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ABSTRACT

A generalized thermodynamics for chemically active multiphase solid-fluid mixtures in turbulent state of motion is formulated. The global equations of balance for each phase are ensemble averaged and the local conservation laws for the mean motions are derived. The averaged form of the Clausius-Duhem inequality is used and the thermodynamics of the chemically active mixtures in turbulent motion is studied. Particular attention is given to the species concentration and chemical reaction effects, in addition to transport and interaction of the phasic fluctuation energies. Based on the averaged entropy inequality, constitutive equations for the stresses, energy, heat and mass fluxes of various species are developed. The explicit governing equations of motion are derived and discussed.

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MASTER

INTRODUCTION

Chemically active multiphase flow has attracted considerable attention due to their many significant industrial applications such as pulverized coal and fluidized bed combustion. Extensive surveys of literature on earlier and recent works were provided by Soo (1969), Smith et al. (1981), Hetsroni (1982), Borghi (1988) and Zhou (1993).

Continuum theories for multiphase mixtures were developed by Truesdell and Toupin (1960), Eringen and Ingram (1965), Drumheller and Bedford (1980), Nunziato and Walsh (1980), Passman et al. (1984), Ahmadi (1982, 1987), Massoudi (1986), and Johnson et al. (1991a,b). Time and volume averaging method were used by Twiss and Eringen (1971), Drew and Lahey (1979), Ishii and Mishima (1984), Ahmadi (1989) and Ahmadi and Ma (1990), among others.

The importance of turbulence kinetic energy in turbulent fluid flows and in developing turbulence models are now well recognized (Launder and Spalding, 1972; Rodi, 1982; Lumley, 1983; Ahmadi, 1985, 1991; Chowdhury and Ahmadi, 1992). Earlier works on modeling dispersed two-phase turbulent flows was reported by Hetsroni and Sokolov (1972), Taweel and Landau (1977), Genchev and Karpuzov (1980), and Chen and Wood (1985). In these models, it was assumed that the particles were simply transported by the carrier fluid flow. The effects of the particulate phase in modifying the fluid turbulence were, thus, totally ignored. Elghobashi and Abou-Arab (1983) developed a model for dilute flows which included, in part, the interaction effects. Kashiwa (1987), Gidaspow et al. (1989), Louge et al. (1991) and Sanjay et al. (1994) proposed more elaborated models that offered certain improvements, but did not consider the fluctuation energy transfer and particle collisions effects for dense multiphase turbulent flows.

Recently, by using the global phasic conservation laws, Ahmadi and Ma (1990) and Abu-Zaid and Ahmadi (1993) developed the basic governing equations for the mean motion and the fluctuation kinetic energies of the multiphase mixture in a turbulent state. The constitutive laws for the mean motions of different species were

also developed. The model included the effects of particle collisions, as well as the phasic fluctuation kinetic energy transfer, and is, therefore, suitable for application to relatively dense multiphase flows. Cao and Ahmadi (1994a,b) used the model to analyze turbulent gas-particle flow in a vertical and inclined channels, and showed that the model predictions are in good agreement with the available experimental data of Tsuji et al. (1984) and Miller and Gidaspow (1992).

In this work, the thermodynamics approach of Ahmadi and Ma (1990) is further generalized and applied to the chemically active multiphase turbulent flow. The fluid is treated as one additional phase with many constituents. The global conservation laws including chemical reactions for different particulate phases and the fluid phase are described. Ensemble averaging method is applied to the integral form of the balance laws, and the local forms of the basic laws of motion for different constituents are developed. Attention was also given to the formulation of mass diffusion of different species. The equations governing the fluctuation kinetic and thermal energies of the particulate phases and the fluid phase are also described. Based on the averaged Clausius-Duhem inequality, constitutive laws for the phasic stress, energy, heat and mass fluxes are developed. The expressions for the phasic interaction momentum supply, the interaction fluctuation kinetic and thermal energy supply, as well as the interaction entropy supply due to chemical reactions are also derived. It is shown that in the absence of the chemical reactions, and turbulence effects, the present model will reduce to the thermodynamical formulation of multiphase mixture theory of Ahmadi and Ma (1990). When the effects of the turbulence and/or the particulate fluctuation kinetic energy are neglected, the equations are consistent with those of Zhou (1993), Nunziato and Walsh (1980), and Baer and Nunziato (1986).

GLOBAL BALANCE LAWS

Consider a dispersed mixture of n distinct particulate phases and m fluid phase. The global balance laws for the α th phase in the multiphase mixture, in the presence of chemical reaction and interfacial mass transfer are given as:

Conservation of mass

$$\frac{\partial}{\partial t} \iiint_V \rho^\alpha dV + \iint_A \rho^\alpha v_j^\alpha n_j dA = \iiint_V \rho^\alpha C^{\alpha+} dV \quad (1)$$

Balance of linear momentum

$$\frac{\partial}{\partial t} \iiint_V \rho^\alpha v_i^\alpha dV + \iint_A \rho^\alpha v_i^\alpha v_j^\alpha n_j dA = \iiint_V \rho^\alpha f_i^\alpha dV + \iint_A t_{ji}^\alpha n_j dA + \iiint_V P_i^\alpha dV \quad (2)$$

Balance of mechanical energy

$$\begin{aligned} \frac{\partial}{\partial t} \iiint_V \rho^\alpha \left(\frac{v_i^\alpha v_i^\alpha}{2} \right) dV + \iint_A \rho^\alpha \left(\frac{v_i^\alpha v_i^\alpha}{2} \right) v_j^\alpha n_j dA &= \iiint_V \rho^\alpha v_i^\alpha f_i^\alpha dV \\ + \iiint_V v_i^\alpha t_{ji}^\alpha n_j dV + \iiint_V v_i^\alpha P_i^\alpha dV - \iiint_V \rho^\alpha C^{\alpha+} \left(\frac{v_i^\alpha v_i^\alpha}{2} \right) dV &\quad (3) \end{aligned}$$

Conservation of energy

$$\begin{aligned} \frac{\partial}{\partial t} \iiint_V \rho^\alpha \left(\frac{v_i^\alpha v_i^\alpha}{2} + e^\alpha \right) dV + \iint_A \rho^\alpha \left(\frac{v_i^\alpha v_i^\alpha}{2} + e^\alpha \right) v_j^\alpha n_j dA &= \iiint_V \rho^\alpha v_i^\alpha f_i^\alpha dV \\ + \iint_A v_i^\alpha t_{ji}^\alpha n_j dA + \iint_A q_i^\alpha n_i dA + \iiint_V (r^\alpha + e^{\alpha+}) dV &\quad (4) \end{aligned}$$

Clausius-Duhem inequality

$$\sum_{\alpha=1}^{n+1} \left[\frac{\partial}{\partial t} \iiint_V \rho^\alpha \eta^\alpha dV + \iint_A \rho^\alpha \eta^\alpha v_j^\alpha n_j dA - \iint_A h_i^\alpha \vartheta^\alpha n_i dA - \iiint_V (r^\alpha \vartheta^\alpha + \eta^{\alpha+}) dV \right] \geq 0 \quad (5)$$

In these equations, V is a fixed volume of space with surface A , \vec{v} is the instantaneous velocity vector, ρ is the density, \vec{n} is the unit normal vector, \vec{f} is the body force per unit mass, t_{ji} is the stress tensor, P_i is the interaction momentum supply per unit volume, e is the internal energy per unit mass, q_i is the heat flux vector pointing outward of an enclosed volume, r is the heat source (due to radiation and nonchemical reaction effects) per unit volume, h_i^α is the entropy flux vectors, $C^{\alpha+}$ is the mass exchange between phases due to chemical reactions, e^+ is the interaction energy supply, η is the entropy per unit mass, η^+ is the interaction entropy supply and ϑ is the coldness defined as

$$\vartheta = 1/\theta \quad (6)$$

where θ is the temperature. The superscript for α ($1 \leq \alpha \leq n$) represents the α th particulate phase and $\alpha = n + 1$ in equations (2)-(5) (superscript f is used later)

denotes the fluid phase. In equation (1), $\alpha = \hat{f}$ ($n + 1 \leq \alpha = \hat{f} \leq n + m$) refers to the m fluid constituents. Throughout this work the regular Cartesian tensor notation with Latin subscripts is used. Thus, indices after a comma denote partial derivatives and d/dt stands for the total time derivative.

For turbulent multiphase flows, the field quantities for all phases vary randomly. These random functions could be decomposed into mean and fluctuation parts. These are:

$$\begin{aligned}
 \rho^\alpha &= \bar{\rho}^\alpha + \rho^{\alpha'}, & \overline{\rho^{\alpha'}} &= 0, \\
 v_i^\alpha &= \bar{v}_i^\alpha + v_i^{\alpha'}, & \overline{v_i^{\alpha'}} &= 0, \\
 P_i^\alpha &= \bar{P}_i^\alpha + P_i^{\alpha'}, & \overline{P_i^{\alpha'}} &= 0, \\
 \theta^\alpha &= \bar{\theta}^\alpha + \theta^{\alpha'}, & \overline{\theta^{\alpha'}} &= 0, \\
 \vartheta^\alpha &= \bar{\vartheta}^\alpha + \vartheta^{\alpha'}, & \overline{\vartheta^{\alpha'}} &= 0, \\
 t_{ij}^\alpha &= \bar{t}_{ij}^\alpha + t_{ij}^{\alpha'}, & \overline{t_{ij}^{\alpha'}} &= 0, \\
 h_i^\alpha &= \bar{h}_i^\alpha + h_i^{\alpha'}, & \overline{h_i^{\alpha'}} &= 0, \\
 q_i^\alpha &= \bar{q}_i^\alpha + q_i^{\alpha'}, & \overline{q_i^{\alpha'}} &= 0, \\
 e^{\alpha+} &= \bar{e}^{\alpha+} + e^{\alpha+'}, & \overline{e^{\alpha+'}} &= 0, \\
 \eta^{\alpha+} &= \bar{\eta}^{\alpha+} + \eta^{\alpha+'}, & \overline{\eta^{\alpha+'}} &= 0, \\
 C^{\alpha+} &= \bar{C}^{\alpha+} + C^{\alpha+'}, & \overline{C^{\alpha+'}} &= 0.
 \end{aligned} \tag{7}$$

Here, a bar on the top of a letter stands for the expected value (ensemble average) and a prime denotes the fluctuating part. The body force acceleration f_i and heat source r are assumed to be nonfluctuating. Following Farve (1965), mass-weighted ensemble averaging for certain field quantities is used to obtain convenient forms of the equations governing the mean motion. Accordingly, the following decompositions are introduced:

$$\begin{aligned}
 v_i^\alpha &= \tilde{v}_i^\alpha + v_i^{\alpha''}, & \tilde{v}_i^\alpha &= \frac{\overline{\rho^\alpha v_i^\alpha}}{\bar{\rho}^\alpha}, & v_i^{\alpha''} &= \frac{\overline{\rho^\alpha v_i^{\alpha'}}}{\bar{\rho}^\alpha}, \\
 C^{\alpha+} &= \tilde{C}^{\alpha+} + C^{\alpha+''}, & \tilde{C}^{\alpha+} &= \frac{\overline{\rho^\alpha C^{\alpha+}}}{\bar{\rho}^\alpha},
 \end{aligned}$$

$$e^\alpha = \tilde{e}^\alpha + e^{\alpha''}, \quad \tilde{e}^\alpha = \frac{\overline{\rho^\alpha e^\alpha}}{\bar{\rho}^\alpha},$$

$$\eta^\alpha = \tilde{\eta}^\alpha + \eta^{\alpha''}, \quad \tilde{\eta}^\alpha = \hat{\eta}^\alpha + \eta^{\alpha T} = \frac{\overline{\rho^\alpha \eta^\alpha}}{\bar{\rho}^\alpha}. \quad (8)$$

Here, a tilde on the top of a letter represents a mass-weighted ensemble averaged quantity and double prime stands for the fluctuating part relative to the mass-weighted average. Equation (8) also shows that $\overline{v_i^{\alpha''}}$ is proportional to the fluctuation velocity-density correlation. Note that the ensemble average of a double prime quantity is not zero, while

$$\overline{\rho^\alpha v_i^{\alpha''}} = \overline{\rho^\alpha C^{\alpha+''}} = \overline{\rho^\alpha e^{\alpha''}} = \overline{\rho^\alpha \eta^{\alpha''}} = 0. \quad (9)$$

The decomposition of the mass-weighted averaged entropy is along the line of Ahmadi (1989). It is assumed that the mean entropy $\tilde{\eta}^\alpha$ is composed of two parts, $\hat{\eta}^\alpha$ and $\eta^{\alpha T}$, corresponding to the molecular and turbulent agitations, respectively. While $\hat{\eta}^\alpha$ is a function of temperature, $\eta^{\alpha T}$ is expected to be a function of the state of fluctuation (turbulence) of α th phase.

