NOTES ON DIFFUSION WITH VOLUME CHANGE

Robert F. Sekerka
Carnegie Mellon University
Pittsburgh, Pennsylvania 15213-3890

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Introduction

We explore some fundamental aspects of diffusion in a binary (chemical species \( A \) and \( B \)) system. The ultimate objective is to better understand the relationship among the various treatments of a one-dimensional diffusion couple when there is volume change on mixing. We begin by examining the relationships among diffusion fluxes that are true irrespective of the nature of constitutive equations. We then introduce constitutive equations and relate the various diffusivities therein. By means of an explicit transformation along the lines suggested by den Broeder [1], we transform the Eulerian description for a one dimensional diffusion couple with volume change to a Lagrangian description, thus eliminating the explicit appearance of a convective term. The resulting equation can be solved by the Boltzmann-Matano method [2,3]. We deduce by purely analytical means the formulae of Wagner [4] for the diffusivity and for the location of the Matano interface. We develop explicit formulae for the movement of this Wagner-Matano interface with respect to the ends of the diffusion couple. We show that the ends of the couple and the Wagner-Matano interface move with respect to one another by amounts that are proportional to \( \sqrt{t} \) where \( t \) is time. We then relate this solution to an alternative description by Sauer and Freise [5] and show explicitly the relationship of the Wagner-Matano interface to the two Matano planes of Sauer and Freise which are fixed with respect to either end of the diffusion couple.

1 Diffusion Formalism

In this section we present the fundamental formalism that underlies diffusion. We first define diffusive fluxes and relate these to one another. These relationships are purely kinematical and hold irrespective of the form of the constitutive equations. Then we introduce constitutive equations and relate diffusivities. We do this in three dimensions and later specialize to one dimension.
1.1 General description of diffusion

**Observed fluxes** We first define observed fluxes of the species (atoms or molecules) of a multicomponent system. We consider a system with two chemical components (species) which we denote by $A$ and $B$.

The *observed flux* of a species, $i$, measured in units of moles $m^{-2} s^{-1}$, is given by

$$J_i := c_i v_i, \quad i = A, B$$

where $c_i$ is the concentration of species $i$, expressed in moles $m^{-3}$, and $v_i$ is the average velocity of species $i$, measured in $m/sec$ with respect to an arbitrary observer. Such a flux depends on the state of motion of the observer, or for an observer fixed in the laboratory, the local relative motion of a portion of the sample, either via motion of the whole sample and/or local flow within the sample. We emphasize that $c_i$ is *concentration* ("stuff" per unit volume), not *composition*, which would be measured in terms of the mole fractions $X := X_B := c_B/c$ and $1 - X = X_A := c_A/c$, where the total concentration (reciprocal of the molar volume) is $c := c_A + c_B$.

Alternatively, we could define observed mass-based fluxes

$$\tilde{J}_i := \rho_i v_i, \quad i = A, B$$

measured in kg $m^{-2} s^{-1}$, where $\rho_i$ is the partial density of species $i$, expressed in kg $m^{-3}$. Here again, we emphasize that $\rho_i$ is a type of *concentration* in the sense of "stuff" per unit volume; the corresponding *composition* would be expressed in terms of mass fractions, $\omega := \omega_B := \rho_B/\rho$ and $1 - \omega = \omega_A := \rho_A/\rho$, where the total density $\rho = \rho_A + \rho_B$.

Provided that each species has a non-vanishing molecular mass (molecular "weight") $m_i$, one has simply $\rho_i = m_i c_i$ and $\tilde{J}_i = m_i J_i$. If one treats a lattice model in which vacancies are considered to be a hypothetical species with zero molecular weight, the connection between a mole-based description and a mass-based description is more complicated. In the following, we limit ourselves to descriptions for which $m_i \neq 0$, in which case the only difference in these observed fluxes is the units in which they are measured.

**Diffusive fluxes** We now define diffusive fluxes, consistent with the notion that diffusion is *relative* motion of species and therefore must be independent of the state of motion of the observer. This requirement is met if the diffusive fluxes are expressed in terms of differences of velocity fields [7]

$$j_i^F := c_i(v_i - v^F) = J_i - c_i v^F$$

where $v^F$ is a velocity field, a vector quantity common to all species that can vary with position and time. The quantity $j_i^F$ is the diffusive flux, measured in moles $m^{-2} s^{-1}$, of species $i$ with respect to the field $v^F$.

We can also define a mass-based diffusive flux,

$$\tilde{j}_i^F := \rho_i(v_i - v^F) = \tilde{J}_i - \rho_i v^F$$

\(^1\)The notation $:= $ means “is defined to be equal to.” We use it to distinguish definitions from results.
Here, $\tilde{j}_i^F$ is the diffusive flux, measured in kg m$^{-2}$ s$^{-1}$, of species $i$ with respect to the field $\mathbf{v}^F$.

**Center of moles, center of mass** For the mole based description, a possible choice for the field $\mathbf{v}^F$ is the velocity field of the local center of moles,

$$\mathbf{v}^* := \frac{c_A \mathbf{v}_A + c_B \mathbf{v}_B}{c} = X_A \mathbf{v}_A + X_B \mathbf{v}_B. \quad (5)$$

The corresponding diffusive fluxes are

$$j_i := c_i (\mathbf{v}_i - \mathbf{v}^*), \quad (6)$$

so $j_A = -j_B$, as may be verified by adding Eq(6) for $A$ and $B$.

The parallel treatment for mass fluxes is to choose $\mathbf{v}^F$ to be the velocity field of the local center of mass (also known as the barycentric velocity)

$$\mathbf{v} := \frac{\rho_A \mathbf{v}_A + \rho_B \mathbf{v}_B}{\rho} = \omega_A \mathbf{v}_A + \omega_B \mathbf{v}_B. \quad (7)$$

The corresponding diffusive fluxes

$$\mathbf{j}_i = \rho_i (\mathbf{v}_i - \mathbf{v}) \quad (8)$$

so $\mathbf{j}_A = -\mathbf{j}_B$. The fluxes $\mathbf{j}_i$ and $\mathbf{j}_i^*$ are not only measured in different units but are measured with respect to different reference velocity fields, so they are not simply related. We can, however, relate them through the observed fluxes which obey $\mathbf{J}_i = m_i \mathbf{J}_i$. Thus

$$\rho_A \mathbf{v} + \mathbf{j}_A = m_A c_A \mathbf{v}^* + m_A \mathbf{j}_A \quad (9)$$
$$\rho_B \mathbf{v} + \mathbf{j}_B = m_B c_B \mathbf{v}^* + m_B \mathbf{j}_B.$$

Adding these equations and recalling that $\rho_i = m_i c_i$ leads to

$$\mathbf{v} - \mathbf{v}^* = \frac{m_B - m_A}{\rho} \mathbf{j}_B = \frac{1}{c} \left( \frac{1}{m_A} - \frac{1}{m_B} \right)^T \mathbf{j}_B. \quad (10)$$

Eq(10) shows that the relationship between $\mathbf{v}$ and $\mathbf{v}^*$ is purely diffusive, and further relates the diffusive fluxes by

$$j_A = \frac{\rho}{c} \frac{\mathbf{j}_A}{m_A m_B}; \quad j_B = \frac{\rho}{c} \frac{\mathbf{j}_B}{m_A m_B} \quad (11)$$

which hold even though the ratio

$$\frac{\rho}{c} = m_A + (m_B - m_A)X = \frac{1}{m_A^{-1} + (m_B^{-1} - m_A^{-1}) \omega} \quad (12)$$

varies with composition.
Center of volume  Another common choice for the field $v^F$ is the velocity field of the local center of volume, which we denote by $v^\Box$. In order to define this field, we note that for a homogeneous system, the differential of the volume is given by

$$
\frac{dV}{V} = \frac{N_A}{M_A} \frac{dM_A}{N_B} = \frac{\beta d\rho}{\beta} + \frac{\alpha dT}{\alpha}
$$

where $N_A$ and $N_B$ are mole numbers of $A$ and $B$, $M_A$ and $M_B$ are masses of $A$ and $B$, $\rho$ is the pressure, $T$ is the temperature, $\beta$ is the isothermal compressibility, and $\alpha$ is the isobaric coefficient of expansion. The coefficients $\tilde{V}_i$ are partial molar volumes and $\tilde{V}_i$ are partial specific volumes, related by the molecular weights such that $\tilde{V}_i = \frac{m_i}{\rho_i}$. Since $V$ is a homogeneous function of degree one in the $N_i$ or the $M_i$, Eq(13) can be integrated by Euler’s theorem$^2$ to give

$$
V = \tilde{V}_A N_A + \tilde{V}_B N_B = \tilde{V}_A M_A + \tilde{V}_B M_B
$$

which holds even when the partial volumes are variables. Division by $V$ yields

$$
1 = \tilde{V}_A c_A + \tilde{V}_B c_B = \tilde{V}_A \rho_A + \tilde{V}_B \rho_B
$$

which are assumed to hold locally, even for an inhomogeneous system.

