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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].

$$\tilde{G}(s) = \frac{k_B T}{\pi a s \left(\Delta \tilde{r}^2(s) \right)} \tag{1}$$

$$G^*(\omega) = \frac{k_B T}{\pi a i\omega \left(\Delta r^2(i\omega) \right)} \tag{2}$$

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 better account for curvature in ln $\langle \Delta r^2(t)\rangle$ versus ln t, which has been expanded on by Dasgupta et al. [7]. Another approach has been used by Tassiero et al. [8] based on the method of Evans [9], which uses a piecewise linear function to determine the Fourier transform. This approach has also been applied to creep data. The algebraic expression proposed by Mason [6] can be written as

$$\left|G^{*}(\omega)\right| \approx \frac{k_B T}{\pi a \left(\Delta r^2(1/\omega)\right) \Gamma\left[1+\alpha(\omega)\right]} \tag{3}$$

with $\alpha(\omega)$ the local power index given by Equation 4 estimated at $t = i\omega$ and Γ is the gamma function, which is an extension of the factorial function and when employed in the above form can be equated with a local Fourier transform of the MSD.

$$\alpha(\omega) = \left.\frac{d\ln\left(\Delta r^2(t)\right)}{d\ln t}\right|_{t=1/\omega} \tag{4}$$

For thermally-driven motion of the probe particles, the slope of the logarithmic time derivative of the mean square displacement will be unity in a purely viscous medium (diffusive motion), zero in an elastic medium (completed arrested motion), and will lie between these extremes in a complex viscoelastic fluid medium. This can be equivocated with the phase angle or phase lag δ measured using dynamic measurements on a rotational rheometer, where $\delta = \pi\alpha(\omega)/2$. Consequently the frequency dependent viscoelastic moduli $G'(\omega)$ and $G''(\omega)$ can be determined using Euler's theorem

$$\begin{aligned} G'(\omega) &= G^{*}(\omega)\cos\left[\pi\frac{\alpha(\omega)}{2}\right] \\ G''(\omega) &= G^{*}(\omega)\sin\left[\pi\frac{\alpha(\omega)}{2}\right] \end{aligned} \tag{5}$$

A relationship between the MSD of a tracer embedded in a viscoelastic fluid and the creep compliance of that fluid $J(t)$ can also be established since in the Laplace frequency domain $J(s) = 1/G(s)$, hence based on Equation 1 it can be shown $J(t)$ and $\langle \Delta r^2(t)\rangle$ are linearly related according to Equation 6 [10–12]. A microrheology experiment can therefore be considered analogous to a mechanical creep test performed in the linear viscoelastic regime and data can be presented in a common rheological format using $J(t)$ without the need for transformation to the frequency domain [13].

$$J(t) = \frac{\pi a}{k_B T}\left(\Delta r^2(t)\right) \tag{6}$$

Furthermore, the mean square displacement in Equation 2 can be substituted with the creep compliance to give the following relation

$$\left|G^{*}(\omega)\right| \approx \frac{1}{J(1/\omega)\Gamma\left[1+\alpha(\omega)\right]} \tag{7}$$

with

$$\alpha(\omega) = \left.\frac{d\ln J(t)}{d\ln t}\right|_{t=1/\omega} \tag{8}$$

Therefore, the methods developed for obtaining viscoelastic properties from the MSD in a microrheology measurement can be equally applied to the creep compliance, thus facilitating an approach for converting the time dependent creep compliance to frequency dependent moduli for measurements made on a rotational rheometer. A key benefit of this approach is that it does not require oversampling of data as with alternative methods [8, 9] hence it can be used to transform existing data obtained at discrete time intervals quite easily so long as an accurate estimate of $\alpha(\omega)$ can be made.

A limitation of the algebraic approach for both microrheology and creep testing is that it requires local differentiation of the $\langle \Delta r^2(t)\rangle$ or $J(t)$ versus time curves, which can lead to errors in the value of $\alpha(\omega)$ and hence the quality of the converted data, particularly $G'(\omega)$ and $G''(\omega)$. Unlike a dynamic oscillatory test where data can be integrated for an extended period at a discrete oscillation frequency, each data point is recorded instantaneously in a creep measurement hence integrating is not really feasible unless the integration window is much smaller than the recorded time increments. Another, option is to fit the data with a polynomial; however, a classical problem of fitting with polynomials is oscillatory artifices, which are further exacerbated on differentiating the data.

