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Interdiffusion Revisited

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Abstract. We define the volume density and basing on the Euler's and Lagrange theorems derive the volume continuity equation. These fundamental formulae define the volume fixed frame of reference in the multicomponent, solid and liquid solutions. The volume velocity is a unique frame of reference for all processes namely, the mass diffusion, charge transport, heat flow, etc. No basic changes are obligatory in the foundations of linear irreversible thermodynamics except recognizing the need to add volume density to the usual list of extensive physical properties undergoing transport in every continuum. The volume fixed frame of reference allows the use of the Navier-Lamé equation of mechanics of solids. Proposed modifications of Navier-Lamé and energy conservation equations are self-consistent with the literature for solid-phase continua dating back to the classical experiments of Kirkendall and their interpretation by Darken. We do show that when Darken constraints are used the general formulae reduce to the Darken expression.

1 Introduction

Studies of diffusion in gases and liquids were at the center of interest of scientists in the second half of the nineteenth century. In the twentieth century, diffusion in solids was a driving force for chemistry of solids. In this work we target on the self-consistent definition of the material reference frame and its use in mechano-chemistry. We focus here on the four discoveries in the 20th century that were crucial and irreversibly affected the theory of mass transport in solids:

1. The concept of mobility and Nernst-Planck flux formula,
2. Common occurrence of defects in solids (Frenkel and others),

3. The nonstoichiometry is a canon, not an exception in solids (Schottky and Wagner) and
4. The lattice sites do not have to be conserved (Kirkendall and Darken).

Very recently, basing upon conflicts noted between tracer- and mass–velocity experiments Brenner has suggested that the fluid's volume velocity (*i.e.*, material velocity or drift velocity) is the proper internal frame of reference [1,2]. The experimental data on the thermal diffusion in binary liquid mixtures [3] support the applicability of the proposed revisions. According to Öttinger [4]: "Something is missing" in the currently accepted mass, energy and entropy transport equations of nonequilibrium irreversible thermodynamics [5, 6] and he proposed incorporating fluctuations into the friction matrix appearing in GENERIC theory [4]. Klimontovich included the self-diffusion-like contribution to the collision term in Boltzmann's equation [7]. The independent theories of Öttinger and Klimontovich lead to identical results and are formally equivalent to Brenner concept of diffuse volume transport [1-3]. These foundlings imply fundamental conflict between the rational mechanics and irreversible thermodynamics concerning the specific momentum density. The proper definition of the material velocity is an open question [1] despite the previous arguments [8].

In all our studies of mass transport we entirely based on the Darken concept [9] and its generalization [10], *i.e.*, we based on the volume fixed reference frame for diffusion. First attempt to combine diffusion and stress based on the Euler's view that was formulated ~250 years ago. Namely, we accepted the velocity of the local mass centre, υ^m, as an internal frame of reference for stress field [11]. The introduction of the partial Cauchy stress tensor [12] was unsuccessful in practical applications due to the unsolved conflict between the two different reference frames. In all papers concerned with mathematical description of mechano-chemical transport process (*e.g.*, the interdiffusion under the stress field) we were not able to avoid the same conflict. Nevertheless, in these works we have generalized and consequently used the volume fixed reference frame to describe the diffusion in multicomponent alloys and solid solutions, including the compressible one. We also postulated the constitutive formula for the mechanical potential in multicomponent systems that is self-consistent with thermodynamical description [13].

Expression $\rho\upsilon^m$ in the momentum flux was formulated by Euler 250 years ago [14]. It originates from the assumption that Newton's laws of motion for solid body are also valid in a case of material domain of known mass density ρ moving within a continuum. Euler was obviously unaware of the diffusion and hidden constitutive assumption implicit in the relation $\rho\upsilon^m$. Since then this relation was questioned only in a very few circumstances [15, 16]. The definitions of the overall velocities: the local mass centre velocity υ^m, local concentration velocity υ^M, and local volume velocity υ, differ from each other and the selection of the proper reference frame for all internal processes (thermodynamics) is crucial.

Following Darken, Brenner and Öttinger's theories we recently postulated that the volume velocity defines the local material velocity at nonequilibrium [17]. It allowed fixing the unique frame of reference for all internal transport processes, thermodynamics in general. No basic changes are required in the foundations of linear irreversible thermodynamics except recognizing the need to add volume density to the usual list of extensive physical properties undergoing transport in every continuum.

Using the Euler's and Lagrange theorems we present here: 1) the rigorous derivation of the volume continuity equation, 2) the consistency of the Newton laws with thermodynamics in the volume fixed reference frame and 3) the equivalence of presented and Darken methods when Darken restriction are introduced.

2 The Volume Continuity, Conservation of Mass, Momentum and Energy

We will consider a motion of a single phase *r*-component mixture, *e.g.*, solid solution. We define the velocity field of the *i*-th component, $\upsilon_i : [\,0\,,\,\infty\,) \times \mathrm{R}^3 \nrightarrow \mathrm{R}^3$, and its density of mass, $\rho_i : [\,0\,,\,\infty\,) \times \mathrm{R}^3 \nrightarrow \mathrm{R}$. The notation $X \nrightarrow Y$ means that the domain of a function is a subset of X. Let Σ denote any subregion of the mixture and for any time $t \geq 0$, let $\Sigma(t)$ to be the set of the points of that belonged to Σ at the moment $t = 0$. Thus, $\Sigma = \Sigma(0)$. The theory must fulfill the following conditions:

1. The local acceleration of the mixture depends on its mass, not on its internal energy.
2. The local centre of mass position cannot be affected by any diffusion process (mass diffusion, heat transport, internal friction etc.).
3. The volume velocity (*i.e.*, the material velocity) is a unique internal frame of reference for all processes: diffusion [9,10], deformation, viscosity, heat transport etc. [1].
4. The nonbalanced diffusion fluxes affect the local volume velocity [9].

