Optimised Methodology for Dynamic Light Scattering (DLS) Microrheology

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Introduction

> Microrheology is termed ‘micro’ since it measures rheological properties on very small (micro) length scales.
> With microrheology the motion of a colloidal probe particle or tracer particle embedded in the sample is measured.
> From this motion the same rheological parameters that are measured in mechanical rheology $G^*$, $G'$, $G''$ and $\eta^*$ can be determined since;
   - Stress is related to the particle size and force acting over the surface of the particle;
   - Strain is related to the mean squared displacement (MSD) resulting from this applied stress;
   - The relative phase difference is related to the change in gradient of the MSD with time.

Benefits of Microrheology

> Measurements require very small sample volumes – typically microlitre-scale volumes, enabling rheological characterization of material types not available in larger volumes e.g. protein-based formulations.
> DLS Microrheology probes a much wider frequency range than conventional mechanical rheometry enabling rheological studies into dilute, weakly-structured macromolecular solutions where critical material dynamics occur on very short timescales.
> Probes a complete range of measurement frequencies simultaneously by measuring ensemble statistics arising from thermal (Brownian) motion of probe particles, which enables a much faster frequency-dependent rheological characterization method e.g. for rapid formulation screening.
> Depending on probe size and surface chemistry, can probe either bulk or localized rheological properties.

How it Works

> DLS Microrheology uses Dynamic Light Scattering to follow the random motion of tracer particles resulting from Brownian forces.

The MSD is related to the correlation function ($g$) according to the formula:

\[
\langle \Delta r^2(t) \rangle = \frac{1}{q} \left[ \log g(0) - \log g(t) \right]
\]

(1)

The Complex Modulus can then be obtained from the Generalised Stokes Einstein equation following Fourier analysis, and the Complex Viscosity obtained:

\[
G^*(\omega) = \frac{k_B T}{\pi \alpha_0 \langle \Delta r^2(\omega) \rangle / \omega}
\]

(2)

Measurement Process

> We do not Fourier transform the data directly but employ an algebraic method based on a power law expansion of the MSD.

\[
G^*(\omega) = \frac{k_B T}{\pi \alpha_0 \langle \Delta r^2(\omega) \rangle / \omega^{1 + \omega / \alpha}}
\]

\[
\alpha(\omega) = \frac{d \ln \langle \Delta r^2(\omega) \rangle}{d \ln \omega}
\]

(3)

The magnitude of the MSD at $1/\omega$ is related to $G^*$ and the logarithmic gradient of the MSD curve can be used to resolve $G'$ and $G''$ since the logarithmic gradient ($\alpha$) of the MSD can be considered analogous to the phase angle in mechanical rheometry, hence

\[
G(\omega) = G^*(\omega) \cos[\pi \alpha(\omega) / 2]
\]

\[
G'(\omega) = G^*(\omega) \sin[\pi \alpha(\omega) / 2]
\]

(4)

REFERENCES


Zeta Potential

> If the tracer particle is large enough to measure the bulk viscosity and tracer size is correct then macro- and micro- rheology data should overlay at low frequencies.
> If the data overlays but a vertical shift is required first then this suggests the probe size used is incorrect.
> Rotational rheology can then be used to estimate the hydrodynamic size of tracer in the sample.
> This may differ from the value measured in continuous phase with no sample present.
> If relative values of $G'$ and $G''$ differ with frequency between two methods this suggests tracer/sample interaction.
> Can be complementary or an alternative measure to zeta potential measurement for possible interaction.

Size Measurement

> The tracer particle size must be measured in the buffer solution to make the microrheology measurement as accurate as possible, since it is the hydrodynamic size of the particles that is important and this is dependent on pH and ionic strength.
> The measured size of the tracer particles should be larger than the dispersed sample phase but small enough to resist settling.
> Tracer particle scattering should completely mask that of the sample as denoted by absence of multiple peaks.
> Increase tracer concentration until a single dominant peak is observed.

Microrheology Measurement

> For thermally-driven motion of the probes, the slope of the logarithmic time derivative of the MSD ($\alpha(\omega)$) will be unity in a purely viscous medium (diffusive motion), zero in an elastic medium (completely arrested motion), and will lie between these extremes in a complex viscoelastic fluid medium.

\[
\alpha(\omega) = \frac{d \ln \langle \Delta r^2(\omega) \rangle}{d \ln \omega}
\]

(5)

Conclusions

> DLS Microrheology uses Dynamic Light Scattering to measure the thermally induced mean square displacement (MSD) of tracer particles in solution.
> The data can be converted into the rheological parameters $G^*$, $G'$, $G''$ and $\eta^*$ using the Generalised Stokes-Einstein equation.
> The measurement protocol allows the optimum particle chemistry, size and concentration to be determined prior to measurement ensuring reliable results.