Mass budget of a fluid mixture[1]: a quick refresher

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Density, concentration and velocity

Let $\delta\Omega$ represent an elemental control domain. According to the continuous media approach, $\delta\Omega$ is to be "infinitely small" from the macroscopic vantage point, and "infinitely large" from the microscopic one. Thus, in the macroscopic model developed hereinafter, the value of the volume of $\delta\Omega$, δV (m^3), is considered arbitrarily small ($\delta V \to 0$) and all variables associated with this control volume can be viewed as pointwise variables.

The abovementioned elemental control volume contains $N+1$ constituents, which are identified by integer subscript n. The latter ranges from 0 (pure water, i.e. $\mathrm{H_2O}$) to N. At time t, the mass of the n-th constituent contained in the elemental domain is $\rho_n(t,\mathbf{x})\delta V$, where $\mathbf{x}=(x,y,z)$ is the position vector and $\rho_n(t,\mathbf{x})$ ($\mathrm{kg\,m^{-3}}$) is the density of the constituent under consideration. At time t and location $\mathbf{x}$, the density of the fluid mixture obviously is

$$\rho(t,\mathbf{x}) = \sum_{n=0}^{N} \rho_n(t,\mathbf{x}) \quad . \tag{1}$$

The associated concentrations, defined as mass fractions, are the following dimensionless variables

$$C_n(t,\mathbf{x}) = \frac{\rho_n(t,\mathbf{x})}{\rho(t,\mathbf{x})} \quad . \tag{2}$$

It is readily seen that the concentrations satisfy

$$0 \le C_n(t,\mathbf{x}) \le 1 \tag{3}$$

and

$$\sum_{n=0}^{N} C_n(t,\mathbf{x}) = 1 \quad . \tag{4}$$

Concentrations may be defined in many ways. In any case, they should be introduced with great care: failing to do so may lead to misconceptions. Transforming one type of concentration into another is no insuperable task. However, to every type of concentration corresponds a specific formulation of the reactive transport equation (e.g. de Groot and Mazur, 1962[2]).

In elemental control domain $\delta\Omega$, the macroscopic velocity $\mathbf{v}_n(t,\mathbf{x})$ of the n-th constituent is defined as the arithmetic mean of the velocities of the molecules of this constituent that are present in $\delta\Omega$. Then, the macroscopic velocity of the fluid mixture, $\mathbf{v}(t,\mathbf{x})$, is defined as the mass-weighted average of the velocities of all the constituents,

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[1] This working note is inspired by the following book: **de Groot S.R. and P. Mazur, 1962, *Non-Equilibrium Thermodynamics*, North-Holland, Amsterdam, 510 pages** (it is still possible to purchase a copy of this treatise from http://store.doverpublications.com/0486647412.html)

[2] Ibid.

$$\mathbf{v}(t,\mathbf{x}) = \frac{\sum_{n=0}^{N} \big(\rho_n(t,\mathbf{x})\delta V\big)\mathbf{v}_n(t,\mathbf{x})}{\sum_{n=0}^{N} \rho_n(t,\mathbf{x})\delta V} \quad , \tag{5}$$

which eventually leads to

$$\boxed{\mathbf{v} = \frac{1}{\rho}\sum_{n=0}^{N} \rho_n \mathbf{v}_n = \sum_{n=0}^{N} C_n \mathbf{v}_n} \tag{6}$$

This velocity may be seen to be equal to that of the centre of mass of all the molecules contained in the elemental control domain, which is why it is usually referred to as the barycentric velocity.

Mass budget of a constituent

Classical mass budget considerations lead to the following equation

$$\frac{\partial \rho_n}{\partial t} = \rho\theta_n - \nabla \bullet (\rho_n \mathbf{v}_n) \quad , \tag{7}$$

where θ_n is the relevant reaction rate (s^{-1})[3]. According to the law of mass conservation usually attributed to Antoine-Laurent de Lavoisier (*nothing is lost, nothing is created, everything is transformed*), the reaction rates satisfy the following constraint

$$\sum_{n=0}^{N} \theta_n(t,\mathbf{x}) = 0 \quad . \tag{8}$$

Mass flux $\rho_n \mathbf{v}_n$ may be transformed to

$$\rho_n \mathbf{v}_n = \rho_n \mathbf{v} + \rho_n(\mathbf{v}_n - \mathbf{v}) \quad , \tag{9}$$

where $\rho_n \mathbf{v}$ is the resolved mass flux associated with macroscopic-scale processes (referred to as advective flux) and

$$\mathbf{q}_n = \rho_n(\mathbf{v}_n - \mathbf{v}) \tag{10}$$

is the macroscopic-scale flux due to unresolved, microscopic-scale phenomena. Fluxes $\mathbf{q}_n$ satisfy the following constraint

$$\sum_{n=0}^{N} \mathbf{q}_n = \underbrace{\sum_{n=0}^{N} \rho_n \mathbf{v}_n}_{=\rho\mathbf{v},\ \text{see (6)}} - \underbrace{\sum_{n=0}^{N} \rho_n \mathbf{v}}_{=\rho\mathbf{v},\ \text{see (1)}} = \rho\mathbf{v} - \rho\mathbf{v} = 0 \quad . \tag{11}$$

Substituting (9)-(10) into (7) allows rewriting (7) as follows:

$$\frac{\partial \rho_n}{\partial t} = \rho\theta_n - \nabla \bullet (\rho_n \mathbf{v} + \mathbf{q}_n) \tag{12}$$

or, equivalently,

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[3] For instance, the reaction rate of a radioative tracer reads $\theta_n = -C_n / \tau_n$, where positive constant τ_n denotes its mean life. The corresponding half-life is $(\log 2)\tau_n \approx 0.7\,\tau_n$.

$$\frac{\partial}{\partial t}(\rho C_n) = \rho\theta_n - \nabla\bullet(\rho C_n \mathbf{v} + \mathbf{q}_n) \tag{13}$$

This equation is also called “reactive transport equation”, for it takes into account the impact of reactions, whaver their very nature, and transport phenomena — at the macroscopic and microscopic scales.

