Regularization Inverse Method for Variable Binary Diffusivity Measurements

Alonso V. Jaques and Jeffrey C. LaCombe

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Boltzmann-Matano (and related) inverse methods are used extensively in the determination of interdiffusivities in alloys. In the course of analyzing experimental data to determine concentration dependent diffusivities, numerical integrations and differentiations of the concentration profile are performed. With experimental data that contains point-to-point scatter, challenges such as calculating the local slope result. Smoothing of the experimental data is often performed prior to analysis using a variety of approaches. This can introduce artifacts into the data and affects the confidence in the estimated interdiffusivities. We present here, a new approach to the so-called Boltzmann-Matano-type inverse method for calculating concentration-dependent interdiffusion coefficients in binary alloys. This method starts with a regularization formulation from the calculus of variations to estimate a smoothed form of the noisy concentration data. This is then integrated into the inverse estimation process through an optimization routine. This process minimizes or eliminates the necessity of arbitrary filtering or smoothing parameters, and does not require foreknowledge of the functional form of $D(C)$. The regularization inverse method presented is less subjective, is self-consistent (i.e., regularized concentration profiles are consistent with the diffusion equation), and results in increased accuracy in the estimated diffusion coefficients in comparison with existing inverse methods.

Keywords binary diffusion, Boltzmann/Matano analysis, concentration profiles, Diffusivity measurements, inverse methods, regularization, variational calculus

1. Introduction

In the determination of concentration-dependent diffusivities of alloys, a “diffusion couple” experimental sample configuration is commonly used.^[1,2] This arrangement involves bonding together two alloys with different compositions. Once bonded, the diffusion process starts, and a smooth concentration profile extends across the initial interface of the diffusion couple (Fig. 1). This concentration profile is the main data product of the experiment, and can be measured quantitatively using compositional analysis techniques such as radioactive tracers, microprobe analysis, and other techniques that generate composition as a function of position in the diffusion zone.

The advantage of the diffusion couple experiment geometry is that it is a system whose analytical representation permits inversion. I.e., given the geometry, boundary, and initial conditions, the diffusivity $D(C)$ can be estimated knowing the concentration profile produced during the

diffusion process. The so-called Boltzmann-Matano-type (BM) methods are the most commonly used inverse methods for this problem (Ref 3-6, summarized for example, in Ref 1, 2). A key advantage of the diffusion couple geometry and the BM methods is that they can be used when the diffusivity is a function of concentration, i.e., non-linear diffusion. However, in practice, the reliability of these methods relies on having an accurate, smooth, error-free concentration profile. This is rarely true when considering real experimental data, due to the fact that there is scatter (arising from measurement uncertainties) in the data.

A common feature of the Boltzmann-Matano methods is that they require the estimation of the gradient of the concentration profile. Having scatter in the concentration data makes it difficult (if not impossible) to produce an accurate estimation of the gradient, as the scatter produces a non-monotonic, non-smooth (no continuity in the second derivative) estimation. In order to overcome this, an estimated (“corrected”) concentration profile, $\hat{C}(x)$, with desirable properties is commonly used in experimental practice. This estimated profile is commonly produced using a variety of methods:

- *Filtering*: Consists of treatment of the original data with a special function (filter) to redistribute the scatter among the data points, producing a smoothed estimation of the data (see Ref 7, 8 for example).
- *Fitting*: A mathematical expression (such as an error function) is fit via regression to the experimental data. Although relatively easy to implement using a non-linear regression methods,^[9] it requires assuming the functional form of $C(x)$ to perform the regression (see Ref 10-13 for example).

Alonso V. Jaques, Departamento de Ingeniería Química y Ambiental, Universidad Técnica Federico Santa María, Casilla 110-V, Valparaíso, Chile; Jeffrey C. LaCombe, Chemical and Materials Engineering Department, University of Nevada, Reno, Reno, NV 89557. Contact e-mail: lacomj@unr.edu.

