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FLUID PHASE  
EQUILIBRIA[www.elsevier.com/locate/fluid](http://www.elsevier.com/locate/fluid)The third industrial fluid properties simulation challenge<sup>☆</sup>

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**Abstract**

The third industrial fluid properties simulation challenge was held from March to September 2006. As in the previous two events contestants were challenged to predict specific, industrially relevant, properties of fluid systems. Their efforts were judged based on the agreement of the predicted values with previously unpublished experimental data (provided by researchers at ExxonMobil and DuPont). The focus of this contest was on the transferability of modeling methods—the ability to predict properties for materials that are chemically different, or at different state points, to those used in model parameterization and validation. Nine groups attempted to compute bubble point pressures for mixtures of 1,1,1,2,3,3,3-heptafluoropropane (HFC-227ea) and ethanol at 343 K, given data for mixtures at 283 K, and given the pure component vapor pressures. They used a range of different techniques including statistical mechanical and molecular simulations-based approaches. Four of the groups were recognized for providing predictions that were significantly more accurate than would be obtained by extrapolation using the NRTL model (the standard engineering approach). Three groups undertook the more challenging “molecular transferability” problem, attempting to predict shear viscosities at two different state points for a range of diols and triols for which little experimental data was available.

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**Keywords:** Molecular simulation; VLE; Phase equilibria; Viscosity; Statistical mechanics; 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. Process simulation has become the main tool for the development, design, scale-up, and optimization of chemical processes. Physical properties (particularly phase equilibria) and kinetic data are the key inputs for the development of such process models. Prediction of physical properties is key in new

<sup>☆</sup> Certain commercially available items may be identified in this paper. This identification does not imply recommendation or endorsement by NIST, nor does it imply that it is the best available for the purposes described.

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product design, and physical properties are also needed for regulatory compliance and product application literature [1]. It can be difficult, time consuming, or expensive, to obtain reliable information, especially for unusual materials, mixtures, or state points far from ambient conditions. Computer simulation holds great promise in this area [2,3].

The industrial fluid properties simulation challenges (IFPSC) were started in 2001 to provide a realistic assessment of the value of methods for predicting thermophysical properties of industrially important fluids. The organizing committee (the authors of this paper, and of the previous two papers in this series [4,5]) 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 concluded in September 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 [4]. Their blind predictions were judged based on agreement with experimental data obtained by the IFPSC benchmark committee [6]. Results from this first challenge showed that in 2002 simulation methods could already provide accurate predictions of density for a wide range of organic fluids, and for two aqueous solutions [7–10]—although care should be taken in selecting an appropriate forcefield. Reasonable results were obtained for vapor–liquid equilibria [11,12]: contestants were asked to predict the vapor–liquid equilibria (VLE) for mixtures of dimethyl ether and propylene at  $-20^{\circ}\text{C}$  (253.15 K) and  $20^{\circ}\text{C}$  (293.15 K), and for mixtures of nitroethane and propylene glycol monomethyl ether at  $80^{\circ}\text{C}$  (353.15 K) and  $40^{\circ}\text{C}$  (313.15 K). The third problem set in the first IFPSC asked contestants to predict the shear viscosity of *n*-nonane, isopropanol, and two mixtures of these fluids [10,13]. These viscosity predictions were less convincing—principally because of large error bars (partially a function of the state of computational resources at that time). A second contest was held in 2004, focusing on molecular simulation methods. Contestants attempted to predict vapor pressures, heats of vaporization, Henry's law constants, and heats of mixing using a wide range of molecular modeling methods and forcefields [5]. Predictions of Henry's constant for  $\text{N}_2$ ,  $\text{CO}_2$ ,  $\text{CH}_4$ , and  $\text{O}_2$  in ethanol, at 323 and 373 K, were judged sufficiently accurate to be of value in an industrial environment [14–16]. Results for vapor pressure and heats of vaporization of acetone and butyramide at a range of temperatures [16,17] were mixed: the winning entry gave good agreement [18], but the range of predictions was large. Reasonable qualitative predictions of heats of mixing were obtained for mixtures of *n*-butylamine with *n*-heptane [16,19]. Results for butylamine with water revealed an area where although, for the most part, the molecular simulation methods were sound, forcefield descriptions were inadequate. Calculations using the COSMO-RS [20] demonstrated that non-molecular simulation methods were capable of greater accuracy than the simulation methods for this system.

The committee actively sought feedback after the first contest, and the second contest provided an opportunity to refine our procedures for communicating with participants and judg-

ing the contest, procedures that we maintained for the third contest. For example, we instigated an initial screening process. Each entry was reviewed by external judges: acknowledged experts in molecular simulation who were not participating in the current contest. The reviewers assessed the overall quality of the entry (statistical significance of results, sufficient supporting evidence, adherence to contest rules, etc.). Entries that failed these criteria were rejected. To ensure full transparency in the judging process the spreadsheets used to assess numerical scores were placed on the IFPSC website (<http://www.fluidproperties.org>) at the start of both the second and the third competition. They will remain there, and we hope that methodology and forcefield developers may find them useful to assess the accuracy of new methods that they develop. The organizing committee would be most interested in hearing about such comparisons.

