Dynamic Light Scattering

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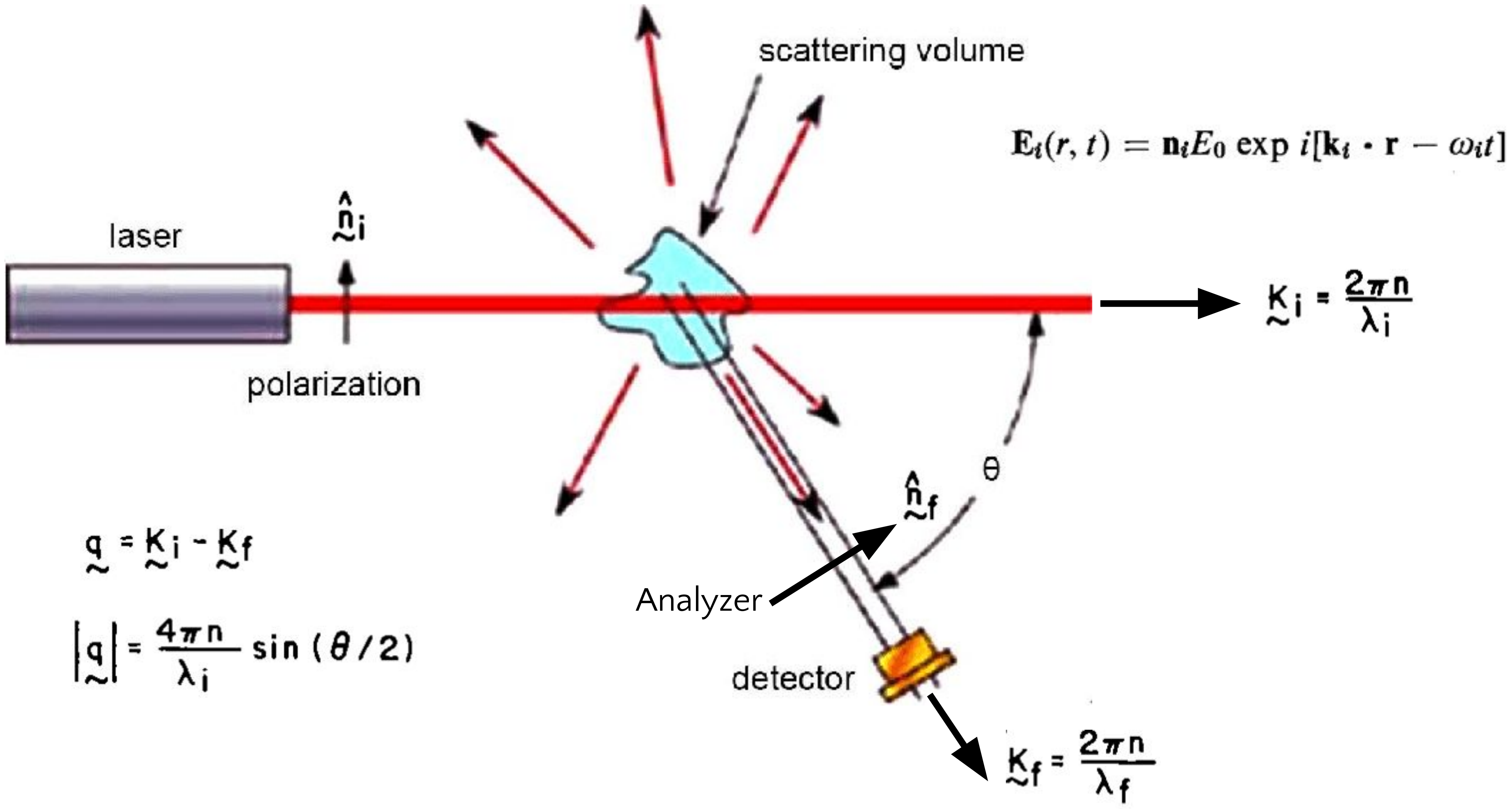
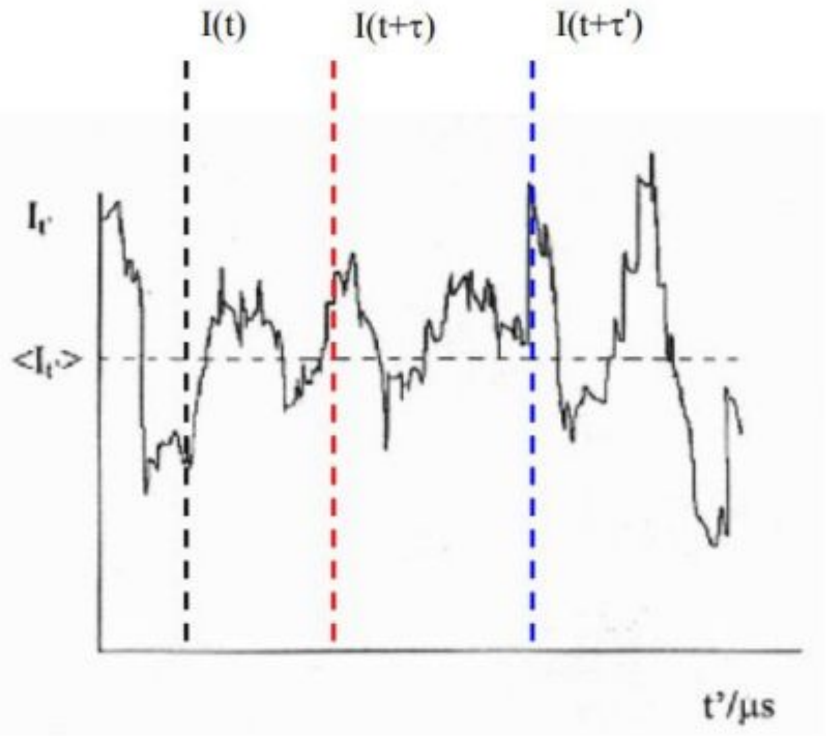
Introduction – Dynamic Light Scattering



