Thin-source concentration-dependent diffusion: A full solution

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A new method of analysis is developed for solving the problem of an initially thin source of impurity ions diffusing into a host solid when the mechanism of transport involves a concentration-dependent diffusivity. In order to extract a diffusivity from experimental data we show that the fundamental experiment required is a measurement of the diffusion profile at two different times. The constant and the concentration-dependent contributions to the diffusivity then can be isolated by requiring the initial measured profile to propagate into the final measured profile. The analytic procedure presented here is shown to be a full solution to the problem of a diffusivity that varies linearly with concentration: $D(C)=D_0(1+\alpha C)$, where α is the strength of the nonlinear term. A matrix of orthogonal functions determines the time evolution for an arbitrary thin-source initial state. We show that the total diffusant amount is conserved and that the solution is naturally expressed as a power series in α. The persistence of curvature on $\ln(C)$-vs-x^2 axes is then derived from the asymptotic (long-time) properties of the nonlinear equation solution. The solution up through order α^2 is then explicitly constructed for an arbitrary thin-source initial state.

I. INTRODUCTION

When a linear diffusion equation with a constant diffusivity is obeyed, the diffusion of an initially thin source of material into a semi-infinite solid gives a Gaussian penetration profile. On $\ln(C)$-vs-x^2 axes, Gaussians plot as straight lines. Curvature in the penetration profile on $\ln(C)$-vs-x^2 axes means a non-Gaussian profile, and this is often taken as an indication of concentration-dependent diffusion, where the diffusivity $D(C)$ depends on the local concentration C. In planar geometry, Fick's laws then give[1]

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} D(C) \frac{\partial C}{\partial x} \ . \tag{1}$$

Although concentration-dependent diffusion (CDD) equations have been formulated for many diverse physical systems, the resulting nonlinear equations have historically proven difficult to analyze, preventing both determining accurate physical parameters from experimental data and hampering quantitative comparison of data with differing CDD models that might be developed for describing the transport physics.

Here, a new method of solution for the nonlinear diffusion equation is developed for the thin-source configuration when the diffusivity varies linearly with concentration. This method uses a matrix of orthogonal functions to describe the time development of the concentration profile and it allows an arbitrary function to be used for the initial state.

For a thin-source experiment, the total amount of diffusant must also be conserved. This is expressed as a conserved side condition of

$$\int_{x=-\infty}^{\infty} C(x,t)dx = K \ , \tag{2}$$

where K is necessarily independent of time, and where reflection symmetry has been used to convert the semi-infinite interval $x = (0, \infty)$ into a double-infinite interval $x = (-\infty, +\infty)$. We show how proper handling of this constraint gives rise to the "persistence of curvature" phenomenon [$\ln(C)$-vs-x^2 axes] which is often associated with CDD systems.

The fundamental experiment which goes along with this solution method is a two-time experiment in which penetration profiles must be measured for an initial and final time t_R and t_F under similar experimental conditions. The initial state $C(x,t_R)$ is propagated forward in time, using the nonlinear analysis technique, to determine a test final state $C(x,t_F)$ with various trial values for the parameters D_0 and α. These test final states can then be compared to a measured final state $C_F(x,t_F)$ to determine D_0 and α.

In addition, having a full solution gives valuable insight into how nonlinearity can affect the solution of partial differential equations.

II. BACKGROUND

A. Origin of concentration-dependent diffusivities

The basic physical mechanism responsible for concentration-dependent diffusion in solid-state systems is generally well understood, and it is due to the vacancy mechanism dominating the diffusion process. It results in $D \sim [v]$, with $[v]$ being the vacancy concentration. For many ionic and covalent solids, the positive ion is more mobile, usually being smaller, and diffusion is then controlled by the concentration of positive-ion vacancies $[v^+]$. When a foreign metal ion enters substitutionally, to balance the charge mismatch of a heterovalent ion, the levels of the $[v^+]$ lattice vacancies will often change. Since the diffusivity D depends on $[v^+]$, the D value then becomes a function of the local diffusant concentration C.

When the diffusing ion has a greater positive charge, it results in a locally enhanced D value, as in the case of

Ca^{2+} diffusion in NaCl and KCl,[2-7] where each Ca atom can bring in an extra vacancy, so that a $[Ca^{2+}]$-$[v^+]$ pair replaces two $[Na^+]$ or $[K^+]$ sites. Conversely, Na^+ diffusion into a Ca-based ionic crystal suppresses the $[v^+]$ concentration, resulting in a locally depressed D value.

The CDD effect is not limited to strongly ionic crystals, but is expected to generally occur in nonmetallic systems where few free electrons are available for screening a heterovalent ion. Indeed, the CDD effect has been observed in oxides[8-14] and in dopant profiles in Si,[15-23] GaAs,[24-31] and CdS.[32,33] What may be different among these diverse systems is the actual form of the CDD interaction. For example, additional factors such as the equilibration between $[v^+]$ and $[v^-]$ sites via the law of mass action also can alter the local vacancy concentration.[34] Even with these additional processes, however, the heterovalent ions still cause appreciable changes in the local $[v^+]$ concentration, resulting in a CDD process within the diffusion zone.

In this work, the simplest CDD model is studied,

$$D(C) = D_0(1 + \alpha C) , \quad (3)$$

which corresponds to each heterovalent ion introducing exactly one extra vacancy, neglecting mass-action law corrections due to vacancy-vacancy interactions. In Eq. (3), α is a measure of the nonlinearity of the system, and it corresponds roughly to the inverse of the intrinsic $[v^+]$ concentration in the absence of the heterovalent ions C.

B. Thin-source geometry and CDD systems

Numerous methods have been developed to approximate the solution of the nonlinear diffusion equation [Eq. (1)] for various $D(C)$ functions and boundary conditions. One large class of solutions is based on a method pioneered by Boltzmann[35] and Matano,[36] where the two independent variables (x,t) can be replaced by one combined variable,

$$\xi^2 = x^2/4D_0t , \quad (4)$$

reducing the partial differential equation for $C(x,t)$ into an ordinary one for $C(\xi)$. However, this method can only be used with certain types of boundary conditions, such as an initial step-function concentration[37-46] or for diffusion out of a finite slab into a well-mixed medium where $C = 0$ on the surface.[47-51]

The thin-source geometry, in contrast, does not readily admit solutions where $C(x,t)$ can be written as a function of ξ only. The few solutions that have been found for this geometry often have undesirable properties, such as propagating discontinuities,[52,53] or they are solutions which do not inherently conserve mass,[5,6] or D_0 must vanish while keeping (αD_0) finite.[54,55]

Whereas the diffusion equation solution for a step function and for the thin-source initial state are simply related in the constant D case, those two boundary conditions are totally different for the CDD process. The reason can be seen from examining Eq. (3). A step function with a maximum concentration of C_0 sets a specific upper limit for $D(C)$ compared to D_0. In contrast, the thin-source

initial state, which is often idealized as a $\delta(x)$ function, or at least a thin tall Gaussian, spans an arbitrarily large range of concentrations, resulting in ratios for $D(C)/D_0$ which initially can be very large.