We now define the velocity field of the local center of volume$^3$ by

$$
v^\Box := \tilde{V}_A c_A v_A + \tilde{V}_B c_B v_B = \tilde{V}_A \rho_A v_A + \tilde{V}_B \rho_B v_B.
$$

The corresponding diffusive fluxes for moles are

$$
j_i^\Box := c_i (v_i - v^\Box)
$$

and $\tilde{V}_A j_A^\Box = -\tilde{V}_B j_B^\Box$. Similarly for the diffusive mass fluxes

$$
j_i^\Box := \rho_i (v_i - v^\Box)
$$

and $\tilde{V}_A j_A^\Box = -\tilde{V}_B j_B^\Box$. Because the reference velocity field is the same for both of these diffusive fluxes, they are simply related by

$$
j_A^\Box = \frac{j_A}{m_A}; \quad j_B^\Box = \frac{j_B}{m_B}.
$$

Relationship of $v^\Box$ to $v^*$ and $v$  We can relate $v^\Box$ to $v^*$ by equating observed fluxes to obtain

$$
c_A v^* + j_A = c_A v^\Box + j_A^\Box
$$

$$
c_B v^* + j_B = c_B v^\Box + j_B^\Box.
$$

$^2$If $f(x_1, x_2, \ldots, x_n) = \lambda^nf(x_1, x_2, \ldots, x_n)$, the function $f$ is said to be homogeneous of degree $n$ in the variables $x_1, x_2, \ldots, x_n$. Then Euler’s theorem states that $nf = \sum_{i=1}^n x_i (\partial f/\partial x_i)$.

$^3$The relationship to a physical center of volume should not be taken too seriously because the partial volumes are defined as derivatives, and one of them can even be negative. If the partial volumes are constants, a physical interpretation is possible.
Adding these equations gives

\[ \mathbf{v}^\square - \mathbf{v}^* = -\frac{(\mathbf{j}_A^\square + \mathbf{j}_B^\square)}{c} = \frac{(\tilde{V}_B - \tilde{V}_A)\mathbf{j}_B^\square}{cV_A} \]  

(21)

whereas multiplying the first equation by \( \tilde{V}_A \) and the second by \( \tilde{V}_B \) and adding gives

\[ \mathbf{v}^\square - \mathbf{v}^* = \tilde{V}_A\mathbf{j}_A + \tilde{V}_B\mathbf{j}_B = (\tilde{V}_B - \tilde{V}_A)\mathbf{j}_B. \]  

(22)

Therefore the difference between \( \mathbf{v}^\square \) and \( \mathbf{v}^* \) is purely diffusive, and comparison of Eq(21) with Eq(22) leads to

\[ \mathbf{j}_A = \frac{\mathbf{j}_A^\square}{cV_B}; \quad \mathbf{j}_B = \frac{\mathbf{j}_B^\square}{cV_A}. \]  

(23)

In a similar way, for the mass fluxes, we obtain

\[ \mathbf{v}^\square - \mathbf{v} = \frac{(\tilde{V}_B - \tilde{V}_A)\mathbf{j}_B^\square}{\rho V_A} = (\tilde{V}_B - \tilde{V}_A)\mathbf{j}_B. \]  

(24)

and

\[ \mathbf{j}_A = \frac{\mathbf{j}_A^\square}{\rho V_B}; \quad \mathbf{j}_B = \frac{\mathbf{j}_B^\square}{\rho V_A}. \]  

(25)

**Solvent field**  Another possible choice for the field \( \mathbf{v}^F \) is \( \mathbf{v}_A \) itself, regarded to be the solvent, with species \( B \) as solute. This leads to a single diffusive flux

\[ \mathbf{j}_B^S := c_B(\mathbf{v}_B - \mathbf{v}_A) = \frac{1}{1 - X} \mathbf{j}_B = \frac{1}{c_A V_A} \mathbf{j}_B^\square \]  

(26)

for the mole based description and

\[ \mathbf{j}_B^S := \rho_B(\mathbf{v}_B - \mathbf{v}_A) = \frac{1}{1 - \omega} \mathbf{j}_B = \frac{1}{\rho_A V_A} \mathbf{j}_B^\square \]  

(27)

for the mass based description. Such a description would only be useful if \( \mathbf{v}_A \) could be determined independently. For example, if species \( A \) in a solid were substitutional and immobile on a rigid lattice and species \( B \) were a mobile interstitial, its motion would be described completely by \( \mathbf{j}_B^S \).

**Lattice or marker field**  We could also choose the field \( \mathbf{v}^F \) to be the local velocity \( \mathbf{v}^L \) of a crystal lattice (not necessarily a rigid lattice) or the velocity \( \mathbf{v}^M \) of inert markers (which might very well move with the lattice). The formalism is the same in either case, so we illustrate it for \( \mathbf{v}^M \) and for the mole based description. The diffusive fluxes relative to markers are

\[ \mathbf{j}_i^M := c_i(\mathbf{v}_i - \mathbf{v}^M). \]  

(28)

Equating observed fluxes gives

\[ c_A \mathbf{v}^M + \mathbf{j}_A^M = c_A \mathbf{v}^* + \mathbf{j}_A \]  

(29)

\[ c_B \mathbf{v}^M + \mathbf{j}_B^M = c_B \mathbf{v}^* + \mathbf{j}_B \]
and adding these equations leads to

\[ \mathbf{v}^M - \mathbf{v}^* = -\frac{(\mathbf{j}_A^M + \mathbf{j}_B^M)}{c}. \]  

(30)

This yields

\[ \mathbf{j}_A = c_A(\mathbf{v}_A - \mathbf{v}^*) = c_A(\mathbf{v}_A - \mathbf{v}^M) + c_A(\mathbf{v}^M - \mathbf{v}^*) = \mathbf{j}_A^M - \frac{c_A(\mathbf{j}_A^M + \mathbf{j}_B^M)}{c}. \]  

(31)

Thus

\[ \mathbf{j}_A = X_B \mathbf{j}_A^M - X_A \mathbf{j}_B^M \]  

(32)

\[ \mathbf{j}_B = -X_B \mathbf{j}_A^M + X_A \mathbf{j}_B^M \]

and

\[ \mathbf{j}_A = c\mathbf{V}_B(X_B \mathbf{j}_A^M - X_A \mathbf{j}_B^M) \]  

(33)

\[ \mathbf{j}_B = c\mathbf{V}_A(-X_B \mathbf{j}_A^M + X_A \mathbf{j}_B^M). \]

Note, however, that it is not possible to solve Eq(32) and Eq(33) for \( \mathbf{j}_A^M \) and \( \mathbf{j}_B^M \) because the determinant of the matrix of their coefficients is zero. This arises because \( \mathbf{j}_A^M \) and \( \mathbf{j}_B^M \) have been introduced as independent fluxes. They can only be related by a detailed theory of marker motion or given by postulated constitutive equations in terms of intrinsic diffusivities, as discussed in the next section.

