

Portland State University

PDXScholar

Physics Faculty Publications and Presentations

Physics

2002

Fluid Dynamics and Energetics in Ideal Gas Mixtures

John D. Ramshaw

Portland State University, jdramshaw@yahoo.com

Follow this and additional works at: https://pdxscholar.library.pdx.edu/phy_fac



Part of the [Fluid Dynamics Commons](#)

Let us know how access to this document benefits you.

Citation Details

Ramshaw, J. (2002). "Fluid Dynamics and Energetics in Ideal Gas Mixtures" *American Journal of Physics* Vol. 70 Iss. 5.

This Article is brought to you for free and open access. It has been accepted for inclusion in Physics Faculty Publications and Presentations by an authorized administrator of PDXScholar. Please contact us if we can make this document more accessible: pdxscholar@pdx.edu.

Fluid dynamics and energetics in ideal gas mixtures

John D. Ramshaw^{a)}

Lawrence Livermore National Laboratory, University of California, P.O. Box 808, L-097, Livermore, California 94551

(Received 4 August 2001; accepted 31 January 2002)

The generalization of fluid dynamics from pure to multicomponent fluids (fluid mixtures composed of different components or species) requires the introduction of new concepts, some of which are rather subtle and are less widely appreciated than they deserve to be. The purpose of this paper is to provide a simple didactic introduction to some of these concepts based on a detailed analysis of the equations governing the flow of ideal gas mixtures. The treatment is based entirely on a continuum description and makes no explicit use of the kinetic theory of gases. We include a straightforward and physically transparent derivation of the additional heat flux arising from the relative motion of the different species, and show why this flux involves species enthalpies rather than energies. Some of the concepts are reminiscent of those used in turbulence modeling, and these analogies are briefly discussed. © 2002 American Association of Physics Teachers.

[DOI: 10.1119/1.1463737]

I. INTRODUCTION

Most fluids of practical interest are multicomponent mixtures containing several different components or chemical species. For many purposes, fluid mixtures behave much like pure fluids and can be described by very similar equations. Mass, momentum, and energy are of course conserved in mixtures as well as pure fluids, and the dynamics of fluid mixtures is consequently described by fluid dynamical mass, momentum, and energy transport equations similar in form to those for a pure fluid. This similarity can be deceptive, however, as pure fluids and mixtures also exhibit some essential differences that are not obvious on casual inspection. The purpose of this paper is to derive and discuss some of these differences, including subtle differences in the definition and interpretation of various familiar quantities such as the stress tensor, heat flux, and internal energy.

For simplicity and concreteness, we restrict our attention to the special case of multicomponent ideal gas mixtures. However, most of the basic ideas apply equally well to dense fluid mixtures as well as multiphase mixtures, where similar considerations lead to very similar results (although there are differences in the details). The main prerequisite assumed of the reader is a general familiarity with the continuity, momentum, and energy equations for a pure fluid, such as that provided by most introductory courses in fluid dynamics. More complete and advanced treatments of multicomponent fluid dynamics may be found in the books of Burgers¹ and Woods,² which are based on the kinetic theory of gases and phenomenological nonequilibrium thermodynamics, respectively. The subject is sufficiently complex, however, that one should not expect these and other treatments to be fully consistent with each other or with the present treatment in all respects.

II. SPECIES DENSITIES, CONCENTRATIONS, AND FRACTIONS

The partial mass density of species i is denoted by ρ_i and is defined as the mass of species i per unit total volume. The total mass density of the mixture is $\rho = \sum_i \rho_i$, and the mass fraction of species i in the mixture is $y_i = \rho_i / \rho$. The molar concentration (moles per unit total volume) of species i is

$c_i = \rho_i / M_i$, where M_i is the molecular weight (mass of a single mole) of species i . The mass of a single molecule of species i is $m_i = M_i / N_0$, where Avogadro's number N_0 is the number of atoms or molecules in a mole. The number density of species i is the number of atoms or molecules of species i per unit total volume and is given by $n_i = \rho_i / m_i = N_0 c_i$. Thus n_i and c_i differ only by a constant factor, and the choice of which to use is merely a matter of taste. The total molar and number densities of the mixture are simply $c = \sum_i c_i$ and $n = \sum_i n_i = N_0 c$, respectively, and the mole fraction of species i is $x_i = c_i / c = n_i / n$. All of these quantities (except of course the constants M_i , m_i , and N_0) are local dependent variables which are functions of the position \mathbf{r} and the time t .