The Liouville transport theorem will be applied to obtain the volume continuity equation and the Darken drift velocity. It will be used to derive all conservation laws in a general case of a compressible, multicomponent mixture showing the different partial molar volumes. Transport theorem generalizes the Gauss-Ostrogradzki theorem and allows compressing the mathematics.

Theorem. If $\upsilon_i : [\,0\,,\,\infty\,) \times \mathrm{R}^3 \nrightarrow \mathrm{R}^3$ *and* $\rho_i : [\,0\,,\,\infty\,) \times \mathrm{R}^3 \nrightarrow \mathrm{R}^3$ are a sufficiently smooth functions defined on the domain of υ_i, then

$$\frac{\mathrm{d}}{\mathrm{d}t} \int_{\Sigma(t)} \rho_i \upsilon_i \, \mathrm{d}x = \int_{\Sigma(t)} \left(\upsilon_i \left(\frac{\partial \rho_i}{\partial t} + \operatorname{div}\left(\rho_i \upsilon_i\right) \right) + \rho_i \left(\frac{\partial \upsilon_i}{\partial t} + \upsilon_i \cdot \operatorname{grad} \upsilon_i \right) \right) \mathrm{d}x . \tag{1}$$

The proof of the above theorem can be found elsewhere [18].

2.1 Extensive and intensive variables

We consider the mass density, $\rho_i = \rho_i(t,x)$, the molar concentration, $c_i = c_i(t,x)$ and the molar ratio, $N_i = N_i(t,x)$ of every mixture component. The mass density, $\rho = \rho(t,x)$, the molar concentration, $c = c(t,x)$, the molar volume, $\Omega = \Omega(t,x)$, and the molar mass, $M = M(t,x)$, of the mixture are given by:

$$\rho := \sum_{i=1}^{r} \rho_i \tag{2}$$

$$c := \sum_{i=1}^{r} c_i \equiv \frac{1}{\Omega} \equiv \frac{\rho}{M} \equiv \sum_{i=1}^{r} \frac{\rho_i}{M_i} \tag{3}$$

$$N_i := c_i / c \tag{4}$$

where M_i denotes the molar mass of the *i*-th component. Volume occupied by the mixture at given temperature and pressure, Ω^*, is an extensive variable [19]. If we write:

$$\Omega = \Omega\left(N_1, \ldots, N_r; T, p\right) \tag{5}$$

as the equation of state of the system giving the molar volume in terms of independent variables: $N_1, \ldots, N_r$ and T, p, we have then for an arbitrary volume Ω^* and number of moles $n_1, \ldots, n_r$

$$\Omega^*\left(kn_1,...,kn_r;T,p\right) = k\Omega^*\left(n_1,...,n_r;T,p\right) \tag{6}$$

which express the fact that the system at a temperature T, pressure p, and containing $kn_1, \ldots, kn_r$ moles of components occupies a volume $k\Omega^*$. This relation is identically satisfied whatever may be the values of $T, p, n_1, \ldots, n_r$ and k, *i.e.*, the factor k multiplies the extensive variables $n_1, \ldots, n_r$ and functions Ω^* and Ω are homogeneous of the first degree with respect to composition, *e.g.*, the number of moles: $n_1, \ldots, n_r$. Thus, the Euler's theorem can be applied in further analysis.[1] This theorem states that the function $f(x_1, \ldots, x_r, \ldots)$ is called homogeneous of the m-th degree in the variables $x_1,\ldots,x_r$ if the identity: $f\left(kx_1, \ldots ,kx_r; \ldots\right) \equiv k^m f\left(x_1, \ldots , x_r; \ldots\right)$ holds [19]. If we differentiate this definition with respect to k the next identity follows

$$\sum_{i=1}^{r} x_i \frac{\partial f\left(kx_1,...,kx_r;...\right)}{\partial kx_i} \equiv mk^{m-1} f\left(x_1,...,x_r;...\right) \tag{7}$$

$$\sum_{i=1}^{r} x_i \frac{\partial f\left(x_1,...,x_r;...\right)}{\partial x_i} \equiv m f\left(x_1,...,x_r;...\right) \quad \text{when} \quad k=1. \tag{8}$$

Eqn. (8) is called Euler's theorem. From the theory of partial differential equations it follows that conversely any function $f(x_1,\ldots, x_r; \ldots)$ which satisfies eqn. (8) is homogeneous of the m-th degree in $x_1, \ldots, x_r$ [20]. In what follows we are concerned with:

i) homogeneous functions of the first degree, $m = 1$. In such a case

$$f\left(kx_1,...,kx_r;...\right) \equiv k f\left(x_1,...,x_r;...\right) \tag{9}$$

and eqn. (8) becomes:

$$\sum_{i=1}^{r} x_i \frac{\partial f\left(x_1,...,x_r;...\right)}{\partial x_i} \equiv f\left(x_1,...,x_r;...\right) \tag{10}$$

ii) homogeneous functions of the zero degree, $m = 0$. In such a case

$$f\left(kx_1,..,kx_r;...\right) \equiv f\left(x_1,...,x_r;...\right) \tag{11}$$

and eqn. (8) becomes:

$$\sum_{i=1}^{r} x_i \frac{\partial f\left(x_1,...,x_r;...\right)}{\partial x_i} \equiv 0 \tag{12}$$

Comparing eqns. (5), (6) and (9) we see that Ω and Ω^* are homogeneous functions of the first degree in the independent variables $N_1,\ldots, N_r$. Consequently, from eqn. (10) it follows:

$$\sum_{i=1}^{r} N_i \frac{\partial \Omega\left(N_1,...,N_r;T,p\right)}{\partial N_i} \equiv \Omega\left(N_1,...,N_r;T,p\right). \tag{13}$$

Differentiating above identity with respect to N_j at constant T and p we have:

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[1] In what follows we do neglect the dimensions of the body and surface energy, *e.g.*, interfaces, grain boundaries, etc.