Taking the ensemble average of equations (1)-(5), and using the decompositions given by equations (7) and (8), the integral form of the balance laws follows. These are:

Conservation of mass

$$\frac{\partial}{\partial t} \iiint_V \bar{\rho}^\alpha dV + \iint_A \bar{\rho}^\alpha \tilde{v}_j^\alpha n_j dA = \iiint_V \bar{\rho}^\alpha \tilde{C}^{\alpha+} dV. \quad (10)$$

Balance of linear momentum

$$\begin{aligned} & \frac{\partial}{\partial t} \iiint_V \bar{\rho}^\alpha \tilde{v}_i^\alpha dV + \iint_A \bar{\rho}^\alpha \tilde{v}_i^\alpha \tilde{v}_j^\alpha n_j dA + \iint_A \overline{\rho^\alpha v_i^{\alpha''} v_j^{\alpha''}} n_j dA \\ & = \iiint_V \bar{\rho}^\alpha f_i^\alpha dV + \iint_A \bar{t}_{ji}^\alpha n_j dA + \iiint_V \bar{P}_i^\alpha dV. \end{aligned} \quad (11)$$

Balance of mechanical energy

$$\begin{aligned} & \frac{\partial}{\partial t} \iiint_V \bar{\rho}^\alpha \left(\frac{\tilde{v}_i^\alpha \tilde{v}_i^\alpha}{2} + k^\alpha \right) dV + \iint_A \bar{\rho}^\alpha \left(\frac{\tilde{v}_i^\alpha \tilde{v}_i^\alpha}{2} + k^\alpha \right) \tilde{v}_j^\alpha n_j dA + \iint_A \overline{\rho^\alpha \frac{v_i^{\alpha''} v_i^{\alpha''}}{2}} v_j^{\alpha''} n_j dA \\ & + \iint_A \overline{\rho^\alpha v_i^{\alpha''} v_j^{\alpha''}} \tilde{v}_i^\alpha n_j dA = \iiint_V \bar{\rho}^\alpha \tilde{v}_i^\alpha f_i^\alpha dV + \iint_V \tilde{v}_i^\alpha \bar{t}_{ji}^\alpha dV + \iiint_V \overline{v_i^{\alpha''} \bar{t}_{ji}^\alpha} dV \\ & + \iint_V \overline{v_i^{\alpha''} \bar{t}_{ji}^{\alpha'}} dV + \iint_V \overline{v_i^\alpha \bar{P}_i^\alpha} dV - \left[\iiint_V \overline{\rho^\alpha C^{\alpha+''} v_i^{\alpha''} \tilde{v}_i^\alpha} dV \right. \\ & \left. + \iint_V \bar{\rho}^\alpha \tilde{C}^{\alpha+} \left(\frac{\tilde{v}_i^\alpha \tilde{v}_i^\alpha}{2} + k^\alpha \right) dV + \iint_V \overline{\rho^\alpha \frac{v_i^{\alpha''} v_i^{\alpha''}}{2}} C^{\alpha+''} dV \right]. \end{aligned} \quad (12)$$

Conservation of energy

$$\begin{aligned}
& \frac{\partial}{\partial t} \iiint_V \bar{\rho}^\alpha \left(\frac{\tilde{v}_i^\alpha \tilde{v}_i^\alpha}{2} + k^\alpha + \tilde{e}^\alpha \right) dV + \iint_A \bar{\rho}^\alpha \left(\frac{\tilde{v}_i^\alpha \tilde{v}_i^\alpha}{2} + k^\alpha + \tilde{e}^\alpha \right) \tilde{v}_j^\alpha n_j dA \\
& + \iint_A \overline{\rho^\alpha \frac{v_i^{\alpha''} v_i^{\alpha''}}{2} v_j^{\alpha''} n_j} dA + \iint_A \overline{\rho^\alpha v_i^{\alpha''} v_j^{\alpha''} \tilde{v}_i^\alpha n_j} dA + \iint_A \overline{\rho^\alpha e^{\alpha''} v_j^{\alpha''} n_j} dA \\
& = \iiint_V \bar{\rho}^\alpha \tilde{v}_i^\alpha f_i^\alpha dV + \iint_A \tilde{v}_i^\alpha \bar{t}_{ji}^\alpha n_j dA + \iint_A \overline{v_i^{\alpha''} \bar{t}_{ji}^\alpha} n_j dA \\
& + \iint_A \overline{v_i^{\alpha''} \bar{t}_{ji}^{\alpha'}} n_j dA + \iint_A \bar{q}_i^\alpha n_i dA + \iiint_V (r^\alpha + \tilde{e}^{\alpha+}) dV. \tag{13}
\end{aligned}$$

Clausius-Duhem inequality

$$\begin{aligned}
& \sum_{\alpha=1}^{n+1} \left[\frac{\partial}{\partial t} \iiint_V \bar{\rho}^\alpha \tilde{\eta}^\alpha dV + \iint_A (\bar{\rho}^\alpha \tilde{\eta}^\alpha \tilde{v}_j^\alpha + \overline{\rho^\alpha \eta^{\alpha''} v_j^{\alpha''}}) n_j dA \right. \\
& \left. - \iint_A (\bar{h}_i^\alpha \tilde{\vartheta}^\alpha + \overline{h_i^{\alpha'} \vartheta^{\alpha'}}) n_i dA - \iiint_V (r^\alpha \tilde{\vartheta}^\alpha + \tilde{\eta}^{\alpha+}) dV \right] \geq 0. \tag{14}
\end{aligned}$$

In these equations, k^α is the fluctuation kinetic energy of the α th phase defined as

$$\bar{\rho}^\alpha k^\alpha = \overline{\rho^\alpha \frac{v_i^{\alpha''} v_i^{\alpha''}}{2}}. \tag{15}$$

Equations (10)-(14) are the statements of global conservation laws for the mean motion of the multiphase mixture.

DIFFERENTIAL BALANCE LAWS

While the instantaneous field variables in a dispersed multiphase turbulent flow are random, discontinuous and non-differentiable functions, their averages are continuous, smoothly varying, differentiable functions of space and time. Applying the divergence theorem to the surface integrals in equations (10)-(14) and rearranging terms, the differential balance laws for the mean motion of the multiphase mixture follows.

The differential forms of the equations of conservation of mass for the α th particulate phase as obtained from equation (10) is given as

$$\frac{\partial \bar{\rho}^\alpha}{\partial t} + \frac{\partial}{\partial x_j} (\bar{\rho}^\alpha \tilde{v}_j^\alpha) = \bar{\rho}^\alpha \tilde{C}^{\alpha+}. \tag{16}$$

When the α th particulate phase is incompressible, it follows that

$$\bar{\rho}^\alpha = \rho_0^\alpha \nu^\alpha, \quad (17)$$

where ν^α is the mean volume fraction of the α th phase. Since ρ_0^α is a constant, equation (16) may now be restated as

$$\frac{\partial \nu^\alpha}{\partial t} + \frac{\partial}{\partial x_j} (\nu^\alpha \tilde{v}_j^\alpha) = \nu^\alpha \tilde{C}^{\alpha+}. \quad (18)$$

Similarly, for the \hat{f} th fluid phase the statement of conservation of mass becomes

$$\frac{\partial \bar{\rho}^{\hat{f}}}{\partial t} + \frac{\partial}{\partial x_j} (\bar{\rho}^{\hat{f}} \tilde{v}_j^{\hat{f}}) = \bar{\rho}^{\hat{f}} \tilde{C}^{\hat{f}+}. \quad (19)$$

The averaged density of the fluid phases is given as

$$\bar{\rho}^f = \sum_{\hat{f}=1}^m \bar{\rho}^{\hat{f}}. \quad (20)$$

The averaged velocity of fluid phases \tilde{v}_i^f is defined as

$$\bar{\rho}^f \tilde{v}_i^f = \sum_{\hat{f}=1}^m \bar{\rho}^{\hat{f}} \tilde{v}_i^{\hat{f}}. \quad (21)$$

We introduce the concentration of species in the fluid phase as

$$c^{\hat{f}} = \frac{\bar{\rho}^{\hat{f}}}{\bar{\rho}^f}, \quad \sum_{\hat{f}=1}^m c^{\hat{f}} = 1. \quad (22)$$

Using equation (22), equation (19) may be restated as

$$\bar{\rho}^f \left(\frac{\partial c^{\hat{f}}}{\partial t} + \tilde{v}_i^{\hat{f}} \frac{\partial c^{\hat{f}}}{\partial x_i} \right) = \frac{\partial J_i^{\hat{f}}}{\partial x_i} + \bar{\rho}^f \tilde{C}^{\hat{f}-}, \quad (23)$$

where the mass flux $J_i^{\hat{f}}$ and source term $\tilde{C}^{\hat{f}-}$ are defined as

$$J_i^{\hat{f}} = -\bar{\rho}^{\hat{f}} (\tilde{v}_i^{\hat{f}} - \tilde{v}_i^f), \quad \bar{\rho}^f \tilde{C}^{\hat{f}-} = \bar{\rho}^{\hat{f}} \tilde{C}^{\hat{f}+} - \bar{\rho}^f \tilde{C}^{f+}. \quad (24)$$

Here

$$\bar{\rho}^f \tilde{C}^{f+} = \sum_{\hat{f}=1}^m \bar{\rho}^{\hat{f}} \tilde{C}^{\hat{f}+}. \quad (25)$$

Equation (23) is a diffusion equation for the \hat{f} th fluid species.

Summing equation (19) for $\hat{f} = 1$ to m and using equations (20) and (21), the continuity equation of the fluid phases follows. i.e.,

$$\frac{\partial \bar{\rho}^f}{\partial t} + \frac{\partial}{\partial x_j} (\bar{\rho}^f \tilde{v}_j^f) = \bar{\rho}^f \tilde{C}^{f+}. \quad (26)$$

Therefore, the fluid (gas) phases may be treated as an additional phase with m different constituents of different concentrations. For an incompressible fluid phase,

$$\bar{\rho}^f = \rho_0^f \nu^f, \quad (27)$$

where density ρ_0^f is also a constant. Equation (26) now may be rewritten as

$$\frac{\partial \nu^f}{\partial t} + \frac{\partial}{\partial x_j} (\nu^f \tilde{v}_j^f) = \nu^f \tilde{C}^{f+}. \quad (28)$$

For fully saturated mixtures, the following constraint is imposed:

$$\bar{\rho} = \bar{\rho}^f + \sum_{\alpha=1}^n \bar{\rho}^\alpha. \quad (29)$$

When the constituents are incompressible, equation (29) leads to

$$\nu^f + \sum_{\alpha=1}^n \nu^\alpha = 1. \quad (30)$$

In addition, the following constraint on the averaged mass exchange due to chemical reactions must hold.

$$\bar{\rho}^f \tilde{C}^{f+} + \sum_{\alpha=1}^n \bar{\rho}^\alpha \tilde{C}^{\alpha+} = 0. \quad (31)$$

Form equation (11), the local forms of balance of linear momentum for the α th particulate phase and for the fluid phase are derived. These are

$$\bar{\rho}^\alpha \frac{d\tilde{v}_i^\alpha}{dt} = \bar{\rho}^\alpha f_i^\alpha + \frac{\partial \bar{\tau}_{ji}^\alpha}{\partial x_j} + \frac{\partial \hat{t}_{ji}^\alpha}{\partial x_j} + \bar{P}_i^\alpha - \bar{\rho}^\alpha \tilde{C}^{\alpha+} \tilde{v}_i^\alpha, \quad (32)$$

and

$$\bar{\rho}^f \frac{d\tilde{v}_i^f}{dt} = \bar{\rho}^f f_i^f + \frac{\partial \bar{t}_{ji}^f}{\partial x_j} + \frac{\partial \hat{t}_{ji}^{fT}}{\partial x_j} + \bar{P}_i^f - \bar{\rho}^f \tilde{C}^{f+} \tilde{v}_i^f. \quad (33)$$

In equation (32) for the particulate phases, the fluctuation (kinetic) stress tensor

