Forum 2000: Fluid Properties for New Technologies, Connecting Virtual Design with Physical Reality

James C. Rainwater,* Daniel G. Friend, Howard J. M. Hanley, Allan H. Harvey, Cynthia D. Holcomb, Arno Laesecke, Joseph W. Magee, and Chris Muzny

Physical and Chemical Properties Division, National Institute of Standards and Technology, 325 Broadway, Boulder, Colorado 80305-3328

Forum 2000 was held at the 14th Symposium for Thermophysical Properties, with all symposium attendees invited. The forum addressed the present needs and priorities for thermophysical properties measurements and the challenges facing the experimental community. Seven distinguished panelists presented brief overviews of issues related to a wide variety of subjects, and three discussion periods were held. Topics included whether simulation can replace experiment, properties needs for new miniaturization techniques, real problems such as nuclear waste cleanup, data needs for electrolyte systems and new generations of electric power plants, and data needs for unconventional materials such as molten metals and soft solids.

Introduction

The future roles and priorities of experiment and simulation, as well as theory and correlation, for thermophysical properties research were the topics of Forum 2000, held on June 29, 2000, as part of the Fourteenth Symposium on Thermophysical Properties in Boulder, Colorado. All participants in the symposium were invited to attend the forum, which was organized by the authors of the present paper. Meetings with similar agendas[1] have been held before, but the forum was unique in bringing together a panel of authorities from academic, government, and private research institutions and funding agencies.

The advance abstract for the forum read as follows: "Advances in miniaturization, decentralization, demand-controlled production, flexible feedstocks, and information technology will catalyze dramatic changes in the fluid-based industries in the 21st century. New technologies are emerging in areas such as waste minimization, advanced fuels, modular power plants, and high-value chemicals. Accelerated design, evaluation, and optimization of these processes require virtual tools based on robust information. Essential to these tools are physical property models, which must be validated with accurate data.

"All stakeholders in technology development reap the benefits from accurate measurements and improved property models. However, economic realities prevent single entities from committing substantial resources to such research. This forum will identify strategic needs for collaborative efforts between experimentalists and developers of database and process modeling tools with direct input from the end users to respond to their fluid property needs. The intent is to bring together competence from industry, academia, and government research with representatives of the funding organizations to assist in the realization of these collaborative efforts. These efforts will result in a stronger connection between virtual design tools and physical reality."

* Corresponding author. E-mail: james.rainwater@nist.gov. Fax: (303)-497-5224.

This report is one of a number of documentations of the forum. Another paper expands on themes from the forum and offers ideas on the future opportunities and challenges for fluid property research.[2] A more detailed report will be released as a NIST Special Publication,[3] and further information is available at the forum website, http://forum2000.boulder.nist.gov.

Presentations of Panelists

The forum was moderated by Howard Hanley of NIST. Each of the seven panelists presented a 10-min talk. There were discussion periods after the second and fourth talks; the last talk was followed by a summary from the moderator and a final discussion period.

Professor Peter T. Cummings with the University of Tennessee, Knoxville, and Oak Ridge National Laboratory, first pointed out how his own career, in which he had started as a theorist, was an example of the trend of the displacement of theory by simulation. Cummings noted the remarkable progress in computational power, citing Moore's law that computing speeds double every 18 months, which is about an order of magnitude every 5 years. There is "tremendous leverage out of the consumer market for computers", driven by demands for computer games and word processing. He asserted that, by comparison, experiment and theory are much more labor-intensive.

The term "molecular modeling" describes molecular dynamics where one solves equations of motion for a system of molecules, Monte Carlo methods where the thermodynamics is computed stochastically, and quantum chemistry where Schrödinger's equation is solved numerically. There are a variety of scales involved, from the lowest (electronic structure) level, through fluid thermodynamic properties, through scales appropriate to polymer modeling.

