

Multicomponent diffusion revisited

S. H. Lam^{a)}

Department of Mechanical and Aerospace Engineering, Princeton University, Princeton, New Jersey 08544

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The derivation of the multicomponent diffusion law is revisited. Following Furry [Am. J. Phys. **16**, 63 (1948)], Williams [Am. J. Phys. **26**, 467 (1958); *Combustion Theory*, 2nd ed. (Benjamin/Cummings, Menlo Park, CA, 1985)] heuristically rederived the classical kinetic theory results using macroscopic equations, and pointed out that the dynamics of the mixture fluid had been assumed inviscid. This paper generalizes the derivation, shows that the inviscid assumption can easily be relaxed to add a new term to the classical diffusion law, and the thermal diffusion term can also be easily recovered. The nonuniqueness of the multicomponent diffusion coefficient matrix is emphasized and discussed. © 2006 American Institute of Physics. [DOI: 10.1063/1.2221312]

I. CLASSICAL KINETIC THEORY RESULTS

The classical multicomponent diffusion law for a mixture of N perfect gases is usually derived using rigorous asymptotics, starting from the Boltzmann's equation of kinetic theory:¹⁻⁴

$$\mathbf{j}_i^* \equiv \frac{\mathbf{j}_i}{\rho Y_i} = - \left(\sum_{j=1}^N D_{ij} \mathbf{d}_j + D_i^{(T)} \nabla (\ln T) \right) [1 + O(\epsilon)], \quad (1a)$$

$$\mathbf{d}_i \equiv \nabla X_i + (X_i - Y_i) \nabla (\ln p) + \mathbf{g}_i, \quad (1b)$$

$$\mathbf{g}_i \equiv \frac{\rho}{p} \left(Y_i \sum_{j'=1}^N Y_{j'} (\mathbf{f}_{j'} - \mathbf{f}_i) \right), \quad (1c)$$

$$i = 1, \dots, N,$$

where ϵ is the ratio of characteristic (intra- and interspecies) collision time to characteristic fluid mechanics time, D_{ij} is the $N \times N$ multicomponent (kinematic) diffusion coefficient matrix, $D_i^{(T)}$ is the (kinematic) thermal diffusion coefficient,⁵ and \mathbf{f}_i is the body force per unit mass acting on the i species, \mathbf{v}_i^* is the mass-averaged diffusion velocity of the i species, and

$$\mathbf{j}_i^* \equiv \rho_i \mathbf{v}_i^* = \text{diffusion mass flux of } i \text{ species}, \quad (2a)$$

$$X_i \equiv \frac{p_i}{p} = \text{partial pressure fraction of } i \text{ species}, \quad (2b)$$

$$Y_i \equiv \frac{\rho_i}{\rho} = \text{mass fraction of } i \text{ species}, \quad (2c)$$

$$p = \sum_{i=1}^N p_i = \text{total mixture pressure}, \quad (2d)$$

$$\rho = \sum_{i=1}^N \rho_i = \text{total mixture density}, \quad (2e)$$

$$\sum_{i=1}^N X_i = 1 \quad \sum_{i=1}^N Y_i = 1. \quad (2f)$$

All species are assumed to have the same temperature T . The summation convention is *not* used in this paper.

Following Furry,⁶ Williams^{7,8} heuristically rederived the above kinetic theory results [i.e., Eqs. (1a) and (1b), except for the thermal diffusion term] starting from the macroscopic conservation equations of all the species. Furry considered a fluid at rest and Williams considered a fluid in motion. Williams made the assumption that the dynamics of all the species—and therefore also the mixture fluid—were inviscid. The questions being addressed here are as follows: What happens to Eq. (1a) and Eq. (1b) when the dynamics of the mixture fluid is known to be viscous? What about the uniqueness of D_{ij} ? These issues shall be addressed here from the macroscopic point of view—without direct dealings with the Boltzmann equation. In addition, thermal diffusion will be included in the present derivation for completeness.

A. Some important properties

The \mathbf{d}_j 's in Eq. (1a) and Eq. (1b) are dimensional and have the physical dimension of reciprocal length. It can readily be verified [using its definition, Eq. (1b), and the help of Eq. (2f)] that they satisfy

$$\sum_{j=1}^N e_j \mathbf{d}_j = 0, \quad e_j \equiv [1, 1, \dots, 1], \quad (3)$$

always—i.e., the \mathbf{d}_j 's are not linearly independent. Hence, given any valid matrix D_{ij} , Eq. (3) guarantees that $D_{ij} + c_i e_j$ is an equally valid matrix also—where the c_i 's are N arbitrary numbers. More on the uniqueness of D_{ij} later.

The diffusion velocities \mathbf{v}_i^* 's are also not linearly independent. They must satisfy the *zero-net-flux condition*:

$$\sum_{i=1}^N \mathbf{j}_i^* = \sum_{i=1}^N \rho_i \mathbf{v}_i^* = 0. \quad (4)$$

Using Eq. (1a) for \mathbf{v}_i^* , this condition can be rewritten as follows:

^{a)}Professor emeritus. Electronic mail: lam@princeton.edu

$$\sum_{j=1}^N \eta_j \mathbf{d}_j = 0, \quad \eta_j \equiv \sum_{i=1}^N \rho_i D_{ij}; \quad (5a)$$

$$\sum_{j=1}^N \rho_i D_i^{(T)} = 0. \quad (5b)$$

Hence, a required property of D_{ij} is that its η_j must satisfy Eq. (5a), and a required property of $D_i^{(T)}$ is that it must satisfy Eq. (5b). Note that Eq. (5a) can be satisfied by either (i) $\eta_j \propto e_j$ —by taking advantage of Eq. (3)—or (ii) $\eta_j=0$. It is emphasized here that option (ii) is a special case of option (i). In other words, $\eta_j=0$ is only a sufficient but *not* a necessary condition to satisfy Eq. (5a). Note also that a diagonal D_{ij} does not satisfy Eq. (5a) unless all $\rho_i D_{ii}$'s are equal.

