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Mass Diffusion and Thermodiffusion in Multicomponent Fluid Mixtures

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Abstract
Fick diffusion and thermodiffusion coefficients of multicomponent mixtures are known to depend on the frame of reference adopted for the mass fluxes. This paper further elucidates a recent proposal on how to define mass- and thermodiffusion coefficients that are independent of the frame of reference. The primary purpose of the paper is to emphasize the simplicity and convenience of using such frame-independent mass- and thermodiffusion coefficients.

Keywords Fick diffusion · Mass diffusion · Multicomponent mixtures · Non-equilibrium thermodynamics · Ternary mixtures · Thermodiffusion

1 Introduction

While the subject of mass- and thermodiffusion in binary liquid mixtures is well understood, the issues regarding mass- and thermodiffusion in multicomponent mixtures are more complex. During the past decade there has been an increased attention to mass- and thermodiffusion in multicomponent mixtures in general and in ternary mixtures specifically. The quality of mass- and diffusion experiments has increased considerably from systematic testing of different experimental techniques on specific benchmark systems, initially for binary liquid mixtures [1–3], and subsequently also for ternary mixtures [4–11]. In addition, comparisons have been made between earth-bound diffusion experiments and convection-free experiments at low gravity [12–15]. Another interesting development is the possibility of measuring mass- and thermodiffusion simultaneously from scattering measurements of non-equilibrium fluctuations in mixtures subjected to a temperature gradient [16–21].

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Attempts to obtain information for mass- and thermodiffusion in ternary mixtures from studying such non-equilibrium fluctuations have also been initiated [22–27].

Fick diffusion represents the linear relation between mass diffusion and a concentration gradient. Thermodiffusion represents the relation between mass diffusion and a temperature gradient. While for binary liquids both the mass diffusion coefficient and the thermodiffusion coefficient are uniquely defined, for multicomponent fluid mixtures the elements of the corresponding Fick diffusion and the thermodiffusion matrices depend on the frame of reference adopted for the definition of the mass fluxes, i.e., whether mass fractions, mole fractions, or volume fractions are used to specify the composition of the mixtures. This frame dependence of the mass- and thermodiffusion matrices introduces considerable complexity in dealing with diffusion research in multicomponent fluids [28–36]. An example of a careful analysis of the dependence of the diffusion matrices of ternary mixtures of different types on the frame of reference can be found in a paper of Shevtsova and coworkers [37].

In contrast to Fick diffusion matrices, Maxwell–Stefan diffusion matrices, which relate mass diffusion not to concentration gradients but to chemical potential gradients, do not depend on the frame of reference [29, 38–42]. However, knowledge of chemical potentials in multicomponent mixtures requires reliable information for the equation of state that is usually not available [43, 44]. Hence, experimentalists measure Fick diffusion coefficients in practice.

My collaborator J.M. Ortiz de Zárate and I have recently proposed how one can define frame-invariant diffusion matrices for multicomponent fluids by applying a simple transformation in terms of matrices that only depend on the concentrations of the components of the mixture [45, 46]. The idea was originally developed by Ortiz de Zárate for thermodiffusion coefficients of multicomponent mixtures [45] and subsequently extended by us to mass diffusion coefficients [46]. The purpose of the present paper is to further clarify the proposed frame-independent mass and thermodiffusion matrices, in part in response to comments received regarding the previous publications on this subject. Specifically, I have concluded that it is conceptually much easier to start by first developing frame-independent Fick diffusion matrices and then extend the concept to thermodiffusion.

There are a variety of possible frames of references defining diffusion fluxes [29, 47]. To elucidate the concept of frame-invariant diffusion matrices, we shall consider here only diffusion fluxes relative to the center of mass velocity, commonly referred to as barycentric velocity [48], and diffusion fluxes relative to the center of molar velocity. Diffusion flux $\boldsymbol{J}_i^{\mathrm{w}}$ of component i of the mixture relative to the center of mass velocity is defined by

$$\boldsymbol{J}_i^{\mathrm{w}} = \rho_i \left[\boldsymbol{u}_i - \left(\sum\nolimits_i w_i \boldsymbol{u}_i \right) \right], \tag{1}$$

where ρ_i is the mass density of component i, $\boldsymbol{u}_i$ the velocity of component i, and $w_i = \rho_i / \rho_{\mathrm{t}}$ the mass fraction of component i with $\rho_{\mathrm{t}} = \sum_j \rho_j$ being the total mass density of the mixture. Diffusion flux $\boldsymbol{J}_i^{\mathrm{x}}$ relative to the center of molar velocity is defined by

$$\boldsymbol{J}_i^{\mathrm{x}} = c_i\left[\boldsymbol{u}_i - \left(\sum_i x_i \boldsymbol{u}_i\right)\right], \quad (2)$$

where c_i is the molar concentration of component i, and $x_i = c_i/c_{\mathrm{t}}$ the mole fraction of component i with $c_{\mathrm{t}} = \sum_j c_j$ being the total molar density of the mixture (equal to the inverse molar volume). In a mixture of n components there are only $n - 1$ independent fluxes, since $\sum_i \boldsymbol{J}_i^{\mathrm{w}} = \sum_i \boldsymbol{J}_i^{\mathrm{x}} = 0$.

