Polydispersity effects on colloidal phase behaviour

The aim of this project was to improve our theoretical understanding of the fundamental effects of polydispersity on the phase behaviour of colloidal systems. We have developed methods for predicting, visualizing and simulating polydisperse phase behaviour (objective 4 and 5 below) and successfully applied these to fundamental statistical mechanics models for colloidal liquid crystals (objectives 1 and 2) and suspensions of spherical colloids (objective 3).

Background

Statistical mechanics was originally developed for the study of large systems of identical particles. However, many materials of industrial and commercial importance which contain colloidal particles or polymers do not fit this description. The particles in a colloidal suspension, for example, are never precisely identical to each other but have a range of radii (and possibly surface charges, shapes etc). Industrially produced polymers always contain macromolecules with a range of chain lengths; and hydrocarbon mixtures occurring in the petrochemical industry often consist of a large number of different molecular species with effectively continuously varying properties across each family of molecules. All these materials are therefore *polydisperse* in that they contain particles with properties depending continuously on one or several parameters. A key issue is what effects polydispersity has on *phase behaviour*: to process a colloidal or polymeric material, one needs to know under which conditions of pressure and temperature it will be stable against demixing, how many phases will result if it does demix, and what their properties are.

The main challenge in studying polydisperse phase equilibria theoretically arises from the effectively infinite number of particle species present; labelling these by the polydisperse attribute σ, the state of a polydisperse system must be described by a density *distribution* $\rho(\sigma)$, rather than a finite number of density variables. The free energy $f[\rho(\sigma)]$ of a polydisperse system 'lives' in an infinite-dimensional space, and the conventional procedure of deriving phase equilibria from tangent (hyper-)planes to a free energy (hyper-)surface becomes useless, both computationally and conceptually.

Polydispersity has routinely been ignored in the past, in the hope that for a narrow density distribution $\rho(\sigma)$ one can treat the system as monodisperse, i.e. containing a single particle species only. However, it has become increasingly clear that there are many aspects of polydisperse phase behaviour which can *only* be understood once polydispersity is taken into account explicitly. These include, for example, nematic-nematic demixing in liquid crystals, solid-solid coexistence in hard sphere colloids (see below), and multiple demixing in random copolymers[1]. This rich behaviour is suggested already by Gibbs' phase rule, where with an infinite number of particle species present there is no a priori limit on the number of phases.

An important feature of polydisperse phase behaviour is *fractionation*: particles may partition themselves unevenly between several coexisting phases as long as—due to particle conservation—the overall composition $\rho^{(0)}(\sigma)$ of the 'parent' phase is maintained. This leads to complex phase diagrams; the conventional gas-liquid binodal of a monodisperse system, for example, connecting the ends of tielines in a density-temperature diagram, splits into a 'cloud' and a 'shadow' curve. These give, respectively, the density at which phase coexistence first occurs and the density of the incipient phase. Because the shadow phase in general differs in composition from the parent, the curves do not coincide, and the critical point is located at their intersection rather than their maximum. In this conventional representation, all information on the composition of the phases—and therefore on fractionation—is projected out; one of the project aims was to investigate how such information can best be retained in more complete visualizations.

The studies of polydisperse phase behaviour in this project made use of the moment free energy (MFE) method developed by the PI and collaborators[1,2]. As reviewed in[3,4], this is substantially more powerful computationally and provides greater physical insight than previous methods. The latter often introduce uncontrolled errors, by 'binning' the density distribution $\rho(\sigma)$ into discrete pseudo-components or imposing the shape of the density distributions in coexisting phases *ad hoc*. The MFE method is also not restricted to nearly monodisperse systems, where controlled perturbation expansions around the monodisperse limit are possible but cannot detect qualitative polydispersity-induced changes in phase behaviour.