We emphasize that these relationships among diffusive fluxes are purely kinematical and independent of constitutive equations.

### 1.2 Constitutive equations

In order to give a complete description of diffusion, we must close the problem by providing a methodology to calculate the fluxes from the mole or mass densities or compositions. This is accomplished by constitutive equations that relate the fluxes to gradients of suitable potentials, and ultimately to gradients of mole density, mass density or composition. Such constitutive equations are often postulated on purely empirical grounds, e.g., Fick’s first law. Alternatively, they can be rationalized on the basis of irreversible thermodynamics. We examine briefly their rationalization, but ultimately adopt them as laws that must be validated by experiment.

**Basis in irreversible thermodynamics**  We consider diffusion in an *isothermal* fluid in terms of a mass based description with diffusion fluxes \( \mathbf{j}_i = \rho_i(\mathbf{v}_i - \mathbf{v}) \) as in Eq(8). Considerations of entropy production and the assumption of a linear relationship between fluxes and thermodynamic forces leads to [8,9]

\[ \mathbf{j}_A = -\tilde{L}_{AA}(\nabla \mu_A - \mathbf{g}_A) - \tilde{L}_{AB}(\nabla \mu_B - \mathbf{g}_B) \]  

(34)

\[ \mathbf{j}_B = -\tilde{L}_{BA}(\nabla \mu_A - \mathbf{g}_A) - \tilde{L}_{BB}(\nabla \mu_B - \mathbf{g}_B) \]
where the $\mu_i$ are (intrinsic) chemical potentials per unit mass and the $g_i$ are species specific external forces per unit mass. For these forces and fluxes [8], the mobility matrix $\bar{L}_{ij}$ has Onsager symmetry, and since $\bar{j}_A + \bar{j}_B = 0$ for these fluxes, the assumption of independent driving forces $\nabla \mu_A - g_A$ and $\nabla \mu_B - g_B$ leads to $\bar{L}_{AA} = -\bar{L}_{BA} = -\bar{L}_{AB} = \bar{L}_{BB}$. Thus Eq(34) contains only one mobility coefficient which we call $\bar{L}$ and can be written in the form

$$\bar{j}_B = -\bar{L} [\nabla (\mu_B - \mu_A) - (g_B - g_A)]$$

(35)

with $\bar{j}_A = -\bar{j}_B$. If the forces per unit mass are due to gravity, which we shall assume, then $g_A = g_B = g$, and we are left with

$$\bar{j}_B = -\bar{L} \nabla (\mu_B - \mu_A) = -\bar{L} \left[ \frac{\partial(\mu_B - \mu_A)}{\partial \omega} \nabla \omega + \frac{\partial(\mu_B - \mu_A)}{\partial p} \nabla p \right].$$

(36)

If $g$ is the Gibbs free energy per unit mass, then $\mu_B - \mu_A = \partial g/\partial \omega$ and Eq(36) can be written

$$\bar{j}_B = -\bar{L} \left[ \frac{\partial^2 g}{\partial \omega^2} \nabla \omega + (V_B - V_A) \nabla p \right]$$

(37)

where we have also identified the pressure derivative. Under many circumstances, the effect of a pressure gradient on the diffusion flux can be neglected relative to that due to the gradient of composition; for an estimate see Appendix B of [10]. We proceed as is customary to neglect the pressure gradient term and adopt a flux law of the form

$$\bar{j}_B = -\rho \bar{D} \nabla \omega$$

(38)

where the diffusivity $\bar{D} = (\bar{L}/\rho)\partial^2 g/\partial \omega^2$. Provided that $\rho$ and $\bar{D}$ are treated as variables, there is no loss of generality in having the density $\rho$ appear explicitly in Eq(38). As we shall see, this choice will result in $\bar{D}$ being the diffusivity in the center of volume description, in accord with common notation.

**Constitutive relations for all fluxes** Whether motivated by irreversible thermodynamics or postulated on empirical grounds, we adopt Eq(38) for the diffusive flux of mass relative to the velocity field of the local center of mass. Then by Eqs(11,19,23,25,26,27) we can write constitutive relations for all of the other fluxes.

From Eq(11) we obtain

$$\bar{j}_B = -\frac{\rho^2}{c m_A m_B} \bar{D} \nabla \omega.$$  

(39)

By taking the derivative of Eq(12), we obtain $d\omega/dX = m_A m_B c^2/\rho^2$, which enables Eq(39) to be rewritten in the form

$$\bar{j}_B = -c \bar{D} \nabla X$$

(40)

which should be compared with Eq(38). Then from Eqs(26,27) we obtain

$$\bar{j}_S = -\frac{\rho}{1-\omega} \bar{D} \nabla \omega$$

(41)

$$\bar{j}_B = -\frac{c}{1-\omega} \bar{D} \nabla X$$

(40)
which are consistent with Wagner’s equation \[4\]

\[
\mathbf{v}_A - \mathbf{v}_B = \mathcal{D} \frac{\nabla \omega}{\omega(1 - \omega)} = \mathcal{D} \frac{\nabla X}{X(1 - X)} \tag{42}
\]

which he used as a definition of \(\mathcal{D}\).

For the diffusive fluxes with respect to \(\mathbf{v}\), Eq(23) and Eq(25) give

\[
\begin{align*}
\mathbf{j}_B^\mathcal{D} & = -c^2 \mathbf{V}_A \mathcal{D} \nabla X \\
\mathbf{j}_B^\mathcal{\Omega} & = -\rho^2 \mathbf{V}_A \mathcal{D} \nabla \omega
\end{align*} \tag{43}
\]

which, although correct, are not in their usual form. To obtain such a form, we return to Eq(13) for an isothermal system and also neglect the term in \(\beta\) to get

\[
d\mathbf{V} = \mathbf{\bar{V}}_A d\mathbf{N}_A + \mathbf{\bar{V}}_B d\mathbf{N}_B = M_A d\mathbf{M}_A + M_B d\mathbf{M}_B. \tag{44}\]

In order to justify Eq(44), some researchers claim to be working at constant pressure, but having no way to control the pressure internally (which might well be a driving force for fluid convection) we prefer to claim that the compressibility \(\beta\) is small for condensed systems, to which we confine our analysis. Comparison of Eq(44) with the differential of Eq(14) then gives

\[
0 = N_A d\mathbf{V}_A + N_B d\mathbf{V}_B = M_A d\mathbf{M}_A + M_B d\mathbf{M}_B. \tag{45}\]

which can be divided by \(\mathbf{V}\) to give

\[
0 = c_A d\mathbf{V}_A + c_B d\mathbf{V}_B = \rho_A d\mathbf{M}_A + \rho_B d\mathbf{M}_B. \tag{46}\]

Comparison of Eq(46) with the differential of Eq(16) then gives

\[
0 = \mathbf{\bar{V}}_A d\mathbf{c}_A + \mathbf{\bar{V}}_B d\mathbf{c}_B = \mathbf{\bar{V}}_A d\rho_A + \mathbf{\bar{V}}_B d\rho_B. \tag{47}\]

Eqs(46,47) are assumed to hold locally. Thus

\[
\begin{align*}
dX & = d \left( \frac{c_B}{c} \right) = \frac{dc_B}{\mathbf{V}_A c^2} \\
d\omega & = d \left( \frac{\rho_B}{\rho} \right) = \frac{d\rho_B}{\mathbf{V}_A \rho^2}. \tag{48}\end{align*}
\]

Eqs(43) therefore lead to

\[
\begin{align*}
\mathbf{j}_A^\mathcal{D} & = -\mathcal{D} \nabla c_A; & \mathbf{j}_B^\mathcal{D} & = -\mathcal{D} \nabla c_B \\
\mathbf{j}_A^\mathcal{\Omega} & = -\mathcal{D} \nabla \rho_A; & \mathbf{j}_B^\mathcal{\Omega} & = -\mathcal{D} \nabla \rho_B \tag{50}\end{align*}
\]

and

\[
\begin{align*}
\mathbf{j}_A^\mathcal{\Omega} & = -\mathcal{D} \nabla \rho_A; & \mathbf{j}_B^\mathcal{\Omega} & = -\mathcal{D} \nabla \rho_B \tag{51}\end{align*}
\]

which have the forms of Fick’s law.

