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# THE FUNDAMENTAL EQUATIONS OF GAS–DROPLET MULTIPHASE FLOW

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**Abstract**—This paper describes the derivation of an equation set for the multiphase flow of small polydispersed liquid droplets in a continuous gas-phase consisting of either a pure vapour (of the same chemical species as the liquid droplets) or a mixture of pure vapour and an inert gas. Some difficulties of previous formulations are resolved by more judicious definitions of the interphase transfer terms. The analysis includes a consistent model to represent the surface energy and entropy of the liquid droplets. Surface effects are normally neglected but must be included if consistency is to be maintained with droplet growth models in which the droplet temperature depends on its radius due to the effects of capillarity. A derivation of the equation for the rate of entropy creation due to departures from equilibrium is also presented. Entropy production in non-nucleating flows can be represented by precisely four terms, three of which are associated individually with the interphase transfer of mass, momentum and energy. The fourth term represents the entropy change due to the homogeneous nucleation of liquid droplets from the vapour and is in exact agreement with the results of classical nucleation theory. The form of the entropy creation equation allows an interpretation using the methods of linear irreversible thermodynamics and indicates that some mathematical models of droplet growth in common use, derived on an informal basis, may not be physically realistic in certain circumstances.

*Key Words:* condensation, droplets, condensing flow, multiphase flow

## INTRODUCTION

The specification of a basic equation set for modelling multiphase flows with phase change is a difficult problem which has not yet been resolved satisfactorily. Because of the sheer variety of flow types, phases and components possible, the derivation of a physically consistent mathematical framework for the analysis of a general multiphase flow is a very daunting task. The present paper has a much more modest aim, however, in attempting a rigorous formulation describing just one type of multiphase flow, namely the flow of small, spherical liquid droplets of various sizes in a continuous gas-phase consisting of either a pure vapour (of the same chemical species as the liquid droplets) or a mixture of a pure vapour and an inert gas. Despite the apparent restrictions, the equations are applicable to a wide range of engineering flow problems including, in particular, those involving the homogeneous nucleation of a supersaturated vapour.

Equation sets for gas–droplet multiphase flow have appeared in the literature before, two well-known examples being those of Marble (1969) and Jackson & Davidson (1983). These provide excellent starting points, but the fact that neither is fully comprehensive and both contain inconsistencies testifies to the difficulty in formally establishing the basic framework. Indeed, a familiarity with the literature on condensing and evaporating flows soon reveals a need for a more rigorous approach at the fundamental level of mathematical modelling. This paper is an attempt to resolve some of the difficulties of previous treatments.

The first part of the paper is concerned with a careful derivation of the conservation equations of mass, momentum and energy. Although this is familiar territory, the division of the equations for the mixture into separate equations for the gas and liquid phases is not a straightforward problem because of the difficulty of specifying precisely the terms representing the interphase transfer of momentum and energy in the presence of condensation or evaporation. By adopting definitions slightly modified from the usual to describe this transport of momentum and energy, the gas and liquid phase equations become symmetrical and the resulting, more elegant, form aids physical interpretation.

The most important modification, however, is the inclusion of a thermodynamically consistent model for the surface energy and entropy of the liquid droplets. The surface terms are invariably neglected in formulating the conservation equations because it is widely believed that their effects are insignificant. Nevertheless, when calculating the temperature of very small condensing or evaporating droplets, the effect of capillarity is always included because, in these circumstances, it can be shown that the deviation of the droplet temperature from the saturation temperature is strongly influenced by the effects of surface tension (Gyarmathy 1963). The two assumptions are not consistent, however, and this becomes evident when deriving the equation for the creation of entropy due to departures from equilibrium. Indeed, a correct form of this equation, with or without the inclusion of surface effects, has never appeared in the literature. Without *any* mathematical approximations *en route*, it is shown below that the production of entropy can be represented by precisely four terms. Three of these are associated individually with the interphase transfer of mass, heat and momentum. The fourth term represents the entropy change associated with the nucleation of liquid droplets from the vapour and is in exact agreement with the results of classical homogeneous nucleation theory. Such a mathematically elegant and physically significant form can only be obtained by the correct inclusion of the liquid surface energy and entropy.

The form of the entropy production equation makes possible an interpretation using the methods of irreversible thermodynamics. Thus, the conjugate fluxes and thermodynamic forces can be identified and the phenomenological equations established for linear departures from equilibrium. These equations provide a formal setting for the theory of droplet growth and indicate that some mathematical models in common use, derived on an informal basis, may not be physically realistic in certain situations.

In deriving the equations, the assumptions and approximations are stated without qualification in order that the main issues are not obscured by less important detail. Most readers will be aware of the range of validity of the equations and, for those who are not, an exhaustive discussion can be found in Gyarmathy (1982). Some approximations can quite easily be relaxed at the cost of greater algebraic complexity but, from a practical point of view, it is probably easier to add additional terms to the equations as presented below, rather than remove unwanted terms from a more general, but less comprehensible, analysis.

## BASIC RELATIONSHIPS

The analysis applies to the unsteady compressible flow of a gas–droplet mixture in one, two or three space dimensions. The continuous phase consists (in the general case) of a mixture of an inert gas (subscript G) and a condensible vapour (subscript v) and is referred to throughout as the gas-phase. The liquid phases are discontinuous and consist of a polydispersed population of spherical droplets. It is assumed that the volume fraction occupied by the droplets is small and hence that droplet–droplet interactions do not occur. The effects of viscosity, thermal conductivity and diffusion in the gas-phase are neglected except in the specification of the interphase transfer processes. The resulting equations are therefore not applicable as they stand to boundary layer and other flows dominated by viscosity.

Consider a mixture of inert gas, condensible vapour and liquid droplets and let the mass of inert gas per unit mass of mixture be $g$. The mass of vapour plus liquid per unit mass of mixture is therefore $(1-g)$. The total wetness fraction $y$ is now defined as the mass of liquid per unit mass of vapour plus liquid (*not mixture*). It therefore follows that the mass of vapour per unit mass of mixture is $(1-g)(1-y)$ and the total mass of liquid per unit mass of mixture is $(1-g)y$. Obviously,

$$g+(1-g)(1-y)+(1-g)y=1. \qquad [1]$$

The above definitions of $g$ and $y$ are very convenient. In the particular case when velocity slip between the gas and liquid phases can be neglected, elemental fluid particles retain their identity in that the total mass of vapour plus liquid contained in the particle remains constant even though condensation or evaporation may occur. For this special condition, it follows that $g$ remains constant along a particle path line in unsteady flow or along a streamline in steady flow. Another advantage is that, for a pure vapour, $g = 0$ and $y$ is synonymous with the conventional definition of the wetness fraction. In passing, note that the specific humidity (defined for mixtures of low vapour content as the ratio of the mass of vapour to the mass of inert gas) is given by $(1-g)(1-y)/g$.

For convenience, the continuous spectrum of droplet sizes is discretized into an arbitrary number of droplet groups. Group-$i$ consists of $n_i$ spherical liquid droplets per unit mass of vapour plus liquid (*not mixture*), all of radius $r_i$, liquid density $\rho_i$ and mass $m_i = 4\pi r_i^3 \rho_i/3$. The contribution to the wetness fraction by group-$i$ droplets is,

$$y_i = n_i m_i, \qquad [2]$$

and the total wetness fraction is therefore,

$$y = \sum y_i, \qquad [3]$$

where the summation sign indicates summation over all droplet groups.

If the partial densities of the inert gas and vapour components are $\rho_G$ and $\rho_v$ respectively, then the density of the gas-phase is,

$$\rho = \rho_G + \rho_v, \qquad [4]$$

and the mixture density $\rho_m$ is given by,

$$\frac{1}{\rho_m} = \frac{g + (1-g)(1-y)}{\rho} + \sum \frac{(1-g)y_i}{\rho_i}. \qquad [5]$$

Often, the volume occupied by the liquid phases is very small and the final term of [5] may be neglected.

Assuming inert gas and vapour to behave as perfect gases with partial pressures $p_G$ and $p_v$,

$$p_v = \rho_v R_v T,$$

$$p_G = \rho_G R_G T, \qquad [6]$$

where $R_G$ and $R_v$ are the specific gas constants of the inert gas and vapour components and $T$ is the temperature of the gas-phase. By Dalton's law, the pressure of the gas-phase $p = p_v + p_G$ is given by,

$$p = \rho R T, \qquad [7]$$

where,

$$R = \frac{g R_G + (1-g)(1-y)R_v}{g + (1-g)(1-y)}, \qquad [8]$$

is the specific gas constant of the gas-phase and varies from point to point in the flowfield.

