Towards a thermodynamically consistent, quantitatively accurate integral equation theory

Daniel Tomazic, Martin Urban, Stefan M. Kast*

Physikalische Chemie III, TU Dortmund, D-44227 Dortmund, Germany
e-mail: daniel.tomazic@tu-dortmund.de

The integral equation (IE) formalism of theories of the liquid and solution state is based on a set of nonlinear equations that connect the total and the direct correlation functions by a convolution product and by a so-called closure relation which also contains the interaction potential. In contrast to explicit molecular simulations the solution to an IE theory allows for fast, noise-free calculations of structural properties such as the pair distribution functions as well as of thermodynamic quantities like the free energy or the chemical potential. The quality of an IE calculation relies on the accuracy of the so-called bridge function that is in principle, though not easily, obtained from simulations, but for which several approximations have been described.

Here we follow-up on our earlier formally exact result concerning conditions on the bridge function leading to thermodynamic consistency in the sense that the free energy is required to be a path-independent state function [1]. We demonstrate for the Lennard-Jones fluid that bridge data taken directly from a simulation can be used in an analytical expression [2] for the free energy which matches reference data from molecular dynamics simulations very accurately. Moreover, a novel exact result is presented by deriving an inequality between the renormalized direct correlation function and the bridge function which is useful for the development of bridge approximations and for controlling the numerical stability of IE solutions [3].

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