

# Multispecies Diffusion in Liquids

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## 1 Basic Equations

These notes are based on the book by Gerard Kuiken. The multi-species diffusion equation is

$$\partial_t (\rho_i) + \nabla \cdot (\rho_i \mathbf{v}) = \nabla \cdot \mathbf{F}_i,$$

where  $i = 1, \dots, N_s$  (I will use the extended notation here where all species are treated on equal footing). Here the baro-centric diffusive flux is

$$\mathbf{F}_i = - \sum_j \mathbf{L}_{ij} \frac{\nabla_T \mu_j}{T} - l_i \frac{\nabla T}{T^2},$$

where  $\mathbf{L}$  is a matrix of Onsager coefficients (symmetric positive-semidefinite with zero row and column sums) and the vector of cross-coupling coefficients  $\mathbf{l}$  sums to zero. This ensures  $\sum_i \mathbf{F}_i = \mathbf{0}$ .

### 1.1 Thermodynamics

The formula for transforming from mass to mole fractions using the molecular masses  $\mathbf{m}$  is

$$x_k = \frac{\bar{m}}{m_k} \mathbf{w}_k = \left( \sum_{i=1}^N \frac{w_i}{m_i} \right)^{-1} \frac{w_k}{m_k},$$

and will be used later. Here

$$\bar{m} = \rho/n = \left( \sum_{i=1}^N \frac{w_i}{m_i} \right)^{-1}$$

is the mixture-averaged molecular mass.

The excess free energy of mixing (over an ideal mixture) is written in the form

$$Q_{\text{ex}}(\mathbf{x}, T, P) = (k_B T) \sum_k x_k \ln \gamma_k,$$

where  $\gamma(\mathbf{x}, T, P)$  are the activity coefficients, usually given in terms of empirical formulae, for example, they can be assumed to be linear functions of the  $x$ 's with some empirical coefficients (see Table D.7 in Appendix D.2 in Krishna/Taylor). The chemical potential (we use chemical potential per mass per molecule, which differs from the more common per mole by a factor of  $mN_A$ ) of a general mixture has the form

$$\mu_k = \mu_k^0(T, P) + \frac{k_B T}{m_k} [\ln(x_k) + \ln(\gamma_k)],$$

so that the derivatives are

$$\frac{\partial \mu_i}{\partial x_j} = \frac{n k_B T}{\rho_i} \left( \delta_{ij} + \frac{\partial \ln \gamma_i}{\partial \ln x_j} \right),$$

where  $n$  is the total number density. For an ideal mixture  $\gamma_k = 0$ .

### 1.1.1 Partial volumes

Introduce the partial volume (denoted by  $v$  in Kuiken's book which is confusing with velocity so we change notation here):

$$\theta_k = \left( \frac{\partial V}{\partial M_k} \right)_{T,P,M'} = \left( \frac{\partial \mu_k}{\partial P} \right)_{T,M},$$

see (4.14) in Kuiken. In Krishna/Taylor the partial molar volume is used,  $\bar{V}_k = \theta_k M_k$ . We are not sure how to model these for liquids, they are related somehow to the EOS and the virial coefficients, see (6.102) in Kuiken and Alej's notes in PartialVolumeNotes. Define also

$$\theta = \sum_i w_i \theta_i = V/M = 1/\rho,$$

see equation right after (6.2) in the book. For certain classes of liquids one can assume  $\theta_i \equiv \theta_i(P, T)$  are independent of composition (e.g., ideal or incompressible mixtures).

### 1.1.2 Thermodynamic factors

Define also the matrix of thermodynamic factors  $\mathbf{\Gamma}$  defined by the relation

$$\nabla_{T,P} \boldsymbol{\mu} = \frac{k_B T}{\bar{m}} \mathbf{W}^{-1} \mathbf{\Gamma} \nabla \mathbf{x},$$

where  $\mathbf{W}$  is a diagonal matrix of mass fractions. In standard chemical engineering textbooks, one of species, say species  $N_s$ , is singled out and chemical potentials are defined relative to that "solvent" species,  $\bar{\mu}_i = \mu_i - \mu_{N_s}$ . Then, one defines the  $(N_s - 1) \times (N_s - 1)$  matrix of thermodynamic factors [Donev: **This is defined wrongly in Kuiken to have pressure instead of  $n k_B T$ , which is only true for ideal systems. The correct definition can be read from Krishna/Taylor (2.2.4) and does not involve pressure**]

$$\bar{\Gamma}_{ij} = \frac{\rho_i}{n k_B T} \left( \frac{\partial \bar{\mu}_i}{\partial x_j} \right)_{T,P,\sum_i x_i=1} = \delta_{ij} + \left( \frac{\partial \ln \gamma_i}{\partial \ln x_j} \right)_{T,P,\sum_i x_i=1},$$

where  $\mathbf{x}$  are the number fractions (adding to unity), and  $\boldsymbol{\gamma}$  are the activity coefficients. The partial derivatives here are taken keeping the mole fractions of all other species fixed except for species  $N_s$ , the mole fraction of which is determined by the constraint  $\sum_i x_i = 1$ .

