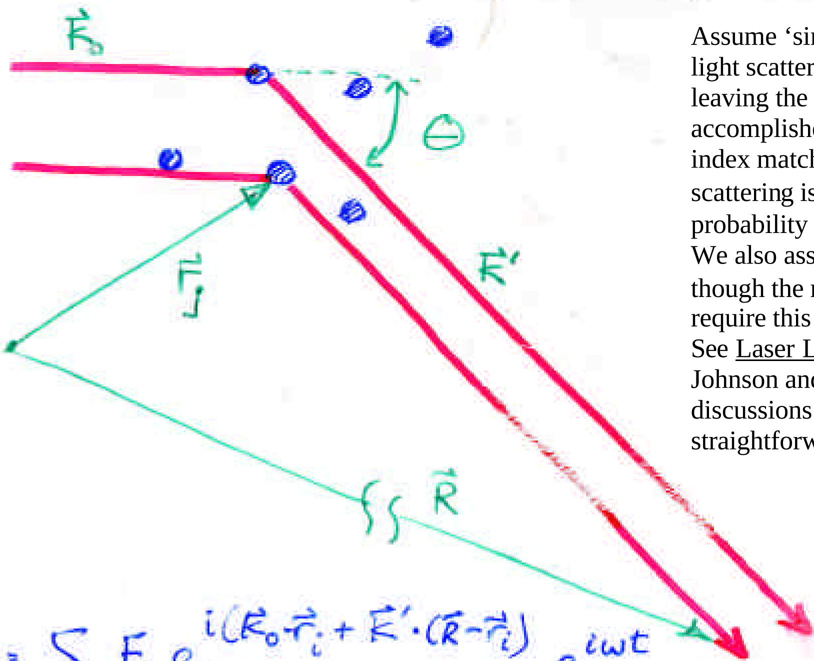
Dynamic Light Scattering (DLS)



Assume 'single scattering', *i.e.* that light scatters only once before leaving the sample. This can be accomplished by near refractive-index matching (the probability of scattering is ε 1, and the probability of scattering twice is ε^2.) We also assume point-like particles, though the result for $g(\tau)$ does not require this assumption.
See <u>Laser Light Scattering</u> by CS Johnson and DA Gabriel for more discussions at a fairly straightforward level.

$$\vec{E}(\vec{R}) = \sum_j E_0 \underbrace{e^{i(\vec{k}_0\cdot\vec{r}_j + \vec{k}'\cdot(\vec{R}-\vec{r}_j))}}_{e^{-i\vec{r}_j\cdot\overbrace{(\vec{k}'-\vec{k}_0)}^{\equiv\vec{q}}}\; e^{i\vec{k}'\cdot\vec{R}}} e^{i\omega t}$$

$$\left(|\vec{q}| = \frac{4\pi}{\lambda}\sin\theta/2\right)$$

$$\langle I(t)\rangle_t = \langle E(t)E^*(t)\rangle_t = \Big\langle |E_0|^2 \sum_{j\,i} \underbrace{e^{-i\vec{q}\cdot(\vec{r}_i - \vec{r}_j(t))}}_{\substack{=1 \quad (i=j)\\ 0 \quad (i\neq j)}}\Big\rangle$$

so $\langle I\rangle = |E_0|^2 N$

... DLS ...

$$\langle I(t)\, I(t+\tau)\rangle = \langle E(t) E^*(t)\, E(t+\tau)\, E^*(t+\tau)\rangle$$

$$= |E_0|^4 \left\langle \sum_{jklm} e^{-i\vec{q}\cdot[\vec{r}_j(t)-\vec{r}_k(t)+\vec{r}_l(t+\tau)-\vec{r}_m(t+\tau)]}\right.$$

(This is a sum over particles.)

[$e^{i\omega\tau}$ & $e^{i\vec{k}'\cdot\vec{R}}$ terms cancel]

* Note $\langle\Sigma \cdots\rangle = \Sigma\langle\cdots\rangle$

we have 3 types of terms ...

A. One subscript (jklm) unique

$$\rightarrow \langle e^{i\vec{q}\cdot(\vec{r}_j(t)-\vec{r}_k(t))}\rangle_t = \underbrace{\langle e^{i\vec{q}\cdot\vec{r}_j(t)}\rangle}_{=0}\underbrace{\langle e^{i\vec{q}\cdot\vec{r}_k(t)}\rangle}_{=0}$$

B. $j=k$, $l=m$ [N^2 of these]

$$\rightarrow \langle |E_0|^4 e^{-i\vec{q}\cdot 0}\rangle = |E_0|^4$$

C. $j=m$, $k=l$ but $j\neq k$ [N^2-N of these]

$$\rightarrow \left\langle |E_0|^4 e^{-i\vec{q}(\vec{r}_j(t)-\vec{r}_j(t+\tau))} e^{i\vec{q}(\vec{r}_k(t)-\vec{r}_k(t+\tau))}\right\rangle$$

$$= |E_0|^4 \underbrace{\langle e^{-i\vec{q}\cdot(\vec{r}_j(t)-\vec{r}_j(t+\tau))}\rangle}_{?}\langle e^{i\vec{q}(\vec{r}_k(t)-\vec{r}_k(t+\tau))}\rangle$$

... DLS ...

