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The Laplace Approach in Microrheology

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ABSTRACT

When coupled with the Generalized Stokes-Einstein (GSE) equation, it is often reported that micro-rheology probes the dynamic properties differently than do macroscopic rheological measurements, especially in relatively condensed systems. In the present work, we empirically examine the GSE in its widely used form: following an analytical continuation, the Fourier transformed particle mean-square displacement (MSD) is used to determine the dynamic moduli [G'(ω) and G''(ω)] and we compare the results with those obtained by direct inverse Laplace transform calculation of the relevant viscoelastic functions (either relaxation modulus or creep compliance) from the MSD. The results show that the inverse Laplace approaches can differ from the Fourier approach and give better agreement with macroscopic rheological measurements when this is the case. Some instances of agreement between the Fourier approach and the direct Laplace transform approaches are also shown. It is recommended that micro-rheology MSD data be interpreted using one of the direct Laplace transform based approaches.

Controlled by the thermally driven Brownian motion, micro-rheology probes complex fluids in a different way than does traditional macroscopic rheology. One significant difference is that micro-rheology can probe the sample at shorter and tunable length scales, generally by changing the size of a probe particle [1]. Another advantage for micro-rheology is that it can be used in a non-invasive setup where viscoelastic properties of the sample can be extracted without applying external forces or perturbations [2]. The important step in micro-rheology is to take the measured response of the particle mean-squared displacement (MSD) and establishing the relationship between the MSD and the continuum viscoelastic properties of the system through the generalized Stokes-Einstein relationship (GSER) as proposed by Mason and Weitz [3]:

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

where $\tilde{G}(s)$ and $\langle \Delta \tilde{r}^2(s) \rangle$ are the Laplace transformed relaxation modulus and the Laplace transformed mean squared displacement (MSD), respectively. s is the Laplace frequency. k_B denotes the Boltzmann constant. T is the temperature in Kelvin, and a is the particle radius. Based on this relationship, Mason [4] further developed the GSER by transforming the modulus into the frequency domain by assuming an analytical continuation ($s = i\omega$) and taking the Fourier transform of $\tilde{G}(s)$ to obtain the complex modulus $G^*(\omega)$:

$$G^*(\omega) = \frac{k_B T}{\pi a i \omega \mathcal{F}\{\langle \Delta r^2(\tau) \rangle\}} \tag{2}$$

where $\mathcal{F}\{\langle \Delta r^2(\tau) \rangle\}$ is the Fourier transformed MSD. The Fourier transformation of the MSD data can be estimated using the gamma function and local differentiations of the MSD data [4]. The storage modulus ($G'(\omega)$) and loss modulus ($G''(\omega)$) can be further calculated. In some instances, e.g. relatively dilute polymer solutions [5,6], the viscoelastic properties of the sample measured from micro-rheology agree well with those obtained from macroscopic rheological measurements. However, upon increasing the concentration in colloidal systems or the number of entanglements in polymer solutions, micro-rheology seems to not fully capture the macroscopic viscoelastic properties of the sample [7,8,9,10,11]. The current understanding of this situation includes the possibility that physically, non-ergodic or heterogeneous concentrated systems have length-scale-dependent dynamics with the consequence that the microscopic viscoelastic behavior may differ from the macroscopic rheological measurements [7,11].

At the same time, with increasing colloidal concentration or number of entanglements in polymer solutions, the shape of the MSD becomes more complex, which can introduce larger errors in the estimation of the Fourier transformed MSD when using the local differentiation of the MSD [5]. Although these sources of error are recognized and there have been mathematical improvements [5,11], there still remain questions about the correct interpretation of the derived rheological properties obtained from the micro-rheological methods using the GSER and this is particularly true of the question of the probe-size dependence of the response, which has ramifications for the understanding of the physics of systems with heterogeneous dynamics or spatial heterogeneity.

