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Opening the "black box": summary of equations used to calculate the Mean Squared Displacement (MSD) and Microrheological quantities from DWS

The DWS RheoLab **measures** the Intensity Correlation Function (ICF**,** sometimes referred to as $g_2(t)$) defined as:

$$g_2(\tau) = \frac{\langle I(t)I(t+\tau)\rangle}{\langle |I(t)|^2\rangle} \qquad 1.$$

The ICF is related to the electric Field Correlation Function (FCF) $g_1(t)$ as follows

$$g_2(\tau) - 1 = \beta |g_1(t)|^2 \qquad 2.$$

Where

$$g_1(\tau) = \frac{\langle E(t)E^*(t+\tau)\rangle}{\langle |E(t)|^2\rangle} \qquad 3.$$

And β is the intercept, determined by the instrument optics

The FCF can be related to the Mean Squared Displacement (MSD), which provides information about particle motion. In the case of single scattering events, the FCF is expressed as follows:

$$g_1(\tau) = e^{-q^2 D\tau} \qquad 4.$$

Where $q = 2k_0 \sin(\theta/2)$ is the wavevector, of magnitude $k_0 = 2\pi n/\lambda$ and D is the diffusion coefficient. The reader will recognize the expression used in Dynamic Light Scattering (DLS), mentioned on our DLS Theory page.

Mean-Squared Displacement

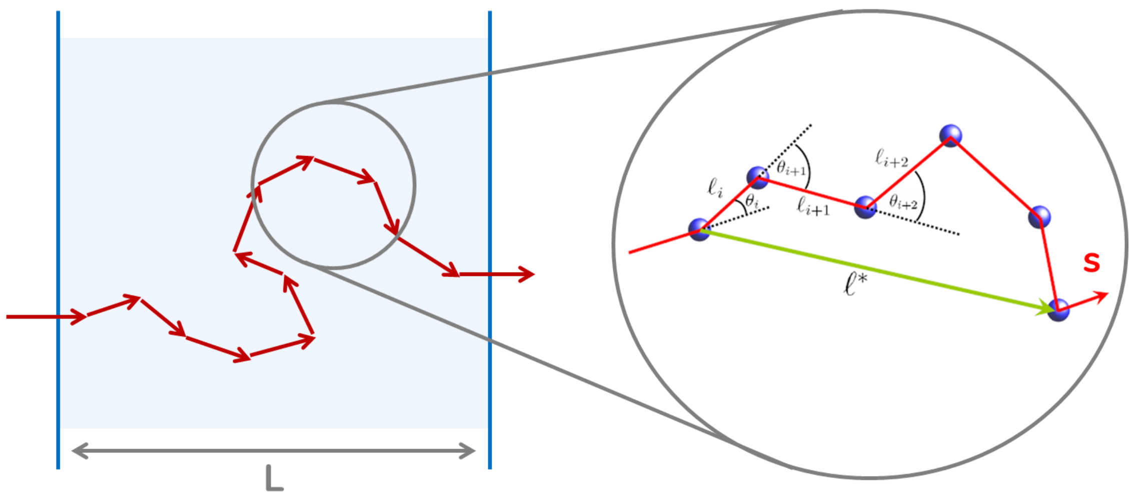
In the context of a 3-dimensional Brownian process, the MSD is directly linked to the diffusion coefficient via:

$$\langle \Delta r^2(\tau) \rangle = 6D\tau \qquad 5.$$

We can thus write:

$$g_1(\tau) = e^{-\frac{1}{6}q^2\langle \Delta r^2(\tau) \rangle} \qquad 6.$$

Diffusing Wave Spectroscopy (DWS) is based on multiple dynamic light scattering. The "diffuse" light propagates randomly through the colloidal sample by means of a series of particle-to-particle scattering events.