The specific internal energy of the gas-phase $e$ is the sum of the specific internal energies of its components $e_G$ and $e_v$. Thus,

$$e = \frac{g e_G + (1-g)(1-y)e_v}{g + (1-g)(1-y)}. \qquad [9]$$

Changes in $e$ at constant $g$ and $y$ are therefore given by,

$$de = c_v \, dT, \qquad [10]$$

where the isochoric specific heat capacity of the gas-phase $c_v$ is given by,

$$c_v = \frac{g c_{vG} + (1-g)(1-y)c_{vv}}{g + (1-g)(1-y)}. \qquad [11]$$

Similarly, the specific enthalpy of the gas-phase $h = e + p/\rho = e + RT$ is given by,

$$h = \frac{g h_G + (1-g)(1-y)h_v}{g + (1-g)(1-y)}, \qquad [12]$$

where $h_G = e_G + p_G/\rho_G = e_G + R_G T$ and $h_v = e_v + p_v/\rho_v = e_v + R_v T$. Changes in $h$ at constant $g$ and $y$ are given by,

$$dh = c_p\, dT, \qquad [13]$$

where the isobaric specific heat capacity of the gas-phase $c_p$ is given by,

$$c_p = \frac{g c_{pG} + (1-g)(1-y)c_{pv}}{g + (1-g)(1-y)}. \qquad [14]$$

Finally, the specific entropy of the gas-phase $s$ is given by,

$$s = \frac{g s_G + (1-g)(1-y)s_v}{g + (1-g)(1-y)}, \qquad [15]$$

where $s_G$ and $s_v$ are the specific entropies of the inert gas and vapour components evaluated at the gas-phase temperature $T$ and the partial pressures $p_G$ and $p_v$.

## THERMODYNAMICS OF A LIQUID DROPLET

In deriving expressions for the energy and entropy of the liquid phases, it is important to include the droplet surface terms in order to obtain a consistent set of equations. Apart from being a matter of principle there are also important practical implications. For large droplets with low surface to volume ratios, numerical errors resulting from neglect of these terms are normally small. However, for self-nucleated flows containing large concentrations of very small droplets, numerical errors can be significant, particularly when calculating entropy production rates. Thus, although the rate of phase-change itself may be computed with acceptable accuracy, the error in the entropy production rate may, in some cases, be comparable with the magnitude of the effect itself.

Although a number of authors have attempted to include the surface terms in the flow conservation equations [for example, see appendix A2 of Gyarmathy (1982)] a correct derivation has not yet appeared in the literature. The following is a more rigorous formulation based on the surface thermodynamics of Gibbs, a clear exposition of which can be found in Ono & Kondo (1960).

In the Gibbs formulation of the thermodynamics of curved surfaces, the real droplet–gas system (with rapidly but, nevertheless, continuously varying properties in the interface region) is replaced by a model consisting of a spherical droplet separated from the gas by a hypothetical dividing surface of zero thickness. Both droplet and gas are assumed to have uniform properties right up to the dividing surface where a discontinuous change takes place. The position of the dividing surface is arbitrary, but it is usually convenient to place the surface at the position where the total mass of the model system equals the total mass of the real system. This is called the equi-molecular position of the dividing surface. However, although the total mass of the system is conserved by this choice, the total energy and entropy are not. The difference between the total energy of the real system and that of the model system (i.e. the sum of the liquid and gas contributions) is called the surface energy and is specifically associated with the dividing surface. The surface entropy is defined similarly.

It is thus assumed that the energy $E_i$ and entropy $S_i$ of a group-$i$ liquid droplet can be represented as the sum of a bulk term (subscript b) and a surface term (subscript s),

$$E_i = E_{bi} + E_{si},$$
$$S_i = S_{bi} + S_{si}. \qquad [16]$$

These expressions can be written,

$$E_i = \tfrac{4}{3}\pi r_i^3 \rho_i e_{bi} + 4\pi r_i^2 e_{si},$$
$$S_i = \tfrac{4}{3}\pi r_i^3 \rho_i s_{bi} + 4\pi r_i^2 s_{si}, \qquad [17]$$

where $e_{bi}$ and $s_{bi}$ are the bulk specific energy and entropy (i.e. per unit mass) and $e_{si}$ and $s_{si}$ are the energy and entropy per unit surface area. The energy and entropy per unit mass of droplet, $e_i$ and $s_i$, are therefore given by,

$$e_i = e_{bi} + \frac{3e_{si}}{\rho_i r_i},$$

$$s_i = s_{bi} + \frac{3s_{si}}{\rho_i r_i}. \qquad [18]$$

In the present analysis, it is assumed that the bulk properties (particularly the temperature) are uniform throughout the droplet (even well away from the surface region). This approximation may be questionable for large droplets but can be relaxed (at the expense of greater complexity) without affecting the basic structure of the equations. [The conditions under which it is permissible to assume uniform droplet temperature are analysed in detail by Gyarmathy (1982)] The condition for mechanical equilibrium of the droplet in a gas at pressure $p$ is,

$$p_i = p + \frac{2\sigma_i}{r_i}, \qquad [19]$$

where $p_i$ is the internal pressure of the droplet and $\sigma_i$ is the surface tension or surface free energy per unit area. Equation [19] is assumed to hold even in non-equilibrium situations.

It is important to note that $e_{bi}$ and $s_{bi}$ must be evaluated at the droplet temperature $T_i$ and *internal* pressure $p_i$ and that the latter may be very large for small droplets.

As shown in texts on surface thermodynamics, the surface energy and entropy $e_{si}$ and $s_{si}$ can be expressed in terms of the surface *free* energy (or surface tension) $\sigma_i$ as,

$$e_{si} = \sigma_i - T_i\frac{d\sigma_i}{dT_i},$$

$$s_{si} = -\frac{d\sigma_i}{dT_i}. \qquad [20]$$

Formally, $\sigma_i$ is defined by the relationship $\sigma_i = (\partial E_{si}/\partial A_i)_{S_{si}}$, where $A_i$ is the surface area of a group-$i$ droplet. $\sigma_i$ is a function of temperature and, in some cases perhaps, of droplet radius (for example in the very early stages of nucleation when the droplet is little more than a large cluster of molecules). The latter possibility is not included here, however. (Note that, in some publications, the surface *free* energy $\sigma_i$ has been confused with the surface energy $e_{si}$.)

Changes in the specific bulk entropy and energy are related by the familiar relationship,

$$T_i\,ds_{bi} = de_{bi} + p_i\,d(1/\rho_i), \qquad [21]$$

where $de_{bi} = c_i\,dT_i$, $c_i$ being the bulk specific heat capacity at constant volume of the liquid. The corresponding relationship between the surface entropy and energy can be derived using the methods of surface thermodynamics as,

$$T_i\,ds_{si} = de_{si}. \qquad [22]$$

[22] implies that the droplet–gas interface has been located at the equi-molecular position so that the mass associated with the surface is zero.

Equations [20] and [22] assume that the surface and bulk liquid are always in thermodynamic equilibrium and hence the "surface temperature" $T_{si}$ is always equal to the bulk temperature $T_i$. Readers unfamiliar with the concept of "surface temperature" should note that it is defined by the relationship $T_{si} = (\partial E_{si}/\partial S_{si})_{A_i}$ and is therefore a well-specified quantity. It is unnecessary to associate the usual physical attributes of temperature with $T_{si}$.

The change in droplet entropy per unit mass $ds_i$ must now be related to the change in droplet energy per unit mass $de_i$. This can be achieved by differentiating [18] and substituting [21] and [22]. Equations [19] and [20] are also used and give, after some manipulation,

$$T_i\,ds_i = de_i + p\,d(1/\rho_i) + \frac{\sigma_i}{\rho_i r_i}\frac{dm_i}{m_i}, \qquad [23]$$

where $m_i$ is the mass of a group-$i$ droplet. Note that the pressure $p$ in [23] is the local gas-phase pressure and *not* the internal pressure of the droplet $p_i$. The droplet enthalpy per unit mass is now *defined* by the relation,

$$h_i = e_i + \frac{p}{\rho_i}, \tag{24}$$

where $p$ represents the gas-phase pressure. Differentiation and substitution of [23] results in,

$$T_i\,\mathrm{d}s_i = \mathrm{d}h_i - \frac{\mathrm{d}p}{\rho_i} + \frac{\sigma_i}{\rho_i r_i}\frac{\mathrm{d}m_i}{m_i}. \tag{25}$$

## CONSERVATION OF DROPLETS

Consider a control volume of volume $V$ bounded by a closed surface $S$. A small volume $\delta V$ within the control volume contains total mass $\rho_m \delta V$ and mass $\rho_m(1-g)\delta V$ of vapour plus liquid. The number of group-$i$ droplets in $\delta V$ is thus $\rho_m(1-g)n_i\delta V$. Let the nucleation rate of group-$i$ droplets per unit mass of *vapour plus liquid* in $\delta V$ be $J_i$.

