JOURNAL OF THERMOPHYSICS AND HEAT TRANSFER
Vol. 14, No. 1, January–March 2000

Technical Comments

Brief discussion of previous investigations in the aerospace sciences and technical comments on papers published in the Journal of Thermophysics and Heat Transfer *are presented in this special department. Entries must be restricted to a maximum of 1000 words, or the equivalent of one* Journal *page including formulas and figures. A discussion will be published as quickly as possible after receipt of the manuscript. Neither the AIAA nor its editors are responsible for the opinions expressed by the correspondents. Authors will be invited to reply promptly.*

Comment on "Different Levels of Modeling for Diffusion Phenomena in Neutral and Ionized Mixtures"

Alexandre Ern*
CERMICS, 77455 Marne la Vallée CEDEX 2, France
and
Vincent Giovangigli†
Centre National de la Recherche Scientifique, 91128 Palaiseau CEDEX, France

IN a recent paper[1] Desmeuzes et al. have considered different models of diffusion processes in neutral and ionized gas mixtures. For diffusion phenomena caused by concentration gradients, they investigated four approaches: Fick's law, a variant called Blottner's approximation with species-dependent diffusion coefficients, Kendal's approximation in which an approximate expression for the system matrix arising in the Stefan–Maxwell–Boltzmann equations is considered, and finally, a direct solve of the Stefan–Maxwell–Boltzmann equations. On the other hand the authors only considered an empirical approximation to evaluate the thermal diffusion coefficients of the mixture and stated in their conclusions that it was necessary to find an accurate and cost-effective expression for their evaluation.

It appears, however, that the authors are not aware of some new results concerning mutlicomponent transport algorithms. These results have been published recently in a book and a series of papers[2–7] and have been developed mainly in the context of reactive flow modeling. However, these results apply to a wide range of applications, including those considered in Ref. 1. In this Comment we briefly summarize the relevant state-of-the-art models for describing multicomponent diffusion. Mathematical, numerical, and physical aspects of the problem are addressed. We then comment on the algorithms used in Ref. 1 to model multicomponent mass diffusion, and in response to the authors' conclusion we also describe accurate and cost-effective approximations for the thermal diffusion coefficients.

The equations governing multicomponent dilute isotropic gas mixtures are derived from the kinetic theory of gases using a generalized Boltzmann equation and the Enskog expansion.[2,6] In particular, the species mass conservation equations read

$$\partial_t(\rho Y_i) + \nabla\cdot(\rho v Y_i) = -\nabla\cdot(\rho Y_i V_i) + \omega_i, \qquad i \in [1,n] \tag{1}$$

where ∂_t and ∇ are the time and space derivative operators, ρ the density, Y_i the mass fraction of the ith species, v the hydrodynamic velocity, V_i the diffusion velocity of the ith species, ω_i its mass production rate, and n the number of species. The species diffusion velocities read

$$V_i = -\sum_{j\in[1,n]} D_{ij}(d_j + \chi_j \nabla \log T), \qquad i \in [1,n] \tag{2}$$

where $D = (D_{ij})_{i,j\in[1,n]}$ is the diffusion matrix, d_j the diffusion driving force for the jth species, and $\chi = (\chi_i)_{i\in[1,n]}$ the thermal diffusion ratios. The diffusion driving forces are given by

$$d_i = \nabla X_i + (X_i - Y_i)\nabla p + \frac{\rho}{p}\sum_{j\in[1,n]} Y_i Y_j (b_j - b_i) \qquad i \in [1,n] \tag{3}$$

where X_i is the mole fraction of the ith species, p the pressure, and b_i the external force acting on the ith species. The thermal diffusion ratios and the diffusion driving forces sum up to zero, i.e.,

$$\sum_{i\in[1,n]} \chi_i = \sum_{i\in[1,n]} d_i = 0$$

On the other hand, the matrix D satisfies the mass conservation relations

$$\sum_{i\in[1,n]} Y_i D_{ij} = 0$$

implying that

$$\sum_{i\in[1,n]} Y_i V_i = 0$$

Moreover, the diffusion matrix is symmetric positive semidefinite and is positive definite on the physical hyperplane of zero sum gradients. These latter properties are closely associated with the entropy production.[2]

An alternate definition of the species diffusion velocities, as considered in Ref. 1, involves the thermal diffusion coefficients $\theta = (\theta_i)_{i\in[1,n]}$ such that $\theta = D\chi$. From a computational viewpoint this approach is not so attractive because, as stated next, the thermal diffusion ratios are easier to evaluate than the thermal diffusion coefficients.[3] Note also that the diffusion matrix considered here relates the mole fraction gradients to the species diffusion velocities. It is also possible, as in Blottner's approximation considered in Ref. 1, to use the mass fraction gradients in the diffusion driving forces and modify the diffusion matrix accordingly. However, this new matrix is not naturally associated with the kinetic theory framework and is no longer symmetric positive semidefinite. These structure properties are not only of fundamental importance but are also very useful for a cost-effective evaluation of the matrix D.[4,5]