We will not work with  $\bar{\mathbf{\Gamma}}$  but rather work directly with  $\mathbf{\Gamma}$ , defined via the unconstrained derivatives,

$$\Gamma_{ij} = \frac{\rho_i}{n k_B T} \left( \frac{\partial \mu_i}{\partial x_j} \right)_{T,P} = \frac{\bar{m} w_i}{k_B T} \left( \frac{\partial \mu_i}{\partial x_j} \right)_{T,P} = \delta_{ij} + \frac{\partial \ln \gamma_i}{\partial \ln x_j},$$

which is to be interpreted as taking any analytical extension of  $\boldsymbol{\mu}(\mathbf{x}, T, P)$  away from the surface  $\sum_i x_i = 1$  and then just differentiating it. The relation between the two is given by the chain rule,

$$\left( \frac{\partial \bar{\mu}_i}{\partial x_j} \right)_{T,P,\sum_i x_i=1} = \frac{\partial \mu_i}{\partial x_j} - \frac{\partial \mu_{N_s}}{\partial x_j} - \frac{\partial \mu_i}{\partial x_{N_s}} + \frac{\partial \mu_{N_s}}{\partial x_{N_s}}.$$

Note that what we do with  $\nabla_{T,P} \boldsymbol{\mu}$  is to multiply it by the Onsager  $\mathbf{L}$ . By using the facts that  $\nabla x_{N_s} = -\sum_{j=1}^{N_s-1} \nabla x_j$ , the above chain rule, and the fact that row and column sums of  $\mathbf{L}$  are zero,

$$\mathbf{L} = \begin{bmatrix} \bar{\mathbf{L}} & -\bar{\mathbf{L}} \mathbf{1} \\ -\mathbf{1}^T \bar{\mathbf{L}} & \mathbf{1}^T \bar{\mathbf{L}} \mathbf{1} \end{bmatrix},$$

it is not hard to prove that for  $1 \leq i \leq N_s - 1$  (see John's brief note for the matrix notation proof),

$$\sum_{j,k=1}^{N_s} L_{ij} \Gamma_{jk} \nabla x_k = \sum_{j,k=1}^{N_s-1} \bar{L}_{ij} \bar{\Gamma}_{jk} \nabla x_k,$$

so that using the unconstrained derivatives will in the end produce the same fluxes.

### 1.1.3 Thermodynamic driving force for diffusion

The most important thermodynamic identity to us is the Gibbs-Duhem relation

$$\sum_i \rho_i \nabla_T \mu_i = \rho \theta \nabla P.$$

Using this, we can rewrite the diffusion force (see (6.2) in Kuiken) in the form **[Donev: This is defined wrongly in Kuiken to have pressure instead of  $nk_B T$ , which is only true for ideal systems.]**

$$\mathbf{d}_i = \frac{\rho_i}{nk_B T} (\nabla_T \mu_i - \theta \nabla P) = \frac{\rho_i}{nk_B T} \left( \nabla_T \mu_i - \sum_j \frac{\rho_j}{\rho} \nabla_T \mu_j \right) \Rightarrow \mathbf{d} = \Theta \nabla_T \mu, \quad (1)$$

where the matrix  $\Theta$  can directly be read to be

$$\Theta = \frac{\rho}{nk_B T} (\mathbf{W} - \mathbf{w} \mathbf{w}^T),$$

where  $\mathbf{w}$  is a vector of mass fractions and  $\mathbf{W}$  is a diagonal matrix of mass fractions.

## 1.2 Low Mach Equations

In the low Mach approximation, we assume that pressure is constant,

$$P(\boldsymbol{\rho}, T) = P_0 = \text{const.}$$

Here we take a simple model for the EOS that assumes incompressible components,

$$\sum_i \frac{\rho_i}{\bar{\rho}_i} = \rho \sum_i \frac{w_i}{\bar{\rho}_i} = 1, \quad (2)$$

where  $w_i = \rho_i / \rho$  is the mass fraction, and  $\bar{\rho}_i(T, P)$  is the pure-component density at pressure  $P_0$  and temperature  $T$ . Note that this is in fact general if one defines

$$\bar{\rho}_i = \frac{1}{\theta_i} = \frac{M_k}{\bar{V}_k},$$

where  $\theta_i$  is the partial volume, see below, which in general depends on composition but not for an incompressible or ideal mixture. **If we assume that the partial molar volumes  $\theta_i$  are independent of composition, which is true if the chemical potentials depend on pressure *only* through the reference state (pure liquid states), then we get a simple low Mach number formulation as given below. Note that this is definitely true for an ideal mixture, but may be assumed more generally so long as the activities  $\gamma$ 's only depend on composition and not on pressure.**