\[\text{This relationship implies that } d\omega/dX = \omega(1 - \omega)/[X(1 - X)] \text{ which is not obvious from Eq(12) but can be verified by taking the logarithmic derivative of } \omega/(1 - \omega) = (m_B/m_A)[X/(1 - X)].\]
Marker diffusivities Following Darken [11], we postulate constitutive equations for the diffusive fluxes relative to markers of the form

\[ j_M^A = -D_M^A \nabla c_A; \quad j_M^B = -D_M^B \nabla c_B \] (52)

where the diffusivities \( D_M^A \) and \( D_M^B \) are marker diffusivities. Such constitutive equations might be rationalized on the basis of atomistic hopping models. The fact that \( \nabla c_A = -(\bar{V}_B/\bar{V}_A) \nabla c_B \) makes them quite general, even though it appears superficially that \( j_M^A \) is driven only by \( \nabla c_A \) and \( j_M^B \) is driven only by \( \nabla c_B \). Substitution into Eq(32) leads to

\[ j_B = X_B D_M^A \nabla c_A - X_A D_M^B \nabla c_B = -c(c_B \bar{V}_B D_M^A + c_A \bar{V}_A D_M^B)\nabla X \] (53)

and similarly

\[ j_B^\square = -(c_B \bar{V}_B D_M^A + c_A \bar{V}_A D_M^B)\nabla c_B. \] (54)

Comparison of Eq(53) with Eq(40) and Eq(54) with Eq(50) reveals that

\[ \mathcal{D} = c_B \bar{V}_B D_M^A + c_A \bar{V}_A D_M^B \] (55)

which is a generalization of Darken’s well-known result \( \mathcal{D} = X_B D_M^A + X_A D_M^B \), which is based on \( \bar{V}_A = \bar{V}_B \).

As pointed out to the author by P. K. Gupta [12], one could also write constitutive relations of the form

\[ \dot{j}_A^M = -c D_M^{MG} \nabla X_A; \quad \dot{j}_B^M = -c D_B^{MG} \nabla X_B. \] (56)

In view of Eq(48) these are equivalent to Eq(52) provided that the diffusivities are related by \( D_M^{MG} = D_M^A \bar{V}_B \) and \( D_B^{MG} = D_B^M \bar{V}_A \). Substitution into Eq(55) then gives

\[ \mathcal{D} = X_B D_M^{MG} + X_A D_B^{MG} \] (57)

which has the same form of Darken’s original result. Note, however, that Eq(57) is expressed in terms of different marker diffusivities than used by Darken. In the special case \( \bar{V}_A = \bar{V}_B = 1/c \), we have \( D_A^{MG} = D_A^M \) and \( D_B^{MG} = D_B^M \), and these diffusivities are the same as those of Darken.

1.3 Conservation laws

Provided that there are no chemical reactions (which we assume throughout these notes), each species is conserved, as expressed by equations of the form

\[ \frac{\partial c_i}{\partial t} + \nabla \cdot \mathbf{J}_i = 0 \] (58)

for the mole-based description, or

\[ \frac{\partial \rho_i}{\partial t} + \nabla \cdot \mathbf{\bar{J}}_i = 0 \] (59)
for the mass-based description, where \( t \) is time and \( \nabla \) is the gradient operator in the reference frame of an arbitrary observer. These equations resemble what is referred to as Fick’s second law, but we emphasize that they are in terms of observed fluxes, not diffusive fluxes. If Eq(58) and Eq(59) are each summed for \( A \) and \( B \), we obtain the continuity equations

\[
\frac{\partial c}{\partial t} + \nabla \cdot (c \mathbf{v}^*) = 0 \\
\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) = 0
\]

which are overall conservation equations for total moles and total mass, respectively. The system can then be described by any pair of independent equations, for example Eq(61) and Eq(59) for species \( B \).

**Diffusion equations** To get diffusion equations, we must introduce diffusive fluxes by means of Eq(3) or Eq(4), which requires specification of the field \( \mathbf{v}^F \), and then substitute into Eq(58) or Eq(59). This gives:

\[
\frac{\partial c_i}{\partial t} + \nabla \cdot (c_i \mathbf{v}^F) + \nabla \cdot \mathbf{j}_i^F = 0 \\
\frac{\partial \rho_i}{\partial t} + \nabla \cdot (\rho_i \mathbf{v}^F) + \nabla \cdot \mathbf{j}_i^F = 0
\]

We have explored several possible choices of \( \mathbf{v}^F \). The general strategy is to make a choice that will simplify the problem of interest. For the choices \( \mathbf{v}^* \) for the mole description and \( \mathbf{v} \) for the mass description, Eqs(62,63) can be simplified by using Eq(60,61) to obtain

\[
c \left[ \frac{\partial X}{\partial t} + \mathbf{v}^* \cdot \nabla X \right] - \nabla \cdot (cD \nabla X) = 0 \\
\rho \left[ \frac{\partial \omega}{\partial t} + \mathbf{v} \cdot \nabla \omega \right] - \nabla \cdot (\rho D \nabla \omega) = 0.
\]

For the choice \( \mathbf{v}^F = \mathbf{v}^\Box \), we proceed to develop the mass based case, that for moles being similar. Eqs(63) become

\[
\frac{\partial \rho_A}{\partial t} + \nabla \cdot (\rho_A \mathbf{v}^\Box - D \nabla \rho_A) = 0 \\
\frac{\partial \rho_B}{\partial t} + \nabla \cdot (\rho_B \mathbf{v}^\Box - D \nabla \rho_B) = 0.
\]

We multiply the first of these by \( \nabla \mathbf{V}_A \) and the second by \( \nabla \mathbf{V}_B \), add the results, and simplify by using Eq(46) and Eq(47) to obtain

\[
\nabla \cdot \mathbf{v}^\Box = \nabla \cdot \mathbf{j}_A^\Box + \nabla \cdot \mathbf{j}_B^\Box = - \frac{D}{\rho_B \nabla \rho_B} \nabla \rho_A \cdot \nabla \mathbf{V}_A.
\]

For the case in which \( \mathbf{V}_A \) (and therefore also \( \mathbf{V}_B \)) is a constant, one has

\[
\nabla \cdot \mathbf{v}^\Box = 0
\]
which can be integrated to give
\[ \mathbf{v} = \nabla \times \mathbf{A} \]  \hspace{1cm} (69)
where \( \mathbf{A} \) is some vector field. In other words, \( \mathbf{v} \) is solenoidal\(^5\) and has no sources or sinks. This results in the total volume of the system being constant, which can be demonstrated as follows: If \( M_A \) and \( M_B \) are the total masses of the system, then
\[ M_A = \int_V \rho_A d^3x; \quad M_B = \int_V \rho_B d^3x \]  \hspace{1cm} (70)
For constant partial specific volumes, we can multiply the first of these by \( \tilde{V}_A \) and the second by \( \tilde{V}_B \) and add to get
\[ \text{constant} = \tilde{V}_A M_A + \tilde{V}_B M_B = \int_V (\tilde{V}_A \rho_A + \tilde{V}_B \rho_B) d^3x = V \]  \hspace{1cm} (71)
where Eq(15) has been used in the last step. For the special case of \( \mathbf{A} = (1/2) \mathbf{B}(t) \times \mathbf{r} \) where \( \mathbf{B}(t) \) is a vector that depends on time but not on space, Eq(69) yields simply
\[ \mathbf{v} = \mathbf{B}(t) \]  \hspace{1cm} (72)
and the vector field \( \mathbf{v} \) becomes a rigid moving frame. We can then choose the observer’s frame to move with the sample such that \( \mathbf{v} = 0 \). This enables Eq(66) to take the simple form
\[ \frac{\partial \rho_A}{\partial t} - \nabla \cdot (\mathbf{D} \nabla \rho_A) = 0 \]  \hspace{1cm} (73)
\[ \frac{\partial \rho_B}{\partial t} - \nabla \cdot (\mathbf{D} \nabla \rho_B) = 0 \]
which is often assumed to hold without justification. For constant partial specific volumes, such a simplification is always possible, but in more than one dimension, \( \mathbf{v} \) can be more complicated, consistent with Eq(69).