Using a diffusivity linearly dependent on concentration to model this initial stage of diffusion thus can give local diffusivity values that are so large that other transport processes can become significant factors. In addition, the mathematical idealization of a thin source as a $\delta(x)$ function cannot be used for nonlinear equations, because algebraic functions of $\delta(x)$ cannot be consistently defined.[56] Because of these factors, the profile in the very initial stages of diffusion can be very non-Gaussian, whereas many of the numerical computations that have been performed[4,57-61] have used a Gaussian to model the thin-source initial state.

These difficulties associated with specifying what occurs during the very initial stages of the thin-source CDD process require using a two-time experiment as the fundamental experiment for this type of boundary condition. A diffusion anneal should first be done for an initial time t_R, followed by a second anneal under similar conditions for a longer time t_F. One may then describe how the thin-source system propagates from an initial $t = t_R$ state into the final $t = t_F$ state. The nonlinearity of the system is then determined by the highest concentration present in the initial $C(x, t_R)$ state. A perturbative solution to the nonlinear equation may then be applied to describe the $t > t_R$ regime, and we derive that solution here up through order α^2. What one gives up for a reduction in net system nonlinearity is that the analysis method has to allow for an arbitrary function as an initial state. A Gaussian or a $\delta(x)$-like function can no longer be assumed to automatically be a good match for the initial $t = t_R$ state.

III. INITIAL STATE

In order to determine what a given initial state propagates into, a parametrization of the initial state is needed. To use a complete orthogonal function set for describing the initial state means that any initial measured profile can be uniquely parametrized by that series, given that the series exists and converges. To do this, we parametrize the initial $t = t_R$ state by using the orthogonal function set that is a generalized thin-source solution to the linear diffusion equation.

The Gaussian thin-source solution for the constant diffusivity case consistent with total mass conservation [Eq. (2)], is

$$C(x,t) = \frac{K}{(4\pi D_0 t)^{1/2}} \exp(-x^2/4D_0t) , \quad (5)$$

and it can be easily generalized into a complete orthogonal function set to allow for a non-Gaussian initial state. One uses the following substitution in Eq. (5):

$$4D_0t \rightarrow X_R^2 + 4D_0(t - t_R) , \quad (6)$$

followed by taking derivatives with respect to x on both sides. This procedure gives a "generalized thin-source" solution to the linear diffusion equation,

$$C(x,t) = \sum_{p=0}^{p=N_i} \frac{B_p}{\Gamma^{(p+1/2)}} H_{2p}(z) \exp(-z^2) \, , \qquad (7a)$$

$$\Gamma = \Gamma_0 + [4D_0(t - t_R)/X_R^2] \, , \qquad (7b)$$

$$z^2 = x^2/(\Gamma X_R^2) \, . \qquad (7c)$$

Here t_R, X_R, Γ_0, and the series $\{B_p; p = (0, N_i)\}$ are all arbitrary constants which specify the initial state, and $H_{2p}(z)$ are the even Hermite polynomials. The $t = t_R$ limit is a complete orthogonal function representation for the thin-source initial state, for both the linear and nonlinear diffusion equations.[62,63]

IV. NONLINEAR DIFFUSION EQUATION

A. General thin-source solution

A concentration-dependent diffusion equation in one rectilinear dimension can be written, using Eq. (3), as

$$\frac{\partial C}{\partial t} = D_0 \frac{\partial}{\partial x}(1 + \alpha C)\frac{\partial C}{\partial x} \, , \qquad (8)$$

where α is a parameter describing the strength of the nonlinearity and D_0 is the intrinsic diffusivity in the absence of nonlinear effects. Transforming from the variables (x,t) to (z,Γ) gives

$$4\Gamma \frac{\partial C}{\partial \Gamma} = \frac{\partial}{\partial z}(1 + \alpha C)\frac{\partial C}{\partial z} + 2z\frac{\partial C}{\partial z} \, , \qquad (9)$$

where Eqs. (7b) and (7c) were used for Γ and z, respectively. The parameter Γ alone defines the time evolution of the system.

One can now select between two possible viewpoints to match experimental data. Suppose D_0 is known beforehand; then $\Gamma = \Gamma_0$ corresponds to the initial state, and $\Gamma > \Gamma_0$ will be the time evolution of that initial state. Alternatively, if D_0 is not known beforehand, and a final state at $t = t_F$ is measured in addition to the initial $t = t_R$ state, then Γ can propagate through the range of possible D_0 values. The particular Γ value which gives a predicted profile that most closely matches the measured final state at $t = t_F$ then determines D_0. For example, if the final $t = t_F$ state were matched well using $\Gamma \approx \Gamma_0$, it would correspond to a diffusivity D_0 that is vanishingly small.

Using the orthogonal function solution to the linear diffusion equation [Eq. (7a), $\alpha = 0$], as a trial solution for to the nonlinear case does not work without substantial modifications. The reason is that each term in Eq. (7a) is of the type $\sim \exp(-z^2)$, and the nonlinear operations will generate terms of the type $\sim \exp(-2z^2)$. These terms can combine, again due to the nonlinearities, to general new terms $\sim \exp(-3z^2)$ and $\sim \exp(-4z^2)$, which then generate even higher-order terms. Thus a minimum spanning space of functions to solve Eq. (9) is

$$C(z,\Gamma) = \sum_{n=1}^{\infty} \sum_{m=0}^{\infty} g(m,n)H_{2m}(z\sqrt{n}) \exp(-nz^2) \, . \qquad (10)$$

We will show in succeeding sections that Eq. (10) does indeed solve the nonlinear diffusion equation of Eq. (9), where the coefficients $g(m,n)$ can be recursively calculated, and are functions of Γ only, Γ being a normalized time parameter. In addition, we will show that the series solution represented by Eq. (10) is, in general, convergent, and that it (1) uniquely specifies the time development from an initial $t = t_R$ state, (2) conserves net diffusant amount, and (3) predicts the persistence of curvature [on $\ln(C)$-vs-x^2 axes], specifically due to the nonlinear nature of the diffusion equation.

B. Overview of the nonlinear diffusion equation solution

In this section we provide an overview of the full solution being developed here. This overview serves not only as a guide through the full solution but also it shows which elements of the full solution become related together due to the nonlinearity of the system.

