Modeling Diffusion and Thermodiffusion Coefficients in Multicomponent Mixtures

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The goal of the present work is to establish theoretically rigorous way of modeling diffusion and thermodiffusion coefficients in multicomponent mixtures.

At present the governing equations describing the multicomponent mass transfer are well established, and the theory behind them is far developed, in the form of the non-equilibrium thermodynamics or the Maxwell-Stefan relations. However, the transport coefficients entering these equations remain unknown, especially, for realistically complex mixtures. Only in the ideal gas limit the Boltzmann theory provides rigorous and rather precise estimates of the transport properties. Several models for diffusion and thermodiffusion coefficients in dense multicomponent mixtures have been developed. However, these models are largely based on empirical arguments. The lack of experimental data (only few sets of datapoints for ternary diffusion, difficulties in measurements of the thermodiffusion ratios) reduces even more predictability of these models.

Diffusion in an n-component mixture is described by n(n-1)/2 diffusion coefficients. Additional (n-1) coeffiecients are needed in order to describe thermodiffusion. There is no known functional dependence between these coefficients, and they cannot be determined separately in different experiments, but only all together.

In order to compensate for deficiency of the existing experimental data, a better theoretical understanding of the structure of the transport coefficients is required. Our goal is not to provide a specific model, but to produce a rigorous physical framework for future modeling. Such a framework is constructed by means of the theory of fluctuations around an equilibrium state, described both by the methods of the statistical mechanics and by the theory of Markov processes.

The rate of diffusion in the mixture may be described in terms of three factors: 1) the thermodynamic factor, determined by the structure of the mixture and the system of thermodynamic coordinates, in which diffusion is expressed, 2) the kinetic factor, or the rate of the molecular motion, and 3) the resistance factor, determined by the fact that other molecules may serve the obstacles on the way of a given molecule. For thermodiffusion, the fourth energetic factor should be added. The methods developed in the present work make it possible to obtain exact expressions for all the three factors and find the right way of their combination and expressing in terms of the equilibrium properties. The resistance factor is expressed in terms of the newly introduced penetration lengths of the molecules. These are also equilibrium properties, although their expression in terms of the standard properties (pressure, temperature etc.) is not straightforward. The penetration lengths can be determined by molecular dynamics simulations or modeled exceeding from obvious physical considerations and experimental data available. For validation of the models developed, we compare them with the available sets of experimental data and, also with other models available for multicomponent diffusion and thermodiffusion coefficients.