The paper is organized as follows. In Sect. 2 we reconsider isothermal diffusion in a binary mixture with the aim of clarifying why the Fick diffusion coefficient of a binary mixture is independent of the frame of reference. We then proceed with an analysis of isothermal diffusion in ternary mixtures in Sect. 3. Specifically, we show how one can define a frame-independent Fick diffusion matrix for ternary mixtures by generalizing what we have learned from binary mixtures. Generalizing the procedure to multicomponent mixtures is straightforward as shown in Sect. 4. In Sect. 5 we similarly consider thermodiffusion in binary mixtures and in Sect. 6 thermodiffusion in ternary and multicomponent mixtures. The general case of non-isothermal diffusion is then obtained as the sum of the Fick diffusion and the thermodiffusion contributions as shown in Sect. 7. Our conclusions are summarized in Sect. 8.

2 Isothermal Diffusion in a Binary Mixture

In a binary mixture there is only one independent flux $\boldsymbol{J}^{\mathrm{w}} = \boldsymbol{J}_1^{\mathrm{w}}$ or $\boldsymbol{J}^{\mathrm{x}} = \boldsymbol{J}_1^{\mathrm{x}}$ with one mass fraction variable $w = w_1$ and one mole fraction variable $x = x_1$. According to Fick's law [29]

$$\boldsymbol{J}^{\mathrm{w}} = -\rho_{\mathrm{t}} D \nabla w, \quad (3)$$

or

$$\boldsymbol{J}^{\mathrm{x}} = -c_{\mathrm{t}} D \nabla x, \quad (4)$$

where D is a single diffusion coefficient. In accordance with Eqs. 1 and 2, the mass diffusion flux relative to the center of mass velocity is

$$\boldsymbol{J}^{\mathrm{W}} = \boldsymbol{J}_1^{\mathrm{w}} = \rho_1\left[\boldsymbol{u}_1 - \left\{w_1\boldsymbol{u}_1 + \left(1 - w_1\right)\boldsymbol{u}_2\right\}\right] = \rho_{\mathrm{t}} w_1\left(1 - w_1\right)\left(\boldsymbol{u}_1 - \boldsymbol{u}_2\right), \quad (5)$$

and the molar diffusion flux relative to the molar velocity is

$$\boldsymbol{J}^{\mathrm{x}} = \boldsymbol{J}_1^{\mathrm{X}} = \rho_1\left[\boldsymbol{u}_1 - \left\{x_1\boldsymbol{u}_1 + \left(1 - x_1\right)\boldsymbol{u}_2\right\}\right] = c_{\mathrm{t}} x_1\left(1 - x_1\right)\left(\boldsymbol{u}_1 - \boldsymbol{u}_2\right). \quad (6)$$

From Eqs. 5 and 6 we conclude that the two fluxes are related by

$$\frac{\boldsymbol{J}^{\mathrm{w}}}{\rho_{\mathrm{t}} w_1\left(1 - w_1\right)} = \frac{\boldsymbol{J}^{\mathrm{x}}}{c_{\mathrm{t}} x_1\left(1 - x_1\right)}. \quad (7)$$

Since the mass fraction w_1 is related to the mole fraction x_1 by $w_1 = x_1 M_1 / \left[x_1 M_1 + \left(1 - x_1 \right) M_2 \right]$ where M_1 and M_2 are the molar weights of components 1 and 2, respectively, it follows that the concentration gradients are related by

$$\frac{\nabla w_1}{w_1 \left(1 - w_1 \right)} = \frac{\nabla x_1}{x_1 \left(1 - x_1 \right)}. \tag{8}$$

Substitution of Eq. 7 into Eq. 3 for $\boldsymbol{J}_1^{\mathrm{w}}$ with Eq. 8 for ∇w_1 reproduces Eq. 4 with only one single diffusion coefficient D for a binary mixture, independent of the frame of reference ($D^{\mathrm{w}} = D^{\mathrm{x}} = D$).