In this Letter, we compare the above described widely used micro-rheological method where the analytical continuation ($s = i\omega$) and the Fourier transformed MSD are used to obtain frequency dependent viscoelastic properties (the Fourier Approach, Equation (2)), with the calculation of the time-domain response obtained by directly taking the inverse of the Laplace transform of Equation (1) along with the continuum viscoelastic identity (in Laplace space) $s\tilde{J}(s)\tilde{G}(s) = 1$ [12] to extract the system compliance information ($J(t)$, the Compliance Approach), which is directly proportional to the MSD [13]

$$J(t) = \left[\frac{\pi a}{k_B T}\right]\langle \Delta r^2(t)\rangle \qquad (3)$$

This approach of calculating the creep compliance was proposed by Xu et al [14] in their study on actin filament networks, but it has not been widely used in studies of concentrated systems. From the $J(t)$ information, the relaxation modulus, $G(t)$, can be calculated by numerical evaluation of the convolution integral proposed by Hopkins and Hamming [15] as well as the linear interpolation method from Evans et al [16]

$$\int_0^t J(\tau)G(t-\tau)d\tau = t \tag{4}$$

Despite having the same starting point of equation (1), unlike the Fourier Approach, the Compliance Approach does not use the analytical continuation ($s = i\omega$) to switch the Laplace space into the Fourier space. Also, directly relating the creep compliance to the MSD (equation 3) greatly reduces mathematical errors during the calculations. In the present work, we compare the two micro-rheology methods using MSD data for three different systems (a PS-PNIPAM/AA model soft colloidal glass, a Laponite suspension, and a concentrated giant-micelle solution). To better show the comparisons, and test the validity of the analytical continuation ($s = i\omega$), a third Fourier-free calculation method (Laplace Approach) is introduced where a direct numerical inversion (Talbot method [17]) on the Laplace transformed modulus $\tilde{G}(s)$ was performed to obtain the relaxation modulus G(t). Then the $G'(\omega)$, $G''(\omega)$, and $J(t)$ information can be calculated using basic viscoelastic interconversions [18]. A diagram of the three calculation methods used in the present work is given in Figure 1.

First, we present results for a soft colloidal suspension from our own measurements, which led to the present findings, and we provide related analysis of MSD data reported in the literature. In all instances we are interested in the conversion from MSD data to the viscoelastic domain. For our own work, multi-speckle diffusing-wave spectroscopy (DWS) in backscattering geometry was used to characterize the dynamics of the sample and the MSD was determined from the intensity autocorrelation function $g_2(t)$ [19]. The samples were illuminated by polarized light from a coherent laser source (Melles Griot) with a wavelength of 633 nm. A CCD camera

