned}&\theta(0,t)=N_{A,0}/2n_i+(1+N_{A,0}^2/4n_i^2)^{1/2},\\&\theta(x,0)=\theta(\infty,t)=1,\end{aligned} \tag{15}$$

$$\sigma(x,0)=\sigma(0,t)=\sigma(\infty,t)=0. \tag{16}$$

Rigorously speaking, our flux expressions from the phenomenological equations are formulated in a fixed spatial coordinate system in which the sum of fluxes $(J_A+J_B+J_V)$ across any plane (except the surface plane) perpendicular to x is zero. It is tacitly assumed

[5] S. M. Hu and T. H. Yeh, J. Appl. Phys. 40, 4615 (1969).

that only vacancies and impurity atoms, but not host lattice atoms, can flow across the surface. Since, in general, the sum (J_A+J_v) at the surface will not be zero, the conservation of lattice sites in a plane demands the surface to move relative to the fixed coordinate, and we have a moving-boundary problem. However, an approximate estimation gives a movement of the boundary on the order of $(\pi^{-1/2}N_{A,0}/N_S)2(D_At)^{1/2}$, which is less than 1% of the impurity diffusion length under typical conditions. This justifies the assumption of a fixed boundary at $x=0$.

The set of equations (13)–(16) admits a Boltzmann transformation. Defining $\eta=x/t^{1/2}$ and denoting differentiation with respect to η by primes, one obtains

$$2\eta(\theta-\theta^{-1})'+D_A^*[(1+\sigma)(\theta^2)']'=0, \quad (17)$$

$$2\eta[\theta(1+\sigma)]'+D_v^*(\theta\sigma')'=0, \quad (18)$$

$$\theta(\eta)=\theta_0 \text{ at } \eta=0, \quad \theta(\eta)=1 \text{ as } x\to\infty, \quad (19)$$

$$\sigma(\eta)=0 \text{ at } \eta=0 \text{ and } \infty. \quad (20)$$

While an analytical solution to Eqs. (17)–(20) appears unavailable, an upper bound for $|\sigma|$ can be estimated using inequality relations. It is shown in the Appendix that $|\sigma| \lesssim 8D_A(0)/D_v$, which is negligibly small.

III. NUMERICAL RESULTS

Numerical solutions of the continuity equations (17)–(20) have been obtained using finite difference approximation. The enormous difference between D_A^* and D_v^* results in a vacancy diffusion length a few orders of magnitude larger than the impurity diffusion length. This has required the use of a nonuniform grid point spacing and difference approximations which have recently been utilized in degenerate boundary-value problems.[6,7]

In the example calculated, we have considered a case characterized by these physical parameters: $D_A^*=10^{-14}$ cm^2 sec^{-1}; $D_v^*=10^{-6}$ cm^2 sec^{-1}; $N_{A,0}=2.5\times10^{20}$ cm^{-3}; $N_v^*=10^{13}$ cm^{-3}; $n_i=10^{19}$ cm^{-3}. These values of rounded figures are considered to be appropriate to diffusion in silicon between 1000–1100°C. The value of n_i was from

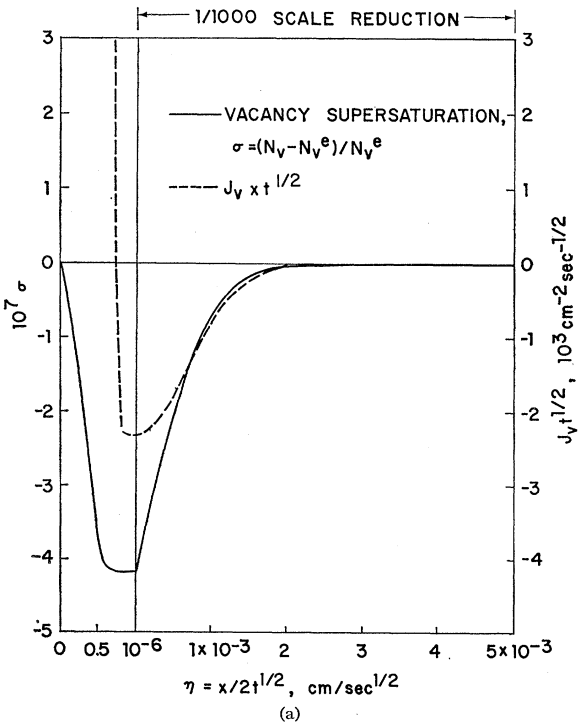

FIG. 1. (a) Fractional departure of vacancy concentration versus η. (b) $N_A(\eta)$ versus $N_v(\eta)$ [see $\sigma(\eta)$ in (a)].

