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A mean-field description of two-phase flows with phase changes

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Abstract

A new version of the two-fluid model is developed, specially devoted to liquid–vapour two-phase mixtures, but also relevant to liquid-gas and liquid–liquid mixtures. It is well-known that, over a large range of volume fractions, liquid–vapour mixtures behave as dispersions of particles in a carrier fluid. But the "particles" belong to one phase at the beginning of the phase change, and to the second phase at the end. Within the present model, the dispersed phase is not prescribed at the outset but is merely the one with the lower volume fraction. To simplify the issue, surface tension and interfacial properties are neglected. However, the differences of pressure, temperature and velocity between the two phases are taken into account. The exchanges of mass, momentum and energy between phases are split into a "mean-field" part corresponding to the average conditions imposed by the whole mixture on the dispersed phase, and a part specifically due to the disturbances created by the particles. Constraints on constitutive relations are obtained from the overall dissipation rate, and result in a closed set of seven equations for seven state variables including one volume fraction. We insist on the general form of the equations but not on the details of the closure relations. The limits of this simple model are clearly stated, and we discuss possible improvements, including a better account of small-scale kinetic phenomena, as well as an eighth equation for the density of interfaces.

Keywords: Suspensions; Averaged equations; Phase changes; Mass and heat transfer

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1. Introduction

The two-fluid model for two-phase mixtures is established on firm grounds (Ishii, 1975; Nigmatulin, 1979; Drew, 1983) and is sufficiently general to be able to describe any type of mixtures. The price to pay for its generality is its lack of suitability for dispersed mixtures in which one phase appears in the form of particles dispersed throughout the second phase. In fact, many researchers (Buyevich and Schelchkova, 1978; Nigmatulin, 1979; Prosperetti and Jones, 1984) have long admitted the necessity of deriving a two-fluid model in a form specially suited to dispersed mixtures. If we consider the momentum balance for example, the recent work by Marchioro et al. (1999) is the last descendant of a long series of works that distinguish the particulate phase from the carrier fluid phase. The same status can be given to the work by Zhang and Prosperetti (1997) concerning the energy balance. While these recent results are quite motivating, they are still not suitable for liquid–vapour mixtures in which the particles are vapour bubbles at the beginning of the boiling process and liquid drops at the end. *We would like to have a "symmetric" system of equations which acknowledges for the existence of a dispersed phase while not prescribing at the outset which phase it is*. We here give some hints towards a new version of the standard two-fluid model. In this new version, the two phases are placed on an equal footing but the interactions between phases involve a mean-field contribution which depicts the mean conditions in which the minority phase is embedded. As a result, whenever one of the two phases happens to be dilute, the new set of equations looks very much like that for a dispersed mixture. Although simplistic in that it neglects the role of all kinds of small-scale fluctuations, the mean-field model takes into account phase transitions as well as the differences of pressure, temperature, chemical potential and velocity between the two phases. Since this model relies in part on thermodynamic considerations, we first review in Section 2 the thermodynamics of two-phase mixtures, insisting on the underlying assumptions. Then we turn to the general form of the mean-field equations of motion in Section 3, and consider the kinetics of phase transitions and its consequences in Section 4. Section 5 will dwell on the total dissipation rate and on the way the two phases are sharing the total dissipation. Section 6 will sum up the results and will give an example of unusual results concerning the momentum balances, while Section 7 will consider the necessary extensions of this first-step model. The link between the standard two-fluid model and its mean-field version, as well as the definitions of the mean-field quantities in terms of averaged small-scale quantities, are presented in Appendix A.

2. Thermodynamics of a multi-phase mixture

The thermodynamic relations of a multi-phase (or multi-component) mixture are presented in well-known text-books (Ishii, 1975; Nigmatulin, 1990). We write them to clarify our list of symbols, but above all to stress on the underlying assumptions. The thermodynamic behaviour of a given phase (or component) in the mixture is supposed to be similar to the behaviour of the pure phase, provided the space sharing is taken into account through the use of volume fractions. This fundamental assumption, when written for the unit mass of a phase labelled n, appears as

$$\varepsilon_n = \mu_n + T_n s_n - (\phi_n/\rho_n)p_n \quad \text{and} \quad \mathrm{d}\varepsilon_n = T_n\,\mathrm{d}s_n - p_n\,\mathrm{d}(\phi_n/\rho_n) \tag{1}$$

with the consequence

$$\mathrm{d}\mu_n = (\phi_n/\rho_n)\,\mathrm{d}p_n - s_n\,\mathrm{d}T_n. \tag{2}$$

Here, μ_n, T_n and p_n are the chemical potential, temperature and pressure of phase n, ε_n and s_n are the internal energy and entropy per unit mass, while ϕ_n is the volume fraction and ρ_n is the apparent mass per unit volume of the mixture, so that ρ_n/ϕ_n is the true mass per unit volume of pure phase n. The above thermodynamic relations hold for fluid-like phases. They also hold for solid-like particles, provided they undergo homogeneous compressions or expansions only (i.e. one excludes any change of shape), and in that case the pressure must be understood as the trace of the elastic stress.

The total mass, total momentum, total entropy and total energy per unit volume of the mixture are defined as

$$\rho = \Sigma_n \rho_n, \tag{3}$$

$$\rho \mathbf{V} = \Sigma_n \rho_n \mathbf{V}_n, \tag{4}$$

$$\rho s = \Sigma_n \rho_n s_n \tag{5}$$

and

$$\rho e = \Sigma_n \rho_n (\varepsilon_n + \tfrac{1}{2} V_n^2), \tag{6}$$

where V_n is the mean velocity of component n. The above relations are well-known and have a rather intuitive meaning but the assumptions which underlie them are very restrictive:

- all interfacial phenomena are neglected,
- energy and entropy of mixing are neglected,
- all fluctuations around $\mathbf{V}_n$ are neglected,
- all fluctuations around μ_n, T_n and p_n are neglected.

The first restriction means that all the effects connected with surface tension are neglected. The second one means we exclude colloidal suspensions and consider particles with a size larger than about ten micro-meters. The third one means we neglect the “added-mass” kinetic energy and the pulsation kinetic energy in case of bubbles. Let us comment on the fourth restriction and consider the temperature field of phase n for example. $T_n(x,t)$ is to be understood as the average temperature at point x and time t. A “point” in the mixture can be figured out as a tiny volume containing all components and within this tiny volume the local temperature of phase n is likely to display spatial variations and time fluctuations. When writing the above thermodynamic relations, all the details of the small-scale temperature field were supposed to be irrelevant except for its average value. The same assumption was made concerning the pressure field and the chemical potential field. The irrelevance of any moment but the average is a very strong assumption underlying (1), (2) and (6). In what follows we will use this thermodynamic description and will neglect all kinds of small-scale fluctuations. Hence, we will be concerned mainly with the modelling of a collision-free and non-Brownian dispersed two-phase mixture, without surface tension or any other interfacial properties. These assumptions seem stringent at first sight, but they are necessary to build up a (first step) comprehensible model.

