An investigation of photon correlation spectroscopy data analysis packages "discrete" and "contin" using the Schulz-Zimm distribution

Usman Abdul Aziz Qazi
University of Nevada, Las Vegas
INFORMATION TO USERS

This manuscript has been reproduced from the microfilm master. UMI films the text directly from the original or copy submitted. Thus, some thesis and dissertation copies are in typewriter face, while others may be from any type of computer printer.

The quality of this reproduction is dependent upon the quality of the copy submitted. Broken or indistinct print, colored or poor quality illustrations and photographs, print bleedthrough, substandard margins, and improper alignment can adversely affect reproduction.

In the unlikely event that the author did not send UMI a complete manuscript and there are missing pages, these will be noted. Also, if unauthorized copyright material had to be removed, a note will indicate the deletion.

Oversize materials (e.g., maps, drawings, charts) are reproduced by sectioning the original, beginning at the upper left-hand corner and continuing from left to right in equal sections with small overlaps. Each original is also photographed in one exposure and is included in reduced form at the back of the book.

Photographs included in the original manuscript have been reproduced xerographically in this copy. Higher quality 6" x 9" black and white photographic prints are available for any photographs or illustrations appearing in this copy for an additional charge. Contact UMI directly to order.
An investigation of photon correlation spectroscopy data analysis packages "discrete" and "contin" using the Schulz-Zimm distribution

Qazi, Usman Abdul Aziz, M.S.
University of Nevada, Las Vegas, 1991
AN INVESTIGATION OF PHOTON CORRELATION SPECTROSCOPY
DATA ANALYSIS PACKAGES "DISCRETE" AND "CONTIN"
USING THE SCHULZ-ZIMM DISTRIBUTION

by
Usman Qazi

A thesis submitted in partial fulfillment
of the requirements for the degree of

Master of Science
in
Physics

Department of Physics
University of Nevada, Las Vegas
August 1991
The thesis of Usman Qazi for the degree of Master of Science in Physics is approved.

Chairperson, J. C. Selser, Ph. D.

Examiner Committee Member, B. Zygelman, Ph. D.

Examiner Committee Member, P. Hintzen, Ph. D.

Graduate Faculty Representative, A. Muleshkov, Ph. D.

Graduate Dean, R. W. Smith, Ph. D.

University of Nevada, Las Vegas
August, 1991
ABSTRACT

DISCRETE and CONTIN are standard data analysis packages employed in the field of Photon Correlation Spectroscopy in order to investigate noisy autocorrelation functions. Their efficacy and resolution were studied by using simulated autocorrelation functions based on the Schulz-Zimm distribution of polymer radii.

Intensity autocorrelation functions with various levels of noisy were fitted to DISCRETE and CONTIN. The results of the CONTIN output were studied in order to see what indications of the features of the original distribution were retained. It was found that autocorrelation functions calculated for broader distributions of radii yielded correspondingly broader distributions in radius space when inverted by means of CONTIN. It was found that features such as the skewness of the original Schulz-Zimm distribution could not be recovered by this process except in the case of narrow distributions of radii that may be approximated as monodisperse. The addition of noise was not found to seriously affect the performance of DISCRETE and CONTIN, however, a narrowing of the recovered radius distribution, attributable to the CONTIN feature of parsimony, was observed.

It was also remarked that the output of CONTIN did not preserve many essential features of the original distribution of radii when the latter were very broad, which indicates that CONTIN results do tend to depend on the breadth of the original radius distribution, but an exact correspondence is difficult to find.
TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Chapter I  Characterization of polymers</th>
<th>1</th>
</tr>
</thead>
<tbody>
<tr>
<td>I.1 Molecular weight distributions of polymer samples</td>
<td>1</td>
</tr>
<tr>
<td>I.2 Types of molecular weights</td>
<td>2</td>
</tr>
<tr>
<td>I.3 Theoretical molecular weight distributions of polymer samples</td>
<td>4</td>
</tr>
<tr>
<td>References</td>
<td>5</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Chapter II  Theory and techniques of light scattering</th>
<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td>II.2 Photon correlation spectroscopy of Brownian motion</td>
<td>8</td>
</tr>
<tr>
<td>II.4 Rayleigh scattering</td>
<td>11</td>
</tr>
<tr>
<td>II.5 Scattering of light by macromolecules in solution</td>
<td>12</td>
</tr>
<tr>
<td>III.6 Temporal averages and autocorrelation functions</td>
<td>15</td>
</tr>
<tr>
<td>II.7 Discrete-time computation of autocorrelation functions</td>
<td>16</td>
</tr>
<tr>
<td>II.8 The spectral density</td>
<td>17</td>
</tr>
<tr>
<td>II.9 Nomenclature of autocorrelation functions</td>
<td>18</td>
</tr>
<tr>
<td>II.10 The scattered field autocorrelation function</td>
<td>19</td>
</tr>
<tr>
<td>II.11 Link between polarizability fluctuations and Brownian motion</td>
<td>19</td>
</tr>
<tr>
<td>II.12 Field and intensity autocorrelation functions</td>
<td>22</td>
</tr>
<tr>
<td>II.13 Form factor for any geometry of the scatterer</td>
<td>29</td>
</tr>
<tr>
<td>II.13.1 The static form factor for a rigid rod</td>
<td>32</td>
</tr>
<tr>
<td>II.13.2 The static form factor for a random coil</td>
<td>35</td>
</tr>
<tr>
<td>II.14 Static light scattering and molecular weight determinations</td>
<td>39</td>
</tr>
<tr>
<td>II.15 The dynamic form factor of a macromolecule</td>
<td>40</td>
</tr>
<tr>
<td>II.16 Description of the experimental setup</td>
<td>41</td>
</tr>
<tr>
<td>References</td>
<td>43</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Chapter III  Analytic study of light scattering from polydisperse systems</th>
<th>45</th>
</tr>
</thead>
<tbody>
<tr>
<td>III.1 Application of the Schulz-Zimm distribution to dynamic light scattering</td>
<td>45</td>
</tr>
<tr>
<td>III.2 The &quot;polydisperse&quot; electric field autocorrelation function</td>
<td>47</td>
</tr>
<tr>
<td>Appendix</td>
<td>52</td>
</tr>
<tr>
<td>References</td>
<td>53</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Chapter IV  Data analysis</th>
<th>54</th>
</tr>
</thead>
<tbody>
<tr>
<td>IV.1 General discussion</td>
<td>54</td>
</tr>
<tr>
<td>IV.2 Some common techniques of data analysis</td>
<td>55</td>
</tr>
<tr>
<td>IV.3 Method of cumulants</td>
<td>56</td>
</tr>
<tr>
<td>IV.4 DISCRETE and CONTIN</td>
<td>58</td>
</tr>
<tr>
<td>References</td>
<td>64</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Chapter V  Results</th>
<th>66</th>
</tr>
</thead>
<tbody>
<tr>
<td>V.1 Introduction to the results section</td>
<td>66</td>
</tr>
<tr>
<td>V.2 Pure exponentials</td>
<td>69</td>
</tr>
<tr>
<td>Section</td>
<td>Page</td>
</tr>
<tr>
<td>------------------------------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>V.2.1 Exponential with no noise</td>
<td>70</td>
</tr>
<tr>
<td>V.2.2 Exponential with a high level of noise</td>
<td>71</td>
</tr>
<tr>
<td>V.2.3 Exponential with a low level of noise</td>
<td>73</td>
</tr>
<tr>
<td>V.3 Intensity autocorrelation functions for various values of z</td>
<td>74</td>
</tr>
<tr>
<td>V.3.1 Intensity autocorrelation function for ( z = 100 ) with no noise</td>
<td>75</td>
</tr>
<tr>
<td>V.3.2 Intensity autocorrelation function for ( z = 100 ) with low noise</td>
<td>78</td>
</tr>
<tr>
<td>V.3.3 Intensity autocorrelation function for ( z = 100 ) with high noise</td>
<td>81</td>
</tr>
<tr>
<td>V.3.4 Intensity autocorrelation function for ( z = 10 ) with no noise</td>
<td>83</td>
</tr>
<tr>
<td>V.3.5 Intensity autocorrelation function for ( z = 10 ) with low noise</td>
<td>87</td>
</tr>
<tr>
<td>V.3.6 Intensity autocorrelation function for ( z = 10 ) with high noise</td>
<td>90</td>
</tr>
<tr>
<td>V.3.7 Intensity autocorrelation function for ( z = 1 ) with no noise</td>
<td>93</td>
</tr>
<tr>
<td>V.3.8 Intensity autocorrelation function for ( z = 1 ) with low noise</td>
<td>95</td>
</tr>
<tr>
<td>V.3.9 Intensity autocorrelation function for ( z = 1 ) with high noise</td>
<td>98</td>
</tr>
<tr>
<td>V.4 Discussion</td>
<td>100</td>
</tr>
<tr>
<td>References</td>
<td>104</td>
</tr>
</tbody>
</table>
ACKNOWLEDGEMENTS