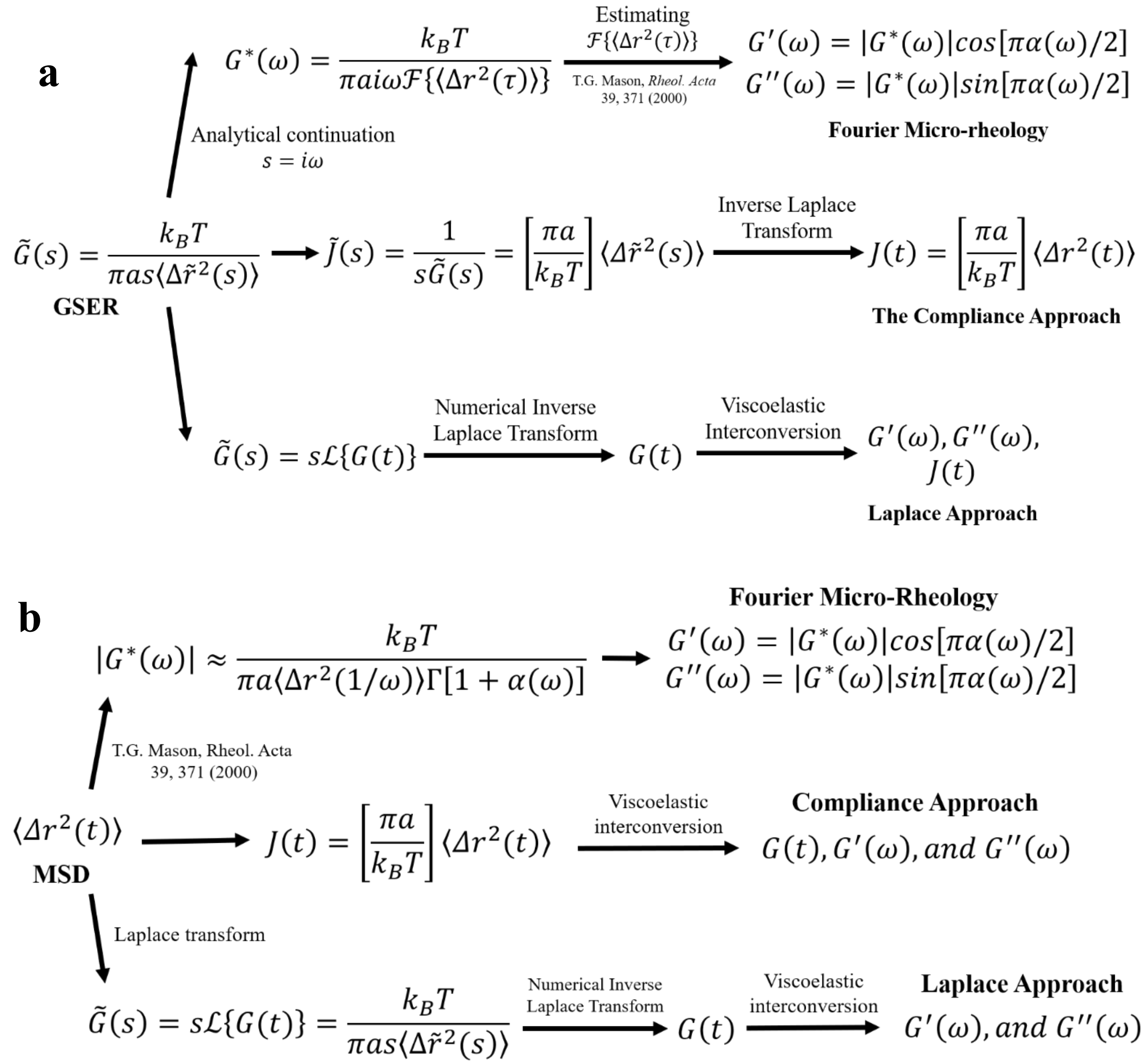

Figure 1. **(a)** A summary of the calculation routes used in this work. **(b)** A detailed calculation processes for the three approaches based on the mean squared displacements (MSD).

(Basler acA640-120uc) at 120 frames/s was used to collect the multiply scattered light. The soft colloidal system used in this work is a 16.0 wt% polystyrene (PS)-poly(N-isopropylacrylamide) (PNIPAM)/ acrylic acid (AA) (PS-PNIPAM/AA) latex system as previously investigated with a final particle diameter of 210.7 nm (23 °C) [19,20]. 2 μm polystyrene microsphere probes

(Polybead® Microspheres, Polysciences, Inc.) were used in the DWS experiments and the concentration of probe particles was 1.0 vol%. Macroscopic rheological measurements were performed using a stress-controlled rotary rheometer (AR-G2, TA Instruments) equipped with a cone-plate geometry having a diameter of 40 mm and cone angle of 2^o. The colloidal sample was surrounded by Krytox oil to prevent solvent evaporation during testing. All measurements were performed after sudden volume fraction increases (up-jumps) from the liquid state at low volume fraction to various final high volume fractions, and then aged into an intransient state, where the response became independent of time, thus the final measurements are for samples that have achieved a metastable equilibrium.