Further information about this contest, the judging procedures, our motivation and aims, can be found in the overview papers for the first and second contest [4,5], and at the IFPSC website. The website provides a link to the IFPSC vision and strategic planning document, which outlines a range of other activities proposed by the group. The website also provides information about the fourth IFPSC challenge.

## 2. The challenge problems

### 2.1. The state-condition transferability problem

The ability of computer modeling to predict properties for state points that are challenging, inaccessible to experiment, or simply missing, is often used as a justification for its development. The objective of this challenge problem was to test and validate this capability. A common task in chemical and related industries is to use mixture phase equilibria information obtained at one isotherm or isobar and extrapolate to state conditions at other temperatures, pressures, and/or compositions. This extrapolation may be required with or without the knowledge of experimental pure component properties.

Entrants were provided with the experimental bubble point (or total pressure) for 15 mixture compositions of 1,1,1,2,3,3,3-heptafluoropropane (HFC-227ea, CAS# 431-89-0) and ethanol (CAS# 64-17-5) at 283.17 K ( $10.02^{\circ}\text{C}$ ), and of the pure materials at 343.13 K, as shown in Table 1. They were challenged to compute the bubble points for seven mixture compositions at  $T=343.13\text{ K}$  ( $69.98^{\circ}\text{C}$ ). There was no limitation on the experimental data for the individual components that could be used to parameterize a model. No mixture data (binary and/or higher order) for the specified system could be used other than the experimental data provided in Table 1. Entries using any theory/modeling/simulation method were welcome, provided they follow the rules with respect to parameterization.

Entries were judged based on a simple scoring system:

$$F = \frac{100}{7} \sum_i^7 \left| \frac{P_{i,\text{exp}} - P_{i,\text{calc}}}{P_{i,\text{exp}}} \right|$$



Table 1  
Experimental bubble point pressures for mixtures of HFC-227ea and ethanol provided to IFPSC contest entrants

Mole fraction ethanol	Bubble point pressure			
	283.17 K		343.13 K	
	N/m <sup>2</sup>	psia	N/m <sup>2</sup>	psia
0	2.80E+05	40.63	1.487E+06	215.72
0.0545	2.70E+05	39.13		
0.1123	2.64E+05	38.28		
0.2152	2.56E+05	37.15		
0.3173	2.49E+05	36.07		
0.4137	2.40E+05	34.87		
0.5097	2.30E+05	33.32		
0.6066	2.10E+05	30.45		
0.7328	1.76E+05	25.466		
0.7893	1.49E+05	21.538		
0.8553	1.08E+05	15.632		
0.9001	7.63E+04	11.071		
0.9392	4.78E+04	6.939		
0.967	2.76E+04	3.999		
1	3.08E+03	0.446	7.274E+04	10.55

The experimental data was measured by scientists at DuPont as discussed in the following paper and results for the mixtures at 343.13 K were kept secret until all the entries had been received.

The system is industrially relevant: hydrofluorocarbons are widely used, often as mixtures with other fluids, as replacements for environmentally hostile chlorofluorocarbon refrigerants, and as cleaning solutions, fire retardants, and propellants. It is also chemically interesting: the possibility of hydrogen bonding interactions between the HFC-227ea proton and ethanol is likely to lead to asymmetric interactions (the interaction between HFC-227ea and ethanol will not be well modeled by simple mixing rules).

For many years chemical engineers and chemists involved with chemical process simulations have relied on well-known local composition  $G^E$  models [21] (e.g., UNIQUAC, NRTL, Wilson) to describe cases where non-ideal behavior in the liquid phase plays an important role [21] – but experience has shown that these models do not provide sufficient accuracy for mixtures – particularly asymmetric mixtures.

In recent years a number of molecular simulation approaches have been proposed for predicting vapor–liquid equilibria. Molecular simulations methods have been frequently applied in previous IFPSC's [4,5], and were the focus of the second IFPSC [5]. Briefly, in a molecular simulation, a physically realistic model of a small portion of fluid (typically a few tens of nanometer cube) is created. If the model is an accurate one, the properties and behavior of the simulated system will predict the properties and behavior of the real material. Accuracy is determined by the realism of the inter-atomic interactions (the functional form and parameters of the forcefield) [22], and by the strategies for creating and manipulating the model to provide property predictions (the molecular simulations methods used). Typical molecular simulations approaches that have been used for VLE prediction of mixtures include configurational-bias Monte Carlo simulations (Gibbs ensemble and the combination of Grand-

Canonical Monte Carlo and histogram reweighting) [23–27], the Gibbs–Duhem integration method [28–30], the NPT dynamics plus test particle method (Widom's insertion method) [31,32], the bubble point pseudo-ensemble method [33], and the Grand Equilibrium method [34].

COSMO-RS – a technique that combines aspects of both statistical mechanics and simulations approaches – has also been applied to predictions of VLE [20,35–37]. The winning entry for the VLE challenge in the first IFPSC used COSMO-RS [11].