B. An identity involving \mathbf{d}_i

Replacing X_i by p_i/p in Eq. (1b), one can manipulate it to arrive at the following exact mathematical identity involving \mathbf{d}_i :

$$\mathbf{d}_i = -\frac{1}{p} \{ \mathbf{F}_i - Y_i \mathbf{F} \}, \quad (5c)$$

where

$$\mathbf{F}_i \equiv -\nabla p_i + \rho_i \mathbf{f}_i, \quad (5d)$$

$$\mathbf{F} \equiv \sum_{i'=1}^N \mathbf{F}_{i'} = -\nabla p + \rho \mathbf{f}, \quad (5e)$$

$$\mathbf{f} \equiv \frac{1}{\rho} \sum_{i'=1}^N \rho_{i'} \mathbf{f}_{i'}. \quad (5f)$$

The physical dimensions of both \mathbf{F}_i and \mathbf{F} are the force per unit volume. They are readily recognized as the net external force per unit volume acting on the i species and the fluid mixture, respectively—excluding all *interspecies* collisional momentum exchanges.

II. THE FURRY-WILLIAMS APPROACH

The Furry-Williams approach⁶⁻⁸ proceeds by using species-specific macroscopic conservation laws, leaving kinetic theory concepts in the background—to be called upon only when numerical values of the interspecies collisional cross sections are needed. What follows is an extension and generalization of this approach.

A. The perfect gas assumption

In any kinetic theory formulation, the perfect gas assumption plays a crucial role. In the Furry-Williams approach, the perfect gas assumption is not crucial.

The partial pressure fraction X_i and mass fraction Y_i are dimensionless and they are related by their respective equations of state. When all the species are perfect gases, X_i and Y_i are related by

$$X_i = \frac{Y_i \mathcal{M}_i}{\sum_{j'=1}^N (Y_{j'} \mathcal{M}_{j'})}, \quad Y_i = \frac{X_i \mathcal{M}_i}{\sum_{j'=1}^N (X_{j'} \mathcal{M}_{j'})}$$

where the \mathcal{M}_i 's are the molecular weights of the i species. Thus $X_i - Y_i > 0$ if the i species is a lighter species relative to the others. If the mixture components are not perfect gases, then the associated X_i and Y_i relations are more complicated.

B. The macroscopic continuity equations

Let \mathbf{V}_i , n_i , and m_i denote the mass averaged velocity, the number density, and the molecular mass of the i species, respectively.

The species-specific macroscopic continuity equations can readily be written down from first principles:

$$\frac{\partial \rho_i}{\partial t} + \nabla \cdot (\rho_i \mathbf{V}_i) = W_i, \quad \rho_i = n_i m_i, \quad (6)$$

where W_i represents the net mass production rate (per unit volume) of the i species coming from chemical reactions. Since mass can either be created or destroyed by chemical reactions, the W_i 's always satisfy

$$\sum_{i'=1}^N W_{i'} = 0. \quad (7)$$

The diffusion velocity of the i species \mathbf{v}_i^* is defined by

$$\mathbf{v}_i^* \equiv \mathbf{V}_i - \mathbf{V}, \quad (8)$$

where the mass averaged velocity \mathbf{V} of the mixture fluid is given by

$$\mathbf{V} \equiv \frac{1}{\rho} \sum_{i'=1}^N \rho_{i'} \mathbf{V}_{i'} = \sum_{i'=1}^N Y_{i'} \mathbf{V}_{i'}. \quad (9)$$

In terms of \mathbf{V} and \mathbf{v}_i^* , Eq. (6) becomes

$$\frac{\partial \rho_i}{\partial t} + \nabla \cdot (\rho_i \mathbf{V}) + \nabla \cdot (\rho_i \mathbf{v}_i^*) = W_i. \quad (10)$$

By its definition, \mathbf{v}_i^* (and thus \mathbf{j}_i^*) must satisfy the zero-net-flux condition, Eq. (4). The mixture macroscopic fluid continuity equation is obtained by summing Eq. (10) over all species and using Eq. (7) and Eq. (4):

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{V}) = 0. \quad (11)$$

In the classical approach, one would now go to Eq. (1a)—provided by kinetic theory—to eliminate $\rho_i \mathbf{v}_i^*$ in Eq. (10) to obtain the convective-diffusive governing partial differential equations for the ρ_i 's (or the X_i 's, or Y_i 's). The present derivation goes instead to the species-specific macroscopic momentum equations to “derive” Eq. (1a).

C. The macroscopic momentum equations

The macroscopic momentum equation for the i species can be written from first principles as follows:

$$\frac{\partial(\rho_i \mathbf{V}_i)}{\partial t} + \nabla \cdot (\rho_i \mathbf{V}_i \mathbf{V}_i) = \mathbf{F}_i + \mathbf{G}_i. \quad (12)$$

The left hand side contains familiar conventional terms. On the right hand side, the first term \mathbf{F}_i [defined by Eq. (5d)] represents the net external force per unit volume acting on the i species (*excluding* all momentum exchanges by interspecies collisions), and the last term \mathbf{G}_i represents *only* interspecies collisional momentum exchanges per unit time per unit volume between the i species and all other species (both elastic and inelastic, *including* the momenta being brought in and removed via chemical reactions). Instead of limiting the term $\rho_i \mathbf{f}_i$ in \mathbf{F}_i to represent only body forces,^{6–8} it is now used to represent “all other complications” not so far included, such as the viscous force per unit volume.⁹ In other words, $\rho_i \mathbf{f}_i$ is now a “catch-all” term that simply tags along, to be exploited later.

