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Irreversible Thermodynamics For Spray Behavior

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Abstract. An irreversible thermodynamic theory is developed in order to study a non-homogeneous system, having a multisize set of droplets inmersed in a multicomponent mixture of gases. Conservation and balance equations are considered to be valid for the whole system and we derive the equations of motion for any gas component and for each class of droplets classified according to their size. The interaction between the droplets and the gases is taken into account through mass, momentum and energy sources in the corresponding balance equations.

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1. Introduction

Spray behavior is important in some industrial processes like hydrocarbon combustion, food drying, pulverizing of some products, etc.. In this kind of processes the spray is inmersed in a gas flow thus provoking between spray and gas an interaction through the mass, momentum and energy interchanges. There exist in the literature [1,2] some approaches to study such systems. Many of them consider the spray (dispersed matter) and the gas flow (continuum) as independent systems, and introduce in a later stage some convenient approximations in order to take into account the interaction between them. Other studies assume that the spray and the gas together form a uniform fluid in physical and chemical local equilibrium, consequently the usual fluid mechanics equations are the starting point of their developments [3-5]. A characteristic of these last approaches is that they tend to neglect the interaction between the spray and the gas, a crude approximation *per se*, which is partially solved by introducing the dispersed matter properties based on the behavior of an individual droplet [6-10]. In this work we try to take advantage from both approaches; we consider the spray and the gas as a one continuous media, but we separate the gas flow equations from the dispersed matter equations. This is done at the expense of introducing source terms into the mass, momentum and energy equations. These sources will be taken alternatively from a numerical simulation of the problem based on the properties of individual droplets, or from a kinetic theory treatment.

From the point of view of irreversible thermodynamics, our approach contrasts with some others in the literature [11,12], where the droplets and the gas are taken separately. Those papers do not take a unified view of the system and the interaction is not taken properly. In fact, we consider as a starting point the balance equations for the whole system to emphasize our main hypothesis, which is that the mixture of gases together with the droplets are the system we are working with.

In Section 2 we define the system characteristics and introduce the notation to be used. In Section 3 we establish the mass conservation, while in Section 4 we do it for the momentum. At last in Sections 5 and 6 we discuss the energy balance equations, and give some concluding remarks.

2. Multisize-multicomponent systems

The system we are interested in this work consists of a two phase inhomogeneous fluid, for example: *i)* mixtures of gases in which there are droplets immersed in; *ii)* a liquid carrying bubbles with it. In both cases we distinguish a continuum phase interacting with a dispersed one. We are specially interested in a dispersed phase formed by a very large number of droplets having a size distribution. The initial size distribution is determined by external conditions, like the atomizer characteristics. As time elapses the droplets change their size according to a vaporization rate and the corresponding size distribution also changes. The droplets are all inmersed in a multicomponent mixture of gases having a temperature distribution and moving with some velocity. Such a system is what we call a spray. In particular for the hydrocarbons combustion we have the following model: **i)** The continuum phase is a multicomponent mixture of nitrogen, oxygen and fuel vapors at a higher temperature than the liquid fuel in the droplets. **ii)** As we said before the heat flux induces vaporization of droplets, the vapors become a part of the continuum phase, but also the droplets size decrease until they disappear. When the droplets size becomes smaller there is also a change in the momentum, mainly because the drag force exerted by the continuum changes according to the droplets' radius.

Now we will define some useful quantities in order to describe such a system. First of all, the continuum phase is an inert mixture of N gases, its density $\rho_c(\mathbf{x},t)$ depending on position and time and can be written in terms of the densities $\rho_\gamma(\mathbf{x},t)$ of the species γ in the mixture

$$\rho_c(\mathbf{x},t) = \sum_{\gamma=1}^{N} \rho_\gamma(\mathbf{x},t). \tag{1}$$

The hydrodynamic velocity $\mathbf{u}_c(\mathbf{x},t)$ is defined through the corresponding hydrodynamic velocities $\mathbf{v}_\gamma(\mathbf{x},t)$ of the species γ

$$\rho_c(\mathbf{x},t)\mathbf{u}_c(\mathbf{x},t) = \sum_{\gamma=1}^{N} \rho_\gamma(\mathbf{x},t)\mathbf{v}_\gamma(\mathbf{x},t). \tag{2}$$

Any given property $\psi_c(\mathbf{x},t)$ of the continuum phase may be written as

$$\rho_c(\mathbf{x},t)\psi_c(\mathbf{x},t) = \sum_{\gamma=1}^{N} \rho_\gamma(\mathbf{x},t)\psi_\gamma(\mathbf{x},t), \tag{3}$$

provided ψ is a linear function of the hydrodynamic variables.

