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The second industrial fluid properties simulation challenge

Fiona Case [a], Anne Chaka [b], Daniel G. Friend [c], David Frurip [d], Joseph Golab [e], Peter Gordon [f], Russell Johnson [b], Petr Kolar [g], Jonathan Moore [d], Raymond D. Mountain [b,*], James Olson [h], Rick Ross [i], Martin Schiller [j]

[a] *Case Scientific, Essex Junction, VT, USA*
[b] *NIST, 100 Bureau Drive Stop 8380, Gaithersburg, MD 20899-8380, USA*
[c] *NIST, Boulder, CO, USA*
[d] *The Dow Chemical Company, Midland, MI, USA*
[e] *BP, Naperville Complex, Naperville, IL, USA*
[f] *ExxonMobil, Annandale, NJ, USA*
[g] *Mitsubishi Chemical Corporation, Kurashiki, Japan*
[h] *The Dow Chemical Company, S. Charleston, WV, USA*
[i] *3M Company, St. Paul, MN, USA*
[j] *DuPont, Germany*

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Abstract

The industrial fluid properties simulation challenge was established in 2001 to provide a realistic assessment of the value of molecular simulation methods for predicting thermophysical properties of industrially important fluids. The organizing committee (the authors of this paper) wished to establish reliable comparisons between the available methods, to assess the state of the art, and to enhance alignment of academic efforts with industrial needs. The first contest was held in 2002. Commercial modeling companies, academic groups and government laboratories were challenged to predict vapor–liquid equilibria, densities, and viscosities for a specified set of organic fluids, mixtures and aqueous solutions. Based on the success of that endeavor a second contest was held, concluding in September 2004. Modeling groups from around the world attempted to predict vapor pressure and heats of vaporization, Henry's law constants, and heats of mixing using molecular simulation methods (the focus of this contest). The contestants applied a wide range of different methods, and different forcefields. Accurate benchmark values were obtained, based on experimental data, by a team from NIST and Dow Chemical and used to assess the accuracy of the predicted values. Predictions of Henry's constant were judged sufficiently accurate to be of value in an industrial environment. The results for vapor pressure and heats of vaporization were mixed. Reasonable qualitative predictions of heats of mixing were obtained for an organic/organic mixture. But results for aqueous solutions revealed an area where although, for the most part, the methods by which predictions were made are sound, the forcefield descriptions are inadequate.

Keywords: Molecular simulation; Heats of mixing; Gas solubility; Henry's constant; Vapor pressure; Heats of vaporization; Molecular dynamics; Monte Carlo

1. Introduction

1.1. Background and motivation for this contest

Accurate physical property data are critical in process and materials design, but it can be difficult to obtain reliable information, especially for unusual materials, mixtures, or

* Corresponding author. Tel.: +1 301 975 2484; fax: +1 301 869 4020.
E-mail address: raymond.mountain@nist.gov (R.D. Mountain).

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state points far from ambient conditions. Computer simulation holds great promise in this area.

In 1999 the Technology Roadmap for computational chemistry held out a future vision of molecular simulation as a "breakthrough" technology [1] – a technology that would take us significantly beyond the current methods to new levels of efficiency, accuracy, and applicable regimes of molecular types and state conditions. A workshop on 'Predicting the Thermophysical Properties of Fluids by Molecular Simulation' held at the National Institute of Standards and Technology, USA (NIST) in 2001 [2] concluded that one of the main barriers to industrial application of these tools was a lack of validation of different methods, and of reliable comparison studies. The industrial fluid properties simulation challenge was established to meet this need. Our aims are to:

(a) Formalize methods for the evaluation and validation of simulation results with experimental data;
(b) Assess the state of the art;
(c) Drive improvements in the practice of molecular modeling;
(d) Enhance alignment of academic efforts with industrial needs; and
(e) Provide examples and tools that are of value for modeling groups to assess the accuracy of new methods and forcefields.

In the first industrial fluid properties simulation challenge [3–12] academic groups and commercial molecular modeling companies were challenged to predict vapor–liquid equilibria, densities, and viscosities for a specified set of organic fluids, mixtures and aqueous solutions. Accurate benchmark values for the specified properties, based on experimental data, were obtained by teams at NIST and The Dow Chemical Company, and only revealed after entries had been submitted. The contest was judged primarily on the agreement between predicted and experimental data, although the judging teams also awarded a portion of their score based on a more qualitative assessment of the transferability and "true predictability" of the methods. Although in practice this qualitative assessment made no difference to the ranking, some competitors were concerned with the lack of transparency in the judging process.

The results from the first challenge (announced at the AIChE Annual Meeting, 2002, and published in a special edition of Fluid Phase Equilibria [3–12]) showed that simulation methods could already provide accurate predictions of density for a wide range of molecule types – although care should be taken in selecting an appropriate forcefield for a given material. Reasonable results were obtained for vapor–liquid equilibria. The viscosity predictions were less convincing – principally because the calculations did not converge (insufficient simulation time). The organizing committee felt the initiative provided valuable information and served to promote the industrial application of these techniques.

The success of the first challenge encouraged us set up a second industrial fluid properties simulation challenge, which was completed in September 2004, and is the subject of this special edition of Fluid Phase Equilibria. One of the difficulties associated with conducting the first contest was that we did not have formal definition of what constituted a molecular simulation method. For the second contest we adopted the formal definition that a molecular simulation is any method that involves an ensemble of many molecules whose coordinates are "evolved in accordance with a rigorous calculation of intermolecular energies or forces" [13]. Only those entries that were consistent with this definition were eligible for the awards in this particular challenge – although papers describing prediction of the contest properties using other approaches were encouraged at the conference session, and one is included in this special edition of Fluid Phase Equilibria.

Further information about this contest, our motivation and aims, and a list of Frequently Asked Questions (and our answers to those questions) are available at the industrial fluid properties simulation challenge website: http://www.fluidproperties.org [3].

The committee would be interested to receive suggestions and comments – email can be sent to Raymond.Mountain@nist.gov. You are invited to join the Fluid Properties newsletter list at our website [3] to keep informed of the progress of this initiative.

1.2. Problem selection

The challenge in selecting problems for this contest was to identify questions that would be representative of the type of property prediction required in an industrial setting, but also amenable to accurate measurement by our benchmark data committee.

Most molecular simulation methods require some level of parameterization using experimental data. Experimental values are fitted to obtain the parameters for forcefields, which are used to predict the relative stability of different molecular conformations, or of different compositions in the case of mixed systems. To make this a test of the predictive capabilities of molecular simulation, materials and state points were selected that had not previously been well characterized (little or no experimental data existed in the literature). This minimizes the chance that experimental values for the properties we were asking the contestants to predict contributed to the parameterization of methods they used (this issue is particularly important for forcefields that have been in existence for many years, and added to by many different groups).

Naturally, at the start of the process we had a large number of potential problems – there were many different properties and materials that we would have liked the contestants to study. After much debate, and a review of the proposed problems by external modeling experts, we settled on predictions of vapor pressure and heats of vaporization, Henry's law constants, and heats of mixing. The systems we selected were simpler than those typically studied in an industrial situation.