It is also useful to define the volume fraction of species i in the mixture, which we denote by α_i . These volume fractions are more common and familiar in the description of multiphase mixtures, but they are also of fundamental importance in the multicomponent gas mixtures of present interest. In this case, however, the constituent species are intimately mixed together on the atomic or molecular level, so in order to define α_i we must first define the partial volume occupied by species i in the mixture. To this end, we imagine that the species contained within any small volume V are separated into subvolumes V_i without changing their temperatures T_i (which are equal in most cases, although they need not be^{1,3}) or the total pressure p . The number of molecules of species i contained in V is $n_i V$, so the number density of species i within its subvolume is $n_i V / V_i$. (Similarly, the mass of species i contained in V is $\rho_i V$, so the mass density of pure species i within its subvolume is $\rho_i V / V_i$. These mass densities are important variables in multiphase mixtures, but they do not play a significant role in the multicomponent gas mixtures of present interest.) Because we are dealing with ideal gases, the pressure of species i within its subvolume then becomes $(n_i V / V_i) k T_i$, where k is Boltzmann's constant. By equating these subvolume pressures to the total pressure p , we obtain $p V_i = n_i k T_i V$, which determines V_i . For this definition of V_i to be sensible, however, we must verify that $\sum_i V_i = V$ (Amagat's law). This relation indeed follows from

the fact that $p = \sum_i p_i$, where $p_i = n_i k T_i$ is the partial pressure of species i in the original unseparated mixture. The volume fractions can then be defined as $\alpha_i = V_i/V = p_i/p \equiv z_i$. The volume fraction of species i in a multitemperature multicomponent ideal gas mixture is therefore the same as its pressure fraction z_i . In the special case when all the species temperatures T_i are equal, z_i trivially reduces to the mole fraction x_i , so that $\alpha_i = x_i$ and the species volume fractions become identical to their mole fractions.

III. SPECIES AND MIXTURE CONTINUITY EQUATIONS

In the absence of chemical reactions or other mass exchange between species, the mass of each species is conserved, so that each species obeys a continuity equation of the same form as that for a pure fluid:

$$\frac{\partial \rho_i}{\partial t} + \nabla \cdot (\rho_i \mathbf{u}_i) = 0, \quad (1)$$

where \mathbf{u}_i is the mean velocity of species i . Equation (1) is not restricted to ideal gas mixtures, but applies equally well to dense fluid mixtures and multiphase mixtures. If we sum over i , we obtain the total continuity equation for the mixture:

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{u}) = 0, \quad (2)$$

where $\mathbf{u} = \sum_i y_i \mathbf{u}_i$ is the mass-weighted mean fluid velocity of the mixture. Equation (1) is usually written in the form

$$\frac{\partial \rho_i}{\partial t} + \nabla \cdot (\rho_i \mathbf{u}) = -\nabla \cdot \mathbf{J}_i, \quad (3)$$

where $\mathbf{J}_i = \rho_i \mathbf{w}_i$ and $\mathbf{w}_i = \mathbf{u}_i - \mathbf{u}$. Clearly \mathbf{J}_i is the mass flux (mass flow per unit area per unit time) of species i relative to \mathbf{u} . The fluxes \mathbf{J}_i may be considered the fundamental variables that carry information about the relative velocities of the different species.

IV. THE VOLUME-WEIGHTED MEAN VELOCITY

The volume-weighted mean fluid velocity is defined by $\mathbf{u}_v = \sum_i \alpha_i \mathbf{u}_i$, which becomes $\sum_i z_i \mathbf{u}_i$ in the ideal gas mixtures of present interest. Both \mathbf{u} and \mathbf{u}_v are fundamental for different purposes, and the distinction between them is an essential difference between the flow of pure and multicomponent fluids. Consider a small fixed surface with unit normal vector \mathbf{n} . The mass of species i crossing this surface per unit area per unit time is $\rho_i \mathbf{u}_i \cdot \mathbf{n}$, so the total mass crossing this surface per unit area per unit time is $\rho \mathbf{u} \cdot \mathbf{n}$. Thus there is no net mass flow across a surface moving with velocity \mathbf{u} . Similarly, the volume of species i crossing such a surface per unit area per unit time is $\alpha_i \mathbf{u}_i \cdot \mathbf{n}$. The total volume crossing such a surface per unit area per unit time is therefore $\mathbf{u}_v \cdot \mathbf{n}$, so there is no net volume flow across a surface moving with velocity \mathbf{u}_v . Relations based on volume changes consequently involve \mathbf{u}_v rather than \mathbf{u} , as will be seen in what follows. A simple example is the familiar relation⁴

