7. DYNAMIC LIGHT SCATTERING

7.1 First order temporal autocorrelation function.

- Dynamic light scattering (DLS) studies the properties of inhomogeneous and *dynamic media*. A generic situation is illustrated in Fig. 1, where a plane wave scatters on a system of randomly moving particles.

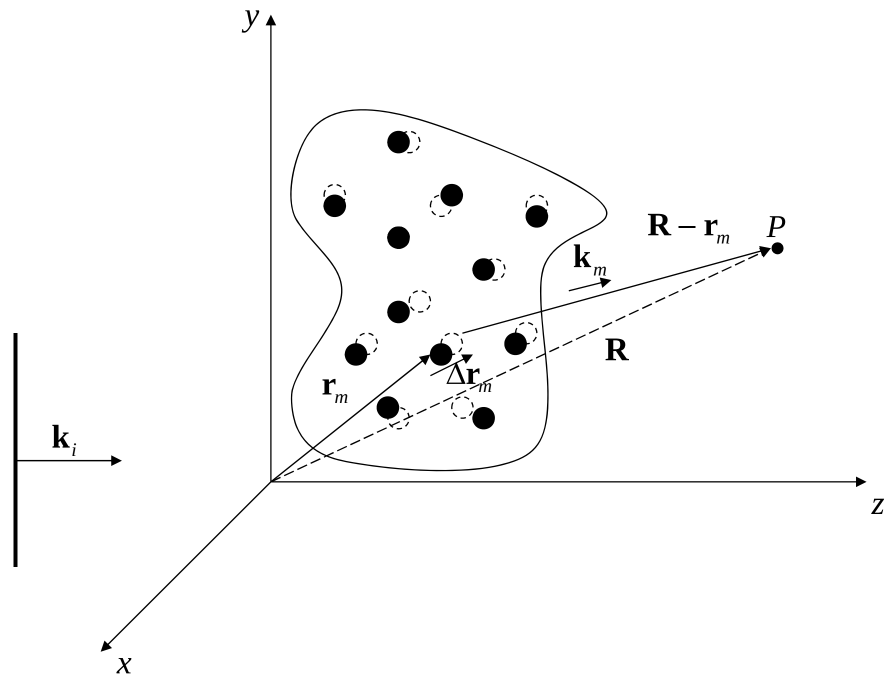

Figure 7-1. Light scattering on a system of moving particles.

- At observation point P of vector position **R**, particle *m*, of fluctuating position $\mathbf{r}_m(t)$, scatters along direction $\mathbf{R}-\mathbf{r}_m(t)$.
- For weakly scattering media, the problem can be described by the Born approximation, where we consider the scattering medium to be discrete and the particle positions to fluctuate in time.
- Define a *dynamic scattering potential*, as a collection of point scatterers.

$$F(\mathbf{r},t)=F_0(\mathbf{r})*\sum_j \delta\left[\mathbf{r}-\mathbf{r}_j(t)\right]. \qquad (7.1)$$

- Equation 1 is analogous to the earlier equation when describing *static* scattering under the Born approximation, now the particle positions change in time.
- F_0 is the scattering potential of a single particle and the summation is over all the particles. Variable *t* is due to fluctuations in particle positions and should not be confused with the reciprocal variable of optical frequency ω.

- The scattering potential is still in the frequency domain, $F(\mathbf{r},\omega)$; we ignored the explicit ω argument for simplicity. The *dynamic* scattering amplitude is given by the Fourier transform of Eq. 1,

$$f(\mathbf{q},t) = f_0(\mathbf{q}) \cdot \sum_j e^{i\mathbf{q}\mathbf{r}_j(t)}, \tag{7.2}$$