3. The mean-field equations of motion of a two-phase mixture

3.1. What we (should) all agree on

There is a general agreement on the way to write the conservations laws for the total mass, total momentum, total energy as well as the balance law for the total entropy of the mixture. These equations are shared by all types of continuous media and can be presented as

$$\mathrm{d}\rho/\mathrm{d}t + \rho\nabla\cdot\mathbf{V} = 0, \tag{7}$$

$$\rho\,\mathrm{d}\mathbf{V}/\mathrm{d}t + \nabla\cdot\boldsymbol{\Pi} = \rho\mathbf{g}, \tag{8}$$

$$\rho\,\mathrm{d}e/\mathrm{d}t + \nabla\cdot[\mathbf{V}\cdot\boldsymbol{\Pi} + \mathbf{Q}] = \rho\mathbf{g}\cdot\mathbf{V} \tag{9}$$

and

$$\rho\,\mathrm{d}s/\mathrm{d}t + \nabla\cdot\mathbf{H} = \Delta, \tag{10}$$

where $\boldsymbol{\Pi}$ is the mixture stress tensor, $\mathbf{Q}$ is the mixture energy flux, $\mathbf{H}$ is the mixture entropy flux, while $\mathbf{g}$ is the external force field per unit mass and Δ is the (positive) entropy production rate. $\mathbf{V}$ is the mixture velocity defined in (4) and $\mathrm{d}/\mathrm{d}t$ is defined as $\mathrm{d}/\mathrm{d}t \equiv \partial/\partial t + \mathbf{V}\cdot\nabla$. There is also a general agreement on the way to express the mass balance for each phase. For a two-phase mixture, they are generally presented as

$$\partial\rho_1/\partial t + \nabla\cdot\rho_1\mathbf{V}_1 = -\Gamma, \tag{11}$$

$$\partial\rho_2/\partial t + \nabla\cdot\rho_2\mathbf{V}_2 = \Gamma, \tag{12}$$

where $\Gamma = \Gamma_\mathrm{N} + \Gamma_\mathrm{G}$ is the mass exchange rate due to phase transitions. This mass exchange comes from nucleation processes (Γ_N) and from growth at already existing interfaces (Γ_G). From definitions (3) and (4), it is clear that the sum of the two above mass balances results in the overall conservation law expressed in (7).

3.2. The primary phasic balance laws

3.2.1. Momentum balance

The mean-field type of equations were first proposed by Nigmatulin (1979). They are here written in a slightly modified form

$$\rho_1\mathrm{d}_1\mathbf{V}_1/\mathrm{d}t = \phi_1(-\nabla p + \nabla\cdot\boldsymbol{\tau}) - \mathbf{F} - \Gamma(\mathbf{V}^* - \mathbf{V}_1) + \rho_1\mathbf{g}, \tag{13}$$

$$\rho_2\mathrm{d}_2\mathbf{V}_2/\mathrm{d}t = \phi_2(-\nabla p + \nabla\cdot\boldsymbol{\tau}) + \mathbf{F} + \Gamma(\mathbf{V}^* - \mathbf{V}_2) + \rho_2\mathbf{g}, \tag{14}$$

where $\mathrm{d}_n/\mathrm{d}t \equiv \partial/\partial t + \mathbf{V}_n\cdot\nabla$ ($n = 1, 2$). Note that the sum of these two balances gives back the conservation law (8) with

$$\boldsymbol{\Pi} = p\boldsymbol{I} - \boldsymbol{\tau} + (\mathbf{V}_2 - \mathbf{V}_1)\otimes\mathbf{J}, \tag{15}$$

where $\boldsymbol{I}$ is the unit tensor while $\mathbf{J}$ is the relative mass flux between the two phases

$$\mathbf{J} = (\rho_1\rho_2/\rho)(\mathbf{V}_2 - \mathbf{V}_1). \tag{16}$$

The right-hand side of the above momentum balances contain four contributions. The contribution of gravity needs no further comment. The contribution due to phase transitions displays the average impulse $\Gamma\mathbf{V}^*$ of the mass exchanged between the two phases. An expression for $\mathbf{V}^*$ in terms of $\mathbf{V}_1$ and $\mathbf{V}_2$ will be obtained in Section 4. The two remaining contributions mean that each phase interacts with the other through a mutual interaction force F (precisely defined in Appendix A), and through the "mean-field" stress $p\boldsymbol{I} - \boldsymbol{\tau}$ created by both phases. The force associated with the mean-field stress acts on each phase in proportion to their volume fraction. This mean stress is made of a viscous stress $\boldsymbol{\tau}$ and a pressure stress involving the *mean* pressure

$$p = \phi_1 p_1 + \phi_2 p_2. \tag{17}$$

This way of writing the interphase momentum exchange can also be understood as a splitting between a generalized Archimedes force, and all the other forces gathered into $\mathbf{F}$. While the presence of ∇p in the Archimedes force is not a surprise, the presence of $\nabla \cdot \boldsymbol{\tau}$ is a little bit more puzzling. In fact, as will be seen in Section 5, this presence is necessary for the viscous stress $\boldsymbol{\tau}$ to depend on the gradients of the volume-averaged velocity of the mixture (Batchelor, 1970)

$$\mathbf{U} = \phi_1 \mathbf{V}_1 + \phi_2 \mathbf{V}_2 \tag{18}$$

and *not* on the gradients of the mass-averaged velocity $\mathbf{V}$. This role of $\mathbf{U}$ can be understood as follows: the small-scale viscous stress tensor depends on the small-scale velocity gradient $\nabla\mathbf{v}^\circ$. Since the averaging procedure involves the probabilities of presence (and nothing connected to the phase densities), the mixture viscous stress will depend on $\langle \chi_1 \nabla \mathbf{v}_1{}^\circ + \chi_2 \nabla \mathbf{v}_2{}^\circ \rangle$. And since the small-scale velocity is continuous on the interfaces, the mixture viscous stress ultimately depends on the gradient of $\langle \chi_1 \mathbf{v}_1{}^\circ + \chi_2 \mathbf{v}_2{}^\circ \rangle$, i.e. on the gradient of the above-defined $\mathbf{U}$. It is clear that when the same averaging procedure is applied to quantities like $\rho^\circ \mathbf{v}^\circ$ (which depend explicitly on densities), the result will involve $\mathbf{V}$ and not $\mathbf{U}$. This is why $\mathbf{V}$ appears in the average momentum while $\nabla\mathbf{U}$ has to appear in the average mixture stress.