Calculations that provided better predictions than could have been obtained using the NRTL (non-random two liquid model) extrapolation were recognized as being industrially relevant.

## 2.2. The molecule transferability problem

A great deal of effort has been put into the development of forcefields for molecular simulations that can cover a wide range of chemical species. Typically forcefield parameters are fit to some variety of physical property information for a limited number of compounds. A desirable property of such forcefields, then, is the transferability of the forcefield to describe the properties of molecules with similar chemical makeup but different molecular connectivity. The molecule transferability problem was designed to test this aspect of forcefields.

Contestants were asked to predict the low-strain rate limit (Newtonian) viscosity for five diols and triols (Fig. 1), at two state points:  $T=373$  K,  $P=0.1$  MPa, and  $T=373$  K,  $P=250$  MPa. These molecules represent chemically similar species for which only limited experimental data is available. In particular, atmospheric pressure data is available for 1,*n*-butanediols over a limited temperature range, but there is no known data for 1,2,4-butanetriol, 2-methyl-1,3-propanediol. In addition, no data at elevated pressures for any of these species. The challenge problem required all properties to be predicted with a single intermolecular potential. This was stipulated to test the transferability of parameters that comprise a forcefield to molecules of similar chemical makeup but differing connectivity. We also note that viscosity is not a property typically used to fit intermolecular forcefield parameters. This aspect provides an additional test of the predictive capability of the forcefields.

Viscosity is a fundamental transport property in lubrication, impacting heat transfer, friction and wear characteristics, and the energy efficiency of lubricated contacts. Fluids entrained in lubricated contacts of non-conforming surfaces typically are compressed to very high pressures, in the range of 1 GPa or

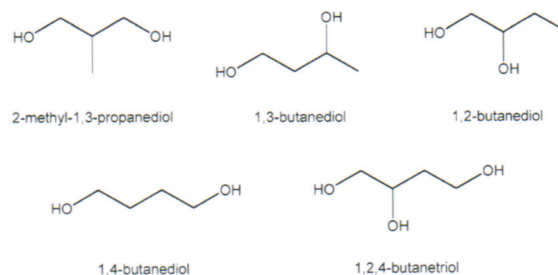


Fig. 1. Diol and triol structures for fluids in the viscosity prediction challenge.



more. In general, experimental data describing viscosity at such pressures are scarce, and are not easily predicted on the basis of viscosity data at atmospheric pressure.

Lubricating fluids are typically comprised of many components. Composition of the lubricant basestock, the main carrying fluid, controls the viscosity, and is characterized by the molecular weight distributions of classes of similar molecule types, such as paraffins, naphthenes, 1-ring aromatics, and so on. Within these classes, however, the effect of isomer distribution is generally ignored, but can have a large impact on the viscosity. The molecules selected for this challenge problem demonstrate this point, as was revealed when the experimental data was released: there is a significant spread in the viscosities of the same molecular weight species.

While real lubricants are typically of larger molecular weight than the small molecules considered in this challenge, a forcefield that successfully demonstrates the properties of transferability demanded in this contest challenge could be used to predict the properties of larger diol and triols of interest as potential lubricant basestock components.

The entries were judged based on their quantitative accuracy, comparing their predictions to experimental data (measured by researchers at ExxonMobil and not revealed until after all the contest entries had been received). This accounted for 50% of their scores. Twenty-five percent of the score rested on the accuracy of the relative viscosities within the set of molecule species, and the final 25% was awarded based on the success of each method in predicting the relative viscosity increase:  $\eta_{250 \text{ MPa}}/\eta_{0.1 \text{ MPa}}$ .

A number of different strategies have been proposed for calculating shear viscosities from molecular simulations. Equilibrium molecular dynamics (EMD) methods sample the time dependence of thermal fluctuations in the stress or momentum flux tensors, which can be related to the viscosity using linear response theory [38]. For example, the results of a long simulation could be analyzed using a Green–Kubo equation that links the viscosity with the autocorrelation function of the  $xy$  component of the stress tensor [38,39]:

$$\eta = \frac{V}{k_B T} \int_0^\infty \langle P_{xy}(0) P_{xy}(t) \rangle dt \quad (1)$$

The champions in the viscosity challenge for the first IFPSC used EMD. The integral in Eq. (1) converges slowly, and requires long simulation times to achieve good statistics. An alternative approach to computing viscosity is offered by a class of methods known as non-equilibrium molecular dynamics (NEMD), in which the system is driven away from equilibrium and the response is monitored. There are two non-equilibrium methods that make use of steady-state shear: sliding boundary conditions, for instance Lees–Edwards boundary conditions or the SLLOD algorithm [39–41], can be used to set up planar Couette flow. Alternatively, a periodic shear flow can be set up using conventional periodic boundary conditions [42]. In these NEMD methods the shear rate,  $\dot{\gamma}$ , is imposed, the resulting momentum flux or off diagonal component of the stress tensor,  $P_{xy}$ , are

measured. The ratio provides the shear viscosity:

$$\eta = \frac{P_{xy}}{\dot{\gamma}}$$

These methods can also be compute-intensive, as low shear imposed shear rates may be required to reach the Newtonian limit of the fluid. In the reverse non-equilibrium molecular dynamics (RNEMD) method the momentum flux of the molecules is imposed and the resulting shear rate or velocity profile is measured [43]. Other approaches include momentum impulse relaxation (MIR) [44], in which a Gaussian velocity profile is imposed on an equilibrated system, and its decay is monitored as a function of time.

