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The use of the diffusion velocity in conservation equations for multicomponent gas mixtures

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Abstract—The nature of the diffusion velocity for ordinary diffusion is carefully examined. It is shown that its physical character is different to the forced diffusion velocity in that it is not necessary to associate diffusion stresses and kinetic energy with ordinary diffusion. As a consequence, momentum and energy conservation equations based on coexisting-continua models found in the literature are shown to be of doubtful utility, and are often incorrectly interpreted. In addition, a widely seen form of the thermal energy equation is shown to be in error. A single continuum model is proposed for non-ionized gas mixtures that is adequate for practical use. An appropriate form of the coexisting-continua model conservation equations is given for plasma when forced diffusion is the dominant diffusion mechanism. © 1998 Elsevier Science Ltd. All rights reserved.

1. INTRODUCTION

The conservation equations for gas mixtures in common use are derived from coexisting-continua or kinetic-theory models. In both models, the phenomena of diffusion are introduced by defining the absolute velocity of a chemical species to have a component due to diffusion, called the diffusion velocity, $\hat{\mathbf{v}}_i$. The resulting derivations of species and mass conservation equations are straightforward. However, when using the coexisting-continua model to derive the mixture momentum conservation equations, momentum fluxes $-\Sigma_i\rho_i\hat{\mathbf{v}}_i\hat{\mathbf{v}}_i$ appear that are interpreted as a 'diffusion stress tensor'. Similarly, the mixture energy equation contains terms that are associated with a 'kinetic energy of diffusion', $\Sigma_i\frac{1}{2}\rho_i\hat{v}_i^2$. Kinetic-theory models yield conservation equations that contain similar terms, either explicitly or implicitly. Often these quadratic diffusion terms are concealed by new definitions, are discarded based on scaling arguments, or are simply ignored.

In general, the diffusion velocity has four components: these are associated with ordinary, forced, pressure, and thermal diffusion. It will be shown that the diffusion velocities for ordinary and forced diffusion are fundamentally different. The former is an arbitrarily defined average value for molecules in thermal motion; the latter is a 'drift' velocity that can be specified as a component of the velocity of each molecule. The result is that quadratic terms involving these velocities have different physical meanings for ordinary and forced diffusion. It will be shown that the only practical use of the ordinary diffusion velocity is in a product with a measure of species concentration to give a mass, mole or molecular flux. There is no need to define quantities such as the diffusion stress tensor and kinetic energy of diffusion for ordinary diffusion since they have no separate existence. The diffusion pressure is a portion of the thermodynamic pressure; the kinetic energy of diffusion is a portion of the thermodynamic internal energy. These terms are often said to be discarded based on scaling arguments when, in fact, they have not been discarded. Use of thermodynamic pressure ensures that the diffusion pressure for ordinary diffusion is included. Use of the thermodynamic internal energy ensures that the kinetic energy of ordinary diffusion is included. On the other hand, the forced diffusion velocity does give diffusion stresses and a kinetic energy of diffusion that are distinct physical quantities. If these terms are to be considered, they need to be specified separately. The kinetic energy of forced diffusion is energy in addition to the thermodynamic internal energy.

In Section 2 the physics of diffusion is discussed, and in Section 3 some definitions from the kinetic theory of gases are used to illuminate the simple physics of Section 2. In Section 4 a brief development of a coexisting-continua model of gas mixtures is given, followed by an evaluation of the model and comments on the relevant literature. Section 5 recommends new continuum models for gas mixtures, first for non-ionized gas mixtures and then when forced diffusion is dominant. Finally, in Section 6 the nature of the ordinary-diffusion velocity in continuum models is revisited.

2. THE PHYSICS OF DIFFUSION

2.1. *Continuum model of ordinary diffusion*

When concentration gradients exist in a gas mixture, the random (thermal) motion of molecules causes ordinary diffusion to occur. In a continuum model, ordinary diffusion in a binary mixture can be described by Fick's law in the form,

NOMENCLATURE

a	rate of mass gain
$\mathbf{c}$	peculiar velocity relative to average species velocity
$\bar{c}$	mean thermal speed $(8RT/\pi)^{1/2}$
$\mathbf{C}$	peculiar velocity relative to mass average velocity
D/Dt	substantial derivative
D_{ij}	multicomponent diffusion coefficient
D_i^T	thermal diffusion coefficient
$\mathscr{D}$	binary diffusion coefficient
e	total energy
ϵ	elementary electric charge
E	electric field strength
$\mathbf{f}$	external force per unit mass
f	velocity distribution function
g	gravitational acceleration
h	enthalpy
$\mathbf{j}$	mass diffusion flux
$\mathscr{J}$	molecular diffusion flux
k	thermal conductivity
$\mathscr{k}$	Boltzmann constant
Kn	Knudsen number
$\mathscr{G}$	mean free path
L	length scale
m	mass fraction
$\mathscr{m}$	mass of a molecule
n	absolute mass flux
$\mathscr{N}$	number density
P	pressure
$\mathbf{q}$	heat/energy flux
$\dot{Q}_{Vi}$	internal (volumetric) heat generation rate
$\dot{r}$	mass generation rate due to homogeneous reactions
R	gas constant
Re	Reynolds number
Sc	Schmidt number
t	time
T	temperature
u	internal energy
$\mathbf{v}$	velocity
v	molecule absolute velocity
V	volume
x	mole fraction
z	spatial coordinate.

Greek symbols

ζ	friction force
κ	bulk viscosity
μ	viscosity; mobility of an ion
ξ	rate of energy dissipation due to interaction stresses
ρ	density
σ	total stress
τ	viscous stress
ϕ	rate of energy accumulation
Φ	dissipation function.

Subscripts

i	species i
s	subsurface, adjacent to a solid
P	particle
1, 2	species 1, 2.

Superscripts and overscores

C	conduction
CC	Chapman and Cowling
D	diffusion
DC	diffusional conduction (Dufour effect)
FD	forced diffusion
OD	ordinary diffusion
TD	thermal diffusion
W	Woods
$'$	relative to the mass average velocity
$*$	relative to the molecule average velocity;
$*$, $^+$, $\dagger$, tr	various definitions of internal energy [see equations (44), (45), (48) and (49)]
$\tilde{}$	partial property not equivalent to its pure gas counterpart.

$$\mathbf{j}_1 = -\rho\mathscr{D}_{12}\nabla m_1. \tag{1}$$

The diffusion velocity relative to the mass average velocity $\hat{\mathbf{v}}_1$ can be defined by the relation

$$\mathbf{j}_1 = \rho_1\hat{\mathbf{v}}_1. \tag{2}$$

Comparing equations (1) and (2),

$$\hat{\mathbf{v}}_1 = -\mathscr{D}_{12}\nabla \ln m_1. \tag{3}$$

Consider now the simple situation depicted in Fig. 1. In the connecting tube, steady one-dimensional diffusion takes place in an isothermal mixture of two species of essentially equal molecular weights (e.g. CO and N_2). The mixture may be taken to be stationary. The gradient ∇m_1 is constant along the tube, as is the flux $\mathbf{j}_1$, but $\hat{\mathbf{v}}_1$ varies nonlinearly along the tube. Since $\rho_1 = \rho$ at $z = 0$, $\hat{\mathbf{v}}_1 = \mathbf{j}_1/\rho$ at $z = 0$, and, since $\rho_1 \to 0$ as $z \to L$, $\hat{\mathbf{v}}_1 \to \infty$ as $z \to L$. If the diffusion velocity $\hat{\mathbf{v}}_1$ were a relevant physical velocity we would be surprised and concerned by such behavior. In a continuum model, however, $\hat{\mathbf{v}}_1$ is an artificial velocity defined by equation (2), in what may be viewed as a flow model of ordinary diffusion. Only the product $\rho_1\hat{\mathbf{v}}_1 = \mathbf{j}_1$ has physical significance.