3.2.2. Entropy balance

The mean-field evolution equations are

$$\rho_1 \mathrm{d}_1 s_1/\mathrm{d}t = \Delta_1 - \phi_1 \nabla \cdot \mathbf{h} - \Sigma - \Gamma(s^* - s_1), \tag{19}$$

$$\rho_2 \mathrm{d}_2 s_2/\mathrm{d}t = \Delta_2 - \phi_2 \nabla \cdot \mathbf{h} + \Sigma + \Gamma(s^* - s_2), \tag{20}$$

where Δ_n is the (positive) entropy production rate inside phase n while $\mathbf{h}$ is the averaged entropy flux created by both phases. These balance equations are the extension for non-dilute mixtures of Michaelides and Feng (1996) approach of the transient heat transfer on a single particle. These authors have split the total heat exchange into a bare (undisturbed) part which exists in the absence of the particle, and a perturbation part induced by the particle. Here, $\phi_n \nabla \cdot \mathbf{h}$ plays the role of the bare part and Σ the role of the particle perturbation. Note that, as a result of definition (5), the two above balances imply the overall entropy balance (10) with

$$\Delta = \Delta_1 + \Delta_2 \quad \text{and} \quad \mathbf{H} = \mathbf{h} + (s_2 - s_1)\mathbf{J}. \tag{21}$$

The analogous roles of $\mathbf{h}$ and $p\boldsymbol{I} - \boldsymbol{\tau}$ is made clear when comparing (15) and (21). There is no interfacial entropy production in conformity with our neglect of all interfacial quantities. The entropy exchanges linked to phase transitions are represented by Γs^*, and s^* will be given an explicit expression in Section 4. The entropy exchanges at the interfaces are split into a mean-field part involving $\nabla \cdot \mathbf{h}$ and a part Σ representing the remaining contributions (a definition of Σ in terms of averaged small-scale quantities is given in Appendix A). As will be seen later on, this role of $\nabla \cdot \mathbf{h}$ is also necessary for the thermal dissipation to depend on the gradients of the mixture temperature defined as

$$T = \phi_1 \, T_1 + \phi_2 \, T_2. \tag{22}$$

This role of T in the mixture heat flux has the same origin as the role of $\mathbf{U}$ in the mixture viscous stress. It can be understood after noticing that the small-scale heat flux is proportional to ∇T°, the gradient of the small-scale temperature. The averaging procedure will express the mean heat flux in terms of $\langle \chi_1 \nabla T_1{}^\circ + \chi_2 \nabla T_2{}^\circ \rangle$, i.e. in terms of the gradient of the above-defined temperature T (taking into account the continuity of the small-scale temperature at interfaces).

3.2.3. Volume fraction balance

The mean-field evolution equations are

$$\begin{aligned} \partial\phi_2/\partial t + \nabla \cdot \phi_2 \mathbf{V}_2 &= \phi_2 \nabla \cdot \mathbf{U} + A + \Gamma/\rho^*, \\ \partial\phi_1/\partial t + \nabla \cdot \phi_1 \mathbf{V}_1 &= \phi_1 \nabla \cdot \mathbf{U} - A - \Gamma/\rho^*. \end{aligned} \tag{23}$$

Note that these two equations are not independent of each other because of the constraint $\phi_2 + \phi_1 = 1$. We wrote the second equation just to stress on the similarities of structure with the momentum and entropy balances. The velocity $\mathbf{U}$ plays for the volume fractions a mean-field role similar to that of $\mathbf{h}$ and $p\boldsymbol{I} - \boldsymbol{\tau}$. Basically, the above equations mean that the volume fractions are transported with the same velocity as the mass, and that two processes influence their evolution: the first one is linked to the mass exchange (phase transformations) and it involves a mass density ρ^* to be determined in Section 4. The second one represents the role of the mixture compressibility. This role is expressed with two terms, one of them linked to the "mean-field" compressibility $\nabla \cdot \mathbf{U}$, and the other by A. The definition of A in terms of small-scale quantities is given in Appendix A.

3.3. The secondary balance laws

All the other balance laws can be deduced from the above basic ones.

3.3.1. Internal energy

Taking the thermodynamic relations (1) into account, one easily deduces the evolution of the internal energies

$$\rho_1 \mathrm{d}_1 \varepsilon_1/\mathrm{d}t = T_1[\Delta_1 - \phi_1 \nabla \cdot \mathbf{h} - \Sigma - \Gamma(s^* - s_1)] - p_1[\phi_1 \nabla \cdot \mathbf{U} - A - \Gamma(1/\rho^* - \phi_1/\rho_1)],$$

$$\rho_2 \mathrm{d}_2 \varepsilon_2/\mathrm{d}t = T_2[\Delta_2 - \phi_2 \nabla \cdot \mathbf{h} + \Sigma + \Gamma(s^* - s_2)] - p_2[\phi_2 \nabla \cdot \mathbf{U} + A + \Gamma(1/\rho^* - \phi_2/\rho_2)].$$

3.3.2. Total energy

The evolutions of the kinetic energies are a direct consequence of the momentum balances and are obtained from the dot product of (13) with $\mathbf{V}_1$ and (14) with $\mathbf{V}_2$. A mere addition of the evolutions equations for the kinetic and internal energies leads to the evolution equations for the total phasic energies $\varepsilon_1 + (1/2)V_1^2$ and $\varepsilon_2 + (1/2)V_2^2$. Summing these two equations we obtain

$$\begin{aligned}
&\rho_1 \mathrm{d}_1/\mathrm{d}t(\varepsilon_1 + \tfrac{1}{2}V_1^2) + \rho_2 \mathrm{d}_2/\mathrm{d}t(\varepsilon_2 + \tfrac{1}{2}V_2^2) + \Gamma(\varepsilon_2 + \tfrac{1}{2}V_2^2 - \varepsilon_1 - \tfrac{1}{2}V_1^2) \\
&\quad = T_1\Delta_1 + T_2\Delta_2 - \boldsymbol{\tau} : (\nabla \mathbf{U})^s + \mathbf{h}\cdot\nabla T + (\mathbf{V}_2 - \mathbf{V}_1)\cdot\mathbf{F} + (T_2 - T_1)\Sigma - (p_2 - p_1)A \\
&\qquad + \Gamma[\mu_2 - \mu_1 + s^*(T_2 - T_1) - (1/\rho^*)(p_2 - p_1) + (V_1 - V^*)^2/2 - (V_2 - V^*)^2/2] \\
&\qquad + \nabla\cdot[\mathbf{U}\cdot\boldsymbol{\tau} - p\mathbf{U} - T\mathbf{h}] + \rho\mathbf{g}\cdot\mathbf{V},
\end{aligned}$$

where $(\nabla \mathbf{U})^s$ is the symmetric gradient of the volume-averaged velocity while ∇T is the gradient of the volume-averaged temperature. The overall energy being defined as in (6), the above result must be compatible with the conservation law (9). This forces the total dissipation rate to be expressed as

$$\begin{aligned}
T_1\Delta_1 + T_2\Delta_2 = {}& \boldsymbol{\tau} : (\nabla \mathbf{U})^s - \mathbf{h}\cdot\nabla T - (\mathbf{V}_2 - \mathbf{V}_1)\cdot\mathbf{F} - (T_2 - T_1)\Sigma + (p_2 - p_1)A \\
& - \Gamma[\mu_2 - \mu_1 + s^*(T_2 - T_1) - (1/\rho^*)(p_2 - p_1) + (V_1 - V^*)^2/2 - (V_2 - V^*)^2/2].
\end{aligned} \tag{24}$$