For the control volume, the conservation of group-$i$ droplets can be written,

$$\frac{\partial}{\partial t}\left\{\iiint \rho_m(1-g)n_i\,\mathrm{d}V\right\} + \iint \rho_m(1-g)n_i\mathbf{u}_i\cdot\mathrm{d}\mathbf{A} = \iiint \rho_m(1-g)J_i\,\mathrm{d}V, \tag{26}$$

where $\mathbf{u}_i$ is the vectorial velocity of group-$i$ droplets and $\delta A$ is a vectorial element of area on the control surface with direction equivalent to an outward pointing normal vector. The triple integrals represent integration over the control volume $V$ and the double integrals represent integration over the closed control surface $S$. Applying Gauss's theorem and allowing $\delta V$ to become infinitesimally small (while still containing many droplets), gives the differential form,

$$\frac{\partial}{\partial t}\{\rho_m(1-g)n_i\} + \nabla\cdot\{\rho_m(1-g)n_i\mathbf{u}_i\} = \rho_m(1-g)J_i. \tag{27}$$

Note that a separate equation must be written for each droplet group. Equations valid for a pure vapour can be obtained by setting $g = 0$.

A special case arises when the relative velocity between the gas and liquid phases is negligible as in many self-nucleated flows where the droplets are very small. As shown in the next section, $g$ then remains constant along a path line and, using [35] below,

$$\frac{\mathrm{D}n_i}{\mathrm{D}t} = J_i, \tag{28}$$

where $D/Dt = \partial/\mathrm{d}t + \bar{\mathbf{u}}\cdot\nabla$ is the substantive derivative following a fluid particle and $\bar{\mathbf{u}}$ is the common velocity of the phases. Thus, in the absence of nucleation, the $n_i$ remain constant along the fluid path lines. (This is why it is generally much more convenient to work in terms of $n_i$, defined as the number per unit *mass* of vapour plus liquid rather than the more common "number density" defined as the number per unit volume.)

## MASS CONTINUITY EQUATIONS

In the elemental volume $\delta V$, the mass of inert gas is $g\rho_m\delta V$, the mass of vapour is $\rho_m(1-g)(1-y)\delta V$ and the mass of group-$i$ liquid droplets is $\rho_m(1-g)y_i\delta V$. The continuity equation for the mixture as a whole can therefore be written in control volume form as,

$$\frac{\partial}{\partial t}\iiint \rho_m\,\mathrm{d}V + \iint \rho_m[g + (1-g)(1-y)]\mathbf{u}\cdot\mathrm{d}\mathbf{A} + \sum\iint \rho_m(1-g)y_i\mathbf{u}_i\cdot\mathrm{d}\mathbf{A} = 0, \tag{29}$$

where $\mathbf{u}$ is now the velocity of the gas-phase and $\Sigma$ represents summation over all the droplet groups. Applying Gauss's theorem and allowing $\delta V$ to become infinitesimally small (while still containing many droplets), gives the differential form,

$$\frac{\partial\rho_m}{\partial t} + \nabla\cdot\{\rho_m[g + (1-g)(1-y)]\mathbf{u}\} + \sum\nabla\cdot\{\rho_m(1-g)y_i\mathbf{u}_i\} = 0. \tag{30}$$

As before, the equations for a pure vapour carrier can be obtained by setting $g = 0$. The species continuity equation for the inert gas, derived similarly, is,

$$\frac{\partial}{\partial t}(\rho_{\mathrm{m}} g) + \nabla \cdot (\rho_{\mathrm{m}} g \mathbf{u}) = 0. \qquad [31]$$

The mass continuity equation for droplet group-$i$ is obtained by multiplying the droplet conservation equation [27] by $m_i$,

$$\frac{\partial}{\partial t}\{\rho_{\mathrm{m}}(1-g)y_i\} + \nabla \cdot \{\rho_{\mathrm{m}}(1-g)y_i \mathbf{u}_{\mathrm{i}}\} = \rho_{\mathrm{m}}(1-g)(n_i \dot{m}_i + m_i J_i), \qquad [32]$$

where $\dot{m}_i = \partial m_i/\partial t + \mathbf{u}_{\mathrm{i}} \cdot \nabla m_i$ is the *condensation* rate on a group-$i$ droplet. With the possible exception of condensation on very small, freshly nucleated droplets containing only a few molecules, $\dot{m}_i$ is a well-defined quantity. The continuity equation for the gas-phase is obtained by subtracting from [30] the summation over all groups of [32]. Thus,

$$\frac{\partial}{\partial t}\{\rho_{\mathrm{m}}[g + (1-g)(1-y)]\} + \nabla \cdot \{\rho_{\mathrm{m}}[g + (1-g)(1-y)]\mathbf{u}\} = -\rho_{\mathrm{m}}(1-g)\sum(n_i \dot{m}_i + m_i J_i). \quad [33]$$

The species continuity equation for the vapour component alone may then be obtained by subtracting [31] from [33].

For zero relative velocity between the gas and liquid phases, the mixture continuity equation [30] becomes,

$$\frac{\partial \rho_{\mathrm{m}}}{\partial t} + \nabla \cdot (\rho_{\mathrm{m}} \bar{\mathbf{u}}) = 0, \qquad [34]$$

where $\bar{\mathbf{u}}$ is the common velocity of the phases. Equation [31] for the inert gas component reduces to,

$$\frac{\mathrm{D}g}{\mathrm{D}t} = 0, \qquad [35]$$

showing that the mass fraction $g$ remains constant along a fluid particle path line. For droplet group-$i$, [32] becomes,

$$\frac{\mathrm{D}y_i}{\mathrm{D}t} = (n_i \dot{m}_i + m_i J_i), \qquad [36]$$

and for the vapour component alone, [33] becomes,

$$\frac{\mathrm{D}(1-y)}{\mathrm{D}t} = -\sum(n_i \dot{m}_i + m_i J_i). \qquad [37]$$

## MOMENTUM EQUATIONS

In deriving the momentum equations, care must be taken in specifying the force acting on the control surface when droplet surface tension is included. Consider a group-$i$ droplet intersected by the control surface as shown in figure 1. The internal pressure of the droplet is $(p + 2\sigma_i/r_i)$ and this acts normal to the control surface within the droplet. However, the excess pressure $2\sigma_i/r_i$ integrated over the relevant area is just balanced by the surface tension force acting on the droplet perimeter where it is cut by the control surface. Hence, the total force acting on the control surface is simply obtained by integrating the *gas-phase* pressure over the whole surface including that intersected by the droplets.

Neglecting viscous shear forces, the momentum equation for the mixture as a whole is,

$$\frac{\partial}{\partial t}\left\{\iiint \rho_{\mathrm{m}}[g + (1-g)(1-y)]\mathbf{u}\,\mathrm{d}V + \sum \iiint \rho_{\mathrm{m}}(1-g)y_i \mathbf{u}_{\mathrm{i}}\,\mathrm{d}V\right\} + \iint p\,\mathrm{d}\mathbf{A}$$
$$+ \iint \rho_{\mathrm{m}}[g + (1-g)(1-y)]\mathbf{u}(\mathbf{u} \cdot \mathrm{d}\mathbf{A}) + \sum \iint \rho_{\mathrm{m}}(1-g)y_i \mathbf{u}_{\mathrm{i}}(\mathbf{u}_{\mathrm{i}} \cdot \mathrm{d}\mathbf{A}) = 0. \quad [38]$$

The differential form is obtained by applying Gauss's theorem, allowing $\delta V$ to become infinitesimally small and introducing the continuity equation [31]–[33]. The result is,