The set of functions in the nonlinear equation solution $g(m,n)$ can be arranged in a matrix form as follows:

$$G(\Gamma) = \begin{bmatrix} g(0,1) & g(1,1) & g(2,1) & g(3,1) & \cdots \\ g(0,2) & g(1,2) & g(2,2) & g(3,2) & \cdots \\ g(0,3) & g(1,3) & g(2,3) & g(3,3) & \cdots \\ \cdots & \cdots & \cdots & \cdots & \cdots \\ \cdots & \cdots & \cdots & \cdots & \cdots \end{bmatrix} . \qquad (11)$$

Each $g(m,n)$ term will be a function of Γ only, primarily due to the fact that each row (distant n value) is a complete orthogonal function expansion by itself. Since Γ is a time-evolution parameter, the equation governing each $g(m,n)$ term will be first order in Γ, since the original diffusion equation is first order in time. Each $g(m,n)$ term will then have a separate constant that must be determined from the $t = t_R$ initial state.

The first row ($n = 1$) in the $G(\Gamma)$ matrix will also correspond to a full thin-source solution to the linear diffusion equation; thus one will be able to match any given finite initial state just by using this part of the nonlinear equation solution.

Once a particular initial state is matched using the $g(m,n = 1)$ functions, all the other functions, $g(m,n > 1)$, must then be set to vanish at the initial time t_R so as to not alter the shape of that initial state. Mathematically, this criteria becomes the following constraint for $n > 1$:

$$\lim_{\Gamma \to \Gamma_0} g(p, n > 1) = 0 \, . \qquad (12)$$

This constraint then assigns a specific value to all the "arbitrary" constants that appear in the $G(\Gamma)$ matrix. Matching the linear equation solution as given in Eqs. (7a)–(7c) then determines the initial state for the set of $g(m,n)$ functions,

$$G(\Gamma = \Gamma_0) = \begin{bmatrix} B_0/\Gamma_0^{1/2} & B_1/\Gamma_0^{3/2} & B_2/\Gamma_0^{5/2} & B_3/\Gamma_0^{7/2} & \cdots \\ 0 & 0 & 0 & 0 & \cdots \\ 0 & 0 & 0 & 0 & \cdots \\ \cdots & \cdots & \cdots & \cdots & \cdots \end{bmatrix} . \tag{13}$$

For the linear diffusion equation ($\alpha = 0$), the time evolution of $G(\Gamma)$ is simply

$$G(\Gamma, \alpha = 0) = \begin{bmatrix} B_0/\Gamma^{1/2} & B_1/\Gamma^{3/2} & B_2/\Gamma^{5/2} & B_3/\Gamma^{7/2} & \cdots \\ 0 & 0 & 0 & 0 & \cdots \\ 0 & 0 & 0 & 0 & \cdots \\ \cdots & \cdots & \cdots & \cdots & \cdots \end{bmatrix} , \tag{14}$$

reflecting the fact that for linear systems, each orthogonal function component propagates in time independently of all others. Similarly, any orthogonal function coefficient which vanishes for the initial state remains zero for all times thereafter in the linear equation case.

For the nonlinear equation, however, individual $g(m,n)$ components will grow from being zero at the initial state. Determining this time evolution for individual elements in the $G(\Gamma)$ matrix then completes the nonlinear equation solution. It is during this part of the calculation that the special properties of Eq. (10) become evident as being the true equation solution, instead of being just a good approximation.

While the time evolution of the $g(m,n)$ functions is governed by first-order differential equations, they could have formed a system that was neither linear nor recursively calculable. However, for the particular series chosen in Eq. (10), the systems of $g(m,n)$ equations are recursively calculable and consist entirely of first-order linear equations. In addition, this solution also rigorously preserves total diffusant amount [Eq. (2)], which is a physical requirement of thin-source diffusion. Together, strict mass conservation and recursivity allow the asymptotic form of the $G(\Gamma)$ matrix to be determined. What we then find, for the long-time (large-Γ) limit, is that the $G(\Gamma)$ matrix asymptotically approaches

$$G(\Gamma) = \begin{bmatrix} B_0/\Gamma^{1/2} & B_1/\Gamma^{3/2} & B_2/\Gamma^{5/2} & B_3/\Gamma^{7/2} & \cdots \\ 0 & \sim 1/\Gamma^1 & \sim 1/\Gamma^1 & \sim 1/\Gamma^1 & \cdots \\ 0 & \sim 1/\Gamma^{3/2} & \sim 1/\Gamma^{3/2} & \sim 1/\Gamma^{3/2} & \cdots \\ 0 & \sim 1/\Gamma^{3/2} & \sim 1/\Gamma^{3/2} & \sim 1/\Gamma^{3/2} & \cdots \\ \cdots & \cdots & \cdots & \cdots & \cdots \end{bmatrix} . \tag{15}$$

The terms that are involved in total mass conservation are all in the first column, and as Eq. (15) shows, only one term, $g(0,1)$, is nonvanishing, and that term is from the linear part of the equation solution. This solution thus automatically preserves net diffusant amount.

The absolute conservation of total diffusant amount has a second, very important consequence. Had those nonlinear contributions in the first column not identically vanished, as could be true in an approximate solution, they would have had a time dependence which behaves like ($1/\Gamma^{1/2}$), which is the same overall size as a fundamental Gaussian solution from the linear equation [Eq. (5)]. That time dependence would then propagate from the first column out into every other column of the $G(\Gamma)$ matrix. One could then erroneously conclude that the size of the nonlinear contributions could swamp out the linear equation fundamental Gaussian. However, with total mass conservation strictly assured, the proper asymptotic form, as shown in Eq. (15), can be derived for each $g(m,n)$ function.

C. Persistence of curvature

The experimentally observed signature most often associated with concentration-dependent diffusion is a persistence of curvature [$\ln(C)$-vs-x^2 axes] observed in diffusion profiles for a thin-source geometry. A persistence of curvature is equivalent to a persistence of non-Gaussian contributions in the time development of a diffusion profile. These non-Gaussian contributions are exactly the higher-order Hermite polynomials, $H_{2m}(z\sqrt{n})$ of Eq. (10), in the solution of the nonlinear diffusion equation.

How these non-Gaussian components decay in time (large-Γ limit), compared to the linear diffusion equation, determines the time evolution of the penetration profiles on $\ln(C)$-vs-x^2 axes. The large-Γ limit of the linear equation solution has all the non-Gaussian components decreasing successively faster and faster in time [Eqs. (7a) and (14)]. Thus, when the linear equation is obeyed, any curvature, or non-Gaussian quality in an initial diffusion

profile "heals out" very quickly. "Curvature" for the linear equation system, therefore, does not persist.