Fig. 1 Schematic representation of diffusion couple experiment setup. As the diffusion proceeds ($t > 0$), the initially sharp interface at $x = 0$ evolves into a smooth concentration profile with finite gradient at all points across the sample. In practice, the smooth profile is approximated by scattered discrete measurements of $C(x, t)$

- *Smoothing Splines*: This technique^[14] uses splines to represent the original data (see Ref 15,16 for example). The nodes of the splines are selected based on the differences between the original and smoothed data and controlling the degree of smoothness of the second order derivatives of the smoothed data.
- *Regularization*: In this method (present study), a variational function is created to incorporate information characterizing how the original data (without experimental scatter) should appear. This allows the incorporation of information, in the form of a so-called regularization function, leading to the minimization of the scattering. With the exception of the regularization method, the above approaches all require making assumptions about the form of $D(C)$ and/or introduce artifacts into the estimated concentration profile, $\hat{C}(x)$. This requires that caution be exercised, as subjective decisions on how to generate $\hat{C}(x)$ affect the reliability of the estimated $D(\hat{C})$. As will be shown here, regularization methods (summarized well in Ref 17-19) do not require any such actions, and thus offer a desirable alternative in inverse methods to estimating concentration-dependent diffusion coefficients.

The regularization method implemented here generally consists of the formulation of a variational functional, $F[\hat{C}(x)]$, that includes a weighted, least-squares estimation of the deviation between the experimental concentration data and the estimated “corrected” data point. It also incorporates a regularization “measure” functional $G[\hat{C}(x)]$, which weights in the characteristics required for the data to be regularized. This functional is expressed with these two respective terms as

$$F[\hat{C}(x)] = \left\| \frac{C(x) - \hat{C}(x)}{\sigma(x)} \right\|^2 + \lambda \|G[\hat{C}(x)]\|^2, \quad (\text{Eq 1})$$

where the $\| \cdot \|$ brackets denote the norm of the function over its domain. For continuous cases, this norm is written as

$$\|f(x)\| = \sqrt{\int_a^b f^2(x) dx},$$

and for discrete data,

$$\|f(x)\| = \sqrt{\sum f^2(x_i)}.$$

The first term on the right side of (Eq 1), $\sigma(C)$ corresponds to a local concentration-dependent error. The second (regularization) parameter, weights the value of the regularization measure function, in the variational expression. Thus, minimizing $F[\hat{C}(x)]$ should produce an estimated concentration profile by minimizing the deviation with the experimental data while complying with the constraints specified by the regularization measure. There are several common alternatives for the regularization function; each one is designed to produce certain characteristics (ex: smoothness) in the estimated data.^[20-25] These are summarized below:

- *Tikhonov regularization*: This is commonly used for ill-conditioned regression, for example, when it is not possible to invert the coefficient matrix in linear regression. It has been used in inverse problems and parameter estimation,^[22] with the $G[\hat{C}(x)]$ from (Eq 1) written as:

$$G[\hat{C}(x)] = [D(C) - D(\hat{C})].$$

However, this method requires that $D(\hat{C})$ be estimable directly from the scattered experimental data.

- *Data smoothing*: It is possible to use regularization to produce an estimate of a numerical differentiation. Several implementations have been proposed.^[20,24,25] This method has been proposed to produce a reliable estimation during the numerical differentiation of noisy data. For example,

$$G[\hat{C}(x)] = \frac{d^2 \hat{C}}{dx^2}$$

has been used for the estimation of the first^[24] and second^[25] spatial derivatives of the concentration by spline interpolation.

The regularization formulations for smoothing and differentiation in the literature^[20,24,25] can be applied to the diffusion process. We present here an adapted formulation that specifically incorporates the physics of diffusion and what is therefore “expected” of the concentration profile, i.e., that it be consistent with a nonlinear diffusion process, governed by Fick’s laws. In this way, a “custom made” regularization measure is proposed for this specific purpose.

2. Description of Non-Linear Diffusion

The well-known formulation of non-linear diffusion in a binary diffusion couple (single phase) is described by the

following partial differential equation and boundary conditions:

$$\frac{\partial C(x, t)}{\partial t} = \frac{\partial}{\partial x} \left(D(C') \frac{\partial C(x, t)}{\partial x} \right), \quad -\infty \leq x \leq +\infty \quad (\text{Eq 2})$$

such that

$$\begin{aligned} C(x < 0, 0) &= C^- & C(-\infty, t) &= C^- \\ C(x > 0, 0) &= C^+ & C(+\infty, t) &= C^+. \end{aligned}$$