I would like to express my thanks to Dr. J. C. Selser for his extensive advice and supervision. I am also grateful to Dr. K. Devanand for his close help in all matters. This work was greatly aided by my getting access to the facilities of the Computer Science Department, and I would like to record my appreciation for the consideration I received from there.
Chapter I

**Characterization of Polymers**

1.1 Molecular weight distributions of polymer samples

The problem here concerns the characterization of polymers, which is a process that follows the preparation of a particular polymer as the physical properties and the structure of the product have to be understood. Often the chemical structure of a polymer is known by its method of synthesis but some aspects of its configuration, conformation or isomerism need to be investigated using physical characterization methods such as light scattering.\(^1,2,3\)

A high polymer is taken to be one for which a considerable upward change in its molecular weight does not cause a marked change in its properties. This definition excludes certain polymers such as polyethylene of a molecular weight of 6000 amu, but it is adequate for the polymer samples studied here, such as polyethylene oxide, which are characterized by a molecular weight of over a million.

Using Avogadro's hypothesis that equal volumes of gases contain the same number of molecules under the same conditions of temperature and pressure, it is possible to determine the molecular weights of chemical substances. Molecular weights of gases and volatile liquids may be measured using this principle. The laws for the behavior of dilute
solutions were developed in analogy to nonideal gases by Van't Hoff (1884), which permitted the molecular weights to be determined from colligative properties. Other methods were developed in this century using physical properties of solutions approaching ideal behavior at infinite dilution.

Polymers are polydisperse systems in which the molecular weight does not aid in obtaining the molecular formula, but rather explains the change in the physical properties when several components of different chain lengths combine in various proportions. For example, the tensile strength and elongation at break increase steeply for some polymers in the molecular weight range of 50,000 amu to 200,000 amu. A wide distribution of molecular weights changes the magnitude of these properties in certain expected directions and a knowledge of the distribution of molecular weights may help in obtaining optimum physical properties by controlling the process of polymerization.

1.2 Types of polymer molecular weights

Nonuniform molecular weight distributions can be due to the presence of impurities in a sample. The sources of these impurities may however be identified and removed. But it is not possible by means of a process of synthesis to produce uniform molecular weights and in many cases a wide range of molecular weights is produced. Polymers can be better characterized by a distribution of molecular weights. For some applications the determination of one or more types of average molecular weight of the sample may provide the necessary information.
There are several kinds of average molecular weight of a polymer sample, depending on the particular physical property employed. The number-average molecular weight, $M_n$, is obtained by counting the number of molecules, $n_i$ present in a certain weight category, $M_i$,

$$M_n = \frac{\sum n_i M_i}{\sum n_i}.$$  

(1)

This measure of the molecular weight is especially sensitive to the presence of small molecules in the sample as more of these may be present per sample mass than any other species.

The weight average molecular weight, $M_w$, is the sum of contributions based on the weight fraction of each species, $w_i$, showing a sensitivity to components of high molecular weight,

$$M_w = \frac{\sum w_i M_i}{\sum w_i} = \frac{\sum n_i M_i^2}{\sum n_i}.$$  

(2)

This quantity may be accessed by means of static light scattering and ultracentrifugation, for example.

Finally, the z-averaged molecular weight, obtained by for example, measurements of the radial distribution of of the refractive-index gradient in equilibrium centrifugation, or size exclusion chromatography, is defined as

$$M_z = \frac{\sum n_i M_i^3}{\sum n_i M_i^2}.$$  

(3)

Average molecular weights are given in atomic mass units.
1.3 Theoretical molecular weight distributions of polymers

Molecular weight distributions of polymers are generally presented as the relative number of each species against its molecular weight. One method of obtaining a curve of this kind uses calculations based on the molecular weights of the sample. If two different average molecular weights such as $M_n$ and $M_w$ are known for the sample and a particular distribution of molecular weights is assumed from prior knowledge of the process by which the sample is prepared, then these average values can be used to obtain the average distribution curve. There are several distribution functions available, such as that of Lansing and Kraemer, and the one used in this study, which is the "most probable" distribution function of Schulz and Zimm, and is discussed at length in Chap. III. This method requires good accuracy for the two average molecular weights and a correct idea of the distribution function. Also, noting that the curves obtained for the Schulz-Zimm distribution are markedly skewed to the right for low values of $z$ and tend more and more toward a delta peak as the value of $z$ gets higher, it is obvious that a given distribution showing a different skewness will not be well fitted by a theoretical distribution of this type.
REFERENCES


Chapter II

Theory and Techniques of Light Scattering

II.1 Introduction to light scattering

A beam of light traversing a uniform medium will only be "scattered" in the forward direction. The scattering occurs because the medium consists of molecules that are surrounded by loosely bound electrons, which can be viewed as a charge distribution with multipolar moments. A light wave carries a time varying electric field which sets up oscillations in the charge distribution within the medium. The dipole component of the interaction is far more important than all other moments and the scattering of light can be viewed as dipole scattering. The light is only scattered in the forward direction because all the other components of the scattered electric field are cancelled by destructive interference i.e. by phase cancellation.

However, thermal energy causes density fluctuations to occur in otherwise homogeneous fluids, one of the consequences of which is the well known phenomenon of Brownian motion. In binary systems concentration fluctuations will occur as a result of thermal fluctuations. Such fluctuations cause the incident light to be scattered in all
directions. A pure fluid with no variation in its density will scatter light only in the forward direction, but a thermally caused inhomogeneity in the fluid will cause light to be scattered in other directions as well.

A polymer solution can thus be pictured as undergoing local concentration fluctuations which lead to fluctuation in its index of refraction which scatter incident laser light. The dimensions of the scattering macromolecule are of the order of the wavelength of visible light, which is why laser light in the visible range is used in photon correlation spectroscopy experiments. The macromolecule in solution is actually undergoing Brownian motion which may be described by the Langevin equation. The Einstein diffusion relationship shows its mean displacement to be a function of its coefficient of diffusion, \( D \), i.e., in one dimension

\[
<x^2> = 2Dt, \tag{1}
\]

where \( x \) denotes the instantaneous displacement of the particle and \( t \) the time. In three dimensions this relationship is

\[
<r^2> = 6Dt \tag{2}
\]

where \( r \) is the instantaneous position of the particle.

Information on the diffusion coefficient can be obtained by studying the temporal variation of the scattered light intensity in a particular direction. The autocorrelation function of the scattered intensity can be measured directly in an experiment. This quantity is actually used to obtain the electric field autocorrelation function of the scattered light, which in many cases for polymer solutions may be viewed as a sum of several decaying exponentials, each of which reflects the decay from a particular mode of motion in the
solution which may come from one or several molecular weight species present in the solution.

II.2 Photon correlation spectroscopy of Brownian motion

Quite often it is not known whether the scattered field autocorrelation function contains only one component as there are factors such as aggregation, problems with instrumentation, in some instances the presence of strongly scattering impurities, or the manifestation of an unknown phenomenon that could lead to extra components. Also, the principal aim of a PCS experiment can very well be the study of the polydispersity of a given sample, per se. Thus it may become necessary to represent the first order (electric field) autocorrelation function as a linear combination of independent contributions.

II.3 Phenomenological description of light scattering

Light propagating in space may usually be considered to consist of transverse electromagnetic waves that vary sinusoidally in space and time. When light interacts with a material medium, it is by means of a coupling between the electric field of the incident light and the multipolar charge distributions that exist in the medium. The time varying electric field causes the electronic charges with which it couples to accelerate and emit radiation as a consequence.
A plane electromagnetic wave incident on a nonmagnetic, nonconducting, nonabsorbing and homogeneous medium with a dielectric constant \( \varepsilon_0 \) can be described as

\[
E_i(r,t) = n_i E_0 e^{i(k_i r - \omega t)}.
\]

In the present notation the unit vector \( n_i \) represents the direction of polarization of the incident electric field; \( E_0 \) is the electric field amplitude; \( \omega \) the angular frequency of the incident radiation, \( |k_i| = 2\pi n/\lambda_i \) and \( |k_f| = 2\pi n/\lambda_f \) represent the incident and the scattered wavevectors in terms of the incident and the scattered wavelengths in vacuum, respectively. The subscript \( i \) refers to quantities relating to the incident electric field, while \( f \) characterizes those connected with the scattered electric field.