In contrast, for the nonlinear equation, all the higher-order Hermite polynomial terms will be shown to decay with similar rates: $g(p>1, n=2)\sim\Gamma^{-1}$ and $g(p>1, n=3,4,\ldots)\sim\Gamma^{-3/2}$. Thus these terms remain comparable in size to or larger than the first non-Gaussian component of the linear equation solution $g(1,1)\sim\Gamma^{-3/2}$. Thus all the non-Gaussian structure in the initial state remains for a much longer time in the nonlinear case, which is exactly the persistence of curvature phenomenon.

V. SOLUTION OF THE NONLINEAR DIFFUSION EQUATION

A. Equations governing the nonlinear time evolution

In this section the solution to the nonlinear diffusion equation [Eq. (9)] is determined for an arbitrary thin-source initial state [Eqs. (6) and (7)] by constructing the time-evolution matrix $G(\Gamma)$ as given in Eqs. (10)–(15).

Throughout this section and following sections we will often make use of a generalized Kronecker's delta, $\delta\{\ \}$, which keeps track of additional constraints on the indices. The notation using $\delta\{\ \}$-type functions simplifies much of the accounting when permutations are done involving summations. The value of $\delta\{\ \}$ is 1 whenever the relational expression inside the braces is true and $\delta\{\ \}$ is

zero otherwise. Using the generalized Kronecker's delta allows constraints on the indices to be manipulated algebraically within each summation, and it is critical for the accurate derivation of many of the formulas here.

Using the following shorthand notation:

$$g(m,n)\equiv g_{m,n}(\Gamma)$$

(implicit function of Γ assumed) ,   (16a)

$$g'(m,n)=\frac{d}{d\Gamma}g(m,n)$$

(implicit derivative of Γ assumed) ,   (16b)

$$q(2m,n)=H_{2m}(z\sqrt{n})\exp(-nz^2)$$

(implicit function of z assumed) ,   (16c)

it results in the linear part of Eq. (9) becoming

$$4\Gamma\frac{\partial C}{\partial\Gamma}-\frac{\partial^2 C}{\partial z^2}-2z\frac{\partial C}{\partial z}$$

$$=\sum_{n=1}^{\infty}\sum_{m=0}^{\infty}[4\Gamma g'(m,n)+2(2m+1)g(m,n)$$

$$-(n-1)g(m-1,n)]q(2m,n) ,   (17)$$

where we have used the additional definition $g(-1,n)=0$. Substituting Eq. (10) into the nonlinear part gives

$$\alpha\left[C\frac{\partial^2 C}{\partial z^2}+\left[\frac{\partial C}{\partial z}\right]^2\right]=(\alpha n/2)\sum_{n_1,n_2=1}^{\infty}\sum_{m_1,m_2=0}^{\infty}g(m_1,n_1)g(m_2,n_2)\delta\{n_1=na^2\}\delta\{n_2=nb^2\}$$

$$\times[a^2q(2m_1+2,n_1)q(2m_2,n_2)+b^2q(2m_1,n_1)q(2m_2+2,n_2)$$

$$+2abq(2m_1+1,n_1)q(2m_2+1,n_2)] ,   (18a)$$

$$a^2\equiv(n_1/n) ,   (18b)$$

$$b^2\equiv(n_2/n) .   (18c)$$

Equating coefficients of $\sim\exp(-nz^2)$ when both Eqs. (17) and (18a) are substituted into Eq. (9) then isolates all the terms with the same exponential factor. Each distinct $\sim\exp(-nz^2)$ term can then be multiplied by $H_{2p}(z\sqrt{n})d(z\sqrt{n})$, and integrating over all $z=(-\infty,+\infty)$ then isolates a separate equation for each $g(p,n)$ function:

$$4\Gamma g'(p,n)+2(2p+1)g(p,n)-(n-1)g(p-1,n)$$

$$=(\alpha n/2)\sum_{n_1,n_2=1}^{\infty}\sum_{m_1,m_2=0}^{\infty}\delta\{n_1+n_2=n\}g(m_1,n_1)g(m_2,n_2)\theta(m_1,m_2,n_1,n_2;p,n) .   (19)$$

The $\delta\{n_1+n_2=n\}$ restriction in Eq. (19) means that each $g(p,n)$ function depends only on index values less than n, decoupling the nonlinearity of the original diffusion equation into a set that can be recursively calculated. Equation (19) also represents a system of first-order linear equations, which together determine the $G(\Gamma)$ matrix.

The function $\theta(m_1,m_2,n_1,n_2;p,n)$ corresponds to the following integral:

$$\theta(m_1,m_2,n_1,n_2;p,n)=[\pi^{1/2}(2p)!2^{2p}]^{-1}\delta\{n_1=na^2\}\delta\{n_2=nb^2\}$$

$$\times\int\delta\{a^2+b^2=1\}H_{2p}(y)\exp(-y^2)[a^2H_{2m_1+2}(ay)H_{2m_2}(by)+b^2H_{2m_1}(ay)H_{2m_2+2}(by)$$

$$+2abH_{2m_1+1}(ay)H_{2m_2+1}(by)]dy ,   (20)$$

where $a^2 \equiv n_1/n$ and $b^2 \equiv n_2/n$ was used again, and where the implicit limits on the integral are from $y = (-\infty, +\infty)$.

What is noteworthy is that all the arguments in the θ function are integer indices. It is a pure number, containing neither physical parameters (D_0, α) nor parameters derived from the initial state $C(x, t_R)$. The role of the θ function is to prescribe strengths of the mode-mode couplings, since each element of the orthogonal function expansion (mode) is coupled to the others by the nonlinearity of the diffusion equation.

Finally, since the nonlinearity parameter α appears only as a coefficient multiplying the entire right-hand side of Eq. (19), each $g(p, n)$ function is proportional to the $(n-1)$ power of α. Thus the $C(z, \Gamma)$ solution naturally appears as a power series in the nonlinearity parameter α. One can then speak of a solution to order α [involving $g(p, 1)$ and $g(p, 2)$ only] or a solution to order α^2 [involving $g(p, 1)$ through $g(p, 3)$] or a solution to higher order in α.

B. Initial state for the nonlinear equation system

The thin-source solution to the nonlinear diffusion equation of Eq. (9) must be able to fit an arbitrary initial-state profile $C(x, t_R)$ that would be measured at the initial time t_R. We demonstrate this property of the Eq. (19) solution first.

