Definition of frame-invariant Soret coefficients for ternary mixtures

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When a steady temperature gradient is applied to a multi-component liquid mixture thermodiffusion induces a separation of its components, and concentration gradients develop in the system. In the case of a binary liquid mixture, after some transient, a non-equilibrium steady state is reached where a constant (in time) concentration gradient is established. In isotropic fluids the applied temperature gradient and the induced concentration gradient are always parallel (or antiparallel). To quantify thermodiffusion in binary mixtures, the so-called Soret coefficient S_T (units of K^{-1}) is defined as proportional to the ratio of these steady concentration and temperature gradients, namely,

$$x(1-x)S_T\,\nabla T = -\nabla x, \tag{1}$$

with x is the (average) concentration of the mixture in mole fraction. The concentration prefactor $x(1-x)$ in the definition (1) of the Soret coefficient of a binary mixture makes the S_T value invariant under change in concentration representation. Indeed, if w is concentration in mass fraction, one has:

$$\frac{\nabla x}{x(1-x)} = \frac{\nabla w}{w(1-w)}, \tag{2}$$

and, consequently, the numerical value of S_T will be identically the same, independently of whether it is computed like in Eq. (1) with concentrations in mole fraction x, or by

$$w(1-w)S_T\,\nabla T = -\nabla w, \tag{3}$$

with concentration in mass fraction w.

In a ternary mixture there are two independent concentrations, x_1 and x_2, so that one initially needs two independent Soret coefficients $S_{T,1}$ and $S_{T,2}$ to describe thermodiffusion in it. Our purpose here is to show how to introduce a concentration prefactor in the definition of Soret coefficients for a ternary mixture that retains the frame-invariance that the S_T of Eq. (1) has for binaries. The inconvenience is that such a prefactor has to be in the form of a matrix. Then, if for a steady state one defines Soret coefficients in a ternary mixture as:

$$\begin{bmatrix} x_1(1-x_1) & -x_1x_2 \\ -x_1x_2 & x_2(1-x_2) \end{bmatrix} \begin{pmatrix} S_{T,1} \\ S_{T,2} \end{pmatrix} \nabla T = -\begin{pmatrix} \nabla x_1 \\ \nabla x_2 \end{pmatrix}, \tag{4}$$

the resulting Soret coefficients, $S_{T,1}$ and $S_{T,2}$, are independent of whether concentrations are expressed in mole or mass fraction. This can be shown by simple differentiation of the relationship between concentrations in mass and mole fractions in a ternary mixture, which gives:

$$\begin{bmatrix} x_1(1-x_1) & -x_1x_2 \\ -x_1x_2 & x_2(1-x_2) \end{bmatrix}^{-1} \begin{pmatrix} \nabla x_1 \\ \nabla x_2 \end{pmatrix} = \begin{bmatrix} w_1(1-w_1) & -w_1w_2 \\ -w_1w_2 & w_2(1-w_2) \end{bmatrix}^{-1} \begin{pmatrix} \nabla w_1 \\ \nabla w_2 \end{pmatrix}, \tag{5}$$

similar to Eq. (2) for binaries.

The frame-invariance ideas presented here can be extended [1] to unsteady situations, by introducing frame-invariant thermodiffusion coefficients, as well as to generic multi-component mixtures.

References

[1] J. M. Ortiz de Zárate: *Definition of frame-invariant thermodiffusion and Soret coefficients for ternary mixtures*. Eur. Phys. J. E **42**, accepted (2019).