$t_{ji}^{\alpha T}$ and the collisional stress tensor $t_{ji}^{\alpha c}$ are combined. i.e.,

$$\bar{\tau}_{ji}^{\alpha} = \bar{t}_{ji}^{\alpha c} + t_{ji}^{\alpha T}, \quad t_{ji}^{\alpha T} = -\overline{\rho^{\alpha} v_j^{\alpha''} v_i^{\alpha''}}, \quad (34)$$

and

$$\hat{t}_{ji}^{\alpha} = \bar{t}_{ji}^{\alpha} - \bar{t}_{ji}^{\alpha c}, \quad (35)$$

is the average stress tensor in the absence of collisional effects. The fluid turbulent stress tensor t_{ji}^{fT} is defined as

$$t_{ji}^{fT} = -\overline{\rho^f v_j^{f''} v_i^{f''}}. \quad (36)$$

Using equations (16), (26) and (31), the equation of mass conservation for the entire mixture becomes

$$\frac{\partial \bar{\rho}}{\partial t} + \frac{\partial}{\partial x_j} (\bar{\rho} \tilde{v}_j) = 0, \quad (37)$$

where the density of mixture $\bar{\rho}$ is defined by equation (29) and the velocity of mixture \tilde{v}_j are defined as

$$\bar{\rho} \tilde{v}_j = \bar{\rho}^f \tilde{v}_j^f + \sum_{\alpha=1}^n \bar{\rho}^{\alpha} \tilde{v}_j^{\alpha}. \quad (38)$$

The balance of linear momentum for the entire mixture follows by adding equation (32) and (33) for all the species. i.e.,

$$\bar{\rho} \frac{d\tilde{v}_i}{dt} = \bar{\rho} f_i + \frac{\partial \tau_{ji}}{\partial x_j}, \quad (39)$$

where the total mixture stress is defined as

$$\tau_{ji} = \sum_{f=1}^m (\bar{t}_{ji}^f + t_{ji}^{fT} - \bar{\rho}^f \tilde{v}_i^f \tilde{v}_j^f) + \sum_{\alpha=1}^n (\bar{\tau}_{ji}^{\alpha} + \hat{t}_{ji}^{\alpha} - \bar{\rho}^{\alpha} \tilde{v}_i^{\alpha} \tilde{v}_j^{\alpha}) + \bar{\rho} \tilde{v}_i \tilde{v}_j. \quad (40)$$

In the derivation of equation (39), the conditions that the net interaction momentum supply must be zero. i.e.,

$$\bar{P}_i^f + \sum_{\alpha=1}^n \bar{P}_i^{\alpha} = 0, \quad (41)$$

and

$$\bar{\rho}^f \tilde{C}^{f+} \tilde{v}_i^f + \sum_{\alpha=1}^n \bar{\rho}^\alpha \tilde{C}^{\alpha+} \tilde{v}_i^\alpha = 0, \quad (42)$$

are used.

Equation (12) for the balance of mechanical energy may be restated in differential form as

$$\begin{aligned} \bar{\rho}^\alpha \frac{dk^\alpha}{dt} &= \bar{\tau}_{ji}^\alpha \tilde{v}_{i,j}^\alpha - \overline{v_i^{\alpha''} p_i^\alpha} + K_{j,j}^\alpha - \bar{\rho}^\alpha \epsilon^\alpha + \bar{\rho}^\alpha s^\alpha \\ &\quad - \overline{\rho^\alpha C^{\alpha+''} v_i^{\alpha''} \tilde{v}_i^\alpha} - 2\bar{\rho}^\alpha \tilde{C}^{\alpha+} k^\alpha - \overline{\rho^\alpha \frac{v_i^{\alpha''} v_i^{\alpha''}}{2} C^{\alpha+''}}, \end{aligned} \quad (43)$$

where,

$$\bar{\rho}^\alpha \epsilon^\alpha = \bar{\rho}^\alpha (\epsilon^{\alpha c} + \epsilon^{\alpha v}), \quad \bar{\rho}^\alpha \epsilon^{\alpha c} = \overline{t_{ij}^{\alpha c} v_{i,j}^\alpha}, \quad \bar{\rho}^\alpha \epsilon^{\alpha v} = \overline{t_{ij}^{\alpha v} v_{i,j}^{\alpha''}}. \quad (44)$$

In these equations, ϵ^α is the dissipation rate for α th phase per unit mass, $\epsilon^{\alpha c}$ and $\epsilon^{\alpha v}$ are the particulate collisional and viscous dissipation rates and $t_{ij}^{\alpha v} = t_{ij}^{\alpha} + p^\alpha \delta_{ij}$ is the viscous (dissipative) part of t_{ij}^{α} . Here

$$K_j^\alpha = -\overline{\rho^\alpha \frac{v_i^{\alpha''} v_i^{\alpha''}}{2} v_j^{\alpha''}} + \overline{v_i^{\alpha''} t_{ji}^{\alpha v}} + \overline{v_i^{\alpha''} t_{ji}^{\alpha c}} - \overline{v_j^{\alpha''} p^{\alpha'}}, \quad (45)$$

is the particulate fluctuation energy flux vector, and

$$\bar{\rho}^\alpha s^\alpha = \overline{v_i^\alpha P_i^\alpha} - \overline{P_i^\alpha \tilde{v}_i^\alpha} = \overline{v_i^{\alpha''} P_i^\alpha}, \quad (46)$$

is the particulate interaction fluctuation energy supply term. In equation (43), the particulate fluctuation pressure-velocity gradient correlation term $\overline{v_i^{\alpha''} p^{\alpha'}}$ was neglected.

For the fluid phase equation (43) may be restated as

$$\begin{aligned} \bar{\rho}^f \frac{dk^f}{dt} &= t_{ji}^{fT} \tilde{v}_{i,j}^f - \overline{v_i^{f''} p_i^f} + K_{j,j}^f - \bar{\rho}^f \epsilon^f + \bar{\rho}^f s^f \\ &\quad - \overline{\rho^f C^{f+''} v_i^{f''} \tilde{v}_i^f} - 2\bar{\rho}^f \tilde{C}^{f+} k^f - \overline{\rho^f \frac{v_i^{f''} v_i^{f''}}{2} C^{f+''}}, \end{aligned} \quad (47)$$

where the fluid turbulent kinetic energy k^f and fluid dissipation rate ϵ^f are defined

as

$$\bar{\rho}^f k^f = \overline{\rho^f \frac{v_i^{f''} v_i^{f''}}{2}}, \quad \bar{\rho}^f \epsilon^f = \overline{t_{ji}^{fv} v_{i,j}^{f''}}, \quad (48)$$

respectively. Here,

$$K_j^f = -\overline{\rho^f \frac{v_i^{f''} v_i^{f''}}{2} v_j^{f''}} + \overline{v_i^{f''} t_{ji}^{fv}} - \overline{v_j^{f''} p^{f'}}, \quad (49)$$

is the fluid fluctuation energy flux vector, and

$$\bar{\rho}^f s^f = \overline{v_i^f P_i^f} - \bar{P}_i^f \bar{v}_i^f = \overline{v_i^{f''} P_i^f}, \quad (50)$$

is the fluid fluctuation energy supply term. The instantaneous stress tensor in the fluid phase is expressed as $t_{ji}^f = -p^f \delta_{ij} + t_{ji}^{fv}$, where t_{ji}^{fv} is the viscous part of the fluid stress tensor and p^f is the fluid hydrodynamic pressure. Equations (43) and (47) show that the fluctuation energies are being produced by the action of the total fluctuation (kinetic plus collisional for the particulate phases) stresses in a mean shear field, transported by convection and diffusion and are dissipated. Furthermore, fluctuation energies could be supplied or extracted through the interaction source terms. There are also a secondary source terms related to the product of the density-velocity correlation and mean pressure gradient fields.

Subtracting the mechanical energy equation given by (12) from equation (13) and using the divergence theorem, it follows that

$$\begin{aligned} \bar{\rho}^\alpha \frac{d\bar{\epsilon}^\alpha}{dt} &= \bar{q}_{j,j}^\alpha + q_{j,j}^{\alpha T} + \bar{\rho}^\alpha \epsilon^\alpha + \overline{\hat{t}_{ji}^\alpha \tilde{v}_{j,i}^\alpha} - \overline{v_i^\alpha P_i^\alpha} - \overline{\bar{p}^\alpha v_{i,i}^{\alpha''}} + r^\alpha + \bar{\epsilon}^{\alpha+} \\ &- \bar{\rho}^\alpha \bar{C}^{\alpha+} (\bar{\epsilon}^\alpha - \frac{\overline{\tilde{v}_i^\alpha \tilde{v}_i^\alpha}}{2} - k^\alpha) + \overline{\rho^\alpha \frac{v_i^{\alpha''} v_i^{\alpha''}}{2} C^{\alpha+}} + \overline{\rho^\alpha C^{\alpha+} v_i^{\alpha''} \tilde{v}_i^\alpha}, \end{aligned} \quad (51)$$

and

$$\begin{aligned} \bar{\rho}^f \frac{d\bar{\epsilon}^f}{dt} &= \bar{q}_{j,j}^f + q_{j,j}^{fT} + \bar{\rho}^f \epsilon^f + \overline{\hat{t}_{ji}^f \tilde{v}_{j,i}^f} - \overline{v_i^f P_i^f} - \overline{\bar{p}^f v_{i,i}^{f''}} + r^f + \bar{\epsilon}^{f+} \\ &- \bar{\rho}^f \bar{C}^{f+} (\bar{\epsilon}^f - \frac{\overline{\tilde{v}_i^f \tilde{v}_i^f}}{2} - k^f) + \overline{\rho^f \frac{v_i^{f''} v_i^{f''}}{2} C^{f+}} + \overline{\rho^f C^{f+} v_i^{f''} \tilde{v}_i^f}. \end{aligned} \quad (52)$$

where

$$q_j^{\alpha T} = \overline{\rho^\alpha e^{\alpha''} v_j^{\alpha''}}, \quad q_j^{fT} = \overline{\rho^f e^{f''} v_j^{f''}}. \quad (53)$$

are the α th particulate and the fluid turbulent heat flux vectors. Note that for all phases, the net energy exchange should be zero. i.e.,

$$\bar{e}^{f+} + \sum_{\alpha=1}^n \bar{e}^{\alpha+} = 0. \quad (54)$$

Equations (51) and (52) are the statement of the local form of the conservation of energy for the α th particulate and the fluid phases. In these equations, the fluctuation pressure-velocity gradient correlation terms $\overline{p^{\alpha'} v_{i,i}^{\alpha''}}$ and $\overline{p^{f'} v_{i,i}^{f''}}$ were also neglected.

The entropy inequality equation as given by (14) may be restated in differential form as:

$$\sum_{\alpha=1}^{n+1} \left[\bar{\rho}^{\alpha} \dot{\eta}^{\alpha} - (\bar{h}_i^{\alpha} \bar{\vartheta}^{\alpha})_{,i} - R_{i,i}^{\alpha T} - r^{\alpha} \bar{\vartheta}^{\alpha} + \bar{\rho}^{\alpha} \dot{\eta}^{\alpha T} - S_{i,i}^{\alpha T} - \bar{\eta}^{\alpha+} + \bar{\rho}^{\alpha} \tilde{C}^{\alpha+} \dot{\eta}^{\alpha} \right] \geq 0. \quad (55)$$

where the turbulent entropy flux vector $S_i^{\alpha T}$ and the heat flux-coldness correlation vector $R_i^{\alpha T}$ are defined as

$$S_i^{\alpha T} = -\overline{\rho^{\alpha} v_i^{\alpha''} \eta^{\alpha''}}, \quad (56)$$

and

$$R_i^{\alpha T} = \overline{h_i^{\alpha'} \vartheta^{\alpha'}}. \quad (57)$$

The net entropy exchange for all phases should also be zero. i.e.,

$$\bar{\eta}^{f+} + \sum_{\alpha=1}^n \bar{\eta}^{\alpha+} = 0. \quad (58)$$

The phasic Helmholtz free energy functions for the mean thermal and turbulent fluctuations are defined as (Ahmadi and Ma, 1990)

$$\begin{aligned} \hat{\psi}^{\alpha} &= \bar{e}^{\alpha} - \hat{\eta}^{\alpha} / \bar{\vartheta}^{\alpha}, & \psi^{\alpha T} &= k^{\alpha} - \eta^{\alpha T} / \vartheta^{\alpha T}, \\ \hat{\psi}^f &= \bar{e}^f - \hat{\eta}^f / \bar{\vartheta}^f, & \psi^{f T} &= k^f - \eta^{f T} / \vartheta^{f T}. \end{aligned} \quad (59)$$

In these equations, $\vartheta^{\alpha T}$ and $\vartheta^{f T}$ are the particulate fluctuation and the fluid turbulence coldness defined analogous to the thermal coldness.

