

Unified Description of Interdiffusion in Solids and Liquids

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This work presents a mathematical description of mass transport in multicomponent solution based on the Darken concept of drift velocity. The diffusion of components depends on the chemical potential gradient and on the stress that can be induced by diffusion and by boundary and initial conditions. The key postulate is cubic symmetry of a solid alloy, which implies a precise form for the stress tensor. In such a quasi-continuum, the energy, momentum, and mass transport are diffusion controlled, and the fluxes are given by the Nernst-Planck formulae. A modified form the Navier-Lame equation is postulated, and the resulting form of the continuity equation for energy is derived. It is shown that the Darken method is valid for multicomponent solid solutions as well as for liquids.

1. Introduction

A new understanding of diffusion in multicomponent systems started with Kirkendall experiments on the interdiffusion (ID) between Cu and Zn. Experiments proved that diffusion by direct interchange of atoms, the prevailing idea of the day, was incorrect and that a less-favored theory, the vacancy mechanism, must be considered. In 1946, Kirkendall, along with his student, Alice Smigelskas, coauthored a paper asserting that ID between Cu and Zn in brass showed movement of the interface between the “initially different phases” due to ID. This discovery, forever after known as the “Kirkendall Effect” supported the idea that atomic diffusion occurs through vacancy exchange [1947Smi]. It shows the different intrinsic diffusion fluxes of the components that cause swelling (creation) of one part and shrinking (annihilation) of the other part of the diffusion couple. The key conclusion is that local movement in a solid (its lattice) and liquid is due to diffusion and is a real process. Once the solution is nonuniform and the mobilities differ from each other, then a vast number of phenomena can occur: Kirkendall marker movement, Kirkendall-Frenkel voids, stress, etc. The Kirkendall paper was submitted to *Trans. of AIME*, but publication was delayed for six months because leading scientists at the time thought he was wrong. The concepts initiated by Kirkendall played a decisive role in the development of diffusion theory [1948Dar, 1993Dan]. The progress in the understanding of the ID phenomenology [1994Hol] nowadays allows attempts to further generalize the Darken method.

The Darken Method for a multicomponent solution is based on the postulate that total mass flow is a sum of diffusion and drift flow [1994Hol]. The force arising from

gradients causes the atoms of a particular component to move with a velocity, which may generally differ from the velocities of atoms of other components. In a single common medium for all the species, all fluxes are coupled, thus their local changes can affect the common drift velocity v^{drift} . The physical laws that govern the process are continuity equations and the postulate that the total molar concentration of the solution is constant. The extended Darken method in one-dimensional solid solution [1994Hol] allows modeling of the positions of the solution boundaries, densities, and drift velocity. The physical laws are the same as in the original Darken model. The important differences are in formulation of initial and boundary conditions that allow simulation of the reactions and many other situations. The uniqueness and existence of the solution, the effective methods of numerical solution, and successful modeling of the up-hill diffusion (“diffusional structures”) prove the universality of the drift concept [1993Dan, 1994Hol]. It provides the sole opportunity to describe ID in real solutions in three dimensions, an objective of this work.

Navier-Stokes “was revisited” recently by Brenner [2005Bre]. He postulated a revision of Newton’s law of viscosity appearing in the deviatoric stress tensor in the Navier-Stokes equation for the case of compressible fluids, both gaseous and liquid. The postulated modification is equivalent to the Darken concept.