In such circumstances a more viable approach may be to model the data with an appropriate functional form and to perform the conversion on the fitted data, hence minimizing errors due to local noise. Such an approach is common and indeed necessary when using DLS to determine the size distribution of a dispersion, where the Autocorrelation Function (ACF) is fitted using the method of cumulants to give a Z-average diameter and polydispersity index [13] or a multiple exponential decay function to give a size distribution, with each relaxation time corresponding with a particular size class [15, 16]. Such a function may be expected to fit rheological data similarly well if demonstrating typical Maxwell like behavior, however, when probing short time dynamics of viscoelastic materials which can demonstrate pseudo-gel behavior as with microrheology, there is a need to account for Kelvin-Voigt behavior also. Hence, a more suitable model is the Burgers model or Creep model (Equation 9) which is commonly used for fitting creep compliance curves and is a standard rheological model for describing linear viscoelastic behavior [17–19].

$$J(t) = J_o + \sum_n J_n\left(1 - e^{t/\tau_n}\right) + \frac{t}{\eta_o} \tag{9}$$

Because of the linear relationship between creep compliance and mean square displacement the Burgers model is equally applicable to microrheology also. Furthermore, the Burgers model is similar to the coupled harmonically bound Brownian particle (c-HBBP) model discussed by Khan and Mason for describing microrheological behavior of generalized linear viscoelastic (GLVE) complex fluids, further justifying its use for probe based microrheology [20]. A key advantage of fitting with a functional form of this type which is monotonically increasing is that it respects a-priori knowledge about the system; that is we expect that the mean squared displacement or creep compliance is monotonically increasing with time (its derivative is positive-semi definite). Furthermore, as the determination of the intercept is crucial for determining the mean square displacement in a DLS-microrheology measurement, since $\langle \Delta r^2(t) \rangle \propto [\log g(0) - \log g(t)]$, then shorter diffusion times or delay times can lead to negative values of the mean square displacement which are then unusable in the determination of $\alpha(\omega)$. An approach which involves fitting J_o, the intercept in the Burgers model, allows one to fit out any such uncertainties.

Fitting a retardation spectrum to $J(t)$ curves obtained from microrheology measurements has previously been presented by Mason et al. [12]. In this work they calculated the retardation spectrum by fitting a Kelvin-Voigt model with multiple retardation times and used this to calculate the viscoelastic moduli. While the data fit was good over times where the material showed Kelvin-Voigt behavior, at longer times this was likely due to the exclusion of a Maxwell term in the fitting function, something which a Burgers model addresses. In this paper we demonstrate the applicability of Equation 7 for converting creep compliance to viscoelastic moduli and the use of the Burgers model for accurately fitting $\langle \Delta r^2(t) \rangle$ and $J(t)$ to improve the quality of the conversion process.

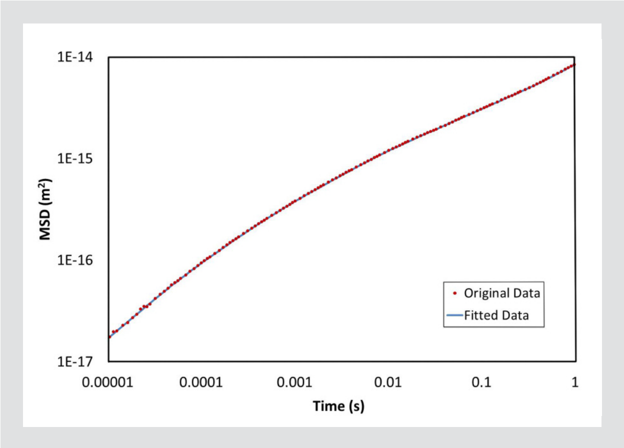

Figure 1: MSD versus time plot comparing original data and fitted data (Burgers model).

2 MATERIALS AND METHODS

FLOPAAM 3230s polymer (Polyacrylamide powder supplied by SNF Floerger) with a molecular weight ranging between 6–8 MDaltons was dispersed in deionized water to give a final concentration of 1 mg/ml. Carboxylated Melamine microspheres with a particle diameter of 1.1 μm were used as tracers for the DLS-microrheology measurements, which were performed on a Zetasizer Nano ZSP (Malvern Instruments) using the non-invasive back-scattering (NIBS) configuration, which uses a scattering angle of 173 ° and a moving lens arrangement [21]. Zeta potential measurements were used to ensure minimal interaction between tracer particle and sample by comparing the zeta potential of tracer in solvent with and without polymer present [22, 23]. A sufficient concentration of tracers was added to each sample to ensure dominant scattering over the polymer. This criterion was considered to have been met when the particle size distribution determined on the same instrument, contained a single peak attributable to the tracer particles. In this case 5 μg of the 10 %(w/v) tracer suspension in 1000 μL of sample was found to be sufficient. Creep and oscillatory measurements were made using a Kinexus Pro+ rotational rheometer with a cone-plate measuring system. All microrheology and rotational rheometer measurements were made at 25 °C.