In the isothermal case, differentiating this constraint in time we get

$$\sum_i \frac{\partial_t(\rho_i)}{\bar{\rho}_i} = \sum_i \frac{1}{\bar{\rho}_i} \nabla \cdot \mathbf{F}_i - \left( \sum_i \frac{\rho_i}{\bar{\rho}_i} \right) \nabla \cdot \mathbf{v} - \mathbf{v} \cdot \nabla \left( \sum_i \frac{\rho_i}{\bar{\rho}_i} \right) = \sum_i \frac{1}{\bar{\rho}_i} \nabla \cdot \mathbf{F}_i - \nabla \cdot \mathbf{v} = 0,$$

giving the equivalent velocity constraint **[Donev: This is in fact not general but rather only works if  $\bar{\rho}_i$ 's are independent of composition so they can be pulled inside the divergence – otherwise the base pressure  $P_0$  won't be constant, see John's notes]**

$$\nabla \cdot \mathbf{v} = \nabla \cdot \left( \sum_i \frac{\mathbf{F}_i}{\bar{\rho}_i} \right).$$

If all components have the same density than this becomes the usual  $\nabla \cdot \mathbf{v} = 0$ .

## 2 Diffusion

### 2.1 Diffusion ala Stefan-Maxwell

The Stefan-Maxwell relations are [Donev: This matches (5.48) in the book by Kjelstrup (which does not include barodiffusion), except that the temperature term is written as  $(D_i^T - D_j^T) \nabla T$  which is probably due to some slight difference in notation from Kuiken.]

$$\mathbf{d}_i = \frac{\rho_i}{nk_B T} (\nabla_T \mu_i - \theta \nabla P) = \sum_{j \neq i} \frac{x_i x_j}{D_{ij}} \left[ E_{ij} \frac{\nabla T}{T} + (\mathbf{v}_i - \mathbf{v}_j) \right], \quad (3)$$

where  $\mathbf{v}_i = \mathbf{F}_i / \rho_i$  is the diffusive barocentric slip velocity. Here I introduced the shorthand notation

$$E_{ij} = \frac{E_j}{w_j} - \frac{E_i}{w_i},$$

where  $\mathbf{E}$  are the thermodiffusion coefficients (denoted with  $D_i^T$  in the book but this is cumbersome to write). It can be proven relatively easily that if all the Stefan-Maxwell diffusion constants  $D_{ij} = D_{ji}$  are positive the entropy production is also positive. Therefore it is much better to work with these diffusion constants than the Onsager coefficients  $L_{ij}$ .

We can write (3) in matrix form as

$$\mathbf{d} = -\rho^{-1} \mathbf{\Lambda} \mathbf{W}^{-1} \mathbf{F} + \frac{\nabla T}{T} \mathbf{e}.$$

Here the vector of thermo-diffusion coefficients is

$$e_i = \sum_{j \neq i} \frac{x_i x_j}{D_{ij}} E_{ij} = \sum_{j \neq i} \frac{x_i x_j}{D_{ij}} \left( \frac{E_j}{w_j} - \frac{E_i}{w_i} \right),$$

and note that  $\sum_i e_i = 0$ . The positive semi-definite matrix  $\mathbf{\Lambda}$  (this follows from  $D_{ij} \geq 0$ ) has the form

$$\Lambda_{ij} = -\frac{x_i x_j}{D_{ij}} \text{ if } i \neq j, \quad (4)$$

and diagonal elements that are determined from the condition of zero row and column sums,

$$\Lambda_{ii} = -\sum_{j \neq i} \Lambda_{ij}.$$

Note that  $\mathbf{\Lambda} \mathbf{1} = \mathbf{0}$  so this matrix is not positive definite (or invertible). The range of  $\mathbf{\Lambda}$  are vectors that sum to zero.

Let us now introduce the projection matrix

$$\mathbf{Q} = \mathbf{I} - \mathbf{1} \mathbf{w}^T,$$

which satisfies  $\mathbf{Q}^T \mathbf{w} = \mathbf{Q} \mathbf{1} = \mathbf{0}$ ; therefore, pre-multiplying a matrix by  $\mathbf{Q}^T$  ensures that it has a range consisting of vectors that sum to zero, and post-multiplying by  $\mathbf{Q}^T$  ensures that it has  $\mathbf{w}$  in its null-space. Now, let us define the symmetric positive-semidefinite *matrix of diffusion coefficients*

$$\chi = \mathbf{Q} \mathbf{\Lambda}^{-1} \mathbf{Q}^T. \quad (5)$$

Note that this makes sense even though  $\mathbf{\Lambda}$  is not invertible because  $\mathbf{Q}^T \mathbf{x}$  is in the range of  $\mathbf{\Lambda}$  for any  $\mathbf{x}$ . Alternatively, one can use

