## Excitement on the Smallest Scale

Microrheology is in its early stages, but it has the potential to expand the range and enhance the application of rheological characterization. Here's how.



By Steve Carrington, Product Marketing Manager - Rheology, Malvern Instruments, Malvern, Worcestershire, UK.

Those of us who treasure rheology recognise that it offers a unique perspective on material properties at all levels from an academic understanding of how underlying molecular dynamics and microstructure drive complex bulk material deformation and flow properties, more applied measurements that to optimise product performance can or troubleshoot processing problems. Rheological characterization supports the formulation of highly sophisticated personal care products, for example, and foods that deliver market-leading consumer appeal at competitive cost.

Conventional rotational rheometers are highly sophisticated instruments that enable changes, sometimes over decades, to the critical control parameters that determine viscoelastic properties, such as applied stress, strain and frequency. However, mechanical rheometry has fundamental limits, primarily arising from the effects of mechanical inertia, which prevent complete characterization across all complex fluid types.

Imagine that you could apply rheometry on a micro-scale and remove the inertia limitations, enabling you to perform high frequency measurements that capture short timescale dynamics of low viscosity formulations. Imagine a drive force of such low applied stress and sensitivity that the onset of molecular aggregation or denaturation processes can be followed, within the linear regime of the most highly strain-sensitive systems. Imagine the ability to probe different material length scales, from bulk properties down to mapping localized spatial dynamics at a microstructural level. Then consider the sample volume for this thought-experiment - of course, that's on a micro(litre)-scale too - a real positive for high value, scarce materials as biotherapeutic proteins or such engineered polymers. Make novel this thought-experiment real, and you have microrheology.

The term microrheology describes a range of techniques that extract the rheological properties of soft materials by measuring and analyzing the motion of colloidal tracer particles dispersed in the sample. Passive microrheology exploits thermal diffusion of the tracers, whereas active microrheology drives probe particles using laser or magnetic tweezers. My focus is on passive dynamic light scattering (DLS) microrheology, where the average motion of an ensemble of tracer particles undergoing Brownian motion is tracked by light scattering. The way in which a particle diffuses is intimately linked to the rheology of the dispersion medium. For Newtonian fluids, the relationship between viscosity, particle size and particle diffusion is given by Stokes-Einstein, but for viscoelastic fluids it is far more complex. It has been the extension of the Generalized Stokes-Einstein Relation (GSER) to Non-Newtonian fluids, and in particular the linking of particle diffusion with linear

viscoelastic moduli, that has formed the basis of modern microrheology (1).

Currently, microrheology sits firmly in the research laboratory, and while the promise of the technique is palpable, there are potential pitfalls for the unwary. The choice of probe particle is critical and requires careful investigation and assessment—from suitable tracer chemistry to minimize sample interactions, to tracer size and concentration to ensure robust data. Sample preparation is vital for microrheology, and elements of this can be involved and non-trivial.

The rewards resulting from this careful sample preparation, however, are substantial: a quick and easy rheological test using tiny sample volumes. An ideal screening tool in fact. Just as importantly, microrheology allows the behaviour of samples to be assessed in ways that conventional methods do not. For example, we've used DLS microrheology to look at the onset of gelation in protein solutions caused by denaturation and aggregation (2), and to extend the characterization of dilute polymer solutions into the high frequency regime.

While I find microrheology an absorbing, and potentially valuable proposition, the technique is still in embryonic form and it is collaborations across the scientific community, including those working at the forefront of commercial product development, that will provide a thorough assessment of its value. Consider this an invite to get involved!

## References

- T. G. Mason and D. A. Weitz, "Optical measurements of frequency dependent linear viscoelastic moduli of complex fluids", Phys. Rev. Lett. 74:1250-1253 (1995).
- S. Amin, C. A. Rega and H. Jankevics, "Detection of viscoelasticity in aggregating dilute protein solutions through dynamic light scattering-based optical microrheology", Rheol. Acta 51: 329–342 (2012).