



A View on the Future of Applied Thermodynamics

Jean-Charles de Hemptinne, Georgios M. Kontogeorgis, Ralf Dohrn, Ioannis G. Economou, Antoon ten Kate, Susanna Kuitunen, Ljudmila Fele Žilnik, Maria Grazia de Angelis, Velisa Vesovic

► To cite this version:

Jean-Charles de Hemptinne, Georgios M. Kontogeorgis, Ralf Dohrn, Ioannis G. Economou, Antoon ten Kate, et al.. A View on the Future of Applied Thermodynamics. Industrial and engineering chemistry research, 2022, 61 (39), pp.14664-14680. 10.1021/acs.iecr.2c01906 . hal-03941335

HAL Id: hal-03941335

<https://ifp.hal.science/hal-03941335>

Submitted on 16 Jan 2023

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Distributed under a Creative Commons Attribution - NonCommercial - NoDerivatives 4.0 International License

A View on the Future of Applied Thermodynamics

Jean-Charles de Hemptinne,* Georgios M. Kontogeorgis, Ralf Dohrn, Ioannis G. Economou, Antoon ten Kate, Susanna Kuitunen, Ljudmila Fele Žilnik, Maria Grazia De Angelis, and Velisa Vesovic



Cite This: *Ind. Eng. Chem. Res.* 2022, 61, 14664–14680



Read Online

ACCESS |

Metrics & More

Article Recommendations

ABSTRACT: Thermodynamics is the science of the interactions between energy and matter. It was formalized in the late 19th century and remains an essential piece in solving many technological challenges that society faces today. Yet, it is often considered complex and challenging, perhaps because it is often taught within a rigid mathematical framework, without highlighting the extensive range of applications and the tools that it offers for understanding and elaborating a sustainable future. The authors of this paper have performed an industrial survey (Kontogeorgis et al., *Ind. Eng. Chem. Res.*, 2021, **60**, 13, 4987–5013), which pointed out that thermodynamics is indeed a cornerstone of many processes in a large range of industries, but that as of today, many questions and needs remain unanswered. Some missing answers are caused by a lack of knowledge of the existing tools (educational issue), some by the unavailability of models, parameters or by the lack of transferability of the concepts from one system to another. In other cases, simply, no generally accepted approach exists, and fundamental research is required for understanding the phenomena. In all cases, data are needed, either to understand, develop, or validate the models. Specific recent examples of applied thermodynamics research relevant to industrial practice are discussed. This manuscript aims not only at promoting research but also at encouraging highly trained professionals to engage in education, laboratory work, fundamental developments, and/or model validation. Such professionals should find positions both in academia and in industry, as well as with software vendors. Collaboration between academia, industry, and software vendors is essential in order to foster new developments and serve the goals of sustainable development and circular economy.



1. INTRODUCTION

The Working Party (WP) on Thermodynamics and Transport Properties (TTP) of the European Federation of Chemical Engineering (EFCE) has recently published a review¹ of the industrial needs after having surveyed 37 industrial companies. It is a follow up of a review published a decade earlier.² The objective of the recent paper¹ was to summarize, as faithfully as possible, the comments made by industry. It is a long and detailed document, containing numerous and yet sometimes conflicting suggestions. In view of this, some journal reviewers have suggested that the authors should provide additional expert opinion on important issues that are raised. The present paper fulfills this request by first summarizing the main items raised in the review and by proposing a concise vision of the state of the art and of the main directions that we believe the applied thermodynamics community should adopt in the coming decade. In the analysis, we have relied not only on the survey results, but also on various documents, including the five symposium reports^{3–7} on the Industrial Use of Thermodynamics, which are results of the Working Party industrial task group.

The following important topics were raised in the survey:

- New fields of application: The global challenges related to water, health, energy, and waste management open up

new needs. These may be related not only to the types of mixtures (in particular bio-based molecules and electrolytes), but also to different properties that require innovative and accurate tools. In particular, properties under confinement and at interfaces or in the presence of external fields as well as transport and non-equilibrium phenomena require increased interest.

- Predictive modeling: An essential step in the industrial applications of thermodynamics is the selection and parameterization of an appropriate model in a process simulator. This choice is however far from straightforward. The answer will depend on the scope of the simulation task, the mixture at hand, the operating conditions, and most importantly, the availability of data for validation. Each of these issues should be further investigated, but it appears that industry prefers to have a 'predictive' approach that works accurately for a large

Received: May 30, 2022

Revised: July 12, 2022

Accepted: July 12, 2022

Published: September 20, 2022



SUSTAINABLE DEVELOPMENT GOALS



Figure 1. UN's 17 Sustainable Development Goals (SDGs).⁹

range of conditions. Several such approaches are discussed in the survey: PSRK-VTPR, SAFT and its variants, and COSMO-RS/SAC models are the most widely quoted, and an expert opinion on their strengths and limitations is clearly needed.

- Data: Regardless of its predictive ability, any model must be validated and parameterized using data. Databases do exist, but no strategy exists to exploit them in a way that would be beneficial to the community at large. Such a strategy would need to consider: (1) evaluating the quality of the existing data, (2) assessing the need for new data and performing the relevant measurements, and (3) making the data available in some convenient and standardized form. Perhaps new tools using artificial intelligence could help in this direction.
- Education and training: the expertise needed to develop innovations require time and experts. Quality training is therefore needed, not only at the diploma level, but also at the level of continuing education. Industry needs sufficiently trained thermo experts to maintain its capacity to quickly adapt to the changing context. The practicing engineer will increasingly need both the access to a high-level expertise and the capacity to adapt to the vocabulary and concepts of different disciplines. Novel teaching methodologies do exist but must be evaluated for relevance, keeping in mind that some thermodynamic fundamentals do remain the same.

The present paper follows the above structure.

2. FIELDS OF APPLICATION

The first and probably most important issue to discuss is what is applied thermodynamics good for? Our modern society faces a multitude of grand challenges, and we believe that our technical knowledge can help in the resolution of many of them.

In response to the grand challenges the United Nations defined and agreed to 17 Sustainable Development Goals (or

SDGs) aiming at creating a better world by 2030, by ending poverty, fighting inequality, and addressing the urgency of climate change, among others.⁸ The full list of SDGs is shown in Figure 1. World-wide substantive attention is addressed to these SDGs and their related thematic issues, including water, energy, climate, oceans, urbanization, transport, science and technology.⁹

As stated by the American Chemical Society (ACS), "chemistry plays an essential role in helping society achieve the Sustainable Development Goals (SDGs). The chemistry enterprise has a broad reach into technology, the economy, and human health, and there are already many ways chemists are working to support global sustainable development."¹⁰

More specifically, ACS identified seven priority SDGs where chemistry and chemical technology can and should play an important role in achieving them. They are listed in Table 1. From these SDGs and the illustrated example cases, one could extract a number of overarching challenges where applied thermodynamics plays a crucial role. In our attempt, we have arrived at the following list of important topics:

- Energy efficiency, energy conversion, and energy carriers

Human developments have always required energy. Yet, since the beginning of the industrial revolution, the energy consumption per capita has increased up to the point that it endangers the future of the planet. Three types of actions can be taken to reduce our human energy footprint: the first is reduce the use; the second is improve the use; and the third is search for alternative, sustainable resources. While the first implies a change of lifestyle, the second and third types of action will require engineering solutions. The second, improved use of resources (meaning use less for the same result), is a topic for which thermodynamic concepts are extremely well designed: it defines the upper limit of what is feasible in terms of work delivery of various processes. The concept of exergy, or energy quality, has been developed using these principles.^{5,11,12} This concept is

Table 1. Seven Priority SDGs (as Identified by ACS) with Essential Role for Chemistry and Chemical Engineering for Achieving Them, Adapted from Ref¹⁰

SDG	chemistry & chemical technologies examples to meet this SDG
2 zero hunger	<ul style="list-style-type: none"> drought protection for crops phosphate recovery and reuse targeted crop protection agents active packaging to prevent food spoilage
3 good health and well-being	<ul style="list-style-type: none"> tools for greener chemical manufacturing (green) pharmaceuticals enhance bioavailability of pharmaceuticals with low water solubility environmental improvement
6 clean water and sanitation	<ul style="list-style-type: none"> solar-assisted desalination processes heavy metal removal
7 affordable and clean energy	<ul style="list-style-type: none"> chemistry and energy storage energy conversion
9 industries, innovation, and infrastructure	<ul style="list-style-type: none"> sustainable & green chemistry green coatings transforming & advancing separation science
12 responsible consumption and production	<ul style="list-style-type: none"> recycling materials biobased feedstocks second generation biofuels
13 climate action	<ul style="list-style-type: none"> design principles of green and sustainable chemistry

now used in some Swiss cantons to deliver authorization for new systems or tools.¹³ It is also used for Life Cycle Analysis.¹⁴

One of the important challenges encountered in energy management today is energy storage. Yet, as such, energy cannot be stored; storage means in fact converting the energy in a thermal, mechanical, electrochemical, or chemical product that can be retrieved with the least possible loss.¹⁵ The choice depends on many local and use-related criteria, but in all cases, a thermodynamic analysis is required to identify the feasible solutions. The long-term viability of the hydrogen economy, for example, should be challenged by the large amount of energy required to produce this high energy-containing molecule. Similarly, the use of CO₂ as low energy carbon source can be challenged from an energy efficiency point of view, as demonstrated by a thermochemical analysis.¹⁶

Among the most well-known energy conversion systems, one should mention the thermal energy cycles that make it possible to convert heat into work (as in power cycles or internal combustion engines), work into lower temperature (as in refrigerators or cooling systems), or low temperature heat into high temperature heat (as in heat pumps), all of which are based on various types of thermodynamic cycles. The optimal design of these cycles often rests on the selection of an adequate working fluid.¹⁷

• Water

Water is a key element for life! It is essential for drinking and agriculture. In engineering applications, it is an essential solvent in many processes, heat duty agent (steam), stripping agent, a reactant (from hydrolysis to

H₂ production), or byproduct (e.g., condensation reactions). Its safeguard is key for political stability in many places worldwide. The importance of fundamental understanding of water properties is obvious, yet its thermodynamic behavior is still subject to discussion and remains challenging: water exhibits a number of anomalous thermodynamic behavior, two of the most well-known being the maximum in density around 4 °C and shrinking upon melting.¹⁸

• Solvents as a key to sustainable, green chemistry and to cyclic economy

If our society wants to preserve its resources and treat the waste in a proper way, the key is to be able to extract specific molecules from one medium and concentrate them in another. This is the role of solvents. The solvent molecules often cannot be entirely removed from the final product, which means that they end up in the application with potential human exposure and eventually in the environment. In the past, petrochemical-based products were often used, but the increasing environmental awareness creates the need for using novel molecules that are bio-based, non-toxic, and/or compatible with the environment. Solvents are also needed for enhancing reactive systems or in electrochemical devices. The European regulations are now increasingly severe for putting new products on the market, which enhances the need to know the properties in advance (REACH regulations).¹⁹

Several types of new such solvents have been identified in the recent past, ranging from ionic liquids, deep eutectic solvents, supercritical CO₂, or solids such as zeolites, metal organic frameworks, etc. Yet, very often, the most efficient solvent is water. The reason for its efficiency as a solvent is its low molecular weight and low volatility as well as its capacity to dissolve salts into ionic species. This unfortunately may also lead to undesirable effects such as corrosion. Water (rarely pure) is used for recycling metals from waste batteries, removing CO₂ from flue gases, or as reaction medium for biological treatments, among many other uses. Yet, the behavior of these complex salt-containing solvent mixtures (electrolyte mixtures) are often poorly known and need to be further investigated.

• Health and nutrition, or bio-sciences

Life sciences entail significant thermodynamic complexity, as they combine the presence of highly concentrated electrolytic and reactive systems, confined in micro- and sometimes nano-sized entities. In addition, they are almost entirely driven by non-equilibrium phenomena, although without going into the full complexity, food production or pharmaceuticals are two domains where equilibrium phenomena are also important and need to be better understood.¹ The biggest challenge today is related to the complexity of the molecules that are relevant in these processes: proteins, enzymes, amino acids, and pharmaceuticals, among others, need to be synthesized, isolated, and delivered. They may exhibit various solid phases. An important effort to understand the behavior of these molecules in their environment is therefore needed.