The general equations governing the scattering process, writing the energies of the incident and scattered photons as \( W_i \) and \( W_f \), can be given as

\[
W_f - W_i = \hbar \omega, \quad \text{(inelastic scattering)}
\]

\[
W_f - W_i = 0, \quad \text{(elastic scattering)}
\]

\[
\hbar k_f - \hbar k_i = \hbar q, \quad \text{(2)}
\]

where \( \hbar \omega \) and \( \hbar q \) are the energy and momentum transfers, respectively. Also in elastic scattering both energy and momentum are conserved and thus \( |k_f| \) and \( |k_i| \) are equal. The magnitude of the scattering vector \( q \) determines the characteristic sizes that may be probed in a particular experiment. The scattering situation is shown in Fig 2. The vector \( q \) is defined as

\[
q = k_i - k_f \quad \text{(3)}
\]
The angle between the vectors $k_i$ and $k_f$ is called the scattering angle. As in Rayleigh scattering, $|k_i| = |k_f|$, and the scattering wavevector magnitude is given by

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

as shown in Fig. 1(iii) below.

Fig. 1 The essentials of Photon Correlation Spectroscopy. (i) shows intensity fluctuations in scattered light resulting from Brownian motion. The intensity fluctuates around a mean value $\langle I \rangle$. (ii) depicts the resulting intensity autocorrelation function. (iii) corresponds to equations (3) and (4) in this section. (iv) shows the interference among wavelets scattered from two identical particles. All figures in this chapter are taken from [20]

Inter- and intra-molecular motions come into play in the calculation of autocorrelation functions of electric field scattered from macromolecules in solution. Using Huygens'
notion of diffraction it can be said that different parts of a particular scattering macromolecule do not lie on the same wavefront, hence interference occurs between wavelets originating from different portions of the macromolecule.

For convenience in calculation, macromolecules are divided into point-like scattering segments whose size $l$ is negligible compared to the magnitude of the inverse of the scattering vector $q$, or

$$q l << 1$$  \hspace{1cm} (5)

II.4 Rayleigh scattering

It is possible to characterize many situations in the scattering of light.\textsuperscript{3} There are two especially interesting cases: (i) Raman scattering, where the scattered light contains frequencies that are not present in the incident light and (ii) Rayleigh scattering where the frequency suffers essentially no change. Raman scattering occurs when the incident light causes a change in the quantum-mechanical state of the scattering molecule, while Rayleigh scattering leaves the internal state of the molecule unchanged and occurs when the mean free path of the scattering molecules is much smaller compared to the wavelength $\lambda$ of the incident light. In the case of a dilute solution of polymers, Rayleigh scattering is caused by fluctuations of polymer concentration in the solution whose spatial dimensions are of the order of $\lambda^3$. A local change in concentration is accompanied by a change $\delta \varepsilon$ in the permittivity of the medium.
II.5 Scattering of light by macromolecules in solution

In the scattering of light by macromolecules in solution undergoing diffusion, the scattering is not perfectly elastic or energy conserving due to Doppler effects. This leads to the nomenclature 'quasi-elastic light scattering' with

\[ \omega_i \equiv \omega_f \text{ and } \lambda_i \equiv \lambda_f. \]  

Light scattering in dilute polymer solutions usually depends on concentration fluctuations that occur at all times in solutions and the scattered light yields information about the motions of the various scattering centers. Here, the discussion will be limited to situations in which the Rayleigh-Debye approximation is valid, i.e. the electric field causing dipole radiation is the same as the incident radiation that propagates in the sample. Then, the light rays scattered from each center have a definite phase relationship (Mie scattering covers certain situations that occur when this approximation is not valid). First, a phenomenological description based on fluctuations in the dielectric constant of the scattering medium will be given. Later, in order to get specific, the discussion will focus on the molecular polarizability.

The local dielectric constant of the medium is represented by

\[ \varepsilon(r,t) = \varepsilon_0 I + \delta\varepsilon(r,t). \]  

Here \( \varepsilon_0 \) is the mean dielectric constant in the absence of fluctuations, \( I \) is the second rank unit tensor and \( \delta\varepsilon(r,t) \) is the fluctuation in the dielectric constant.
It is assumed in what follows that the incident electric field is sufficiently weak that the response of the scattering system consisting of the solvent and suspended macromolecules can be assumed to be linear.

The actual response of a system of charges to a sinusoidally varying electric field is that of a damped driven harmonic oscillator. Electromagnetic theory yields the following sum for the contribution of all volume elements $d^3r$ located at $r$ for an observer located at the point $R$ (Fig. 2).

$$E_s(R,t) = \frac{E_0}{4\pi Re_0} \exp(i(k_f R) \int_{\text{volume of scattering}} d^3r \exp(i(q \cdot r - \omega t)) [n_f \cdot (k_f \times (\delta \epsilon(r,t)).n_i)] .$$

(3)

This equation may be rewritten by considering a spatial Fourier transform of the dielectric fluctuation

$$\delta \epsilon(q,t) = \int_{\text{volume of scattering}} d^3r \exp(iq \cdot r) \delta \epsilon(r,t)$$

(4)

and the following relationship is obtained

$$E_s(R,t) = \frac{E_0}{4\pi Re_0} \int_{\text{volume of scattering}} d^3r \exp(i(k_f R - \omega t)) [n_f \cdot (k_f \times (\delta \epsilon(q,t)).n_i)] ,$$

(5)

which may be simplified to

$$E_s(R,t) = \frac{-k_f^2 E_0}{4\pi Re_0} \exp(i(k_f R - \omega t)) \delta \epsilon_{tt}(q,t)) ,$$

(6)
where the component of the tensor $\varepsilon$ along the initial and final polarization directions is given as

$$\delta \varepsilon_{ii}(q,t) = n_f \cdot \varepsilon(q,t) \cdot n_l.$$  

Thus the Fourier transform of the dielectric fluctuation is observed in a light scattering experiment.

Fig. 2 The net field arriving at the detector is the sum of the fields scattered from all infinitesimal volume elements $d^3r$ located at position $r$ with respect to the center of the illuminated particle. The detector is located at position $R$. 
II.6 Temporal averages and autocorrelation functions

At this point it is necessary to introduce the notion of an autocorrelation function which facilitates the observation of interesting phenomena such as dielectric constant fluctuations.

Any measurement of a bulk property \( A \) of a system that is a function of the positions and momenta of its constituent particles has to involve a process of averaging. Due to the presence of thermal noise, the magnitude of the property will fluctuate around a certain mean value at equilibrium.5

For a measurement lasting from an instant \( t_0 \) to an instant \( t_0 + T \), where \( T \) is ideally infinitely large, the average value of property \( A \) is

\[
\overline{A}(t_0) = \lim_{T \to \infty} \frac{1}{T} \int_{t_0}^{t_0+T} dt \ A(t).
\]  

(1)

with the understanding that

\[
T = \int_{t}^{t+T} dt'.
\]  

(2)

If the bulk property \( A \) is stationary (i.e. \( \overline{A} = 0 \)), then its average value is independent of the initial instant \( t_0 \). In that case its time average is given as

\[
\langle A \rangle = \lim_{T \to \infty} \frac{1}{T} \int_{0}^{T} dt \ A(t).
\]  

(3)
The scattered electric field intensity is a dynamic function of time. Due to thermal fluctuations occurring in the medium, its value is subject to constant change. Its value at an initial time \( t \) will not be greatly different from the value at a subsequent time \( t + \tau \) provided \( \tau \) is small. The temporal autocorrelation function of a time dependent quantity \( A(t) \) is a measure of the similarity between two signals. It is defined as

\[
C(\tau) = \langle A(t)^* A(t+\tau) \rangle = \lim_{T \to \infty} \frac{1}{T} \int_t^{t+T} dt \ A(t)^* A(t+\tau) ,
\]

where \( A^* \) is the complex conjugate of the quantity \( A \).