Using equations (43), (47), (51)-(52) and (59) in equation (55), the result may be restated as

$$\begin{aligned}
& \sum_{\alpha=1}^n \bar{\vartheta}^{\alpha} \left[-\bar{\rho}^{\alpha} \left(\dot{\psi}^{\alpha} - \bar{\eta}^{\alpha} \frac{\dot{\vartheta}^{\alpha}}{(\bar{\vartheta}^{\alpha})^2} \right) + \bar{q}_{j,j}^{\alpha} + q_{j,j}^{\alpha T} + \hat{t}_{ji}^{\alpha} \tilde{v}_{j,i}^{\alpha} + \bar{\rho}^{\alpha} \epsilon^{\alpha} \right. \\
& - \frac{1}{\bar{\vartheta}^{\alpha}} (\bar{h}_i^{\alpha} \bar{\vartheta}^{\alpha})_{,i} - \tilde{v}_i^{\alpha} \bar{P}_i^{\alpha} - \bar{\rho}^{\alpha} s^{\alpha} - \bar{p}^{\alpha} \overline{v_{i,i}^{\alpha}} - \frac{1}{\bar{\vartheta}^{\alpha}} R_{i,i}^{\alpha T} + \bar{e}^{\alpha+} - \frac{1}{\bar{\vartheta}^{\alpha}} \bar{\eta}^{\alpha+} \\
& + \frac{1}{\bar{\vartheta}^{\alpha}} \bar{\rho}^{\alpha} \tilde{C}^{\alpha+} \bar{\eta}^{\alpha} - \bar{\rho}^{\alpha} \tilde{C}^{\alpha+} \bar{e}^{\alpha} \\
& + \bar{\rho}^{\alpha} \left(\frac{\tilde{v}_i^{\alpha} \tilde{v}_i^{\alpha}}{2} + k^{\alpha} \right) \tilde{C}^{\alpha+} + \frac{\overline{\rho^{\alpha} v_i^{\alpha} v_i^{\alpha} C^{\alpha+}}}{2} + \overline{\rho^{\alpha} C^{\alpha+} v_i^{\alpha} \tilde{v}_i^{\alpha}} \left. \right] \\
& + \bar{\vartheta}^f \left[-\bar{\rho}^f \left(\dot{\psi}^f - \bar{\eta}^f \frac{\dot{\vartheta}^f}{(\bar{\vartheta}^f)^2} \right) + \bar{q}_{j,j}^f + q_{j,j}^{fT} + \hat{t}_{ji}^f \tilde{v}_{j,i}^f + \bar{\rho}^f \epsilon^f \right. \\
& - \frac{1}{\bar{\vartheta}^f} (\bar{h}_i^f \bar{\vartheta}^f)_{,i} - \tilde{v}_i^f \bar{P}_i^f - \bar{\rho}^f s^f - \bar{p}^f \overline{v_{i,i}^f} - \frac{1}{\bar{\vartheta}^f} R_{i,i}^{fT} + \bar{e}^{f+} - \frac{1}{\bar{\vartheta}^f} \bar{\eta}^{f+} \\
& + \frac{1}{\bar{\vartheta}^f} \bar{\rho}^f \tilde{C}^{f+} \bar{\eta}^f - \bar{\rho}^f \tilde{C}^{f+} \bar{e}^f \\
& + \bar{\rho}^f \left(\frac{\tilde{v}_i^f \tilde{v}_i^f}{2} + k^f \right) \tilde{C}^{f+} + \frac{\overline{\rho^f v_i^f v_i^f C^{f+}}}{2} + \overline{\rho^f C^{f+} v_i^f \tilde{v}_i^f} \left. \right] \\
& + \sum_{\alpha=1}^n \vartheta^{\alpha T} \left[-\bar{\rho}^{\alpha} \left(\psi^{\alpha T} - \eta^{\alpha T} \frac{\dot{\vartheta}^{\alpha T}}{(\vartheta^{\alpha T})^2} \right) + \bar{\tau}_{ji}^{\alpha} \tilde{v}_{i,j}^{\alpha} \right. \\
& - \bar{\rho}^{\alpha} \epsilon^{\alpha} - \overline{v_i^{\alpha} p_i^{\alpha}} + K_{j,j}^{\alpha} + \bar{\rho}^{\alpha} s^{\alpha} - \frac{1}{\vartheta^{\alpha T}} S_{i,i}^{\alpha T} \\
& - 2\bar{\rho}^{\alpha} \tilde{C}^{\alpha+} k^{\alpha} - \frac{\overline{\rho^{\alpha} v_i^{\alpha} v_i^{\alpha} C^{\alpha+}}}{2} - \overline{\rho^{\alpha} C^{\alpha+} v_i^{\alpha} \tilde{v}_i^{\alpha}} \left. \right] \\
& + \vartheta^{fT} \left[-\bar{\rho}^f \left(\psi^{fT} - \eta^{fT} \frac{\dot{\vartheta}^{fT}}{(\vartheta^{fT})^2} \right) + t_{ji}^{fT} \tilde{v}_{i,j}^f \right. \\
& - \bar{\rho}^f \epsilon^f - \overline{v_i^{fT} p_i^f} + K_{j,j}^f + \bar{\rho}^f s^f - \frac{1}{\vartheta^{fT}} S_{i,i}^{fT} \\
& - 2\bar{\rho}^f \tilde{C}^{f+} k^f - \frac{\overline{\rho^f v_i^{fT} v_i^{fT} C^{f+}}}{2} - \overline{\rho^f C^{f+} v_i^{fT} \tilde{v}_i^f} \left. \right] \geq 0. \tag{60}
\end{aligned}$$

Equation (60) is the statement of averaged form of Clausius-Duhem inequality for chemically active turbulent multiphase flows.

CONSTITUTIVE EQUATIONS

In this section, based on averaged entropy inequality as given by (60), a set of constitutive equations for the mean turbulent multiphase flow are developed. Following Ahmadi and Ma (1990), in analogy with classical thermodynamics, we assume

$$\begin{aligned}
\bar{h}_i^\alpha &= \bar{q}_i^\alpha, & \bar{h}_i^f &= \bar{q}_i^f - \sum_{j=1}^m j^j \bar{\mu}^j, \\
R_i^{\alpha T} &= q_i^{\alpha T} \bar{\vartheta}^\alpha, & S_i^{\alpha T} &= K_i^\alpha \vartheta^{\alpha T}, \\
R_i^{f T} &= (q_i^{f T} - \sum_{j=1}^m j^{j T} \bar{\mu}^j) \bar{\vartheta}^f, & S_i^{f T} &= K_i^f \vartheta^{f T} - E_i^f.
\end{aligned} \tag{61}$$

That is the mean entropy flux for the particulate phase is assumed to be equal to the mean heat flux, while that of the fluid phase includes the products of mass diffusion of the f th species and the corresponding chemical potential $\bar{\mu}^f$. The turbulence entropy flux is assumed to be equal to the product of the energy flux vector and the corresponding coldness. For the fluid phase a vector \vec{E}^f is introduced in equation (61) to account for the possible differences.

Using equation (61), inequality (60) may be restated as

$$\begin{aligned}
& \sum_{\alpha=1}^n \bar{\vartheta}^\alpha \left[-\bar{\rho}^\alpha \left(\dot{\psi}^\alpha - \dot{\eta}^\alpha \frac{\dot{\vartheta}^\alpha}{(\bar{\vartheta}^\alpha)^2} \right) - \frac{1}{\bar{\vartheta}^\alpha} Q_i^\alpha \bar{\vartheta}_{,i}^\alpha + \hat{t}_{ji}^\alpha \bar{v}_{j,i}^\alpha + \bar{\rho}^\alpha \epsilon^\alpha \right. \\
& - \bar{v}_i^\alpha \bar{P}_i^\alpha - \bar{\rho}^\alpha s^\alpha - \bar{\rho}^\alpha \overline{v_{i,i}^{\alpha''}} + \bar{e}^{\alpha+} - \frac{1}{\bar{\vartheta}^\alpha} \bar{\eta}^{\alpha+} - \bar{\rho}^\alpha \bar{C}^{\alpha+} \bar{e}^\alpha \\
& \left. + \bar{\rho}^\alpha \left(\frac{\bar{v}_i^\alpha \bar{v}_i^\alpha}{2} + k^\alpha \right) \bar{C}^{\alpha+} + \frac{\overline{\rho^\alpha v_i^{\alpha''} v_i^{\alpha''} C^{\alpha+}}}{2} + \overline{\rho^\alpha C^{\alpha+} v_i^{\alpha''} \bar{v}_i^\alpha \right] \\
& + \bar{\vartheta}^f \left[-\bar{\rho}^f \left(\dot{\psi}^f - \dot{\eta}^f \frac{\dot{\vartheta}^f}{(\bar{\vartheta}^f)^2} \right) - \frac{1}{\bar{\vartheta}^f} Q_i^f \bar{\vartheta}_{,i}^f + \frac{1}{\bar{\vartheta}^f} \sum_{j=1}^m (J^j \bar{\mu}^j \bar{\vartheta}^f)_{,i} + \hat{t}_{ji}^f \bar{v}_{j,i}^f + \bar{\rho}^f \epsilon^f \right. \\
& - \bar{v}_i^f \bar{P}_i^f - \bar{\rho}^f s^f - \bar{\rho}^f \overline{v_{i,i}^{f''}} + \bar{e}^{f+} - \frac{1}{\bar{\vartheta}^f} \bar{\eta}^{f+} - \bar{\rho}^f \bar{C}^{f+} \bar{e}^f \\
& \left. + \bar{\rho}^f \left(\frac{\bar{v}_i^f \bar{v}_i^f}{2} + k^f \right) \bar{C}^{f+} + \frac{\overline{\rho^f v_i^{f''} v_i^{f''} C^{f+}}}{2} + \overline{\rho^f C^{f+} v_i^{f''} \bar{v}_i^f \right] \\
& + \sum_{\alpha=1}^n \vartheta^{\alpha T} \left[-\bar{\rho}^\alpha \left(\psi^{\alpha T} - \eta^{\alpha T} \frac{\dot{\vartheta}^{\alpha T}}{(\vartheta^{\alpha T})^2} \right) + \hat{r}_{ji}^\alpha \bar{v}_{i,j}^\alpha \right. \\
& - \overline{v_i^{\alpha''} \bar{p}_{,i}^\alpha} - \bar{\rho}^\alpha \epsilon^\alpha + \bar{\rho}^\alpha s^\alpha - \frac{1}{\vartheta^{\alpha T}} K_i^\alpha \vartheta_{,i}^{\alpha T} \\
& \left. - 2\bar{\rho}^\alpha \bar{C}^{\alpha+} k^\alpha - \frac{\overline{\rho^\alpha v_i^{\alpha''} v_i^{\alpha''} C^{\alpha+}}}{2} - \overline{\rho^\alpha C^{\alpha+} v_i^{\alpha''} \bar{v}_i^\alpha \right] \\
& + \vartheta^{f T} \left[-\bar{\rho}^f \left(\psi^{f T} - \eta^{f T} \frac{\dot{\vartheta}^{f T}}{(\vartheta^{f T})^2} \right) + \hat{r}_{ji}^f \bar{v}_{i,j}^f \right. \\
& - \overline{v_i^{f''} \bar{p}_{,i}^f} - \bar{\rho}^f \epsilon^f + \bar{\rho}^f s^f - \frac{1}{\vartheta^{f T}} K_i^f \vartheta_{,i}^{f T} + \frac{1}{\vartheta^{f T}} E_{i,i}^f \\
& \left. - 2\bar{\rho}^f \bar{C}^{f+} k^f - \frac{\overline{\rho^f v_i^{f''} v_i^{f''} C^{f+}}}{2} - \overline{\rho^f C^{f+} v_i^{f''} \bar{v}_i^f \right] \geq 0,
\end{aligned} \tag{62}$$

where Q_i^α and Q_i^f are the total heat flux vectors defined as

$$\begin{aligned}
Q_i^\alpha &= \bar{q}_i^\alpha + q_i^{\alpha T}, \\
Q_i^f &= \bar{q}_i^f + q_i^{fT}, \\
J^f &= \bar{j}^f + j^{fT}.
\end{aligned} \tag{63}$$