• Novel and complex materials

As a result of increasing interest in renewability and circularity, novel materials are constantly developed and

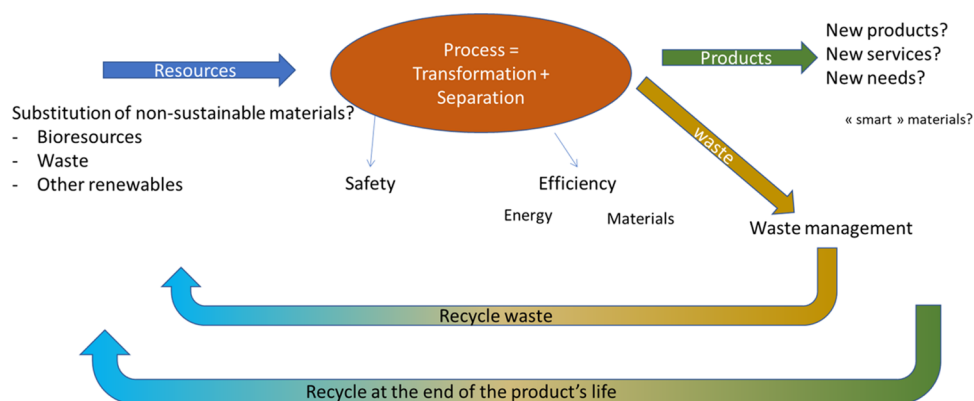


Figure 2. Concise view of the process and the challenges related to it.

introduced into processes, as raw materials, intermediates, and products, or as auxiliary materials like solvents, e.g., deep eutectic solvents (DES). These materials can be multifunctional, especially oxygenated compounds, and are therefore polar, featuring more complex phase behavior than fossil-based materials, which were the major focus of work until now.

Many industrial applications involve multiphase systems, like emulsions and dispersions. Often, these systems are in a metastable state. In spite of considerable knowledge, there are still gaps in appropriate fundamental understanding of their phenomenological behavior. A better understanding is anticipated to drive innovation toward further development of sustainable materials.

Structured product design is key to enhancing development of these novel and/or complex materials. Product design is sometimes mentioned as the 3rd paradigm in chemical engineering, yet in practice there is still much ground to be covered before it is sufficiently mature for widespread application.²⁰

In process design, we calculate the relevant physical and chemical properties of different streams from the given composition. In product design the reverse is done, and compounds and compositions are calculated that provide certain functionality. Big challenges in product design are related to this reverse calculation, as well as how to define the desired functionality in quantitative terms; thus, one key aspect is the translation of product functionality to target properties.²¹ To be successful, this will require a cultural change in how product design is done in practice.²⁰

- Advanced materials recovery and precision technology

Higher efficiency is sought to separate and purify the desired products, within the constraints of reducing manufacturing costs, lowering energy usage and keeping a small environmental footprint. The product recovery needs to be achieved for a wide range of systems, from biochemical systems, enhanced oil recovery, and mining to standard recovery from chemical reaction mixtures. The concentration from which the product needs to be recovered can vary considerably. It can be high as in chemical reaction mixtures, but also low as in fermentation broths.

Following the multilayered approach from a chemical engineering perspective, as offered by Gani et al.,²² the process

is at the heart of activities, essentially comprising pretreatment and transformation of material and subsequent separation²³ into the desired products. Yet, in this view, a process may also be an energy conversion unit. In short, the process and its challenges can be described as shown in Figure 2.

Figure 2 illustrates the challenges from a chemical engineering perspective. It shows the key changes that will need to take place in the future to grow toward a more sustainable industry:

- The resources change. In the past, we very often used fossil material, while increasingly, non-fossil resources or waste will be used as input.
- The products change. Products were often bulk chemicals, but there is an increased need to target the product to very specific consumer needs that may include complex materials, based on nanoencapsulations or other organized multiphase “smart” products. An increasing attention must be paid to the ultimate service to be delivered rather than to a material product.
- The waste may come from the process itself, but also when the desired product reaches the end of its useful life. It may be solid, liquid, gaseous, or even heat (energy) and must be managed intelligently, in other words by recycling or integrating into a new process. The first action in that regard is an improved process efficiency, so that less waste is created. Exergy analysis and Life Cycle Assessments will be increasingly used.
- Finally, the process safety will remain in all cases a key factor, meaning that all possible accidents will need to be analyzed and avoided. Accurate knowledge of toxicity, flammability explosivity, heats of reactions, and other properties necessary to ensure process safety is needed.

Even though the concise view presented here is based on a chemical process point of view, it can be further extended to other undertakings, like mining processes, medical devices, or even to the entire ecosystem that is nothing but a very complex process.

The development of adequate responses to the grand challenges goes most often through the use of software tools that contain models and are able to simulate the behavior of the complexity of nature. These tools contain physical models that are calibrated on measured data. This is why the next two sections will focus on these essential contributions to the engineering use of thermodynamics. Yet, software tools are used by people, and at the end, they are the ones responsible for choosing the appropriate tools, providing relevant inputs,

and interpreting the numerical results. Additionally, even before using the software tools, people with proper knowledge of thermodynamics and physical properties can substantially save time and expenses in the process and product design by steering efforts to the most promising ideas. This is why the final section of this work will discuss the need for training and for investing in human resources.

In conclusion, applied thermodynamics can and should play a strong role in addressing the grand challenges. As thermodynamics is the science of interaction between energy and matter, it is very well positioned to help us achieve the SDGs to arrive at a better world. It is at the heart of the multilayered process view that is shown above, where its role is to understand and help in the design and optimization of the increasingly complex processes and products.

3. MODELS AND SIMULATION

All of the applications discussed so far require at some point, either the computation of physicochemical properties, with an input that is usually the operating condition and fluid composition (in the case of process design), or a target property with the aim to identify the compound or mixture that best fulfills the requirements (in the case of product design). Models are needed for this purpose. Although there is an increased trend to use machine learning (ML) and chemoinformatic approaches to predict compound properties, we do not believe that they will replace the physically grounded models that are the legacy of more than a century of research.²⁴ We would like to stress, however, the important effort that remains to be done in view of improving the predictivity of the models: data, as will be discussed later, are very expensive to generate and are therefore often unavailable for tuning the models. In particular, product design tools²⁵ cannot be developed unless such predictive models are further improved.

We will discuss in what follows the so-called macroscopic models, which are found in most process simulators, as well as the microscopic tools that are now available through molecular simulation. Macroscopic transport property models are presented separately as they deal with non-equilibrium properties.

3.1. Macroscopic Thermodynamic Models for Equilibrium Properties (Equations of State (EoS) and Other Models). The property that is most difficult to describe accurately is the chemical potential that drives the phase equilibrium: it allows for computing how compounds partition between the various phases, which may be solid, liquid, or gaseous. The equilibrium between solid phases is a topic that is investigated at length for metallurgical processes. Solid–fluid equilibria, encountered in chemical processes, often consider pure solids, leading to a very simplified property model,²⁶ that uses melting point and phase change properties as input. In the case of solid solutions, activity coefficient models are often used to represent possible non-idealities. In what follows, we will focus on fluid phases that are generally much more complex to describe.

The expectation from the user community is to have access to tools that provide “automatically” correct numerical results. This is called “fully predictive”. Unfortunately, such an infallible ‘push-button’ tool does not exist today. The best that is offered are documents that help the engineer select the most appropriate model.^{27–31} Yet, the choice is very often limited to the availability of the model in process simulators

including an extensive parameterization, and documentation.⁴ From this perspective, the academic developers should be strongly encouraged to aim toward a standardized development: avoid developing case-specific models, but prefer using existing ones and build upon accepted parameter sets.

As a community of experts, we however strongly stress the fact that “automatic” tools will never remove the need for a trained person to plan the simulation scenarios and interpret the result. Non-intuitive phenomena may occur, with the consequence of loss of time, money, and sometimes the creation of safety issues. Below, we discuss very briefly the limitations of the existing models and identify the most important developments that we believe are needed in the near future in light of the industrial survey.¹

3.1a. Predictive Power. At first, one should be cautious with the word ‘predictive’. The models that are under study here are mathematical equations with parameters fitted to experimental data. Predictivity can point to extrapolating to other process conditions, mixture composition, or properties or to other or similar compounds via Group Contribution (GC) methods and related schemes. It is a key quality of EoS models to be able to describe many properties in a consistent manner, which is less true for activity coefficient models, and even less so for correlative approaches based on ML. This is why the form of the equation is critical. Yet, when the quality of temperature extrapolations is not adequate, it often happens that temperature-dependent parameters are used, making it possible to describe almost any temperature function: this is typically the case with the energy and interaction parameter functions in cubic EoS. Le Guennec *et al.*³² have discussed limitations in this type of temperature formulations. For gas processors or working fluid specialists, who have access to a large experimental database, Span and colleagues have developed highly precise models³³ based on the 64 parameter modified Benedict–Webb–Rubin (MBWR) EoS.³⁴ The GERG consortium (European Gas Research Group) widely uses these models³⁵ that have also inspired the NIST RefProp database in gas or working fluid applications.³⁷ These EoS may be classified as predictive because of their capacity to cover all properties in a consistent way, although their numerous adjustable parameters have been trained by means of a large amount of data. They are widely used and have been recently extended to simple mixtures.³⁶ Yet, it should be noted that very few studies have been presented for evaluating the predictive power of other types of EoS (cubic or higher order ones) for thermal and derivative properties, as compared to phase equilibrium behavior; thus, capabilities of many models are not well-known. This is certainly an area to focus on in the future.

Yet, the predictivity is often referred to as the capacity to describe a fluid mixture without experimental data. This may be needed when process concept feasibility evaluations are needed on a short notice for troubleshooting or for product design. The model parameters must then be computed starting from molecular descriptors in some way. The most common type of descriptors refers to the molecular groups. The first industrial GC model was proposed by Fredenslund with the UNIFAC activity coefficient model.³⁸ Using Huron–Vidal type mixing rules,³⁹ the model is now commercialized through an EoS under the name PSRK⁴⁰ and more recently VTPR.⁴¹ GC models are now widely developed, both with cubic EoS (PPR78)^{42,43} and within the SAFT framework.^{44–47} Many gaps remain to be filled in parameter tables for GC methods, both activity coefficient models (UNIFAC) and EoS (e.g.,

VTPR), and of course also for association theories when GC schemes are used. Such gaps as well as the uncertainty related to multifunctional groups and neighboring group effects limit the use of these models for predictive applications including their implementation in computer-aided design methods. It should be pointed out that NIST provides, through their 'Thermo Data Engine' (TDE), a novel method for extending the UNIFAC parameter table.^{48,49} Other descriptors can be alternatively used. Within the SAFT framework, several innovative attempts exist with the use of *ab initio* descriptors, through neural network-type approaches.⁵⁰ The COSMO models⁵¹ use as descriptors the so-called sigma profiles that also originate from *ab initio* calculations. Alternative approaches based on artificial intelligence are seriously investigated. This topic is further discussed later in the section about experimental data.

In practice, however, it may be considered convenient to have access to adjustable parameters whenever data are available because no model exists today that can combine both predictivity and accuracy for a very extensive range of systems and conditions.

3.1b. On the Application Range of the Most Well-Known Equations. When it comes to the "classical" predictive thermodynamic models, there are a lot of similarities in the statements made by the industry in the two surveys that the EFCE WP conducted,^{1,2} despite them being 10 years apart. Moreover, no real new modeling trends have appeared since the first survey.² The cubic EoS also with advanced mixing rules (PSRK and VTPR), UNIFAC, association models (like SAFT and CPA), and the COSMO-RS approach appear to be among the most widely used methods, especially in the petrochemical/chemical industries. Local composition models like NRTL and UNIQUAC are also useful as tools for multicomponent systems once binary parameters are available. All these models are still much used by industry, and there is a clear understanding that having a single predictive model for all applications is most likely an impossible task.

