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The dangerous nexus of process simulation, molecular modelling and physical reality

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The paper explores the dangers for careful process design using new materials and processes that may arise because of the state of understanding of the properties of those materials. Evolution of the sciences of molecular modelling and of thermophysical property theory is explored and it is clear that both have a considerable amount to contribute to careful process design in the future. However, it is equally argued that the evolution of the experimental database upon which the design of conventional processes has been based may not be evolving in such a favourable direction. By means of examples it is shown that what was the basis for the past success of thermophysical property provision, is being undermined by modern scientific behaviour and that there is ample evidence that when new materials are encountered the system that has been in place to validate data is simply lacking its full force.

The consequences of this lack of rigour in property provision for the databases on novel, perhaps especially biological processes, needs careful consideration.

Key words: Process simulation, thermophysical properties, transport properties, experimental technique, process design software

INTRODUCTION

In the search for a more sustainable future for the world the chemicals and materials industries have sought to make their processes more efficient in terms of energy use, to reduce waste products and to use greener process routes to create products that are capable of re-use or recycling. In addition, there is a demand to move to feedstocks that are themselves renewable unlike traditional fossil feedstocks. The tools of the modern era of process-simulation have made it possible to conduct automated, intelligent searches of alternate process routes to products using these feedstocks [1]. At the same time the world of science has, in many areas, particularly in thermophysical property research moved away from the value attached to careful experimentation in favour of molecular modelling and cavalier experiments with excitement value! Such work is simpler, quicker and cheaper than careful experiments and leads to faster career enhancement!

At the same time, there is ample evidence that when inadequate comprehension of physical reality is combined with over enthusiastic simplification of either experimental design and implementation or automated design processes, gross errors of process design can occur even for conventional processes and materials. When the materials and/or processes are new or untried the likelihood of gross errors is exacerbated.

The development of the tools employed by the industry to design and optimise processes has been carried through by a combination of scientists and engineers with a relatively well-defined set of starting points and objective functions. A vast array of experience has been accumulated based upon processes of a conventional kind. As the simplest possible example Fig. 1 shows many of the elements of a conventional process that involve the familiar unit operations of mixing, heating, reaction, cooling and separation. Even if one does not consider alternative process routes to the same product the design of such a simple process requires a knowledge of the thermodynamic and transport properties of all the materials involved, the kinetics of the reactions and of the relationship of the design variables to those properties.

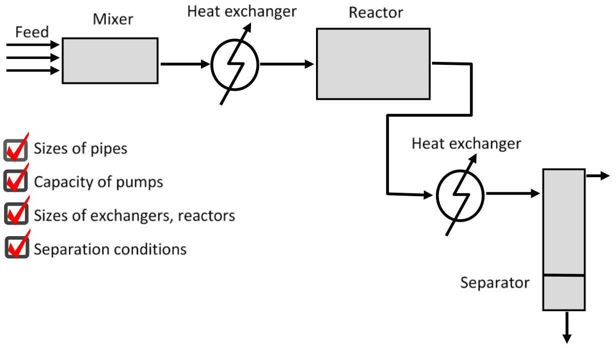

Fig. 1. Exemplar chemical process.

Let us take just one unit, a heat exchanger, illustrated in Fig. 2. Its design requires a specification of the needed duty, a selection of the type and then a deduction of the area of the exchanger based upon long-established empirical correlations of heat transfer for conventional

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materials and the thermophysical properties of the fluids involved. Both elements are now incorporated into design software that is available commercially and which has been thoroughly tested and validated. That this process of testing and validation is important is illustrated by the indication in the figure that costs accompany an over (or under) design of the exchanger. The costs can be expressed in financial terms for convenience but they can also be expressed in terms of environmental damage or waste [2]. The likely costs for an entire process are of course additive and depend upon the number of units.

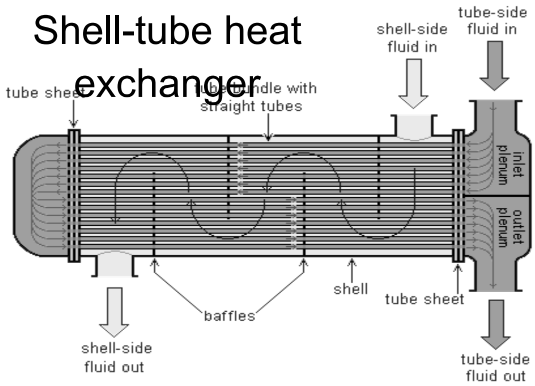

Fig. 2. Heat exchanger.

If some efficiency is attempted, as illustrated in the methanol synthesis reactor sketched in Fig. 3, then the problem potentially becomes more acute because here the heat exchanger is combined into the reactor so that any overdesign in the exchanger has consequences for the design and construction of the reactor as well [2].

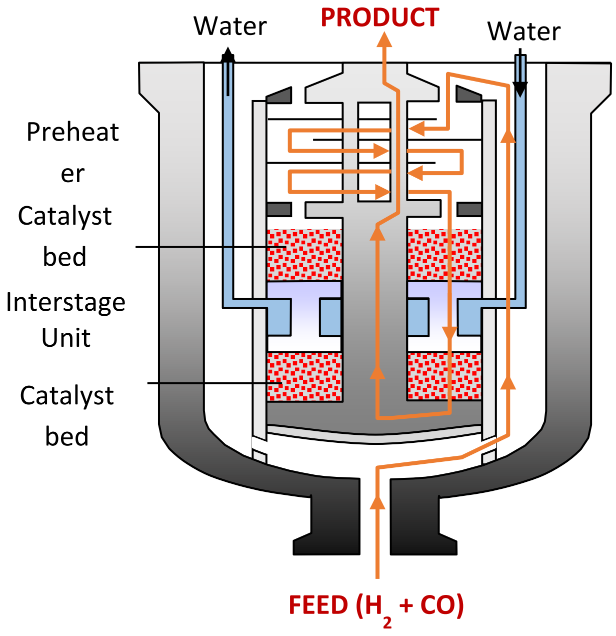

Fig. 3. Integrated methanol synthesis reactor.