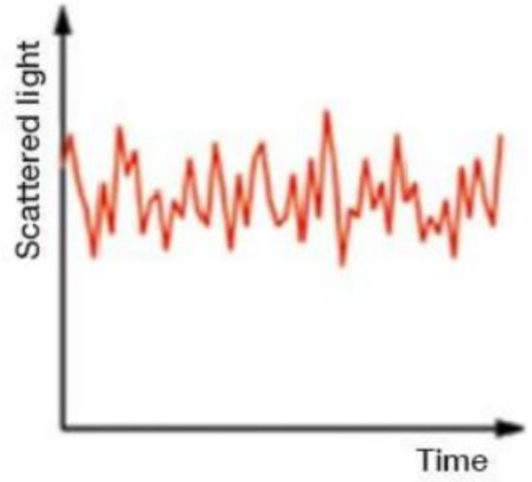
Introduction – Dynamic Light Scattering ……Contd.

- The suspended particles of the colloidal dispersion under investigation undergo Brownian motion.
- This motion results in fluctuations in the distances between the particles and hence also in fluctuations of the phase relations of the scattered light.
- Due to the random motion of the suspended particles within the sample, the interference can be either constructive or destructive.
- The number of particles within the scattering volume may vary in time
- The net result is fluctuating intensity
- Scattered waves interference generates a net scattered light intensity I_s(t).

