ME 451C
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Week # 4

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Abstract

We now embark on some interesting issues in multi-component fluid mechanics—dealing with diffusion and chemical reactions. The materials in these notes here will probably take more than one week to cover. Read it, and bring your questions to class.

To avoid confusion, the Einstein summation convention is *not* adopted here.

1 Continuum Phenomenological Formulation

Diffusion of things can happen when the distribution of something is non-uniform in space. If temperature is non-uniform, diffusion of heat occurs. If concentration of a species is non-uniform, diffusion of matter occurs.

The simplest mass diffusion problem is the diffusion of a trace of inert gas (*e.g* perfume) in a environment of inert gas (air). One can easily accept the phenomenological diffusion law for the mass diffusion flux $\mathbf{j}^*$ of the trace gas:

$$\mathbf{j}^* = -D(\nabla X + \ldots) \tag{1}$$

where D, a scalar (for isotropic materials) or a 3×3 a matrix (for anisotropic materials), is the diffusion coefficient and X denotes the "concentration' (we will define concentration later) of the trace gas. To do a trace gas diffusion problem (and ignore any potential interaction between mass and heat diffusion), we just need D to formulate the problem.

Two questions we shall address are: what happens when we have a (isotropic) mixture of N species, and when these species react with each other chemically?

When there are N distinct species with concentrations denoted by Y_α's, there will be N mass diffusion fluxes $\mathbf{j}^*_\alpha$'s. The so-called *Fickian* relation between the $\mathbf{j}^*_\alpha$'s and the ∇X_α's, assuming linearity and isotropicity, is:

$$\mathbf{j}^*_\alpha = -\sum_{\beta=1}^{N} D_{\alpha\beta} \nabla (X_\beta + \ldots), \tag{2}$$

where $D_{\alpha\beta}$ is now a matrix (*i.e.* a tensor). To do a general multi-component diffusion problem (and ignoring any potential interaction between heat and mass diffusion) for an isotropic fluid, we need the full $N \times N$ $D_{\alpha\beta}$ matrix.

1.1 The Onsager Reciprocity Relation

More frequently than it should, some authors claim that the matrix $D_{\alpha\beta}$ is symmetric, and attribute the claim to the *Onsager Reciprocity Relation*. This is not correct. It was pointed by Coleman and Truesdell [7] that *such (sloppily stated) claims are without merit*, since the symmetry property of the relevant matrix can be changed by a simple linear transformation—on either $\mathbf{j}^*_\alpha$ or ∇X_β or both. The Onsager Reciprocity Relation needs to be stated much more carefully. See discussion on top of page 13 of [8]. We shall talk a bit more about it next week.

As we shall see later, we shall need to bring the Duham-Gibbs equation into the discourse, plus the concept of *microscopic reversibility* introduced in the original Onsager papers [9, 10].

2 Derivation of Diffusion Laws

The derivation of the classical multi-component diffusion law is revisited here. Following Furry [1], Williams [2, 3] pointed out that the dynamics of the mixture fluid had been assumed inviscid in the derivation. This paper shows that this assumption is easily relaxed, yielding a new term to the diffusion law. The theoretical consequences of this new term for viscous flow problems is briefly discussed.

2.1 Results Derived via Classical Kinetic Theory

The well known classical multi-component diffusion law for a mixture of N perfect gases can readily be derived starting from the Boltzmann Equation of kinetic theory [4, 5]:[1]

$$\mathbf{v}_\alpha^* \equiv \frac{\mathbf{j}_\alpha^*}{\rho Y_\alpha} = -\sum_{\beta=1}^{N} D_{\alpha\beta}\mathbf{d}_\beta - D_\alpha^{(T)}\nabla \log T, \tag{3}$$

$$\mathbf{d}_\alpha = \nabla X_\alpha + (X_\alpha - Y_\alpha)\nabla(\log p) + \frac{\rho}{p}\left(Y_\alpha \sum_{\beta=1}^{N} Y_\beta(\mathbf{f}_\beta - \mathbf{f}_\alpha)\right), \tag{4}$$

$$\alpha = 1, \ldots, N,$$

where ρ, p and T are the density, (scalar) pressure and temperature of the mixture fluid, X_α, Y_α, $\mathbf{v}_\alpha^*$ and $\mathbf{j}_\alpha^*$ are the mole fraction (p_α/p), the mass fraction (ρ_α/ρ), the mass-averaged diffusion velocity and the diffusion mass flux ($\rho_\alpha \mathbf{v}_\alpha^*$) of the α species, respectively,[2] $D_{\alpha\beta}$ is the diffusion coefficient matrix, $D_\alpha^{(T)}$ is the thermal diffusion coefficient, and $\mathbf{f}_\alpha$ is the body force per unit mass acting on the α species. As a direct consequence of their definitions, the mole and mass fractions satisfy

$$\sum_{\alpha=1}^{N} X_\alpha = 1, \quad \sum_{\alpha=1}^{N} Y_\alpha = 1, \tag{5}$$

[1] Compare the kinetic theory derived results with the phenomenological Fickian diffusion law Eq.(2).