Many companies have still traditional views on the model choice with the first category of the aforementioned models (cubic EoS, local-composition activity coefficients models) being far more used than the latter ones (association EoS and COSMO-RS), even if the latter ones are getting more popular. In this context, it is worth noting that these latter methods offer better prospects for multifunctional and complex materials, like bio-based and "smart" materials, and therefore may attract increased attention in the future. Even among the more "traditional sectors" (oil & gas and chemicals), association models need much more development if they are to be of wider use: better characterization schemes for oil components, improvements in computational efficiency, and predictive schemes for estimating the SAFT parameters especially for complex chemicals are some of the examples of the improvements that are needed. An area where we see much promise in the future and where possible breakthroughs can occur is related to SAFT parameterization from *ab initio* quantum mechanics calculations. This could significantly reduce the dependency on experimental data.⁵² Moreover, there are far too many SAFT variants (unlike UNIFAC where by now one version – Dortmund – has become dominant⁵³). Industry is confused and new tools⁵⁴ that permit open comparisons of SAFT models may assist in the future in the clarification of this rather confusing picture.

The use of the "standard database" by Jaubert and co-workers⁵⁵ may also be useful in providing a fair comparison of models at least for binary VLE systems. Of course, the real success of SAFT-type approaches vs cubic EoS and UNIFAC should be expected for multicomponent and multiphase behavior of complex systems (e.g., VLLE, CCS applications, properties beyond phase behavior, etc.) but still needs to be proven. An area where essentially all SAFT approaches suffer is the representation of the critical point, even compared to classical cubic EoS.⁵⁶ In many practical applications, e.g., for use in petroleum applications, thermodynamic models should deliver accurate and reliable results even very close to the critical point. Thus, a crucial aspect for SAFT-type models is the performance at the critical point as well as being able to characterize oil and gas to facilitate their subsequent use in process simulations.

3.1c. Need for Further Developments. While all the above indicate areas where future developments toward better predictive models are needed, there are three fields which require particular attention: electrolytes, polymers, and systems containing complex multifunctional compounds.

Regarding electrolyte solutions, we have observed¹ that many companies are users of the e-NRTL model, and many requests were related to this model (more parameters for important systems including radioactive ones, better education on the use of this model, etc.). Challenges appear at high salt content, with mixed solvents (with possible liquid–liquid demixing) or at high temperatures, typically where few data exist.

We therefore encourage the development of predictive, possibly GC-based, electrolyte models. We believe that the very active research area of development of electrolyte equations of state should continue as it may lead to more predictive and generally applicable models for electrolyte solutions. Prior to arriving to ultimate successful electrolyte versions of EoS models, there is a wide range of practical and fundamental issues that need to be overcome. Some of these issues include identification of the most appropriate theories for ion–ion and ion–solvent interactions,⁵⁷ determination or clarification of the appropriate balance for electrostatic and physical terms, role and importance of solvent relative permittivity, frameworks for standard states of solids and for mixed solvents, role of individual ion activity coefficient data recently appeared, just to mention a few, and all of these at very different concentration levels.

It is important to mention that for such electrolyte solutions, the ultimate aim is to describe different types of phase equilibria using a single set of binary interaction parameters, namely, combined prediction of phase and chemical equilibria and prediction in the absence of experimental data, different hydrate forms of organic salts, crystallization of electrolytes, mixed salts and mixed solvent solution at concentrated condition, corrosion due to electrolytes in bio-processes, polyelectrolytes, etc. All in all, a very demanding task indeed!

Especially relevant are truly predictive models for electrolytes with limited requirement for adjustable parameters. Data regressions are often required over extensive temperature and pressure ranges and at high concentrations, including speciation behavior, which may have a huge impact on the system behavior. The ranges of interest are sometimes not easily accessible experimentally, and some of the required data falls outside the traditional area of thermophysical property measurement. Identifying the best approach to parameterize

electrolyte models for general applications is considered a difficult task where future research should also be focused.⁷

Polymers and their solutions play an important role in industry for their widespread use in packaging as well as in chemical engineering processes like membrane separations. While polymeric mixture properties in the liquid and rubbery state can be represented fairly well with activity coefficient models developed for macromolecular solutions like the free volume-corrected UNIFAC,⁵⁸ the Flory–Huggins equation,⁵⁹ or EoS models like the lattice fluid⁶⁰ or SAFT theories, the situation becomes more complicated when a glassy or semi-crystalline system is concerned. In both cases, polymer density cannot be predicted *a priori* as the system is frozen in a non-equilibrium or constrained condition, and models developed for liquid or rubbery solutions assumed amorphous and at thermodynamic equilibrium fail. Appropriate protocols need to be established, which account for the non-equilibrium condition or for the crystalline fraction. The density of the glassy system was found to be a simple and effective order parameter to describe the polymer-fluid solubility by the non-equilibrium thermodynamics for glassy polymers (NET-GP) approach⁶¹ that is now a well-established tool due to its flexibility, which makes it a proper extension to the glassy domain of most equilibrium EoS models (NE-LF and NE-SAFT). For semi-crystalline polymers, several attempts were made at describing the effect of crystalline domains on the polymer solution properties, i.e., by introducing an additional constraint pressure.⁶² No theory seems yet predominant, and there is still a need for development, especially considering that most commodity polymers, like polyethylene and polypropylene, are semi-crystalline, as well as many new biodegradable materials like polylactic acid (PLA) and poly hydroxyalkanoates (PHA). The availability of EoS parameters for several polymeric systems is still an issue, which could be solved using Group Contribution,^{63,64} ML, or molecular simulation methods. Data-driven methods have recently been proposed to design polymers with specific properties.⁶⁵

Finally, there are several applications containing complex multifunctional molecules, which could benefit from reliable thermodynamic models, but the consensus is that due to the complexity of the molecules involved as well as associated conditions (polymorphism, precipitation, crystallization, etc.), essentially, no successful predictive models exist for the needs of the industry with complex products, (e.g., comprising surface active materials), like pharma, biotech home & personal care, agrochemical, and mining. Over these 10 years, we have observed an increased interest by the pharma/biotech industry in thermodynamic models, as a comparison of the results from the two surveys^{1,2} shows.

It has been pointed out in the surveys^{1,2} that UNIFAC and GC versions of SAFT cannot successfully handle even a small number of the molecules (active ingredients) of relevance to the industry with complex products. More complex molecules like peptides, proteins, enzymes, etc. can be even more challenging. Such systems are typically multicomponent mixtures (including water, organic solvents, dissolved solids, dissolved gases, ionic species, and macromolecules), and this adds to the complexity, which needs to be implemented in successful models. We lack today predictive models that can cover such a wide range of conditions and systems containing complex molecules, and this is a very challenging area where future research needs to focus.

3.2. Transport Properties. Both industrial surveys carried out by the Working Party^{1,2} have indicated that the transport property predictive models are still lacking when compared with the thermodynamic models. This is certainly true in general, but there are regions of phase space and particular systems where the transport property models are not only available but also accurate and reliable. For instance, for gases at low pressure in a dilute gas limit, we can calculate the transport properties (shear viscosity, thermal conductivity, and self and binary diffusion coefficients) to an accuracy that is commensurate with the best experimental data. Such calculations have been carried out for a number of simple molecules and their binary mixtures, by means of the combination of the kinetic theory of polyatomic gases, classical trajectory method, and *ab initio* intermolecular potential.^{66,67} Hence, for several industrially important mixtures like natural gas, including sour and CO₂-rich natural gas, accurate and reliable transport properties can be computed. The developed technique for computing the transport properties in the dilute gas state has an additional advantage, because of its accuracy, that allows creation of pseudo-experimental data to supplement the available ones and/or allows for discrimination between inconsistent experimental data measured in different laboratories. Thus, we have means of addressing the need for data at very low and high temperatures, where accurate measurements are scarce and for toxic, highly corrosive, or explosive gases that cannot be easily handled.

Another area where transport properties data are available is for a number of pure fluids of industrial interest.⁶⁸ This work is being carried out under the auspices of the International Union of Pure and Applied Chemistry (IUPAC). The starting point is to make use of the best available experimental data, selected based on a critical analysis of the measurement methods. This information is complemented with guidance available from theory to produce accurate, consistent, and theoretically sound correlations of the viscosity and thermal conductivity of industrially important fluids over the widest range of temperature and pressure possible. The available viscosity and thermal conductivity correlations are IUPAC recommended representations analogous to NIST/IUPAC/GERG pure species EoS.³⁶

The development of generic models for the prediction of transport properties over the whole range of temperatures, pressures, and compositions of interest to industry is hampered by the lack of a rigorous and comprehensive molecular theory for dense fluids. Hence, it is not possible to evaluate transport properties based on a theoretical molecular description starting from the intermolecular potential directly. Consequently, one has either to rely on different approximate approaches or molecular dynamics simulations (see the next section). The former developments suffer from a lack of rigor that invariably translates to higher uncertainty in predicting transport properties while the latter is currently limited by the use of simple intermolecular potentials that require fitting the scaling parameters. Nevertheless, both approaches have shown marked improvements in recent years, as described in the Advances in Transport Properties, which summarizes the state of the field.⁶⁶

The approximate approaches can be broadly divided into three groups, depending on the theoretical starting point used in developing the model; kinetic theory-based models, corresponding-states based models, and models that exploit links with thermodynamics.^{66,69–74} Although conceptually

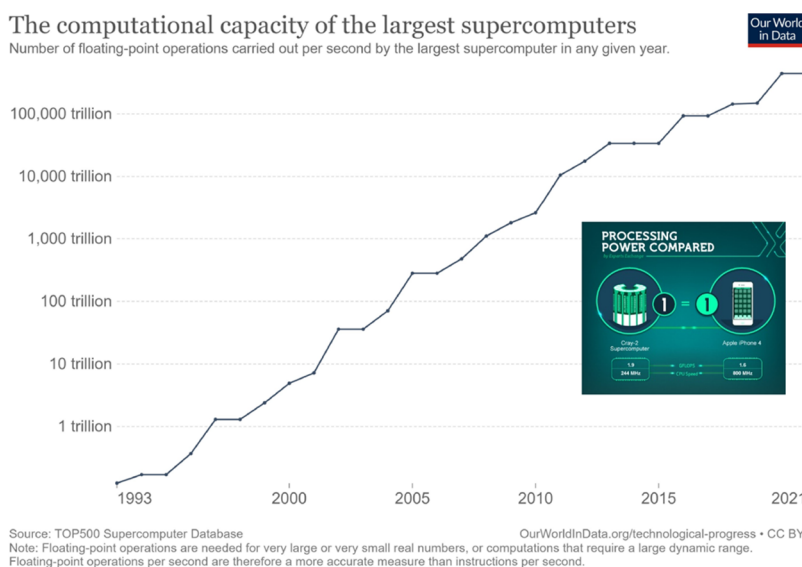


Figure 3. Largest supercomputer power in FLOPS from 1993 to 2021. In the inset, a comparison in computing power between the Cray 2 Supercomputer and Apple iPhone 4 is shown. Taken from: <https://ourworldindata.org/technological-progress>.

different, all these models require experimental data to determine the number of effective parameters of the model. Furthermore, most available methods require mixing rules, which are invariably based on averaging of pure fluid characteristics without recourse to interaction parameters. So far, most of the models have been used for mixtures of interest to the oil and gas industry and petrochemicals.

No comprehensive comparison between different models, even for hydrocarbon systems, has been undertaken. Instead, each model developer performed limited validation of their own model against, more often than not, selected experimental data. All models validated in this fashion show good agreement. Overall, the predictive power of currently available models is fluid-dependent, unless the effective parameters, sometimes expressed as a function of thermodynamic state, are also linked to molecular properties by a further correlation. The lack of experimental data and funding has precluded the use of such models more generally. Thus, we have a paradoxical situation that although significant research efforts both financially and timewise went into developing a plethora of models, the resulting predictions of transport properties are for some mixtures unreliable. This includes mixtures of even simple molecules that belong to very different chemical families, asymmetric mixtures (e.g., methane–*n*-decane or carbon dioxide–*n*-decane), mixtures at high pressure, mixtures where strong hydrogen bonds are present including aqueous mixtures, or mixtures that contain very large molecules that are poorly defined as pure species. Furthermore, most of the efforts have gone into describing the properties of fluids that display Newtonian rheological behavior. For instance, models for predicting the viscosity of non-Newtonian fluids are scarce, as are methods that indicate which type of rheology is to be expected.