### 3. Challenge results and discussion

Details of the simulations carried out by each of the teams are given in companion papers in this special issue of Fluid Phase Equilibria.

#### 3.1. Results for the state-condition transferability problem: predictions of VLE for mixtures of HFC-227ea and ethanol at 343.13 K

Nine teams entered this section of the third IFPSC. They used a wide range of techniques. Four of the entries provided predictions that were more accurate than could have been obtained by NRTL extrapolation. The entries are summarized in Table 2. Results using Raoult's law plus the ideal gas law; from direct fitting of data using the NRTL-PR and Wilson-PR; using NRTL-PR and Wilson-PR approaches with parameters fit to the 10 °C isotherm; and using the commercial version of COSMO-RS [45,46] plus the ideal gas law, are reported in Table 3 for com-

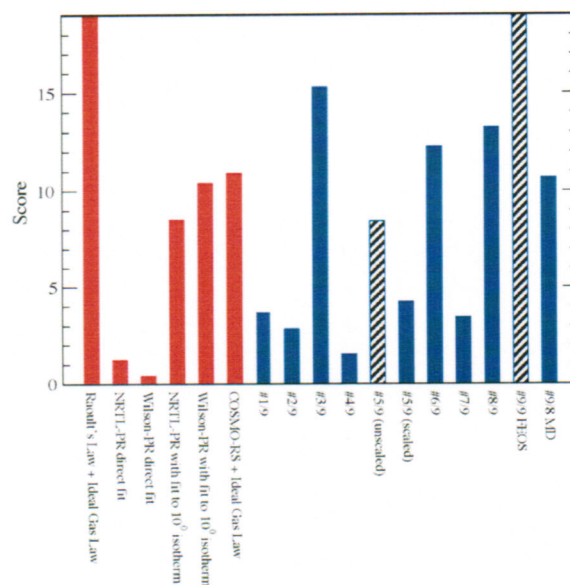


Fig. 2. Scores for entries into the state conditions transferability problem, compared with calculations using other approaches.



Table 2

Percent error for submitted bubble point pressures for the specified mixture compositions of HFC-227ea and ethanol

$x(\text{HFC-227ea})$	$x(\text{EtOH})$	#1/9	#2/9	#3/9	#4/9	#5/9	#6/9	#7/9	#8/9	#9/9
0.06	0.94	8.73	0.47	28.46	0.37	0.15	28.30	3.99	26.90	32.66
0.15	0.85	5.98	2.68	21.33	1.38	3.48	34.04	6.65	19.86	29.72
0.27	0.73	1.48	10.83	18.05	1.34	8.70	10.25	5.60	18.75	2.99
0.48	0.52	3.75	2.07	15.52	1.98	11.82	6.14	0.54	15.37	0.75
0.67	0.33	3.88	2.60	12.01	3.13	5.26	4.10	3.45	7.31	2.62
0.88	0.12	1.51	0.29	6.66	1.61	0.15	2.21	2.46	1.98	3.87
0.94	0.06	0.74	0.85	5.00	0.77	0.15	0.71	1.35	2.38	2.05

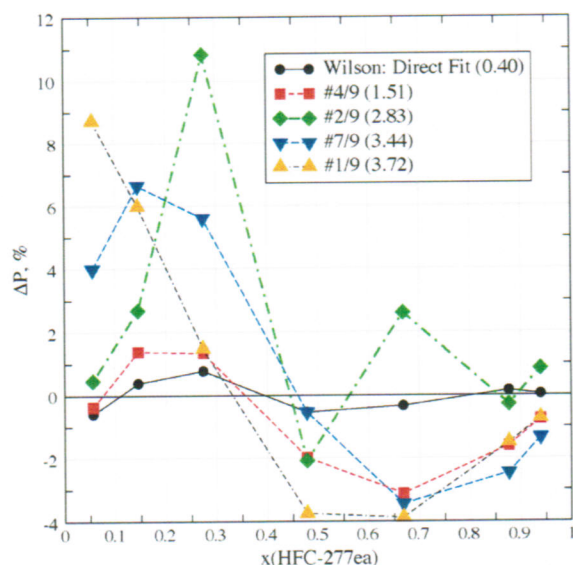


Fig. 3. Pressure deviation from experimental values for predicted bubble pressures of mixtures of ethanol and HFC-227ea at 343.13 K. The top four entries.

parison. The entries are also compared graphically in Figs. 2–4. Some of the teams (entries 6/9, 2/9, 8/9) chose not to fit to the lower temperature data for HFC-227ea/ethanol mixtures supplied as part of the contest problem description. Others supplied a second set of predicted bubble points (in addition to their official contest entry) showing how their methods performed without fitting to the mixture data. The scores for these entries illustrate the capabilities of these techniques for predicting properties of mixtures for which no experimental data is available.