If the dimensionless concentration ratio is defined as, $\chi = \frac{2C - (C^+ + C^-)}{(C^+ - C^-)}$ and a transformation substitution of $\xi \equiv x/\sqrt{t}$ is used (along with $\partial \xi / \partial x = 1/\sqrt{t}$, $\partial \xi / \partial t = x/2t\sqrt{t}$), it is possible to recast (Eq 2) (refer to Eq 13.3.17 in Ref 26, or 1-55 in Ref 27) as a nonlinear ordinary differential equation of the form:

$$-\frac{\xi}{2} \frac{d\chi(\xi)}{d\xi} = \frac{d}{d\xi} \left(D(\chi) \frac{dC(\xi)}{d\xi} \right), \quad (\text{Eq 3})$$

such that

$$\chi(-\infty) = -1 \text{ and } \chi(+\infty) = +1.$$

Following the approach of Liukov^[26] (similar to that described by Crank^[21]), this expression has an implicit solution of the form:

$$\chi(\xi) = A \int_0^\xi \frac{1}{D} \exp \left[- \int_0^{\xi'} \frac{\xi}{2D} d\xi \right] d\xi' + B. \quad (\text{Eq 4})$$

After application of the boundary conditions to (Eq 4), the dimensionless concentration profile for a diffusion couple with variable diffusivity $D = D(C)$ can be developed into the implicit expression (adapted from Ref 2, 26):

$$\chi(\xi) = \frac{\int_{-\infty}^\xi \frac{1}{D} \exp \left[- \int_0^{\xi'} \frac{\xi}{2D} d\xi \right] d\xi' - \int_{\xi}^{+\infty} \frac{1}{D} \exp \left[- \int_0^{\xi'} \frac{\xi}{2D} d\xi \right] d\xi'}{\int_{-\infty}^{+\infty} \frac{1}{D} \exp \left[- \int_0^{\xi'} \frac{\xi}{2D} d\xi \right] d\xi'}. \quad (\text{Eq 5})$$

Expressing (Eq 5) in terms of the original variables $C(x, t)$:

$$\begin{aligned} C(x, t) &= \frac{(C^+ - C^-)}{2 \int_{-\infty}^{+\infty} \frac{1}{D} \exp \left[- \int_0^{\xi'} \frac{x}{2Dt} dx \right] dx'} \\ &\cdot \left(\int_{-\infty}^\xi \frac{1}{D} \exp \left[- \int_0^{\xi'} \frac{x}{2Dt} dx \right] dx' - \int_x^{+\infty} \frac{1}{D} \exp \left[- \int_0^{\xi'} \frac{x}{2Dt} dx \right] dx' \right) \\ &+ \frac{(C^+ + C^-)}{2}. \end{aligned} \quad (\text{Eq 6})$$

Note that because the diffusivity is a function of concentration, (Eq 6) needs to be evaluated iteratively. That is, first a tentative concentration profile, $C(x)$, needs to be proposed, thus allowing the evaluation of the variable diffusivity $D(x)$ for each location x .

As introduced earlier, current inverse methods for determining $D(C)$ involve numerical evaluations of integrals and derivatives of discrete experimental $C(x)$ data. These are collectively known as Boltzmann-Matano (BM) methods. An efficient implementation of the BM method for variable diffusivity estimation was given by Sauer, Freise and den Broeder (SFdB).^[5,6] The SFdB method has the advantage over the BM method of not requiring a priori knowledge of the diffusion couple's initial interface location. The SFdB method evaluates the concentration-dependent diffusivity from the concentration profile using the following differential-integral expression:

$$D(C) = \frac{(C^- - C) \int_{x'}^{+\infty} (C - C^+) dx + (C - C^+) \int_{-\infty}^{x'} (C^- - C) dx}{2t \left(\frac{dC}{dx} \right)_{x'} (C^+ - C^-)}, \quad (\text{Eq 7})$$

where $D(C)$ is the diffusivity corresponding to experimentally-measured concentration C at location x' , C^- and C^+ are the concentration at the left and right sides of the diffusion couple, and t is the diffusion time.