[2] I am using fairly standard kinetic theory notation here where X_α denotes mole fraction while Y_α denotes mass fraction. Unfortunately, I used X_n to denote mass fraction in my Week # 3 notes. Here, I use asterisk '*' to mark entities associated with diffusion.

and the diffusion mass fluxes satisfy:

$$\sum_{\alpha=1}^{N} \mathbf{j}_\alpha^* = \sum_{\alpha=1}^{N} \rho_\alpha \mathbf{v}_\alpha^* = 0. \tag{6}$$

Under the assumption that all species in the mixture are perfect gases and all have the same temperature, X_α and Y_α are related by:

$$X_\alpha = \frac{Y_\alpha/\mathcal{M}_\alpha}{\sum_{\beta=1}^{N}(Y_\beta/\mathcal{M}_\beta)} \tag{7}$$

where the $\mathcal{M}_\alpha$'s are the molecular weights of the α species. Thus $X_\alpha - Y_\alpha > 0$ if the α species is a light species relative to the others. The fluid pressure p is the sum of all the (partial) pressures of the components. Summing the perfect gas (for each component) equations of state, we have:

$$p = \sum_{\alpha=1}^{N} p_\alpha = \rho R T \tag{8}$$

where

$$R \equiv \mathcal{R} \sum_{\alpha=1}^{N} \frac{Y_\alpha}{\mathcal{M}_\alpha} \tag{9}$$

and $\mathcal{R}$ is the *universal gas constant*. The important observation is: the fluid gas constant R is not a constant anymore—unless the Y_α's are constants. It is a function of the Y_α's which may be time and space dependent.

Following Furry [1], Williams [2, 3] rederived the essence of the above kinetic theory results in an elementary and insightful way—starting from the macroscopic momentum equations of all the species. The derivation invoked the assumption that the dynamics of all the species—and therefore also the mixture fluid—was inviscid. The question being addressed here is: What happens to Eq.(3) and Eq.(4) when the dynamics of the mixture fluid is known to be viscous? This is an important theoretical issue since Eq.(3) and Eq.(4) have been freely used for viscous flow problems for a very long time.

3 The Elementary Derivation

The elementary derivation [2, 3] proceeds by using macroscopic conservation laws, leaving kinetic theory concepts in the background to be called upon only when needed. In the present discourse, thermal diffusion effects will be omitted. See Furry [1] for his insightful exposition on this topic.

3.1 The Continuity Equations

Let n denote the total number density of all the molecules in the mixture fluid, $\mathbf{V}_\alpha$, n_α and m_α denote the mass averaged velocity, the number density and the molecular mass of the α species, respectively.

The species-specific macroscopic continuity equations are readily written down:

$$\frac{\partial \rho_\alpha}{\partial t} + \nabla \cdot (\rho_\alpha \mathbf{V}_\alpha) = W_\alpha \tag{10}$$

where W_α represents the net mass production rate (per unit volume) of the α species from chemical reactions, and ρ_α, the mass density of the α species, is related to ρ, the mixture fluid density, by:

$$\rho_\alpha = n_\alpha m_\alpha = \rho Y_\alpha, \quad (\rho \equiv \sum_{\alpha=1}^{N} \rho_\alpha), \tag{11}$$

where Y_α denotes mass fraction. Since mass can be neither be created or destroyed by chemical reactions, we have

$$\sum_{\alpha=1}^{N} W_\alpha = 0. \tag{12}$$

The diffusion velocity of the α species $\mathbf{v}^*_\alpha$ is defined by:

$$\mathbf{v}^*_\alpha \equiv \mathbf{V}_\alpha - \mathbf{V}. \tag{13}$$

where $\mathbf{V}$ is the mass averaged velocity of the mixture fluid defined by:

$$\mathbf{V} \equiv \frac{1}{\rho} \sum_{\alpha=1}^{N} \rho_\alpha \mathbf{V}_\alpha = \sum_{\alpha=1}^{N} Y_\alpha \mathbf{V}_\alpha. \tag{14}$$