$$\sum_{i=1}^{r} N_i \frac{\partial\Omega}{\partial N_i \partial N_j} + \frac{\partial\Omega}{\partial N_j} \equiv \frac{\partial\Omega}{\partial N_j}, \tag{14}$$

whence

$$\sum_{j=1}^{r} N_i \frac{\partial^2\Omega}{\partial N_i \partial N_j} \equiv 0. \tag{15}$$

Upon introducing the usual definition of the partial molar volume Ω_i:

$$\Omega_i = \Omega_i\left(T,p\right) := \frac{\partial\Omega\left(N_1,...,N_r;T,p\right)}{\partial N_i} \tag{16}$$

eqn. (13) can be written in usual, concise form

$$\Omega \equiv \sum_{i=1}^{r} \Omega_i N_i, \tag{17}$$

which gives the relation between the molar volume of the mixture and partial molar volumes of the components. Relation between partial molar volumes, eqn. (15), upon combining with eqn. (16) becomes:

$$\sum_{i=1}^{r} N_i \frac{\partial\Omega_i}{\partial N_j} \equiv 0. \tag{18}$$

From the above identity it follows that partial molar volumes depend on each other. For binary system at constant temperature and pressure one gets:

$$N_1 \frac{\partial\Omega_1}{\partial N_1} + N_2 \frac{\partial\Omega_2}{\partial N_1} \equiv 0 \tag{19}$$

Upon comparing eqns. (12) and (18) it is obvious that partial molar volumes are homogeneous functions of the zero degree ($m = 0$) and

$$\Omega_i\left(kn_1,...,kn_r;T,p\right) = \Omega_i\left(n_1,...,n_r;T,p\right) \quad \text{for all } i \tag{20}$$

Thus, the partial molar volumes are intensive variables and can be expressed as functions of the other intensive variables, *e.g.*, T, p, N_1, … ,N_r

The overwhelming majority of authors dealing with interdiffusion in solids simplifies the problem and assumes constant and/or equal partial molar volumes. In general case it is obvious that volume is not conserved. From definition (3) and identity (17) the following identities hold:

$$\sum_{i=1}^{r} \frac{\Omega_i}{\Omega} N_i \equiv \sum_{i=1}^{r} \frac{\Omega_i c_i}{\Omega c} \equiv \sum_{i=1}^{r} \Omega_i c_i \equiv \sum_{i=1}^{r} \rho_i^V \equiv 1 \tag{21}$$

the variable $\Omega_i c_i = \rho_i^V$ is the volume density of the i-th component. Thus, we have shown that the volume density of the arbitrary multicomponent mixture is conserved and equals one[2], eqn. (21). The fluxes and velocities of the local centre of mass, υ^m, composition, υ^M and volume, υ, are defined by respective densities:

$$\rho\upsilon^m = \sum_{i=1}^{r} J_i^m = \sum_{i=1}^{r} \rho_i \upsilon_i \quad \text{and} \quad \upsilon^m := \sum_{i=1}^{r} \frac{\rho_i}{\rho} \upsilon_i, \tag{22}$$

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[2] Unless we consider/allow the formation of the cracks and/or voids.

$$c\upsilon^M = \sum_{i=1}^{r} J_i^M = \sum_{i=1}^{r} c_i \upsilon_i \quad \text{and} \quad \upsilon^M := \sum_{i=1}^{r} \frac{c_i}{c} \upsilon_i \,, \tag{23}$$

$$\Omega c \upsilon = \sum_{i=1}^{r} J_i^V = \sum_{i=1}^{r} \Omega_i c_i \upsilon_i \quad \text{and} \quad \upsilon := \sum_{i=1}^{r} \frac{\Omega_i c_i}{\Omega c} \upsilon_i \,, \tag{24}$$

where Ωc and $\Omega_i c_i$ denote the total $(\Omega c \equiv 1)$ and partial volume densities, compare eqns. (20) and (21).
Above velocities differ from each other and the local mass centre velocity given by eqn. (22), υ^m, must be reconsidered as an adequate description of the local momentum flux [1], *e.g.*, compare the expressions $\rho\upsilon^m$ vs. $\rho\upsilon^M$ and $\rho\upsilon$. We will show that only the volume velocity, eqn. (24), can serve as a unique reference frame for all internal processes (thermodynamics), *e.g.*, the mass diffusion processes, heat transport, deformation etc.

2.2 Diffusion

The diffusion velocity of every component can be expressed by an appropriate formula, *e.g.*, by the Nernst-Planck equation [21, 22], 1st Fick law [23], Onsager flux [24] or the mechano-chemical flux [13]:

$$\upsilon_i^d = -B_i \operatorname{grad}\left(\mu_i^{ch} + \mu_i^{el}\right) \quad \text{where} \quad \mu_i^{el} = z_i \mathrm{F} V \,, \tag{25}$$

$$\upsilon_i^d = -D_i \operatorname{grad} \ln c_i \,, \tag{26}$$

$$\upsilon_i^d = \frac{1}{c_i} \sum_{j=1}^{k} L_{ij} X_j \,, \tag{27}$$

$$\upsilon_i^d = -B_i \operatorname{grad}\left(\mu_i^{ch} + \frac{\Omega_i^0}{\Omega^0} \Omega p\right) = -B_i \operatorname{grad}\left(\mu_i^{ch} + \mu_i^m\right) \quad \text{where} \quad \sum_{i=1}^{r} c_i \mu_i^m = p \,, \tag{28}$$

where B_i, D_i, z_i denote mobility, diffusivity and valence of the *i*-th component, respectively. F and *V* are the Faraday constant and electric potential. $\Omega = \Omega(t,x)$ is the molar volume of the mixture, Ω^0 and Ω_i^0 denote molar volumes of the mixture and of the i-th component at standard conditions.[3] In what follows we use the mechano-chemical flux formula, eqn. (28).
The local drift velocity in the mixture, υ^{drift}, is a result of the deformation, υ^{σ}, of the Darken drift due to diffusion, υ^D and translation, υ^{tr}

$$\upsilon^{\text{drift}} = \upsilon^{\sigma} + \upsilon^D + \upsilon^{tr} \,. \tag{29}$$

The Darken's drift, υ^D, denotes the local common velocity generated within a mixture by nonbalanced diffusion fluxes: $\sum_{i=1}^{r} J_i^d \neq 0$, [9,10]. In what follows all velocities denote the volume velocity.