The MFE method exploits systematically the fact that many polydisperse systems are described by free energies whose non-ideal (excess) part only depends on certain generalized *moments* $\rho_i = \int d\sigma \, w_i(\sigma)\rho(\sigma)$ of the density distribution $\rho(\sigma)$. In the simplest case, $w_i(\sigma) = \sigma^i$, the ρ_i reduce to conventional moments. The phase equilibrium conditions in such 'truncatable' systems reduce from integral equations for the density distributions to nonlinear equations for a finite number of parameters. The MFE method takes this insight further, to the level of the free energy itself: for any given parent distribution one can construct a *moment free energy* depending *only* on the moments ρ_i. This is done by eliminating the dependence of the true free energy on the full $\rho(\sigma)$—arising from the ideal free energy term $T \int d\sigma \, \rho(\sigma) \ln \rho(\sigma)$ that is present even for truncatable systems—by minimizing over $\rho(\sigma)$ for given values of the ρ_i. The key

result is that, if the ρ_i are viewed as densities of a finite number of quasi-species of particles and the conventional tangent plane construction is applied to the MFE, the onset of phase coexistence, i.e. cloud and shadow curves, are found *exactly*. The same holds for spinodals and (multi-)critical points. Beyond the onset of phase separation the results are not exact, but can be refined by including extra moments in the description. By tuning the weight functions defining these extra moments, the properties of the coexisting phases can then be calculated with in principle arbitrary accuracy[5].

The importance of polydispersity effects on phase behaviour was recognized already within the EPSRC Physics Network in Soft Condensed Matter (1998–2001), where it was the topic of one of the most active working groups. Since then the area has received growing attention both nationally and internationally, as regards both the bulk phase behaviour that this project was concerned with[6–10] and e.g. interfacial[11,12] and dynamical[13] effects.

Key advances and supporting methodology

Objective 1 — Lyotropic liquid crystals

The paradigmatic model of colloidal liquid crystals is that of Onsager which treats particles as hard, i.e., interacting only via an infinite repulsion on overlap; in the limit of long thin rods, an exact expression for the free energy can be found. This has been widely used to model *lyotropic* liquid crystals, where transitions from isotropic (I) to orientationally ordered nematic (N) phases are primarily controlled by changes in density; see references in[14–16]. We focussed on the effects of polydispersity in particle lengths. Previous work in this area had been concerned with bi- and tridisperse mixtures (rods with two or three different lengths), and with perturbative effects for near-monodisperse systems. From these the behaviour of fully polydisperse systems as regards e.g. the possibility of N–N and I–N–N demixing cannot be naively inferred: in the bidisperse case it is known that sufficiently disparate lengths do produce phase coexistence involving two nematic phases, but the same is not guaranteed in polydisperse systems just because they always contain *some* rods of very different lengths.

To make progress we first extended the MFE formalism to include continuously varying non-conserved degrees of freedom (the rod angles with the nematic axis). We were able to show that this extended MFE approach continues to locate the onset of phase coexistence and of spinodal instabilities exactly, as long as these are approached starting from an isotropic phase[14]. Within this framework we then studied a simplified $\mathcal{P}_2$ Onsager model involving one conserved and one non-conserved moment. This model is obtained by truncating the expansion of the excluded volume interaction in the excess free energy, which in principle involves an infinite number of different moments, after the first nontrivial term; from work on the monodisperse case it was expected to give reliable results.

We found that the $\mathcal{P}_2$ Onsager model was indeed able to predict N–N and I–N–N coexistence, thus improving on a simpler model with rods oriented along one of three perpendicular axes[5] which failed in this respect. These features did not occur in unimodal (single-peaked) Schulz distributions, however, requiring instead bimodal parent length distributions containing a small number of rods with lengths substantially above the average. This suggested that length distributions which were unimodal but had fat tails towards large lengths should also show phase coexistence involving two nematic phases. We studied in detail the case of log-normal parent length distributions[4,15], and did indeed find an I–N–N coexistence region. Unusually tough, this is very narrow and not connected to an N–N region, separating instead two different regions of I–N coexistence. This novel effect arises because the orientational ordering in the nematic phase is most favourable, i.e. reduces excluded volume most strongly, for long rods. The resulting fractionation is so strong that at the onset of phase separation the nematic phase develops a second peak in its length distribution at the maximal rod length present in the system; the I–N–N coexistence arises essentially from the transition of this unusual nematic to a more conventional one.