Expanding the left hand side of Eq. (12) and using Eq. (6), one obtains¹⁰

$$\rho_i \frac{D_i \mathbf{V}_i}{Dt} = \mathbf{F}_i + \mathbf{G}_i^{\text{coll}}, \quad (13)$$

where D_i/Dt denotes the substantial derivative of the i species:

$$\frac{D_i}{Dt} \equiv \frac{\partial}{\partial t} + \mathbf{V}_i \cdot \nabla \quad (14)$$

and $\mathbf{G}_i^{\text{coll}}$ now represents the net impacts of *all* interspecies collisional momentum exchanges:

$$\mathbf{G}_i^{\text{coll}} \equiv \mathbf{G}_i - W_i \mathbf{V}_i. \quad (15)$$

Note that $\mathbf{G}_i^{\text{coll}}$ includes a contribution from the left hand side of Eq. (12) via Eq. (6). This new term cancels an identical term inside \mathbf{G}_i so that \mathbf{G}^{coll} is now properly Galilean invariant. Since interspecies collisions conserve total momentum, the sum of $\mathbf{G}_i^{\text{coll}}$ over all species must be identically zero:

$$\sum_{i'=1}^N \mathbf{G}_{i'}^{\text{coll}} = 0. \quad (16)$$

Summing Eq. (13) over all species, one obtains the exact macroscopic momentum equation of the mixture fluid:

$$\sum_{i'=1}^N \left(\rho_{i'} \frac{D_{i'} \mathbf{V}_{i'}}{Dt} \right) = \mathbf{F}. \quad (17)$$

The $\rho \mathbf{f}$ inside \mathbf{F} [see Eq. (5e)] is the *net catch-all force per unit volume* acting on the mixture fluid. It is duly noted that the left hand side is not yet in its familiar form.

1. The interspecies collisional term $\mathbf{G}_i^{\text{coll}}$

Intuitively, $\mathbf{G}_i^{\text{coll}}$ should be zero if all the \mathbf{V}_i 's are the same. Thus, it is heuristically reasonable to expect $\mathbf{G}_i^{\text{coll}}$ to be some linear combination of the \mathbf{v}_i^* 's—any missing term can be accounted for later by the catch-all term $\rho_i \mathbf{f}_i$. Using insights from elementary kinetic theory (and assuming that only binary collisions need to be considered), one can express $\mathbf{G}_i^{\text{coll}}$ in the Stefan-Maxwell form^{7,8} using only macroscopic variables:

$$\mathbf{G}_i^{\text{coll}} = \sum_{j=1}^N \bar{m}_{ij} \nu_{ij} (\mathbf{V}_j - \mathbf{V}_i) = \sum_{j=1}^N \bar{m}_{ij} \nu_{ij} (\mathbf{v}_j^* - \mathbf{v}_i^*), \quad (18)$$

where $\bar{m}_{ij} = m_i m_j / (m_i + m_j)$ is the “reduced mass” and ν_{ij} is the collision frequency (per unit volume) of collisions between i and j molecules. All elements of these two symmetric matrices are positive numbers. Kinetic theory calculations on the detailed dynamics of the elastic and inelastic (e.g., chemically active) interspecies collisions are needed to generate numerical values for ν_{ij} .¹¹

It is convenient to rewrite Eq. (18) as follows:

$$\mathbf{G}_i^{\text{coll}} = - \sum_{j=1}^N K_{ij} \mathbf{v}_j^*, \quad (19)$$

where K_{ij} is defined by

$$K_{ij} \equiv \delta_{ij} \sum_{j'=1}^N \bar{m}_{ij'} \nu_{ij'} - \bar{m}_{ij} \nu_{ij}, \quad (20)$$

and δ_{ij} is the Kronecker delta. Note that K_{ij} is always symmetric, and it always automatically satisfies

$$\sum_{i=1}^N K_{ij} = 0, \quad (21)$$

Eq. (21) says K_{ij} is a singular matrix—which is a direct consequence of Eq. (16). The rank of K_{ij} is assumed to be $N-1$.

2. The nonsingular matrix \hat{K}_{ij}

Equation (13) can now be rewritten as follows:

$$\rho_i \frac{D_i \mathbf{V}_i}{Dt} = \mathbf{F}_i - \sum_{j=1}^N K_{ij} \mathbf{v}_j^*. \quad (22)$$

If K_{ij} were not a singular matrix, one could immediately use its inverse to solve for \mathbf{v}_i^* directly from Eq. (22). Since K_{ij} is definitely singular, this is not possible. Moreover, one must also make sure that the \mathbf{v}_i^* 's always honor Eq. (4), the zero-net-flux condition.