The two key aspects of molecular modeling are force fields and computational methods. Cummings noted that far more funding has gone into force fields for pharmaceutical drug design than into force fields suitable for chemical processing. Drug design applications involve a small range of temperatures, 25 to 35 °C, and low pressures. In

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contrast, chemical processing requires density ranges (for example, between liquid and vapor) of orders of magnitude, pressure ranges of several decades, and temperature ranges of hundreds of kelvins. However, the state of the art has improved to the extent that simulations are predicting data subsequently confirmed by experiment and are locating errors in databases, and some properties such as enthalpies of formation and reaction are now routinely obtained by some companies through computational chemistry. A recent multiagency study (see http://www.itri.loyola.edu/molmodel/welcome.htm) discusses current applications of molecular modeling.

Cummings concluded with a prediction that, by 2020, many properties of pure low molecular weight systems will be predictable computationally with better accuracy and higher precision than from experiment. Certain problems will remain a challenge to simulation, for example when quantum effects are important or when there are disparities in time scales. His conclusion was that “I don’t think theory is gone by any stretch of the imagination, or experiment,” but that molecular modeling has become a very powerful and important tool for thermophysical properties prediction.

Dr. Ward TeGrotenhuis, Chief Engineer, Environmental Technology Division of the Pacific Northwest National Laboratory (Richland, WA), spoke about research on miniaturized devices and the associated physical property needs. A goal is to develop chemical process equipment typically 2 orders of magnitude smaller in size than traditional equipment, without sacrificing capacity. Typical length scales are microchannel widths ranging from 1 μm to 1 mm, pumps and valves at the centimeter scale, reactors and heat exchangers of 10 cm, and an entire system ~1 m in length. As a specific example, he cited a recently developed vaporizer for an automotive fuel processor that could process 1400 standard liters of gasoline vapor per minute in a volume of only one-third of a liter. Other projects included one for NASA to develop a miniature plant to produce propellants from carbon dioxide in the Martian atmosphere and a project for the Department of Defense on a portable system for cooling a soldier in the field.

TeGrotenhuis noted that property issues have not been of much importance to date in the exploratory stages of the devices but will become more important with actual design and development. Conventional properties such as density, thermal conductivity, and electrical conductivity will be useful. Additionally, at these small length scales, wall effects can dominate, so there is a greater need for such properties as surface tension, surface energy, and wettability. The flows may involve multiphase fluids, and the dynamics will be at small time and length scales. New models and instrumentation will be required to measure properties in small channels and to characterize what is happening.

Dr. James A. Poppiti, Team Leader of In-Tank Characterization, Department of Energy, Office of River Protection, discussed an urgent practical problem, the cleanup of radioactive waste at the Hanford, WA, site. He first reviewed the history of the site, back to its contribution to the first nuclear weapon detonated at Alamogordo, NM. He also reviewed the geography of the site, which is 560 mi^2 (1450 km^2) in area and has a west and an east area separated by 5 mi (8 km), across which large amounts of contaminated fluid must be transferred.

This project calls for models, but Poppiti said that, to date, his experience with models from contractors has been “pretty bad.” In one instance, Hanford engineers needed an estimate of the cooling requirements for a tank. From the amount of water used in cooling, the estimate was 100 000 Btu/h (29 kW), but the estimate from heat generated by waste samples was 30 000 to 40 000 Btu/h (8.8 to 11.7 kW). It was necessary to assume the larger figure, but in the end the smaller figure was closer to the truth, possibly because the ventilation system may not have been accounted for properly in the model.

In another instance, they needed a state permit for the atmospheric emissions resulting from a transfer of radioactive waste from a single-shell to a double-shell tank. A model provided an initial estimate of 20 parts per million of organic carbon, and the site got a permit for 50 parts per million. However, in the first hour of the actual transfer, 500 parts per million was released. The problem was subsequently corrected, but the original model had failed to account for a radiolysis reaction that produced volatile byproducts including heptene. These examples showed that there are important real-life problems where experts in fluids and chemistry can contribute.

Dr. Andrzej Anderko, Vice President, Properties of Fluids and Materials at OLI Systems, Inc. (Morris Plains, NJ), discussed research and development involving the properties of electrolyte systems. This is an area in which the current database is inadequate, particularly at high temperature. More experimental work on thermophysical properties will be necessary, because molecular simulation cannot yet handle the complex interactions realistically. The particular technologies of interest were corrosion simulation, crystallization simulation, flow assurance software, and environmental simulation.