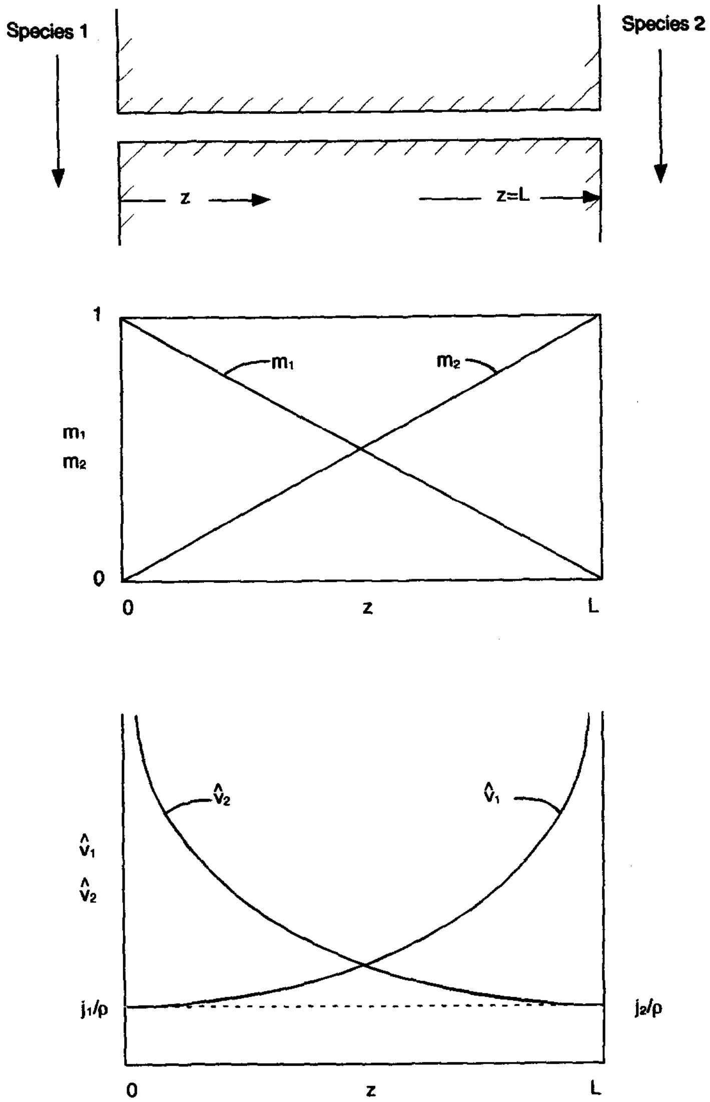

Fig. 1. Steady one-dimensional interdiffusion of two species with equal molecular weights.

The diffusion velocity can be very large in many familiar physical situations. For example, consider oxidation of solid carbon by oxygen to form carbon monoxide. At sufficiently high temperatures, the reaction is diffusion controlled and chemical equilibrium data indicate that the partial density of oxygen adjacent to the carbon, $\rho_{O_2,s}$, is very small. The diffusion flux of oxygen to the surface is finite; thus, $\hat{v}_{O_2,s} = j_{O_2,s}/\rho_{O_2,s}$ is very large. Similar situations occur in most diffusion-controlled reactions: the flux of reactant to the surface is finite but the diffusion velocity at surface is very large.

2.2. *Molecular model of ordinary diffusion*

In anticipation of dealing with kinetic theory models, consider the molecular equivalent of equation (1). Mass and molecule average velocities are equal for equal molecular weights, thus we can write

$$\mathscr{J}_1 = -\mathcal{N}\mathscr{D}_{12}\nabla n_1. \tag{4}$$

Also, dividing equation (2) by the mass of a molecule gives

$$\mathscr{J}_1 = \mathcal{N}_1\hat{\mathbf{v}}_1. \tag{5}$$

On a molecular level, the behavior of $\hat{\mathbf{v}}_1$ in Fig. 1 is simply explained. As $\mathcal{N}_1$ decreases, the number of 'carriers' for the constant diffusion flux $\mathscr{J}_1$ decreases: hence the diffusion velocity associated with these molecules must increase.

A molecular equivalent of the situation depicted in Fig. 1 was investigated by G. A. Bird using the direct simulation Monte Carlo (DSMC) method [1]. The purpose was to calculate the self-diffusion coefficient of argon. Identical argon molecules were designated species 1 and 2. The number density was $\mathcal{N} = 1.4\times10^{20}$ m^{-3} and temperature $T = 273$ K

($P \cong 1/20\,000$ atm). A plane layer 1 m thick was considered with pure species 1 adjacent to the plane at $z = 0$, and pure species 2 adjacent to the plane at $z = L = 1$ m. The initial condition was $\mathcal{N}_1 = \mathcal{N}_2 = 0.5$ and the steady state solution obtained is shown in Fig. 2. Concentration 'jumps' are in evidence at $z = 0$ and $z = 1$ m due to the low pressure ($Kn \simeq 0.02$). The diffusion velocities were calculated by sampling and averaging: values of 160 m s^{-1} are seen as $z \to 0$ and $z \to 1$ m for $\hat{\mathbf{v}}_2$ and $\hat{\mathbf{v}}_1$, respectively.

But what is the relevance of these diffusion velocities? The argon molecules are in random motion characterized by the average molecular speed $\bar{c} = (8RT/\pi)^{1/2}$. Ordinary diffusion is a net flux of molecules that occurs when there is a concentration gradient: at any plane $z =$ constant there are more molecules of species 1 crossing from left to right than from right to left. This flux is constant and independent of the local number fraction of species, n_1; it depends only on the gradient of n_1. The diffusion velocity $\hat{\mathbf{v}}_1 = \mathcal{J}_1/\mathcal{N}n_1$ increases with z as n_1 decreases, but the intrinsic thermal molecular motion does not change. All the molecules are identical and the gas is in equilibrium. The mixture as a whole has a Maxwellian velocity distribution that does not vary with z. The diffusion velocities are non-zero because they belong to subsets of molecules that, on an average, happen

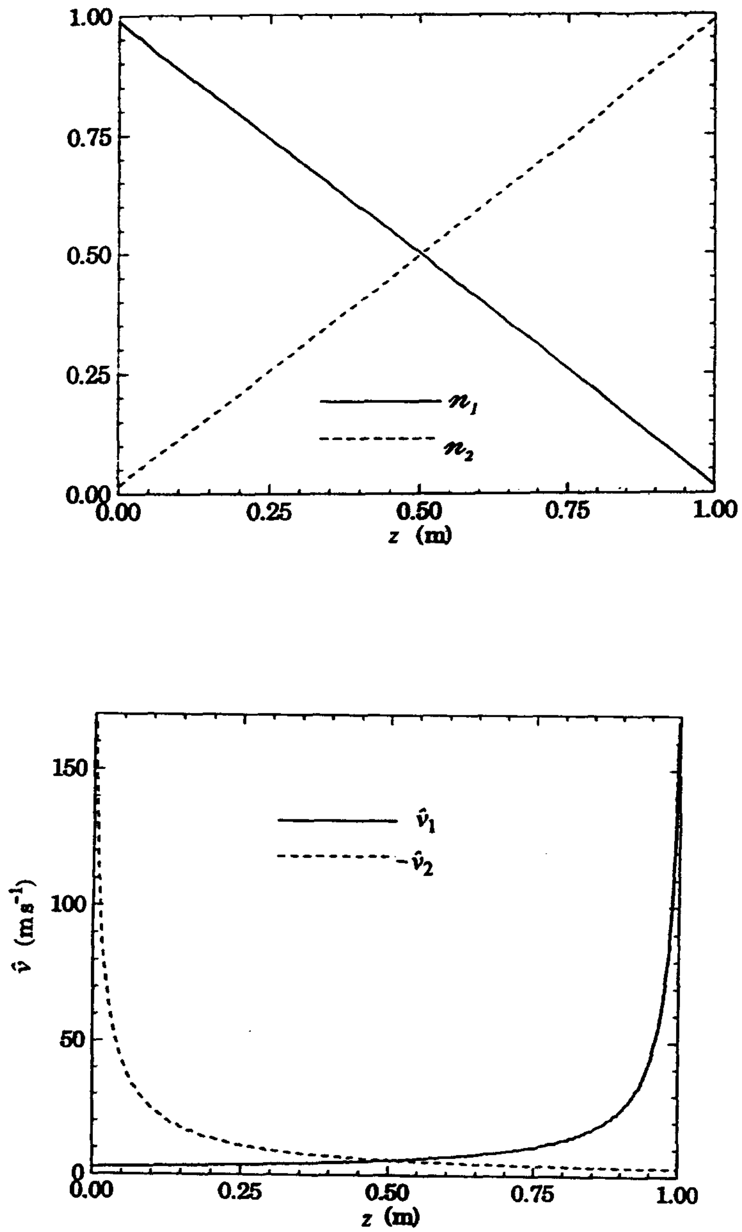

Fig. 2. Self-diffusion of argon: results of G. A. Bird's DSMC calculations.

to be moving from left to right (species 1) or right to left (species 2). As a consequence there can be no pressure or kinetic energy associated with the diffusion velocities that is not already accounted for in the thermodynamic pressure and internal energy. In Section 3 we will return to this issue.

2.3. *Forced diffusion*

As an example, consider an electric field applied to an ionized gas. Negatively charged electrons diffuse to the anode while the positively charged ions migrate to the cathode. The molecular flux of a singly-ionized species is

$$\mathscr{J}_i^{*F} = \mu_i E n_i \tag{6}$$

where E is the electric field strength or voltage gradient, and μ_i is the mobility of species i. The Nernst–Einstein equation is used to relate mobility to the effective binary diffusion coefficient,

$$\mu_i = \frac{e\mathscr{D}_{im}}{kT} \tag{7}$$

Notice that $\mu_i E$ has the units of velocity and is the forced diffusion, or cataphoretic velocity, $\hat{\mathbf{v}}_i^{\mathrm{FD}}$. It is a 'drift' velocity that can be assigned to all the molecules of species i as an average over an appropriate time scale. It is not a component of the thermal velocity of the molecules. The forced diffusion velocity can be very large: for example, cadmium ions in a helium-calmium laser have a forced diffusion velocity of $\sim 3000\ \mathrm{m\,s^{-1}}$. There are momentum fluxes and kinetic energy associated with the forced diffusion velocity that are not accounted for in the thermodynamic pressure and internal energy.