Moreover, the energy flux appearing in (9) is found to be related to $\mathbf{h}$, $\boldsymbol{\tau}$ and $\mathbf{J}$ in the form

$$\mathbf{Q} = T\mathbf{h} + (\mathbf{V} - \mathbf{U})\cdot(\boldsymbol{\tau} - p\boldsymbol{I}) + [\varepsilon_2 - \varepsilon_1 + (1 - 2c_2)(V_2 - V_1)^2/2]\mathbf{J}. \tag{25}$$

We have now written the complete set of equations describing a two-phase mixture. This set is composed of the seven equations (11)–(14), (19), (20), (23) for the seven fundamental variables ρ_1, ρ_2, $\mathbf{V}_1$, $\mathbf{V}_2$, s_1, s_2 and ϕ_2. These equations contain six yet undetermined quantities $\boldsymbol{\tau}$, $\mathbf{h}$, $\mathbf{F}$, Σ, A and Γ which appear in the six contributions to the total dissipation rate (24). The clear meaning of these six contributions, together with the role of $\nabla\mathbf{U}$ and ∇T are arguments in favour of the proposed equations. For the set of equations to be closed, one has (a) to express s^*, ρ^* and $\mathbf{V}^*$ in terms of the seven basic variables, (b) to propose constitutive relations for $\boldsymbol{\tau}$, $\mathbf{h}$, $\mathbf{F}$, Σ, A and Γ, and (c) to split the total dissipation rate into its components $T_1\Delta_1$ and $T_2\Delta_2$.

4. Kinetics of phase transitions

According to the dissipation rate (24), the thermodynamic force driving the phase transitions is a rather complicated expression involving s^*, ρ^* and $\mathbf{V}^*$ together with the differences $\mu_2 - \mu_1$, $T_2 - T_1$, $p_2 - p_1$ and $\mathbf{V}_2 - \mathbf{V}_1$ (see also Nigmatulin (1990) and Hütter (2001) for different approaches with similar conclusions). On physical grounds, one expects this thermodynamic force to depend on the *deviation from saturation conditions*. For small deviations, we expect it to be proportional to the difference $p - p_S(T)$ or $T_S(p) - T$ where p and T are the average pressure and temperature defined in (17) and (22), while $p_S(T)$ is the saturation pressure at temperature T and $T_S(p)$ the saturated temperature at pressure p. For this proportionality to appear, one must adopt the special values

$$s^* = \phi_1 s_2 + \phi_2 s_1, \tag{26}$$

$$1/\rho^* = \phi_1(\phi_2/\rho_2) + \phi_2(\phi_1/\rho_1) \tag{27}$$

and

$$\mathbf{V}^* = (\mathbf{V}_1 + \mathbf{V}_2)/2, \tag{28}$$

so that one can write *for moderate deviations from equilibrium*

$$\mu_2 - \mu_1 + s^*(T_2 - T_1) - (1/\rho^*)(p_2 - p_1) + (V_1 - V^*)^2/2 - (V_2 - V^*)^2/2$$
$$\approx (\phi_2/\rho_2 - \phi_1/\rho_1)(p - p_S(T)) \approx (s_2 - s_1)(T_S(p) - T).$$

In the limit of a very small ϕ_2, phase 2 is the dispersed phase and from (26) and (27) one finds $s^* = s_2$, $\rho^* = \rho_2/\phi_2$. Conversely, when ϕ_1 is small, $s^* = s_1$, $\rho^* = \rho_1/\phi_1$. These are results conform to intuition. On intuitive grounds also, one would expect the velocity $\mathbf{V}^*$ of the exchanged mass to be that of the dispersed phase. However, this intuition is correct only for the mass grown from already existing particles. At variance, because of the small size of nuclei, the nucleated mass appears with the velocity of the dominant phase and so, it is not obvious to assess what $\mathbf{V}^*$ should be. Let Γ_N be the mass exchange rate due to nucleation processes. Then, $\Gamma_G = \Gamma - \Gamma_N$ represents the mass grown from already existing interfaces. It is likely that Γ_G appears with the velocity $\phi_1\mathbf{V}_2 + \phi_2\mathbf{V}_1$ (see also Appendix A) while the nucleated mass appears with the average mixture velocity, let us say with $\mathbf{U}$. Then, the momentum exchange due to mass exchange is presumably

$$\Gamma\mathbf{V}^* = \Gamma_G(\phi_1\mathbf{V}_2 + \phi_2\mathbf{V}_1) + \Gamma_N\mathbf{U} \tag{29}$$

and result (28) corresponds to the special case $\Gamma_N = \Gamma_G = \Gamma/2$. While the factor 1/2 is dubious, the trend is correct. Moreover, were $\mathbf{V}^*$ different from $(\mathbf{V}_1 + \mathbf{V}_2)/2$, the thermodynamic force would not vanish at saturation, i.e. whenever $p = p_S(T)$ or $T = T_S(p)$. Hence, it could be possible to induce phase transitions in a saturated mixture just because of the relative motion between the two phases. To avoid this unphysical role of the relative velocity we cannot but adopt the Solomonic value (28) for $\mathbf{V}^*$.

5. Results from thermodynamics of irreversible processes

The second law of thermodynamics requires the total entropy production rate $\Delta_1 + \Delta_2$ to be positive. In the present modelling of dissipative processes the only quantity we obtain unambiguously is the dissipation rate $T_1\Delta_1 + T_2\Delta_2$, and it is this quantity that will be required to be positive

$$T_1\Delta_1 + T_2\Delta_2 \geqslant 0.$$

There are many ways to meet that requirement. We present below the simplest one in which the six contributions to the entropy production rate (24) are considered as *mutually independent*

$$\begin{aligned}
&\boldsymbol{\tau} = 2\eta(\nabla\mathbf{U})^s,\\
&T\mathbf{h} = -\lambda\nabla T,\\
&\mathbf{F} = -\phi_1\phi_2\xi(\mathbf{V}_2 - \mathbf{V}_1),\\
&T\Sigma = -\phi_1\phi_2\beta(T_2 - T_1),\\
&A = \phi_1\phi_2\alpha(p_2 - p_1),\\
&\Gamma = \gamma_p(\phi_1/\rho_1 - \phi_2/\rho_2)(p - p_S(T)) = \gamma_T(s_1 - s_2)(T_S(p) - T).
\end{aligned} \tag{30}$$

The transport coefficients η, λ, ξ, β, α, γ_p and γ_T are all supposed to be positive while the $\phi_1\phi_2$ factor is to remind that the related quantities stem from exchanges at the interfaces and disappear whenever one of the two phases disappears. We refrained from applying this $\phi_1\phi_2$ factor to Γ because of the nucleated mass which can appear even when $\phi_1\phi_2 = 0$. On dimensional grounds, one expects the following relations

$$\xi \sim \eta/R^2, \quad \beta \sim \lambda/R^2, \quad \alpha \sim 1/\eta, \quad \gamma_p \sim 1/\eta(\phi_1/\rho_1 - \phi_2/\rho_2)^2, \tag{31}$$

where R is some microstructure length (the particle size for dilute mixtures) and the $\sim$ sign means that the two quantities are proportional to each other, the proportionality factor being a non-dimensional but otherwise undetermined number.