It is worth noting that the recent Industrial Fluid Properties Simulation Challenge,^{75,76} designed to compare different molecular simulation models in their ability to predict the temperature and pressure dependence of the viscosity of complex molecules, is a positive step in addressing the predictive capabilities of some of the current models.

There are plentiful anecdotal examples that, even if a particular model works for a specific set of mixtures, there is no guarantee that it can be used for mixtures of species belonging to another chemical family.⁶⁶ This is especially true for viscosity, which changes significantly when the fluid is in the vicinity of the solidification line or when a process under consideration leads to a preferential change in composition of small or large molecules. However, there are also success stories where a model originally developed for hydrocarbons was used to successfully predict the viscosity of deep eutectic solvents (DES).⁷⁷ Nevertheless, this relied on having reliable viscosity data on pure components making up the mixture. Overall, the currently available models have the appropriate basis to be used for prediction of transport properties of at least non-electrolyte and Newtonian fluids. However, it is unlikely that any of the current models can become a generic tool for predicting transport properties without recourse to good experimental data both for fitting the parameters and also for the validation purposes.

There are several avenues that could prove fruitful for future research. Development of Group Contribution approaches would have potential to promote some of the current modeling tools into the more predictive realm, in particular models based on corresponding states or hard sphere representation. Links with SAFT-EoS that are currently explored by some research groups can provide an impetus for a more unified approach. The models based on residual entropy is one such example.⁷⁸ More such theoretical or even semi-theoretical approaches, capable of underpinning a practical model, should be sought, for example on how to include hydrogen bonding within the transport property framework. This would open the way to a more predictive analysis for a plethora of mixtures. Further research in developing models that use effective characteristics, as a proxy for a full fluid composition, to describe a particular mixture are also welcomed. For many fluids of industrial interest that may contain a large number of components, isomeric species, or ill-defined large species, forfeiting the full compositional formulation is the only way forward.

3.3. Molecular Simulation and Its Use. Molecular simulation refers to mathematical modeling of matter (solid,

liquid, or vapor, either pure components or mixtures) at the molecular level by accounting for the inter- and intramolecular interactions using appropriate potential functions known as force fields. The method was originally developed in the 1950s, and for several decades, it was restricted to relatively simple systems due to the heavy computational needs. The tremendous continuous increase of computing power at affordable prices allows us today to perform large computations at different scales (in time and spatial dimensions) and to understand accurately complex phenomena in nature or in the lab. Molecular simulation has evolved into a powerful engineering tool, thanks also to the emergence of start-up companies that develop and support methods, codes, and databases for the simulation of complex systems of industrial interest. Several of these business initiatives are rooted in academic research groups.

Development of new computer architectures continues to support the rise of computing power at reasonable price. In Figure 3, the capacity of the largest supercomputers in terms of FLOPS is shown from 1993 until 2020. Moore's law continues to be valid without any sign of slowing down. With the computing power rising, it is expected that in the future, scientists and engineers will be able to simulate more challenging systems, in terms of inter- and intramolecular complexity and for longer simulation times with profound effects for the design of more advanced processes and materials.

The available computing power is used today in many different ways.

3.3a. Upscaling for Developing 'Predictive' Tools. When it comes to chemical process industry, hierarchical multiscale computational methods are used to design and model accurately chemical processes and new materials. A very successful example refers to the use of molecular dynamics simulation to predict accurately the diffusivity of reactants and products in the catalytic nanopores at the actual temperature and pressure conditions of the gas-to-liquid (GTL) process.⁷⁹ GTL is an industrial process where synthesis gas (syngas, H_2 , and CO) is converted into liquid hydrocarbon fractions, namely, paraffins (from *n*-hexane to waxes), olefins, and to a smaller extent oxygenates (e.g., alcohols). Predictions from molecular simulation were used to parameterize an empirical model used for the optimization of the GTL process in a major industrial site in Qatar.

In Figure 4, the interconnectivity of methods used by chemical engineers is shown schematically. Subatomic quantum mechanics calculations allow the development of accurate molecular force fields to describe intra- and intermolecular interactions of complex chemical systems including aqueous mixtures, macromolecular systems, biological molecules, nanoconfined systems, etc. These force fields are used in molecular simulations, such as molecular dynamics, Monte Carlo simulations, Brownian dynamics, etc., in order to predict physical properties of complex chemical systems. These predictions are very accurate in reproducing the real system.⁸⁰

3.3b. Accompanying and Complementing Experimental Work. Molecular simulation results are always compared with existing experimental data as a way of validation. Yet, it is nowadays also used to guide experimental work for new molecules or chemical systems and previously unexplored temperature and pressure conditions. An example refers to the measurement of thermophysical properties of fluid mixtures related to the GTL process that were originally predicted by

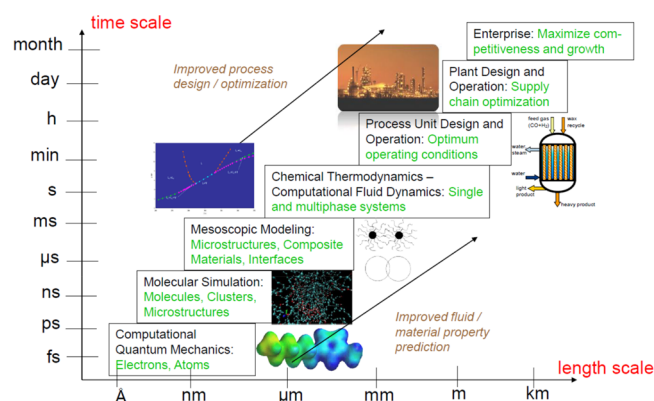


Figure 4. Hierarchical multiscale process design and modeling spans the entire spectrum of length and time scales.

molecular simulation.⁸¹ Dynamic light scattering data ended up being in excellent agreement with such predictions. As a manifestation of the accuracy of simulation methods in predicting physical properties, the *Journal of Chemical and Engineering Data*, a premier journal in publishing highly accurate thermodynamic data, accepts since 2010 publication of papers that contain molecular simulation data of *real* systems without any experimental work.

A powerful approach to reduce computing time without loss of accuracy in representing chemical and/or biological systems is the use of coarse-grained molecular models. In this approach, a group of atoms, or even molecules, is represented by a single interaction unit. Originated within the biochemistry simulation community, this approach is gaining importance in the oil & gas research community. Such an approach has not been validated widely for many different systems; yet, it is estimated that it provides predictions within a few percent for primary thermodynamic properties and around 10% or more for derivative and transport properties.

Furthermore, ML methods can be trained using data measured experimentally or generated by molecular simulation and this approach can be used to predict physical properties at significantly lower computational effort compared to molecular simulation alone. As an example, Snurr and co-workers at Northwestern University developed an ML predictive model for the design of metal–organic frameworks (MOFs) to be used for gas separations and other applications.⁸²

Molecular simulations of glassy and semi-crystalline solids would be surely more predictive than EoS, but the computational effort is high, due to the long equilibration times required by the glassy systems, or by the large size of the simulation box of semi-crystalline solids.⁸³ An improvement is expected from the development of multiscale methods, which combine the low computational cost of macroscopic models with the accuracy and predictive ability of molecular simulations,⁸⁴ which can for instance inspect the thermodynamic state of the amorphous–crystalline interface.

Last but not least, molecular simulation can be used to predict properties of very toxic, corrosive, or other systems and conditions where experimental work is impossible. However, it remains so that despite the fast-improving quality of molecular simulation results, they will never reduce the need for high quality actual experimental measurements.

3.3c. Description of Key Phenomena that Occur at the Nanoscale. Molecular simulation can be combined with other computational methods such as quantum mechanics calcu-

lations for the elucidation of elementary molecular processes at interfaces, including for instance catalytic processes. In a typical application, a cluster of molecules near a catalytic nanoparticle is modeled using *ab initio* wavefunction methods or semiempirical Hartree–Fock (HF) methods and results are used to parameterize a molecular force field that can be used subsequently in molecular simulations.⁸⁵

Molecular simulation has also been used extensively to predict properties of fluid under confinement with a diverse range of industrial applications that include CO₂ sequestration, H₂ storage, and many others. In most of these cases, experimental measurement of thermophysical properties is very cumbersome or even impossible. Molecular simulation can predict within reasonable accuracy both equilibrium, as well as transport properties of these systems and provides very valuable information on the effect of confinement, especially in the case where experimental data do not exist.⁸⁶ It can also generate accurate data that can be used at a higher coarse grain level, in such a way that calculations can be accelerated and/or systems at larger scales can be examined.⁸⁷

4. DATA

Data for thermodynamic and transport properties play a crucial role in process and product design, optimization of processes, sustainable energy usage, and safety assessment in a number of diverse disciplines, such as environmental, chemical, and mechanical engineering, biotechnology, and materials science. The ability to calculate the behavior of pure components, mixtures, certain process steps, entire plants, or even larger systems relies on the fact that the model needs to have information on the interaction between the molecules. Usually, this input information is supplied by pure-component and mixture parameters of thermophysical property models. These parameters are determined either by fitting them to experimental data or in their absence to data estimated using predictive property models, like group-contribution methods, molecular simulation, or COSMO-RS. Clearly, true experimental values are preferred, and we will next provide a summary of the existing vs non-existing experimental data. In a second section, we will discuss their quality, which is probably even more important than their availability. We will end this section with some recommendations.

4.1. Lack of Data. Although several property data banks (DETERM,^{88,92} DDB,⁸⁹ NIST-TRC,⁹⁰ DIPPR,⁹³ etc.) are available and grow every year by including newly measured data from the literature, there remains a general lack of data. This trend is increasing with time, as an increasing number of molecularly complex substances becomes of interest to industry, while the measurement capacities remain constant or tends to decrease in some parts of the world, as also pointed out by the survey.¹ Measurements are generally not directly funded; they are byproducts of funding programs dedicated to certain practical needs. Measurements funded by industry are usually confidential and data cannot be published, or only with a delay of several years.

Experimental data are available for about 100 compounds in a wide range of temperatures and pressures so that fundamental equations of state explicit in the Helmholtz energy have been developed to describe their thermodynamic properties with high accuracy.^{37,94} Many accurate and reliable property data are needed to fit the numerous EoS parameters. Fundamental EoS are of high value for industrial applications,^{33,94} e.g., for all calculations that need high accuracy and

even to support the evaluation of experimental raw data. Fundamental EoS for more pure substances are needed, but they can only be developed if high-quality property data will become available in a wide range of temperatures and pressures.

For almost 2000 pure components, data exist for the most important thermophysical properties, like the liquid density and the vapor pressure, as a function of temperature. They have been validated by the DIPPR consortium⁹¹ and high quality correlations are made available. Yet, it must be stressed that whenever data are missing (which may be the case for interfacial or transport properties), predictive approaches are used to develop the said correlations.

For thousands of other pure components, which are available in commercial data banks and in process simulators, only very few experimental data are known, e.g., the melting point. Pharmaceuticals and agrochemical substances become more complex and often are high-molecular-weight multifunctional compounds for which no or only few data are available.

For mixtures, the lack of data is even worse, e.g., for phase equilibrium data of non-ideal mixtures including electrolyte systems, data at high pressures, data in dilute conditions, cryogenic conditions, and for reactive multiphase systems. The required needs for measurements include all types of phase equilibria (VLE, LLE, VLLE, SLE, and SLVE), density, thermal, surface and derivative properties, e.g., heat capacities, and transport properties like viscosity, diffusion coefficients, and thermal conductivity.¹ Multicomponent system data are important for model validation, especially multicomponent LLE.

Literature searches may be frustrating because the Web of Knowledge and SciFinder, for example, provide natural-language searches with incomplete responses contaminated by a large amount of irrelevant references. In addition, we are convinced that many classified data exist, covered by long-gone confidentiality protections. It would be a great asset to the community at large to find resources for assessing them in a comprehensive way.

If no data are available and no predictive methods can be applied, then the analysis of the behavior of similar systems for which data exist can be very helpful to solve industrial problems. Therefore, research activities on the general behavior of classes of mixtures is also of interest for industrial applications.