From the DWS measurement, the $g_2(t)$ information for the soft PS-PNIPAM/AA colloids can be obtained. We emphasize that the samples were all aged into metastable equilibrium states after the concentration jumps. From the $g_2(t)$ information, the corresponding MSD can be calculated. In the backscattering geometry the relevant calculation method comes from Scheffold and coworkers [7]:

$$g_2(t) - 1 = exp\left[-2\gamma\sqrt{k_0^2\langle\Delta r^2(t)\rangle + b} + 2\gamma\sqrt{b}\right] \qquad \textbf{(5)}$$

where γ quantifies the low-order scattering, and here we take $\gamma = 1.9$ [7], b is a parameter characterizing the deviation of the current geometry from that of an idealized semi-infinite slab, and $b = 0.0035$ [7]. $k_0 = 2\pi/\lambda$ is the wave number. From the MSD information, the creep compliance was calculated using the three methods shown in Figure 1 (the Fourier micro-rheology (Fourier App.), the Compliance Approach (Compliance App.), and the Laplace approach (Laplace App.)). The results are shown in Figures 2. Importantly, the compliance response calculated from the Compliance Approach for the 2 μm probe measurements agrees with that from the creep compliance measured in the macroscopic rheology, indicating the size of the probe particles is large enough compared with the structural length-scales of the system that the scattering signals observed by DWS were all from the probe particles and that the micro-rheological analysis is valid for this case. Second, among the three different calculation methods, the results from the Compliance Approach and the Laplace Approach agree with macroscopic rheological measurements. However, the Fourier Approach gives smaller values of J(t). This difference in J(t) shows that the Compliance Approach gives better estimations of the viscoelastic properties of the system than does the Fourier Approach.

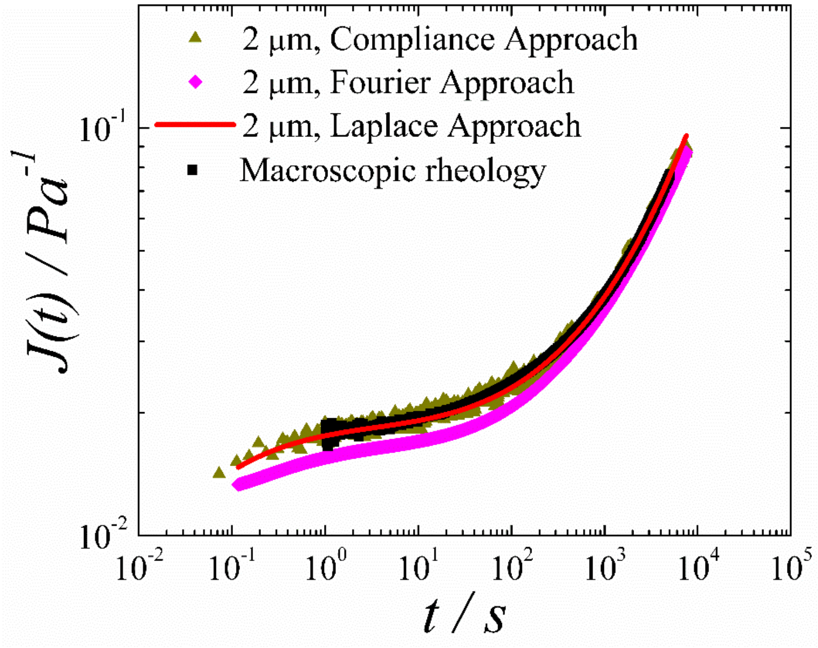

Figure 2. Compliance calculated with the Compliance Approach, the Fourier Approach, as well as the Laplace Approach for a 16.0 wt% PS-PNIPAM/AA system with 2 μm probes (probe concentration 1.0 vol%). Black squares indicate the creep compliance measured by macroscopic rheology for a same system.

We remark that the difference between the Fourier Approach and the Laplace Approach is that the Laplace Approach takes the Laplace transform of the Laplace space relaxation modulus while in the Fourier approach, an analytical continuation ($s = i\omega$) is assumed to hold and one goes from the Laplace relaxation modulus to the frequency dependent complex modulus via the Fourier transform of the MSD. The above data show us straightforwardly that the Fourier approach can be problematic when being used to interpret microrheological responses in complex fluids such as the soft colloidal glass examined here.

