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Minimum Error Fickian Diffusion Coefficients for Mass Diffusion in Multicomponent Gas Mixtures

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Abstract

Mass diffusion in multicomponent gas mixtures is governed by a coupled system of linear equations for the diffusive mass fluxes in terms of thermodynamic driving forces, known as the generalized Stefan–Maxwell equation. In computations of mass diffusion in multicomponent gas mixtures, this coupling between the different components results in considerable computational overhead. Consequently, simplified diffusion models for the diffusive mass fluxes as explicit functions of the driving forces are an attractive alternative. These models can be interpreted as an approximate solution to the Stefan–Maxwell equation. Simplified diffusion models require the specification of "effective" diffusion coefficients which are usually expressed as functions of the binary diffusion coefficients of each species pair in the mixture. Current models for the effective diffusion coefficients are incapable of providing *a priori* control over the error incurred in the approximate solution.

In this paper a general form for diagonal approximations is derived, which accounts for the requirement imposed by the special structure of the Stefan–Maxwell equation that such approximations be constructed in a reduced-dimensional subspace. In addition, it is shown that current models can be expressed as particular cases of two general forms, but not all these models correspond to the general form for diagonal approximations. A new minimum error diagonal approximation (MEDA) model is proposed, based on the criterion that the diagonal approximation minimize the error in the species velocities. Analytic expressions are derived for the MEDA model's effective diffusion coefficients based on this criterion. These effective diffusion coefficients automatically give the correct solution in two important limiting cases: for that of a binary mixture, and for the case of arbitrary number of components with identical binary diffusivities. Although these minimum error effective diffusion coefficients are more expensive to compute than existing ones, the approximation will still be cheaper than computing the exact Stefan–Maxwell solution, while at the same time being more accurate than any other diagonal approximation. Furthermore, while the minimum error effective diffusion coefficients in this work are derived for bulk

diffusion in homogeneous media, the minimization procedure can in principle be used to derive similar coefficients for diffusion problems in heterogeneous media which can be represented by similar forms of the Stefan–Maxwell equation. These problems include diffusion in macro- and microporous catalysts, adsorbents, and membranes.

1. Introduction

In this paper a rational approach to constructing diagonal approximations to the Stefan–Maxwell equation which governs mass-diffusion in multicomponent gaseous mixtures is presented. These approximations, like the Fickian diffusion assumption, decouple the full linear system by specifying effective binary diffusion coefficients, thereby reducing computational expense. The necessary background for mass diffusion in multicomponent gas mixtures is established in Section 2. In order to familiarize the reader with some of the previous modeling efforts, three important simplified diffusion models are described in Section 3. The modeling issues associated with constructing simplified diffusion models are itemized in Section 4. In Section 5 the solution of the Stefan–Maxwell equation is detailed, which leads to the resolution of some of these modeling issues. This section also helps to establish a clear connection between the general form of existing approximations, which is given in Section 6, and the Stefan–Maxwell solution. The Stefan–Maxwell solution for two special limiting cases is explored in Section 7, which reveals the special structure of this equation. With the aid of this development a critical appraisal of existing models is given in Section 8. In Section 9 a new approach to constructing simplified diffusion models is described, and the general form of diagonal approximations is given in Section 10. The particular form of these diagonal models that minimizes the error incurred in the approximation is derived in Section 11. Implications of this work are discussed in Section 12, and the salient conclusions are summarized in the final section. The minimization procedure developed in this work can also be used to derive similar effective diffusion coefficients for diffusion problems in heterogeneous media which can be cast in the Stefan–Maxwell equation framework.

2. Background

Consider a multicomponent ideal gas mixture with N different chemical species. This system may be characterized by the mixture mass density ρ, the mass-averaged velocity $\mathbf{u}$, the internal energy e, and the species mass fractions Y_α, $\alpha = 1, \ldots, N$, which together constitute $N+5$ unknowns. The mass fraction Y_α of species α is defined as

$$Y_\alpha = \rho_\alpha / \rho, \quad \alpha = 1, \ldots, N, \tag{1}$$

where ρ_α is the mass density of the α species (note that $\sum_\alpha \rho_\alpha = \rho$, whence $\sum_\alpha Y_\alpha = 1$). These $N+5$ unknowns (ρ, $\mathbf{u}$, e, Y_α) are related by $N+5$ conservation equations of mass, momentum, energy and species [1]. In particular, the species

conservation equation is:

$$\rho\frac{\partial Y_\alpha}{\partial t}+\rho\mathbf{u}\cdot\nabla Y_\alpha = S_\alpha - \nabla\cdot[\rho Y_{(\alpha)}\mathbf{V}_{(\alpha)}],\quad \alpha=1,\ldots,N, \tag{2}$$

which states that following the mass-average motion of the fluid, the species mass fraction Y_α can change only by chemical reaction S_α, or by diffusion. The quantity $\rho Y_{(\alpha)}\mathbf{V}_{(\alpha)}$ is termed the diffusive mass flux of species α. The summation convention in this paper is that repeated indices are summed over unless they are bracketed like in the diffusive mass flux term of equation (2).

If $\mathbf{u}_\alpha$ denotes the average velocity of molecules of species α, then the mass-averaged velocity of the mixture $\mathbf{u}$ is determined by the relation

$$\mathbf{u} = Y_\alpha\mathbf{u}_\alpha. \tag{3}$$

The mass diffusion velocity of species α, denoted $\mathbf{V}_\alpha$, is defined as the difference between the mean molecular velocity of species α and the mass-averaged velocity of the mixture,

$$\mathbf{V}_\alpha \equiv \mathbf{u}_\alpha - \mathbf{u}. \tag{4}$$

Note that equations (3) and (4) together imply that the mass diffusion velocity must satisfy the constraint

$$Y_\alpha\mathbf{V}_\alpha = \mathbf{0}. \tag{5}$$

The diffusive mass flux of species α relative to the mass-averaged velocity of the mixture $\mathbf{u}$, is defined as

$$\mathbf{J}_\alpha \equiv \rho_{(\alpha)}[\mathbf{u}_{(\alpha)}-\mathbf{u}] = \rho Y_{(\alpha)}\mathbf{V}_{(\alpha)}. \tag{6}$$

The N species conservation equations (eq. (2)) together with the 5 conservation equations for ρ, $\mathbf{u}$, and e, form a closed set in terms of the $N+5$ unknowns, provided quantities such as the reaction rates S_α and the diffusion fluxes $\rho Y_{(\alpha)}\mathbf{V}_{(\alpha)}$ can be related to the variables (ρ, $\mathbf{u}$, e, Y_α), and their gradients. In this paper we are concerned with the closure of the mass diffusion terms. The closure equation for the mass diffusion fluxes in terms of the mass-fraction gradients as given by the complete kinetic theory [1], is the Stefan–Maxwell equation.

2.1. The generalized Stefan–Maxwell equation

Following Ramshaw [2], the generalized Stefan–Maxwell equation for the mass diffusion velocities $\mathbf{V}_\alpha$ is written as a linear system of the form

$$\sum_\beta \frac{X_{(\alpha)}X_{(\beta)}}{D_{\alpha\beta}}[\mathbf{V}_{(\beta)}-\mathbf{V}_{(\alpha)}] = \mathbf{G}_\alpha, \tag{7}$$

where X_α is the mole fraction of species α, $D_{\alpha\beta}$ is the binary diffusivity for the species pair (α, β) and the driving forces $\mathbf{G}_\alpha$ are given by

$$\mathbf{G}_\alpha = \nabla X_\alpha + (X_\alpha - Y_\alpha)\nabla \ln p + K_\alpha \nabla \ln T - \frac{1}{p}[\rho_{(\alpha)}\mathbf{F}_{(\alpha)} - Y_\alpha \rho_\beta \mathbf{F}_\beta], \tag{8}$$

where p is the pressure, T is the temperature, and $\mathbf{F}_\alpha$ is the body force per unit mass acting on species α. The coefficients K_α are related to the thermal diffusion coefficients $D_{T,\beta}$ [1], [2] by the relation

$$K_\alpha = \sum_\beta \frac{X_{(\alpha)}X_{(\beta)}}{\rho D_{\alpha\beta}}\left(\frac{D_{T,\alpha}}{Y_{(\alpha)}} - \frac{D_{T,\beta}}{Y_{(\beta)}}\right). \tag{9}$$

When the only non-zero contribution to the driving forces $\mathbf{G}_\alpha$ is due to concentration gradients ∇X_α, equation (7) is commonly referred to as the Stefan–Maxwell equation [1]. When the driving forces are generalized to include the contributions due to pressure gradients, temperature gradients and body forces [2], equation (7) is referred to as the generalized Stefan–Maxwell equation. The sum of the driving forces $\mathbf{G}_\alpha$ over all species is zero:

$$\sum_\alpha \mathbf{G}_\alpha = \mathbf{0}. \tag{10}$$

Since the species conservation equation (eq. (2)) is in terms of mass fractions, it is convenient to express the mole-fraction gradients $\mathbf{G}_\alpha$ (for simplicity, and without loss of generality, hereinafter it is assumed that the only non-zero contribution to the driving forces arises from concentration gradients) in equation (8) as a linear combination of mass fraction gradients $\mathbf{H}_\beta \equiv \nabla Y_\beta$:

$$\mathbf{G}_\alpha = \nabla X_\alpha = \frac{\partial X_\alpha}{\partial Y_\beta}\nabla Y_\beta = T_{\alpha\beta}\mathbf{H}_\beta, \tag{11}$$

where the transformation matrix $T_{\alpha\beta}$ is given by

$$T_{(\alpha)(\alpha)} = \frac{X_{(\alpha)}}{Y_{(\alpha)}}[1 - X_{(\alpha)}] \tag{12}$$

$$T_{\alpha\beta} = \frac{X_\alpha X_{(\beta)}}{Y_{(\beta)}}, \quad \alpha \neq \beta. \tag{13}$$

With the relation between $\mathbf{G}_\alpha$ and $\mathbf{H}_\beta$, it is easy to see that equation (7) represents a closure of the diffusion flux in terms of mass fraction gradients. The sum of the driving forces $\mathbf{H}_\alpha$ over all species is also zero:

$$\sum_\alpha \mathbf{H}_\alpha = \mathbf{0}. \tag{14}$$

It is well known that the Stefan–Maxwell equation (eq. (7)) alone does not determine the mass diffusion velocities $\mathbf{V}_\alpha$ uniquely [2]. The additional constraint on the mass-diffusion velocity $Y_\alpha \mathbf{V}_\alpha = \mathbf{0}$ is needed to uniquely determine $\mathbf{V}_\alpha$. Since equation (7) is only a statement concerning velocity differences, its solution is indeterminate to within a constant vector.

This indeterminacy implies that equation (7) may also be written in terms of the species velocity with $\mathbf{u}_\alpha = \mathbf{V}_\alpha + \mathbf{u}$ in place of $\mathbf{V}_\alpha$ as

$$\sum_\beta \frac{X_{(\alpha)} X_{(\beta)}}{D_{\alpha\beta}} [\mathbf{u}_{(\beta)} - \mathbf{u}_{(\alpha)}] = \mathbf{G}_\alpha. \tag{15}$$

The additional constraint is now $Y_\alpha \mathbf{u}_\alpha = \mathbf{u}$, where $\mathbf{u}$ is determined by the momentum equation, and may be regarded as known.

Some approximations to the Stefan–Maxwell equation also use the *molar* diffusion velocity $\mathbf{V}'_\alpha$, which is defined as the difference between the mean molecular velocity of species α and the molar-averaged velocity of the mixture:

$$\mathbf{V}'_\alpha \equiv \mathbf{u}_\alpha - \mathbf{u}', \tag{16}$$

where the molar-averaged velocity of the mixture $\mathbf{u}'$ is given by the relation

$$\mathbf{u}' = X_\alpha \mathbf{u}_\alpha. \tag{17}$$

Note that equations (17) and (16) together imply that the molar diffusion velocity must satisfy the constraint

$$X_\alpha \mathbf{V}'_\alpha = \mathbf{0}. \tag{18}$$

Substituting

$$\mathbf{u}_\alpha = \mathbf{V}'_\alpha + \mathbf{u}'$$

from equation (16) into equation (15) results in the Stefan–Maxwell equation in terms of the molar diffusion velocity:

$$\sum_\beta \frac{X_{(\alpha)} X_{(\beta)}}{D_{\alpha\beta}} [\mathbf{V}'_{(\beta)} - \mathbf{V}'_{(\alpha)}] = \mathbf{G}_\alpha. \tag{19}$$

The system of equations expressed in equations (7), (15) and (19) can be represented in a single general matrix form as

$$M_{\alpha\beta} \mathbf{W}_\beta = \mathbf{\Pi}_\alpha, \tag{20}$$

where

$$M_{\alpha\beta} = \mathscr{A}_{\alpha\beta},\ \alpha \neq \beta,$$
$$M_{(\alpha)(\alpha)} = -\sum_{\gamma} \mathscr{A}_{\alpha\gamma}, \quad \gamma \neq \alpha, \tag{21}$$

and

$$\mathscr{A}_{(\alpha)(\beta)} = \frac{X_{(\alpha)}X_{(\beta)}}{D_{\alpha\beta}}.$$

In this general matrix representation of the Stefan–Maxwell equation (eq. (20)), $\mathbf{W}_\beta$ can represent either the mass diffusion velocity $\mathbf{V}_\beta$, the species velocity $\mathbf{u}_\beta$, or the molar diffusion velocity $\mathbf{V}'_\beta$, and $\mathbf{\Pi}_\alpha$ can represent either the driving forces in terms of mole-fraction gradients $\mathbf{G}_\alpha$, or the driving forces in terms of mass fraction gradients $T_{\alpha\beta}\mathbf{H}_\beta$. The reason for considering all possible combinations of velocities and driving forces is that approximations to the Stefan–Maxwell equation are formulated with different combinations of velocities and driving forces. This general representation, which subsumes all such combinations, is useful in deriving general forms for existing approximations. This general matrix form is also used later to show that, while all combinations are equivalent as far as the full Stefan–Maxwell equation is concerned, the same is *not* true when constructing diagonal approximations to the equation.