[6] H. J. Kushner, SIAM J. Num. Anal. 5, 664 (1968).
[7] C. D. Hill, SIAM, J. Num. Anal. 5, 717 (1968).

Morin and Maita[8]; D_A^* is of typical experimental values of group-V donors[9]; N_v^* is estimated from the calculated energy of vacancy formation[10] of 2.35 eV; D_v^* is obtained from the relationship $D_v^* N_v^* = D_B^* N_S$, where D_B^* is the silicon self-diffusivity, and is given an approximate value[11] of 10^{-16} cm^2/sec; and N_S, the concentration of lattice sites, is taken to be 5.5×10^{22} cm^{-3}. The results of the numerical computation are shown in Figs. 1(a), 1(b), and 2.

In Fig. 1(a), the fractional departure of the vacancy concentration from its equilibrium value, the latter being a function of local $N_A(\eta)$, is plotted against η. In this example, we obtained a maximum $|\sigma|$ of $(4.17\pm0.05)\times10^{-7}$. The error estimate given is empirical, based on successive calculations with different numbers of grid points. σ is negative everywhere except at the boundaries, indicating a general vacancy undersaturation at all times during the diffusion process. However, σ is so small that its effect on the impurity diffusion is entirely negligible.

The vacancy flux J_v normalized by a factor of $t^{1/2}$, is also plotted in the same figure to show the spatial relationship of σ and J_v. The results show that the vacancy flux is in the outward direction in the region of large η, and there is a reversal of flux direction in the region of small η. The point of zero flux $x(J_v=0)$ moves in with $t^{1/2}$, as demanded by the $J_v t^{1/2}$-versus-η plot. Figure 1(b) shows the profiles $N_A(\eta)$ and $N_v(\eta)$ in the same example and serves to connect the spatial relationship between $N_A(\eta)$ and $\sigma(\eta)$ in Fig. 1(a). These $N_A(\eta)$ profiles are the same to the extent of numerical accuracy with those calculated on the assumption of local vacancy equilibrium.[12] Figure 2 shows a log-log plot of $(J_v+3\times10^3)$ versus x at a diffusion time of 1 sec. The constant of 3×10^3 cm^{-2} sec^{-1} was added to J_v to make possible the representation of J_v in the log-log plot in its full range including negative values. Even with a value of $\sim7\times10^7$ cm^{-2} sec^{-1} at the surface, J_v is very small in comparison with the impurity flux $J_A\sim10^{14}$ cm^{-2} sec^{-1} at the surface.

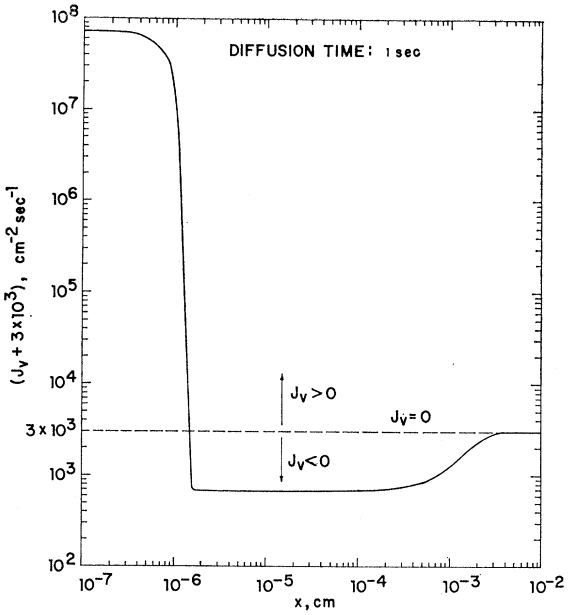

FIG. 2. Log-log plot of $(J_v+3\times10^3)$ versus x at a diffusion time of 1 sec.