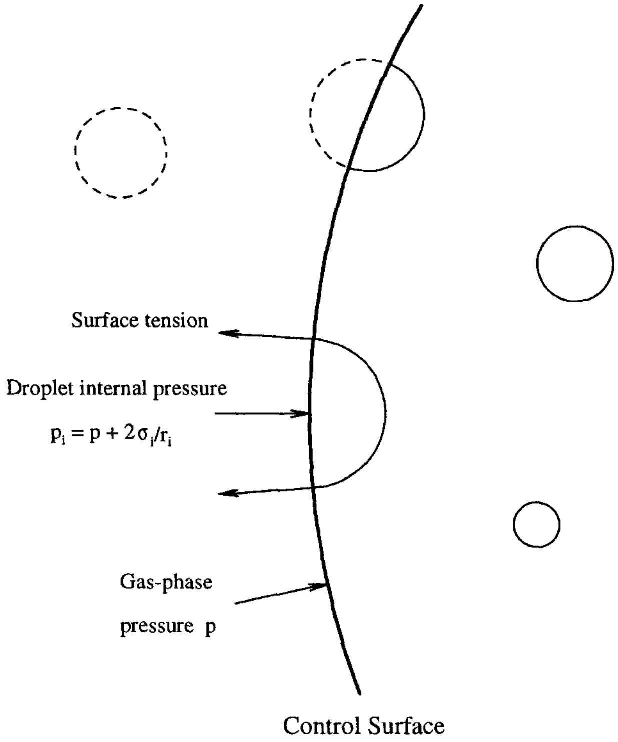

Figure 1. Droplets intersected by the control surface.

$$[g+(1-g)(1-y)]\frac{D\mathbf{u}}{Dt}+(1-g)\sum y_i\frac{D\mathbf{u}_i}{Dt_i}+\frac{\nabla p}{\rho_m}=(1-g)\sum n_i\dot{m}_i(\mathbf{u}-\mathbf{u}_i), \qquad [39]$$

where $D/Dt = \partial/\partial t + \mathbf{u}\cdot\nabla$ is the substantive derivative associated with a gas-phase fluid particle and $D/Dt_i = \partial/\partial t + \mathbf{u}_i\cdot\nabla$ is the substantive derivative associated with the group-$i$ liquid droplets. In deriving [39], it has been assumed that freshly nucleated droplets travel with the gas-phase velocity.

The derivation of the momentum equations for the separated gas and liquid phases has caused some confusion in previous publications. The problem involves the specification of the momentum exchange between a droplet and the gas-phase when phase-change is occurring simultaneously with the presence of velocity slip. A discussion can be found in appendix 1, where it is shown that a well-defined formulation of the momentum equation for group-$i$ droplets is,

$$y_i\left(\frac{D\mathbf{u}_i}{Dt_i}+\frac{\nabla p}{\rho_i}\right)=n_i\mathbf{f}_i+n_i\dot{m}_i(\tilde{\mathbf{u}}_i-\mathbf{u}_i), \qquad [40]$$

where $(\mathbf{f}_i - m_i\nabla p/\rho_i)$ represents the net rate of momentum transfer from the gas-phase to a group-$i$ droplet measured in a co-ordinate system moving at an arbitrary velocity $\tilde{\mathbf{u}}_i$. In the absence of phase-change, $\mathbf{f}_i$ is similar to the force on a solid particle and (assuming the Basset and virtual mass effects are negligible) can usually be approximated by a suitable expression for the steady-state drag force. If phase-change is present, however, the form of $\mathbf{f}_i$ may change to include the effects (not necessarily additive) of net condensation or evaporation. Because of the definition of $\mathbf{f}_i$, [40] is valid irrespective of the sign of the interphase mass transfer rate $\dot{m}_i$ and it is unnecessary to differentiate between cases of net positive or negative phase-change in the manner of Jackson & Davidson (1983). (In passing, it should also be noted that the term representing the force on the droplet due to the pressure gradient is incorrectly specified in the Jackson & Davidson paper.)

The momentum equation for the gas-phase is obtained by summing [40] multiplied by $(1-g)$ over all droplet groups and subtracting from [39] to give,

$$[g+(1-g)(1-y)]\left(\frac{D\mathbf{u}}{Dt}+\frac{\nabla p}{\rho}\right)=(1-g)\sum[-n_i\mathbf{f}_i+n_i\dot{m}_i(\mathbf{u}-\tilde{\mathbf{u}}_i)], \qquad [41]$$

where $\rho$ is the gas-phase density.

Although $\bar{\mathbf{u}}_i$ is an arbitrary velocity, a useful simplification and ordering of the energy and entropy equations results from the choice $\bar{\mathbf{u}}_i = (\mathbf{u} + \mathbf{u}_i)/2$, a definition which is adopted herewith. Physically, this choice implies that the interphase momentum transfer is measured with respect to a co-ordinate system moving at the mean velocity of the two phases and it is this symmetrical viewpoint of the momentum exchange which is responsible for later simplifications.

For negligible gas–liquid relative velocity, [39] for the mixture becomes,

$$\frac{D\bar{\mathbf{u}}}{Dt} + \frac{\nabla p}{\rho_m} = 0. \tag{42}$$

As discussed by Marble (1969), care must be exercised when taking the limit $(\mathbf{u} - \mathbf{u}_i) \to 0$ in the equations for the individual phases because the $\mathbf{f}_i$ remain finite. The correct procedure is to write [40] as,

$$y_i\left(\frac{D\bar{\mathbf{u}}}{Dt} + \frac{\nabla p}{\rho_i}\right) = n_i \mathbf{f}_i, \tag{43}$$

where $\bar{\mathbf{u}}$ is the common velocity of the phases and this equation defines the $\mathbf{f}_i$ for inclusion in the gas-phase momentum equation [41] which then becomes,

$$[g + (1-g)(1-y)]\left(\frac{D\bar{\mathbf{u}}}{Dt} + \frac{\nabla p}{\rho}\right) = -(1-g)\sum n_i \mathbf{f}_i. \tag{44}$$

## ENERGY EQUATIONS

In deriving the energy equation for the mixture, the effects of heat conduction, viscosity and diffusion in the gas-phase are neglected. As before, we consider a control volume of volume $V$ and bounding surface area $S$. In order to specify the work done by the pressure forces in transporting the flow through the control volume, we imagine, following Jackson & Davidson (1983), the control surface to be sub-divided into sub-surfaces passing each phase alone. Thus, each element of control surface area $\delta\mathbf{A}$ is composed of area elements passing the gas and liquid phases separately,

$$\delta\mathbf{A} = \delta\mathbf{A}_G + \sum \delta\mathbf{A}_i. \tag{45}$$

As shown by Jackson & Davidson, the continuity relationships then require,

$$\begin{aligned} \delta\mathbf{A}_G &= \frac{\rho_m[g + (1-y)(1-g)]}{\rho}\,\delta\mathbf{A}, \\ \delta\mathbf{A}_i &= \frac{\rho_m(1-g)y_i}{\rho_i}\,\delta\mathbf{A}. \end{aligned} \tag{46}$$

The energy equation for the mixture in control volume form can therefore be written,

$$\begin{aligned} &\frac{\partial}{\partial t}\left\{\iiint \rho_m[g + (1-g)(1-y)]\left(e + \frac{u^2}{2}\right)dV + \sum \iiint \rho_m(1-g)y_i\left(e_i + \frac{u_i^2}{2}\right)dV\right\} \\ &+ \iint \rho_m[g + (1-g)(1-y)]\left(e + \frac{u^2}{2}\right)\mathbf{u}\cdot d\mathbf{A} + \sum \iint \rho_m(1-g)y_i\left(e_i + \frac{u_i^2}{2}\right)\mathbf{u}_i\cdot d\mathbf{A} \\ &+ \iint \frac{\rho_m[g + (1-g)(1-y)]}{\rho}\,p\mathbf{u}\cdot d\mathbf{A} + \sum \iint \frac{\rho_m(1-g)y_i}{\rho_i}\,p\mathbf{u}_i\cdot d\mathbf{A} = 0. \end{aligned} \tag{47}$$

