Perturbation Theory Based Equation of State for Small Systems under Confinement

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Equations of state (EOS) based on perturbation theory are useful tools in thermodynamics due to their ability to provide insight on the behavior of model fluids. One example is the Baker Henderson perturbation theory (BHPT) [1]. For fluids confined in small geometries, there is currently a lack of successful methods to predict thermodynamic properties from EOS, as thermodynamics of small systems is known to deviate from the classical thermodynamic description [2]. Popular tools for obtaining thermodynamic properties can therefore not be directly applied without doing some modifications.

We show how such modifications can be made to the BHPT so that it can be applied to fluids under confinement. The extended theory is referred to as BHPT-small. The reference system of BHPT is the hard sphere fluid, meaning that the perturbation terms are calculated from the radial distribution function (RDF) of this system. Two major findings were made by investigating how the RDF of a hard sphere fluid, confined by a spherical geometry differs from the bulk RDF. Due to the non-periodic boundaries of the confined system, the RDF will approach zero for at indefinitely pair-distances, instead of tending towards unity. In addition, particles adsorb on the boundary of the spherical confinement, which leads to a depletion of particles in its center. The density experienced by the particles in the center is therefore not equal to the average density of the fluid.

We further demonstrate how BHPT-small can be formulated for pores of different sizes and shapes. The extended perturbation theory provides a tool to compute thermodynamic properties of nanosystems that is applicable to a variety of examples.

References

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