By this definition, Eq.(6) follows immediately. Equation (10) can be rewritten as:

$$\frac{\partial \rho_\alpha}{\partial t} + \nabla \cdot (\rho_\alpha \mathbf{V}) + \nabla \cdot (\rho_\alpha \mathbf{v}^*_\alpha) = W_\alpha \tag{15}$$

The mixture macroscopic fluid continuity equation is obtained by summing Eq.(15) over all species:

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{V}) = 0. \tag{16}$$

Using Eq.(16), we can rewrite Eq.(15) as follows:

$$\rho \frac{DY_\alpha}{Dt} + \nabla \cdot \mathbf{j}^*_\alpha = W_\alpha. \tag{17}$$

where D/Dt is the conventional substantial derivative.

Thus, in the absence of chemistry $W_\alpha = 0$ and mass diffusion $\mathbf{j}^*_\alpha = 0$, we have Y_α =constant following any fluid parcel in the flow field. Thus, if the fluid coming into the flow field of interest has constant Y_α's, then the Y_α's are constant in the flow field of interest. That is why we usually don't worry about the Y_α's.

But, as should be obvious, whenever we are interested in mass diffusion or gas phase chemistry, then the Y_α's are not constants, and we need to find equations for them, somehow. Usually, one goes to kinetic theory to get the formulas displayed in Eq.(3) and Eq.(4) for the diffusion mass flux vector, $\mathbf{j}^*_\alpha$ (or $\rho_\alpha \mathbf{v}^*_\alpha$) in Eq.(16). Here, the elementary derivation goes instead to the species-specific momentum equation to "derive" the same formulas.

If we use the simple Fickian Law Eq.(2) in Eq.(17), we have:

$$\rho \frac{DY_\alpha}{Dt} + \nabla \cdot \sum_{\beta=1}^{N} (D_{\alpha\beta} \nabla Y_\beta) = W_\alpha. \tag{18}$$

This is a diffusion equation and gives us advanced notice that we will need to worry about boundary conditions for the Y_α's.

3.1.1 Duham-Gibbs again

The Duham-Gibbs equation, eq.(54) in Week # 3 Notes, was written for an identified "system." When the identified system is a moving glob of fluid, we use the substantial derivative to follow the system as it moves. We have:

$$\rho T \frac{Ds}{Dt} = \rho \frac{Dh}{Dt} - \frac{Dp}{Dt} - \sum_{\alpha=1}^{N} \mu_\alpha \rho \frac{DY_\alpha}{Dt}. \tag{19}$$

In Week #3 Notes, I had used X_n to denote the mass fraction. Here, I am following the kinetic theory notation and use Y_α for the mass fraction. I apologize for the change of notation in midstream.

There are three terms on the right hand side of Eq.(19). We can see that the first term involves the global energy equation, the second term involves the global momentum equation, and the last term involves all the individual species continuity equations.

Using Eq.(17) in Eq.(19), we have:

$$\rho T \frac{Ds}{Dt} = \rho \frac{Dh}{Dt} - \frac{Dp}{Dt} + \sum_{\alpha=1}^{N} \mu_\alpha \left(\nabla \cdot \mathbf{j}_\alpha^* - W_\alpha . \right). \tag{20}$$

We now see why we never bothered with the last term when mass diffusion and gas phase chemistry are neglected. We shall put this equation aside for a while and come back to it later.

Using the global energy and momentum equations for the first two terms of Eq.(20), we have (after some well-known manipulations):

$$\rho T \frac{Ds}{Dt} = -\nabla \cdot \mathbf{q} + \bar{\bar{\tau}} : \nabla \mathbf{V} + \sum_{\alpha=1}^{N} \mu_\alpha \left(\nabla \cdot \mathbf{j}_\alpha^* - W_\alpha . \right). \tag{21}$$

where $\mathbf{q}$ and $\bar{\bar{\tau}}$ are heat flux (energy per unit area per unit time) by conduction and viscous stress tensor (force per unit area), respectively. We see that the specific entropy s of the fluid parcel can change due to these three effects. (Can you pin point precisely where did we commit our fluid parcel to be in "thermodynamic equilibrium?" Ask me in class if you are not sure.)

We shall come back to Eq.(21) later.