It should be noted that $e$ is the specific internal energy of the gas-phase and $e_i$ is the energy per unit mass of the group-$i$ droplets *including the surface energy*. Introducing the definitions of the specific enthalpies of the gas-phase ($h = e + p/\rho$) and of the group-$i$ droplets ($h_i = e_i + p/\rho_i$) gives,

$$\frac{\partial}{\partial t}\left\{\iiint \rho_{\mathrm{m}}[g+(1-g)(1-y)]\left(h+\frac{u^2}{2}\right)\mathrm{d}V+\sum\iiint \rho_{\mathrm{m}}(1-g)y_i\left(h_i+\frac{u_i^2}{2}\right)\mathrm{d}V\right\}-\iiint\frac{\partial p}{\partial t}\,\mathrm{d}V$$
$$+\iint \rho_{\mathrm{m}}[g+(1-g)(1-y)]\left(h+\frac{u^2}{2}\right)\mathbf{u}\cdot\mathrm{d}\mathbf{A}+\sum\iint \rho_{\mathrm{m}}(1-g)y_i\left(h_i+\frac{u_i^2}{2}\right)\mathbf{u}_{\mathrm{i}}\cdot\mathrm{d}\mathbf{A}=0. \quad [48]$$

The differential form is obtained by applying Gauss's theorem, allowing $\delta V$ to become infinitesimally small and introducing the continuity equations [31]–[33]. The result is,

$$g\frac{\mathrm{D}}{\mathrm{D}t}\left(h_{\mathrm{G}}+\frac{u^2}{2}\right)+(1-g)(1-y)\frac{\mathrm{D}}{\mathrm{D}t}\left(h_{\mathrm{v}}+\frac{u^2}{2}\right)+(1-g)\sum y_i\frac{\mathrm{D}}{\mathrm{D}t_i}\left(h_i+\frac{u_i^2}{2}\right)-\frac{1}{\rho_{\mathrm{m}}}\frac{\partial p}{\partial t}$$
$$=(1-g)\sum(n_i\dot{m}_i+m_iJ_i)\left[\left(h_{\mathrm{v}}+\frac{u^2}{2}\right)-\left(h_i+\frac{u_i^2}{2}\right)\right]. \quad [49]$$

It should be noted that, if the vapour and inert gas components behave as perfect gases, $g\,\mathrm{D}h_{\mathrm{G}}/\mathrm{D}t+(1-g)(1-y)\,\mathrm{D}h_{\mathrm{v}}/\mathrm{D}t=[g+(1-g)(1-y)]c_{\mathrm{p}}\,\mathrm{D}T/\mathrm{D}t$, where $c_{\mathrm{p}}$ is defined by [14].

The thermodynamic form of the energy equation is obtained by subtracting from [49] the scalar product of $\mathbf{u}$ and [41], and the scalar product of $(1-g)\mathbf{u}_{\mathrm{i}}$ and [40] for each droplet group. Adopting the definition $\tilde{\mathbf{u}}_{\mathrm{i}}=(\mathbf{u}+\mathbf{u}_{\mathrm{i}})/2$ gives,

$$g\left[\frac{\mathrm{D}h_{\mathrm{G}}}{\mathrm{D}t}-\frac{1}{\rho}\frac{\mathrm{D}p}{\mathrm{D}t}\right]+(1-g)(1-y)\left[\frac{\mathrm{D}h_{\mathrm{v}}}{\mathrm{D}t}-\frac{1}{\rho}\frac{\mathrm{D}p}{\mathrm{D}t}\right]+(1-g)\sum y_i\left[\frac{\mathrm{D}h_i}{\mathrm{D}t_i}-\frac{1}{\rho_i}\frac{\mathrm{D}p}{\mathrm{D}t_i}\right]$$
$$=(1-g)\sum[(n_i\dot{m}_i+m_iJ_i)(h_{\mathrm{v}}-h_i)+n_i\mathbf{f}_{\mathrm{i}}\cdot(\mathbf{u}-\mathbf{u}_{\mathrm{i}})]. \quad [50]$$

One of the advantages of this particular choice for $\tilde{\mathbf{u}}_{\mathrm{i}}$ is now evident as the terms on the right hand side of [50] naturally separate into two parts. The first represents the rate at which "latent heat" is released at the droplet surface due to phase-change and the second represents the rate of dissipation of kinetic energy by the "effective drag force" $\mathbf{f}_{\mathrm{i}}$. It is only for this particular choice of $\tilde{\mathbf{u}}_{\mathrm{i}}$ that such a separation occurs.

The energy equation for a liquid droplet is complicated by, among other things, the inclusion of the surface energy terms and a correct formulation has not appeared previously in the literature. A derivation is presented in appendix 2, where it is shown that a well-specified formulation of the energy equation for group-$i$ droplets is,

$$y_i\left[\frac{\mathrm{D}h_i}{\mathrm{D}t_i}-\frac{1}{\rho_i}\frac{\mathrm{D}p}{\mathrm{D}t_i}\right]=n_i\dot{m}_i(h_{\mathrm{v}}-h_i)+n_iq_i, \quad [51]$$

where $q_i$ is the heat transfer rate from the gas-phase to a group-$i$ droplet. (The precise definition of $q_i$ can be found in appendix 2.)

The energy equation for the gas-phase is obtained by summing [51] over all droplet groups, multiplying by $(1-g)$ and subtracting from [50] for the mixture to give,

$$g\left[\frac{\mathrm{D}h_{\mathrm{G}}}{\mathrm{D}t}-\frac{1}{\rho}\frac{\mathrm{D}p}{\mathrm{D}t}\right]+(1-g)(1-y)\left[\frac{\mathrm{D}h_{\mathrm{v}}}{\mathrm{D}t}-\frac{1}{\rho}\frac{\mathrm{D}p}{\mathrm{D}t}\right]$$
$$=(1-g)\sum[-n_iq_i+m_iJ_i(h_{\mathrm{v}}-h_i)+n_i\mathbf{f}_{\mathrm{i}}\cdot(\mathbf{u}-\mathbf{u}_{\mathrm{i}})]. \quad [52]$$

For zero relative velocity between the gas and liquid phases, the energy equation for the mixture becomes,

$$g\frac{\mathrm{D}h_{\mathrm{G}}}{\mathrm{D}t}+(1-g)(1-y)\frac{\mathrm{D}h_{\mathrm{v}}}{\mathrm{D}t}+(1-g)\sum y_i\frac{\mathrm{D}h_i}{\mathrm{D}t}+\frac{\mathrm{D}}{\mathrm{D}t}\left(\frac{\tilde{u}^2}{2}\right)-\frac{1}{\rho_{\mathrm{m}}}\frac{\partial p}{\partial t}$$
$$=(1-g)\sum(n_i\dot{m}_i+m_iJ_i)(h_{\mathrm{v}}-h_i), \quad [53]$$

and the thermodynamic form is,

$$g\frac{\mathrm{D}h_{\mathrm{G}}}{\mathrm{D}t}+(1-g)(1-y)\frac{\mathrm{D}h_{\mathrm{v}}}{\mathrm{D}t}+(1-g)\sum y_i\frac{\mathrm{D}h_i}{\mathrm{D}t}-\frac{1}{\rho_{\mathrm{m}}}\frac{\mathrm{D}p}{\mathrm{D}t}=(1-g)\sum(n_i\dot{m}_i+m_iJ_i)(h_{\mathrm{v}}-h_i). \quad [54]$$

The energy equation for group-*i* droplets takes the form,

$$y_i\left[\frac{\mathrm{D}h_i}{\mathrm{D}t}-\frac{1}{\rho_i}\frac{\mathrm{D}p}{\mathrm{D}t}\right]=n_i\dot{m}_i(h_\mathrm{v}-h_i)+n_i\mathrm{q}_i, \qquad [55]$$

and [52] for the gas-phase becomes,

$$g\left[\frac{\mathrm{D}h_\mathrm{G}}{\mathrm{D}t}-\frac{1}{\rho}\frac{\mathrm{D}p}{\mathrm{D}t}\right]+(1-g)(1-y)\left[\frac{\mathrm{D}h_\mathrm{v}}{\mathrm{D}t}-\frac{1}{\rho}\frac{\mathrm{D}p}{\mathrm{D}t}\right]=(1-g)\sum[-n_iq_i+m_iJ_i(h_\mathrm{v}-h_i)]. \qquad [56]$$

## ENTROPY PRODUCTION

The conservation equations of momentum and energy derived in the previous sections reveal a pleasing form and symmetry which aids physical interpretation and has been lacking in other formulations. A comparison of the present equations with those of Marble (1969) and Jackson & Davidson (1983), for example, shows that by careful definition of the interphase transfer terms $\mathbf{f}_\mathrm{i}$ and $q_i$, it has been possible to eradicate some of the small terms which otherwise appear in the equations tending to obscure their significance.

It will also be observed that the incorporation of the droplet surface energy has not altered the basic form of the equations. The surface energy is contained within the droplet specific enthalpy term $h_i$ and only appears in the energy equations. The analysis has demonstrated, however, that the correct form is $h_i=e_i+p/\rho_i$ rather than $h_i=e_i+p_i/\rho_i$ as might otherwise have been suspected.