2 One Dimensional Diffusion Couple

In this section, we examine the problem of a strictly one dimensional diffusion couple, for which the only spatial variable is \( x \). This is a non-trivial simplification which can only be approximated in certain real experiments. For a solid, the cross section of the sample would have to remain constant throughout the diffusion process, although the sample could lengthen or shorten along \( x \). This might be approximately true for a sufficiently thick sample. For a liquid in a cylinder with pressurized movable end caps, one might maintain a constant cross section but it would seem to be very difficult to prevent buoyancy driven convection, which would be intrinsically multidimensional. Even in strictly zero gravity, the no slip condition at the container walls would result in multidimensional flows as the total volume of the system changes.

\(^5\)A “solenoidal” vector field forms closed loops, as do the lines of the magnetic field \( \mathbf{B} \) for a solenoid.
We shall proceed to treat a diffusion couple with left end located at \( x_L(t) \) and right end at \( x_R(t) \), as measured by an observer. In the treatment of this problem by Sauer and Freise [5], the observer is in a frame fixed with respect to either the right end or the left end of the couple, which are located in that frame at \( -\infty \) and \( \infty \), respectively. We will also treat a very long couple in the sense that \( x_R(t) - x_0(t) \) and \( x_0(t) - x_L(t) \) are both assumed to be very large compared to \( \sqrt{Dt} \), where \( x_0(t) \), which will turn out to be the location of the Matano interface, is somewhere within the couple such that the initial discontinuity of composition is at \( x_0(0) \). This will allow us to make a correspondence between Wagner’s treatment, which is based on a unique Matano interface (hereafter the Wagner-Matano or WM interface) and the two Matano planes of Sauer and Freise, one fixed in a frame that moves with \( x_L(t) \) and the other fixed in a frame that moves with \( x_R(t) \).

2.1 Lagrangian Transformation

We use a mass based description of diffusion (the mole treatment is similar) and take the governing equations in the form

\[
\rho \left[ \frac{\partial \omega}{\partial t} + v \frac{\partial \omega}{\partial x} \right] = \frac{\partial}{\partial x} \left( \rho D \frac{\partial \omega}{\partial x} \right) \tag{74}
\]

\[
\frac{\partial \rho}{\partial t} + \frac{\partial (\rho v)}{\partial x} = 0 \tag{75}
\]

which are the one dimensional versions of Eq(65) and Eq(61). As suggested by den Broeder [1], we make a transformation to a new variable \( n(x,t) \). Although den Broeder stated that \( dn = \rho dx \), this is insufficient to define \( n \) so we proceed to specify

\[
\left( \frac{\partial n}{\partial x} \right)_t = \rho(x,t); \quad \left( \frac{\partial n}{\partial t} \right)_x = -\rho(x,t)v(x,t). \tag{76}
\]

Then by means of Eq(75) we have

\[
\frac{\partial^2 n}{\partial t \partial x} = \frac{\partial^2 n}{\partial x \partial t} \tag{77}
\]

which is necessary for \( dn \) to be an exact differential. This defines \( n \) up to an additive constant.\(^6\) From the differential

\[
dn = \rho(x,t)dx - \rho(x,t)v(x,t)dt \tag{78}
\]

we deduce that

\[
v(x,t) = \left( \frac{\partial x}{\partial t} \right)_n \tag{79}
\]

so that

\[
\left( \frac{\partial \omega}{\partial t} \right)_n = \left( \frac{\partial \omega}{\partial t} \right)_x + \left( \frac{\partial \omega}{\partial x} \right)_t \left( \frac{\partial x}{\partial t} \right)_n = \left( \frac{\partial \omega}{\partial t} \right)_x + v \left( \frac{\partial \omega}{\partial x} \right)_t \tag{80}
\]

\(^6\)We could replace \( n \) by \( \chi \rho_0 \) where \( \rho_0 \) is a constant with dimensions of density. Then the new variable \( \chi \) would have dimensions of length, and this transformation would more nearly resemble a transformation to Lagrangian coordinates.
which appears on the left hand side of Eq(74). Likewise

\[ \rho \left( \frac{\partial}{\partial n} \right) = \left( \frac{\partial}{\partial x} \right) \]

so Eq(74) becomes, after cancellation of a factor of \( \rho \neq 0 \),

\[ \left( \frac{\partial \omega}{\partial t} \right) = \frac{\partial}{\partial n} \left( \rho^2 D \frac{\partial \omega}{\partial n} \right) \]

which is a diffusion equation with an effective diffusivity \( \rho^2 D \) but without a convective term.\(^7\)

We proceed to obtain a first integral of Eq(82) for a very long diffusion couple with initial condition

\[ \omega(x, 0) = \begin{cases} \omega^- & \text{for } x < x_{00} \\ \omega^+ & \text{for } x > x_{00} \end{cases} \]

where \( x_{00} \) is a constant. Then by Boltzmann’s scaling argument,

\[ \omega = \tilde{\omega}(\lambda); \quad \lambda := \frac{(n - n_0)}{\sqrt{t}} \]

where \( n_0 \) is a constant, independent of both \( x \) and \( t \). We note that \( \rho \) and \( D \) depend only on \( \omega \), and hence also on \( \lambda \). Thus after cancellation of a factor of \( 1/t \), Eq(82) takes the form

\[ -\frac{\lambda}{2} \frac{d\tilde{\omega}}{d\lambda} = \frac{d}{d\lambda} \left( \rho^2 D \frac{d\tilde{\omega}}{d\lambda} \right). \]

**Wagner-Matano interface** We integrate Eq(85) from \( \lambda_L := (n_L - n_0)/\sqrt{t} \approx -\infty \) to \( \lambda_R := (n_R - n_0)/\sqrt{t} \approx \infty \) where \( n_L(t) = n(x_L(t), t) \) and \( n_R(t) = n(x_R(t), t) \) correspond to the left and right ends of the diffusion couple. This yields

\[ \int_{\lambda_L}^{\lambda_R} \lambda \frac{d\tilde{\omega}}{d\lambda} d\lambda = 0 \]

where we have used \( d\tilde{\omega}/d\lambda = 0 \) at \( \lambda = \lambda_L \) and \( \lambda = \lambda_R \). We proceed to evaluate Eq(86) by breaking the integral at \( \lambda = 0 \) and integrating by parts to obtain

\[ \int_{\lambda_L}^{\lambda_R} \lambda \frac{d\tilde{\omega}}{d\lambda} d\lambda = \int_{\lambda_L}^{0} \lambda \frac{d(\tilde{\omega} - \omega^-)}{d\lambda} d\lambda + \int_{0}^{\lambda_R} \lambda \frac{d(\tilde{\omega} - \omega^+)}{d\lambda} d\lambda \\
= -\int_{\lambda_L}^{0} (\tilde{\omega} - \omega^-) d\lambda - \int_{0}^{\lambda_R} (\tilde{\omega} - \omega^+) d\lambda. \]

Thus

\[ \int_{\lambda_L}^{0} (\tilde{\omega} - \omega^-) d\lambda + \int_{0}^{\lambda_R} (\tilde{\omega} - \omega^+) d\lambda = 0, \]

\(^7\)If \( \chi \) had been used instead of \( n \), the effective diffusivity would have been \( (\rho/\rho_0)^2 D \), which has the usual units of a diffusivity.
where we recall that $\lambda_L \approx -\infty$ and $\lambda_R \approx \infty$ but choose to retain the finite values for assistance in conversion to an integral over $x$ and to other representations.