2.3 Volume Continuity Equation and Darken Drift

In nonreversible thermodynamics the molar volumes are intensive parameters and are not conserved, Eqs. (5) and (20). However, these properties are transported by the velocity field of every mixture component. Contrary, the molar volume density of the mixture equals one is conserved during an arbitrary transport process in continuum, eqn. (21). From eqn. (21) it follows:

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[3] The standard molar volumes of the mixture can be given by an appropriate constitutive equation, *e.g.*, by Vegard's law: $\Omega^0 := \sum_{i=1}^{r} N_i \Omega_i^0$

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_{\Sigma(t)}\sum_{i=1}^{r}c_i\Omega_i\,\mathrm{d}x=\frac{\mathrm{d}}{\mathrm{d}t}\int_{\Sigma(t)}c\Omega\,\mathrm{d}x=0\,. \tag{30}$$

Unfortunately, eqn. (30) is irrelevant to transport process. One need to know the time evolution of the volume velocity in order to separate the all internal processes from the momentum of the mixture itself and to define the unique internal reference frame for all local transport processes [1]. The partial molar volumes as well as partial volume densities are non-conservative properties and evolution of the partial volume density, $\rho_i^V=c_i\Omega_i$, occurs during the transport, eqn. (24). Only the total volume density must be conserved[4], eqns. (3) and (30). The partial molar volume density is defined on the domain of υ_i. Consequently, from the Liouville transport theorem, eqn. (1), and relation (30) it follows:

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_{\Sigma(t)}\sum_{i=1}^{r}c_i\Omega_i\,\mathrm{d}x=\int_{\Sigma(t)}\left(\sum_{i=1}^{r}\frac{\partial c_i\Omega_i}{\partial t}+\operatorname{div}\left(\sum_{i=1}^{r}c_i\Omega_i\upsilon_i\right)\right)\mathrm{d}x=0\,. \tag{31}$$

Combining eqns. (21) and (31) and since the subregion $\Sigma(t)$ was chosen arbitrarily, then:

$$\operatorname{div}\left(\sum_{i=1}^{r}c_i\Omega_i\upsilon_i\right)=0\,. \tag{32}$$

Above relation can be called the volume continuity equation or the law of conservation of the molar volume density, $c\Omega$.

Eqn. (32) allows analyzing an arbitrary transport process in the multicomponent mixture. Let us consider the diffusion process in compressible multicomponent mixture: $c_i\Omega_i\upsilon_i=c_i\Omega_i\upsilon_i^d$, for i =1, 2,…, r. Kirkendall experimentally [25], Darken theoretically in binary alloy [9] and one of the authors in multicomponent solid mixtures [10] have shown that the local sum of diffusion fluxes has not to be zero or constant, $\operatorname{div}\left(\sum_{i=1}^{r}c_i\Omega_i\upsilon_i^d\right)\neq 0$ *i.e.*, the law of conservation of lattice sites does not exist [9]. Thus, the volume continuity implies that the "new" average velocity, Darken velocity, υ^D, has to be generated during, such "pure" diffusion process and from eqn. (32) it follows:

$$\begin{gathered}\operatorname{div}\left(\sum_{i=1}^{r}c_i\Omega_i\upsilon^D+\sum_{i=1}^{r}c_i\Omega_i\upsilon_i^d\right)=\operatorname{div}\left(c\Omega\upsilon^D+\sum_{i=1}^{r}c_i\Omega_i\upsilon_i^d\right)\Rightarrow\\ \upsilon^D(t,x)=-\sum_{i=1}^{r}\frac{c_i\Omega_i}{c\Omega}\upsilon_i^d+\upsilon^{tr}(t)=-\sum_{i=1}^{r}c_i\Omega_i\upsilon_i^d+\upsilon^{tr}(t)\end{gathered} \tag{33}$$

the Darken drift velocity, υ^D, is a volume average velocity generated by diffusion and $\upsilon^{tr}(t)$ is the translation velocity. In the same manner we will define the local diffusion velocity of the mixture, υ^d, as volume velocity of the diffusion:

$$c\Omega\upsilon^d=\sum_{i=1}^{r}c_i\Omega_i\upsilon_i^d=\upsilon^d\,. \tag{34}$$

Using eqns. (24) and (34) allows adding the fluxes of the all mixture components[5]

$$\upsilon=\sum_{i=1}^{r}\frac{\Omega_ic_i}{\Omega c}\left(\upsilon^D+\upsilon^\sigma+\upsilon^{tr}+\upsilon_i^d\right)=\upsilon^D+\upsilon^\sigma+\upsilon^{tr}+\sum_{i=1}^{r}\frac{\Omega_ic_i}{\Omega c}\upsilon_i^d=\upsilon^D+\upsilon^\sigma+\upsilon^{tr}+\upsilon^d\,. \tag{35}$$

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[4] Unless voids and/or cracks are formed.

[5] In this work we do consider the deformation, translation and Darken velocities. Their sum results in the drift velocity in the mixture. Incorporation velocity due to the thermal expansion, etc. does not affect the formalism.

Eqn. (35) defines the flux of the *i*-th component in the volume fixed reference frame:

$$J_i = c_i\upsilon_i = c_i\upsilon^D + c_i\upsilon^\sigma + c_i\upsilon^{tr} + c_i\frac{\Omega_i}{\Omega}\upsilon_i^d = c_i\upsilon^{drift} + c_i\frac{\Omega_i}{\Omega}\upsilon_i^d = c_i\upsilon^{drift} + J_i^d\,. \tag{36}$$

where $\upsilon^{drift} = \upsilon^D + \upsilon^\sigma + \upsilon^{tr}$ and J_i^d are the drift velocity and the diffusion flux of the *i*-th component in the volume fixed reference frame. Note that common for all components drift velocity is affected by all internal process.