In the first set of $g(p, n)$ functions when $n = 1$, the constraint $\delta\{n_1 + n_2 = n\}$ is never satisfied, and the right-

hand side of Eq. (19) then vanishes. The dependence of each $g(p, n)$ function on the $g(p-1, n)$ term preceding it also vanishes for $n = 1$. The equations for the $n = 1$ case reduce to

$$4\Gamma g'(p, 1) + 2(2p + 1)g(p, 1) = 0 . \tag{21}$$

Each element in the $n = 1$ set is thus independent of all others. As a first-order linear equation, each has one arbitrary constant, giving

$$g(p, 1) = B_p \Gamma^{-(p+1/2)} , \tag{22}$$

where the p index ranges from $p = (0, N_i)$ to match the initial state of Eq. (7a). One thus recovers the generalized thin-source solution to the linear diffusion equation as the first part of the solution to the nonlinear equation. Equation (22) explicitly demonstrates that an arbitrary initial state is allowed by this solution.

C. Normalization preservation

A necessary property of any thin-source solution to the diffusion equation is that the net diffusant amount must be conserved [Eq. (2), normalization preservation]. That constraint turns out to be the key requirement for generating the proper full solution to the nonlinear diffusion equation.

Demonstrating normalization preservation begins by direct substitution of the solution [Eq. (10)] into the normalization condition of Eq. (2). It results in

$$K = \int_{x=-\infty}^{\infty} C(z, \Gamma)dx = X_R \Gamma^{1/2} \int_{z=-\infty}^{\infty} C(z, \Gamma)H_0(z\sqrt{n})dz$$
$$= X_R \Gamma^{1/2} \sum_{(m,n)} g(m, n) \int_{z=-\infty}^{\infty} H_{2m}(z\sqrt{n})H_0(z\sqrt{n})\exp(-nz^2)dz , \tag{23}$$

where H_0 is the first Hermite polynomial, which is $H_0 = 1$, and where Eq. (7c) was used for z. The orthogonality of Hermite polynomials means that only the $m = 0$ terms contribute to the sums in Eq. (23), giving

$$K = X_R \Gamma^{1/2} \sum_{n=1}^{\infty} g(0, n)(\pi/n)^{1/2} . \tag{24}$$

The $g(0, n)$ equations are described by the $p = 0$ case of Eq. (19), which is

$$4\Gamma g'(0, n) + 2g(0, n)$$
$$= (\alpha n/2) \sum_{n_1, n_2} \sum_{m_1, m_2} \delta\{n_1 + n_2 = n\}g(m_1, n_1)$$
$$\times g(m_2, n_2)$$
$$\times \theta(m_1, m_2, n_1, n_2; 0, n) . \tag{25}$$

The constant K representing total diffusant amount necessarily must be both independent of time and the nonlinearity parameter α. However, the right-hand sides of both Eqs. (24) and (25) seem to show that K is an explicit function of both time (i.e., Γ) and α. The resolution of how mass conservation can still be embodied in this

solution comes from a detailed examination of the $\theta(m_1, m_2, n_1, n_2; p = 0, n)$ function.

The $p = 0$ case of the θ function can be expressed as sum of integrals solved by Bailey,[64-67] denoted by $I(p, q; a, b)$,

$$I(p, q; a, b)$$
$$= \int_{y=-\infty}^{+\infty} H_p(ay)H_q(by)\delta\{a^2 + b^2 = 1\}\exp(-y^2)dy$$
$$= (-1)^{(p-q)/2}2^{(p+q)}b^p a^q \Gamma[(p + q + 1)/2] , \tag{26}$$

where $\Gamma[\ ]$ denotes the gamma function and where $p + q$ equals an even integer. Examining the $g(0, n)$ equations and substituting in Bailey's integral immediately results in

$$\theta(m_1, m_2, n_1, n_2; p = 0, n) \equiv 0 . \tag{27}$$

This result means that the mode-mode coupling identically vanishes for those terms involving the net diffusant amount. The nonlinear part to the $g(0, n)$ equations has gone away, leaving

$$4\Gamma g'(0, n) + 2g(0, n) = 0 . \tag{28}$$

The only solution to this system for $n > 1$ obeying the initial condition restriction of Eq. (12) is for all the functions $g(0, n > 1)$ to identically vanish. Thus only the $g(0,1)$ function is involved in matching the net diffusant amount and, as with the linear diffusion equation, net diffusant amount is conserved.

D. First nonlinear corrections: Order-α solution

We next construct the first nonlinear corrections of the diffusion equation solution. The functions $g(p, n = 2)$ are the order-α contributions to the nonlinear diffusion equation solution. For $n = 2$, Eq. (19) becomes

$$4\Gamma g'(p,2) + 2(2p+1)g(p,2) - g(p-1,2)$$
$$= \alpha \sum_{m_1,m_2=0} g(m_1,1)g(m_2,1)\theta(m_1,m_2,1,1;p,2) \ .$$

$$(29)$$

Here two functions from the linear equation part ($n = 1$ case) are multiplied together, to create a nonlinear contribution. A product of two functions appears here, because this nonlinear diffusion equation [Eq. (9)] is inherently quadratic in concentration. But now the entire effect of the diffusion equation nonlinearity is to create an inhomogeneous term in the linear first-order equations for the $g(p,2)$ functions, making the system exactly solvable. The detailed solution of systems like Eq. (29) are given in the Appendix. The following equations for the order-α solution then result.

The B_p coefficients which describe the initial state [Eq. (7a), $p = (0, N_i)$] first become coupled together, via the mode-mode coupling integral [Eq. (20)] to create new constants in the right-hand side of Eq. (29),

$$R(s,p) = \sum_{m_1=\max(0,s-N_i)}^{\min(s,N_i)} B_{m_1} B_{s-m_1}\theta(m_1,s-m_1,1,1;p,2) \ .$$

$$(30)$$

Solving the system of equations in Eq. (29) couples the $R(s,p)$-array elements together, giving new lumped constants,

$$\hat{Q}(p,t,s) = \sum_{q=0}^{\min(t,s)} \frac{(-1)^{t-q} R(s,q+1)}{(p-t-1)!(t-q)!4^{p-q}} \ .$$

$$(31)$$

Using this array, the $g(p, n = 2)$ functions then become

$$g(p,2) = \alpha \sum_{t=0}^{p-1} \sum_{s=0}^{2N_i} \frac{\hat{Q}(p,t,s)}{t-s+1/2}$$
$$\times (\Gamma^{-s-1} - \Gamma_0^{t-s+1/2}\Gamma^{-t-3/2}) \ . \quad (32)$$

Equation (32) represents the exact order α solution to the original nonlinear diffusion equation, specifying the time development (via the Γ-parameter) of any given initial state. Equation (32) is composed of two algebraically distinct series in descending powers of Γ. The first series, with integer powers, arises from the system being nonlinear. The second series, with half-integer powers, arises from the boundary condition that the $g(p,2)$-functions

must initially vanish ($\Gamma \to \Gamma_0$).