Anderko described corrosion as a complex process involving thermodynamic and transport properties, speciation, surface electrochemical processes, and the breakdown of passive films on metals. Speciation is the most important; the pH of the fluid is the simplest characterization, but the presence of other complexing agents must also be considered. As an example, anhydrous hydrogen fluoride is noncorrosive, but when mixed with water it becomes very corrosive. Anderko discussed other processes such as supercritical water oxidation and the production of inorganic materials, in particular piezoelectric ceramics.

There are many thermophysical property needs in these areas. Transport properties are poorly known, and diffusivity and viscosity are needed to compute mass transfer effects in corrosion. Modeling phase equilibria, densities, and enthalpies in multicomponent systems is important in designing supercritical water oxidation processes. An accurate equation of state is available for this purpose, but parameters are established for only a few systems due to lack of experimental data. For ceramics, the main limitation is lack of thermochemical data for the multiple solid phases involved. Phenomena such as adsorption, ion exchange, and surface complexation are also important.

Dr. Thomas J. O’Brien of the Department of Energy, National Energy Technology Laboratory (Morgantown, WV), discussed a DOE program for electrical power generation from fossil fuels. The program, known as Vision 21, sets the ambitious goal of increasing power plant efficiencies to 75%, compared with 60% for current state-of-the-art designs and 35% for typical coal-fired plants now in operation, while at the same time preserving the environment. Coal and natural gas will continue to be important fuels, although opportunities to use biofuels will be considered. Envisioned technologies include upstream separation of oxygen from air, gasification of the initial materials into a higher-intensity fuel, a cascade of conversion devices first with fuel cells at high temperature and pressure and then with more fuel cells at lower temperature and pressure, and a turbine to burn the reject fuel. There will be serious control problems as different stages in the cascade are integrated.

Related to the new plant technologies is a DOE project to model plants by computer. O'Brien noted that, in previous years, the U.S. government provided billions of dollars for demonstration plants but that support will not continue indefinitely, so that simulation must at least partly replace expensive demonstration plants. The fossil-fuel power industry, which has not had extensive experience in scientific computing, will use as models other efforts, such as the simulation of nuclear explosions by the DOE weapons program and the simulation of space exploration by NASA. There will also be interactions with process simulation and computer graphics companies. He ended by noting that science, previously based on analysis and experiment, is now a "three-legged stool" based on analysis, experiment, and simulation.

Dr. Paul M. Mathias, Principal Advisor with Aspen Technology (Cambridge, MA), gave a process engineering perspective on thermophysical properties research and reviewed how data are used in the simulation of industrial plants of various kinds. He described the stages of plant development, from conceptual design to operation. He commended NIST (and the National Bureau of Standards, as it was called until 1988) for standardization of thermodynamic models for simple fluids. He emphasized the importance of education and offered his opinion that companies do not understand their processes in great detail anymore and some previous core compentencies have drifted away. He felt that often when something important is missed, it is due to lack of education rather than lack of capability. On the other hand, the emergence of the Internet will allow more institutions to participate in the field of thermodynamic modeling.

Mathias spoke of "conventional" properties, where at least most of the concepts are in place, and unconventional properties. For the former, he noted that transport property research had been unduly neglected because of the greater importance of phase equilibria. He felt that molecular modeling of condensed phase properties was currently weak and questioned whether some modeling was really just a sophisticated data-fitting exercise. The role of molecular modeling, in his view, was to understand trends and build hybrid models. He also regarded as important the kinetics of solid−liquid equilibrium and, echoing Anderko, speciation in electrolyte systems. He saw an opportunity for sensors that would relate the variable that one really wanted to control in a process (such as molecular weight in a polymerization reaction) to a property that could be more easily measured on-line.

Unconventional properties, for example those of polymers, are often history-dependent, and even the conceptual frameworks are not yet established. Mathias noted that it is difficult to set up a reasonable simulation when properties are history-dependent. He concluded that much work is needed in this area, including databases for history-dependent processes.

