PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

Colloids, grains and dense suspensions: under flow and under arrest

Michael E. Cates, Wilson C. K. Poon and Paul Bartlett

Phil. Trans. R. Soc. A 2009 **367**, 4989-4991
doi: 10.1098/rsta.2009.0201

PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A

Phil. Trans. R. Soc. A (2009) **367**, 4989–4991
doi:10.1098/rsta.2009.0201

INTRODUCTION

Colloids, grains and dense suspensions: under flow and under arrest

This Theme Issue reports papers presented at a Discussion Meeting intended to bring together those working on colloids (suspended particles small enough to have strong Brownian motion) with those working on non-Brownian systems such as dry granular matter, dense suspensions of larger particles and pastes.

A better understanding of flow and arrest in these systems is of potential value to wide areas of chemical engineering, materials processing and the design of soft materials. Such knowledge is relevant to personal-care products, oilbore-drilling fluids, wastewater processing and handling of slurries, ceramic pastes and dry powders. Although these topics do not necessarily ignite the imagination of the general public when discussed in abstract terms, many people are fascinated by the behaviour of jammable suspensions such as dense cornstarch or tomato ketchup, and intrigued to learn that these pose mysteries that are yet to be answered by scientists. The similarities between such materials and quicksand, landslides and avalanches serve as a reminder that such topics make a valid claim on publicly funded research budgets.

Historically, those studying dense particulate materials have tended to divide according to whether or not a fluid medium surrounds the particles and whether, if a solvent is present, the particles are small enough to be Brownian and hence amenable to an equilibrium statistical mechanical description. Increasing focus on non-equilibrium phenomena, even in colloids, means that these divisions are increasingly indefensible. Moreover, within each area there has evolved strong interdisciplinarity in the sense of involving scientists from physics, chemical engineering and other subject backgrounds. Nonetheless, the Brownian versus granular divide remains substantive.

The existence of such a divide is understandable since over several decades quite different experimental techniques have been developed for the various cases, and the theoretical gap between equilibrium statistical mechanics (colloids only) and far non-equilibrium (the rest) remains hard to bridge. However, there is now an experimental convergence on real-space methods that track individual particle motions (whether by microscopy, MRI or other means), allowing large datasets to be interrogated by computer; likewise, conceptual links between equilibrium and granular statistical mechanics are finally being built. Moreover, it is realized that the presence of solvent interfaces (capillary bridges, free surfaces) can create forces that entirely suppress Brownian motion even within the colloidal domain, as can the non-equilibrium phenomenon of glass formation.

One contribution of 12 to a Discussion Meeting Issue ‘Colloids, grains and dense suspensions: under flow and under arrest’.

In planning the meeting, the organizers were mindful of the fact that high-precision experimental work, often involving direct particle imaging, has shed new mechanistic light on both sides of the granular/colloid divide, highlighting similarities as well as differences between granular and colloidal dynamics. An instance is in the formation of separate regions of static and flowing material under homogeneous stress conditions to create 'shear bands'. In dry granular flows, these are usually microscopic (a few grains across) whereas for colloidal systems they are often macroscopic (occupying a substantial fraction of the width of the sample cell). This difference is not understood; yet shear banding (as well as jamming, see below) underlies the physics of thixotropy—a theme explored in the contribution of Bonn and colleagues in this volume (Moller *et al.* 2009). Shear banding also poses important challenges to the modelling of dense granular flows, exemplified here by the contribution of Pouliquen & Forterre (2009) on the development of non-local rheological models for such flows. A second example of shared ground between colloidal and granular sytems is represented by capillary forces, arising at fluid–fluid–solid contact lines. These can be used to template colloidal self-assembly—a technique taken to new heights in the contribution of Lewis and colleagues (Harris *et al.* 2009). Yet they also play a central role in wet granular mechanics, where capillary bridges cause adhesion between particles that dominate their mechanics, as explored in the contribution of Radjai & Richefeu (2009).

An important theoretical advance of recent years has been to develop the connection between 'jamming' in granular and colloidal materials and concepts of the glass transition. In colloids, the Brownian diffusion of particles becomes so hindered at high concentrations that particles remain effectively confined to cages, resulting in an ageing amorphous solid with a yield stress: the colloidal glass. The contribution of Vlassopoulos and colleagues (Christopolou *et al.* 2009) investigates this complex macroscopic nonlinear behaviour for a class of soft colloids made from multi-arm star polymers, while that of Fuchs and colleagues (Henrich *et al.* 2009) develops quantitative theoretical models for such flow behaviour based on the successful mode-coupling approaches to the quiescent glass transition. A closely related contribution is that of Trappe and co-workers (Sessoms *et al.* 2009), which establishes a fascinating link between macroscopic behaviour and short-scale spatiotemporal fluctuations (dynamic heterogeneity) within a dense assembly of microgel beads.