II.7 Discrete-time computation of autocorrelation functions

In the laboratory, the scattered intensity (not the electric field) is recorded by means of a photomultiplier tube coupled with an amplifier/discriminator which produces digital pulses proportional to the number of photons that are incident on the photomultiplier face. A discussion of the calculation of the discrete average and autocorrelation function of property \( A \) is therefore required. By considering discrete intervals of time \( \Delta t \) it is possible to write \( t = i \ \Delta t, \tau = n \ \Delta t \) and the value of the property \( A \) at the beginning of the \( j \)-th time interval as \( A_j \). The discrete version of the sum in (II.7.3) above is

\[
\langle A \rangle \equiv \lim_{N \to \infty} \frac{1}{N} \sum_{i=1}^{N} A_i ,
\]

while the discrete version of (II.7.4) is given by
\[ \langle A(0) A(\tau) \rangle \equiv \lim_{N \to \infty} \frac{1}{N} \sum_{i=1}^{N} A_i A_{i+n}. \]  

(2)

The above expression gives the value of the autocorrelation function at time shift \( \tau \). Theoretically, in the case of a monotonically decaying \( C(\tau) \), the calculation can be extended to any length of time, but in practice it is truncated when it is believed that the interesting features of the decay have been recorded and the "baseline" regime has been reached. This expression supposes stationarity and thus an arbitrary temporal origin may be chosen for the calculation.

If \( A \) represents a nonconserved, nonperiodic property that fluctuates about an average value \( \langle A \rangle \), its autocorrelation function either remains equal to its initial value (meaning that \( A \) is a constant of the motion of the system) or decays from the initial value to a value \( \langle A \rangle^2 \) for a large \( \tau \). Thus

\[ \langle A^2(0) \rangle \geq \langle A(0) A(\tau) \rangle. \]  

(3)

II.8 The spectral density

The Fourier transform of the temporal autocorrelation function is known as the spectral density. In the general case of a complex quantity \( A \) it is given as

\[ I_A(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt \, e^{-i\omega t} \langle A^*(0)A(t) \rangle. \]  

(1a)
Also,

\[ \langle A^*(0)A(t) \rangle = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt \, e^{i\omega t} I_A(\omega), \quad (1b) \]

i.e. \( I_A(\omega) \) and \( C(\tau) \) are a Fourier transform pair.

II.9 Nomenclature of autocorrelation functions

The autocorrelation functions of relevance here are always of a temporal character. The first order (scattered electric field) autocorrelation function is denoted as \( G^{(1)} \) if it is un-normalized and \( g^{(1)} \) in case it is normalized. The normalization is expressed as

\[ g^{(1)}(q,t) = \frac{\langle E^*(0) E(t) \rangle}{|E^*(0)|^2}. \quad (1) \]

Similarly, the temporal intensity autocorrelation function is referred to as \( G^{(2)} \) in case it is un-normalized and \( g^{(2)} \) in case it is normalized.

\( G^{(1)}(r, t) \) means the first order space-time electric field correlation function and the corresponding Fourier transform is usually written as \( G^{(1)}(q, \omega) \).

The Fourier transform in time of \( G^{(1)}(r, t) \) will be denoted \( G^{(1)}(r, \omega) \) and that of \( G^{(1)}(q, t) \) written as \( G^{(1)}(q, \omega) \). \( G^{(1)}(q, \omega) \) may be measured using a spectrum analyzer, such as a Fabry-Perrot interferometer.
II.10 The scattered electric field autocorrelation function

A temporal autocorrelation function of the scattered electric field can therefore be written as

\[ \langle E_s^*(R,0)E_s(R,t) \rangle = \frac{k^4|E_0|^2}{16\pi^2R^2\varepsilon_0^2} \langle \delta e_{if}(q,0)\delta e_{if}(q,t) \rangle e^{-i\omega t} \]  

(1)

This relationship shows the link between the scattered electric field autocorrelation function and the autocorrelation function of fluctuations in the dielectric constant. The physical mechanism causing dielectric constant fluctuations may therefore be studied by means of the scattered electric field autocorrelation function, as discussed below.

II.11 Link between polarizability fluctuations and Brownian motion

So far scattering on the basis of fluctuations in the dielectric constant has been considered. In the study of dilute polymer solutions by means of laser light scattering, information is sought on motions of macromolecules undergoing Brownian motion in the solvent. These macromolecules have a much larger polarizability \( \alpha \) than the solvent molecules and their diffusion is much slower than that of the solvent molecules. The scattered electric field autocorrelation function needs to be formulated in terms of the
polarizability of the macromolecule. The polarizability is an intrinsic property of the macromolecule.

An outside electric field distorts a charge distribution within matter by inducing a dipole moment $\mu$ which varies as a function of time. This is called polarization of the field and is governed by the relation

$$\mu(t) = \alpha(r, t) E$$

(1)

The coefficient $\alpha$ is a tensor, and the above equation is expressed in cartesian three dimensional form as

$$\begin{bmatrix}
\mu_x \\
\mu_y \\
\mu_z 
\end{bmatrix} =
\begin{bmatrix}
\alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\
\alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\
\alpha_{zx} & \alpha_{zy} & \alpha_{zz}
\end{bmatrix}
\begin{bmatrix}
E_x \\
E_y \\
E_z
\end{bmatrix}.$$ 

(2)

The tensor $\alpha$ reflects the geometry of the macromolecule in terms of the distribution of its loosely bound outer electrons.

An accelerating charge such as a time-varying dipole is a source of electromagnetic radiation. The radiated or scattered electric field reaching the detector can be shown as being proportional to

$$k_f \times k_f \times \ddot{\mu}(t')$$

(3)

where $t'$ is the retarded time, defined as

$$t' = t - |r' - r| n/c .$$

(4)

and $\ddot{\mu}$ is the second time derivative of $\mu$. 
The quantity \( |r' - r|/c \) is the time taken by light in traveling from \( r \) to the detector. Here \( r' \) refers to the location of the detector in a reference-frame attached to the laboratory. \( t \) is the time at which light emitted at an earlier time \( t' \) is detected.

A calculation similar to that in Sec. II.5 using of (3) shows that the scattered electric field at the detector characterized by polarization \( n_f \) is proportional to \( \alpha_{lf}(t)e^{i\mathbf{q}\cdot\mathbf{r}(t)} \) where \( \mathbf{r}(t) \) now characterizes the position of the center of mass (CM) of the scattering macromolecule. The coefficient \( \alpha_{lf}(t) \) is time dependent due to its rotational and vibrational motions so that the field scattered by the macromolecule varies in time. Translation of the CM of the macromolecule enters the phase factor \( e^{i\mathbf{q}\cdot\mathbf{r}(t)} \) via the instantaneous position \( \mathbf{r}(t) \).

Making the approximation of a weak coupling between the motions of neighboring macromolecules, the net electric field scattered by all the macromolecules in the volume of the solution illuminated by the incident laser beam becomes a linear superposition of the fields scattered by individual macromolecules. The total scattered field then becomes

\[
E_{\text{scat}} = \sum_i E^{(i)}_{\text{scat}}. \tag{5}
\]

It is important to note that macromolecules in solution will also suffer collisions which will produce a distortion in their electronic clouds and thus produce changes in the scattered electric field. Such changes are short lived and do not enter the approximation used here.

The total scattered electric field amplitude is then

\[
E_{\text{scat}} = \sum_k \alpha^k_{lf}(t)e^{i\mathbf{q}\cdot\mathbf{r}(t)} \tag{6}
\]

where only the molecules within the illuminated volume enter into the sum.
II.12 Field and intensity autocorrelation functions

Photon correlation spectroscopy relies on optical mixing to extract information from scattered light. There are two principal techniques for the calculation of autocorrelation functions in a light scattering experiment.

*Heterodyne light scattering* combines the scattered light with a component of the incident light (known as the local oscillator) to produce interference. This technique requires high precision and is difficult to realize experimentally.