IV. DISCUSSION

In the preceding sections, a quantitative study has been made on the vacancy transient phenomenon and the extent of the induced vacancy concentration undersaturation during a diffusion process. The results show that the fractional departure of the vacancy concentration from its local equilibrium value is negligibly small, with a maximum σ of -4.17×10^{-7} for the example studied. An inequality estimation of the upper bound for $|\sigma|$ is $O(8D_A/D_v^*)$. This justifies the assumption of an equilibrium vacancy concentration during the diffusion process. Quite obviously, the theory of equilibrium vacancy concentration using the assumptions of local charge neutrality and of Boltzmann statistics is itself a grosser approximation.

The preceding analysis is based on the tight-binding model of impurity diffusion of Ref. 2. This model is considered to be appropriate for the diffusion of substitutional impurities in semiconductors. In cases where this model becomes inappropriate, the conclusion regarding vacancy undersaturation arising from intrinsic transients would be different. We may examine the extreme case of Seitz's chemical-pump model[3] which, though physically unrealistic, may nevertheless serve to demonstrate certain model processes in which significant vacancy undersaturation can occur. We rewrite Eq. (2) in the following form of equation of continuity:

$$\frac{\partial\sigma}{\partial t}=D_v\frac{\partial\sigma}{\partial x}\left(\frac{\partial\sigma}{\partial x}-\frac{(D_A-D_B)}{D_v}\frac{1}{N_v^*}\frac{\partial N_A}{\partial x}\right). \quad (21)$$

We may assume $N_A(\eta)$ to be bounded such that $N_{A,0}\geq N_A(\eta)\geq0$, and to practically vanish at $\eta\gtrsim O(D_A{}^{1/2})$. The boundary conditions for σ are $\sigma(x,0)=\sigma(0,t)=\sigma(\infty,t)=0$, and the Boltzmann transform of Eq. (21) is

$$-2\eta\sigma'=D_v\sigma''-[(D_A-D_B)/N_v^*]N_A''. \quad (22)$$

Equation (22) is a linear differential equation of the first order in σ' and can be twice integrated directly to

[8] F. J. Morin and J. P. Maita, Phys. Rev. **96**, 28 (1954).
[9] For example, see B. I. Boltaks, *Diffusion in Semiconductors* (Academic Press Inc., New York, 1963).
[10] For example, see A. Seeger and M. L. Swanson, in *Lattice Defects in Semiconductors*, edited by R. R. Hasiguti (University of Tokyo Press, Tokyo, 1968), p. 93 ff.
[11] J. M. Fairfield and B. J. Masters, J. Appl. Phys. **38**, 3148 (1967).
[12] S. M. Hu and S. Schmidt, J. Appl. Phys. **39**, 4272 (1968).

give

$$\sigma(\eta)=\tfrac{1}{2}\sqrt{(\pi)}\frac{D_A-D_B}{D_vN_v^*}$$
$$\times\left\{-\operatorname{erf}\eta_0\int_0^\infty N_A''(\rho)e^{\rho^2/\eta_0^2}\operatorname{erfc}\left(\frac{\rho}{\eta_0}\right)d\rho\right.$$
$$\left.+\int_0^\eta N_A''(\rho)e^{\rho^2/\eta_0^2}\left[\operatorname{erfc}\left(\frac{\rho}{\eta_0}\right)-\operatorname{erfc}\left(\frac{\eta}{\eta_0}\right)\right]d\rho\right\}, \quad (23)$$

where $\eta_0\equiv D_v^{1/2}$. For values of $\eta\ll\eta_0$, Eq. (23) reduces to

$$\sigma(\eta)\approx-[(D_A-D_B)/D_vN_v^*]$$
$$\times\{N_A(0)-[1+O(\eta/\eta_0)]N_A(\eta)\}+O(\eta^2/\eta_0^2). \quad (24)$$

It is then easily seen that a limiting value of σ exists at some $\eta=O(D_A^{1/2})\ll\eta_0$, at which Eq. (24) becomes

$$\sigma_{\min}\approx-(D_A-D_B)N_{A,0}/(D_vN_v^*)$$
$$=-(D_A-D_B)N_{A,0}/D_BN_S, \quad (25)$$

for we know at some $\eta=O(D_A^{1/2})$, $N_A(\eta)/N_A(0)\approx0$, and that D_v is several orders of magnitude larger than D_A.

