An Algebraic Approach for Determining Viscoelastic Moduli from Creep Compliance through Application of the Generalised Stokes-Einstein Relation and Burgers Model

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ABSTRACT:

DLS Microrheology involves tracking the time dependent motion or mean square displacement of dispersed tracer particles of known size using Dynamic Light Scattering (DLS) in order to determine viscoelastic properties of the dispersion medium. The viscoelastic moduli are calculated using a generalised form of the Stokes-Einstein equation which requires Fourier Transformation of the MSD. An alternative approach for estimating the viscoelastic moduli uses a modified algebraic form of the generalized Stokes-Einstein equation, which employs a power law expression to describe the local change in MSD with time. Since the mean square displacement is linearly related to the creep compliance, it can be shown that the same algebraic approach can also be applied to creep measurements made on a rotational rheometer, giving access to the low frequency moduli in a fraction of the time required for oscillatory testing. Furthermore, the quality of the conversion process can be improved by fitting a Burgers model to the time domain data prior to conversion thus minimising errors associated with local differentiation, which is fundamental to the conversion approach.

KEY WORDS:

Burgers model, creep compliance, microrheology, viscoelastic modulus, low frequency, interconversion

1 INTRODUCTION

Microrheology techniques involve tracking the motion of dispersed probe (or tracer) particles in a complex fluid, to extract local and bulk rheological properties of the matrix. Analogous to mechanical rheometry techniques, a stress is applied to the system by motion of the probe particle, and the deformation (or strain) is measured through changes in the probe particle position. Dynamic Light Scattering (DLS) Microrheology is classified as a passive technique, whereby the colloidal probe particles undergo thermal fluctuations in a system at thermodynamic equilibrium. The Mean Square Displacement (MSD) or $\langle \Delta r^2(t) \rangle$ of the probe particles with time is followed by DLS, to enable linear viscoelastic parameters for the complex fluid matrix to be extracted [1-4]. In the implementation of microrheology, the viscoelastic moduli of a sample from the mean square displacement of embedded tracers is calculated using a generalised form of the Stokes-Einstein equation (Equation 1) as outlined by Mason and Weitz [1]. This requires Fourier transformation of $\langle \Delta r^2(t) \rangle$, which was initially achieved by performing a Laplace transform to obtain the shear modulus G(s) in terms of the Laplace frequency and then using analytical continuation on the basis that $s = i\omega$ to determine $G^*(\omega)$ [5].

$$\tilde{G}(s) = \frac{k_{B}T}{\pi as(\Delta \tilde{r}^{2}(s))}$$
(1)

$$G^{*}(\omega) = \frac{k_{B}T}{\pi a i \omega (\Delta r^{2}(i\omega))}$$
(2)

Mason proposed an alternative approach for estimating the required Fourier transform of the MSD algebraically by using a power law expression to describe the change in the local MSD with time at any given time point [6]. A benefit of this approach is that it does not require the use of numerical transforms (and associated truncation errors) or arbitrary functional forms implicit with the Fourier transformation. Mason, highlighted the need to

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Figure 4: Plots of G' and G" against angular frequency using data generated from microrheology, creep, and oscillation testing.

become trapped within the entanglement mesh (d > a), particle diffusion is governed by the relaxation rate of the polymer. Consequently one would expect good agreement between microrheological and bulk rheological measurements if (d > a) providing there is minimal interaction between tracer and sample.

4 CONCLUSIONS

DLS-microrheology can be used to extend rheological measurements in to the high frequency domain using an algebraic form of the generalised Stokes Einstein equation. Since the mean square displacement is linearly related to the creep compliance, the same approach can also be applied to creep measurements on a rotational rheometer, giving access to the low frequency moduli in a fraction of the time required for oscillatory testing. Furthermore, the quality of the conversion process can be improved by fitting a Burgers model to the time domain data prior to conversion thus minimizing errors associated with local differentiation, which is fundamental to the conversion approach.