In the dispersed phase the number of droplets in a small macroscopic volume element is very large, so we can classify them according to their size. The set of droplets with radius between R_k and $R_k + \Delta R_k$ are called "size-k" and each "size-k" is characterized by some local thermodynamic properties. The dispersed matter is composed of M sets of droplets. Each size-k has a density $\rho_k(\mathbf{x},t)$ defined as the mass of droplets of size-k divided by the total volume of the system, so that the dispersed phase density is given by

$$\rho_d(\mathbf{x},t) = \sum_{k=1}^{N} \rho_k(\mathbf{x},t), \tag{4}$$

the hydrodynamic velocity

$$\rho_d(\mathbf{x},t)\mathbf{u}_d(\mathbf{x},t) = \sum_{k=1}^{M} \rho_k(\mathbf{x},t)\mathbf{v}_k(\mathbf{x},t). \tag{5}$$

and any linear property ψ_d is given by

$$\rho_d(\mathbf{x},t)\psi_d(\mathbf{x},t) = \sum_{k=1}^{M} \rho_k(\mathbf{x},t)\psi_k(\mathbf{x},t). \tag{6}$$

The whole system is characterized by the density ρ, the total hydrodynamic velocity $\mathbf{U}$ and any property ψ is given by :

$$\rho(\mathbf{x},t) = \rho_c(\mathbf{x},t) + \rho_d(\mathbf{x},t), \tag{7}$$

$$\rho(\mathbf{x},t)\mathbf{U}(\mathbf{x},t) = \rho_c(\mathbf{x},t)\mathbf{u}_c(\mathbf{x},t) + \rho_d(\mathbf{x},t)\mathbf{u}_d(\mathbf{x},t), \tag{8}$$

$$\rho(\mathbf{x},t)\psi(\mathbf{x},t) = \rho_c(\mathbf{x},t)\psi_c(\mathbf{x},t) + \rho_d(\mathbf{x},t)\psi_d(\mathbf{x},t). \tag{9}$$

Finally we define the relative velocities $\mathbf{w}_k(\mathbf{x},t)$ for any size-k and $\mathbf{w}_\gamma(\mathbf{x},t)$ for the γ component in the continuum as follows

$$\mathbf{w}_k(\mathbf{x},t) = \mathbf{v}_k(\mathbf{x},t) - \mathbf{U}(\mathbf{x},t), \tag{10}$$

$$\mathbf{w}_\gamma(\mathbf{x},t) = \mathbf{v}_\gamma(\mathbf{x},t) - \mathbf{U}(\mathbf{x},t), \tag{11}$$

We include here the relationship

$$\rho\mathbf{U}\psi = \sum_{i=1} \rho_i \mathbf{v}_i \psi_i + \sum_{i=1} \rho_i \mathbf{w}_i (\psi - \psi_i) \tag{12}$$

because it is useful in some later calculations. Hereafter we will use the index i in the summation symbol in order to shorten the equations, thus the terms from $i = 0$ to $i = M$ represent the size-k terms of the dispersed phase and the terms from $i = M + 1$ to $i = M + N$ represent the N components in the continuum phase.

3. Mass Conservation

As we said before, the system is formed by two kinds of continuous media, one is represented by the mixture of gases, where we know the balance equations to be written. The droplets are also considered as a continuous media but it is not a trivial matter to guess the corresponding balance equations. To circumvent this difficulty, we will take the system as a whole and write the usual conservation and balance equations for it. In a further step and consistently with the definitions given in Section 2, we will assume that the species and each size-k set properties are additive. To undertake the validity of this hypothesis in the equations of motion, we will introduce some sources there, then we separate the equations for each species and each size-k set of droplets.