There are many ways to proceed. For example, one could select one judiciously chosen component of Eq. (22) and replace it by Eq. (4) such that the resulting $N \times N$ matrix operating on \mathbf{v}_i^* is now nonsingular. To highlight the fact that the formal result is nonunique, the present paper proceeds by introducing \hat{K}_{ij} , which is defined by

$$\hat{K}_{ij} \equiv K_{ij} + \omega_i \rho_j, \quad i, j = 1, \dots, N, \quad (23)$$

where the ω_i 's are N arbitrary numbers (with a physical dimension of reciprocal time) that satisfy

$$\sum_{i=1}^N \omega_i \neq 0. \quad (24)$$

Note that \hat{K}_{ij} is, in general, nonsymmetric unless one chooses $\omega_i = b \rho_i$, where b is independent of i .¹²

Unlike the original singular K_{ij} , this new (nonunique) \hat{K}_{ij} —which respects Eq. (24)—is no longer singular:

$$\sum_{i=1}^N \hat{K}_{ij} = \left(\sum_{i=1}^N \omega_i \right) \rho_j \neq 0. \quad (25)$$

The singular K_{ij} in Eq. (19) [and Eq. (22)] can now be replaced by the nonsingular (nonunique and most probably nonsymmetric) \hat{K}_{ij} —while honoring Eq. (4) at the same time:

$$\mathbf{G}_i^{\text{coll}} = - \sum_{j=1}^N \hat{K}_{ij} \mathbf{v}_j^*. \quad (26)$$

The inverse of \hat{K}_{ij} now exists, and can be applied to both sides of the new equation (22) to obtain

$$\mathbf{v}_i^* = \sum_{j=1}^N [\hat{K}]_{ij}^{-1} \left(\mathbf{F}_j - \rho_j \frac{D_j \mathbf{V}_j}{Dt} \right). \quad (27a)$$

Using Eq. (5c) to eliminate \mathbf{F}_j , one obtains

$$\mathbf{v}_i^* = - \rho \sum_{j=1}^N [\hat{K}]_{ij}^{-1} \left(\mathbf{d}_j - \frac{Y_j}{\rho} \left\{ \mathbf{F} - \rho \frac{D_j \mathbf{V}_j}{Dt} \right\} \right). \quad (27b)$$

Formally, Eq. (27a) and Eq. (27b) are both an *exact* alternative representation of Eq. (12), the original species-specific macroscopic momentum equations. No approximation had been used, and Eq. (27a) and Eq. (27b) are valid for whatever one may have chosen for the catch-all term $\rho_i \mathbf{f}_i$ —while honoring Eq. (4) always. Both are not yet the final diffusion law—because $D_j \mathbf{V}_j / Dt$ on their right hand sides depends on \mathbf{v}_j^* . The perfect gas law made no appearance.

3. The species-specific accelerations

It is easy to be convinced that $\hat{K}_{ij} = O(1/\epsilon)$, or $[\hat{K}]_{ij}^{-1} = O(\epsilon)$. Since $\mathbf{G}_i^{\text{coll}}$ must be $O(1)$ for asymptotically small ϵ , Eq. (19) says the leading approximation for \mathbf{v}_i^* in the small ϵ limit must be

$$\mathbf{v}_i^* = O(\epsilon). \quad (28)$$

In other words, to leading order all species move with the same \mathbf{V} , the mass-averaged velocity of the mixture fluid. Hence, to leading order the species-specific acceleration can be approximated by the acceleration of the mixture fluid:

$$\frac{D_i \mathbf{V}_i}{Dt} = \frac{D\mathbf{V}}{Dt} + \left(\frac{D\mathbf{v}_i^*}{Dt} + \mathbf{v}_i^* \cdot \nabla (\mathbf{V} + \mathbf{v}_i^*) \right), \quad (29a)$$

$$= \frac{D\mathbf{V}}{Dt} [1 + O(\epsilon)]. \quad (29b)$$

Using Eq. (29b) in Eq. (17), one obtains the familiar macroscopic momentum equation for the total mixture fluid:

$$\rho \frac{D\mathbf{V}}{Dt} = \mathbf{F} [1 + O(\epsilon)]. \quad (30)$$

III. MACROSCOPIC DERIVATION RESULTS

So far, only macroscopic conservation laws have been involved.

The macroscopic derivation began by replacing the singular K_{ij} in the macroscopic momentum equations with the nonsingular but nonunique \hat{K}_{ij} , and using its inverse. Using Eq. (29b) and Eq. (30) in Eq. (27b), one obtains the leading approximation for \mathbf{v}_i^* :

$$\mathbf{v}_i^* = - \sum_{j=1}^N D_{ij} \mathbf{d}_j [1 + O(\epsilon)], \quad (31a)$$

where

$$D_{ij} = \rho [\hat{K}]_{ij}^{-1} + c_i e_j, \quad (31b)$$

and the additive modifications (with arbitrary c_i 's) are allowed, as mentioned previously in Sec. I A. *The macroscopic derivation is done.* The diffusion coefficient matrix D_{ij} has been related to \hat{K}_{ij} —which depends on all $N(N-1)/2$ inter-species collisional parameters—by simple manipulations of the macroscopic conservation equations. It is clear that D_{ij} is nonunique. See Sec. III B later.

With the caveat that the thermal diffusion term is still missing, the above results are identical to Eq. (1a) and Eq. (1b)—when $\rho_i \mathbf{f}_i$ is limited to represent only the body force. By allowing it to be a catch-all force, the Furry-Williams results are easily generalized beyond inviscid flows. Note that the $O(\epsilon)$ error terms displayed in Eqs. (29b), (30), and (31a) all arose from approximating the species-specific accelerations by the mixture fluid acceleration. The effects of the neglected higher order terms—those in the curly brackets on the right hand side of Eq. (29a)—can be approximately accounted for by iteration using Eq. (31a) or Eq. (1a) as the first iterant to obtain a more accurate $D_i \mathbf{V}_i / Dt$ to be used in Eq. (27a) or Eq. (27b).

