Accurate Kirkwood-Buff Integrals from Molecular Dynamics Simulations

Authors:
R. Wedberg, PhD stud., DTU Chemical Engineering, Technical University of Denmark
J.P. O'Connell, Professor, Dept. of Chemical Engineering, University of Virginia
G.H. Peters, Assoc. Prof., DTU Chemistry, Technical University of Denmark and MEMPHYS - Centre for Biomembrane Physics, University of Southern Denmark
J. Abildskov, Assoc. Prof., DTU Chemical Engineering, Technical University of Denmark

Abstract:
We seek to develop a rigorous approach for extracting Kirkwood-Buff (KB) integrals, i.e. spatial integrals of the molecular pair-distribution functions [1, 2], from molecular dynamics simulations in the NVT or NPT ensemble. Computing the KB integrals of a mixture at different compositions allows one to calculate several derivatives of thermodynamic functions (activities, partial molar volumes, isothermal compressibility) easily [3]. However, direct numerical integration of the g(r) obtained from MD is fragile since the tail deviates from the desirable, grand-canonical distribution function. Various empirical approaches to extend the MD results to large r, and thus obtain an accurate integral, have been explored previously [4, 5].

In this work, we utilize the asymptotic behavior of the direct correlation function, c(r), which at large r approaches the Mayer function, and connect this with the total correlation function, h(r), via the Ornstein-Zernike relation [6]. The g(r) obtained from MD is assumed to be correct for r < R for a certain R. An extension is sought, that is consistent with a c(r) exhibiting the proper behavior when r > R. Together with the requirement that g(r) and c(r) satisfy the Ornstein-Zernike equation one obtains a closed form integral equation, which is efficiently solved using Newton's method. This resembles an approach proposed by Verlet [7]. Our method is tested on the Lennard-Jones fluid. MD simulations are carried out covering a broad range of temperatures and densities. Verification of the results is done by comparing the isothermal compressibilities derived from the KB integrals with those obtained from the equation of state by Johnson et. al. [8], which results from smoothing PVT data obtained from a large number of MD simulation with the Lennard-Jones potential. The two routes are found to be in good agreement.

The paper describes the results obtained so far, and results of current work on rationalizing the choice of R, and extending the method to angle-dependent potentials.

References
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