3. Existing Simplified Diffusion Models

In order to gain an appreciation for the issues involved in the construction of simplified diffusion equations which are approximations to the Stefan–Maxwell equation, some of the past work in this area is briefly reviewed. Subsequently in Section 6 it will be shown that these simplified diffusion equations are special cases of a general class of approximations.

3.1. Fickian diffusion model

For binary mixtures ($N=2$) the exact solution to the Stefan–Maxwell equation simplifies to:

$$\mathbf{V}_\alpha = -\frac{D_{12}}{Y_{(\alpha)}}\mathbf{H}_\alpha, \quad \alpha = 1, 2, \tag{22}$$

(note that it is assumed that $D_{12}=D_{21}$). The above equation is also known as Fick's Law, and it is exact for binary mixtures, and also for equal diffusivity mixtures with arbitrary number of species [1]. Its characteristic feature is that the diffusion velocity of the αth species is purely a function of the αth driving force.

For the general multicomponent case ($N>2$, and diffusivities not necessarily equal) the exact solution to the Stefan–Maxwell equation does not have any such simple

representation. The Fickian diffusion approximation (FDA)[1)] generalizes the form in equation (22) for the general multicomponent case ($N>2$) to get:

$$\mathbf{V}_\alpha^e = -\frac{D_{(\alpha)}^e}{Y_{(\alpha)}}\mathbf{H}_\alpha, \quad \alpha = 1, \ldots, N, \tag{23}$$

where $\mathbf{V}_\alpha^e$ represents the FDA model for mass diffusion velocity. There are two important features associated with the FDA model. First, the FDA model for the diffusion velocity is easier to compute than solving the full Stefan–Maxwell linear system. Secondly, it assumes that the coupling between driving forces and diffusion velocities is purely diagonal, since $\mathbf{V}_\alpha$ is independent of $\mathbf{H}_\beta$, $\beta \neq \alpha$. It is possible to construct a model that has the first feature, but does not make this assumption, and such a model will be described in Section 3.3.

The effective diffusion coefficient D_α^e is used to model the diffusion velocity of species α in terms of the driving force associated with species α in a manner analogous to the binary case. It is taken to be some function of the binary diffusivities of all the species pairs, and the species mole fractions:

$$D_\alpha^e = f(D_{\gamma\beta}, \mathbf{X}).$$

For the FDA model these effective diffusion coefficients are specified as:

$$D_\alpha^e = \frac{[1 - X_{(\alpha)}]}{\sum_{\beta\neq\alpha} X_{(\beta)}/D_{(\alpha)(\beta)}}. \tag{24}$$

While these effective diffusion coefficients are qualitatively correct, there is no real justification for this specification from a quantitative standpoint: i.e., this specification takes no cognizance of the error it implies between the Fickian model for diffusion velocity and the true solution to the Stefan–Maxwell equation. It is important to note that if equation (23) is applied to all the N species, then the modeled mass diffusion velocities violate the constraint given in equation (5), i.e.

$$Y_\alpha \mathbf{V}_\alpha^e \neq \mathbf{0}.$$

The FDA model can also be written in terms of molar diffusion velocities as

$$\mathbf{V}_\alpha'^e = -\frac{D_{(\alpha)}^e}{X(\alpha)}\mathbf{G}_\alpha, \quad \alpha = 1, \ldots, N, \tag{25}$$

where $\mathbf{V}_\alpha'^e$ is the FDA model for the molar diffusion velocity of species α. Again, if equation (25) is applied to all the N species, then the modeled molar diffusion

[1)] In this paper we make a distinction between the terms Fickian diffusion approximation and effective binary diffusion approximation. See Section 12.3 for details.

velocities violate the constraint given in equation (18), i.e.

$$X_\alpha \mathbf{V}'^{e}_{\alpha} \neq 0.$$

This deficiency motivates the next simplified diffusion model.

3.2. Modified Fickian diffusion model

In this model the simplified diffusion equation given in equation (23) (or eq. (25)) is applied to only N–1 species:

$$\mathbf{V}^{em}_{\alpha} = -\frac{D^{e}_{(\alpha)}}{Y_{(\alpha)}}\mathbf{H}_\alpha, \quad \alpha = 1, \ldots, N-1 \tag{26}$$

$$\mathbf{V}'^{em}_{\alpha} = -\frac{D^{e}_{(\alpha)}}{X_{(\alpha)}}\mathbf{G}_\alpha, \quad \alpha = 1, \ldots, N-1. \tag{27}$$

The appropriate constraint on the diffusion velocity (eq. (5) for $\mathbf{V}^{em}_{\alpha}$ and eq. (18) for $\mathbf{V}'^{em}_{\alpha}$) then determines the Nth species' diffusion velocity to be:

$$\mathbf{V}^{em}_{N} = \frac{1}{Y_N}\sum_{\alpha=1}^{N-1} D^{e}_{(\alpha)}\,\mathbf{H}_\alpha, \tag{28}$$

$$\mathbf{V}'^{em}_{N} = \frac{1}{X_N}\sum_{\alpha=1}^{N-1} D^{e}_{(\alpha)}\,\mathbf{G}_\alpha. \tag{29}$$

It is important to note that the modified FDA model has an undesirable dependence on the ordering of the species.

3.3. Self-consistent effective binary diffusion model

The self-consistent effective binary diffusion (SCEBD) model proposed by Ramshaw [2], and reformulated by Ramshaw and Chang [3], addresses the modified FDA model's dependence on species order. The SCEBD model for the species velocity is

$$\mathbf{u}^{sc}_{\alpha} = \mathbf{a} - \frac{D^{sc}_{(\alpha)}}{X_{(\alpha)}}\mathbf{G}_\alpha, \tag{30}$$

where $\mathbf{a}$ is a constant vector which is the same for all the species, and the effective diffusion coefficient D^{sc}_{α} is defined as

$$D^{sc}_{\alpha} \equiv \left(1 - \frac{w_\alpha}{w}\right)\left[\sum_{\beta\neq\alpha}\frac{X_{(\beta)}}{D_{(\alpha)(\beta)}}\right]^{-1}. \tag{31}$$

In equation (31) the quantity w_α is a weighting factor associated with the αth species, and $w = \sum_\alpha w_\alpha$. Ramshaw and Chang [3] propose different choices for the weighting factors which include $w_\alpha = X_\alpha$ and $w_\alpha = Y_\alpha$.

The constraint on the species velocity (eq. (3)) is used to determine the constant vector **a**, resulting in

$$\mathbf{a} = \mathbf{u} + \sum_\beta Y_{(\beta)} \frac{D^{sc}_{(\beta)}}{X_{(\beta)}} \mathbf{G}_\beta. \tag{32}$$

This value of **a** can be substituted back into equation (30) to get the final form of the SCEBD model:

$$\mathbf{u}^{sc}_\alpha = \mathbf{u} - \frac{D^{sc}_{(\alpha)}}{X_{(\alpha)}} \mathbf{G}_\alpha + \sum_\beta Y_{(\beta)} \frac{D^{sc}_{(\beta)}}{X_{(\beta)}} \mathbf{G}_\beta. \tag{33}$$

The following features of the SCEBD model are noteworthy:

(a) The SCEBD model is formulated in terms of the species velocity, whereas the modified FDA is formulated in terms of diffusion velocity.
(b) In the SCEBD model the species velocity is modeled in terms of mole-fraction gradients, but the species velocity constraint which is used to determine the constant vector **a** corresponds to the mass-average velocity.
(c) The SCEBD effective diffusion coefficients are formulated in terms of weighting factors which, when chosen to be mole fractions, reduce to the effective diffusion coefficients in the FDA model.
(d) Unlike the Fickian diffusion models, in the SCEBD model the velocity of the αth species depends on $\mathbf{G}_\beta$, $\beta \neq \alpha$, for all N species. This point is further elucidated in Section 12.3.

4. Modeling Issues

With a description of the important simplified diffusion models in hand, it is seen that the following modeling issues are still unresolved.

1. What space should the model be formulated in ? i.e., species velocity $\mathbf{u}_\beta$, mass diffusion velocity $\mathbf{V}_\beta$, or molar diffusion velocity $\mathbf{V}'_\beta$, in terms of mole-fraction gradients $\mathbf{G}_\gamma$ or mass-fraction gradients $\mathbf{H}_\gamma$?
   Each simplified diffusion model can be viewed as a transformation from the space of driving forces to the space of velocities. From the description of the FDA, modified FDA and the SCEBD models in the previous section, it is clear that there is a lack of consensus as to which space the model should be formulated in.
2. What exactly are the existing models approximations to ?
   None of the existing models clearly describe how the matrix equations implied by their effective diffusion coefficients relate to the original matrix **M**.

3. What is the correct behaviour that a model must reproduce in limiting cases, and what does this imply for the form of the model?
   The exact solution to the Stefan–Maxwell equation is known for the binary ($N=2$) diffusion case, and for the case where all the component pairs have identical diffusivities. While the FDA and modified FDA models reproduce these limiting case solutions, the behaviour of the SCEBD model in these limiting cases is dependent on the specification of the weighting factors. It is shown in Section 5 that the solution to the Stefan–Maxwell equation in these limiting cases reveals the structure of this linear system, which can then be used to construct simplified diffusion models.
4. How many model coefficients (effective diffusion coefficients) can be independently specified in a diagonal approximation ? N, or $N-1$?
   This issue is resolved in Section 9.5.
5. Is there a rational way to construct a model that will minimize the error in the diagonal approximation?
   All the models considered so far make no mention of the error incurred in the approximations. It is shown in Section 11 that not only can an expression for the error by derived, but in fact the model coefficients can be chosen so as to minimize the 2-norm of the error.
6. Can we construct diagonal approximations that are not dependent on species order?

The question of species order is addressed in Section 12.4.

5. Naive Solution to the Stefan–Maxwell Equation

In order to gain insight into these modeling issues, it is worthwhile to first investigate the form of the solution to the Stefan–Maxwell equation (eq. 20) using a naive approach. The elements of matrix $\mathbf{M}$ in equation (20) depend on the binary diffusivities (which are in turn dependent on the chemical species present in the mixture), and also on the mole fractions X_α, which are functions of space and time in general. Assuming that all the X_α are non-zero[2)], and under the reasonable assumption that the diffusivities $D_{\alpha\beta}$ are finite non-zero quantities, $\mathbf{M}$ is a singular matrix whose rank is exactly $N-1$. While formally this implies there is a one-parameter family of solutions to the least-squares problem

$$\min_{\mathbf{W}_\beta} \|M_{\alpha\beta}\mathbf{W}_\beta - \mathbf{\Pi}_\alpha\|_2$$

corresponding to the matrix equation (20), clearly there is an unique member of this family, which is the solution to the physical problem, that solves equation (20) exactly[3)]. This family of solutions can be written as [4]

$$\mathbf{W}_\beta = M^+_{\beta\gamma}\mathbf{\Pi}_\gamma + \mathbf{W}^n_\beta, \tag{34}$$

[2)] The case where some of the X_α are exactly zero is discussed separately in Section 12.6.
[3)] How this unique member of the family is selected is explained shortly.

where $\mathbf{M}^+$ denotes the pseudo-inverse of $\mathbf{M}$ [5], and $\mathbf{W}^n_\beta$ represents the indeterminate part of $\mathbf{W}_\beta$ which lies in the null space of matrix $\mathbf{M}$.