The belief that measurements are expensive is mainly true for the first few data points since the apparatus needs to be set up and evaluated and the staff needs to be trained. Therefore, the measurement of many data points in a specialized apparatus is often less expensive than the individual measurements of each data point. During the last few decades, the number of experimental apparatuses that are available in industrial property labs has decreased. Methods focus on properties that are of importance for process and product design, e.g., measurements of phase equilibria and pure-component properties. To perform measurements with external partners is a valuable option, which has to deal with a couple of issues: (a) tight schedule, (b) confidential substances, (c) safety issues due to substances of (yet) not fully evaluated hazards, (d) issues with equipment suitability (e.g., corrosion), (e) availability and transport of sufficient amounts of substances, (f) administrative and legal issues, to name a few. Non-technical aspects, such as signing the contracts, transport of materials, and so on, may pose a

challenge for these external measurements, especially when the project time frame is tight.

4.2. Quality of Data. From the industrial point of view, there is also a widespread concern^{1,2} regarding data quality. The increasing number of publications on experimental thermophysical property data has enhanced the effort needed for data validation,⁹⁵ particularly due to the increase in the percentage of low-quality data being published.⁹⁶ For example, if several authors measure property data for the same system and they all claim an accuracy of 1% for their data, but the deviations between the data sets are 10% or even larger, strong doubts arise as discussed by Peper et al.⁹⁷ Before these data can be used for industrial applications an data quality evaluation has to be performed. A fit of model parameters to all existing data for a certain task often leads to a bad result since a few erroneous data points can have a huge negative impact on the quality of the fitted model. The trust in data published in the major international journals of thermophysical property data is in general high. Five journals have joined efforts (Journal of Chemical and Engineering Data, The Journal of Chemical Thermodynamics, Fluid Phase Equilibria, Thermochemica Acta, and International Journal of Thermophysics) for defining a quality standard in their accepted publications.⁹⁸ However, many new journals have come up and not all have a peer review process of the same specific expertise as the major thermophysical property journals resulting in the publication of low quality or even erroneous data. For example, a manuscript on high-pressure phase equilibria submitted to a journal of membrane science, green chemistry or energy technology will most likely have reviewers with a different expertise, than those from the thermophysical property community.

Many publications do not fulfill the requirements of Good Reporting Practice,⁹⁹ so that the quality of data is difficult to evaluate, e.g., data are not given in numerical format or the substances and methods are not sufficiently specified. There is a need to report systematically the experimental errors, to check the thermodynamic consistency of the finally reported values and to compare them with all available literature data. For several systems, many data sets have been published, e.g., for phase equilibria of CO₂–ethanol, including bad quality data. If one of those systems is used to validate the accuracy of an apparatus or an experimental method, it is easy to find a data set that agrees with own measurements, even if there is a disagreement with most of the other data sets. Often, only a few data points for a system are published, which makes the evaluation of data quality difficult. Good measurements are not easy to perform since many experimental challenges must be overcome.¹⁰⁰ A well-trained research staff that is aware of the many error sources is essential. This knowledge is usually generated in groups with long-established experimental expertise. Many industrial colleagues regret the decline of the number of these groups in Europe and North America. For all groups it is highly recommended to perform reference measurements in regular intervals to evaluate the accuracy of the apparatus and the method. This applies to both commercial and for self-developed equipment.

4.3. What Could be Done about the Lack and the Quality of Data?

1. Appraisal of the importance of data and recognition of experimentalists who can perform these demanding

measurements to obtain accurate and reliable quality data.

2. Guidelines for experimentalists for reporting data, e.g., Bazyleva *et al.*⁹⁹ or Chirico *et al.*⁹⁸ should become common knowledge. Authors, reviewers, and editors should be strict in preventing the publication of low-quality data. **Bad data are like fake news:** Once published, they will not disappear. An IUPAC project to promote reliability of VLE data is on-going.
3. False incentives should be avoided for researchers from funding agencies and universities, e.g., to publish many articles instead of publishing high-quality articles. Publication in one of the five journals⁹⁸ that have agreed on quality criteria (or possibly others if they commit themselves to the same quality criteria) should be highly recommended (if not imposed).
4. Further development of a set of test systems with recommended high-quality data in a wide range of temperatures and pressures.⁵⁵ All apparatuses and methods should be checked in regular intervals against at least one of the test systems, particularly in the temperature and pressure range of interest.
5. Development of experimental expertise in more groups in academia and/or contract research organizations, e.g., in collaboration with industrial partners.
6. Encourage public funding toward data measurement to fill important gaps and toward an understanding of the behavior of classes of mixtures.
7. Extend consortia with industrial partners to fill data gaps, e.g., by measuring phase equilibria and excess enthalpies to determine missing parameters of GC methods.
8. To reduce the lack of data on properties that are not easily accessible via measurement computational methods like molecular simulations or methods based on quantum chemistry like COSMO-RS can be used.
9. There is a need to simplify administrative efforts of publicly funded projects. Several companies do no longer accept money in publicly funded projects due to excessive administrative issues before, during, and after the project.
10. Development and applications of hybrid models (combination of thermophysical models and ML algorithms) for interpolation of data, to improve predictive methods, or to find correlations between properties.

5. EDUCATION, TRAINING, AND NETWORKING

5.1. Diploma Education. In the survey on “Industrial Requirements for Thermodynamic and Transport Properties: 2020”,¹ special attention was given to education and training, as well as collaboration. Chemical engineering education and the role of thermodynamics were discussed quite extensively by many participants of the survey, mainly the shortening of studies (Bologna process) in some European countries, but also noting the lack of knowledge of basic thermodynamics and associated models. To bridge this gap, additional education and training is required. Education on different levels was perceived as a key to successful application of thermodynamics in industry. Therefore, not only the education on the basic level, e.g., undergraduate or graduate education, but life-long education and training should be encouraged. An analysis of the thermodynamic education in both undergraduate and post-

graduate programs in Europe and the United States was presented more than 10 years ago in a survey, carried out under the auspices of the WP on TTP,¹⁰¹ where teaching in terms of quantity, content, and structure (teaching methods) of the TTP courses as well as textbooks were discussed. Some differences between the USA and Europe were noted with regard to the descriptions on the atomistic/molecular level and on the relative amount of problem-based learning as well as home assignments.

Any chemical engineer should have a basic idea of phase equilibria and of the main models, but beyond that, there is a need to train experts in the field. The most efficient way to that end is doctoral training. This kind of education is limited by (1) the capacity to find interested students, (2) the number of PhD grants, and (3) the career opportunities that can be offered to the graduates. On this last point, a decrease in industrial experts is an issue of concern since it undermines the capability of industry to debottleneck and innovate. Applied thermodynamics is essential for many chemical engineering calculations and designs, and errors will reduce, or possibly even overshadow, the efficiency of process improvements. Nonetheless, a trend of declining expertise is observed in many companies. It is a worrying development not only for the health of the companies but also for the attractiveness of future generations to develop themselves as specialists.

5.2. Life-Long Education. Due to the various challenges and applications of thermodynamics in industrial processes that an engineer needs to face during his/her career, there is a need for life-long education and training of industrial professionals. In an early career, the process engineer must be aware of some basic thermodynamics including the models that might be suitable for a specific application/system. This is paramount as the practicing engineer will come across a variety of different simulators with thermodynamic models embedded. Due to new emerging application areas, sustainable processes, advanced materials, and new components that industry faces, the field of thermophysical properties is evolving and the engineers using thermodynamic tools need to be aware of the strengths and limitations of these tools. They must know when to consult a thermodynamic expert in case of need, and the expert must remain up to date. The role of the industrial expert is often undervalued: the presence of such an expert helps speed up innovation because of a faster understanding of feasible pathways, reduce cost because they will be able to optimize the simulation tools to better fit the physical behavior, and avoid accidents, as their training will alert them to pre-empt unexpected events. The expert will likewise facilitate the interactions with academic and possible consortium partners by expressing the industrial vision and needs, thus avoiding waste of time, energy, and funding.

The role of the expert is to be aware of the new developments,¹⁰² actively attending, and perhaps developing educational and training methods (among which one finds workshops, seminars, summer schools, conferences, webinars, on-line courses, publications and books).

5.3. Conferences and Workshops. The organization of workshops, summer schools, or webinars^{103,104} are efficient ways for the participants to learn about the new developments in a particular area. This is especially useful for graduate students to develop additional skills, knowledge, and experience for future employees.

Conferences are extremely well-suited for learning about new developments and for meeting other participants both

from academia, industry, and software suppliers. The human factor is very important for exchanging ideas that go both ways: academics can learn about industrial needs and challenges, while practicing engineers learn about new developments. The COVID-19 pandemic has had a very negative impact on this process that was only partly redeemed by the development of remote interactions. One area that is perhaps not sufficiently developed in engineering conferences is workshops and tutorials that provide a more detailed examination of particular topics. It is key to be able to strike a balance between the number of conferences that cannot be too many; otherwise, the selection becomes difficult and industrial professionals may not be able to attend. On the other side, the size of the conference is playing also an important role on intensity of ideas exchanged. Smaller conferences are more appropriate for true and long-lasting interactions, but at larger conferences, the participants may widen their horizon and have a possibility to find more interdisciplinary connections.

As an example of successful workshops within chemical engineering conferences, special mention should be given to the 'Industrial Use of Thermodynamics' (IUT), symposia,^{3–7} initiated by the EFCE TTP WP, and mainly organized within the framework of the other, larger, conferences. During each IUT Symposium, a round table discussion was organized to give the opportunity to both industrial and academic professionals to present their view on various topics of interest.

Among the number of Thermodynamic Conferences, the ESAT (European Symposium on Applied Thermodynamics) as well as PPEPPD (Properties & Phase Equilibria for Product & Process Design) Conferences and the Boulder Symposium on Thermophysical Properties should be highlighted. These conferences offer forum for academic and industrial researchers to meet and communicate on the development and trends in thermophysical properties, phase equilibria, modeling, and simulations, with importance to design of processes and products.

5.4. Specific Initiatives. As pointed out during several of the IUT sessions, software providers have an important responsibility in the transfer of new technologies to their engineering customers. They offer customer support through different channels, as well as through training sessions organized across the globe or online and by providing examples in their manuals. In addition, courses on Chemical Thermodynamics for Process Simulation for academia and industry were regularly organized in the past by Oldenburg University in Germany and nowadays by Rareytec Europe Online, where participants become familiar with the capabilities and limitations of currently used methods and models. The behavior of multicomponent mixtures is covered, with special attention to phase equilibria, also electrolyte systems and various approaches to process engineering problems using modern thermodynamic methods are presented. Different courses are also offered by software providers.

Being a member of different consortia (UNIFAC, DIPPR, CERE, KT-Consortium, EleTher, etc.) also brings benefits to industrial partners. For example, the UNIFAC consortium was organized to support the revision, extension, and further development of the Group Contribution Methods UNIFAC, modified UNIFAC (Dortmund), and the Predictive Equations of State PSRK and VTPR. Moreover, such consortia provide a welcome platform for the company specialist to meeting each other (peer contact), which is a valuable and important attribute in the current situation of shrinking expert groups in

Thermodynamics as a driver for sustainable development

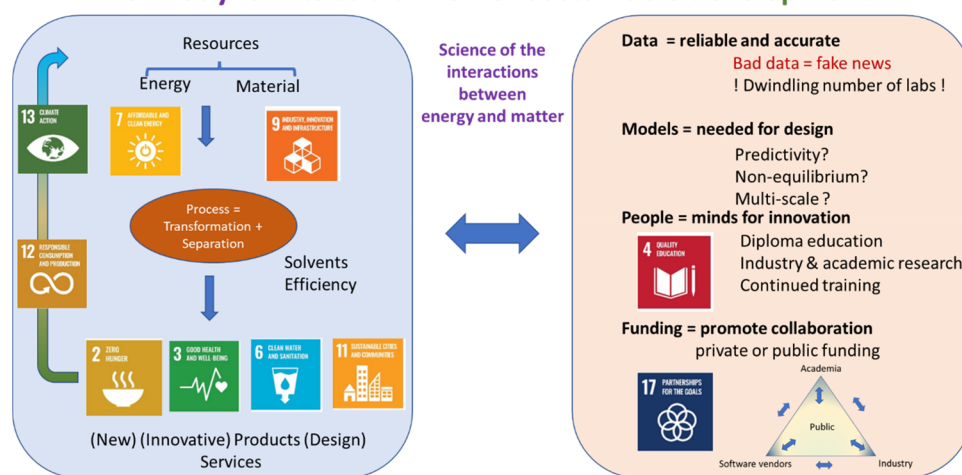


Figure 5. Main messages to remember from this paper.

industry. The models developed by the mentioned consortia are used worldwide for the synthesis and design of separation processes and many further applications of industrial interest, while DIPPR represents the industry standard for pure component physical properties, which are critically evaluated.