Table 3

Percent error for bubble point pressures calculated or fitted using other methods

$x(\text{HFC-227ea})$	$x(\text{EtOH})$	Raoult's law + ideal gas law	NRTL-PR direct fit	Wilson-PR direct fit	NRTL-PR using parameters fitted to 10 °C isotherm	Wilson-PR using parameters fitted to 10 °C isotherm	COSMO-RS + ideal gas law
0.06	0.94	54.44	1.31	0.59	24.90	23.77	6.26
0.15	0.85	56.98	0.48	0.39	20.63	20.35	18.38
0.27	0.73	50.43	1.46	0.78	10.87	11.24	23.43
0.48	0.52	34.21	0.52	0.54	0.63	2.36	17.43
0.67	0.33	18.65	2.03	0.34	1.92	7.50	8.56
0.88	0.12	4.73	1.81	0.15	0.25	4.69	1.60
0.94	0.06	1.88	0.93	0.04	0.22	2.78	0.58

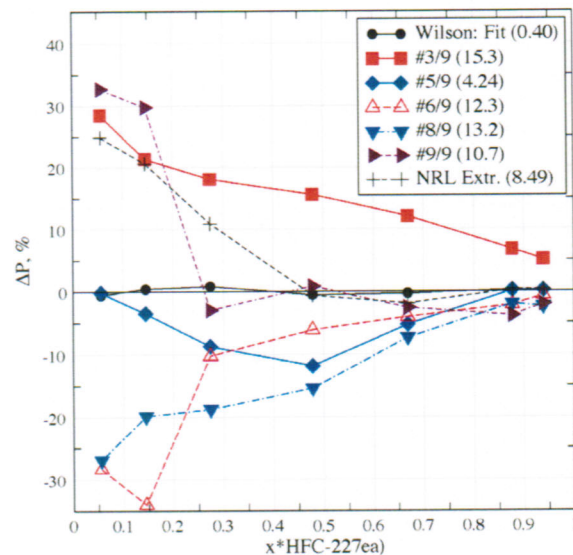


Fig. 4. Pressure deviation from experimental values for predicted bubble pressures of mixtures of ethanol and HFC-227ea at 343.13 K. The remaining five entries compared with the results of extrapolation from the lower temperature data using NRTL.

Entry 1/9 was provided by Matthias Kleiner and Gabriele Sadowski from the Lehrstuhl für Thermodynamik at the Universität Dortmund, using their Perturbed Hard Chain Statistical Association Fluid Theory method (PC-SAFT) [47]. Conventional equations of state (EOS) involve variations on hard-sphere or mean-field models of fluids. These are insufficient for fluids in which the molecules are highly non-spherical or associate due to specific chemical interactions (hydrogen bonding, dipole–dipole interactions, etc.). In SAFT, molecules are modeled as chains



of beads (segments), providing shape information. Terms are included to model intramolecular segment–segment interactions (the result of van der Waals interactions between the molecules); and specific associations between molecules (such as hydrogen bonding) [21]. PC-SAFT provides a more sophisticated approach to modeling of attractive interactions than the original SAFT [47]. The molecular model can be refined by individually accounting for association (hydrogen bonding) and polar interactions (dipolar and quadrupolar), and has been shown to model phase-behavior in a number of polar and non-polar fluids [48]. For this contest the authors introduce a new strategy for modeling asymmetric mixtures—mixtures in which the intermolecular interactions cannot be estimated using simple mixing rules. Their predictions were recognized as being significantly more accurate than could have been obtained by fitting to a standard NRTL model.

Entry 2/9 was provided by Bernhard Eckl, Yow-Lin Huang, Jadran Vrabec and Han Hasse from the Institut für Technische Thermodynamik und Thermische Verfahrenstechnik, at the Universität Stuttgart. This team used a molecular simulation approach. Geometric and electrostatic forcefield parameters were obtained from quantum mechanics simulations of isolated molecules (using the Conductor-like Screening Model, COSMO to model the effect of the solvent environment on the electrostatic charges [49]). A Lennard-Jones model for the inter-atomic van der Waals and short repulsions was parameterized by fitting to experimental data for pure ethanol and pure HFC-227ea. The team used their Grand Equilibrium method to predict the VLE for each mixture composition [34]. The error bars obtained were rather large (due to the poor statistics of Widom's insertion method used to calculate the pressure-dependent chemical potentials of the species in the liquid mixtures)—but the accuracy was good. Their predictions were recognized as being significantly more accurate than could have been obtained by fitting to a standard NRTL model. This was the second place entry in this section of the third IFPSC.