In any realistic situation and perhaps especially if attempts are made to explore novel methodologies then there are many possible process routes to explore and need for confidence in the tools of design become ever more important. As an example, we consider Fig. 4 which depicts a solar capture system developed in Nevada, USA to generate electricity. USA DoE recently invested $737 million into the Crescent Dunes Solar Energy Project in Nevada, which will generate energy well into the night by using molten salt as an energy storage medium. To do this the plant will focus nearly 20,000 heliostats upon a solar power tower filled with salt, heating the material to 840 K.

The use of a molten inorganic salt as the heat transfer and storage medium means that its thermophysical properties are important. As we shall see later the data on the properties of such molten salts are by no means well known and agreed even for the most familiar of them. It is the thesis of this paper that the tools of testing and validation that have been applied to date for these designs are now either under threat or falling into disuse and that this trend is dangerous. In order to make the argument we review the various parts of the validation process in turn and then point out why it may be less robust for new processes that employ different feedstocks and aim at different products.

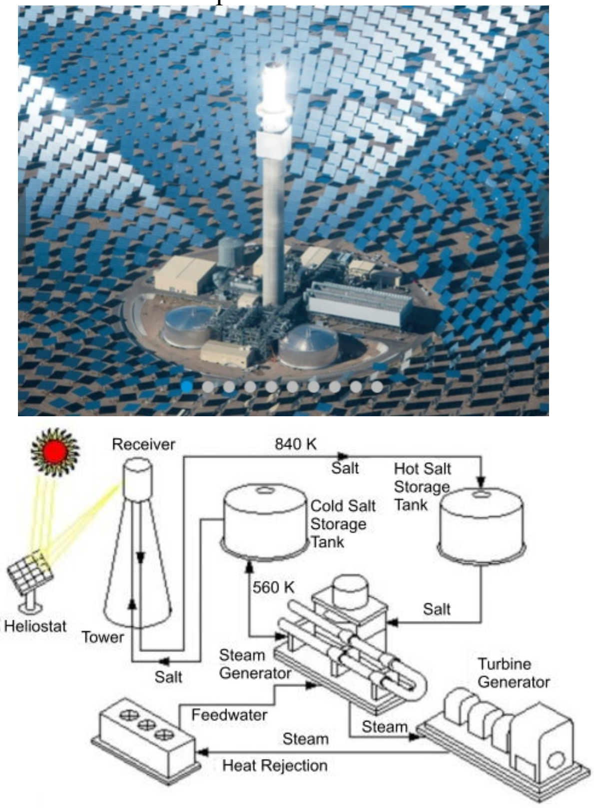

Fig. 4. Crescent Dunes Solar Energy Project in Nevada.

VALIDATION PROCESSES

There are various elements of the validation process with which we are concerned here which is the provision of reliable thermophysical property data for the fluid systems under study. A similar argument might be advanced about the familiar correlations of the process industries, but we have sought to confine our consideration to the area we know best. They are:

- Molecular Theory.
- Molecular modelling
- Experimental measurements
- Internationally accepted data and correlations

Molecular Theory

The only state of matter for which we have a rigorous, tractable analytic theory is the dilute gas. In that case we now have knowledge of the intermolecular pair potential for all the monatomic species and that allows the evaluation of all of their properties from a rigorous theory [3]. In the last few years it has become possible to extend this approach to polyatomic systems of very modest complexity such as carbon dioxide and water vapour but no further [4]. These developments have reached the point now, after about 100 years work, where the calculations are more reliable than experiment [4, 5], but it is important to recognise that was achieved in part by the existence of very careful experimental property measurements in the first place. Certainly, the dominant species of interest in the process industries and the states of matter of interest cannot be treated in this way.

Table 1 [47] contains experimental results, using the best possible experimental methods for both the viscosity and the thermal conductivity of the five monatomic gases at a temperature of 308.15 K and in the limit of zero density.

The measurements are independent of each other and absolute. The results are used to evaluate the Eucken Factor, *Eu,* defined by [3] as

$$Eu = \frac{2M\lambda_0}{3\eta_0 RF(T)} = 2.5\ (exactly) \qquad (1)$$

where the factor *F(T),* is an almost, model-independent factor from theory very close to unity and *R* is the Universal Gas constant.

Cencek *et al.* [6] developed the most accurate pair potential energy surface to date for Helium and used it to calculate properties of Helium. They recommended

λ_{He} (298.15 K, 0.1 MPa) = (155.000 8 ± 0.001 5) mW m^{-1} K^{-1}

Experimentally we find

λ_{exp}(298.15 K, 0.1 MPa) = (154.96 ± 0.30) mW m^{-1} K^{-1}

These results and many other like them summarised in Refs [4, 7] demonstrate the mutual agreement of theory with the best experiments and, of course, provide mutual support for both. This is indeed very important when the same experimental methods are applied to other systems because the methods themselves can be said to be validated.

That the same can now be done for small polyatomic systems is shown in Fig. 5 [5] where the deviations of the experimental results for the viscosity and thermal conductivity of methane are compared with theoretical calculations using a modern intermolecular potential for methane. The agreement is really excellent.

Molecular modelling

In most cases of course this exact theoretical route is not available, either because the theory is not tractable (dense fluids) or because we lack intermolecular pair potentials for more complex systems. The approach of molecular modelling has been adopted to obviate these difficulties in one of two main ways.

The first, which was the only practical way forward until recently, was the adoption of simple molecular models of fluids that were tractable to approximate, or, occasionally, exact theory. Examples of this approach are various forms of corresponding states approaches to the prediction of the properties of fluids. The properties involved can be equilibrium or non-equilibrium and the systems involved can be single component fluids or mixtures.

The basic idea is founded upon the conformality of the pair potential for the interaction of molecules in the system so that all interactions in the reduced form

$$U/\varepsilon = f(r/\sigma) \qquad (2)$$

are identical. Here ε is an energy scaling parameter and σ a length scaling parameter.