Indeed, the transformation from $(n, t)$ to $(x, t)$ can be written in the form

$$x(n, t) - x_0(t) = \int_{n_0}^{n} \left( \frac{\partial x}{\partial n'} \right)_t \, dn' = \int_{n_0}^{n} \frac{1}{\bar{\rho}(n', t)} \, dn' = \sqrt{t} \int_0^{\lambda} \frac{1}{\bar{\rho}(\lambda')} \, d\lambda' \quad (89)$$

where $x_0(t) \equiv x(n_0, t)$ and $\bar{\rho}(\lambda) := \bar{\rho}(n, t) = \rho(x, t)$. Eq(89) shows that

$$\lambda_x := \frac{x - x_0(t)}{\sqrt{t}} = h(\lambda) \quad (90)$$

where $h(\lambda)$ is an isotonic function of $\lambda$. Relating back to the initial conditions Eq(83) we see that $x_{00} = x_0(0) = x(n_0, 0)$. Thus $\bar{\omega}(n, t) = \bar{\omega}(\lambda) = \omega(\lambda_x) = \omega(x, t)$ and Eq(88) can be transformed at any fixed $t$ to

$$\int_{x_L(t)}^{x_0(t)} \rho(\omega - \omega^-) \, dx + \int_{x_0(t)}^{x_R(t)} \rho(\omega - \omega^+) \, dx = 0 \quad (91)$$

where we have used $d\lambda = (1/\sqrt{t})(\partial(n - n_0)/\partial x) \, dx = (\rho/\sqrt{t}) \, dx$. Eq(91) is equivalent to Eq(5) of Wagner (with a corrected relative sign between his integrals) which was stated without derivation. We regard it as defining a unique Wagner-Matano (WM) interface located at $x_0(t)$. If the weighting factor of $\rho$ in the integrals were a constant, one would obtain the usual Matano interface.

**Formula for $D$** To obtain a formula for the diffusivity $D$ that is independent of the location of the Matano interface (Eq(4.12) of Sauer and Freise [5], Eq(14) of Wagner [4], Eq(9) of den Broeder [1]) in a simple way, we proceed as follows. We integrate Eq(85) from $\lambda_L$ to $\lambda^*$ and then from $\lambda^*$ to $\lambda_R$ to obtain the pair of equations

$$-\frac{1}{2} \int_{\lambda_L}^{\lambda^*} \lambda \frac{\partial \bar{\omega}}{\partial \lambda} \, d\lambda = \left( \rho^2 D \frac{d\bar{\omega}}{d\lambda} \right)_{\lambda^*} \quad (92)$$

$$-\frac{1}{2} \int_{\lambda^*}^{\lambda_R} \lambda \frac{\partial \bar{\omega}}{\partial \lambda} \, d\lambda = - \left( \rho^2 D \frac{d\bar{\omega}}{d\lambda} \right)_{\lambda^*} \quad (93)$$

We then integrate by parts as above to obtain

$$\lambda^*(\bar{\omega}^* - \omega^-) - \int_{\lambda_L}^{\lambda^*} (\bar{\omega} - \omega^-) \, d\lambda = -2 \left( \rho^2 D \frac{d\bar{\omega}}{d\lambda} \right)_{\lambda^*} \quad (93)$$

$$-\lambda^*(\bar{\omega}^* - \omega^+) - \int_{\lambda^*}^{\lambda_R} (\bar{\omega} - \omega^+) \, d\lambda = 2 \left( \rho^2 D \frac{d\bar{\omega}}{d\lambda} \right)_{\lambda^*} \quad (93)$$

where $\bar{\omega}^* := \bar{\omega}(\lambda^*)$. We multiply the first of Eqs(93) by $(\bar{\omega}^* - \omega^+)$ and the second by $(\bar{\omega}^* - \omega^-)$ and add the resulting equations to get

$$-(\bar{\omega}^* - \omega^+) \int_{\lambda_L}^{\lambda^*} (\bar{\omega} - \omega^-) \, d\lambda - (\omega^* - \omega^-) \int_{\lambda^*}^{\lambda_R} (\bar{\omega} - \omega^+) \, d\lambda = 2(\omega^+ - \omega^-) \left( \rho^2 D \frac{d\bar{\omega}}{d\lambda} \right)_{\lambda^*} \quad (94)$$

---

8For brevity, we use the same functional notation for the corresponding function of one or two variables, either $(n, t)$ or $\lambda$ with a tilde, or $(x, t)$ and $\lambda_x$ without a tilde.
Eq(94) can be simplified by introducing the dimensionless composition

\[
\bar{Y} := \frac{\bar{\omega} - \omega^-}{\omega^+ - \omega^-}
\]

(95)

to obtain

\[
(1 - \bar{Y}^*) \int_{\lambda_*}^{\lambda_*} \bar{Y} d\lambda + \bar{Y}^* \int_{\lambda_*}^{\lambda_*} (1 - \bar{Y}) d\lambda = 2(\bar{\rho}^*)^2 \bar{D}^* \frac{d\bar{Y}^*}{d\lambda^*}
\]

(96)

where \( \bar{Y}^* \), \( \bar{\rho}^* \) and \( \bar{D}^* \) are the corresponding values of \( Y \), \( \rho \) and \( D \) at \( \lambda = \lambda^* \). We then convert Eq(96) for any fixed time to an integral over \( x \) to obtain

\[
D^* = \frac{(1 - Y^*) \int_{x_L(t)}^{x_R(t)} \rho Y dx + Y^* \int_{x_L(t)}^{x_R(t)} \rho (1 - Y) dx}{2 \rho^* t (\partial Y^*/\partial x^*)_t}
\]

(97)

where \( Y(x, t) = (\omega(x, t) - \omega^-)/(\omega^+ - \omega^-) \), \( Y^* = Y(x^*, t) \), and \( D^* \) and \( \rho^* \) are the corresponding values of \( D \) and \( \rho \) at composition \( \omega(x^*, t) \). Here, \( x^* \) is related to \( \lambda^* \) through Eq(90), although it can be chosen to lie anywhere between \( x_L(t) \) and \( x_R(t) \) when applying Eq(97). We note that Eq(97) is independent of the location \( x_0(t) \) of the Wagner-Matano interface, which makes it very useful.

**Relative motion of \( x_L(t) \), \( x_0(t) \) and \( x_R(t) \)** Our diffusion couple is assumed to be so long that the compositions at the ends of the couple are practically unchanged for diffusion over the time \( t \) under consideration. Nevertheless, the ends of the couple move with respect to one another, and with respect to the WM interface, located at \( x_0(t) \), because of composition and concomitant volume change within the couple. For a one dimensional problem, Eq(24) becomes

\[
v(x, t) - v^\square(x, t) = (\bar{V}_B - \bar{V}_A) \rho D \frac{\partial \omega}{\partial x}
\]

(98)

where we have used the one dimensional version of Eq(38) to express the flux. Thus at the ends of the couple we have

\[
\frac{dx_L(t)}{dt} = v(x_L(t), t) = v^\square(x_L(t), t) = v_A(x_L(t), t) = v_B(x_L(t), t)
\]

(99)

\[
\frac{dx_R(t)}{dt} = v(x_R(t), t) = v^\square(x_R(t), t) = v_A(x_R(t), t) = v_B(x_R(t), t)
\]

The one dimensional version of Eq(67) is

\[
\frac{\partial v^\square(x, t)}{\partial x} = \frac{D}{\rho_B \bar{V}_B} \frac{\partial \rho A}{\partial x} \frac{\partial \bar{V}_A}{\partial x} = G(x, t).
\]

(100)

Integration of Eq(100) from \( x_L(t) \) to \( x \) yields

\[
v^\square(x, t) - \frac{dx_L}{dt} = \int_{x_L(t)}^{x} G(x', t) dx'.
\]