Our studies also showed that the $\mathcal{P}_2$ Onsager model, while sufficiently close to the full Onsager model for many purposes, cannot predict the N–N demixing known to take place at larger densities in e.g. bidisperse systems. We showed that the same applies to any finite truncation of the Onsager excluded volume interaction[14]. To assess the reliability of our novel predictions for fat-tailed length distributions we therefore carried out an exact numerical study of the onset of phase coexistence in the full polydisperse Onsager model[16]. We found (as confirmed by later approximate results[6]) that the effects were in fact more pronounced: there is again an I–N–N coexistence region, but the incipient nematic phase can now be entirely dominated by the longest rods in the system, and the density at which phase separation begins decreases to zero as the maximal rod length increases. This conclusion holds generally for length distributions with fatter than exponential tails. In the limiting case of a Schulz distribution, behaviour dominated by the longest rods can still occur but only if the width of the distribution is above some non-trivial threshold. We thus have a complete characterization of length polydispersity effects on the onset of nematic order in lyotropic liquid crystals. Similar effects on N–N demixing at higher densities

and their dependence on the length distribution remain to be clarified; as explained, truncated Onsager models do not capture the full physics here, while a direct attack on the full Onsager model would be a formidable numerical undertaking. Progress using improved truncatable approximations to the Onsager model may be possible, however; see below.

Objective 2 — Thermotropic liquid crystals

In contrast to lyotropics, in *thermotropic* liquid crystal the important control parameter is temperature. Here anisotropy of long-range attractions between particles is considered the key driving force behind orientational ordering, as described in the simplest form within the Maier-Saupe model. Our objective was to establish whether N–N and I–N–N demixing could occur also here once polydispersity was taken into account; again only limited results for binary mixtures and perturbative calculations for nearly monodisperse systems existed. We used an appropriate generalization of the Maier-Saupe theory, with the common assumption that interaction strengths between different particle species factorize. All polydispersity effects are then controlled by the distribution of interaction strengths, and the results apply independently of whether the latter arises through polydispersity in, say, particle lengths or polarizabilities. We found[17] that for a sufficiently broad distribution of interaction strengths coexistence of two or more nematic phases does in fact occur, also in combination with an additional isotropic phase. This is accompanied by a strong broadening of the temperature range where I–N coexistence is observed, to the extent that re-entrant I–N separation can occur as temperature is lowered. The Maier-Saupe model is by its nature too simple to include smectic or crystalline phases, and transitions to these might mask some of the predicted phase behaviour. Nevertheless, our results make clear that polydispersity can have very significant effects also in lyotropic liquid crystals.

Objective 3 — Spherical colloids

Part I: Hard spheres. The simplest model for suspensions of spherical colloid particles is that of hard spheres, experimentally realized e.g. as latex particles sterically stabilized by a polymer coating. Monodisperse hard spheres exhibit a freezing transition as density is increased, but it was realized early on that polydispersity in the sphere diameters should destabilize the colloidal crystal phase, inhibiting freezing above a certain 'terminal' polydispersity (measured as the width of the size distribution normalized by its mean) of between 5% and 10%. Theoretical studies prior to our work (see references in [18,19]) had suggested that for slightly less polydisperse systems, a transition to a re-entrant fluid should be observed; coexistence of several solid phases, with strong size fractionation between them, had also been found. These predictions involved drastic—and differing—approximations, however, leaving the relative importance of these two phenomena unclear. Simulation work had showed the importance of fractionation but had been carried out at imposed distribution of chemical potentials, leading to strong variations of the particle size distribution across the phase diagram at variance with the experimental situation. A clearer picture of the equilibrium phase behaviour was particularly desirable as a baseline against which to assess the influence of non-equilibrium effects (growth kinetics, glass transitions and possibly gravitational settling) on experimental observations.