We will begin with the well known mass conservation equation for the total inhomogeneous system

$$\frac{\partial \rho}{\partial t} + \operatorname{div}(\rho\mathbf{U}) = 0. \tag{13}$$

Direct substitution of Eqs. (1)- (8) into Eq. (13) and the introduction of the source term allows us to obtain the equations of motion for ρ_k and ρ_γ, after a separation of each term in the summation namely,

$$\frac{\partial}{\partial t}\rho_k + \operatorname{div}(\rho_k \mathbf{v}_k) = -\phi_k^m, \tag{14}$$

$$\frac{\partial}{\partial t}\rho_\gamma + \operatorname{div}(\rho_\gamma \mathbf{v}_\gamma) = \phi_\gamma^m, \tag{15}$$

where ϕ_k^m and ϕ_γ^m are the mass sources for each size-k and each component respectively. The source ϕ_γ^m is the mass rate of species γ added to the continuum phase per unit volume, it is always positive because we assumed only the existence of droplet vaporization. This fact eliminates condensation of species γ into a droplet. Then, ϕ_γ^m is the amount of mass which is being fed into the continuum phase. The droplets in each size-k vaporize and the fuel vapors go to enrich the species γ so we can write

$$\phi_\gamma^m = \sum_{k=1}^{M} \phi_{k\to\gamma}^m, \tag{16}$$

where $\phi_{k\to\gamma}^m$ gives us the mass contribution to species γ coming from size-k droplets. When the combustion reactions occur it is necessary to include in these sources the reaction rate between different chemical species γ and γ' for each reaction

$$\phi_\gamma^m = \sum_{k=1}^{M} \phi_{k\to\gamma}^m + \sum_{\gamma'=1}^{L} \phi_{\gamma'\gamma}^m \tag{17}$$

here we have assumed that there are L independent chemical reactions and $\phi_{\gamma'\gamma}^m$ are the corresponding rates.

The $-\phi_k^m$ in Eq. (14) represents a mass sink for each size-k droplets, namely, the mass lost in size-k produced mainly by vaporization. Thus, the mass of vapors enters into the continuum phase and the droplets become smaller. When the size of the droplets in size-k decreases to the range R_{k-1} they contribute to size-$(k-1)$, at the same time the set size-$(k+1)$ is loosing droplets which are going to size-k as well as to the vapor phase. Thus,

$$\phi_k^m = \sum_{\gamma=1}^{N} \phi_{k\to\gamma}^m + \sum_{k'=1}^{M} \phi_{k'k}^m. \tag{18}$$

The important terms in this equation are: $\phi_{k+1\to k}^m$ which gives us the mass transferred from size-$(k+1)$ to size-k by the reduction in size of droplets, and $\phi_{k\to k-1}^m$ which is the mass lost by the size-k, it is proportional to the number of droplets that after vaporization become of size-$(k-1)$. In order to satisfy Eq. (13) it is obvious that we must require that these sources are to be restricted by :

$$\sum_{\gamma=1}^{N} \phi_\gamma^m - \sum_{k=1}^{M} \phi_k^m = 0 \tag{19}$$

The physical meaning of this equation is now very simple: the rate of mass lost by the dispersed phase is fed into the continuum in such a way that the total mass is conserved.

4. Momentum balance equations

Following the same steps as in Section 3, we will assume the total momentum of the system obeys the usual balance equation given by

$$\frac{\partial}{\partial t}\rho\mathbf{U} + \mathrm{div}(\rho\mathbf{U}\mathbf{U} + \mathbb{P}) = \rho\mathbf{f}, \tag{20}$$

where $\mathbb{P}$ is the total pressure tensor. Here, the pressure tensor is introduced in the same spirit as it is done in the usual theory, but we need an interpretation for it. To be specific we want to express it as a superposition of two tensors coming from the gases and the droplets. This is an additional assumption which can be justified by means of analyzing the physical meaning of any pressure tensor. Any pressure tensor measures the momentum transport in the system, but in our case the gases as well as the droplets transport momentum, giving rise to a different kind of contribution, then