2. Darken Method and Stress

The interdiffusion process inherently generates a stress field within the diffusion zone. The Kirkendall and Kirkendall-Frenkel effects are experimental evidences of diffusion induced deformation and stress in solids. An unquestionable explanation of these phenomena was given by Darken [1948Dar]. The core of his method is mass balance equation:

$$\frac{\partial \rho_i}{\partial t} = -\text{div} J_i \quad \text{for } i = 1, \dots, r \quad (\text{Eq 1})$$

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where ρ_i is the mass density and J_i denotes the postulated form of the flux of i -th element that contains the diffusive and drift terms:

$$J_i = J_i^d + \rho_i v^{\text{drift}} \quad \text{for } i = 1, \dots, r \quad (\text{Eq 2})$$

where v^{drift} denotes the drift velocity, J_i^d is the diffusion flux, and r is the number of components in the solution. The mass balance equation can be written in an internal reference frame (relative to the drift velocity). Thus, from Eq 1 and 2 it follows:

$$\left. \frac{D\rho_i}{Dt} \right|_{v^{\text{drift}}} = -\text{div} J_i^d - \rho_i \text{div} v^{\text{drift}} = -\text{div}(\rho_i v_i^d) - \rho_i \text{div} v^{\text{drift}} \quad \text{for } i = 1, \dots, r \quad (\text{Eq 3})$$

where v_i^d is diffusion velocity. The operator in Eq 1 is changed from a partial derivative to a Lagrangian derivative when Eq 2 is substituted into Eq 1 and only the i -th component is considered; thus $[\mathbf{D}\rho_i/\mathbf{D}t]_{v^{\text{drift}}} = \partial\rho_i/\partial t + v^{\text{drift}} \text{grad} \rho_i$, which simplifies to $\partial\rho_i/\partial t + v^{\text{drift}} \partial\rho_i/\partial x$ for a unidirectional concentration gradient and where v^{drift} is the drift velocity.

The derivative in Eq 3 is called Lagrangian, substantial or material derivative:

$$\left. \frac{D\rho_i}{Dt} \right|_{v^{\text{drift}}} = \frac{\partial\rho_i}{\partial t} + v^{\text{drift}} \text{grad} \rho_i \quad (\text{Eq 4})$$

and it gives the rate of density changes at the point moving with an arbitrary velocity; here it is the drift velocity.

Upon expressing the diffusion flux by the Nernst-Planck equation [1889Ner, 1890Pla], the Darken method of interdiffusion [1948Dar] with his concept of drift velocity can be extended to include the stress effect:

$$J_i^d = \rho_i B_i F_i \quad (\text{Eq 5})$$

where B_i and F_i are, respectively, the mobility of i -th component and the forces affecting the mobility:

$$F_i = -\text{grad}(\mu_i + \Omega_i p) \quad (\text{Eq 6})$$

where μ_i , Ω_i , and p denote the chemical potential, the partial molar volume of the i -th element of the solution, and the pressure.

Upon combining Eq 3, 5, and 6 the continuity equation becomes:

$$\left. \frac{D\rho_i}{Dt} \right|_{v^{\text{drift}}} = \text{div}[\rho_i B_i \text{grad}(\mu_i + \Omega_i p)] - \rho_i \text{div} v^{\text{drift}} \quad \text{for } i = 1, \dots, r \quad (\text{Eq 7})$$

The total strain can be defined using the deformation-gradient tensor \mathbf{H} [1987Lan]:

$$\mathbf{H} = \text{grad} \mathbf{u} \quad (\text{Eq 8})$$

where \mathbf{u} denotes a displacement vector. The total dilatation is defined as a mean of the normal total strains [1987Lan]:

$$e^{\text{TOT}} = \frac{1}{3} \text{trace} \boldsymbol{\varepsilon}^{\text{TOT}} \quad (\text{Eq 9})$$

where $\text{trace} \boldsymbol{\varepsilon} = \sum \varepsilon_{kk}$.

The total strain tensor is the sum of elastic, plastic and stress-free strain tensors:

$$\boldsymbol{\varepsilon}^{\text{TOT}} = \boldsymbol{\varepsilon}^E + \boldsymbol{\varepsilon}^P + \boldsymbol{\varepsilon}^{\text{SF}} \quad (\text{Eq 10})$$

The stress-free tensor can be a product of the diffusion or other processes. The pressure is defined by:

$$p = -\frac{1}{3} \text{trace} \boldsymbol{\sigma} \quad (\text{Eq 11})$$

where $\boldsymbol{\sigma}$ is the Cauchy stress tensor.

