

The Industrial Fluids Simulation Challenge: Highlights of the First Event and a Preview of the Second

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Abstract

This poster describes the results, activities, and philosophy of the Industrial Fluids Simulation Challenge. The recently completed open competition challenged practitioners of molecular simulation to calculate accurate physical properties for pure materials and mixtures at specific state points. The chosen properties were vapor-liquid equilibria, density, and viscosity. It is anticipated that this competition will be a recurring event for the purpose of driving improvements in the practice of molecular simulation, formalizing methods for the evaluation and validation of simulation results with experimental data, and ensuring relevance of simulation activities to industrial needs. The goal of the first Industrial Fluid Properties Simulation Challenge was to obtain an in-depth and objective assessment of current abilities and inabilities in the prediction of physical properties for fluids with industrial relevance. With ten entries to the three problems, the contest ended recently with the announcement of the Champions at the 2002 Annual Meeting of the AIChE (Nov 3-8, 2002). Cash prizes were awarded from generous contributions by BP and The Dow Chemical Company. The Computational Molecular Science and Engineering Forum (CoMSEF) of the AIChE sponsored the contest and NIST administered the event. The paper summarizes the choice of contest problems, the results of the contest, and the elements of the second contest, ending in 2004.

Note that much of the following discussion relating to the first contest is extracted from a more detailed article to appear in a special issue of Fluid Phase Equilibria [1]. Readers are encouraged to consult that issue and associated articles for more information relating to the competition, philosophy, entries, judging, and benchmark data.

1. Introduction

The Industrial Fluid Properties Simulation Challenge [2] was established to promote the use of molecular simulation methods to predict materials' properties of industrial relevance. The goals of the Challenge were to encourage the development of intermolecular potentials and associated molecular simulation methods for the prediction of physical properties for industrially challenging fluids. The results of these competitions will provide an accurate assessment of current abilities to address significant industrial problems. The organizing committee (most of the authors of this paper) also wished to establish reliable comparisons between the available methods that could assist modelers in choosing the most appropriate approach for a particular property or system. The Challenge was open to anyone outside of the institutions or companies represented on the organizing committee.

Entries were received from three commercial companies, one national lab, and a number of universities. In this first Challenge, participants were asked to predict vapor-liquid equilibria, densities, and viscosities for a specified set of organic fluids, mixtures and aqueous solutions. Accurate experimental measurements of the specified properties were obtained by teams at NIST and The Dow Chemical Company. Entries were 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 "true predictability" of the method. Most of the groups that accepted the Challenge only entered one of the sections. Only one team attempted predictions in all three sections of the contest. This indicates the challenging nature of the problems and the current state-of-the-art for molecular simulations. We would like to recognize the significant efforts made by all the entrants. Their work is summarized in this poster and is described in greater detail in the papers contributed by most of the contestants to a special edition of FPE (unknown publication date at the time of writing). Building on this success we plan a Second Industrial Fluid Properties Challenge to end in Fall, 2004. The current organizing committee (all the authors of this paper) welcome your suggestions for suitable Challenge problems. Some details of the second event are included in this paper.

2. The Need for a Competition

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 state points far from ambient conditions where experimental determination becomes costly, unsafe, or too time consuming. Some data are available in the literature or can be estimated using empirical correlations based on literature data. Resources exist to aid the experimental evaluation of data at NIST, in the AIChE Design Institute for Physical Properties (DIPPR) consortium, and at contract measurement laboratories. Computer simulation holds out great promise in this area. In the future we hope to be able to build models of sufficient accuracy to confidently predict physical properties, even for materials that have never been studied experimentally.

A workshop on "Predicting the Thermophysical Properties of Fluids by Molecular Simulation" was organized by NIST in June 2001 [3]. It was attended by modelers from both industry and academia. The participants concluded that the lack of validation of different methods and of reliable comparison studies was a major limitation to the industrial application of atomistic scale simulation. These limitations were also recognized recently in a detailed study of the future of the U.S. chemical industry: Technology Vision 2020 [4]. In particular, the Technology Roadmap for Computational Chemistry [5] specifically lists the same limitations noted above as technology barriers to the increased use of Computational Chemistry. To address this problem the group established the Industrial Fluids Properties Simulation Challenge. Commercial modeling companies and academic groups that develop modeling techniques were challenged to predict a specified set of properties for a range of industrially-relevant small-molecule organic fluids and solutions.

The competition was announced in the fall of 2001 at the AIChE Annual Meeting. Contestants were given just under a year to provide predictions in one or more sections of the competition. In parallel, scientists from NIST and The Dow Chemical Company obtained accurate experimental benchmark data for the competition problems. The entries were judged anonymously by teams from industrial modeling groups and national labs based on criteria established before any manuscripts were seen. The majority of the score was based on the agreement between predicted and experimental data. Each team also included a more qualitative assessment of the “true predictability” of the method (Was it a prediction? What is the likelihood of transferability?). The results were announced and the champions recognized at the 2002 AIChE National Meeting in Indianapolis. Cash prizes were awarded resulting from generous donations by BP and The Dow Chemical Company.

The members of the Contest Committee firmly believe that it is important for this event to continue for a number of reasons. If Molecular Simulation methodology is to truly become a “breakthrough” application for the modern chemical industry in the next few years, the methods, tools (both commercial and academic), force field development and availability, academic research direction, and related government funding *must* continue to be more closely aligned with the needs of the chemical industry. A Challenge event like this offers a unique opportunity for this alignment to occur. *However, the success of this event is greatly dependent on the acceptance of this premise by all parties involved. Consequently, we offer a plea to those interested parties (academicians, industrial practitioners, and commercial software developers) to work with the Contest Committee in close partnership to make these events a success.* The first Challenge was far from perfect, but with the enlightened input from many people, we think the next event will be significantly better in many ways including the problem selection and judging process. We encourage all practitioners and interested parties to register as an entrant or as an observer at the Contest web site [2].