$$\mathbb{P} = P\mathbb{I} + \mathbb{P}_c + \mathbb{P}_d, \tag{21}$$

where P is the isotropic part of the pressure tensor and it will be interpreted as the usual hydrostatic pressure for the whole system, $\mathbb{I}$ is the unit tensor, $\mathbb{P}_c$ is the usual viscous tensor for the mixture of gases. In contrast, the meaning of the "viscous" tensor $\mathbb{P}_d$ is not clear from a phenomenological point of view, we introduce it here in the same spirit as is done in other works [11-12] and we attempt to give it a kinetic interpretation elsewhere [13]. In fact we can say that it is somehow related to the average correlation function of the relative velocities for the droplets.

Both tensors $\mathbb{P}_c$ and $\mathbb{P}_d$ can be written as

$$\mathbb{P}_c = \sum_{\gamma=1}^{N}\mathbb{P}_\gamma, \qquad \mathbb{P}_d = \sum_{k=1}^{M}\mathbb{P}_k. \tag{22}$$

Finally in Eq. (20) $\rho\mathbf{f}$ is the bulk external force, which can also be written as a superposition of the bulk forces acting on each species and each size-k set of droplets.

$$\rho\mathbf{f} = \sum_{i=0}\rho_i\mathbf{f}_i. \tag{23}$$

Direct substitution of Eqs. (1)-(8), (22) and (23) in Eq. (20) leads us to the sought momentum balance equations, namely,

$$\frac{\partial}{\partial t}(\rho_\gamma\mathbf{v}_\gamma) + \mathrm{div}(\rho_\gamma\mathbf{v}_\gamma\mathbf{v}_\gamma - \rho_\gamma\mathbf{w}_\gamma\mathbf{w}_\gamma + \mathbb{P}_\gamma) + \beta_\gamma\nabla P - \rho_\gamma\mathbf{f}_\gamma = -\boldsymbol{\phi}_\gamma^P, \tag{24}$$

$$\frac{\partial}{\partial t}(\rho_k \mathbf{v}_k) + \operatorname{div}(\rho_k \mathbf{v}_k \mathbf{v}_k - \rho_k \mathbf{w}_k \mathbf{w}_k + \mathbb{Z}_k) + \beta_k \nabla P - \rho_k \mathbf{f}_k = \boldsymbol{\phi}_k^P. \tag{25}$$

The pressure gradient affects both the dispersed phase and the continuum phase, thus contributing to all equations. The β_γ and β_k phenomenological coefficients measure the effect of this pressure gradient and they satisfy the following condition

$$\sum_{i=0} \beta_i = 1. \tag{26}$$

The momentum sources $\boldsymbol{\phi}_k^P$ and $\boldsymbol{\phi}_\gamma^P$ also satisfy a restriction condition similar to Eq. (19) in order to maintain the validity of global momentum balance as indicated in (20). Therefore,

$$\sum_{k=1}^{M} \boldsymbol{\phi}_k^P - \sum_{\gamma=1}^{N} \boldsymbol{\phi}_\gamma^P = 0. \tag{27}$$

These sources can also be written as a superposition of effects coming from the corresponding phases

$$\boldsymbol{\phi}_\gamma^P = \sum_{k=1}^{M} \boldsymbol{\phi}_{\gamma \to k}^P, \tag{28}$$

$$\boldsymbol{\phi}_k^P = \sum_{\gamma=1}^{N} \boldsymbol{\phi}_{\gamma \to k}^P + \sum_{k'=1}^{M} \boldsymbol{\phi}_{k'k}^P. \tag{29}$$

Here $\boldsymbol{\phi}_{\gamma \to k}^P$ is the rate of momentum per unit volume transferred from species γ to size-k and $\boldsymbol{\phi}_{k'k}^P$ is the rate of momentum density transferred from size-k' droplets to size-k droplets.