The Maxwell constitutive relations relate plastic and elastic strain to stress [1988Ste] in an isotropic solid:

$$e^E = -\frac{1-2\nu}{E} p \quad (\text{Eq 12})$$

$$\boldsymbol{\varepsilon}^E = \frac{1+\nu}{E} (\boldsymbol{\sigma} + p\mathbf{1}) + e^E \mathbf{1} \quad (\text{Eq 13})$$

$$e^P = 0 \quad (\text{Eq 14})$$

$$\left. \frac{D\boldsymbol{\varepsilon}^P}{Dt} \right|_{v^D} = \frac{1}{2\eta} (\boldsymbol{\sigma} + p\mathbf{1}) \quad (\text{Eq 15})$$

where E , ν , and η are the Young's modulus, the Poisson's ratio and the shear viscosity, respectively, and $\mathbf{1}$ denotes a unit matrix.

The first quantitative descriptions of the stress induced interdiffusion are by Stephenson [1988Ste] and Beke [1996Bek].

Stephenson [1988Ste] simplified the stress problem to avoid mathematical and numerical difficulties. He postulated a noncompressible flow, $\text{div} v^{\text{drift}} = 0$ in the Eq 3, and reduced the mass balance equation:

$$\left. \frac{D\rho_i}{Dt} \right|_{v^{\text{drift}}} = -\text{div} J_i^d \quad \text{for } i = 1, \dots, r \quad (\text{Eq 16})$$

where the diffusion flux is given by Eq 5 and 6.

The substantial derivatives of $\boldsymbol{\varepsilon}^{\text{TOT}}$, U , and \mathbf{H} were related by [1988Ste]:

$$\left. \frac{D\boldsymbol{\varepsilon}^{\text{TOT}}}{Dt} \right|_{v^{\text{drift}}} = \left. \frac{DU}{Dt} \right|_{v^{\text{drift}}} = \frac{1}{2} \left(\left. \frac{D\mathbf{H}}{Dt} \right|_{v^{\text{drift}}} + \left. \frac{D\mathbf{H}^T}{Dt} \right|_{v^{\text{drift}}} \right) \quad (\text{Eq 17})$$

where U is symmetric stretch tensor [1987Lan]. The problem was further simplified by postulating:

$$\left. \frac{De^{\text{TOT}}}{Dt} \right|_{v^{\text{drift}}} = \frac{1}{3} \text{div} v^{\text{drift}} \quad (\text{Eq 18})$$

Consequently, he derived the final set of coupled nonlinear differential equations describing the spatial evolution of the system (the unknowns ρ_i and p):

$$\left. \frac{D\rho_i}{Dt} \right|_{v^{\text{drift}}} = \text{div} \left(\frac{D_i}{kT} \rho_i \text{grad} (\mu_i + \Omega_i p) \right) \quad \text{for } i = 1, \dots, r \quad (\text{Eq 19})$$

$$\left. \frac{Dp}{Dt} \right|_{v^{\text{drift}}} = \frac{2E}{9(1-\nu)} \sum_{i=1}^r \left\{ \Omega_i \text{div} \left(\frac{D_i}{kT} \rho_i \text{grad} (\mu_i + \Omega_i p) \right) \right\} - \frac{E}{6\eta(1-\nu)} P \quad (\text{Eq 20})$$

$$\text{div} v^{\text{drift}} = \sum_{i=1}^r \Omega_i \text{div} \left(\frac{D_i}{kT} \rho_i \text{grad} (\mu_i + \Omega_i p) \right) \quad (\text{Eq 21})$$

where D_i is the diffusion coefficient and the other terms have already been defined.