Small though these alterations to the theory may appear, they have a very significant effect in the derivation and interpretation of the equation for the rate of production of entropy due to departures from equilibrium. A formally correct version of this equation has never appeared in the literature, all previous derivations being plagued with small but unwanted terms which destroy the expected symmetry and sometimes run counter to physical intuition.

Let the rate of production of entropy *per unit mass of mixture* be $\omega$. The entropy production equation in control volume form is then,

$$\iiint\rho_\mathrm{m}\omega\,\mathrm{d}V=\frac{\partial}{\partial t}\left\{\iiint\rho_\mathrm{m}[g+(1-g)(1-y)]s\,\mathrm{d}V+\sum\iiint\rho_\mathrm{m}(1-g)y_is_i\,\mathrm{d}V\right\}$$
$$+\iint\rho_\mathrm{m}[g+(1-g)(1-y)]s\mathbf{u}\cdot\mathrm{d}\mathbf{A}+\sum\iint\rho_\mathrm{m}(1-g)y_is_i\mathbf{u}_\mathbf{i}\cdot\mathrm{d}\mathbf{A}, \qquad [57]$$

where $s$ is the specific entropy of the gas-phase and $s_i$ is the entropy per unit mass of a group-*i* droplet *including the surface entropy*. The differential form is obtained by applying Gauss's theorem, allowing $\delta V$ to become infinitesimally small and introducing the continuity equations [31]–[33]. The result is,

$$\omega=g\frac{\mathrm{D}s_\mathrm{G}}{\mathrm{D}t}+(1-g)(1-y)\frac{\mathrm{D}s_\mathrm{v}}{\mathrm{D}t}+(1-g)\sum y_i\frac{\mathrm{D}s_i}{\mathrm{D}t_i}-(1-g)\sum(n_i\dot{m}_i+m_iJ_i)(s_\mathrm{v}-s_i). \qquad [58]$$

The changes in specific entropy of the inert gas and vapour components are described by the thermodynamic relationships,

$$T\frac{\mathrm{D}s_\mathrm{G}}{\mathrm{D}t}=\frac{\mathrm{D}h_\mathrm{G}}{\mathrm{D}t}-\frac{1}{\rho_\mathrm{G}}\frac{\mathrm{D}p_\mathrm{G}}{\mathrm{D}t},\quad T\frac{\mathrm{D}s_\mathrm{v}}{\mathrm{D}t}=\frac{\mathrm{D}h_\mathrm{v}}{\mathrm{D}t}-\frac{1}{\rho_\mathrm{v}}\frac{\mathrm{D}p_\mathrm{v}}{\mathrm{D}t}, \qquad [59]$$

which together can be written,

$$T\left[g\frac{\mathrm{D}s_\mathrm{G}}{\mathrm{D}t}+(1-g)(1-y)\frac{\mathrm{D}s_\mathrm{v}}{\mathrm{D}t}\right]=g\left[\frac{\mathrm{D}h_\mathrm{G}}{\mathrm{D}t}-\frac{1}{\rho}\frac{\mathrm{D}p}{\mathrm{D}t}\right]+(1-g)(1-y)\left[\frac{\mathrm{D}h_\mathrm{v}}{\mathrm{D}t}-\frac{1}{\rho}\frac{\mathrm{D}p}{\mathrm{D}t}\right]. \qquad [60]$$

The change in specific entropy of a group-*i* droplet is given by [25],

$$T_i\frac{\mathrm{D}s_i}{\mathrm{D}t_i}=\frac{\mathrm{D}h_i}{\mathrm{D}t_i}-\frac{1}{\rho_i}\frac{\mathrm{D}p}{\mathrm{D}t_i}+\frac{\sigma_i}{\rho_ir_im_i}\dot{m}_i. \qquad [61]$$

Substituting [60] and [61] in [58] and combining with the energy equations [51] and [52] gives,

$$\omega = (1-g)\sum\left\{n_i q_i\left[\frac{1}{T_i}-\frac{1}{T}\right] + n_i\dot{m}_i\left[\frac{(h_v-h_i)}{T_i}-(s_v-s_i)+\frac{\sigma_i}{\rho_i r_i T_i}\right]\right.$$
$$\left. + \frac{n_i\mathbf{f}_i\cdot(\mathbf{u}-\mathbf{u}_i)}{T} + m_i J_i\left[\frac{(h_v-h_i)}{T}-(s_v-s_i)\right]\right\}. \qquad [62]$$

The terms associated with mass transfer and nucleation can be simplified as shown in appendix 3. Equation [62] then becomes,

$$\frac{\omega}{R_v} = (1-g)\sum\left\{\frac{n_i q_i}{R_v T_i}\left[\frac{T-T_i}{T}\right] + \frac{n_i\dot{m}_i}{R_v}\left[\frac{(h_v-h_{bi})}{T_i}-(s_v-s_{bi})\right] + \frac{n_i\mathbf{f}_i\cdot(\mathbf{u}-\mathbf{u}_i)}{R_v T} - \frac{4\pi r_i^2\sigma_i J_i}{3R_v T}\right], \qquad [63]$$

where $s_{bi}$ and $h_{bi} = e_{bi} + p_i/\rho_i$ are the specific entropy and enthalpy of the bulk liquid composing a group-$i$ droplet. Both terms must be evaluated at the droplet temperature $T_i$ and internal pressure $p_i$. Equation [63] involves no approximation whatsoever and follows directly from the original mathematical model of the multiphase flow. However, with the very minor approximation discussed in appendix 3, the equation takes the more significant form,

$$\frac{\omega}{R_v} = (1-g)\sum\left\{\frac{n_i q_i}{R_v T_i}\left[\frac{T-T_i}{T}\right] + n_i\dot{m}_i\log_e\left[\frac{p_v}{p_s(T_i, r_i)}\right] + \frac{n_i\mathbf{f}_i\cdot(\mathbf{u}-\mathbf{u}_i)}{R_v T} - \frac{4\pi r_i^2\sigma_i J_i}{3R_v T}\right\}, \qquad [64]$$

where $p_v$ is the partial pressure of the vapour in the gas-phase and $p_s(T_i, r_i)$ is the saturation pressure (corrected for the effects of surface curvature) at temperature $T_i$ for a droplet of radius $r_i$. $p_s(T_i, r_i)$ is related to the "flat surface" saturation pressure $p_s(T_i)$ by the Kelvin–Helmholtz equation $p_s(T_i, r_i) = p_s(T_i)\exp(2\sigma_i/\rho_i R_v T_i r_i)$.

There are several noteworthy features about the entropy production rate equation. Excluding for the moment the term involving nucleation, it is evident that the creation of entropy is associated with the three interphase exchange processes of mass, heat and momentum transfer. This conclusion is not, of course, new but it is the first time in which an equation has been derived whereby the three contributions appear as three clearly identifiable, separate terms. Equation [63] follows directly from the basic mathematical model and there are *no* approximations *en route*. That such a formulation is possible hinges on the precise definitions of $q_i$ and $\mathbf{f}_i$ and the correct inclusion of the surface energy and entropy terms.

The term representing the entropy generation rate due to nucleation is notable because it is always negative and hence appears to contradict the second law of thermodynamics. It will be recalled, however, that in classical nucleation theory, the initial growth of a liquid cluster to the critical radius (at constant temperature) is associated with a work *input* of magnitude $4\pi r_i^2\sigma_i/3$. For nucleation at the rate of $J_i$ per unit mass of vapour plus liquid, this implies a dissipation or entropy production rate per unit mass of mixture of,

$$\frac{\omega}{R_v} = -(1-g)\left[\frac{4\pi r_i^2\sigma_i J_i}{3R_v T}\right]. \qquad [65]$$

The result from classical nucleation theory is therefore in exact agreement with [63].