In contrast, the diffusion velocity for ordinary diffusion cannot be assigned as a 'drift' velocity to the molecules: if this is done, a simple mean-free-path kinetic theory argument will show that ordinary diffusion would be accounted for twice.

3. ADVANCED KINETIC THEORY MODELS

In kinetic theory the Boltzmann equation describes the change of the velocity distribution function f. It is common practice to derive the transport equation (or equation of change, or conservation equation) for a molecular property ϕ from the Boltzmann equation. In the literature we find two distinct formulations of transport equations. One is due to Chapman and Cowling [2], and is also presented by Hirschfelder, Curtiss and Bird [3] and Williams [4]. The other is due to Woods [5, 6]. Both formulations commence by defining the linear velocity v_i of a molecule of species i. The absolute velocity of species i, present at number density $\mathcal{N}_i$, is defined as

$$\mathbf{v}_i = \frac{1}{\mathcal{N}_i}\int v_i f_i \,\mathrm{d}v_i \tag{8}$$

where $f_i(\mathbf{r}_i, v_i, t)$ is the velocity distribution function of species i. The mass average velocity is then defined as

$$\mathbf{v} = \frac{1}{\rho}\sum_i \mathcal{N}_i m_i \mathbf{v}_i. \tag{9}$$

The diffusion velocity of species i with respect to the mass average velocity is

$$\hat{\mathbf{v}}_i = \mathbf{v}_i - \mathbf{v}. \tag{10}$$

The molecule peculiar velocity is defined in two ways. Chapman and Cowling (CC) define it relative to mass average velocity,

$$\mathbf{C}_i = v_i - \mathbf{v}. \tag{11}$$

Woods (W) defines it relative to the absolute velocity of the species,

$$\mathbf{c}_i = v_i - \mathbf{v}_i. \tag{12}$$

For a single component gas we set $\phi = m$, $m\mathbf{C}$ and $\frac{1}{2}mC^2$ to obtain transport equations for mass, momentum and energy. In the CC formulation for a gas mixture we set $f = f_i$ and $\phi = m_i$, $m_i\mathbf{C}_i$ and $\frac{1}{2}m_iC_i^2$ to give transport equations for each species. These sets of equations are immediately summed to give transport equations for the mixture. In the W formulation we set $\phi = m_i$, $m_i\mathbf{c}_i$ and $\frac{1}{2}m_ic_i^2$ to obtain transport equations for each species. These equations are then manipulated before summing to give transport equations for the mixture. The difference in the formulations is in the choice of definition of the peculiar velocity: the two definitions are related as:

$$\mathbf{C}_i = \mathbf{c}_i + \hat{\mathbf{v}}_i. \tag{13}$$

Both formulations give the same species equations; the differences arise in the momentum and energy equations. To explain the difference we will look at the energy of the mixture. We subtract the kinetic energy associated with the mass average velocity, namely $\frac{1}{2}\rho v^2$, and examine the W formulation treatment of the remaining energy. Woods defines a mixture energy of a purely thermodynamic nature for monatomic molecules as

$$\rho u^{\mathrm{W}} = \sum_i \rho_i u_i^{\mathrm{W}} = \sum_i \frac{1}{2}\rho_i\overline{c_i^2} \tag{14}$$

and a mixture energy relative to the mass average velocity (as used in the CC formulation)

$$\rho u^{\mathrm{CC}} = \sum_i \frac{1}{2}\rho_i\overline{C_i^2}. \tag{15}$$

Using $\mathbf{C}_i = \mathbf{c}_i + \hat{\mathbf{v}}_i$ we obtain

$$\rho u^{\mathrm{CC}} = \rho u^{\mathrm{W}} + \sum_i \frac{1}{2}\rho_i\hat{v}_i^2 = \rho u^{\mathrm{W}} + \mathrm{K.E.}^{\mathrm{D}} \tag{16}$$

where $\mathrm{K.E.}^{\mathrm{D}} = \Sigma_i \frac{1}{2}\rho_i\hat{v}_i^2$ is the kinetic energy associated with the diffusion velocities. Woods goes on to state ([5] p. 79), "It is usual to take ρu^{CC} as defining the energy density, but as will be explained later (Sections 23.5, 53.2), in process thermodynamics this mixing together of energy due to purely random motions and energy due to the often controllable relative fluid velocities is sometimes unsatisfactory." To examine this statement by Woods let us return to G. A. Bird's argon self-diffusion problem of Section 2.2.

The mixture of molecules 1 and 2 is a stationary pure gas in thermodynamic equilibrium. The internal energy is

$$\rho u = \sum_i \frac{1}{2}\rho_i \overline{C_i^2} = \rho u^{\mathrm{CC}} \tag{17}$$

and is uniform $0 < z < L$. That is, the thermodynamic internal energy is identified as the kinetic energy of the monatomic molecules, which have a Maxwellian velocity distribution that is associated with the thermal agitation of the molecules. Also from equations (15) and (16)

$$\rho u^{\mathrm{CC}} = \sum_i \frac{1}{2}\rho_i \overline{c_i^2} + \sum_i \frac{1}{2}\rho_i \hat{v}_i^2 = \rho u^{\mathrm{W}} + \mathrm{K.E.}^{\mathrm{D}} \tag{18}$$

There is clearly no extra energy associated with ordinary diffusion; the $\mathrm{K.E.}^{\mathrm{D}}$ is portion of the thermodynamic internal energy of the gas. The subdivision of internal energy in equation (18) is unnecessary; it is also troublesome because $\mathrm{K.E.}^{\mathrm{D}} \to \infty$ as $\rho_i \to 0$, and ρu^{W} has no physical meaning except as the difference between ρu and $\mathrm{K.E.}^{\mathrm{D}}$. Similar considerations apply to the pressure. The diffusion pressure is defined as

$$P^{\mathrm{D}} = \frac{1}{3}\sum_i \rho_i \hat{v}_i^2 \tag{19}$$

but is simply a portion of the thermodynamic pressure. There is no extra pressure associated with ordinary diffusion.

A quite different situation is obtained when we consider forced diffusion. Equation (6) defines a forced diffusion velocity $\hat{\mathbf{v}}_i^{\mathrm{FD}} = \mu_i \mathbf{E}$ for an electric field applied to an ionized gas, and this velocity is a 'drift' velocity possessed by all molecules of species 1. In situations where forced diffusion is the only diffusion mechanism of concern, the subdivision of internal energy in equation (16) is useful if the kinetic energy of diffusion is defined for forced diffusion only,

$$\mathrm{K.E.}^{\mathrm{D}} = \Sigma \tfrac{1}{2}\rho_i \hat{v}_i^{\mathrm{FD}^2}. \tag{20}$$

This issue will be returned to in Section 5.2.

The important point is that the ordinary diffusion velocity and forced diffusion velocity are essentially different physical quantities. No problems are encountered when these velocities are added in the species conservation equation (because, in fact, it is diffusion fluxes that are added). On the other hand, a number of difficulties arise if we attempt to add these velocities in deriving momentum and energy conservation equations, since quadratic terms in diffusion velocity are obtained. This issue is discussed in Section 4.

4. COEXISTING-CONTINUA MODELS OF GAS MIXTURES

Currently used continuum derivations of the conservation equations for a multicomponent chemically reacting gas mixture are based on models that imagine the components of the mixture to be coexisting continua. Thus all components (species) can simultaneously exist at each space point. Each component is taken to have a partial density ρ_i, velocity vector $\mathbf{v}_i$, partial pressure $\tilde{P}_i$ and internal energy $\tilde{u}_i$. The tilde overscore indicates a property that will generally prove to be different to its pure fluid counterpart. Some authors, e.g. Woods [6] derive conservation equations for each component separately, including terms that account for interactions between continua. These equations are then manipulated and summed to obtain 'one-fluid' equations, i.e., conservation equations for the mixture. Other authors, e.g., Williams [4] immediately write down conservation equations for the mixture to avoid specification of all the interaction terms. The presentation that follows is similar to that of Woods, but there are significant differences. Only pertinent results will be given here: for more complete derivations the reader is referred to Woods [6] or Williams [4].

4.1. *Species and mass conservation*

In this derivation and the derivations that follow, the conservation principle will be stated for a control volume V, and followed by the resulting differential equation.