To further explore the problem, we used literature MSD data for a concentrated giant-micelle solution: hexa-ethylene glycol mono n-hexadecyl ether ($C_{16}E_6$) surfactant solution (100 mg/mL) with sulfate polystyrene latex spheres (diameter 720 nm) embedded as tracer particles. The experimental MSD data used come from Cardinaux et al [7] and was determined by DWS in both backscattering and transmission geometries with a sample thickness of 2 mm. Macroscopic rheological data were also reported in [7]. We compare the dynamic moduli $G'(\omega)$ and $G''(\omega)$ calculated from the MSD using both the Fourier and the Compliance Approaches in Figure 3(a) and 3(b). We remark that the MSD data from Cardinaux et al [7] is smooth and not noisy or

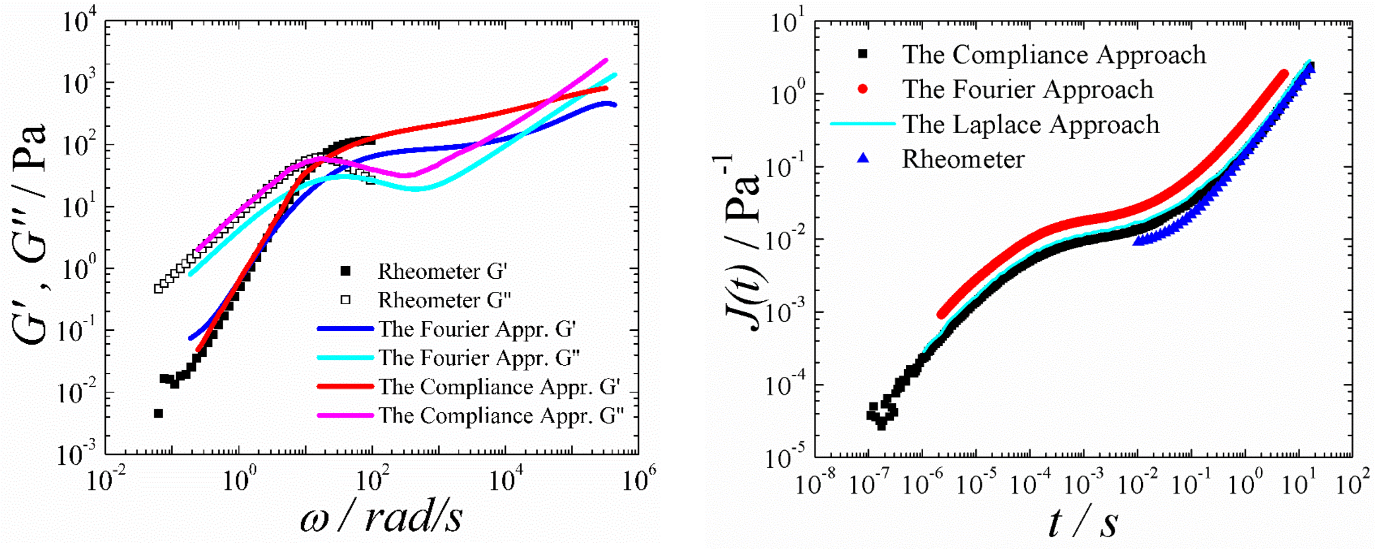

Figure 3. (a) Storage modulus, $G'(\omega)$, and loss modulus, $G''(\omega)$, from direct calculations using the Fourier Approach, and from viscoelastic interconversion from J(t) calculated with the Compliance Approach, compared with macro-rheological measurements from Cardinaux et al [7]. **(b)** The calculated J(t) from the three different micro-rheological methods. Rheometric J(t) is calculated from frequency sweep test results in Figure 3(a).

fluctuating, thus minimizing the errors in the numerical treatment of the MSD data when using the Fourier Approach [5]. It is clear to see that in Figure 3(a), the dynamic moduli ($G'(\omega)$ and $G''(\omega)$) calculated from the Compliance Approach are closer to the macroscopic measurements than the values calculated from the Fourier Approach and in the data range at high frequencies the two approaches differ from the Fourier Approach which gives lower modulus values. Of interest is that this deviation is the opposite of that seen in the compliance calculations shown above.