Professor William A. Wakeham, Pro Rector (Research) of the Imperial College of Science, Technology, and Medicine (London), whose plenary lecture for the 14th Symposium on Thermophysical Properties on the history and future prospects of the profession had generated considerable discussion throughout the week, presented the viewpoint of an experimentalist and data provider. He also spoke of conventional and unconventional properties. Within the conventional, he said that the oil and gas industries, and combustion, will continue to be very important. In studying combustion, part of the problem is obtaining properties of reacting mixtures where some species are short-lived and cannot be studied in isolation. For oil and gas production, the process of thermal diffusion in near-critical hydrocarbon mixtures could be an important factor in determining the phase distribution in reservoirs. The so-called "mushy" region of metals in which solid and liquid phases coexist in a nonequilibrium state is important, but the ill-characterized nature of the state meant that much of the existing work was not useful. Other multiphase systems were also important to study, especially those involving membranes and multiple fluid phases.

Wakeham noted that the health and food industries would always be important. There are property needs for "soft solids", such as soap, food, powders and pastes, and cosmetics. He also mentioned tissue engineering, where bone can be grown now, and scientists will be able to grow lung lobes within the next 5 years and liver tissue shortly thereafter. Because the processes involved are essentially those involved in any chemical reactor, there is an opportunity for the thermophysical properties community to contribute to the description of such processes, although they have done little so far.

Wakeham showed widely varying predictions from several structure-based estimation techniques of the phase diagram of a hydrocarbon system, none of which was in close agreement with reality. He noted that the correspondence of virtual reality to physical reality can only be determined by experiment. But he asserted that we can never conduct all necessary experiments. Even if there were only 15 pure components in the world, the experimental effort required to study all possible mixtures would be astronomical. For the tens of thousands of substances actually in use, the task is clearly impossible. In conclusion, Wakeham called for a balance between simulation, theory, and experiment.

After Wakeham's talk, Hanley, as moderator, gave an impromptu summary. He commented that two important gaps existed, first between simulation and experiment, and second between property information and process demands. He mentioned nanotechnology, surfactants, and colloids as areas that perhaps should be considered within the realm of thermophysical properties to a greater extent than they currently are. He also stated the importance of multidisciplinary studies and of contact with industrial experts, mentioning an example from his own research where a phone call to the right person at a clay products company clarified questions that had concerned him for 3 years.

Discussion

The discussion periods covered a variety of topics. More details will be given in the Special Publication;[3] here we summarize the main themes. Most of the discussion can be categorized in terms of four challenges facing the thermophysical properties community. The first came from simulation and the question of whether simulations could supplant experiment for obtaining accurate property data. Second were structural issues, including funding availability. Third was the challenge to help solve "real-life" problems, and fourth was the need to move toward new materials and new properties.

Simulations. An audience member noted that advances in algorithms were a greater factor in improvement of the speed of simulations than improvements in computing speed itself, and while Moore's law predicted increases in speed of 2 orders of magnitude per decade, the improvement of algorithms made the overall simulation speed go up by 4 or 5 orders of magnitude, an observation with which Cummings agreed.

It was asked what error bars could be put on simulated property data. Cummings commented that real validation comes from experiments that are performed after the simulations and agree with them. He agreed that simulation data are ultimately useful to an engineer only if they come with error bars, that the largest uncertainties come from the force fields but are hard to quantify, and that the simulation community has not done very much in this area. Another audience member pointed out that, like experiments, simulations could be subject to systematic errors and that there were published examples where this had happened.

The measurement of properties of alternative refrigerants was brought up as an example. These fluids had been largely ignored until about 15 years ago, but when ozone depletion became a major concern, their properties were measured extensively worldwide. The question was posed whether, in a similar situation, the simulation community today would say experiments were unnecessary and all data could be simulated. Cummings replied that simulated properties are useful in the early design stages of a plant, but at the final design and production stages, almost everyone agrees that real experimental data are necessary.

