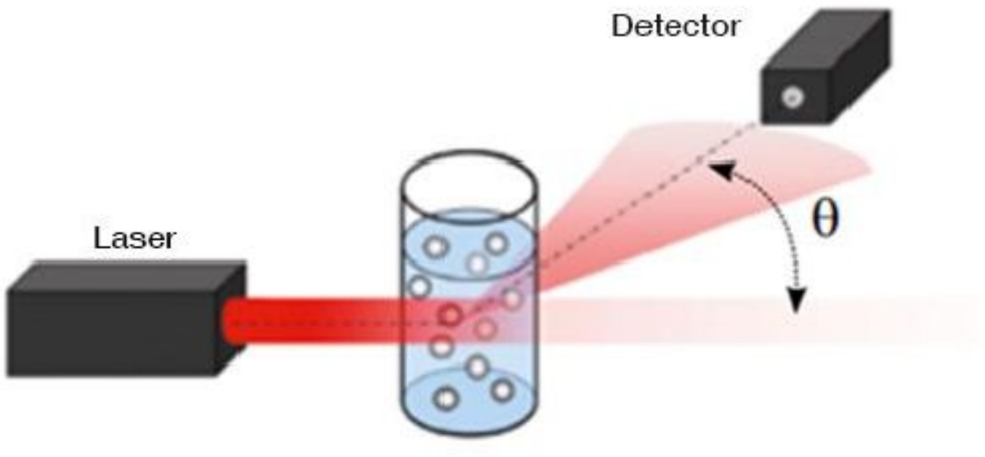
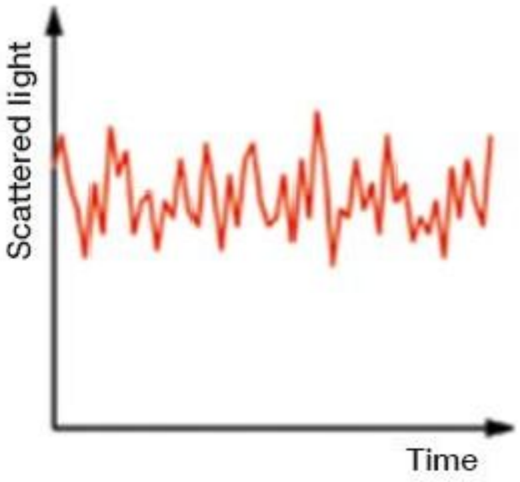
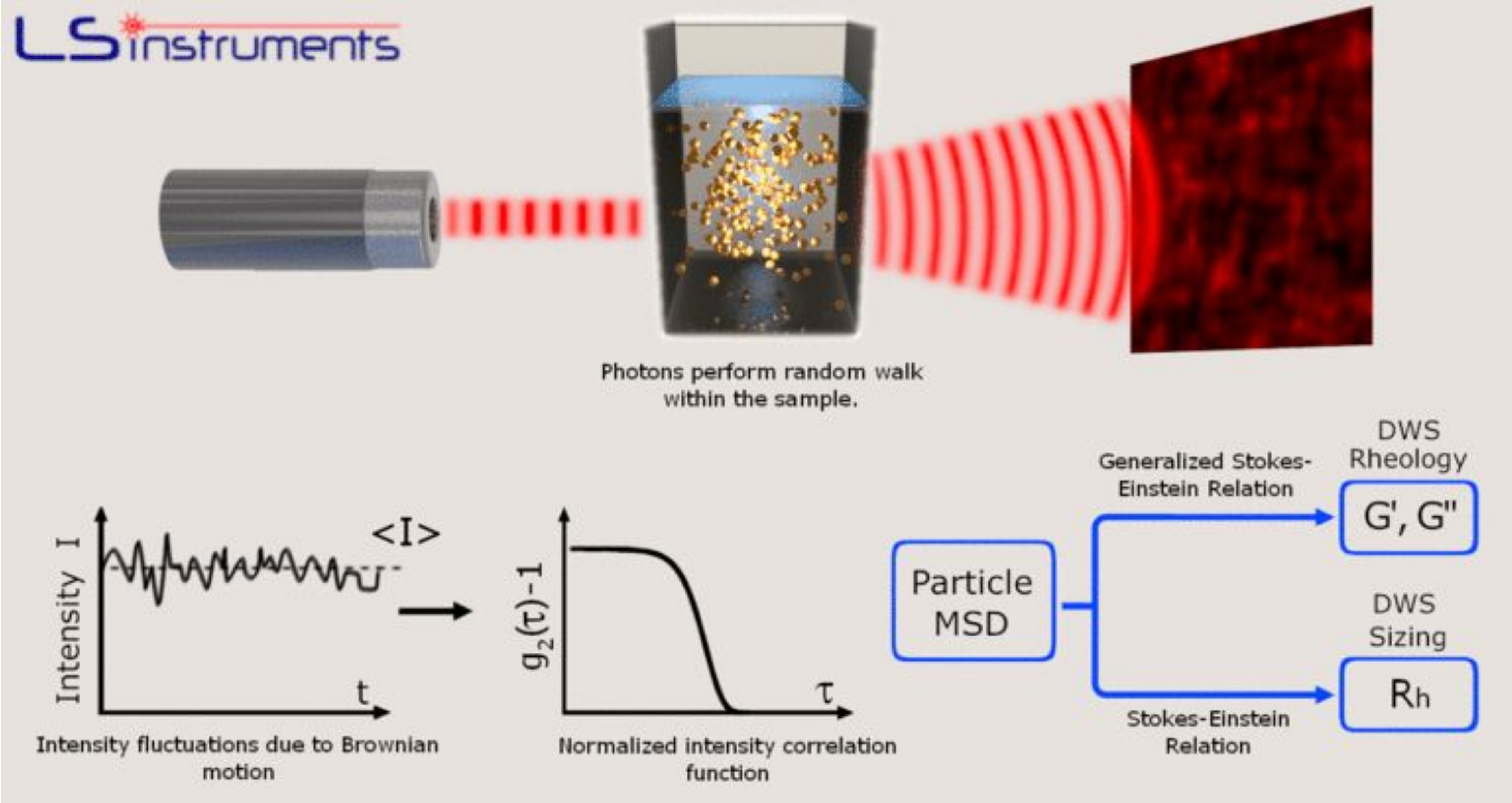
Dynamic Light Scattering

