Definitions of diffusion coefficients

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November 2023

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1 Introduction

Diffusion- and thermal diffusion coefficients can be defined in a plethora of ways, which can quickly lead to confusion. This memo aims to clearly state how diffusion coefficients computed using the KineticGas package with various options are defined, and serve as a starting point for users that wish to use the KineticGas package together with other definitions of diffusion and thermal diffusion coefficients.

2 Diffusion Coefficients

When defining the diffusion coefficients we must make a set of choices:

- What frame of reference do the coefficients apply to?

- What basis are the fluxes measured in?

- What forces are our driving forces?

- Are we using an independent or dependent set of driving forces?

- If we are using an independent set: What is the dependent driving force?

In this memo, the notation $J_i^{(x,f)}$ is used to denote a flux on the x basis, in the f frame of reference, such that a molar flux in the mole-centre frame of reference is denoted $J_i^{(n,n)}$, and the corresponding mass flux is $J_i^{(m,n)}) = m_i J_i^{(n,n)}$, where m_i is the molar mass of species i. Diffusion coefficients are denoted $D_{ij}^{(f,l)}$, where the indices indicate

- i : The flux the diffusion coefficient applies to.

- j : The force the diffusion coefficient applies to.

- f : The frame of reference the diffusion coefficient applies to.

- l : The index of the dependent force. The index l is omitted for diffusion coefficients defined using a dependent set of forces.

This indexing may at first seem excessive, but it is required in order to accurately differentiate between the different definitions discussed here. Using this notation, we can write Ficks' law on a molar basis in the centre of moles (CoN) frame of reference (FoR) for an arbitrary multicomponent mixture as

$$J_i^{(n,n)} = -\sum_{j \neq l} D_{ij}^{(n,l)} \nabla c_j \tag{1}$$

where we have used the molar concentrations as driving forces, and chosen to use an independent set of driving forces, as the dependent gradient ∇c_l is given by

$$\nabla c_l = -\sum_{j \neq l} \nabla c_j. \tag{2}$$

For a binary mixture, taking $l = 2$, this reduces to

$$J_1^{(n,n)} = -D_{11}^{(n,2)} \nabla c_1, \quad J_2^{(n,n)} = -D_{21}^{(n,2)} \nabla c_1,$$
$$J_1^{(n,n)} = -J_2^{(n,n)} \iff D_{11}^{(n,2)} = -D_{21}^{(n,2)}, \tag{3}$$

a commonly known formulation of Ficks' law in binary mixtures.

To most easily expand our formulation of Ficks' law from binary to multicomponent mixtures, and to facilitate keeping track of indices, the KineticGas always[1] returns an $N \times N$ diffusion matrix, defined through

$$\begin{pmatrix} J_1 \\ J_2 \\ \vdots \\ J_N \end{pmatrix}^{(n,f)} = - \begin{bmatrix} D_{11} & D_{12} & \dots & D_{1N} \\ D_{21} & D_{22} & \dots & D_{2N} \\ \vdots & \vdots & \ddots & \vdots \\ D_{N1} & D_{N2} & \dots & D_{NN} \end{bmatrix}^{(f,l)} \begin{pmatrix} \nabla c_1 \\ \nabla c_2 \\ \vdots \\ \nabla c_N \end{pmatrix} \tag{4}$$

where the dependent species, l, is selected with the `dependent_idx` option (default is last component, $l = N$). For the described binary case mentioned above (CoN FoR, species 2 as the dependent species), this reduces to

$$\begin{pmatrix} J_1 \\ J_2 \end{pmatrix}^{(n,n)} = - \begin{bmatrix} D_{11} & 0 \\ D_{21} & 0 \end{bmatrix}^{(n,2)} \begin{pmatrix} \nabla c_1 \\ \nabla c_2 \end{pmatrix} \tag{5}$$

where, as described above, the coefficients fulfill $D_{11}^{(n,2)} = -D_{21}^{(n,2)}$. If we select species 1 as the dependent component, the resulting matrix is

$$\begin{pmatrix} J_1 \\ J_2 \end{pmatrix}^{(n,n)} = - \begin{bmatrix} 0 & D_{12} \\ 0 & D_{22} \end{bmatrix}^{(n,1)} \begin{pmatrix} \nabla c_1 \\ \nabla c_2 \end{pmatrix} \tag{6}$$

where, because for a binary mixture at isothermal, isobaric conditions, $\nabla c_1 = -\nabla c_2$, and in the CoN FoR, $J_1^{(n,n)} = -J_2^{(n,n)}$, we have $D_{12}^{(n,1)} = -D_{11}^{(n,2)}$ and $D_{22}^{(n,1)} = -D_{12}^{(n,1)} = D_{11}^{(n,2)}$. Because the binary system is often of interest, and we only need on diffusion coefficient to describe the system, using the option `use_binary=True` with the `interdiffusion` method, will return the diffusion coefficient

$$D^{(f)} = D_{11}^{(f,2)} = D_{22}^{(f,1)} = -D_{12}^{(f,1)} = -D_{21}^{(f,2)} \tag{7}$$

where f indicates the frame of reference, such that

$$J_1^{(n,n)} = -D^{(n)} \nabla c_1, \tag{8}$$

the common formulation of Ficks' law in the CoN FoR.