$$\chi = \mathbf{Q} \left[ \mathbf{\Lambda} + \text{Trace}(\mathbf{\Lambda}) \frac{\mathbf{1} \mathbf{1}^T}{4} \right]^{-1} \mathbf{Q}^T = \mathbf{Q} \tilde{\mathbf{\Lambda}}^{-1} \mathbf{Q}^T,$$

which leads to a symmetric positive definite matrix (the prefactor  $\text{Trace}(\mathbf{\Lambda})$  was chosen arbitrarily with the idea of having the same order of magnitude as the rest of the matrix). An alternative formula that comes from Giovangigli is to use

$$\boldsymbol{\chi} = \left( \mathbf{\Lambda} + \alpha \mathbf{w} \mathbf{w}^T \right)^{-1} - \alpha^{-1} \mathbf{1} \mathbf{1}^T, \quad (6)$$

where  $\alpha$  is arbitrary but a good choice is  $\alpha = \text{Trace}(\mathbf{\Lambda})$ . These formulae can be computed using Cholesky factorization of  $\tilde{\mathbf{\Lambda}}$ , but we expect this will have numerical problems when some of the species vanish. An alternative is to use an iterative numerical procedure [1]

$$\boldsymbol{\chi} = \left[ \sum_{j=0}^{\infty} (\mathbf{Q} \mathbf{N})^j \right] \mathbf{Q} \mathbf{M}^{-1} \mathbf{Q}^T,$$

where  $\mathbf{N} = \mathbf{I} - \mathbf{M}^{-1} \mathbf{\Lambda}$ , and  $\mathbf{M}$  is a diagonal matrix with entries

$$M_{ii} = \frac{x_i}{1 - w_i} \sum_{j \neq i} \frac{x_j}{D_{ij}}.$$

The sum converges rapidly so only a few terms in the sum are needed to compute  $\boldsymbol{\chi}$  without having to do matrix inverses, but the speed of convergence is hard to access a priori so we will need to test numerically. We already have code to do the above sum and we can use that. It is important to note that, as explained in GG's book, the truncated sum to  $m$  terms gives an approximation  $\boldsymbol{\chi}_m \approx \boldsymbol{\chi}$  that is symmetric positive semi-definite, and satisfies the properties  $\boldsymbol{\chi}_m \mathbf{w} = \mathbf{0}$  as it must. It is therefore perfectly consistent with thermodynamics to just approximate  $\boldsymbol{\chi}$  with  $\boldsymbol{\chi}_m$ .

### 2.1.1 Summary of linear algebra

Here is a quick summary of the key relations derived in [1]:

1.  $\mathbf{\Lambda} \mathbf{1} = \mathbf{0}$  and  $\mathbf{\Lambda}$  is SPD on  $\mathbf{w}^\perp$ .
2.  $\boldsymbol{\chi} \mathbf{w} = \mathbf{0}$  and  $\boldsymbol{\chi}$  is SPD on  $\mathbf{1}^\perp$ .
3.  $\boldsymbol{\chi}$  and  $\mathbf{\Lambda}$  are generalized inverses of each other,  $\boldsymbol{\chi} \mathbf{\Lambda} \boldsymbol{\chi} = \boldsymbol{\chi}$  and  $\mathbf{\Lambda} \boldsymbol{\chi} \mathbf{\Lambda} = \mathbf{\Lambda}$ .
4. More specifically,  $\mathbf{\Lambda} \boldsymbol{\chi} = \mathbf{Q}^T$  and  $\boldsymbol{\chi} \mathbf{\Lambda} = \mathbf{Q}$ .
5. The SPD matrices

$$\tilde{\mathbf{\Lambda}} = \mathbf{\Lambda} + \alpha \mathbf{w} \mathbf{w}^T = \tilde{\boldsymbol{\chi}}^{-1} = \left( \boldsymbol{\chi} + \alpha^{-1} \mathbf{1} \mathbf{1}^T \right)^{-1}$$

are inverses of each other, and  $\tilde{\mathbf{\Lambda}} \equiv \mathbf{\Lambda}$  on the subspace  $\mathbf{1}^\perp$  and  $\tilde{\boldsymbol{\chi}} = \boldsymbol{\chi}$  on the subspace  $\mathbf{w}^\perp$ .