3.2 The Momentum Equations

The macroscopic momentum equation for the α species can be written as follows:

$$\frac{\partial(\rho_\alpha \mathbf{V}_\alpha)}{\partial t} + \nabla \cdot (\rho_\alpha \mathbf{V}_\alpha \mathbf{V}_\alpha) = -\nabla p_\alpha + \rho_\alpha \mathbf{h}_\alpha + \mathbf{G}_\alpha. \tag{22}$$

The left hand side are familiar conventional terms. On the right hand side, the first term represents the net surface force by (scalar) pressure (p_α is the partial pressure of the α gas), and the last term represents momentum exchange per unit time of the α species via inter-species (elastic and inelastic) collisions. The middle term, $\rho_\alpha \mathbf{h}_\alpha$, represents "all other complications" not so far included (or properly accounted for), such as body and/or viscous surface forces[3]. We shall let this

[3]Furry [1] and Williams [2, 3] assumed $\rho_\alpha \mathbf{h}_\alpha$ represented body forces only. We hereby allow the possibility that it may represent "all other" otherwise unaccounted for forces. In order for it to represent surface forces, $\rho_\alpha \mathbf{h}_\alpha$ *must* be a divergence of some stress tensor.

"catch-all" term simply tag along, and exploit it later. Whatever complaints you may have about this equation, blame it on this term.

Expanding the left hand side of Eq.(22) and using Eq.(10), we obtain:

$$\rho_\alpha \frac{D_\alpha \mathbf{V}_\alpha}{Dt} = -\nabla p_\alpha + \rho_\alpha \mathbf{h}_\alpha + \mathbf{G}_\alpha^{coll} \tag{23}$$

where D_α/Dt denotes the substantial derivative of the α species:

$$\frac{D_\alpha}{Dt} \equiv \frac{\partial}{\partial t} + \mathbf{V}_\alpha \cdot \nabla \tag{24}$$

and $\mathbf{G}_\alpha^{coll}$, defined by

$$\mathbf{G}_\alpha^{coll} \equiv \mathbf{G}_\alpha - W_\alpha \mathbf{V}_\alpha, \tag{25}$$

and is seen to include a contribution (from the left hand side) arising from chemical reactions, represents all inter-species collisional momentum exchange. Since inter-species collisions conserves total momentum, the sum of $\mathbf{G}_\alpha^{coll}$ over all species must be identically zero:

$$\sum_{\alpha=1}^{N} \mathbf{G}_\alpha^{coll} = 0. \tag{26}$$

Summing Eq.(23) over all species, we obtain the momentum equation of the mixture fluid:

$$\sum_{\alpha=1}^{N} \left(\rho_\alpha \frac{D_\alpha \mathbf{V}_\alpha}{Dt} \right) = -\nabla p + \sum_{\alpha=1}^{N} \rho_\alpha \mathbf{h}_\alpha \tag{27}$$

where p is pressure of the mixture fluid (the sum of all the p_α's). The left hand side of Eq.(27) needs additional attention to make it look totally familiar.

3.2.1 The Inter-Species Collisional Term $\mathbf{G}_\alpha^{coll}$

It is intuitively clear that $\mathbf{G}_\alpha^{coll}$ must be zero if all species in the mixture fluid move with identical mass averaged velocities. Thus, $\mathbf{G}_\alpha^{coll}$ is expected to be some linear combination of the $\mathbf{v}_\alpha^*$'s. Using concepts from elementary kinetic theory, we can rewrite $\mathbf{G}_\alpha^{coll}$ as follows [2, 3]:

$$\mathbf{G}_\alpha^{coll} = \sum_{\beta=1}^{N} \bar{m}_{\alpha\beta} \nu_{\alpha\beta} (\mathbf{V}_\beta - \mathbf{V}_\alpha) = \sum_{\beta=1}^{N} \bar{m}_{\alpha\beta} \nu_{\alpha\beta} (\mathbf{v}_\beta^* - \mathbf{v}_\alpha^*) \tag{28}$$

where $\bar{m}_{\alpha\beta} = m_\alpha m_\beta/(m_\alpha + m_\beta)$ is the "reduced mass" and $\nu_{\alpha\beta}$ is the collision frequency (per unit volume) of collisions between α and β molecules. Detailed kinetic theory calculations on the dynamics of elastic and inelastic (*i.e.* chemically active) collisions are needed to generate $\nu_{\alpha\beta}$ from first principles.[4] It is convenient to further rewrite Eq.(28) as follows:

$$\mathbf{G}_\alpha^{coll} = -\sum_{\beta=1}^{N} K_{\alpha\beta}\mathbf{v}_\beta^*, \tag{29}$$

where $K_{\alpha\beta}$ is defined by

$$K_{\alpha\beta} \equiv \delta_{\alpha\beta}\sum_{\beta'=1}^{N} \bar{m}_{\alpha\beta'}\ \nu_{\alpha\beta'} - \bar{m}_{\alpha\beta}\nu_{\alpha\beta} \tag{30}$$

and $\delta_{\alpha\beta}$ is the Kronecker Delta. Note that $K_{\alpha\beta}$ as defined is symmetric (because both $\bar{m}_{\alpha\beta}$ and $\nu_{\alpha\beta}$ are symmetric) and automatically satisfies

$$\sum_{\alpha=1}^{N} K_{\alpha\beta} = 0. \tag{31}$$

Equation (31) is consistent with Eq.(26).