3. The Problems Chosen for the First Challenge

Problem Set 1 – Prediction of Vapor-liquid Equilibria (VLE)

Knowledge of vapor-liquid equilibria (VLE) for mixtures is critical in the design of industrial processes such as distillation and fluid transport. VLE is also an important consideration for solvent selection, coolants, refrigerants, control of volatile organic chemicals for paints and building materials, and for design of fragrances.

The VLE challenge problem consisted of two parts:

Part 1-a) Determine the P_x curve for a mixture of dimethyl ether and propylene at $-20\text{ }^\circ\text{C}$ (253.15 K) with explicit pressures for $x=0, 0.2, 0.4, 0.6, 0.8, 1.0$ and the pressure at $20\text{ }^\circ\text{C}$ (293.15 K) for $x=0.5$

Part 1-b) Determine the pressure and composition of the azeotropic point for a mixture of nitroethane and propylene glycol monomethyl ether at $80\text{ }^\circ\text{C}$ (353.15 K) and at $40\text{ }^\circ\text{C}$ (313.15 K), and the bubble point pressure for $x=0.2$ (nitroethane) and $x=0.5$

Several criteria were used to select these systems for the Simulation Challenge problems. In addition to a lack of published data at a range of state points and compositions, the molecules were relatively small and contained functional groups of interest to industry.

Problem Set 2 - Prediction of Density

Density prediction was selected as one of the challenge problems because it is strongly correlated with other materials properties. If a simulation method cannot provide accurate density prediction, it is unlikely to be able to predict relevant properties such as vapor pressure, mechanical properties, energies of mixing, viscosity/flow properties, or refractive index. Density prediction is also a particularly stringent test for an atomistic simulation method. Accurate results suggest that both the shapes of the individual molecules and the intermolecular packing are correctly modeled.

Because density can be predicted relatively quickly, we used this section to challenge the breadth of the different techniques and their performance away from ambient conditions. Few commercial products contain only one chemical species. If a modeling technique is to be useful in an industrial setting, it should be applicable to many different materials and should reliably predict properties for new materials and mixtures. The ability of a force field to do this is termed its “transferability”. For this first challenge most of the materials were single component organic fluids. They were selected to cover a wide range of chemistries (alkanes, alcohols, amines, halogenated compounds, etc.). We also included water and two aqueous solutions (methanol in water and a choline chloride salt solution) in recognition of the ubiquitous role of water as a solvent in commercial processes and as a major component in many consumer products (such as foods, cosmetics, paint, cleaning and personal care products). For each material we requested density predictions at two state points: one close to ambient conditions (1 atmosphere pressure, 298K) and the other at higher temperature and/or pressure. The materials included in the density section of the challenge are listed in table 1.

Table 1 – Definition of systems for the density section of the First Industrial Fluid Properties Simulation Challenge [2].

part #	System	State Point 1	State Point 2
a	Water	0.1 MPa, 293 K	2.0 MPa, 423 K
b	Cyclohexane	0.1 MPa, 300 K	20 MPa, 400 K
c	Isopropanol	0.1 MPa, 298.15 K	5 MPa, 400 K
d	Diethanol amine	0.1 MPa, 330 K	5 MPa, 400 K
e	1,2,3-trichloropropane	0.1 MPa, 290 K	1.5 MPa, 400 K
f	Triethylene glycol	0.1 MPa, 310 K	2 MPa, 280 K
g	Pyridine	0.1 MPa, 298 K	10 MPa, 375 K
h	Water + choline chloride (Aqueous choline chloride)	0.1 MPa, 298 K, 20% choline Cl by weight	1 MPa, 305 K, 10% choline Cl by weight
i	Water + methanol (50:50 by mass fraction)	0.1 MPa, 325 K	10 MPa, 400 K

Problem Set 3 - Prediction of Viscosity

Viscosity was chosen as the third simulation challenge problem because it is the key transport property in industrial technology. Viscosity data are important for the design of chemical processing units and as a measure of a fluid's efficacy for particular applications, for example lubrication. Molecular simulation of viscosity [6] would be especially valuable when the data are needed at extreme conditions such as high temperature and pressure, where the corresponding experimental measurements are particularly difficult [7]. Molecular simulation has also been successful in predicting the temperature- [8-10] and pressure-dependence [7, 11] of viscosity and discriminating between mutually-inconsistent correlations of experimental data [12].

The accuracy of a viscosity calculation is determined in part by the quality of the intermolecular potential, or force field, that is used in the simulation. Unlike the two other properties considered in this simulation challenge, force fields are not commonly fitted to viscosity data. Instead, force fields that were fitted to other properties (e.g. liquid density or VLE) are used to predict viscosities. Thus, it is reasonable to expect less accuracy from viscosity calculations than from density, for example, if no viscosity data are used to adjust the model parameters.

The systems for which the shear viscosity was predicted are listed in table 2. The pure components, 2-propanol and n-nonane, and their mixtures were chosen for the challenge problem because the large specific forces due to the hydrogen-bonding of the alcohol molecules might be expected to lead to mixture

viscosities far removed from a linear mole-fraction mixing rule. In addition, and key to this competition, no mixture data had been published for this system.