When evaluating (Eq 7) using experimental data, it is required to differentiate the concentration as a function of position using the profile data. When experimental scatter is present in the data, this operation becomes non-trivial. Here, an implementation of the regularization method with the objective of the estimation of $D(C)$ through the incorporation of (Eq 7) is proposed. Because the concentration gradient appears in the denominator of (Eq 7), it is evident that any errors in the estimation of this gradient will influence the estimated value of $D(C)$. This influence is worsened in the presence of scattering of the experimental data, where a point-to-point estimate of the concentration gradient would oscillate between large positive and negative values.^[20,24]

Traditional alternatives such as curve fitting, smoothing splines, and data filtration (e.g., Ref 10, 28), have been used to handle the effects of data scatter in diffusivity estimations. Although easy to implement, curve fitting requires a priori knowledge (or assumption) of the analytical expression representing the concentration profile. I.e., an assumed functional form is required to estimate the unknown $D(\hat{C})$. For non-linear diffusivity, this functional form is generally unknown.^[2] Similarly, smoothing splines require making subjective or arbitrary assumptions about the noiseless concentration profile shape, and can also incorporate "artifacts" in the final results.

To formulate a regularization method for BM methods, having an analytical expression for the concentration gradient will prove useful. From (Eq 6) it is possible to obtain an analytical expression for the concentration gradient by taking the partial derivative of the concentration profile with respect to position:

$$\frac{\partial C}{\partial x} = \frac{(C^+ - C^-) \left(\frac{1}{D(C)} \exp \left[- \int_0^{\xi'} \frac{x}{2D(C)t} dx \right] \right)}{\int_{-\infty}^{+\infty} \frac{1}{D(C)} \exp \left[- \int_0^{\xi'} \frac{x}{2D(C)t} dx \right] dx}. \quad (\text{Eq 8})$$

It is important to note that both the gradient in equation (Eq 8) and the SFdB expression for $D(C)$ in

(Eq 7) require the evaluation of integrals with limits going to $\pm\infty$. To accomplish the numerical evaluation of these expressions (which clearly cannot actually integrate to limits of infinity), one approach is to artificially truncate the integrals. However, in practice this can produce numerical artifacts in the results, especially near the extreme values of the concentration range present in the data, C^- and C^+ .^[13] To address this, an alternative approach is presented here, where the estimations of the integrals in (Eq 7) and (Eq 8) are handled piecewise, without truncation.

It should be noted that the evaluation of (Eq 6) requires the evaluation of improper integrals, i.e., with integration limits going to $\pm\infty$. In order to deal with this and reduce the associated numerical errors, the improper integral is divided to separate out an interval where data is available, from where it is not available, but where boundary conditions may apply. I.e., the available range of experimental data of the diffusion couple is denoted as $L^\pm$, and no integrable discrete data is known beyond the interval of $[L^-, L^+]$. The behavior outside of this interval is instead estimated by recognizing that due to the nature of the solution for the non-linear diffusion equation, the concentration profile should approach the end composition values, $C^\pm$, asymptotically. Thus as an approximation, the following treatment is proposed *outside* of the interval $[L^-, L^+]$:

$$\begin{aligned} D[C(x > L^+)] &\approx D(C^+) = D^+ \\ D[C(x < L^-)] &\approx D(C^-) = D^-. \end{aligned} \quad (\text{Eq 9})$$

This approximation is valid only if $C(L^\pm) \approx C^\pm$. Considering this, and splitting the integrals over these intervals, the previous approximation of the integral in the denominator of (Eq 8) can be expressed over the separate intervals:

$$\begin{aligned} &\int_{-\infty}^{+\infty} \frac{1}{D} \exp \left[- \int_0^{x'} \frac{x}{2Dt} dx \right] dx' \\ &\approx \sqrt{\frac{\pi t}{D^-}} \exp \left[\frac{(L^-)^2}{4D^-t} \right] \left(1 + \operatorname{erf} \left[\frac{L^-}{2D^-t} \right] \right) \exp \left[- \int_0^{L^-} \frac{x}{2Dt} dx \right] \\ &+ \int_{L^-}^{L^+} \frac{1}{D} \exp \left[- \int_0^{x'} \frac{x}{2Dt} dx \right] dx' \\ &+ \sqrt{\frac{\pi t}{D^+}} \exp \left[\frac{(L^+)^2}{4D^+t} \right] \left(1 + \operatorname{erf} \left[\frac{L^+}{2D^+t} \right] \right) \exp \left[\int_0^{L^+} \frac{x}{2Dt} dx \right]. \end{aligned} \quad (\text{Eq 10})$$