The pseudo-inverse $\mathbf{M}^+$ is the unique matrix that solves the least-squares problem with $\mathbf{W}_\beta = M^+_{\beta\gamma}\mathbf{\Pi}_\gamma$ having the smallest 2-norm in the set of all solutions to the least-squares problem. Details of various properties (including uniqueness) of the pseudo-inverse may be found in Golub and Van Loan [5] (pp. 256–257) and Lawson and Hanson [4] (pp. 36–40).

Given a basis for the null space of $\mathbf{M}$, the entire family of solutions can be represented by different values of a scalar parameter which when multiplied by the basis yields a different $\mathbf{W}^n_\beta$ in equation (34), corresponding to each member of the set of solutions to the least-squares problem. Since $\mathbf{W}^n_\beta$ lies in the null space of $\mathbf{M}$, it satisfies the relation

$$M_{\alpha\beta}\mathbf{W}^n_\beta = 0. \tag{35}$$

Furthermore, since the matrix $\mathbf{M}$ has special structure, the indeterminate part of the solution $\mathbf{W}^n_\beta$ has a matrix form. The matrix $\mathbf{M}$ is a *pair-wise exchange* matrix since it is symmetric and has the property

$$M_{(\alpha)(\alpha)} = -\sum_\gamma M_{\alpha\gamma}. \tag{36}$$

This implies that

$$\mathbf{W}^n_\beta = \mathbf{c}e_\beta, \tag{37}$$

where $\mathbf{c}$ is a constant vector which is the same for all species, and e_β is a unit vector in the β-direction of species space.

It is convenient to rewrite the solution given by equation (34) for the two different cases corresponding to $\mathbf{\Pi}_\gamma$ being expressed in terms of mole-fraction gradients or mass-fraction gradients. When $\mathbf{\Pi}_\gamma = \mathbf{G}_\gamma$, equation (34) becomes

$$\mathbf{W}_\beta = M^+_{\beta\gamma}\mathbf{G}_\gamma + \mathbf{W}^n_\beta, \tag{38}$$

and when $\mathbf{\Pi}_\gamma = T_{\gamma\eta}\mathbf{H}_\eta$ it can be written as

$$\mathbf{W}_\beta = N^+_{\beta\eta}\mathbf{H}_\eta + \mathbf{W}^n_\beta, \tag{39}$$

where

$$N^+_{\beta\eta} = M^+_{\beta\gamma}T_{\gamma\eta}. \tag{40}$$

Of course the indeterminate parts of the solution in equations (38) and (39) will be different, but they span the same space.

The value of the constant vector $\mathbf{c}$ in equation (37) is determined by imposing the appropriate constraint on the velocity, which depends on which velocity is represented by $\mathbf{W}_\beta$. The constraints corresponding to the different choices can be written as

$$\mathbf{W}_\beta = \begin{cases} \mathbf{V}_\beta & : \quad Y_\beta \mathbf{V}_\beta = 0 \\ \mathbf{V}'_\beta & : \quad X_\beta \mathbf{V}'_\beta = 0 \\ \mathbf{u}_\beta & : \quad Y_\beta \mathbf{u}_\beta = \mathbf{u} \\ \mathbf{u}_\beta & : \quad X_\beta \mathbf{u}_\beta = \mathbf{u}' \end{cases} \tag{41}$$

While the appropriate constraint uniquely determines $\mathbf{W}_\beta$ from the family of solutions expressed in equation (34), it is important to note that this $\mathbf{W}_\beta$ still only solves equation (20) in the least-squares sense, i.e. it minimizes the quantity

$$\varepsilon_{LS}^2 = \| M_{\alpha\beta} \mathbf{W}_\beta - \mathbf{\Pi}_\alpha \|_2^2.$$

For arbitrary $\mathbf{\Pi}_\alpha$ which may have non-zero components in the null-space of matrix $M_{\alpha\beta}$, the quantity ε_{LS} will in general be non-zero. This means that for arbitrary $\mathbf{\Pi}_\alpha$ the uniquely determined $\mathbf{W}_\beta$ does not solve equation (20) exactly. It is only by virtue of the constraint on the driving forces $\sum_\alpha \mathbf{\Pi}_\alpha = \mathbf{0}$, that the Stefan–Maxwell solution, which is the constrained member of the family of solutions expressed by equation (34), is unique and exact.

As a specific example of the solution procedure, we first consider the mole-fraction gradient case where $\mathbf{\Pi}_\gamma = \mathbf{G}_\gamma$, in which case the solution $\mathbf{W}_\beta$ is given by equation (38). If $\mathbf{W}_\beta$ is the molar diffusion velocity $\mathbf{V}'_\beta$, the constraint equation can be written as

$$X_\beta \mathbf{V}'_\beta = X_\beta M^+_{\beta\gamma} \mathbf{G}_\gamma + X_\beta \mathbf{c} e_\beta = \mathbf{0}, \tag{42}$$

where the expression for $\mathbf{V}'_\beta$ from equation (38) has been substituted. Solving for the constant $\mathbf{c}$ yields

$$\mathbf{c} = -X_\beta M^+_{\beta\gamma} \mathbf{G}_\gamma, \tag{43}$$

which results in the following expression for $\mathbf{V}'_\beta$:

$$\mathbf{V}'_\beta = M^+_{\beta\gamma} \mathbf{G}_\gamma - X_\eta M^+_{\eta\gamma} \mathbf{G}_\gamma e_\beta. \tag{44}$$

The above equation may be rewritten in a more compact form as

$$\mathbf{V}'_\beta = M^{+c'}_{\beta\gamma} \mathbf{G}_\gamma, \tag{45}$$

where $M^{+c'}_{\beta\gamma}$ represents the matrix pseudo-inverse of $\mathbf{M}$ after the constraint corresponding to the molar diffusion velocity has been imposed, and is given by

$$M^{+c'}_{\beta\gamma} = M^+_{\beta\gamma} - X_\eta M^+_{\eta\gamma}. \tag{46}$$

If instead of the molar diffusion velocity, $\mathbf{W}_\beta$ is taken to be the species velocity $\mathbf{u}_\beta$ and the constraint of equation (17) is imposed, one obtains

$$X_\beta \mathbf{u}_\beta = X_\beta M^+_{\beta\gamma} \mathbf{G}_\gamma + X_\beta \mathbf{c} e_\beta = \mathbf{u}'. \tag{47}$$

The resulting final form for the species velocity is then

$$\mathbf{u}_\beta = M^{+e'}_{\beta\gamma} \mathbf{G}_\gamma + \mathbf{u}'. \tag{48}$$

Clearly this solution is exactly equivalent to that expressed in equation (45).

In an entirely analogous fashion one can write the solution for any of the other $\mathbf{W}_\beta$, i.e. the mass diffusion velocity or the species velocity (with the mass-averaged velocity constraint) in terms of the mole-fraction gradients. It turns out that regardless of whether the solution is expressed in terms of the species of velocity or the diffusion velocities, all the solutions are equivalent to

$$\mathbf{V}'_\beta = M^{+c'}_{\beta\gamma} \mathbf{G}_\gamma \tag{49}$$

or

$$\mathbf{V}_\beta = M^{+c}_{\beta\gamma} \mathbf{G}_\gamma, \tag{50}$$

where

$$M^{+c}_{\beta\gamma} = M^+_{\beta\gamma} - Y_\eta M^+_{\eta\gamma}. \tag{51}$$

The same conclusions hold true for the mass-fraction gradient case ($\mathbf{\Pi}_\gamma = T_{\gamma\eta} \mathbf{H}_\eta$), where the solution $\mathbf{W}_\beta$ is given by equation (39). Again, regardless of whether the solution is expressed in terms of the species velocity or the diffusion velocities, all the solutions are equivalent to

$$\mathbf{V}'_\beta = N^{+c'}_{\beta\gamma} \mathbf{H}_\gamma \tag{52}$$

or

$$\mathbf{V}_\beta = N^{+c}_{\beta\gamma} \mathbf{H}_\gamma, \tag{53}$$

where

$$N^{+c'}_{\beta\gamma} = N^+_{\beta\gamma} - X_\eta N^+_{\eta\gamma} \tag{54}$$

$$N^{+c}_{\beta\gamma} = N^+_{\beta\gamma} - Y_\eta N^+_{\eta\gamma}. \tag{55}$$

Since all the solutions are entirely equivalent to the expressions for the mass and molar diffusion velocities, there is no reason to model in terms of species velocity (cf. modeling issue #1). Other advantages of formulating the problem in terms of the diffusion velocity are detailed in Section 12.2.

6. General Form of Previous Approximations

Given the form of the solution to the Stefan Maxwell equation (eqs. (49), (50), (52), and (53)) it is easy to ascertain the exact nature of the approximation implied by existing models. However, it is advantageous to first cast the existing models in their most general forms.

The FDA model and its modified version are of the form

$$\mathbf{V}_{\alpha}^{e/em} = K_{\alpha\beta}^{e/em}\mathbf{H}_{\beta}. \tag{56}$$

For the standard FDA model

$$\mathbf{K}^{e} = \begin{bmatrix} -D_1^e/Y_1 & 0 & 0 & \cdots & 0 \\ 0 & -D_2^e/Y_2 & 0 & \cdots & 0 \\ \cdots & \cdots & \cdots & \cdots & \cdots \\ 0 & 0 & 0 & \cdots & -D_N^e/Y_N \end{bmatrix}, \tag{57}$$

and for the modified version of the FDA model

$$\mathbf{K}^{em} = \begin{bmatrix} -D_1^e/Y_1 & 0 & 0 & \cdots & 0 & 0 \\ 0 & -D_2^e/Y_2 & 0 & \cdots & 0 & 0 \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\ 0 & 0 & 0 & \cdots & -D_{N-1}^e/Y_{N-1} & 0 \\ D_1^e/Y_N & D_2^e/Y_N & D_3^e/Y_N & \cdots & D_{N-1}^e/Y_N & 0 \end{bmatrix}. \tag{58}$$

Comparing equation (56) with equation (53) shows that both $K_{\beta\gamma}^{e}$ and $K_{\beta\gamma}^{em}$ are models for $N_{\beta\gamma}^{+c}$ (cf. modeling issue #2).

Similarly the SCEBD model can be cast in the form

$$\mathbf{V}_{\alpha}^{sc} = L_{\alpha\beta}^{sc}\mathbf{G}_{\beta}, \tag{59}$$

where

$$\mathbf{L}^{sc} = \begin{bmatrix} (Y_1-1)D_1^{sc}/X_1 & Y_2D_2^{sc}/X_2 & Y_3D_3^{sc}/X_3 & \cdots & Y_ND_N^{sc}/X_N \\ Y_1D_1^{sc}/X_1 & (Y_2-1)D_2^{sc}/X_2 & Y_3D_3^{sc}/X_3 & \cdots & Y_ND_N^{sc}/X_N \\ \cdots & \cdots & \cdots & \cdots & \cdots \\ Y_1D_1^{sc}/X_1 & Y_2D_2^{sc}/X_2 & Y_3D_3^{sc}/X_3 & \cdots & (Y_N-1)D_N^{sc}/X_N \end{bmatrix}. \tag{60}$$

Again comparing equation (59) with equation (50) reveals that $L_{\alpha\beta}^{sc}$ is a model for $M_{\alpha\beta}^{+c}$ (cf. modeling issue #2).

An important observation stemming from equation (60) is that the SCEBD model is not a Fickian type approximation, in that $\mathbf{L}^{sc}$ has non-zero off-diagonal entries for all species. In particular, one should not be misled by the SCEBD model expression given by equation (30), which would result in a diagonal approximation only if the

constant vector **a** were exactly equal to the mass-averaged velocity: i.e., $\mathbf{a} = \mathbf{u}$. However, expressing the SCEBD model in terms of mass diffusion velocities shows the contribution of $\mathbf{G}_\beta$, $\beta \neq \alpha$ to $\mathbf{V}_\alpha^{sc}$:

$$\mathbf{V}_\alpha^{sc} = -\frac{D_{(\alpha)}^{sc}}{X_{(\alpha)}}\mathbf{G}_\alpha + \sum_\beta Y_{(\beta)}\frac{D_{(\beta)}^{sc}}{X_{(\beta)}}\mathbf{G}_\beta. \tag{61}$$

The following points concerning a non-diagonal approximation are worth noting. It is considerably more difficult to minimize the error in approximating a matrix (such as $M_{\alpha\beta}^{+c}$) by a non-diagonal matrix, than by a diagonal one. Also it is shown in Section 9.5 that it is easier to reproduce the exact Stefan–Maxwell solution for certain limiting cases with a diagonal approximation. It is remarkable that the SCEBD model, which is a non-diagonal approximation, does reproduce the correct limiting case behaviour for one choice of the weighting factor ($w_\alpha = X_\alpha$).