3 RESULTS AND DISCUSSION

Figure 1 shows a plot of the calculated MSD against time for the polyacrylamide solution and the corresponding multiple Burgers model fit, based on 10 retardation time constants. The observed curvature in the MSD demonstrate regions of sub-diffusive behavior characteristic of a viscoelastic fluid and such behavior seems to be well described by the Burgers model with no discernible difference between the original data and fitted data observed. For the range of data shown the difference in the fitted and original values of the MSD compared at each discrete time point was less than 2 %. Fig-

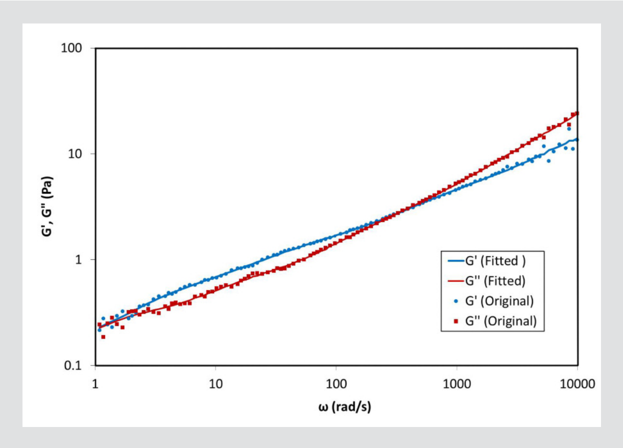

Figure 2: Plots of G' and G" against angular frequency following conversion from MSD using original data (filled symbols) and fitted data (lines).

ure 2 shows *G'* and *G"* plotted against angular frequency following conversion of both the original and fitted MSD. Clearly there is an improvement in the quality of the converted data following model fitting while retaining all the key features of the original data set.

Figure 3 shows $G'(\omega)$ and $G''(\omega)$ plotted against angular frequency following conversion from $J(t)$. The top chart in Figure 3 shows an overlay of data converted with and without the use of the Burgers model. As with the MSD this demonstrates that the Burgers model provides a good fit to the creep data and improves the quality of the conversion process. The bottom chart in Figure 3 shows the model fitted data plotted alongside oscillatory data. The agreement between the two data sets is excellent thus validating the use of Equation 7 for transforming creep data measured on a rotational rheometer. A key benefit of this approach is the measurement time needed to access low frequency data. To get to 0.001 rad/s as shown in Figure 3 would take 1000 seconds or about 17 minutes using a creep test. Since each time point corresponds with an angular frequency then theoretically all frequencies up to $1/t$ can be sampled continuously, subject to sample and instrument constraints. In comparison a full oscillation cycle at 0.001 rad/s would take 6283 seconds, which equates to approximately 1 hour 45 minutes, and that corresponds to a single data point at that frequency. While the use of partial wave or multiwave oscillatory testing may reduce the time for testing over a range of frequencies it would still be considerable compared with a direct time or creep measurement.

Through using a combination of microrheology, on length scales corresponding with bulk material behavior, and rotational rheometry in creep and oscillatory modes, it is therefore possible to access a wide range of timescales and frequencies. This is demonstrated in Figure 4 which combines data from Figure 2 (right) and Figure 3 (right). In this particular case rheological properties have been determined over 8 decades of frequency. To further validate the approach another polyacrylamide sample (Hengfloc 63026 supplied by Beijing Hengu) was evaluated at two different concentrations (1 and 2 mg/ml) in a brine solution with $1\,\mu$m PEGylated polystyrene beads used as tracers. PEGylated tracers worked better than carboxylated melamine in these brine systems with the latter showing evidence of sample interaction and aggregation. The results are shown in Figure 5 and as with the Flopaam sample show excellent agreement between rotational rheometry (creep and oscillation) and microrheology measurements while clearly demonstrating the effect of concentration on viscoelastic behavior.

The excellent agreement between rotational rheometry and microrheology measurements on polyacrylamide solutions has also been observed by Pomella et al. [24]. They studied dilute polyacrylamide solutions with very low viscoelasticity using optical tweezers and bulk rheology and found 'remarkable' agreement between these two techniques. Such agreement is supported by the work of Cai et al., who used scaling theory to derive the time dependence of the mean-square displacement $\langle \Delta r^2(t) \rangle$ of spherical probe particle of different sizes in polymer solutions and melts [25]. Three different cases for particle diffusion were proposed depending on the relative size of the particle with respect to the correlation length ξ and the tube diameter a of an entangled polymer system. They showed that for probe particles which are large enough to