5. Kinetic and potential energy balance

The kinetic energy balance equations are directly obtained from the momentum equation upon taking the scalar product with the velocity. From Eq. (25) we obtain that,

$$\begin{aligned} &\frac{\partial}{\partial t}\left(\tfrac{1}{2}\rho_k v_k^2\right) + \operatorname{div}\left[\tfrac{1}{2}\rho_k v_k^2 \mathbf{v}_k - \rho_k \mathbf{w}_k(\mathbf{v}_k \cdot \mathbf{w}_k) + \mathbf{v}_k \cdot \mathbb{Z}_k\right] + \rho_k \mathbf{w}_k \mathbf{w}_k : \nabla \mathbf{v}_k \\ &\qquad = \mathbb{Z}_k : \nabla \mathbf{v}_k - \beta_k \mathbf{v}_k \cdot \nabla P + \rho_k \mathbf{v}_k \cdot \mathbf{f}_k + \mathbf{v}_k \cdot \boldsymbol{\phi}_k^P + \tfrac{1}{2} v_k^2 \phi_k^m, \end{aligned} \tag{30}$$

This equation is valid for each size-k droplets set ($k = 1, \ldots, M$). The kinetic energy equation for the γ species ($\gamma = 1, \ldots, N$) is given by

$$\frac{\partial}{\partial t}\left(\tfrac{1}{2}\rho_\gamma v_\gamma^2\right) + \operatorname{div}\left[\tfrac{1}{2}\rho_\gamma v_\gamma^2 \mathbf{v}_\gamma - \rho_\gamma \mathbf{w}_\gamma(\mathbf{v}_\gamma \cdot \mathbf{w}_\gamma) + \mathbf{v}_\gamma \cdot \mathbb{Z}_\gamma\right] + \rho_\gamma \mathbf{w}_\gamma \mathbf{w}_\gamma : \nabla \mathbf{v}_\gamma$$
$$= \mathbb{Z}_\gamma : \nabla \mathbf{v}_\gamma - \beta_\gamma \mathbf{v}_\gamma \cdot \nabla P + \rho_\gamma \mathbf{v}_\gamma \cdot \mathbf{f}_\gamma - \mathbf{v}_\gamma \cdot \boldsymbol{\phi}_\gamma^P - \tfrac{1}{2} v_\gamma^2 \phi_\gamma^m. \qquad (31)$$

Eqs. (30) and (31) assume the validity of the mass conservation and momentum balance equation, but they contain no other additional hypothesis. Notice should be made of the fact that in these equations the momentum and mass sources are added to the usual kinetic energy sources as we could expect to be the case.

It is also useful to have the balance equations for the squared relative velocity, since it represents in a crude way the dispersion of the velocities with respect to the hydrodynamic velocity of the system. Those equations are obtained in a straightforward way by taking the difference between Eqs. (20) and (25), then we take the scalar product with $\mathbf{w}_k$ or $\mathbf{w}_\gamma$,

$$\frac{\partial}{\partial t}\left(\tfrac{1}{2}\rho_k w_k^2\right) + \operatorname{div}\left[\tfrac{1}{2}\rho_k w_k^2 \mathbf{U}\right] - \tfrac{1}{2} w_k^2 \operatorname{div}(\rho_k \mathbf{U}) + \rho_k \mathbf{w}_k \mathbf{w}_k : \nabla \mathbf{U}$$
$$+ \mathbf{w}_k \cdot \left[\operatorname{div}\left(\mathbb{Z}_k - \frac{\rho_k}{\rho}\mathbb{Z}\right) + \mathbb{Z} \cdot \nabla\left(\frac{\rho_k}{\rho}\right)\right]$$
$$= \mathbf{w}_k \cdot \left[-\beta_k \nabla P + \rho_k(\mathbf{f}_k - \mathbf{f}) + \boldsymbol{\phi}_k^P + \left(\mathbf{U} - \tfrac{1}{2}\mathbf{w}_k\right)\phi_k^m\right] \qquad (32)$$