Entry 3/9 was provided by Amanda Sans and Richard Elliot from the Chemical and Biomolecular Engineering Department at the University of Akron. Their Step Potential Equilibria And Discontinuous Molecular Dynamics (SPEADMD) method [18] was adapted to characterize the interaction potentials in perfluorinated hydrocarbons, and their mixtures with *n*-alkanes. The innovation provided by the step potential [50] is fitting of the functional form for inter-atomic interactions (other molecular simulation methods assume a functional form such as Lennard-Jones and simply fit the parameters). Their study recommends a softer, stepped, potential for perfluorinated hydrocarbons, and they obtain good predictions for vapor pressure and density for a wide range of structures. Fluorine parameters are directly transferred from the perfluorinated hydrocarbons to model HFC-227ea, and parameters for the additional CFH interaction are obtained by fitting to experimental data. For the ethanol/HFC-227ea mixture interactions between CH<sub>x</sub> and F are transferred from their perfluorinated hydrocarbon/*n*-alkane simulations. The authors suggest a number of ways that their forcefield model could be refined, but note that these would detract from the transferability of the method.

Entry 4/9 was provided by Steen Christensen, Günther Peters, Flemming Hansen, and Jens Abildskov from the Danmarks Tekniske Universitet (DTU), and John O'Connell from the University of Virginia. This team has recently developed a new method for predicting binary vapor–liquid isotherms. Starting with a NPT-MD molecular simulation of the liquid phase for each mixture composition they use fluctuation solution theory to provide a link between the predicted microscopic structure (from the calculated radial distribution function), and the parameters needed to optimize a G<sup>E</sup> model for the liquid phase. They assume that the vapor phase is ideal and calculate the bubble pressure (for the 343.13 K predictions they treat the vapor phase as an ideal solution since the challenge is set at a pressure that is too high to assume an ideal gas). For this contest they modified the CHARMM forcefield, optimizing the Lennard-Jones parameters for the –CHF– part of the HFC-227ea molecule to fit experimental densities. This team generated the most accurate predictions of VLE behavior for the HFC-227ea/ethanol mixture. They were declared the champions in this section of the third IFPSC. Figs. 5 and 6 shows the award being presented the 2006 AIChE Annual Meeting in San Francisco.

Entry 5/9 was provided by Neeraj Rai, Jake Rafferty, and Ilia Siepmann from the University of Minnesota. This team used the Gibbs ensemble Monte Carlo approach to predict VLE using molecular simulations. This approach involves two simulation boxes: one containing the liquid phase and the other containing the vapor phase. A range of Monte Carlo moves are used to equilibrate the fluids in each box; and two moves (volume changes and interbox transfers) are used to equilibrate the two phases. The TraPPE forcefield [51] was extended to model HFC-227ea, and good agreement was obtained between the predicted and experimental critical constants, boiling temperature, and vapor–liquid coexistence curve for the neat fluid. The team provided two sets of predicted bubble point pressures for the HFC-227ea/ethanol mixture at 343.13 K. In the spirit of a transferability challenge, parameters for the first set of predictions were fit without using the binary data provided for the system at 283.17 K. For the second set of predictions the team introduced a novel scaling approach to incorporate the experimental data. Their second set of predictions was recognized as being significantly more accurate than could have been obtained by fitting to a standard NRTL model. This team also provided structural insight into the fluid mixture revealing that at higher temperatures free ethanol molecules will, at least weakly, bond to surrounding HFC-227ea molecules.

Entry 6/9 was provided by Xiaofeng Le, Jianxing Dai and Huai Sun from the School of Chemistry and Chemical Technology at Shanghai Jiao Tong University. This team also employed NPT Gibbs ensemble Monte Carlo molecular simulations to predict VLE. They extended their TEAM forcefield [9] to model fluoroalkanes, introducing a new method for deriving transferable van der Waals parameters. In the TEAM forcefield (and in other forcefields) electrostatic and intramolecular valence parameters (bond lengths, bond angles, etc.) are obtained by fitting to the results of quantum mechanics simulations of molecules or molecular fragments. However, van der Waals parameters for every atom type have traditionally been obtained by fitting to





Fig. 5. Anne Chaka presents the award for the state conditions transferability problem to Jens Abildskov at the special IFPSC session during the 2006 AIChE Annual Meeting.

experimental condensed phase data. The new approach derives charge-dependent van de Waals parameters, which can be fit using atomic ionization energies and polarizabilities calculated from *ab initio* methods. This reduces the need for experimental data (this team did not fit their model using the experimental VLE data at 283.17 K). Validation work showed that the new methods could provide excellent predictions of condensed phase properties for the pure fluids, and good predictions of bubble pressures for the mixture system at 283.17 K.

Entry 7/9 was provided by Andreas Klamt and Frank Eckert from COSMOlogic. The COSMO-RS technique combines a molecular simulation method (quantum density functional theory, DFT) with a statistical thermodynamics description of the VLE. A DFT simulation is used to optimize the conformation of the ethanol and HFC-227ea molecules (using the COSMO

continuum solvation model), and to calculate the charge density at the surface of each molecule. This provides a description of the surface polarity. The interaction energies between segments of the surfaces of each molecule are then calculated, providing an *ab initio* prediction of molecular interactions in the liquid phase that includes specific interactions such as dipole–dipole interactions and hydrogen bonding. Less specific van der Waals interactions are generally approximated using element specific dispersion coefficients. However, for this challenge problem the authors introduce a new strategy for adjusting the van der Waals parameters. They fit the F–F parameter using the lower temperature VLE data provided, resulting in a marked improvement in their predictions. Their predictions were recognized as being significantly more accurate than could have been obtained by fitting to a standard NRTL model.