Table 1. The Experimental values of the Eucken factors for the monatomic gases For reference see above [47]

Gas	η_o (μPa s)	λ_o (mW m- K^{-1})	$F(T)$	Eu (Experimental)
He	20.31 ± 0.02	158.4 ± 0.30	1.0042	2.494 ± 0.01
Ne	32.47 ± 0.03	50.41 ± 0.10	1.0035	2.503 ± 0.01
Ar	23.24 ± 0.02	18.18 ± 0.03	1.0012	2.503 ± 0.01
Kr	26.15 ± 0.03	9.722 ± 0.02	1.0006	2.497 ± 0.01
Xe	23.84 ± 0.02	5.656 ± 0.01	1.0001	2.497 ± 0.01

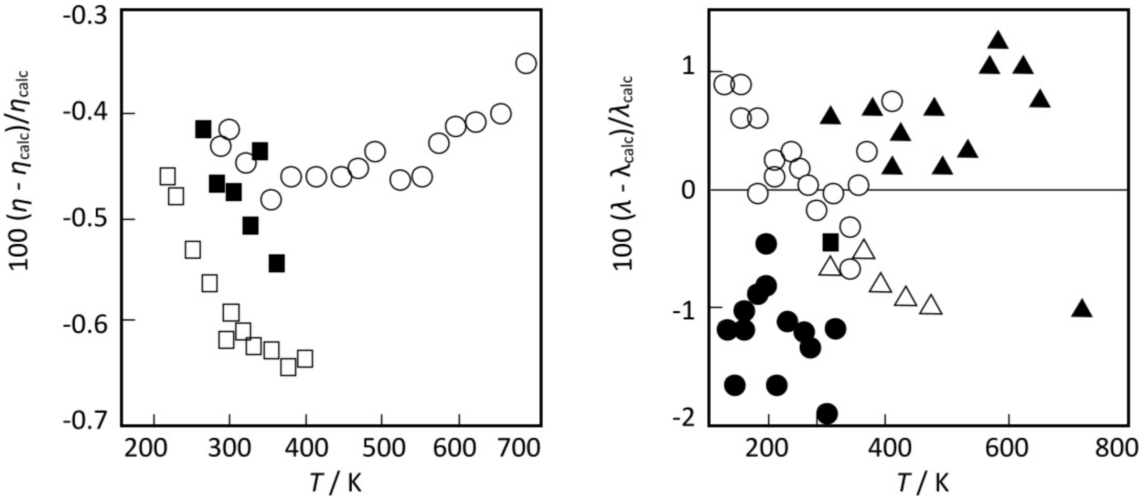

Fig. 5. Deviations of the experimental results for the viscosity and thermal conductivity of methane from theoretical calculations using a modern intermolecular potential for methane **[5]**

In the case of non-equilibrium properties it was possible to apply this idea to the representation of large numbers of pure and multicomponent mixtures of a wide range of spherical and indeed non-spherical molecules at low densities with a high degree of confidence supported by a large set of very accurate experimental data on viscosity, thermal conductivity and diffusion coefficients [8]. U/εAs just one example of hundreds Fig. 6 contains deviations of the measured viscosity of a number of multicomponent polyatomic gases from the predicted values.

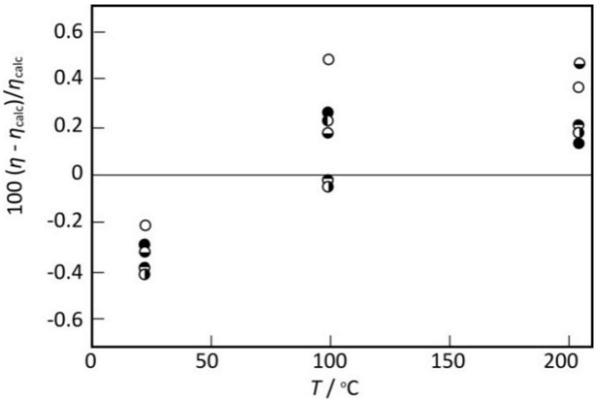

Fig. 6. Comparison between calculated and measured viscosity: ○ CH_4-CO_2-CF_4; ◐ CO_2-CF_4-SF_6; ◑ CH_4-CF_4-SF_6; ◒ CH_4-CO_2-SF_6; ● CH_4-CO_2-CF_4-SF_6 [9]

This approach gave a prediction capability for one property based upon measurements of another and over a wider range of temperature than the measurements could be performed.

Of course, the need is often for properties at elevated pressures or densities and, in this case, the dilute gas analysis was supplemented by a different molecular model for hard-spheres where the approximate Enskog theory of dense fluids [10, 11] could be applied to describe the density dependence. This allowed the development by Vesovic and Wakeham [11, 12] of methods for predicting the properties of dense gas mixtures using only the properties of the pure gases and some results from rigid sphere theory. Again, these methods have been validated for predictions using a wide range of accurate experimental data on well characterised fluid systems [12]. That gives confidence in the application of the procedures for the prediction of data on systems where there have been no measurements. As an example of what can be achieved using this VW method and experimental data for pure fluids only, Fig. 7 shows the deviations between the predictions of the revised VW scheme [11] and the measurements of Schley *et al.* [13] for natural gas containing only traces of higher hydrocarbons. The scheme performance deteriorates somewhat if the same model is used for heavier long chain hydrocarbons although recent improvements have been made [12].

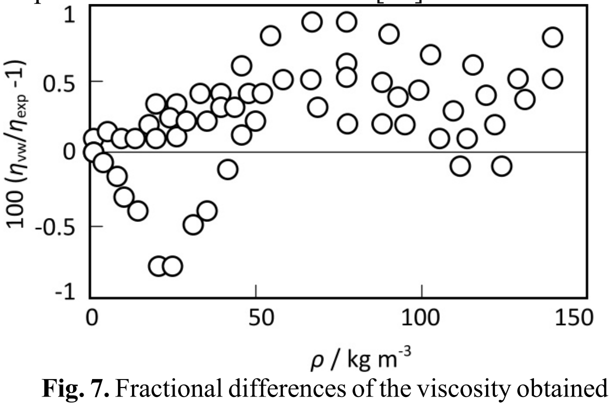

Fig. 7. Fractional differences of the viscosity obtained using VW-sphere, η_{vw}, from the experimental data for natural gas of Schley et al. [13], η_{exp}, as a function of the density ρ.