7. Special Limiting Cases

Two limiting cases are considered where the exact solution to the Stefan–Maxwell equation is known. One reason for considering these cases is to understand the structure of the linear system under these limiting conditions. It is found that understanding this structure is crucial to constructing models that will eventually reproduce the exact solution under these limiting conditions.

7.1. Stefan–Maxwell solution for $N = 2$

For the seemingly trivial case of a binary mixture, it is well known that the Stefan–Maxwell diffusion velocities are given by equation (22), or equation (25) (with $N = 2$). Nevertheless, it is still useful to formally solve the Stefan–Maxwell equation.

First the solution of molar diffusion velocity in terms of mole-fraction gradients as given by equation (49) is considered. In the binary mixture case the matrix **M** can be written as

$$\mathbf{M} = \begin{pmatrix} -a & a \\ a & -a \end{pmatrix}, \tag{62}$$

where

$$a = \frac{X_1 X_2}{D_{12}}.$$

The pseudo-inverse $\mathbf{M}^+$ of the matrix **M** is found to be

$$\mathbf{M}^+ = \begin{bmatrix} -1/(4a) & 1/(4a) \\ 1/(4a) & -1/(4a) \end{bmatrix}. \tag{63}$$

Substituting this into the expression in equation (46) for the constrained pseudo-inverse $\mathbf{M}^{+c'}$ yields

$$\mathbf{M}^{+c'} = \frac{1}{4a}\begin{pmatrix} -2X_2 & 2X_2 \\ 2X_1 & -2X_1 \end{pmatrix}. \tag{64}$$

On applying the constraint $\mathbf{G}_2 = -\mathbf{G}_1$ (eq. 10), the solution for the molar diffusion velocity turns out to be

$$\mathbf{V}'_\alpha = -\frac{D_{12}}{X_{(\alpha)}}\mathbf{G}_\alpha, \quad \alpha = 1, 2. \tag{65}$$

The following important conclusions emerge:

(i) Although the molar diffusion velocity solution for the two species are decoupled (i.e., the expression for $\mathbf{V}'_\alpha$ in equation (65) involves only $\mathbf{G}_\alpha$, and not $\mathbf{G}_\beta$, $\beta \neq \alpha$), the solution matrix $M^{+c'}$ is *not* diagonal ! This implies that if a diagonal model of the form

$$\mathbf{V}'^m_\alpha = L_{(\alpha)(\alpha)}\mathbf{G}_\alpha,$$

is proposed which seeks to "approximate"[4] $\mathbf{M}^{+c'}$, then it is clear from the solution to this extremely simple case that $(\mathbf{V}'_\alpha, \mathbf{G}_\alpha)$ is not the correct space in which diagonal models should be constructed.

(ii) The decoupled form emerges only after the constraint on $\mathbf{G}_\beta$ is imposed. All the models which were considered in Section 3 have only imposed the constraint on velocity, but the constraint on $\mathbf{G}_\beta$ has not been explicitly incorporated into the models. Since this constraint is what renders the velocity solution to the Stefan–Maxwell equation exact, it should be reflected in any simplified diffusion model. Further implications of neglecting the constraint on the driving forces are discussed in Section 9.

7.2. Equal diffusivity case

If $D_{\alpha\beta} = D \ \forall\, \alpha, \beta = 1, \ldots, N$, then the molar diffusion velocity solution can be written as

$$\mathbf{V}'_\alpha = -\frac{D}{X_{(\alpha)}}\mathbf{G}_\alpha, \tag{66}$$

which satisfies

$$M_{\alpha\beta}\mathbf{V}'_\beta = \mathbf{G}_\alpha.$$

In terms of the mass-diffusion velocity, the solution

$$\mathbf{V}_\alpha = -\frac{D}{Y_{(\alpha)}}\mathbf{H}_\alpha, \tag{67}$$

[4] in the sense of some appropriate matrix norm

satisfies

$$M_{\alpha\beta}\mathbf{V}_\beta = \mathbf{H}_\alpha.$$

However, the mass-diffusion velocity solution $\mathbf{V}_\beta$ to the equation

$$M_{\alpha\beta}\mathbf{V}_\beta = \mathbf{G}_\alpha,$$

is *not* of this diagonal, decoupled form. Note that $\mathbf{H}_\alpha = T^{-1}_{\alpha\beta}\mathbf{G}_\beta$, where the inverse transformation $\mathbf{T}^{-1}$ is given by

$$T^{-1}_{(\alpha)(\alpha)} = \frac{Y_{(\alpha)}}{X_{(\alpha)}}[1 - Y_{(\alpha)}] \tag{68}$$

$$T^{-1}_{\alpha\beta} = -\frac{Y_\alpha Y_{(\beta)}}{X_{(\beta)}}, \quad \alpha \neq \beta. \tag{69}$$

(The quantity $T^{-1}_{\alpha\beta}$ refers to the (α,β) element of the matrix $\mathbf{T}^{-1}$, and not the reciprocal of $T_{\alpha\beta}$). Substituting $T^{-1}_{\alpha\beta}\mathbf{G}_\beta$ for $\mathbf{H}_\alpha$ in equation (67), and using the inverse transformation relations given in equations (68–69), results in

$$\mathbf{V}_\alpha = -D\frac{[1 - Y_{(\alpha)}]}{X_{(\alpha)}}\mathbf{G}_\alpha + \sum_{\beta\neq\alpha} D\frac{Y_{(\beta)}}{X_{(\beta)}}\mathbf{G}_\beta. \tag{70}$$

In matrix form this mass-diffusion velocity solution is

$$\begin{pmatrix} \mathbf{V}_1 \\ \mathbf{V}_2 \\ \cdot \\ \mathbf{V}_N \end{pmatrix} = -D \begin{bmatrix} (1-Y_1)/X_1 & -Y_2/X_2 & -Y_3/X_3 & \cdots & -Y_N/X_N \\ -Y_1/X_1 & (1-Y_2)/X_2 & -Y_3/X_3 & \cdots & -Y_N/X_N \\ \cdots & \cdots & \cdots & \cdots & \cdots \\ -Y_1/X_1 & -Y_2/X_2 & -Y_3/X_3 & \cdots & (1-Y_N)/X_N \end{bmatrix} \begin{pmatrix} \mathbf{G}_1 \\ \mathbf{G}_2 \\ \cdot \\ \mathbf{G}_N \end{pmatrix}. \tag{71}$$

Thus it is clear that the mass-diffusion velocities do not decouple if $\mathbf{V}_\alpha$ is expressed in terms of the mole-fraction gradients $\mathbf{G}_\alpha$. This implies that if the model is to be a Fickian (i.e., diagonal) approximation, and is to reduce to the exact solution in this limiting case, the modeling should be in the pairs $(\mathbf{V}'_\alpha, \mathbf{G}_\alpha)$ or $(\mathbf{V}_\alpha, \mathbf{H}_\alpha)$, and not in $(\mathbf{V}_\alpha, \mathbf{G}_\alpha)$ (cf. modeling issue #3). If the model is proposed in $(\mathbf{V}_\alpha, \mathbf{G}_\alpha)$, then it cannot be diagonal and also satisfy the equal diffusivity limiting case solution.

The SCEBD model is an example of a non-diagonal model that does satisfy the equal diffusivity limiting case solution for a particular choice of the weighting factor ($w_\alpha = X_\alpha$). However, Ramshaw and Chang do not recommend X_α as the preferred choice for the weighting factor since it does not give the highest accuracy in terms of the normalized Stefan–Maxwell residuals [3]. Since it is easier to construct a diagonal approximation which provides error control and satisfies the limiting case

solutions by working in the pairs $(\mathbf{V}'_\alpha, \mathbf{G}_\alpha)$ or $(\mathbf{V}_\alpha, \mathbf{H}_\alpha)$, the velocity-driving force combination of $(\mathbf{V}_\alpha, \mathbf{G}_\alpha)$ is not chosen for the new model proposed in this paper.

8. Comparison of Previous Models

Based on the foregoing development, a comparative assessment of the models described in Section 3 is presented in this section. The common deficiency of all these models is that their choice of the effective diffusion coefficients is not governed by an *a priori* characterization of the approximation error.

8.1. Fickian diffusion model

This is a diagonal approximation that correctly reproduces both limiting case solutions but does not satisfy the velocity constraint $Y_\alpha \mathbf{V}_\alpha = 0$. Clearly this deficiency alone renders it an unsatisfactory model.

8.2. Modified FDA model

This model correctly reproduces both limiting case solutions, and satisfies the velocity constraint, but is dependent on species order. It is also no longer a fully diagonal approximation. The dependence on species order is certainly undesirable, but without a thorough investigation into the nature of this dependence it is premature to dismiss this model as unsatisfactory.

8.3. SCEBD model

The SCEBD model satisfies the velocity constraint without dependence on species order. It was shown in Section 6 that it is a non-diagonal approximation. The SCEBD model's limiting case behaviour depends on a model parameter, which is the weighting factor in equation (31).

For what the authors call the ''conventional'' choice of the weighting factor $(w_\alpha/w = X_\alpha)$ [3], the SCEBD model reproduces the correct limiting case solution for both the binary case, and the equal diffusivity case. For the choice of weighting factors equal to the mass fractions $(w_\alpha/w = Y_\alpha)$, the SCEBD model does not give the correct limiting case solution for either the binary or equal diffusivity cases. For the recommended choice of the weighting factor (equal to the normalized geometric mean of the mole and mass-fraction choices), the SCEBD model gives the correct limiting case solution for the binary case, but not for the equal diffusivity case. In this work it is shown that the correct limiting case behavior does not have to be sacrificed in order to resolve issues of error control and species order dependence. Another feature of the current work, which is lacking in the other modeling efforts discussed, is a thorough exploration of the exact nature of the issue of dependence on species order.

Ramshaw and Chang [3] claim that the effect of adding the constant vector **a** removes the indeterminacy corresponding precisely to that of the original Stefan–Maxwell equation itself. This correspondence is not entirely clear for the following reason.

The Stefan–Maxwell equation (eq. 7) is a singular system of N equations in N unknowns. Assuming all the mole fractions X_α are non-zero, and the diffusivities $D_{\alpha\beta}$ are finite, non-zero quantities, only $N-1$ equations in the Stefan–Maxwell system are linearly independent. Using the additional constraint equations (eqs. (5) and (10)) results in a closed, fully determined system of $N-1$ equations for $N-1$ unknowns without the need for any additional indeterminate constants. Further details are provided in Section 9.

9. New Approach to Constructing Approximations

The following features are common to the modeling approach taken by all the existing models described in Section 3:

(i) The models are approximations to either the matrix $N^{+c}_{\beta\gamma}$, or $M^{+c}_{\alpha\beta}$.
(ii) A general form for the velocity (species, mass-diffusion, or molar-diffusion) in terms of the driving force is specified, and then the appropriate constraint on the velocity is imposed.
(iii) The fact that the driving forces are constrained is not represented in the models.

Ignoring the constraint on the driving forces implies that the Stefan–Maxwell equation (eq. 7) in conjunction with the velocity constraint (eq. 5) is an over-determined system, which is clearly not the case. In Section 5 it was shown that the solution to equation (20) as expressed in equations (49), (50), (52), and (53) are all exact only because the constraint on the driving forces ensures that the component of driving forces in the null space of matrix **M** is exactly zero.

The new modeling approach pursued in this paper is based on the observation that the constraints on the velocity and driving force vector (in species space) restrict them to span lower-dimensional subspaces. If the linear system expressed by the Stefan–Maxwell equation is transformed to this lower-dimensional subspace, then the solutions automatically satisfy the constraints. It is also shown that when the matrix form of the Stefan–Maxwell equation (eq. 20) is transformed to the appropriate subspace, the matrices associated with the limiting cases trivially become diagonal! In view of this important observation, the new modeling approach requires that diagonal approximations be constructed in this subspace. An explicit characterization of the error incurred by such diagonal approximations with respect to the exact solution to the Stefan–Maxwell equation constitutes the next step in the new modeling approach. Finally, the effective diffusion coefficients are determined by simply minimizing the approximation error.

In this section the special properties of the Stefan–Maxwell equation which derive from the constraints on the velocity and driving force are explained. Subsequent sections deal with the rest of the steps in the new modeling approach.

9.1. Special properties of the Stefan–Maxwell equation

Since the mass-diffusion problem as characterized by the Stefan–Maxwell equation is isotropic in physical space, a single spatial dimension is considered for simplicity of

notation. Let the molar-diffusion velocity, mole fractions and the mole-fraction gradient in this one-dimensional physical system be represented by the following N-dimensional vectors in species space:

$$\mathscr{V}' = V'_\alpha, \tag{72}$$

$$\mathscr{X} = X_\alpha, \tag{73}$$

$$\mathscr{G} = G_\alpha, \quad \alpha = 1, \ldots, N. \tag{74}$$

In species space, the molar-diffusion velocity vector is related to the mole-fraction gradient vector by the following matrix form of the Stefan–Maxwell equation:

$$M\mathscr{V}' = \mathscr{G}, \tag{75}$$

where the elements of the matrix **M** are given by equation (21). The above equation can be viewed as a linear transformation of the N-dimensional vector of mole-fraction gradients to the N-dimensional vector of molar-diffusion velocities in species space. As noted earlier in Section 5, **M** is a singular matrix. In addition, it is now shown that equation (75) represents a constrained, singular system.

