A Schoolboy Dreams of the Stars

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I was honoured and delighted to be awarded a Gold Medal from the society that has been an academic home since the first year of my PhD! I am especially happy to have received a medal alongside Mike Cates – more of Mike anon, but the reappearance here of some of the characters he wrote about in the last issue will illustrate how closely connected the international rheological community is. I will follow Mike in telling my "rheological story": the BSR itself has been to me a continuous source of new academic friendships, and many important lessons along the way. Let the reader draw their own, if any, from the following. I recall one of my very first BSR conferences at the University of Kent, and with it a memorable encounter. On emerging into the coffee break after giving a talk on molecular rheology of branched polymers (some things never change, do they?) I was buttonholed by a rather agitated industrial participant. "We don't want all these complicated equations!", he protested, "we just want simple equations that we can solve and predict how our polymers will process!". I think I mumbled something apologetic about nature just being complicated sometimes and that that was the way things were … but the ringing criticism and appeal for simplicity I never forgot.

2009 BSR Gold Medallist –Professor Tom McLeish FInstP FRSC

But I'd like to go back and explain why I became involved in rheology in the first place, and fascinated by branched polymers in the second. My first scientific love was actually astronomy: from an early age I kept records of sunspot activity and solar rotation, took photographs of galaxies and planets, mapped Jupiter's storms during 5 hour observation sessions at the school telescope in bleak midwinter, got to know Patrick Moore – even managed an "O-level" in the subject (astronomy, not P. Moore that is, and a vital career move as it later turned out to be). Physics at university was clearly the route to a life spent with the stars, but I was very keen to take a "gap year" before that, ideally being paid to do something scientific. I was pointed towards companies that offered "thick sandwich" sponsorships with periods of industrial experience before and after a degree course, and finding that only two would consider physicists, did not take long to send off applications. GEC turned me down but Courtaulds offered a place. From that moment my fate was sealed: a year at their Coventry research labs polymerising acrylonitrile, extruding polyethylene fibres at high rates, wondering at the strange spiral instabilities and "spurt effects", observing the properties of highly-filled melts in flow sent me scuttling off to the company library in the firm conviction that there *had* to be some science behind all this (no one in my research group seemed to be aware of any!). And there they were – a row of books on "Rheology" (one by a certain N. Cogswell) which I devoured happily, yet without complete satisfaction: even in the literature no-one really talked in depth about what the molecules were doing.

Then at Cambridge I set about the physics I would need to do professional astronomical research. At that point there were no undergraduate courses in the subject; only the chance to follow a final year project in the area; these often led onto a PhD. I latched on to the exciting field of X-ray astronomy and a project suggested by Andy Fabian (now a world leader in X-ray emissions from accretion disks). That was the good bit; those who know me will wince when they hear that the project itself involved writing a long and complicated Fortran code. Six weeks of frustration later I wrote a note of resignation to Fabian, opted for the problem paper instead of a project, and left astronomy for clear nights at the bottom of the garden.

I was temporarily at a loss for what to do, wistful musings about those weird polymer fluids at Courtaulds seeming to lead nowhere, until someone, I cannot recall who, asked me if I had heard about the "polymer physics" that Sam Edwards and his group were developing right under my nose in Cambridge. The words sounded right, and I was already one of the physics students totally under Sam's spell as the magician who had lectured us (magically but fortunately unexaminably) on classical mechanics. Wouldn't it be better to follow a PhD in this group rather than return to Courtaulds unenlightened? My suggested supervisor, Robin Ball told me about schemes called CASE awards that might satisfy both myself and the company, and a new idea called the "Doi-Edwards theory" of polymer melts that might prove a good starting point for explanations of phenomena that had puzzled me on the pilot plant. Sam even gave me a pre-print just arrived from some young turk at Bell Labs called Ron Larson. I can still remember the title page: "Fibre-Spinning with the Doi-Edwards Equation".

Turning over, the next page had me hooked, for there was *a differential equation using tensors and describing polymer molecules*! This was what I wanted to do!