In the *homodyne light scattering* technique, all information about the scattered laser light field is obtained by means of a photomultiplier tube which counts photons via the intensity of the light reaching it. The output of the photomultiplier tube is fed to a digital correlator which calculates the temporal intensity autocorrelation function of the scattered light over a period of time. The photomultiplier tube gives a signal proportional to the number of photons it receives, which is a measure of the intensity of the incoming light. If this intensity at a given time \( t \) is represented by \( I(t) \) then

\[
<I(0) I(t)> \propto <|E(0)|^2 |E(t)|^2>
\]  

(1)

The Gaussian approximation states that \( G^{(1)}(q,t) \) can be obtained from \( G^{(2)}(q,t) \) under the approximation that the fluctuation in the molecular polarizability (II.11.6) is a Gaussian stochastic variable. Only under this assumption does the *Siegert relationship* apply:

\[
G^{(2)}(q,t) = A |G^{(1)}(q,t)|^2 + B.
\]  

(2)
where the experimentally obtained intensity autocorrelation function is denoted by $G^{(2)}(q,t)$, the corresponding scattered electric field autocorrelation function as $G^{(1)}(q,t)$ and $A$ and $B$ are constants. $B$ is known as the baseline.
Model for the decay of dielectric constant fluctuations

The heterodyne technique gives an autocorrelation function defined for the purpose of discussion here as

$$I_1(t) = \langle E_{\text{scat}}^*(0) E_{\text{scat}}(t) \rangle$$  \hspace{1cm} (3)

While the homodyne technique yields

$$I_2(t) = \langle |E_{\text{scat}}(0)|^2 |E_{\text{scat}}(t)|^2 \rangle$$  \hspace{1cm} (4)

From eq. (II.11.6) above it is apparent that $I_1(t)$ and $I_2(t)$ are respectively proportional to quantities $F_1$ and $F_2$ defined as \textsuperscript{9}

$$F_1(q, t) = \langle \psi^*(q, 0) \psi(q, t) \rangle$$  \hspace{1cm} (5)

$$F_2(q, t) = \langle |\psi^*(q, 0)|^2 |\psi(q, t)|^2 \rangle$$  \hspace{1cm} (6)

where

$$\psi(q, t) \equiv \sum_{k=1}^{N} b_k(t) \exp(i \mathbf{q} \cdot \mathbf{r}_k) = \int_V d^3r \sum_{k=1}^{N} \delta(r - \mathbf{r}_k(t)) \exp(i \mathbf{q} \cdot \mathbf{r})$$  \hspace{1cm} (7)

and $b_k$ is a function defined as being equal to one if the k-th segment is inside the scattering volume $V$ and equal to zero otherwise. Assuming that in a sufficiently dilute solution macromolecules rarely encounter each other, (5) can be written as
\[ F_1(q, t) = \left( \sum_{k=1}^{N} b_k(0)b_k(t) \exp i \mathbf{q} \cdot [\mathbf{r}_k(t) - \mathbf{r}_k(0)] \right). \] (8)

The time scale for a variation in the product \( b_j(0)b_j(t) \) is indicated by the time it takes for the scattering macromolecule to move out of the illuminated region. If this volume is supposed to have the characteristic dimension \( L \) (typically less than 1mm), the time \( \tau \) required for the macromolecule undergoing diffusive motion to traverse this volume is

\[ \tau \sim L^2/D. \] (9)

The complex exponential \( \exp i\mathbf{q} \cdot [\mathbf{r}_k(t) - \mathbf{r}_k(0)] \) is significantly different from unity when

\[ q^{-1} \ll |\mathbf{r}_k(t) - \mathbf{r}_k(0)|. \] (10)

For a macromolecule undergoing diffusive motion this time scale is given as

\[ \tau_q = (q^2D)^{-1}. \] (11)

From the ratio

\[ \tau/\tau_q = (q^2L)^2, \] (12)

a typical value for \( \tau/\tau_q \) is \( 10^6 \) as \( q \) and \( L \) are of the order of \( 10^5 \) cm\(^{-1} \) and 0.01cm respectively. This implies that the variation in \( b_j(0)b_j(t) \) is much slower than that in the complex exponential, known as the self-intermediate scattering function

\[ F_S(q,t) = \exp \{i\mathbf{q} \cdot [\mathbf{r}_k(t) - \mathbf{r}_k(0)]\}. \] (13)

\( F_S(q,t) \) is also statistically independent from \( b_j(0)b_j(t) \) as it does not depend on the macromolecule being in the scattering volume. It is possible to approximate the variation
\[ b_j(0) b_j(t) \text{ as } b_j(0)^2, \text{ which is actually equal to } b_j(0) \text{ given that the only two possible values for } b_j(0) \text{ are zero or one. It is also obvious that the average number of particles in the scattering volume is given by } <N>. \]

\[ \sum_{k=1}^{N} \langle b_k(0) \rangle = \langle N \rangle . \tag{14} \]

It is then possible to write (8) as

\[ F_1(q, t) = (N) F_S(q, t) . \tag{15} \]

The self-intermediate scattering function defined in (13) is also the spatial Fourier transform of the Van Hove self space-time correlation function denoted as \( G_S (R, t) \) and defined as

\[ G_S (R, t) = <\delta (R - [r_k(t) - r_k(0)])>. \tag{16} \]

Thus,

\[ F_S (q, t) = \int d^3 R \ e^{i q \cdot R} G_S (R, t) . \tag{17} \]

From the definition of \( G_S (R, t) \) it is clear that

\[ G_S (R, 0) = <\delta (R)> \tag{18} \]

with

\[ F_S (q, 0) = 1 \tag{19} \]
The function $G_S(R,t)d^3R$ can be viewed as the probability of finding a macromolecule within an infinitesimally small neighborhood $d^3R$ of a point whose vector coordinate is $R$ at an instant $t$. For a macromolecule undergoing diffusive motion, $G_S(R,t)$ is then a solution to the diffusion equation subject to the initial condition (18)

$$\frac{\partial G_S(R,t)}{\partial t} = D \nabla^2 G_S(R,t). \tag{20}$$

Its Fourier transform is then

$$\frac{\partial F_S(q,t)}{\partial t} = -q^2 D \nabla^2 F_S(q,t), \tag{21}$$

subject to the boundary condition

$$F_S(q, 0) = 1.$$

This yields the fundamentally important solution

$$F_S(q,t) = \exp(-q^2Dt) = \exp(-q^2Dt) = \exp\left(-\frac{t}{\tau_q}\right) \tag{22}$$

with $\tau_q$ being the relaxation time defined in (11). The scattered electric field autocorrelation function is thus seen to be an exponentially decaying function of time.

The Einstein diffusion relationship gives the self-diffusion coefficient $D$ in terms of the friction coefficient $\zeta$ as

$$D = k_B T/\zeta, \tag{23}$$

where $k_B$ and $T$ are the familiar notations for the Boltzmann constant and the temperature, respectively.
Further, the theory of Brownian motion assumes that the Langevin equation describes the motion of a Brownian particle, which could be a massive macromolecule suspended in solvent consisting of smaller molecules. Assuming the Brownian particle of mass $M$ moves with a velocity $\mathbf{V}$, and is subjected to a fluctuating force $F(t)$ arising from collisions with solvent molecules, the corresponding Langevin equation is

$$\frac{MdV}{dt} = -\zeta \mathbf{V} + F(t). \tag{24}$$

In the Stokes approximation for a diffusing sphere with "stick boundary conditions", meaning that at the surface of the sphere (the macromolecule) the velocity of the fluid (meaning the solvent) is zero relative to the velocity of the particle, i.e. at the surface the solvent rotates or translates with the particle,\textsuperscript{11} the friction coefficient is given as

$$\zeta = 6\pi \eta a \tag{25}$$

where $\eta$ is the viscosity of the pure solvent and $a$ the radius of the sphere. Typical values for aqueous solutions of macromolecules are $\eta \sim 0.01$ Poise, giving $D \sim 10^{-13}/a$. The magnitude of the scattering vector for visible light and at a scattering angle of 90°, or example, is $q \sim 10^5 \text{cm}^{-1}$. Thus $q^2D \sim 10^{-3}/a$. The decay of $F_S(q,t)$ is therefore slower the faster the macromolecule. For spheres of radius 0.01\,µm $q^2D = 1/\tau_q \sim 10^{+3}$ sec.

The scattered electric field correlation function then turns out to be

$$F_S(q,t) = \langle N \rangle \exp(-q^2D t), \tag{26}$$

and it permits the measurement of the diffusion coefficient of a macromolecule via the decay constant $\tau_q$. A plot of $\tau_q$ versus $q^2$ will give the diffusion coefficient.
In the limit of extreme dilution the relationship between the diffusion coefficient and the molecular weight of a flexible monodisperse linear polymer is given as

\[ \lim_{c \to 0} D(c) = A M^{-\nu}, \]  

(27)

where \( c \) is the polymer concentration and the exponent \( \nu \) generally varies between 0.5 and 0.6.