3 Isothermal Diffusion in a Ternary Mixture

In a ternary mixture there are two independent fluxes, say $\boldsymbol{J}_1^{\mathrm{w}}$ and $\boldsymbol{J}_2^{\mathrm{w}}$ or $\boldsymbol{J}_1^{\mathrm{X}}$ and $\boldsymbol{J}_2^{\mathrm{X}}$, with two independent concentration variables w_1 and w_2 or x_1 and x_2. Fick's law relates the two fluxes to the two concentration gradients such that [29]

$$\begin{pmatrix} \boldsymbol{J}_1^{\mathrm{w}} \\ \boldsymbol{J}_2^{\mathrm{w}} \end{pmatrix} = -\rho_{\mathrm{t}} \mathrm{D}^{\mathrm{w}} \times \begin{pmatrix} \nabla w_1 \\ \nabla w_2 \end{pmatrix} \quad \text{with} \mathrm{D}^{\mathrm{w}} = \begin{bmatrix} D_{11}^{\mathrm{w}} D_{12}^{\mathrm{w}} \\ D_{21}^{\mathrm{w}} D_{22}^{\mathrm{w}} \end{bmatrix}, \tag{9}$$

or

$$\begin{pmatrix} \boldsymbol{J}_1^{\mathrm{X}} \\ \boldsymbol{J}_2^{\mathrm{X}} \end{pmatrix} = -c_{\mathrm{t}} \mathrm{D}^{\mathrm{X}} \times \begin{pmatrix} \boldsymbol{\nabla}_{x_1} \\ \boldsymbol{\nabla}_{x_2} \end{pmatrix} \quad \text{with} \, \mathrm{D}^{\mathrm{X}} = \begin{bmatrix} D_{11}^{\mathrm{X}} & D_{12}^{\mathrm{X}} \\ D_{21}^{\mathrm{X}} & D_{21}^{\mathrm{X}} \end{bmatrix}. \tag{10}$$

Here, D^{w} and D^{x} are two-dimensional Fick diffusion matrices, but the problem is that the elements depend on the chosen frame of reference, so that $\mathrm{D}^{\mathrm{w}} \neq \mathrm{D}^{\mathrm{x}}$.

For a binary mixture we found that the frame independence of the diffusion coefficient was a direct consequence of the relationships (7) and (8) between the fluxes and the concentration gradients. Hence, we want to generalize these relationships between the fluxes and the concentration gradients to a ternary mixture. This goal can be readily accomplished by introducing two concentration-dependent matrices defined by

$$\mathrm{W} = \begin{bmatrix} w_1 \left(1 - w_1 \right) & -w_1 w_2 \\ -w_1 w_2 & w_2 \left(1 - w_2 \right) \end{bmatrix} \tag{11}$$

and

$$\mathrm{X} = \begin{bmatrix} x_1 \left(1 - x_1 \right) & -x_1 x_2 \\ -x_1 x_2 & x_2 \left(1 - x_2 \right) \end{bmatrix}. \tag{12}$$

In terms of these matrices the fluxes are related by

$$\frac{1}{\rho_t}\begin{pmatrix} \boldsymbol{J}_1^{\mathrm{W}} \\ \boldsymbol{J}_2^{\mathrm{W}} \end{pmatrix} = \frac{1}{c_t}\mathrm{W}\cdot\mathrm{X}^{-1}\cdot\begin{pmatrix} \boldsymbol{J}_1^{\mathrm{X}} \\ \boldsymbol{J}_2^{\mathrm{X}} \end{pmatrix}, \tag{13}$$

while the concentration gradients are related by

$$\mathrm{W}^{-1}\cdot\begin{pmatrix} \nabla w_1 \\ \nabla w_2 \end{pmatrix} = \mathrm{X}^{-1}\cdot\begin{pmatrix} \boldsymbol{\nabla} x_1 \\ \boldsymbol{\nabla} x_2 \end{pmatrix}. \tag{14}$$

For a binary mixture $\boldsymbol{J}_2^{\mathrm{w}} = 0$, $\boldsymbol{J}_2^{\mathrm{x}} = 0$, $w_2 = 0$, $x_2 = 0$ and Eqs. 13 and 14 reduce to Eqs. 7 and 8 for a binary mixture. And indeed, it is well known that the Fick diffusion matrices are related by a similarity transformation such that (see, e.g., Eq. 3.2.11 in Ref. [29])

$$\mathrm{W}^{-1}\cdot\mathrm{D}^{\mathrm{w}}\cdot\mathrm{W} = \mathrm{X}^{-1}\cdot\mathrm{D}^{\mathrm{x}}\cdot\mathrm{X} \tag{15}$$