One may quickly notice that for entirely possible physical cases where $(D_A-D_B)N_{A,0}/D_BN_S>1$, Eq. (25) would give $\sigma_{\min}<-1$, meaning the existence of a negative vacancy concentration, which is physically impossible. The explanation lies in the failure of the simple model of Eq. (2) under the condition of significant nonequilibrium vacancy concentration. This physical defect of the model can be removed (while the correlation effect remains neglected) by modifying Eq. (2) into

$$J_v=(D_A-D_B)(N_v/N_v^*)(\partial N_A/\partial x)-D_v\partial N_v/\partial x. \quad (26)$$

Either with Eq. (2) or (26), a considerable vacancy undersaturation can be expected if $(D_A-D_B)N_{A,0}/(D_BN_S)$ is not negligibly small compared to unity. In binary metal alloys, where both the impurity and the vacancy concentrations are high, one may expect considerable extent of vacancy nonequilibrium. These form the classical examples in the study of the Kirkendall effect, but are complicated by the presence of dislocations.

APPENDIX: ESTIMATION OF UPPER BOUND FOR $|\sigma|$

A knowledge of the general characteristics of the impurity profile $N_A(X)$ allows us to make the following assumptions:

(a) $\theta(\eta)\leq\theta(0)$,
(b) $\theta'(\eta)\leq0$, (A1)
(c) $\theta(\eta)\simeq1$ for $\eta\geq\eta^*$,

where η^* is some point sufficiently larger than the impurity diffusion length. η^*, in general, will be a few orders of magnitude smaller than $\sqrt{D_v}$. The following conditions are readily established:

(a) $\sigma(\eta)\leq0$,
(b) $\sigma(\eta)>-1$,
(c) $\sigma(\eta)$ has no local maximum and has a unique minimum at $\bar{\eta}$, (A2)
(d) $\sigma(\eta)$ is a complementary error function for $\eta\geq\eta^*$; thus, $\bar{\eta}\leq\eta^*$, since erfc has no local extremum.

Condition (d) in (A2) is a consequence of (c) in (A1) because, then, Eq. (2–12) reduces to

$$2\eta\sigma'+D_v^*\sigma''=0, \quad \eta\geq\eta^*. \quad (A3)$$

With $\sigma(\propto)=0$, (A3) admits a solution of the form

$$\sigma(\eta)=K\operatorname{erfc}(\eta/\sqrt{D_v^*}), \quad \eta\geq\eta^* \quad (A4)$$

where K is a constant determinable by matching the solution for $\eta\leq\eta^*$. We rewrite Eq. (18) in the following form:

$$[\theta\sigma'e^{\eta^2/D_v^*}]'=-\frac{2\eta}{D_v^*}\theta'(1+\sigma)e^{\eta^2/D_v^*}$$
$$\leq-\theta'\frac{2\eta}{D_v^*}e^{\eta^2/D_v^*}. \quad (A5)$$

Integrating (A5) from η to $\bar{\eta}$, using $\sigma'(\bar{\eta})=0$, we obtain

$$-\theta\sigma'e^{\eta^2/D_v^*}\leq\int_\eta^{\bar{\eta}}(-\theta')\frac{2\eta}{D_v^*}e^{\eta^2/D_v^*}d\eta$$
$$\leq\frac{2\bar{\eta}}{D_v^*}e^{\bar{\eta}^2/D_v^*}\int_\eta^{\bar{\eta}}-\theta'd\eta$$
$$\leq\frac{2\bar{\eta}}{D_v^*}e^{\bar{\eta}^2/D_v^*}\theta(\eta), \quad (A6)$$

or

$$-\sigma'\leq\frac{2\bar{\eta}}{D_v^*}e^{(\bar{\eta}^2-\eta^2)/D_v^*}\leq\frac{2\bar{\eta}}{D_v^*}e^{\bar{\eta}^2/D_v^*}. \quad (A7)$$

Integrating from 0 to η, we obtain

$$|\sigma(\bar{\eta})|\leq\frac{2\bar{\eta}^2}{D_v^*}e^{\bar{\eta}^2/D_v^*}. \quad (A8)$$

We estimate $\bar{\eta}^2$ to be of the order of

$$4D_A(0)=4D_A^*[N_{A,0}/2n_i+(1+N_{A,0}^2/4n_i^2)]^{1/2}.$$

Taking the values of the physical parameters as given in Sec. III, we obtain $|\sigma|\leq2\times10^{-6}$, which is consistent with the numerical result given in Sec. III.