II.13 Form Factor for any geometry of the scatterer

Inter- and intra-molecular forces come into play in the calculation of autocorrelation functions of electric field scattered from macromolecules in solution. Using Huygens' notion of diffraction, it can be said that different parts of a particular scattering macromolecule do not lie on the same wavefront, hence interference occurs between wavelets originating from different portions of the macromolecule. This intramolecular interference leads to the notion of the form factor, which is a function containing information about the geometry of the scattering macromolecule. It is discussed here and then further in Chap. III.

In order to avoid interference due to intramolecular scattering, the scattering macromolecule may be considered to be composed of many point scatterers or scattering segments of a typical length \( l \) smaller than the reciprocal of the scattering vector \( q \) or

\[ ql \ll 1. \]  

(1)
This consideration leads to the Rayleigh criterion for scattering, which stipulates that the macromolecule with typical length $l$ must satisfy

$$\frac{\lambda}{l} < 20. \quad (2)$$

Then the expression for $g^{(1)}(q, t)$ at time $t=0$ becomes

$$g^{(1)}(q, 0) = (n_i n_f)^2 \left\langle \sum_{i,j,m} \alpha_i \alpha_j \exp iq \cdot (r_i - r_j) \right\rangle \quad (3)$$

Here $r_i$ represents the position and $\alpha_i$ the polarizability of the $i$-th scattering segment of the $i$-th macromolecule. In the limit of a dilute solution there is no correlation between the motions of different segments of any two different macromolecules corresponding to terms for which $i \neq j$. The above expression permits us to define the molecular form factor $S(q)$ in terms of the molecular polarizability,

$$\alpha_M = n \alpha \quad (4)$$

where $n$ is the number of scattering units in a segment. The molecular form factor is then defined as

$$S(q) = \frac{1}{n^2} \left\langle \sum_{i,m} \exp iq \cdot (r_i - r_m) \right\rangle, \quad (5)$$

with

$$g^{(1)}(q, 0) = (n_i n_f)^2 \langle N \rangle \alpha_M^2 S(q), \quad (6)$$

$\langle N \rangle$ being the time average of the total number of macromolecules in the sample.
Scattering from a suspended macromolecule whose conformation and position is constantly changing due to Brownian motion is discussed in the context of the dynamic form factor.
II.13.1 The static form factor for a rigid rod

Fig. 3 Scattering by a rigid rod of length $L$. The net field arriving at the detector is the result of interference between wavelets originating at each point on the rod.

The calculation of the form factor of a macromolecule having the conformation of a long and thin rigid rod is quite simple and is included as an illustration of the method.
The diameter of the rod is assumed to be small so that no significant phase difference exists between light scattered from two different points across the diameter of the rod. It is also assumed to have uniform polarizability. Equation (II.13.5) then takes the form

$$S(q) = \left\langle \sum_k \frac{1}{n} \exp iq \cdot u r_k \right\rangle,$$

(1)

where \( r_k \) is an arbitrary segment of the rod, \( u \) is a unit vector parallel to the length of the rod, and \( n \) is the total number of segments, which is taken to be very large so that in the limit of a continuous distribution of infinitesimally small segments, the sum in equation (1) may be replaced by an integral in the following manner:

$$\lim_{n \to \infty} \frac{1}{L} \sum_1^n \exp iq \cdot u r_l = \frac{1}{L} \int_{-\Delta}^{\Delta} \exp iq \cdot u r \, dr = J_0 \left( \frac{q \cdot u L}{2} \right),$$

(2)

\( J_0 \) is the zero-th order Bessel function,

$$J_0(w) = \frac{\sin(w)}{w}.$$  

(3)

In a spherical coordinate system chosen such that \( q \) coincides with the z-axis, it is seen that

$$q \cdot u = q \cos(\theta).$$  

(4)

(1) can be rewritten as

$$S(q) = \left\langle J_0 \left( \frac{x \cos(\theta)}{2} \right)^2 \right\rangle$$

(5)

with

$$x = qL.$$  

(6)
The averaging in (5) is carried out over all possible orientations of the rod, which are all equally probable. Thus

\[ S(q) = \frac{1}{4\pi} \int_0^{2\pi} d\phi \int_0^\pi d\theta \sin(\theta) \left| J_0\left(\frac{x\cos(\theta)}{2}\right)\right|^2. \]  

(7)

Effecting an integration over \( \phi \) and making a change of variable from \( \theta \) to \( y = \cos(\theta) \) it is seen that

\[ S(q) = \frac{1}{2} \int_{-1}^{1} dy \left| J_0\left(\frac{xy}{2}\right)\right|^2. \]  

(8)

Noting the identity (3) and using another change of variable

\[ z = \frac{xy}{2} \]  

(9)

gives

\[ J_0^2\left(\frac{xy}{2}\right) = \frac{1}{2} \left(1 - \cos(2z)\right). \]  

(10)

The integral (8) after this change of variable is

\[ S(q) = \frac{1}{2x} \int_{-x^2}^{x^2} dz \left(1 - \cos(2z)\right) = -\frac{1}{x} \int_{-x^2}^{x^2} dz \frac{\cos(2z)}{z^2}. \]  

(11)

After a further integration the form factor takes the form

\[ S(q) = \frac{x}{x} \int_0^x dz \frac{\sin z}{z} - \left(\frac{x}{2} \sin \left(\frac{x}{2}\right)\right). \]  

(12)

Here \( x = qL \). The Sine integral is a commonly used tabulated function.\(^{12}\)
II.13.2 The static form factor for a random coil

The calculation of the structure factor of a random coil was first made by Debye. The Pecora treatment for the dynamic form factor of the random coil relied on the Rouse-Zimm bead-and-spring model of the random coil. This calculation considered coils to be monodisperse, ideal and free-draining.

Gaussian Coil

A Gaussian coil is formed from a distribution of segments for which the mean squared distance between segments separated by p links is proportional to p

\[ \langle r^2(p) \rangle = l^2 p, \quad (1) \]

where \( l \) is considered to be the length of a statistical segment.

This model of a random coil follows the Gaussian probability distribution of a particle moving a distance \( r_{ij} \) in a large number of steps. If it is assumed that the polymer is highly flexible, then the probability \( p(r_{ij}) \) that any two segments i and j are separated by a distance vector \( r_{ij} \) follows a Gaussian distribution:

\[ p(r_{ij}) = \left[ \frac{3}{2\pi\langle r^2(m) \rangle} \right]^{3/2} \exp \left( -\frac{3}{2\langle r^2(m) \rangle} r_{ij}^2 \right). \quad (2) \]
Calculation of the static form factor

The static form factor is obtained by carrying out the averaging of $e^{i\mathbf{q} \cdot \mathbf{r}}$ with the probability distribution function $p(r_{ij})$

$$S(q) = \frac{1}{n^2} \sum_{i,j} \left[ \frac{3}{2\pi \langle r^2(m) \rangle} \right]^{3/2} \int \exp \left[ i \mathbf{q} \cdot \mathbf{r}_{ij} \right] \exp \left[ -\frac{3}{2\langle r^2(m) \rangle} r_{ij}^2 \right] d^3 r_{ij}.$$  \hspace{1cm} (3)

The integration yields

$$S(q) = \frac{1}{n^2} \sum_{i,j} \exp \left[ -\frac{q^2 \langle r^2(m) \rangle}{6} \right].$$  \hspace{1cm} (4)

As it is supposed that the coil consists of a large number of segments, an integration can be carried out over $p$, the number of links separating $n$ segment pairs

$$S(q) = \frac{1}{n^2} \int_0^n v(p) \exp \left[ -\frac{q^2 \langle r^2(m) \rangle}{6} \right] dp.$$  \hspace{1cm} (5)

$v(p)$ can be calculated by considering the Gaussian distribution of coil segments. There will be more pairs of segments separated by a small number of links than by a large number of links. The total number of pairs separated by $p$ links is proportional to $n-p$, this is

$$v(p) = k (n-p)$$  \hspace{1cm} (6)

where $k$ is a constant of proportionality.
As there are \( n \) segments, there are a total of \( n^2 \) pairs of segments. Then the value of \( k \) can be found from

\[
\int_0^n v(p) \, dp = n^2 \quad \text{and therefore} \quad k = \frac{n^2}{\int_0^n (n - p) \, dp} = 2.
\]

The expression for \( S(q) \) is then

\[
S(q) = \frac{2}{n^2} \int_0^n (n - p) e^{-q^2 \rho^2 / 6} \, dp
\]

since \( \langle r^2(p) \rangle = \pi l^2 / 6 \).