Flowable colloids can also jam up under stress (the cornstarch effect) and this has been thought of as a 'stress-induced' glass transition. The relation between this concept and dilatancy, particularly in relation to density inhomogeneities, is explored in a commentary by Haw (2009), based on remarks made at the meeting and included in this Theme Issue. Progress may be possible using the concept of effective temperature to describe the unpredictable part of the particle motion under strong flow. This concept, while longstanding for fast granular flows (where it describes kinetic energy), is increasingly being developed for slow flows and static systems, where instead it describes the fact that a non-equilibrium system resides much higher up on the potential energy (or free energy) landscape than would its equilibrium counterpart. This avenue is explored in the contribution of Bi & Chakraborty (2009), which introduces a new temperature-like variable conjugate to applied stress. Effective temperature is one of several unresolved factors in the crossover in

granular materials from collisional to frictional flow regimes as jamming is approached—a problem addressed in the contribution of Menon and co-workers (Gardel *et al.* 2009).

The contribution of Pusey *et al.* (2009) gives a new twist on an old problem, namely, the role of the glass transition in suppressing the formation of crystals. This reminds us of a different role for colloids, namely, their use as model systems to test a range of fundamental ideas in statistical physics and material science. This has been a fruitful research avenue for Peter Pusey (and the group he founded at Edinburgh) over several decades—with his experimental work illuminating in turn the entropy-driven crystallization of hard spheres, their arrest as amorphous glass phases, the role of attractive forces in driving liquid–liquid and liquid–solid phase transitions, and the effect of such forces on glass formation. The organizers were particularly pleased to be able to organize this Discussion Meeting at a time that could also mark Peter Pusey's formal retirement (after several years in a part-time position) from the University of Edinburgh. We dedicate this Theme Issue to him, with our very best wishes for a long and happy retirement.

Michael E. Cates[1,*], Wilson C. K. Poon[1] and Paul Bartlett[2]
[1]*School of Physics and Astronomy, University of Edinburgh, JCMB Kings Buildings, Mayfield Road, Edinburgh EH9 3JZ, UK*
[2]*School of Chemistry, University of Bristol, Bristol BS8 1TS, UK*
*Author for correspondence (m.e.cates@ed.ac.uk).

References

Bi, D. & Chakraborty, B. 2009 Rheology of granular materials: dynamics in a stress landscape. *Phil. Trans. R. Soc. A* **367**, 5073–5090. (doi:10.1098/rsta.2009.0193)

Christopoulou, C., Petekidis, G., Erwin, B., Cloitre, M. & Vlassopoulos, D. 2009 Ageing and yield behaviour in model soft colloidal glasses. *Phil. Trans. R. Soc. A* **367**, 5051–5071. (doi:10.1098/rsta.2009.0166)

Gardel, E., Seitaridou, E., Facto, K., Keene, E., Hattam, K., Easwar, N. & Menon, N. 2009 Dynamical fluctuations in dense granular flows. *Phil. Trans. R. Soc. A* **367**, 5109–5121. (doi:10.1098/rsta.2009.0189)

Harris, D. J., Conrad, J. C. & Lewis, J. A. 2009 Evaporative lithographic patterning of binary colloidal films. *Phil. Trans. R. Soc. A* **367**, 5157–5165. (doi:10.1098/rsta.2009.0157)

Haw, M. D. 2009 Volume fraction variations and dilation in colloids and granulars. *Phil. Trans. R. Soc. A* **367**, 5167–5170. (doi:10.1098/rsta.2009.0182)

Henrich, O., Weysser, F., Cates, M. E. & Fuchs, M. 2009 Hard discs under steady shear: comparison of Brownian dynamics simulations and mode coupling theory. *Phil. Trans. R. Soc. A* **367**, 5033–5050. (doi:10.1098/rsta.2009.0191)

Moller, P., Fall, A., Chikkadi, V., Derks, D. & Bonn, D. 2009 An attempt to categorize yield stress fluid behavior. *Phil. Trans. R. Soc. A* **367**, 5139–5155. (doi:10.1098/rsta.2009.0194)

Pouliquen, O. & Forterre, Y. 2009 A non-local rheology for dense granular flows. *Phil. Trans. R. Soc. A* **367**, 5091–5107. (doi:10.1098/rsta.2009.0171)

Pusey, P. N., Zaccarelli, E., Valeriani, C., Sanz, E., Poon, W. C. K. & Cates, M. E. 2009 Hard spheres: crystallization and glass formation. *Phil. Trans. R. Soc. A* **367**, 4993–5011. (doi:10.1098/rsta.2009.0181)

Radjai, F. & Richefeu, V. 2009 Bond anisotropy and cohesion of wet granular materials. *Phil. Trans. R. Soc. A* **367**, 5123–5138. (doi:10.1098/rsta.2009.0185)

Sessoms, D. A., Bischofberger, I., Cipelletti, L. & Trappe, V. 2009 Multiple dynamic regimes in concentrated microgel systems. *Phil. Trans. R. Soc. A* **367**, 5013–5032. (doi:10.1098/rsta.2009.0178)