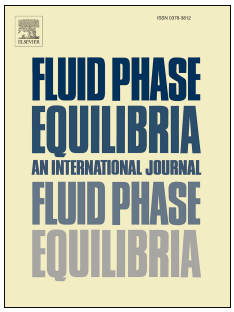

Detailed pedagogical review and analysis of Wertheim's thermodynamic perturbation theory

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Detailed pedagogical review and analysis of Wertheim's Thermodynamic Perturbation Theory

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Abstract

The Thermodynamic Perturbation Theory (TPT) developed by Michael S. Wertheim in the years 1984 to 1986 provides a powerful framework for modeling directional attractive interactions. TPT is successful, for example, in describing fluids with hydrogen-bonding interactions and it leads to accurate models of non-spherical chain fluids. The theory of Wertheim is elegant in many ways, but his original work is not easy to read and does not effortlessly reveal all of its beautiful features. Our study aims at providing a review of the graph-theoretical development that led Wertheim to the TPT. Our motive is to (1) develop appreciation for the ingenious development of Wertheim, (2) make the assumptions behind TPT transparent, and (3) thereby possibly facilitate further development in the theory of fluids. This review is mainly pedagogical and we intend to alleviate the lack of scientific novelty to a small extent by formulating the TPT of arbitrary order.

Keywords: Thermodynamic Perturbation Theory, TPT, association, hard chain, Wertheim

1. Introduction

A perturbation theory in statistical thermodynamics allows to approximately predict the thermodynamic properties of a target fluid with defined intermolecular potential. What is needed is a reference fluid with two requirements: First, the reference fluid must have well-known properties (such as Helmholtz energy, two-body correlation function, and possibly higher-body correlation functions). Secondly, the structure of the reference fluid should preferably be similar to the structure of the target fluid. With structure, we refer to the average arrangement of molecules around one another, as captured in the two- and higher-body correlation functions. The properties of a fluid with highly directional interactions, such as those arising from hydrogen-bonding interactions, are difficult to describe because there is no reference fluid that fulfills both of these requirements. Michael S. Wertheim in the years from 1984 to 1987 developed a powerful perturbation theory where a simple reference fluid, with a spherically symmetric pair potential suffices for describing a target fluid with highly directional interactions[1, 2, 3, 4]. The theory of Wertheim is original and intriguing in its graph theoretical roots and this review is intended to disclose these accomplished developments to non-expert readers.

The basic idea of perturbation theories was developed by van der Waals[5]. While early studies[6, 7, 8, 9] deal with special cases of perturbation theory, the first general perturbation expansion for the Helmholtz energy is given by Zwanzig[10]. The starting point for a modern perturbation theory is usually the division of the target fluid's intermolecular (pair) potential into the intermolecular potential of the reference fluid and a residual part, u_P, referred to as perturbing potential. One scales the perturbing potential u_P with a coupling parameter λ, in order to make a continuous transition from the reference fluid ($\lambda = 0$) to the

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