A. Thermal diffusion

Can the catch-all term $\rho_i \mathbf{f}_i$ recover the missing thermal diffusion term? Since thermal diffusion does not exert a net force per unit volume on the fluid mixture, the needed catch-all $\rho_i \mathbf{f}_i$'s must honor

$$\rho \mathbf{f} = \sum_{i=1}^N \rho_i \mathbf{f}_i = 0. \quad (32)$$

Comparing Eq. (1a) with Eq. (31a) and using $\rho_i \mathbf{f}_i$'s that honor Eq. (32) to represent the thermal diffusion term, one obtains

$$D_i^{(T)} \nabla (\ln T) = - \sum_{j=1}^N [\hat{K}]_{ij}^{-1} \rho_j \mathbf{f}_j. \quad (33)$$

Solving for $\rho_i \mathbf{f}_i$ and using \hat{K}_{ij} from Eq. (23) on both sides, one obtains

$$\rho_i \mathbf{f}_i = - \nabla (\ln T) \sum_{j=1}^N (K_{ij} + \omega_i \rho_j) D_j^{(T)}. \quad (34)$$

Since $\rho_i D_i^{(T)}$ honors Eq. (5b),¹³ one obtains

$$\rho_i \mathbf{f}_i = -\nabla(\ln T) \sum_{j=1}^N K_{ij} D_j^{(T)}. \quad (35)$$

Hence, this catch-all term recovers the thermal diffusion term. Equation (32) is satisfied because K_{ij} honors Eq. (21).

Since the physical origin of the thermal diffusion term is interspecies collisional momentum exchanges, it is more satisfying to “derive” it by adding a physically meaningful term to $\mathbf{G}_i^{\text{coll}}$ in Eq. (26). This additional term is a vector. Heuristically, this vector is expected to be parallel to the temperature gradient. Hence a vector with this property is inserted into Eq. (26), yielding

$$\mathbf{G}_i^{\text{coll}} = -\sum_{j=1}^N \hat{K}_{ij} [\mathbf{v}_j^* + D_j^{(T)} \nabla(\ln T)], \quad (36a)$$

$$= \sum_{j=1}^N \bar{m}_{ij} \nu_{ij} [(\mathbf{v}_j^* - \mathbf{v}_i^*) + (D_j^{(T)} - D_i^{(T)}) \nabla(\ln T)]. \quad (36b)$$

The thermal diffusion term is thus heuristically “derived.”

A formula for $D_i^{(T)}$ that honors Eq. (5b) is

$$D_i^{(T)} = \tilde{D}_i^{(T)} - \sum_{j=1}^N Y_j \tilde{D}_j^{(T)}, \quad (37)$$

where the newly introduced scalar $\tilde{D}_i^{(T)}$ is heuristically expected to depend only on the properties of the i species. Note that the $D_i^{(T)}$'s in Eq. (36b) can be replaced by the $\tilde{D}_i^{(T)}$'s without other changes.

The physical dimension of $\tilde{D}_i^{(T)}$ is the velocity length. Heuristically, it should be the product of the random thermal velocity and a mean-free path associated with the i species. If $\tilde{D}_i^{(T)}$ is assumed positive, then Eq. (37) is consistent with the observations that heavier molecules are pushed in the direction opposite to ∇T .

B. Uniqueness of D_{ij}

The fact that D_{ij} is fundamentally nonunique is clearly documented in the literature.^{1-4,14-18} It is emphasized that for given spatial nonuniformities (i.e., the \mathbf{d}_i 's), the corresponding diffusion fluxes (i.e., \mathbf{j}_i^* 's) are always unique.¹⁹ Only the elements of the diffusion coefficient matrix D_{ij} are nonunique. It is unfortunate that this nonuniqueness is seldom given the emphasis it deserves. The following exposition is an attempt to shed light on this issue—using only macroscopic concepts.

Using only dimensional arguments along with heuristic reasonings, one can express ν_{ij} as follows:

$$\nu_{ij} = n_i n_j C_{ij} \sigma_{ij}, \quad (38)$$

where C_{ij} is a characteristic collisional velocity, σ_{ij} is a characteristic (momentum) cross section of i - j collisions, and both are positive entities. There are $N(N-1)/2$ physically meaningful (temperature dependent) σ_{ij} 's. Substituting Eq. (20) into Eq. (23) and using Eq. (38), one obtains

$$\hat{K}_{ij} = \delta_{ij} \frac{p \rho_i}{\rho} \sum_{j'=1}^N \frac{\rho_{j'}}{\mathcal{D}_{ij'}} + \rho_i \rho_j \Delta_{ij}, \quad (39a)$$

where

$$\Delta_{ij} \equiv \frac{\omega_i}{\rho_i} - \frac{p}{\rho \mathcal{D}_{ij}}, \quad (39b)$$

and \mathcal{D}_{ij} , commonly referred to as the *binary mass diffusion coefficient*, is shorthand notation for

$$\mathcal{D}_{ij} \equiv \left(\frac{m_i + m_j}{C_{ij} \sigma_{ij}} \right) \frac{p}{\rho}, \quad (39c)$$

which is a *symmetric* matrix that contains all the relevant binary interspecies collisional parameters. While D_{ij} is kinematic and has the physical dimension of velocity-length, \mathcal{D}_{ij} has the physical dimension of mass density-velocity-length. The diagonal elements \mathcal{D}_{ii} 's are called the *coefficients of self-diffusion*.² Most importantly, $\rho \mathcal{D}_{ij}/p$ depends only on the relevant binary collision parameters and not on the composition of the mixture.

The nonunique \hat{K}_{ij} depends on all the arbitrary ω_i 's [that must honor Eq. (24)]. The matrix D_{ij} is related to the inverse of \hat{K}_{ij} and allows additional nonunique modifications, as indicated by Eq. (31b). The arbitrariness may be freely exploited. Aside from the option of setting $D_{ii}=0$ chosen by Ref. 2, p. 477, another option is to set one column of D_{ij} to zero—preferably the column pointing to the most uninteresting major species in the mixture. Another popular option is to choose $\omega_i = b \rho_i$ so that Δ_{ij} (and therefore \hat{K}_{ij}) is symmetric,^{4,14-17} and to impose the optional condition $\eta_i = 0$ at the same time. The various nonunique D_{ij} 's so determined are exact, usually nondiagonal, but *they are all correct*.