Working in the Edwards group taught us so many things that in retrospect are perhaps of more consequence than the physics we did at the time: all that contributes to the identity of a research group, the clear signal that we could and should steer our own projects as much as possible, the idea that the PhD students were valued highly for the new work we were doing (I once heard Sam reply in answer to a conference question criticising his lecture, "Well, you know, we have some very bright research students in Cambridge, and if something were really wrong with what I've told you, I'm sure that one of them would have spotted it."). Added to this was the presence of external visitors – both Masao Doi and Ed Samulski were resident during my first year – all making for a quite exhilarating atmosphere.

The CASE award meant that I was reading through as much industrially related literature as physics. It was this that brought to my attention the strange vortices that formed upstream of constriction flows in branched polyethylene melts (LDPE) but not in equivalent the linear (HDPE) melts. Understanding as I did by then that Doi-Edwards theory elevated the molecular *topology* of a polymer melt to the highest physical status, I naturally started to wonder if the explanation of this topologically-determined effect might already lie implicitly within the new framework. The problem was that no one had any idea of the real molecular structures lurking in LDPE. But browsing through recent copies of *Macromolecules* in the library one afternoon I came across an extraordinary paper. A Canadian group had claimed to have synthesised, from polystyrene, a melt whose every molecule had the topology of a capital H. Not only that, but they had measured the linear rheology and shown it to be quite different from either linear or star-shaped melts. The author was Jacques Roovers, and I knew I had struck gold (and along the way might be able to finish writing a PhD). If not LDPE, then perhaps the H-polymer melt might be the next step? The conceptual problems were considerable, as illustrated by a brief conversation with Sam Edwards one day:

> **SFE**: "*Well Tom, you've got a year left of your PhD, what are you going to do with it?*"
> **TCBM**: "*I thought I'd take a look at entangled branched polymers and how they flow*"
> **SFE**: **....Pause ....** "*But why should they flow at all?*"

Although Sam and Masao had never written about it, they had clearly understood that, with reptation suppressed, the viscosities of highly branched melts would diverge exponentially (a problem that Robin Ball and I later returned to, first in the context of star polymers). Two other people were the source of encouragement to keep my sights on the ramifications of this problem. One was Mike Cates, by then back in Cambridge from Exxon and Santa Barbara. I had been reading Mike's beautiful thesis on the statistical physics of "polymeric fractals" (aka branched polymers!) and was impressed that once the statistics determining the ensemble were known, Mike had successfully calculated the linear rheology in the unentangled case.

"*What about the non-linear rheology, Mike*?",

"*No chance*".

"*Because there's no tube model*?"

"*Something like that*".

Perhaps the reason I have never forgotten that conversation is that, at the annual Society of Rheology conferences in the USA, I had started to hold regular conversations with Ron Larson (of "*Fibre-Spinning with the Doi-Edwards Equation*" fame and much besides by then) about the LDPE problem. Ron convinced me that the situation was much worse than the lack of a molecular theory of LDPE – there wasn't even a phenomenological constitutive equation that came qualitatively close to describing its shear-thinning and extension-hardening behaviour in all geometries. Might Ron's unmatched grasp of the structure of rheological models, combined with my background in molecular theory, help find the missing model? It is, however, hard to make real progress with a tough problem from a distance, especially for a post-doc looking for a job.

The job problem was solved by Sheffield University department of physics by placing quite the most extraordinary advertisement I have ever seen for a lecturer: "*Junior lecturer wanted to start a new research activity not currently followed in the department, e.g Polymer Physics / Should also be able to teach astronomy*". There it was pinned up on the Cavendish Laboratory jobs board. They told me afterwards that it really was the astronomy "O-level" that swung it. My wife Julie was very supportive of the move north, even though it meant an interruption to the planned course of her medical qualifications (in the end a very positive one as it turned out). We saw Mike quite frequently in Sheffield ("*Nearest place to Cambridge you can go for a walk*"), giving us the chance to develop his ideas on "living" polymers made of surfactants. The other kindness I received from former Cambridge colleagues was from a thoughtful Athene Donald. Times have changed now, but at that time it was possible to walk into a lectureship without any discussion of research funding, grant proposals and the like. Athene pointed out that an application on the theory of branched polymers to the Agricultural and Food Research Council might be looked on favourably (actually I think I could have been forgiven for not having thought of that one!). I'm very grateful for that first leg up onto the research funding ladder – such kindnesses of voluntary mentoring are still needed by newly appointed academics.