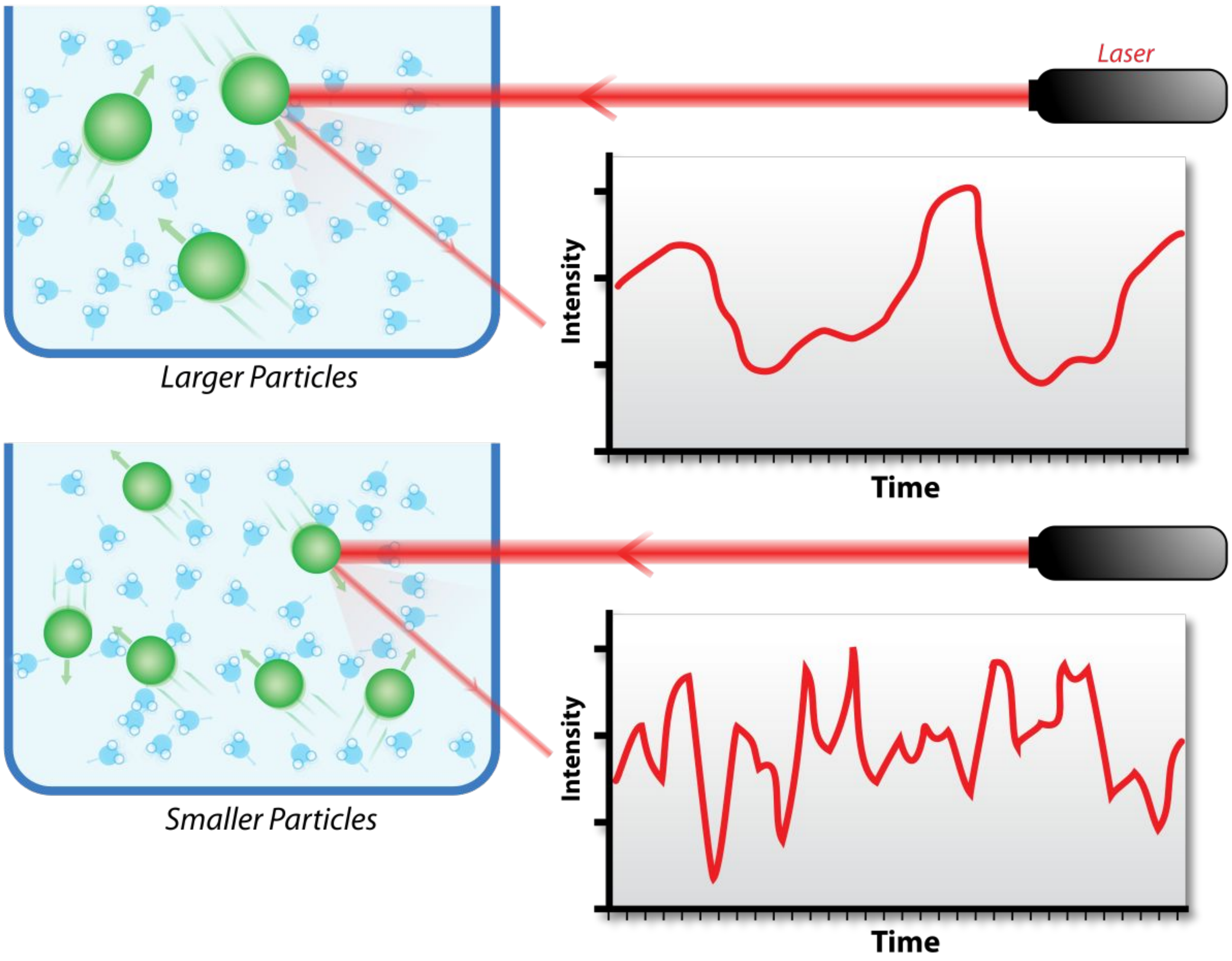
(Photon Correlation Spectroscopy)