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[1] See note on the option `use_binary=True`.

2.1 Dependent driving forces

When translating between definitions of the diffusion coefficient it may be convenient to have access to diffusion coefficients defined using a *dependent* set of driving forces. These are then computed by selecting the option `use_independent=False`, and are defined through

$$
\begin{pmatrix} J_1 \\ J_2 \\ \vdots \\ J_N \end{pmatrix}^{(n,f)} = - \begin{bmatrix} D_{11} & D_{12} & \dots & D_{1N} \\ D_{21} & D_{22} & \dots & D_{2N} \\ \vdots & \vdots & \ddots & \vdots \\ D_{N1} & D_{N2} & \dots & D_{NN} \end{bmatrix}^{(f)} \begin{pmatrix} \nabla c_1 \\ \nabla c_2 \\ \vdots \\ \nabla c_N \end{pmatrix}
\tag{9}
$$

and in the binary case reduce to

$$
\begin{aligned}
J_1^{(n,f)} &= -D_{11}^{(f)} \nabla c_1 - D_{12}^{(f)} \nabla c_2 \\
J_2^{(n,f)} &= -D_{21}^{(f)} \nabla c_1 - D_{22}^{(f)} \nabla c_2.
\end{aligned}
\tag{10}
$$

Note that this diffusion matrix is not unique, and not invertible. It is primarily of interest because it gives easy access to the coefficients given in Eq. (19) of Ref. [1]. For practical calculations it is recommended to always use an independent set of driving forces.

2.2 Frames of Reference

In the centre of moles (CoN, default) frame of reference (FoR), the molar fluxes are subject to the constraint

$$
\sum_i J_i^{(n,n)} = 0.
\tag{11}
$$

in e.g. CFD calculations, we are typically more interested in fluxes in the centre of mass (CoM, barycentric) FoR. These are subject to the constraint

$$
\sum_i J_i^{(m,m)} = \sum_i m_i J_i^{(n,m)} = 0.
\tag{12}
$$

We compute diffusion coefficients that apply in the CoM FoR by using the option `frame_of_reference='CoM'` with the `interdiffusion` method, which returns the matrix of diffusion coefficients corresponding to the equation

$$
\begin{pmatrix} J_1 \\ J_2 \\ \vdots \\ J_N \end{pmatrix}^{(n,m)} = - \begin{bmatrix} D_{11} & D_{12} & \dots & D_{1N} \\ D_{21} & D_{22} & \dots & D_{2N} \\ \vdots & \vdots & \ddots & \vdots \\ D_{N1} & D_{N2} & \dots & D_{NN} \end{bmatrix}^{(m,l)} \begin{pmatrix} \nabla c_1 \\ \nabla c_2 \\ \vdots \\ \nabla c_N \end{pmatrix}
\tag{13}
$$

where, again, l indicates the dependent component (default is last component), and $D_{il} = 0$ for all i. This matrix is related to the diffusion matrix in the CoN FoR by the transformation matrix given in the supporting material to Ref. [1].

For all frames of reference (Exception: See section on Ortiz de Zárate.) the definition used for the diffusion coefficients returned by the KineticGas package is that in Eq. (4), that is:

- The fluxes are on a *molar basis.*

- The driving forces are the *molar concentration gradients.*

3 Thermal Diffusion

Thermal diffusion coefficients are defined through an extension of the equations in Sec. 2, using the same notation as is present there, thermal diffusion coefficients computed using the KineticGas package are defined through

$$
\begin{pmatrix} J_1 \\ J_2 \\ \vdots \\ J_N \end{pmatrix}^{(n,f)} = \begin{pmatrix} D_{T,1} \\ D_{T,2} \\ \vdots \\ D_{T,N} \end{pmatrix}^{(f,l)} \nabla \ln T - \begin{bmatrix} D_{11} & D_{12} & \dots & D_{1N} \\ D_{21} & D_{22} & \dots & D_{2N} \\ \vdots & \vdots & \ddots & \vdots \\ D_{N1} & D_{N2} & \dots & D_{NN} \end{bmatrix}^{(f,l)} \begin{pmatrix} \nabla c_1 \\ \nabla c_2 \\ \vdots \\ \nabla c_N \end{pmatrix} \tag{14}
$$

or, more compactly

$$
\mathbf{J}^{(n,f)} = \mathbf{D}_T^{(f,l)} \nabla \ln T - \underline{\boldsymbol{D}}^{(f,l)} \nabla \mathbf{c}. \tag{15}
$$