We therefore carried out a comprehensive investigation of the phase behaviour of polydisperse hard spheres, based on accurate free energy expressions with truncatable structure[18,19]. This showed that, at equilibrium, re-entrant melting is prevented by size fractionation: even a fluid with polydispersity above 10% can freeze by separating off a solid with a much narrower size distribution. A terminal polydispersity remains well-defined for solids, however, which are unstable to phase separation above polydispersities of 6–7%. At high densities this separation is into multiple solids as predicted earlier, though with more complicated fractionation phenomena whereby denser solids have narrower size distributions. Our study also made the novel prediction that coexistence between a fluid and multiple solids should occur in some regions of the phase diagram. Surprisingly, the fluid then has a wider size distribution than the parent, because it contains left-over particle sizes that do not fit comfortably into the solid phases. Overall, these results give the first comprehensive account of the equilibrium phase behaviour of polydisperse hard spheres and constitute a significant step forward. They will of course need to be confronted with direct simulations, where non-equilibrium effects can be excluded to a large extent (see below); for the simpler situation of imposed chemical potentials we already find very good agreement.

Part II: Colloid-polymer mixtures. We extended this work on hard sphere colloids to mixtures of colloids and polymers. These are of fundamental interest because the polymers induce a depletion interaction between the colloids, causing the appearance of a (colloidal) gas-liquid coexistence region in the phase diagram. For the simplest case of colloids with hard interactions and polymers at their θ-point, the Asakura-Oosawa model (see references in [20,21]) has been widely used; it treats the polymer coils as spherical particles that can interpenetrate freely with each other, but not with the colloids. For monodisperse colloid

particles, the resulting behaviour is well understood, with gas-liquid separation seen above a threshold value ξ_c of the polymer-colloid size ratio; otherwise only limited perturbative results for narrow colloid size distributions existed.

We therefore undertook the first study of the AO model with polydisperse colloids[20]. By applying a free-volume approximation we were able to derive a truncatable free energy, involving four moments of the colloid density distribution and in addition the polymer density. The presence of colloid polydispersity, which can cause coexistence of several solids and a fluid, combines with possible gas-liquid phase separation to give a rich variety of possible phase diagrams, which we were able to calculate and rationalize. Quantitatively, colloid polydispersity disfavours fluid-solid against gas-liquid coexistence. Even a polydispersity of only 10% can significantly lower the threshold value ξ_c; this resolves the long-standing puzzle of why theoretical predictions for ξ_c have in the past been persistently above the experimental value of $\xi_c \approx 0.25$. In the presence of polymer, solid-solid coexistence is predicted even at moderate colloid densities, opening up the exciting possibility that such behaviour, previously unobserved in experiment, may become kinetically accessible in colloid-polymer mixtures.

We also studied polydispersity in the *polymer chain lengths*[21]. An important question here is how to characterize the typical polymer size appropriately. We investigated a number of common choices and found that, if the weight-average chain length is used, phase behaviour is nearly independent of polymer polydispersity; this should provide useful guidance for the interpretation of experimental data. We were also able to clarify some counter-intuitive results obtained earlier for imposed polymer chemical potentials, which arose from the variation of the actual polymer length distribution across the phase diagram.

Part III: Lennard-Jones mixtures. The results for colloid-polymer mixtures and our simultaneous progress in simulation techniques (see below) stimulated us to investigate polydispersity effects also for colloidal suspensions with direct—rather than polymer-mediated—attractive interactions. We modelled these theoretically by augmenting our free energies for polydisperse hard spheres with an attractive van der Waals term. For the case where particle size affects only the range of the attraction, the MFE results give good qualitative agreement with simulations of Lennard-Jones mixtures[22,23]. This includes in particular the shift with increasing polydispersity of the critical temperature for the gas-liquid transition, for which an earlier study had predicted an incorrect sign. Intriguingly, the critical point is very near the maximum of cloud and shadow curves, and the latter almost coincide when plotted in terms of colloid volume fraction. We were able to establish theoretically[10] that these 'pseudo-monodisperse' features of the phase behaviour are in fact generic for systems where polydispersity affects only the range of the interaction between colloids. For the case where also the attraction *strength* is affected, both theory and simulation find that the onset of gas-liquid separation is dominated by the largest particles in the system. This demonstrates for the first time that extreme fractionation effects similar to those we found for liquid crystals can appear also in spherical colloids[24].