- $\mathbf{q} = \mathbf{k}_s - \mathbf{k}_i$
- The dynamic signal originates in the superposition of scattered fields with fluctuating phases. To characterize these fluctuations, we calculate the *temporal* autocorrelation of the field scattered along $\mathbf{k}_s$, as

$$\begin{aligned}\Gamma(\mathbf{q},\tau) &= \left\langle f(\mathbf{q},t) \cdot f^*(\mathbf{q},t+\tau) \right\rangle \\ &= \left| f_0(\mathbf{q}) \right|^2 \left\langle \sum_{m,n} e^{i\mathbf{q}\left[\mathbf{r}_m(t+\tau)-\mathbf{r}_n(t)\right]} \right\rangle.\end{aligned} \tag{7.3}$$

- Γ is the *first-order (field) correlation* function, to be distinguished from the *intensity correlation*. In Eq. 3, the angular brackets denote temporal averaging, $\left\langle f(t)\right\rangle = \frac{1}{T}\int_{-T/2}^{T/2} f(t)\,dt$. Assume particles move independently from one another, always true for a sparse distribution of particles. Under these circumstances, correlations between displacements of different particles vanish,

$$\left\langle e^{i\mathbf{q}\left[\mathbf{r}_m(t+\tau)-\mathbf{r}_n(t)\right]}\right\rangle = 0, \text{ for } m \neq n. \tag{7.4}$$

- Combining Eqs. 3 and 4, we obtain

$$\begin{aligned}\Gamma(\mathbf{q},\tau) &= \sigma_d(\mathbf{q})\left\langle \sum_m e^{i\mathbf{q}\left[\mathbf{r}_m(t+\tau)-\mathbf{r}_m(t)\right]}\right\rangle, \\ &= N\sigma_d(\mathbf{q})\left\langle e^{i\mathbf{q}\left[\mathbf{r}(t+\tau)-\mathbf{r}(t)\right]}\right\rangle\end{aligned} \tag{7.5}$$

- $\sigma_d(q) = |f_0(q)|^2$ is the differential cross section associated with a single particle and N is the total number of particles in the scattering volume.
- We assumed that all terms in the summation are equal, i.e. all particles are governed by the same statistics. The temporal autocorrelation Γ is typically normalized to give

$$g_1(\mathbf{q},\tau) = \frac{\Gamma(\mathbf{q},\tau)}{N\sigma_d(q)} = \left\langle e^{i\mathbf{q}\left[\mathbf{r}_m(t+\tau)-\mathbf{r}_m(t)\right]} \right\rangle \tag{7.6}$$

- The subscript 1 indicates that g_1 is a *first-order correlation function*.

7.2 Second-order correlation function. The Siegert relationship.

- In practice, one only has access to the intensity scattered along direction $\mathbf{k}_s$. An intensity autocorrelation function is the measurable quantity, defined as

$$g_2(\tau) = \frac{\langle I(t) \cdot I(t+\tau) \rangle}{\langle I(t)^2 \rangle}, \qquad (7.7)$$

- where

$$I(t) = \sum_{m,n} U_m(t) \cdot U^*_n(t), \qquad (7.8)$$

- The angular brackets denote temporal average, and the double summation is over the ensemble of the scattered fields. Combining Eqs. 7 and 8, we obtain

$$g_2(\tau) = \frac{1}{\langle I(t)^2 \rangle} \cdot \left\langle \sum_{m,n} U_m(t) \cdot U_n^*(t) \cdot \sum_{k,l} U_k(t+\tau) U_l^*(t+\tau) \right\rangle. \quad (7.9)$$

- In Eq. 9, there are two different contributions:
  - for $m = n = k = l$, summation gives $\left\langle I(t)^2 \right\rangle$
  - for $m=l$ and $n=k$, $m \neq n$, we obtain terms of the form $\left\langle \sum_m I_m g_1(\tau) \cdot \sum_n I_n g_1{}^*(\tau) \right\rangle$. Because the particles scattered independently from one another, all the other terms vanish.
- Thus, Eq. 9 becomes

$$q_2(\tau) = \frac{1}{\left\langle I(t)^2 \right\rangle} \cdot \left[\left\langle I(t)^2 \right\rangle + \left\langle I(t)^2 \right\rangle \cdot \left| g_1(\tau) \right|^2 \right], (7.10)$$