Having observed differences between the Fourier Approach and the Compliance or Laplace approaches and the use of the approach is widespread, the question arises as to whether or not there are instances in which the results are the same? To answer this question, the Fourier Approach and the Compliance Approach were used to analyze MSD data for a Laponite® clay dispersion (1 wt%) obtained by multiple particle tracking micro-rheology (MPT) [21]. The probe particles were Fluoresbite® YG Carboxylate Microspheres having sizes of 110 nm, 161 nm, 258 nm, and 463 nm. Figure 4 presents the J(t) calculated from the MSD of a 45-min-aged Laponite with probes of different sizes. In the Laponite system, the Compliance Approach and the Fourier Approach give similar results and show the same probe size effects. In this case, the two approaches seem to probe the system heterogeneity in a similar way. Thus, in some situations, the Fourier approach seems adequate to capture the heterogeneous dynamics in an equivalent fashion to the Compliance or Laplace Approaches.

From the results above for the three different systems several things are clear. First, the different results calculated from the Compliance Approach and the Fourier Approach do not simply originate from the fitting of the MSD data since the results are from the same MSD data. Second, we remark that the different results between these two approaches seem to arise from the

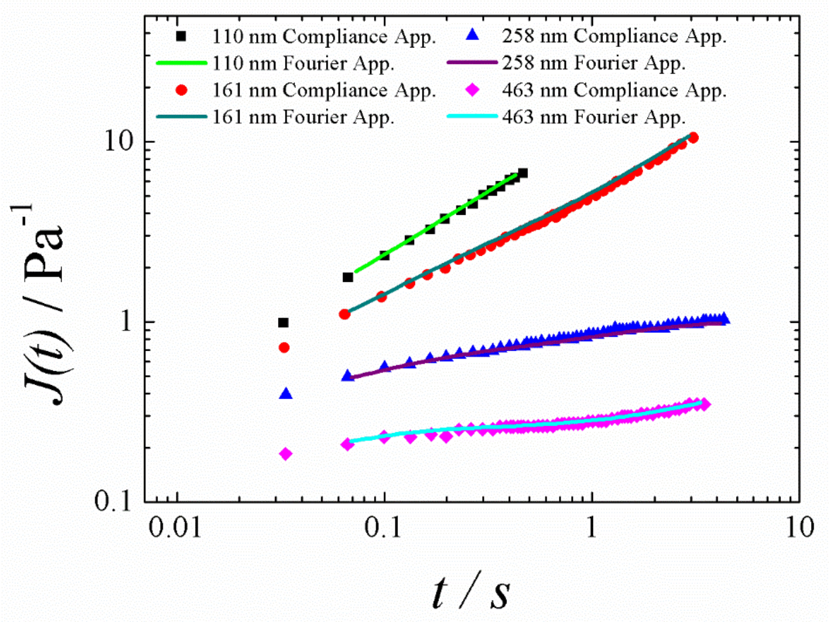

Figure 4. Calculated J(t) using the Compliance Approach and the Fourier Approach for 1 wt% Laponite dispersion with four different sizes of probes after aging of 45 minutes. J(t) calculated from MSD data from Rich et al [21].

analytic continuation ($s = i\omega$) approximation. Equation (2) is derived from Equation (1) by assuming an analytic continuation. This assumption switches the Laplace transform in Equation (1) into a Fourier transform equation in Equation (2). Mathematically, the Fourier space is an imaginary part of the Laplace space ($s = \sigma + i\omega$). However, in a relaxation process, both the real and the imaginary parts affect the results when converting time domain data into the frequency domain. It is important to note that not only has the Laplace transform been used in going from time to frequency domain in dielectric spectroscopy[22,23,24] but there have also been discussions of the use of Fourier transforms being problematic in transforming time domain data with corrections applied to specific functional forms for the time domain behavior [25,26]. We have not identified the underlying mathematical reason for the problem, but we can say from the work presented above and from an empirical perspective the use of the Fourier transform may be problematic [27,28] and it seems appropriate to recommend that microrheology data in general should be treated with one of the approaches based on the Laplace transform. Even though the full implications of the present results require further investigation, this analytic continuation 'crisis' provides a partial explanation for discrepancies between macro- and micro-rheological results in non-ergodic (or heterogeneous) systems such as colloidal glasses or gels [7,11] and beyond the arguments related to length-scale dependent dynamics, which can exist but need to be treated carefully as the quantitative values can depend on the method of data analysis used to go from the time domain to the frequency domain as illustrated in the above results.