## LINEAR IRREVERSIBLE THERMODYNAMICS

It is instructive to apply the formalism of linear irreversible thermodynamics to a gas–droplet multiphase flow. Linearizing [64] and omitting the nucleation term gives,

$$\frac{\omega}{R_v} = (1-g)\sum\left\{\frac{n_i q_i}{R_v T_i}\left[\frac{T-T_i}{T}\right] + n_i\dot{m}_i\left[\frac{p_v - p_s(T_i, r_i)}{p_v}\right] + \frac{n_i\mathbf{f}_i\cdot(\mathbf{u}-\mathbf{u}_i)}{R_v T}\right\}, \qquad [66]$$

Adopting the terminology of irreversible thermodynamics, [66] allows the identification of three pairs of conjugate fluxes and thermodynamic forces which characterize the departures from equilibrium. These are: (i) a heat flux $q_i/R_v T_i$ associated with a force $(T - T_i)/T$; (ii) a mass flux $\dot{m}_i$ associated with a force $[p_v - p_s(T_i, r_i)]/p_v$; and (iii) a momentum flux $\mathbf{f}_i/\sqrt{R_v T}$ associated with a force $(\mathbf{u} - \mathbf{u}_i)/\sqrt{R_v T}$.

The condition for flow equilibrium corresponds to zero entropy production. From [66] this can only occur if, for every droplet group, $T_i = T$ (equality of temperature), $p_s(T_i, r_i) = p_v$ (equality of chemical potential) and $\mathbf{u}_i = \mathbf{u}$ (zero relative velocity). The condition for mechanical equilibrium $p_i = p + 2\sigma_i/r_i$ has been assumed throughout the analysis and hence there is no entropy production term associated with departures from this type of equilibrium.

The following shorthand notation is now adopted:

$$J_m = \dot{m}_i, \quad J_q = \frac{q_i}{R_v T_i}, \quad \mathbf{J}_u = \frac{\mathbf{f}_i}{\sqrt{R_v T}},$$
$$\Delta p = \frac{p_v - p_s(T_i, r_i)}{p_v}, \quad \Delta T = \frac{T - T_i}{T}, \quad \Delta \mathbf{u} = \frac{\mathbf{u} - \mathbf{u}_i}{\sqrt{R_v T}}. \qquad [67]$$

For convenience the subscript $i$ on the fluxes and thermodynamic forces has been dropped, it being understood that the resulting equations apply to droplets of group-$i$ with radius $r_i$.

In the theory of irreversible thermodynamics, a linear relation may exist between each flux and each thermodynamic force. It will be noted, however, that the components of the conjugate pairs $(J_m, \Delta p)$ and $(J_q, \Delta T)$ are scalar quantities, while those of the pair $(\mathbf{J}_u, \Delta \mathbf{u})$ are vectors. According to the Curie symmetry principle (de Groot & Mazur 1962) fluxes and thermodynamic forces of different tensorial character do not couple. The resulting linear dependence can therefore be represented by the three equations,

$$J_m = L_{mm} \Delta p + L_{mq} \Delta T$$
$$J_q = L_{qm} \Delta p + L_{qq} \Delta T$$
$$\mathbf{J}_u = L_{uu} \Delta \mathbf{u} \qquad [68]$$

where $L_{mm}$, $L_{mq}$, $L_{qm}$, $L_{qq}$ and $L_{uu}$ are scalar quantities known as phenomenological coefficients. Onsager's reciprocal theorem then demands the equality $L_{mq} = L_{qm}$.

The phenomenological coefficients cannot be deduced by thermodynamic reasoning alone and must be obtained from suitable models based on continuum fluid mechanics and the kinetic theory of gases. The literature on this subject is now very large and the reader is referred to Gyarmathy (1982) for an extremely comprehensive review and synthesis of the published theories. It should be appreciated, however, that most mathematical models of droplet growth have been derived rather informally and sometimes do not fit comfortably into the formal framework of [68]. Even Gyarmathy's impressive synthesis concentrates exclusively on three terms which, given the insight provided by the theory of irreversible thermodynamics, can be identified as $L_{mm}$, $L_{qq}$ and $L_{uu}$. These are, indeed, the dominating terms for many cases of quasi-steady droplet growth or evaporation particularly where an inert carrier gas is present. However, even in the simplest case of steady-state droplet growth in a stationary atmosphere of pure vapour, it is found that $\Delta p$ is effectively zero and hence that $J_m$ is controlled by the term $L_{mq} \Delta T$ irrespective of the magnitude of the coefficient $L_{mm}$. In cases of transient droplet growth, of course, the off-diagonal terms may totally dominate.

Any complete theory should therefore examine the mathematical form and physical interpretation of all the phenomenological coefficients. A start has been made in this direction by a number of publications [see, for example, Young (1991)] but more work is required before satisfactory models are available covering the very wide range of conditions experienced by droplets in multiphase fluid flowfields.

## CONCLUSIONS

The derivation of an equation set for the flow of small polydispersed spherical droplets in a pure vapour with or without an inert gas component has been described. Some difficulties of previous formulations have been resolved by the adoption of more suitable definitions of the interphase transfer terms and the analysis includes a consistent model to represent the surface energy and entropy of the liquid droplets. All these modifications are essential to obtain a correct formulation of the equation for the creation of entropy due to departures from equilibrium. The form of this equation allows an interpretation in terms of linear irreversible thermodynamics and the fluxes and thermodynamic forces of Onsager's theory are clearly identifiable. The resulting phenomenological equations give the correct form for the interphase transfer processes and show that some informally derived droplet growth models may require modification.

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## APPENDIX 1

### *Interphase Momentum Transfer*

The equation of motion of a spherical droplet in the absence of phase-change has been discussed, for example, by Maxey & Riley (1983). In most cases of practical interest, the main force acting on the droplet is due to steady-state drag. Other terms, such as the Basset and virtual mass forces, are usually small and are generally neglected. In the present analysis, the force due to the pressure gradient is included explicitly for the sake of symmetry with the gas-phase momentum equation. It gives rise to the term $\nabla p/\rho_l$ in [40].

Even in the absence of phase-change, the steady-state drag force is difficult to specify because the range of droplet radii of practical interest is very large. Thus, an expression for the drag force is often required to be valid from the continuum flow limit, through the slip and transition regimes to the other extreme of free molecule flow. Such a multi-range equation has been proposed by Gyarmathy (1982), [125], and the reader is referred to this very comprehensive publication for all details of the deviation and assumptions involved.

When phase-change is occurring simultaneously, the situation is much more complex. The approach adopted by Marble (1969), Gyarmathy (1982) and Jackson & Davidson (1983) is to assume that the momentum transferred from the gas-phase to the droplet consists of two additive contributions, one associated with the steady-state drag (written as if phase-change were absent) and the other associated with the net interphase mass transfer. Jackson & Davidson make the assumption that the net mass transferred carries the momentum associated with the velocity of the phase from which it originates (i.e. the gas-phase for net condensation and the liquid-phase for net evaporation). Gyarmathy and Marble qualify this assumption by associating the interphase mass transfer always with the liquid-phase velocity except in the case of net condensation in free molecule flow.

In practice, however, the transfer of momentum due to viscous drag and interphase mass transfer are inextricably linked and their total effect cannot be represented by a simple linear combination. That this is so, can easily be appreciated by reference to a laminar boundary layer flow over a flat plate with and without suction. In the case without suction, the surface shear stress is given, for zero pressure gradient, by the Blasius solution. The solution to the problem with suction can be found in Schlichting (1979, p. 383). In the asymptotic limit, the surface shear stress equals $-\rho v_0 u_\infty$, where $u_\infty$ is the free stream velocity and $v_0$ is the normal velocity at the surface. The solution, in this limiting case, bears no relation to the Blasius result.

Nevertheless, it is advantageous to write the separate droplet and gas-phase momentum equations unambiguously in terms of a quantity, which, although difficult to specify, is at least well-defined.

Consider, therefore, the conservation of momentum applied to a group-$i$ droplet over a time interval $\delta t$ during which its mass changes from $m_i$ to $m_i + \delta m_i$ and its velocity from $\mathbf{u}_i$ to $\mathbf{u}_i + \delta \mathbf{u}_i$. $\mathbf{f}_i'$ is defined to be the total net rate of momentum transfer from the gas-phase to the droplet, measured in a co-ordinate frame moving at an arbitrary velocity $\tilde{\mathbf{u}}_i$. In the absence of phase-change, $\mathbf{f}_i'$ is independent of the frame of reference but for simultaneous net phase-change its form may need to be adjusted depending on the choice of $\tilde{\mathbf{u}}_i$. The conservation of momentum is expressed by,

$$(m_i + \delta m_i)(\mathbf{u}_i + \delta \mathbf{u}_i) - m_i \mathbf{u}_i = \mathbf{f}_i' \delta t + \delta m_i \tilde{\mathbf{u}}_i, \qquad [A1]$$

which, in the limit as $\delta t$ tends to zero, becomes,

$$m_i \frac{\mathrm{D}\mathbf{u}_i}{\mathrm{D}t_i} = \mathbf{f}_i' + \dot{m}_i(\tilde{\mathbf{u}}_i - \mathbf{u}_i) \qquad [A2]$$

Defining $\mathbf{f}_i = \mathbf{f}_i' + m_i \nabla p/\rho_i$ (where the final term represents the negative of the force on the droplet due to the imposed pressure gradient) gives the result,

$$m_i\left(\frac{\mathrm{D}\mathbf{u}_i}{\mathrm{D}t_i} + \frac{\nabla p}{\rho_i}\right) = \mathbf{f}_i + \dot{m}_i(\tilde{\mathbf{u}}_i - \mathbf{u}_i). \qquad [A3]$$

It is shown in the paper that a judicious choice for $\tilde{\mathbf{u}}_i$ is $\tilde{\mathbf{u}}_i = (\mathbf{u} + \mathbf{u}_i)/2$.