http://www.schaefer-tec.it/en/cat-prodotti/diffusing-wave-spectroscopy

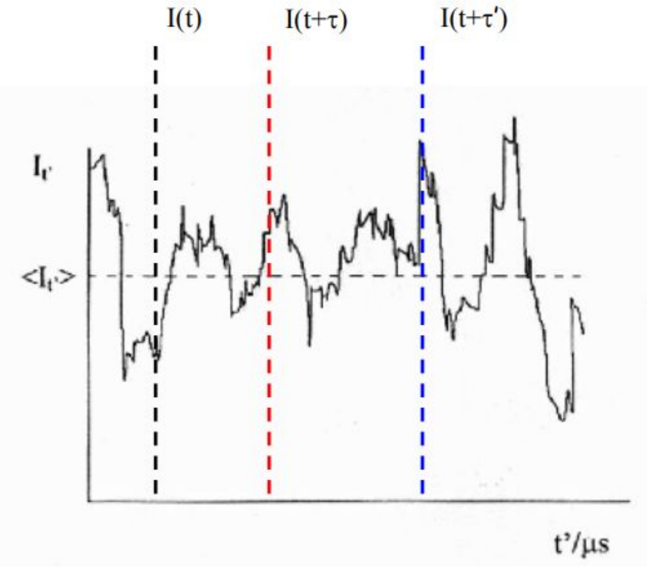

Laser
Larger Particles
Intensity
Time
Smaller Particles
Intensity
Time

$$R_f(t) \equiv \lim_{T\to\infty} \frac{1}{2T} \int_{-T}^{T} f(\tau) f(t+\tau)\, d\tau$$

Autocorrelation Function

Definition 1: The **autocorrelation function** (**ACF**) **at lag *k***, denoted ρ_k, of a stationary stochastic process is defined as $\rho_k = \gamma_k/\gamma_0$ where $\gamma_k = \text{cov}(y_i, y_{i+k})$ for any *i*.

