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Report on the PhD 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 *MSc Bernadeta Jasiok*

The undersigned, Catinca Secuianu, habilitated university professor at the University Politehnica of Bucharest, Bucharest, Romania, I was appointed on April 18, 2023, by the Scientific Council of the Institute of Chemistry of the University of Silesia in Katowice to review the doctoral dissertation of Bernadeta Jasiok, MSc. The promoter of this doctorate is Prof. Mirosław Chorążewski.

The doctoral dissertation with the title “*Approaches based on the theory of thermodynamic fluctuations and molecular dynamics for predicting properties of molecular and ionic liquids under high pressures”* is a collection of six scientific papers published in very high impact journals that form a guidebook. The thesis contains 109 pages, including an appendix summarizing the author’ scientific activity. The thesis is structured in six chapters, the first one being an Introduction, and the last one the Conclusions, and ends with References. Chapters 2-4 present coherently the main contributions published in the six papers.

It is worth mentioning that the candidate is the ***first author*** for four out of the six papers of the PhD thesis, and she also co-authored another five high-quality papers, participated in numerous conferences, was awarded a grant and several prizes, as it follows from her activity mentioned at the end of doctoral thesis. Another important aspect is that for each paper that constitutes this thesis, the candidate's contributions are clearly highlighted.

In the ***Introduction*** the candidate presents the scientific context and motivation of the thesis and its aim to investigate predictive methods and their relations to the structural changes which may occur in compressed liquids in high-pressure regions. The candidate explains the importance of the properties selected for investigation (high pressure density, isobaric thermal expansion coefficient, heat capacity, isothermal compressibility, speed of sound, etc.), and their meaning. The candidate also describes which tools are used to investigate the properties and their relationship.

Chapter 2 entitled "*Variation of the isothermal compressibility as one of the key parameters allowing predicting the density of liquids at highly elevated pressures*" summarizes the findings of the first two papers (**P1**, **P2**) included in the thesis. Thus, the first paper – **P1**, with the title "***The prediction of high-pressure volumetric properties of compressed liquids using the two states model***" is a complex study proposing a different strategy approach built on the rejection of a single equation of state intended to replicate volumetric properties across the entire range of pressures at which they exist in the liquid state in favor of combining two equations of state that are valid for different ranges of the supplied density with the crossover rule for switching between them, or the two states model. The author's hypothesis is supported by experimental data showing that liquids behave differently elastically, as shown by their bulk moduli and reduced density fluctuations.

The advantage of this new approach ("*Two State Model*") is a predictive scheme that requires only the prior knowledge of some temperature dependent physico-chemical data easily to be obtained experimentally at atmospheric pressure (the speed of sound, the density, and the isobaric heat capacity).

The predictive capacity of the proposed approach is confirmed by performing a comparative analysis of different prototypical molecular liquids (n-alkanes, n-alcohols, and benzene, silicone oil 9981 LTNV-70). The case study revealed that the accuracy agrees with real physical high-pressure experiments up to a GPa range.

As experimental data are not always available or they are not available in the required range for testing the new models, the author also developed a method for predicting these data. The candidate used machine learning as an algorithm for gradient boosting on decision trees – CATBOOST which is presented in the second paper of the thesis, **P2**: "***The CATBOOST as a tool to predict the isothermal compressibility of ionic liquids***". The author used as the input quantities just few properties (i.e., the density at 298.15 K, the critical temperature and pressure, the molar mass, and the acentric coefficient) of individual ionic liquids and using the machine learning algorithms aimed to predict isothermal compressibility at 298.15 K. The candidate selected 35 ionic liquids and with the CATBOOST-based algorithm successfully predicted the isothermal compressibility at atmospheric pressure. The results are significantly better compared with other models such as SAFT-based EoS.

The ***third chapter*** entitled "***Substantiation of the approach for predicting the density and the speed of sound as based on the theory of thermodynamic fluctuations: applications to molecular and ionic liquids***" is based on papers **P3** and **P4** and describes the development of a sequential simultaneous approach based on the theory of thermodynamic fluctuations and Taylor's series expansion of the elevated pressure as a function of either the density or the speed of sound.

P3, entitled ***"Prediction of high-pressure properties of complex mixtures without knowledge of their composition as a problem of thermodynamic linear analysis***" proposes a mathematical framework in order to predict thermodynamic properties of molecular liquids and their mixtures at elevated pressures using their properties measured at ambient conditions only by considering such procedure as a modified analogue to the linear analysis procedure known from the theory of dynamical system when time is replaced by one of PVT quantities.

The candidate demonstrates that the proposed approach using the isothermal Fluctuation Theory-based Equation of State has universal effectiveness for different classes of liquid. The paper also includes the generalization of this line of reasoning on the case of the speed of sound and other thermodynamic quantities, which can be derived from such data via the acoustic route. The success of the proposed approach is also by SRS diesel calibrating liquid, for which a new original set of experimental data for a wide range of temperatures and pressures is reported.

"***Prediction of the speed of sound in ionic liquids as a function of pressure***" is the ***fourth paper*** of this thesis in which the candidate demonstrates the possibility of calculating the speed of sound of ionic liquids as a function of temperature and pressure using the fluctuation-based approach. The density, speed of sound, and heat capacity at atmospheric pressure are used for the calculations. The accuracy of the method is remarkable, and it was proved using nine ionic liquids.

Chapter 4 is entitled "***Determination of physicochemical properties of selected halogenoalkanes based on computer simulation methods"*** and it is based on papers **P5** and **P6**. The two papers present a systematic investigation of several halogenoalkanes by molecular dynamics (MD) simulations with the aim to obtain thermodynamic and structural information in a wide range of temperatures and pressures. The candidate aims to connect experimentally defined thermodynamic particularities with the atomistic structure of liquids.

The study published in the ***fifth paper*** entitled "***Liquid dibromomethane under pressure: a computational study"*** is not only a complex investigation but also shows the ability of the candidate to learn fast and perform very well, as part of the work was done in six months of academic exchange that the candidate spent at the University of Lorraine in France.

The investigation is continued in the ***sixth paper***, "***Thermophysical properties of chloropropanes in liquid phase: Experiments and simulations***" which also provides the MD simulation details.

Finally, the thesis ends with the general conclusions and summarizes the main findings: accurate predictions of density and isothermal compressibility up to very high pressures of the range of GPa using the Two States Model, ii) the speed of sound using an extension of the fluctuating equation of state, and iii) the thermal expansion, the isobaric and isochoric heat capacities, the isothermal compressibility, and the speed of sound using MD simulations.

The thesis is a logical sequence of high-quality scientific articles published by the candidate and the rapporteur recognizes the value and complexity of the work presented by Bernadeta Jasiok and considers that this work is worthy of being presented before a jury with a view to obtaining the degree of Doctor.

I conclude that the doctoral dissertation meets the conditions specified in Article 13(1) of the Act of 14 March 2003 on Scientific Degrees and Academic Title and Degrees and Title in Art (Journal of Laws of 2017, item 1789) and Article 179 of the Act of 3 July 2018, and I request the Scientific Council of the Institute of Chemistry of the University of Silesia in Katowice to admit Ms Bernadeta Jasiok, M.Sc. to further stages of the doctoral dissertation.

Prof. habil. dr. Catinca Secuianu

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