Dymond and Assael [14] have made use of a slightly different form of the Enskog theory to develop a methodology for representing and predicting the transport properties of dense liquid systems, particularly hydrocarbons. There have been several extensions of the Dymond and Assael scheme to higher densities [14].

There are, of course, equivalent approaches for equilibrium properties including phase equilibrium for well characterised systems simple molecular models, such as that which leads to the Van der Waals equation and its derivatives, and have achieved considerable success. Perturbation theories have also enjoyed considerable success

One of the most successful modern schemes for predictions and representations for more complex fluids is based upon the SAFT equation of state which, again, exploits simple molecular models for those systems. This has recently found application in transport properties as well as equilibrium properties [15]

There are numerous other examples of prediction methods for properties based upon different molecular models and the state of the art is summarised in Refs [11, 14-16].

A second strand of molecular modelling is more recent and exploits modern computing power. Using moderately realistic potential models for two or more body interactions it is now possible, via molecular dynamics simulations or Monte-Carlo-equilibrium simulations to calculate the transport properties or equilibrium properties of a modest ensemble of molecules that can be argued to be representative of the real fluid. This approach has developed rapidly, and quite complicated systems can now be studied. In that context water in the condensed state is a particularly interesting material because of its complex structure driven by hydrogen bonding. Although early calculations using proposed potential models were only able to predict the transport properties of water qualitatively, the most recent attempts, exemplified by the use of a potential from 2005 [17, 18] achieve quantitative agreement. The results are somewhat better for other hydrogen-bonding liquids such as alcohols where deviations of about 20% are found. Fig. 8 contains a comparison of the results of simulation for water with experiment. The attempts to perform such calculations have progressed much more rapidly than the experiments of high accuracy on such systems. They are now beginning to be simulations of complex systems such as might be involved in new green and biological processes.

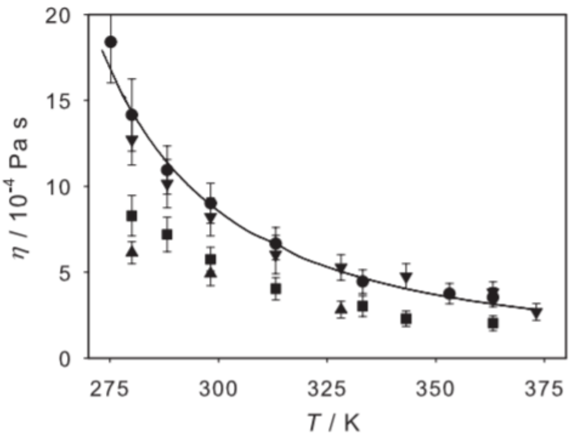

Fig. 8. Temperature dependence of the predicted shear viscosity of pure liquid water at 0.1 MPa.

Experimental Measurements

We wish to concentrate here on transport properties which are our own main interest but we must say few words about equilibrium properties. The measurements of the equilibrium properties of fluid systems have been carried out for several hundred years, in the case of the density for example, because it was possible to conduct measurements of this kind with very simple equipment. For example, even the simplest form of specific gravity bottle enabled liquid densities to be measured. The phase behaviour of simple two component often two-phase systems could also be measured by visual observation and this formed the initial sort of data used for testing and validation of equations of state. Slowly the measurement techniques became ever more precise and with that followed the refinement of equations of state capable of representing all the equilibrium properties of pure fluids. An example is the IUPAC Equation of State for Ethylene [19]. The equations were often able to reveal inconsistencies in experimental data for different properties by virtue of the precision of some data and were thus able to highlight experiments that were in error. There are now commercial companies manufacturing devices for very high precision measurements of equilibrium properties of fluids such as the vibrating-tube densimeter for liquids [20, 21], the Rubotherm magnetic balance devices for gas and gas mixture density [21, 22] and the differential scanning calorimeter for heat capacities [21, 23]. It remains true that the quality of the results obtained with these devices depends upon the users and their understanding of the method. However, that has not prevented hundreds of papers being published in the scientific literature every year reporting, for example, excess volumes of binary and ternary mixtures of liquids over a very limited temperature range around ambient. The papers usually make entirely hand-waving deductions about the intermolecular forces and the sign of the excess volume. The next paper from the same laboratory then does the same thing for another pair of liquids from bottles on the laboratory shelf. This habit has earned the name of such work 'stamp-collecting' because it has neither scientific utility nor engineering value since the systems studied are usually simple ones rather than useful ones!

It is interesting that not until the 1970's did precise and accurate means of measuring the transport properties of fluids became available [24, 25]. The probable reason was that all such properties involve a dynamic process in a non-equilibrium state and in most cases it is very difficult in a fluid to isolate one dynamic process free from all others so that a mathematical model of the experimental process can be developed for analysis of an experiment. The most obvious example is the fact that, on earth, natural convection and radiation accompany the process of thermal conduction in any fluid within a temperature gradient where that gradient is not everywhere aligned with and opposite to the gravitation acceleration. Another important reason was that for many years the measurements had been the preserve of chemists and they tended to work in glass with little regard for mathematical analysis of the often complicated, processes involved in the measurement. Improved comprehension of all these features and the involvement of engineers and physicists in the field have changed the approach of careful experimenters markedly. However, this has not been a universal phenomenon.