Equation (23) can now be rewritten as follows:

$$\rho_\alpha \frac{D_\alpha \mathbf{V}_\alpha}{Dt} = -\nabla p_\alpha + \rho_\alpha \mathbf{h}_\alpha - \sum_{\beta=1}^{N} K_{\alpha\beta}\mathbf{v}_\beta^* \tag{32}$$

Since $K_{\alpha\beta}$ is a singular matrix (clearly indicated by Eq.(31)), it is not possible to algebraically solve Eq.(32) directly for the N components of the $\mathbf{v}_\alpha^*$ vector. In addition, Eq.(6) must be honored by the solution. There are many ways to proceed. One way is to replace one judiciously chosen component of Eq.(31) by Eq.(6) such that the resulting new square $N \times N$ matrix operating on $\mathbf{v}_\alpha^*$ is non-singular. Another way is to bring in Eq.(6) as the $(N+1)$th component of Eq.(31), and to solve for the $\mathbf{v}_\alpha^*$ using the pseudo-inverse [11] of the resulting (full rank) rectangular matrix. Still another way is to introduce $\widehat{K}_{\alpha\beta}$ defined by:

$$\widehat{K}_{\alpha\beta} = K_{\alpha\beta} + c_\alpha \rho_\beta, \quad \alpha, \beta = 1, \ldots, N, \tag{33}$$

[4]It is important to emphasize that *both* elastic and inelastic collisions contribute to $K_{\alpha\beta}$. It is a useful exercise to work out—by dimensional analysis—how $\nu_{\alpha\beta}$ depends on collision cross-section, averaged thermal velocities, and number densities of the collision partners.

where the c_α's are N *arbitrary* constants that satisfy $\sum_{\alpha=1}^{N} c_\alpha \neq 0$. Unlike $K_{\alpha\beta}$ which is singular because of Eq.(31), $\widehat{K}_{\alpha\beta}$ is no longer singular:

$$\sum_{\alpha=1}^{N} \widehat{K}_{\alpha\beta} = (\sum_{\alpha=1}^{N} c_\alpha)\rho_\beta \neq 0. \tag{34}$$

In view of Eq.(6), we have:

$$\sum_{\beta=1}^{N} \widehat{K}_{\alpha\beta}\mathbf{v}_\beta^* = \sum_{\beta=1}^{N} K_{\alpha\beta}\mathbf{v}_\beta^*, \tag{35}$$

which allows us to replace $K_{\alpha\beta}$ in Eq.(32) by $\widehat{K}_{\alpha\beta}$. Applying the inverse of $\widehat{K}_{\alpha\beta}$ on the resulting new Eq.(32) to solve for $\mathbf{v}_\alpha^*$, we have, without any approximation:

$$\mathbf{v}_\alpha^* = \sum_{\beta=1}^{N} \left[\widehat{K}\right]_{\alpha\beta}^{-1} \left(-\nabla p_\beta + \rho_\beta \mathbf{h}_\beta - \rho_\beta \frac{D_\beta \mathbf{V}_\beta}{Dt}\right). \tag{36}$$

The nonuniqueness of the answer—as highlighted by the arbitrariness of the c_α's—is well known in the literature [4, 5, 6].[5]

Formally, Eq.(36) is an *exact* alternative representation of Eq.(32), the species momentum equations, and is valid for whatever we may have chosen for $\rho_\alpha \mathbf{h}_\alpha$, while honoring Eq.(6) always.

3.2.2 The Continuum Limit: $\left[\widehat{K}\right]_{\alpha\beta}^{-1} \to 0$

Let U and L denote the characteristic velocity and length of the problem under study. The characteristic fluid mechanics timescale is then L/U. Let τ_{coll} denote a characteristic collision timescale of the mixture fluid, and is representative of *both* inter and intra-species collisions. We denote the timescale ratio $U\tau_{coll}/L$ by ϵ, which in the continuum limit is an asymptotically small number. It is easy to be convinced that $\widehat{K}_{\alpha\beta} = O(1/\epsilon)$, or $\left[\widehat{K}\right]_{\alpha\beta}^{-1} = O(\epsilon)$. Since $\mathbf{G}_\alpha^{coll}$ must have a finite limit for asymptotically small ϵ, the leading approximation for $\mathbf{v}_\alpha^*$ must be:

$$\mathbf{v}_\alpha^* = \mathbf{V}_\alpha - \mathbf{V} = O(\epsilon). \tag{37}$$

[5]For example, it is possible to impose a "cosmetic" requirement that the diagonal elements of $[\widehat{K}]_{\alpha\beta}^{-1}$ be zeros.