Table 2 – Specification of fluid systems for the viscosity prediction section of the First Industrial Fluid Properties Simulation Challenge [2].

	system	State Point
a	n-nonane	0.1 MPa, 300 K
b	isopropanol	0.1 MPa, 300 K
c	n-nonane + isopropanol (0.5 mole fraction)	0.1 MPa, 300 K
d	n-nonane + isopropanol (0.75 mole fraction isopropanol)	0.1 MPa, 300 K

4. Challenge Results & Discussion

Problem Set 1 - Vapor-liquid Equilibria

Two of the three teams that entered this section of the challenge used classical molecular simulations models to describe bulk dimethyl ether, propylene, nitroethane, propylene glycol monomethylether, and their mixtures. The third entrant in this section (Andreas Klamt from COSMOLogic GmbH [13]) used an approach based on a combination of quantum mechanics and electrostatic interactions that differed significantly from the force field/statistical mechanics methods of other entrants. The COSMO method provided the most accurate prediction of vapor-liquid equilibria for mixtures of dimethyl ether/propylene and of nitroethane/propylene glycol monomethylether and was declared the champion in this section.

The teams also used different approaches for creating realistic configurations for the bulk fluids. Full details are given in their papers, including analysis of the strengths and weaknesses of their approach, discussions of errors, and timings [1].

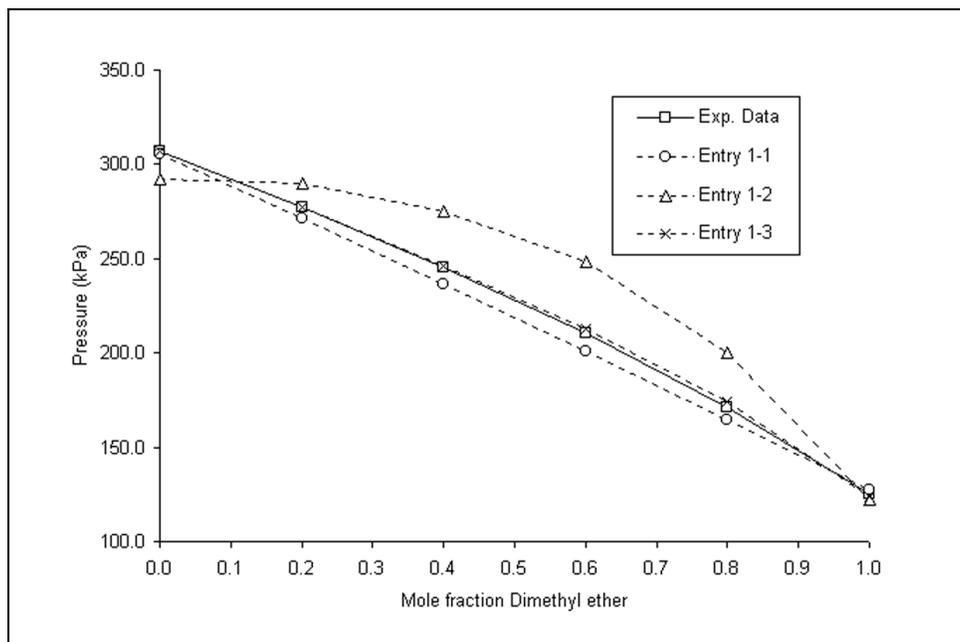


Figure 1 – P_x curve for a mixture of dimethyl ether and propene at $-20\text{ }^\circ\text{C}$.
The source of the experimental data may be found in [1].

The results from the three entries (identified as 1-1, 1-2, and 1-3) for problem 1a are shown in figure 1. The winner was determined to be Entry 1-1, the entry from COSMOLogic GmbH. It should be noted that Entrant 1-3 had submitted a set of revised results to part 1b that was received too late after the deadline to be included in the judging. The revised submission corrected a mistake and significantly improved the accuracy of the results. The revised results are included in the figures below, along with the original submission, to enable a fair assessment of the performance of the methodology of Entrant 1-3.

Problem Set 2 - Prediction of density

The four teams who entered this section used a variety of approaches to create models of the bulk materials and used different force fields describing inter-molecular and intra-molecular interactions. Valence parameters (bond lengths, angles, torsions, and their force constants) and atom charges are often obtained by fitting to quantum mechanical data. Van der Waals parameters are usually obtained by fitting to experimental data. Two important issues, highlighted by this section of the Challenge, are the transferability of force fields (Can parameters fitted to experimental data for one material be used to model another, similar, material for which experimental data are not available?), and their ability to predict properties at state points far from experimental data. Most of the teams have published full details of their entries in a special issue of Fluid Phase Equilibria [1], including analysis of the strengths and weaknesses of their approach, discussions of errors, and timings.