Fig. 6. Left to right: Huai Sun, Xiaofeng Li, Lifeng Zhao, Jianxing Dai and Xijun Wang with the award for the molecule transferability problem (awardee Ling Wang is not shown).



Entry 8/9 was provided by A. Özgür Yazaydin and Marcus Martin from Sandia National Laboratories. This group decided on a pragmatic approach—one that would be likely to be taken by an industrial molecular simulation practitioner. They calculated bubble pressures for the ethanol/HFC-227ea mixtures using the MCCC'S Towhee Monte Carlo molecular simulation program, which is freely available (<http://towhee.sourceforge.net>). They selected the TraPPE-UA forcefield for the ethanol since it has already been well validated for predicting VLE for this molecule [52]; and they tested the ability of four public available forcefields (CHARMM22, DREIDING, OPLS-2001 and UFF) for their ability to predict experimental vapor liquid coexistence curves and critical data for HFC-227ea, finally selecting UFF for this molecule. They used simple geometric mixing rules for the interactions between the TraPPE-UA ethanol and the UFF HFC-227ea molecules.

Entry 9/9 was provided by V.B. Rogankov and O.G. Bytner, from the Physics Department at the Odessa State Academy of Refrigeration. This team used a combination of a fluctuation-based equation of state and molecular dynamics. The equation of state part was used to determine the formal location of the bubble points and to generate state-dependent Lennard-Jones parameters. The molecular dynamics used the state-dependent Lennard-Jones potentials to determine the pressures.

### 3.2. Entries for the molecule transferability problem

Three teams entered this section of the contest. Details of their work can be found in their papers in this special edition of Fluid Phase Equilibria. Figs. 7–9 compare their results with the experimental data (which was not revealed until after all the

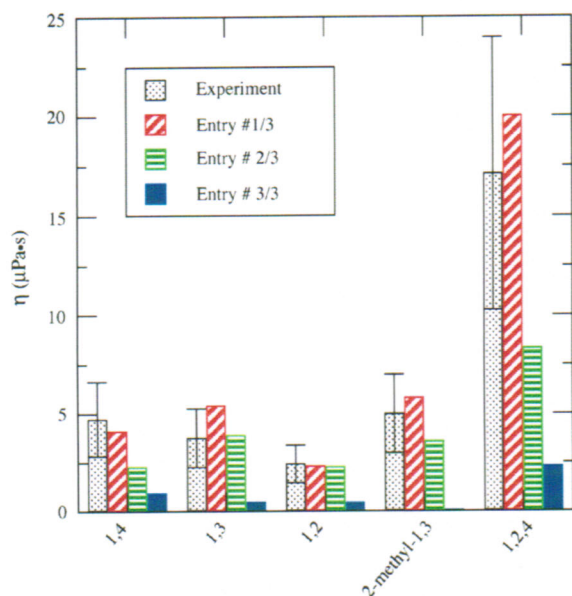


Fig. 7. Quantitative comparisons of predicted and experimental viscosities at the low pressure state point (0.1 MPa). Error bars on experimental data reflect the range for which simulation predictions were awarded partial credit.

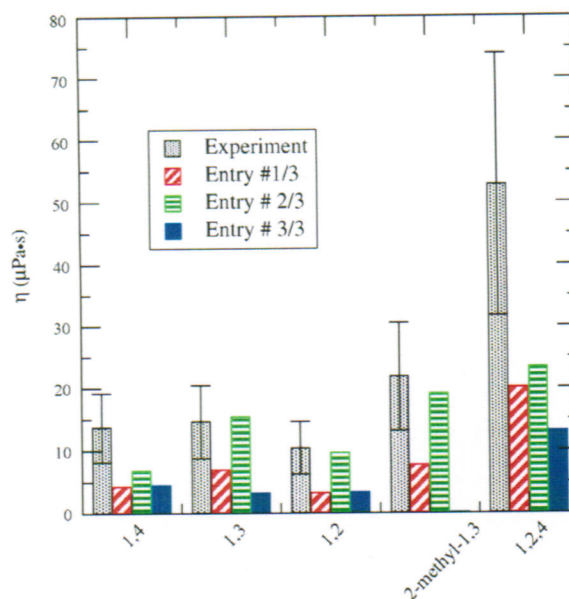


Fig. 8. Quantitative comparisons of predicted and experimental viscosities at the high pressure state point (250 MPa).

contest entries had been received). The committee was pleased to note that entrants were much more rigorous in benchmarking and validating their methods than was the case in the first IFPSC. Viscosity predictions are computationally intensive, and are becoming increasingly realistic. However, further improvements may require forcefield developers to fit their parameters to dynamic properties such as viscosity.