The other element of very good fortune in the move to Sheffield became apparent during a visit to Exxon the summer before I started there. Talking to Lew Fetters, one of the great anionic synthetic chemists interested in branched polymers, I mentioned my new institution. "Sheffield!", he started, "Ron Young's there – best anionic chemist in the UK". Indeed so it proved, and showed me how powerful, and how pleasurable, a close collaboration between chemistry and physics could be.

I should say more about my version of the "american connection" during those years. Through sharing an office with Mike in the Cavendish I had been introduced to Scott Milner (mostly through answering the telephone to Scott's daily calls about the problem of lamellae under shear – see Mike's article in the last issue). Annual trips across the atlantic would take in Scott, who was also interested in polymer dynamics, as well as the matchless theory/experiment pair of Mike Rubinstein and Ralph Colby at Kodak's Rochester labs. Mike and Ralph were enabled by Kodak to create a group as strong as any university team anywhere in the field. It also supplied them with funds for visiting fellows that, in retrospect, did a huge amount to keep the international community in polymer physics connected. There for the first time we saw how the entangled dynamics of a complex branched melt might be calculated, and Ralph set off devising a clean experiment that might test it. Both strands took several years to come to fruition.

Working with the best people in the world for a few days a year is a good start, but as noted above, cannot really substitute for sustained collaboration when the nuts you want to crack are especially hard ones. Another stroke of good fortune helped solve the impasse, again through the good offices of Mike Cates. Mike had proposed, together with Ken Walters and Anthony Pearson, a 6-month programme on the "Dynamics of Complex Fluids" at the Newton Institute, Cambridge in 1996. But then came his move to Edinburgh, and did not feel he could immediately disappear from his new responsibilities for so long. By then I had been in Leeds a couple of years, so was more mobile. I set about ensuring that two people would be able to spend extended visits to the programme – their names were Ron Larson and Scott Milner. Getting both of them to Cambridge for the 6 months might solve that problem of limited discussion time at annual visits and conferences. Indeed that time proved memorable, as those if us gathered once more in Cambridge for the 10 year review meeting recently testified. After six weeks, Ron and I had written down and started to compute with the system now known as the "Pom-Pom" constitutive theory for branched entangled polymers, and by the end of the programme has shown its inequivalence to existing theories, and its qualitative capturing of LDPE's phenomena. In a strange twist of conceptual history, I later realised that the Pom-pom structure lay buried in the rather complicated theory of H-polymers I had worked out for my thesis, and which had caused affront to the industrialist at that early BSR meeting. Perhaps the plea for simplicity had struck home.

I'd like to say a little more about the vital role of industrial science in the UK. After the Courtaulds CASE, ICI had sponsored my post-doc in Cambridge, and a kindly soul from that company called Richard Buscall supported my first PhD student, Kevin O'Connor in Sheffield. Sam had always taught us to value (by example as in everything) the continual flux of interesting new problems that industrial visitors brought us. One of them, the delightful and accomplished Giancarlo Cappaccio from BP Chemicals seemed to have the closest interest in the polymer rheology problems I was tackling, and promised that if the company ever had need of a deep study of long chain branching, he would contact me. Good to his word, several years later, as I was moving to Leeds, the new metallocene catalysts for olefin polymerisation were looking promising, and the possibility of designing molecular structures for processing began to look realistic. True to his word, Giancarlo did get in touch, so beginning over a decade of fruitful collaboration with BP. But more than that, it was a consortium of UK industry including BP, ICI and Courtaulds that initiated the vision that became the multidisciplinary "Microscale Polymer Processing" project. I can take no credit for the concept – I more or less did what I was told in championing the idea (at a meeting of the Polymer Engineering Group in York as matter of fact). So the chemistry-physics collaboration could be extended to chemical engineering and applied mathematics, and into industrial teams in a deeply collaborative way, assisted by some very enlightened planning at EPSRC, an organisation which we are quick to criticise but that perhaps doesn't get enough credit when it is due.