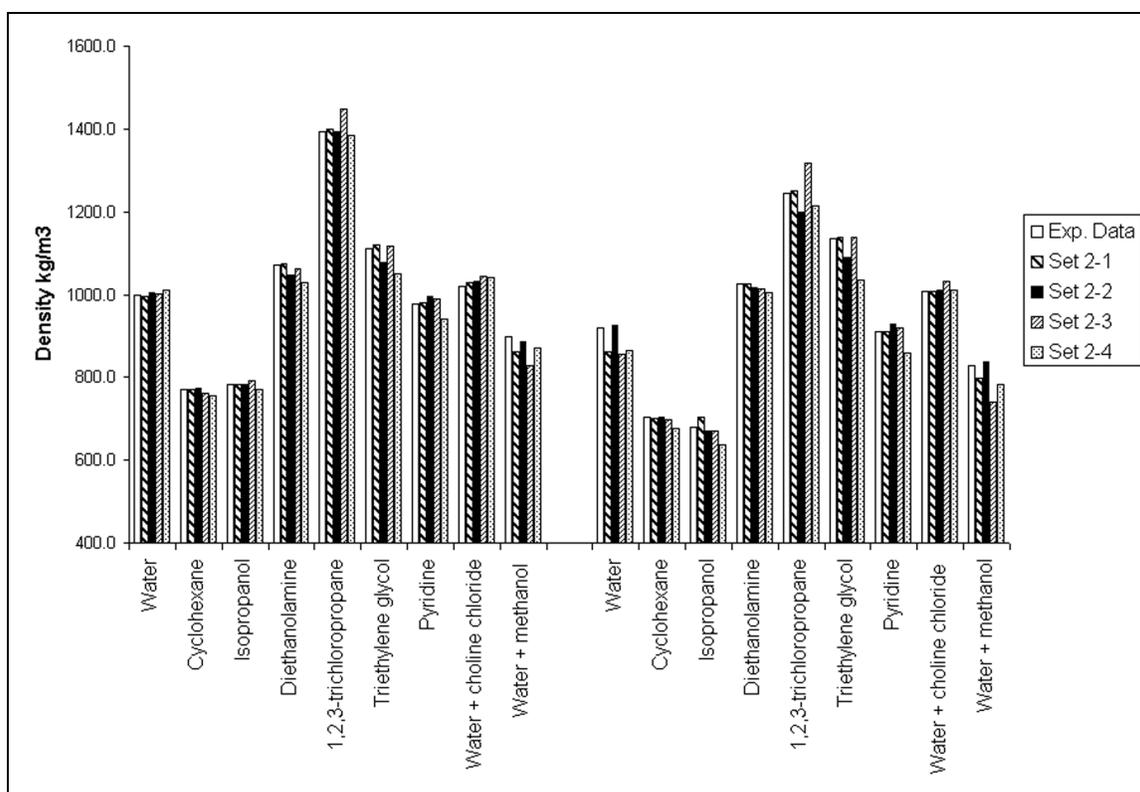


Figure 2 – Comparison of predicted and experimental densities for the systems at state point 1 (close to ambient conditions), and at state point 2 (higher temperature and/or pressure), as listed in table 1. The sources of the experimental data may be found in [1].

Entry #2-1 (Huai Sun, Aeon Technology, San Diego [14]) presented results from a new force field (based on a well know functional form) developed specifically for the compounds in the challenge. He obtained impressive results showing the capabilities of molecular simulations and was declared the champion in the density section.

Entry #2-2 was submitted by the only team to enter all three sections of the First Industrial Fluid Properties Simulation Challenge. By doing this they demonstrated what could be achieved by a scientist who wished to predict both thermodynamic and transport properties for an organic fluid for which little or no experimental data existed. This team provided the most accurate predictions for water and the aqueous solutions.

Entry #2-3 was of comparable accuracy to entry 2-2 for materials other than water and the aqueous solutions. Results were obtained using a commercially available modeling package without any additional fitting or parameterization.

Entry #2-4 was a pragmatic approach. Results were averaged over several force fields that were available in the public domain. With the exception of triethylene glycol, results were within 4% of experimental values for all the materials at the first state point (close to ambient conditions), and within 7% for the second state point. This shows what could be achieved by a molecular modeler without access to commercial force fields and without any re-parameterization.

Problem Set 3 - Prediction of Viscosity

A summary of the entries in the viscosity prediction section is given in table 4. The systems were defined in table 2. The three teams that entered all used molecular dynamics approaches. Both entry 3-1 and entry 3-3 used standard force fields from the literature without modification. Entry 3-2 used a combination of parameters obtained in several different ways including fitting to pure component viscosity data for nonane and isopropanol. Most of the teams have published full details of their entries in [1], including analysis of the strengths and weaknesses of their approach, discussions of errors, and timings.

Table 3 – Predicted and experimental viscosities (in mPa x s) for a series of materials from the first Challenge [2]. The sources of the experimental data may be found in [1].

	n-nonane	isopropanol	50/50 mixture	25/75 mixture
Experimental	0.650±0.007	1.986±0.021	0.756± 0.008	1.040±0.011
Entry 3-1	0.450±0.05	1.600±1	0.220±0.05	0.190±0.04
Entry 3-2	0.533	2.09	0.823	0.939
Entry 3-3	0.910±0.05	3.000±0.3	0.780±0.06	1.320±0.05

Based on the criteria established by the viscosity judging team, Marcus Martin and Aidan Thompson of Sandia National Laboratories (entry 3-3) [15] were declared the champions in this section. Note that the contestants' estimates of the uncertainties in their calculations were not factored into the scoring except in the case of Entry 3-1 where the large uncertainty in the calculated isopropanol viscosity made it difficult to assess the consistency of deviation. The judging team noted that entry 3-2 did not report uncertainties for

the zero-shear viscosities but did report values for the shear-rate-dependent viscosities that were used to estimate the zero-shear viscosities.

The disagreements among the entries suggest that the viscosity problem was the most challenging of the three, and this supports an assertion that transport properties are inherently more difficult to predict than static properties. Furthermore, two of the three contestants used force fields that had not been fit to any viscosity data. Thus, it comes as no surprise that the viscosity predictions were generally less accurate than those of density and VLE.

5. The Second Contest

At the time of writing this, the Contest Committee (currently all the authors of this paper) is in the midst of putting together the second event. We have decided to extend the timeline for the conclusion of Challenge II to the fall of 2004 and again we will announce the winners at a special session of the fall AIChE meeting, under the auspices of the CoMSEF Group. This extension was made for several reasons. First it allows the Contest Committee to spend adequate time carefully formulating the problems ensuring alignment with the contest mission (see discussion below). Also, the extension should allow for more practitioners to participate since it allows more time for planning use of critical resources and schedules. In addition we felt that the extra year helps ensure adequate time for individual and group discussions about the first event (including feedback), and publicity at scientific gatherings such as FOMMS. Finally we allow more time to ensure adequate financial support from corporate donors. (Approximately half of the prize monies generously donated by BP and The Dow Chemical Company were held back for the second event).

