Reference frames and negative main Fick diffusion coefficients

V. Shevtsova[1], T. Janzen[2], S. Kozlova[3], I. Ryzhkov[3], A. Mialdun[1], J. Vrabec[2]

[1]Microgravity Research Center, Université libre de Bruxelles (ULB), Brussels, Belgium
[2]Thermodynamics and Process Engineering, Technical University Berlin, Berlin, Germany
[3]Institute of Computational Modelling SB RAS, Krasnoyarsk, Russia
*vshev@ulb.ac.be

Recently, the scientific community has taken ternary mixtures more into focus because they can be seen as prototypes for truly multicomponent mixtures. Fick diffusion coefficients depend on the order of components because in Fick's law for a ternary mixture the fluxes of two components are written explicitly, while the third component serves as a reference component. Moreover, the numerical values also depend on the reference frame, for which the diffusive fluxes are expressed. Only the eigenvalues of the Fick diffusion matrix are independent on the order of components and the reference frame. There are three common reference frames for expressing Fick's law: volume-, mass- or molar-averaged. There is therefore a variety of diffusion coefficients in use. The Fickian diffusion coefficients are measured in the volume reference frame, the governing equations for thermodiffusion (Soret) are written in the mass reference frame and molecular dynamic simulation are done in the molar reference frame. Understanding the bridge between them is of particular interest for the researchers [1].

Another important point concerns the existence of negative main Fick diffusion coefficients in non-ideal solutions sometimes discussed in literature. The thermodynamic stability conditions [2] require that the sum of the main diffusion coefficient has to be positive

$$D_{11}+D_{22} > 0$$

and does not require the main diffusion coefficients to be individually positive. Negative main Fick diffusion coefficients violate physical intuition because they indicate that species oppose their dilution even in the absence of cross diffusion effects. Note that the negative main diffusion coefficients reported in the literature usually appeared in the course of transformations between different reference frames or when changing the order of components

In this study, the dependence of diffusion coefficients on the reference frame is thoroughly analyzed for seven ternary mixtures of different types. The key finding of this study is that negative values of main diffusion coefficients in ternary only appear in molar reference frame due to relatively large experimental uncertainties of cross diffusion coefficients measured in volume reference frame, which are propagated and amplified by frame transformation. Another highlight of this study is the existence of a strong similarity between main diffusion coefficients in the volume and mass reference frames for seven considered mixtures of different types.

References

[1] S. Kozlova, A. Mialdun, I. Ryzhkov, T. Janzen, J. Vrabec, V. Shevtsova*: Do ternary liquid mixtures exhibit negative main Fick diffusion coefficients?* Phys.Chem.Chem.Phys. **21**, 2140 (2019).

[2] D. G. Miller, V. Vitagliano, R. Sartorio: *Some comments on multicomponent diffusion: negative main term diffusion coefficients, second law constraints, solvent choices, and reference frame transformations*, J. Phys. Chem. **90**, 1509–1519 (1986).