The constitutive independent variables are

$$\bar{\rho}^\alpha, \bar{\rho}^f, c^f, \bar{\vartheta}^\alpha, \vartheta^{\alpha T}, \bar{\vartheta}^f, \vartheta^{fT}, \bar{\vartheta}_{,i}^\alpha, \vartheta_{,i}^{\alpha T}, \bar{\vartheta}_{,i}^f, \vartheta_{,i}^{fT}, \bar{d}_{ij}^\alpha, \tilde{d}_{ij}^{\alpha T}, \epsilon^\alpha, \epsilon^f, \bar{\mu}^f. \tag{64}$$

These are all frame-indifferent tensors and \bar{d}_{ij}^α and \tilde{d}_{ij}^f are the mean deformation rate tensors defined as

$$\bar{d}_{ij}^\alpha = \frac{1}{2}(\tilde{v}_{i,j}^\alpha + \tilde{v}_{j,i}^\alpha), \quad \tilde{d}_{ij}^f = \frac{1}{2}(\tilde{v}_{i,j}^f + \tilde{v}_{j,i}^f). \tag{65}$$

Along the line of Ahmadi and Ma (1990), the following set of frame-indifferent constitutive equations are proposed:

$$\begin{aligned}
\hat{\psi}^\alpha &= \hat{\psi}^\alpha(\bar{\rho}^\alpha, \bar{\vartheta}^\alpha), \quad \psi^{\alpha T} = \psi^{\alpha T}(\bar{\rho}^\alpha, \vartheta^{\alpha T}, \epsilon^\alpha), \\
\hat{\psi}^f &= \hat{\psi}^f(\bar{\rho}^f, \bar{\vartheta}^f, c^f), \quad \psi^{fT} = \psi^{fT}(\bar{\rho}^f, \vartheta^{\alpha T}, \epsilon^f), \\
\bar{\tau}_{ij}^\alpha &= \bar{\tau}_{ij}^\alpha(\bar{\rho}^\alpha, \bar{\vartheta}^\alpha, \bar{d}_{ij}^\alpha), \quad \hat{t}_{ij}^\alpha = \hat{t}_{ij}^\alpha(\bar{\rho}^\alpha, \vartheta^{\alpha T}, \bar{d}_{ij}^\alpha, \epsilon^\alpha), \\
\bar{t}_{ij}^f &= \bar{t}_{ij}^f(\bar{\rho}^f, \bar{\vartheta}^f, \bar{d}_{ij}^f), \quad t_{ij}^{fT} = t_{ij}^{fT}(\bar{\rho}^f, \vartheta^{fT}, \bar{d}_{ij}^f, \epsilon^f) \\
Q_i^\alpha &= Q_i^\alpha(\bar{\rho}^\alpha, \bar{\vartheta}^\alpha, \bar{\vartheta}_{,i}^\alpha), \quad K_i^\alpha = K_i^\alpha(\bar{\rho}^\alpha, \vartheta^{\alpha T}, \vartheta_{,i}^{\alpha T}, \epsilon^\alpha), \\
Q_i^f &= Q_i^f(\bar{\rho}^f, \bar{\vartheta}^f, \bar{\vartheta}_{,i}^f), \quad K_i^f = K_i^f(\bar{\rho}^f, \vartheta^{fT}, \vartheta_{,i}^{fT}, \epsilon^f), \\
\bar{v}_i^{\alpha'''} &= \bar{v}_i^{\alpha'''}(\bar{\rho}^\alpha, \bar{\rho}_{,i}^\alpha, \bar{\vartheta}^\alpha, \bar{\vartheta}_{,i}^\alpha, \vartheta^{\alpha T}, \epsilon^\alpha), \\
\bar{v}_i^{f'''} &= \bar{v}_i^{f'''}(\bar{\rho}^f, \bar{\rho}_{,i}^f, \bar{\vartheta}^f, \bar{\vartheta}_{,i}^f, \vartheta^{fT}, \epsilon^f), \\
E_i^f &= E_i^f(\bar{\rho}^f, \vartheta^{fT}, \vartheta_{,i}^{fT}, \epsilon^f, \epsilon_{,i}^f), \\
J_i^f &= J_i^f((\bar{\rho}^f, \bar{\vartheta}^f, c^f, \bar{\mu}_i^f).
\end{aligned} \tag{66}$$

For incompressible constituents the respective densities could be replaced by the corresponding volume fraction in the constitutive relations given by equation (66). Furthermore, according to the principle of equipresence of continuum mechanics all the constitutive dependent variables must, in general, be functions of all the independent constitutive variables. For simplicity of analysis, only the most relevant variables are included in the constitutive equations given by (66).

Employing (66), inequality (60) may be restated as

$$\begin{aligned}
& \sum_{\alpha=1}^n \bar{\vartheta}^{\alpha} \left[-\bar{\rho}^{\alpha} \left(\frac{\partial \hat{\psi}^{\alpha}}{\partial \bar{\vartheta}^{\alpha}} - \frac{\hat{\eta}^{\alpha}}{(\bar{\vartheta}^{\alpha})^2} \right) \dot{\bar{\vartheta}}^{\alpha} - \frac{1}{\bar{\vartheta}^{\alpha}} Q_i^{\alpha} \bar{\vartheta}_{,i}^{\alpha} + (\hat{t}_{ji}^{\alpha} + \bar{p}^{\alpha} \delta_{ij}) \bar{v}_{,i}^{\alpha} + \bar{\rho}^{\alpha} \epsilon^{\alpha} \right. \\
& - \bar{v}_i^{\alpha} \bar{P}_i^{\alpha} - \bar{\rho}^{\alpha} s^{\alpha} - \bar{p}^{\alpha} \overline{v_{i,i}^{\alpha}} + \bar{e}^{\alpha+} - \frac{1}{\bar{\vartheta}^{\alpha}} \bar{\eta}^{\alpha+} - \bar{\rho}^{\alpha} \bar{C}^{\alpha+} \bar{e}^{\alpha} \\
& \left. + \bar{\rho}^{\alpha} \left(\frac{\bar{v}_i^{\alpha} \bar{v}_i^{\alpha}}{2} + k^{\alpha} \right) \bar{C}^{\alpha+} + \frac{\overline{\rho^{\alpha} v_i^{\alpha} v_i^{\alpha} C^{\alpha+}}}{2} + \overline{\rho^{\alpha} C^{\alpha+} v_i^{\alpha} \bar{v}_i^{\alpha}} \right] \\
& + \bar{\vartheta}^f \left[-\bar{\rho}^f \left(\frac{\partial \hat{\psi}^f}{\partial \bar{\vartheta}^f} - \frac{\hat{\eta}^f}{(\bar{\vartheta}^f)^2} \right) \dot{\bar{\vartheta}}^f - \frac{1}{\bar{\vartheta}^f} Q_i^f \bar{\vartheta}_{,i}^f + (\hat{t}_{ji}^f + \bar{p}^f \delta_{ij}) \bar{v}_{,i}^f + \bar{\rho}^f \epsilon^f \right. \\
& \left. + \sum_{f=1}^m \left[(\bar{\mu}^f - \frac{\partial \hat{\psi}^f}{\partial c^f}) J_{i,i}^f + \frac{1}{\bar{\vartheta}^f} J_i^f (\bar{\mu}^f \bar{\vartheta}^f)_{,i} - \bar{\rho}^f \frac{\partial \hat{\psi}^f}{\partial c^f} \bar{C}^f - \right] \right. \\
& - \bar{v}_i^f \bar{P}_i^f - \bar{\rho}^f s^f - \bar{p}^f \overline{v_{i,i}^f} + \bar{e}^{f+} - \frac{1}{\bar{\vartheta}^f} \bar{\eta}^{f+} - \bar{\rho}^f \bar{C}^{f+} \bar{e}^f \\
& \left. + \bar{\rho}^f \left(\frac{\bar{v}_i^f \bar{v}_i^f}{2} + k^f \right) \bar{C}^{f+} + \frac{\overline{\rho^f v_i^f v_i^f C^{f+}}}{2} + \overline{\rho^f C^{f+} v_i^f \bar{v}_i^f} \right] \\
& + \sum_{\alpha=1}^n \vartheta^{\alpha T} \left[-\bar{\rho}^{\alpha} \left(\frac{\partial \psi^{\alpha T}}{\partial \vartheta^{\alpha T}} - \frac{\eta^{\alpha T}}{(\vartheta^{\alpha T})^2} \right) \dot{\vartheta}^{\alpha T} + (\bar{\tau}_{ji}^{\alpha} + p^{\alpha T} \delta_{ij}) \bar{v}_{,i}^{\alpha} \right. \\
& - \bar{\rho}^{\alpha} \epsilon^{\alpha} - \overline{v_i^{\alpha} \bar{p}_{,i}^{\alpha}} + \bar{\rho}^{\alpha} s^{\alpha} - \frac{1}{\vartheta^{\alpha T}} K_i^{\alpha} \vartheta_{,i}^{\alpha T} - \bar{\rho}^{\alpha} \frac{\partial \psi^{\alpha T}}{\partial \epsilon^{\alpha}} \dot{\epsilon}^{\alpha} \\
& \left. - 2\bar{\rho}^{\alpha} \bar{C}^{\alpha+} k^{\alpha} - \frac{\overline{\rho^{\alpha} v_i^{\alpha} v_i^{\alpha} C^{\alpha+}}}{2} - \overline{\rho^{\alpha} C^{\alpha+} v_i^{\alpha} \bar{v}_i^{\alpha}} \right] \\
& + \vartheta^{fT} \left[-\bar{\rho}^f \left(\frac{\partial \psi^{fT}}{\partial \vartheta^{fT}} - \frac{\eta^{fT}}{(\vartheta^{fT})^2} \right) \dot{\vartheta}^{fT} + (t_{ji}^{fT} + p^{fT} \delta_{ij}) \bar{v}_{,i}^f \right. \\
& - \bar{\rho}^f \epsilon^f - \overline{v_i^f \bar{p}_{,i}^f} + \bar{\rho}^f s^f - \frac{1}{\vartheta^{fT}} K_i^f \vartheta_{,i}^{fT} + \frac{1}{\vartheta^{fT}} E_{i,i}^f - \bar{\rho}^f \frac{\partial \psi^{fT}}{\partial \epsilon^f} \dot{\epsilon}^f \\
& \left. - 2\bar{\rho}^f \bar{C}^{f+} k^f - \frac{\overline{\rho^f v_i^f v_i^f C^{f+}}}{2} - \overline{\rho^f C^{f+} v_i^f \bar{v}_i^f} \right] \geq 0, \tag{67}
\end{aligned}$$

where

$$\begin{aligned}
\bar{p}^{\alpha} &= (\bar{\rho}^{\alpha})^2 \frac{\partial \hat{\psi}^{\alpha}}{\partial \bar{\rho}^{\alpha}}, & p^{\alpha T} &= (\bar{\rho}^{\alpha})^2 \frac{\partial \psi^{\alpha T}}{\partial \bar{\rho}^{\alpha}}, \\
\bar{p}^f &= (\bar{\rho}^f)^2 \frac{\partial \hat{\psi}^f}{\partial \bar{\rho}^f}, & p^{fT} &= (\bar{\rho}^f)^2 \frac{\partial \psi^{fT}}{\partial \bar{\rho}^f}. \tag{68}
\end{aligned}$$

The consistency conditions for pressures require that

$$p^{\alpha T} = \gamma^{\alpha} \bar{\rho}^{\alpha} k^{\alpha}, \quad p^{fT} = \frac{2}{3} \bar{\rho}^f k^f, \tag{69}$$

where γ^{α} is a parameter which is a strong function of solid volume fraction ν^{α} .