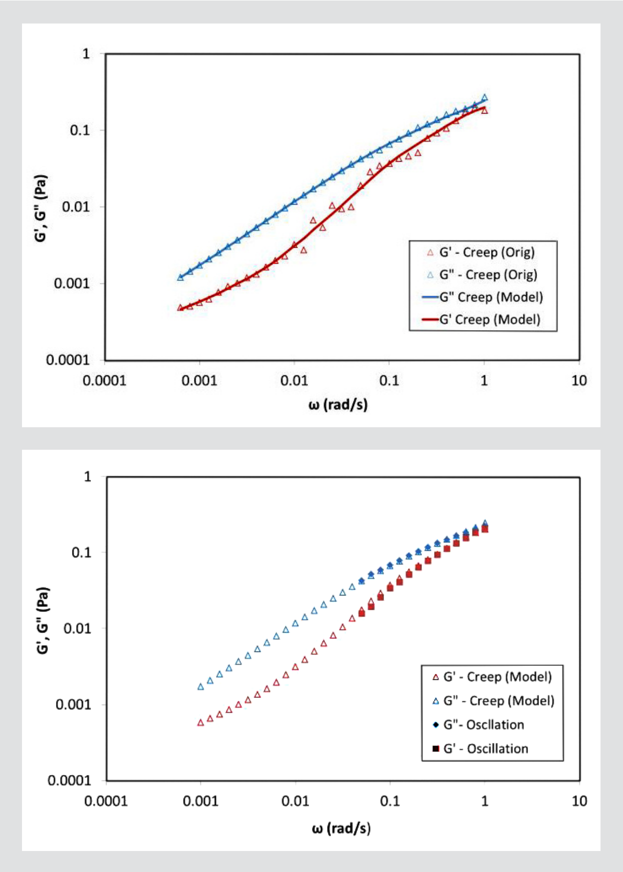

Figure 3: Plots of G' and G" against angular frequency following conversion from J(t) measured on a rotational rheometer using (top) original data and (bottom) fitted data compared with oscillatory data.

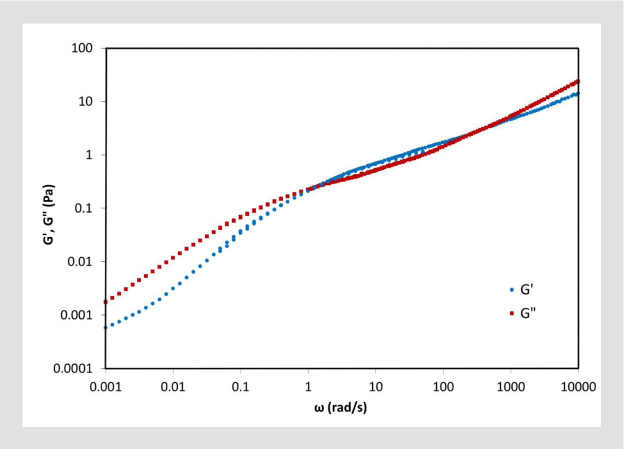

Figure 4: Plots of G' and G" against angular frequency using data generated from microrheology, creep, and oscillation testing.

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.

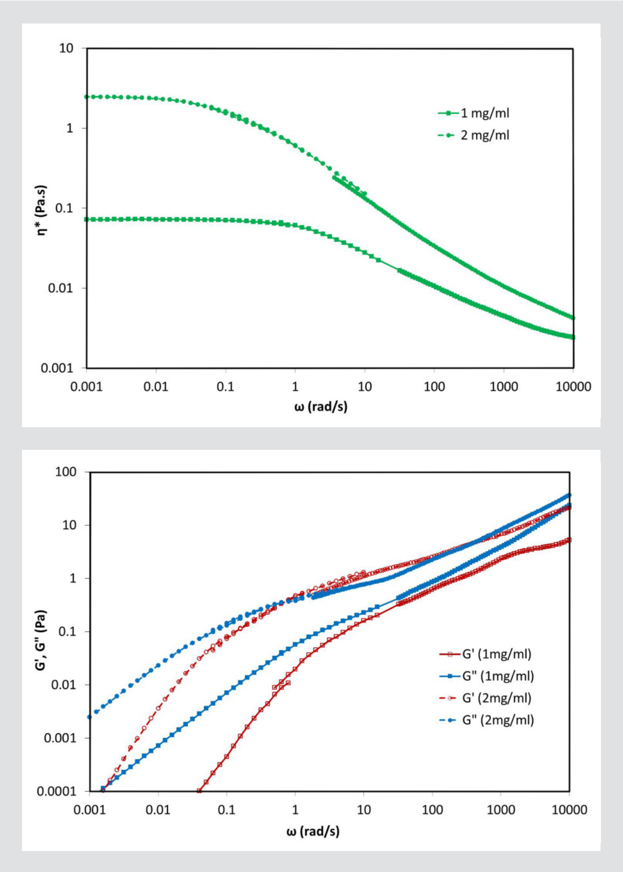

Figure 5: Plots of η^* (top) and G' as well as G" (bottom) against angular frequency for Hengfloc 63026 in brine using data generated from microrheology, creep, and oscillation testing.

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