Note that two of these three intervals have analytical expressions for the integral solutions. Similarly, this approach can be applied to evaluate the integrals in the SFdB expression (Eq 6):

$$\begin{aligned} &\int_{-\infty}^x \frac{1}{D} \exp \left[- \int_0^{x'} \frac{x}{2Dt} dx \right] dx' \\ &\approx \sqrt{\frac{\pi t}{D^-}} \exp \left[\frac{(L^-)^2}{4D^-t} \right] \left(1 + \operatorname{erf} \left[\frac{L^-}{2D^-t} \right] \right) \exp \left[- \int_0^{L^-} \frac{x}{2Dt} dx \right] \\ &+ \int_{L^-}^x \frac{1}{D} \exp \left[- \int_0^{x'} \frac{x}{2Dt} dx \right] dx', \end{aligned} \quad (\text{Eq 11})$$

and

$$\begin{aligned} &\int_{x'}^{+\infty} \frac{1}{D} \exp \left[- \int_0^{x'} \frac{x}{2Dt} dx \right] dx' \\ &\approx + \int_x^{L^+} \frac{1}{D} \exp \left[- \int_0^{x'} \frac{x}{2Dt} dx \right] dx' \\ &+ \sqrt{\frac{\pi t}{D^+}} \exp \left[\frac{(L^+)^2}{4D^+t} \right] \left(1 + \operatorname{erf} \left[\frac{L^+}{2D^+t} \right] \right) \exp \left[- \int_0^{L^+} \frac{x}{2Dt} dx \right]. \end{aligned} \quad (\text{Eq 12})$$

Thus, this approach can make reasonable estimations of integrals outside of the range for which experimental data is actually available. This is favored over truncation of the integrals, which can produce errors by under-estimation of the contribution of these region(s) of the integrals. The significance of the impact of such as truncation for a given experimental data set will vary, but can be estimated by comparing the first and third terms on the RHS of (Eq 10) with the entire RHS.

3. Regularized Inverse Method (RIM) Formulation

Regularization (in the present context) involves the introduction of additional information into the regression scheme to avoid ill-posed problems or prevent over-fitting.^[20] In the problem analyzed here, the regularization goal is to obtain a differentiable concentration profile from noisy data that may then be used with the conventional SFdB inverse method to estimate the diffusivity. That is, the regularization serves as an approach to finding the best estimate for the concentration profile, minimizing the effect of data scattering from experimental error. If a *smooth* tentative concentration profile, $\hat{C}(x)$, representing the (noisy) experimental data $C(x)$ can be obtained, it would then be possible to obtain an estimate for the gradient of $\hat{C}(x)$ via numerical differentiation $\Delta\hat{C}/\Delta x$, and the associated diffusivity estimation, $D(\hat{C})$, through evaluation of the SFdB expression (Eq 7).

Having the estimate of the diffusivity, $D(\hat{C})$, it is then possible to “close the loop” by obtaining an estimate of the

concentration gradient via the analytical expression in equation (Eq 8). If the tentative concentration profile, $\hat{C}(x)$, corresponds to a suitable solution for the non-linear diffusion solution in (Eq 6), both the numerical and the analytical evaluations for the concentration gradient should coincide.

The following regularization measure is proposed to minimize the difference between the theoretical (as estimated by SFdB) gradient (Eq 8), and that calculated through numerical differentiation. Following the form of (Eq 1) this is written:

$$G[\hat{C}(x)] = \frac{(C^+ - C^-) \left(\frac{1}{D} \exp \left[- \int_0^x \frac{x'}{2Dt} dx' \right] \right)}{\int_{-\infty}^{+\infty} \frac{1}{D} \exp \left[- \int_0^x \frac{x'}{2Dt} dx' \right] dx'} - \frac{\Delta C}{\Delta x}. \quad (\text{Eq 13})$$