The diffusion matrix and the thermal diffusion ratios are not given explicitly by the kinetic theory, but from the solution of linear systems. The corresponding system matrices depend on the choice made for polynomial expansions used to solve approximately the Boltzmann equations. For the diffusion matrix the simplest approach yields the system matrix Δ of size n given by

$$\Delta_{ij} = -\frac{X_i X_j}{\mathcal{D}_{ij}}, \qquad i \neq j, \qquad \Delta_{ii} = \sum_{j\neq i} \frac{X_i X_j}{\mathcal{D}_{ij}}, \qquad i \in [1,n] \tag{4}$$

where $\mathcal{D}_{ij}$ are the species binary diffusion coefficients. The matrix Δ is symmetric positive semidefinite, and introducing the vectors

Received 23 March 1998; accepted for publication 2 August 1999.

*Research Scientist and Applied Mathematics Professor, Ecole Nationale des Ponts et Chaussées, 6 et 8 av. Blaise Pascal.

†Senior Research Scientist, Centre de Mathématiques Appliquées, Ecole Polytechnique.

$U = (1)_{i \in [1,n]}$ and $Y = (Y_i)_{i \in [1,n]}$, the matrix $\Delta + Y \otimes Y$ is symmetric positive definite and we have

$$D + U \otimes U = (\Delta + Y \otimes Y)^{-1} \tag{5}$$

Note that considering the matrix $D + U \otimes U$ instead of just D in the species conservation equations may suppress artificial singularities in discretized equations.[8,9] Equivalently, it is also possible to consider the Stefan–Maxwell–Boltzmann equations providing the species diffusion velocities

$$\sum_{j \in [1,n]} \Delta_{ij} V_j = -(d_i + \chi_i \nabla \log T), \qquad i \in [1, n] \tag{6}$$

Considering the symmetric positive definite matrix $\Delta + Y \otimes Y$ for a direct numerical inversion instead of the nonsymmetric matrix used in Ref. 1 is computationally more efficient because the Choleski algorithm can then be used at approximately half the computational cost of a standard LU decomposition. Note also that the Cramer expressions considered in Ref. 1 are much more expensive, even for a modest number of species.

On the other hand, the evaluation of the thermal diffusion ratios requires the solution of a symmetric positive definite linear system. The standard approach consists in considering polynomial expansions in both the translational and internal energy of the molecules and yields a system matrix of size $2n$. A new approach developed by the authors[3] uses polynomial expansions in the total energy of the molecules and yields a system matrix of size n. The linear system is detailed in Ref. 3. The resulting thermal diffusion ratios are within a few percent accuracy of those obtained with the standard method. The same approach can also be applied to the thermal diffusion coefficients. The standard and new linear system involve, respectively, a symmetric positive semidefinite matrix of size $3n$ and $2n$ and are thus larger than those associated with the thermal diffusion ratios.

Based on a tradeoff between costs and accuracy, several strategies may be considered for evaluating the diffusion matrix and the thermal diffusion ratios. For the diffusion matrix the simplest approximation is to represent the diffusion driving forces by the mass fraction gradients and to assume that the diffusion matrix is diagonal. It is shown in Ref. 8 that this simplification is possible if and only if all of the binary diffusion coefficients $\mathcal{D}_{ij}$, for $i, j \in [1, n]$ and $i \neq j$, are equal. In this situation we have $Y_i V_i = -\mathcal{D}(\nabla Y_i + \chi_i \nabla \log T)$ for $i \in [1, n]$, where $\mathcal{D}$ denotes the common value of the quantities $\mathcal{D}_{ij}$. A similar result is also given in Ref. 8 for mole fraction gradients. If species-dependent diffusion coefficients are to be retained, as in Blottner's approximation, it is necessary to add a mass correction velocity.

A theory for multicomponent transport algorithms has been derived recently.[2] First, the mathematical structure of the transport linear systems has been obtained under very general assumptions.[6] In particular, it was proven that all of the transport coefficients can be expanded as convergent series.[4,5] Accurate approximate expressions are then obtained by truncation. For the diffusion matrix we consider a splitting of the form $\Delta = M - Z$ and set $T = M^{-1} Z$. The matrix M is chosen to be symmetric positive definite such that $M + Z$ has the same properties. A projected iterative scheme is introduced in such a way that each iterate satisfies all of the physical constraints.[7] We introduce the projector matrix

$$P = P_{Y^{\perp}, U} = I - \frac{U \otimes Y}{\Sigma_{\, i \in [1,n]} Y_i}$$

where I is the identity matrix, and we point out that the spectral radius of T is $\rho(T) = 1$ while $\rho(PT) < 1$. We then have

$$D = \sum_{k=0}^{\infty} (PT)^k P M^{-1} P^t$$

and the partial sums

$$D^{[l]} = \sum_{k=0}^{l} (PT)^k P M^{-1} P^t, \qquad l \geq 0 \tag{7}$$

are symmetric, satisfy the mass conservation constraint, yield a positive entropy production, and converge toward D as $l \to \infty$. The associated diffusion velocities read

$$V_i^{[l]} = -\sum_{k=0}^{l} (PT)^k P M^{-1} P^t (d_i + \chi_i \nabla \log T), \qquad i \in [1, n] \tag{8}$$

