Thermophysical Property Measurements: the Journey from Accuracy to Fitness for Purpose

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Until the early 1960's much of the experimental work on the thermophysical properties of fluids was devoted to the development of methods for the measurement of the properties of relatively simple fluids under relatively benign conditions of temperature and pressure. By the end of that period a number of methods had emerged that brought together a rigorous mathematical description of the experimental method with modern technical innovation to render measurements accurate enough to provide a rigorous test for theories of fluids in both gas and liquid phases. These studies demonstrated that, for the gas phase at least, the theories were exceedingly reliable and soundly based and led to some real physical insight about simple molecular interactions.

The basic thesis of this presentation is that since those successes there has been a divergence of experimental effort in the field and that future effort need to focus very much more on in-situ measurement of properties in process fluids. The argument is based upon the changes in the balance between the accuracy of a result and its utility and economic value and upon technical developments which have rendered cheap, reliable and small sensors of properties readily available and robust.

Some work has sought to repeat the success of the early work through the study of slightly more complicated molecules over the same sort of conditions together with an extension to extended ranges of thermodynamic states with the same philosophy and accuracy. It has led to the seemingly, never-ending repetition of measurements of the properties of some systems with very small improvements in accuracy achieved by careful experimental design. The properties of a relatively small number of fluids have been determined in this way over a wide range of conditions with a significantly smaller state range being covered for the bulk of fluids. The exact statistical mechanical theories of fluids have proved much less tractable for the majority of molecular systems so that much less detailed information on molecular interactions has been gleaned. However, the same experimental data have permitted semi-empirical applications of the statistical-mechanical theories have provided ways of using the results over a wide range of states for a limited number of systems to predict (albeit less accurately) the properties of more fluids and their mixtures. This approach is now mature and it is doubtful whether much can be gained by further refinement of the methods or the systems to which they are applied.

A second sort of study has been confined to particular situations where precision and accuracy are paramount. Such studies include the near critical region for fluids, where there are very particular questions about the physics to be answered that have required considerable care and accuracy in measurement over a relatively narrow range of thermodynamic states, and the provision of standard reference data for calibration. There evidently remains much to be done in this area guided by theory because there remain a number of unanswered questions.

A third type of study that is of increasing importance and frequency includes the measurements of the properties of the real and particular fluids in use in industry either in situ (within the plant, process or natural environment) or in the laboratory. Such measurements are seldom performed with high accuracy and it is seldom needed because the value of the measurement to the process lies in the fact that a number is known at all within a prescribed uncertainty and not in the intrinsic accuracy of the result. It also follows that the motivation is not, usually, to enable the testing of theories or the development of semi-empirical predictions but, rather, so that the result of the measurement can be used in the evaluation or improvement of the process studied. The challenge in this type of work is therefore to design instrumentation that can be applied in environments that are often aggressive, at the extremes of temperature and pressure. The call is therefore often for novel and small instrumentation with modest but known accuracy. The operating principles of this instrumentation are often quite different from those that characterized the previous generation of experiments.

It is argued that the trend towards this kind of study is increasing in intensity and that it offers thermophysicists the opportunity to secure new ground for their field in territory previously not available to the discipline.