Conservation of species i requires that the time rate of storage of species i within V plus the net rate of outflow across the boundary surface S equal the production rate of species i within V due to chemical reactions. Hence,

$$\frac{\partial \rho_i}{\partial t} + \nabla \cdot \rho_i \mathbf{v}_i = \dot{r}_i. \tag{21}$$

Writing the absolute velocity $\mathbf{v}_i$ as the sum of the mass average velocity $\mathbf{v}$ and diffusion velocity $\hat{\mathbf{v}}_i$, and introducing the diffusion flux $\mathbf{j}_i = \rho_i \hat{\mathbf{v}}_i$ gives

$$\frac{\partial \rho_i}{\partial t} + \nabla \cdot (\rho_i \mathbf{v}) = -\nabla \cdot \mathbf{j}_i + \dot{r}_i. \tag{22}$$

Defining a_{ij} [kg m^{-2} s] as the total rate at which continuum i gains mass from continuum j due to one or more chemical reactions (or ionization processes) and introducing the substantial derivative gives the alternative form,

$$\frac{D\rho_i}{Dt} + \rho_i \nabla \cdot \mathbf{v} = -\nabla \cdot \mathbf{j}_i + \sum_j (a_{ij} - a_{ji}). \tag{23}$$

Summing over all species gives the mass conservation equation as

$$\frac{\partial \rho}{\partial t}+\nabla\cdot\rho\mathbf{v}=0. \tag{24}$$

4.2. *Momentum conservation*

The stress tensor for continuum i is defined as

$$\tilde{\sigma}_i=-\tilde{P}_i I+\tilde{\tau}_i \tag{25}$$

where $\tilde{\tau}_i$ is the viscous stress in continuum i. The interaction forces between continua are viewed as producing a net body force, and it is written as $\rho_i\zeta_i$, where ζ_i is the friction force per unit mass of species i resulting from the relative motion of all other species past species i. We shall write

$$\rho_i\zeta_i=\sum_j \zeta_{ij} \quad (i\neq j) \tag{26}$$

where ζ_{ij} is the force acting on species i due to species j, per unit volume.

Newton's second law of motion applied to continuum i requires that the rate of change of momentum of the fluid within the volume plus the net rate of outflow of momentum equal the sum of the surface integral of the stress vector, the volume integral of the net volume forces, and the volume integral of the net rate of change of momentum associated with production of species i; hence the continuum momentum equation is

$$\frac{\partial}{\partial t}(\rho_i\mathbf{v}_i)+\nabla\cdot\rho_i\mathbf{v}_i\mathbf{v}_i=\nabla\cdot\tilde{\sigma}_i+\rho_i(\mathbf{f}_i+\zeta_i)+\sum_j(a_{ij}\mathbf{v}_j-a_{ji}\mathbf{v}_i). \tag{27}$$

Using the species conservation equation, an alternative form is derived as

$$\rho_i\frac{D_i}{Dt}\mathbf{v}_i=\nabla\cdot\tilde{\sigma}_i+\rho_i(\mathbf{f}_i+\zeta_i)+\sum_j a_{ij}(\mathbf{v}_j-\mathbf{v}_i) \tag{28}$$

where

$$\frac{D_i}{Dt}\equiv\frac{\partial}{\partial t}+\mathbf{v}_i\cdot\nabla.$$

Summing equation (27) over all species gives the mixture momentum conservation equation. The net rate of production of momentum due to all reactions is zero, and the sum of the interaction forces between continua add to zero by Newton's third law of motion. From equation (25)

$$\sum_i\nabla\cdot\tilde{\sigma}_i=-\nabla\tilde{P}+\nabla\cdot\tilde{\tau}$$

where a prescription for the mixture viscosity is implied in writing $\tilde{\tau}=\Sigma_i\tilde{\tau}_i$. Then the result of the summation is

$$\frac{\partial}{\partial t}\sum_i\rho_i\mathbf{v}_i+\nabla\cdot\sum_i\rho_i\mathbf{v}_i\mathbf{v}_i=-\nabla\tilde{P}+\nabla\cdot\tilde{\tau}+\sum_i\rho_i\mathbf{f}_i. \tag{29}$$

Introducing $\mathbf{v}_i=\mathbf{v}+\hat{\mathbf{v}}_i$ and using the mass conservation equation with the relation $\Sigma_i\rho_i\hat{\mathbf{v}}=\Sigma_i\mathbf{j}_i=0$, allows equation (29) to be rewritten as

$$\rho\frac{D\mathbf{v}}{Dt}+\nabla\cdot\sum_i\rho_i\hat{\mathbf{v}}_i\hat{\mathbf{v}}_i=-\nabla\tilde{P}+\nabla\cdot\tilde{\tau}+\Sigma\rho_i\mathbf{f}_i. \tag{30}$$

Defining the diffusion stress tensor $\tau^{\mathrm{D}}=-\Sigma_i\rho_i\hat{\mathbf{v}}_i\hat{\mathbf{v}}_i$, equation (30) becomes

$$\rho\frac{D\mathbf{v}}{Dt}=-\nabla\tilde{P}+\nabla\cdot[\tilde{\tau}+\tau^{\mathrm{D}}]+\Sigma\rho_i\mathbf{f}_i. \tag{31}$$

Notice that the diagonal components of the diffusion stress tensor give rise to the diffusion pressure.

$$P^{\mathrm{D}}=\frac{1}{3}\sum_i\rho_i\hat{v}_i^2. \tag{32}$$

4.3. *Energy conservation*

The first law of thermodynamics applied to continuum i requires that the rate at which energy accumulates in the control volume equal the net inflow of energy across the boundary, plus heat transfer across the boundary, plus the work done on the continuum by pressure, viscous stresses and volume forces, plus energy added due to production of species i plus energy added due to a difference in temperatures $\tilde{T}_i$ and $\tilde{T}_j$, plus dissipation heat generated by the interaction stresses, plus flow work required to introduce newly produced species i into the continuum, plus other internally produced energy. The resulting total energy conservation equation is

$$\begin{aligned}\frac{\partial}{\partial t}\rho_i\left(\tilde{u}_i+\frac{1}{2}v_i^2\right)+\nabla\cdot\rho_i\left(\tilde{u}_i+\frac{1}{2}v_i^2\right)\mathbf{v}_i\\ =-\nabla\cdot\tilde{\mathbf{q}}_i+\nabla\cdot[\mathbf{v}_i\cdot\tilde{\sigma}_i]+\rho_i\mathbf{v}_i(\mathbf{f}_i+\zeta_i)\\ +\sum_j\left[\phi_{ij}+\xi_{ij}+a_{ij}\left(\tilde{u}_j+\frac{\tilde{P}_j}{\rho_j}+\frac{1}{2}v_j^2\right)\right.\\ \left.-a_{ji}\left(\tilde{u}_i+\frac{\tilde{P}_i}{\rho_i}+\frac{1}{2}v_i^2\right)\right]+\dot{Q}_{Vi}\end{aligned} \tag{33}$$

where $\tilde{\mathbf{q}}_i$ is a contribution to conduction and diffusional conduction (Dufour effect) by the continuum i, ϕ_{ij} is the rate at which energy is accumulated in continuum i if $\tilde{T}_i\neq\tilde{T}_j$, and ξ_{ij} is the rate of energy dissipation due to the interaction stresses.

As was done for the momentum equation, the species conservation equation can be used to obtain the alternative form

$$\begin{aligned}\rho_i\frac{D_i}{Dt}\left(u_i+\frac{1}{2}v_i^2\right)=-\nabla\cdot\tilde{\mathbf{q}}_i+\nabla\cdot[\mathbf{v}_i\cdot\tilde{\sigma}_i]\\ +\rho_i\mathbf{v}_i\cdot(\mathbf{f}_i+\zeta_i)+\sum_j\left[\phi_{ij}+\xi_{ij}+a_{ij}\left(\tilde{u}_j+\frac{\tilde{P}_j}{\rho_j}+\frac{1}{2}v_j^2\right.\right.\\ \left.\left.-\tilde{u}_i-\frac{1}{2}v_i^2\right)-a_{ji}\frac{\tilde{P}_i}{\rho_i}\right]+\dot{Q}_{Vi}.\end{aligned} \tag{34}$$

Consistent with the postulate that continuum i has a velocity $\mathbf{v}_i$, we form its mechanical energy equation by taking the scalar product of $\mathbf{v}_i$ with equation (28),

$$\rho_i \frac{D_i}{Dt}\left(\frac{1}{2}v_i^2\right) = \mathbf{v}_i \cdot [\nabla \cdot \tilde{\sigma}_i] + \rho_i \mathbf{v}_i \cdot (\mathbf{f}_i + \zeta_i) + \sum_j a_{ij}(\mathbf{v}_i \cdot \mathbf{v}_j - v_i^2). \quad (35)$$

Subtracting equation (35) from equation (34) gives

$$\rho_i \left[\frac{D_i}{Dt}\tilde{u}_i + \tilde{P}_i \frac{D_i}{Dt}\left(\frac{1}{\rho_i}\right)\right] = -\nabla \cdot \tilde{\mathbf{q}}_i - \tilde{\tau}_i \cdot \nabla \mathbf{v}_i + \sum_j \left\{\phi_{ij} + \xi_{ij} + a_{ij}\left[\tilde{u}_j + \frac{\tilde{P}_j}{\rho_j} - \left(\tilde{u}_i + \frac{\tilde{P}_i}{\rho_i}\right) + \frac{1}{2}(\mathbf{v}_j - \mathbf{v}_i)^2\right]\right\} + \dot{Q}_{Vi} \quad (36)$$

which in analogy to a pure fluid we will term a 'thermal' energy equation. Notice that there are no work terms in this energy equation; the work term $\rho_i \mathbf{v}_i(\mathbf{f}_i + \zeta_i)$ in the total energy equation gets subtracted out by the corresponding term in the mechanical energy equation.

