Institution: Imperial College London

Unit of Assessment: 12 Aeronautical, Mechanical, Chemical and Manufacturing Engineering

Title of case study: 14. Advanced thermodynamic modelling for complex fluids

1. Summary of the impact (indicative maximum 100 words)

The **SAFT-VR** family of thermodynamic models has made it possible to predict reliably the behaviour of the many complex and challenging fluids that are found across a range of industrial sectors, including oil & gas, chemicals (refrigerants, surfactants, polymers), energy (carbon capture solvents, carbon dioxide-rich streams) and pharmaceuticals.

The SAFT-VR models have had a wide impact on industrial practice. At BP, they have been used to design novel surfactants that have increased the lifetime of oil fields up to five-fold, avoiding maintenance interventions costing millions of dollars and increasing productivity by 50% (worth $2-3 million per year per well). At Borealis, they have been used to understand how to increase the productivity of the reactor in the flagship Borstar process by 30%. At ICI and Ineos/Mexichem, they have been used to design efficient processes for producing replacement refrigerants with much reduced reliance on extreme and expensive experiments involving hydrogen fluoride, a highly corrosive substance. Industrial demand for access to the predictive capabilities of SAFT-VR has been such that Imperial College has licensed the software in 2013 to a UK SME in order to distribute it worldwide to users.

2. Underpinning research (indicative maximum 500 words)

Fluid mixtures form an integral part of our modern lifestyle, from the use of simple solvents in chemical processing to opto-electronic devices with liquid crystalline and polymeric materials. The prediction of the phase behaviour of these fluids (e.g., in what phase(s) they exist at given temperature, pressure and composition) and of their thermophysical properties, underpins the ability to design efficient and competitive manufacturing processes. Yet, until recently, it had not been possible to accurately model the phase behaviour of complex mixtures involving, for example, water, oil, surfactants and salts. With the Statistical Associating Fluid Theory for potentials of Variable Range (SAFT-VR) platform, the Imperial College group consisting of Professors Claire Adjiman (1998-date), Amparo Galindo (2000- date) and George Jackson (1998-date) has played a central role in developing a theoretical approach for the description of molecular interactions such as hydrogen bonding, dipolar forces and chain flexibility, which are of crucial importance in industrially-relevant fluids. This body of work represents a major advance in the application of formal statistical mechanics to realistic molecular interactions. Due to its predictive accuracy, which has been validated experimentally, its versatility and its firm molecular foundation, the SAFT approach is rapidly superseding well established chemical engineering equations of state, putting the UK at the leading edge of molecular modelling of multicomponent fluids.

The SAFT-VR equation of state, initially developed by Galindo and Jackson, brought significant flexibility to the modelling of complex molecular interactions, allowing hydrogen-bonding, dipolar and other strong interactions to be modelled within a unified approach [1]. The framework has been demonstrated to offer exceptional predictive capabilities for complex fluids including polymers, polar fluids (e.g., carbon dioxide, refrigerants), strongly associating / hydrogen bonding fluids (e.g., carboxylic acids, hydrogen fluoride, water), mixed electrolytes (e.g., inorganic salts, charged surfactants), gas hydrates and asphaltenes. The same models can be used to describe the behaviour of a given mixture across wide temperature and pressure ranges. The group has published 54 papers on the technique and its improvements and applications since the late 90s, and the approach has been widely taken up by other academic researchers.

A key milestone in the development of the theory is the extension to mixtures containing electrolytes and exhibiting salting-out behaviour, which are pervasive in the oil and fine chemicals industries. This work, undertaken in collaboration with Schlumberger, showed that a broad range

of electrolytic mixtures could be treated within a single framework, with transferable parameters for the ions, thereby maintaining the predictive capabilities of the approach [2].

A further milestone was reached with the development of a group contribution version, SAFT-γ, by PhD student Alexandros Lymperiadis (2003-2008; supervisors Adjiman, Galindo, Jackson). In this version, the basic building blocks are atomic groups (e.g., CH_3 or OH), rather than whole molecules [3]. This dramatically increased the predictive capabilities of the methodology, by allowing the thermodynamic properties of new molecules or mixtures to be represented reliably, in the absence of any experimental data.

While there have been many applications of SAFT-VR to fluids of industrial relevance, those with the highest impact on practice include the modelling of hydrofluorocarbon (HFC) replacement refrigerants by a number of PhD students and PDRAs (1998-2008; supervisors Adjiman, Galindo, Jackson); this need arose since the original chlorofluorocarbon (CFC) refrigerants are responsible for the depletion of ozone in the upper atmosphere. The production of HFCs invariably involves mixtures containing HF, a highly corrosive material, which renders experiments very expensive and complex. SAFT-VR models were shown to predict their behaviour well, while standard methods fail due to the extreme association between the molecules in these mixtures [4]. At the other end of the molecular scale, SAFT has been found to provide an excellent description of the phase equilibria of aqueous solutions of hydrocarbons and micellar solutions of alkyl polyoxyethylene surfactants by PDRA Blanca Garcia (1998-2000; supervisor Jackson) and PhD student Gary Clark (2005-2008; supervisors Galindo, Jackson); the phase diagrams of these non-ionic surfactants and polymers are characterized by closed-loop cloud curves denoting large regions of re-entrant miscibility which require a specific treatment of molecular association [5]. Finally SAFT has been used by PDRA Andrew Haslam (2002 to date; supervisors Galindo, Jackson) to provide a very effective representation of the phase behaviour (adsorption) in gas phase polymerisation reactions [6]; e.g., a gas phase comprising the ethene monomer and but-1-ene co-monomer in contact with a reacting polyethylene grain.