In other words, in this limit all species move with approximately the same $\mathbf{V}$, the mass-averaged velocity of the mixture fluid. Using $\mathbf{V}_\alpha = \mathbf{V} + O(\epsilon)$ on the left hand side of Eq.(27), we obtain the following as our momentum equation for the total mixture fluid:

$$\rho \frac{D\mathbf{V}}{Dt} = -\nabla p + \rho \mathbf{h} + O(\epsilon) \tag{38}$$

where the *net* "otherwise unaccounted force" (per unit mass) $\mathbf{h}$ is

$$\mathbf{h} \equiv \sum_{\alpha=1}^{N} Y_\alpha \mathbf{h}_\alpha \tag{39}$$

and the original species-specific acceleration $D_\alpha \mathbf{V}_\alpha / Dt$ has been approximated by $D\mathbf{V}/Dt$, the acceleration of the mixture fluid. Using the same approximation again on the right hand side of Eq.(36), we obtain the next approximation for $\mathbf{v}^*_\alpha$:

$$\mathbf{v}^*_\alpha = \sum_{\beta=1}^{N} \left[\widehat{K}\right]^{-1}_{\alpha\beta} \left(-\nabla p_\beta + \rho_\beta \mathbf{h}_\beta - \rho_\beta \frac{D\mathbf{V}}{Dt}\right) + O(\epsilon^2). \tag{40}$$

Using Eq.(38) to eliminate $D\mathbf{V}/Dt$ from Eq.(40), we obtain:

$$\mathbf{v}^*_\alpha = -\sum_{\beta=1}^{N} D_{\alpha\beta} \left\{\nabla X_\beta + (X_\beta - Y_\beta)\nabla(\log p) + \mathbf{H}_\beta\right\} + O(\epsilon^2) \tag{41}$$

where

$$D_{\alpha\beta} \equiv p \left[\widehat{K}\right]^{-1}_{\alpha\beta}, \tag{42}$$

$$\mathbf{H}_\beta \equiv \frac{1}{p}\left(\rho_\beta \mathbf{h} - \rho_\beta \mathbf{h}_\beta\right) \tag{43}$$

$$= \frac{\rho}{p}\left(Y_\beta \sum_{\beta'=1}^{N} Y_{\beta'}(\mathbf{h}_{\beta'} - \mathbf{h}_\beta)\right). \tag{44}$$

Note that all $O(\epsilon)$ and $O(\epsilon^2)$ error terms displayed in Eq.(38), Eq.(40) and Eq.(41) arose from approximating the species-specific acceleration by the mixture fluid acceleration.

Furry [1] limited his derivations for a mixture fluid at rest. Williams [2, 3] dealt with a mixture fluid in motion, but neglected the "non-diagonal elements of the pressure tensor" and chose to include *only* body forces ($\mathbf{h}_\alpha = \mathbf{f}_\alpha$) in his species-specific momentum equation—thus tacitly assumed the dynamics for the mixture fluid to be inviscid. Williams recovered the essence of the well known results of classical kinetic theory (see eq.(E-18,19) of [3]) but gave explicit answers only for the binary case. The derivation here gives explicit results for the general multi-component case, directly confronting the singular nature of $K_{\alpha\beta}$ by the use of $\widehat{K}_{\alpha\beta}$. The key message of this approach is that

> *the derived diffusion law is simply an alternative (approximate) representation of the species momentum equations while honoring Eq.(6) at the same time.*

The catch-all term $\rho_\alpha \mathbf{h}_\alpha$ is available to account for *all otherwise unaccounted for terms*—it is not restricted to represent only body forces. Most importantly, whatever $\rho_\beta \mathbf{h}_\beta$ appeared in Eq.(38) *must* also appear in eqs.(40,43 and 44), and *vice versa*.[6]

4 Some Speculations

What happens when we deal with problems that need the full Navier Stokes momentum equation for the mixture fluid?