Several things were learned from the first event which will help us ensure continued success in the second event. Many people (in particular the entrants) provided constructive feedback (including criticism) which the committee has welcomed, discussed at great length, and taken to heart. Certainly, the scope and complexity of the problems was perhaps (in hindsight) slightly over ambitious in the sense that most entrants were only able to tackle one of the problems due to lack of time and resources. The only entrant to attempt all three problem areas (the so-called "Great Lakes Regressors") was a consortium of several academic groups. This team, lead by Prof. Ilja Siepmann of the University of Minnesota, was highly praised for the time and coordinated effort extended!

We also learned that the judging criteria need to be very carefully chosen, well thought out to ensure alignment with the mission and to minimize potential ambiguities, and publicly available at the time of announcement of the problems. To accomplish the latter, we have decided that for the next event, details of the judging criteria for each problem will be posted on the Challenge web site concurrently with the problem set. At the end of the contest, entrants will be able to determine exactly how well they performed compared to the posted experimental results, and eventually compared to the other entrants.

Perhaps the most difficult (and controversial) part of the judging process in the first event was the qualitative score which was different for each problem. Consequently a decision was made for the second Challenge to judge the entries solely on unambiguous, quantitative means such as deviation from the answer (the experimental benchmark) or predicting the correct trend or temperature dependence of some key variable. All of the latter lend themselves to quantitative, unambiguous assignment of a numerical score. Considerations that otherwise might be included in a qualitative score (e.g. likelihood of transferability) would be handled in two ways. First, we would try to design the problem carefully and cleverly enough to allow an assessment of the issue without resorting to a subjective rating. For example, those in industry are very interested in the reliability of the various methods. Thus a qualitative question like: "is the method likely capable of accurate extrapolations?" can be answered by designing the problem to require an extrapolation of the model outside its bounds. This results in a "number" which then can be objectively scored. Another example of a qualitative factor is the type of data used for the model parameterization. Clearly a model parameterized directly using experimental data for a property which is then used to "predict" that same property at a slightly different condition is more curve fitting than prediction. In this case the problem could be framed in such a way to not allow certain data or data in a particular temperature range from being used in the force field parameterization. Also, we decided that we

would set an immediate high standard for the threshold of entry. To accomplish this, the work and report must be of recognized publication quality as judged by recognized, expert practitioners in the field.

The Problem Set for the Second Challenge

Although the details of the problems have not been explicitly defined at the time of writing we have reached consensus on some general aspects which we can share. Included in this paper is some general discussion about the second contest problem sets but exact details may be found on the Challenge web site (<http://www.cstl.nist.gov/FluidSimulationChallenge>) and, for the FOMMS Conference attendees, at the poster session where this contribution is included.

We have decided to offer Challenge problems in the following three general property areas:

- **Vapor pressure and enthalpy of vaporization of liquids,**
- **Gas solubility in liquids,**
- **Enthalpy of mixing.**

A brief background of each property follows including some justification of why each was chosen. The reader is encouraged to visit the Contest web site for the most up-to-date information regarding the second Challenge [2]. In each problem presented below, restrictions may be applied to the use of certain data in the parameterization of the force fields used.

Problem Involving Vapor Pressure and Enthalpy of Vaporization of Liquids

Vapor pressure is an extremely valuable property in the chemical industry used mainly in the design of separation processes. It is also an important parameter in evaluating environmental and safety hazards of chemicals. One VLE problem was included in the first challenge but due to its critical importance in the chemical industry, we decided to include a related problem in the second contest. Heat of vaporization is also an important quantity in the design of heat exchangers and other chemical process units. Also, enthalpy of vaporization is ~~also~~ used to calculate solubility parameters that are useful to determine the mutual compatibility of chemicals.

Vapor pressure is a fundamental thermodynamic property of a liquid. It is the pressure generated at a particular temperature by pure component which has liquid (or solid) and vapor in equilibrium in a closed vessel. The vapor pressure of a liquid increases with temperature between the triple point and the critical point.

Vapor pressure gives a measure of the escaping tendency of a material. The difference in vapor pressure between chemicals is the driving force for separation by distillation: The measure of separability for an ideal mixture of two components is the relative volatility, $\alpha_{(1\Rightarrow 2)}$, defined as,

$$\alpha_{(1\Rightarrow 2)} = P_{sat1}/P_{sat2} \quad (1)$$

where P_{sat1} and P_{sat2} are the vapor pressures. Few liquid mixtures are ideal so at low to moderate pressures this relative volatility equation usually contains activity coefficient terms, for which the vapor pressure is essentially the reference fugacity.

The most common vapor-pressure equation as a function of the temperature, T , is,

$$\text{Log } P_{sat} = A - B/(T+C) \quad (2)$$

which was suggested by Antoine in 1888. High-accuracy use of the Antoine equation is restricted to a short range, typically 1 to 200 kPa. Thus the Antoine equation is often used for calculations related to

atmospheric or vacuum distillations. The Antoine equation can cautiously be used to give vapor pressure data to $\pm 15\%$ over the temperature range where vapor pressure increases from 1 kPa to the critical pressure.

The Riedel equation is,

$$\ln P_{\text{sat}} = A + B/T + C \ln T + DT^N \quad (3)$$

where A, B, C, D, and N are adjustable parameters (N is usually an integer from 1 to 6). The temperature, T, must be absolute temperature, K. The Riedel equation is used to fit data over the entire liquid range from the triple point to the critical point with a precision of 0.5 to 2%. It also has the correct derivative behavior ($d(\ln P)/d(1/T)$) over most of the liquid range.

