Dynamic Light Scattering

Doi, "Introduction to Polymer Physics" p. 82

K. S. Schmitz. "An Introduction to Dynamic Light Scattering by Macromolecules" p.31

B. Chu, "Laser Light Scattering: Basic Principles and Practice, Second Edition", Academic Press, 1991.

M. Bee, "Quasielastic Neutron Scattering: Principles and Applications in Solid State Chemistry, Biology and Materials Science", 1988.

Dynamic light scattering, as well as dynamic neutron and x-ray scattering (recently), is a main tool to understand and verify models pertaining to the dynamics of polymers in dilute solution. Because it is an analytic technique unfamiliar to the majority of polymer scientists a brief overview is given here.

As mentioned above, the autocorrelation function C(t), or correlation function for position is given by:

$$C(t) = <x(0)\ x(t)>$$

When monochromatic, collimated visible light irradiates matter the state of polarization of the molecules oscillates at the frequency of the irradiating light. This results in an electric field $\mathbf{E}(t)$ associated with the position of the molecules at a given time. This oscillating electric field produces light of the same wavelength as the incident light that is irradiated from the molecules essentially in a uniform manner in space. Constructive interference between the emitted light from two molecules or parts of a polymer separated by a vector, $\mathbf{r}$, results in the scattering pattern. The observed intensity is proportional to the square of the resulting electric field associated with the combination of light emanating from the irradiated volume.

A photomultiplier tube of quantum efficiency Q_e records the scattered intensity associated with a separation distance $\mathbf{R}$ at a fixed angle as a function of time t,

$$I(\mathbf{R}, t) = Q_e\ \mathbf{E}_s{}^*(\mathbf{R}, t')^T \cdot \mathbf{E}_s(\mathbf{R}, t')$$

where t' is the time of irradiation and emission and t is the time of observation by the PMT (there is an incidental time lag in measurement). "*" indicates the complex conjugate and "T" the transpose (this is how you square a complex vector). The angle is usually converted to wavevector, $\mathbf{K} = 2\ \sin(\ /2)/\ $, or momentum transfer vector $\mathbf{q} = 2\ \mathbf{k}$. q is related to size r by r = $2\ /q = 1/K$.

The time average intensity is given by,

$$\langle I(\mathbf{R}) \rangle = Q_e \langle \mathbf{E}_s{}^*(\mathbf{R}, t')^T \cdot \mathbf{E}_s(\mathbf{R}, t') \rangle$$

Since the electric field vector relies on the presence of scattering matter at position $\mathbf{R}$ at time t', it is expected that there is a relationship between C(t) and the intensity correlation function,

$$\langle I(0)I(t) \rangle = \langle I(0)^2 \rangle + Q_e{}^2 \langle |\mathbf{E}^*(0)^T \cdot \mathbf{E}(t)| \, |\mathbf{E}^*(t)^T \cdot \mathbf{E}(0)| \rangle$$

If the intensity correlation function is normalized by $\langle I(0)^2 \rangle$ the autocorrelation function results,

$$C(t) = \langle I(0)I(t) \rangle / \langle I(0)^2 \rangle = 1 + K \, g^{(2)}(t)$$

where $g^{(2)}(t)$ is the square of the normalized autocorrelation function for electric field, $g^{(2)}(t) = |g^{(1)}(t)|^2$.

Dynamic light scattering offers a direct measure of $C_v(t)$.

The dynamic light scattering instrument will require a high power laser, typically an Argon gas laser, a temperature controlled sample cell, a sensitive detector such as a photomultiplier tube, and a time correlator capable of recording intensity (or current from the photomultipler tube) on an extremely short time scale (nanoseconds). The correlator usually calculates the intensity correlation function directly. The DLS instrumentation is well described in B. Chu's book cited above.

Center of Mass Diffusion and DLS:
Application of Fick's second law for diffusion to scattering in $\mathbf{K}$-space results in the following expression for the molecular correlation function for center of mass motion,

$$G_1(\mathbf{K}, t) = \langle (\Delta C(\mathbf{K}, 0))^2 \rangle \exp(-D_m K^2 t)$$

where D_m is the mutual diffusion coefficient and ΔC is the concentration change as a function of time and wavevector, $\mathbf{K}$. Normalizing by $\langle (\Delta C(\mathbf{K}, 0))^2 \rangle$ yields the electric field correlation function, $g^{(1)}$,

$$g^{(1)}(t) = g^{(1)}(\mathbf{K}, t) = \exp(-D_m K^2 t)$$

The mutual diffusion coefficient is dependent on the wavevector (scattering angle) since at different size scales, $r = 1/K$, the mechanisms of diffusion differ. In the limit of K goes to 0, i.e. large size scales, the mutual diffusion coefficient, D_m, is defined by the **Stokes-Einstein relationship**,

$$D_m = (1/N_A f_m) \; (d\Pi/dc)_{T,\mu'}$$

where f_m is the mutual friction factor, $(d\Pi/dc)_{T,\mu'}$ is the osmotic susceptibility. At infinite dilution $(d\Pi/dc)_{T,\mu'} = N_A kT$, so at infinite dilution (no interactions) and $K = 0$ (size scales much larger than the particles of interest), $D_m = kT/f_m$, as previously discussed.

Center of mass diffusion is the simplest case to describe. Other types of diffusion will effect dynamic scattering depending on the complexity of the material, i.e. internal modes of relaxation, hydrodynamic interactions and interactions between chains such as entanglements. These will be of great importance to the dynamics of polymers.