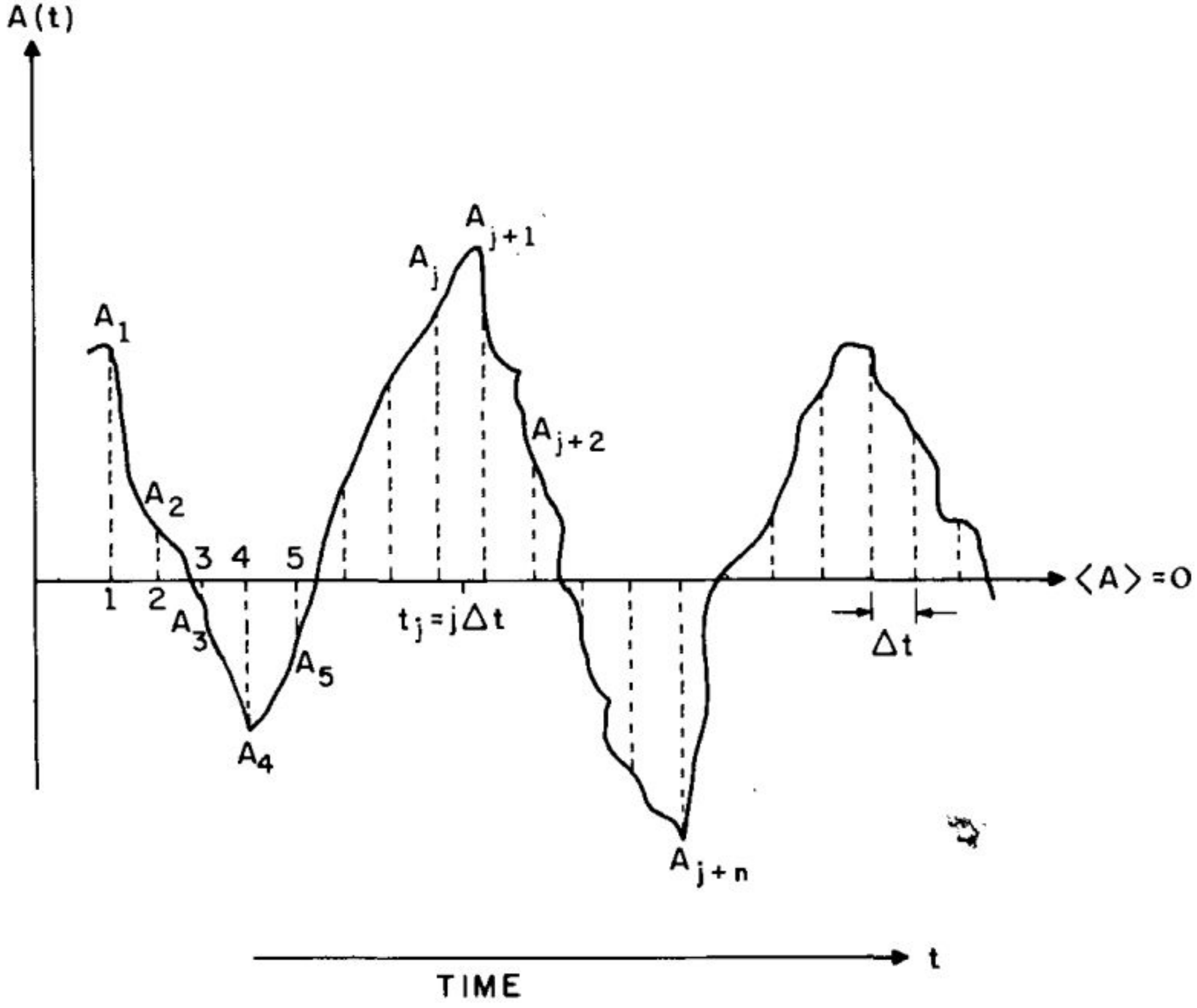


Dynamic Light Scattering – Time Correlation

- Spectral characteristics of the scattered lights depend on motion of scatters in time scale
- The objective of scattered light experiment is to measure time correlation functions of scattered field and/or scattered intensity
- Time correlation functions and their spectral densities are central to light scattering experiments
- Due to erratic thermal molecular motion, scattered field varies randomly at the detector.
- Time dependent correlation functions related to noise and fluctuation are relevant for the study of DLS