A second wide-range vapor-pressure equation is the Wagner equation which is given in reduced form: the temperature and pressure variables are divided by the critical temperature, T_c , and the critical pressure, P_c ,

$$\ln Pr = [a + b(1-Tr)^{1.5} + c(1-Tr)^3 + d(1-Tr)^6]/Tr \quad (4)$$

where $Tr = T/T_c$ and $Pr = P_{\text{sat}}/P_c$. There are many other vapor-pressure equations but the Antoine, Riedel, and Wagner equations are the three most commonly used in the chemical industry.

Heat of vaporization is the difference in heat content between coexisting liquid and vapor;

$$\Delta H_{\text{vap}} = H_V - H_L \quad (5)$$

For a process where energy is absorbed or liberated at constant pressure, heat of vaporization is called enthalpy of vaporization. It usually has a maximum value at the triple point and decreases with temperature, going to zero at the critical point. The heat of vaporization can be determined from direct calorimetric measurements (rare) or derived from accurate vapor pressure data via the Clapeyron equation which is generally valid at low reduced temperatures:

$$\Delta H_{\text{vap}} = -R\Delta Z_{VL} [d(\ln P)/d(1/T)] \quad (6)$$

where ΔZ_{VL} is the difference in compressibility factor ($Z = PV/nRT$) between coexisting vapor and liquid.

In recent years, there are a growing number of industrially important chemicals whose vapor pressures and heats of vaporization need to be determined outside of the ranges of ordinary experimental apparatus (e.g., highly volatile compounds at closely subcritical conditions, thermally unstable chemicals, low volatile compounds with high melting points, etc.). Molecular Simulation could offer an attractive alternative to these difficult laboratory measurements. Some examples of the application of Molecular Simulation methods to the prediction of VLE/vapor pressure and heats of vaporization may be found in references [16-19] and [20-23] respectively.

At the time of writing, (subject to change prior to official announcement [2]), the Contest Committee has decided to challenge the entrants to determine the vapor pressure and heat of vaporization of two organic materials, each at four temperatures. For scoring, a numerical score will be computed as the sum of the absolute values of the percentage difference for each of four state points from the experimental benchmark data. Appropriate weighting will be applied to each part of the problem to reflect their relative difficulty.

Problem Involving Gas Solubility in Liquids

The solubilities of gases in liquids are properties of great industrial importance since, for example, dissolved gases are a key component of many industrial chemical processes. The inherent experimental difficulties associated with certain gas/solvent mixtures (e.g. the risk of explosion during measurement of oxygen solubility) make them promising candidates for the application of molecular simulation as a tool for physical property prediction.

The Henry's law constant (HLC) is a measure of the limiting solubility of a solute in a solvent. The HLC of solute 2 in solvent 1 ($H_{2,1}$) at constant temperature can be expressed as [24]

$$H_{2,1} = \lim_{x_2 \rightarrow 0} \frac{f_2}{x_2} \quad (7)$$

where x_2 is the mole fraction of the solute in the solvent, f_2 is the fugacity of the solute, and equation (7) is known as Henry's law. The solubility of a solute in a solvent is often observed to be proportional to the solutes' gas phase partial pressure

$$x_2 = \frac{p_2}{C} = \frac{y_2 P}{C} \quad (8)$$

as long as the partial pressure is not too large. In equation (8), p_2 is the partial pressure of the solute, y_2 is the mole fraction of the solute in the gas phase, P is the total pressure, and C is a constant of proportionality. Equations (7) and (8) are consistent if the gas-phase fugacity of the solute is assumed to be equal to its partial pressure (i.e. an ideal gas) and C is identified as the Henry's law constant.

A number of authors have attempted to use molecular simulation to understand and predict the solubility of a solute in a low molecular weight solvent [25-34] or in a polymer [35-38]. Historically, the approach most commonly taken has been to estimate the infinite dilution residual chemical potential of the solute in the solvent, $\mu_2^{r\infty}$, which can be related to Henry's constant according to [25]

$$H_{2,1} = \rho_{liq} RT \exp\left(\frac{\mu_2^{r\infty}}{kT}\right) \quad (9)$$

where ρ_{liq} is the molar density of the liquid. Note that various methods for estimating chemical potential by molecular simulation have recently been discussed [39-41].

At the time of writing (subject to change prior to official announcement ([2]), we have decided to challenge the entrants to calculate the Henry's law constants of 4 gases in 1 liquid at 2 temperatures. For scoring:

- 20 % of the score will be based on predicting the correct trend with temperature for each gas.
- 40 % of the score will be based on a quantitative comparison of the predicted Henry's constants with the experimental values, but only in a relative sense.
- 40 % of the score will be based on an absolute quantitative comparison of the predicted Henry's constants with the experimental values.

Problem Involving Enthalpy of Mixing

Real binary mixture behavior is frequently described through the excess properties [24]. For liquids far away from the critical point, properties are not strongly influenced by pressure. The properties of primary interest are G^E , the excess Gibbs energy, and its temperature derivatives, particularly H^E , the excess enthalpy of mixing or short heat of mixing:

$$H^E = -RT^2 \left(\frac{\partial G^E / RT}{\partial T} \right)_{P,x} \quad (10)$$

The logarithm of the activity coefficient γ_i is the partial molar property with respect to the dimensionless excess Gibbs energy:

$$\ln \gamma_i = \left(\frac{\partial(nG^E/RT)}{\partial n_i} \right)_{T,P,n_j} \quad (11)$$

One the premier challenges for modeling thermal separation processes (e.g., absorption, distillation, extraction, etc.) is the ability to describe activity coefficients of the components of interest over the whole concentration and temperature range of interest with sufficient accuracy.