The essential features of a good measurement of a physical property, whether equilibrium or not are:

1. A recognition that a thermophysical property, such as thermal conductivity, is only really defined for a single-phase material in the bulk.
    - materials may be anisotropic but must be otherwise homogeneous.
    - only using this definition is it possible to assert, without ambiguity, that the property is a function of the thermodynamic state variables (P,V,T,x) alone.
2. It is perfectly legitimate in engineering terms to discuss the properties of multiphase materials and inhomogeneous materials as 'effective' or 'apparent' properties.
    - but the results obtained for the effective property could depend upon the method of measurement or the size of the sample employed.
    - the size of the sample may also be an issue when surface effects can dominate bulk effects such as in very thin films.
3. The measurement should involve a minimal disturbance of an equilibrium state.
    - therefore, we use small departures from equilibrium, so that the accompanying equilibrium state can easily be defined.
    - high sensitivity of measured variables to quantity being measured is essential.
4. A theoretical working equation or a numerical solution of sufficient accuracy for the governing differential equations that describe the experiment.
5. A practical realisation of the experiment that has small departures from the theoretical model is essential.
6. Each of the departures from the ideal model can be analysed to introduce small corrections to the working equation that can be quantitatively evaluated through theory and applied to the results.
7. It should be possible to demonstrate that the theory of the experiment exactly describes what is observed.
8. If possible conduct absolute measurements in which all parameters of the instrument are determined independently and by means traceable to fundamental units or constants.
9. If an absolute measurement is not possible, calibration to determine one parameter of the instrument with the aid of a standard reference material is possible.
    - The parameter determined should agree with direct evaluations of the same quantity from theory within its estimated uncertainty.

It has proven possible to satisfy all these conditions in some laboratories with respect to the properties of fluids. We would single out the laboratories of

- Joseph Kestin in Brown University, USA, for viscosity and thermal conductivity over a wide range of conditions,
- Mike Moldover and his colleagues in NIST, Gaithersburg over many years beginning in the 1930's,
- Akira Nagashima in Keiuo University, Japan,
- Marc Assael, from Aristotle University in Thessaloniki,
- Peter Dunlop in University of Adeleid Australia,
- Eckhard Vogel in Rostock University and Alfred Leipertz in Erlangen University and their colleagues in Germany, and
- Harald Oye in Norwegian University of Technology in Norway.

However, it has never been the norm to perform such careful experiments and we now see the dangerous signs of a complete disintegration of the protocols that stem from the principles set out above. We shall provide some illustrations of the good and then rather more examples of the bad extending over almost a century and it will become clear that the situation is deteriorating for reasons upon which we shall speculate.

Some Good Practice

We choose three examples only which illustrate good practice.

The first is the capillary viscometry carried out in NIST where, over some 25 years, across World War II an instrument was developed to make absolute measurements of the viscosity of liquid water at 20 ◦C [26]. The resulting value of the viscosity of water is still the standard value adopted universally today. More recently NIST have used capillary viscosity in gases in conjunction with the best possible pair potentials for the interactions among monatomic gases to make exceedingly precise measurements [7].

Those values have supplemented those made with our second example, the oscillating disk viscometer employed in USA, Japan and Germany to provide standard reference values for the viscosity of gases. The concept of the torsional pendulum comprising a flat disk suspended in the fluid originates with Maxwell but Kestin and his colleagues [27] employed careful fluid mechanical analysis of the complex flow pattern around such a disk to design and then build instruments where it was possible to make absolute measurements of viscosity over wide ranges of conditions These devices also took several decades of work to achieve their result with the work of Vogel in Germany the most recent [28] We have referred to the validation of these results earlier.

The third is the transient hot-wire technique for the measurement of the thermal conductivity of fluids. It is in essence a very simple technique in which a very thin metallic wire is heated by ohmic dissipation when immersed in the fluid. It is possible to analyse this technique almost exactly mathematically, initially analytically and now numerically so that there exists an exact theory of the method. In its current form it was pioneered by Haarman [29, 30] and made possible by modern electronics because the entire heating process can be limited to a duration of one second during which time convection has a negligible effect on the heat transfer. It is also possible to confirm that the method operates in accord with the theory of it, as Fig. 9 illustrates. Here we compare the predicted behaviour of the temperature of the heated wire with the observations in one fluid.

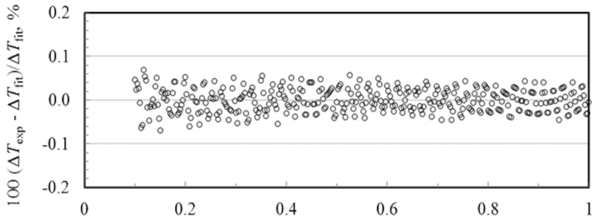

Fig. 9. Differences between the experimental temperature rise of the hot wire in water from the theoretical values, as a function of time.

The deviations are random and exceedingly small. These instruments employed in the laboratories of the authors [31, 32], Nieto de Castro *et al.* [33] and Perkins *et al.* [34] are responsible for most of the accurate thermal conductivity data for fluids.

Some Bad Practice

We provide here rather more examples of bad practice in measurement than of good because, that is the balance in the field at present and because we wish to make the point that modern measurements are not to be trusted unless the full pedigree of the method is exposed and tested by researchers. In part, this is because of the growth of the popularity of commercial instruments for measurement and the fact that modern research (or possibly researchers) cannot spend decades to perfect a technique. Readers should note that these comments apply to thermodynamic and transport property measurements and not, for example, to measurements of time or length or voltage where commercial instruments have long been validated against agreed and accurate standards.

We begin with what is called variously the Transient Hot-Wire probe or the Transient Needle Probe. It is illustrated schematically in Fig. 10, and it consists of a wire and a resistance thermometer embedded within a solid powder itself held within a stainless steel sheath. The entire probe is immersed in the fluid of interest and the wire heated electrically while ‘its’ temperature rise is measured with the thermometer. The word ‘its’ is in quotation marks because it is not clear that the thermometer is measuring anything but its own temperature.

The theory applied to this device to deduce the thermal conductivity of the fluid is exactly that which we illustrated above for a very thin wire immersed directly in the fluid despite the obvious differences. The manufacturers themselves, who designed the device for on-site measurements of the thermal conductivity of rocks and concrete in a civil engineering context, seem to be aware of this problem as exemplified by their literature. Researchers looking for rapid results and instant fame are not it seems!