Entry 1/3 was provided by Jake L. Rafferty, Manish S. Kelkar, J. Ilja Siepmann and Edward Maginn. They used coupled-

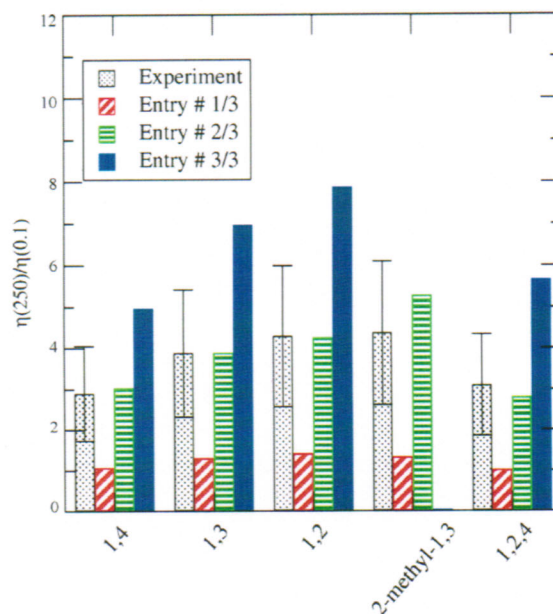


Fig. 9. Comparison of predicted and experimental pressure rise.



decoupled configurational-bias Monte Carlo (CMBC) simulations to compute the liquid densities of each fluid. Then they used NVT reverse non-equilibrium molecular dynamics (RNEMD), at the calculated densities, to predict viscosities. Their forcefield was based on TraPPE-UA with the addition of harmonic bond stretching potentials for the MD simulations (with parameters taken from the AMBER forcefield). Validation work showed that the TraPPE-UA forcefield was able to reproduce the correct order of boiling points, and critical temperatures and pressures, for polyhedral alcohols for which experimental data was available. In many cases they also obtained good quantitative agreement. Their viscosity predictions for the contest molecules were quite good at the lower pressure state point. After the contest submission deadline, it was found that incorrect densities were mistakenly employed in their high pressure viscosity state point calculations, resulting in poor predictions at 250 MPa. Corrected predictions can be found in the authors' paper.

Entry 2/3 was provided by Lifeng Zhao, Xijun Wang, Ling Wang and Huai Sun. This team also used CMBC to calculate the density of the fluids. They then used NEMD with a periodic shear flow [42] to predict viscosity. They used the OPLS-AA forcefield without modification [53]. In this method the predicted viscosity depends on the amplitude,  $\Lambda$ , of the acceleration profile, reflecting the shear rate dependence of the measured response. Smaller amplitudes reflect conditions closer to the Newtonian limit, but require longer simulation times for the same degree of convergence. The team carried out simulations with different amplitudes and linearly extrapolated to  $\Lambda=0$ . They validated their method by calculating viscosities for liquid ethanol at five different temperatures, obtaining good agreement with experimental data. Their predictions of viscosity for the contest molecules were the most accurate we received, particularly at the higher pressure point, and this team was declared the champions of this section of the third IFPSC.

Entry 3/3 was provided by David van der Spoel and Paul J. van Maaren. This group equilibrated their fluid models using NPT molecular dynamics, and then used NEMD with a periodic shear flow [42] to predict viscosity. In contrast to the previous entry, however, they chose an acceleration amplitude  $\Lambda=0.1$  nm/ps, on the assumption that the viscous response is shear rate independent below this limit. This choice was validated with calculations for glycerol, which, they noted, is a particularly challenging material with a strong temperature effect. They found that predictions for glycerol using the OPLS-AA and AMBER forcefields deviated significantly from experiment at all temperatures, and so chose to create a polarizable forcefield, transferring parameters from the ethanol model of Noskov [54]. Implementation of this forcefield for the contest molecules was challenging and highlighted the issues of force-field transferability that were at the heart of this IFPSC contest problem.

### 3.3. The "best of show" award

As in the previous IFPSC contest, an award was presented to the group that performed best over both contest problems. The motivation for this "best of show" award is the recognition that in an industrial setting modeling and theory practitioners are called on to predict a wide range of physical properties. The team lead by J. Ilja Siepmann and Edward Maginn attempted both the state conditions transferability problem (VLE prediction) and the molecule transferability problem (viscosity prediction). Their VLE entry was recognized as providing more accurate results than could be obtained using standard engineering approaches. Their viscosity prediction entry took second place in the molecule transferability problem, and their efforts in providing comprehensive documentation of their methods and validation are to be commended. Fig. 10 shows them receiv-



Fig. 10. Peter Gordon presents the "best in show" award to Edward Maginn, Manish Kelkar, and Ilja Siepmann during the special IFPSC session at the 2006 AIChE Annual Meeting.



ing the award for the best in show. The importance of “property transferability” – the ability of one modeling approach (or force-field) to handle a wide range of property predictions – will be highlighted in the fourth IFPSC challenge. Details are available at [www.fluidproperties.org](http://www.fluidproperties.org).

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