Introduction to Dynamic Light Scattering (DLS)

Yeling Dai, April 30, 2008
Outline

Basic of conventional DLS
- DLS principle
- Brownian motion and autocorrelation function
- Accessible time range and length scale
- Advantages and disadvantages

Improvement of DLS
- Multispeckle wide-angle DLS
- Ultralow angle DLS
DLS principle

- Dynamic light scattering measures variation in scattered intensity with time at a fixed scattering angle (typically $90^\circ$), while static light scattering measures scattered intensity as a function of angle.
Brownian Motion—Doppler Effect

First observed By Robert Brown (1827)

Mathematical description by Albert Einstein (1905)
Brownian Motion—Doppler Effect II

- Many particles—various velocities and directions

![Diagram]

Spectrum is Lorentzian:

\[ P(\omega) = \langle I \rangle \frac{\Delta \omega / \pi}{(\omega - \omega_0)^2 + (\Delta \omega)^2} \]

\[ \Delta \omega = D q^2 \]

diffusion coefficient of translational motion
Stoke-Einstein relation:

\[
D = \frac{k_B T}{6\pi \eta}
\]

visible light: \( q \sim 10^5 \text{ cm}^{-1} \)

\( D \sim 10^{-5} \text{ to } 10^{-10} \text{ cm}^2/\text{s} \)

\[ \Rightarrow \quad \Delta \omega = Dq^2 \sim 10^0 - 10^5 \text{ Hz} \]

Cannot be measured spectroscopically:

Required resolution \( \frac{\omega}{\Delta \omega} = \frac{10^{14}}{\Delta \omega} \approx 10^9 - 10^{14} \)

Best Fabry-Perrot interferometer \( \frac{\omega}{\Delta \omega} \sim 10^7 \)
Study time correlations instead of frequency

\[ P(\omega) = \int g^1(t) \exp(i\omega t) dt \]

\[ g^1(t) = \langle E(0)E(t) \rangle \quad \text{field correlation function} \]

\[ g^1(t) = \exp(-\Delta \omega \cdot t) = \exp(-\Gamma t) = \exp(-Dq^2 t) \]

Experimentally we can measure:

\[ g^2(t) = \langle I(0)I(t) \rangle \quad \text{intensity correlation function} \]

\[ g^2(t) = 1 + \beta |g^1(t)|^2 \quad \text{Siegert relation} \]

\[ (\beta \approx 1) \]
Autocorrelation Function

**Autocorrelation function of the intensity**

\[
G^2(\tau) = \lim_{T \to \infty} \frac{1}{2T} \int_0^T I(t)I(t + \tau)dt = \langle I(t)I(t + \tau) \rangle
\]

**Normalized autocorrelation function of the intensity**

\[
g^2(\tau) = \frac{\langle I(t)I(t + \tau) \rangle - \langle I(t) \rangle^2}{\langle I(t) \rangle^2} = \frac{G^2(\tau) - \langle I(t) \rangle^2}{\langle I(t) \rangle^2}
\]
Experimental Set-up

- PM-Tube & Amplifier
- Optical fiber
- Computer with Correlator
- Cryostat or Oven
- Sample
- Laser
- Lens

Graph: Intensity vs. Elapsed time (correlation vs. Time (s))
Time and length range of DLS

Time range: typically $10^{-7} - 10^3$ s!
Length range: typically $10^{-9} - 10^{-6}$ m!
Q-range: typically $0.6 - 2 \times 10^{-3}$ Å$^{-1}$

DLS is therefore suitable for diffusional studies of macromolecules, such as polymers and large biomolecules!
Advantages and Disadvantages

- Wide time range
- Digital correlators are commercially available
- Simple experimental set-up
- Probability to analyze samples containing broad distribution of different molecular masses

- Time consuming, especially for slow dynamics
- Only transparent sample
- Sensitive for mechanical disturbances
- Lack of selectivity and relatively low signal strength

A statistical uncertainty of 1% requires a measurement over 10000 characteristic decay times of the correlation function!!
Multispeckle DLS (DLS with CCD)

- Using CCD as an area detector instead of a photomultiplier and replacing time averaging partly by ensemble averaging to shorten sampling time and improve the statistical accuracy

Apollo P.Y. Wong and P. Wiltzius, Dynamic light scattering with a CCD camera, 1993
Divide the speckle pattern into ten concentric rings which are 1 pixel wide each. Each ring has a radius 20 pixels longer than the previous one.

Calculate 4400 correlation functions in parallel for 10 q values (10 rings).

\[ \delta I(q, t) = I(q, t) - \langle I(q, t) \rangle_{q_0} \]

\[ G(q_0, \tau) = \langle \delta I(q, t_0) \delta I(q, t_0 + \tau) \rangle_{q_0} \]

\[ g(q, \tau) = \langle I(q, t) I(q, t + \tau) \rangle_t \]

Apollo P.Y. Wong and P. Wiltzius, Dynamic light scattering with a CCD camera, 1993
q = 14832, 20834, 29748 cm\(^{-1}\), fit G \sim \exp(- \Gamma \tau), \ \Gamma = Dq^2

**FIG. 3.** The intensity autocorrelation functions at 51 °C measured by the new method. Three different q's were shown in this graph (see text for the value of q's). The backgrounds have been subtracted. The solid lines were the single-exponential fits.

**FIG. 4.** The decay rates of the correlation functions vs the square of wave vectors. The solid line is a linear fit forced through the origin. The circles denote the results from the CCD setup. The filled square denotes the result from the ALV correlator.

Apollo P.Y. Wong and P. Wiltzius, Dynamic light scattering with a CCD camera, 1993

Sample is a solution of 0.215-um diam latex spheres diffusing in glycerol.
Ultralow-angle DLS with CCD

Low angle $\Rightarrow$ small $q$ $\Rightarrow$ slow dynamics

Stray light scattered from the optical components should be subtracted

Luca Cipelletti and D.A. Weitz, RSI, 1999
Summary: DLS technique

DLS principle: intensity fluctuation

- Time scales: \( \sim 10^{-7} - 10^3 \) s
- Length scales: \( \sim \text{nm} - \mu\text{m} \)
- Wave vectors: \( \sim 10^{-3} \text{ Å}^{-1} \)

Improvement of DLS

- Multispeckle DLS
- Lowangle DLS
Thank you!
Autocorrelation function
\[ \vec{q} = \vec{k}_s - \vec{k}_i \]
\[ \omega = \omega_z - \omega_i \]
Hydrodynamic Radius

\[ \frac{1}{R_{\text{hyd}}} \overset{\text{def}}{=} \frac{1}{N^2} \langle \sum_{i \neq j} \frac{1}{r_{ij}} \rangle \]

- where \( r_{ij} \) is the distance between subparticles \( i \) and \( j \), and where the angular brackets \( \langle \ldots \rangle \) represent an \textit{ensemble average}. 
Brownian Motion

Explanation:
A suspended particle is constantly and randomly bombarded from all sides by molecules of the liquid. If the particle is very small, the number of hits it takes from one side at a given time will be stronger than the bumps from other side. This make the particle jump. These small random jumps are what make up Brownian motion.

Stoke-Einstein relation:

\[ D = \frac{k_B T}{6\pi \eta r} \]