$$\langle e^{-i\vec{q}\cdot\Delta\vec{r}(t,\tau)}\rangle = ?$$

Note: $\langle f \rangle = \int_{-\infty}^{\infty} f(x)\, P(x)\, dx$

so $\langle e^{-i\vec{q}\cdot\Delta\vec{r}(t,\tau)}\rangle = \int_{-\infty}^{\infty} d(\Delta\vec{r})\, P(\Delta\vec{r},\tau)\, e^{i\vec{q}\cdot\Delta\vec{r}(\tau)}$

t-averaged Probability of displacement $\Delta\vec{r}$ in interval τ

(Green's fn solution of Diffusion eqn)

$$\frac{dP(\vec{r},t)}{dt} = D\nabla^2 P(\vec{r},t)$$

solve in Fourier space: $P(\vec{r},t) = \frac{1}{2\pi}\int_{-\infty}^{\infty} dq\, e^{-i\vec{q}\cdot\vec{r}}\, \tilde{P}_q$

$\times e^{i\vec{q}\cdot\vec{r}}$ and integrate ...

$$\frac{d\tilde{P}_q}{dt} = -q^2 D\tilde{P}_q \Rightarrow \tilde{P}_q(t) = e^{-q^2 Dt}$$

normalization!
$\tilde{P}_0 = \int dr\, P(r) = 1$

so $\langle e^{-i\vec{q}\cdot\Delta\vec{r}(t,\tau)}\rangle_t = \tilde{P}_q(\tau) = e^{-q^2 D\tau}$ *

$= \langle e^{+i\vec{q}\cdot\Delta\vec{r}(t,\tau)}\rangle$

(* Can also prove by expanding $\langle e^{i\vec{q}\cdot\Delta\vec{r}}\rangle$ in Taylor Series)

... DLS ...

Add up terms ...

$$\langle I(t)\, I(t+\tau)\rangle = |E_0|^4 \left[N^2 + (N^2 - N)\, e^{-2q^2 D\tau} \right]$$

divide by $\langle I\rangle^2 = N^2 |E_0|^4$

$$\boxed{g(\tau) = \frac{\langle I(t)\, I(t+\tau)\rangle}{\langle I\rangle^2} = 1 + e^{-2q^2 D\tau}}$$

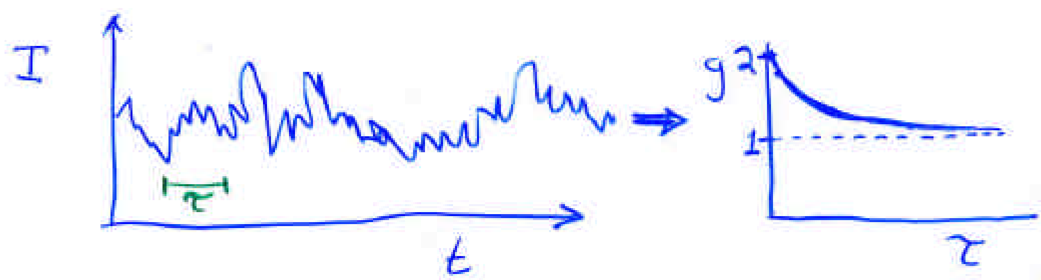
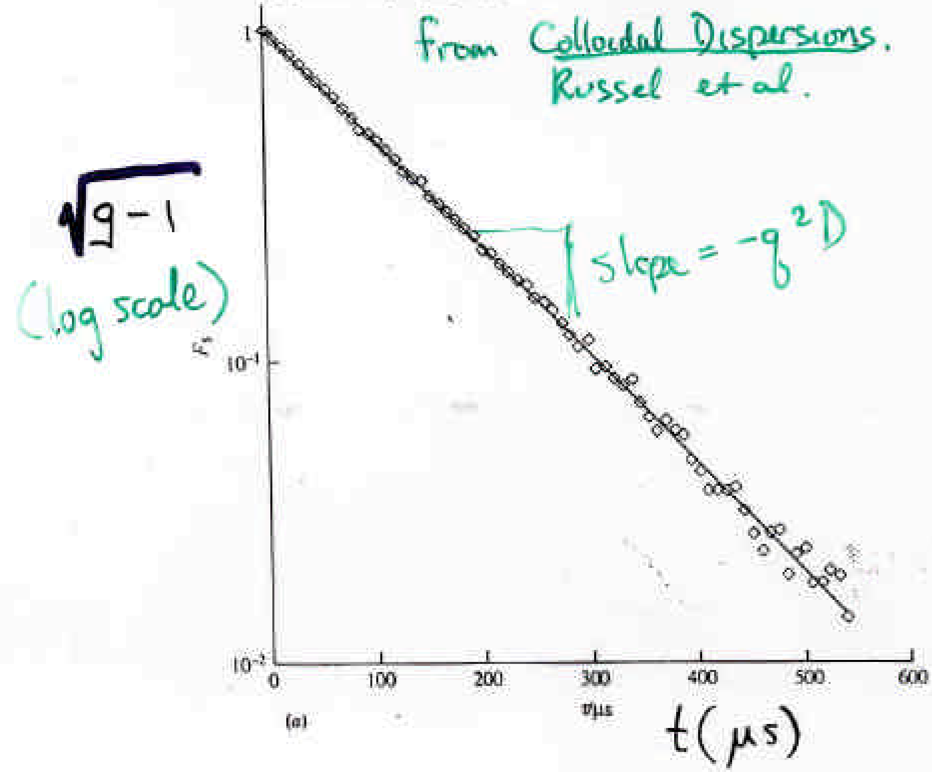


Fig. 3.4. (*a*) Autocorrelation function for dilute polystyrene latex spheres with $a = 0.30\,\mu m$ showing experimental points (□) and single exponential decay (—) expected from (3.4.6).
(*b*) Confirmation of the q^2 dependence of the decay constant for $2a = 0.357\,\mu m$ (●) and $0.091\,\mu m$ (■) polystyrene latices (Lee, Tscharnuter, & Chu, 1972).



Polystyrene spheres
in water, $R = 0.30\,\mu m$