(101)
But for any fixed $t$,  
\[ G(x', t)dx' = \frac{1}{\sqrt{t}} \left( -\frac{D}{\rho_B V_B} \frac{d\rho_A}{dV_A} \right) d\lambda'_x = \frac{1}{\sqrt{t}} H(\lambda'_x) d\lambda'_x. \]  
(102)  
where $\lambda'_x = (x' - x_0(t))/\sqrt{t}$. Thus Eq(101) can be integrated to obtain\(^9\)  
\[ v \odot (x, t) - \frac{dx_L}{dt} = \frac{1}{\sqrt{t}} \int_{\lambda_{xL}}^{\lambda_x} H(\lambda'_x) d\lambda'_x \]  
(103)  
where $\lambda_x := (x - x_0(t))/\sqrt{t}$ and $\lambda_{xL} := (x_L(t) - x_0(t))/\sqrt{t} \approx -\infty$. Substituting Eq(103) into Eq(98) gives  
\[ v(x, t) - \frac{dx_L}{dt} = \frac{1}{\sqrt{t}} \left[ (\tilde{V}_B - \tilde{V}_A)\rho D \frac{d\omega}{d\lambda_x} + \int_{\lambda_{xL}}^{\lambda_x} H(\lambda'_x) d\lambda'_x \right] \]  
(104)  
For general $x$, and hence general $\lambda_x$, the dependence of Eqs(103,104) on $t$ is rather complicated, but for $x = x_R(t)$ and $x = x_0(t)$ there is enlightening simplification. For $x = x_R(t)$, either of Eqs(103,104) become  
\[ \frac{dx_R}{dt} - \frac{dx_L}{dt} = g_{\infty} \]  
(105)  
where  
\[ g_{\infty} := \int_{\lambda_{xL}}^{\lambda_x} H(\lambda'_x) d\lambda'_x \approx \int_{-\infty}^{\infty} H(\lambda'_x) d\lambda'_x \]  
(106)  
and $\lambda_{xL} \approx -\infty$ and $\lambda_{xR} := (x_R(t) - x_0(t))/\sqrt{t} \approx \infty$ have been used in the last step. In obtaining Eq(106), Eq(99) has been used to identify $dx_R/dt$. Integration of Eq(106) then leads to  
\[ x_R(t) - x_L(t) = x_R(0) - x_L(0) + 2g_{\infty} \sqrt{t} \]  
(107)  
which determines the lengthening or shortening of the entire diffusion couple with time. For $x = x_0(t)$, Eq(103) becomes  
\[ v \odot (x_0(t), t) - \frac{dx_L}{dt} = \frac{1}{\sqrt{t}} g_{\infty} \]  
(108)  
where  
\[ g_{\infty} := \int_{\lambda_{xL}}^{0} H(\lambda'_x) d\lambda'_x \approx \frac{1}{\sqrt{t}} \int_{-\infty}^{0} H(\lambda'_x) d\lambda'_x. \]  
(109)  
Similarly Eq(104) becomes  
\[ v(x_0(t), t) - \frac{dx_L}{dt} = \frac{1}{\sqrt{t}} \left( g_{\infty} + g_0 \right) \]  
(110)  
\(^9\)Eq(103) plays the same role as Eqs(2.16), (4.4) and (4.5) of Sauer and Freise [5] but the notation is different. These S&F equations are based on a coordinate system in which $dx_L/dt = 0$ and which has a different origin. See later for a detailed comparison.
where
\[ g_0 := \left( \bar{V}_B - \bar{V}_A \rho D \frac{d\omega}{d\lambda_x} \right)_{\lambda_x=0}. \]

The velocities \( v^\square(x_0(t), t) \) and \( v(x_0(t), t) \) that appear on the left hand sides of Eqs(108,110) are functions of time only. We shall proceed to show that \( v^\square(x_0(t), t) = dx_0(t)/dt \) which will enable Eq(110) to be integrated. Expanding the notation somewhat, Eq(79) can be written
\[ \left( \frac{\partial x(n,t)}{\partial t} \right)_n = \tilde{v}(n,t) = \tilde{v}(n(x,t), t) = v(x,t) \]
but since \( x_0(t) = x(n_0, t) \) where \( n_0 \) is a constant, we have
\[ \frac{dx_0}{dt} = \left( \frac{\partial x(n_0,t)}{\partial t} \right)_{n_0} = v(x_0(t), t). \]
Thus Eq(110) becomes
\[ \frac{dx_0}{dt} - \frac{dx_L}{dt} = \frac{1}{\sqrt{t}} \left( g_\infty^- + g_0 \right) \]
which integrates to
\[ x_0(t) - x_L(t) = x_0(0) - x_L(0) + 2(g_\infty^- + g_0) \sqrt{t}. \]
Subtracting Eq(115) from Eq(107) then leads to
\[ x_R(t) - x_0(t) = x_R(0) - x_0(0) + 2(g_\infty^+ - g_0) \sqrt{t}. \]
where
\[ g_\infty^+ := g_\infty - g_\infty^+ = \int_0^{x_L} H(x'_\lambda) d\lambda_x' \approx \int_0^\infty H(x'_\lambda) d\lambda_x'. \]

Eqs.(115,116) show that the Wagner-Matano interface moves like \( \sqrt{t} \) with respect to either end of the diffusion couple. This should be contrasted with the two Matano planes of Sauer and Freise [5], one of which is at rest with respect to the left end of the diffusion couple, and the other of which is at rest with respect to the right end. We unravel this apparent paradox in the next section.

2.2 Reconciliation of Wagner with Sauer and Freise

We proceed to reconcile the relationship between the unique Wagner-Matano interface, which moves with respect to either end of the diffusion couple, and the two Matano planes of Sauer and Freise, which are fixed with respect to either end. To do this, we define coordinates \( x^L \) and \( x^R \) which are measured in frames that are at rest with respect to \( x_L(t) \) and \( x_R(t) \) respectively. The specific transformations are:
\[ x^L - x^L_M = x - x_L(t) - [x_0(0) - x_L(0)] \]
\[ x^R - x^R_M = x - x_R(t) - [x_0(0) - x_R(0)] \]
where $x_L^M$ and $x_R^M$ are constants that correspond\textsuperscript{10}, respectively, to the two Matano planes of Sauer and Freise. At $t = 0$, $x_L - x_L^M = x - x_0(0) = x_R - x_R^M$. Following Sauer and Freise, we require the coordinates $x_L$ and $x_R$ to be the same at $t = 0$. This requires the constants $x_L^M$ and $x_R^M$ to be equal, so we designate either of them by $x_M$ and write Eqs (118,119) in the form
\begin{align*}
x_L - x_M &= x - x_L(t) - [x_0(0) - x_L(0)] \quad (120) \\
x_R - x_M &= x - x_R(t) - [x_0(0) - x_R(0)]. \quad (121)
\end{align*}
Subtracting Eq (121) from Eq (120), we obtain
\begin{equation}
x_L - x_R = [x_R(t) - x_L(t)] - [x_R(0) - x_L(0)] = 2g_\infty \sqrt{t} \tag{122}
\end{equation}
in agreement with Eq (5.9) of Sauer and Freise. At the “left Matano plane” of Sauer and Freise, $x_L = x_M$, so this plane is located at coordinate $x_L = x_M - 2g_\infty \sqrt{t}$. Similarly, at the “right Matano plane” of Sauer and Freise, $x_R = x_M$, so this plane is located at coordinate $x_L = x_M + 2g_\infty \sqrt{t}$.