Mixture energy equations are useful only when all the continua are in thermal equilibrium, that is $\tilde{T}_i = \tilde{T}_j$ for all i; then, from its definition, $\phi_{ij} = 0$. In summing equation (33) over all species, the work done by and dissipation due to the continua interaction forces sum to zero, as do the reaction terms. Then, with $\dot{Q}_V = \Sigma \dot{Q}_{Vi}$ and $\Sigma \tilde{\mathbf{q}}_i = \tilde{\mathbf{q}}^{\mathrm{C}} + \tilde{\mathbf{q}}^{\mathrm{DC}}$ the result is

$$\begin{aligned}
&\frac{\partial}{\partial t}\left[\rho\left(\tilde{u} + \frac{1}{2}v^2 + \sum_i \frac{1}{2}m_i \hat{v}_i^2\right)\right] \\
&\quad + \nabla \cdot \rho\left(\tilde{u} + \frac{1}{2}v^2 + \sum_i \frac{1}{2}m_i \hat{v}_i^2\right)\mathbf{v} + \nabla \cdot \sum_i \mathbf{j}_i \tilde{u}_i \\
&\quad + \nabla \cdot \rho\left(\sum_i \frac{1}{2}m_i \hat{v}_i^2 \hat{\mathbf{v}}_i\right) + \nabla \cdot \rho \sum_i m_i(\mathbf{v} \cdot \hat{\mathbf{v}}_i)\hat{\mathbf{v}}_i \\
&= -\nabla \cdot (\tilde{\mathbf{q}}^{\mathrm{C}} + \tilde{\mathbf{q}}^{\mathrm{DC}}) + \nabla \cdot \tilde{P}\mathbf{v} + \nabla \cdot [\mathbf{v} \cdot \tilde{\tau}] + \nabla \cdot \sum_i \hat{\mathbf{v}}_i \tilde{P}_i \\
&\quad + \nabla \cdot \left[\sum_i \hat{\mathbf{v}}_i \cdot \tilde{\tau}_i\right] + \rho \mathbf{v} \cdot \mathbf{f} + \sum_i \mathbf{j}_i \cdot \mathbf{f}_i + \dot{Q}_V. \qquad (37)
\end{aligned}$$

Using the mass conservation equation and introducing the substantial derivative gives

$$\begin{aligned}
&\rho \frac{D}{Dt}\left(\tilde{u} + \frac{1}{2}v^2 + \sum_i \frac{1}{2}m_i \hat{v}_i^2\right) + \nabla \cdot \rho \sum_i m_i(\mathbf{v} \cdot \hat{\mathbf{v}}_i)\hat{\mathbf{v}}_i \\
&= \nabla \cdot (\tilde{\mathbf{q}}^{\mathrm{C}} + \tilde{\mathbf{q}}^{\mathrm{DC}}) - \nabla \cdot \sum_i \mathbf{j}_i u_i - \nabla \cdot \sum_i \hat{\mathbf{v}}_i \tilde{P}_i \\
&\quad - \nabla \cdot \rho\left(\sum_i \frac{1}{2}m_i \hat{v}_i^2 \hat{\mathbf{v}}_i\right) + \nabla \cdot \tilde{P}\mathbf{v} + \nabla \cdot [\mathbf{v} \cdot \tilde{\tau}] \\
&\quad + \nabla \cdot [\Sigma \hat{\mathbf{v}}_i \cdot \tilde{\tau}_i] + \rho \mathbf{v} \cdot \mathbf{f} + \sum_i \mathbf{j}_i \cdot \mathbf{f}_i + \dot{Q}_V. \qquad (38)
\end{aligned}$$

A mixture 'thermal' energy equation is obtained by summing the continua thermal energy equations, equation (36). The result is

$$\rho \frac{D\tilde{u}}{Dt} = -\tilde{P}\nabla \cdot \mathbf{v} - \nabla \cdot (\tilde{\mathbf{q}}^{\mathrm{C}} + \tilde{\mathbf{q}}^{\mathrm{DC}}) - \nabla \cdot \left(\sum_i \mathbf{j}_i \tilde{u}_i\right) - \sum_i \tilde{P}_i \nabla \cdot \hat{\mathbf{v}}_i + \tilde{\mu}\Phi + \tilde{\mu}\Phi^{\mathrm{D}} + \dot{Q}_V. \quad (39)$$

where $\tilde{\mu}\Phi = -\tau \cdot \nabla \mathbf{v}$ and $\tilde{\mu}\Phi^{\mathrm{D}} = -\Sigma_i \tau_i \cdot \nabla \hat{\mathbf{v}}_i$.

4.4. *Evaluation of the coexisting-continua model*

The momentum and energy conservation equations derived using coexisting-continua models have a number of serious shortcomings. Three issues of particular concern are as follows:

(1) The equations are obtained in terms of partial properties that do not have their usual meaning for pure fluids.
(2) The total energy equations are unwieldy due to the large number of terms related to the kinetic energy of diffusion.
(3) The 'thermal' energy equation does not express conservation of all the thermal energy of the mixture.

These issues will now be discussed in turn.

4.4.1. *Partial properties.* For example, consider the derivation of the energy conservation equation in which the total energy of the continuum is taken to be the sum of an 'internal' energy $\tilde{u}_i$ and kinetic energy $\frac{1}{2}\rho_i v_i^2$. The mixture total energy is then

$$e = \sum_i e_i = \sum_i \rho_i\left(\tilde{u}_i + \frac{1}{2}v_i^2\right). \quad (40)$$

But $\mathbf{v}_i = \mathbf{v} + \hat{\mathbf{v}}_i$, and $\Sigma_i \rho_i \hat{\mathbf{v}}_i = \Sigma_i \mathbf{j}_i = 0$. Hence

$$e = \Sigma \rho_i \tilde{u}_i + \tfrac{1}{2}\rho v^2 + \tfrac{1}{2}\Sigma \rho_i \hat{v}_i^2. \quad (41)$$

The last term is the kinetic energy of diffusion that was discussed in Section 3. Thus, in terms of the kinetic theory model of a gas mixture and equation (14),

$$\tilde{u}_i = u_i^{\mathrm{W}} = \tfrac{1}{2}\rho_i \overline{c_i^2} \quad (42)$$

where $\mathbf{c}_i$ is the peculiar velocity relative to the species absolute velocity. As was discussed in Section 3, u_i^{W} is not the usual thermodynamic (equilibrium) species internal energy; portion has been subtracted out as kinetic energy of diffusion.

Similar considerations apply to other properties. The partial pressure $\tilde{P}_i$ is not the thermodynamic pressure because portion has been subtracted out as a contribution to the diffusion pressure. The viscous stress tensor $\tilde{\tau}_i$ does not sum to the usual mixture counterpart; a portion is missing because it is included in the diffusion velocity terms.

Of perhaps greater concern is that the partial properties cannot be identified without a term by term comparison of the resulting conservation equations with the corresponding equations obtained from kinetic theory, as was done by Williams [4]. The coexisting-continua model is, in a sense, redundant since it adds nothing new. There is little meaning to the statement by Williams [4] that there is an 'equivalence of the continuum theory and kinetic theory results.'

4.4.2. *The total energy equations.* The issue here is that the numerous diffusion velocity terms need not be separated out in most applications; as will be demonstrated in Section 5.1. Also, these terms are often physically meaningless.

4.4.3. *The 'thermal' energy equation.* In the preceding development a continuum mechanical energy equation, equation (35), was obtained that was consistent with the postulate of a continuum velocity $\mathbf{v}_i$. A continuum 'thermal' energy equation, equation (39), was obtained in the usual way for pure fluids by subtracting the mechanical energy equation from the total energy equation. The mixture 'thermal' energy equation (39), was then obtained by summation. The problem with equation (39) is that it does not express conservation of all the thermal energy of the mixture. A portion has been associated with ordinary diffusion and subtracted out by including it in the kinetic energy of each continuum. Thus equation (39) has a rather obscure physical meaning, and it is doubtful if it is of any practical use.

4.5. *Comments on relevant literature*

It is fair to say that the literature on coexisting-continua models and their use contains much that is confusing and difficult to reconcile with a consistent theory. Some examples follow.

4.5.1. *L. Lees* [7]. In his seminal paper on boundary layers with mass transfer, Lees presents a scaling of the diffusion stresses for a boundary-layer flow by comparing τ_{xy}^{D} to the "ordinary stress" $\mu \partial u/\partial y$: this ratio is found to be order $1/Re_{\mathrm{L}}\, Sc^2$, where L is a characteristic length in the flow direction, and hence τ_{xy}^{D} is negligible in boundary layers. He also states that the ratio of the kinetic energy of diffusion to the 'complete enthalpy' is of the same order. In a footnote he states that Baron [8] does not make it clear that the diffusion stress tensor exists whenever concentration gradients exist in a mixture. It appears that Lees regarded diffusion stresses and kinetic energy of diffusion as additions to the usual stresses and internal energy. In his analysis, which considered only ordinary diffusion, his scaling was unnecessary since his use of the 'usual' stress tensor and internal energy is exact.