The (low speed) Navier-Stokes momentum equation for the mixture fluid is:

$$\rho \frac{D\mathbf{V}}{Dt} = -\nabla p + \nabla \cdot (\mu \nabla \mathbf{V}) \tag{45}$$

where μ is the mixture fluid viscosity and is a function of the composition of the mixture. From elementary kinetic theory of gases, $\mu = O(\rho a^2 \tau_{coll})$ where a is a characteristic "speed of sound" of the mixture fluid. Hence, the Reynolds number of the problem ($R_e = \rho U L/\mu$) is $O(M^2/\epsilon)$ where M is the characteristic Mach number, U/a. From the vantage point of asymptotics, the viscous term in Eq.(45) is $O(1/R_e) = O(\epsilon/M^2)$. Hence for flows with finite M, the viscous term is formally a "higher order" term in small ϵ asymptotics. Hence, whenever the viscous term in Eq.(45) is deemed important, the characteristic Mach number M of viscous flow problems must be $O(\epsilon^{1/2})$ so that the viscous term remains $O(1)$ in the $\epsilon \to 0$ limit.

Since the sum of all the species momentum equations must always agree with Eq.(38) and Eq.(45), a "viscous" surface stress term must

[6] It is interesting to note that when $\mathbf{h} = 0$, *i.e.* when there is no net external "otherwise unaccounted force," it is possible that the $Y_\alpha \mathbf{h}_\alpha$'s are not zeros. They just need to sum to zero.

appear in some (at least one) of the species momentum equations whenever the viscous term is kept in Eq.(45). And the sum of all these terms must equal to $\nabla \cdot (\mu \nabla \mathbf{V})$.

We can now exploit the catch-all term $\rho_\alpha \mathbf{h}_\alpha$. Since viscous forces are surface forces, $\rho_\alpha \mathbf{h}_\alpha$ must be in the form of a divergence. The simplest empirical model is:

$$\rho_\alpha \mathbf{h}_\alpha = \nabla \cdot (\mu_\alpha \nabla \mathbf{V}) \tag{46}$$

where μ_α is the viscosity of the α species in this particular mixture—it is emphasized that it is *not* the viscosity of a pure α species gas[7]. Comparing Eq.(38) with Eq.(45), we find that the μ_α's must be related to the mixture fluid viscosity μ by

$$\mu = \sum_{\alpha=1}^{N} \mu_\alpha . \tag{47}$$

Using Eq.(46) for $\rho_\alpha \mathbf{h}_\alpha$ in Eq.(43), we obtain:

$$\mathbf{H}_\beta = \frac{1}{p} \left[Y_\beta \nabla \cdot (\mu \nabla \mathbf{V}) - \nabla \cdot (\mu_\beta \nabla \mathbf{V}) \right] . \tag{48}$$

This is the new term in the multi-component diffusion law (using Eq.(46) as the model) in response to the viscous term in Eq.(45) being important to the dynamics of the mixture fluid.[8]

Theoretically, μ_α must depend on all the Y_α's (and/or the X_α's), and it must obey Eq.(47). In analogy to $p_\alpha = X_\alpha p$, a simple-minded model for μ_α is:

$$\mu_\alpha = X_\alpha \mu , \tag{49}$$

where μ itself is dependent on the composition of the mixture. The resulting $\mathbf{H}_\beta$ is:

$$\mathbf{H}_\beta = \frac{1}{p} \left((Y_\beta - X_\beta) \nabla \cdot (\mu \nabla \mathbf{V}) - \mu (\nabla X_\beta \cdot \nabla) \mathbf{V} \right) . \tag{50}$$

Another simple-minded model for μ_α is:

$$\mu_\alpha = Y_\alpha \mu . \tag{51}$$

[7]Equation (46) has taken advantage of Eq.(37) in the continuum limit. If the flow is not low speed, an additional term analogous to the bulk viscosity term would be needed.

[8]Note that the new term involves tensors. See page 13, the paragraph following eq.(10) of [8] on comments on the "absurd branch" of this literature.

The resulting $\mathbf{H}_\beta$ is:

$$\mathbf{H}_\beta = -\frac{\mu}{p}(\nabla Y_\beta \cdot \nabla)\mathbf{V}. \tag{52}$$

Intuitively, Eq.(50) is more pleasing than Eq.(52) because the latter says nothing special happens when the molecular weights of the colliding species are the same. However, it is not possible to pass unequivocal judgment on which, if any, of the above speculations is correct without a detailed and careful analysis based on first principles.