$$\nabla \cdot \mathbf{u} = \lim_{V \rightarrow 0} \frac{1}{V} \frac{dV}{dt}, \quad (4)$$

where V is the volume of a small Lagrangian volume element whose surface moves with the local mass-weighted fluid velocity \mathbf{u} . This relation remains valid in a multicomponent fluid, but it no longer has the same interpretation because $V^{-1} dV/dt$ no longer has the significance of the intrinsic local relative expansion rate of the fluid. The reason is that the surface of V does not move with velocity \mathbf{u}_v , so there is a net flow of volume across it which causes V to change even in the absence of expansion or contraction of the fluid itself. To obtain a proper measure of expansion or contraction divorced from the effects of transport, it is necessary to consider a small volume element V' with no net volume flow across its surface; that is, a volume element whose surface moves with velocity \mathbf{u}_v rather than \mathbf{u} . We then have

$$\nabla \cdot \mathbf{u}_v = \lim_{V' \rightarrow 0} \frac{1}{V'} \frac{dV'}{dt}, \quad (5)$$

which now represents the intrinsic local relative expansion rate of the fluid mixture. The condition for incompressible flow is that this expansion rate vanishes, so the incompressibility condition in a multicomponent fluid takes the form $\nabla \cdot \mathbf{u}_v = 0$ rather than $\nabla \cdot \mathbf{u} = 0$. In a pure fluid $\mathbf{u}_v = \mathbf{u}$, and the incompressibility condition then reduces to its usual familiar form $\nabla \cdot \mathbf{u} = 0$.

Even though \mathbf{u} and \mathbf{u}_v are both important, it is inconvenient to retain both of them in the description. Because \mathbf{u} is directly related to mass and momentum conservation, it is customary to eliminate \mathbf{u}_v in terms of \mathbf{u} . This elimination may be done by means of the easily verified identity

$$\mathbf{u}_v = \mathbf{u} + \sum_i (\alpha_i / \rho_i) \mathbf{J}_i. \quad (6)$$

V. SPECIES AND MIXTURE MOMENTUM EQUATIONS

We are concerned with ideal gases, in which the effects of intermolecular collisions are negligible by definition. This implies that viscous stresses can be neglected, and for simplicity we shall also neglect external forces such as gravity. If intermolecular collisions were completely absent, the molecules of each species in an ideal gas mixture would be completely unaware of the presence of the other species, so that the momentum equation for each species would have exactly the same form as that for a pure inviscid (zero viscosity) ideal gas. To make things more realistic, however, we shall include the effects of collisions between molecules of *different* species, while still neglecting intermolecular collisions between molecules of the *same* species. Strictly speaking this assumption is somewhat inconsistent, but it will allow us to focus more clearly on the effects of interest without extraneous complications. The momentum equation for species i will then still have the same form as that for a pure inviscid ideal gas, but with additional terms representing the forces exerted on species i by each of the other species:

$$\frac{\partial(\rho_i \mathbf{u}_i)}{\partial t} + \nabla \cdot (\rho_i \mathbf{u}_i \mathbf{u}_i) = -\nabla p_i + \sum_{j \neq i} \mathbf{F}_{ij}, \quad (7)$$

where $\mathbf{F}_{ij} = -\mathbf{F}_{ji}$ is the force per unit volume of species j on species i . If we sum over i , we obtain the total momentum equation for the mixture:

$$\frac{\partial(\rho\mathbf{u})}{\partial t} + \nabla \cdot \sum_i \rho_i \mathbf{u}_i \mathbf{u}_i = -\nabla p, \quad (8)$$

which may be rewritten in the form

$$\frac{\partial(\rho\mathbf{u})}{\partial t} + \nabla \cdot (\rho\mathbf{u}\mathbf{u}) = \nabla \cdot \boldsymbol{\sigma}, \quad (9)$$

where

$$\boldsymbol{\sigma} = -p\mathbf{U} + \mathbf{R} \quad (10)$$

is the total stress tensor, \mathbf{U} is the unit tensor, and

$$\mathbf{R} = -\sum_i \rho_i \mathbf{w}_i \mathbf{w}_i \quad (11)$$

is an additional stress arising from the relative motion of the different species. This additional stress is a purely multicomponent phenomenon and vanishes in a pure fluid.