and for the components

$$\frac{\partial}{\partial t}\left(\tfrac{1}{2}\rho_\gamma w_\gamma^2\right) + \operatorname{div}\left[\tfrac{1}{2}\rho_\gamma w_\gamma^2 \mathbf{U}\right] - \tfrac{1}{2} w_\gamma^2 \operatorname{div}(\rho_\gamma \mathbf{U}) + \rho_\gamma \mathbf{w}_\gamma \mathbf{w}_\gamma : \nabla \mathbf{U}$$
$$+ \mathbf{w}_\gamma \cdot \left[\operatorname{div}\left(\mathbb{Z}_\gamma - \frac{\rho_\gamma}{\rho}\mathbb{Z}\right) + \mathbb{Z} \cdot \nabla\left(\frac{\rho_\gamma}{\rho}\right)\right]$$
$$= \mathbf{w}_\gamma \cdot \left[-\beta_\gamma \nabla P + \rho_\gamma(\mathbf{f}_\gamma - \mathbf{f}) - \boldsymbol{\phi}_\gamma^P - \left(\mathbf{U} - \tfrac{1}{2}\mathbf{w}_\gamma\right)\phi_\gamma^m\right]. \qquad (33)$$

The balance equation for the total kinetic energy is obtained by adding the equations over all the species γ and all size-k sets of droplets in the system. The result is the well known kinetic energy equation

$$\frac{\partial}{\partial t}\left(\tfrac{1}{2}\rho U^2\right) + \operatorname{div}\left(\tfrac{1}{2}\rho U^2 \mathbf{U} + \mathbf{U} \cdot \mathbb{Z}\right) = \mathbf{U} \cdot \nabla P + \rho \mathbf{U} \cdot \mathbf{f} + \mathbb{Z} : \nabla \mathbf{U}. \qquad (34)$$

- In order to derive the potential energy balance equation we first assume that all the bulk forces acting on the system are derived from time independent scalar functions representing the potential energy per unit mass, namely,

$$\mathbf{f}_k = -\nabla\varphi_k, \qquad \mathbf{f}_\gamma = -\nabla\varphi_\gamma. \tag{35}$$

The total bulk force can be written as

$$\rho\mathbf{f} = -\rho\nabla\varphi + \rho\sum_{i=0}\varphi_i\nabla\left(\frac{\rho_i}{\rho}\right), \tag{36}$$

where φ denotes the total potential energy. If we now take the time derivative of $\rho\varphi$ we obtain that

$$\frac{\partial}{\partial t}\rho\varphi + \mathrm{div}(\rho\mathbf{U}\varphi) = -\rho\mathbf{f}\cdot\mathbf{U} - \sum_{i=0}\varphi_i\nabla\cdot(\rho_i\mathbf{w}_i) + \sum_{\gamma=1}^{N}\varphi_\gamma\phi_\gamma^m + \sum_{k=1}^{M}\varphi_k\phi_k^m, \tag{37}$$

which is the sought balance equation for the potential energy density $\rho\varphi$.

6. Energy conservation

The total energy E of the system we are studying is a superposition of the kinetic, potential and internal energies, namely,

$$\rho E = \tfrac{1}{2}\rho U^2 + \rho\varphi + \rho e, \tag{38}$$

where e is the internal energy per unit mass. The total energy flux $\mathbf{J}_E$ is defined as

$$\mathbf{J}_E = \rho e\mathbf{U} + \mathbb{Z}\cdot\mathbf{U} + \mathbf{q} + \sum_{i=0}\rho_i\mathbf{w}_i\varphi_i, \tag{39}$$

where $\rho e\mathbf{U}$ represents the convective energy flow, $\mathbb{Z}\cdot\mathbf{U}$ is the mechanical work, $\mathbf{q}$ is the heat flux and the last term is produced by the diffusion fluxes $\rho_i\mathbf{w}_i$. We assume that the total energy is a conserved quantity, so it satisfies a continuity equation

$$\frac{\partial}{\partial t}\rho E + \mathrm{div}\,\mathbf{J}_E = 0 \tag{40}$$

Direct substitution of Eqs. (38), (39), (34) and (37) in Eq. (40) allows us to write a balance equation for the internal energy in our system

$$\frac{\partial}{\partial t}\rho e + \mathrm{div}(\rho e\mathbf{U} + \mathbf{q}) = -\mathbb{Z} : \nabla\mathbf{U} + \sum_{i=0}\rho_i\mathbf{w}_i\cdot\mathbf{f}_i + \sum_{k=1}^{M}\varphi_k\phi_k^m + \sum_{\gamma=1}^{N}\varphi_\gamma\phi_\gamma^m. \tag{41}$$

According to the well established framework for irreversible thermodynamics [14], we are allowed to recognize Eq. (41) as the local form of the first law of thermodynamics. That framework also contains the local equilibrium hypothesis, which we will use here to derive the balance equations, of the entropy and the enthalpy of the system.