5.5. Handbooks and Publications. Last but not least, a continued transfer of knowledge is provided through publications and handbooks. Several high impact journals propose review papers that make it possible for a larger community to have access to the latest developments in thermodynamics and transport properties (Fluid Phase Equilibria, Journal of Chemical and Engineering Data, Journal of Physical Chemistry B, International Journal of Thermodynamics, Journal of Chemical Thermodynamics, Journal of Physical and Chemical Reference Data, etc.). The high cost of subscribing to different journals may be an issue for general public or private companies, but increasing care is given to open access options and non-edited versions of these documents are often available in open access archives. Very interesting textbooks also exist that explain sometimes complex topics at length and make them thus more easily accessible to practicing engineers.^{27–30,105–108} Even though writing such documents implies generally a very large investment of time and resources by the author(s), such efforts should be highly recommended as it adds to long-lasting and easily accessible bank of information that is available both for teaching and for applications. More recently, an initiative has appeared proposing a guide for selecting models through a web application.³¹

6. CONCLUSIONS

This document aims at sharing the views of the authors, who are all members of the EFCE Working Party on Thermodynamics and Transport Properties, on the big challenges that lie ahead in their domain of activity. It arises in a response to the recent survey carried out by the EFCE Working Party on industrial needs in the area of applied thermodynamics.¹ An attempt to summarize the main messages is proposed in Figure 5.

The paper is organized so as to first put thermodynamics in the context of the current drive to developing sustainable and circular economy. This is illustrated in the left part of the figure and in the first section of the paper. In the right part of the

figure, we discuss the answers that the engineering community can offer to these societal challenges. We believe that applied thermodynamics has a very important role to play in economic transition to sustainable and circular economy by providing models, tools, and data to the engineering community for reducing the environmental impact of human activity while maintaining a reasonable standard of living in our societies. In other words, it remains of crucial importance that public and private funds be invested, and that young bright and motivated people choose a career path in the field of applied thermodynamics. The link between applications and the science of thermodynamics may not always be obvious to recognize, but we have attempted in this paper to illustrate it through some examples.

In the second and third section, we considered the issues that have been revealed by a recent survey that was conducted by the working party regarding property modeling and experimental data. The outcomes of the survey indicate several industrial needs that are not fully satisfied. We specifically recommend that the future research should focus on complex poly functional molecules (pharmaceuticals, bio-based materials, surface active agents, etc.), polymers, and electrolytes as in these areas the current approaches are not satisfactory. We also highlighted the increasing capacity of molecular simulation not only to help in understanding the different phenomena and providing reliable data but also for designing models and processes that rely on microscopic phenomena.

Reliable and accurate data play an essential role in any further progress. Even though there have been great improvements in our computational powers to generate data, the importance of keeping high-quality experimental labs and expertise is paramount. The overwhelming majority of models used in industry is based on parameters that have been fitted to experimental data and the lack of reliable data is enormous. We provided a list of 10 points that summarizes in our opinion the areas that need to be addressed.

We believe that future progress will necessarily require collaborative efforts between academia, software vendors and industry, and like to insist on the importance of allocating both public and private funding for such endeavors. The funding agencies should encourage close collaboration of the editors of scientific journals with reviewers and researchers. Motivating public funders is often found to be difficult because the applied

thermodynamics field is very transverse, technical, and long-established. The latter implying to most funders that there are no longer any problems worth solving. Private funders are primarily concerned about their competitive interest and may therefore not want to share the latest developments. We strongly believe that applied thermodynamics plays a key role and has a lot to offer both to companies and to society in general. Employing experts in the field as well as participating to joint efforts, are essential for innovations toward a more sustainable future. There is a clear need for our community to communicate this more successfully to policymakers, higher management, and other funders.

In a final section, we have highlighted the importance of the people. Attracting and educating young and enthusiastic collaborators in this field is essential. Yet, probably even more so is being able to collaborate with other domains. This implies an open mind, but also tools that make it possible to keep ahead of the latest developments. Several modes of communicating about the new developments are presented. We stressed in particular that successful communication goes both ways. It is important that thermodynamic experts are aware of the new challenges that industry faces, but it is equally important that practicing chemical engineers know about the strengths and limitations of their models and about the innovations that may be of interest for their applications, not only in the chemical industry but also in other areas ranging from mining to medicine. Education and training are essential in this respect.

AUTHOR INFORMATION

Corresponding Author

Jean-Charles de Hemptinne – IFP Energies nouvelles, Rueil-Malmaison 92852, France; orcid.org/0000-0003-1607-3960; Email: jean-charles.de-hemptinne@ifpen.fr

Authors

Georgios M. Kontogeorgis – Center for Energy Resources Engineering (CERE), Department of Chemical and Biochemical Engineering, Technical University of Denmark, Lyngby DK-2800, Denmark; orcid.org/0000-0002-7128-1511

Ralf Dohrn – Bayer AG, Process Technologies, Leverkusen 51368, Germany

Ioannis G. Economou – Chemical Engineering Program, Texas A&M University at Qatar, Doha 23874, Qatar; orcid.org/0000-0002-2409-6831

Antoon ten Kate – Nouryon, Deventer 7418 AJ, The Netherlands

Susanna Kuitunen – Neste Engineering Solutions Oy, Porvoo FI-06101, Finland

Ljudmila Fele Žilnik – Department of Catalysis and Chemical Reaction Engineering, National Institute of Chemistry, Ljubljana 1001, Slovenia

Maria Grazia De Angelis – Institute for Materials and Processes, School of Engineering, University of Edinburgh, Edinburgh EH9 3FB, UK; Department of Civil, Chemical, Environmental and Materials Engineering University of Bologna, Bologna 40131, Italy

Velisa Vesovic – Department of Earth Science and Engineering, Imperial College London, South Kensington Campus, London SW7 2AZ, United Kingdom

Complete contact information is available at:
<https://pubs.acs.org/10.1021/acs.iecr.2c01906>

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The free access fee is paid by the EleTher IFP-School chair.

ABBREVIATIONS

CERE	Center for Energy Resources Engineering (DTU consortium)
COSMO-RS	CONductor like Screening Model-Real Solvent
COSMO-SAC	CONductor like Screening Model-Segment Activity Coefficient
DIPPR	Design Institute for Physical Properties (AIChE consortium)
EleTher	Electrolyte Thermodynamics (IFPEN consortium)
e-NRTL	electrolyte Non Random Two Liquids (activity coefficient model)
GC	Group Contribution
GERG	Groupe Européen de Recherche Gazières (multiparameter equation of state)
IUPAC	International Union for Pure and Applied Chemistry
NIST	National Institute for Standards and Technology
NRTL	Non Random Two Liquids (activity coefficient model)
PSRK	Predictive Soave-Redlich-Kwong (equation of state)
REACH	Registration, Evaluation, Authorization and restriction of Chemicals (EU regulation)
SAFT	Statistical Associating Fluid Theory (equation of state)
SDG	Sustainable Development Goals
TDE	Thermo Data Engine
UNIFAC	Universal Functional Activity Coefficients (activity coefficient model)
UNIFAC(Do)	Universal Functional Activity Coefficients (Dortmund version) (activity coefficient model)
VTPR	Volume-Translated Peng-Robinson (equation of state)

REFERENCES

- (1) Kontogeorgis, G. M.; Dohrn, R.; Economou, I. G.; de Hemptinne, J.-C.; TEN, A.; Kuitunen, S.; Mooijer, M.; Žilnik, L. F.; Vesovic, V. Industrial Requirements for Thermodynamic and Transport Properties: 2020. *Ind. Eng. Chem. Res.* **2021**, 60, 4987–5013.
- (2) Hendriks, E.; Kontogeorgis, G. M.; Dohrn, R.; de Hemptinne, J. C.; Economou, I. G.; Žilnik, L. F.; Vesovic, V. Industrial Requirements for Thermodynamics and Transport Properties. *Ind. Eng. Chem. Res.* **2010**, 49, 11131–11141.
- (3) Kontogeorgis, G. M.; Jaubert, J.-N.; de Hemptinne, J.-C. Editorial. *Oil Gas Sci. Technol.* **2013**, 68, 187–215.
- (4) Economou, I. G.; de Hemptinne, J.-C.; Dohrn, R.; Hendriks, E.; Keskinen, K.; Baudouin, O. Industrial use of thermodynamics workshop: Round table discussion on 8 July 2014. *Chem. Eng. Res. Des.* **2014**, 92, 2795–2796.
- (5) de Hemptinne, J.-C.; Ferrasse, J.-H.; Gorak, A.; Kjelstrup, S.; Maréchal, F.; Baudouin, O.; Gani, R. Energy efficiency as an example of cross-discipline collaboration in chemical engineering. *Chem. Eng. Res. Des.* **2017**, 119, 183–187.