2.4 Conservation of Mass

The molar mass of the mixture component, $m_i(t)$, contained in $\Sigma(t)$ at the moment t is:

$$m_i(t) = \int_{\Sigma(t)} c_i\,\mathrm{d}x \tag{37}$$

The principle of conservation of mass states that the mass in $\Sigma(t)$ is conserved.[6] Thus,

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_{\Sigma(t)} c_i\,\mathrm{d}x = 0\,. \tag{38}$$

By Liouville theorem $(\upsilon_i \equiv 1)$ from (1) and (38) we get,

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_{\Sigma(t)} c_i\,\mathrm{d}x = \int_{\Sigma(t)}\left(\frac{\partial c_i}{\partial t} + \mathrm{div}(c_i\upsilon_i)\right)\mathrm{d}x = 0\,, \tag{39}$$

Since the subregion $\Sigma(t)$ was chosen arbitrarily, then

$$\frac{\partial c_i}{\partial t} + \mathrm{div}(c_i\upsilon_i) = 0\,, \tag{40}$$

Upon summing up for all components partial continuity equations, eqns. (40), one can get the global conservation law:

$$\frac{\partial c}{\partial t} + \mathrm{div}(c\upsilon) = 0\,, \tag{41}$$

Equations (40) and (41) are known as the partial and global continuity equations.

2.5 Balance of Momentum

The momentum of a multicomponent mixture in an evolving subregion $\Sigma(t)$ is:

$$\left[\text{momentum in } \Sigma(t)\right] = \int_{\Sigma(t)} \rho\upsilon\,\mathrm{d}x\,. \tag{42}$$

By the Newton's law the rate of momentum change in $\Sigma(t)$ equals the total force acting on mass in $\Sigma(t)$:

$$\mathrm{F}_{\text{total}} = \frac{\mathrm{d}}{\mathrm{d}t}\int_{\Sigma(t)} \rho\upsilon\,\mathrm{d}x\,. \tag{43}$$

We assume that the following forces act on the mass in $\Sigma(t)$[7]:

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[6] To simplify the relations, in this work we do not consider the chemical and/or nuclear reactions in the mixture, *i.e.*, we do neglect the local sources and sinks of mass.

[7] We do not consider here the electromagnetic field. *e.g.*, the diffusion of the charged species (ions).

1. The force of elastic stress, $\boldsymbol{F}_\sigma$, acting on the surface $\partial\Sigma(t)$

$$\mathrm{F}_\sigma = \int_{\partial\Sigma(t)} \sigma^e \,\mathrm{d}x = \int_{\Sigma(t)} \mathrm{div}\sigma^e \,\mathrm{d}x, \tag{44}$$

where $\sigma^e : [0,\infty) \times \mathbb{R}^3 \to \mathrm{L}(\mathbb{R}^3, \mathbb{R}^3)$ is the stress tensor and $L(\mathbb{R}^3, \mathbb{R}^3)$ is the space of linear mappings from $\mathbb{R}^3$ to $\mathbb{R}^3$ [15]. In eqn. (44) we postulate that the mechanical properties of the mixture, the temperature and its entropy, are represented by the average values. The deformation velocity is given by:

$$\upsilon^\sigma = \frac{\partial u^\sigma}{\partial t} \tag{45}$$

where u^σ denotes the deformation vector of the mixture.

2. The viscosity force acting on the mass in $\Sigma(t)$, is a result of the non-uniform volume velocity field. The area was extensively studied and the vast number of constitutive equations is known [15]. Here it is sufficient to use the basic expression:

$$\mathrm{F}_\nu = -\int_{\partial\Sigma(t)} \eta \,\mathrm{grad}\, \upsilon^{drift} \cdot \mathrm{n}\mathrm{d}a = -\int_{\Sigma(t)} \mathrm{div}\left(\eta \,\mathrm{grad}\upsilon^{drift}\right)\mathrm{d}x = \int_{\Sigma(t)} \mathrm{div}\sigma^p \,\mathrm{d}x. \tag{46}$$

3. The net chemical force acting on mass in $\Sigma(t)$. This part of the stress tensor is called the stress free deformation tensor[8] [26]. In nonideal systems the net chemical force equals:

$$\mathrm{F}_{\mathrm{chem}} = -\sum_{i=1}^{\mathrm{r}} \int_{\Sigma(t)} c_i \mathrm{grad}\mu_i^{ch} \,\mathrm{d}x, \tag{47}$$

4. The external force, f^{ext}, acting on the mass in the volume $\Sigma(t)$ is given by:

$$\mathrm{F}_{\mathrm{ext}} = \int_{\Sigma(t)} \rho f^{ext} \,\mathrm{d}x = -\int_{\Sigma(t)} \rho \,\mathrm{grad} V^{ext} \,\mathrm{d}x. \tag{48}$$

An external force can be, *e.g.*, the gradient of a gravitational potential, $f^{ext} = -\nabla V^{ext}$.
The total force acting on mass in $\Sigma(t)$ is the sum of all forces listed above. Consequently:

$$\mathrm{F}_{\mathrm{total}} = \mathrm{F}_\sigma + \mathrm{F}_\nu + \mathrm{F}_{\mathrm{chem}} + \mathrm{F}_{\mathrm{ext}} \tag{49}$$

Applying the formulae (42) and (44) … (49) results in:

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_{\Sigma(t)} \rho\upsilon \,\mathrm{d}x = \int_{\Sigma(t)} \mathrm{div}\sigma^e \,\mathrm{d}x + \int_{\Sigma(t)} \mathrm{div}\sigma^p \mathrm{d}x - \sum_{i=1}^{\mathrm{r}} \int_{\Sigma(t)} c_i \,\mathrm{grad}\mu_i^{ch} \,\mathrm{d}x - \int_{\Sigma(t)} \rho \,\mathrm{grad} V^{ext} \,\mathrm{d}x. \tag{50}$$

Using the Liouville theorem the left hand side of eqn. (50) becomes:

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}\int_{\Sigma(t)} \rho\upsilon \,\mathrm{d}x &= \int_{\Sigma(t)} \left(\upsilon\left(\frac{\partial\rho}{\partial t} + \mathrm{div}(\rho\upsilon) \right) + \rho\left(\frac{\partial\upsilon}{\partial t} + \upsilon \cdot \mathrm{grad}\upsilon \right) \right) \mathrm{d}x = \\ \int_{\Sigma(t)} \left(\frac{\partial\rho\upsilon}{\partial t} + \upsilon \,\mathrm{div}(\rho\upsilon) + \rho\upsilon \cdot \mathrm{grad}\upsilon \right) \mathrm{d}x &= \int_{\Sigma(t)} \left(\frac{\partial\rho\upsilon}{\partial t} + \mathrm{div}(\rho\upsilon \otimes \upsilon) \right) \mathrm{d}x.\end{aligned} \tag{51}$$

Substituting eqn. (51) into eqn. (50) one gets

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[8] The stress free deformation tensor equals zero in a case of an ideal mixture.

$$\int_{\Sigma(t)}\left(\frac{\partial\rho\upsilon}{\partial t}+\mathrm{div}\left(\rho\upsilon\otimes\upsilon\right)\right)\mathrm{d}x=\int_{\Sigma(t)}\mathrm{div}\sigma^{e}\mathrm{d}\,x+\int_{\Sigma(t)}\mathrm{div}\sigma^{p}\mathrm{d}x-\sum_{i=1}^{\mathrm{r}}\int_{\Sigma(t)}c_i\;\mathrm{grad}\mu_i^{ch}\mathrm{d}x-\int_{\Sigma(t)}\rho\,\mathrm{grad}\,V^{ext}\mathrm{d}\,x \tag{52}$$

Since the subregion $\Sigma(t)$ was chosen arbitrarily one can omit integrals and eqn. (52) becomes:

$$\left(\frac{\partial\rho\upsilon}{\partial t}+\mathrm{div}\left(\rho\upsilon\otimes\upsilon\right)\right)=\mathrm{div}\sigma^{e}+\mathrm{div}\sigma^{p}-\sum_{i=1}^{\mathrm{r}}c_i\;\mathrm{grad}\mu_i^{ch}-\rho\,\mathrm{grad}\,V^{ext}. \tag{53}$$

Upon using continuity equation, eqn. (40), it is easy to show that

$$\rho\left.\frac{\mathrm{D}\upsilon}{\mathrm{D}t}\right|_{\upsilon}=\mathrm{div}\left(\sigma^{e}+\sigma^{p}\right)-\sum_{i=1}^{r}c_i\mathrm{grad}\mu_i^{ch}-\rho\;\mathrm{grad}V^{ext}. \tag{54}$$

Equations (53) and (54) we shall call the equation of motion.

2.6 Balance of Energy

The total energy of the mixture in $\Sigma(t)$ can be written:

$$\begin{array}{ccccccc} e(t) & = & e_k(t) & + & e_I(t) & + & e_P(t) \\ \begin{bmatrix}\text{total energy of}\\ \text{mass in }\Sigma(t)\end{bmatrix} & = & \begin{bmatrix}\text{kinetic}\\ \text{energy}\end{bmatrix} & + & \begin{bmatrix}\text{internal}\\ \text{energy}\end{bmatrix} & + & \begin{bmatrix}\text{potential}\\ \text{energy}\end{bmatrix}\end{array}$$

The kinetic energy contained in the moving subregion $\Sigma(t)$ with a velocity υ is:

$$e_k(t)=\int_{\Sigma(t)}\frac{1}{2}\rho\upsilon^2dx. \tag{55}$$

We shall use the fundamental canonical equation of thermodynamics:

$$U=U\left(S,\Omega^*,m_1,m_2,\ldots,m_r\right)$$

It is convenient to analyze the transport in unit volume moreover, the volume, Ω^*, is considered as the reference frame. Thus:

$$\overset{\vee}{\varepsilon}=\overset{\vee}{\varepsilon}\left(\overset{\vee}{s},\rho_1,\rho_2,\ldots,\rho_r\right)$$

where $\overset{\vee}{\varepsilon}$ and $\overset{\vee}{s}$ denote the internal energy and the entropy that are expressed per unit volume. Consequently, the fundamental canonical equation of thermodynamics becomes

$$\overset{\vee}{\varepsilon}=\rho\varepsilon=\overset{\vee}{\varepsilon}\left(\rho s,\rho_1,\rho_2,\ldots,\rho_r\right) \tag{56}$$

ε and s are an internal energy and entropy per mass unit. Transition from fundamental canonical form to the eqn. (56) implies introduction of the mechanical potential. In such a case, the Gibbs equation becomes:

$$\mathrm{d}\left(\rho\varepsilon\right)=T\mathrm{d}\left(\rho s\right)+\sum_{i=1}^{r}\mu_i^{*}M_i^{-1}\mathrm{d}\rho_i=T\mathrm{d}\left(\rho s\right)+\sum_{i=1}^{r}\left(\mu_i^{ch}+\mu_i^{m}\right)\mathrm{dc}_i \tag{57}$$

μ_i^{ch}, μ_i^{m} and μ_i^{*} are the chemical, mechanical and mechanochemical potentials of components. The mechanical potential due to the deformation can be given by any proper formula, *e.g.*, by eqn. (28). The integral form of the Gibbs equation follows from eqn. (57):

$$\rho\varepsilon = Ts\rho + \sum_{i=1}^{r}\mu_i^{*}c_i = Ts\rho + \sum_{i=1}^{r}\mu_i^{ch}c_i + \sum_{i=1}^{r}\mu_i^{m}c_i\,. \tag{58}$$