Here, we go one step further introducing a new Fick diffusion matrix D defined by

$$\mathrm{D} \equiv \mathrm{W}^{-1}\cdot\mathrm{D}^{\mathrm{w}}\cdot\mathrm{W} = \mathrm{X}^{-1}\cdot\mathrm{D}^{\mathrm{x}}\cdot\mathrm{X}. \tag{16}$$

Equations 10 and 11 for Fick's law can then be rewritten as

$$\begin{pmatrix} \boldsymbol{J}_1^{\mathrm{w}} \\ \boldsymbol{J}_2^{\mathrm{w}} \end{pmatrix} = -\rho_t\mathrm{W}\cdot\mathrm{D}\cdot\mathrm{W}^{-1}\cdot\begin{pmatrix} \boldsymbol{\nabla} w_1 \\ \boldsymbol{\nabla} w_2 \end{pmatrix}, \tag{17}$$

$$\begin{pmatrix} \boldsymbol{J}_1^{\mathrm{x}} \\ \boldsymbol{J}_2^{\mathrm{x}} \end{pmatrix} = -c_t\mathrm{X}\cdot\mathrm{D}\cdot\mathrm{X}^{-1}\cdot\begin{pmatrix} \boldsymbol{\nabla} x_1 \\ \boldsymbol{\nabla} x_2 \end{pmatrix}, \tag{18}$$

in terms of a Fick diffusion matrix D whose components are now independent of the frame of reference.

4 Isothermal Diffusion in Multicomponent Mixtures

The formulation of Fick's law in terms of a frame-independent diffusion matrix can be readily generalized to mixtures with an arbitrary number of components n. For this purpose we define $(n-1)\times(n-1)$ concentration matrices W and X with elements W_{ij} and X_{ij} defined by

$$W_{ij} = w_i\delta_{ij} - w_i w_j, \tag{19}$$

$$X_{ij} = x_i\delta_{ij} - x_i x_j, \tag{20}$$

where δ_{ij} are Kronecker deltas. Just as Eqs. 17 and 18 for Fick's law in ternary mixtures, Fick's law for a mixture of n components can now be written as

$$\begin{pmatrix} \boldsymbol{J}_1^{\mathrm{w}} \\ \vdots \\ \boldsymbol{J}_{n-1}^{\mathrm{w}} \end{pmatrix} = -\rho_{\mathrm{t}} \mathrm{W} \cdot \mathrm{D} \cdot \mathrm{W}^{-1} \cdot \begin{pmatrix} \nabla w_1 \\ \vdots \\ \nabla w_{n-1} \end{pmatrix}, \tag{21}$$

$$\begin{pmatrix} \boldsymbol{J}_1^{\mathrm{x}} \\ \vdots \\ \boldsymbol{J}_{n-1}^{\mathrm{x}} \end{pmatrix} = -c_{\mathrm{t}} \mathrm{X} \cdot \mathrm{D} \cdot \mathrm{X}^{-1} \cdot \begin{pmatrix} \nabla x_1 \\ \vdots \\ \nabla x_{n-1} \end{pmatrix}, \tag{22}$$

in terms of a $(n-1) \times (n-1)$ Fick diffusion matrix D whose components are again independent of the frame of reference.

5 Thermodiffusion in a Binary Mixture

The thermodiffusion coefficient D_T of a binary mixture relates the mass flux $\boldsymbol{J}^{\mathrm{w}}$ or $\boldsymbol{J}^{\mathrm{x}}$ resulting from a temperature gradient ∇T [1, 3]:

$$\boldsymbol{J}^{\mathrm{w}} = -\rho_{\mathrm{t}} w(1-w) D_T \nabla T, \tag{23}$$

or

$$\boldsymbol{J}^{\mathrm{x}} = -c_{\mathrm{t}} x(1-x) D_T \nabla T. \tag{24}$$

Note the concentration-dependent prefactors $w(1-w)$ and $x(1-x)$ in the definition of the thermodiffusion coefficient D_T. These factors are necessary to make the thermodiffusion coefficient D_T of a binary mixture independent of the frame of reference [48]. And indeed, substitution of Eq. 7 for $\boldsymbol{J}^{\mathrm{w}}$ into Eq. 23 reproduces Eq. 24. Instead of the thermodiffusion coefficient D_T, one often considers in liquid mixtures a Soret coefficient S_T which is related to the thermodiffusion coefficient as $S_T = D_T/D$. Frame independence of D_T and of D implies frame independence of S_T [45].