The integration yields the result obtained by Debye.

\[
S(q) = \frac{2}{q^4 R_G^4} \left\{ \exp \left[ -q^2 R_G^2 \right] - 1 + q^2 R_G^2 \right\},
\]

where \( R_G \) is the radius of gyration of a random coil, defined in the following paragraph.

**Radius of gyration of a random coil**

The root mean-square radius of a macromolecule relative to its CM is its radius of gyration, \( R_G \). It is defined here in terms of the vector coordinate \( \mathbf{R} \) of the center of mass of the macromolecule and a vector \( \mathbf{r}_i \) serving as the coordinate of the \( i \)-th segment of the macromolecule.
In case all \( n \) segments have the same mass \( m \), this mass can be factored out, and thus

\[
R_G^2 \equiv \frac{\left\langle \sum_{i=1}^{n} m_i (r_i - R)^2 \right\rangle}{\sum_{i=1}^{n} m_i}.
\]  

(10)

In case all \( n \) segments have the same mass \( m \), this mass can be factored out, and thus

\[
R_G^2 \equiv \frac{m}{n} \left\langle \sum_{i=1}^{n} (r_i - R)^2 \right\rangle.
\]  

(11)

**Expression for the form factor of a random coil**

In the limit of a large \( N \), with \( l \) being the length of a single segment of the polymer chain, the values of the radius of gyration \( R_G \) in two typical cases are given as:

(i) Linear, freely jointed chain

\[
R_G^2 = n l^2 / 6.
\]  

(12)

(ii) Rigid rod

\[
R_G^2 = n l^2 / 12.
\]  

(13)
II.14 Static light scattering and molecular weight determinations$^{17,18}$

For a given value of the scattering vector, the scattered intensity at a given time is

\[ I_{if}(q) = KS(q) \]  

(1)

Here \( I_{if} \) refers to the scattering per unit volume while \( S(q) \) is the form factor, normalized such that \( S(0) = 1 \).

In case of unpolarized light of intensity \( I_0 \) striking a unit volume of polymer solution of concentration \( c \) the scattered intensity \( I(\theta) \) at a point at distance \( R \) and making an angle \( \theta \) with the incident beam is given by

\[
\frac{I(\theta)}{I_0} = \frac{K(1+\cos^2(\theta))c(1-q^2R_G^2/3+\ldots)}{R^2(1/M_w+2A_2c+\ldots)},
\]

(2)

with

\[
K = \frac{2\pi^2n^2(dn/dc)^2}{\kappa\lambda^4}
\]

(3)

In the above expressions \( n \) is the refractive index of the solution, \( \lambda \) the vacuum wavelength of the incident light, \( \kappa \) (Avogadro's number), \( A_2 \) the second virial coefficient, \( R_G^2 \) the mean-square radius of gyration, \( q = \frac{4\pi n \sin(\theta/2)}{\lambda} \) and \( M_w \) is the weight average molecular weight (cf. Chap. I).

The formula (2) can be simplified by introducing the Rayleigh ratio...
\[ R_\theta = \frac{R^2 I(\theta)}{I_0(1 + \cos^2 \theta)}, \]  

(4)

as

\[ \frac{K_c}{R_\theta} = \left( \frac{1}{M_w} + 2A_2c + \ldots \right) \left( 1 + \frac{q^2 R_G^2}{3} + \ldots \right). \]  

(5)

Thus quantities such as \( M_w, A_2 \) and \( R_G^2 \) can be experimentally obtained using graphical tools such as the Zimm plot.

II.15 The dynamic form factor of a macromolecule

The double Fourier transform (temporal as well as spatial) of the time-dependent conformation of a macromolecule undergoing Brownian motion is known as the dynamic structure factor \( S(q, t) \) defined as

\[ S(q, t) = \frac{1}{n^2} \left\{ \sum_{i,j} \exp \left( i q \cdot [r_i(t) - r_j(0)] \right) \right\} \]  

(1)

By definition

\[ S(q, 0) = S(q) \]  

(2)

In order to evaluate (1), it is convenient to view the instantaneous position of the macromolecule \( r(t) \) as

\[ r(t) = R(t) + b_j(t) \]  

(3)
Where $R(t)$ is the instantaneous position of the center of mass of the macromolecule and $b_j(t)$ is the position of the j-th segment with respect to the center of mass.

It is then possible to write the expression of the dynamic form factor using

$$R_t = R(t) - R(0)$$

as

$$S(q, t) \equiv \frac{1}{n^2} \left\{ \exp \left[ \frac{iq \cdot R_t}{\sum_{i,j} \exp \left[ iq \cdot \left[ b_j(t) - b_j(0) \right] \right]} \right] \right\}$$

Further in the approximation of negligible intramolecular interference (meaning that max $q|b_j(t) - b_j(0)| \ll 1$) it can be shown that

$$S(q, t) \sim \exp \left( -Dq^2t \right)$$

In case the macromolecule is assumed to propagate by means of translational diffusion, this leads to an essential relationship

$$S(q, t) \sim \exp \left( -Dq^2t \right)$$

II.16 Description of the experimental setup

In photon correlation spectroscopy experiments done here, the intensity of the scattered light incident on the detector by employing a photomultiplier tube that counts the number of incoming photons. An temporal autocorrelation function of the intensity for a given value
of the scattering vector $q$ (that is for a fixed scattering angle, wavelength and refractive index) is calculated by a digital correlator according to a numerical scheme.\textsuperscript{19}

Fig. 4 Instrumentation used in a Photon Correlation Spectroscopy experiment. A polarized laser beam is focused on a dilute polymer solution in a temperature controlled environment. Some of the scattered light impinges on a photomultiplier tube, which generates electric pulses that are passed on to a hardwired digital correlator via an amplifier/discriminator.
REFERENCES


3. see p. 30 of [1].

4. see p. 11 of [1].

5. see p. 15 of [1].


7. see p. 19 of [1],

8. see p. 57 of [1]

9. see p. 50 of [1].


Chapter III

Analytic study of light scattering from polydisperse systems

III.1 Application of the Schulz-Zimm distribution to dynamic light scattering

The Schulz-Zimm distribution may be used to characterize the size distributions of polymers. It is then possible to calculate the intensity autocorrelation function that such a distribution would yield in a dynamic light scattering experiment. It can then be compared to experimentally obtained autocorrelation functions in order to determine the size distributions of actual polymer samples.

The unimodal Schulz distribution gives the fraction of particles with a size $r$ as a function of a parameter $z$, which characterizes the shape of the size distribution. The fraction of particles having a size $r$ is given in terms of the average particle size $\bar{r}$ as

$$f_z(r) = \frac{1}{z!} \left( \frac{z+1}{\bar{r}} \right)^{z+1} r^2 \exp\left(-\frac{(z+1)r}{\bar{r}}\right),$$

(1)

$$z = 0, 1, 2,...$$
Fig. 1 The Schulz-Zimm distribution. There are two plots due to scaling differences. The first shows three distributions corresponding to \( z = 1, 5, 10 \). The second shows the distribution for \( z = 10, 100, 1000 \).
III.2 The "polydisperse" electric field autocorrelation function

In correspondence with (II.13.9) and (II.15.7), using a slightly different notation, the scattered electric field autocorrelation function for scatterers undergoing translational Brownian motion can be written as

\[ I(q,t) = I(q) e^{q^2D t} = A N \alpha^2(r) P(qr) e^{q^2D t}. \]  

(1)

Here \( A \) is a constant, \( \alpha(r) \) the polarizability per molecule, \( N \) the number of molecules, \( P(qr) \) the form factor of the scatterer and \( D \) is the coefficient of translational diffusion. In order to perform analytic integrations, one assumes that \( D \sim 1/r \), in accordance with the Stokes-Einstein relationship, without explicitly specifying what measure of size is being used. This dependence will be denoted as \( D(r) \). The average diffusion coefficient of the polydisperse distribution can then be denoted as \( \overline{D} = D(1/r) \), with \( D = \overline{r D} \).