Beke [1996Bek] analyzed the stress problem in a binary alloy. The different partial molar volumes and mobilities of the diffusing species generate an imbalance in the volume transport. This is equivalent to the creation of a nonuniform stress-free strain [1988Ste, 1996Bek]. Beke used the relationship between the velocity field and the strain rate analogous as in the Stephenson approach, Eq 18. Mass balance and stresses were described by Eq 3 and 10. The stress-free strain for a binary alloy is related in his model to the volume transport by the relation:

$$\left. \frac{De^{\text{SF}}}{Dt} \right|_{v^{\text{drift}}} = -\frac{1}{3} (\Omega_1 \text{div} J_1^d + \Omega_2 \text{div} J_2^d) \quad (\text{Eq 22})$$

He used the Maxwell constitutive relations to relate plastic and elastic strain to stress (Eq 12-14) postulated noncompressible flow and the Vegard law as the equation of state. Consequently, the diffusion was described by:

$$\left. \frac{D\rho_i}{Dt} \right|_{v^{\text{drift}}} = \Omega_2 (\rho_1 \text{div} J_2^d - \rho_2 \text{div} J_1^d) + 3\rho_1 \frac{1-2\nu}{E} \left. \frac{Dp}{Dt} \right|_{v^{\text{drift}}} \quad (\text{Eq 23})$$

$$\left. \frac{Dp}{Dt} \right|_{v^{\text{drift}}} = \frac{2E}{9(1-\nu)} \sum_{i=1}^2 \left\{ \Omega_i \text{div} \left(\frac{D_i}{kT} \rho_i \text{grad} (\mu_i + \Omega_i p) \right) \right\} - \frac{E}{6\eta(1-\nu)} P \quad (\text{Eq 20})$$

$$\Omega_1 \rho_1 + \Omega_2 \rho_2 = 1 \quad (\text{Eq 24})$$

Thus, the whole problem of diffusion and stress was reduced to one diffusion equation.

3. Diffusion and Stress in the Multicomponent Solution

In this section, the authors derive the momentum and the energy conservation equations based entirely on the concept of drift velocity. They differ from the previously presented formula, Sec. 2, in rigorous definition of the internal and external reference frames. Or, in other words, provide the mandatory invariance of the diffusion velocity when defined in the proper (Kirkendall) frame of reference. In the case when both the stress field and the Kirkendall effect are considered, the Darken concept of drift velocity has to be generalized. It is postulated here that the drift velocity is a sum of Darken drift velocity v^D (generated by the interdiffusion) and the deformation velocity v^σ (generated by the stress):

$$v^{\text{drift}} = v^D + v^\sigma \quad (\text{Eq 25})$$

Darken postulated that diffusion fluxes are local and defined exclusively by the local forces (e.g., the chemical potential gradient, stress field, electric field etc.). He postulated the existence of a unique average velocity that he called the drift velocity. In this work, the authors generalize the original Darken concept to include the elastic deformation of an alloy. The Darken drift velocity is given by [1948Dar]:

$$v^D = \frac{1}{c} \sum_{i=1}^r c_i v_i - \frac{1}{c} \sum_{i=1}^r c_i v_i^d - v^\sigma \quad (\text{Eq 26})$$

where the average total and the diffusion velocities are:

$$v = \frac{1}{c} \sum_{i=1}^r c_i v_i \quad (\text{Eq 27})$$

$$v^d = \frac{1}{c} \sum_{i=1}^r c_i v_i^d \quad (\text{Eq 28})$$

The diffusion velocity of the i -th component and concentration of the solution are defined by:

$$J_i^d = c_i v_i^d \quad (\text{Eq 29})$$

$$c = \sum_{i=1}^r c_i \quad (\text{Eq 30})$$

From Eq 25-29, the following relations for the flux of the i -th element and its velocity hold:

$$J_i = J_i^d + c_i v^D + c_i v^\sigma \quad (\text{Eq 31})$$

$$v_i = v^D + v^\sigma + v_i^d = v^{\text{drift}} + v_i^d \quad (\text{Eq 32})$$

Upon summing Eq 31 for all components, the average local velocities satisfy the Eq 26:

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$$\sum_{i=1}^r c_i v_i^d = \sum_{i=1}^r c_i v_i - c v^D - c v^\sigma$$

and from Eq 27, 28, and 31 it follows:

$$v^d = v - v^{\text{drift}} = v - v^D - v^\sigma \quad (\text{Eq 33})$$

3.1 Mass Balance

For all the processes that obey the mass conservation law and when the chemical and/or nuclear reactions are not allowed, the reaction term can be omitted in the mass conservation law. Thus, the equation of mass conservation is given by Eq 3. Using Eq 33, one can rewrite Eq 3 in the following form:

$$\left. \frac{Dc_i}{Dt} \right|_{v^{\text{drift}}} + \text{div} J_i^d + c_i \text{div} v^{\text{drift}} = 0 \quad (\text{Eq 34})$$

Summing Eq 34 over all components one obtains:

$$\left. \frac{Dc}{Dt} \right|_{v^{\text{drift}}} + \text{div} \left(\sum_{i=1}^r J_i^d \right) + c \text{div} v^{\text{drift}} = 0 \quad (\text{Eq 35})$$

Using Eq 26 and 33 it becomes:

$$\left. \frac{Dc}{Dt} \right|_{v^{\text{drift}}} + \text{div}(c v) - \text{div}(c v^{\text{drift}}) + c \text{div} v^{\text{drift}} = 0$$

and upon further rearrangement:

$$\left. \frac{Dc}{Dt} \right|_{v^{\text{drift}}} + \text{div}(c v) - v^{\text{drift}} \text{grad} c = 0$$

and finally using Eq 4:

$$\frac{\partial c}{\partial t} + \text{div}(c v) = 0 \quad (\text{Eq 36})$$

Thus, the well-known formula was obtained for the mass conservation in the multicomponent solution.

3.2 Stress and Strain Relations

The general form of the equation of motion for an elastic solid is complex. Here the relations for an isotropic material are used. In such a case, the equation of motion is the vector equation $\mathbf{f} = (\lambda + \mu) \text{grad div} \mathbf{u} + \mu \text{div grad} \mathbf{u}$, where \mathbf{f} is the density of the force induced by the displacement vector \mathbf{u} , where $\mathbf{u} = \mathbf{x} - \mathbf{X}$. It shows that isotropic material is completely described by the two elastic constants. To obtain the equation of motion for such a material, one can set $\mathbf{f} = \rho \partial^2 \mathbf{u} / \partial t^2$ and when any body forces like gravity etc. are neglected [1964Fey]:

$$\rho \partial^2 \mathbf{u} / \partial t^2 = (\lambda + \mu) \text{grad div} \mathbf{u} + \mu \text{div grad} \mathbf{u}$$

An elastic body is defined as a material, for which the stress tensor is an exclusive function of a deformation tensor \mathbf{F} :

$$\boldsymbol{\sigma} = \boldsymbol{\sigma}(\mathbf{F}) \quad (\text{Eq 37})$$

In this work, it is postulated that the displacements are small. In such a case the displacement gradient \mathbf{H} is defined as the gradient of the displacement vector:

$$\mathbf{H} = \text{grad} \mathbf{u} = \mathbf{F} - \mathbf{1} \quad (\text{Eq 38})$$

and the strain tensor is the symmetric part of \mathbf{H}

$$\boldsymbol{\varepsilon} = \frac{1}{2} (\mathbf{H} + \mathbf{H}^T) \quad (\text{Eq 39})$$

where

$$\varepsilon_{kl} = \varepsilon_{lk} = 1/2 (u_{k,l} + u_{l,k})$$

The constitutive equation of an isotropic, linear and elastic body is known as the Hooke's law [1964Cot]:

$$\boldsymbol{\sigma} = (\lambda \text{trace} \boldsymbol{\varepsilon}) \mathbf{1} + 2\mu \boldsymbol{\varepsilon} \quad (\text{Eq 40})$$

where λ and μ denote the Lamé coefficients:

$$\lambda = \frac{\nu E}{(1 + \nu)(1 - 2\nu)} \quad \text{and} \quad \mu = \frac{E}{2(1 + \nu)} \quad (\text{Eq 41})$$

where E , as previously, denotes the Young's modulus and ν is the Poisson number.