DLS – Autocorrelation Function



$$\langle A(0)A(\tau)\rangle = \lim_{T\to\infty}\frac{1}{T}\int_0^T dt\, A(t)A(t+\tau)$$

In general, autocorrelation function decays like exponential function

$$\langle A(0)A(\tau)\rangle = \langle A\rangle^2 + \{\langle A^2\rangle - \langle A\rangle^2\}\exp\frac{-\tau}{\tau_r}$$

Where τ_r is the relaxation time or correlation time

The autocorrelation function is the measure of similarities two signals, namely $A(t)$ and $A(t+\tau)$.

DLS – Particle Sizing Governing Equations

The corresponding measured normalized intensity correlation function is written as:

$$g_2(q,\tau) = \frac{\langle I_s(q,t) I_s(q,t+\tau)\rangle}{\langle |I_s(q,t)|^2\rangle},$$

By means of the Siegert relation can be related to the electric field correlation function $g_1(q,\tau)$:

$$g_2(q,\tau) = 1 + \beta\,|g_1(q,\tau)|^2$$

β being the so-called intercept and where the field correlation function $g_1(q,\tau)$ is defined as

$$g_1(q,\tau) = \frac{\langle E_s(q,t)) E_s^*(q,t+\tau)\rangle}{\langle |E_s(q,t,)|^2\rangle}$$

The field correlation function may be used to determine the diffusion coefficient D of the scatterers. For a monodisperse sample, is fitted to an exponential function

$$g_1(q,\tau) = \exp(-\Gamma\tau)$$

yielding the decay rate Γ. From its definition:

$$\Gamma = q^2 D$$

one obtains the diffusion coefficient D and by using the Stokes-Einstein equation one can calculate the hydrodynamic radius

$$R = \frac{kT}{6\pi\eta D}$$

DLS – Particle Sizing Example

Source: Jia, Z.; Li, J.; Gao, L.; Yang, D.; Kanaev, A. Dynamic Light Scattering: A Powerful Tool for In Situ Nanoparticle Sizing. *Colloids Interfaces* **2023**, *7*, 15. https://doi.org/10.3390/colloids7010015

Particle Size Characterization in Colloids

Colloids: Colloids are mixtures in which one substance is dispersed as relatively large solid particles or liquid droplets throughout a solid, liquid, or gaseous medium.

Colloids are crucial in paints, pigments, pharmaceuticals, food, cosmetics, ceramics, and personal care. Particle size, polydispersity, shape, and surface characteristics significantly influence formulation efficacy.

Methods for measuring particle size:

Microscopic Imaging
High resolution but requires counting numerous particles

Electrical sensing (Coulter) counters
Quick, direct; challenges with non-spherical particles

Hydrodynamic or field flow fractionation
Efficient, struggles with polydisperse samples

Disc centrifuge particle sizing
High res, time-consuming and complex process

Size exclusion chromatography
Suitable for macromolecules

Scattering techniques
Valuable info, may require complex data analysis

Scattering Techniques

Static Light Scattering (SLS)

- Measures scattering intensity at various angles.
- Limited to particles similar or larger than the wavelength of light..

Dynamic Light Scattering (DLS)