Demanding that the entropy inequality (67) holds for all independent variations of $\bar{\vartheta}^\alpha$, $\bar{\vartheta}^f$, $\vartheta^{\alpha T}$ and ϑ^{fT} , it follows that

$$\hat{\eta}^\alpha = (\bar{\vartheta}^\alpha)^2 \frac{\partial \hat{\psi}^\alpha}{\partial \bar{\vartheta}^\alpha}, \quad \eta^{\alpha T} = (\vartheta^{\alpha T})^2 \frac{\partial \psi^{\alpha T}}{\partial \vartheta^{\alpha T}}, \quad (70)$$

$$\hat{\eta}^f = (\bar{\vartheta}^f)^2 \frac{\partial \hat{\psi}^f}{\partial \bar{\vartheta}^f}, \quad \eta^{fT} = (\vartheta^{fT})^2 \frac{\partial \psi^{fT}}{\partial \vartheta^{fT}}. \quad (71)$$

Furthermore,

$$\bar{\mu}^f = \frac{\partial \hat{\psi}^f}{\partial c^f}. \quad (72)$$

The inverse of the mean coldness are now defined as

$$\hat{\theta}^\alpha = \frac{1}{\bar{\vartheta}^\alpha}, \quad \hat{\theta}^f = \frac{1}{\bar{\vartheta}^f}. \quad (73)$$

In general, $\hat{\theta}^\alpha$ and $\hat{\theta}^f$ are different from the mean temperatures $\bar{\theta}^\alpha$ and $\bar{\theta}^f$. They are equal only within the limit of a linearized theory.

Following Ahmadi and Ma (1990), it is assumed that

$$\vartheta^{\alpha T} = C^{\alpha T}/k^\alpha, \quad \vartheta^{fT} = C^{fT}/k^f, \quad (74)$$

where $C^{\alpha T}$ and C^{fT} are some positive parameters corresponding to the energy capacities of turbulent fluctuations. Using equations (71)-(73), inequality (67) reduces to

$$\begin{aligned} & \sum_{\alpha=1}^n \frac{1}{\hat{\theta}^\alpha} \left[\frac{1}{\hat{\theta}^\alpha} Q_i^\alpha \hat{\theta}_{,i}^\alpha + (\hat{t}_{ji}^\alpha + \bar{p}^\alpha \delta_{ij}) \tilde{v}_{j,i}^\alpha + \bar{p}^\alpha \epsilon^\alpha \right. \\ & \quad - \tilde{v}_i^\alpha \bar{P}_i^\alpha - \bar{p}^\alpha s^\alpha - \bar{p}^\alpha \overline{v_{i,i}^{\alpha''}} + \bar{e}^{\alpha+} - \hat{\theta}^\alpha \bar{\eta}^{\alpha+} - \bar{p}^\alpha \tilde{C}^{\alpha+} \bar{e}^\alpha \\ & \quad \left. + \bar{p}^\alpha \left(\frac{\tilde{v}_i^\alpha \tilde{v}_i^\alpha}{2} + k^\alpha \right) \tilde{C}^{\alpha+} + \frac{\rho^\alpha v_i^{\alpha''} v_i^{\alpha''} C^{\alpha+}}{2} + \overline{\rho^\alpha C^{\alpha+} v_i^{\alpha''} \tilde{v}_i^\alpha} \right] \\ & \quad + \frac{1}{\hat{\theta}^f} \left\{ \frac{1}{\hat{\theta}^f} Q_i^f \hat{\theta}_{,i}^f + (\hat{t}_{ji}^f + \bar{p}^f \delta_{ij}) \tilde{v}_{j,i}^f + \bar{p}^f \epsilon^f \right. \\ & \quad \left. + \sum_{f=1}^m \left[\hat{\theta}^f J_i^f \left(\frac{\bar{\mu}^f}{\hat{\theta}^f} \right)_{,i} - \bar{p}^f \bar{\mu}^f \tilde{C}^{f+} \right] \right. \\ & \quad \left. - \tilde{v}_i^f \bar{P}_i^f - \bar{p}^f s^f - \bar{p}^f \overline{v_{i,i}^{f''}} + \bar{e}^{f+} - \hat{\theta}^f \bar{\eta}^{f+} - \bar{p}^f \tilde{C}^{f+} \bar{e}^f \right. \\ & \quad \left. + \bar{p}^f \left(\frac{\tilde{v}_i^f \tilde{v}_i^f}{2} + k^f \right) \tilde{C}^{f+} + \frac{\rho^f v_i^{f''} v_i^{f''} C^{f+}}{2} + \overline{\rho^f C^{f+} v_i^{f''} \tilde{v}_i^f} \right\} \end{aligned}$$

$$\begin{aligned}
& + \sum_{\alpha=1}^n \frac{C^{\alpha T}}{k^{\alpha}} \left[(\bar{\tau}_{ji}^{\alpha} + \gamma^{\alpha} \bar{\rho}^{\alpha} k^{\alpha} \delta_{ij}) \tilde{v}_{i,j}^{\alpha} - \bar{\rho}^{\alpha} \epsilon^{\alpha} \right. \\
& - \overline{v_i^{\alpha} p_i^{\alpha}} + \bar{\rho}^{\alpha} s^{\alpha} + \frac{1}{e^{\alpha}} K_i^{\alpha} k^{\alpha}_{,i} - \bar{\rho}^{\alpha} \frac{\partial \psi^{\alpha T}}{\partial \epsilon^{\alpha}} \dot{\epsilon}^{\alpha} \\
& \left. - 2\bar{\rho}^{\alpha} \tilde{C}^{\alpha} + k^{\alpha} - \frac{\overline{\rho^{\alpha} v_i^{\alpha} v_i^{\alpha} C^{\alpha+}}}{2} - \overline{\rho^{\alpha} C^{\alpha+} v_i^{\alpha} \tilde{v}_i^{\alpha}} \right] \\
& + \frac{C^{fT}}{k^f} \left[(t_{ji}^{fT} + \frac{2}{3} \bar{\rho}^f k^f \delta_{ij}) \tilde{v}_{i,j}^f - \bar{\rho}^f \epsilon^f \right. \\
& - \overline{v_i^{fT} p_i^f} + \bar{\rho}^f s^f + \frac{1}{k^f} K_i^f k^f_{,i} + \frac{k^f}{C^{fT}} E_{i,i}^f - \bar{\rho}^f \frac{\partial \psi^{fT}}{\partial \epsilon^f} \dot{\epsilon}^f \\
& \left. - 2\bar{\rho}^f \tilde{C}^f + k^f - \frac{\overline{\rho^f v_i^{fT} v_i^{fT} C^{f+}}}{2} - \overline{\rho^f C^{f+} v_i^{fT} \tilde{v}_i^f} \right] \geq 0. \tag{75}
\end{aligned}$$

Based on the Clausius-Duhem inequality given by (75), thermodynamically consistent constitutive equations may be formulated. Ahmadi and Ma (1990) described a set of isotropic quasi-linear constitutive equations for the stresses. These are:

$$\hat{t}_{ij}^{\alpha} = -(\bar{p}^{\alpha} + \frac{2}{3} \mu^{\alpha} \tilde{d}_{mm}^{\alpha}) \delta_{ij} + 2\mu^{\alpha} \tilde{d}_{ij}^{\alpha}, \tag{76}$$

$$\bar{\tau}_{ij}^{\alpha} = -(\gamma^{\alpha} \bar{\rho}^{\alpha} k^{\alpha} + \frac{2}{3} \mu^{\alpha T} \tilde{d}_{mm}^{\alpha}) \delta_{ij} + 2\mu^{\alpha T} \tilde{d}_{ij}^{\alpha}, \tag{77}$$

$$\bar{t}_{ij}^f = -(\bar{p}^f + \frac{2}{3} \mu^f \tilde{d}_{mm}^f) \delta_{ij} + 2\mu^f \tilde{d}_{ij}^f, \tag{78}$$

$$t_{ij}^{fT} = -\frac{2}{3} (\bar{\rho}^f k^f + \mu^{fT} \tilde{d}_{mm}^f) \delta_{ij} + 2\mu^{fT} \tilde{d}_{ij}^f. \tag{79}$$

Here, μ^{α} and μ^f are the coefficients of viscosity given by

$$\mu^{\alpha T} = C^{\alpha\mu} \bar{\rho}^{\alpha} d^{\alpha} (k^{\alpha})^{1/2}, \quad \mu^{fT} = C^{f\mu} \bar{\rho}^f (k^f)^2 / \epsilon^f, \tag{80}$$

where $C^{\alpha\mu}$ and $C^{f\mu}$ are parameters which depend on ρ^{α} and ρ^f , and d^{α} is an appropriate length scale of the α th particulate phase. Generalized rate-dependent and nonlinear constitutive equations for the phasic turbulent stresses were derived by Abu-Zaid and Ahmadi (1993). However, those more general formulation are not considered in this study.

The constitutive equation for the fluid species mass fluxes are given by

$$J_i^f = D^f \frac{\partial c^f}{\partial x_i}, \quad (81)$$

where

$$\hat{D}^f = C_D \frac{\partial(\bar{\mu}^f/\hat{\theta}^f)}{\partial c^f} = C_D \frac{\partial}{\partial c^f} \left(\frac{1}{\hat{\theta}^f} \frac{\partial \hat{\psi}^f}{\partial c^f} \right), \quad (82)$$

with C_D being a constant. The constitutive equations for the density-velocity correlations are given as

$$\overline{v_i^{\alpha''}} = -\frac{\mu^{\alpha T}}{\sigma^{\alpha p} \bar{\rho}^\alpha k_\alpha} \bar{p}_{,i}^\alpha, \quad \overline{v_i^{f''}} = -\frac{\mu^{f T}}{\sigma^{fp} \bar{\rho}^f k_f} \bar{p}_{,i}^f, \quad (83)$$

where $\sigma^{\alpha p}$ and σ^{fp} are parameters which are in general functions of ρ^α and ρ^f .

The fluctuation energy fluxes are assumed to be given as

$$K_i^\alpha = \frac{\mu^{\alpha T}}{\sigma^{\alpha k}} \bar{k}_{,i}^\alpha, \quad K_i^f = \left(\mu^f + \frac{\mu^{f T}}{\sigma^{fk}} \right) \bar{k}_{,i}^f. \quad (84)$$

where $\sigma^{\alpha k}$ and σ^{fk} are parameters corresponding to the Prandtl numbers for turbulence energy fluxes. It is also assumed that the heat fluxes satisfy the extended Fourier law of conduction. i.e.,

$$Q_i^\alpha = (\kappa^\alpha + \kappa^{\alpha T}) \hat{\theta}_{,i}^\alpha, \quad Q_i^f = (\kappa^f + \kappa^{f T}) \hat{\theta}_{,i}^f, \quad (85)$$

where κ 's are heat conductivity and superscript T refers to turbulence.

The entropy inequality given by (75) also imposes the following restriction on the parameters:

$$\begin{aligned} \mu^\alpha &\geq 0, & \mu^f &\geq 0, & \mu^{\alpha T} &\geq 0, & \mu^{f T} &\geq 0, \\ \kappa^\alpha &\geq 0, & \kappa^f &\geq 0, & \kappa^{\alpha T} &\geq 0, & \kappa^{f T} &\geq 0, \\ \sigma^{\alpha p} &\geq 0, & \sigma^{fp} &\geq 0, & \sigma^{\alpha k} &\geq 0, & \sigma^{fk} &\geq 0, \end{aligned}$$

$$\hat{D}^f \geq 0. \quad (86)$$

Assuming that the fluctuation velocity and the mass supply due to chemical reactions are statistically independent, it follows that

$$\overline{\rho^\alpha C^{\alpha''} v_i^{\alpha''} v_i^{\alpha''}} = \overline{\rho^\alpha C^{\alpha''} v_i^{\alpha''}} = 0, \quad (87)$$

$$\overline{\rho^f C^{f''} v_i^{f''} v_i^{f''}} = \overline{\rho^f C^{f''} v_i^{f''}} = 0. \quad (88)$$