Structural Issues. Discussion of structural issues echoed the remark of Mathias that lack of education and expertise was more often an impediment than lack of capability. The near disappearance of corporate engineering groups was lamented. Pressures to cut costs and the availability of software and specialized services from vendors have largely changed the role of engineers in industry from specialists to generalists. Engineering specialists, often with Ph.D.s, provided essential expertise to their companies and a link to academic and government researchers. Process simulation software has replaced them in part, but key decisions are now made by people with limited thermodynamics education. Companies rely on consultants but may not be able to judge their competence properly. Product design knowledge, the ability of a person in industry to know what data are needed for a given product, is something of a lost art, and it is even unclear if it is being taught anymore.

Wakeham's comment about the huge data needs for only 15 pure components prompted some discussion. O'Brien noted that it would also be a huge job to do all the needed simulations for the mixtures. It was noted that theory had been rather underemphasized in the discussion, and estimating properties of all the mixtures called for some good mixture theorists, but that funding agencies are not doing a particularly good job of encouraging theory.

Although not envisioned as a primary concern of the forum, issues of research funding inevitably arose. The way in which "turf battles" inhibit cross-agency funding was mentioned, as was the way agencies such as DOE were stretched thin between basic and applied research and user facilities, with political pressures as an added complication. Frustrations were expressed that funding agencies sometimes fail to inform researchers of what they really want, saying they want to support science but instead focusing on short-term fixes. It was mentioned that the problems in areas such as environmental cleanup were so complex that even identifying the basic science needs was difficult. Poppiti seconded this on the basis of his experience with a problem universally regarded as urgent, where he had extensive funding at his disposal but had difficulty finding how and where to spend it to get the needed answers.

Real-Life Problems. The challenges provided by formidable "real-life" problems were addressed. Poppiti commented that his stories of modeling failures were just two that he picked out, and he could tell many more. Modeling deficiencies have already had a significant negative impact, including the temporary shutdown of a major activity.

Hanley said that "academic people", loosely defined, who wanted to contribute should visit sites and see firsthand large tanks rotting away and other evidence of the problems. He also commented that these problems are gigantic and complex and might make a good subject for a proposal, but people in the room hardly know what questions to ask and are not informed of what data are needed. On such problems, it was suggested that there is probably some basic research that would help, but somebody has to provide a bridge between the basic science and engineering needs, and it was unclear who would be in a position to do that.

New Materials and Technologies. The talks by TeGrotenhuis and Wakeham brought up challenges and opportunities in new areas such as microtechnology and soft solids. It was clarified that usual bulk properties are still useful in microtechnology, the construction of devices about 2 orders of magnitude less in size than conventional devices, as opposed to nanotechnology that involves much smaller size scales at the molecular level. Hanley asked TeGrotenhuis if his miniaturized devices used ordinary bulk property information or if new information was needed, while pointing out that at some scale use of bulk properties would break down. TeGrotenhuis replied that, so far, traditional properties from standard chemical reference sources worked, but at some point with further miniaturization there would be nonidealities associated with scale.

TeGrotenhuis was asked what fluid−surface interaction studies would be useful to him and what specific surface material was of interest. He replied that his group mostly worked with metals, because of high-temperature application, but that others in the microtechnology world used glass, silicon, or plastic. Wakeham reiterated his recommendation for studies of thermal properties of tissues, and there was some discussion as to whether this area was appropriate for traditional thermophysical properties laboratories.

Conclusions

Overall, the forum raised many questions, but there was some consensus. While there were differences of opinion on the capabilities of simulation, it was clear that it has not rendered experiment obsolete and that experiments will need to be continued for, among other reasons, the validation of simulation predictions. Still, simulation is now an important player in the determination of thermophysical properties and will become more so with improvements in computer speed and algorithms. Clearly there are opportunities in new materials and properties, microtechnology, soft solids, and elsewhere. The profession can contribute to complex problems such as nuclear waste cleanup, but important liaisons between properties experts and those tasked with solving practical problems, such as corporate engineering groups, have been disappearing.

NIST hopes to continue its leadership in fostering dialogue on the future of thermophysical properties research and is considering organizing more such events.

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