Combining the constitutive relation for Γ with γ_p as given in (31) leads to

$$\Gamma \sim [\eta(\phi_1/\rho_1 - \phi_2/\rho_2)]^{-1}(p - p_S(T)).$$

Hence, the mass of the discrete phase increases if the continuous fluid is lighter and the mixture is supersaturated ($p > p_S(T)$) or if it is denser and the mixture is depressurised ($p < p_S(T)$). This expression for Γ reminds of the Hertz-Knudsen formula deduced from a kinetic theory approach. In fact, kinetic theory suggests that the mass exchange rate depends not only on $p - p_S(T)$ but also on the temperature difference (Takata et al., 1998). This means a coupling between Γ and Σ which was not taken into account by the simplest expressions (30). In fact, more general flux-force relationships can be written because the Curie symmetry principle (De Groot and Mazur, 1962) allows a coupling between the two vectors $\mathbf{F}$ and $\mathbf{h}$ on one hand, and between the three scalars A, Σ and Γ on the other hand. These general relations are lengthy and will not be written, but a representative example of unusual coupling will be given at the end of Section 6.

We have now constitutive relations for all the unknown terms appearing in the phasic balances with one exception: the entropy dissipation rates Δ_1 and Δ_2. We know what the total dissipation rate is, but how to share it between the two phases? The dissipation connected to $\boldsymbol{\tau}$ and $\mathbf{h}$ is distributed all over the mixture and has contributions from both phases. It seems natural to split it according to the volume fractions of the respective phases. The dissipation connected with the inter-phase exchanges $\mathbf{F}$, Σ, A and Γ is localized close to the interfaces, but for a dilute mixture it is concentrated mostly on the continuous phase side. For non-dilute mixtures we will suppose that the dissipation in inter-phase exchanges is also shared according to the respective volume fractions. Hence we propose, for want of something better,

$$T_1\Delta_1 = \phi_1[T_1\Delta_1 + T_2\Delta_2] \quad \text{and} \quad T_2\Delta_2 = \phi_2[T_1\Delta_1 + T_2\Delta_2]. \tag{32}$$

6. The mean-field model

The final form of the balance equations is

$$\begin{aligned}
&\partial\rho_1/\partial t + \nabla\cdot\rho_1\mathbf{V}_1 = -\Gamma,\\
&\partial\rho_2/\partial t + \nabla\cdot\rho_2\mathbf{V}_2 = \Gamma,\\
&\partial\phi_2/\partial t + \nabla\cdot\phi_2\mathbf{V}_2 = \phi_2\nabla\cdot\mathbf{U} + A + \Gamma/\rho^*,\\
&\rho_1 \mathrm{d}_1\mathbf{V}_1/\mathrm{d}t = \phi_1(-\nabla p + \nabla\cdot\boldsymbol{\tau}) - \mathbf{F} + \Gamma(\mathbf{V}_1 - \mathbf{V}_2)/2 + \rho_1\mathbf{g},\\
&\rho_2 \mathrm{d}_2\mathbf{V}_2/\mathrm{d}t = \phi_2(-\nabla p + \nabla\cdot\boldsymbol{\tau}) + \mathbf{F} + \Gamma(\mathbf{V}_1 - \mathbf{V}_2)/2 + \rho_2\mathbf{g},\\
&\rho_1 \mathrm{d}_1\varepsilon_1/\mathrm{d}t = \phi_1[\boldsymbol{\tau} : (\nabla\mathbf{U})^s - \mathbf{h}\cdot\nabla T + (\mathbf{V}_1 - \mathbf{V}_2)\cdot\mathbf{F}] - T^*\Sigma - \phi_1 T_1\nabla\cdot\mathbf{h} + p^*A\\
&\qquad\qquad - \phi_1 p_1\nabla\cdot\mathbf{U} + \Gamma(\varepsilon_1 - \mu^* - T^*s^* + p^*/\rho^*),\\
&\rho_2 \mathrm{d}_2\varepsilon_2/\mathrm{d}t = \phi_2[\boldsymbol{\tau} : (\nabla\mathbf{U})^s - \mathbf{h}\cdot\nabla T + (\mathbf{V}_1 - \mathbf{V}_2)\cdot\mathbf{F}] + T^*\Sigma - \phi_2 T_2\nabla\cdot\mathbf{h} - p^*A\\
&\qquad\qquad - \phi_2 p_2\nabla\cdot\mathbf{U} - \Gamma(\varepsilon_2 - \mu^* - T^*s^* + p^*/\rho^*),
\end{aligned} \tag{33}$$

where all stared quantities are defined in analogy with (26) and (27)

$$T^* = \phi_1 T_2 + \phi_2 T_1, \quad p^* = \phi_1 p_2 + \phi_2 p_1 \quad \text{and} \quad \mu^* = \phi_1 \mu_2 + \phi_2 \mu_1. \tag{34}$$

Note that we have written the internal energy balances instead of the entropy balances just because most previous works have insisted on internal energy rather than entropy. Note however that the internal energy balances have a somehow complex writing because they result from both the entropy and volume fraction balances.

The second law of thermodynamics requires $\boldsymbol{\tau}$, $\mathbf{h}$, $\mathbf{F}$, Σ, A and Γ to satisfy the inequality

$$\begin{aligned}&\boldsymbol{\tau} : (\nabla \mathbf{U})^s - \mathbf{h} \cdot \nabla T - \mathbf{F} \cdot (\mathbf{V}_2 - \mathbf{V}_1) - \Sigma(T_2 - T_1) + A(p_2 - p_1) \\ &\quad - \Gamma(\phi_2/\rho_2 - \phi_1/\rho_1)(p - p_S(T)) \geqslant 0.\end{aligned} \tag{35}$$

It is to be stressed that the set of constitutive relations compatible with (35) is amazingly rich. The simplest example was given in (30), but we already mentioned a possible dissipative coupling between the two vectors $\mathbf{F}$ and $\mathbf{h}$ on the one hand, and between the three scalars A, Σ and Γ on the other hand. These couplings were dictated by the Curie symmetry principle which holds for isotropic systems. In case the mixture has a non-uniform concentration, isotropy is destroyed and the number of possible couplings is much enlarged. We consider below a coupling which is particularly important when calculating the velocity profile of flowing mixtures with non-uniform concentrations. This (rather unusual) coupling concerns $\mathbf{F}$ and $\boldsymbol{\tau}$ and can be presented in the form

$$\begin{aligned}\mathbf{F} &= -\boldsymbol{\xi} \cdot (\mathbf{V}_2 - \mathbf{V}_1) - \mathbf{C} \cdot (\nabla \mathbf{U})^s, \\ \boldsymbol{\tau} &= \boldsymbol{\eta} : (\nabla \mathbf{U})^s + (\mathbf{V}_2 - \mathbf{V}_1) \cdot \mathbf{C}.\end{aligned}$$

