Predicting self-diffusion and transport diffusion coefficients using entropy scaling and PC-SAFT

J. Mele[1]*, M. Hopp[1], A. Bardow[2], J. Gross[1]

[1]University of Stuttgart, Institute of Thermodynamics and Thermal Process Engineering, Stuttgart, Germany
[2]RWTH Aachen University, Chair of Technical Thermodynamics, Aachen, Germany
*mele@itt.uni-stuttgart.de

Many approaches for the prediction of transport diffusion coefficients D_{ij} require knowledge of self-diffusion coefficients of pure substances D^{self} or diffusion coefficients at infinite dilution D^0. With the scarce availability of experimental data, we show approaches for the calculation of these properties in our study.

To describe and even predict self-diffusion D^{self} using only a thermal equation of state, the entropy scaling method proposed by Rosenfeld [1] provides an impressively simple but accurate approach. Rosenfeld found a monovariable dependence between residual entropy and transport properties. We use the PCP-SAFT equation of state [2] to calculate residual entropies. With a suitable correlation function the entropy scaling method for self-diffusion coefficients shows good agreement with experimental data for all available systems. We show results for various chemical families in the entire fluid region [3].

For the calculation of diffusion coefficient at infinite dilution D^0 most approaches from literature use variations of the Stokes-Einstein (SE) Equation [4]. Despite the crude assumptions inherent in the SE equation for molecular species, some approaches lead to satisfying results for many systems, but require many input parameters and some define various equations for specific chemical families. To overcome these problems, we develop a modified SE approach to estimate D^0 using only D^{self} and viscosity η of the corresponding pure substances. Both, D^{self} and η [5], are calculated through entropy scaling. Further, we extended our new approach by an entropy dependent function to correct for inaccuracies of SE concerning solved gases. So far, we achieved promising results in the calculation of D^0 for mixtures of various species. The next step of our work will be the application of the presented approaches for D^0 and D^{self} into well-known approaches for D_{ij}.

References

[1] Y. Rosenfeld: *Relation between the transport coefficient and the internal entropy of simple systems.* Phys. Rev. **15**, 2545–2549 (1977).

[2] J. Gross, G. Sadowski: *Pertubed-Chain SAFT: An equation of state based on a pertubation theory for chain molecules.* Ind. Eng. Chem. Res. **40**, 1244–1260 (2001).

[3] M. Hopp, J. Mele, J. Gross: *Self-diffusion coefficients from entropy scaling using the PCP-SAFT equation of state.* Ind. Eng. Chem. Res. **57**, 12942–12950 (2018).

[4] A. Einstein: *Über die von der molekularkinetischen Theorie der Wärme geforderte Bewegung von in ruhenden Flüssigkeiten suspendierten Teilchen.* Annalen der Physik **17**, 549-560 (1905).

[5] O. Lötgering-Lin, J. Gross: *Group contribution method for viscosities based on entropy scaling using the Perturbed-Chain Polar Statistical Associating Fluid Theory.* Ind. Eng. Chem. Res. **54**, 7942–7952 (2015).

Financial support of the Deutsche Forschungsgemeinschaft (DFG) through project GR 2948/2-2 is greatly acknowledged.