- which readily simplifies to

$$g_2(\tau) = 1 + \left| g_1(\tau) \right|^2 \qquad (7.11)$$

- Equation 11 connects the first-order and the second-order correlation functions and is known as the *Siegert relationship*. To evaluate the average $\left\langle e^{i\mathbf{q}\Delta\mathbf{r}(\tau)}\right\rangle$, with Δr the displacement of a single particle, we need information regarding the physical phenomenon that generates fluctuations in the particle positions. This will provide the displacement probability density, to evaluate the average.
- Let us assume that this probability density is $\psi(\mathbf{r},t)$. The average of interest can be calculated as an *ensemble average*,

$$\begin{aligned}\left\langle e^{iq\mathbf{r}(t)}\right\rangle &= \int_V \psi(\mathbf{r},t)\cdot e^{i\mathbf{q}\mathbf{r}(t)} d^3\mathbf{r} \\ &= \tilde{\psi}(\mathbf{q},t)\end{aligned} \qquad (7.12)$$

- The average is simply the 3D spatial Fourier transform of the probability density $\psi(\mathbf{r},t)$. In the following section, we determine ψ and the average $\left\langle e^{i\mathbf{q}\mathbf{r}(t)}\right\rangle$ for *diffusive particles*, which is a situation widely encountered in practice.

7.3 Particles under Brownian motion.

- For particles fluctuating at thermal equilibrium, undergoing Brownian motion, the probability density associated with a particle at position **r** and time *t* verifies the (homogeneous) diffusion equation

$$D\nabla^2\psi(\mathbf{r},t)-\frac{\partial}{\partial t}\psi(\mathbf{r},t)=0. \qquad (7.13)$$

- *D* is the diffusion coefficient, which for a spherical particle of radius *a* is given by the Stokes-Einstein equation

$$D=\frac{k_B T}{6\pi\eta a} \qquad (7.14)$$

- k_B is the Boltzmann constant, $\left(k_B=1.38\cdot10^{-23}\,\mathrm{J}/\mathrm{K}\right)$, T is the absolute temperature (*T*=298K for room temperature), η the viscosity of the surrounding fluid ($\eta\simeq10^{-3}\,\mathrm{N\cdot s}/\mathrm{m}^2\simeq10^{-2}\,\mathrm{Pa\cdot s}$ for water at room temperature).

- Taking the spatial Fourier transform of Eq. 13, we obtain

$$\frac{\partial \tilde{\psi}(\mathbf{q},t)}{\partial t} = Dq^2 \tilde{\psi}(\mathbf{q},t) \qquad (7.15)$$

- The first order differential equation in time immediately yields

$$\tilde{\psi}(q,t) = e^{-Dq^2 t} \qquad (7.16)$$

- It follows from Eqs 6, 13 and 16 that the first order correlation function for Brownian particles has the form

$$\begin{aligned} g_1(\mathbf{q},\tau) &= \left\langle e^{i\mathbf{qr}(\tau)} \right\rangle \\ &= e^{-Dq^2\tau}. \end{aligned} \qquad (7.17)$$

- Equation 17 is commonly used in dynamic light scattering. It establishes, for measurements at a fixed scattering angle θ, which corresponds to $q = \frac{4\pi}{\lambda} \sin \theta/2$, the field correlation function has a characteristic time $\tau_0 = 1/Dq^2$.

- The larger the scattering angle and the larger the diffusion coefficient, the shorter the correlation time τ_0. For example, a particle of 1μm diameter, suspended in water at room temperature, has a characteristic $\tau_0 \simeq 2.5\text{ms}$.
- Experimentally one has access directly to the second-order correlation function and, using the Siegert relationship, information about the diffusion coefficient can be obtained via

$$g_2(\tau) = 1 + e^{-2Dq^2\tau}. \qquad (7.18)$$

- Figure 2 shows a qualitative description of the measured intensity and $g_2(\tau)$ for two different correlation times.