Each $g(p,2)$-term contains decreasing powers of Γ, but the leading power in each of these order-α terms is still $(1/\Gamma)$, and that leading power is what gives rise to the persistence of curvature phenomenon. The solution for $C(z,\Gamma)$, through order α is then

$$C(z,\Gamma) = \sum_{p=0}^{N_i} \frac{B_p}{\Gamma^{(p+1/2)}} H_{2p}(z) \exp(-z^2)$$
$$+ \sum_{p=1}^{N_a} g(p,2) H_{2p}(z\sqrt{2}) \exp(-2z^2) \ , \quad (33)$$

where the sum for the order-α part has been truncated at an upper p-index limit of N_a, with $N_a \to \infty$ corresponding to the full order-α contribution.

E. Second nonlinear corrections: Order-α^2 solution

The order-α^2 solution proceeds much like the order-α case. It is the $n = 3$ case of Eq. (19),

$$4\Gamma g'(p,3) + 2(2p+1)g(p,3) - 2g(p-1,3)$$
$$= 3\alpha \sum_{m_1,m_2=0}^{\infty} g(m_1,1)g(m_2,2)\theta(m_1,m_2,1,2;p,3) \ ,$$

$$(34)$$

where $g(0,2) \equiv 0$, as required by Eqs. (12) and (28).

Here, both the linear and the order-α solution can be substituted directly into Eq. (34), and terms collected to form groups of constants. The starting point for the order-α solution was the R array [Eq. (30)], which was a coupling of the initial-state parameters to themselves. An equivalent starting point for the order-α^2 case is a coupling of the initial state to the order-α solution. The cognate to the R array is the following array in the order-α^2 solution denoted $W(u,v;p)$:

$$W(u,v;p)$$
$$= \sum_{(m_1)} \sum_{m_2=v-m_1}^{N_a-1} \delta\{m_1+m_2 \geq p-2\}$$
$$\times B_{m_1} \frac{\hat{Q}(m_2+1,v-m_1,u-m_1)}{v-u+1/2}$$
$$\times \theta(m_1,m_2+1,1,2;p,3) \ , \quad (35a)$$

$$m_1(\min) = \max(0, u-2N_i, v-N_a+1) \ , \quad (35b)$$

$$m_1(\max) = \min(N_i, u, v) \ . \quad (35c)$$

where $m_1 + m_2 \geq p-2$ is required and the $\hat{Q}$ array was defined by Eq. (31).

The solution of Eq. (34) then couples the $W(u,v;p)$-array elements together, creating these new lumped constants:

$$\hat{Q}_a(p,t,u) = \frac{3}{2} \sum_{v=v_1}^{v_2} \sum_{q=0}^{t} \frac{(-1)^{t-q} 2^{q-p} W(u,v;q+1)}{(p-t-1)!(t-q)!} \ ,$$

$$(36a)$$

$$\hat{Q}_b(p,t,v) = \frac{3}{2} \sum_{u=u_1}^{u_2} \sum_{q=0}^{t} \frac{(-1)^{t-q} 2^{q-p} W(u,v;q+1)}{(p-t-1)!(t-q)!}$$
$$\times \Gamma_0^{v-u+1/2} . \tag{36b}$$

These functions for the order-α^2 solution are cognates to the $\hat{Q}(p,t,s)$ array of the order-α solution [Eq. (31)] except that they use the $W(u,v;p)$ array. In Eqs. (36a) and

(36b), the limits on each sum are as follows:

$$v_1 = \max(0, u-2N_i), \quad v_2 = (N_a-1) + \min(u,N_i), \tag{37a}$$

$$u_1 = \max(0, v-N_a+1), \quad u_2 = 2N_i + \min(v,N_i) . \tag{37b}$$

It results in the following expressions for the $g(p,3)$ functions:

$$g(p,3) = \alpha^2 \sum_{t=0}^{p-1} \sum_{u=0}^{3N_i} \hat{Q}_a(p,t,u) \left[\frac{(1-\delta\{t=u\})}{t-u}(\Gamma^{-u-3/2} - \Gamma_0^{t-u}\Gamma^{-t-3/2}) + \delta\{t=u\}\Gamma^{-t-3/2}\ln\frac{\Gamma}{\Gamma_0} \right]$$
$$-\alpha^2 \sum_{t=0}^{p-1} \sum_{v=0}^{N_i+N_a-1} \hat{Q}_b(p,t,v) \frac{1}{t-v-1/2}(\Gamma^{-v-2} - \Gamma_0^{t-v-1/2}\Gamma^{-t-3/2}) . \tag{38}$$

Each $g(p,3)$ function has the same leading term, $(1/\Gamma^{3/2})$, so these terms also help curvature to persist, compared to the purely linear equation. However, these terms decay faster than the $g(p,2)$ functions, which all had a leading term of $(1/\Gamma)$. Thus the long-time non-Gaussian part of the penetration profile will be primarily determined by the order-α correction to a purely linear equation. With Eqs. (30)–(32) and (35)–(38) determined, the order α^2 construction is complete for any given initial-state thin-source profile.

VI. SUMMARY AND CONCLUSIONS

In this work we have developed a new method of analysis for concentration-dependent diffusion with a thin-source initial state. This method used a matrix of orthogonal functions to develop a complete solution to the problem of diffusion from a thin source into a semi-infinite medium when the diffusivity varies linearly with concentration. It is based on a generalized thin-source solution to the linear diffusion equation, which is composed of Hermite polynomials multiplied by a fundamental Gaussian.

We showed that the nonlinear diffusion equation

$$\frac{\partial C}{\partial t} = D_0 \frac{\partial}{\partial x}(1+\alpha C)\frac{\partial C}{\partial x} , \tag{39}$$

could be decoupled into a recursive set of first-order inhomogeneous linear equations. That entire set of equations are all of a particular generic type, and the full solution to that class of equations was developed, reducing the problem to algebra. This solution was then explicitly constructed to order α [Eqs. (30)–(33)] and order α^2 [Eqs. (35)–(38)].

While many previous methods and approximations have been historically developed, we showed that for thin-source diffusion the requirement of conservation of total diffusant amount is crucial to the full nonlinear equation solution. Our solution was shown to automatically preserve net diffusant amount, and the solution developed predicts a unique final state $C(x, t > t_R)$ from a specific initial state $C(x, t_R)$.

If the physical constraint of mass conservation had not been preserved by the mathematical formalism, the total diffusant amount would have become an apparent function of both time and the nonlinearity parameter α. In addition, the calculated long-time limit for the solution would have incorrectly shown that the order-α, order-α^2, and higher-order terms were comparable or larger than the fundamental Gaussian solution. Instead, with mass conservation assured, these nonlinear contributions were all found to asymptotically vanish compared to the fundamental Gaussian.