Note that because in the presence of a temperature gradient, the Gibbs-Duhem equation no longer reduces to

$$
\sum_i \nabla c_i = 0 \tag{16}
$$

the choice of dependent component (l) will not only effect the diffusion matrix $\underline{\boldsymbol{D}}^{(f,l)}$, but also the thermal diffusion vector $\mathbf{D}_T^{(f,l)}$. Just as for the diffusion matrix, the frame of reference and choice of dependent component for thermal diffusion coefficients is selected with the options `frame_of_reference` and `dependent_idx`, with the `thermal_diffusion_coeff` method.

Also, just as for the diffusion matrix, thermal diffusion coefficients computed using the KineticGas package are defined through Eq. (14), i.e. with $\nabla \ln T$ and the *molar concentration gradients* as the driving forces, and with the fluxes on a *molar* basis.

4 Ortiz de Zárate

Ortiz de Zárate showed that one may define the diffusion- and thermal diffusion coefficients such that they are equivalent in the centre of mass (CoM) and centre of moles (CoN) frame of reference (FoR). We denote these frame-independent coefficients as $\mathbf{D}_T^{(z)}$ and $\underline{\boldsymbol{D}}^{(z)}$, and they are defined through

$$
\begin{pmatrix} J_1 \\ J_2 \\ \vdots \\ J_{N-1} \end{pmatrix}^{(n,n)} = -c \left\{ \underline{\boldsymbol{X}} \begin{pmatrix} D_{T,1} \\ D_{T,2} \\ \vdots \\ D_{T,N-1} \end{pmatrix}^{(z)} \nabla T + \underline{\boldsymbol{X}} \begin{bmatrix} D_{11} & D_{12} & \dots & D_{1,N-1} \\ D_{21} & D_{22} & \dots & D_{2,N-1} \\ \vdots & \vdots & \ddots & \vdots \\ D_{N-1,1} & D_{N-1,2} & \dots & D_{N-1,N-1} \end{bmatrix}^{(z)} \underline{\boldsymbol{X}}^{-1} \begin{pmatrix} \nabla x_1 \\ \nabla x_2 \\ \vdots \\ \nabla x_{N-1} \end{pmatrix} \right\} \tag{17}
$$

or, more compactly

$$
\mathbf{J}^{(n,n)} = c \left\{ \underline{\boldsymbol{X}} \mathbf{D}_T^{(z)} \nabla T + \underline{\boldsymbol{X}} \underline{\boldsymbol{D}}^{(z)} \underline{\boldsymbol{X}}^{-1} \nabla \mathbf{x} \right\}, \tag{18}
$$

where we have arbitrarily chosen the last component as the dependent component for ease of notation, and $\underline{\boldsymbol{X}}$ is the matrix

$$
X_{ij} = \delta_{ij} x_i - x_i x_j. \tag{19}
$$

Ortiz de Zárate shows that these coefficients simultaneously fulfill

$$
\mathbf{J}^{(m,m)} = \rho \left\{ \underline{\boldsymbol{W}} \mathbf{D}_T^{(z)} \nabla T + \underline{\boldsymbol{W}} \underline{\boldsymbol{D}}^{(z)} \underline{\boldsymbol{W}}^{-1} \nabla \mathbf{w} \right\}, \tag{20}
$$

where w denote the mass fractions, ρ denotes the mass density, and $\underline{\boldsymbol{W}}$ is the matrix

$$
W_{ij} = \delta_{ij} w_i - w_i w_j. \tag{21}
$$

for details on how these are related to other diffusion coefficients, see the memo on binary limits.

To compute the coefficients $\mathbf{D}_T^{(z)}$ and $\underline{\boldsymbol{D}}^{(z)}$, use the option `frame_of_reference='zarate'`. For direct access to the coefficients

$$\underline{\boldsymbol{D}}^{(x)} = \underline{\boldsymbol{X}}\underline{\boldsymbol{D}}^{(z)}\underline{\boldsymbol{X}}^{-1}, \quad \text{and}$$
$$\underline{\boldsymbol{D}}^{(w)} = \underline{\boldsymbol{W}}\underline{\boldsymbol{D}}^{(z)}\underline{\boldsymbol{W}}^{-1} \tag{22}$$

use the options `frame_of_reference='zarate_x'` and `frame_of_reference='zarate_w'`

References

[1] V. G. Jervell and O. Wilhelmsen, "Revised Enskog theory for Mie fluids: Prediction of diffusion coefficients, thermal diffusion coefficients, viscosities, and thermal conductivities," *The Journal of Chemical Physics*, vol. 158, p. 224101, 06 2023.