The constraints on the molar-diffusion velocity and mole-fraction gradients, given by equations (18) and (10) respectively, can be written in vector notation as:

$$\mathscr{X}^{\mathrm{T}}\mathscr{V}' = 0 \tag{76}$$

$$\sum_\alpha \mathscr{G}_\alpha = 0, \tag{77}$$

where $\mathscr{X}^{\mathrm{T}}$ is the transpose of the column vector $\mathscr{X}$. These constraints imply that the vectors $\mathscr{V}'$ and $\mathscr{G}$ span the subspaces S_{V} and S_G respectively, whose dimension is only $(N-1)$. The subspace S_V is defined such that its orthogonal complement $S_V^{\perp} = \mathrm{span}\,\{\mathscr{X}\}$, and S_G is defined such that its orthogonal complement $S_G^{\perp} = \mathrm{span}\,\{[1, 1, \ldots, 1]^{\mathrm{T}}\}$ [5]. One important implication of the constraints on the linear system in equation (75) is that this is really an $(N-1) \times (N-1)$ problem.

Now the transformation of the original matrix equation expressed in equation (75) to the lower-dimensional subspace is described. Consider the transformations

$$\mathscr{V}' = \mathbf{R}\mathscr{V}'^{r} \tag{78}$$

$$\mathscr{G} = \mathbf{P}\mathscr{G}^{r}, \tag{79}$$

where $\mathscr{V}'^{r}$ and $\mathscr{G}^{r}$ are $N-1$ vectors which are referred to as the reduced representations of $\mathscr{V}'$ and $\mathscr{G}$ in the subspaces S_V and S_G. From equations (78) and (79) it is clear that **R** and **P** are non-square, $N \times (N-1)$ matrices. Substituting the reduced representations given by equations (78) and (79) in the original matrix

equation (eq. 75), results in the transformed matrix equation:

$$\mathbf{MR}\mathscr{V}'^{r} = \mathbf{P}\mathscr{G}^{r}, \tag{80}$$

which can be written as

$$\mathbf{A}\mathscr{V}'^{r} = \mathscr{G}^{r}, \tag{81}$$

where the matrix $\mathbf{A}$ is defined as

$$\mathbf{A} = \mathbf{P}^{-}\mathbf{MR}. \tag{82}$$

In equation (82), the $(N-1)\times N$ matrix $\mathbf{P}^{-}$ satisfies the following relation[5]:

$$\mathbf{P}^{-}\mathbf{P} = \mathbf{I}_{(N-1)\times(N-1)}, \tag{83}$$

where $\mathbf{I}_{(N-1)\times(N-1)}$ represents the $(N-1)\times(N-1)$ identity matrix. Since the transformed linear system in equation (81) incorporates the constraints on both the velocity and the driving forces, it is claimed that this is the correct space in which approximations to the Stefan–Maxwell equation by simplified diffusion models should be constructed. Clearly such models will be automatically consistent. In the next subsection the transformation matrices $\mathbf{R}$ and $\mathbf{P}$ are specified.

9.2. The transformation matrices

One form for the matrix $\mathbf{R}$ leads to the equation:

$$\begin{aligned}\mathscr{V}' &= \mathbf{R}_{N\times(N-1)}\mathscr{V}'^{r} \\ &= \begin{bmatrix} 1 & 0 & \cdots & \cdots & 0 \\ 0 & 1 & \cdots & \cdots & 0 \\ \cdots & \cdots & \cdots & \cdots & \cdots \\ 0 & 0 & \cdots & 0 & 1 \\ -X_1/X_N & -X_2/X_N & \cdots & -X_{N-2}/X_N & -X_{N-1}/X_N \end{bmatrix}\mathscr{V}'^{r}.\end{aligned} \tag{84}$$

Note that the mole fraction vector $\mathscr{X}$ is orthogonal to each column of the transformation matrix $\mathbf{R}$, so that their inner product is always zero. This means that the molar-diffusion velocity vector $\mathscr{V}'$ expressed in the above form will automatically satisfy its constraint.

[5] It should be noted that $\mathbf{P}^{-}$ is not one of the two pseudo-inverses that can be defined for a non-square matrix $\mathbf{P}$ [4], namely $\mathbf{P}^{+(1)} = (\mathbf{P}^{\mathrm{T}}\mathbf{P})^{+}\mathbf{P}^{\mathrm{T}}$ or $\mathbf{P}^{+(2)} = \mathbf{P}^{\mathrm{T}}(\mathbf{P}\mathbf{P}^{\mathrm{T}})^{+}$. However, like $\mathbf{P}^{+(2)}$ it satisfies equation (83).

One form for the matrix **P** can be expressed in the following relation:

$$\mathscr{G} = \mathbf{P}_{N\times(N-1)}\mathscr{G}^r = \begin{bmatrix} 1 & 0 & \cdots & 0 & 0 \\ 0 & 1 & \cdots & 0 & 0 \\ \cdots & \cdots & \cdots & \cdots & \cdots \\ 0 & 0 & \cdots & 0 & 1 \\ -1 & -1 & -1 & \cdots & -1 \end{bmatrix} \mathscr{G}^r. \tag{85}$$

The mole-fraction gradient vector written in this way also automatically satisfies its constraint.

It should be noted that the transformation matrices are non-unique. The implications of this non-uniqueness will be discussed in Section 12.4. With these expressions for the transformation matrices, the matrix **A** in the transformed linear system can now be formed.

9.3. The matrix A

The form for the matrix $\mathbf{P}^-$ which corresponds to the specific expression for **P** given in equation (85) is

$$\mathbf{P}^-_{(N-1)\times N} = \begin{bmatrix} 1 & 0 & 0 & \cdots & 0 & 0 \\ 0 & 1 & 0 & \cdots & 0 & 0 \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\ 0 & 0 & 0 & \cdots & 1 & 0 \end{bmatrix}. \tag{86}$$

Now the matrix **A** whose dimension is $(N-1)\times(N-1)$ can be constructed for arbitrary N by using the relation

$$\mathbf{A}_{(N-1)\times(N-1)} = \mathbf{P}^-\mathbf{M}\mathbf{R}. \tag{87}$$

It is interesting to investigate the structure of the **A** matrix in the limiting cases of a binary mixture, and a multicomponent mixture with equal diffusivities.

9.4. Limiting cases: solution for $N=2$

For the binary mixture case, the matrix **A** has only one element, which is given by equation (87) to be:

$$\mathbf{A}_{1\times1} = [1\ 0]\begin{pmatrix} -a & a \\ a & -a \end{pmatrix}\begin{bmatrix} 1 \\ -X_1/X_2 \end{bmatrix} = -\frac{a}{X_2} = -\frac{X_1}{D_{12}}, \tag{88}$$

where the value of $a = (X_1X_2)/D_{12}$ has been substituted.

The solution for the molar-diffusion velocity is then trivially

$$\mathscr{V}'^r_1 = -\frac{D_{12}}{X_1}\mathscr{G}^r_1. \tag{89}$$

In terms of $\mathscr{V}$, the solution is

$$V_1' = -\frac{D_{12}}{X_1}\mathscr{G}_1, \tag{90}$$

$$V_2' = -\frac{D_{12}}{X_2}\mathscr{G}_2. \tag{91}$$

The solution in the transformed space for this simple case resolves the issue of why the solution matrix in the original space $\mathbf{M}^{+c'}$ is not diagonal, although the molar-diffusion velocity solution for each species is decoupled. The diagonal form emerges only when the Stefan–Maxwell equation is transformed to the appropriate subspace.

9.5. Limiting cases: equal diffusivity case

For the equal diffusivity case with N species, the matrix $\mathbf{A}$ as given by equation (87) is an $(N-1)\times(N-1)$ diagonal matrix which can be written as:

$$\mathbf{A} = \mathrm{diag}\left(-\frac{X_1}{D}, -\frac{X_2}{D}, \ldots, -\frac{X_{N-1}}{D}\right). \tag{92}$$

Note that only $N-1$ diagonal values are needed to completely specify the solution to the equal-diffusivity N-component problem (cf. modeling issue #4). The number of degrees of freedom in a diagonal model is further discussed in Section 12.2.

The modeling implication of the form of the matrix $\mathbf{A}$ in this equal diffusivity limiting case is that diagonal approximations to $\mathbf{A}$ would satisfy the constraints automatically and could be expected to reduce to the correct expressions in the limiting cases (cf. modeling issue #3).

9.6. Mass-diffusion velocity formulation

Frequently the formulation of multicomponent diffusion is in terms of mass-diffusion velocities and mass-fraction gradients. The development of the new modeling approach for this formulation is very similar to that for the molar-diffusion velocity. The salient features of this formulation are presented in this subsection.

Let the mass-diffusion velocity, mass fractions and the mass-fraction gradient in a one-dimensional physical system be represented by the following N-dimensional vectors in species space:

$$\mathscr{V} = V_\alpha, \tag{93}$$

$$\mathscr{Y} = Y_\alpha, \tag{94}$$

$$\mathscr{H} = H_\alpha, \quad \alpha = 1, \ldots, N. \tag{95}$$

In species space, the mass-diffusion velocity vector is related to the mass-fraction gradient vector by the following matrix form of the Stefan–Maxwell equation:

$$\mathbf{M}\mathscr{V} = \mathbf{T}\mathscr{H}. \tag{96}$$

The constraints on the mass-diffusion velocity and mass-fraction gradients, given by equations (5) and (14) respectively, can be written in vector notation as:

$$\mathscr{Y}^{\mathrm{T}}\mathscr{V} = 0 \tag{97}$$

$$\sum_{\alpha} \mathscr{H}_{\alpha} = 0, \tag{98}$$

where $\mathscr{Y}^{\mathrm{T}}$ is the transpose of the column vector $\mathscr{Y}$. These constraints imply that the vectors $\mathscr{V}$ and $\mathscr{H}$ span lower-dimensional subspaces, whose dimension is only $(N-1)$. Now the transformation of the original matrix equation expressed in equation (96) to the lower-dimensional subspace is described. Consider the transformations

$$\mathscr{V} = \tilde{\mathbf{R}}\mathscr{V}^{r} \tag{99}$$

$$\mathscr{H} = \tilde{\mathbf{P}}\mathscr{H}^{r}, \tag{100}$$

where $\mathscr{V}^{r}$ and $\mathscr{H}^{r}$ are $N-1$ vectors which are referred to as the reduced representations of $\mathscr{V}$ and $\mathscr{H}$ in their respective lower-dimensional subspaces. Substituting the reduced representations given by equations (99) and (100) in the original matrix equation (eq. 96), results in the transformed matrix equation:

$$\mathbf{M}\tilde{\mathbf{R}}\mathscr{V}^{r} = \mathbf{T}\tilde{\mathbf{P}}\mathscr{H}^{r}, \tag{101}$$

which can be written as

$$\tilde{\mathbf{A}}\mathscr{V}^{r} = \mathscr{H}^{r}, \tag{102}$$

where the matrix $\tilde{\mathbf{A}}$ is defined as

$$\tilde{\mathbf{A}} = \tilde{\mathbf{P}}^{-}\mathbf{T}^{-1}\mathbf{M}\tilde{\mathbf{R}}. \tag{103}$$

In equation (103), the $(N-1)\times N$ matrix $\tilde{\mathbf{P}}^{-}$ satisfies the following relation:

$$\tilde{\mathbf{P}}^{-}\tilde{\mathbf{P}} = \mathbf{I}_{(N-1)\times(N-1)}. \tag{104}$$

One form for the matrix $\tilde{\mathbf{R}}$ can be expressed in the form:

$$\mathscr{V} = \tilde{\mathbf{R}}_{N\times(N-1)}\mathscr{V}^{r} = \begin{bmatrix} 1 & 0 & \cdots & 0 & 0 \\ 0 & 1 & \cdots & 0 & 0 \\ \cdots & \cdots & \cdots & \cdots & \cdots \\ 0 & 0 & \cdots & 0 & 1 \\ -Y_1/Y_N & -Y_2/Y_N & -Y_3/Y_N & \cdots & -Y_{N-1}/Y_N \end{bmatrix} \mathscr{V}^{r}. \tag{105}$$