This work also showed how the persistence of curvature [$\ln(C)$-vs-x^2 axes] develops due to the nonlinear interactions. For the linear equation case, the non-Gaussian components decay increasingly faster with time. In the nonlinear equation, those components contribute to an overall order-α term which decays only as slow as $(1/t)$, and the order-α^2 and beyond terms decay only as slow as $(1/t)^{3/2}$. It is this slow decay which gives rise to the persistence of curvature phenomenon.

Finally, based on general properties of the nonlinear system, we found that measurement of the diffusion profile for two different times under similar conditions is necessary to extract information about D_0 and α from experimental data. The solution presented here also allows for an arbitrary thin-source initial state to handle this difficult but important requirement.

APPENDIX: DETERMINING THE $G(\Gamma)$ MATRIX

In this appendix we derive a method to solve the system of first-order linear inhomogeneous equations [Eq. (19)], which together determine the time evolution of the nonlinear diffusion equation. A helpful transformation is first applied:

$$g(p,n) = \alpha^{(n-1)} L(p,n) e(p,n) / \Gamma^{p+1/2} , \qquad (A1)$$

where $L(p,n)$ are the following set of constants:

$$L(p,n) = \left[\delta\{n=1\} + \left[\frac{n-1}{4} \right]^p \right] . \qquad (A2)$$

Substituting the $e(p,n)$ functions into Eq. (19) for $g(p,n)$ gives

$$e(p,n)' - (1 - \delta\{n=1\}) e(p-1,n) = \tilde{f}^{-1}(p,n;\Gamma) , \qquad (A3)$$

where $\tilde{f}^{-1}(p,n;\Gamma)$ is the following:

$$\tilde{f}^{-1}(p,n;\Gamma) = \frac{n}{8L(p,n)} \sum_{n_1=1}^{\infty} \sum_{n_2=1}^{\infty} \sum_{m_1=0}^{\infty} \sum_{m_2=0}^{\infty} \frac{e(m_1,n_1) e(m_2,n_2)}{\Gamma^{(m_1+m_2-p+3/2)}}$$

$$\times \delta\{n_1+n_2=n\} \delta\{m_1+m_2 \geq p-1\} L(m_1,n_1) L(m_2,n_2)$$

$$\times \theta(m_1,m_2,n_1,n_2;p,n) , \qquad (A4)$$

where both restrictions $n_1+n_2=n$ and $m_1+m_2 \geq p-1$ must be applied. Here, the $\delta\{n_1+n_2=n\}$ restriction makes each $\tilde{f}^{-1}(p,n;\Gamma)$ function independent of the nonlinearity parameter α. The additional restriction in Eq. (A4) of $\delta\{m_1+m_2 \geq p-1\}$ is an indirect result of the orthogonality of Hermite polynomials, and it arises from the specific form of the θ function.

The initial condition that $g(p,n>1)$ vanish at Γ_0 translates into the functions $e(p,n>1)$ also vanishing there. The solution for $e(p,n=1)$, matching what was derived earlier [Eqs. (7a) and (22)], is simply

$$e(p,n=1) = B_p , \qquad (A5)$$

since the right-hand side of Eq. (A4) vanishes for $n=1$.

We next define a new function, based on Eq. (A4), which is the result of $(q+1)$ integrals on the $\tilde{f}^{-1}(p,n;\Gamma)$ function:

$$\tilde{f}^{+q}(p,n;\Gamma) \equiv \int_{\Gamma_0}^{\Gamma} d\Gamma_1 \int_{\Gamma_0}^{\Gamma_1} d\Gamma_2 \int_{\Gamma_0}^{\Gamma_2} d\Gamma_3 \int_{\Gamma_0}^{\Gamma_3} d\Gamma_4 \cdots \int_{\Gamma_0}^{\Gamma_q} d\Gamma_{q+1} \tilde{f}^{-1}(p,n;\Gamma_{q+1})$$

$$\equiv \frac{1}{q!} \int_{\Gamma_0}^{\Gamma} (\Gamma - W)^q \tilde{f}^{-1}(p,n;W) dW , \qquad (A6)$$

where a multiple integral transform[68] was used for the last step. In terms of these new functions, the $e(p,n)$ which solve Eq. (A3) are

$$e(p,n) = \sum_{q=0}^{p-1} \tilde{f}^{+q}(p-q,n;\Gamma) \equiv \sum_{q=0}^{p-1} \tilde{f}^{(p-q-1)}(q+1,n;\Gamma) . \qquad (A7)$$

This solution is easily verified by direct substitution. Also, because the $e(p,n)$ functions are made up of integrals extending over the entire range of (Γ_0, Γ), the boundary condition that $e(p,n)$ vanishes at Γ_0 is automatically satisfied. Equation (A7) is also implicitly consistent with the mass conservation condition of

$$g(p=0, n>1) = e(p=0, n>1) = 0 , \qquad (A8)$$

which was derived earlier [Eq. (28)].

The classes of functions which appear in Eqs. (A4) and (A6) are all of the same type, requiring multiple integrals of $[\ln(\Gamma)]^r / \Gamma^\nu$. Thus the entire time dependence reduces to variations on the following integral:

$$\Phi(\lambda,r,q;\Gamma,\Gamma_0) = \frac{1}{q!} \int_{\Gamma_0}^{\Gamma} (\Gamma - W)^q W^\lambda (\ln W)^r dW$$

$$\equiv \frac{1}{q!} \sum_{s=0}^{q} \begin{bmatrix} q \\ s \end{bmatrix} (-1)^s \Gamma^{q-s} \left[\delta\{s+\lambda+1=0\} \frac{\delta\{-1 \geq \lambda \geq -(q+1)\}}{(r+1)} [(\ln\Gamma)^{r+1} - (\ln\Gamma_0)^{r+1}] \right.$$

$$+ (1 - \delta\{s+\lambda+1=0\}) \sum_{k=0}^{r} \frac{(-1)^{r-k} r!}{k!(s+\lambda+1)^{r-k+1}}$$

$$\left. \times [\Gamma^{s+\lambda+1} (\ln\Gamma)^k - \Gamma_0^{s+\lambda+1} (\ln\Gamma_0)^k] \right] . \qquad (A9)$$

The whole set of $e(p,n)$ functions is this determined from knowing the two functions: $\theta(m_1,m_2,n_1,n_2;p,n)$, describing the intrinsic coupling due to nonlinearities, and $\Phi(\lambda,r,q;\Gamma,\Gamma_0)$, describing the rate of time evolution behavior.