Thus, from eqn. (58) the internal energy of mass contained by $\Sigma(t)$ is given by:

$$e_{\mathrm{I}} = \int_{\Sigma(t)}\rho\varepsilon\,\mathrm{d}\,x = \int_{\Sigma(t)}\left(Ts\rho + \sum_{i=1}^{r}\mu_i^{*}c_i\right)\mathrm{d}\,x = \int_{\Sigma(t)}\left(Ts\rho + \sum_{i=1}^{r}\mu_i^{ch}c_i + \sum_{i=1}^{r}\mu_i^{m}c_i\right)\mathrm{d}\,x \tag{59}$$

The potential energy of mass in $\Sigma(t)$ is represented by its potential per the mass unit,

$$e_P = \int_{\Sigma(t)}\rho V^{ext}\,\mathrm{d}\,x\,. \tag{60}$$

By the First Law of Thermodynamics the total energy of mass contained by $\Sigma(t)$ can be affected by the heat flow and the work done on it. Thus, from eqns. (55) … (60):

$$\begin{aligned}&\frac{\mathrm{d}}{\mathrm{dt}}\int_{\Sigma(t)}\left(\frac{1}{2}\rho\upsilon^2 + Ts\rho + \sum_{i=1}^{r}\mu_i^{*}c_i + V^{ext}\rho\right)\mathrm{d}\,x = \\ &= \int_{\partial\Sigma(t)}\sigma^e\cdot\upsilon\mathrm{d}a - \int_{\partial\Sigma(t)}\sigma^p\cdot\upsilon\mathrm{d}a - \int_{\Sigma(t)}\mathrm{div}\,J_q\mathrm{d}x = \int_{\Sigma(t)}\mathrm{div}\left(\sigma^e\cdot\upsilon + \sigma^p\cdot\upsilon - J_q\right)\mathrm{d}x\end{aligned} \tag{61}$$

where J_q denotes the heat flux, which is given by the proper constitutive formula. Applying the Liouville theorem eqn. (61) becomes:

$$\begin{aligned}&\int_{\Sigma(t)}\left(\frac{\partial}{\partial t}\left(\frac{1}{2}\rho\upsilon^2 + T\rho s + \sum_{i=1}^{r}c_i\mu_i^{*} + \rho V^{ext}\right) + \mathrm{div}\left(\frac{1}{2}\rho\upsilon^2\upsilon + Ts\rho\upsilon + \upsilon\sum_{i=1}^{r}c_i\mu_i^{*} + \rho\upsilon V^{ext}\right)\right)\mathrm{d}\,x = \\ &= \int_{\Sigma(t)}\mathrm{div}\left(\sigma^e\cdot\upsilon\right)\mathrm{d}x + \int_{\Sigma(t)}\mathrm{div}\left(\sigma^p\cdot\upsilon\right)\mathrm{d}x - \int_{\Sigma(t)}\mathrm{div}\,J_q\mathrm{d}x\end{aligned} \tag{62}$$

Since the subregion $\Sigma(t)$ was chosen arbitrarily, the integral in eqn. (62) can be omitted and using the mass continuity equation, it can be written in the condensed form as

$$\sum_{i=1}^{r}\rho_i\frac{\mathrm{D}}{\mathrm{D}t}\left(\frac{1}{2}\upsilon^2 + Ts + \frac{\mu_i^{*}}{M_i} + V^{ext}\right)\Bigg|_{\upsilon} = \mathrm{div}\left(\sigma^e\cdot\upsilon\right) + \mathrm{div}\left(\sigma^p\cdot\upsilon\right) - \mathrm{div}\,J_q \tag{63}$$

The left hand side of the eqn. (63) can be rearranged to

$$\rho\upsilon\frac{\mathrm{D}\upsilon}{\mathrm{D}t}\bigg|_{\upsilon} + \sum_{i=1}^{r}\rho_i\frac{\mathrm{D}}{\mathrm{D}t}\left(Ts + \frac{\mu_i^{*}}{M_i} + V^{ext}\right)\Bigg|_{\upsilon} = \mathrm{div}\left(\sigma^e\cdot\upsilon\right) + \mathrm{div}\left(\sigma^p\cdot\upsilon\right) - \mathrm{div}\,J_q \tag{64}$$

Upon multiplying the momentum conservation equation, eqn. (54), by the volume velocity υ we have:

$$\rho\upsilon\frac{\mathrm{D}\upsilon}{\mathrm{D}t}\bigg|_{\upsilon} = \upsilon\,\mathrm{div}\left(\sigma^e + \sigma^p\right) - \upsilon\sum_{i=1}^{r}c_i\,\mathrm{grad}\mu_i^{ch} - \rho\upsilon\,\mathrm{grad}V^{ext} \tag{65}$$

Consequently, upon combining eqns. (60), (64) and (65), the equation of the internal energy conservation becomes:

$$\sum_{i=1}^{r}\rho_i\frac{\mathrm{D}}{\mathrm{D}t}\left(Ts + \frac{\mu_i^{*}}{M_i} + V^{ext}\right)\Bigg|_{\upsilon} = \sigma^e\text{: }\mathrm{grad}\upsilon + \sigma^p\text{: }\mathrm{grad}\upsilon + \upsilon\sum_{i=1}^{r}c_i\,\mathrm{grad}\mu_i^{ch} + \rho\upsilon\mathrm{grad}V^{ext} - \mathrm{div}\,J_q\,. \tag{66}$$

When an external force field does not depend on time, $\left(V^{ext}=V^{ext}\left(x\right)\right)$, it further reduces to:

$$\rho\left.\frac{\mathrm{D}\varepsilon}{\mathrm{D}t}\right|_{\upsilon}=\rho\left.\frac{\mathrm{D}Ts}{\mathrm{D}t}\right|_{\upsilon}+\sum_{i=1}^{r}c_i\left.\frac{\mathrm{D}\mu_i^*}{\mathrm{D}t}\right|_{\upsilon}=\sigma^e\mathrm{:grad}\,\upsilon+\sigma^p\mathrm{:grad}\,\upsilon+\upsilon\sum_{i=1}^{r}c_i\mathrm{grad}\mu_i^{ch}-\mathrm{div}\,J_q\,, \tag{67}$$

The formulae (66) and (67) express the first law of thermodynamics in multicomponent continuum.