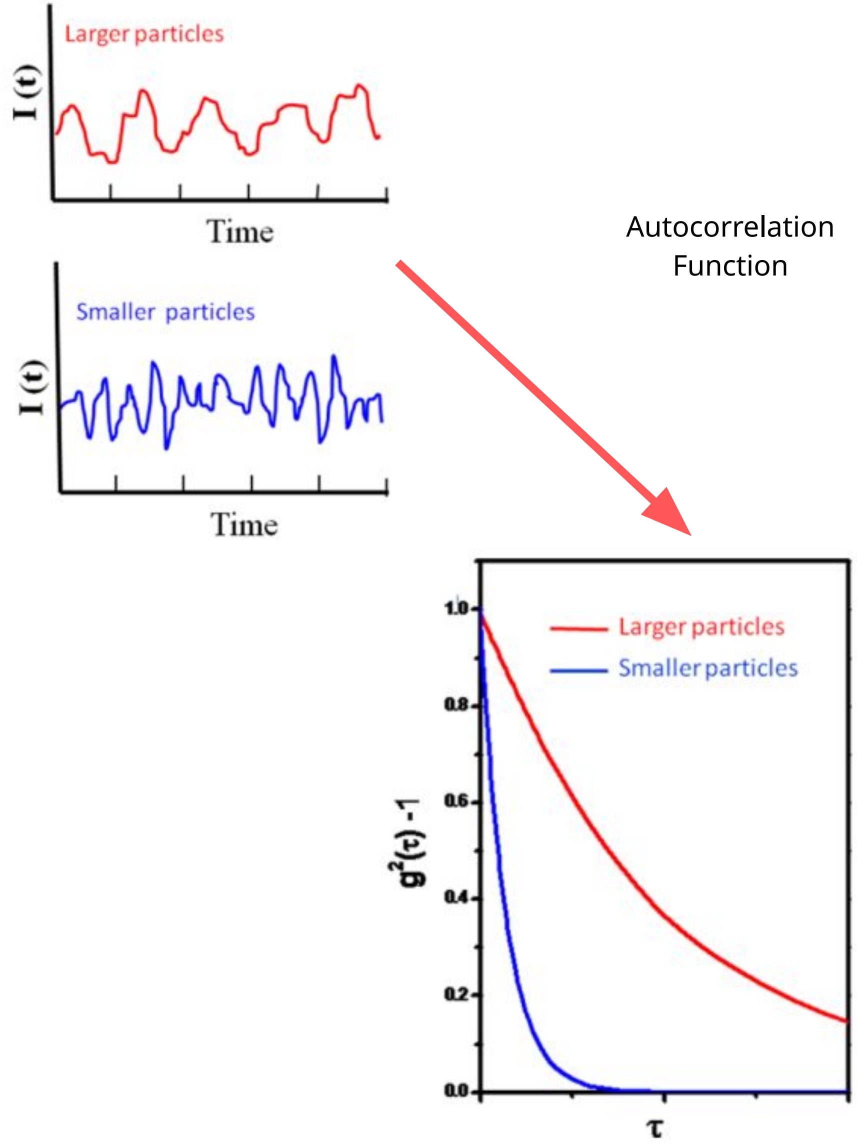
- Utilizes Brownian motion-induced intensity fluctuations.
- Measures dynamic size changes in particles undergoing random motion.
- Ensemble-averaged submicron size estimates.
- Fast data acquisition

Analyzing Particle Size via Intensity Fluctuations

- Utilizes speckle patterns resulting from scattered light
- Measures temporal fluctuations in intensity to determine particle size
- Autocorrelation function helps determine particle diffusion coefficients
- Characterizes intensity fluctuations by comparing signal at different times

Autocorrelation Function: $g^2(\tau) = \frac{\langle I(t)I(t+\tau)\rangle}{\langle I(t)\rangle^2}$

When τ equals zero, g2(τ) equals 1, indicating that the signal is perfectly correlated at this point, reflecting uniform particle movement



