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Review of the Ph. D. Thesis entitled "Approaches based on the theory of thermodynamic fluctuations and molecular dynamics for predicting properties of molecular and ionic liquids under high pressures", by Bernadeta Jasiok.

The doctoral dissertation of mgr. inz. Bernadeta Jasiok was entitled "Approaches based on the theory of thermodynamic fluctuations and molecular dynamics for predicting properties of molecular and ionic liquids under high pressures". It has been developed in the University of Silesia, specifically in the Institute of Chemistry, Faculty of Science and Technology, located at Katowice. Her doctoral supervisor is dr. hab. Mirosław Chorążewski, professor of this university. Her scientific tutor is Eugene B. Postnikov, from Kursk State University, Russia. The dissertation was organized as a collection of six papers, with an initial text in the form of a guidebook that summarizes the work carried on and the main results of her research during her Ph. D. education stage.

The dissertation consists on seven chapters, it has 109 pages and 40 references, if those given in the papers are not considered. The first chapter is an introduction, the next three ones explain the three main lines of the candidate's research, and the fourth presents the main conclusions of the Ph. D. thesis. The articles, with a brief description of each author's contribution, are shown in chapter six, and in the seventh one, a description of the researching activities of the candidate is presented. It must be

highlighted that the candidate is coauthor of another five articles, besides those presented in the Ph. D. Thesis, which sum up a total of eleven articles, a quite large number of publications for a Ph. D. student. Moreover, it must be pointed out that all publications were done in high impact factor journals, a fact that avails the quality of the scientific work.

The main subject of the Ph. D. thesis is the prediction of the thermodynamic properties of liquid substances. This is developed using two methodologies: equations of state and molecular simulation under the molecular dynamics approach. The candidate wisely splits the work in three parts, which are explained with the chapters 2, 3 and 4 of the dissertation. Moreover, there is also a correspondence between each chapter and the articles shown in chapter six: the chapter 2 would comprise the two first papers -P1 and P2, using candidate's notation-, the next two are dealt in the chapter 3 and the last two, which involve molecular simulation, are explained in chapter 4.

The first paper is devoted to the presentation of the fluctuation theory-based two state model, and the authors validate it using a large and precise dataset for alkanes, alkanols, benzene, and a silicone oil of industrial interest. It is important to stress that in spite of the results being pure predictions, the agreement between experimental and predicted values is very good; density shows deviations lower than 1% for most data. The second paper develops a machine learning methodology for the calculation of the isothermal compressibility of ionic liquids, a key property for the prediction methodology presented in the first article. The comparison of the predictions given by this machine learning algorithm with the experimental data were fairly good, with deviations of only few

percent. Considering the uncertainty that the original data have, the methodology proposed in the paper is highly valuable.

In the third paper, a prediction procedure for density and speed of sound prediction is presented. The density and heat capacity a liquid with unknown composition (SRS calibration fluid) were experimentally determined at atmospheric pressure. Moreover, the speed of sound over a wide pressure range was also measured. Using an integration procedure based on the experimental data, the density at high pressure was also obtained, and the fluctuation theory-based equation of state is used for density prediction, obtaining satisfactory results. Moreover, it is shown that the equations for carrying on this task can be determined from a mathematical framework analogous to that used in dynamical systems when the independent variable (time) is replaced by the density. Thus, the authors obtained the fluctuation theory-based equation of state from this procedure. Besides, using a linearization procedure for the speed of sound, the authors obtain an equation for speed of sound. They show that the predicted values are very close to the experimental ones, although they found that the curvature can be improved by adding a correction term, which depends on temperature. Finally, the authors evaluate the prediction capabilities of the two approximations using heptane, dodecane and diesel fuels. In the fourth paper, the procedure described in the previous article was used for ionic liquids speed of sound prediction. Data for density, speed of sound and heat capacity at atmospheric pressure were used as the input data, and the speed of sound is predicted at high pressure for a set of ionic liquids. The results were highly satisfactory, obtaining a relative average absolute deviation close to 0.85%.

The fifth and sixth papers constitute a different approach to the study of the thermodynamic properties of liquids, since they are based on molecular simulation, specifically, the molecular dynamics approximation to the problem was used. This is a more fundamental methodology, since it goes from a microscopic model of the liquid and, applying basic concepts of Statistical Physics, the thermodynamic properties are calculated. However, the downside of this methodology is the large computational resources needed for its implementation, compared with the simple calculations to be made with the analytic equations of state presented in the first part of the dissertation. The candidate simulated four molecules in liquid phase, covering wide temperature and pressure ranges. In the fifth paper, dibromethane was studied. The molecule was modelled using ab initio calculations and GAFF2 force field, although some modifications were made in order to improve it. The candidate calculated density and its derived properties (isobaric thermal expansivity and isothermal compressibility), isobaric and isochoric hear capacities, and compared with the experimental results. Moreover, other properties, as, for instance, speed of sound, are presented in the paper. The results from simulation and experiment satisfactorily agree. Finally, in the last paper, the thermodynamic properties of three chloropropanes, namely 1-chloropropane, 2-chloropropane and 1,2 dichloropropane are investigated. The authors use an integration procedure to obtain the thermodynamic properties at high pressure. They perform molecular dynamics simulation for 1-chloropropane and 2-chloropropane, using ab initio calculations to model the interaction potential. Moreover, they fit the experimental data to the Span –Wagner equation of state, and compare the results with the simulation data, obtaining quite satisfactory agreement.

Questions

1) The prediction methodology based on equations of state was applied to organic and ionic liquids. What would be its performance for water and aqueous solutions?
2) The equation of state used in the Ph. D. thesis was used for high pressure volumetric properties. Would it be possible to devise a similar scheme for prediction of isobaric and isochoric heat capacities?
3) The molecular dynamics calculation scheme was satisfactorily used for dibromomethane and chloroalkanes. What would the capabilities of this method be for ionic liquids? How would these compounds be modelled?

Award request

I would like to propose the distinction of the doctoral dissertation of Ms. Bernadeta Jasniok, if the conditions for this award are met. This is justified by the important achievements she has attained:

1) She was able to construct a methodology for density and speed of sound prediction at high pressure using simple but robust and physical-grounded equations, with very good results.
2) She has carried on molecular dynamic simulations to obtain the thermophysical properties of three molecules and compared the obtained results with experimental data, obtained quite good agreement. The work carried on in this field was not only calculations in the molecular dynamics framework, but she

also developed and improved the available force fields for the studied compounds using ab initio techniques.

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