The resulting Clausius-Duhem inequality (75) then becomes:

$$\begin{aligned} & \sum_{\alpha=1}^n \frac{1}{\hat{\theta}^\alpha} \left[-\tilde{v}_i^\alpha \bar{P}_i^\alpha - \bar{\rho}^\alpha s^\alpha + \bar{e}^{\alpha+} - \hat{\theta}^\alpha \bar{\eta}^{\alpha+} - \bar{\rho}^\alpha \tilde{C}^{\alpha+} \bar{e}^\alpha + \bar{\rho}^\alpha \left(\frac{\tilde{v}_i^\alpha \tilde{v}_i^\alpha}{2} + k^\alpha \right) \tilde{C}^{\alpha+} \right] \\ & + \frac{1}{\hat{\theta}^f} \left[-\tilde{v}_i^f \bar{P}_i^f - \bar{\rho}^f s^f + \bar{e}^{f+} - \hat{\theta}^f \bar{\eta}^{f+} - \bar{\rho}^f \tilde{C}^{f+} \bar{e}^f + \bar{\rho}^f \left(\frac{\tilde{v}_i^f \tilde{v}_i^f}{2} + k^f \right) \tilde{C}^{f+} - \sum_{\hat{f}=1}^m \rho^{\hat{f}} \bar{\mu}^{\hat{f}} \tilde{C}^{\hat{f}-} \right] \\ & + \sum_{\alpha=1}^n \frac{C^{\alpha T}}{k^\alpha} \left[\bar{\rho}^\alpha s^\alpha - 2\bar{\rho}^\alpha \tilde{C}^{\alpha+} k^\alpha \right] + \frac{C^{fT}}{k^f} \left[\bar{\rho}^f s^f - 2\bar{\rho}^f \tilde{C}^{f+} k^f \right] \geq 0. \end{aligned} \quad (89)$$

Now let

$$\tilde{C}^{\hat{f}-} = \sum_{\hat{l}=1}^m c^{\hat{f}} c^{\hat{l}} \nu^{\hat{l}} \xi^{\hat{l}}, \quad (90)$$

where $\nu^{\hat{l}}$ is proportional to stoichiometric coefficients of constituent \hat{f} in the $\hat{l}th$ chemical reaction, and $\xi^{\hat{l}}$ is the rate of advancement of reaction \hat{l} . Inequality (89) now implies that

$$\bar{\rho}^f \sum_{\hat{l}=1}^m A^{\hat{l}} \xi^{\hat{l}} \geq 0, \quad (91)$$

where $A^{\hat{l}}$ is the affinity of the $\hat{l}th$ chemical reaction defined by

$$A^{\hat{l}} = - \sum_{\hat{f}=1}^m c^{\hat{f}} c^{\hat{l}} \nu^{\hat{l}} \bar{\mu}^{\hat{f}}. \quad (92)$$

From (91), it follows that

$$\xi^{\hat{l}} = \xi_0^{\hat{l}} (\hat{\theta}^f) A^{\hat{l}}, \quad (93)$$

and

$$\tilde{C}^{\hat{f}-} = \sum_{\hat{l}=1}^m c^{\hat{f}} c^{\hat{l}} \Lambda^{\hat{l}}(\hat{\theta}^f), \quad (94)$$

where

$$\Lambda^{\hat{l}}(\hat{\theta}^f) = \xi_0^{\hat{l}} (\hat{\theta}^f) \nu^{\hat{l}} A^{\hat{l}}. \quad (95)$$

Note that the summation over \hat{l} covers the fluid constituents and the particulate species that participate in the chemical reactions. Equation (94) is an averaged form of the Arrhenius law for binary reactions.

Inequality (89) now may be restated as

$$\sum_{\alpha=1}^n \frac{1}{\hat{\theta}^\alpha} \left[-(\tilde{v}_i^\alpha - \tilde{v}_i^f) \bar{P}_i^\alpha + \bar{\rho}^\alpha \left(\frac{\tilde{v}_i^\alpha \tilde{v}_i^\alpha}{2} - \frac{\tilde{v}_i^f \tilde{v}_i^f}{2} \right) \tilde{C}^{\alpha+} \right]$$

$$\begin{aligned}
& + \sum_{\alpha=1}^n \frac{C^{\alpha T}}{k^{\alpha}} \bar{\rho}^{\alpha} s^{\alpha} + \frac{C^{fT}}{k^f} \bar{\rho}^f s^f + \sum_{\alpha=1}^n \frac{1}{\hat{\theta}^{\alpha}} \bar{e}^{\alpha+} + \frac{1}{\hat{\theta}^f} \bar{e}^{f+} \\
& - 2 \left(\sum_{\alpha=1}^n C^{\alpha T} \bar{\rho}^{\alpha} \tilde{C}^{\alpha+} + C^{fT} \bar{\rho}^f \tilde{C}^{f+} \right) \\
& + \sum_{\alpha=1}^n \frac{1}{\hat{\theta}^{\alpha}} \left[-\bar{\rho}^{\alpha} s^{\alpha} - \hat{\theta}^{\alpha} \bar{\eta}^{\alpha+} - \bar{\rho}^{\alpha} \tilde{C}^{\alpha+} \bar{e}^{\alpha} + \bar{\rho}^{\alpha} k^{\alpha} \tilde{C}^{\alpha+} - \tilde{v}_i^f \bar{P}_i^{\alpha} + \bar{\rho}^{\alpha} \frac{\tilde{v}_i^f \tilde{v}_i^f}{2} \tilde{C}^{\alpha+} \right] \\
& + \frac{1}{\hat{\theta}^f} \left[-\bar{\rho}^f s^f - \hat{\theta}^f \bar{\eta}^{f+} - \bar{\rho}^f \tilde{C}^{f+} \bar{e}^f + \bar{\rho}^f k^f \tilde{C}^{f+} - \tilde{v}_i^f \bar{P}_i^f + \bar{\rho}^f \frac{\tilde{v}_i^f \tilde{v}_i^f}{2} \tilde{C}^{f+} \right] \geq 0 \quad (96)
\end{aligned}$$

Entropy inequality (96) admits the following constitutive equations for the mean interaction momentum supply:

$$\bar{P}_i^{\alpha} = D_{ij}^{\alpha} (\tilde{v}_j^f - \tilde{v}_j^{\alpha}) + \frac{1}{2} \bar{\rho}^{\alpha} \tilde{C}^{\alpha+} (\tilde{v}_i^{\alpha} + \tilde{v}_i^f). \quad (97)$$

Furthermore, \bar{P}_i^f may be obtained from equations (41) and (97). i.e.,

$$\bar{P}_i^f = \sum_{\alpha=1}^n \left[D_{ij}^{\alpha} (\tilde{v}_j^{\alpha} - \tilde{v}_j^f) - \frac{1}{2} \bar{\rho}^{\alpha} \tilde{C}^{\alpha+} (\tilde{v}_j^{\alpha} + \tilde{v}_j^f) \right]. \quad (98)$$

where D_{ij}^{α} is a positive definite matrix given as

$$D_{ij}^{\alpha} = D_0^{\alpha} \delta_{ij} + 2L^{\alpha} \tilde{d}_{ij}^f. \quad (99)$$

In this equation, D_0^{α} and L^{α} correspond to the drag and shear lift coefficients. For a dilute suspension of spherical particles in an incompressible fluid of density ρ^f and viscosity μ_0^f ,

$$D_0^{\alpha} = \frac{18\mu_0^f \nu^{\alpha} [1 + 0.1(R_{ed}^{\alpha})^{0.75}]}{(d^{\alpha})^2 (1 - \nu^{\alpha}/\nu_m^{\alpha})^{2.5\nu_m^{\alpha}}}, \quad L^{\alpha} = \frac{2.181(\rho^f \mu_0^f)^{1/2} \nu^{\alpha}}{d^{\alpha} (\tilde{d}_{ij}^f \tilde{d}_{ji}^f)^{1/4}}, \quad (100)$$

were suggested by Ahmadi and Ma (1990). Here, d^{α} is the diameter of the α th particulate phase, and the particle Reynolds number is defined as

$$R_{ed}^{\alpha} = \frac{\rho^f d^{\alpha} |\vec{v}^f - \vec{v}^{\alpha}|}{\mu_0^f}. \quad (101)$$

In equation (100), ν_m^{α} is limiting dense packing volume fraction for shear flows. For a single size spherical particulate phase, $\nu_m = 0.64356$ (Ma and Ahmadi, 1986).

Entropy inequality (96) imposes the following restriction on the fluctuation kinetic energy source terms

$$\sum_{\alpha=1}^n \frac{C^{\alpha T}}{k^{\alpha}} \bar{\rho}^{\alpha} s^{\alpha} + \frac{C^{fT}}{k^f} \bar{\rho}^f s^f \geq 0. \quad (102)$$

Based on inequality (102), Abu-Zaid and Ahmadi (1993) obtained

$$\bar{\rho}^{\alpha} s^{\alpha} = 2D_0^{\alpha}(ck^f - k^{\alpha}), \quad (103)$$

$$\bar{\rho}^f s^f = 2 \sum_{\alpha=1}^n D_0^{\alpha}(k^{\alpha} - k^f) + \sum_{\alpha=1}^n s_1^{\alpha} D_0^{\alpha}(\tilde{v}_i^{\alpha} - \tilde{v}_i^f)(\tilde{v}_i^{\alpha} - \tilde{v}_i^f), \quad (104)$$

where

$$c = \frac{1}{1 + \tau^{\alpha}/T_L}, \quad T_L = 0.165 \frac{k^f}{\epsilon^f}, \quad \tau^{\alpha} = \frac{\bar{\rho}^{\alpha}}{D_0^{\alpha}}, \quad (105)$$

and s_1^{α} is a positive parameter with $1 \geq s_1^{\alpha} \geq 0$. Note the second term in equation (104) accounts for the generation of fluid phase turbulence due to the mean particle-fluid slip velocity.

Inequality (96) also implies that

$$\sum_{\alpha=1}^n \frac{1}{\hat{\theta}^{\alpha}} \bar{e}^{\alpha+} + \frac{1}{\hat{\theta}^f} \bar{e}^{f+} \geq 0. \quad (106)$$

Using equation (54), the expressions for $\bar{e}^{\alpha+}$ and \bar{e}^{f+} satisfying inequality (106) are given as

$$\bar{e}^{\alpha+} = e_0^{\alpha}(\hat{\theta}^f - \hat{\theta}^{\alpha}), \quad (107)$$

$$\bar{e}^{f+} = \sum_{\alpha=1}^n e_0^{\alpha}(\hat{\theta}^{\alpha} - \hat{\theta}^f), \quad (108)$$

where e_0^{α} is a positive function of $\hat{\theta}^f$ and $\hat{\theta}^{\alpha}$.

Equations (97), (98), (103), (104), (107) and (108) imply that the transport of momentum, and the fluctuation and thermal energies occur between each particulate phase and the fluid-phase. Thus, the direct transport between the particulate phases is ignored. Further generalization to include such effect is not considered in this study.

The resulting entropy inequality now becomes

$$\sum_{\alpha=1}^n \frac{1}{\hat{\theta}^{\alpha}} \left[-\bar{\rho}^{\alpha} s^{\alpha} - \hat{\theta}^{\alpha} \bar{\eta}^{\alpha+} - \bar{\rho}^{\alpha} \tilde{C}^{\alpha+} \bar{e}^{\alpha} + \bar{\rho}^{\alpha} k^{\alpha} \tilde{C}^{\alpha+} - \tilde{v}_i^f \bar{P}_i^{\alpha} + \bar{\rho}^{\alpha} \frac{\tilde{v}_i^f \tilde{v}_i^f}{2} \tilde{C}^{\alpha+} \right]$$

$$+\frac{1}{\hat{\theta}^f} \left[-\bar{\rho}^f s^f - \hat{\theta}^f \bar{\eta}^{f+} - \bar{\rho}^f \tilde{C}^{f+} \tilde{e}^f + \bar{\rho}^f k^f \tilde{C}^{f+} - \tilde{v}_i^f \bar{P}_i^f + \bar{\rho}^f \frac{\tilde{v}_i^f \tilde{v}_i^f}{2} \tilde{C}^{f+} \right] \geq 0. \quad (109)$$

Inequality (109) admits the following expressions for the entropy fluxes:

$$\begin{aligned} \bar{\eta}^{\alpha+} = & \frac{1}{\hat{\theta}^\alpha} \left[-2D_0^\alpha (ck^f - k^\alpha) - \bar{\rho}^\alpha \tilde{C}^{\alpha+} \tilde{e}^\alpha + \bar{\rho}^\alpha k^\alpha \tilde{C}^{\alpha+} \right. \\ & \left. - D_{ij}^\alpha (\tilde{v}_j^f - \tilde{v}_j^\alpha) \tilde{v}_i^f - \bar{\rho}^\alpha \frac{\tilde{v}_i^\alpha \tilde{v}_i^f}{2} \tilde{C}^{\alpha+} \right], \end{aligned} \quad (110)$$

$$\begin{aligned} \bar{\eta}^{f+} = & \frac{1}{\hat{\theta}^f} \left[-2 \sum_{\alpha=1}^n D_0^\alpha (k^\alpha - k^f) - \sum_{\alpha=1}^n s_1^\alpha D_0^\alpha (\tilde{v}_i^\alpha - \tilde{v}_i^f) (\tilde{v}_i^\alpha - \tilde{v}_i^f) \right. \\ & \left. - \bar{\rho}^f \tilde{C}^{f+} \tilde{e}^f + \bar{\rho}^f k^f \tilde{C}^{f+} - \sum_{\alpha=1}^n D_{ij}^\alpha (\tilde{v}_j^\alpha - \tilde{v}_j^f) \tilde{v}_i^f - \bar{\rho}^f \frac{\tilde{v}_i^f \tilde{v}_i^f}{2} \tilde{C}^{f+} \right]. \end{aligned} \quad (111)$$

Equations (76)-(86), (94), (97), (98), (103), (104), (107), (108), (110) and (111) are thermodynamically consistent constitutive relationships for multiphase turbulent reactive flows. Further generalization to include nonlinear and/or stress transport type model could be done along the line of Abu-Zaid and Ahmadi (1993). But this further generation is left for the future studies.