As a result of these advances, the academics have been invited to present keynote lectures at leading international conferences, including at the Thermodynamics Conference Series (Jackson, UK, 1999; Adjiman, Greece, 2011), European Symposium on Applied Thermodynamics (ESAT – Jackson, Greece, 2000 and Denmark, 2006; Galindo, St Petersburg, 2011), the EFCE International Workshops on Methods for Product and Process Design (Jackson, Germany, 2010, 2013), Properties and Phase Equilibria for Product and Process Design (PPEPPD – Jackson, Japan, 2001; Galindo, China, 2010), Foundations of Molecular Modeling and Simulation (FOMMS; Adjiman, USA, 2012), the American Institute of Chemical Engineers Annual meetings (AIChE; Jackson, USA, 2012). The group launched the SAFT Workshop Series in 2010; two workshops have taken place so far, in Spain and France.

In addition PhD students and postdocs from the group have undertaken numerous consultancies (e.g., BP, Shell, Total, Exxon, Schlumberger, Ciba, BMS, Pfizer, P&G), and as a result of the group interactions a number of our staff are now employed in key companies (BP, Shell, Qatar Petroleum, Air Products, Aspen Technology, Genesis Oil & Gas, KBC Advanced Technologies, Process Systems Enterprise, Solvay etc.).

3. References to the research (indicative maximum of six references)
* References that best indicate quality of underpinning research.

*[1] P. Paricaud, A. Galindo, G. Jackson, “Recent advances in the use of the SAFT approach in describing electrolytes, interfaces, liquid crystals and polymers”, Fluid Phase Equilibria, Vol 194, pp. 87-96, (2002) ISSN:0378-3812, DOI: 10.1016/S0378-3812(01)00659-8

[2] B.H. Patel, P. Paricaud, A. Galindo, G.C. Maitland, “Prediction of the salting-out effect of strong electrolytes on water plus alkane solutions”, Industrial & Engineering Chemistry Research, Vol 42, pp. 3809-3823, (2003) ISSN:0888-5885, DOI: 10.1021/ie020918u

*[3] A. Lymperiadis, C.S. Adjiman, A. Galindo, G. Jackson, “A group contribution method for associating chain molecules based on the statistical associating fluid theory (SAFT-gamma)”, Journal of

Chemical Physics, Vol 127, pp. 234903-234903-22, (2007) ISSN:0021-9606, DOI: 10.1063/1.2813894

[4] A. Galindo, S.J. Burton, G. Jackson, D.P. Visco, D.A. Kofke, "Improved models for the phase behaviour of hydrogen fluoride: chain and ring aggregates in the SAFT approach and the AEOS model", Molecular Physics, Vol 100, pp. 2241-2259, (2002) ISSN:0026-8976, DOI: 10.1080/00268970210130939

[5] G.N.I. Clark, A. Galindo , G. Jackson, S. Rogers and A.N. Burgess, "Modeling and understanding closed-loop liquid - Liquid immiscibility in aqueous solutions of poly(ethylene glycol) using the SAFT-VR approach with transferable parameters", Macromolecules, Vol 41, pp. 6582-6595, (2008), ISSN:0024-9297, DOI: 10.1021/ma8007898

*[6] A. J. Haslam, Ø. Moen, C.S. Adjiman, A. Galindo, G. Jackson in "Multiscale Modelling of Polymer Properties", Laso, M. and Perpète, E.A. ed. (Elsevier Science, Amsterdam), pp. 301-332, (2006), ISBN-13: 978-0444521873, DOI: 10.1016/S1570-7946(06)80015-5

4. Details of the impact (indicative maximum 750 words)

A molecular description of matter using statistical mechanical theories and computer simulation is the key to understanding and predicting the thermophysical properties of dense fluids and materials. Building on the theoretical advances in the development of the SAFT-VR equation of state, and its success in modelling a wide range of complex fluids, SAFT-VR has attracted increasing attention from industry. The application of the SAFT-VR approach to industrial problems has occurred primarily through collaborative projects, secondments and consultancies.
Among the more than 20 consultancy and collaborative projects that have been completed successfully using the SAFT-VR technology, we highlight the following impacts:

- Design of manufacturing processes for the production of replacement refrigerants (Chief Scientist, ICI/AkzoNobel [7]): a huge challenge in the design of such processes is the need for phase equilibria data for mixtures involving hydrogen fluoride (HF). This is a highly corrosive and dangerous substance, making experiments difficult, costly and undesirable. In traditional distillation columns, each tray incurs an additional cost of £1m in material costs due to the corrosive nature of HF. Thanks to its predictive capabilities, SAFT-VR was used in lieu of experiments to generate the data required for process design. SAFT-VR has also been used to identify erroneous experimental data, in cases where the formation of two liquid phases had not been correctly identified, thereby lowering the risk of process development by avoiding costly design errors.