The divergence of the stress tensor defined by the Eq (40) can be expressed by [1987Lan, 1964Fey]:

$$\text{div} \boldsymbol{\sigma} = (\lambda + \mu) \text{grad div} \mathbf{u} + \mu \text{div grad} \mathbf{u} \quad (\text{Eq 42})$$

3.3 Momentum Balance

The Navier and Navier-Lamé equations describe the momentum balance in the compressible fluid and isotropic solid [1987Lan]. The relations for the momentum and the moment of momentum obtained in the theory of mass transport in a continuum in which diffusion takes place [1994Dan1] permit the following relation for a multicomponent solution to be defined:

$$\rho_i \left. \frac{Dv_i}{Dt} \right|_{v^{\text{drift}}} = \text{div} \sigma_i^* + \rho_i \mathbf{f}_b \quad (\text{Eq 43})$$

When the interdiffusion is analyzed, it is convenient to express momentum balance as a function of concentrations. Thus upon dividing Eq 43 by the molar mass of i -th component and using Eq 32:

$$c_i \left. \frac{Dv_i^{\text{drift}}}{Dt} \right|_{v^{\text{drift}}} = \text{div} \sigma_i + c_i \mathbf{f}_b - c_i \left. \frac{Dv_i^d}{Dt} \right|_{v^{\text{drift}}} \quad (\text{Eq 44})$$

where σ_i and \mathbf{f}_b denote partial Cauchy stress tensor and body force, respectively. The partial Cauchy stress tensor σ_i for the i -th component is defined as follows:

$$\sigma_i = \frac{\Omega_i N_i}{\Omega M_i} \sigma \quad (\text{Eq 45})$$

where σ and Ω denote the overall stress tensor defined by Eq 40 and the alloy molar volume, respectively. It is postulated here that the alloy normal molar volume (at $p = 10^5$ Pa) is given by the Vegard law:

$$\Omega = \sum_{i=1}^r N_i \Omega_i = \sum_{i=1}^r \frac{c_i}{c} \Omega_i \quad (\text{Eq 46})$$

where N_i and Ω_i denote the molar fraction and partial molar volume of the i -th component in solution.

In Eq 43, it is postulated that the drift velocity defines the local (Kirkendall) frame of reference. In the analyzed case of the cubic and elastic crystal, the partial stress tensor obeys the following relation [1987Lan, 1988Ste]:

$$\sigma_i - \sigma_i^T = 0 \quad (\text{Eq 47})$$

Summing Eq 44 and using relations 26-28 and 32-35 yields:

$$c \frac{Dv^{\text{drift}}}{Dt} \Big|_{v^{\text{drift}}} = \text{div} \bar{\sigma} + c \mathbf{f} - c \frac{Dv^{\text{d}}}{Dt} \Big|_{v^{\text{drift}}} + v \text{div}(c v^{\text{d}}) \quad (\text{Eq 48})$$

$$\mathbf{f} = \mathbf{f}_b + \frac{1}{c} \sum_{i=1}^r c_i v_i^{\text{d}} \text{grad} v_i \quad (\text{Eq 49})$$

$$\bar{\sigma} = \sum_{i=1}^r \bar{\sigma}_i = \sum_{i=1}^r (\sigma_i - c_i v_i^{\text{d}} v_i) = \sum_{i=1}^r \left(\frac{N_i \Omega_i}{M_i \Omega} \sigma - c_i v_i^{\text{d}} v_i \right) \quad (\text{Eq 50})$$

$$\begin{aligned} \text{div} \bar{\sigma}_i &= \frac{N_i \Omega_i}{M_i \Omega f_0} (\lambda + \mu) \text{grad} \text{div} v^\sigma \\ &+ \frac{N_i \Omega_i}{M_i \Omega f_0} \mu \text{div} \text{grad} v^\sigma - \text{div}(c_i v_i^{\text{d}} v_i) \quad \text{for } i = 1, \dots, r \end{aligned} \quad (\text{Eq 51})$$

where $v^\sigma = \mathbf{u} f_0$ denotes the “velocity” of internal process produced by stress and f_0 denotes the frequency of the internal process (vibration of the atoms).