6 Thermodiffusion in Multicomponent Mixtures

To formulate the frame independence of the thermodiffusion coefficient for multicomponent mixtures, we note from the definitions (19) and (20) of the concentration matrices W and X that for binary mixtures $\mathrm{W} = w(1-w)$ and $\mathrm{X} = x(1-x)$, so that Eqs. 23 and 24 can be rewritten as

$$\boldsymbol{J}^{\mathrm{w}} = -\rho_{\mathrm{t}} \mathrm{W} D_T \nabla T, \tag{25}$$

$$\boldsymbol{J}^{\mathrm{x}} = -c_{\mathrm{t}} \mathrm{X} D_T \nabla T. \tag{26}$$

This form can be immediate generalized to multicomponent mixtures. Specifically, we obtain for a ternary mixture

$$\begin{pmatrix} \boldsymbol{J}_1^{\mathrm{w}} \\ \boldsymbol{J}_2^{\mathrm{w}} \end{pmatrix} = -\rho_{\mathrm{t}} \mathrm{W} \cdot \begin{pmatrix} D_{T,1} \\ D_{T,2} \end{pmatrix} \boldsymbol{\nabla} T, \tag{27}$$

$$\begin{pmatrix} \boldsymbol{J}_1^{\mathrm{x}} \\ \boldsymbol{J}_2^{\mathrm{x}} \end{pmatrix} = -c_{\mathrm{t}} \mathrm{X} \cdot \begin{pmatrix} D_{T,1} \\ D_{T,2} \end{pmatrix} \boldsymbol{\nabla} T, \tag{28}$$

where the matrices W and X are now defined by Eqs. 11 and 12, and where the thermal diffusion coefficients $D_{T,1}$ and $D_{T,2}$ are now independent of the frame of reference. As discussed by Ortiz de Zárate [45], this result solves several complications encountered in the literature dealing with thermodiffusion in ternary mixtures. For a corresponding frame-independent formulation of the Soret coefficients $S_{T,1}$ and $S_{T,2}$ the reader is also referred to the earlier work of Ortiz de Zárate [45].

For a mixture of n components we obtain similarly

$$\begin{pmatrix} \boldsymbol{J}_1^{\mathrm{w}} \\ \vdots \\ \boldsymbol{J}_{n-1}^{\mathrm{w}} \end{pmatrix} = -\rho_{\mathrm{t}} \mathrm{W} \cdot \begin{pmatrix} D_{T,1} \\ \vdots \\ D_{T,n-1} \end{pmatrix} \boldsymbol{\nabla} T, \tag{29}$$

$$\begin{pmatrix} \boldsymbol{J}_1^{\mathrm{x}} \\ \vdots \\ \boldsymbol{J}_{n-1}^{\mathrm{x}} \end{pmatrix} = -c_{\mathrm{t}} \mathrm{X} \cdot \begin{pmatrix} D_{T,1} \\ \vdots \\ D_{T,n-1} \end{pmatrix} \boldsymbol{\nabla} T, \tag{30}$$

where the matrices W and X are now defined by Eqs. 19 and 20, and where the thermal diffusion coefficients $D_{T,i}$ are again independent of the frame of reference.

7 Non-isothermal Diffusion in Multicomponent Mixtures

For the general case of non-isothermal diffusion in multicomponent mixtures, we just add the Fick diffusion contributions and the thermodiffusion contributions, so that

$$\begin{pmatrix} \boldsymbol{J}_1^{\mathrm{w}} \\ \vdots \\ \boldsymbol{J}_{n-1}^{\mathrm{w}} \end{pmatrix} = -\rho_{\mathrm{t}} \left[\mathrm{W} \cdot \mathrm{D} \cdot \mathrm{W}^{-1} \cdot \begin{pmatrix} \nabla w_1 \\ \vdots \\ \nabla w_{n-1} \end{pmatrix} + \mathrm{W} \cdot \begin{pmatrix} D_{T,1} \\ \vdots \\ D_{T,n-1} \end{pmatrix} \boldsymbol{\nabla} T \right], \tag{31}$$

$$\begin{pmatrix} \boldsymbol{J}_1^{\mathrm{x}} \\ \vdots \\ \boldsymbol{J}_{n-1}^{\mathrm{x}} \end{pmatrix} = -c_{\mathrm{t}} \left[\mathrm{X} \cdot \mathrm{D} \cdot \mathrm{X}^{-1} \cdot \begin{pmatrix} \nabla x_1 \\ \vdots \\ \nabla x_{n-1} \end{pmatrix} + \mathrm{X} \cdot \begin{pmatrix} D_{T,1} \\ \vdots \\ D_{T,n-1} \end{pmatrix} \boldsymbol{\nabla} T \right], \tag{32}$$

where the elements D_{ij} of the Fick diffusion matrix D and the thermodiffusion coefficients $D_{T,i}$ are all independent of the frame of reference.