### 2.2 Onsager matrix (for fluctuations)

Combining relations we get

$$\mathbf{d} = \Theta \nabla_T \boldsymbol{\mu} = -\rho^{-1} \mathbf{\Lambda} \mathbf{W}^{-1} \mathbf{F} + \frac{\nabla T}{T} \mathbf{e},$$

which together with the condition  $\mathbf{1}^T \mathbf{F} = 0$  determines the fluxes. It can be shown (one can prove this by noting that  $\mathbf{\Lambda} \mathbf{Q} \mathbf{\Lambda}^\dagger = \mathbf{\Lambda} \mathbf{\Lambda}^\dagger = \mathbf{I} - N_s^{-1} \mathbf{1} \mathbf{1}^T$  is an identity operator on the subspace of zero-sum vectors) that the solution of this linear system of equations can be written in form

$$\mathbf{F} = -\rho \mathbf{W} \boldsymbol{\chi} \left[ \Theta \nabla_T \boldsymbol{\mu} - \mathbf{e} \frac{\nabla T}{T} \right] = -\mathbf{L} \frac{\nabla_T \boldsymbol{\mu}}{T} - \mathbf{l} \frac{\nabla T}{T^2},$$

which by comparison of terms gives the relation

$$\mathbf{L} = \rho T \boldsymbol{\chi} \Theta = \frac{\rho^2 T}{n k_B T} \mathbf{W} \mathbf{Q} \tilde{\mathbf{\Lambda}}^{-1} \mathbf{Q}^T (\mathbf{W} - \mathbf{w} \mathbf{w}^T) = \frac{\rho^2}{n k_B} \mathbf{W} \mathbf{Q} \tilde{\mathbf{\Lambda}}^{-1} \mathbf{Q}^T \mathbf{W}.$$

The final result is therefore

$$\mathbf{L} = \frac{\bar{m}\rho}{k_B} \mathbf{W} \boldsymbol{\chi} \mathbf{W} \quad (7)$$

which makes it clear that the Onsager matrix is symmetric positive semidefinite. In fluctuating hydrodynamics we can generate the stochastic fluxes as

$$\widetilde{\mathbf{F}} = (2k_B \mathbf{L})^{\frac{1}{2}} \mathbf{Z} = \sqrt{2\bar{m}\rho} \mathbf{W} \mathbf{A} \mathbf{Z},$$

where  $\mathbf{A}$  is the Cholesky factor of  $\boldsymbol{\chi} = \mathbf{A} \mathbf{A}^T$ , and  $\mathbf{Z}$  denotes spatio-temporal white noise.

For the Soret effect we get

$$\mathbf{l} = -\rho T \mathbf{W} \boldsymbol{\chi} \mathbf{e} = \mathbf{L} \boldsymbol{\xi} = \frac{\bar{m}\rho}{k_B} \mathbf{W} \boldsymbol{\chi} \mathbf{W} \boldsymbol{\xi} \quad \text{and in PRE notation} \quad \mathbf{l} = \frac{k_B T}{\bar{m}} \mathbf{L} \tilde{\boldsymbol{\chi}} = \rho T \mathbf{W} \boldsymbol{\chi} \mathbf{W} \tilde{\boldsymbol{\chi}},$$

leading to the identification

$$\mathbf{e} = -\frac{\bar{m}}{k_B T} \mathbf{W} \boldsymbol{\xi} \quad \text{and in PRE notation} \quad \frac{\bar{m}}{k_B T} \boldsymbol{\xi} \equiv \tilde{\boldsymbol{\chi}}.$$

### 2.3 Diffusion ala Fick

In the actual code we do not work with gradients of chemical potentials but rather gradients of number densities, pressure, and temperature. To do this, we use the chain rule

$$\mathbf{d}_i = \frac{\rho_i}{nk_B T} (\nabla_T \mu_i - \theta \nabla P) = \frac{\rho_i}{nk_B T} \left( \frac{\partial \mu_i}{\partial x_j} \right)_{T,P,\sum_k x_k=1} \nabla x_j + \frac{\rho_i}{nk_B T} \left( \frac{\partial \mu_k}{\partial P} \right)_{T,M} \nabla P - \frac{\rho_i}{nk_B T} \theta \nabla P$$

which gives the relation **[Donev: The first term here matches Kuiken but the second one has  $P$  rather than  $nk_B T$ ]**

$$\mathbf{d}_i = \Gamma_{ij} \nabla x_j + \frac{\rho_i}{nk_B T} (\theta_i - \theta) \nabla P. \quad (8)$$

Note that an alternative, perhaps clearer, way to write the barodiffusion term is

$$\rho_i (\theta_i - \theta) \nabla P = (\varphi_i - w_i) \nabla P,$$

where  $\varphi_i = \rho_i \theta_i = \rho_i \bar{V}_i / M_i$  is the volume fraction. In ideal gas mixtures  $\varphi_i = x_i$ . Recall also that  $n = \rho / \bar{m}$ .

