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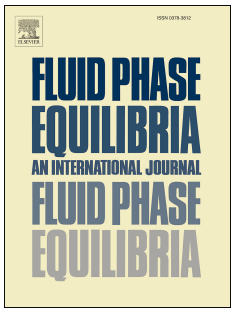

Perturbation Theories of the Thermodynamics of Polar and Associating Liquids: A Historical Perspective

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Perturbation Theories of the Thermodynamics of Polar and Associating Liquids: a Historical Perspective

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Abstract

A historical account is given of the development of perturbation theories for polar and associating liquids. A perturbation expansion of the free energy of a polar liquid about that for a liquid of spherical, non-polar molecules was first proposed by J.A. Barker in 1951, but its further development had to await the successful development of theories for simple, non-polar molecules, which did not occur until the late 1960's. The development of such approaches was further catalyzed by the first molecular simulation results for such polar liquids in the early 1970's. Although the Barker expansion did not converge well for strong electrostatic forces, a resummation using a Padé approximant due to G. Stell and coworkers gave excellent results for the free energy and other thermodynamic properties. A further major advance was the theory proposed by M.S. Wertheim in the mid-1980's, which accounted for the effects of highly directional forces that result in molecular association (H-bonding, charge transfer, etc.). Over the past 30 years this theory has been extended and found to give very good results for a wide variety of applications, including mixtures containing strongly associating molecules such as water, polymers, proteins, and other complex molecules.

1. Introduction

The search for a satisfactory theory of simple liquids of spherical, nonpolar molecules, such as hard spheres or Lennard-Jones molecules, occupied much effort in the first part of the 20th century. In particular, the period 1953 to 1970 saw the introduction of integral equation theories and perturbation theories that were finally successful for such fluids, first for hard spheres and subsequently for liquids of simple molecules with attractive forces, such as Lennard-Jones and square-well fluids. These developments were much catalyzed by the appearance of the first