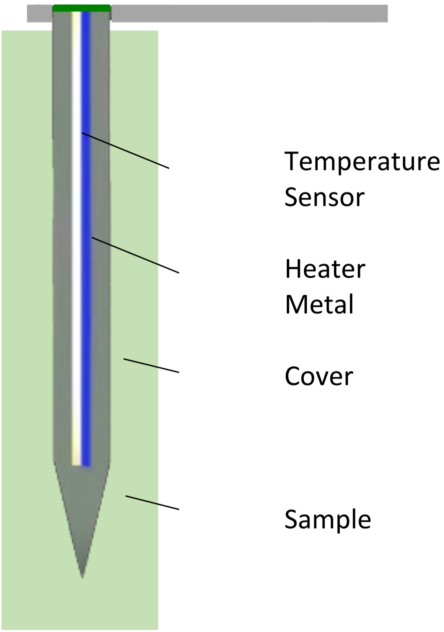

Fig. 10. Transient Hot-Wire probe.

A second device which has proved very popular is the transient hot disk, developed originally for solids. Its sensor is illustrated in Fig. 11 and its working principle is that an electrical current flows in the spiral that comprises the disk and heats the spiral, at a rate determined in part by the thermal diffusivity of the surrounding fluid. Unfortunately commercial versions of this device do not make use of the full theory of the instrument, which is mostly available, but they simplify it. In addition, the timescale of measurements in fluids are such that convective heat transfer is inevitable although its presence is universally ignored and no tests for its presence are applied.

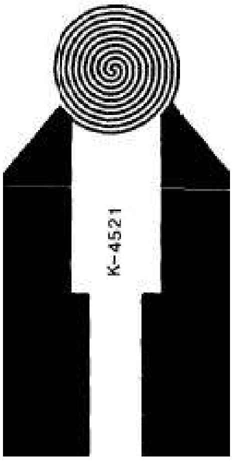

Fig. 11. Transient hot disc.

Thirdly, a technique known as the 3-omega technique was developed for solids where it is very successful for certain classes of material and is extremely elegant. It is illustrated in Fig. 12. A wire in contact with the test material is heated with an alternating current at a frequency ω. As a result there is, of course, a voltage change across the wire which oscillates at a frequency 3ω. The rate of evolution of that harmonic voltage change, which can be monitored by modern lock-in amplifiers can be related to the thermal diffusivity of the material. This technique, which is operated in essentially a continuous mode, has also been applied to fluids. It seems not to have occurred to its users that as well as the component of the voltage oscillating at 3ω there are other components, in particular a unidirectional temperature increase which, of course, drives convection for which no account is taken.

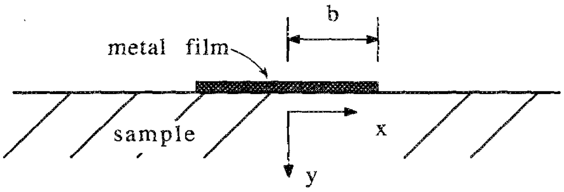

Fig. 12. The 3-ω technique.

The fourth example is from capillary viscometry, which is, perhaps, the oldest technique for measuring a transport property. The Montreal Protocol on the phasing out of certain refrigerants in favour of those less damaging to the Ozone layer in 1987 stimulated an intense fashion in conducting measurements of the properties of the proposed replacements. This fashion led to an enormous increase in the number of people interested in property measurement. Indeed, the measurement of the properties was sorely needed. However, among those attracted to the study were many with no previous experience of the field. They rushed in where angels had feared to tread and set out with simplistic equipment and theories of it to be the first to conduct measurements on the new systems. One such technique adopted was the sealed capillary viscometer illustrated schematically in Fig. 13 which was applied to the measurement of the viscosity of 1,1,1,2-tetrafluoromethane (R134A) very early on in the study of the fluid.

An example from diffusion of bad practice is the development of the Taylor dispersion technique for diffusivity measurements in liquids [36]. In this technique a small pulse of one fluid is injected into a stream of a second fluid flowing in a long circular section tube. The combined action of the laminar velocity profile in the tube and radial diffusion lead to an eluted pulse of the second material downstream from the point of injection whose width is a measure of the mutual diffusion coefficient of the two species. In order to make the measurement possible it is necessary to use a capillary tube a few mm in diameter and some 30 meters long. To make the system practical it is coiled so as to be able to immerse it in a thermostatic enclosure. Unfortunately, early proponents of this system did not realise that when the capillary tube is coiled a new velocity component is generated in the flow in the tube which affects mixing. The effect is large unless the Reynolds number is small and the coil radius large so the neglect led to large errors in early work before the full theory was evaluated.

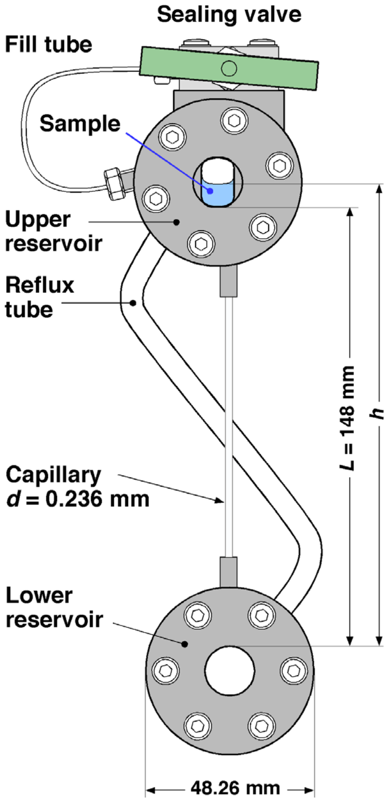

Fig. 13. Sealed gravitational capillary viscometer with straight vertical capillary developed at NIST [35].

Finally, returning to thermal conductivity many authors have been attracted by the idea of using a very much shorter hot-wire system, illustrated in Fig. 14, with the same theory as we set out earlier essentially for an infinitely long wire.

They seemed to forget that in such a case the longitudinal heat conduction to the supports of the wire can dominate radial conduction through the medium under test so that nowhere does the wire attain the temperature of an infinite wire so that the entire measurement is invalid. This has not prevented its use and papers being published! More recently a few authors [37, 38] have implemented computer solutions of the full heat conduction problem including the axial conduction in solids although it remains unclear what particular advantages this device holds over the more conventional system.