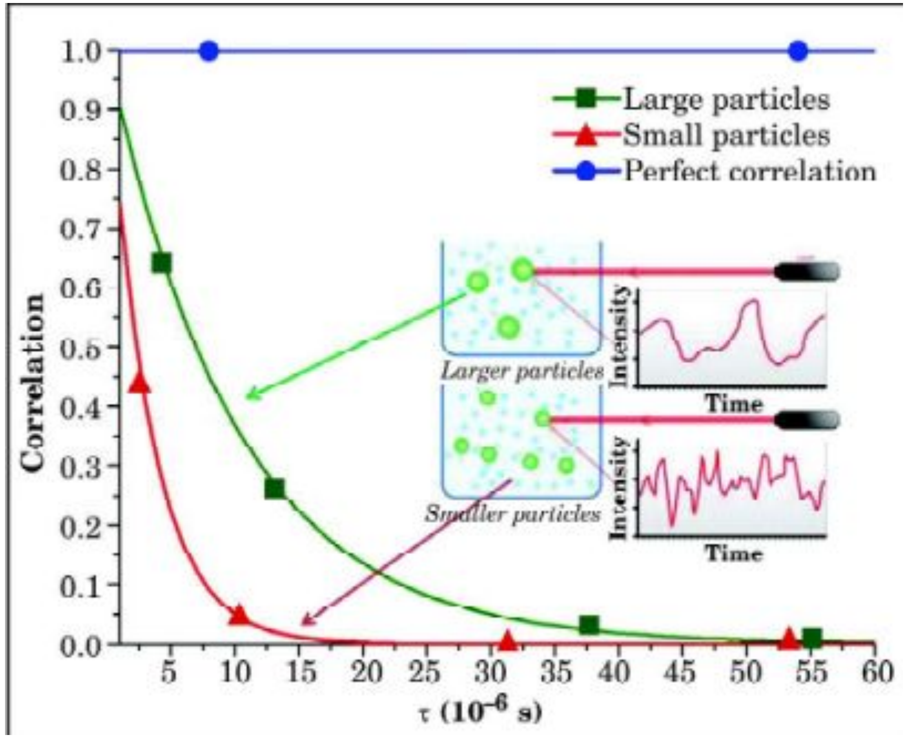
ANALYSIS OF AUTOCORRELATION FUNCTION

Objective

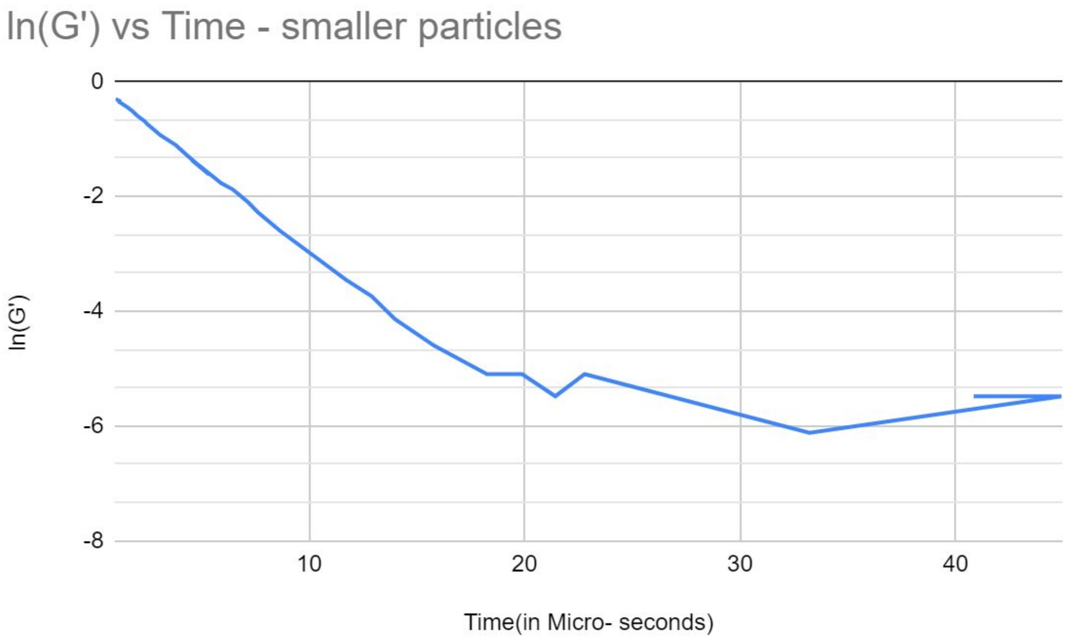
- Compare the particle sizes based on an analysis of the graph depicting the correlation as a function of delay time