The coupling displays the Onsager symmetry (De Groot and Mazur, 1962) which is here represented by the third-order tensor $\mathbf{C}$ (with $C_{ijk} = C_{ikj}$), while $\boldsymbol{\xi}$ is a second-order non-symmetric mobility tensor and $\boldsymbol{\eta}$ is a fourth-order completely symmetric viscosity tensor. It happens that such a coupling is the way the shear-induced diffusion phenomena come into play. The shear-induced diffusion can be separated into a longitudinal diffusion (Wang and Mauri, 1999) and a transverse diffusion (Leighton and Acrivos, 1987). The longitudinal diffusion is basically a two-particle process while the transverse diffusion involves a minimum of three particles. In what follows we consider longitudinal diffusion only and, to provide a simple example, we limit our discussion to the dilute case ($\phi_2 \ll 1$) for which the above expressions simplify into

$$\begin{aligned}\mathbf{F} &= -\boldsymbol{\xi} \cdot (\mathbf{V}_2 - \mathbf{V}_1) - c\eta_1 \phi_2 (\nabla \mathbf{U})^s \cdot \nabla \phi_2, \\ \boldsymbol{\tau} &= \eta_1 (1 + \tfrac{5}{2}\phi_2)(\nabla \mathbf{U})^s + c\eta_1 \phi_2 [(\mathbf{V}_2 - \mathbf{V}_1) \otimes \nabla \phi_2]^s,\end{aligned}$$

where c is a numerical constant close to unity and slightly depending on the type of flow represented by $(\nabla \mathbf{U})^s$ (Wang and Mauri, 1999). The explicit form of the drag and lift forces associated with the dilute-limit expression for ξ will not be written. It is astonishing that the extra stress tensor associated with longitudinal shear diffusion has exactly the form proposed long ago by Ishii (1975). Needless to say that the $\phi_2 \nabla \phi_2$ dependence of this extra stress, characteristic of a two-particle process, could not be anticipated by Ishii. Hence, despite its apparent simplicity, the dissipation rate (35) can cope with many physical phenomena. The issue is to combine results from micro-hydrodynamics to write the most general form of $\boldsymbol{\tau}$, $\mathbf{h}$, $\mathbf{F}$, Σ, A and Γ, and then check that these expressions are compatible with (35). The mean-field model is only a new framework in which constitutive relations must be introduced. It is of no help for finding new closure relations except for the constraint (35). But it is helpful in presenting balance equations in a form which acknowledges that the mixture is a dispersion when one of the volume fractions is very small and which proposes a reasonable interpolation when the mixture is non-dilute.

7. Concluding remarks

The thermodynamic description of a two-phase mixture is still in its infancy and denies any role to the fluctuations of the main thermodynamic variables. *The balance equations cannot but reflect that simplicity*. With this in mind, we have developed a closed set of seven balance equations specially devoted to two-phase mixtures with phase changes. The concept of a mean-field influence of the embedding fluid, which was previously used for the momentum balances only, has been systematically applied to the other balances laws. The resulting model has the advantage of being thermodynamically consistent but it relies on stringent assumptions. Among the four main restrictions listed in Section 2, the first three ones can be easily released as follows.

The energy and entropy of mixing are important when dealing with colloidal suspensions of micron-sized particles. They were taken into account by Lhuillier (2001) but with the assumption of equal pressure and equal temperature between the two phases. The main novelty (as compared to the present model) is a non-dissipative contribution to **F** that accounts for concentration-diffusion as well as thermo-diffusion.

The fluctuations relative to the mean velocity play an important role in the analysis of added-mass effects or when considering the pulsating motion in a bubbly fluid. The way to deal with these phenomena is to replace (6) by

$$\rho e = \Sigma_n \rho_n (\varepsilon_n + \tfrac{1}{2} V_n^2 + \tfrac{1}{2} \langle (\Delta v_n)^2 \rangle)$$

and to write the fluctuating kinetic energy in terms of the seven basic variables of the mean-field model. It appears that the added-mass kinetic energy induces non-dissipative contributions to $\boldsymbol{\tau}$ and **F**, while the pulsation kinetic energy induces non-dissipative contributions to $\boldsymbol{\tau}$ and A (Nigmatulin, 1990; Zhang and Prosperetti, 1994).

Up to that point, the number of equations was kept unchanged in spite of the various improvements. Restoring interfacial quantities is likely to introduce *three* new balance laws on the interfaces. The number of equations would thus be increased up to ten unless one considers a temperature-dependent surface tension as the only interfacial quantity, and one makes some simplifying assumption concerning the temperature of the interfaces.

It has long been suggested that to take into account the coalescence or break-up of particles, an equation describing the evolution of the density of interfaces was compulsory (Ishii, 1975; Delhaye, 2001). The reason is that coalescence and break-up are volume and mass conserving so they cannot be involved in the balances of mass or volume. Another reason is that the intensity of some inter-phase exchanges are not easily expressed in terms of the seven basic variables only. And this is the case in particular for **F** and Σ which, according to (31), involve some microstructure length scale R: for our mean-field set of equations to be closed, one must in fact *simulate* the coalescence and break-up phenomena by relating this length scale to the volume fraction, and the actual relation is far from evident. As a bonus for introducing the area density as an eighth variable (governed by an eighth evolution equation) is the simplicity with which the interfacial energy is taken into account. Hence, an eight-equation model is likely to supersede the present model but many of the above results will need minor modifications only to cope with this extension.

Appendix A. Statistical basis of the mean-field model

A.1. Evolution of the volume fraction

The two phases share the total volume, so that $\phi_1 + \phi_2 = 1$ and we focus on the volume fraction of phase 2 for example. Phase 2 is characterized by its (Heaviside-like) function of presence $\chi_2(\mathbf{x}, t)$ with $\chi_2 = 1$ when point $\mathbf{x}$ is occupied by phase 2 at time t and $\chi_2 = 0$ otherwise. This (small-scale) function of presence satisfies the two relations

$$\nabla\chi_2 = -\mathbf{n}_2\delta_I \quad \text{and} \quad \partial\chi_2/\partial t + \mathbf{v}_I \cdot \nabla\chi_2 = 0, \tag{A.1}$$

where $\delta_I(\mathbf{x}, t)$ is the (Dirac-like) function of presence of the interfaces between the two phases, $\mathbf{v}_I$ is the velocity of these interfaces and $\mathbf{n}_2$ is the normal to the interfaces which points outwards phase 2. From the above two relations one deduces

$$\partial\chi_2/\partial t + \nabla \cdot (\chi_2\mathbf{v}_2{}^\circ) = \chi_2\nabla \cdot \mathbf{v}_2{}^\circ + (\mathbf{v}_I - \mathbf{v}_2{}^\circ) \cdot \mathbf{n}_2\delta_I,$$

where $\mathbf{v}_2{}^\circ$ is the small-scale velocity of phase 2. The volume fraction ϕ_2 is a coarse-grained quantity which is nothing but the statistical average $\langle\chi_2\rangle$. Taking the statistical average of the above equation one obtains

$$\partial\phi_2/\partial t + \nabla \cdot \langle\chi_2\mathbf{v}_2{}^\circ\rangle = \langle\chi_2\nabla \cdot \mathbf{v}_2{}^\circ\rangle + \langle(\mathbf{v}_I - \mathbf{v}_2{}^\circ) \cdot \mathbf{n}_2\delta_I\rangle.$$