5 Theoretical Consequences

To clear the air immediately, we note that the new term is of no importance in problems dealing with conventional diffusion boundary layers in large Reynolds number flows. This is because in boundary layer problems the interesting component of the diffusion velocity $\mathbf{v}^*_\alpha$ is its component perpendicular to $\mathbf{V}$, while the new $\mathbf{H}_\alpha$ vector—according to either Eq.(50) or Eq.(52)—is parallel to $\mathbf{V}$.

What happens in finite or low Reynolds number (*e.g.* Stokes flows) problems? There is no question—based on the derivation presented here—that the use of classical diffusion law cannot be justified, since for this class of problems the viscous term is not a "higher order" term. It is worth repeating that whatever $\rho_\beta \mathbf{h}_\beta$ appeared in Eq.(38) *must* also appear in eqs.(40,43 and 44), and *vice versa*.

In theories of shock and detonation structures, it is known that the viscous term cannot be neglected from 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. Whether the new term plays a practically significant role for laminar flame studies remains to be clarified. When M is considered independent of ϵ, the $\mathbf{H}_\beta$ term in Eq.(41) arising from viscosity is *formally* of the same order as the neglected "higher order" (*i.e.* $O(\epsilon^2)$) terms. This is probably the rationale for not keeping the viscous terms in the current literature [2, 3].

In normal applications, one seldom, if ever, deals with all N components of a mixture fluid. Often, one of the species—say the N-th species—is removed from the list of unknowns using Eq.(5). The governing equations are then the mixture fluid continuity and momentum equations, plus the species-specific continuity equations and the diffusion laws for the remaining $(N-1)$ species. What happens when the classical (inviscid) diffusion law is adopted for these $(N-1)$ species when the mixture fluid momentum equation is viscous? According to the present paper, the above procedure is equivalent to assuming that the "removed" species' diffusion law is responsible for the full burden of the viscous term in the mixture fluid momentum equation! Clearly this unspoken assumption can not be justified.

6 Homeworks

1. Let us denote specific *Gibb's free energy* of a substance by g:

$$g = h - Ts, \tag{53}$$

and the chemical potential of its α component by μ_α (as defined by eq.(53) of Week # 3 notes):

$$\mu_\alpha = h_\alpha - Ts_\alpha. \tag{54}$$

The mole fraction is denoted by X_α, and the mass fraction is denoted by Y_α. All symbols without subscript refer to the values of the mixture (pressure is p, density is ρ, etc.). All components are at the same T. Assume all components to be perfect gas (with constant specific heat) in the interested range of the parameters.

Find the following in terms of species properties ($p_\alpha, \rho_\alpha, R_\alpha, C_{p,\alpha}, \gamma_\alpha$, etc.) and X_α, Y_α:

a p, ρ. (OK, these are for warming up).

b h. (remember, we may be interested in chemical reactions among the species.).

c s. This is what the warm-ups are leading to. First find s_α, then proceed from there. Compare the relations between p and p_α, ρ and ρ_α, h and h_α with s and s_α.

d Say something interesting when all μ_α's have the same value.

2. The Fickian Law of mass diffusion, Eq.(2), is phenomenological. Nevertheless, it must satisfy Eq.(6). Show that Eq.(2) can be

alternatively written as follows:

$$\mathbf{j}^*_\alpha = \sum_{\beta=1}^{N} \widehat{D}_{\alpha\beta} \nabla Y_\beta \tag{55}$$

where

$$\widehat{D}_{\alpha\beta} = D_{\alpha\beta} + c_\alpha \sum_{\alpha'=1}^{N} D_{\alpha'\beta}. \tag{56}$$

and c_α is any (arbitrary) real N-dimensional (dimensionless) vector. Discuss the issue of uniqueness of Fickian Law of mass diffusion. How meaningful is a claim on the symmetry properties of $D_{\alpha,\beta}$ in Eq.(2) whenever Eq.(6) must be respected?

3. Consider the term $\bar{m}_{\alpha\beta}\nu_{\alpha\beta}$. By dimensional analysis, express it in terms of the following parameters: $m_\alpha, m_\beta, \sigma_{\alpha\beta}, c_{\alpha\beta}$ (collision cross-section and average random collision velocity between the colliding particles), ρ_α, ρ_β.

4. Work out the mass diffusion law for a binary mixture, and express the diffusion coefficient(s) in terms of the parameters in item #2 above.

5. Suppose you have worked out the diffusion coefficients for a binary mixture of species 1 and 2, and separately the diffusion coefficients for a binary mixture of species 1 and 3. Now, you are interested in mixture that contains all three species. Obviously, having done the above problem, you can do this one also. Suppose you want to guess at what the right answer is going to be before doing the math. What would be your guesses?

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