4.5.2. *S. S. Penner* [9]. In his monograph *Chemical Reactions in Flow Systems*, Penner presents momentum and energy conservation equations that he attributes to von Karman. The stress terms in his momentum equation are $\nabla \cdot (\tau^{\mathrm{v}} + \tau^{\mathrm{D}})$, where the 'viscous stress tensor' τ^{v} is defined in terms of velocity gradients in the usual way. His energy equation is written in terms of $u + \mathrm{K.E.}^{\mathrm{D}}$ where u is the 'specific internal energy of the gas mixture'. Like Lees, it is clear that Penner regarded the diffusion stresses and kinetic energy of diffusion as additions to the usual viscous stresses and internal energy, even though his only real concern was with ordinary diffusion.

4.5.3. *F. A. Williams* [4]. In his text on combustion theory, Williams presents a detailed derivation of the conservation equations using a coexisting-continua model. By comparing his results with Chapman–Enskog kinetic theory definitions of stresses, energy and heat flux, he identifies the various continuum partial properties that were defined for his model. (As was done in Section 4.4.1 for the kinetic energy of diffusion.) However, he does not examine the utility of his equations with respect to ordinary diffusion on one hand and forced diffusion on the other. For example, he concludes his discussion of the diffusion terms with the statement, "therefore, it has not been fruitful to study the diffusion terms which, in a sense, may be viewed as artifacts of the continuum approach." If ordinary diffusion is of concern, as is the case in combustion theory, these terms are, indeed, artifacts as has been demonstrated in Section 4.4. However, if forced diffusion is a concern, then the diffusion terms associated with forced diffusion are distinct momentum fluxes and energy that should be kept separate from those associated with the thermal motion of molecules. In situations where these terms cannot be neglected they must be kept separate if the equations are to have practical utility. Indeed, it can be said that not having separate terms for forced diffusion is an artifact of the Chapman–Enskog kinetic theory resulting from the definition of peculiar velocity employed.

A related and troublesome issue concerns the 'thermal' energy equation. The derivation given by Williams differs from that given in Section 4.3. Williams does not actually write down continuum momentum and total energy equations. Rather, he immediately writes down mixture momentum and total energy equations in terms of summations where appropriate. In this way he avoids having to specify continua interaction terms that sum to zero. Then, in order to obtain a mixture 'thermal' energy equation, he forms the scalar product of the mass average velocity and the mixture momentum equation and subtracts the results from the mixture total energy equation. His result is

$$\rho \frac{Du}{Dt} = P \nabla \cdot \mathbf{v} - \nabla \cdot \mathbf{q} + \tau : \nabla \mathbf{v} + \Sigma \mathbf{j}_i \cdot \mathbf{f}_i \qquad (43)$$

where u, P, q and τ are defined following Chapman–Enskog kinetic theory. At first sight this equation is more satisfactory than the form derived as equation (39) in Section 4.3, because all the energy associated with the thermal motion of the molecules is contained in this equation: the portion associated with ordinary diffusion has not been subtracted out. As will be shown later, this equation is appropriate if species dependent external forces are absent. In general, however, equation (43) is unsatisfactory because it also contains total energy conservation associated with forced diffusion; in particular it contains a work term $\Sigma \mathbf{j}_i \cdot \mathbf{f}_i$. We do not see work terms in the thermal energy equation for a pure fluid because mechanical work can only affect thermal energy via a reversible heating by compression, or by an irreversible viscous dissipation. Bird, Stewart and Lightfoot [10] have a clear presentation of these issues for a pure fluid. The source of the work term is as follows. In the total energy equation the work done by external forces is $\Sigma \rho_i \mathbf{f}_i \cdot \mathbf{v}_i$; however, in taking the scalar product of the mass average velocity and the mixture momentum equation the term $\mathbf{v} \cdot \Sigma \rho_i \mathbf{f}_i$ is obtained. Clearly the latter term is not the true work because the point of application of $\mathbf{f}_i$ does not follow $\mathbf{v}$. The difference of the two terms appears as a residual in the Williams thermal-energy equation.

Of course, the Williams equation is mathematically correct; but the relevant issues are whether it is physically meaningful and of practical use. Actually, a 'thermal' energy equation of similar form is also given in most kinetic theory derivations of the conservation equations from the Boltzmann equation, for example, by Hirschfelder, Curtiss and Bird [3], as will be discussed in Section 4.5.9.

4.5.4. *de Groot and Mazur* [11]. In their treatise on nonequilibrium thermodynamics, these authors define the internal energy of a mixture as the total energy minus the barycentric kinetic energy (ignoring the potential energy that they included). Since

$$e = \tilde{u} + \Sigma \tfrac{1}{2} m_i v_i^2 = \tilde{u} + \tfrac{1}{2} v^2 + \Sigma \tfrac{1}{2} m_i \hat{v}_i^2$$

their internal energy, denoted u^+ here, is

$$u^+ = \tilde{u} + \Sigma \tfrac{1}{2} m_i \hat{v}_i^2 \tag{44}$$

Then, referring to their Section 3.4, equation (32), they define a 'different' internal energy u^*

$$u^* = u^+ - \Sigma \tfrac{1}{2} m_i \hat{v}_i^2 = \tilde{u}. \tag{45}$$

They state "since the internal energy should only contain contributions from thermal agitation and the short range molecular interactions, the quantity u^* has perhaps more right to this name than the quantity u^+" and note that the Gibbs relation is in terms of u^*. However, as demonstrated in Section 4.4.1, $u^* = \tilde{u}$ is missing a portion of the thermal internal energy that was artificially separated out as a kinetic energy of ordinary diffusion in using a coexisting-continua formulation. As a result, the validity of the ensuing development of the entropy balance equation is suspect.

4.5.5. *Truesdell and Noll* [12]. These authors employ continuum partial properties. A partial stress $\tilde{\sigma}_i$ is defined, and their equation (215.1) gives the 'total' stress as

$$\sigma = \sum_i \tilde{\sigma}_i + \tau^{\mathrm{D}}. \tag{46}$$

Similarly, they define a partial internal energy $\tilde{u}_i$ and their equation (243.1) gives the 'total' energy as the sum of the partial internal energies plus the kinetic energies of diffusion, i.e., the same as u^+ defined by de Groot and Mazur; from equation (44),

$$u^+ = \tilde{u} + \sum_i \frac{1}{2} m_i \hat{v}_i^2.$$

The internal energy u^+ equals u^{CC} of kinetic theory [see equation (15)], and equals the thermodynamic internal energy if ordinary diffusion is the only diffusion mechanism present. Like Williams [4], these authors are careful to reconcile their property definitions with Chapman–Enskog kinetic theory.

4.5.6. *Slattery* [13]. Slattery's coexisting continua model defines the total energy of the mixture as

$$e = u + \sum_i \frac{1}{2} m_i v_i^2 \tag{47}$$

where u is the thermodynamic internal energy, and then obtains the left side of the 'thermal' energy equation as $\rho(D/Dt)(u + \Sigma_i \frac{1}{2} m_i \hat{v}_i^2)$. He asserts that the kinetic energy of diffusion is expected to be small compared to u and 'we are prepared to neglect it'. He subsequently refers to Truesdell and Noll [12] and de Groot and Mazur [11] to note that a new internal energy $u^\dagger$ can be defined as

$$u^\dagger = u + \sum_i \frac{1}{2} m_i \hat{v}_i^2 \tag{48}$$

to obtain the thermal energy equation in terms of $u^\dagger$, but that 'unfortunately, this simplification disappears when we use the fundamental constitutive equation for a thermodynamically homogeneous material which requires that u is not an explicit function of the motion of the material.'

Slattery has misquoted refs. [11] and [12], neither of whom define an internal energy $u^\dagger$. In fact, for ordinary diffusion only, u^+ of de Groot and Mazur [11] is equal to u, and

$$u^\dagger = u^+ + \Sigma \tfrac{1}{2} m_i \hat{v}_i^2 \tag{49}$$

that is, the kinetic energy of diffusion has been accounted for twice. Truesdell and Noll [12] only define u^+ [see equation (44)].

The error in Slattery's formulation is a common one, namely, a failure to recognize that, if a continuum is defined to have a velocity $\mathbf{v}_i$ that includes the ordinary diffusion velocity, then the internal energy of the continuum cannot be the usual thermodynamic internal energy. This error is similar to the one made by Lees and by Penner, who viewed the diffusion stresses to be in addition to the usual stress tensor.