For free molecule drag with simultaneous phase-change, an expression for $\mathbf{f}_i$ can be derived from the kinetic theory of gases and is limited only by the difficulty of specifying the various accomodation coefficients (Brock 1964). The specification of $\mathbf{f}_i$ for continuum flow is more difficult and must await the publication of the analysis of flow around a sphere with suction and blowing. Often, however, condensation and evaporation rates are so low that $\mathbf{f}_i$ can be approximated by the conventional viscous drag force without incurring severe penalties.

## APPENDIX 2

### *Interphase Energy Transfer*

The derivation of the energy equation for a droplet requires careful attention to detail. During a time interval $\delta t$, the increase in energy of the droplet is,

$$(m_i + \delta m_i)\left[\left(e_i + \frac{u_i^2}{2}\right) + \delta\left(e_i + \frac{u_i^2}{2}\right)\right] - m_i\left(e_i + \frac{u_i^2}{2}\right), \qquad [B1]$$

where $e_i$ is the energy per unit mass of the droplet *including the contribution from the surface energy*. From [A2], the work done *on* the droplet by the momentum transfer from the gas-phase in time $\delta t$ is,

$$\mathbf{u}_i \cdot [\mathbf{f}_i' \, \delta t + \delta m_i(\tilde{\mathbf{u}}_i - \mathbf{u}_i)] = m_i \delta(u_i^2/2), \qquad [B2]$$

and the work done *on* the droplet by the gas-phase due to the change in droplet volume is,

$$-p\delta(m_i/\rho_i) = -m_i\delta(p/\rho_i) - (p/\rho_i)\delta m_i + (m_i/\rho_i)\delta p. \qquad [B3]$$

$\delta E$ is now *defined* as the remaining energy transfer from the gas-phase to the droplet in time $\delta t$ in a co-ordinate system translating with the droplet. This is a well-specified quantity which, in principle at least, can be evaluated by the methods of kinetic theory. $\delta E$ is represented as the sum of a convective vapour enthalpy flux *defined* by $h_v(T, p_v)\delta m_i$ ($h_v = e_v + p_v/\rho_v$) and a heat flux $q_i \delta t$,

$$\delta E = h_v(p_v, T)\delta m_i + q_i \delta t. \qquad [B4]$$

[B4] *defines* $q_i$ as the heat transfer rate from the gas-phase to the droplet. Being non-condensible, the inert gas, if present, makes no contribution to the convective term but it can have a strong effect on $q_i$. In the absolute co-ordinate system, the total energy transfer *to* the droplet from the gas-phase in time $\delta t$ is therefore,

$$[h_v(p_v, T) + u_i^2/2]\delta m_i + q_i \delta t. \qquad [B5]$$

Combining the expressions [B1]–[B3] and [B5] results in an equation representing the conservation of energy for the droplet,

$$m_i(\delta h_i - \delta p/\rho_i) = (h_v - h_i)\delta m_i + q_i \delta t, \qquad [B6]$$

where $h_i = e_i + p/\rho_i$. Note that all the kinetic energy terms cancel, a result which is in keeping with the physical principle that a change in droplet velocity can only be effected by a transfer of kinetic energy and not by an exchange of thermal energy. Dividing by $\delta t$ and taking the limit $\delta t \to 0$ gives the energy equation for a group-$i$ droplet,

$$m_i\left[\frac{Dh_i}{Dt_i} - \frac{1}{\rho_i}\frac{Dp}{Dt_i}\right] = \dot{m}_i(h_v - h_i) + q_i. \qquad [B7]$$

The specification of the interphase heat transfer rate $q_i$ is discussed at length by Gyarmathy (1982). For small relative velocity, $q_i$ is dominated by conduction heat transfer through the gas-phase surrounding the droplet. At higher relative velocities, however, the heat transfer coefficient is dependent on the relative Reynolds number. The Knudsen number also has an important influence. A multi-range expression for $q_i$ has been proposed by Gyarmathy (1982), [123], and the reader is referred to this publication for further details.

## APPENDIX 3

### *Simplification of [62]*

First consider the coefficient of $n_i \dot{m}_i$ in [62]. By the substitution of [18]–[20] and [24], this can be written,

$$\left[\frac{(h_v - h_i)}{T_i} - (s_v - s_i) + \frac{\sigma_i}{\rho_i r_i T_i}\right] = \frac{(h_v - h_{bi})}{T_i} - (s_v - s_{bi}), \qquad [C1]$$

where $h_{bi} = e_{bi} + p_i/\rho_i$ is the specific enthalpy and $s_{bi}$ is the specific entropy of the bulk liquid. Both these quantities are evaluated at droplet temperature $T_i$ and droplet internal pressure $p_i = p + 2\sigma_i/r_i$. Further simplification results from the expansion,

$$(h_v - h_{bi}) - T_i(s_v - s_{bi}) = [h_v(T, p_v) - h_v(T_i, p_v)] - T_i[s_v(T, p_v) - s_v(T_i, p_v)] + [\mu_v(T_i, p_v) - \mu_i(T_i, p_i)], \qquad [C2]$$

where $\mu_v(T_i, p_v) = h_v(T_i, p_v) - T_i s_v(T_i, p_v)$ is the chemical potential of the vapour component at temperature $T_i$ and partial pressure $p_v$ and $\mu_i(T_i, p_i) = h_{bi}(T_i, p_i) - T_i s_{bi}(T_i, p_i)$ is the chemical potential of the liquid at temperature $T_i$ and internal pressure $p_i$. According to the Kelvin–Helmholtz relation, a droplet of radius $r_i$ and temperature $T_i$ would be in equilibrium with vapour at temperature $T_i$ and pressure $p_e = p_s(T_i, r_i) = p_s(T_i)\exp(2\sigma_i/\rho_i R_v T_i r_i)$, where $p_s(T_i)$ is the saturated vapour pressure at temperature $T_i$. Hence, $\mu_i(T_i, p_i) = \mu_v(T_i, p_e)$. Assuming the vapour to behave as a perfect gas, [C2] can therefore be written,

$$(h_v - h_{bi}) - T_i(s_v - s_{bi}) = c_{pv}(T - T_i) - c_{pv} T_i \log_e\left(\frac{T}{T_i}\right) + R_v T_i \log_e\left(\frac{p_v}{p_s(T_i, r_i)}\right). \qquad [C3]$$

With only second order error, the first two terms on the right hand side cancel and hence,

$$\left[\frac{(h_v - h_i)}{T_i} - (s_v - s_i) + \frac{\sigma_i}{\rho_i r_i T_i}\right] \approx R_v \log_e\left(\frac{p_v}{p_s(T_i, r_i)}\right). \qquad [C4]$$

Now consider the coefficient of $J_i$ in [62]. According to isothermal classical nucleation theory, droplets of critical radii are nucleated at a temperature equal to that of the gas-phase, i.e. $T_i = T$. Using [18]–[20] and [24] as before,

$$m_i\left[\frac{(h_v - h_i)}{T} - (s_v - s_i)\right] = m_i\left[\frac{(h_v - h_{bi})}{T} - (s_v - s_{bi}) - \frac{\sigma_i}{\rho_i r_i T}\right]. \qquad [C5]$$

For a droplet of critical radius, $\mu_v(T, p_v) = \mu_i(T, p_i)$ and hence $h_v - Ts_v = h_{bi} - Ts_{bi}$. Thus,

$$m_i\left[\frac{(h_v - h_i)}{T} - (s_v - s_i)\right] = -\frac{4\pi r_i^2 \sigma_i}{3T}. \qquad [C6]$$