3.4 Diffusion and Other Fluxes

The diffusion flux of the i -th component depends on both, the stress and the chemical potential gradient and is given by Nernst-Planck formula, relations 5 and 6:

$$J_i^{\text{d}} = -c_i B_i \text{grad}(\mu_i + \Omega_i p) \quad (\text{Eq 52})$$

The free energy density is limited to the isostatic stress com-

ponent. Keeping only the diagonal terms [1988Ste, 1996Phi] one gets:

$$p = -1/3 \text{ trace} \sigma \quad (\text{Eq 53})$$

The free energy density (pressure) gradient will induce the diffusion flux of elements if their molar volumes differ from each other [1996Phi]. The Nernst-Einstein equation relates the mobility and the self diffusion coefficient [1996Phi]:

$$D_i = B_i k T \quad (\text{Eq 54})$$

where k is the Boltzmann constant and T the absolute temperature.

3.5 Physical Laws

The integral form of the mass conservation law has a form:

$$\frac{D}{Dt} \Big|_{v^{\text{drift}}} \int_{\beta(t)} c d\vartheta + \int_{\partial\beta(t)} c v^{\text{d}} ds = 0$$

Using Eq 33, it can be written in terms of drift velocity. Thus, the following formulas form the integral balance equations for multicomponent solution:

$$\frac{D}{Dt} \Big|_{v^{\text{drift}}} \int_{\beta(t)} c d\vartheta + \int_{\partial\beta(t)} c v ds - \int_{\partial\beta(t)} c v^{\text{drift}} ds = 0 \quad (\text{Eq 55})$$

$$\frac{D}{Dt} \Big|_{v^{\text{drift}}} \int_{\beta(t)} c v d\vartheta = \int_{\partial\beta(t)} \bar{\sigma} ds + \int_{\beta(t)} c \mathbf{f} d\vartheta \quad (\text{Eq 56})$$

$$\frac{D}{Dt} \Big|_{v^{\text{drift}}} \int_{\beta(t)} \mathbf{x} \times c v d\vartheta = \int_{\partial\beta(t)} \mathbf{x} \times \bar{\sigma} ds + \int_{\beta(t)} \mathbf{x} \times c \mathbf{f} d\vartheta \quad (\text{Eq 57})$$

$$\begin{aligned} \frac{D}{Dt} \Big|_{v^{\text{drift}}} \int_{\beta(t)} \left(c e + \sum_{i=1}^r \frac{1}{2} c_i (v^{\text{drift}} + v_i^{\text{d}})^2 \right) d\vartheta = \\ \int_{\partial\beta(t)} v \bar{\sigma} ds - \int_{\partial\beta(t)} \mathbf{q}_T ds + \int_{\beta(t)} c f v d\vartheta + \int_{\beta(t)} \mathbf{q}_B d\vartheta \end{aligned} \quad (\text{Eq 58})$$

$$\frac{D}{Dt} \Big|_{v^{\text{drift}}} \int_{\beta(t)} c \eta d\vartheta \geq - \int_{\partial\beta(t)} \frac{\mathbf{q}_T}{T} ds + \int_{\beta(t)} \frac{\mathbf{q}_B}{T} d\vartheta \quad (\text{Eq 59})$$

where e , \mathbf{q}_T , \mathbf{q}_B , and η denote the specific internal energy, heat flux (vector of heat transfer), vector of heat source per unit mass produced by internal sources and density of energy production, respectively. $\beta(t)$ and $\partial\beta(t)$ denote the solution volume, which in general can depend on time.