- Surfactants: SAFT-VR was used in a collaborative project with BP Exploration to understand the behaviour of surfactants used in enhanced oil recovery to extend oil field lifetimes by a factor of up to 5. BP North Sea Operations Manager [8], our collaborator at BP Exploration, commented that the use of SAFT-VR removed the need for a large experimental programme to identify a surfactant formulation for squeeze treatment, focusing the effort onto half a dozen options only, out of an essentially infinite formulation space. He stated the following: *"Large cost savings can be achieved by extending the squeeze lifetimes: the average cost of an intervention on BPA's Magnus asset is £130K (with deferred oil costs) and annual treatment costs run to several million pounds.I could also point to some side-benefits: one of the wells in the North Sea was shut in at 8mbd [mbd=thousand barrels per day] for a scale squeeze. When it was squeezed with the glycol ether treatment, it came back on at 12mbd. The accelerated value of this production would be significant, I would imagine order 2-3mm$ [million $] (1.4 million barrels per year accelerated by 1 year at 20$/bbl, say). Also the business was developed and transferred to TR Oil Services, creating additional work and benefits to the wider UK oil industry. (…) I have rarely seen an academic project yield quite such direct insights and benefits and it remains one of the highlights for me of what can be done with quality research and development."*

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- Increased productivity in polyethylene gas phase reactor (Dr Moen, Borealis [9]). SAFT-VR was used to identify a mechanism to increase reactor productivity by 30% during polymerisation in Borealis' Borstar process [6]. Such an increase in productivity is key to the production of such a commodity product as polyethylene. By changing the "inert" gas used in the process, it was shown that the solubility of the key reactant, ethylene monomer, could be increased significantly, resulting in an increased reaction rate. Such a prediction is made possible by SAFT-VR's ability to model the behaviour of highly non-ideal polymer-solvent mixtures.

The collaborative and consultancy projects created demand for making SAFT-VR more widely available to industrial users. To enable this, the software for the SAFT-VR family of models was licensed in 2009 via Imperial Innovations to Process Systems Enterprise Ltd (PSE), a thriving SME spun out of Imperial in 1997. In 2012, with customers impressed by the accuracy and versatility of the platform, PSE acquired the full rights to the software, which is now marketed as gSAFT [10], [11] and [12]. gSAFT is a key technological element in the £3m project (partly funded by ETI, [13], on end-to-end modelling of carbon capture and storage (CCS) chains; this project alone has created four full-time highly skilled jobs at PSE's UK headquarters [10]. The development and marketing of gSAFT as a strategic technology by PSE (Weblink [14]) has re-inforced its impact across multiple industries.

5. Sources to corroborate the impact (indicative maximum of 10 references.)

[7] Chief Scientist, AkzoNobel previously ICI to confirm the use of the SAFT-VR approach for the for the production of replacement refrigerants

[8] North Sea Operations Manager, BP to Impact on increased lifetime and productivity of oil fields through squeeze treatment:

[9] Senior Advanced Process Control Manager, Borealis Group to confirm the Impact on polymerisation reactor productivity

[10] Marketing Director & Deputy Managing Director, Process Systems Enterprise (PSE) Ltd. to confirm Impact on oil industry and UK process modelling SME via licensing

Weblinks

[11] "News and Events- One of the most cited pieces of research gets its due" Imperial College London (2007) http://www3.imperial.ac.uk/newsandeventspggrp/imperialcollege/newssummary/news_12-10-2007-9-51-21 (Archived at https://www.imperial.ac.uk/ref/webarchive/wrf on 5th September, 2013)

[12] "gSAFT- Revolutionising physical property prediction for complex fluids" Process Systems Enterprise www.psenterprise.com/gproms/options/physprops/saft/index.html (Archived at https://www.imperial.ac.uk/ref/webarchive/xrf on 5th September, 2013)

[13] "UK's ETI launches £3 million carbon capture and storage project" Energy Efficiency News (2011) http://www.energyefficiencynews.com/uk/i/4479/ (Archived at https://www.imperial.ac.uk/ref/webarchive/yrf on 5th September, 2013)

[14] TCE article "Future foods- Coding caviar to avoid species extinction" www.psenterprise.com/gproms/options/physprops/saft/data/tce_saft_feb10.pdf Archived here at 17/09/2013