Here, the first part of the regularization function is the gradient evaluated using (Eq 8) with the diffusivity estimated by the numerical inverse method of (Eq 7) (SFdB). The second part corresponds to the gradient obtained through a numerical differentiation of the smoothed data, using a point-to-point estimation. As the regularization function becomes minimized, the smoothness of the concentration profile is better assured. The regularization function in (Eq 1) is written:

$$F[\hat{C}(x)] = \left\| \frac{C(x) - \hat{C}(x)}{\sigma(C)} \right\|^2 + \lambda \left\| \frac{(C^+ - C^-) \left(\frac{1}{D} \exp \left[- \int_0^x \frac{x'}{2Dt} dx' \right] \right)}{\int_{-\infty}^{+\infty} \frac{1}{D} \exp \left[- \int_0^x \frac{x'}{2Dt} dx' \right] dx'} - \frac{\Delta C}{\Delta x} \right\|^2. \quad (\text{Eq 14})$$

The weighted least square portion (first term) requires knowing (or at least an estimate of) the concentration uncertainty, $\sigma(C)$. This information is typically available for most experimental methods. For example in electron microprobe analysis, the secondary electrons are detected via wavelength dispersive analysis. In this case, the error associated with the measured concentration results from the counting time of x-rays in the detector.^[29] The statistics of signal detection are used to make an estimation of the uncertainty in the measured concentration, and this is usually reported along with the concentration data. This information can be used directly in the regularization measure function. In cases where no estimate for the concentration uncertainty is available, a constant value estimate for $\sigma(C)$ can be used.

Thus the regularization problem can be described as using the original experimental concentration profile to find a diffusivity that minimizes the regularization function of (Eq 14):

$$\min F[\hat{C}(x)] \Rightarrow D[\hat{C}(x)]. \quad (\text{Eq 15})$$

That is, the regularized concentration profile, $\hat{C}(x)$, allows a reliable estimation of the non-linear diffusivity, $D[\hat{C}(x)]$, to be produced using an inverse BM-type method. This method was implemented using MatLab[®]. Details of the implementation are described in the Appendix, with an outline given as follows:

1. Generate an initial tentative (guess) solution concentration profile, $\hat{C}_0(x, t)$, which can be obtained by using the analytical expression for the concentration profile.
2. Determine the corresponding $D(\hat{C}_i)$ using a BM method (like SFdB), where the subscript i represents the optimization iteration number.
3. Evaluate $F(\hat{C}_i)$ using (Eq 14) with λ fixed to a value on the order of 1×10^{-6} (discussed below).
4. Using a minimization algorithm procedure, generate a new tentative concentration profile and $F(\hat{C}_{i+1})$, and keep if $F(\hat{C}_{i+1}) < F(\hat{C}_i)$.
5. Repeat 2-4 iteratively until a stop criterion is achieved. This criterion can be gradient based (i.e., when the magnitude of the gradient of the objective function $\nabla[F(\hat{C}_i)] \rightarrow 0$), a convergence tolerance, or a maximum number of iterations. The choice of the value of the regularization parameter λ , in (Eq 14), is strictly not a closed problem. However, during case studies, the specific value of λ used was found to have minimal affect

on the regularized concentration profile. When the value λ was too small, the solution did not converge to a monotonic concentration profile. When too large, insufficient regularization of the initial concentration data, $C(x)$, resulted. After numerous case studies, a “weak” assumption of $\lambda = 10^{-6}$ was determined to yield consistent and valid results, with little dependence of the results on λ near this value. This behavior of the regularization parameter is commonly observed, in regularization problems, and a more formal approach may be implemented in the regularization optimization process (for example, see Section 2.5 of Ref 30). Here however, a quick estimation for λ was readily made after a few iterations, judging the stability and convergence of the estimated $\hat{C}(x)$ or $D(\hat{C})$ with respect to the choice of λ .

4. Case Study

An example concentration-dependent diffusivity data set (Fig. 2) is used to test the proposed RIM. This hypothetical

data set was chosen to include several characteristics that often make the inverse-estimation of $D(\hat{C})$ a complex, non-trivial issue. First, the data are non-monotonic, with a local minimum and maximum. Second, the data exhibit significant changes in order of magnitude and curvature. Additionally, the intermediate values for the diffusivity have been estimated by linear interpolation, producing a segmented shape for $D(\hat{C})$, as presented in Fig. 2. A concentration profile C_i^0 was generated using equation (Eq 6) with the diffusivity data in Fig. 2. That is, this concentration profile represents the original concentration as generated by the diffusion process. To further simulate an experimentally

