Institution: King's College London

Unit of Assessment: Department of Mathematics

Title of case study: Conceptual insights and numerical methods for polydisperse phase behaviour

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

Research by Prof Sollich and collaborators has led to new ways of looking at the problem of understanding the phase behaviour (phase transitions like freezing and melting, or demixing in oil-water mixtures) of systems which are polydisperse in that they contain an effectively infinite number of different particle species. This is the situation with many industrially important materials: e.g. in emulsion paint, the colloidal paint particles have an essentially continuous spread of diameters. Beyond conceptual progress, the research has resulted in efficient numerical algorithms for predicting phase equilibria. Specifically, it has led to significant savings in industrial research processes and thus has had both economic impact and impact on practitioners and professional services.

2. Underpinning research (indicative maximum 500 words)

The underlying research relates to understanding and predicting phase behaviour: transitions between different states of matter or "phases", like ice, water, steam or the various phases of anisotropic molecules used in liquid crystal displays (LCDs); or demixing transitions into two or more phases, as in liquid mixtures like oil and water that may separate at room temperature but remain mixed at different temperature. The challenge is to predict, from the properties of the constituent molecules, the number of coexisting phases and their properties, and how these change when one varies external control parameters like temperature or pressure, or in typical "soft matter" systems like colloidal suspensions (paint) or emulsions (mayonnaise) the overall dilution of the system.

There are well established approaches for predicting phase behaviour in simple systems: a "free energy" is calculated as a function of the concentrations of all of the species of molecules present, and phase separation regions can be found by constructing tangent planes to this free energy surface. However, in soft systems one has the added complication that e.g. colloidal particles are never all identical but typically have variations in size (or shape, electrical charge etc). This makes them very different from atoms or small molecules. In the colloidal case, as particle sizes are fixed by the process of chemical synthesis, the number of particles in each small range of sizes is fixed, and so each such range has to be treated as a separate particle species. Because the size distribution is continuous (rather than a mixture of a few distinct sizes), the system is *polydisperse*: it is a mixture of an effectively infinite number of particle species. The traditional procedures for predicting phase behaviour then become unmanageable both conceptually and numerically.

Polydisperse systems are very widespread in industrial applications. Most commercially available surfactants (soaps) are polydisperse, and so are polymer additives, often highly so. Home and personal care product formulations are sophisticated blends of surfactants, polymers and colloids, and control of phase behaviour is essential for processability and usability.

The research described here successfully tackled the problem of predicting phase behaviour in polydisperse systems. It was carried out by Peter Sollich in collaboration with Michael Cates and Patrick Warren from early 1997 to March 2000. The main research underpinning the impact, particularly as regards the development of efficient numerical algorithms, was done by Peter Sollich

with Alessandro Speranza from September 1999 until September 2002.

The key insight was that the free energy expressions for many polydisperse mixtures contain the full details of the polydispersity (the size distribution, in the colloids example) only in the “entropy of mixing” term. The remainder of the free energy represents the interactions between molecules of different species and can normally be written as a function of only a few moments of the size distribution. The research proposed a method of constructing for such free energies a “moment free energy”, which depends on only as many concentration variables as the number of moments required. Remarkably, this can then be treated like the free energy of a simple mixture of a few effective particle species, while preserving exactly many properties of the original free energy and giving accurate approximations for others. Peter Sollich was instrumental in developing these theoretical insights (with Cates and Warren), which provide a new and conceptually powerful way of looking at polydisperse phase equilibria. He also developed computer code for evaluating the predictions of the moment free energy method efficiently. Crucially, this code is generic in that in can be applied to any free energy with the required moment structure. The further research with Speranza led to an efficient computational method for extending the approach to be numerically essentially exact, overcoming the need to approximate in certain regions of the phase diagram.

Key researchers

- Professor Peter Sollich
  - King’s College London since 01/1999
    initially as Lecturer, promoted to Reader Sept 2002, promoted to Professor Oct 2004
- Dr Alessandro Speranza
  - King’s College London Oct 1999 to Sept 2002, PhD student
- Professor Michael E Cates
  - University of Edinburgh
- Dr Patrick B Warren
  - scientist at Unilever PCL at Port Sunlight (UK)

3. References to the research (indicative maximum of six references)

1) P. Sollich, P. B. Warren and M. E. Cates, Moment free energies for polydisperse systems. *Advances in Chemical Physics* (I Prigogine and S A Rice, editors), 116:265-336, 2001. DOI:10.1002/9780470141762.ch4, Citation counts as of 09/2012: 57 (google scholar), 52 (ISI)

2) P. Sollich, Predicting phase equilibria in polydisperse systems (invited topical review). *Journal of Physics: Condensed Matter*, 14:R79-R117, 2002. DOI:10.1088/0953-8984/14/3/201, Citation counts as of 09/2012: 129 (google scholar), 104 (ISI)

3) A. Speranza and P. Sollich, Simplified Onsager theory for isotropic-nematic phase equilibria of length polydisperse hard rods. *Journal of Chemical Physics*, 117:5421-5436, 2002. DOI:10.1063/1.1499718, Citation counts as of 09/2012: 51 (google scholar), 45 (ISI)

Grant support:

- EPSRC Fast Stream Grant, awarded to Peter Sollich (sole investigator), Polydispersity effects on colloidal phase behaviour, Oct 2001- Sep 2004, £63K (PhD studentship; funding amount limited by rules for Fast Stream Grants). In the assessment at the end of the grant, both assessors rated the research overall as "outstanding" (highest rating), and described it

as an "outstanding project" producing "research ... of the very highest quality" and leading to "significant ... advances [in] new theoretical and computational developments".