Previously we obtained the fluxes from  $\mathbf{d}$ ,  $\mathbf{F} = -\rho \mathbf{W} \boldsymbol{\chi} [\mathbf{d} - \mathbf{e} \frac{\nabla T}{T}]$ , giving **[Donev: It seems that  $\nabla P / P$  would make more sense?]**

$$\mathbf{F} = -\rho \mathbf{W} \boldsymbol{\chi} \left[ \Gamma \nabla \mathbf{x} + (\phi - \mathbf{w}) \frac{\nabla P}{nk_B T} + \frac{\bar{m}}{k_B T} \mathbf{W} \boldsymbol{\xi} \left( \frac{\nabla T}{T} \right) \right]. \quad (9)$$

**[Donev: This seems different from what is in the PRE since there we write the thermodiffusion as**

$$\frac{\bar{m}}{k_B T} \mathbf{X} \boldsymbol{\xi} \left( \frac{\nabla T}{T} \right) \equiv \mathbf{X} \tilde{\boldsymbol{\chi}} \frac{\nabla T}{T}$$

**which has an  $\mathbf{X}$  rather than  $\mathbf{W}$ . Must have done something wrong...]** Note that the Gibbs-Duhem this implies that  $\mathbf{1}^T \mathbf{F} = \mathbf{1}^T \mathbf{d} = 0$  and this must be discretely true on every face of the grid. This implies that we also require  $\mathbf{1}^T \Gamma \nabla \mathbf{x} = 0$  numerically and discretely as well on every face of the grid. Note that in the paper on gas mixtures we wrote things in terms of the matrix  $\mathbf{C} = \rho \mathbf{W} \boldsymbol{\chi}$  (so it was not quite right to call this a matrix of diffusion coefficients since it has units of density times diffusion coefficient).

It is also possible to use gradients of mass fractions instead of gradients of mole fractions, by using the chain rule

$$\mathbf{\Gamma} \nabla \mathbf{x} = \mathbf{\Gamma} \left( \frac{\partial \mathbf{w}}{\partial \mathbf{x}} \right) \nabla \mathbf{w} = \frac{\rho}{P} \mathbf{W} \left( \frac{\partial \boldsymbol{\mu}}{\partial \mathbf{x}} \right)_{T,P} \left( \frac{\partial \mathbf{x}}{\partial \mathbf{w}} \right) \nabla \mathbf{w}.$$

The Jacobian matrix

$$\mathbf{\Upsilon} = \left( \frac{\partial \boldsymbol{\mu}}{\partial \mathbf{w}} \right)_{T,P} = \left( \frac{\partial \boldsymbol{\mu}}{\partial \mathbf{x}} \right)_{T,P} \left( \frac{\partial \mathbf{x}}{\partial \mathbf{w}} \right) = \mathbf{\Upsilon}^T$$

can be seen to be proportional to the Hessian of the free energy with respect to mass fractions,  $\mathbf{\Upsilon} \sim \partial^2 H / \partial \mathbf{w}^2$ , and must therefore be symmetric. This is a sort of Maxwell relation that has to be obeyed and any model for  $\mathbf{\Gamma}$  must be constructed to obey this property.

## 2.4 Binary Mixture

Note that converting from mass to mole fraction derivatives is done using

$$\frac{\partial x_1}{\partial w_1} = \frac{\bar{m}^2}{m_1 m_2} = \frac{x_1 x_2}{w_1 w_2},$$

where  $\bar{m} = m_1 m_2 / (w_1 m_2 + w_2 m_1) = \rho / n$ . This gives

$$\frac{\partial \mu_1}{\partial w_1} = \frac{\partial \mu_1}{\partial x_1} \frac{\partial x_1}{\partial w_1} = \frac{\bar{m}^2}{m_1 m_2} \frac{n k_B T}{\rho} \frac{\Gamma_{11}}{w_1} = \frac{k_B T}{w_1 (w_1 m_2 + w_2 m_1)} \Gamma_{11},$$

and similarly for other derivatives. This gives

$$\frac{\partial \mu}{\partial w} = \left( \frac{\partial \bar{\mu}_1}{\partial w_1} \right)_{w_1 + w_2 = 1}$$

as

$$\frac{\partial \mu}{\partial w} = \frac{\partial x_1}{\partial w_1} \left[ \left( \frac{\partial \mu_1}{\partial x_1} - \frac{\partial \mu_2}{\partial x_1} \right) - \left( \frac{\partial \mu_1}{\partial x_2} - \frac{\partial \mu_2}{\partial x_2} \right) \right] = \frac{\bar{m} k_B T}{m_1 m_2} \left( \frac{\Gamma_{11}}{w_1} - \frac{\Gamma_{21}}{w_1} - \frac{\Gamma_{12}}{w_2} + \frac{\Gamma_{22}}{w_2} \right) = \frac{\bar{m} k_B T}{m_1 m_2} \cdot \frac{\bar{\Gamma}}{w_1 w_2},$$

where the reduced thermodynamic factor

$$\bar{\Gamma} = w_2 (\Gamma_{11} - \Gamma_{21}) - w_1 (\Gamma_{12} - \Gamma_{22})$$

is directly related to the constrained derivative denoted with  $\partial \mu / \partial c$  in our binary and low Mach papers. For an ideal binary mixture,  $\Gamma_{ij} = \delta_{ij}$ ,  $\bar{\Gamma} = 1$  and we get

$$\frac{\partial \mu}{\partial w} = \frac{\bar{m} k_B T}{m_1 m_2} \cdot \frac{1}{w_1 w_2} = \frac{k_B T}{w_1 w_2 (w_1 m_2 + w_2 m_1)},$$

consistent with the formula in the binary paper.