Continuity equation

Taking the sum of (13) over all the constituents leads to

$$\frac{\partial}{\partial t}(\rho \underbrace{\sum_{n=0}^{N} C_n}_{\substack{=1 \\ \text{see (4)}}}) = \rho \underbrace{\sum_{n=0}^{N} \theta_n}_{\substack{=0 \\ \text{see (8)}}} - \nabla\bullet(\rho \underbrace{\sum_{n=0}^{N} C_n}_{\substack{=1 \\ \text{see (4)}}} \mathbf{v} + \underbrace{\sum_{n=0}^{N} \mathbf{q}_n}_{\substack{=0 \\ \text{see (11)}}}) \ , \tag{14}$$

which simplifies to continuity equation

$$\frac{\partial\rho}{\partial t} = -\nabla\bullet(\rho\mathbf{v}) \tag{15}$$

This mass conservation equation of the whole fluid mixture has the same form as the continuity equation of a single-constituent fluid. This is due to the definitions introduced above for the density, concentration and velocity.

Fick's law, Boussinesq approximation and turbulent fluxes

In a two-constituent fluid mixture, unresolved mass fluxes are generally parameterised with the help of Fick's law, i.e.

$$\left.\begin{array}{l} \mathbf{q}_1 = -\rho\kappa\nabla C_1 \\ \mathbf{q}_2 = -\rho\kappa\nabla C_2 \end{array}\right\} \Rightarrow \ \mathbf{q}_1 + \mathbf{q}_2 = -\rho\kappa\nabla\underbrace{(C_1 + C_2)}_{=1} = 0 \ . \tag{16}$$

where $\kappa(t,\mathbf{x})$ is the appropriate molecular diffusivity ($\mathrm{m^2\,s^{-1}}$), which is positive definite. When there are more than two constituents, the relevant parameterisations may be much more intricate.

If the density of the fluid mixture exhibits small variations, then the Boussinesq approximation may be resorted to. This essentially consists in replacing the $\rho(t,\mathbf{x})$ by constant reference density $\rho_\bullet$ (which is of the order of 1,025 $\mathrm{kg\,m^{-3}}$ for seawater). In addition, relation (2) is to be simplified to $C_n(t,\mathbf{x}) \approx \rho_n(t,\mathbf{x})/\rho_\bullet$. Finally, (13) and (15) transform to

$$\frac{\partial C_n}{\partial t} = \theta_n - \nabla\bullet(C_n\mathbf{v} + \rho_\bullet^{-1}\mathbf{q}_n) \tag{17}$$

and

$$\nabla\bullet\mathbf{v} = 0 \tag{18}$$

For turbulent flows, an appropriate averaging operator must be applied to the relevant equations and variables, leading to the introduction of turbulent mass flux $\mathbf{q}_{t,n}$. Then, (17) modifies to

$$\frac{\partial C_n}{\partial t} = \theta_n - \nabla \bullet (C_n \mathbf{v} + \rho_\bullet^{-1} \mathbf{q}_n + \rho_\bullet^{-1} \mathbf{q}_{t,n}) \quad . \tag{19}$$

All of the variables in the above equations are suitably-averaged ones, but, for the sake of simplicity, the notations have not been modified. The unresolved mass flux, $\mathbf{q}_n + \mathbf{q}_{t,n}$, is usually parameterised *à la* Fourier-Fick, leading to

$$\mathbf{q}_n + \mathbf{q}_{t,n} = -\rho_\bullet \mathbf{K} \bullet \nabla C_n \quad , \tag{20}$$

where **K** denotes the diffusivity tensor, which must be symmetric and positive definite[4]. Combining (19) and (20) yields

$$\frac{\partial C_n}{\partial t} = \theta_n - \nabla \bullet (C_n \mathbf{v} - \mathbf{K} \bullet \nabla C_n) \tag{21}$$

Unsurprisingly, by taking the sum of (21) over all the constituents, one obtains the Boussinesq form of the continuity equation:

$$\overbrace{\frac{\partial}{\partial t} \underbrace{\sum_{n=0}^{N} C_n}_{=1}}^{=0} = \underbrace{\sum_{n=0}^{N} \theta_n}_{=0} - \nabla \bullet (\underbrace{\sum_{n=0}^{N} C_n}_{=1} \mathbf{v} - \overbrace{\mathbf{K} \bullet \nabla \underbrace{\sum_{n=0}^{N} C_n}_{=1}}^{=0}) \quad , \tag{22}$$

which simplifies to $\nabla \bullet \mathbf{v} = 0$.

Momentum and thermodynamic equations

The dominant constituent of seawater is, by far, pure water (H_2O). Therefore, it is believed that the momentum and thermodynamic equations may be established as if there was only one constituent. It is only when the evolution of the concentration of a given constituent is to be studied that the multi-constituent nature of the fluid under study must be taken into account explicitly.

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[4] See, e.g., http://www.climate.be/php/users/ericd/doc/TurbulenceClosure.pdf