The local equilibrium assumption is quantified by the Gibbs relationship written in the Lagrangian system, namely,

$$T\frac{Ds}{Dt} = \frac{De}{Dt} + P\frac{D}{Dt}\frac{1}{\rho} - \sum_{i=0} \mu_i \frac{D}{Dt}\frac{\rho_i}{\rho}, \tag{42}$$

where s is the specific entropy, T the local temperature, μ_i are the local chemical potentials and $\frac{D}{Dt} \equiv \frac{\partial}{\partial t} + \mathbf{U}\cdot\nabla$ is the Lagrangian or substantial derivative. The rest of the symbols have already been defined.

From the mass conservation and the internal energy balance equations we obtain an entropy balance equation which can be written in the following form:

$$\frac{\partial}{\partial t}\rho s + \operatorname{div}\mathbf{J}_s = \sigma, \tag{43}$$

where

$$\mathbf{J}_s = \rho s\mathbf{U} + \frac{1}{T}\left(\mathbf{q} - \sum_{i=0}\rho_i\mu_i\mathbf{w}_i\right) \tag{44}$$

is the entropy flow, and

$$\begin{aligned}\sigma = \mathbf{q}\cdot\nabla\left(\frac{1}{T}\right) - \mathbb{Z} : \nabla\mathbf{U} - \frac{1}{T}\sum_{\gamma=1}^{N}\left[(\mu_\gamma + \varphi_\gamma)\,\phi_\gamma^m + \rho_\gamma\mathbf{w}_\gamma\cdot\left(T\nabla\frac{\mu_\gamma}{T} - \mathbf{f}_\gamma\right)\right] \\ + \frac{1}{T}\sum_{k=1}^{N}\left[(\mu_k + \varphi_k)\,\phi_k^m - \rho_k\mathbf{w}_k\cdot\left(T\nabla\frac{\mu_k}{T} - \mathbf{f}_k\right)\right]\end{aligned} \tag{45}$$

is the entropy source, or entropy production.

The entropy flux has a convective term, a contribution of the heat flux and the diffusive fluxes. The entropy source has the same characteristics as that for a simple fluid, but the mass sources ϕ_k^m and ϕ_γ^m appear in it. When there are chemical reactions in the system, the mass sources multiplied by the chemical potential give us the product of the corresponding affinity of the reaction and the reaction rate.

At last we write the enthalpy balance equation because it is specially useful when the combustion reactions are taking place. We start with the conventional thermodynamical relationship, namely

$$\frac{Dh}{Dt} = T\frac{Ds}{Dt} + \frac{1}{\rho}\frac{DP}{Dt}, \tag{46}$$

where h is the specific enthalpy. Eq. (46) is a straightforward consequence of the local equilibrium assumption. Now we express the enthalpy as the superposition of enthalpies for the size-k sets of the droplets and the species in the continuum phase. After some cumbersome algebra we obtain the enthalpy equation for the size-k, namely,

$$\begin{aligned}\frac{D}{Dt}\frac{1}{\rho}(\rho_k h_k) = \beta_k \frac{DP}{Dt} - \frac{1}{\rho}(\rho_k \mathbf{w}_k)\cdot\left(T\nabla\frac{\mu_k}{T} - \mathbf{f}_k\right) - \frac{T}{\rho}\nabla\cdot\left[\frac{1}{T}(\mathbf{q}_k - \rho_k\mu_k\mathbf{w}_k)\right] \\ + \frac{T}{\rho}\mathbf{q}_k\cdot\nabla\frac{1}{T} - \frac{1}{\rho}\mathbb{Z}_k : \nabla\mathbf{U} - \frac{1}{\rho}(\mu_k - \varphi_k)\phi_k^m + \phi_k^h,\end{aligned} \tag{47}$$