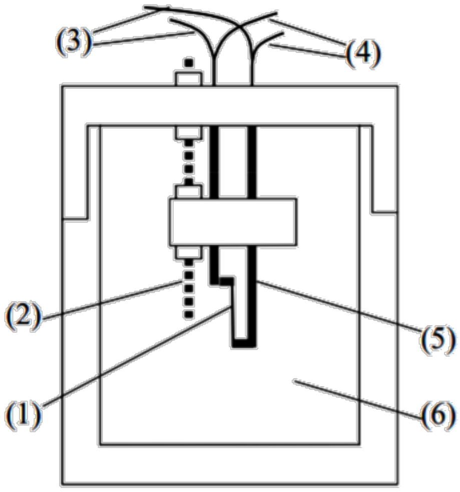

Fig. 14. Short transient hot wire (10 mm length, 50 μm radius). (1) Hot wire; (2) thermocouple; (3) voltage leads; (4) current leads; (5) Pt holder; (6) vessel.

The results

This catalogue of failures in proper experimental protocol of course leads to varying degrees of chaos in the field as we shall illustrate here. First, let us look at the simplest system of all perhaps, which is toluene. Its thermal conductivity has been measured for almost a century and the value appears to have been decreasing in time as Fig. 15 shows.

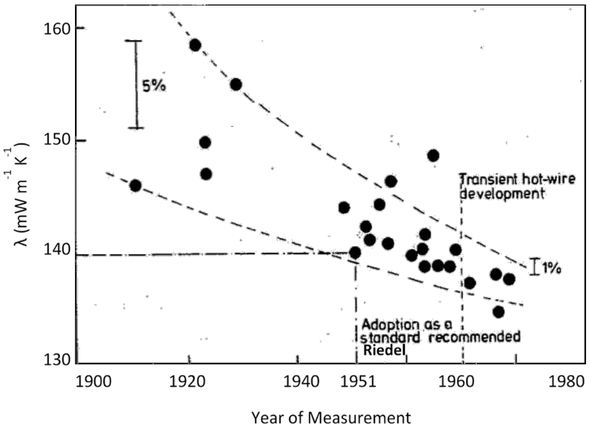

Fig. 15. Reported thermal conductivity of toluene as a function of the year of measurement.

The decrease was slowed when a standard recommendation was made, possibly because it was thought the ‘right answer’ was known! This illustrates the tendency to conform among researchers to an accepted result, which is one obvious danger.

In Fig. 16 we plot the deviations of two sets of early viscosity measurements for R134A from the latest validated values. These measurements were conducted in coiled and sealed capillary systems and it is clear that the measurements were up to 35% in error because of a neglect of these two effects.

If we consider less straightforward systems such as the molten metals, Fig. 17 illustrates the variation that can be found between the results of various measurements reported by a variety of techniques over time. A similar situation persists for molten salts as Fig. 18 exemplifies.

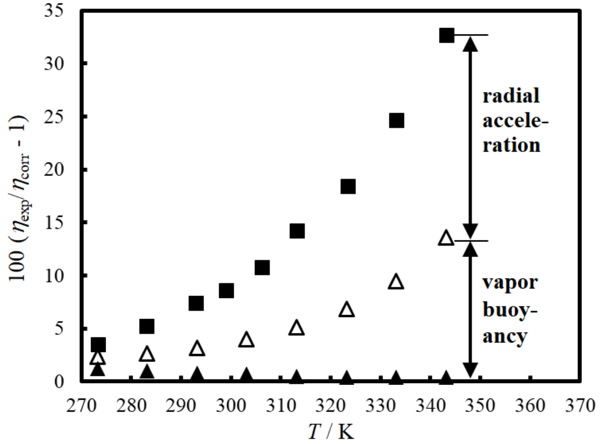

Fig. 16. Fractional deviations of the measured viscosity, for 1,1,1,2-tetrafluoroethane (R134a) from the accepted value, as a function of temperature.

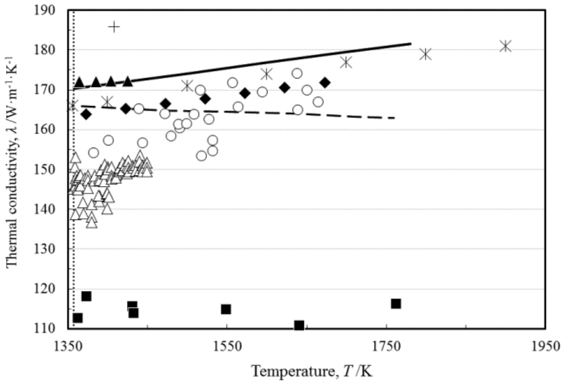

Fig. 17. Measurements of the thermal conductivity of molten copper.

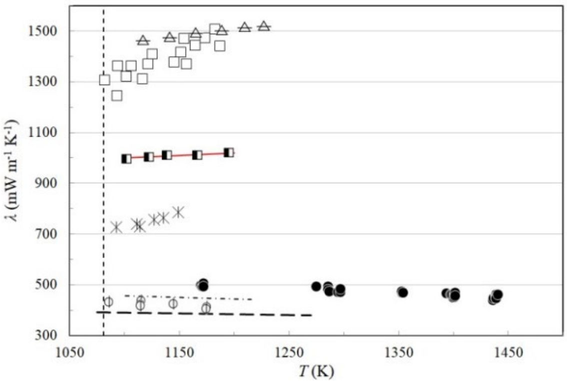

Fig. 18. Measurements of the thermal conductivity of molten NaCl.

It may be thought that this is all in the past but we shall now show you that the situation persists in the 21st Century. The relevant world became very excited in 1995 when it was claimed by Choi *et al.* [39] that the thermal conductivity of a base coolant such as water could be improved by 300% by adding a few volume percent of nanoparticles of alumina. The implications of this for heat transfer systems of all kinds were obvious and it stimulated an enormous stream of papers on the subject. Some showed the same effect, others no effect; some espoused theories to explain the phenomenon and there were computer simulations purporting to explain it. When you review all the evidence dispassionately a depressing picture emerges as illustrated in Fig. 19.