One form for the matrix $\tilde{P}$ can be expressed in the following relation:

$$\mathscr{H} = \tilde{\mathbf{P}}_{N\times(N-1)}\mathscr{H}^r = \begin{bmatrix} 1 & 0 & \cdots & 0 & 0 \\ 0 & 1 & \cdots & 0 & 0 \\ \cdots & \cdots & \cdots & \cdots & \cdots \\ 0 & 0 & \cdots & 0 & 1 \\ -1 & -1 & -1 & \cdots & -1 \end{bmatrix} \mathscr{H}^r. \tag{106}$$

The form for the matrix $\tilde{\mathbf{P}}^-$ which corresponds to the specific expression for $\tilde{\mathbf{P}}$ given by equation (106) is

$$\tilde{\mathbf{P}}^-_{(N-1)\times N} = \begin{bmatrix} 1 & 0 & 0 & \cdots & 0 & 0 \\ 0 & 1 & 0 & \cdots & 0 & 0 \\ \cdots & \cdots & \cdots & \cdots & \cdots & \\ 0 & 0 & 0 & \cdots & 1 & 0 \end{bmatrix}. \tag{107}$$

Now the matrix $\tilde{\mathbf{A}}$ can be constructed for arbitrary N by using the relation

$$\tilde{\mathbf{A}}_{(N-1)\times(N-1)} = \tilde{\mathbf{P}}^-\mathbf{T}^{-1}\mathbf{M}\tilde{\mathbf{R}}. \tag{108}$$

10. General Form for Diagonal Approximations

The next step in the new modeling approach is to propose a general diagonal model in the transformed space. The general form for diagonal approximations in the transformed space is:

$$\mathscr{V}'^{ra} = \mathbf{L}^r\mathscr{G}^r, \tag{109}$$

where $\mathscr{V}'^{ra}$ is a model for the molar-diffusion velocity in the transformed space which is expressed as the product of a diagonal matrix $\mathbf{L}^r = \mathrm{diag}(l_1^r, l_2^r, \ldots, l_{N-1}^r)$ and the transformed mole-fraction gradients $\mathscr{G}^r$. Comparing this equation to the transformed Stefan–Maxwell equation (eq. 81) shows that $\mathbf{L}^r$ is an approximation to $\mathbf{A}^{-1}$.

Similar approximations can be constructed for the mass-diffusion velocity $\mathscr{V}^r$ in terms of mass-fraction gradients $\mathscr{H}^r$. The corresponding general form for diagonal approximations in the transformed space is:

$$\mathscr{V}^{ra} = \mathbf{K}^r\mathscr{H}^r, \tag{110}$$

where $\mathscr{V}^{ra}$ is a model for the mass-diffusion velocity in the transformed space which is expressed as the product of a diagonal matrix $\mathbf{K}^r = \mathrm{diag}(k_1^r, k_2^r, \ldots, k_{N-1}^r)$ and the transformed mass-fraction gradients $\mathscr{H}^r$. Comparing this equation to the transformed Stefan–Maxwell equation (eq. 102) shows that $\mathbf{K}^r$ is an approximation to $\tilde{\mathbf{A}}^{-1}$.

10.1. Form of diagonal approximation models in original space

It is interesting to see what matrix structure is implied in the original space, by diagonal approximations in the transformed space. Substituting equation (109) for $\mathscr{V}'^{ra}$, the diagonal approximation to molar-diffusion velocity in the transformed space, in equation (80) yields the form of the approximation in the original space to be

$$\mathscr{V}'^{a} = \mathbf{L}\mathscr{G}, \tag{111}$$

where the matrix $\mathbf{L}$ denotes $\mathbf{L}^r$ transformed back to the original space using the relation

$$\mathbf{L} = \mathbf{R}\mathbf{L}'^{r}\mathbf{P}^{-}.$$

Substituting the expressions for the specific forms of these matrices results in

$$\mathbf{L} = \begin{bmatrix} l_1^r & 0 & 0 & \cdots & 0 & 0 \\ 0 & l_2^r & 0 & \cdots & 0 & 0 \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\ 0 & 0 & 0 & \cdots & l_{N-1}^r & 0 \\ -l_1^r X_1/X_N & -l_2^R X_2/X_N & -l_3^r X_3/X_N & \cdots & -l_{N-1}^r X_{N-1}/X_N & 0 \end{bmatrix} \tag{112}$$

A similar expression can be derived for $\mathbf{K}$, the matrix corresponding to $\mathbf{K}^r$ in the original space. Using the relation

$$\mathbf{K} = \tilde{\mathbf{R}}\mathbf{K}^{r}\tilde{\mathbf{P}}^{-},$$

results in

$$\mathbf{K} = \begin{bmatrix} k_1^r & 0 & 0 & \cdots & 0 & 0 \\ 0 & k_2^r & 0 & \cdots & 0 & 0 \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\ 0 & 0 & 0 & \cdots & k_{N-1}^r & 0 \\ -k_1^r Y_1/Y_N & -k_2^r Y_2/Y_N & -k_3^r Y_3/Y_N & \cdots & -k_{N-1}^r Y_{N-1}/Y_N & 0 \end{bmatrix} \tag{113}$$

The similarity of the form of the modified FDA model in equation (58) to the form of the matrix $\mathbf{K}$ in equation (113) is striking. This provides a justification and new interpretation for the form of the modified FDA model: namely, that it corresponds to a diagonal approximation in the reduced-dimensional subspace. However, the exact values of the effective diffusion coefficients in the modified FDA model are still not justified on any quantitative basis.

11. The Minimum Error Diagonal Approximation (MEDA) Model

Using the form of the diagonal approximation in the reduced-dimensional subspace, a new simplified diffusion model is proposed in this section. The effective diffusion coefficients are determined by the requirement that they minimize the 2-norm of the

error between the modeled diffusion velocity vector in species space with respect to the exact Stefan–Maxwell solution.

Let $\mathscr{V}^{\prime r e}$ denote the molar-diffusion velocity vector which is the exact solution to the Stefan–Maxwell equation in the reduced-dimensional space (eq. 81):

$$\mathbf{A}\mathscr{V}^{\prime r} = \mathscr{G}^{r}.$$

Let $\mathscr{V}^{\prime r a}$ be the modeled molar-diffusion velocity corresponding to a diagonal model as in equation (109). The error in the molar-diffusion velocity is given by the vector:

$$\delta\mathscr{V}^{\prime r} \equiv \mathscr{V}^{\prime r a} - \mathscr{V}^{\prime r e}.$$

Using equations (81) and (109), it can be shown that the 2-norm of the error can be written as

$$\|\delta\mathscr{V}^{\prime r}\|_2^2 = \sum_{\alpha=1}^{N-1} \mathscr{Z}_{(\alpha)}\sigma_{(\alpha)}^2\mathscr{Z}_{(\alpha)}, \tag{114}$$

where $[\sigma_1, \sigma_2, \ldots, \sigma_{N-1}]$ are the singular values of the matrix

$$\mathbf{C} = [\mathbf{L}^{\mathrm{r}}\mathbf{A} - \mathbf{I}_{(\mathrm{N}-1)\times(\mathrm{N}-1)}],$$

and

$$\mathscr{Z} = \mathbf{Q}^{\mathrm{T}}\mathscr{V}^{\prime r e},$$

where $\mathbf{Q}^{\mathrm{T}}$ is the right orthogonal matrix in the singular value decomposition

$$\mathbf{C} = \mathbf{U}\boldsymbol{\Sigma}\mathbf{Q}^{\mathrm{T}}$$

of the matrix $\mathbf{C}$. See the appendix for details. The squares of the singular values $\boldsymbol{\Sigma} = \mathrm{diag}\{\sigma_1, \sigma_2, \ldots, \sigma_{N-1}\}$ represent the component-wise multiplication factors which when multiplied by the square of the transformed velocity component $\mathscr{Z}_{(\alpha)}$ sum to the 2-norm of the error in molar-diffusion velocity.

Clearly minimizing the quantity

$$\sum_{\alpha=1}^{N-1} \sigma_{(\alpha)}^2$$

will minimize the 2-norm of the error in the molar-diffusion velocity. This quantity is simply the square of the Frobenius norm of the matrix $\mathbf{L}^{r}\mathbf{A} - \mathbf{I}_{(N-1)\times(N-1)}$ [5]:

$$\|\mathbf{L}^{r}\mathbf{A} - \mathbf{I}_{(N-1)\times(N-1)}\|_F^2 = \sum_{\alpha=1}^{N-1} \sigma_{(\alpha)}^2. \tag{115}$$

From equation (114) it follows that in order to minimize the 2-norm of the error, the diagonal components of the matrix $\mathbf{L}^r = \mathrm{diag}(l_1^r, l_2^r, \ldots, l_{N-1}^r)$ should be chosen such that they minimize the quantity

$$Q = \|\mathbf{L}^r\mathbf{A} - \mathbf{I}_{(N-1)\times(N-1)}\|_F^2. \tag{116}$$

This resolves modeling issue #5.

Using the definition of the Frobenius norm in terms of the squares of the matrix elements [5], the quantity Q may be written as

$$Q = \sum_{\theta=1}^{N-1}\sum_{\eta=1}^{N-1} |l_{(\theta)}^r \delta_{(\theta)\gamma} A_{\gamma(\eta)} - \delta_{(\theta)(\eta)}|^2. \tag{117}$$

The minimization procedure requires that

$$\frac{\partial Q}{\partial l_\theta^r} = 0, \quad \theta = 1, \ldots, N-1. \tag{118}$$

Differentiating equation (117) results in

$$\begin{aligned}\frac{\partial Q}{\partial l_\theta^r} &= \sum_{\eta=1}^{N-1} 2\{l_{(\theta)}^r A_{(\theta)(\eta)} - \delta_{(\theta)(\eta)}\}A_{(\theta)(\eta)} \\ &= \sum_{\eta=1}^{N-1} 2\{l_{(\theta)}^r A_{(\theta)(\eta)} A_{(\theta)(\eta)} - A_{(\theta)(\theta)}\}.\end{aligned} \tag{119}$$

Setting $\partial Q/\partial l_\theta^r = 0$ in equation (119) yields the desired values of l_θ^r to be

$$l_\theta^r = \frac{A_{(\theta)(\theta)}}{\sum_{\eta=1}^{N-1}\{A_{(\theta)(\eta)}\}^2}. \tag{120}$$

Using the definition of $\mathbf{A}$ from equation (82) we may write

$$A_{\gamma\eta} = P_{\gamma\alpha}^- M_{\alpha\beta} R_{\beta\eta}, \quad \gamma, \eta = 1, \ldots, N-1, \quad \alpha, \beta = 1, \ldots, N. \tag{121}$$

Noting that $R_{\beta\eta}$ may be written as

$$\begin{aligned} R_{\beta\eta} &= \delta_{\beta\eta}, && \beta, \eta = 1, \ldots, N-1, \\ R_{N\eta} &= -X_\eta / X_N, && \eta = 1, \ldots, N-1, \end{aligned}$$

and that $P_{\gamma\alpha}^-$ may be written as

$$\begin{aligned} P_{\gamma\alpha}^- &= \delta_{\gamma\alpha}, && \alpha, \gamma = 1, \ldots, N-1 \\ P_{\gamma N}^- &= 0, && \gamma = 1, \ldots, N-1, \end{aligned}$$

the elements of matrix **A** may be written as

$$\begin{aligned} A_{\gamma\eta} &= \delta_{\gamma\alpha}\left\{M_{\alpha\beta}\delta_{\beta\eta} - M_{\alpha N}\left(\frac{X_\eta}{X_N}\right)\right\}, \quad \alpha,\beta,\gamma = 1,\ldots,N-1 \\ &= M_{\gamma\eta} - M_{\gamma N}\left(\frac{X_\eta}{X_N}\right). \qquad\qquad \alpha,\gamma = 1,\ldots,N-1. \end{aligned} \tag{122}$$

Substituting this expression for $A_{\gamma\eta}$ into equation (120) results in the desired analytic expression for the diagonal elements l_θ^r in terms of the elements of the matrix **M** and mole fractions:

$$l_\theta^r = \frac{M_{(\theta)(\theta)} - M_{(\theta)N}(X_{(\theta)}/X_N)}{\sum_{\eta=1}^{N-1}\{M_{(\theta)(\eta)} - M_{(\theta)N}(X_{(\eta)}/X_N)\}^2}, \quad \theta = 1,\ldots,N-1. \tag{123}$$

In conjunction with the definition of the elements of the matrix **M** in equation (21), and in view of the relation between **L** and $\mathbf{L}^r$ given in equation (112), it is clear that equation (123) represents the specification of the effective diffusion coefficients of equation (111) in terms of the binary diffusivities and mole fractions.

