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ČESKÉ VYSOKÉ UČENÍ TECHNICKÉ V PRAZE

Faculty of Nuclear Sciences and Physical Engineering

Supervisor's assessment of the bachelor thesis by student **Gabriela Spilková** entitled

Optimization of PC-SAFT Equation of State Parameters for Modeling Thermophysical Properties of Fluids

Introduction

The topic of the thesis deals with the modeling of thermophysical properties of fluids and vapor–liquid phase equilibria. A modern physically sound equation of state (EoS) based on the statistical associating fluid theory (SAFT) was selected for the modeling of technically relevant fluids. The research team of the Laboratory of Thermophysical Properties at the Institute of Thermomechanics of the CAS focuses on experimental and theoretical investigation of various types of fluids and fluid mixtures. SAFT EoS represents a useful tool with reasonable accuracy for the description of thermophysical properties, phase equilibria and even phase interfaces over wide temperature, pressure, and composition ranges. For each chemical substance, three to six fluid-specific parameters have to be correlated to the available property data such as density of saturated liquid, vapor pressure or speed of sound. Our laboratory team has own rather historical Fortran code dating back to 2005 based on the Levenberg-Marquardt algorithm allowing for optimization of the EoS parameters. However, the code is not universal enough as it cannot be linked to the advanced programming languages such as Matlab or Python. Recently, Ing. David Celný has therefore developed a new implementation of PC-SAFT EoS, that can be called as the dll library from other environments. Main motivation of the bachelor thesis was to use this library and to investigate various optimization techniques, when own in-house developed algorithms shall be tested together with other packages available, e.g., in Python library SciPy.

Summary of performed work

The first three sections of the thesis represent the review part. A brief introduction into the thermodynamics and the field of thermophysical properties is provided together with general information on various states of matter and phase diagrams. The SAFT-type equations with special focus on the perturbed-chain (PC) version of SAFT, which is the principal fluid model used in the work, are introduced in the second section. The main part of the review given in section three discusses various optimization methods, that can possibly be used for the fitting of fluid-specific parameters of PC-SAFT EoS. Assessment of various optimization approaches represents the main motivation of the presented work.

Section four describes student's experience gained by using the Python programming language. The Levenberg-Marquardt algorithm has been tested on a sample case of fitting the quadratic function through tabulated input data. Obtained results revealed a considerable influence of the numerical difference scheme. The forward difference did not provide sufficiently accurate results and had to be replaced with the central difference.

Main results of the work are presented and summarized in sections 5 and 6. The parameters of PC-SAFT EoS were optimized for two alkanes (methane and pentane) and one polar fluid refrigerant R125 (pentafluorethane) with a dipole moment of 1.563 Debye. Own Levenberg-Marquardt algorithm was compared with two other methods available in the SciPy package; namely the trust region reflective algorithm (trf) and the dogleg algorithm with rectangular trust regions (dogbox).

Assessment

As a supervisor of the bachelor thesis I have to appreciate student's considerable effort in gaining several additional skills necessary for successful preparation of the thesis. At first, Ms. Spilková had to deepen here knowledge in the field of thermodynamics and thermophysical properties, which was not sufficiently covered in her study program. She got valuable experience with the Python programming language, its several freeware distributions and the SciPy library. Gabriela has also learned how to use the online version control system GitHub required for the data and code sharing. Last but not least, she has learned how to write longer research text in English using the TexStudio environment with Latex typesetting system.

Ms. Spilková was in regular touch both with me and the consultant Ing. David Celný, who has developed new version of the PC-SAFT implementation written in Fortran language including its interface for Python and has administrated the GitHub project. The bachelor thesis was also regularly discussed with the language advisor Mgr. Hana Čápová. I have to admit that there occurred several aspects complicating the thesis preparation, which caused an unexpected delay in the fulfillment of some sub-tasks. The COVID pandemic rose during fall 2021 and beginning 2022. Therefore, several meetings had to be organized online via MS Teams. Both the student and the supervisor got COVID positive during the thesis preparation. Moreover, the vapor-liquid phase equilibrium algorithm prepared by the IT CAS team was found not sufficiently robust in the vicinity of the critical point and an additional modification was required, which lasted couple of weeks.

From the content point of view, the student managed to address all tasks given in the thesis definition. Even though, some of them only partly. For example, the review of possible optimization methods might be broader in order to come up with possible strategy of solving problem of local and global minima. The SIMPLEX algorithm or any other non-gradient approach was not implemented due to lack of time.

Formally, the work is in general presented on a good level. Even though some statements are not entirely correct and the text suffers from typos; few examples:

- Tables are not numbered.
- In figure 33 showing the relative deviation of vapor pressure, the y axis shall be dimensionless and not in MPa.
- There are several typos in tables on pages 48 and 49 by the mean square errors, i.e. flipped units by the pressure and the density and strange formatting of powers of 10.

The bachelor thesis shall still be considered as the first larger research work of a student and as such cannot be compared with the standards of full scientific work such as dissertation or an article in an impacted journal in terms of content, level of novelty, and formal aspects. According to my experience with other bachelor theses, I believe Mrs. Spilková has proved considerable skills, knowledge and effort in the preparation of her bachelor thesis. I therefore recommend the thesis for defense and propose grade

B (very good)

Additional comments

For a possible discussion during the defense, I would have following questions:

1. What was the final form of the objective function used for the PC-SAFT parameters fitting? Were the differences of the model results from the input data dimensional or relative? For example, the vapor pressure can differ by several orders of magnitude. What might be the effect on the obtained results?
2. How could be added various weights <0, 1> of the fitted thermophysical property data into the optimization algorithm?
3. Section 2.5.1 describes residual part of the Helmholtz free energy obtained from PC-SAFT EoS. How could be the ideal gas part added in order the full set of thermodynamic properties can be modeled such as speed of sound w or isobaric heat capacity c_p?

Prague, August 9, 2022

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