Some Rheological Reflections

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2009 BSR Gold Medallist - Professor Michael E. Cates

It is a great honour to receive the Gold Medal of the BSR. It is especially pleasing to be receiving it in the same year as Tom McLeish, with whom I shared an office at the Cavendish Laboratory in Cambridge in the 1980s. Tom and I did not collaborate directly then, but we did have some joint papers in the early 1990s, by which time Tom had moved to Sheffield. One of these [1], with my then-student Neil Spenley, was on shear-banding in wormlike micelles. It developed the idea that the mechanical instability inherent in a nonmonotonic flow curve will lead to coexistence of layers of material with different shear-rates at a common stress. Although this idea had been considered previously (for instance by Tom and Robin Ball in the context of polymer melts [2]), entangled micelles offered a unambiguous example of the effect, in an easily-studied class of experimental systems. (These comprise solutions of amphiphilic molecules, such as detergents, that then aggregate into flexible, linear structures resembling polymer chains. They are widely used in shampoos, thickened bleach and similar products [3].) Since then, wormlike micelles have become a testing ground, not just for shear banding, but for a range of rheological instabilities, with links to diverse aspects of dynamical systems theory [4].

OF MICELLES AND MEN

I first heard about these micelles from Fyl Pincus in 1986, when I was a post-doc at UCSB. Sam Safran (then at Exxon) had recently visited and showed Fyl some rheological data, I think from Jean Candau's group in Strasbourg, for the scaling of the viscosity with concentration. This seemed not too far from the prediction of reptation models, but Fyl had a worry: the micelles, unlike conventional polymers, must undergo breakage and fusion events. One day he asked me whether I thought there was any way of handling this within entanglement theories (hoping perhaps that reptation-like scaling would survive). Within a short while I had found that there was a way to do it – but that breakage and recombination can change everything.

It took a few months to figure out some new scaling laws and the linear elastic

modulus G(t) – which approaches a Maxwellian (single exponential) form in the fast breaking regime [5]. This feature had already been seen (but was not known to us physicists) by Heinz Rehage and Heinz Hoffmann, then both at Bayreuth. For me it was a blind prediction; and I'm told that the experimental confirmation of this result convinced P-G de Gennes that the model was, after all, a good one. (Despite later conversations with him on many subjects, I never did find out what his objections had been!) Another year's work was needed to obtain a constitutive equation [6], and a couple more to spot that this predicted nonmonotonic flow curves, and therefore shear banding. The latter realization was prompted by discussions with Rehage and Hoffmann, who by then had shown me a flow curve with an unexplained stress plateau extending for decades in shear rate (reproduced in [1]). Our shear banding picture predicted this to be a composite curve, with coexisting bands in the plateau region – as was later confirmed in many experiments.

This entire sequence of events represented a string of good luck for me as a scientist, coming as it did quite early in my postdoctoral career. On the other hand (according to Pasteur) 'chance favours the prepared mind'. As it happened, my mind had been exceptionally well prepared – not just for this turn of events but for an entire scientific career – by my PhD supervisor, Sir Sam Edwards. Sir Sam led by example as much as by instruction, and during my PhD I had spent several months studying in detail his series of papers on reptation with Masao Doi [7]. These works remain an inspiring example of how statistical physics can contribute to rheology. But there was no direct link with my thesis project: I had read the Doi-Edwards papers for the pleasure of watching these masters in action, and learning some of their craft. Yet my postdoctoral work on micelles directly used all this knowledge within a couple of years of my gaining it.

There is a lesson here, perhaps, for PhD students and early postdocs: of course you have to get the project done, but reading around your subject for the fun of it is not time wasting! It is an essential part of preparing one's mind for future chances unknown.