Objective 4 — Prediction and simulation tools

In parallel with the above investigations of specific physical systems we developed the numerical implementation of the MFE method for phase equilibrium prediction further. In particular, we automated the adaptation of weight functions which is necessary to obtain accurate results in coexistence regions[15]. Using these results as starting points, we found that even the exact (for a truncatable system) phase equilibrium equations can often be solved. Our algorithm switches automatically when this is possible, reverting to the MFE method when a solution to the exact equations cannot be converged. With this, we can now routinely detect up to five phases even for complicated free energies involving five moments[17–20], while competing direct solution approaches remain restricted to two-phase coexistence[7,8] or very simple free energies[1]. As planned, we further generalized our implementation so that phase splits can be tracked along arbitrary paths through any phase diagram. This is useful because it allows us find phase boundaries 'in reverse gear', by locating the point where a phase first disappears rather than where it first appears; the latter is harder to do precisely.

We also made significant progress in the direct *simulation* of polydisperse phase equilibria, in collaboration with Dr Nigel Wilding at Bath. We developed an approach which combines the advantages of grand-canonical Monte Carlo simulations with the experimentally relevant constraint of a fixed parent distribution, exploiting histogram reweighting techniques to adapt the chemical potential distribution appropriately[25]. We have since extended this to allow the first simulations of phase coexistence under imposed parent distribution[22,23], studying in particular polydisperse Lennard-Jones mixtures (s.a.).

Objective 5 — Visualization tools

As planned, we also developed tools for the visualization of complex polydisperse phase behaviour. The issue here is to present predictions to user communities in an intelligible form which nonetheless accurately

conveys the complexities of multi-phase coexistence and fractionation. For polydisperse hard spheres we developed three-dimensional representations showing a chosen property (e.g. density, volume fraction, polydispersity) versus volume fraction and polydispersity of the parent; each phase is then represented transparently as a separate surface[19]. We also showed that the differences in coexisting phases can be highlighted by characterizing them in terms of an optimally chosen moment. This is done by regarding the density distributions predicted across a region of interest in the phase diagram as points in an infinite dimensional space, and applying Principal Component Analysis methods that are designed to select directions of large variance. In the hard sphere case, the optimal moment is essentially the difference in densities of particles with sizes above and below the average, a physically very plausible outcome. We believe this method holds promise particularly for systems with several polydisperse attributes (particle length and diameter, say), where characterizing fractionation 'by hand' becomes more difficult.

Project plan review

The project objectives were essentially all met, and in fact exceeded in several areas. The exception is in the area of thermotropic liquid crystals, where we did not investigate the effect of particle diameter (or joint length and diameter) polydispersity. This decision was taken on the basis of our studies of polydispersity in particle lengths alone, which suggested that it would be prudent to delay further investigations until improved truncatable approximations to the Onsager model have been found. Instead we were able to tackle the effects of polydispersity in spherical colloids with attractive interactions, and develop the first simulation techniques for phase equilibria in systems with fixed polydispersity. We also made significant progress on colloid-polymer mixtures, one of the possible extensions highlighted in the original proposal. For the other optional extension to mixtures of colloidal rods and plates we expect to seek separate funding shortly. With 11 refereed journal publications, plus 1 further submitted and 2 currently in preparation, we regard the science output from this project as highly cost-effective.

