Kirkwood-Buff Integrals from Molecular Simulation

Noura Dawas
Process & Energy Laboratory, TU Delft, Delft, Netherlands

Peter Kruger
Graduate School of Engineering and Molecular Chirality Research Center, University of Chiba, Chiba, Japan

Sondre Schnell
Department of Materials Science and Engineering, NTNU, Trondheim, Norway

Jean-Marc Simon [C, S]
Physical Chemistry, ICB, University of Bourgogne, Dijon, France
jmsimon@u-bourgogne.fr

Thijs Vlugt
Process & Energy Laboratory, TU Delft, Delft, Netherlands

The Kirkwood-Buff (KB) theory provides a rigorous framework to predict thermodynamic properties of isotropic liquids from the microscopic structure. Several thermodynamic quantities relate to KB integrals, such as partial molar volumes. KB integrals are expressed as integrals of RDFs over volume but can also be obtained from density fluctuations in the grand-canonical ensemble. Various methods have been proposed to estimate KB integrals from molecular simulation. In this presentation, we will review the available methods to compute KB integrals from molecular simulations of finite systems, and particular attention is paid to finite-size effects. We will also review various applications of KB integrals computed from simulations. These applications demonstrate the importance of computing KB integrals for relating findings of molecular simulation to macroscopic thermodynamic properties of isotropic liquids [1].

References

[1] Noura Dawass , Peter Krüger , Sondre K. Schnell , Jean-Marc Simon , T.J.H. Vlugt, Fluid Phase Equilibria, 486, 21 (2019)