Additivity of the potential of mean force: Mayer's theory and computer simulation

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Abstract

Mayer derived in 1942 a certain number of equations for a one-component fluid using the grand canonical ensemble (GCE) [1,2]. These equations serve as the starting point for Mayer's integral equation theory and are the one-component equivalent of the McMillan-Mayer (MM) solution theory [3].
Due to the theoretical and practical interest about the thermodynamics of solutions, it is necessary to study first the one-component system. In this work the corresponding equations which relate the pressure, internal energy and density of the system between two different activities z and z*, are obtained in terms of the potential of mean force and the pair correlation function. In the derivation the additivity of the potential of mean force is assumed. Molecular dynamics simulations [4] are used to check the influence of this additivity assumption in the calculation of thermodynamic properties by means of the pressure equation.

References

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