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Review of the doctoral 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, M.Sc.**

1. General Information

The subject of the review is a doctoral dissertation by Mrs. Bernadeta Jasiok, M.Sc., summarizing her scientific achievement entitled: *Approaches based on the theory of thermodynamic fluctuations and molecular dynamics for predicting properties of molecular and ionic liquids under high pressures*.

The dissertation was conducted by and carried out at the Institute of Chemistry of the University of Silesia under the supervision of Prof. Mirosław Chorążewski within the framework of the "Program for new interdisciplinary elements of education at the doctoral level for the field of chemistry" (POWR.03.02.00–00-I010/17). The work supervisor on the part of the program is Prof. Eugene B. Postnikov from Kursk State University.

2. Summary of the Dissertation

The thesis is given in the form of a series of scientific publications along with an appended guidebook encapsulating and briefly summarizing the key assumptions and results of the conducted research in each publication and the respective conclusions. The number of publications in the series is six; in the thesis, they are marked as **P1**-**P6** (I will follow the notation in the following parts of my review). I find such a number reasonable and adequate for a Ph.D. period (approx. 4-5 years). All the publications were submitted to peer-reviewed journals, including two in *Physical Chemistry Chemical Physics* (RSC, IF = 3.945) and the other four in the *Journal of Molecular Liquids* (Elsevier, IF = 6.663). Noteworthy is the fact that in four publications in the series, Mrs. Bernadeta Jasiok, M.Sc., is the very first and/or corresponding author. In scientific papers, this usually means the leading role and the key participation of the author in conducting the research as well as the article submission and revision workflow. This is confirmed by certified statements on the

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contributions of co-authors. The presented statements clearly and unequivocally show that the Ph.D. candidate was responsible for many relevant elements that made up each of the publications. They also demonstrate that the publications are the result of fruitful cooperation between all co-authors indeed.

The dissertation ends with an overall summary of the research output of Mrs. Bernadeta Jasiok, M.Sc., namely, the lists of all the papers published, conference papers given, internships and workshops participated, and awards granted.

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To sum up, I do not find any formal defects nor raise any objections that would prevent the further review or admission of the dissertation to the next stages of the proceedings.

3. Ph.D. Candidate Scientific Activity

The Ph.D. candidate, Mrs. Bernadeta Jasiok, M.Sc., is a co-author of 11 research papers published since 2017 in the indexed scientific journals that are well-recognized and prestigious in the field of physical and industrial chemistry: *Journal of Molecular Liquids* (5 papers), *Physical Chemistry Chemical Physics* (2 papers), *Scientific Reports*, *Fuel*, *Industrial Engineering & Chemistry Research*, *Fuel Processing Technology* (1 paper per each). The overall Impact Factor of the papers is 66.692. The papers were cited 33 times which corresponds to the Hirsch index of H = 4 (Scopus, accessed May 12, 2023). In my opinion, all these parameters/metrics should be considered impressive and deserving of distinction, considering the early stage of the Ph.D. candidate's scientific career.

Mrs. Bernadeta Jasiok, M.Sc., presented seven papers (including 5 in the form of oral presentations) at conferences of both national and international scope. She participated in three abroad internships, including two short ones and one half-year at the University of Lorraine (Nancy, France) financed under the Iwanowska Program by the Polish National Agency of Academic Exchange. Ms. Jasioek also showed initiative in raising funds for research. Since January 17, 2023, he has been managing the PRELUDIUM project "MEDUSA - thermodynamic anomalies in liquids using computer simulations" financially supported by the National Science Center.

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In conclusion, I believe that the presented summary of the research output (including its scientometric parameters) and the scientific activity of Mrs. Bernadeta Jasiok, M.Sc., fully confirm the legitimacy of conducting the doctoral dissertation and applying for the Ph. D.

4. The Guidebook Structure

The guide is 32 pages long; the number of cited works is 40. It was written in very good English. From the editing side, it was prepared almost perfectly (except for a few minor errors and typos, which I will not mention here). The only drawback is the

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lack of illustrations and summary tables, which makes reading comprehension practically impossible without publications at hand.

The content of the most substantive importance has been organized in the form of five chapters, in accordance with the standards of a typical scientific work: introduce, report, and conclude. Chapter 1 aims to introduce the subject of the dissertation (prepared on the basis of well-chosen items from the bibliography) and propose its main theses. It is very concise and to-the-point. In my opinion, it should be a little bit more comprehensive to be clearer for chemists and physicists specialized in different areas than physical chemistry/chemical physics. Chapters 2 to 4 summarize the relevant groups of related publications (Chapter 2: **P1**-**P2**; 3: **P3**-**P4**; 4: **P5**-**P6**). Finally, Chapter 5 presents the final conclusions, in which the doctoral student expresses her conviction about the impact of the obtained results on the development of physical chemistry, in particular the chemical thermodynamics of compressed liquids, and the potential applications of these results in the area of technological processes requiring the high-pressure.