11.1. Limiting case behavior of the MEDA model

For the binary case, it was noted that the matrix **A** has only one element which is given by equation (88). The MEDA matrix $\mathbf{L}^r$ also has only one element which is given by equation (120) to be

$$l_1^r = 1/A_{11} = -\frac{D_{12}}{X_1},$$

which in turn implies that the molar-diffusion velocity in the reduced-dimensional space is given by

$$\mathscr{V}_1^{\prime r} = -\frac{D_{12}}{X_1}\mathscr{G}_1^r.$$

Comparing this with equation (89) reveals that the MEDA model does yield the correct solution for the binary case.

For the equal diffusivity case it was shown in Section 9.5 that the matrix **A** is a diagonal matrix whose elements are given by equation (92). The elements of the diagonal MEDA matrix $\mathbf{L}^r$ as given by equation (120) are simply the reciprocals of the corresponding diagonal elements of matrix **A**. Substituting these effective diffusion coefficients back into equations (109) and (112) reveals that the MEDA model yields the correct solution in the equal diffusivity case also.

It is remarkable that the general minimization procedure when formulated in the correct subspace automatically recovers these limiting case solutions without any extraneous constraints or information.

11.2. MEDA coefficients for mass-diffusion velocity

The procedure for deriving the MEDA model coefficients for mass-diffusion velocity, $\mathbf{K}^r = \mathrm{diag}(k_1^r, k_2^r, \ldots, k_{N-1}^r)$, is identical to that for the molar-diffusion velocity. In this case the quantity to be minimized is

$$\|\mathbf{K}^r \tilde{\mathbf{A}} - \mathbf{I}_{(N-1)\times(N-1)}\|_F^2.$$

The final form of the model coefficients is

$$k_\theta^r = \frac{\{B_{(\theta)(\theta)} - B_{(\theta)N}(Y_{(\theta)}/Y_N)\}}{\sum_{\eta=1}^{N-1}\{B_{(\theta)(\eta)} - B_{(\theta)N}(Y_{(\eta)}/Y_N)\}^2}, \quad \theta = 1, \ldots, N-1, \tag{124}$$

where

$$B_{\theta\eta} = T_{\theta\gamma}^{-1} M_{\gamma\eta}, \quad \theta, \eta, \gamma = 1, \ldots, N.$$

12. Discussion

This section delves into details concerning various aspects of the study which would have otherwise been a digression to the main development. The scope of the analysis in this work, and possible extensions to other mass-diffusion problems is taken up first.

12.1. Scope of the analysis

This work addresses the issue of mass-diffusion in a homogeneous gaseous medium (also termed bulk diffusion in the literature) consisting of a multicomponent ideal gas mixture, as described by the Stefan–Maxwell equations (15). As such this description is valid for gaseous mixtures at low to moderate pressures, and also for thermodynamically ideal liquid mixtures. Extensions to non-ideal fluid mixtures and to heterogenous media[6)] are of interest in various applications. Krishna and Wesselingh [6] provide a comprehensive review of various mass transfer problems which can be formulated using the Stefan–Maxwell approach. Some problems and issues relevant to the preceding analysis are briefly discussed here.

When the mixture is composed of non-ideal fluids, there are two changes to equation (15) that need to be accounted for. The first is that the generalized driving forces need to be written in terms of gradients of the chemical potential, rather than the gradients of mole-fraction. The second is that the effect of thermodynamic non-idealities on the binary diffusion coefficients need to be accounted for by a matrix of thermodynamic factors involving the activity coefficient for each species. The re-defined binary diffusion coefficients do not change the structure of the Stefan–Maxwell equation

[6)] The author is grateful to the anonymous referee whose comments prompted the inclusion of this subsection.

system and the analysis for ideal gas mixtures carries over to the non-ideal fluid mixture case as well. However, the re-defined binary diffusion coefficients for highly non-ideal liquid mixtures exhibit a strong composition dependence, and can exhibit large variations near phase transition and critical points. For such problems, solving the full Stefan–Maxwell equation system is probably a better alternative.

The dusty gas model for diffusion in porous media (which is composed of bulk diffusion and Knudsen diffusion) results in a system of equations similar to the bulk-diffusion Stefan–Maxwell equations (15), but with appropriately modified diffusion coefficients (Krishna and Wesselingh [6]). It is important to note that the presence of Knudsen diffusion changes the special properties of the matrix $M_{\alpha\beta}$ associated with the Stefan–Maxwell equation system for bulk diffusion. In particular, the presence of Knudsen diffusion results in a nonsingular $M_{\alpha\beta}$ matrix. However, the minimization procedure outlined in this work is still applicable, and may be used to determine the corresponding minimum error Fickian diffusion coefficients. Furthermore, the component of the mass flux arising from viscous flow (due to the pressure gradient driving force) can also be represented by the generalized Stefan–Maxwell equations. Therefore, the procedure used in this work to derive minimum-error effective diffusion coefficients can be extended to diffusion in various heterogeneous media, such as macro- and microporous catalysts, adsorbents and membranes.

This discussion would be incomplete without an important caveat concerning the Fickian diffusion approximation. The Fickian diffusion approximation is incapable of describing certain diffusion phenomena such as osmotic diffusion, reverse diffusion, and diffusion barriers, which could be important in certain applications. As a result, even though the minimum error effective diffusion coefficients derived in this work are more accurate than the standard Fickian diffusion coefficients, since these new coefficients are also based on the Fickian approximation, they cannot reproduce these phenomena either.

12.2. Choice of velocity in the Stefan–Maxwell equation

In Section 1 it was shown that the Stefan–Maxwell equation can be written in terms of diffusion velocities (mass or molar) or species velocities. While at first sight the choice of which formulation to use might seem to be more a matter of personal preference, using the diffusion velocity formulation has certain advantages.

One of the advantages of using the mass-diffusion velocity formulation is that in this case the Stefan–Maxwell equation (eq. 7) together with the constraint equation (eq. 5) constitutes an *independent, closed* system of equations for the mass-diffusion velocity. The independence feature derives from the fact that this system provides the necessary closure for the diffusive mass flux in the species conservation equation, without any additional external information.

The disadvantage of using the species velocity form the Stefan–Maxwell equation (eq. 15) is that the corresponding constraint equation requires knowledge of the mass-averaged mixture velocity **u**. This information is extraneous to the problem since the

quantity of interest, namely the diffusive mass flux whose closure is sought, is independent of **u**.

The other advantage of using the diffusion velocity formulation is that it clearly reveals the dimensionality and degrees of freedom of the problem. It shows that while the Stefan–Maxwell equation is singular, by applying the constraints on the velocities and driving forces the original $N \times N$ linear system is transformed to a nonsingular $(N-1) \times (N-1)$ system (under the conditions noted in Section 5). This in turn implies that any diagonal approximation has only $N-1$ degrees of freedom, or model coefficients.

12.3. Fickian diffusion approximation and effective binary diffusion approximation

In this paper we make a distinction between the terms Fickian diffusion approximation (FDA) and effective binary diffusion approximation. By FDA it is meant that the diffusion velocity of the αth species depends only on the αth species' driving force, and not on the driving force associated with any of the other species. As noted previously, the FDA cannot be true for all species since the diffusion velocities and driving forces are constrained to span lower-dimensional spaces, and are therefore coupled. Hence, a decoupling of diffusion velocity-driving force pairs is not possible for all species. However, in the reduced-dimensional representation of the Stefan–Maxwell equation all the diffusion velocities are independent and a full decoupling based on the FDA is possible.

The effective binary diffusion approximation (EBDA) on the other hand models a multicomponent mixture as a binary mixture of species α and a complementary composite species representing all the other species. The species velocity solution $\mathbf{u}_\alpha$ to the Stefan–Maxwell equation can be decomposed into two contributions: one arising from the αth driving force and the other arising from the driving forces of the remaining species. In the SCEBD model which is based on the EBDA, the contribution to the species velocity from the driving forces associated with the remaining species is assumed to be the same for all species. However, as is readily seen from the non-diagonal form of the SCEBD model, driving forces $\mathbf{G}_\beta$, $\beta \neq \alpha$ do affect $\mathbf{V}_\alpha$. Hence, the SCEBD model is a non-Fickian model.

12.4. Non-uniqueness of the transformations and dependence on species order

It has already been noted in Section 9 that the transformation matrices **R** and **P** that define the reduced representations of the velocity and driving forces are non-unique. The source of the non-uniqueness is closely related to the modified FDA model's dependence on species order, and this connection is clarified in this section.

In order to define the reduced representation of the molar-diffusion velocity vector in the subspace S_V, we need to define a basis for S_V. The subspace S_V is defined such that its orthogonal complement $S_V^\perp = \text{span}\{\mathscr{X}\}$. The definition of the orthogonal complement $S_V^\perp$ is

$$S_V^\perp = \{x \in \mathscr{R}^N \,:\, x^{\mathrm{T}} y = 0, \quad \forall y \in S_V\}.$$

This implies that every vector y in S_V, must satisfy the relation

$$\mathscr{X}^{\mathrm{T}} y = 0.$$

It was also noted in Section 9.2 that the mole-fraction vector $\mathscr{X}$ is orthogonal to each column of the transformation matrix **R**, so that their inner product is always zero. So each column vector of **R** belongs to S_V. Without proof we claim that these column vectors are linearly independent, and that they span the subspace S_V, i.e. that the column vectors of **R** form a basis for the subspace S_V.

Clearly there is no unique basis for S_V. This can be shown easily by noting that the following alternative definition of **R** also has column vectors that form a basis for S_V:

$$\begin{bmatrix} -X_2/X_1 & -X_3/X_1 & \cdots & -X_{N-1}/X_1 & -X_N/X_1 \\ 1 & 0 & \cdots & \cdots & 0 \\ 0 & 1 & \cdots & \cdots & 0 \\ \cdots & \cdots & \cdots & \cdots & \cdots \\ 0 & 0 & \cdots & 0 & 1 \end{bmatrix} \tag{125}$$

However, only N of all possible bases for S_V (in conjunction with the appropriately defined basis for S_G) result in diagonal **A** for the equal diffusivity case. If diagonal approximations to **A** are to reproduce the correct solution for the equal diffusivity case, then such approximations must be constructed using one of these N bases. These bases can be constructed in exactly the same way as the alternative form for **R** in equation (125), but by appropriately re-defining and moving the row with the mole fraction entries from 2 through $N-1$. Another way of viewing these N bases is by retaining the form of the matrix **R** which was given in equation (84), but by sequentially changing the definition of the species in the Nth row to each of the N species in turn. In essence this implies that the N different bases for the subspace S_V that result in diagonal **A** for equal diffusivities can be generated by successively interchanging each of the species with the Nth species in equation (84).

It is important to note that the exact solution to the Stefan–Maxwell equation is the same regardless of the choice of basis, although the matrix **A** will of course be different depending on the choice of the basis. This dependence of the matrix **A** on the choice of the basis means that approximations to **A** (diagonal and non-diagonal ones) will also be dependent on the basis.

For the MEDA model the best choice for the basis is simply the one that minimizes the 2-norm of the error between the approximation and the exact solution to the Stefan–Maxwell equation, and is given by

$$\min_{\mathbf{R}} \| \mathscr{V}^{tra} - \mathscr{V}^{tre} \|_2. \tag{126}$$

Clearly it is impossible to determine the best basis without first obtaining the exact solution. Furthermore, the correspondence between minimizing the quantity Q in equation (116) and minimizing the 2-norm of the error in the molar-diffusion

velocity, does not carry over when the basis **R** is changed, i.e. the basis **R** that satisfies the condition

$$\min_{\mathbf{R}} \|\mathbf{L}^r\mathbf{A} - \mathbf{I}_{(N-1)\times(N-1)}\|_F^2,$$

is not guaranteed to be the same basis that satisfies equation (126). Even if the minimization condition on the Frobenius norm were chosen somewhat arbitrarily to define the best basis, it would require considerable computational expense at each point in physical space and time, since **R** depends on the mole fractions. For the MEDA model to be viable, the choice of species order must be independent of the mole or mass fractions.

We now present an alternative approach to resolving the problem of dependence on species order. In the MEDA model it is proposed that the optimal ordering of the species be based on the following principle. Since the objective of the model is to construct diagonal approximations in the reduced space of dimension $N-1$, it is incapable of diagonalizing the equation for one of the species (for the choice of **R** given by eq. (84) this is the Nth species). This species' velocity is determined by the constraint requirement. If the ordering of species is chosen such that the most diagonally dominant row in the linear system is chosen to be the Nth species, then on average this ordering would result in the most accurate approximation. Therefore, in the MEDA model formulation (which uses the transformation matrix given by eq. (84)) the rows in matrix equation (eq. 75) are rearranged so as to place the species that satisfies the following condition

$$\min_{\alpha}\left\{\frac{\sum_{\beta\neq\alpha} D_{\alpha\beta}}{D_{(\alpha)(\alpha)}}\right\} \tag{127}$$

in the last row.