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

The impact of the research described above has been both on the work of large industrial companies (Unilever PLC), as well as industrial research institutes (I2T3). In both cases the methods developed in the research were directly applied to problems of industrial relevance.

I2T3 (Innovazione Industriale Tramite Trasferimento Tecnologico Onlus) is based in Florence and is an industrial research and technology transfer organisation. This was funded for start up, by the Chamber of Commerce of Florence, the Cassa di Risparmio di Firenze, the Fraunhofer Institut and the University of Florence, and brought together industrial and academic partners. Its Vice-President describes direct impact of the methods developed in this research on a technologically relevant project called “MAC-GEO”. The project concerned modelling of the evolution of geothermal reservoirs and I2T3's contribution focused on phase equilibria of geothermal mixtures. The project was worth 800k Euro overall, but involved also data collecting, database organization so that this modelling part had a budget of ca. 200k Euro. Polydispersity came in both as part of the main dynamic model and, of course, in solving the phase equilibrium conditions. I2T3 had a contract to work on phase equilibrium calculation and chemical kinetics between rock matrix and geothermal fluid. I2T3's Vice-President emphasizes that the phase equilibrium calculations were *possible only* because of the efficient numerical methods arising out of the research in this case study. He is also conducting a feasibility analysis for a project for a company that makes compressors and might be interested in developing modelling software in which liquid/gas phase transitions of polydisperse fluids are taken into account.

I2T3's Vice-President also reports several other instances of impact, including modelling of blowdown processes in hydrocarbon pressure vessels (with I2T3 and Snamprogetti spa, at that time part of the ENI group, now sold to SAIPEM), and a project with ENI to model wax formation in pipelines where again hydrocarbon mixtures were involved. The results for the impact at Snamprogetti were presented at a SIMAI (Societa Italiana di Matematica Applicata e Industriale) conference, in a symposium about oil and gas-related mathematical modelling that had significant attendance from industry. More significantly, the moment method was incorporated directly in blowdown process simulation software delivered to Snamprogetti, where it was then used in the pre-design of hydrocarbon pressure vessels.

Unilever is the world's third largest consumer goods company. It owns over 400 brands, including several with annual sales exceeding one billion euros. Its products include foods, beverages, cleaning agents and products for personal care and hygiene. Many of these products are polydisperse in nature. Food products such as mayonnaise or margarine are typically colloidal mixtures of several different ingredients (including plant oil, fatty acids, water and plant-sterols). The same is true for home and personal care products, many of which are sophisticated blends of surfactants, polymers and colloids. It is essential for processability and usability of these substances that they can be designed to be stable against demixing of their components, for the entire range of ambient temperatures at which they are used, stored, or processed.

A substantial amount of work is therefore invested at the Unilever research labs to formulate compositions that ensure such stability of their products. The polydispersity research described in section 3 has provided concepts and insights which have streamlined this work [see for example

"Flory-Huggins theory for the solubility of heterogeneously-modified polymers", P. B. Warren, Macromolecules 40, 6709 (2007)]. Particularly in the area of computer aided formulation, the ideas are expected to lead to significant savings in research efforts, faster development cycles, shorter time-to-market, and improved flexibility and efficiency in the supply chain.

In a supporting letter, a senior scientist at Unilever describes the impact of the research, emphasizing the conceptual impact as follows: “Indeed, I may add that the polydispersity work now shapes my thinking in a deep way. In computer-aided formulation we are investigating of the phase behaviour of alkyl chain terminated surfactants. Polydispersity in the alkyl chain length is a concern, but I think a key insight from the polydispersity work is that it is legitimate to estimate the effect by a 2- or 3-component mixture....” In this way the conceptual insights from the moment free energy have an impact on Unilever's day to day work. Concerning the resulting savings in research efforts for a typical characterisation project, the senior scientist further comments: “... It is difficult to quantify the impact in financial terms though if we say it saved 6 months of characterisation effort, we can make a very rough justification that this corresponds to £50m. This is indicative of the scale of savings that have continued to accrue since.”

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

Information on I2T3 can be found on its website at http://www.i2t3.unifi.it/
Link to KCL-mirror of I2T3 web-site.

Published information about the MAC-GEO project can be found at

- DOI: 10.1685/2010CAIM589
- DOI:10.1016/j.cageo.2011.03.018
- DOI:10.1016/j.ijengsci.2011.05.003

Of these the first document is most relevant as it deals directly with the polydispersity effects on phase equilibria. (documents available on request)

Published information on the impact at Unilever:

"Flory-Huggins theory for the solubility of heterogeneously-modified polymers", P. B. Warren, Macromolecules 40, 6709 (2007), DOI: 10.1021/ma070809x.
http://pubs.acs.org/doi/abs/10.1021/ma070809x

Individual sources:

- Senior scientist at Unilever (testimonial received and available on request).
- Vice-President of I2T3 (also project manager and general coordinator of the Foundation for Research and Innovation, http://www.fondazionericerca.unifi.it), now at KBC Advanced Technologies, London (testimonial received and available on request).
  Link to KCL-mirror of Fondazione Ricerca site.

Impact on blowdown processes:

- http://www.worldscibooks.com/mathematics/5854.html (ISBN: 978-981-256-368-2)
  Link to KCL-mirror of World Scientific page for the Proceedings
- http://www.worldscibooks.com/mathematics/6554.html (ISBN: 978-981-270-938-7)
  Link to KCL-mirror of World Scientific web-page for the Proceedings