The above integral equations allow deriving the self-consistent set of the following differential equations:

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$$\frac{Dc}{Dt}\Big|_{v^{\text{drift}}} + c\text{div}v^{\text{drift}} + \text{div}(cv^{\text{d}}) = 0 \quad (\text{Eq 60})$$

$$\text{div}\bar{\sigma} + c\mathbf{f} - c\frac{Dv^{\text{d}}}{Dt}\Big|_{v^{\text{drift}}} - c\frac{Dv^{\text{drift}}}{Dt}\Big|_{v^{\text{drift}}} + v\text{div}(cv^{\text{d}}) = 0 \quad (\text{Eq 61})$$

$$\begin{aligned} c\frac{De}{Dt}\Big|_{v^{\text{drift}}} - e\text{div}(cv^{\text{d}}) - cv\frac{Dv^{\text{d}}}{Dt}\Big|_{v^{\text{drift}}} + v^2\text{div}(cv^{\text{d}}) \\ + \sum_{i=1}^r c_i v_i \frac{Dv_i^{\text{d}}}{Dt}\Big|_{v^{\text{drift}}} + \text{div}\mathbf{q}_T - \sum_{i=1}^r \frac{1}{2} v_i^2 \text{div}(c_i v_i^{\text{d}}) \\ + \bar{\sigma} : \text{grad}v - \mathbf{q}_B = 0 \end{aligned} \quad (\text{Eq 62})$$

$$\sigma - \sigma^T = 0 \quad (\text{Eq 63})$$

$$\begin{aligned} -c\frac{D\psi}{Dt}\Big|_{v^{\text{drift}}} + \psi\text{div}(cv^{\text{d}}) + cv\frac{Dv^{\text{d}}}{Dt}\Big|_{v^{\text{drift}}} - v^2\text{div}(cv^{\text{d}}) \\ - \sum_{i=1}^r c_i v_i \frac{Dv_i^{\text{d}}}{Dt}\Big|_{v^{\text{drift}}} + \sum_{i=1}^r \frac{1}{2} v_i^2 \text{div}(c_i v_i^{\text{d}}) \\ + \bar{\sigma} : \text{grad}v \geq 0 \end{aligned} \quad (\text{Eq 64})$$

where the free energy is defined as $psi = e - \eta T$.

4. Summary

In 1845 Stokes proposed the rheological constitutive expression for the fluid's deviatoric or viscous stress σ [1845Sto]. Since then the Navier-Stokes equations become a foundation of continuum fluid dynamics, valid for Newtonian fluids (gases and liquids). In these equations, the velocity u is the local center of mass velocity appearing in the continuity equation:

$$\frac{\partial \rho}{\partial t} + \text{div}(\rho u) = 0 \quad (\text{Eq 65})$$

where Eq 65 is obtained by summing Eq 1 over all components.

Regardless of the common acceptance of the original Stokes interpretation, it is proposed that the velocity appearing in Newton's viscosity law should be the drift velocity. Namely, the lattice/Kirkendall velocity in solids, Eq 43 and 48, and the volume velocity in gases and liquids [1994Dan1]. Thus, the key results of the present work lie in postulated modification of the Navier-Stokes and the Navier-Lamé equations for the case of multicomponent solutions, where the concentrations are not uniform and where diffusion occurs. These lead to the prediction of stresses in liquids and solids. This is based on the Kirkendall effect in solids and on experimental data for the movement of sus-

pending particles in fluids under the influence of mass density gradients [2005Bre]; namely, a fundamental distinction between the fluid's tracer velocity as recorded by monitoring the spatio-temporal trajectory of a small particle (marker) introduced into the fluid, and the fluid's velocity as monitored, e.g., by the introduction of a dye into the fluid. In such conditions a dye undergoes diffusion and its velocity differs from the average (volume) velocity.

The presented self-consistent coupling of the Darken method with mass and momentum balance equations allows for quantitative analysis of the transport processes in multicomponent, three-dimensional and bounded systems.

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