

Summary of doctoral dissertation entitled:

Approaches based on the theory of thermodynamic fluctuations and molecular dynamics for predicting properties of molecular and ionic liquids under high pressures

Author: mgr inż. Bernadeta Jasiok

Supervisor: dr hab. Mirosław Chorażewski, prof. UŚ

Scientific tutor: prof. Eugene B. Postnikov

This dissertation addresses the complex problem of developing thermodynamic methods and equations of state to predict density and its derivatives, including the isobaric thermal expansion coefficient, the isothermal compressibility, and the speed of sound in single-phase liquids under increased pressure. This issue is important both from the point of view of fundamental research in the area of physical chemistry or liquid phase physics in general, as well as being relevant in industrial applications, such as where knowledge of the thermodynamic properties of the compressed liquid phase is essential. The former derives from lacking a general, universal, and functional theory of liquids, which mainly gives quantitative values of thermodynamic quantities in the single-phase region. The second, among other things, derives from the need for thermodynamic modeling of fuel injection processes in common-rail diesel engines designed to operate at pressures reaching values of several hundred MPa, as well as, for example, in the problems of high-pressure chemical catalysis (e.g., the problem of the ionic liquid-mediated lignin processing that one of the actual directions of Green Chemistry).

During the last decade (including earlier works in which the author of this dissertation is a co-author), it has been established that the goal of describing the physicochemical properties of simple molecular as well as ionic liquids can be approached by analyzing its connection to the thermodynamic density fluctuations, which in turn can be related to changes in the free volume of the system induced by external pressure. At the same time, this work has identified a set of open problems, the clarification of which is the main goal of this dissertation.

This dissertation discusses the objectives sequentially proceeding from the macroscopic to the microscopic thermodynamic picture of the compressed liquid phase. The first section addresses the limits of the applicability of the density fluctuations-based approach and its possible

extension in the case of applicability of the applied thermodynamic models to high-pressure regions, as well as the determination of the relevant parameters of the proposed isothermal equation of state at atmospheric pressure in such a way that the predicted density values are comparable within the limits of measurement uncertainty with those obtained by direct experiment. The second section presents the detailed mathematical and thermodynamic basis of the approach proposed in the first chapter. This allows generalizing them to the case of the properties of thermodynamic derivatives and the speed of sound, which is the essence of the discussion undertaken in this dissertation. The third section combines a macroscopic thermodynamic picture of the liquid phase with a microscopic one based on the results of molecular dynamics simulations. The latter aims to clarify thermodynamic anomalies and issues during the fluctuation model studies. These include some dissonance between predictions based on fluctuation theory and results based on acoustic and densitometric measurements during the isobaric thermal expansion coefficient of halogenated *n*-alkanes. The synergy of approaches based on molecular dynamics, thermodynamics, and the fluctuation theory of the compressed liquid phase, also allowed differentiating the stereochemical characteristics of the liquid systems studied, which ultimately translated into a multifaceted discussion of the possibility of predicting the thermodynamic properties of liquids under increased pressure.