Ferziger and Kaper made the following comments on the nonuniqueness of D_{ij} (Ref. 4, pp. 175–176): “...there is considerable variation among authors in the... definition of the multicomponent diffusion... coefficients.” It should be clear from the present derivation that the nonunique D_{ij} has no fundamental obligation to be symmetric (Ref. 1; see its Sec. 11.2d), and η_j has no fundamental obligation to be zero. The Appendix shows a collection of valid D_{ij} 's for the binary case.

The often adopted diagonal D_{ij} is an approximation that can be justified (for $N \geq 3$) under at least two scenarios. The first is the trace gas scenario in which the concentrations of all the interesting diffusing species are negligibly low in comparison to their dominant collision partner whose diffusion is of no interest. The second is when \mathcal{D}_{ij} has very weak dependence on i and j so that $\mathcal{D}_{ij} \approx \text{constant}$ is an acceptable approximation. Both allow $\rho_i \rho_j \Delta_{ij}$ to be neglected by choosing the appropriate ω_i 's. Corrections to such leading approximations can easily be obtained by iterations.¹⁹ The η_j 's for diagonal D_{ij} 's are obviously nonzero.

C. Diffusion in viscous flows

For a Newtonian fluid in low speed flows, Eq. (30) is the Navier-Stokes momentum equation for the mixture fluid. Hence, the catch-all term $\rho \mathbf{f}$ for incompressible viscous flows of a mixture fluid must be

$$\rho \mathbf{f} = \nabla \cdot (\mu \nabla \mathbf{V}), \quad (40)$$

where μ is the mixture fluid viscosity and is expected to be a function of the composition of the mixture. When this term is not negligible, the flow is said to be viscous. Hence, for multicomponent viscous flow problems, the $\rho_i \mathbf{f}_i$'s must contain viscous terms—because they must sum up to $\nabla \cdot (\mu \nabla \mathbf{V})$. These nonzero $\rho_i \mathbf{f}_i$'s should contribute to the diffusion flux \mathbf{j}_i^* of the i species. Heuristically, the simplest model is

$$\rho_i \mathbf{f}_i = \nabla \cdot (\mu_i \nabla \mathbf{V}), \quad (41)$$

where μ_i is the viscosity of the i species in this particular mixture—it is *not* the viscosity of a pure i species gas. Using Eq. (5f), one finds that the μ_i 's must be related to the mixture fluid viscosity μ by

$$\mu = \sum_{i=1}^N \mu_i. \quad (42)$$

Using Eq. (41) for $\rho_i \mathbf{f}_i$ in Eq. (1c), one obtains

$$\mathbf{g}_i = \frac{1}{p} [Y_i \nabla \cdot (\mu \nabla \mathbf{V}) - \nabla \cdot (\mu_i \nabla \mathbf{V})]. \quad (43)$$

This is the new term in the multicomponent diffusion law [using Eq. (41) as the model] contributed by the viscous term in the species-specific momentum equations and thus it should be kept whenever the dynamics of the mixture fluid is viscous.

The value of μ_i , the species-specific viscosity, must obey Eq. (42). A simple-minded guess for μ_i is

$$\mu_i = X_i \mu, \quad (44)$$

where the μ of the mixture fluid that itself is dependent on the detailed composition of the mixture. Using Eq. (44) in Eq. (43), one obtains

$$\mathbf{g}_i = \frac{1}{p} [(Y_i - X_i) \nabla \cdot (\mu \nabla \mathbf{V}) - \mu (\nabla X_i \cdot \nabla \mathbf{V})]. \quad (45)$$

To clear the air immediately, one notes that the new term is of no importance in (transverse) diffusion problems in boundary layers of large Reynolds number flows. This is because in such boundary layer problems the interesting component of the diffusion velocity \mathbf{v}_i^* vector is perpendicular to \mathbf{V} , while the new \mathbf{g}_i vector—according to Eq. (45)—is parallel to \mathbf{V} .

If the first term ∇X_i on the right hand side of Eq. (1b) is considered $O(1)$, then the second term $\nabla p/p$ is $O(M^2)$ (where M is the characteristic Mach number of the problem), and the third term \mathbf{g}_i is $O(\epsilon)$. Thus the new viscous term in \mathbf{d}_i is a higher order term from the vantage point of formal asymptotic analysis—when ϵ alone serves as the only small parameter. In other words, this term is properly neglected in

any “leading order” small ϵ expansions.^{7,8} However, the Reynolds number R_e of a problem is formally $O(M^2/\epsilon)$. Thus the order of magnitude of the $\nabla p/p$ term and the \mathbf{g}_i term are comparable for $R_e = O(1)$ problems. In order to be consistent, if one were kept, the other should also be kept.

In the classical kinetic theory approach, one formally needs to go beyond the Chapman-Enskog expansion results to deal with the impacts of the viscous term. In Sec. 15.42 of Chapman and Cowling,³ the next order terms—nine of them—were obtained and displayed. In the present macroscopic approach, the viscous \mathbf{g}_i term appears in the leading approximation via the catch-all term, and can be identified with the terms associated with ϵ_e , ϵ_f , ϵ_h , and ϵ_i in Ref. 3, Eq. (15.42,1). The five other higher order terms there can be identified with the correction terms generated in the present approach when the next approximation to the species-specific acceleration is used in Eq. (27a) or Eq. (27b).