To sum up, despite minor editing shortcomings, I believe that the guidebook was organized in a logical and thoughtful way. This certainly proves the doctoral student's extensive knowledge of the subject of the work and confirms her full understanding of the problem under study and the results of the research.

5. Summary of the Research and its Evaluation

Reviewing a doctoral thesis in the form of a guide to published publications is not an easy task, because the publications have already been assessed by experts assigned by the editorial offices of individual journals.

Therefore, I can assume that the presented publications do not contain significant substantive errors and focus my review on formulating: (1) remarks/comments of a general nature and (2) questions regarding elements that do not result from either the content of the guide or publication content.

Publications **P1**-**P2** refer the problem of the variation of the isothermal compressibility as the key parameter allowing predicting the density of liquids at highly elevated pressures.

In the work **P1**, it is postulated that *PVT* properties of liquids may not be accurately reproduced by using a single equation of state (EoS) for the whole pressure range up to the gigapascals. Such hypothesis addresses the issue of possible dualities in the physical nature of the liquid phase, reflected experimentally if some data on thermophysical and transport properties. Alternative approach to model those properties with two-state-model is proposed and tested for several *n*-alkanes, 1-alcohols, and benzene. The proposed model, being a kind of a merge of Fluctuation Theory EoS (FT-Eos) and the Murnaghan equation, is predictive (i.e., allows for calculating the properties of fluids at elevated pressure) assuming that the required isothermal compressibility at ambient pressure is calculated using density, heat

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capacity and speed of sound data. Results obtained from more than 2000 experimental data points yield the deviations in predicted density of the order of 1%.

In the work **P2**, completely different approach, namely, the machine learning (ML), is applied to model isothermal compressibility of 35 ionic liquids. Sophisticated algorithm called CATBOOST was applied to predict the target property value at T = 298.15 K based on single point of experimental density at T = 298.15 K, molar mass, and critical properties of ionic liquids. The research was motivated by a need to have access to accurate low-pressure isothermal compressibility data to effectively apply the models like the one discussed in **P1**.

Works **P3**-**P4** substantiate the approach for predicting the density and the speed of sound as based on the theory of thermo- dynamic fluctuations: applications to molecular and ionic liquids. In particular, **P3** proposes a very interesting mathematical framework, which argues the possibility 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. In **P4**, in turn, the authors usee some transformations and assumptions from **P3** to derive a formula by which it is possible to estimate the speed of sound in liquids over a wide range of both temperature and pressure. The formula was tested on a variety or simple and complex fluids, including 9 ionic liquids. Unfortunately, I did not find any qualitative comparative analysis against any of the models available in the literature.

Papers **P5**-**P6** change the research method to completely different kind of technique and scale, namely, to the computer simulations, specifically to molecular dynamics (MD). The system under study was also updated, as the MD simulations were performed on dibromomethane (**P5**) and three chloropropanes (**P6**). The papers **P5**-**P6** nicely demonstrate a link between diversity of thermophysical properties and fundamental properties of the matter (interactions on molecular level/forcefield; expressed in MD as a forcefield). Compared to the previous papers, **P5** and **P6** are focused more on isobaric expansion coefficients rather than isothermal compressibility. Thermodynamic "add-on" to the **P6** is an analysis of the chloropropanes' thermophysical data using the Span-Wagner multiparametric EoS.

As can be easily noticed, the works **P1-P6**, are all focused on studies of an impact of high pressure on thermodynamic data of liquids. For a chemist not specialized in physical chemistry, in particular the chemical thermodynamics, such research may seem to be "static" (or even boring). Dissertation of Mrs. Bernadeta Jasiok, M.Sc., demonstrates, however, that high pressure physical chemistry is a very vivid topic which can be tackled from different angles. In other words, the thesis shows that it can be investigated using a great variety of methods. Importance and value of the experimental methods for development in this field is unquestionable. However, Mrs. Bernadeta Jasiok, M.Sc., shows that PVT + speed of sound data "tuple"

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is also a great subject for developing and testing computational diverse tools and methods. Diversity is a keyword in this context. In fact, the spectrum of the methods used by the Ph.D. candidate is very impressive, as covering the range of methods form simple/empirical ML-approach, through thermodynamics, finally to sophisticated computer simulations. The only drawback of the presented series of papers is that it is not consistent in terms of the studied systems. I think it would be more interesting to fix the system under study (e.g., the chemical family of compounds, ionic liquids, ...) to highlight the performance of the modeling itself.