LIFE AT THE CAVENDISH, CIRCA 1990

I returned to the Cavendish in 1988, first as a Trinity College Research Fellow, then in turn a Royal Society URF, University Assistant Lecturer, and Lecturer. Perhaps I'd had too much early success, because at one stage I became convinced I would never do anything useful again and was seriously preparing to give up physics. Rescue from this state of mind came by way of a collaboration on shear-induced phase transitions [8] with Scott Milner (then at Exxon). As we discussed this problem and its unexpected subtleties, compulsive curiosity about the science gradually overcame my feeling of uselessness. (Lesson two: Don't lose heart just

because you achieve nothing for a while. If the threat of failure never haunts you, perhaps you're not aiming high enough!)

This was at a time when the telephone was the normal way of communicating across continents, rather than email; it was also quite expensive. I remember regularly migrating into the secretary's office so as to be able to dial transatlantic after the University switchboard had closed for the day, and there having two-hour phone discussions with Scott concerning our calculations. Incidentally, my PhD thesis had itself been written on a freestanding word processing machine in the same office just a few years earlier. The machine, which served the entire research group, had a booking sheet and large (20cm diameter) floppy disks for storage. To add Greek letters, each sheet of paper had to be fed through the printer for a second time; despairing of this, the equations in my thesis were hand written. (Lesson three to young scientists: when it comes to IT, you don't know how lucky you are!)

At the Cavendish I was fortunate to have many excellent colleagues. I worked not only on micelles but also on several other topics, including granular materials. The granular work had two themes. One was avalanche dynamics in surface flows, which I studied with J-P Bouchaud, Ravi Prakash, and Sir Sam Edwards [9, 10]. This work was well-received, particularly after de Gennes showed that several puzzling phenomena, relating to segregation by size during avalanches, could be explained by extensions to our model. The other theme was on stress propagation in static granular media – of which more below.

In the mid 1990s there was an obvious logjam for promotion at Cambridge: it was not unusual to gain an FRS before being promoted to a Chair (this happened to both John Hinch and Sir Richard Friend). To avoid having to wait patiently for a decade or two, I accepted a Chair in Edinburgh which I took up in 1995.

BUILDING ON SAND?

Work on static granular media continued in Edinburgh, in collaboration with Joachim Wittmer, J-P Bouchaud and Philippe Claudin. Our ideas were radical, and set aside a large body of prior literature. Much of this earlier work rested on the validity, for cohesionless powders, of plasticity concepts that had been developed for conventional solids such as metals, and never fully validated outside that domain. (Arguably, not within it, either – but that's another issue!) While closer study of the literature might have saved us some trouble, it might also have extinguished prematurely the flickering flame of a new, simple, and experiment-provoking idea.

With hindsight, though, perhaps we should not have submitted our work to as prestigious a journal as Nature [11]: the outcome was some ruffled feathers and chorus of criticisms (ranging from the cogent, to the genuinely parrot-like). This episode culminated in a rather fraught workshop at Cargèse, attended by J-P

Bouchaud, myself, and two or three of our staunchest critics. For the only time in my career, a scientific debate became genuinely soured by animosity – to the point where rational communication was, de facto, suspended. Having stayed up all night adapting my talk to rebut views expressed the day before, and furious at being forced to lose a night's sleep, I needed to calm myself down if the talk was not to degenerate into purely a slanging match. To this end, I missed the two talks before mine, and went for a 45 minute run, finishing in time to shower in my room and stroll back to the lecture hall. Suitably purged of adrenalin and mellowed by endomorphins, I got through the talk without losing my cool (or the argument).

Having recounted this story to people in various disciplines, it appears that in many fields such episodes form a quite normal part of academic life! Which brings me to lesson four: We are lucky to work in an area where collegiality far outweighs antagonism, most of the time.