D. Other body forces

It is well known that for any \mathbf{f}_i that is independent of i (such as gravity), the associated \mathbf{g}_i is identically zero. If some of the species are charged particles, the relevant $\rho_i \mathbf{f}_i$'s would be the Lorentz forces. The resulting diffusion laws provide the basis for the Ohm's Law for electrically conducting fluid mixtures.

E. Heat and mass diffusion couplings

If one were to write down all N species-specific macroscopic energy equations and allowed each component species to have their own temperature T_i , a similar analysis could only conclude that $T_i = T + O(\epsilon)$ in the continuum limit (except when there is large disparity in the molecular masses of the species—e.g., electrons and ions). No multicomponent heat conduction law would come out from this line of attack.

Let \mathbf{q} denote the conduction heat flux vector. For a single component medium, the Fourier Law of heat conduction is simply $\mathbf{q} = -\kappa \nabla T$, where κ is the heat conductivity coefficient. For a multicomponent fluid mixture, cross couplings between mass and heat diffusion are expected. The contribution to mass diffusion by temperature gradient is called the *Soret* effect (i.e., thermal diffusion), while contributions to heat flux by concentration gradients is called the *Dufour* effect. These two effects are (indirectly) related by the Onsager *Reciprocity Relation*, which is based on perceptive insights from statistical mechanics and thermodynamics.²⁰ See Coleman and Truesdell²¹ and Ball and James (Ref. 22, p. 13) for succinct commentaries on this topic.

IV. CONCLUDING REMARKS

In the Furry-Williams approach, the values of the momentum cross sections (σ_{ij}) and the thermal diffusion coefficients ($D_i^{(T)}$ or $\tilde{D}_i^{(T)}$) are left alone; they are to be separately handled by detailed calculations of some relevant kinetic theory (temperature-dependent) collision integrals. The derivation here reproduced Eq. (1a), and showed that it is actually the species-specific macroscopic momentum equation after the singular matrix K_{ij} has been rendered nonsingular

with the help of the zero-net-flux condition. The perfect gas assumption is not crucial (and was not used explicitly). The sophistication and complexity of the mathematics involved here are quite low—in comparison to the kinetic theory approach. A major shortcoming of the Furry-Williams approach is that it cannot satisfactorily handle—beyond the dimensional analysis level—transport terms that arise solely from intraspecies collisions (such as viscous stresses and heat conduction in a pure gas). Thus, the viscous term in the species-specific momentum equation had to be deferred to the catch-all term and needed much hand wavings.

Summarizing: the heuristic expression for \mathbf{G}^{coll} in Eq. (36b) is the heart of the Furry-Williams approach. Once it is adopted, the nonunique multicomponent diffusion matrix D_{ij} , which need not be symmetric, is straightforwardly obtained from the species-specific macroscopic momentum equations using any nonsingular \hat{K}_{ij} with the help of some nonunique ω_i 's. Additional nonunique modifications are allowed by Eq. (5a). The only needed approximation was the use of Eq. (29b) instead of Eq. (29a) for the species-specific acceleration term. The catch-all term $\rho_i \mathbf{f}_i$ stands ready to accommodate any additional omissions or oversights. Kinetic theory and the Boltzmann equation stay in the background.

In the continuum diffusion literature, the concepts of entropy, chemical potential, and the Gibbs-Duhem equation play a major role. It is interesting that in the Furry-Williams derivation, none of the above made an appearance. However, they can play a major role when the Dufour effect takes center stage.

Fortunately, the “new” viscous term in the diffusion law is not important in most boundary layer problems, as was explained previously. In theories of shock and detonation structures, the viscous term does play a significant role in the mixture fluid momentum equation. For such problems, the interesting diffusion velocity vector is in the general direction of \mathbf{V} . Hence, this new term could play a significant role in such problems. However, for such problems the continuum assumption itself is marginal, and it is not clear that this new term in the diffusion law is the most important issue to be dealt with.

APPENDIX: THE BINARY MIXTURE CASE

For the binary mixture case, one has

$$X_1 + X_2 = 1, \quad Y_1 + Y_2 = 1, \quad \mathbf{d}_1 + \mathbf{d}_2 = 0, \quad (\text{A1a})$$

$$\bar{m}_{12} \nu_{12} = \bar{m}_{21} \nu_{21} = \rho_1 \rho_2 \frac{p}{\rho D_{12}}, \quad (\text{A1b})$$

$$D_{12} \equiv \frac{p}{\rho} \frac{m_1 + m_2}{C_{12} \sigma_{12}} = D_{21}, \quad (\text{A1c})$$

$$\mathbf{G}_1^{\text{coll}} = -\mathbf{G}_2^{\text{coll}} = \bar{m}_{12} \nu_{12} (\mathbf{v}_2^* - \mathbf{v}_1^*) = -\sum_{j=1}^2 K_{1j} \mathbf{v}_j^*, \quad (\text{A1d})$$

$$K_{ij} = \bar{m}_{12} \nu_{12} \begin{bmatrix} 1 & -1 \\ -1 & 1 \end{bmatrix} = \frac{\rho_1 \rho_2 p}{\rho D_{12}} \begin{bmatrix} 1 & \\ & -1 \end{bmatrix} \begin{bmatrix} 1 & \\ & -1 \end{bmatrix}. \quad (\text{A1e})$$

By taking advantage of Eq. (4), the zero-net-flux condition, the singular matrix K_{ij} can be replaced by the nonsingular matrix \hat{K}_{ij} , whose inverse exists and is readily found:

$$\hat{K}_{ij} = K_{ij} + \begin{bmatrix} \omega_1 \\ \omega_2 \end{bmatrix} \begin{bmatrix} \rho_1 & \rho_2 \end{bmatrix}, \quad (\text{A2})$$

$$[\hat{K}_{ij}]^{-1} = \frac{1}{\rho(\omega_1 + \omega_2)} \begin{bmatrix} 1 + \frac{\omega_2 \rho D_{12}}{\rho_1 p} & 1 - \frac{\omega_1 \rho D_{12}}{\rho_1 p} \\ 1 - \frac{\omega_2 \rho D_{12}}{\rho_2 p} & 1 + \frac{\omega_1 \rho D_{12}}{\rho_2 p} \end{bmatrix}. \quad (\text{A3})$$