The number of scattering events is $N = s/l$, where l is the mean path length between the scattering events and s is the photon path. The average distance for a photon to see its propagation direction randomized, called the transport mean free path l^*, is defined as

$$l^* = \frac{l}{(1 - \langle \cos\theta \rangle)} \qquad 7.$$

where $\langle \cos\theta \rangle$ is the mean of the cosine of the angle θ the photon is scattered by the particles within the photon transport process. Small particles (size much smaller than the wavelength, i.e. Rayleigh-Gans-Debye limit) scatter isotropically and $\langle \cos(\phi) \rangle \approx 0$, hence $l^* \approx l$. However, larger particles scatter preferentially in forward direction, and thus $l^* \gg l$.

Considering the distribution of photon paths $P(s = Nl)$, the FCF can be expressed as follows:

$$g_1(\tau) = \int_0^\infty dsP(s)e^{-\frac{1}{6}\langle q^2 \rangle \langle \Delta r^2(\tau) \rangle N} \qquad 8.$$

Using the definitions above, we have $\langle q^2 \rangle = 2{k_0}^2(1 - \langle \cos(\theta) \rangle) = 2{k_0}^2\left(\frac{l}{l^*}\right)$, and the expression becomes:

$$g_1(\tau) = \int_0^\infty dsP(s)e^{\left[\left(-\frac{s}{3l*}\right)k_0^2\langle \Delta r^2(\tau) \rangle\right]} \qquad 9.$$

In the absence of absorption and in transmission geometry, one can write the FCF as (Weitz, Pine. 1993)[1]:

$$g_1(t) = \frac{(\hat{L} + 4/3)\hat{t}}{(1 + 4/9\,\hat{t}^2)\sinh(\hat{L}\hat{t}) + 4/3\,\hat{t}\cosh(\hat{L}\hat{t})} \qquad 10.$$

using the definitions $\hat{L} = \frac{L}{l^*}$ with L the cuvette thickness, and $\hat{t} = k_0\sqrt{\langle \Delta r(t)^2 \rangle}$.

From there, one can recover the MSD from a DWS experiment in a straightforward manner. In practice, this parameter is displayed in the instrument software.

If absorption is considered, then in transmission geometry (Scheffold 2003, Soft Matter)[2] the previous expression is modified as:

$$g_1(t) = \frac{\left(\sqrt{\hat{t}^2 + 3A}\right)\sinh\left[(\hat{L} + 4/3)\sqrt{3A}\right]}{(\sqrt{3A})\sinh\left[(\hat{L} + 4/3)\sqrt{\hat{t}^2 + 3A}\right]} \qquad 11.$$

with $A = \frac{l^*}{l_a}$ and l_a the absorption length

In the case of reflection (backscattering) Geometry, with absorption, one has

$$g_1(t) = e^{-\gamma\left(\sqrt{\hat{t}^2 + A} - \sqrt{A}\right)} \qquad 12.$$

One may recover the case without absorption letting the absorption length $l_a \to \infty, and\ A = 0$

Viscoelastic properties

The viscoelastic properties are obtained using the Generalized Stokes-Einstein equation, following the work by T. G. Mason in Rheol Acta 39, (2000), equations 10, 11, and 12[3]:

$$|G^*(\omega)| \approx \frac{k_B T}{\pi\alpha\langle \Delta r^2(1/\omega) \rangle \Gamma[1 + \alpha(\omega)]} \qquad 13.$$

[1] D. A. Weitz, J. X. Zhu, D. J. Durian, H. Gang and D. J. Pine, Diffusing-wave spectroscopy: The technique and some applications, Phys. Scr. 610 (1993).
[2] F. Scheffold, P. Schurtenberger, Light Scattering Probes of Viscoelastic Fluids and Solids, Soft Mat. 1, 2 (2003)
[3] T. G. Mason, Estimating the viscoelastic moduli of complex fluids using the generalized Stokes–Einstein equation, Rheol. Acta 39, 371–378 (2000)

$$G'(\omega) = |G^*(\omega)|\cos\left(\frac{\pi\alpha(\omega)}{2}\right) \qquad 14.$$

$$G''(\omega) = |G^*(\omega)|\sin\left(\frac{\pi\alpha(\omega)}{2}\right) \qquad 15.$$

with $\omega = 1/t$, Γ the gamma function, and $\alpha(\omega) \equiv \frac{d \ln \langle \Delta r^2(t) \rangle}{d \ln t}\Big|_{t=1/\omega}$