In the end, our simple new idea was rather too simple, and subsequent experiments did not bear out some of its most distinctive predictions. (That said, they did not bear out anyone else's theories either.) For a while we were undecided whether to attempt life-saving surgery on our model or, in the memorable words of Joachim Wittmer, "give it a good funeral". While it never became a predictive tool for the statics of frictional powders, the work helped usher in progress by others in understanding 'isostatic' packings of frictionless grains. It also remains a useful modelling paradigm for 'fragile matter': materials, such as jammed colloids, whose solid structure only arises because of the stress they are under, melting away again when this stress is removed [12].

A TOUGH OF GLASS

A big attraction of Edinburgh was, and still is, the presence of a lively crowd of experimental soft matter physicists – headed first by Peter Pusey and now by Wilson Poon. A decision I made soon after arrival was to join their group rather than set up a separate theoretical one. I am proud of the group's subsequent expansion to embrace nonequilibrium dynamics, large scale simulation of complex fluids, and statistical mechanical modelling of flowable materials (as well as, latterly, biophysics).

Although rheological constitutive equations are the main focus of this essay, they do not make good cover art. So, when asked to provide some for this issue, I chose an image, generated by Kevin Stratford, from a lattice-Boltzmann simulation of immiscible binary fluids under shear. Such simulations are increasingly powerful for addressing rheological questions that continue to elude traditional theory – in this case, whether sheared binary fluids coarsen indefinitely or reach a steady state with finite, albeit anisotropic, domains [13].

For the past decade, a central concern for both experimentalists and theorists in

our group has been the detailed study of colloidal arrest [14]. In a sufficiently dense suspension, Brownian motion of the colloids becomes so hindered that, on the timescales relevant to experiments, each particle is trapped quasi-permanently in a cage formed by its neighbours. The result is an amorphous solid, with a yield stress, called the 'colloidal glass'.

The yield stress is very modest (say 1–100 Pascals) and thus easily overlooked if samples are not handled carefully. Nonetheless, colloidal glasses serve as an important model system for understanding soft solids, sharing with many other such materials (such as pastes, emulsions and foams) the property of local structural disorder. Moreover, none of these systems, even in the absence of flow, reaches a state of Boltzmann equilibrium. Having no equilibrium state to start from, one needs to use ideas from an active but incomplete area of statistical mechanics – glass physics.

To address the wider class of 'soft glassy materials', Peter Sollich, Francois Lequeux, Pascal Hebraud and I created a minimal rheological picture of arrested matter. Our 'SGR model' [15] shows several interesting regimes including Herschel Bulkley behaviour (which has a yield stress) and power law fluids (which do not, but have infinite zero-shear viscosity). The work was later extended by Sollich, myself and our then-student Suzanne Fielding to address the rheology of aging materials [16].

The SGR model has interesting constitutive behaviour, but is rather vague on detail. Within the narrower domain of colloidal glasses, the rheology of arrested states can be scrutinized theoretically in a more comprehensive fashion. This entails the extension to flow conditions of some formal techniques, known as mode-coupling theory (MCT), which I learned about from Matthias Fuchs (now in Konstanz) while he was a visitor in Edinburgh. The MCT approach predicts only shear thinning behaviour, although shear-thickening can be addressed by plausible extensions of it [17]; it includes a description of arrest, but currently excludes both aging effects and hydrodynamic interactions. In recent work with Matthias Fuchs, Joe Brader and Thomas Voigtmann, this avenue has proven very fruitful, first for steady-state flow curves [18], then for time-dependent shear [19], and finally in the development of a fully tensorial constitutive model [20]. An important future challenge is to confront this model (or simpler ones inspired by it) with a wider range of experimental data – particularly in non-shear flows.

This brings us just about up to date, and thus to the end of this essay. Alongside all those mentioned by name above, I'd like to thank the other colleagues I've worked with over the years, including many on projects unrelated to rheology. (There are far too many of these colleagues to mention individually, but it is impossible to leave out Tom Witten or Didier Roux.) Collaborations, and the lifelong friendships that stem from them, remain one of the great benefits of choosing a scientific career. (And if anyone wants a fifth lesson, let that be it!).

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