To summarize, the micro-rheological behaviors for three different systems (a PS-PNIPAM/AA soft colloidal latex glass, a concentrated $C_{16}E_6$ giant-micelle solution), and a Laponite® dispersion were determined from MSD data using three different calculation methods (Fourier Approach, Compliance Approach and Laplace Approach) and were compared with the corresponding macroscopic rheological properties, when available. It is shown that the use of analytical continuation to go from the Laplace transform of the relaxation modulus to the frequency domain (Fourier) dynamic moduli can be problematic and that a preferred method would be to use the Laplace transform of the MSD directly in order to obtain the creep compliance (Compliance Approach) or the relaxation modulus (Laplace Approach). While in the instance of the Laponite systems we found agreement between the Laplace based methods and the Fourier Approach, this was not observed for the soft colloid or the giant micellar systems and we take a comment famously made by D.J. Plazek 'With compliance comes comprehension' [29] and extend it to microrheology by recommending the use of the Compliance Approach to convert the MSD data to creep compliance, which can then be converted to the dynamic moduli using standard linear viscoelastic interconversions, if necessary, to obtain the dynamic moduli.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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References

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[1] Weitz DA, Pine DJ, in Dynamic Light Scattering: The Method and Some Applications. Oxford Univ. Press, Oxford. pp. 652-720, 1993.

[2] Harden JL, VIasnoff V. Recent advances in DWS-based micro-rheology. Cur. Opi. Colloid & Interface Sci. 2001, 6 (5-6), 438-445.

[3] Mason TG, Weitz DA. Optical measurements of frequency-dependent linear viscoelastic moduli of complex fluids. Phys. Rev. Lett. 1995, 74 (7), 1250.

[4] Mason TG. Estimating the viscoelastic moduli of complex fluids using the generalized Stokes–Einstein equation. Rheol. Acta. 2000, 39 (4), 371-378.

[5] Duffy JJ, Rega CA, Jack R, Amin S. An algebraic approach for determining viscoelastic moduli from creep compliance through application of the Generalised Stokes-Einstein relation and Burgers model. Appl. Rheol. 2016, 26 (1), 10-15.

[6] Dodero A, Williams R, Gagliardi S, Vicini S, Alloisio M, Castellano M. A micro-rheological and rheological study of biopolymers solutions: Hyaluronic acid. Carbohydrate Polym. 2019, 203 (1), 349-355.

[7] Cardinaux F, Cipelletti L, Scheffold F, Schurtenberger P. Microrheology of giant-micelle solutions. *Europhys. Lett.* 2002, 57(5), 738.

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[8] Lu Q, Solomon MJ. Probe size effects on the microrheology of associating polymer solutions. Phys. Rev. E. 2002, 66 (6), 061504.

[9] Dasgupta BR, Weitz DA. Microrheology of cross-linked polyacrylamide networks. Phys. Rev. E. 2005, 71 (2), 021504.

[10] Sarmiento-Gomez E, Montalvan-Sorrosa D, Garza C, Mas-Oliva J, Castillo R. Rheology and DWS microrheology of concentrated suspensions of the semiflexible filamentous fd virus. Euro. Phys. J. E. 2012, 35 (5), 35.

[11] Narita T, Indei T. Microrheological study of physical gelation in living polymeric networks. Macromolecules. 2016, 49 (12), 4634-4646.

[12] Ferry JD. Viscoelasticity Properties of Polymers, 3rd Edition. John Wiley & Sons, New York, USA, 1980.

[13] Squires TM, Mason TG. Fluid Mechanics of Microrheology. Ann. Rev. Fluid Mech. 2010, 42 (1), 413-438.