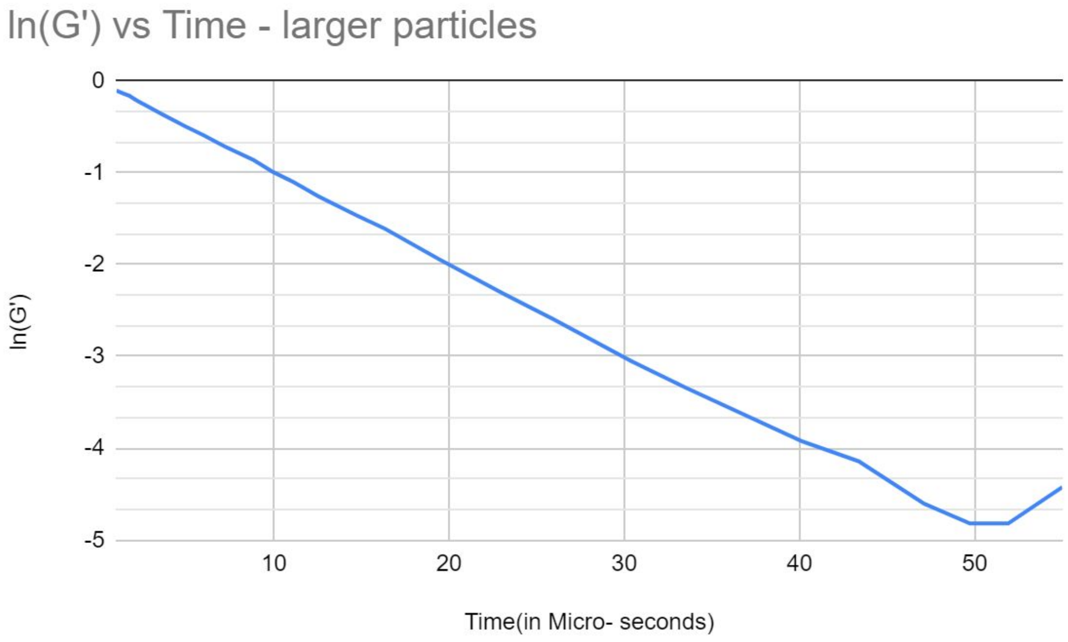
Procedure (Simplified)

- The data set for the large and small particles has been extracted from the given graph.
- The dataset was subjected to a log transformation and then plotted to calculate the slope of the graph.



ANALYSIS OF AUTOCORRELATION FUNCTION ……Contd.





ANALYSIS OF AUTOCORRELATION FUNCTION ……Contd.

For a suspension of spherical particles undergoing Brownian diffusion, the autocorrelation function decays exponentially with the delay time τ and is given as:

$$g^1(\tau) = A \cdot e^{-Dq^2\tau} + B$$

where A: Amplitude of the correlation function

B: Baseline, accounts for any background or noise in the measurements

D: Translational diffusion coefficient of the particles, quantifies the ability of the particles to diffuse or spread out in the suspension. A higher D value implies faster diffusion of the particles.

q is the magnitude of the scattering vector given as $(4\pi n/\lambda) \sin(\theta/2)$. Here, n is the refractive index of the medium.

Slope for smaller particles: -0.2990278052
Slope for larger particles: -0.09175909456

ANALYSIS OF AUTOCORRELATION FUNCTION ……Contd.

For spherical particles, the hydrodynamic radius Rh can be obtained from the translational diffusion coefficient (D) using the Stokes−Einstein relationship:

$$D = kT/(6\pi\eta R_h)$$

where k is the Boltzmann's constant, η is the solvent viscosity, and T is the absolute temperature

From the slopes, assuming the values of T, viscosity and k, we get the values of R as:

R(smaller particles) : 3.344170618

R (larger particles) : 10.89810231

Thank You