The occurrence and physical interpretation of \mathbf{R} become clearer when one reflects upon the significance of the partial pressures p_i . As discussed above, we are neglecting intermolecular collisions between molecules of the same species, and yet p_i still appears in the equations. Thus the pressure in ideal gases does not arise from or represent the effects of intermolecular forces or collisions, which is why the ideal gas law $p = nkT$ involves no cross sections or other collisional parameters. The pressure in the interior of an ideal gas, away from the walls, is therefore not a real physical force per unit area as we are accustomed to thinking (although it is formally equivalent to such a force). In reality, the pressure in an ideal gas is merely an additional momentum flux arising from the fact that the velocities of the atoms or molecules at a given point are not all the same, but are statistically distributed about their mean value at that point.⁴ When this distribution is locally Maxwellian, the gas has a well-defined local temperature to which the local pressure is simply related by the ideal gas law. Even if the velocity distribution were not Maxwellian, however, it would still imply an additional momentum flux appearing as a pressure in the mean momentum equation. This additional momentum flux is indeed the way pressure arises and is defined in the kinetic theory of gases.

Thus the partial pressure p_i in Eq. (7) is simply the mean additional flux of species i momentum resulting from deviations of the molecular velocities of species i from their mean value \mathbf{u}_i . Each of the partial pressures therefore represents the effects of velocity deviations relative to a different mean velocity \mathbf{u}_i . Similarly, $\boldsymbol{\sigma}$ represents the mean additional momentum flux resulting from deviations of the molecular velocities of all species from the mass-weighted mean velocity \mathbf{u} . The additional stress \mathbf{R} simply allows for the difference between the velocities \mathbf{u}_i relative to which the p_i are defined, and the velocity \mathbf{u} relative to which $\boldsymbol{\sigma}$ is defined. Note that \mathbf{R} is inherently dynamical in nature, whereas the partial pressures p_i are purely thermal quantities that are simply related to the species temperatures T_i . Note also that \mathbf{R} has nothing whatever to do with viscous effects, which are completely neglected in the present discussion.

Equations (2) and (9) may be combined to convert the momentum equation into the equivalent nonconservative form

$$\rho \left(\frac{\partial \mathbf{u}}{\partial t} + \mathbf{u} \cdot \nabla \mathbf{u} \right) = \nabla \cdot \boldsymbol{\sigma}. \quad (12)$$

The kinetic energy per unit mass associated with \mathbf{u} is simply $\frac{1}{2}|\mathbf{u}|^2$, a transport equation for which can readily be derived from Eq. (12). The result is

$$\rho \left[\frac{\partial}{\partial t} \left(\frac{1}{2} |\mathbf{u}|^2 \right) + \mathbf{u} \cdot \nabla \left(\frac{1}{2} |\mathbf{u}|^2 \right) \right] = \mathbf{u} \cdot (\nabla \cdot \boldsymbol{\sigma}), \quad (13)$$

which can in turn be expressed in the equivalent conservative form

$$\frac{\partial}{\partial t} \left(\frac{1}{2} \rho |\mathbf{u}|^2 \right) + \nabla \cdot \left(\frac{1}{2} \rho |\mathbf{u}|^2 \mathbf{u} \right) = \mathbf{u} \cdot (\nabla \cdot \boldsymbol{\sigma}). \quad (14)$$