The integral $\theta(m_1,m_1,n_1,n_2;p,n)$ can be worked out to give

$$\theta(m_1,m_2,n_1,n_2;p,n)=\delta\{p\geq 1\}\delta\{m_1+m_2\geq p-1\}(n_1/n)^{m_2-p+1}(n_2/n)^{m_1+p-1}H[2(m_1+m_2-p+1)]$$

$$\times \sum_{k=\max(0,2(p-m_2-1))}^{\min(2m_1,2p-2)}(-1)^k\begin{bmatrix}2m_1\\k\end{bmatrix}\begin{bmatrix}2m_2\\2p-k-2\end{bmatrix}(n_1/n_2)^k\;,\tag{A10}$$

$$H[2m]=(-1)^m(2m)!/m!\;,\tag{A11}$$

where $H[2m]$ is the value of $H_{2m}(y)$ evaluated at $y=0$. Notice that this result vanishes for $p=0$, as it must, as shown in Sec. V C.

For the solution up through order α^2, one needs only the $r=0$ limit of Eq. (A9), and different variations on the following "generic" system:

$$e_p'(\Gamma)-e_{p-1}(\Gamma)=\sum_{r=0}^{N_f(p)}\frac{K_0(r,p)}{\Gamma^{r+\nu(p)}}\;,\tag{A12}$$

where $K_0(r,p)$ is some array of constants. In Eq. (A12), N_f is an integer and ν can be either an integer or half-integer, both of which may depend on the p index. Extensions beyond order α^2 would give rise to additional terms on the right-hand side of Eq. (A12) with powers of $\ln(\Gamma/\Gamma_0)$.

Using Eqs. (A3), (A6), (A7), and (A9), the e_p functions which solve Eq. (A12) then are

$$e_p(\Gamma)=\sum_{q=0}^{p-1}\sum_{r=0}^{N_f(q+1)}\frac{K_0(r,q+1)}{(p-q-1)!}\sum_{s=0}^{p-q-1}\begin{bmatrix}p-q-1\\s\end{bmatrix}(-1)^s\Gamma^{p-q-s-1}\delta\{w=s-r-\nu(q+1)\}$$

$$\times\left[\frac{(1-\delta\{w=0\})}{w}(\Gamma^w-\Gamma_0^w)+\delta\{w=0\}\ln\frac{\Gamma}{\Gamma_0}\right]\;,\tag{A13}$$

where $w=(s-r-\nu)$. The various sums can be manipulated to separate like powers of Γ into one group, and collecting all the constants into another then results in

$$e_p(\Gamma)=\sum_{t=0}^{p-1}\sum_{(s)}Q_0(p,t,s)\Gamma^{p-t-1}$$

$$\times\left[\frac{(1-\delta\{t-s+1=0\})}{t-s+1}\right.$$

$$\times(\Gamma^{t-s+1}-\Gamma_0^{t-s+1})$$

$$\left.+\delta\{t-s+1=0\}\ln\frac{\Gamma}{\Gamma_0}\right]\;,\tag{A14}$$

where the s index advances by unity but may take on half-integer values, and where the Q_0 array is given by

$$Q_0(p,t,s)$$

$$=\sum_{q=0}^{t}(-1)^{t-q}\frac{K_0(s-q-\nu(q+1),q+1)}{(p-t-1)!(t-q)!}$$

$$\times\delta\{N_f(q+1)+\nu(q+1)$$

$$+q\geq s\geq\nu(q+1)+q\}\;.\tag{A15}$$

The $\delta\{\ \}$-constraint in Eq. (A15) serves both to further limit the bounds on the q sum as well as set the ultimate range of the s sum itself. Using this "generic" result, the solution through order α^2 can be constructed.

For the order-α case, terms in Eqs. (A3)–(A5) can be collected together to match the generic format of Eq.

(A12), resulting in

$$e(p,2)'-e(p-1,2)$$

$$=4^{p-1}\delta\{2N_i\geq p-1\}\sum_{q=0}^{2N_i-p+1}\frac{R(p+q-1,p)}{\Gamma^{(q+1/2)}}\;,\tag{A16}$$

where the R array was given by Eq. (30). The solution of Eq. (A16) is now a special case of the generic solution, and after collecting terms as in Eq. (31) together, one can derive

$$e(p,2)=\sum_{t=0}^{p-1}\sum_{s=0}^{2N_i}4^{+p}\frac{\hat{Q}(p,t,s)}{t-s+1/2}$$

$$\times(\Gamma^{p-s-1/2}-\Gamma_0^{t-s+1/2}\Gamma^{p-t-1})\;,\tag{A17}$$

which then gives the order-α solution. For the order-α^2 case, the system of equations to solve becomes

$$e(p,3)'-e(p-1,3)$$

$$=\tfrac{3}{2}2^{p-1}\sum_{(u)}\sum_{(v)}\left[\frac{W(u,v;p)}{\Gamma^{u-p+2}}\right.$$

$$\left.-\Gamma_0^{v-u+1/2}\frac{W(u,v;p)}{\Gamma^{v-p+5/2}}\right]\;,\tag{A18}$$

where Eq. (35) defines the W array, and where the following algebraic tautology was used to permute the u and v

summations:

$$\sum_{(u)} \sum_{(v)} A(u,v) \equiv \sum_{u=0}^{3N_i} \sum_{v=v_1}^{v_2} A(u,v)$$

$$\equiv \sum_{v=0}^{N_i+N_a-1} \sum_{u=u_1}^{u_2} A(u,v) . \qquad (A19)$$

This tautology is valid for any array $A(u,v)$, where the limits (u_1,u_2) and (v_1,v_2) on those summations were given by Eqs. (37a) and (37b).

The generic format of Eq. (A12) is then exactly matched if we separate the $e(p,3)$ functions into two separate pieces:

$$e(p,3) \equiv e_a(p,3) - e_b(p,3) , \qquad (A20)$$

$$e_a(p,3)' - e_a(p-1,3) = \sum_{u=0}^{3N_i} \frac{K_a(u,p)}{\Gamma^{u-p+2}} , \qquad (A21)$$

$$e_b(p,3)' - e_b(p-1,3) = \sum_{v=0}^{N_i+N_a-1} \frac{K_b(v,p)}{\Gamma^{v-p+5/2}} , \qquad (A22)$$

where the constants $K_a(u,p)$ and $K_b(v,p)$ are given by

$$K_a(u,p) = \tfrac{3}{2} 2^{p-1} \sum_{v=v_1}^{v_2} W(u,v;p) , \qquad (A23)$$

$$K_b(v,p) = \tfrac{3}{2} 2^{p-1} \sum_{u=u_1}^{u_2} W(u,v;p) \Gamma_0^{v-u+1/2} . \qquad (A24)$$

The $e(p,3)$ or $g(p,3)$ functions can then be easily derived, with the results as given in Sec. V E of the main text.

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