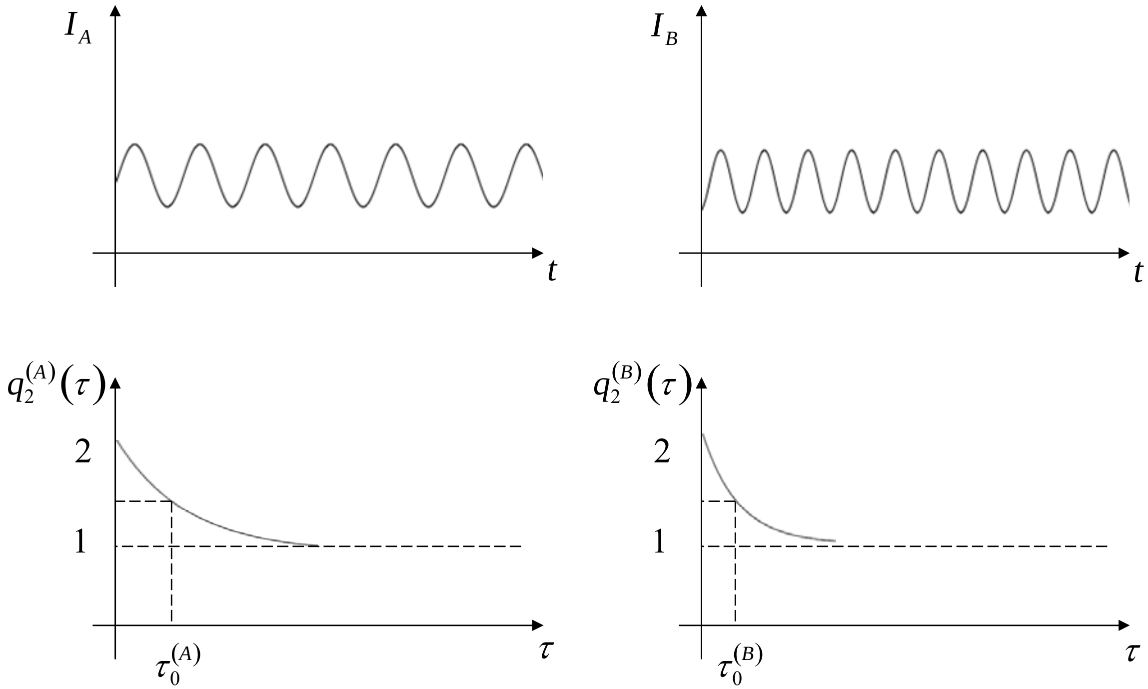

Figure 7-2. DLS signals in two different conditions.

- The decay (correlation) time has the form

$$\tau_0 = \frac{1}{Dq^2} = \frac{6\pi\eta a}{q^2 k_B T} \tag{7.19}$$

- Therefore $\tau_0^{(A)} > \tau_0^{(B)}$ can be obtained in a variety of conditions A and B: $a_A > a_B$, $\eta_A > \eta_B$, $q_A < q_B$, $T_A < T_B$ (all other parameters constant).

- Sometimes, the power spectrum of intensity fluctuations is measured,

$$P(\mathbf{q},\omega) = \int I(\mathbf{q},t) \cdot I(\mathbf{q},t+\tau) e^{-i\omega\tau} d\tau = F\left[g_2(\mathbf{q},t) \right] \tag{7.20}$$

- Equation 20 states that the measured power spectrum is related to $g_2(\tau)$ via a Fourier transform, which simply follows from the Wiener-Kintchin theorem.

- Thus, for diffusive particles, we expect a power spectrum of Lorentzian shape

$$\begin{aligned} P(\omega) &= F\left[e^{-\frac{\tau}{\tau_0}} \right] \\ &= \frac{\Delta\omega}{\omega^2 + (\Delta\omega)^2} \end{aligned}, \qquad (7.21)$$

- With $\Delta\omega = 1/\tau_0$. Thus, the width of the power spectrum is equally informative.