[14] Xu J, Viasnoff V, Wirtz D. Compliance of actin filament networks measured by particle-tracking microrheology and diffusing wave spectroscopy. Rheol. Acta. 1998, 37 (4), 387-398.

[15] Hopkins IL, Hamming RW. On creep and relaxation. J. Appl. Phys. 1957, 28 (8), 906-909.

[16] Evans RML, Tassieri M, Auhl D, Waigh TA. Direct conversion of rheological compliance measurements into storage and loss moduli. Phys. Rev. E. 2009, 80 (1), 012501.

[17] Talbot A. The accurate numerical inversion of Laplace transforms. *IMA J. Appl. Math*. **1979**, 23 (1), 97-120.

[18] Software 'IRIS Rheo-Hub 2014' by Winter HH, Mours M. The cyber infrastructure initiative for rheology. Rheol. Acta. **2006**, 45 (4), 331-338.

[19] Li Q, Peng X, McKenna GB. Long-term aging behaviors in a model soft colloidal system. *Soft Matter*. **2017**, 13 (7), 1396-1404.

[20] Di X, Peng X, McKenna GB. Dynamics of a thermo-responsive microgel colloid near to the glass transition. *J. Chem. Phys*. **2014**, 140(5), 054903.

[21] Rich JP, McKinley GH, Doyle PS. Size dependence of microprobe dynamics during gelation of a discotic colloidal clay. *J. Rheol*. **2011**, 55(2), 273-299.

[22] Mopsik FI. The transformation of time-domain relaxation data into the frequency domain. *IEEE Trans. Electrical Insulation.* **1985**, 6 (1), 957-964.

[23] Simon GP, Williams G. A consideration of the accuracy and application of the Brather approximation for the transformation of dielectric relaxation data from the time domain to the frequency domain. *Polymer*. **1993**, 34 (10), 2038-2044.

[24] Zorn R, Mopsik FI, McKenna GB, Willner L, Richter D. Dynamics of polybutadienes with different microstructures. 2. Dielectric response and comparisons with rheological behavior. *J. Chem. Phys*. **1997**, 107 (9), 3645-3655.

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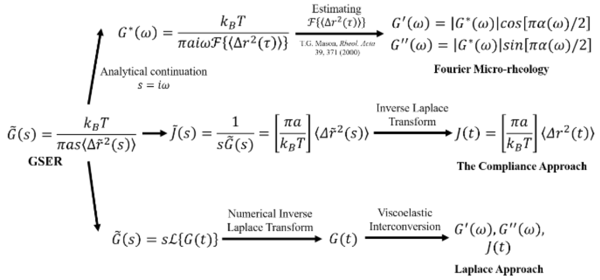
[25] Feldman YD, Zuev YF, Polygalov EA, Fedotov VD. Time domain dielectric spectroscopy. A new effective tool for physical chemistry investigation. *Colloid Polym. Sci*. **1992**, 270 (8), 768-780.

[26] Ferguson R, Arrighi V, McEwen IJ, Gagliardi S, Triolo A. An improved algorithm for the Fourier integral of the KWW function and its application to neutron scattering and dielectric data. *J. Macromolecular Sci., Part B: Phys*. **2006**, 45 (6), 1065-1081.

[27] Oppenheim AV, Willsky AS, Young IA. Signals and Systems. Prentice-Hall, Inc. 1968.

[28] Liu F, Li H, Wang W, Liang B. Initial-condition consideration by transferring and loading reconstruction for the dynamic analysis of linear structures in the frequency domain. *J. Sound and Vibration*. **2015**, 336 (1), 164-178.

[29] Plazek DJ, Echeverría I. Don't cry for me Charlie Brown, or with compliance comes comprehension. *J. Rheol.* **2000**, 44(4), 831-841.



The widely used Fourier micro-rheological approach is empirically examined in concentrated systems, in finding that the direct inverse Laplace approach gives better agreement with macroscopic rheology and reduces the apparent probe-size dependence of the viscoelastic properties deduced from the Fourier micro-rheology approach.