Note that γ_0 is the variance of the stochastic process.



Definition 2: The **mean** of a time series $y_1, \ldots, y_n$ is

$$\bar{y} = \frac{1}{n}\sum_{i=1}^{n} y_i$$

The **autocovariance function at lag** *k*, for $k \geq 0$, of the time series is defined by

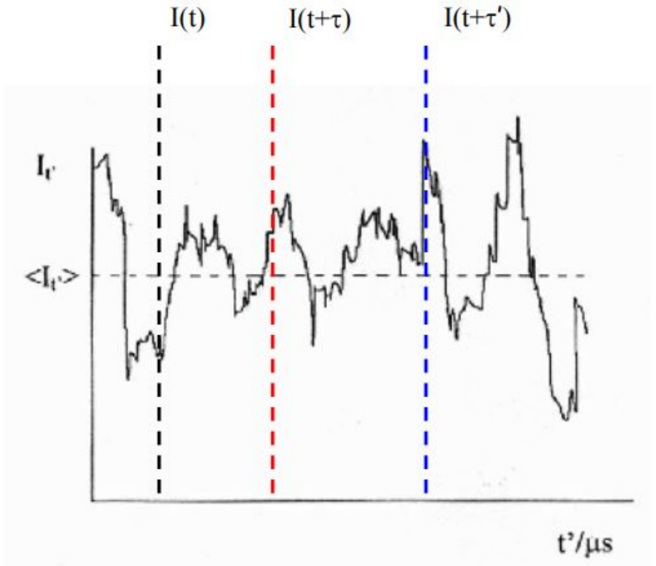
$$s_k = \frac{1}{n}\sum_{i=1}^{n-k}(y_i - \bar{y})(y_{i+k} - \bar{y}) = \frac{1}{n}\sum_{i=k+1}^{n}(y_i - \bar{y})(y_{i-k} - \bar{y})$$

The **autocorrelation function** (**ACF**) **at lag** *k*, for $k \geq 0$, of the time series is defined by

$$r_k = \frac{s_k}{s_0}$$

The **variance** of the time series is s_0. A plot of r_k against *k* is known as a **correlogram**. See Correlogram for information about the standard error and confidence intervals of the r_k, as well as how to create a correlogram including the confidence intervals.

$$G_2(\tau) = B\left[1+\beta\left|g_1(\tau)\right|^2\right]$$



Integrate the difference in distance between particles, assuming Brownian Motion

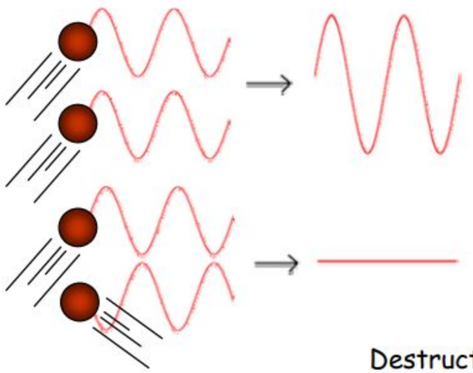
The electric field correlation function describes correlated particle movement, and is given as:

$$G_1(\tau) = \frac{1}{T}\int_0^T E(t)E(t+\tau)d\tau$$

$G_1(t)$ decays as and exponential with a decay constant Γ, for a system undergoing Brownian motion

$$G_1(\tau) = exp^{-\Gamma\tau}$$

Constructive interference



Destructive interference

$$g^{(2)}(\tau) = \frac{\langle I(0)I(\tau)\rangle}{\langle I\rangle^2} \Rightarrow = \frac{1}{T}\int_0^T I(t)I(t+\tau)d\tau$$

Siegert relation

$$g^{(2)}(\tau) = 1 + \beta\left[g^{(1)}(\tau)\right]^2$$

$$= \frac{1}{T}\int_0^T E(t)E(t+\tau)d\tau$$

$$g^{(1)}(\tau) = \exp(-\Gamma\tau)$$

$$\Gamma = -Dq^2 \qquad q = \frac{4\pi n}{\lambda} sin\left(\frac{\theta}{2}\right)$$