8 Conclusions

As shown in Eqs. 31 and 32, it is possible to express mass- and thermodiffusion in multicomponent mixtures in terms of Fick diffusion coefficients D_{ij} and thermodiffusion coefficients $D_{T,i}$ that are independent of the frame of reference. This result is obtained by applying a simple transformation to the Fick's law and thermodiffusion relations in terms of matrices that only depend on the known composition of the mixtures. Unlike Maxwell–Stefan diffusion coefficients, no information about chemical potentials of the mixtures is needed. Listing frame-independent diffusion coefficients in databases would mean that users no longer need to worry how these diffusion coefficients were obtained experimentally. Since recently a considerable amount of experimental Fick diffusion and thermodiffusion data have become available for ternary mixtures [4–11, 30–37, 49–58], this would seem to be an ideal time to establish a data base of frame-independent mass- and thermodiffusion coefficients, at least for ternary mixtures.

Appendix: Volume-Average Frame of Reference

The procedure described above for the formulation of frame-independent mass- and thermodiffusion coefficients can be readily extended to diffusion coefficients obtained when the fluxes are relative to the center of volume velocity:

$$\boldsymbol{J}_i^{\mathrm{V}} = c_i\left[\boldsymbol{u}_i - \left(\sum\nolimits_i \phi_i \boldsymbol{u}_i\right)\right], \tag{33}$$

where $\phi_i = x_i\widehat{V}_i / \sum_j x_j\widehat{V}_j$ is the volume fraction of component i with $\widehat{V}_i$ being the partial molar volume of component i. The corresponding elements $\boldsymbol{\Phi}_{ij}$ of the concentration-dependent matrix Φ for the frame-independent transformation are [29, 46]

$$\boldsymbol{\Phi}_{ij} = x_i\delta_{ij} - \phi_j x_i. \tag{34}$$

Equation 16 becomes

$$\mathrm{D} = \Phi^{-1}\cdot\ \mathrm{D}^{\mathrm{V}}\ \cdot\Phi = \mathrm{W}^{-1}\cdot\mathrm{D}^{\mathrm{w}}\cdot\mathrm{W} = \mathrm{X}^{-1}\cdot\mathrm{D}^{\mathrm{X}}\cdot\mathrm{X}, \tag{35}$$

where D^{V} is now the Fick diffusion matrix in the volume-average frame of reference [29]. Then Eqs. 31 and 32 are supplemented with [46]

$$\begin{pmatrix} \boldsymbol{J}_1^{\mathrm{V}} \\ \vdots \\ \boldsymbol{J}_{n-1}^{\mathrm{V}} \end{pmatrix} = -\left[\Phi\cdot\mathrm{D}\cdot\Phi^{-1}\cdot\begin{pmatrix} \nabla c_1 \\ \vdots \\ \nabla c_{n-1} \end{pmatrix} + \Phi\cdot\begin{pmatrix} D_{T,1} \\ \vdots \\ D_{T,n-1} \end{pmatrix}\boldsymbol{\nabla}T\right]. \tag{36}$$

While the matrices W and X are determined by the composition of the mixture, the matrix Φ requires knowledge of the partial molar volumes, information that may not be so readily available.

Acknowledgments This paper is dedicated to the memory of José M. Ortiz de Zárate, who has been my close collaborator for twenty years.