A particularly interesting choice for the matrix M is to take it diagonal with its elements found by substituting the approximation $D \simeq M^{-1}$ in the exact relation $D\Delta = P$ and identifying the diagonal terms, yielding

$$M_{ii} = \frac{X_i}{D_i^m}, \qquad D_i^m = \frac{\Sigma_{\, j \neq i} Y_j}{\Sigma_{\, j \neq i} (X_j / \mathcal{D}_{ij})} \tag{9}$$

The diffusion velocities associated with the matrix $D^{[0]}$ read $V_i^{[0]} = -D_i^m (\nabla X_i + \chi_i \nabla \log T) + V_c$, where V_c ensures mass conservation and correspond to the well-known Hirschfelder–Curtiss approximated diffusion velocities with a mass correction velocity.[10] As a result, this well-known approximation has a rigorous justification, and the mass correction velocity is obtained here as a direct consequence of the projector matrix P. The next term in the series (7) and (8), namely $D^{[1]}$ and $V^{[1]}$, has been introduced recently.[2,8] From a computational viewpoint the costs of evaluating the diffusion velocities associated with $D^{[0]}$ or $D^{[1]}$ both scale as a multiple of n^2 operations, whereas the costs of the next iterates scale as n^3 iterations. The accuracy of the diffusion matrix $D^{[1]}$ has been tested on several flame problems. This matrix is thus a highly attractive alternative to both $D^{[0]}$ and a direct numerical inversion.[4,5] It is more interesting than Kendal's approximation considered in Ref. 1 because no assumptions on molecular parameters are needed.

The most efficient strategy for evaluating the thermal diffusion ratios is to consider three conjugate gradient iterations for the reduced linear system.[4,5] The resulting approximation for the thermal diffusion ratios is accurate to within a few percent of the actual solution and is computationally much more cost effective than a direct numerical solve. Speedups of more than an order of magnitude have been observed for various flame problems.[5] This result answers a point raised in the conclusions in Ref. 1 regarding the need for accurate and cost-effective approximations for evaluating the thermal diffusion ratios.

To summarize, it is now possible to use accurate and cost-effective approximations in order to model both mass and thermal diffusion processes in dilute gas mixtures. A general-purpose library implementing the preceding algorithms and optimized for both serial and vector architectures is available (Ern, A., and Giovangigli, V., EGlib server and user's manual, http://www.cmap.polytechnique.fr/www.eglib/, 1996).

References

[1] Desmeuzes, C., Duffa, G., and Dubroca, B., "Different Levels of Modeling for Diffusion Phenomena in Neutral and Ionized Gas Mixtures," *Journal of Thermophysics and Heat Transfer*, Vol. 11, No. 1, 1996, pp. 36–44.

[2] Ern, A., and Giovangigli, V., *Multicomponent Transport Algorithms*, Vol. m24, Lecture Notes in Physics, Springer–Verlag, Heidelberg, Germany, 1994.

[3] Ern, A., and Giovangigli, V., "Thermal Conduction and Thermal Diffusion in Dilute Polyatomic Gas Mixtures," *Physica A*, Vol. 214, 1995, pp. 526–546.

[4] Ern, A., and Giovangigli, V., "Fast and Accurate Multicomponent Transport Property Evaluation," *Journal of Computational Physics*, Vol. 120, 1995, pp. 105–116.

[5] Ern, A., and Giovangigli, V., "Optimized Transport Algorithms for Flame Codes," *Combustion Science and Technology*, Vol. 118, 1996, pp. 387–395.

[6] Ern, A., and Giovangigli, V., "The Structure of Transport Linear Systems in Dilute Isotropic Gas Mixtures," *Physical Review E*, Vol. 53, No. 1, 1996, pp. 485–492.

[7] Ern, A., and Giovangigli, V., "Projected Iterative Algorithms with Application to Multicomponent Transport," *Linear Algebra Applications*, Vol. 250, 1997, pp. 289–315.

[8] Giovangigli, V., "Convergent Iterative Methods for Multicomponent Diffusion," *Impact of Computing in Science and Engineering*, Vol. 3, 1991, pp. 244–276.

[9] Giovangigli, V., "Mass Conservation and Singular Multicomponent Diffusion Algorithms," *Impact of Computing in Science and Engineering*, Vol. 2, 1990, pp. 73–97.

[10] Hirschfelder, J. O., and Curtiss, C. F., "Flame Propagation in Explosive Gas Mixtures," *Third Symposium (International) on Combustion*, Reinhold, New York, 1949, pp. 121–127.