VI. SPECIES AND MIXTURE ENERGY EQUATIONS

In accordance with the assumptions made for the species momentum equations, the energy equation for species i has the same form as that for a pure inviscid ideal gas with zero thermal conductivity, but with additional terms representing the exchange of energy between the different species:

$$\frac{\partial(\rho_i E_i)}{\partial t} + \nabla \cdot (\rho_i E_i \mathbf{u}_i) = -\nabla \cdot (p_i \mathbf{u}_i) + \sum_{j \neq i} Q_{ij}, \quad (15)$$

where $E_i = \frac{1}{2}|\mathbf{u}_i|^2 + e_i$ is the total energy per unit mass of species i , e_i is the thermal internal energy per unit mass of species i , and $Q_{ij} = -Q_{ji}$ is the rate per unit volume at which energy is transferred from species j to species i . The total energy per unit volume of the mixture is given by $\rho E = \sum_i \rho_i E_i$, an evolution equation for which may be derived by summing Eq. (15) over all species to obtain

$$\frac{\partial(\rho E)}{\partial t} + \nabla \cdot \sum_i \rho_i E_i \mathbf{u}_i = -\nabla \cdot (p \mathbf{u}_v). \quad (16)$$

We see that the work term in Eq. (16) involves \mathbf{u}_v rather than \mathbf{u} , as might have been anticipated from the fact that work is based on volume changes. Equation (16) can be rewritten as

$$\begin{aligned} \frac{\partial(\rho E)}{\partial t} + \nabla \cdot (\rho E \mathbf{u}) &= -\nabla \cdot (p \mathbf{u}_v) - \nabla \cdot \sum_i E_i \mathbf{J}_i \\ &= -\nabla \cdot (p \mathbf{u}_v) + \nabla \cdot (\mathbf{R} \cdot \mathbf{u}) - \nabla \cdot \mathbf{J}_q \\ &\quad - \nabla \cdot \sum_i e_i \mathbf{J}_i, \end{aligned} \quad (17)$$

where

$$\mathbf{J}_q = \sum_i \frac{1}{2} |\mathbf{w}_i|^2 \mathbf{J}_i. \quad (18)$$

We see that additional heat fluxes \mathbf{J}_q and $\sum_i e_i \mathbf{J}_i$ have arisen due to the conversion from \mathbf{u}_i to \mathbf{u} in the convection term. If we now use Eq. (6) to eliminate \mathbf{u}_v in favor of \mathbf{u} , we obtain

$$\begin{aligned} \frac{\partial(\rho E)}{\partial t} + \nabla \cdot (\rho E \mathbf{u}) &= \nabla \cdot (\boldsymbol{\sigma} \cdot \mathbf{u}) - \nabla \cdot \mathbf{J}_q \\ &\quad - \nabla \cdot \sum_i (e_i + p_i / \rho_i) \mathbf{J}_i \\ &= \nabla \cdot (\boldsymbol{\sigma} \cdot \mathbf{u}) - \nabla \cdot \mathbf{J}_q - \nabla \cdot \mathbf{J}_h, \end{aligned} \quad (19)$$

where

$$\mathbf{J}_h = \sum_i h_i \mathbf{J}_i. \quad (20)$$

and $h_i = e_i + p_i/\rho_i$ is the specific thermal enthalpy of species i . Thus we see that the conversion from \mathbf{u}_v to \mathbf{u} in the work term has the effect of bringing in an additional factor of p_i/ρ_i which combines with e_i to result in the appearance of h_i rather than e_i in \mathbf{J}_h . The flux \mathbf{J}_h is sometimes referred to as “enthalpy diffusion” when the species mass fluxes \mathbf{J}_i are diffusional in character. The quantities \mathbf{J}_h and \mathbf{J}_q both represent additional energy fluxes due to the relative motion between species. These fluxes are inherently multicomponent quantities which are unrelated to ordinary thermal heat conduction and vanish in a pure fluid.

For consistency with the velocity \mathbf{u} determined by the momentum equation, the kinetic energy per unit volume of the mixture must be considered to be $\frac{1}{2}\rho|\mathbf{u}|^2$, which differs from $\sum_i \frac{1}{2}\rho_i|\mathbf{u}_i|^2$. Because of this difference, the internal energy per unit volume $\rho\epsilon \equiv \rho E - \frac{1}{2}\rho|\mathbf{u}|^2$ is not purely thermal in nature, but also contains the relative kinetic energy of the species velocities in a frame moving with \mathbf{u} . We readily find that $\epsilon = e + q$, where $\rho e = \sum_i \rho_i e_i$ is the thermal part of the internal energy density and $\rho q = \sum_i \frac{1}{2}\rho_i|\mathbf{w}_i|^2 = -\frac{1}{2}\mathbf{R}:\mathbf{U}$ is the nonthermal part. A transport equation for ϵ can be obtained by subtracting Eq. (14) from Eq. (19), which gives