- (6) Mathias, P. M.; Soto, A.; Fele-Zilnik, L.; de Hemptinne, J. C.; Bazyleva, A.; Abildskov, J. Data quality and assessment, validation methods and error propagation through the simulation software: Report from the Round-Table Discussion at the 10th World Congress of Chemical Engineering in Barcelona (October 1–5, 2017). *Chem. Eng. Res. Des.* **2018**, *137*, A1–A8.
- (7) Kontogeorgis, G. M.; Kate, A.; ten Huijw-Riberaud, M.; de Hemptinne, J.-C. Conclusions from Round Table Discussion during IUT of ESAT 2021 electrolyte thermodynamics challenges - From industrial needs to academic research. *Fluid Phase Equilib.* **2022**, *556*, 113399.
- (8) *The Global Goals*. <http://www.globalgoals.org/>, consulted 5 january2022.
- (9) United Nations. *The 17 goals for Sustainable Development* (un.org). <https://sdgs.un.org/goals>, consulted 5 january 2022.
- (10) American Chemical Society. *Chemistry & Sustainable Development Goals*. <https://www.acs.org/content/acs/en/sustainability/chemistry-sustainable-development-goals.html>, consulted 5 january 2022.
- (11) Szargut, J. *Exergy method : Technical and ecological applications*. WIT, Southampton, 2005, (xvii), 164.
- (12) Kotas, V. T., ed. *The exergy method of thermal plant analysis*. Butterworth Publishers, 1985.
- (13) Favrat, D.; Marechal, F.; Epelly, O. The challenge of introducing an exergy indicator in a local law on energy. *19th International Conference on Efficiency, Cost, Optimization, Simulation and Environmental Impact of Energy Systems ECOS 2006*, 2008, *33*, 2, 130–136, DOI: 10.1016/j.energy.2007.10.012.
- (14) Peters, J. F. Reinventing exergy as indicator for resource depletion impacts in LCA. *Mater. Technol.* **2020**, *108*, 5–6.
- (15) Michaelides, E. E. Thermodynamics, Energy Dissipation, and Figures of Merit of Energy Storage Systems—A Critical Review. *Energies* **2021**, *14*, 19.
- (16) Müller, K.; Mokrushina, L.; Arlt, W. Thermodynamic Constraints for the Utilization of CO₂. *Chem. Ing. Tech.* **2014**, *86*, 497–503.
- (17) Hu, S.; Yang, Z.; Li, J.; Duan, Y. A Review of Multi-Objective Optimization in Organic Rankine Cycle (ORC) System Design. *Energies* **2021**, *14*, 20.
- (18) Kontogeorgis, G. M.; Holster, A.; Kottaki, N.; Tsochantaris, E.; Topsøe, F.; Poulsen, J.; Bache, M.; Liang, X.; Blom, N. S.; Kronholm, J. Water structure, properties and some applications – A review. *Chem. Thermodyn. Thermal Anal.* **2022**, *6*, 100053.
- (19) Nieto-Draghi, C.; Fayet, G.; Creton, B.; Rozanska, X.; Rotureau, P.; de Hemptinne, J.-C.; Ungerer, P.; Rousseau, B.; Adamo, C. A General Guidebook for the Theoretical Prediction of Physicochemical Properties of Chemicals for Regulatory Purposes. *Chem. Rev.* **2015**, *115*, 13093–13164.
- (20) ten Kate, A. J. B.; Piccione, P. M.; Westbye, P.; Becker, A. F. An industrial and chemical engineering perspective on the formulation of active ingredients in pharmaceuticals and agrochemicals. *Curr. Opin. Chem. Eng.* **2022**, *36*, 100747.
- (21) Enekvist, M. *Computer-Aided Product Design of Organic Coatings*; Danish Technical University: Denmark, 2021.
- (22) Gani, R.; Baldyga, J.; Biscans, B.; Brunazzi, E.; Charpentier, J.-C.; Drioli, E.; Feise, H.; Furlong, A.; van Geem, K. M.; de Hemptinne, J.-C.; ten Kate, A. J.; Kontogeorgis, G. M.; Manenti, F.; Marin, G. B.; Mansouri, S. S.; Piccione, P. M.; Pova, A.; Rodrigo, M. A.; Sarup, B.; Sorensen, E.; Udugama, I. A.; Woodley, J. M. A multi-layered view of chemical and biochemical engineering. *Chem. Eng. Res. Des.* **2020**, *155*, A133–A145.
- (23) Sholl, D. S.; Lively, R. P. Seven chemical separations to change the world. *Nature* **2016**, *532*, 435–437.
- (24) Jirasek, F.; Hasse, H. Perspective: Machine Learning of Thermophysical Properties. *Fluid Phase Equilib.* **2021**, *549*, 113206.
- (25) Abildskov, J.; Kontogeorgis, G. M. Chemical Product Design: A New Challenge of Applied Thermodynamics. *Chem. Eng. Res. Des.* **2004**, *82*, 1505–1510.
- (26) Vidal, J. *Thermodynamics: Applications in Chemical Engineering and the Petroleum Industry*; Editions Technip, 2003.
- (27) Kontogeorgis, G. M.; Folas, G. K. *Thermodynamic Models for Industrial Applications: From Classical and Advanced Mixing Rules to Association Theories*; Wiley, 2010.
- (28) Prausnitz, J. M.; Lichtenthaler, R. N.; Gomes de Azevedo, E. *Molecular Thermodynamics of Fluid Phase Equilibria*; Prentice Hall Int, 1999.
- (29) Poling, B. E.; Prausnitz, J. M.; O'Connell, J. P. *The Properties of Gases and Liquids*; McGraw-Hill Education 2001.
- (30) de Hemptinne, J.-C.; Ledanois, J.-M.; Mougin, P.; Barreau, A. *Select Thermodynamic Models for Process Simulation - A Practical Guide using a Three Steps Methodology*; Editions Technip, 2012.
- (31) IFP-School. Choose my model <https://view.genial.ly/617969334c81c40db6c41ec2/presentation-choose-your-model>.
- (32) Le Guennec, Y.; Privat, R.; Lasala, S.; Jaubert, J.-N. On the imperative need to use a consistent α -function for the prediction of pure-compound supercritical properties with a cubic equation of state. *Fluid Phase Equilib.* **2017**, *445*, 45–53.
- (33) Span, R.; Lemmon, E. W.; Jacobsen, R. T.; Wagner, W.; Yokozeki, A. A reference equation of state for the thermodynamic properties of nitrogen for temperatures from 63.151 to 1000 K and pressures to 2200 MPa. *J. Phys. Chem. Ref. Data* **2000**, *29*, 1361–1433.
- (34) Jacobsen, R. T.; Stewart, R. B. Thermodynamic properties of nitrogen including liquid and vapor phases from 63 K to 2000 K with pressures to 10000 bar. *J. Phys. Chem. Ref. Data* **1973**, *2*, 757–922.
- (35) Jaeschke, M.; Audibert, S.; van Cangehem, P.; Humphreys, A. E.; Janssen-Van, R. R.; Pelle, Q.; Schouten, J. A.; Michels, J. P. J. Accurate prediction of compressibility by the GERG (Groupe européen de recherches gazières) virial equation. *SPE Prod. Eng.* **1991**, *6*, 343–349.
- (36) Kunz, O.; Wagner, W. The GERG-2008 Wide-Range Equation of State for Natural Gases and Other Mixtures – An Expansion of GERG-2004. *J. Chem. Eng. Data* **2012**, *57*, 3032–3091.
- (37) Lemmon, E.; Bell, I. H.; Huber, M. L.; McLinden, M. O. *NIST Standard Reference Database 23: Reference Fluid Thermodynamic and Transport Properties-REFPROP*; National Institute of Standards and Technology. Standard Reference Data Program: Gaithersburg, 2018.
- (38) Fredenslund, A. Unifac and Related Group-Contribution Models for Phase-Equilibria. *Fluid Phase Equilib.* **1989**, *52*, 135–150.
- (39) Huron, M. J.; Vidal, J. New mixing rules in simple equations of state for representing vapour-liquid equilibria of strongly non-ideal mixtures. *Fluid Phase Equilib.* **1979**, *3*, 255–271.
- (40) Holderbaum, T. G.; Gmehling, J. PSRK: A Group Contribution Equation of State Based on UNIFAC. *Fluid Phase Equilib.* **1991**, *70*, 251–265.
- (41) Schmid, B.; Gmehling, J. The universal group contribution equation of state VTPR present status and potential for process development : 12th International Conference on Properties and Phase Equilibria for Product and Process Design. *Fluid Phase Equilib.* **2011**, *302*, 213–219.
- (42) Jaubert, J. N.; Vitu, S.; Mutelet, F.; Corriou, J. P. Extension of the PPR78 model (predictive 1978, Peng-Robinson EOS with temperature dependent $k(ij)$ calculated through a group contribution method) to systems containing aromatic compounds. *Fluid Phase Equilib.* **2005**, *237*, 193–211.
- (43) Qian, J.-W.; Privat, R.; Jaubert, J.-N. Predicting the Phase Equilibria, Critical Phenomena, and Mixing Enthalpies of Binary Aqueous Systems Containing Alkanes, Cycloalkanes, Aromatics, Alkenes, and Gases (N₂, CO₂, H₂S, H₂) with the PPR78 Equation of State. *Ind. Eng. Chem. Res.* **2013**, *52*, 16457–16490.
- (44) Nguyen Thi, T. X.; Tamouza, S.; Tobaly, P.; Passarello, J. P.; de Hemptinne, J. C. Application of Group Contribution SAFT equation of state (GC-SAFT) to model phase behaviour of light and heavy esters. *Fluid Phase Equilib.* **2005**, *238*, 254–261.
- (45) Tihic, A.; Kontogeorgis, G. M.; von Solms, N.; Michelsen, M. L.; Constantinou, L. A predictive Group-Contribution Simplified PC-

SAFT Equation of State: Application to Polymer Systems. *Ind. Eng. Chem. Res.* **2008**, *47*, 5092–5101.

(46) Lymperiadis, A.; Adjiman, C. S.; Galindo, A.; Jackson, G. A group contribution method for associating chain molecules based on the statistical associating fluid theory (SAFT-gamma). *J. Chem. Phys.* **2007**, *127*, 234903.

(47) Mac, D. N.; Pereira, F. E.; Llovel, F.; Blas, F. J.; Adjiman, C. S.; Jackson, G.; Galindo, A. Transferable SAFT-VR Models for the Calculation of the Fluid Phase Equilibria in Reactive Mixtures of Carbon Dioxide, Water, and n-Alkylamines in the Context of Carbon Capture. *J. Phys. Chem. B* **2011**, *115*, 8155–8168.

(48) Kang, J. W.; Diky, V.; Chirico, R. D.; Magee, J. W.; Muzny, C. D.; Abdulagatov, I.; Kazakov, A. F.; Frenkel, M. A new method for evaluation of UNIFAC interaction parameters. *Fluid Phase Equilib.* **2011**, *309*, 68–75.

(49) Kang, J. W.; Diky, V.; Frenkel, M. New modified UNIFAC parameters using critically evaluated phase equilibrium data. *Fluid Phase Equilib.* **2015**, *388*, 128–141.

(50) Ge, K.; Ji, Y. Novel Computational Approach by Combining Machine Learning with Molecular Thermodynamics for Predicting Drug Solubility in Solvents. *Ind. Eng. Chem. Res.* **2021**, *60*, 9259–9268.

(51) Klamt, A. *COSMO-RS: From Quantum Chemistry to Fluid Phase Thermodynamics and Drug Design*; Elsevier Science & Technology, Amsterdam, 2005.

(52) Umer, M.; Albers, K.; Sadowski, G.; Leonhard, K. PC-SAFT parameters from ab initio calculations. *Fluid Phase Equilib.* **2014**, *362*, 41–50.

(53) Gmehling, J.; Wittig, R.; Lohmann, J.; Joh, R. A modified UNIFAC (Dortmund) model. 4. Revision and extension. *Ind. Eng. Chem. Res.* **2002**, *41*, 1678–1688.

(54) Walker, P. J.; Yew, H.-W.; Riedemann, A. Clapeyron.jl: An Extensible, Open-Source Fluid Thermodynamics Toolkit. *Ind. Eng. Chem. Res.* **2022**, *61*, 7130–7153.

(55) Jaubert, J.-N.; Le, Y.; Piña-Martinez, A.; Ramirez-Velez, N.; Lasala, S.; Schmid, B.; Nikolaidis, I. K.; Economou, I. G.; Privat, R. Benchmark Database Containing Binary-System-High-Quality-Certified Data for Cross-Comparing Thermodynamic Models and Assessing Their Accuracy. *Ind. Eng. Chem. Res.* **2020**, *59*, 14981–15027.

(56) Alfradique, M. F.; Castier, M. Critical points of hydrocarbon mixtures with the Peng–Robinson, SAFT, and PC-SAFT equations of state. *Fluid Phase Equilib.* **2007**, *257*, 78–101.

(57) Kontogeorgis, G. M.; Maribo-Mogensen, B.; Thomsen, K. The Debye–Hückel theory and its importance in modeling electrolyte solutions. *Fluid Phase Equilib.* **2018**, *462*, 130–152.

(58) Oishi, T.; Prausnitz, J. M. Estimation of solvent activities in polymer solutions using a group-contribution method. *Ind. Eng. Chem. Process Des. Dev.* **1978**, *17*, 333–339.

(59) Flory, P. J. Thermodynamics of High Polymers Solutions - Letter to the editors. *J. Chem. Phys.* **1941**, *9*, 660–661.

(60) Sanchez, I. C.; Lacombe, R. H. Statistical Thermodynamics of Polymer-Solutions. *Macromolecules* **1978**, *11*, 1145–1156.

(61) de Angelis, M. G.; Sarti, G. C. Solubility of gases and liquids in glassy polymers. *Annu. Rev. Chem. Biomol. Eng.* **2011**, *2*, 97–120.

(62) Atiq, O.; Ricci, E.; Baschetti, M. G.; de Angelis, M. G. Modelling solubility in semi-crystalline polymers: a critical comparative review. *Fluid Phase Equilib.* **2022**, *556*, 113412.

(63) Peters, F. T.; Laube, F. S.; Sadowski, G. Development of a group contribution method for polymers within the PC-SAFT model. *Fluid Phase Equilib.* **2012**, *324*, 70–79.

(64) Gani, R. Group contribution-based property estimation methods: advances and perspectives. *Curr. Opin. Chem. Eng.* **2019**, *23*, 184–196.

(65) Patra, T. K. Data-Driven Methods for Accelerating Polymer Design. *ACS Polymers Au* **2022**, *2*, 8–26.

(66) Assael, M. J.; Goodwin, A. R. H.; Vesovic, V.; Wakeham, W. A. *Advances in Transport Properties of Fluids*; Royal Society of Chemistry: Cambridge, U.K., 2014.

(67) Hellmann, R. Cross Second Virial Coefficients and Dilute Gas Transport Properties of the Systems (N₂ + C₃H₈), (C₂H₆ + C₃H₈), and (H₂S + C₃H₈) from Ab Initio-Based Intermolecular Potentials. *J. Chem. Eng. Data* **2020**, *65*, 4712–4724.