The project also provided excellent training for the project student. His Ph.D. was completed essentially on time, with the thesis submitted one month after the end of the project and accepted by the examiners without any changes in Jan 2005. Work directly from the thesis was published in six peer-reviewed journal papers. The student also had the opportunity to present his work at three national and three international conferences. He was able to gain transferable skills by presenting his work at weekly research group seminars and at research days at King's College London, where he won a 'best poster' prize in Oct 2003. Further training was provided through an EPSRC-sponsored GRAD School as well as the Ph.D. training programme for transferable skills at King's College. The student had several job offers before the end of his Ph.D., and has now taken up a position with Pricewaterhouse Coopers in the area of auditing and operational consultancy, where he is able to use the quantitative, analytical and transferable skills acquired during his Ph.D. to full advantage.

Research impact

The results from this project will be of benefit to the worldwide community of scientists in academia and industry—in fields ranging from physics and chemical engineering to chemistry and applied mathematics—who require a basic science platform for understanding and predicting the phase behaviour of polydisperse systems. Our work has raised awareness of the importance of polydispersity for colloidal phase behaviour, with our review[3] of the area now becoming a fairly standard reference. More specifically, our results on polydisperse hard spheres constitute a solid theoretical basis from which work on non-equilibrium and interfacial effects[11] can now proceed; they will also stimulate systematic simulation studies[7]. Our results for colloid-polymer mixtures have practical implications for how polydisperse polymers are best characterized, and should provide an impetus for exploration of solid-solid coexistence in new experiments and simulations. The same is true for the novel extreme fractionation phenomena that we found in polydisperse lyotropic liquid crystals and, more surprisingly, even spherical colloids with attractive interactions. The generic tools for the prediction and visualization of polydisperse phase behaviour that we have developed should be helpful to an even wider user community, and we hope to make our software available to assist with this. Finally, polydispersity in industrially produced colloidal and polymeric materials is the exception rather than the rule, and the fundamental lessons learned from the model systems studied here should in the longer term also feed into applications; see below.

Explanation of expenditure

Staff costs where spent as budgeted on the project studentship. There was some overspend on exceptional costs (Ph.D. course fees) because of fee increases above the EPSRC allowance for inflation. This was

compensated by savings on equipment, where a computer of slightly higher specification (Dell Precision Workstation 530) could be purchased at somewhat lower cost by the time the grant had started, and on consumables, where no separate computer maintenance contract was necessary. Travel and subsistence expenditure was essentially as budgeted and was used for attendance at the planned number (three) of overseas conferences (APS March Meeting 2004, Montreal; Statphys 2004, Bangalore; Gordon conference on Complex Fluids 2004, New Hampshire) as well as the most relevant meetings in the UK (Condensed Matter and Materials Physics 2002/03/04, Brighton/Belfast/Warwick; Gordon conference on Complex Fluids 2002, Oxford).

Further research and dissemination activities

Transfer of knowledge to beneficiaries from this project was primarily via publication in the open scientific literature and presentation at international conferences and workshops (as listed above, with in addition an invited talk at the 8th UK Frontiers of Polymer Colloids meeting 2002). Preprints were made available on the internet via the PI's home page, and also lodged with the widely used cond-mat preprint archive.

We discussed with MSI in Cambridge the possibility of producing marketable software for the calculation and visualization of polydisperse phase equilibria from the codes developed for this project. Because of a change of priorities at the company, which has since become part of Accelrys, these efforts did not come to fruition. We will nevertheless continue to explore this possibility, while aiming to keep our codes freely available to the academic community. We are also currently in discussion with Prof. George Jackson at Imperial College regarding applications of our work on polydisperse Lennard-Jones systems to the study of complex mixtures in the chemical industry. If this is successful, consultancy for an appropriate industrial partner could be considered.

There are many possible routes for further research. These include the development of better truncatable approximations to the Onsager model for lyotropics; an accurate treatment of the Flory lattice model[26] looks promising here. On this basis, a full study of diameter and joint diameter-length polydispersity effects should then be possible. We also envisage extending this approach to plate-like colloids and rod-plate mixtures, where experiments[27] suggest very strong polydispersity effects. As regards simulation work, we are aiming for further significant progress by developing algorithms for fluid-solid and, eventually, solid-solid coexistence in the experimentally relevant scenario of fixed parent distribution.

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