For a binary mixture of species,

$$\boldsymbol{\chi} = \frac{D_{MS}}{x_1 x_2} \begin{bmatrix} w_2^2 & -w_1 w_2 \\ -w_1 w_2 & w_1^2 \end{bmatrix} = \frac{D_{MS}}{x_1 x_2} \begin{bmatrix} w_2 \\ -w_1 \end{bmatrix} \begin{bmatrix} w_2 & -w_1 \end{bmatrix},$$

where  $D_{MS} = D_{12}$  is the Maxwell-Stefan coefficient.

The deterministic mass flux due to composition gradients is

$$\mathbf{F} = -\rho \mathbf{W} \boldsymbol{\chi} \mathbf{\Gamma} \nabla \mathbf{x} = -\rho D_{MS} \bar{\Gamma} \frac{w_1 w_2}{x_1 x_2} \begin{bmatrix} \nabla x_1 \\ -\nabla x_1 \end{bmatrix}.$$

We can convert this to use gradients of mass fractions as in the previous binary formulation,

$$\mathbf{F}_1 = -\rho D_{MS} \bar{\Gamma} \frac{w_1 w_2}{x_1 x_2} \left( \frac{\partial x_1}{\partial w_1} \right) \nabla w_1 = -\rho D_{MS} \bar{\Gamma} \nabla w_1 = -\rho D_F \nabla w_1,$$

where

$$D_F = D_{MS} \bar{\Gamma} \quad (10)$$

is the Fickian diffusion coefficient, and  $\mathbf{F}_2 = -\mathbf{F}_1$ .

The stochastic flux can be written in the form

$$\widetilde{\mathbf{F}} = \rho \sqrt{\frac{2k_B T}{P} \cdot \frac{D_{MS}}{x_1 x_2}} \mathbf{W} \begin{bmatrix} w_2 \\ -w_1 \end{bmatrix} \mathcal{Z} = \sqrt{2\rho^2 \frac{k_B T}{P} \frac{m_1 m_2}{\bar{m}^2} w_1 w_2 D_{MS}} \begin{bmatrix} \mathcal{Z} \\ -\mathcal{Z} \end{bmatrix}.$$

Let's compare to our previous binary formulation, where the covariance of the stochastic flux was written as

$$2\rho k_B T D_F \left( \frac{\partial \mu}{\partial w} \right)^{-1} = 2\rho k_B T D_{MS} \bar{\Gamma} \left( \frac{\rho k_B T}{\bar{m} P} \right) \left( \frac{\bar{m} k_B T}{m_1 m_2} \cdot \frac{\bar{\Gamma}}{w_1 w_2} \right)^{-1} = 2\rho^2 \frac{k_B T}{P} \frac{m_1 m_2}{\bar{m}^2} w_1 w_2 D_{MS}.$$

This matches the covariance of  $\widetilde{\mathbf{F}}$  so the two formulations are indeed equivalent.

#### 2.4.1 Fluctuations in the Maxwell-Stefan Description (UNFINISHED)

**Donev: This part has not been updated to the new notation**

I will now show that our description of fluctuating hydrodynamics for mixtures is equivalent to the following intuitive system of equations,

$$\begin{aligned} 0 &= - \sum_{j \neq i} \frac{x_i x_j}{D_{ij}} (\mathbf{v}_i - \mathbf{v}_j) + \left( \mathbf{d}_i - \frac{\nabla T}{T} \mathbf{e}_i \right) + \sum_{j \neq i} \left( 2k_B T \frac{x_i x_j}{D_{ij}} \right)^{\frac{1}{2}} \mathcal{W}_{ij} \\ \sum_i \rho_i \mathbf{v}_i &= 0, \end{aligned}$$

where  $\mathcal{W}_{ij} = -\mathcal{W}_{ji}$  are white-noise processes. The physical intuition behind this is as follows. In the MS description of diffusion,  $\frac{x_i x_j}{D_{ij}} (\mathbf{v}_i - \mathbf{v}_j)$  is a friction force between species  $i$  and  $j$ , with friction constant  $\gamma_{ij} = x_i x_j / D_{ij}$ . So the fluctuating (Langevin) force that goes with it is  $\sqrt{2k_B T \gamma_{ij}} \mathcal{W}_{ij}$ , where  $\mathcal{W}_{ij} = -\mathcal{W}_{ji}$  (by Newton's third law) is the random force between the two components. The force  $\mathbf{d} - \frac{\nabla T}{T} \mathbf{e}$  is the thermodynamic driving force due to gradients of chemical potential. So the first equation is just force balance for each component. The second equation makes the velocities uniquely determined (i.e., expressed in the center-of-mass reference frame).