For many years chemical engineers and chemists involved with chemical process simulations have relied on well-known local composition G^E -models (e.g., UNIQUAC, NRTL, Wilson) to model cases where non-ideal behavior in the liquid phase plays an important role. The parameters of those G^E -models require experimental (or if appropriate, predicted) phase equilibrium data. There are many types of phase equilibrium data that can be used for regression, but isothermal vapor-liquid equilibria are probably one of the most common types that is being used in the chemical industry.

One of the inherent problems with using the aforementioned G^E -models is that their built-in capability to extrapolate with high accuracy outside the range of the fitted data is usually quite unreliable. The common way to solve this problem is to use phase equilibrium data for the parameter regression that cover the whole range of temperatures of interest. Introducing an empirical function into the G^E -model that allows the parameters to be temperature dependent usually solves this problem. In practical terms this means that more experimental data needs to be made available. Common practice is to use vapor-liquid equilibria (VLE) data at 2 or 3 temperatures for the parameters regression or sometimes by combining VLE and heat of mixing data. There are practical consequences from the selection of which phase equilibrium data should be chosen for parameter regression, but those consequences are less important for this competition.

Equations (10) and (11) show that if it is desirable to describe activity coefficients as functions of temperature with high accuracy, any G^E -model used needs to be able to describe the heat of mixing properly as well. As a consequence, inaccurate activity coefficients may result in erroneous predictions of phase equilibria which will in turn lead to a less than optimal design of the separation equipment. The result could be over-design or worse under-design of the equipment making the targeted separation more expensive or even impossible than with an optimal design.

Some examples of the application of Molecular Simulation methods to the prediction of mixing heats may be found in references [42-45]. At this time, (subject to change prior to official announcement [2]), we have decided that the task will be to calculate the heat of mixing for 2 binary systems at 4 equally spaced compositions and 2 temperatures (a total of 16 state points). The temperatures will be about 50 K apart and low reduced temperatures will be selected to avoid the influence of the pressure dependence ($P < 10$ bar) on the heat of mixing. For scoring:

- 20% of the score will be based on predicting the correct trend with temperature (or the slope $\Delta H^E/\Delta T$) for each system.
- 80% of the score will be based on a quantitative comparison of the predicted H^E values with the experimental values.

Summary of the Status of Contest II

At the time of writing this paper, the Committee is well into the decision process for choosing the actual systems and state points to offer the entrants. As discussed above, we are also close to finalizing the quantitative judging criteria which will be made public at the time of formal announcement of the problems. We plan on publicly soliciting input about the problems (without revealing the specific systems and state points) prior to the actual announcement. By the time of the FOMMS Conference, this announcement of the actual contest problems will have taken place [2].

6. Conclusions

The First Industrial Fluid Properties Simulation Challenge was established to promote the use of molecular simulation methods to predict industrially relevant materials' properties. Because of the successful outcome, we were gratified to see that the Simulation community responded so positively to this type of activity. Clearly, there is a need in this field (and probably in other fields) to use activities such as these to bring together, for a common purpose, the developers, commercial software suppliers, and industrial users. The results from this first Challenge show that simulation methods can already provide accurate predictions of density for a wide range of molecule types – although care should be taken in selecting an appropriate force field for a given material. Reasonable results can be obtained for vapor-liquid equilibria and viscosity. We believe that this initiative has already provided valuable information and served to promote the industrial application of these techniques. The Contest Committee intends to build on this success by the continuation of the competition.

The second event will last two years, allowing more time for careful formulation of the problems and judging criteria and also allow more time for prospective entrants to complete the calculations. Furthermore, we hope to convince other industrial partners to financially support the contest. Overall we anticipate participation in the contest to increase and to include more of the well-known leaders in the field. It is our desire to build the momentum of this effort to ensure that it becomes established as a long term, scientifically credible, and respected competition. If you are a practitioner in the field, the authors would like to extend an invitation to you to consider entering all or part of the upcoming contests. If you are an industrial user, we encourage you to become active in the planning of the event, even if it is a suggestion for an important industrial problem. Consult the Challenge web page [2] for the latest information.

7. Acknowledgements

We would like to thank the attendees at the 2001 “Workshop in Predicting the Thermophysical Properties of Fluids by Molecular Simulation” [3] who started this whole process. We would like to thank NIST for their assistance in organizing this challenge, AIChE for their sponsorship, and The Dow Chemical Company and BP for financial support. We would like to particularly recognize those from NIST and The Dow Chemical Company who provided the experimental data (the answers to the challenge problems). Also, we thank the AIChE DIPPR organization, in particular George Thomson, for arranging the use of unpublished experimental data for the VLE problem. Finally we would like to thank all the participants for their willingness to commit considerable time and resources to this Challenge.

8. References

- [1] Special Issue of *Fluid Phase Equilibria*, P. Cummings, Ed., Unknown publication date at the time of writing. This volume will contain contributions from most of the entrants to the first contest, articles on the determination of the benchmark data, and a detailed summary of the first Challenge including much more detail on the problems, the entries, and the winning results.
- [2] <http://www.cstl.nist.gov/FluidSimulationChallenge/> ; note also that this web site contains details of the first Challenge, including the benchmark data.
- [3] <http://www.ctcms.nist.gov/~fstarr/ptpfms/home.html>
- [4] Chemical Industry Vision 2020 Technology Partnership, sponsored by AIChE, ACS, and CCR, <http://www.chemicalvision2020.org/>
- [5] "Chemical Industry of the Future, Technology Roadmap for Computational Chemistry", Tyler Thompson, ed., 1999, <http://www.ccrhq.org/vision/index/roadmaps/complete.html>