2.7 Separation of mechanical and thermal terms

The separation of the entropy and mechanical energy terms in eqn. (67) is convenient in many applications [15]. Thus, one can write eqn. (67) as:

$$\sum_{i=1}^{r}c_i\left.\frac{\mathrm{D}\mu_i^*}{\mathrm{D}t}\right|_{\upsilon}=\sigma^e:\mathrm{grad}\,\upsilon+\upsilon\sum_{i=1}^{r}c_i\;\mathrm{grad}\mu_i^{ch} \tag{68}$$

$$\rho\left.\frac{\mathrm{D}Ts}{\mathrm{D}t}\right|_{\upsilon}=\sigma^p:\mathrm{grad}\,\upsilon-\mathrm{div}\,J_q \tag{69}$$

To complete the separation of the mechanical and entropy terms, Eqs. (68) and (69) must be extended to include the dissipation of energy due to the diffusion [15]. From eqns. (56) and (57), the Gibbs-Duhem relation has the form:

$$\rho s\mathrm{d}T=-\sum_{i=1}^{r}c_i\mathrm{d}\mu_i^*=-\sum_{i=1}^{r}c_i\mathrm{d}\left(\mu_i^{ch}+\mu_i^m\right) \tag{70}$$

and the energy dissipated due to the diffusion, *i.e.*, the work done by the chemical forces (diffusion forces) equals:

$$w_{diffusion}=-\sum_{i=1}^{r}c_i\upsilon_i^d\;\mathrm{grad}\,\mu_i^* \tag{71}$$

This work has to be included into the energy balance, eqns. (68) and (69), in such a way that it will not change the total energy conservation equation, eq. (67) [15]. Consequently we get:

$$\sum_{i=1}^{r}c_i\left.\frac{\mathrm{D}\mu_i^*}{\mathrm{D}t}\right|_{\upsilon}=\sigma^e:\mathrm{grad}\,\upsilon+\upsilon\sum_{i=1}^{r}c_i\mathrm{grad}\mu_i^{ch}+\sum_{i=1}^{r}c_i\upsilon_i^d\;\mathrm{grad}\,\mu_i^*\,, \tag{72}$$

$$\rho\left.\frac{\mathrm{D}Ts}{\mathrm{D}t}\right|_{\upsilon}=\sigma^p:\mathrm{grad}\,\upsilon-\mathrm{div}\,J_q-\sum_{i=1}^{r}c_i\upsilon_i^d\;\mathrm{grad}\,\mu_i^*\,. \tag{73}$$

The last terms in eqns. (72) and (73) describe the fact that diffusion does not affect internal energy of the mixture. Entropy is produced at the expense of mechanical energy of the mixture. One may note that, upon adding eqns. (72) and (73) we get eqn. (67).

3 Summary

The drift velocity is the unique frame of reference for the diffusion and the volume continuity equation allows defining it quantitatively:

$$\mathrm{div}\left(\sum_{i=1}^{r}c_i\Omega_i\upsilon_i\right)=\mathrm{div}\left(\upsilon^{drift}+\sum_{i=1}^{r}c_i\Omega_i\upsilon_i^d\right)=\mathrm{div}\left(\upsilon^{drift}+\sum_{i=1}^{r}\Omega_iJ_i^d\right)=0\,.$$

The local momentum density depends on the diffusion of mass as well as on all other transport processes. However, the momentum due to the diffusion can be locally compensated by the Darken velocity. In such a case the overall volume velocity in the momentum balance is: $\upsilon = \upsilon^{\sigma} + \upsilon^{tr}$. Such form of the balance of momentum, eqn. (54), fulfills the condition, that the local acceleration of the body depends on its mass, not on its internal energy and that the local centre of mass position is not affected by diffusion.

When the pure diffusion in ideal solid solution is considered then: $\upsilon(0,x) = \upsilon^{\sigma}(0,x) = 0$ and $\upsilon^{tr}(0,x) = 0$, the concentrations are equal to the activities $c_i = a_i$ and $c = const$. Consequently, the term that describes nonbalanced chemical potentials, eqn. (47), equals zero:

$$\sum_{i=1}^{\mathrm{r}} c_i \mathrm{grad}\mu_i^{ch} = \sum_{i=1}^{\mathrm{r}} c_i RT \mathrm{grad}\,\ln a_i \overset{a_i = c_i}{=} RT \sum_{i=1}^{\mathrm{r}} \mathrm{grad}\, c_i = RT \mathrm{grad}\, c = 0\,. \tag{74}$$

From eqn. (54) it follows that centre of mass position is not affected by diffusion: $\rho \left.\frac{\mathrm{D}\upsilon}{\mathrm{D}t}\right|_{\upsilon} = 0$

Eqn. (33) allows analyzing an arbitrary transport process. Let us consider the Darken's diffusion in non-compressible multicomponent solution where $\Omega = \Omega_i = const$ for every component. Thus, from eqns. (3) and (33), the Darken velocity equals:

$$\upsilon^{D}(t,x) = -\sum_{i=1}^{r} c_i \Omega_i \upsilon_i^{d} = -\frac{1}{c}\sum_{i=1}^{r} c_i \upsilon_i^{d}$$

Thus, we have proved the identity of the presented and Darken methods when Darken constraints are valid.

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