BASIC EQUATIONS

Using the constitutive relationships derived in previous section in equations (23), (32), (33), (43), (47), (51) and (52), the resulting governing equations are:

Fluid Species Concentration

$$\bar{\rho}^f \left(\frac{\partial c^f}{\partial t} + \tilde{v}_i^f \frac{\partial c^f}{\partial x_i} \right) = \frac{\partial}{\partial x_i} \left(D^f \frac{\partial c^f}{\partial x_i} \right) + \bar{\rho}^f \sum_{l=1}^m c^f c^l \Lambda^{fl}(\theta^f) \quad (112)$$

Linear Momentum

$$\begin{aligned} \bar{\rho}^\alpha \frac{d\tilde{v}_i^\alpha}{dt} = & \bar{\rho}^\alpha f_i^\alpha - \frac{\partial}{\partial x_i} \left[\bar{p}^\alpha + \gamma^\alpha \bar{\rho}^\alpha k^\alpha + \frac{2}{3} (\mu^\alpha + \mu^{\alpha T}) \tilde{v}_{m,m}^\alpha \right] \\ & + \frac{\partial}{\partial x_j} \left[(\mu^\alpha + \mu^{\alpha T}) \left(\frac{\partial \tilde{v}_i^\alpha}{\partial x_j} + \frac{\partial \tilde{v}_j^\alpha}{\partial x_i} \right) \right] + \left(D_{ij}^\alpha + \frac{1}{2} \bar{\rho}^\alpha \tilde{C}^{\alpha+} \delta_{ij} \right) (\tilde{v}_j^f - \tilde{v}_j^\alpha) \end{aligned} \quad (113)$$

$$\begin{aligned} \bar{\rho}^f \frac{d\tilde{v}_i^f}{dt} = & \bar{\rho}^f f_i^f - \frac{\partial}{\partial x_i} \left[\bar{p}^f + \frac{2}{3} \bar{\rho}^f k^f + \frac{2}{3} (\mu^f + \mu^{fT}) \tilde{v}_{m,m}^f \right] \\ & + \frac{\partial}{\partial x_j} \left[(\mu^f + \mu^{fT}) \left(\frac{\partial \tilde{v}_i^f}{\partial x_j} + \frac{\partial \tilde{v}_j^f}{\partial x_i} \right) \right] + \sum_{\alpha=1}^n \left(D_{ij}^\alpha + \frac{1}{2} \bar{\rho}^f \tilde{C}^{\alpha+} \delta_{ij} \right) (\tilde{v}_j^\alpha - \tilde{v}_j^f) \end{aligned} \quad (114)$$

Fluctuation Energy

$$\begin{aligned}\bar{\rho}^\alpha \frac{dk^\alpha}{dt} &= -(\gamma^\alpha \bar{\rho}^\alpha k^\alpha + \frac{2}{3} \mu^{\alpha T} \tilde{v}_{m,m}^\alpha) \frac{\partial \tilde{v}_i^\alpha}{\partial x_i} + \mu^{\alpha T} \left(\frac{\partial \tilde{v}_i^\alpha}{\partial x_j} + \frac{\partial \tilde{v}_j^\alpha}{\partial x_i} \right) \frac{\partial \tilde{v}_i^\alpha}{\partial x_j} + \frac{\partial}{\partial x_i} \left(\frac{\mu^{\alpha T}}{\sigma^{\alpha k}} \frac{\partial k^\alpha}{\partial x_i} \right) \\ &- \overline{v_i^{\alpha''}} \frac{\partial \bar{p}^\alpha}{\partial x_i} - \bar{\rho}^\alpha \epsilon^\alpha + 2D_0^\alpha (ck^f - k^\alpha) - 2\bar{\rho}^\alpha \tilde{C}^{\alpha+} k^\alpha\end{aligned}\quad (115)$$

$$\begin{aligned}\bar{\rho}^f \frac{dk^f}{dt} &= -\frac{2}{3} (\bar{\rho}^f k^f + \mu^{fT} \tilde{v}_{m,m}^f) \frac{\partial \tilde{v}_i^f}{\partial x_i} + \mu^{fT} \left(\frac{\partial \tilde{v}_i^f}{\partial x_j} + \frac{\partial \tilde{v}_j^f}{\partial x_i} \right) \frac{\partial \tilde{v}_i^f}{\partial x_j} + \frac{\partial}{\partial x_i} \left[\left(\mu^f + \frac{\mu^{fT}}{\sigma^{fk}} \right) \frac{\partial k^f}{\partial x_i} \right] \\ &- \overline{v_i^{f''}} \frac{\partial \bar{p}^f}{\partial x_i} - \bar{\rho}^f \epsilon^f + 2 \sum_{\alpha=1}^n D_0^\alpha (k^\alpha - k^f) \\ &+ \sum_{\alpha=1}^n s_1^\alpha D_0^\alpha (\tilde{v}_i^\alpha - \tilde{v}_i^f) (\tilde{v}_i^\alpha - \tilde{v}_i^f) - 2\bar{\rho}^f \tilde{C}^{f+k^f}\end{aligned}\quad (116)$$

Heat Transfer

$$\begin{aligned}\bar{\rho}^\alpha \frac{d\tilde{e}^\alpha}{dt} &= \frac{\partial}{\partial x_i} \left[(\kappa^\alpha + \kappa^{\alpha T}) \frac{\partial \hat{\theta}^\alpha}{\partial x_i} \right] - \left(\bar{p}^\alpha + \frac{2}{3} \mu^{\alpha T} \tilde{v}_{m,m}^\alpha \right) \frac{\partial \tilde{v}_i^\alpha}{\partial x_i} + \frac{\partial}{\partial x_j} \left[\mu^\alpha \left(\frac{\partial \tilde{v}_i^\alpha}{\partial x_j} + \frac{\partial \tilde{v}_j^\alpha}{\partial x_i} \right) \right] \frac{\partial \tilde{v}_i^\alpha}{\partial x_j} \\ &- \bar{p}^\alpha \overline{v_i^{\alpha''}} + \bar{\rho}^\alpha \epsilon^\alpha + \bar{\rho}^\alpha \bar{r}^\alpha - 2D_0^\alpha (ck^f - k^\alpha) - \tilde{v}_i^\alpha D_{ij}^\alpha (\tilde{v}_j^f - \tilde{v}_j^\alpha) \\ &- \bar{\rho}^\alpha \tilde{C}^{\alpha+} \left(\frac{1}{2} \tilde{v}_j^f \tilde{v}_j^\alpha + \tilde{e}^\alpha - k^\alpha \right) + e_0^\alpha (\hat{\theta}^f - \hat{\theta}^\alpha)\end{aligned}\quad (117)$$

$$\begin{aligned}\bar{\rho}^f \frac{d\tilde{e}^f}{dt} &= \frac{\partial}{\partial x_i} \left[(\kappa^f + \kappa^{fT}) \frac{\partial \hat{\theta}^f}{\partial x_i} \right] - \left(\bar{p}^f + \frac{2}{3} \mu^{fT} \tilde{v}_{m,m}^f \right) \frac{\partial \tilde{v}_i^f}{\partial x_i} + \frac{\partial}{\partial x_j} \left[\mu^f \left(\frac{\partial \tilde{v}_i^f}{\partial x_j} + \frac{\partial \tilde{v}_j^f}{\partial x_i} \right) \right] \frac{\partial \tilde{v}_i^f}{\partial x_j} \\ &- \bar{p}^f \overline{v_i^{f''}} + \bar{\rho}^f \epsilon^f + \bar{\rho}^f \bar{r}^f - \sum_{\alpha=1}^n s_1^\alpha D_0^\alpha (\tilde{v}_i^\alpha - \tilde{v}_i^f) (\tilde{v}_i^\alpha - \tilde{v}_i^f) - \sum_{\alpha=1}^n \tilde{v}_i^f D_{ij}^\alpha (\tilde{v}_j^\alpha - \tilde{v}_j^f) \\ &- \bar{\rho}^f \tilde{C}^{f+} \left(\frac{1}{2} \tilde{v}_j^f \tilde{v}_j^\alpha + \tilde{e}^f - k^f \right) + \sum_{\alpha=1}^n e_0^\alpha (\hat{\theta}^\alpha - \hat{\theta}^f)\end{aligned}\quad (118)$$

where the $\overline{v_i^{\alpha''}}$ and $\overline{v_i^{f''}}$ in the equations (115)-(118) are given by Abu-Zaid and Ahmadi (1993) as

$$\overline{v_i^{\alpha''}} = -\frac{\mu^{\alpha T}}{\sigma^{\alpha p} \bar{\rho}^\alpha k^\alpha} \left(\frac{\partial \bar{p}^\alpha}{\partial \bar{\rho}^\alpha} \frac{\partial \bar{\rho}^\alpha}{\partial x_i} + \frac{\partial \bar{p}^\alpha}{\partial \hat{\theta}^\alpha} \frac{\partial \hat{\theta}^\alpha}{\partial x_i} \right), \quad (119)$$

$$\overline{v_i^{f''}} = -\frac{\mu^{fT}}{\sigma^{fp} \bar{\rho}^f k^f} \left(\frac{\partial \bar{p}^f}{\partial \bar{\rho}^f} \frac{\partial \bar{\rho}^f}{\partial x_i} + \frac{\partial \bar{p}^f}{\partial \hat{\theta}^f} \frac{\partial \hat{\theta}^f}{\partial x_i} \right). \quad (120)$$

Here it is assumed that \bar{p}^α and \bar{p}^f are the functions of $\bar{\rho}^\alpha$, $\hat{\theta}^\alpha$ and $\bar{\rho}^f$, $\hat{\theta}^f$, respectively. For an incompressible dispersed mixture and when surface tension and Brownian motion effects are negligible, it may be assumed that (Ahmadi and Ma, 1990)

$$\bar{p}^\alpha = \nu^\alpha p^f, \quad \bar{p}^f = \nu^f p^f. \quad (121)$$

where p^f is the mean pressure in the fluid phase.

When dissipation rates ϵ^α and ϵ^f are specified, equations (109)-(115), (18), (28) and (30) may be used to determine phasic mean velocities, solid volume fraction, fluctuation energies and temperatures for an chemically active multiphase turbulent mixture flows. Algebraic expressions and the transport equation for the dissipation rates were suggested by Ahmadi and Ma (1990), Abu-Zaid and Ahmadi (1993) and Cao and Ahmadi (1994a,b).

Equations (16), (19) and (112)-(118) are the governing equations for densities, mean velocities, fluctuation kinetic energies and thermal energies of different species. When no chemical reaction occurs, the present model equations will reduce to the thermodynamical formulations of multiphase turbulent flows of Ahmadi and Ma (1990). When the effects of the particulate fluctuation energies are neglected, the resulting governing equations are consistent with those suggested by Zhou (1993). In the absence of turbulence effects, the present formulation resembles those of Nunziato and Walsh (1980), and Baer and Nunziato (1986).

CONCLUSIONS

The governing equations for the motion of chemically active multiphase turbulent flows are studied. The averaged form of the Clausius-Duhem inequality and the generalized thermodynamics of mixtures in turbulent state are used in the analysis. Thermodynamically consistent constitutive equations for stresses, heat and energy fluxes of various species are developed. The explicit system of governing equations are derived and discussed. The resulting model accounts for the fluctuation and thermal energy transport and interactions. Furthermore, the chemical reactions effects are included in the formulation. Thus, the developed model is suitable for applicable to chemically active multiphase turbulent flows at relative high particulate concentrations.

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