It is clear from the above that the problem of species order is not easy to resolve for either the modified FDA model or for the MEDA model, but the above approach provides a reasonable solution without compromising any of the other advantages of the MEDA model. It is noteworthy that while adding undetermined constants to the modified FDA model removes the species dependence, it does not address the fundamental issue of which species order gives the least approximation error and preserves limiting case solutions.

12.5. Generality of the minimization procedure

It is of interest to determine if non-diagonal approximations can be constructed using the same minimization procedure. Unfortunately it turns out that it is only for diagonal approximations that the error in the diffusion velocity of species α is determined solely by the effective diffusion coefficient associated with that species. This permits us to write out the solution to the minimization problem, namely the values of these effective diffusion coefficients, explicitly without resorting to a matrix

solution procedure. For non-diagonal approximations this is not possible, and the original matrix problem is now simply replaced with a new one, which finally only yields an approximate solution.

12.6. Case of some species with zero mole or mass fractions

It is not unusual to encounter this situation in mass-diffusion problems. The MEDA model as formulated in terms of molar or mass-diffusion velocity will give infinite diffusion coefficients due to possible division by zero in equations (123) and (124). These equations are easily modified to account for the general case where some mole fractions are zero.

Let Z denote the set of N_Z species whose mole fractions are zero such that

$$Z = \{\zeta : X_\zeta = 0\}.$$

Then the rank of matrix $\mathbf{M}$ is $(N-1-N_Z)$, and its elements are zero according as

$$\begin{aligned} M_{\zeta\beta} &= 0, \quad \beta = 1, \ldots, N, \quad \zeta \in Z \\ M_{\beta\zeta} &= 0, \quad \beta = 1, \ldots, N, \quad \zeta \in Z \end{aligned} \tag{128}$$

This has the effect of deleting the row and column associated with the ζth species in the matrix equation for the molar-diffusion velocity formulation.

The expression for the elements of the matrix $\mathbf{A}$ in equation (122) needs to be modified to read

$$A_{\gamma\eta} = M_{\gamma\eta} - (1 - \delta_{N\zeta}) M_{\gamma N} \left(\frac{X_\eta}{X_N} \right), \quad \zeta \in Z, \tag{129}$$

where it is implied that the division by zero mole fraction is not attempted if the term involving the delta function evaluates to zero. Finally the expression for the diagonal elements l_θ^r becomes

$$l_\theta^r = \frac{M_{(\theta)(\theta)} - (1 - \delta_{N\zeta}) M_{(\theta)N} (X_{(\theta)}/X_N)}{\sum_{\eta \notin Z} \{ M_{(\theta)(\eta)} - (1 - \delta_{N\zeta}) M_{(\theta)N} (X_{(\eta)}/X_N) \}^2}, \quad \theta \notin Z, \quad \zeta \in Z. \tag{130}$$

Consistent with the fact that the matrix equation rows and columns corresponding to the θth species ($\theta \in Z$) are zero, the corresponding molar-diffusion velocity and diagonal coefficient must also be zero:

$$l_\theta^r = 0, \quad \theta \in Z \tag{131}$$

$$\mathscr{V}^{\prime r a} = 0, \quad \theta \in Z. \tag{132}$$

The expression for the diagonal coefficients of the mass-diffusion velocity approximation involves the inverse transformation matrix $\mathbf{T}^{-1}$, and therefore the effect of zero mole fractions on its elements must be ascertained. The mole fraction

$X_{(\gamma)}$ always appears in the denominator of the elements of $\mathbf{T}^{-1}$ in conjunction with the corresponding mass fraction $Y_{(\gamma)}$ in the numerator. In view of the relation

$$\frac{Y_{(\gamma)}}{X_{(\gamma)}} = \frac{\mathscr{W}_\gamma}{\mathscr{W}_\alpha X_\alpha},$$

where $\mathscr{W}_\gamma$ is the molecular weight of species γ, the expression for the elements of the transformation matrix given by eqs. (68)–(69) can be rewritten as

$$T^{-1}_{(\alpha)(\alpha)} = \frac{\mathscr{W}_{(\alpha)}}{\bar{\mathscr{W}}}[1 - Y_{(\alpha)}] \tag{133}$$

$$T^{-1}_{\alpha\beta} = -\frac{Y_\alpha \mathscr{W}_{(\beta)}}{\bar{\mathscr{W}}}, \quad \alpha \neq \beta, \tag{134}$$

where $\bar{\mathscr{W}} = \mathscr{W}_\alpha X_\alpha$. It is clear from the above that all the elements of $\mathbf{T}^{-1}$ are finite quantities even when the mole fractions go to zero.

As a consequence the rank of matrix $B_{\theta\eta} = T^{-1}_{\theta\gamma} M_{\gamma\eta}$ is $(N - 1 - N_Z)$, and its elements are zero according as

$$\begin{aligned} B_{\zeta\beta} &= 0, \quad \beta = 1, \ldots, N, \quad \zeta \in Z \\ B_{\beta\zeta} &= 0, \quad \beta = 1, \ldots, N, \quad \zeta \in Z \end{aligned} \tag{135}$$

This has the effect of deleting the row and column associated with the ζth species in the matrix equation for the mass-diffusion velocity formulation.

Similarly redefining the expression for the elements of the matrix $\tilde{\mathbf{A}}$ (where it is implied that the division by zero mole fraction is not attempted if the term involving the delta function evaluates to zero), results in the general expression for the diagonal elements k^r_θ

$$k^r_\theta = \frac{B_{(\theta)(\theta)} - (1 - \delta_{N\zeta}) B_{(\theta)N}(Y_{(\theta)}/Y_N)}{\Sigma_{\eta \notin Z}\{B_{(\theta)(\eta)} - (1 - \delta_{N\zeta}) B_{(\theta)N}(Y_{(\eta)}/Y_N)\}^2}, \quad \theta \notin Z, \quad \zeta \in Z. \tag{136}$$

Again consistent with the fact that the matrix equation rows and columns corresponding to the θth species ($\theta \in Z$) are zero, the corresponding mass-diffusion velocity and diagonal coefficient must also be zero:

$$k^r_\theta = 0, \quad \theta \in Z, \tag{137}$$

$$\mathscr{V}^{ra} = 0, \quad \theta \in Z. \tag{138}$$

12.7. Computational considerations

It is arguable that with the advent of powerful computers and linear algebra software packages, the computational expense associated with solving the full Stefan–

Maxwell equations is no longer excessive. However, the comparison of computational expense for the full Stefan–Maxwell system and a simplified diffusion model should not be made on the basis of solving these equations at a single point in physical space. This is because fully 3-D hydrodynamic codes must use some computational stencil to represent the mole-fraction gradients that appear in the driving forces. Under the Fickian approximation the decoupling of the species evolution equations allows each of these equations to be solved independently and efficiently. However, solving the full Stefan–Maxwell system means that the species evolution equations must all be solved in a coupled fashion. In the context of iterative methods used to solve the matrix equations in many hydrodynamic codes, this could result in a significant computational overhead due to slower convergence of the iteration procedure. Therefore, the appropriate figure of merit for comparison is the total computational cycles consumed in solving the species evolution equation system for a 3-D problem, divided by the total number of species and the total number of grid points in physical space. The asymptotic behavior of this figure of merit for large number of species and large number of grid points would provide the definitive answer of relative computational expense.

Also several computer codes use the Fickian diffusion approximation, and the standard diffusion coefficients used in these codes can be easily replaced with the new minimum-error ones derived in the paper to give improved results. Finally, even if the utility of these improved diffusion coefficients and simplified diffusion models is being rendered obsolete by faster computers, the analysis serves to clarify our understanding of simplified diffusion models and may also have some pedagogical value.

13. Summary

A systematic approach to understanding approximations to the Stefan–Maxwell equation is presented. General forms for existing models are derived and important features of the corresponding approximations are identified. It is shown that constraints on the velocity and driving forces imply that the diffusion problem can be transformed to a lower-dimensional subspace where for limiting cases the Stefan–Maxwell equation has a diagonal matrix structure. A new modeling approach is proposed which consists of constructing approximations in this transformed space. A novel procedure to minimize the approximation error for diagonal approximations is used to construct a new MEDA simplified diffusion model. This model automatically satisfies the constraints on diffusion velocities and reproduces the correct limiting case solutions. The new model (given by eqs. (112) or (113)) replaces the standard Fickian approximation (eq. (58)) with the minimum error effective diffusion coefficients given by equations (130) and (136). It also has exactly as many model coefficients ($N-1$) as there are degrees of freedom for a diagonal approximation. The dependence on species order of approximations in the transformed space is dealt with in a systematic fashion. The new model is more accurate than any other diagonal simplified diffusion model.

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Appendix

The 2-norm of the error in the modeled molar-diffusion velocity, $\|\delta\mathscr{V}^{\prime r}\|_2^2$, can be written as

$$\|\delta\mathscr{V}^{\prime r}\|_2^2 = \delta\mathscr{V}^{\prime r\mathrm{T}}\delta\mathscr{V}^{\prime r}. \tag{139}$$

Given the definition of the error in the molar-diffusion velocity,

$$\delta\mathscr{V}^{\prime r} \equiv \mathscr{V}^{\prime r a} - \mathscr{V}^{\prime r e},$$

and using equation (109) and the fact that $\mathscr{V}^{\prime r e}$ satisfies

$$\mathbf{A}\mathscr{V}^{\prime r e} = \mathscr{G}^r,$$

one may write

$$\delta\mathscr{V}^{\prime r} = (\mathbf{L}^r - \mathbf{A}^{-1})\mathscr{G}^r. \tag{140}$$

Substituting this into the right hand side of equation (139) for the 2-norm of the error results in

$$\begin{aligned}\|\delta\mathscr{V}^{\prime r}\|_2^2 &= \delta\mathscr{V}^{\prime r^{\mathrm{T}}}\delta\mathscr{V}^{\prime r} \\ &= \mathscr{G}^{r^{\mathrm{T}}}(\mathbf{L}^r - \mathbf{A}^{-1})^{\mathrm{T}}(\mathbf{L}^r - \mathbf{A}^{-1})\mathscr{G}^r.\end{aligned} \tag{141}$$

Substituting $\mathscr{G}^r = \mathbf{A}\mathscr{V}^{\prime r e}$ into equation (141) gives

$$\begin{aligned}\|\delta\mathscr{V}^{\prime r}\|_2^2 &= \mathscr{V}^{\prime r e^{\mathrm{T}}}\mathbf{A}^{\mathrm{T}}(\mathbf{L}^r - \mathbf{A}^{-1})^{\mathrm{T}}(\mathbf{L}^r - \mathbf{A}^{-1})\mathbf{A}\mathscr{V}^{\prime r e} \\ &= \mathscr{V}^{\prime r e^{\mathrm{T}}}(\mathbf{L}^r\mathbf{A} - \mathbf{I}_{(N-1)\times(N-1)})^{\mathrm{T}}(\mathbf{L}^r\mathbf{A} - \mathbf{I}_{(N-1)\times(N-1)})\mathscr{V}^{\prime r e}.\end{aligned} \tag{142}$$

If the matrix $\mathbf{L}^r\mathbf{A} - \mathbf{I}_{(N-1)\times(N-1)}$ is denoted by the matrix $\mathbf{C}$, then

$$\|\delta\mathscr{V}^{\prime r}\|_2^2 = \mathscr{V}^{\prime r e^{\mathrm{T}}}\mathbf{C}^{\mathrm{T}}\mathbf{C}\mathscr{V}^{\prime r e}. \tag{143}$$

Further let the singular value decomposition (SVD) of the matrix $\mathbf{C}$ be written as

$$\mathbf{C} = \mathbf{U}\boldsymbol{\Sigma}\mathbf{Q}^{\mathrm{T}}, \tag{144}$$

where $\mathbf{U}$ and $\mathbf{Q}$ are orthogonal matrices, and $\mathbf{\Sigma} = \mathrm{diag}\{\sigma_1, \sigma_2, \ldots, \sigma_{N-1}\}$ is a diagonal matrix of singular values.

If the vector $\mathscr{Z} = [\mathscr{Z}_1, \mathscr{Z}_2, \ldots, \mathscr{Z}_{N-1}]$ is given by

$$\mathscr{Z} = \mathbf{Q}^{\mathrm{T}} \mathscr{V}'^{re},$$

then the expression for the 2-norm of the error can be written as

$$\|\delta \mathscr{V}'^{r}\|_2^2 = \mathscr{Z}^{\mathrm{T}} \mathbf{\Sigma}^2 \mathscr{Z} = \sum_{\alpha=1}^{N-1} \mathscr{Z}_{(\alpha)} \sigma_{(\alpha)}^2 \mathscr{Z}_{(\alpha)}. \tag{145}$$

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