$$\frac{\partial(\rho\epsilon)}{\partial t} + \nabla \cdot (\rho\epsilon\mathbf{u}) = \boldsymbol{\sigma}:\nabla\mathbf{u} - \nabla \cdot \mathbf{J}_h - \nabla \cdot \mathbf{J}_q \quad (21)$$

in which the additional energy fluxes \mathbf{J}_h and \mathbf{J}_q still appear. It is also instructive to derive an evolution equation for the nonthermal internal energy per unit mass q , which is readily found to be

$$\frac{\partial(\rho q)}{\partial t} + \nabla \cdot (\rho q\mathbf{u}) = \mathbf{R}:\nabla\mathbf{u} - \sum_i \mathbf{w}_i \cdot \nabla p_i - \Phi - \nabla \cdot \mathbf{J}_q, \quad (22)$$

where $\Phi = -\sum_{ij} \mathbf{w}_i \cdot \mathbf{F}_{ij}$. By subtracting Eq. (22) from Eq. (21), we obtain a similar evolution equation for e :

$$\frac{\partial(\rho e)}{\partial t} + \nabla \cdot (\rho e\mathbf{u}) = -p\nabla \cdot \mathbf{u} + \sum_i \mathbf{w}_i \cdot \nabla p_i + \Phi - \nabla \cdot \mathbf{J}_h. \quad (23)$$

The terms $\sum_i \mathbf{w}_i \cdot \nabla p_i$ and Φ appear with opposite signs in Eqs. (22) and (23), so they evidently represent an exchange of energy between nonthermal and thermal internal energy. The former term represents reversible work done by the partial pressure of each species on itself, while Φ represents work done on each species by the other species via the forces \mathbf{F}_{ij} . This term is nonzero because even though the forces of species i and j on each other are equal and opposite, the work done by these forces is nevertheless not equal and opposite due to the fact that the species move with different velocities.

It is of interest to specialize to the common case in which the forces between species are purely frictional in nature, so that \mathbf{F}_{ij} takes the form³

$$\mathbf{F}_{ij} = \alpha_{ij}(\mathbf{u}_j - \mathbf{u}_i) = \alpha_{ij}(\mathbf{w}_j - \mathbf{w}_i) \quad (24)$$

and $\alpha_{ij} = \alpha_{ji}$. We then find

$$\Phi = \frac{1}{2} \sum_{ij} \alpha_{ij} |\mathbf{w}_j - \mathbf{w}_i|^2 = \frac{1}{2} \sum_{ij} \alpha_{ij} |\mathbf{u}_j - \mathbf{u}_i|^2 > 0, \quad (25)$$

so that Φ represents a sink term in the nonthermal internal energy equation and an equal and opposite source term in the

thermal internal energy equation. In this case, Φ therefore represents the rate at which the nonthermal internal energy q is irreversibly dissipated into thermal internal energy e by the frictional drag forces between species.

VII. SIMPLIFICATIONS DUE TO SMALL RELATIVE VELOCITIES

The above relations contain a number of unfamiliar terms because they are valid in the general case where the differences between the species velocities are not necessarily small. Most of these terms become negligible when the species velocities \mathbf{u}_i differ only slightly from \mathbf{u} , that is, when the \mathbf{w}_i are small. This occurs, in particular, when the frictional force coefficients α_{ij} are large. The individual species momentum equations then reduce to the Stefan–Maxwell equations of multicomponent diffusion theory, and the species mass fluxes \mathbf{J}_i become diffusional in character.³

When the \mathbf{w}_i are small, terms of order $|\mathbf{w}_i|^2$ may be neglected and the equations then simplify considerably. In particular, the stress tensor $\boldsymbol{\sigma}$ then simply reduces to $-p\mathbf{U}$, so that $\nabla \cdot \boldsymbol{\sigma}$ reduces to $-\nabla p$ and the momentum and kinetic energy equations (9) and (14) reduce to their usual inviscid forms. Moreover, q then becomes negligible compared to e , so that there is no longer any distinction between ϵ and e . Equations (21) and (23) correspondingly become identical, because \mathbf{J}_q also becomes negligible compared to \mathbf{J}_h , while the terms Φ and $\sum_i \mathbf{w}_i \cdot \nabla p_i$ can be neglected because they are both of second order in \mathbf{w}_i . [The fact that the latter term is of order $|\mathbf{w}_i|^2$ can be verified by eliminating ∇p_i using Eq. (7).] Note, however, that the flux \mathbf{J}_h is *linear* in the \mathbf{w}_i and therefore cannot be neglected. This flux represents an absolutely essential contribution to the total heat flux, and failure to include it can result in serious errors in the temperature and pressure.