To sum up, I rate the value substantial content of the work as very high. Particularly noteworthy is the variety of methods used. It proves that the candidate is scientifically mature, has an open mind, easily adapts to learning new research techniques, and willingly participates in interdisciplinary projects. All these features make up the figure of a modern scientist.

6. Comments and Questions

I have only a few major questions regarding the works **P1** and **P2**. I guess the answers to some of them will answer my doubts ref. the remaining publications.

Work P1:

1. I did not find ionic liquids (ILs) in this work. Why is the reason for that? I can only suspect that the idea of involving ILs came later. If so, was the two-state approach tested on ILs in the range of pressure the data are available? If not, what the results expected.
2. Did you perform a sensitivity analysis of the resulting model? It would be interesting to demonstrated how the prediction accuracy is changed when the experimental input data are varied.
3. I also did not find any kind of comparison of the proposed model to any kind of the "flagship" reference EoS, e.g., the PC-SAFT (or any other SAFT-based approach), or cubic equations of state - even for a limited range of pressure. I believe that every paper presenting a new model/theory/computational tool should include such a comparison. Of course, I do not postulate that SAFT would perform better. Nevertheless, such a comparison would be very valuable.
4. Is the unit of isothermal compressibility misspelled in Fig. 5? The values at the y-axis (at $P = 0$) suggest that Pa^{-1} should be applied rather than MPa^{-1}.

Work P2:

1. Did you try to use other method(s) to model the studied dataset? There are plenty of them implemented in Python, MATLAB, ... I think that the **P2** is a very solid contribution, but the lack of the section showing differences between various technique is the weakest point of it.

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2. What is the final number of the parameters fitted during the model training and how does it compare to the number of data points in the training set?
3. The model's generalization capacity was evaluation using so called "leave-one-out" method (LOO). Did you check how the result would change, if you changed it to (35 - *k*) + *k* approach, where $k > 1$. LOO is indeed suitable for such small data sets, but on the other hand, folded cross-validation with k equal approx. of 20% of the data set size is also a standard procedure in evaluating ML-based models. Besides, I did not find any statistical summary of the model performance in terms of determination coefficients like R^2 and Q^2 (see: *J. Chem. Inf. Model.* **2009**, 49, 1669-1678, or OECD guide for developing QSAR models).
4. The model is based on critical properties of ILs, which are the result of calculations using the group-contribution approach by Valderrama et al. The problem is that those are properties which cannot be measured directly due to ILs non-volatility. The only way to get reasonable data is to regress surface tension data or perform computer simulation. Those technique suggest that the value of T_c should be at level of 1000-1500 K. In turn, the results used in **P2** show the values which are in many cases comparable with water. Could you please comment on that? My point is that I think we (as a community) should not derive very complicated and elaborated ML models using potentially invalid data, or the data which validity cannot be checked.

Conclusion

The thesis fulfilled the set objectives using suitable and modern methodology. Furthermore, I find the thesis as well as the overall research output of the candidate is very valuable, and I think that they may have a significant impact on further development of physical chemistry.

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 Mrs. Bernadeta Jasiok, M.Sc., to further stages of the doctoral dissertation.

In addition, to emphasize not only the high quality of the doctoral thesis but also the overall research output of Mrs. Bernadeta Jasiok, M.Sc., and the interdisciplinary nature of the studies presented in the publications she co-authored, I apply to the Council to distinguish the dissertation.

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Stwierdzam, że rozprawa doktorska spełnia warunki określone w art. 13 ust. 1 ustawy z dnia 14 marca 2003 r. o stopniach naukowych i tytule naukowym oraz o stopniach i tytule w zakresie sztuki (Dz. U. z 2017 r. poz. 1789) oraz art. 179 ustawy z dnia 3 lipca 2018 r. i wnoszę do Rady Naukowej Instytutu Chemii Uniwersytetu Śląskiego w Katowicach o dopuszczenie Pani mgr inż. Bernadety Jasiok do dalszych etapów przewodu doktorskiego.

Ponadto chcąc podkreślić zarówno wysoki poziom rozprawy doktorskiej, jak również całkowity dorobek Pani mgr inż. Bernadety Jasiok oraz interdyscyplinarny charakter badań prezentowanych w jej publikacjach, wnioskuję do Rady Naukowej o wyróżnienie pracy.

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