544f Multilevel Modeling of Complex Systems

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Abstract

Most chemical systems can only be fully understood based on physical and chemical property data. Property data can not be calculated in a fully rigorous fashion. Normally semi-empirical property prediction models (SEPP) are used but they all have weaknesses and limitations concerning size and complexity of the molecules and mixtures when applied outside a proven range. They are also quite data-demanding to develop and maintain. In a highly competitive climate, chemical engineers are forced to rely increasingly on predicted data. The purpose of this project is to develop a methodology for extracting maximum information from available experimental data. We combine SEPP models with computational chemistry to give qualified predictions of pure and mixture behavior of novel compound groups to minimize extensive experimental data generation.

1 Introduction

Chemical industries have focused on specialty chemicals for several years. Commonly few physical property data exist for specialty chemicals. Measurement of high-quality data takes quite some expertise and experience within a single organization. Together with economic and time-to-market considerations, this often prevents extensive experimental work from taking place. This makes traditional model development difficult. In general, data driven approaches will become more and more difficult to develop and maintain, since R & D expenditures for experimental research is declining relative to R & D expenditures for atomic scale modeling - at least on a relative scale. In this work, we wish to generate pseudo experimental data through computational chemistry and combine these with experimental data to obtain a more complete picture of the behavior of 'new' species. The results of the simulations are together with experimental data used to generate missing parameters for different SEPP models. An example could be a functional group with unknown properties and with special structural details. Here one possibility would be to extend an existing group contribution method with new first or second-order group [1, 2, 3]. Thereby increasing the pure property predictions for the novel group. This however, requires data.

A second area is mixture properties where the amount of experimental work needed becomes quite comprehensive when one considers all relevant solute/solvents combinations. As an alternative to experimental work we have made molecular dynamics (MD) simulations of binary liquid mixtures for a set of compounds representing a 'new' functional group. The results of MD simulations can be obtained for comparison with measurements based on more or less sophisticated analysis depending upon the property of interest. The (x,g)-datasets for mixtures with molecules having a 'new' functional group can then be used to generate viz. UNIFAC interaction parameters between a new main group and other existing main groups [4].

2 Methodology

The methodology can be divided into two main parts (see Figure 1). The first part is the traditional approach where experimental data is collected for the new compound group. This is followed by testing the predictive power of the SEPP models in their current form. If the predictions do not have an acceptable precision the normal procedure is to extend the models. After the traditional steps it is evaluated whether the predictive capability of the models are acceptable. Are the parameters based on a too narrow range of experimental data? Are all relevant model parameters determined? This is critical for screening alternatives for a purification step.

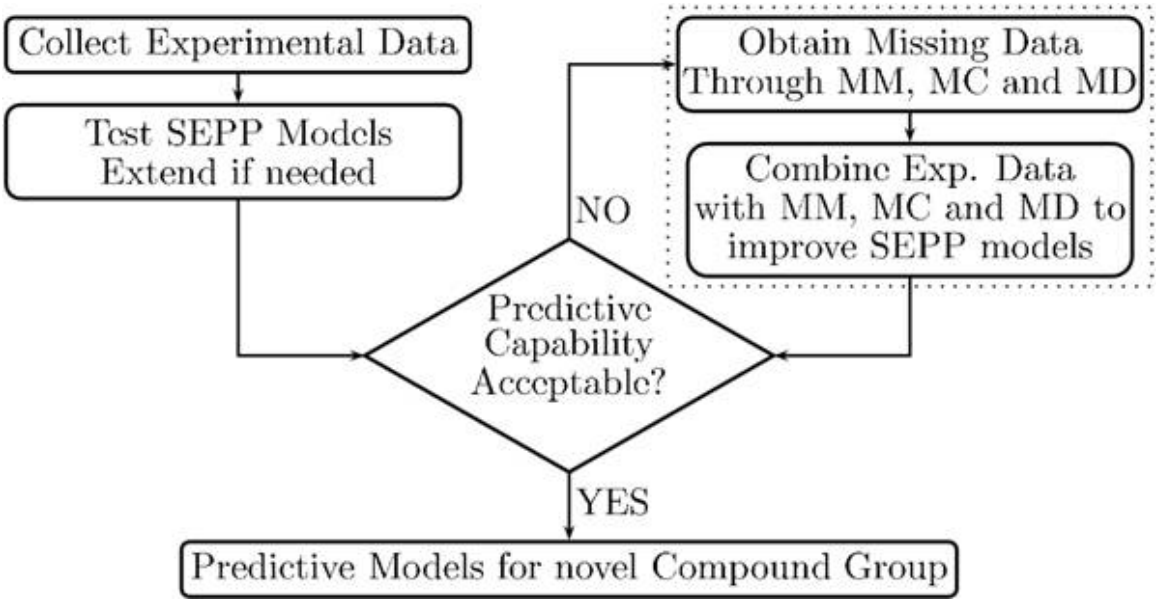

Figure 1: Methodology for Combining experimental and pseudo-experimental data to improve SQPP models.

If the results from the traditional approach are not satisfactory new simulations can be made. MM, MC and MD simulations of pure compounds and mixtures of interest. From analysis of the simulations a wide variety of thermodynamic properties can be derived. The result of analysis is referred to as pseudo-experimental data. The experimental data and the pseudo-experimental data is then combined and used to regress parameters for different models of interest. Afterwards the question is repeated: Is the predictive capability acceptable? One case could be that the solvents of the ketone group did not give acceptable results for in the design phase and it is decided to study possible ethers and thereby repeating the second part of the methodology again, just for mixture properties with a new compound group. The cycle of generating pseudo-experimental data and using it in a SEPP model is repeated until the process design problem has been given a range of predictive models making it possible to solve.

3 Application

An industrial case study deals with the lactone group which are cyclic esters and their corresponding hydroxy-carboxylic acids. The small lactones are good solvents for industrial cleaning products. They also have application as a chemical intermediate in agrochemicals, pharmaceuticals and dyes. The medium sized lactones are known as fragrances naturally occurring in fruits. The lactones are currently purified by distillation. To improve the purification and fractioning of lactones further knowledge is needed about their pure compound properties and mixture phase behavior. A database has been generated with all open literature information known to us. Then the ability of group contribution models to predict the boiling points, heat of formation etc. was compared with experimental data. A new UNIFAC main group has been constructed to describe the lactones. Work has been initiated to complement the lactone liquid phase database through generation of pseudo experimental data. A series of molecular dynamic (MD) simulations of binary mixtures have been initiated to reconstruct existing data and afterwards develop new data. If such simulations are made at different conditions, we expect to be able to calculate thermodynamic quantities of relevance in phase equilibria over extended ranges. Thereby we may extend the experimental data base with pseudo experimental data, to allow parameters in macroscopic models such as UNIFAC to be regressed with greater confidence.

References

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