Introducing the function of presence $\chi_1 = 1 - \chi_2$, the small-scale velocity $\mathbf{v}_1{}^\circ$ of phase 1, and the unit vector $\mathbf{n}_1 = -\mathbf{n}_2$, one can manipulate the right-hand side of this equation and transform it into

$$\begin{aligned}\partial\phi_2/\partial t + \nabla \cdot \langle\chi_2\mathbf{v}_2{}^\circ\rangle &= \phi_2\nabla \cdot \langle\chi_1\mathbf{v}_1{}^\circ + \chi_2\mathbf{v}_2{}^\circ\rangle + \phi_1\langle\chi_2\nabla \cdot \mathbf{v}_2{}^\circ\rangle - \phi_2\langle\chi_1\nabla \cdot \mathbf{v}_1{}^\circ\rangle \\ &\quad + \phi_1\langle(\mathbf{v}_I - \mathbf{v}_2{}^\circ) \cdot \mathbf{n}_2\delta_I\rangle - \phi_2\langle(\mathbf{v}_I - \mathbf{v}_1{}^\circ) \cdot \mathbf{n}_1\delta_I\rangle.\end{aligned} \tag{A.2}$$

We insist that (A.2) is not a true balance equation but a mere consequence of the topological relations (A.1). The issue is to prove that the mean-field equation (23) is a consistent approximation for the exact equation (A.2).

The mean fluxes $\rho_n\mathbf{V}_n$ and the rate of mass exchange Γ_G at interfaces are defined as

$$\rho_n\mathbf{V}_n = \langle\chi_n\rho_n{}^\circ\mathbf{v}_n{}^\circ\rangle \quad \text{and} \quad -\langle\rho_1{}^\circ(\mathbf{v}_I - \mathbf{v}_1{}^\circ) \cdot \mathbf{n}_1\delta_I\rangle = \langle\rho_2{}^\circ(\mathbf{v}_I - \mathbf{v}_2{}^\circ).\mathbf{n}_2\delta_I\rangle = \Gamma_\mathrm{G},$$

where $\rho_n{}^\circ$ is the small-scale mass density of phase n. The thermodynamic description presented in Section 2 supposes that the mean pressure and mean temperature are pertinent quantities but not their fluctuating parts. Accordingly, one can neglect the small-scale fluctuations of $\rho_n{}^\circ$ and write

${\rho_n}^{\circ} = \rho_n/\phi_n$ whether at interfaces or in the bulk of phase n. Hence, for coherence with the thermodynamic description one is led to the following approximations:

$$\langle\chi_n\mathbf{v}_n{}^{\circ}\rangle \approx \phi_n\mathbf{V}_n, \quad \langle(\mathbf{v}_I - \mathbf{v}_2{}^{\circ})\cdot\mathbf{n}_2\delta_I\rangle \approx \Gamma_{\mathrm{G}}\phi_2/\rho_2 \quad \text{and} \quad \langle(\mathbf{v}_I - \mathbf{v}_1{}^{\circ})\cdot\mathbf{n}_1\delta_I\rangle \approx -\Gamma_{\mathrm{G}}\phi_1/\rho_1.$$

From definitions (18) and (27) together with the following definition of A:

$$A = \phi_1\langle\chi_2\nabla\cdot\mathbf{v}_2{}^{\circ}\rangle - \phi_2\langle\chi_1\nabla\cdot\mathbf{v}_1{}^{\circ}\rangle$$

it is clear that (A.2) is transformed into

$$\partial\phi_2/\partial t + \nabla\cdot\phi_2\mathbf{V}_2 = \phi_2\nabla\cdot\mathbf{U} + A + \Gamma_{\mathrm{G}}/\rho^*. \tag{A.3}$$

Result (A.3) does not include the role of nucleated volume. For dilute suspensions, the nucleated mass presumably appears with the mass density of the dilute phase. We infer that, for non-dilute suspensions, the volume exchange due to nucleation is closer to $\Gamma_{\mathrm{N}}/\rho^*$ than to any other value. Adding this contribution to the right-hand side of (A.3), one obtains the mean-field evolution equation (23).

A.2. Evolution of entropy

The statistical average of the small-scale entropy balance of phase n is

$$\partial\rho_n s_n/\partial t + \nabla\cdot(\rho_n s_n V_n) + \nabla\cdot\langle\chi_n\rho_n{}^{\circ}s'\mathbf{v}'\rangle = \langle\chi_n\Delta_n{}^{\circ}\rangle - \langle\chi_n\nabla\cdot\mathbf{h}_n{}^{\circ}\rangle + \langle\rho_n{}^{\circ}s_n{}^{\circ}(\mathbf{v}_I - \mathbf{v}_n{}^{\circ})\cdot\mathbf{n}_n\delta_I\rangle,$$

where superscript ° means a small-scale quantity and a prime ′ means a fluctuation relative to the mean values s_n or $\mathbf{V}_n$. $\Delta_n{}^{\circ}$ is the entropy production rate and $\mathbf{h}_n{}^{\circ}$ is the entropy flux of phase n. In what follows we focus on one phase, say phase 1. Instead of the standard two-fluid model based on the identity $\langle\chi_1\nabla\cdot\mathbf{h}_1{}^{\circ}\rangle \equiv \nabla\cdot\langle\chi_1\mathbf{h}_1{}^{\circ}\rangle + \langle\mathbf{h}_1{}^{\circ}\cdot\mathbf{n}_1\delta_I\rangle$, we will start from an alternative identity

$$\begin{aligned}\langle\chi_1\nabla\cdot\mathbf{h}_1{}^{\circ}\rangle \equiv{}& \phi_1\nabla\cdot\langle\chi_1\mathbf{h}_1{}^{\circ} + \chi_2\mathbf{h}_2{}^{\circ}\rangle + \phi_2\langle\chi_1\nabla\cdot\mathbf{h}_1{}^{\circ}\rangle - \phi_1\langle\chi_2\nabla\cdot\mathbf{h}_2{}^{\circ}\rangle \\ & + \phi_1(\langle\mathbf{h}_1{}^{\circ}\cdot\mathbf{n}_1\delta_I\rangle + \langle\mathbf{h}_2{}^{\circ}\cdot\mathbf{n}_2\delta_I\rangle).\end{aligned}$$

Taking into account the boundary condition on the interfaces (remember we neglect any interfacial quantity including the interfacial entropy production), the entropy balance of phase 1 can be presented in the form

$$\begin{aligned}&\partial\rho_1 s_1/\partial t + \nabla\cdot(\rho_1 s_1\mathbf{V}_1) + \nabla\cdot\langle\chi_1\overset{\circ}{\rho}_1 s'\mathbf{v}'\rangle \\ &\quad = \langle\chi_1\Delta_1{}^{\circ}\rangle - \phi_1\nabla\cdot\langle\chi_1\mathbf{h}_1{}^{\circ} + \chi_2\mathbf{h}_2{}^{\circ}\rangle - \phi_2\langle\chi_1\nabla\cdot\mathbf{h}_1{}^{\circ}\rangle + \phi_1\langle\chi_2\nabla\cdot\mathbf{h}_2{}^{\circ}\rangle \\ &\qquad - \phi_1\langle\rho_2{}^{\circ}s_2{}^{\circ}(\mathbf{v}_I - \mathbf{v}_2{}^{\circ})\cdot\mathbf{n}_2\delta_I\rangle + \phi_2\langle\rho_1{}^{\circ}s_1{}^{\circ}(\mathbf{v}_I - \mathbf{v}_1{}^{\circ})\cdot\mathbf{n}_1\delta_I\rangle.\end{aligned} \tag{A.4}$$