Boltzmann Constant

temperature

$$D = \frac{kT}{6\pi\mu r} = \frac{\text{thermodynamic}}{\text{hydrodynamic}}$$

viscosity

particle radius

Multiexponential Decay

$$g^{(1)}(\tau) = \int G(\Gamma)\exp(-\Gamma\tau)d\Gamma$$

$$\exp(-\Gamma\tau) = \exp(-\bar{\Gamma}\tau)\exp\left[-(\Gamma-\bar{\Gamma})\tau\right],$$

$$\bar{\Gamma} = \int \Gamma G(\Gamma)d\Gamma$$

$$g^{(1)}(\tau) = \exp(-\bar{\Gamma}\tau)\left[1 + \frac{1}{2}\mu_2\tau^2 - \frac{1}{3!}\mu_3\tau^3 + \frac{1}{4!}\mu_4\tau^4 - \dots\right]$$

$$\mu_n = \int (\Gamma-\bar{\Gamma})^n G(\Gamma)d\Gamma$$

$$g^{(2)}(\tau) = B + \beta\left\{\exp(-\bar{\Gamma}\tau)\left[1 + \frac{1}{2}\mu_2\tau^2 - \frac{1}{3!}\mu_3\tau^3 + \frac{1}{4!}\mu_4\tau^4 - \dots\right]\right\}^2$$

$$ln\, c(\tau) = ln\left[\frac{G_2(\tau) - B}{B}\right] = ln\,\beta - 2\,ln\, g_1(\tau)$$

$$\boxed{ln\left[\frac{G_2(\tau) - B}{B}\right] = ln\,\beta - 2\overline{\Gamma}\tau + K_2{}^2\tau^2 - \dots}$$

Note:
Multiplied
by 2

intercept

average decay

Polydispersity index

$$\gamma = \frac{k_2}{\overline{\Gamma}^2}$$

Sample of Cumulant Expansion

390 nm Beads

	Gamma (s^{-1})	Diff. Coef. ($cm^2\ s^{-1}$)	Eff. Diam. (nm)	Poly	Skew	Kurtosis	RMS Error
Linear:	5.741e+02	1.078e-08	455.3				7.9000e-03
Quadratic:	6.498e+02	1.220e-08	402.3	0.241			2.6170e-03
Cubic:	6.588e+02	1.237e-08	396.8	0.284	0.27		1.4565e-03
Quartic:	6.647e+02	1.248e-08	393.2	0.330	0.76	3.63	1.2057e+00

linear $$\ln\left[\frac{G_2(\tau)-B}{B}\right]=\ln\beta-\boxed{2\overline{\Gamma}\tau}$$

Gamma

quadratic $$\ln\left[\frac{G_2(\tau)-B}{B}\right]=\ln\beta-2\overline{\Gamma}\tau+\boxed{K_2{}^2\tau^2}$$

~ Poly

cubic $$\ln\left[\frac{G_2(\tau)-B}{B}\right]=\ln\beta-2\overline{\Gamma}\tau+K_2{}^2\tau^2-\boxed{\frac{K_3{}^3}{3}}\tau^3$$

~ Skew

quartic $$\ln\left[\frac{G_2(\tau)-B}{B}\right]=\ln\beta-2\overline{\Gamma}\tau+K_2{}^2\tau^2-\frac{K_3{}^3}{3}\tau^3+\boxed{\frac{K_4{}^4}{12}}\tau^4$$

~ Kurtosis

Expressed in mathematical terms

$g_1(\tau)$ can be described as the movements from individual particles; where $G(\Gamma)$ is the intensity-weighted coefficient associated with the amount of each particle.

$$g_1(\tau) = \sum_i G_i(\Gamma) e^{-\Gamma_i \tau}$$

For example, consider a mixture of particles:

0.30 intensity-weighted of 100 nm particles,
0.25 intensity-weighted of 200 nm particles,
0.20 intensity-weighted of 300 nm particles,
0.15 intensity-weighted of 400 nm particles,
0.10 intensity-weighted of 500 nm particles.