4.5.7. *L. C. Woods* [6]. In Chapter 9 of his text *Thermodynamics of Fluid Systems*, Woods has a very comprehensive development of the coexisting-continua model that is followed quite closely in Sections 4.2–4.4 of this paper. However, like Slattery (see Section 4.5.6), Woods takes $\tilde{u}_i = u_i$, thereby failing to recognize that a portion of the thermodynamic internal energy has been artificially separated out by including the ordinary diffusion velocity as a component of each continuum velocity. Similarly, he takes $\tilde{P}_i = P_i$. His comments on the quadratic diffusion terms include the following:

(1) "The diffusion pressure is often included as part of the total pressure, but to do this means a departure from the purely thermodynamic significance of pressure."
(2) "It is misleading to describe u^+ as being the 'internal energy', as the application of either heat or work affects u and $\Sigma_i \frac{1}{2} m_i \hat{v}_i^2$ differently ... the concepts of heat and work are blurred in mixture theory."
(3) "The one-fluid model is practical only when the quadratic terms ... involving the diffusion velocity are negligible."

It is relevant to note that a primary concern of Woods was to have a formulation that was practical for plasma transport problems, for which forced diffusion is usually the dominant mode of diffusion. Thus he ensured that the quadratic terms associated with the forced diffusion velocity are kept separate; indeed, if ordinary diffusion is negligible, his formulation is quite satisfactory. It is for the same reason that Woods, in his text *An Introduction to the Kinetic Theory of Gases and Magnetoplasmas* [5], develops a kinetic theory formulation that differs from the traditional Chapman–Enskog theory in defining a molecule peculiar velocity relative to the species absolute velocity rather than the mass average velocity (as described in Section 3 of this paper). This kinetic theory formulation yields conservation equations of identical form to his coexisting-continua formulation.

4.5.8. *Hirschelder, Curtiss and Bird* [3]. In their text *The Molecular Theory of Gases and Liquids* the authors present a widely used treatment of the Chapman–Enskog kinetic theory of gases. Their conservation equations are identical to those used by Williams (see Section 4.5.2) to reconcile his coexisting continua model with kinetic theory. Their 'thermal' energy equation, equation (7.2-49), is in terms of an internal energy for monatomic molecules defined as

$$u^{\mathrm{tr}} = \frac{1}{\rho} \sum_i \frac{1}{2} \mathcal{N}_i m_i \overline{C_i^2} \tag{50}$$

and thus combines the forced diffusion motion with the thermal motion. A corresponding 'kinetic theory' temperature is defined, and equation (7.2-49) is rewritten in terms of this temperature as equation (7.2-50). This form of the energy equation has already been commented on in Section 4.5.2: it is mathematically correct but of doubtful practical utility.

Subsequently, in Section 7.6 they extend their energy equation, equation (7.2-49) to a polyatomic reacting gas mixture by replacing u^{tr} with the 'thermodynamic internal energy' $u = \Sigma_i m_i u_i$, to obtain equation (7.6-7). In so doing they replace a kinetic theory definition of internal energy with the thermodynamic definition, without comment. Their step is valid only if the kinetic energy associated with forced diffusion is negligible, and then, to the same order they should have deleted the work term $\Sigma_i \mathbf{j}_i \cdot \mathbf{f}_i$ from the equation. In Chapter 11 they rewrite equation (7.6-7) as equation (11.1-4) and add thermal and caloric equations of state,

$$P = P(V, T) \tag{51}$$

$$u = u(V, T). \tag{52}$$

Again no mention is made of replacing kinetic theory definitions of P and u with thermodynamic definitions, and the work term remains in the equation. In the various applications that follow, P and u (or T) in the conservation equations are taken to be thermodynamic values, and, since none of the applications involve external forces (and, indeed, do not involve thermal or pressure diffusion), the equations used are correct. But their inconsistent use of internal energy definitions has been a possible source of the same inconsistency in derivative works, for example in the text by Bird, Stewart and Lightfoot [10].

4.5.9. *Bird, Stewart and Lightfoot* [10]. In their widely used text *Transport Phenomena* these authors present various forms of the energy conservation equation in Table 18.3.-1. For example, their equation (10) reads

$$\rho \frac{Du}{Dt} = -\nabla \cdot \mathbf{q} - (\sigma : \nabla \mathbf{v}) + \sum_i \mathbf{j}_i \cdot \mathbf{f}_i. \tag{53}$$

Nowhere in this text is u defined to be other than the thermodynamic internal energy and there is no mention of a 'kinetic theory' temperature. Thus, to the order of the approximation used, namely $u^+ = u$, the term $\Sigma_i \mathbf{j}_i \cdot \mathbf{f}_i$ should not appear in this equation, and in the subsequent forms that are in terms of thermodynamic temperature. It is particularly troublesome to see a work term in a thermal energy equation since, as mentioned before, mechanical work can only affect thermal energy via a reversible heating by compression or an irreversible viscous dissipation.

4.5.10. *Curtiss and Bird* [14]. In a very recent paper dealing with multicomponent diffusion in polymeric liquids, these authors have an appendix devoted to clarifying the nature of the partial stresses that must be defined when using a coexisting-continua model to derive a species momentum equation. However, like Williams [4], no attempt is made to distinguish between ordinary and forced diffusion.

5. PROPOSED CONTINUUM MODELS FOR GAS MIXTURES

In Section 4 it was shown that momentum and energy conservation equations based on coexisting-continua models have serious shortcomings. The difficulties are essentially due to an attempt to have general equations that apply when both ordinary and forced diffusion are present. However, in most heat and mass transfer problems there are no species dependent external forces, and hence forced diffusion is absent. Thus, in Section 5.1 a continuum model is presented for these situations. When forced diffusion is present, ordinary diffusion is often negligible. In Section 5.2 simplified coexisting-continua conservation equations are given for such situations.

5.1. *A continuum model for nonionized gas mixtures*

In this model the gas mixture is modeled as a single continuum with the following definitions of properties and fluxes:

Density $\rho = \Sigma_i \rho_i$. Pressure $P = \Sigma_i P_i$ (usual thermodynamics definition). Internal energy $u = \Sigma_i m_i u_i$ (usual thermodynamics definition). Species production rate $\dot{r}_i$. Species absolute mass flux $\mathbf{n}_i = \rho_i \mathbf{v} + \mathbf{j}_i$, where $\mathbf{v} = (1/\rho)\Sigma \mathbf{n}_i$ is the mass average velocity, $\mathbf{j}_i$ = diffusion flux relative to $\mathbf{v}$. Stress tensor $\sigma = -P\mathbf{I} + \tau$. Energy flux relative to the mass average velocity $\mathbf{q}$. Gravitational acceleration $\boldsymbol{g}$.

The flux laws are obtained from the Chapman–Enskog kinetic theory of gases

$$\mathbf{j}_i = \sum_j m_i m_j D_{ij}[\nabla x_j + (x_i - m_j)\nabla \ln P] - D_i^T \nabla \ln T \tag{54}$$

$$\tau = \mu(\nabla \mathbf{v} + (\nabla \mathbf{v})^T) + (\tfrac{2}{3}\mu - \kappa)(\nabla \cdot \mathbf{v})\delta \tag{55}$$

$$\mathbf{q} = \mathbf{q}^{\mathrm{C}} + \sum_i \mathbf{j}_i h_i + \mathbf{q}^{\mathrm{DC}} = -k\nabla T + \sum_i \mathbf{j}_i h_i + RT \sum_i \sum_j \frac{x_i D_i^T}{M_i \mathscr{D}_{ij}} \left(\frac{\mathbf{n}_i}{\rho_i} - \frac{\mathbf{n}_j}{\rho_j} \right) \tag{56}$$

where μ and k are the mixture viscosity and thermal conductivity. Notice that there is no tilde overscores; all partial properties are the same as those defined for a pure gas; all mixture properties are the same as those defined for a uniform mixture.

Consistent with the statement of the principle of conservation of species given in Section 4.1, the resulting equation is now

$$\frac{\partial \rho}{\partial t} + \nabla \cdot \mathbf{n}_i = \dot{r}_i. \tag{57}$$

Substituting $\mathbf{n}_i = \rho_i \mathbf{v} + \mathbf{j}_i$ gives

$$\frac{\partial \rho_i}{\partial t} + \nabla \cdot \rho_i \mathbf{v} = -\nabla \cdot \mathbf{j}_i + \dot{r}_i. \tag{58}$$

Since we have postulated a single continuum, the derivations of the momentum and energy conservation equations are identical to those for a pure fluid as presented in standard texts. The results are, for momentum,

$$\frac{\partial}{\partial t}\rho \mathbf{v} + \nabla \cdot \rho \mathbf{v}\mathbf{v} = -\nabla P + \nabla \cdot \tau + \rho \boldsymbol{g} \tag{59}$$

for total energy,

$$\frac{\partial}{\partial t}\rho\left(u + \frac{1}{2}v^2\right) + \nabla \cdot \rho\left(u + \frac{1}{2}v^2\right)\mathbf{v} = -\nabla \cdot \mathbf{q} + \nabla \cdot [\mathbf{v} \cdot \sigma] + \rho \boldsymbol{g} \cdot \mathbf{v} \tag{60}$$

and for thermal energy,

$$\rho \frac{Dh}{Dt} = \frac{DP}{Dt} - \nabla \cdot \mathbf{q} + \mu \Phi. \tag{61}$$

In these equations μ and k are uniform mixture properties, while $\mathbf{j}$ and $\mathbf{q}$ are given by equations (54) and (56), respectively.