References

1. J.K. Platten, M.M. Bou-Ali, P. Costesèque, J.F. Dutrieux, W. Köhler, C. Leppla, S. Wiegand, G. Wittko, Philos. Mag. **83**, 1965 (2003)
2. A. Köninger, B. Meier, W. Köhler, Philos. Mag. **89**, 907 (2009)
3. A. Mialdun, V. Yasnou, V. Shevtsova, A. Köninger, W. Köhler, D.A. de Mezquia, M.M. Bou-Ali, J. Chem. Phys. **136**, 244512 (2012)
4. A. Mialdun, V. Sechenyh, J.C. Legros, J.M. Ortiz de Zárate, V. Shevtsova, J. Chem. Phys. **139**, 104903 (2013)
5. M. Gebhardt, W. Köhler, Eur. Phys. J. E **38**, 24 (2015)
6. A. Ahadi, M. Saghir, Eur. Phys. J. E **38**, 25 (2015)
7. Q. Galand, S. Van Vaerenbergh, Eur. Phys. J. E **38**, 26 (2015)
8. A. Mialdun, J.-C. Legros, V. Yasnou, V. Sechenyh, V. Shevtsova, Eur. Phys. J. E **38**, 27 (2015)
9. M. Larrañaga, M.M. Bou-Ali, D.A. de Mezquia, D.A.S. Rees, J.A. Madariaga, C. Santamaría, J.K. Platten, Eur. Phys. J. E **38**, 28 (2015)
10. O.A. Khlybov, I.I. Ryzhkov, T.P. Lyubimova, Eur. Phys. J. E **38**, 29 (2015)
11. M.M. Bou-Ali, A. Ahadi, D.A. de Mezquia, Q. Galand, M. Gebhardt, O. Khlybov, W. Köhler, M. Larrañaga, J.C. Legros, T. Lyubimova, A. Mialdun, I. Ryzhkov, M.Z. Saghir, V. Shevtsova, S. Van Vaerenbergh, Eur. Phys. J. E **38**, 30 (2015)
12. T. Triller, H. Bataller, M.M. Bou-Ali, M. Braibanti, F. Croccolo, J.M. Ezquerro, Q. Galand, J. Gavaldà, E. Lapeira, A. Leverón-Simavilla, T. Lyubimova, A. Mialdun, J.M. Ortiz de Zárate, J. Rodríguez, X. Ruiz, I.I. Ryzhkov, V. Shevtsova, S. Van Vaerenbergh, W. Köhler, Microgravity Sci. Technol. **30**, 295 (2018)
13. A. Mialdun, H. Bataller, M.M. Bou-Ali, M. Braibanti, F. Croccolo, A. Errarte, J.M. Ezquerro, J.J. Fernández, Y. Gaponenko, L. García-Fernández, J. Rodríguez, V. Shevtsova, Eur. Phys. J. E **42**, 87 (2019)
14. M. Schraml, T. Trillert, H. Sommermann, W. Köhler, Acta Astronaut. **160**, 251 (2019)
15. A. Mialdun, M.M. Bou-Ali, M. Braibanti, F. Croccolo, A. Errarte, J.M. Ezquerro, J.J. Fernández, L. García-Fernández, Q. Galand, Y. Gaponenko, F. Gavaldá, W. Köhler, T. Lyubimova, J.M.O. de Zárate, J. Rodríguez, X. Ruiz, I.I. Ryzhkov, M. Schraml, V. Shevtsova, S. Van Vaerenbergh, V. Yasnou, H. Bataller, Acta Astronaut. **176**, 204 (2020)
16. F. Croccolo, F. Scheffold, H. Bataller, C. R. Mec. **341**, 378 (2013)
17. F. Croccolo, H. Bataller, F. Sheffold, J. Chem. Phys. **137**, 234202 (2012); ibid. **141**, 219902 (2014).
18. C. Giraudet, H. Bataller, F. Croccolo, Eur. Phys. J. E **37**, 107 (2014)
19. W. Wu, J.H. Jander, M.H. Rausch, A.P. Fröbas, C. Giraudet, J. Chem. Phys. **153**, 144201 (2020)
20. D. Zapf, W. Köhler, J. Chem. Phys. **153**, 224902 (2020)
21. A.T. Ndjaka, L. García-Fernández, D.E. Bouyou Bouyou, A. Lassin, M. Azaroual, F. Croccolo, H. Bataller, Eur. Phys. J. E **44**, 1–12 (2021)
22. J.M. Ortiz de Zárate, J.L. Hita, J.V. Sengers, C. R. Mec. **341**, 399 (2013)
23. J.M. Ortiz de Zárate, C. Giraudet, H. Bataller, F. Croccolo, Eur. Phys. J. E **37**, 77 (2014)
24. P.M. Pancorbo, J.M. Ortiz de Zárate, H. Bataller, F. Croiccolo, Eur. Phys. J. E **40**, 22 (2017)
25. H. Bataller, T. Triller, B. Pur, W. Köhler, J.M. Ortiz de Zárate, F. Croccolo, Eur. Phys. J. E **40**, 35 (2017)
26. L. García-Fernández, P. Fruton, H. Bataller, J.M. Ortiz de Zárate, F. Croccolo, Eur. Phys. J. E **42**, 124 (2019)
27. J.M. Ortiz de Zárate, L. García-Fernández, H. Bataller, F. Croccolo, J. Stat. Phys. **181**, 1 (2020)
28. D.C. Miller, V. Vitagliano, R. Sartorio, J. Phys. Chem. **90**, 1509 (1986)
29. R. Taylor, R. Krishna, *Multicomponent Mass Transfer* (Wiley, New York, 1993)
30. M.M. Bou-Ali, J.K. Platten, J. Non-Equilib. Thermodyn. **30**, 385 (2005)
31. A. Leahy-Dios, M.M. Bou-Ali, J.K. Platten, A. Firoozabadi, Eur. Phys. J. E, in press
32. J. Wambui Mutoru, A. Firoozabadi, J. Chem. Thermodyn. **43**, 1192 (2011)