VIII. ANALOGIES TO TURBULENCE MODELING

This final section is addressed to readers conversant with turbulence and turbulence modeling,⁵ who will note that several of the concepts discussed above have close turbulent analogs. In particular, the additional stress \mathbf{R} is analogous to a Reynolds stress and arises in much the same way. It is an additional momentum flux resulting from the averaged effects of internal nonthermal velocity variations which do not contribute to the mass-weighted mean velocity field \mathbf{u} . Similarly, the excess kinetic energy per unit mass associated with these internal velocities is q , which is analogous to the turbulent kinetic energy per unit mass. Consequently, the relation between q and \mathbf{R} is formally the same as that in turbulence. And just as in turbulence, the evolution equation for q contains a source term $\mathbf{R}:\nabla\mathbf{u}$ and a sink term Φ , which represents the rate at which q is dissipated to thermal energy and which appears as an equal but opposite source term in the thermal internal energy equation. All of these features are quite general, and simply arise from the fact that in contrast to ordinary single-component laminar fluid dynamics, we now have two kinds of internal energy: the usual thermal internal energy e , and a nonthermal dynamical internal energy q which represents the kinetic energy of internal velocity deviations or fluctuations that do not contribute to and hence are not contained in \mathbf{u} . This circumstance then gives

rise to various coupling terms and mechanisms by which q and e exchange energy with each other and with the kinetic energy of the mean flow.

In the present context, however, it should be noted that it is not necessary, and would in fact be undesirable, to simultaneously solve the transport equations for both q and e . The reason is that q is already known as a simple algebraic function of the species velocities \mathbf{u}_i , which are determined by the species momentum equations or their diffusional approximation. It is therefore merely necessary to solve the transport equation (21) for the total internal energy per unit mass ϵ , which is simpler in form than Eq. (23) for e , whereupon e can be obtained from ϵ simply by subtracting out q . Moreover, Eq. (21) looks very much like the usual thermal internal energy equation in a single-component fluid, which can therefore be used in the present context simply by including R in σ and inserting the \mathbf{J}_h and \mathbf{J}_q terms, provided that we also *reinterpret* the internal energy as $e+q$ as discussed above.

ACKNOWLEDGMENTS

I am grateful to C. H. Chang and Larry Cloutman for many helpful discussions and thoughtful comments on the manuscript. This work was performed under the auspices of the U.S. Department of Energy by the University of California, Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48.

^aElectronic mail: ramshaw@llnl.gov

¹J. M. Burgers, *Flow Equations for Composite Gases* (Academic, New York, 1969).

²L. C. Woods, *The Thermodynamics of Fluid Systems* (Oxford University Press, Oxford, 1975).

³J. D. Ramshaw, "Hydrodynamic theory of multicomponent diffusion and thermal diffusion in multitemperature gas mixtures," *J. Non-Equilib. Thermodyn.* **18**, 121–134 (1993).

⁴P. A. Thompson, *Compressible-Fluid Dynamics* (McGraw-Hill, New York, 1972).

⁵D. C. Wilcox, *Turbulence Modeling for CFD* (DCW Industries, La Cañada, CA, 1998), 2nd ed.



Aeliophile. This linear version of Hero's engine was made by the firm of James W. Queen of Philadelphia, who described it in their 1881 catalogue as "Hero's Engine. With straight jet, mounted, with lamp, on a neat car." They sold it for \$8.00. In use, steam generated by boiling water in the spherical brass container was shot horizontally to propel the car using the rocket principle. This example is at Amherst College; a similar one is at Williston Academy a few miles to the southwest. (Photograph and notes by Thomas B. Greenslade, Jr., Kenyon College)