An absolutely key collaborator during those Leeds "MuPP" years is our current BSR President, Oliver Harlen. Arriving at Leeds from Cambridge soon after me, it is no exaggeration to say that Oliver rescued me (and a very able PhD student, Graeme Bishko) from disaster. I had taken on two students, with the idea that one would work on the molecular theory of branched polymers, while the other (Graeme) would solve the consequent complex flows using a new type of finite element flow solver, the Lagrangian scheme first suggested by Ole Hassager. But it soon became apparent that this development was not a straightforward application of textbook mathematics. Oliver already knew this from personal experience and proved the ideal co-leader of the Leeds team, including the laboratory of rheologists we established (run by David Groves formerly of ICI at that time). I had long wished for such a theory-experiment mix "at home" since seeing how effective was the Colby-Rubinstein collaboration at Kodak. Graeme produced the first version of *flowSolve* in his thesis work, and, now with the Pom-Pom equations in hand, we saw for the first time *in computations* those contraction vortices form that had first alerted me to the fascination of multiscale phenomena in branched polymer melts. In Tim Nicholson's hands, the combination went on to predict flow phenomena seen later by Malcolm Mackley's collaborating group in Cambridge, while David Groves brought me one day the first 12-decade experimental mechanical spectrum of a highly entangled (polyisoprene) H-polymer melt. There were all the features we had predicted years before visible in a flash. It remains the only moment at which I have burst into tears over a page of experimental data!

Like Mike I know that there are many people I would like to mention and should, but two more I must. Daniel Read came to Leeds for a PhD, to work on microphase separation problems in polymer networks. He rapidly became our expert in the theory of neutron scattering in polymeric systems, and vital to our collaborations with the groups of Julia Higgins at Imperial College and Dieter Richter in Jülich. Among other things, he carried though an enormously complex extension of the Random Phase Approximation for a stretched and quenched ensemble of partially-labelled H-polymers that was essential to the experimental and theoretical rheology programme. It was only a matter of time before Daniel would get to the molecular rheology itself, but I have to confess that it would have been sooner had I not capitulated to a temptation of supervisors of extremely clever people to keep just *something* back for themselves. It couldn't last, and after wrestling with a calculation of the linear rheological statistics of metallocene branched polymers for weeks (this was around 2000), I mentioned the problem to Daniel. I think he had the linear result after two days and the non-linear by the following week (the "seniorities" and "priorities" for the aficionados).

Alexei Likhtman has already been in Leeds, working with Sasha Semenov, before joining the MuPP team to work on molecular rheology. His lesson for me was to guard against a self-delusional satisfaction in any theoretical framework with which one is simply familiar. He has also taught me, with Scott Milner, the shortcomings of my own lack of ability for computer simulations, and the rich way these can be interleaved at different resolutions and coarse-grainings to throw light on the conceptual theories. I hope that many colleagues will enjoy using the excellent REPTATE software, developed by Alexei and colleagues and now freely downloadable, that processes and analyses rheological data and theories in a very powerful environment, enabling what used to take us weeks to be done in minutes.

Rheology knows no bounds, but did you know that it can even make your childhood dreams come true? So it was that, in a second international workshop on Complex Fluids, this time in Santa Barbara in 2002, I was drawn by irresistible and atavistic yearnings to the astrophysics conference sessions of the parallel programme. There was a poster on magnetic dynamics of the internal convection zone of the Sun – with – no mistaking it - *the ROUSE EQUATION*. No they hadn't heard of "polymer physics"; yes, this was a good approximation of "magnetohydrodynamics"; no, they had no idea of how a fluid containing such string-like magnetic objects would behave. But I did! So began one of those deeply satisfying collaborations that happen in physics when hard work over many years in one field can be carried over with minor modifications into another. The astrophysicists and I co-wrote a paper for *Astrophysical Journal*. It's even becoming moderately well cited – once by Andy Fabian (yesss!!). Gives a whole new meaning to "star polymers", doesn't it?