In matrix notation, we can write this as

$$\boldsymbol{\zeta} \mathbf{v} = \mathbf{d} - \frac{\nabla T}{T} \mathbf{e} + \sqrt{2k_B T} \mathbf{K} \mathbf{W},$$

where  $\mathbf{W}$  is a vector of  $N_s(N_s - 1)$  independent white noise processes and  $\mathbf{K}$  is an  $N_s \times [N_s(N_s - 1)]$  matrix that is easy to construct in Maple. Here the invertible matrix

$$\boldsymbol{\zeta} = \boldsymbol{\zeta}' + \alpha \mathbf{1} \otimes \boldsymbol{\rho}^T$$

has entries (similar to  $\mathbf{B}$  but without the  $\rho$ 's),

$$\zeta'_{ij} = -\delta_{ij} x_i \sum_{k \neq i} \frac{x_k}{D_{ik}} + (1 - \delta_{ij}) \frac{x_i x_j}{D_{ij}}.$$



We can therefore write:

$$\mathbf{F} = \boldsymbol{\varrho} \mathbf{v} = \boldsymbol{\varrho} \boldsymbol{\zeta}^{-1} \left( \mathbf{d} - \frac{\nabla T}{T} \mathbf{e} \right) + \sqrt{2k_B T} \boldsymbol{\varrho} \boldsymbol{\zeta}^{-1} \mathbf{K} \mathbf{W}. \quad (11)$$

Comparing the deterministic flux to the previous relation

$$\mathbf{F} = \mathbf{B}^\dagger \left( \mathbf{d} - \frac{\nabla T}{T} \mathbf{e} \right)$$

we identify  $\mathbf{B}^\dagger = \boldsymbol{\varrho} \boldsymbol{\zeta}^{-1}$  or  $\mathbf{B} = \boldsymbol{\zeta} \boldsymbol{\varrho}^{-1}$ , which I have confirmed in Maple.

The stochastic mass flux is  $\tilde{\mathbf{F}} = \sqrt{2k_B T} \boldsymbol{\varrho} \boldsymbol{\zeta}^{-1} \mathbf{K} \mathbf{W}$ , and its covariance is

$$\langle \tilde{\mathbf{F}} \tilde{\mathbf{F}}^T \rangle = k_B \mathbf{L}' = 2k_B T \boldsymbol{\varrho} \boldsymbol{\zeta}^{-1} \mathbf{K} \mathbf{K}^T \boldsymbol{\zeta}^{-T} \boldsymbol{\varrho}.$$

Using Maple, I have confirmed (but do not know how to prove on paper) that

$$\mathbf{L}' = \mathbf{L} = -T \mathbf{B}^\dagger \mathbf{C}$$

for up to four species. Therefore, (11) description is identical to our present description:

$$\mathbf{F} = \mathbf{B}^\dagger \left( \mathbf{d} - \frac{\nabla T}{T} \mathbf{e} \right) + (k_B \mathbf{L})^{\frac{1}{2}} \widetilde{\mathbf{W}}$$

In the MS description derived here, however, the fluctuating flux is constructed explicitly without using Cholesky factorization! But, it uses  $N_s(N_s - 1)$  random numbers  $\mathbf{W}$  instead of only  $N_s - 1$  random numbers  $\widetilde{\mathbf{W}}$  as does the Cholesky factorization method. So the MS description here is mostly of theoretical interest. It is elegant and nice and shows the physics of the fluctuating flux. It also proves that  $\mathbf{L}$  is positive semi-definite since  $\mathbf{L}'$  is a covariance matrix.

### 3 Empirical models (UNFINISHED)

Ternary mixture empirical model:

$$D_{ij} = \eta^{-1} \left( \frac{k_B T}{\alpha \sigma_i} \right)^{x_i} \left( \frac{k_B T}{\alpha \sigma_j} \right)^{x_j} \left[ \left( \frac{k_B T}{\alpha} \right) \left( \frac{\sqrt{\eta_i \eta_j}}{\sigma_i \sigma_j \eta_k} \right)^{\frac{1}{2}} \right]^{x_k}.$$

### References

- [1] Vincent Giovangigli. Convergent iterative methods for multicomponent diffusion. *IMPACT of Computing in Science and Engineering*, 3(3):244–276, 1991.