Fig. 2 “True” diffusivity data, $D(C)$, used for the test case study (hollow points) and the estimated diffusivity (solid points) resulting from the RIM analysis. Note that the input test data include features that typically make inverse estimations of $D(C)$ difficult, such as a non-monotonic functional form and point-to-point changes in order of magnitude and sign of the gradient

Fig. 3 Simulated original concentration profile (with and without noise added) and the reconstructed concentration profile produced during the regularization inverse method. The regularized profile features a smooth gradient at all positions, and agrees well with the initial (noise free) data used in the test

observed concentration profile, C_i^e , a normally distributed experimental error δC_i is added:

$$C_i^e = C_i^0 + \delta C_i, \quad \frac{\delta C_i}{C_i} \sim N(0, \sigma^2(C_i)), \quad (\text{Eq 16})$$

where $\sigma(C_i)$ is the standard deviation associated with the concentration analysis. For the case study, $\sigma_C = 0.05\%$ was used. The end compositions for the simulated diffusion couple were $C^- = 0.95$ and $C^+ = 0.05$. Both the simulated original and the simulated “observed” (with experimental scatter) concentration profiles are shown in Fig. 3. The algorithm for the RIM estimation was implemented using MatLab®, with the reconstructed concentration profile also shown in Fig. 3. In order to implement the minimization technique, a simulated annealing (SA) method,^[21] combined with the Broyden, Fletcher, Goldfarb and Shanno (BFGS) method,^[9] was used. The idea was to combine a heuristic method (SA) to obtain a good initial estimate for a candidate solution for the concentration profile. Afterward, the deterministic method (BFGS) is used to improve the solution. This hybrid approach has been performed successfully previously in diffusion related problems.^[31]

The results for the reconstructed regularization profile (Fig. 3) show good agreement between the simulated observed concentration profile, C_i^e (hollow points) and the regularized concentration profile $\hat{C}_i$ (solid line). However, there are some discrepancies, with deviations on the order of the scatter that was introduced, $\sigma(C)$.

Figure 2 permits a comparison of the original “True” diffusivity and the estimated diffusivity produced by the RIM method. There is good agreement in the general trend, and for most of the concentration range, there is very good agreement between the true $D(C)$ and estimated $D(\hat{C})$ data. Although there is some lack of agreement at the local maximum (near 0.2 at.%), the difference is less than an order of magnitude. Note that the diffusivity estimated by the RIM method in this case study also includes any effects of numerical errors due to the numerical integration and differentiation in the SFdB steps embedded in the RIM approach (Eq 7).

It should be noted that in addition to the case study presented here, similar results have been obtained for a number of test cases. In these additional cases, diffusivities with simpler concentration dependence produced still-better agreement between the test and the calculated diffusivities. In all cases, using the RIM approach made it possible to obtain an estimate for $D(C)$ using scattered experimental data with no “strong” assumptions regarding the pre-treatment of the data or the functional form of the diffusivity, as would be required for traditional BM or SFdB inverse methods.

5. Conclusions

Experimental concentration data that include scatter due to instrument errors are often difficult or impossible to use directly in “traditional” BM inverse methods. To analyze such data generally requires subjective data pre-processing, such as smoothing or filtering, and regressions of the data to

generate smooth functions (representing the data) requires making assumptions regarding the functional shape of the concentration profiles. As real profiles almost always include noise (point-to-point scatter), the RIM (presented here) has a significant advantage of not requiring any subjective data pre-processing or assumptions about the functional forms of either $C(x)$ or $D(C)$.

With this method, it is possible to estimate a regularized concentration profile that has the desired smoothness and monotonicity, and is also consistent with the fundamental equations governing the diffusion process (Eq 2). Once the regularization step has produced a smooth concentration profile, the concentration-dependent diffusivity, $D(\hat{C})$, is then estimated via (Eq 7). These steps are repeated iteratively, updating and optimizing the estimates of the diffusivity (Eq 15). It is noteworthy that the estimates are made without using any “strong” assumptions other than compliance with the diffusion equation. I.e., there are no choices to be made regarding the true functional forms of $D(C)$ or $C(x)$, which is necessary for regression-based methods, or for noise reduction, it is not necessary to specify the size of moving averages, spline or local fitting parameters (Savitzky-Golay smoothing), or truncation of data from the ends of the couple. The use of adjustable parameters and assumptions in the regularization inverse method’s process is minimal (insensitive) in the present implementation, and can be completely eliminated through incorporation into the optimization process. In this way, no subjective human decisions or judgments are required for the implementation of the method, even when concentration data sets contain considerable amounts of scatter. It follows that the regularization inverse method is particularly robust in comparison with other methods for inverse diffusivity estimation.