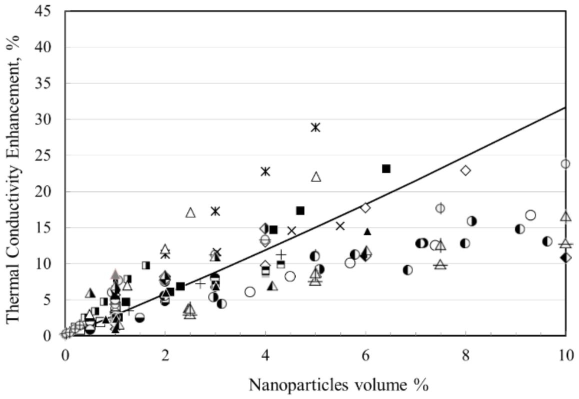

Fig. 19. Measurement of the enhancement of the thermal conductivity of H_2O when alumina nanoparticles are added.

This plot shows the enhancement of the thermal conductivity of the base fluid by the addition of nano particles for an $H_2O+Al_2O_3$ system as measured by a wide range of authors and techniques; most of which we have described. It is clear that there is no consensus. We note, in the context of earlier observations, that many of the authors of these papers have no previous record of having been engaged in the measurement of the thermal conductivity of any homogenous materials.

However, if we eliminate from consideration the techniques that do not have a proper theory or were not applied properly, the picture becomes clearer (Fig. 20) and we see that there is a modest increase in the thermal conductivity which is very close to that expected from a simple theory originating from Maxwell [40]. Indeed, the increase is usually so modest that any heat transfer benefits are usually offset by the concomitant increase in the viscosity of the system.

The amount of money, energy and scientific effort devoted to this situation, merely driven by an experimental error, is frightening. The reader will, of course, note the role of fashion and excitement in this example!

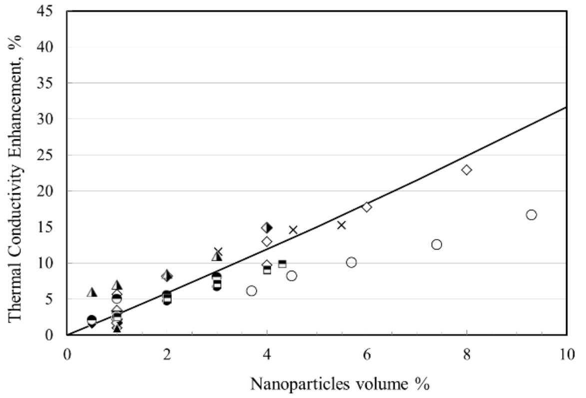

Fig. 20. Selected measurements of the enhancement of the thermal conductivity of H_2O when alumina nanoparticles are added.

Internationally accepted data and correlations

Driven, in part by this failure of past experimental studies of properties to be informed by careful, theoretically-sound methodology, the international community has relied upon an alternative method to determine validated data for the transport and equilibrium properties of fluids.

The effort was initiated by the International Association for the Properties of Steam (IAPS-Now IAPWS) in the 1920's. As its name suggests it was set up to produce internationally agreed values for the properties of Water and Steam largely for the steam boiler and turbine industries. Its initial product will be familiar to those of a certain age as the International Steam Tables [41]. These replaced, or were the source of, National Steam Tables used by engineers for all designs involving water and steam, and their international pedigree ensured transportability of designs across international borders replacing the disputes about the properties of Steam that were then extant. The work took many years and transcended hot and cold wars, and involved all countries of the world including those at war!

The effort continues today although the product is now a set of equations to describe all the properties of water, ice and steam as well as of heavy water [42]. The equations are available inside most respectable design software.

The basic approach of the international task group was to examine critically every measurement made of the properties of water and steam, to select the best measurements using the criteria we have outlined earlier, to reject all others or give them a small weight, to use theory where appropriate and then to produce a set of properties or an equation best representing the acceptable data. Of course, this process stimulated many more good measurements as well as generating enmity when particular measurements were deemed unacceptable.

This same methodology was adopted by two subcommittees of the Thermodynamics Commission of the International Union of Pure and Applied Chemistry (IUPAC). One, for thermodynamic properties, established in the 1950's a small group in London devoted to the production of books of the tables of the thermodynamic properties of important single substances. An example is the text on ethylene [19] which is a substance traded internationally in large quantities. For the process of custody transfer it was helpful (to say the least) if both sides of the border agreed on the density of ethylene at the transfer point because what was transferred was measured in volume but paid for by mass!

The second subcommittee, for transport properties (now the International Association for Transport Properties (IATP)) [43] had an obvious focus and is still operating today. It has produced many representations of the transport properties of fluids from the simplest low density gases to organic liquids to molten metals and molten inorganic salts, as well as three books [25, 44, 45]. Again, this work is endorsed internationally and is incorporated into modern design software. Work of a similar kind is conducted still in NIST, in USA and promoted through the Journal of Physical and Chemical Reference Data [46] but on a much smaller scale than hitherto and without international endorsement.

The future for processes including biological and novel other materials

The near universal adoption of computer-based design software means that the properties of the materials embedded in this software often have an unknown pedigree. In what we have said above it is clear that for familiar and important materials encountered in the process industries to date there are many reasons to have faith in the numbers embedded in the codes. However, we have also shown that whenever materials are new and the topic becomes hot or fashionable, there is a rush to experimental measurements of properties by researchers ill-equipped for the task with little experience and the results are often very inaccurate. Because the materials and measurements are new there is no oversight or perspective on these results and none of the international validation. The rush to follow fashion in this way is driven by the increasing need for (particularly) young faculty to perform at a high level and make a name for themselves in a field to progress their career. This is a dangerous trend in many ways but not the least is its encouragement of speed over rigour in the area of Thermophysics where care and time are essential.

We suggest that the fluid systems that are part of the project which is the subject of this workshop may well involve new materials and new chemistry/biochemistry. They therefore fall into the category identified above and therefore we advise very careful scrutiny of the data and its sources in process designs. We do not argue that the consequences of errors in properties will lead to designs that are physically dangerous but they may well not perform as expected thus tending to undermine your argument for their efficacy.

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