Modelling of thermal diffusion and thermodynamic restrictions

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A B S T R A C T

Upon a review of the balance equations for a mixture, diffusion fluxes are shown to satisfy an evolution equation which, with slight differences, describes diffusion relative to a constituent or relative to the barycentric reference. As a consequence, the particular case of binary mixtures is considered with the view of establishing a connection with the current models. The fact that the diffusion flux is governed by a balance (evolution) equation is quite unusual in the literature since customary models are based on constitutive equations (Fick's law, Soret and Dufour models). This in turn motivates the analysis for a more appropriate thermodynamic setting. The second law for the whole mixture, along with some constitutive assumptions in classical (nonequilibrium) thermodynamics, is shown to provide the constitutive equations which are currently applied in the literature. Instead, the model of diffusion flux through a balance equation proves to be fully consistent with rational thermodynamics and the assumption that the functions, relative to a single constituent, depend on variables pertaining to that constituent whereas interaction terms are allowed to depend also on quantities pertaining to the other constituents.

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1. Introduction

Diffusion means the movement of a constituent of a mixture relative to another constituent or relative to an appropriate reference. The movement may originate by inhomogeneities of, e.g., mass density, temperature, pressure. Thermal diffusion, or Soret (or Ludwig–Soret) effect, indicates the movement originated by a temperature gradient. This effect occurs and is investigated in both liquid and solid mixtures. Meanwhile we may have energy flux originated by a temperature gradient (heat conduction) and also by a gradient of mass density (Dufour effect).

The literature provides models of thermal diffusion within different settings. A classical thermodynamic setting is that of the so-called nonequilibrium thermodynamics or thermodynamics of irreversible processes (see, e.g., De Groot & Mazur, 1984; Fitts, 1962). In addition, kinetic arguments are applied to support the models or to estimate phenomenological coefficients (see, e.g., Asaro, Farkas, & Kulkarni, 2008; Brenner, 2006; Morozov, 2009). Other settings are widely used such as rational thermodynamics (Truesdell, 1984), rational extended thermodynamics (Müller & Ruggeri, 1998), and extended irreversible thermodynamics (Jou, Casas-Vázquez, & Lebon, 2010). A review of the settings and models for thermal diffusion is given in Rahman and Saghir (2014) and Pavelka, Marsik, and Klika (2014) along with an extensive list of references on the subject.

Diffusion may denote the motion of the constituents of a mixture, relative to the mixture as a whole, or to a reference constituent, as is the case for solute and solvent or that of a constituent relative to markers in a crystal lattice (Sekerka, 2004). It is then natural to set diffusion within the theory of mixtures (Bowen, 1976). Of course, the idea is not new in

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the literature and there are many papers in this regard. Yet, a thorough application of the theory of mixtures shows that the diffusion flux is governed by a balance equation (Morro, 2013, 2014; Müller, 1975, 2001). Strangely enough, apart from very few papers, this feature seems to be ignored. The diffusion flux is customarily modelled by an appropriate constitutive equation; Fick's law is the simplest constitutive equation. It is then of interest to investigate the modelling of mass diffusion, due to mass density and temperature gradients, via the appropriate balance equations versus known models based on constitutive equations.

The purpose of this paper is twofold. First, to review the balance equations for a mixture and to show that any diffusion flux satisfies an evolution equation which, with slight differences, describes diffusion relative to a constituent or relative to the barycentric reference. As a consequence, the particular case of binary mixtures is considered with the view of establishing a connection with the current models. The second fold deals with the appropriate thermodynamic setting of diffusion. We will show that the second law for the whole mixture and some constitutive assumptions in classical (nonequilibrium) thermodynamics leads naturally to the constitutive equations which are currently applied in the literature (Fick's law, Soret and Dufour models). Instead, as we expect it to be, no restriction is placed by thermodynamics on the diffusion fluxes if we argue within rational thermodynamics and assume that the functions, relative to a single constituent, depend on variables pertaining to that constituent whereas interaction terms are allowed to depend also on quantities pertaining to the other constituents.

2. Balance equations for single constituents

Throughout we consider a fluid mixture of n constituents occupying a time-dependent region $\Omega \subset \mathbb{R}^3$. The vector $\mathbf{x}$ denotes the position of a point, in Ω, relative to a chosen origin and $t \in \mathbb{R}$ is the time. The subscripts $\alpha, \beta = 1, 2, \ldots, n$ label the quantities pertaining to the constituents of the mixture. The symbol ∇ denotes the gradient with respect to the position $\mathbf{x}$ and ∂_t is the partial derivative with respect to the time t. The superscript T means transpose.

The mass density ρ_α and the velocity $\mathbf{v}_\alpha$ are required to satisfy the continuity equations

$$\partial_t \rho_\alpha + \nabla \cdot (\rho_\alpha \mathbf{v}_\alpha) = \tau_\alpha, \tag{1}$$

where τ_α is the mass produced, per unit time and unit volume, of the αth constituent, $\alpha = 1, 2, \ldots, n$. The overall conservation of mass requires that

$$\sum_\alpha \tau_\alpha = 0. \tag{2}$$

Hereafter it is understood that summation runs over $\alpha = 1, 2, \ldots, n$. The mass density of the mixture, ρ, and the barycentric velocity, $\mathbf{v}$, are defined by

$$\rho = \sum_\alpha \rho_\alpha, \quad \rho \mathbf{v} = \sum_\alpha \rho_\alpha \mathbf{v}_\alpha. \tag{3}$$

Hence summation of (1) over α provides

$$\partial_t \rho + \nabla \cdot (\rho \mathbf{v}) = 0. \tag{4}$$

Let a superposed dot stand for the derivative along the barycentric motion, namely $\dot{\psi} = \partial_t \psi + \mathbf{v} \cdot \nabla \psi$ for any function on $\Omega \times \mathbb{R}$. Hence we can write (4) in the form

$$\dot{\rho} + \rho \nabla \cdot \mathbf{v} = 0. \tag{5}$$

The mass fraction ω_α and the diffusion velocity $\mathbf{u}_\alpha$ are defined by

$$\omega_\alpha = \frac{\rho_\alpha}{\rho}, \quad \mathbf{u}_\alpha = \mathbf{v}_\alpha - \mathbf{v}.$$

Since $\sum_\alpha \omega_\alpha = 1$ we may regard $\omega_1, \ldots, \omega_{n-1}$ and ρ as n variables in 1–1 correspondence with $\rho_1, \rho_2, \ldots, \rho_n$.
Let

$$\mathbf{h}_\alpha := \rho_\alpha \mathbf{u}_\alpha.$$

Substitution of ρ_α with $\rho \omega_\alpha$ in (1) and use of (5) provides

$$\rho \dot{\omega}_\alpha = -\nabla \cdot \mathbf{h}_\alpha + \tau_\alpha. \tag{6}$$

The vector $\mathbf{h}_\alpha$ is termed the diffusion flux. It follows that

$$\sum_\alpha \mathbf{h}_\alpha = 0. \tag{7}$$

Still within the Eulerian description we write the equations of motion in the form

$$\partial_t (\rho_\alpha \mathbf{v}_\alpha) + \nabla \cdot (\rho_\alpha \mathbf{v}_\alpha \otimes \mathbf{v}_\alpha) = \nabla \cdot \mathbf{T}_\alpha + \rho_\alpha \mathbf{f}_\alpha + \mathbf{m}_\alpha, \tag{8}$$