- [6] *Cummings, P. T. and Evans, D. J., 1992, Ind. Eng. Chem. Res. 31, 1237-1252.*
- [7] *McCabe, C., Cui, S., Cummings, P. T., Gordon, P. A., and Saeger, R. B., 2001, J. Chem. Phys. 114, 1887-1891.*
- [8] *Moore, J. D., Cui, S. T., Cummings, P. T., and Cochran, H. D., 1997, AIChE J. 43, 3260-3263.*
- [9] *Moore, J. D., Cui, S. T., Cochran, H. D., and Cummings, P. T., 2000, J. Chem. Phys. 113, 8833-8840.*
- [10] *McCabe, C., Cui, S., and Cummings, P. T., 2001, Fluid Phase Equilib. 183-184, 363-370.*
- [11] *Mundy, C. J. and Klein, M. L., 1996, J. Phys. Chem. 100, 16779-16781.*
- [12] *McCabe, C., Bedrov, D., Smith, G. D., and Cummings, P. T., 2001, Ind. Eng. Chem. Res. 40, 473-475.*
- [13] <http://www.cosmologic.de/>
- [14] <http://www.aeontechnology.com/>
- [15] <http://www.cs.sandia.gov/projects/towhee/index.html>,
<http://www.cs.sandia.gov/~sjplimp/lammmps.html>
- [16] *Panagiotopoulos, A. Z., 1996, Direct determination of fluid phase equilibria by simulation in the Gibbs ensemble: A Review. in Molecular Simulation and Industrial Applications: Methods, Examples and Prospects, edited by K.E. Gubbins and N. Quirke, (Gordon and Breach Publishers) pp. 183-205.*
- [17] *Errington, J. R. and Panagiotopoulos, A. Z., 1999, J. Chem. Phys. 111, 9731-9738.*
- [18] *Martin, M. G. and Siepmann, J. I., 1998, J. Phys. Chem. B 102, 2569-2577.*
- [19] *Ungerer, P., Beauvais, C., Delhommelle, J., Boutin, A., Rousseau, B., and Fuchs, A. H., 2000, J. Chem. Phys. 112, 5499-5510.*
- [20] *Potter, S. C., Tildesley, D. J., Burgess, A. N., and Rogers, S. C., 1997, Mol. Phys. 92, 825-833.*
- [21] *Jorgensen, W. L., Maxwell, D. S., and Tirado-Rives, J., 1996, J. Am. Chem. Soc. 118, 11225-11236.*
- [22] *Spyriouni, T., Economou, I. G., and Theodorou, D. N., 1999, J. Am. Chem. Soc. 121, 3407-3413.*
- [23] *Faller, R., Schmitz, H., Biermann, O., and Müller-Plathe, F., 1999, J. Comput. Chem. 20, 1009-1017.*
- [24] *Prausnitz J.M., Lichtenthaler R.N., de Azevedo E.G., "Molecular Thermodynamics of Fluid Phase Equilibria", 3rd Edition, Prentice Hall PTR, 1999.*
- [25] *Shing, K. S., Gubbins, K. E., and Lucas, K., 1988, Mol. Phys. 65, 1235-1252*
- [26] *Chialvo, A. A., 1990, J. Chem. Phys. 92, 673-679.*
- [27] *Sadus, R. J., 1997, J. Phys. Chem. B 101, 3834-3838.*
- [28] *Bonifácio, R. P., Pádua, A. A. H., and Gomes, M. F. C., 2001, J. Phys. Chem. B 105, 8403-8409.*

- [29] *Errington, J. R. and Panagiotopoulos, A. Z., 1999, J. Chem. Phys. 111, 9731-9738.*
- [30] *Boulougouris, G. C., Voutsas, E. C., Economou, I. G., Theodorou, D. N., and Tassios, D. P., 2001, J. Phys. Chem. B 105, 7792-7798.*
- [31] *Iwai, Y., Uchida, H., Koga, Y., Mori, Y., and Arai, Y., 1995, Fluid Phase Equilib. 111, 1-13.*
- [32] *Murad, S. and Gupta, S., 2000, Chem. Phys. Lett. 319, 60-64.*
- [33] *Murad, S. and Gupta, S., 2001, Fluid Phase Equilib. 187-188, 29-37.*
- [34] *Slusher, J. T., 1999, J. Phys. Chem. B 103, 6075-6079.*
- [35] *Müller-Plathe, F., 1991, Macromolecules 24, 6475-6479.*
- [36] *de Pablo, J. J., Laso, M., and Suter, U. W., 1993, Macromolecules 26, 6180-6183.*
- [37] *Kikuchi, H., Kuwajima, S., and Fukuda, M., 2001, J. Chem. Phys. 115, 6258-6265.*
- [38] *Zervopoulou, E., Mavrantzas, V. G., and Theodorou, D. N., 2001, J. Chem. Phys. 115, 2860-2875.*
- [39] *Kofke, D. A. and Cummings, P. T., 1997, Mol. Phys. 92, 973-996.*
- [40] *Kofke, D. A. and Cummings, P. T., 1998, Fluid Phase Equilib. 150-151, 41-49.*
- [41] *Martin, M. G. and Siepmann, J. I., 1998, Theoretical Chemistry Accounts 99, 347-350.*
- [42] *Chitra, R. and Smith, P. E., 2001, J. Chem. Phys. 115, 5521-5530.*
- [43] *Tanaka, H. and Gubbins, K. E., 1992, J. Chem. Phys. 97, 2626-2634.*
- [44] *Lee, S., Lee, J. G., Lee, H., and Mumby, S. J., 1999, Polymer 40, 5137-5145.*
- [45] *Madkour, T. M., 2001, Chem. Phys. 274, 187-198.*