REFERENCES

- Waigh TA: Microrheology of complex fluids, Rep. Prog. Phys. 68 (2005) 685-742.
- [2] Gardel ML, Valentine MT, Weitz D: Microscale diagnostic techniques, Springer-Verlag, Berlin (2005).
- [3] Cicuta P, Donald AM: Microrheology: A review of the method and applications, Soft Matter 3 (2007) 1449–1455.
- [4] Squires TM, Mason TG: Fluid mechanics of microrheology, Annu. Rev. Fluid Mech. 42 (2010) 413–438.
- [5] Mason TG, Weitz DA: Optical measurements of frequency-dependent linear viscoelastic moduli of complex fluids, Phys. Rev. Lett. 74 (1995) 1250 – 1253.
- [6] Mason TG: Estimating the viscoelastic moduli of complex fluids using the generalized Stokes-Einstein equation, Rheol. Acta 39 (2000) 371–378.
- [7] Dasgupta BR, Tee S-Y, Crocker JC, Frisken BJ, Weitz DA: Microrheology of polyethylene oxide using diffusing



Figure 5: Plots of η^* (top) and G' as well as G" (bottom) against angular frequency for Hengfloc 63026 in brine using data generated from microrheology, creep, and oscillation testing.

wave spectroscopy and single scattering, Phys. Rev. E 65 (2002) 051505.

- [8] Tassieri M, Evans RML, Warren RL, Bailey NJ and Cooper JM: Microrheology with optical tweezers: Data analysis, New J. Phys. 14 (2012) 115032.
- [9] Evans RML, Tassieri M, Auhl D and Waigh T: Direct conversion of rheological compliance measurements into storage and loss moduli, Phys. Rev. E 80 (2009) 012501.
- [10] Ferry JD: Viscoelastic properties of polymers, Wiley, New York (1980).
- [11] Palmer A, Zu J, Wirtz D: High-frequency viscoelasticity of crosslinked actin filament networks measured by diffusing wave spectroscopy, Rheol. Acta 37 (1998) 97.
- [12] Mason TG, Gisler T, Kroy K, Frey E, and Weitz DA: Rheology of F-Actin solutions determined from thermally driven tracer motion, J. Rheol. 44 (2000) 917–928.
- [13] van Zanten JH, Amin S, Abdala AA: Brownian motion of colloidal spheres in aqueous PEO solutions, Macromolecules 37 (2004) 3874-3880.
- [14] Koppel DE: Analysis of macromolecular polydispersity in intensity correlation spectroscopy: The method of cumulants, J. Chem. Phys. 57 (1972) 4814–4820.
- [15] Provencher S: Inverse problems in polymer characterization: Direct analysis of polydispersity with photon correlation spectroscopy, Makromol. Chem. 180 (1979) 201–209.
- [16] Stepanek P: Data analysis in dynamic light scattering, In Dynamic Light Scattering, Oxford University, Oxford (1993) 177-240.
- [17] Barnes HA, Hutton J.F and Walters K: An introduction to rheology, Elsevier (1989).

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- [18] Barnes HA: Handbook of Elementary Rheology, Institute of Non-Newtonian Fluid Mechanics, University of Wales (2000).
- [19] Malkin AY, Isayev AI: Rheology: Concepts, methods, and applications, ChemTec Publishing (2006).
- [20] Khan M, Mason TG: Trajectories of probe spheres in generalized linear viscoelastic complex fluids, Soft Matter 10 (2014) 9073
- [21] Peters R: Fiber optic device for detecting the scattered light or fluorescent light from a suspension, US Patent No 6,016 (2000) 195.
- [22] Amin S, Rega C, Jankevics H: Detection of viscoelasticity in aggregating dilute protein solutions through dynamic

light scattering-based optical microrheology, Rheol. Acta 51 (2012) 1–14.

- [23] Technical Note: Microrheology Running measurements on the Zetasizer ZSP/ZS, Malvern Instruments.
- [24] Pommella A, Prezios V, Caserta S, Cooper JM, Guido S and Tassieri M: Using optical tweezers for the characterization of polyelectrolyte solutions with very low viscoelasticity, Langmuir 29 (2013) 9224–9230.
- [25] Cai LH, Panyukov S, Rubinstein M: Mobility of spherical probe objects in polymer liquids macromolecules. 44(19) (2011) 7853-7863.