With the definitions

$$\Delta_1 \equiv \langle\chi_1\Delta_1{}^{\circ}\rangle, \quad \mathbf{h} \equiv \langle\chi_1\mathbf{h}_1{}^{\circ} + \chi_2\mathbf{h}_2{}^{\circ}\rangle, \quad \Sigma \equiv \phi_2\langle\chi_1\nabla\cdot\mathbf{h}_1{}^{\circ}\rangle - \phi_1\langle\chi_2\nabla\cdot\mathbf{h}_2{}^{\circ}\rangle$$

and the approximations bound to the neglect of small-scale fluctuations

$$\langle\chi_1\rho_1{}^{\circ}s'\mathbf{v}'\rangle \approx 0, \quad \langle\rho_2{}^{\circ}s_2{}^{\circ}(\mathbf{v}_I - \mathbf{v}_2{}^{\circ})\cdot\mathbf{n}_2\delta_I\rangle \approx \Gamma_{\mathrm{G}}s_2, \quad \langle\rho_1{}^{\circ}s_1{}^{\circ}(\mathbf{v}_I - \mathbf{v}_1{}^{\circ})\cdot\mathbf{n}_1\delta_I\rangle \approx -\Gamma_{\mathrm{G}}s_1$$

it is clear that the entropy balance of phase 1 becomes

$$\partial \rho_1 s_1 / \partial t + \nabla \cdot (\rho_1 s_1 \mathbf{V}_1) = \Delta_1 - \phi_1 \nabla \cdot \mathbf{h} - \Sigma - \Gamma_{\mathrm{G}} s^*, \tag{A.5}$$

where s^* is defined in (26). Since the entropy of the nucleated mass is that of the dispersed phase for dilute mixtures, it is likely to be s^* for non-dilute ones and the contribution $-\Gamma_{\mathrm{N}} s^*$ is to be added on the right-hand side of (A.5). We thus recover the entropy balance written in (19). The entropy balance (20) of phase 2 is obtained by a similar method.

A.3. Evolution of the momentum

The statistical average of the small-scale momentum balance is

$$\partial \rho_n \mathbf{V}_n / \partial t + \nabla \cdot (\rho_n \mathbf{V}_n \mathbf{V}_n) + \nabla \cdot \langle \chi_n \rho_n{}^\circ \mathbf{v}'\mathbf{v}' \rangle = \langle \chi_n \nabla \cdot \boldsymbol{\sigma}_n{}^\circ \rangle + \langle \rho_n{}^\circ \mathbf{v}_n{}^\circ (\mathbf{v}_I - \mathbf{v}_n{}^\circ) \cdot \mathbf{n}_n \delta_I \rangle + \rho_n \mathbf{g},$$

where $\sigma_n{}^\circ$ is the small-scale stress of phase n. Following the procedure used above for the entropy balance, we find that the momentum balance of phase 1 can be written in the form

$$\begin{aligned} &\partial \rho_1 \mathbf{V}_1 / \partial t + \nabla \cdot (\rho_1 \mathbf{V}_1 \mathbf{V}_1) + \nabla \cdot \langle \chi_1 \rho_1{}^\circ \mathbf{v}'\mathbf{v}' \rangle \\ &\quad = \phi_1 \nabla \cdot \langle \chi_1 \boldsymbol{\sigma}_1{}^\circ + \chi_2 \boldsymbol{\sigma}_2{}^\circ \rangle + \rho_1 \mathbf{g} + \phi_2 \langle \chi_1 \nabla \cdot \boldsymbol{\sigma}_1{}^\circ \rangle - \phi_1 \langle \chi_2 \nabla \cdot \boldsymbol{\sigma}_2{}^\circ \rangle \\ &\qquad + \phi_2 \langle \rho_1{}^\circ \mathbf{v}^\circ{}_1 (\mathbf{v}_I - \mathbf{v}_1{}^\circ) \cdot \mathbf{n}_1 \delta_I \rangle - \phi_1 \langle \rho_2{}^\circ \mathbf{v}_2{}^\circ (\mathbf{v}_I - \mathbf{v}_2{}^\circ) . \mathbf{n}_2 \delta_I \rangle. \end{aligned} \tag{A.6}$$

With the definitions

$$\boldsymbol{\tau} - p\boldsymbol{I} \equiv \langle \chi_1 \boldsymbol{\sigma}_1{}^\circ + \chi_2 \boldsymbol{\sigma}_2{}^\circ \rangle, \qquad \mathbf{F} \equiv \phi_1 \langle \chi_2 \nabla \cdot \boldsymbol{\sigma}_2{}^\circ \rangle - \phi_2 \langle \chi_1 \nabla \cdot \boldsymbol{\sigma}_1{}^\circ \rangle$$

and the approximations

$$\langle \chi_1 \rho_1{}^\circ \mathbf{v}'\mathbf{v}' \rangle \approx 0, \quad \langle \rho_2{}^\circ \mathbf{v}_2{}^\circ (\mathbf{v}_I - \mathbf{v}_2{}^\circ) \cdot \mathbf{n} \delta_I \rangle \approx \Gamma_{\mathrm{G}} \mathbf{v}_2, \quad \langle \rho_1{}^\circ \mathbf{v}^\circ (\mathbf{v}_I - \mathbf{v}_1{}^\circ) . \mathbf{n}_1 \delta_I \rangle \approx -\Gamma_{\mathrm{G}} \mathbf{v}_1,$$

one obtains the mean-field approximation for (A.6)

$$\partial \rho_1 \mathbf{V}_1 / \partial t + \nabla \cdot (\rho_1 \mathbf{V}_1 \mathbf{V}_1) = \phi_1 (\nabla \cdot \boldsymbol{\tau} - \nabla p) - \mathbf{F} - \Gamma_{\mathrm{G}} (\phi_1 \mathbf{V}_2 + \phi_2 \mathbf{V}_1) + \rho_1 \mathbf{g}. \tag{A.7}$$

This equation does not take the nucleated momentum into account. For a dilute mixture the nucleated mass appears with the velocity of the continuous phase (due to the quite small nucleus size). For a non-dilute mixture, it is likely to appear with the mean velocity $\mathbf{U}$ defined in (18). Hence, a contribution $-\Gamma_{\mathrm{N}} \mathbf{U}$ is to be added to the right-hand side of (A.7). The modified form of (A.7) is thus in agreement with (13) provided $\Gamma \mathbf{V}^*$ is defined like in (29). It was shown in Section 4 that the special value $\mathbf{V}^* = (\mathbf{V}_1 + \mathbf{V}_2)/2$ is the only one for which the mass exchange is driven by the deviations from saturation exclusively.

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