and the enthalpy balance equation for each γ-species,

$$\begin{aligned}\frac{D}{Dt}\frac{1}{\rho}(\rho_\gamma h_\gamma) = \beta_\gamma \frac{DP}{Dt} - \frac{1}{\rho}(\rho_\gamma \mathbf{w}_\gamma)\cdot\left(T\nabla\frac{\mu_\gamma}{T} - \mathbf{f}_\gamma\right) - \frac{T}{\rho}\nabla\cdot\left[\frac{1}{T}(\mathbf{q}_\gamma - \rho_\gamma\mu_\gamma\mathbf{w}_\gamma)\right] \\ + \frac{T}{\rho}\mathbf{q}_\gamma\cdot\nabla\frac{1}{T} - \frac{1}{\rho}\mathbb{Z}_\gamma : \nabla\mathbf{U} + \frac{1}{\rho}(\mu_\gamma - \varphi_\gamma)\phi_\gamma^m + \phi_\gamma^h.\end{aligned} \tag{48}$$

In Eqs. (47) and (48) the quantities ϕ_k^h and ϕ_γ^h are the enthalpy sources arising from the interaction between the droplets and the species of the gas mixture. They satisfy a restriction equation similar to the ones satisfied by the mass and momentum sources, namely,

$$\sum_{k=1}^{M}\phi_k^h + \sum_{\gamma=1}^{N}\phi_\gamma^h = 0. \tag{49}$$

7. Concluding remarks

The equations we have constructed in this work are valid for the spray system, which is composed of a multicomponent mixture of gases and M sets of droplets having different sizes. The equations are consistent with the general scheme of the usual irreversible thermodynamic theory. Accordingly the mass, momentum and energy balance equations for the whole system are taken as a starting point for the development of our treatment. The corresponding equations for one species of the mixture or a size-k set of droplets are obtained from the general equations by the introduction of the sources, which are not known from a phenomenological point of view.

Alternatively, it is possible to take another way to arrive to the same equations of motion; *i.e.* we take the balance equations of the system as a whole, the equations of motion of the mixture of gases, which in fact are well known, and we separate the equations for the dispersed phase by means of the introduction of the sources, which measure the interaction between the gases and the droplets, so the introduction of the sources is the price we paid to separate the equations.

In order to have an expression for these sources, we have to take some models about the vaporization rate and the drag force acting on the droplets, some of these models are well known in the literature [15], here we are not concerned with a particular model, so we can not calculate those terms. In the following paper [13], we give them a kinetic interpretation as well as an expression in terms of distribution functions.

The energy equations we constructed here are not all necessary in a practical problem, the leading special conditions indicate the relevant variables and then the equations to be considered.

We emphasize that the balance equations are not closed and we have to add the constitutive equations for the fluxes and the equations of state, as it is done in any usual thermodynamic theory [14]. As we said before, the applicability of these equations is a very broad one, it goes from combustion chemistry to drying of food. It is clear that the constitutive equations and the equations of state are specific of the problem we are interested in. Our treatment tries to be a general one and we do not want to particularize it with additional assumptions concerning a specific situation.

At last, we notice that our set of equations can also be used to study other systems like polidisperse solutions. There we also have a size distribution for the particles inmersed in a solvent, but there is no vaporization, in such a way that the equations can be significantly simplified. It is obvious that the equations necessary to close the set, will be very different from the case where the particles vaporize.

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Resumen. En este trabajo se estudia la termodinámica irreversible para un sistema inhomogéneo formado por un gran número de gotas inmersas en una mezcla multicomponente de gases. Se considera que las ecuaciones de conservación y balance son válidas para el sistema completo, ello permite escribir ecuaciones de balance para las variables correspondientes a los gases y a las gotas, que a su vez se clasifican de acuerdo a su tamaño. La interacción entre gotas y gases se toma en cuenta mediante la inclusión de fuentes de masa, momento y energía en las ecuaciones de balance.