In many situations pressure and thermal diffusion are negligible and are discarded leaving ordinary diffusion as the only mechanism of diffusion. Then the above equations are exact in the sense that no effects due to ordinary diffusion have been omitted. If pressure or thermal diffusion are included then the equations are approximate in that diffusion stresses and kinetic energy associated with pressure and thermal diffusion are then ignored. However, the drift velocities due to pressure and thermal diffusion are usually of third order, and the resulting stresses and energy associated with these velocities are of an even lower order. Thus, deleting such terms will invariably be an approximation of no concern. Indeed, this issue is always ignored when using conservation equations derived from the kinetic theory of gases and the Boltzmann equation.

5.2. *A continuum model for forced diffusion*

Forced diffusion drift velocities in ionized gas mixtures can be very large. As noted in Section 2, cadmium ions in a helium–cadmium laser have a drift velocity of ~3000 m s^{-1}. Even though only about 1% of the cadmium molecules present are ionized at any given instant of time, the resulting forced diffusion flux of cadmium is also large. It is then often possible to neglect ordinary diffusion (and pressure and thermal diffusion), and it is useful to have appropriate and simple momentum and energy conservation equations. We return to the coexisting-continua model of Section 4, with $\mathbf{v}_i = \mathbf{v} + \hat{\mathbf{v}}_i^{\mathrm{FD}}$ and remove all the tilde overscores. The species equation is then

$$\frac{\partial \rho_i}{\partial t} + \nabla \cdot \rho_i(\mathbf{v} + \hat{\mathbf{v}}_i^{\mathrm{FD}}) = \dot{r}_i \tag{62}$$

or

$$\frac{\partial \rho_i}{\partial t} + \nabla \cdot \rho_i \mathbf{v} = -\nabla \cdot \mathbf{j}_i^{\mathrm{FD}} + \dot{r}_i. \tag{63}$$

The mixture momentum equation from equation (30) is

$$\rho \frac{D\mathbf{v}}{Dt} = -\nabla P + \nabla \cdot \tau - \nabla \cdot \sum_i \rho_i \hat{\mathbf{v}}_i^{\mathrm{FD}} \hat{\mathbf{v}}_i^{\mathrm{FD}} + \sum_i \rho_i \mathbf{f}_i \qquad (64)$$

and from equation (39) the mixture thermal energy equation is

$$\rho \frac{Du}{Dt} = -P\nabla \cdot \mathbf{v} + \nabla \cdot (\mathbf{q}^{\mathrm{C}} + \mathbf{q}^{\mathrm{DC}}) + \nabla \cdot \sum_i \mathbf{j}_i^{\mathrm{FD}} u_i$$

$$- \sum_i P_i \nabla \hat{\mathbf{v}}_i^{\mathrm{FD}} + \mu\Phi + \mu\Phi^{\mathrm{FD}} + \dot{Q}_V \qquad (65)$$

where τ and $\mathbf{q}$ are defined in equations (55) and (56) and $\mu\Phi = -\tau \cdot \nabla \mathbf{v}$, $\mu\Phi^{\mathrm{FD}} = -\Sigma_i \tau_i \cdot \nabla \hat{\mathbf{v}}_i^{\mathrm{FD}}$. We see in equation (64) diffusion stresses associated with forced diffusion, and in equation (65) terms related to heat of compression and viscous dissipation associated with forced diffusion.

These equations can be used to scale the forced diffusion quadratic terms in order to see whether they are negligible. And, for example, equation (64) can be used to investigate whether the diffusion stresses play a role in establishing the axial pressure gradient in a helium-cadmium laser (though, related phenomena, such as the force imbalance associated with the continuous generation of ions, appear to be of greater significance [15, 16]).

6. THE ORDINARY DIFFUSION VELOCITY REVISITED

In using continuum models for mass transfer analysis we routinely apply a boundary condition of zero concentration as a good approximation to the actual physical condition: the diffusion controlled reactions mentioned in Section 2.1 are examples. As a result, the diffusion velocity for ordinary diffusion has a singularity at the boundary. For this reason we solve the species conservation equation in terms of fluxes, not velocities, in order to avoid having to deal with the singularity. However, in the momentum and energy conservation equations derived from the coexisting-continua model, such singularities cannot be so easily avoided. We will use the one-dimensional diffusion problem of Section 2.1 as a simple example. The diffusion pressure P^{D} defined by equation (32) and given by the diagonal components of τ^{D} appearing in the momentum conservation equation, equation (31), has singular terms at $z = 0, L$. Hence, application of equation (31) as $z \to 0$ and $z \to L$ is not straightforward. Similarly, equation (37) contains the term $\nabla \cdot \rho(\Sigma_i \frac{1}{2} m_i \hat{v}_i^2 \hat{\mathbf{v}}_i)$ that is singular at $z = 0, L$. As a result this equation is of questionable practical use.

This singular behavior is even more troublesome in its implications for the definition of the partial internal energy $\tilde{u}$. When only ordinary diffusion is present the thermodynamic internal energy u is

$$u = \tilde{u} + \sum_i \frac{1}{2} m_i \hat{v}_i^2. \qquad (66)$$

Again referring to the one-dimensional diffusion problem of Section 2.1, u is constant and thus at $z = 0, L$ where a $\hat{v}_i \to \infty$, $\tilde{u} \to -\infty$! This awkward result is a feature of the continuum model. A check of the corresponding molecular model shows that the concentration jump at the boundaries precludes $\hat{\mathbf{v}}_i$ becoming large enough for a similar anomaly to occur.

As mentioned in Section 2.1, we really should not be concerned by this anomalous behavior of the quadratic diffusion velocity terms because, in the continuum model, the diffusion velocity is an artificial one, obtained by dividing the diffusion flux $\mathbf{j}_i$ by a density ρ_i, which has no relevance to the physical phenomenon (it could be argued that $\mathbf{j}_i/\rho$ gives a more useful velocity). Physically meaningful momentum fluxes or kinetic energy cannot be associated with the ordinary diffusion velocity. In this sense the suggestion that the velocity is artificial or fictitious seems appropriate, though some might argue that this is a question of semantics.

In closing it is of interest to comment on a related situation, that of diffusion of small aerosol particles. Brownian diffusion is described by

$$\mathcal{J}_{\mathrm{P}} = -\mathcal{D}_{\mathrm{P}} \nabla \mathcal{N}_{\mathrm{P}}. \qquad (67)$$

In most situations, capture of particles by surfaces is very efficient and the usual boundary condition applied to particle conservation equations at surfaces is $\mathcal{N}_{\mathrm{P}} \to 0$. If a diffusion velocity is defined for particles by the relation

$$\mathcal{J}_{\mathrm{P}} = \mathcal{N}_{\mathrm{P}} \hat{\mathbf{v}}_{\mathrm{P}} \qquad (68)$$

then $\hat{\mathbf{v}}_{\mathrm{P}} \to \infty$ at the surface. The idea of the particle velocity becoming singular as it approaches a surface is unacceptable, and for this reason the concept of a diffusion velocity for Brownian diffusion is a not used in the aerosol literature. On the other hand, thermal diffusion of particles (called thermophoresis) is described by a relation

$$\mathcal{J}_{\mathrm{P}}^{\mathrm{TD}} = \mathcal{N}_{\mathrm{P}} \hat{\mathbf{v}}_{\mathrm{P}}^{\mathrm{TD}} \qquad (69)$$

where $\hat{\mathbf{v}}_{\mathrm{P}}^{\mathrm{TD}}$ is independent of particle concentration [17]. Thus, it is customary practice in the aerosol literature to include thermophoresis with convection on the left side of the particle conservation equation, and to have Brownian diffusion on the right side of the equation. Similarly, one could agree that forced diffusion in gas mixtures should be included with the convection terms on the left side of the species conservation equation, rather than with ordinary diffusion on the right side of the equation.

7. CONCLUSIONS

(1) The diffusion velocity for ordinary diffusion requires careful use: it is perhaps best viewed as an artificial velocity.

(2) The kinetic energy of diffusion associated with ordinary diffusion is portion of the ther-

modynamic internal energy: it is not additional energy. Similarly the diffusion pressure is a portion of the thermodynamic pressure: there is no additional pressure exerted in a gas mixture due to ordinary diffusion.

(3) The kinetic energy of diffusion and diffusion pressure associated with forced diffusion are in addition to their thermodynamic counterparts, and should be kept separate.

(4) Coexisting–continua models yield momentum and energy conservation equations that have no intrinsic value, since the kinetic theory of gases is required to identify many of the terms that appear. Furthermore, in their usual form they have little practical utility.

(5) It is incorrect to include the work term $\Sigma \mathbf{j}_i \cdot \mathbf{f}_i$ in equations describing change of thermodynamic internal energy, and in derivative equations.

(6) It is possible to derive useful conservation equations for nonionized gas mixtures using a simple single-continuum model.

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