(68) Velliadou, D.; Antoniadis, K. D.; Assael, M. J.; Huber, M. L. Reference Correlation for the Viscosity of Propane-1,2-diol (Propylene Glycol) from the Triple Point to 452 K and up to 245 MPa. *Int. J. Thermophys.* **2022**, *43*, 42.

(69) Llovel, F.; Marcos, R. M.; Vega, L. F. Free-Volume Theory Coupled with Soft-SAFT for Viscosity Calculations: Comparison with Molecular Simulation and Experimental Data. *J. Phys. Chem., B* **2013**, *117*, 8159–8171.

(70) de Wijn, A. S.; Riesco, N.; Jackson, G.; Martin Trusler, J. P.; Vesovic, V. Viscosity of liquid mixtures: The Vesovic-Wakeham method for chain molecules. *J. Chem. Phys.* **2012**, *136*, 74514.

(71) Lötgering-Lin, O.; Gross, J. Group Contribution Method for Viscosities Based on Entropy Scaling Using the Perturbed-Chain Polar Statistical Associating Fluid Theory. *Ind. Eng. Chem. Res.* **2015**, *54*, 7942–7952.

(72) Hopp, M.; Gross, J. Thermal Conductivity from Entropy Scaling: A Group-Contribution Method. *Ind. Eng. Chem. Res.* **2019**, *58*, 20441–20449.

(73) López, E. R.; Pensado, A. S.; Comuñas, M. J. P.; Pádua, A. A. H.; Fernández, J.; Harris, K. R. Density scaling of the transport properties of molecular and ionic liquids. *J. Chem. Phys.* **2011**, *134*, 144507.

(74) Motahhari, H.; Satyro, M. A.; Taylor, S. D.; Yarranton, H. W. Extension of the Expanded Fluid Viscosity Model to Characterized Oils. *Energy Fuels* **2013**, *27*, 1881–1898.

(75) McCabe, C.; Bair, S.; Moore, J. eds. *10th Industrial Fluid Simulation Challenge*; Elsevier: 2020.

(76) Raymond Mountain *Industrial Fluid Properties Simulation Collective*. <http://fluidproperties.org/>.

(77) Gajardo-Parra, N. F.; Cotroneo-Figueroa, V. P.; Aravena, P.; Vesovic, V.; Canales, R. I. Viscosity of Choline Chloride-Based Deep Eutectic Solvents: Experiments and Modeling. *J. Chem. Eng. Data* **2020**, *65*, 5581–5592.

(78) Novak, L. T. Fluid Viscosity-Residual Entropy Correlation. *Int. J. Chem. React. Eng.* **2011**, *9*, 1.

(79) Papavasileiou, K. D.; Peristeras, L. D.; Bick, A.; Economou, I. G. Molecular Dynamics Simulation of Pure n-Alkanes and Their Mixtures at Elevated Temperatures Using Atomistic and Coarse-Grained Force Fields. *J. Phys. Chem. B* **2019**, *123*, 6229–6243.

(80) Krokidas, P.; Moncho, S.; Brothers, E. N.; Castier, M.; Economou, I. G. Tailoring the gas separation efficiency of metal organic framework ZIF-8 through metal substitution: a computational study. *Phys. Chem. Chem. Phys.* **2018**, *20*, 4879–4892.

(81) Heller, A.; Koller, T. M.; Rausch, M. H.; Fleys, M. S. H.; Bos, A. N. R.; van der Laan, G. P.; Makrodimitri, Z. A.; Economou, I. G.; Fröba, A. P. Simultaneous determination of thermal and mutual diffusivity of binary mixtures of n-octacosane with carbon monoxide, hydrogen, and water by dynamic light scattering. *J. Phys. Chem. B* **2014**, *118*, 3981–3990.

(82) Rosen, A. S.; Iyer, S. M.; Ray, D.; Yao, Z.; Aspuru-Guzik, A.; Gagliardi, L.; Notestein, J. M.; Snurr, R. Q. Machine learning the quantum-chemical properties of metal–organic frameworks for accelerated materials discovery. *Matter* **2021**, *4*, 1578–1597.

(83) Vergadou, N.; Theodorou, D. N. Molecular Modeling Investigations of Sorption and Diffusion of Small Molecules in Glassy Polymers. *Membranes* **2019**, *9*, 98.

(84) Ricci, E.; Minelli, M.; de Angelis, M. G. A multiscale approach to predict the mixed gas separation performance of glassy polymeric membranes for CO₂ capture: the case of CO₂/CH₄ mixture in Matrimid®. *J. Membr. Sci.* **2017**, *539*, 88–100.

(85) Papavasileiou, K. D.; Peristeras, L. D.; Bick, A.; Economou, I. G. Molecular Dynamics Simulation of the n-Octacosane–Water Mixture Confined in Graphene Mesopores: Comparison of Atomistic and Coarse-Grained Calculations and the Effect of Catalyst Nanoparticle. *Energy Fuels* **2021**, *35*, 4313–4332.

- (86) Mercier Franco, L. F.; Castier, M.; Economou, I. G. Diffusion in Homogeneous and in Inhomogeneous Media: A New Unified Approach. *J. Chem. Theory Comput.* **2016**, *12*, 5247–5255.
- (87) Apostolopoulou, M.; Santos, M. S.; Hamza, M.; Bui, T.; Economou, I. G.; Stamatakis, M.; Striolo, A. Quantifying Pore Width Effects on Diffusivity via a Novel 3D Stochastic Approach with Input from Atomistic Molecular Dynamics Simulations. *J. Chem. Theory Comput.* **2019**, *15*, 6907–6922.
- (88) Westhaus, U.; Droge, T.; Sass, R. DETHERM - a thermophysical property database. *Fluid Phase Equilib.* **1999**, *158-160*, 429–435.
- (89) DDB DDBST Software and Separation Technology, 1997.
- (90) NIST TRC Web Thermo Table - Version 2–2011-1-Pro; NIST:Gaithersburg, MD, 2011; <http://wtt-pro.nist.gov/wtt-pro>, 2011.
- (91) Rowley, J. R.; Wilding, W. V.; Oscarson, J. L.; Knotts, T. A.; Giles, N. F. DIPPR (R) Data Compilation of Pure Chemical Properties.
- (92) Detherm. *Thermophysical properties of pure substances and mixtures, version 2017.0*, 2018.
- (93) Bloxham, J. C.; Redd, M. E.; Giles, N. F.; Knotts, T. A.; Vincent Wilding, W. Proper Use of the DIPPR 801 Database for Creation of Models, Methods, and Processes. *J. Chem. Eng. Data* **2021**, *66*, 3–10.
- (94) Span, R.; Beckmüller, R.; Hielscher, S.; Jäger, A.; Mickoleit, E.; Neumann, T.; Pohl, S.; Semrau, B.; Thol, M. TREND. *Thermodynamic Reference and Engineering Data 5.0*. https://www.thermo.ruhr-uni-bochum.de/thermo/forschung/zustandsgleichung_reinstoffe.html.en.
- (95) Diky, V.; Bazyleva, A.; Paulechka, E.; Magee, J. W.; Martinez, V.; Riccardi, D.; Kroenlein, K. Validation of thermophysical data for scientific and engineering applications. *J. Chem. Thermodyn.* **2019**, *133*, 208–222.
- (96) Peper, S.; Fonseca, J. M. S.; Dohrn, R. High-pressure fluid-phase equilibria: Trends, recent developments, and systems investigated (2009–2012). *Fluid Phase Equilib.* **2019**, *484*, 126–224.
- (97) Peper, S.; Haverkamp, V.; Dohrn, R. Measurement of phase equilibria of the systems CO₂+styrene and CO₂+vinyl acetate using different experimental methods. *J. Supercrit. Fluids* **2010**, *55*, 537–544.
- (98) Chirico, R. D.; Loos, T. W.; de Gmehling, J.; Goodwin, A. R. H.; Gupta, S.; Haynes, W. M.; Marsh, K. N.; Rives, V.; Olson, J. D.; Spencer, C.; Brennecke, J. F.; Trusler, J. P. M. Guidelines for reporting of phase equilibrium measurements (IUPAC Recommendations 2012). *Pure Appl. Chem.* **2012**, *84*, 1785–1813.
- (99) Bazyleva, A.; Abildskov, J.; Anderko, A.; Baudouin, O.; Chernyak, Y.; de Hemptinne, J.-C.; Diky, V.; Dohrn, R.; Elliott, J. R.; Jacquemin, J.; Jaubert, J.-N.; Joback, K. G.; Kattner, U. R.; Kontogeorgis, G. M.; Loria, H.; Mathias, P. M.; O'Connell, J. P.; Schröer, W.; Smith, G. J.; Soto, A.; Wang, S.; Weir, R. D. Good reporting practice for thermophysical and thermochemical property measurements (IUPAC Technical Report). *Pure Appl. Chem.* **2021**, *93*, 253–272.
- (100) Dohrn, R.; Fonseca, J. M. S.; Peper, S. Experimental methods for phase equilibria at high pressures. *Annu. Rev. Chem. Biomol. Eng.* **2012**, *3*, 343–367.
- (101) Ahlström, P.; Aim, K.; Dohrn, R.; Elliot, R. J.; Jackson, G.; Jaubert, J. N.; Macedo, E. A.; Pokki, J. P.; Reczey, K.; Victorov, A. I.; Fele-Zelnik, L.; Economou, I. G. A Survey of the Role of Thermodynamics and Transport Properties in ChE University Education in Europe and the USA. *Chem. Eng. Educ.* **2010**, *44*, 35–43.
- (102) Summerton, L.; Clark, J. H.; Hurst, G. A.; Ball, P. D.; Rylott, E. L.; Carslaw, N.; Creasey, J.; Murray, J.; Whitford, J.; Dobson, B.; Sneddon, H. F.; Ross, J.; Metcalf, P.; McElroy, C. R. Industry-Informed Workshops to Develop Graduate Skill Sets in the Circular Economy Using Systems Thinking. *J. Chem. Educ.* **2019**, *96*, 2959–2967.
- (103) *Thermodynamic and Transport Properties Working Party. Electrolyte Thermodynamics challenges from industrial needs to academic research*. <https://www.youtube.com/watch?v=kKjsUuY8tbM>.
- (104) *Thermodynamics and Transport Properties Working Party. Thermodynamic tools for CO₂ capture*. <https://www.youtube.com/watch?v=ZQHxxcOuFFw>.
- (105) Gmehling, J.; Kolbe, B.; Kleiber, M.; Rarey, J. *Chemical Thermodynamics for Process Simulation*. Wiley-VCH verlag GmbH&Co. KGaA, 2012, 1–730.
- (106) Michelsen, M. L.; Møllerup, J. *Thermodynamic Models: Fundamental and Computational Aspects*; Tie-Line Publications, 2004.
- (107) Kleiber, M. *Process Engineering : Addressing the gap between study and chemical industry*; De Gruyter: Berlin, 2016.
- (108) Kjelstrup, S.; Bedeaux, D. D.; Johannes, A. H.; Gross, J. *Non-Equilibrium Thermodynamics for Engineers*. World Scientific, 2017.

Recommended by ACS

A Benchmark Database for Mixed-Solvent Electrolyte Solutions: Consistency Analysis Using E-NRTL

Fufang Yang, Jean-Charles de Hemptinne, *et al.*

SEPTEMBER 16, 2022
INDUSTRIAL & ENGINEERING CHEMISTRY RESEARCH

READ 

Vapor–Liquid Equilibrium Study of the Monochlorobenzene–4,6-Dichloropyrimidine Binary System

Eniko Haasz, Andras Jozsef Toth, *et al.*

MAY 19, 2022
ACS OMEGA

READ 

Effects of Temperature and Pressure on Interfacial Tensions of Fluid Mixtures. I. CO₂/n-Pentane Binary

Reihaneh Toutouni, Mohammad Piri, *et al.*

APRIL 02, 2021
JOURNAL OF CHEMICAL & ENGINEERING DATA

READ 

Effect of Water Content on Thermodynamic Properties of Compressed Hydrogen

Ahmadreza Rahbari, Thijs J. H. Vlught, *et al.*

APRIL 09, 2021
JOURNAL OF CHEMICAL & ENGINEERING DATA

READ 

Get More Suggestions >