Eqs (120,121) can be rewritten in the form
\begin{align*}
x - x_0(t) &= x_L - x_M - \Delta X_L(t) \quad (123) \\
x - x_0(t) &= x_R - x_M + \Delta X_R(t) \quad (124)
\end{align*}
where
\begin{align*}
\Delta X_L(t) : &= [x_0(t) - x_L(t)] - [x_0(0) - x_L(0)] = 2(g_\infty^- + g_0)\sqrt{t} \quad (125) \\
\Delta X_R(t) : &= [x_R(t) - x_0(t)] - [x_R(0) - x_0(0)] = 2(g_\infty^+ - g_0)\sqrt{t}. \quad (126)
\end{align*}
Thus if we define
\begin{equation}
\lambda^L := \frac{x_L - x_M}{\sqrt{t}}; \quad \lambda^R := \frac{x_R - x_M}{\sqrt{t}} \tag{127}
\end{equation}
we can write Eqs (123,124) in the forms
\begin{equation}
\lambda_x = \lambda^L - 2(g_\infty^- + g_0) = \lambda^R + 2(g_\infty^+ - g_0) \tag{128}
\end{equation}
which also imply that $\lambda^L - \lambda^R = 2(g_\infty^- + g_\infty^+) = 2g_\infty$, in agreement with Eq (5.11) of Sauer and Freise. Eq (128) shows that the variables $\lambda_x$, $\lambda^L$ and $\lambda^R$ differ only by constants. Thus the composition can be written in the functional forms
\begin{equation}
\omega(\lambda_x) = \omega^L(\lambda^L) = \omega^R(\lambda^R) \tag{129}
\end{equation}
and similarly for any other quantities, e.g., $\rho$ and $Y$, that depend on composition. In other words, if a “$\sqrt{t}$ solution” can be found in some reference frame, then a “$\sqrt{t}$ solution” can also be found in any other reference frame that moves with respect to the original frame like $\sqrt{t}$. Three such frames are ones that move with either end of the diffusion couple, or with the Wagner-Matano interface.

\textsuperscript{10}The corresponding notation is $x_L^M = x_M$ and $x_R^M = x_M^+$. Just prior to their Eq (5.11), they show that $x_M = x_M^+$.
We shall now show that Eq.(4.13) and Eq.(5.12) of Sauer and Freise are just two different ways of determining the same constant $x_M$ and follow from transformation of Eq(91) for the Wagner-Matano interface. We first divide Eq(91) by $\omega^+-\omega^-$ and use the definition of $Y$ to write it in the form

$$\int_{x_0(t)}^{x_{R(t)}} \rho(1-Y)dx - \int_{x_L(t)}^{x_{0(t)}} \rho Y dx = 0. \quad (130)$$

Then we add an integral to both sides to obtain

$$\int_{x_0(t)}^{x_{R(t)}} \rho(1-Y)dx - \int_{x_L(t)}^{x_{0(t)}} [\rho - \rho(1-Y)]dx = \int_{x_L(t)}^{x_{0(t)}} [\rho - \rho^-]dx. \quad (131)$$

We make a change of variable to $x^L$ in the integrals on the left hand side of Eq(131) as follows:

$$\int_{x_M+\Delta x_L(t)}^{[x_R(t)-x_L(t)]-[x_0(0)-x_L(0)]+x_M} \rho^L(1-Y^L)dx^L - \int_{-x_0(t)}^{x_M+\Delta x_L(t)} [\rho^- - \rho^L(1-Y^L)]dx^L$$

$$= \int_{-\infty}^{\infty} \rho^L(1-Y^L)dx^L - \int_{-\infty}^{0} [\rho^- - \rho^L(1-Y^L)]dx^L - \rho^- x_M + \rho^- \Delta x_L(t) + \int_{x_L(t)}^{x_{0(t)}} [\rho - \rho^-]dx. \quad (132)$$

We shall proceed to show that

$$\rho^- \Delta x_L(t) + \int_{x_L(t)}^{x_{0(t)}} [\rho - \rho^-]dx = 0 \quad (133)$$

in which case Eq(132) becomes

$$\int_{-\infty}^{\infty} \rho^L(1-Y^L)dx^L - \int_{-\infty}^{0} [\rho^- - \rho^L(1-Y^L)]dx^L = \rho^- x_M \quad (134)$$

which is in precise agreement with Eq(4.13) of Sauer and Freise [5]. To prove Eq(133), we first note that it is true at $t = 0$ because $\Delta x_L(0) = 0$ and because $\rho = \rho^-$ in the domain of integration (initial condition). We shall also proceed to show that its time derivative is zero, and hence it is zero for all time. Indeed,

$$\frac{d}{dt} \int_{x_L(t)}^{x_{0(t)}} [\rho - \rho^-]dx = \frac{d}{dt} \int_{x_L(t)}^{x_{0(t)}} \rho \rho v dx + \int_{x_L(t)}^{x_{0(t)}} \partial \rho \rho v dx$$

$$= \frac{d}{dt} \int_{x_L(t)}^{x_{0(t)}} (\rho v x) dx = \rho^- \frac{d}{dt} \Delta x_L(t).$$
Thus Eq(133) is proven and Eq(134) is established, which can also be written
\[ \int_{x_M}^{\infty} \rho^L(1 - Y^L)dx^L - \int_{-\infty}^{x_M} [\rho^+ - \rho^L(1 - Y^L)]dx^L = 0 \]  
(136)
which should be compared with Eq(130). Moreover, Eq(133) provides a succinct formula for \( \Delta x_L(t) \) that is less explicit than that provided by Eq(115). Eq(133) can be motivated physically by noting that all of the density change in the sample takes place in the interior (near to \( x_0(t) \) but far from \( x_L(t) \)) so that the integral of the density deficiency \( \rho^+ - \rho \) must result in an increase in the length of the “left segment” of the couple, resulting in relative motion of the left end of the couple where the density, \( \rho^+ \), is constant.

The transformation of Eq(130) to one in terms of \( x^R \) follows along similar lines so we present results with less detail. We first rewrite Eq(130) in the form
\[ \int_{x_0(t)}^{x_R(t)} [\rho^+ - \rho]dx - \int_{x_L(t)}^{x_0(t)} \rho Y dx = \int_{x_0(t)}^{x_R(t)} [\rho^+ - \rho]dx \]  
(137)
and then transform the left hand side to integrals over \( x^R \) to obtain
\[ \int_{0}^{\infty} [\rho^+ - \rho^R Y^R]dx^R - \int_{-\infty}^{0} \rho^R Y^R dx^R = \rho^+ x_M - \Delta x_R(t) + \int_{x_0(t)}^{x_R(t)} [\rho^+ - \rho]dx. \]  
(138)
Proceeding in a manner similar to that used to prove Eq(133), we can show that
\[ -\rho^+ \Delta x_R(t) + \int_{x_0(t)}^{x_R(t)} [\rho^+ - \rho]dx = 0 \]  
(139)
which results in
\[ \int_{0}^{\infty} [\rho^+ - \rho^R Y^R]dx^R - \int_{-\infty}^{0} \rho^R Y^R dx^R = \rho^+ x_M \]  
(140)
in precise agreement with Eq(5.12) of Sauer and Freise. Eq(140) can also be written
\[ \int_{x_M}^{\infty} [\rho^+ - \rho^R Y^R]dx^R - \int_{-\infty}^{x_M} \rho^R Y^R dx^R = 0 \]  
(141)
for comparison with Eqs(130,136). We emphasize that Eq(134) and Eq(140) are just two different ways of computing the same number, \( x_M \), but for \( t > 0 \), one such determined Sauer-Freise-Matano plane remains fixed with respect to \( x_L(t) \) while the other remains fixed with respect to \( x_R(t) \). Finally, by combining Eq(133) and Eq(139) we obtain
\[ [x_R(t) - x_L(t)] - [x_R(0) - x_L(0)] = \frac{1}{\rho^+} \int_{x_L(t)}^{x_0(t)} [\rho^- - \rho]dx + \frac{1}{\rho^+} \int_{x_0(t)}^{x_R(t)} [\rho^+ - \rho]dx \]  
(142)
for the lengthening of the entire diffusion couple. Note, however, that Eq(142) requires one to know the location, \( x_0(t) \), of the Wagner-Matano interface, so it is not as simple as it appears.

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References