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6. Appendix: Description of Minimization Method

In order to achieve the best estimate for the diffusivity, a combination of an heuristic method, SA, and deterministic method (BFGS), were implemented. First an estimate for the initial (subscript 0) concentration profile is given by taking the solution for the linear diffusion of a diffusion couple:

$$\hat{C}_0(x) = \left(\frac{C^- + C^+}{2} \right) \operatorname{erfc} \left[\frac{x}{2\sqrt{D_0 t}} \right] + C^+, \quad (\text{Eq 17})$$

where D_0 is the initial estimate for the diffusivity. A good first estimate is obtained by considering the extent of the diffusion couple and the diffusion time:

$$D_0 = \frac{L^+ - L^-}{64t}. \quad (\text{Eq 18})$$

This initial estimate is used for the SA step. This can be described by, adapted from Ref 21

1. Estimate initial solution, $(\hat{C}_i)$, and evaluate $F(\hat{C}_i)$.
2. Estimate a tentative concentration profile $\hat{C}_{i+1}$ by adding a random element, δC , to the concentration profile, $\hat{C}_{i+1} = \hat{C}_i + \delta C$.
3. Evaluate $F(\hat{C}_{i+1})$.
4. If $F(\hat{C}_{i+1}) < F(\hat{C}_i)$, the new solution is accepted, otherwise proceed to the next step.
5. Evaluate the probability for the new solution to be accepted. This is given by Boltzmann distribution: $P_n = \exp \left(-\frac{F(\hat{C}_{i+1}) - F(\hat{C}_i)}{K_n} \right)$, where K_n is a parameter increasing with the number of iterations, this is referred to cooling schedule.^[21]
6. The chance of the new solution being accepted is given by: $P_n > U[0,1]$.
7. If the tentative solution was not accepted, repeat from step 2 to generate a new tentative solution.
8. Incorporated here as an additional step was a relaxation parameter ω , where the new solution is a weighted average to the previous solutions: $\hat{C}_{i+1} = \omega \hat{C}_{i+1} + (1 + \omega) \hat{C}_i$.
9. The process is repeated until the stop criterion (previously determined) is achieved.

The solution obtained here is next used as an initial solution for the BFGS optimization method (a climbing method), where a direction and length of steps are calculated for each iteration, moving towards the local minimum. The BFGS method consists of a “Newton” expression, however, the Hessian is approximated in each step, rather than using a direct numerical evaluation. The implementation of the BFGS method used here (adapted from Ref 9 is presented below).

1. Initialize $B_0 = I$ and define starting concentration profile (from previous step) $\hat{C}_0$.
2. Solve s_i from $B_i s_i = -\nabla F(\hat{C}_i)$.
3. Optimize α_i and evaluate $\hat{C}_{i+1}$ for the minimum value in the objective function according to $\hat{C}_{i+1} = \hat{C}_i + \alpha_i s_i$. The optimization of α_i is done using a parabolic search algorithm.
4. Calculate $\gamma_i = \nabla F(\hat{C}_{i+1}) - \nabla F(\hat{C}_i)$.
5. Update the approximate Hessian Matrix: $B_{i+1} = B_i + \frac{\gamma_i \gamma_i^T}{\gamma_i^T s_i} - \frac{B_i s_i s_i^T B_i}{s_i^T B_i s_i}$.
6. Repeat 2 through 5 until convergence is achieved. The convergence criteria in this case is given by setting a tolerance ε between consecutive solutions: $\left| \frac{F(\hat{C}_{i+1}) - F(\hat{C}_i)}{F(\hat{C}_i)} \right| < \varepsilon$. As an additional note, if interpolation is required between the data of the tentative concentration profile, cubic spline interpolation is used. All the routines were implemented using MatLab®.

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