33. J.C. Legros, Y. Gaponenko, A. Mialdun, T. Triller, A. Hammon, C. Bauer, W. Köhler, V. Shevtsova, Phys. Chem. Chem. Phys. **17**, 27713 (2015)
34. V. Shechenyh, J.C. Legros, A. Mialdun, J.M. Ortiz de Zárate, V. Shevtsova, J. Phys. Chem. B **120**, 535 (2016)
35. G. Guevara-Carrion, R. Fingerhut, J. Vrabec, Nat./Sci. Rep. **11**, 12319 (2021)
36. A. Mialdun, M.M. Bou-Ali, V. Shevtsova, Nat./Sci. Rep. **11**, 17735 (2021)
37. S. Kozlova, A. Mialdun, I. Ryzhkov, T. Janzen, J. Vrabec, V. Shevtsova, Phys. Chem. Chem. Phys. **21**, 2140 (2019)
38. G.D.C. Kuiken, *Thermodynamics of Irreversible Processes* (Wiley, New York, 1994)
39. R. Krishna, J.A. Wesselingh, Chem. Eng. Sci. **52**, 861 (1997)
40. S. Kjelstrup, D. Bedeaux, E. Johannessen, J. Gross, *Non-Equilibrium Thermodynamics for Engineers*, 2nd edn. (World Scientific, Singapore, 2017)
41. Y. Demirel, *Nonequilibrium Thermodynamics* (Elsevier, Amsterdam, 2002)
42. C. Peters, L. Wolff, T.J.H. Vlugt, A. Bardow, in Non-Equilbrium Thermodynamics with Applications, eds. by D. Bedeaux, S. Kjelstrup, J.V. Sengers, Ch. 5 (Royal Society of Chemistry, Cambridge, 2016).
43. O.O. Medvedev, A.A. Shapiro, Fluid Phase Equilib. **208**, 291 (2003)
44. A. Bardow, E. Kriesten, M.A. Voda, F. Casanova, B. Blümich, W. Marquardt, Fluid Phase Equilib. **278**, 27 (2009)
45. J.M. Ortiz de Zárate, Eur. Phys. J. E **42**, 43 (2019)
46. J.M. Ortiz de Zárate, J.V. Sengers, Phys. Chem. Chem. Phys. **22**, 17597 (2020)
47. H.J. Merk, Appl. Sci. Res. A **8**, 73 (1960)
48. S.R. de Groot, P. Mazur, *Non-Equilibrium Thermodynamics* (North-Holland, Amsterdam, 1962)
49. T. Grossmann, J. Winkelmann, J. Chem. Eng. Data **54**, 405 (2009)
50. T. Grossmann, J. Winkelmann, J. Chem. Eng. Data **54**, 485 (2009)
51. G.B. Ray, D.G. Leaist, J. Chem. Eng. Data **55**, 1814 (2010)
52. P. Bianco, M.M. Bou-Ali, J.K. Platten, D.A. de Mezquia, J.A. Madariaga, C. Santamaría, J. Chem. Phys. **132**, 114506 (2010)
53. M. Gebhardt, W. Köhler, A. Mialdun, V. Yasnou, V. Shevtsova, J. Chem. Phys. **138**, 114503 (2013)
54. A. Mialdun, V. Shevtsova, J. Chem. Phys. **138**, 161102 (2013)
55. M. Larrañaga, M.M. Bou-Ali, I. Lizarraga, J.A. Madariaga, C. Santamaría, J. Chem. Phys. **143**, 024202 (2015)
56. M. Gebhardt, W. Köhler, J. Chem. Phys. **142**, 084506 (2015)
57. H. Matsuutra, Y. Nagasaka, Rev. Sci. Instrum. **89**, 024903 (2018)
58. M. Schraml, H. Bataller, C. Bauer, M.M. Bou-Ali, F. Croccolo, E. Lapeira, A. Mialdun, P. Möckel, A.T. Ndjaka, V. Shevtsova, W. Köhler, Eur. Phys. J. E **44**, 128 (2021)