Here ω_1 and ω_2 are arbitrary and they satisfy $\omega_1 + \omega_2 \neq 0$. As mentioned previously in Sec. I A, an additional arbitrary term may be added to every column element of each row to obtain D_{ij} :

$$D_{ij} \equiv p[\hat{K}_{ij}]^{-1} + \frac{p}{\rho(\omega_1 + \omega_2)} \begin{bmatrix} \gamma_1 \frac{\rho D_{12}}{p} - 1 & \\ & \gamma_2 \frac{\rho D_{12}}{p} - 1 \end{bmatrix} \begin{bmatrix} 1 & \\ & 1 \end{bmatrix} \\ = \frac{D_{12}}{(\omega_1 + \omega_2)} \begin{bmatrix} \gamma_1 + \frac{\omega_2}{\rho_1} & \gamma_1 - \frac{\omega_1}{\rho_1} \\ \gamma_2 - \frac{\omega_2}{\rho_2} & \gamma_2 + \frac{\omega_1}{\rho_2} \end{bmatrix}. \quad (\text{A4})$$

It is easily verified that $\eta_j = \sum_{i=1}^2 \rho_i D_{ij} \propto \rho_1 \gamma_1 + \rho_2 \gamma_2$; i.e., its η_j is always independent of j . Thus the required property, Eq. (5a), is automatically satisfied (without the need to impose $\eta_j=0$).

The choices for γ_1 and γ_2 are arbitrary—together with ω_1 and ω_2 they provide a total of four arbitrary parameters (the actual degrees of freedom is less). If one chooses $\gamma_1 = -\omega_2/\rho_1$ and $\gamma_2 = -\omega_1/\rho_2$, then D_{ij} has all zeros on the diagonal² and is nonsymmetric. It is interesting to note that if ω_1 , ω_2 , γ_1 , and γ_2 are all proportional to b , then the resulting D_{ij} is independent of the scaling factor b .

While D_{ij} has no fundamental obligation to be symmetric, it can be made symmetric by choosing $\gamma_1 = \omega_1/\rho_1 + c$ and $\gamma_2 = \omega_2/\rho_2 + c$, where c is arbitrary. The resulting symmetric D_{ij} is not yet unique. If the additional (optional) $\eta_j=0$ condition is imposed on this D_{ij} , then $c = -(\omega_1 + \omega_2)/\rho$ must be chosen, yielding^{4,14-17}

$$D_{ij} = \frac{D_{12}}{\rho} \begin{bmatrix} \frac{\rho_2}{\rho_1} & -1 \\ -1 & \frac{\rho_1}{\rho_2} \end{bmatrix}. \quad (\text{A5})$$

One may choose to ignore the optional $\eta_j=0$ condition, and obtain a diagonal D_{ij} by setting $c=0$. Note that for $N \geq 3$ in the general case, D_{ij} cannot be made diagonal this way.

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- ³S. Chapman and T. G. Cowling, *The Mathematical Theory of Non-Uniform Gases* (Cambridge University Press, Cambridge, 1970).
- ⁴K. H. Ferziger and H. G. Kaper, *Mathematical Theory of Transport Processes in Gases* (North-Holland, Amsterdam, 1972).
- ⁵Both D_{ij} and $D_i^{(T)}$ have the physical dimension of velocity-length. The mass diffusion matrix is $\rho_i D_{ij}$; i.e., $\mathbf{j}_i^* = \sum_{j=1}^N (\rho_j D_{ij}) \mathbf{d}_j$.
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- ⁷F. A. Williams, "Elementary derivation of the multicomponent diffusion equation," *Am. J. Phys.* **26**, 467 (1958).
- ⁸F. A. Williams, *Combustion Theory*, 2nd ed. (Benjamin/Cummings, Menlo Park, CA, 1985), Appendix E.
- ⁹When $\rho_i \mathbf{f}_i$ is a surface force, it *must* be in the form of a divergence of a tensor. When \mathbf{f}_i is a viscous surface force, it represents the impacts of collisions with "other" molecules in the vicinity of the physical point of interest.
- ¹⁰In Williams (Refs. 7 and 8), $D_i \nabla_i / Dt$ was approximated here by DV_i / Dt .
- ¹¹Since elastic collisions are usually much more frequent than chemically active inelastic collisions, the latter contributes only a very minor correction to the total.
- ¹²The special choice $\omega_i = b\rho_i$ was made in Refs. 14–16—with b independent of i —so that the resulting \hat{K}_{ij} is symmetric. From the present vantage point, there is no fundamental rationale—except for aesthetics—to *require* \hat{K}_{ij} to be symmetric.
- ¹³The kinematic $D_i^{(T)}$ is denoted by $D_{T,i}/\rho_i$ in Ref. 8. Thus Eq. (5b) is $\sum_{i=1}^N D_{T,i} = 0$.
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- ²⁰Note that a nonsymmetric $\rho_i D_{ij}$ is *not* forbidden by Onsager's Reciprocity Relation (Ref. 1, Sec. 11.2d) because the \mathbf{j}_i^* 's and the \mathbf{d}_i 's are not independent, and—what's more—they are not the appropriate *conjugate* fluxes and forces. However, *the relation is not straightforward*.
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