The "polydisperse" autocorrelation function is written\(^2\)

\[ I_z(q,t) = A I_0 J_0 \int_0^\infty N \alpha^2(r) P(qr) e^{q^2D(1/r)} f_z(r) dr. \]  

(2)

The form factor is generally a complicated expression and in order to perform an integration, Aragón and Pecora\(^2\) expanded the structure factor in a Taylor series around \( X = qr \) which is the average value of \( X' = qr \). In the usual notation

\[ P(X') = \sum_{k=0}^{\infty} \frac{p^{(k)}(X')(X'-\overline{X})^k}{k!}, \]  

(3)

where

\[ p^{(k)}(X') = \frac{d^kP(X')}{dx^k}. \]
Considering that the polarizability depends on particle size via the bulk volume of the particle, an analytical expression for the polarizability may be written

$$\alpha^2(X) = C_\alpha^2 X^p, \quad (5)$$

where $C_\alpha^2$ is a constant of proportionality. To understand $p$, the example of a sphere may be used. In this case the volume is proportional to the cube of the radius. As the polarizability depends on the volume, its square is proportional to the radius of the sphere raised to the sixth power. The characteristic size of discs is given by the radius, giving $p=4$. For thin rods, it is the length, thus $p=2$, and for random coils, for which the mass goes as the mean square radius of gyration, it is the radius of gyration, hence $p=4$.

The value of $p$ for the random coil can be easily verified using (II.13.2.1). For a polymer coil whose mass is proportional to the total number of links $N$, each link having length 1, the mean square radius of gyration is

$$\langle r^2(N) \rangle = l^2 N. \quad (6)$$

Thus

$$N = \frac{1}{l^2} \langle r^2(N) \rangle. \quad (7)$$

Hence the mass of a polymer is assumed to be proportional to the mean square radius of gyration.

The $k$-th integral the series expansion of (4) is given as
\[ V_k(\overline{X}) = \frac{C^2}{z!} \frac{(z+1)^{z+1}}{X^z} \int_0^\infty (X')^2 (X' - \overline{X})^k e^\frac{\Delta}{X} e^{-X'} \, dx', \quad (8) \]

using the notation

\[ \Delta = q^2 \overline{D} \overline{X} \text{ and } \gamma = \frac{(z+1)}{\overline{X}}. \quad (9) \]

Using the binomial expansion in (8) as well as formula (3.471.9) on p. 340 of ref. [4] to carry out the integration, i.e.

\[ \int_0^\infty x^{\nu-1} e^\frac{\Delta}{X} \gamma^x \, dx = 2^{\nu} \frac{\gamma^{\nu+1}}{\nu!} K_\nu(2\sqrt{\Delta \gamma}), \quad (10) \]

results in

\[ V_k(\overline{X}) = \frac{2\alpha^2(\overline{r})\overline{X}^k}{(z+p)!} \sum_{l=0}^{k} \frac{(-1)^l k!}{l! (z+1)^{l-k}} \frac{\Delta^{z+k-1+p-1}}{2} K_{z+p+1-l}(2\sqrt{\Delta \gamma}), \quad (11) \]

with

\[ \alpha_2(\overline{r}) = \frac{\alpha^2(\overline{r})(z+p)!}{z!(z+1)^p} \] ,

(12)

while the function \( K_\nu(y) \) is the modified Bessel function of the second kind of order \( \nu \) discussed in ref. [7]. Given the form of (12), it is easier to work with normalized C-Bessel functions defined as the \( CK_\nu \) given by the relation

\[ CK_\nu(0) = 1, \quad CK_\nu(y) = y^\nu K_\nu(y)/2^{\nu-1}(\nu-1)! \] ,

(13)

\[ \nu = 1, 2, 3... \]

These obey the recurrence relation
\[ CK_{v+1}(y) = CK_v(y) + y^2 CK_{v-1}(y)/4v(v-1) . \] (14)

The exact solution to (4) is

\[ I_z(q,t) = A \alpha_z^2(t) \sum_{k=0}^{\infty} \frac{p^{(k)}(0)X^k}{k!} \frac{X^{z+p+k}}{(z+1)^k(z+p)!} \frac{X}{X_{z+p+1} + (4\Delta \gamma)^{1/2}} . \] (15)

It is shown in [2] that when \( P(X) \) is an even function of \( X \), an adequate approximation for (20) is

\[ I_z(q,t) = A \alpha_z^2(t) P_z(X) CK_{z+p+1} (4\Delta \gamma) \] (16)

where the polydisperse form factor \( P_z(X) \) is given as

\[ P_z(X) = \frac{1}{(z+p)!} \int_0^\infty X^{z+p} P(X)e^{-(z+1)X/X_d}dX. \] (17)

Also \( P_z(X) \) admits the expansion

\[ P_z(X) = \sum_{k=even}^{\infty} \frac{p^{(k)}(0)X^k(z+p+k)!}{k! (z+1)^k(z+p)!} . \] (18)

The form factor for a Gaussian coil of mean square radius of gyration \( R_g = (nb^2/6)^{1/2} \) is given using \( X = qR_g \) is reproduced from (II.13.2.13) \( ^3 \)

\[ P(X) = \frac{2}{X^4}(e^{-X^2} - 1 + X^2). \] (19)

The expression (24) can be evaluated using (22). The integration is straightforward except for the term:

\[ \int_0^\infty X^2 e^{-X} e^{-(z+1)X/X_d}dX. \] (20)
Formula (3.462.1) on p. 337 in [4] gives the solution as

\[
\int_0^\infty x^{\nu-1} e^{-\beta x} x^{\gamma x} \, dx = (2\beta)^{\nu} \frac{\gamma}{\Gamma(\nu)} e^{\frac{\gamma^2}{8\beta}} D_{\nu} \left( \frac{\gamma}{\sqrt{2\beta}} \right)
\]

(21)

Re \( \beta > 0, \text{Re } \nu > 0 \)

\[
P_z(\overline{X}) = \frac{2}{\overline{X}^2} \frac{(z+1)^2}{(z+3)(z+4)} \left[ \overline{X} \frac{2}{(z+2)} + \frac{(z+1)(z+1)^{z+1}}{(z+4)v^{2\overline{X}}} e^{-(z+1)^2/8\overline{X}^2} D_{z-1}(\frac{(z+1)}{\sqrt{2\overline{X}}}) \right].
\]

(22)

\( D_\nu(x) \) is the parabolic cylinder function, it is introduced in [7] and discussed at length in [5].

For \( \nu \) less than approximately -0.20494, \( D_\nu(X) \) is a monotonically decreasing positive function of \( x \). From the contour plot on p. 466 of [5] it is found that

\[ 0.5 < D_{-2}(1) < 0.2, \]

and its value decreases monotonically for higher orders of \( \nu \). In course of the simulations described in Chap. V, \( q = 2.32255 \times 10^5 \) cm and \( r = 1720 \times 10^{-8} \) cm, giving \( \overline{X} = 3.994786 \). Therefore for \( z=1 \),

\[
D_{-2-1}(\frac{z+1}{\sqrt{2} \overline{X}}) = D_{-2}(1.0210),
\]

which is smaller than 0.5. Higher values of \( z \) result in even smaller numbers.

However, noting that the expression for the "polydisperse" scattered electric field autocorrelation function (21) contains unspecified multiplicative constants such as \( A \) and \( C_{\alpha^2} \), it is apparent that the information about the decay for random coils is contained in the factor

\[
CK_{z+5}(\sqrt{4A\gamma}).
\]

Thus \( P_z(\overline{X}) \) may be neglected in the expansion for \( I_z(q, t) \) as the function preserves its shape upon being normalized.
Polydisperse intensity autocorrelation spectra can be represented as

\[ G^{(2)}(\tau) = A \left\{ C K_{z+1} \left[ \sqrt{4q^2 D\tau(z+1)} \right] \right\}^2 + B \]  \hspace{1cm} (23)

where \( A \) is an amplitude and \( B \) is the baseline. Two other parameters required for this expression are the average diffusion coefficient \( \bar{D} \) and the shape parameter \( z \).

**APPENDIX**

A scheme to calculate

\[ I_n = \int_{-\infty}^{\infty} x^n \exp(-ax^2-bx) \, dx \]  \hspace{1cm} (A.1)

was suggested by Dr. A. Muleshkov\(^6\).

Set

\[ x^n = \frac{z^n-1}{2a} (\exp(-2ax-b)) - \frac{b}{2a} x^{n-1} \].  \hspace{1cm} (A.2)

Then

\[ I_n = \frac{1}{2a} \int_{0}^{\infty} x^{n-1} \exp(-ax^2-bx) \, dx - \frac{b}{2a} \int_{0}^{\infty} x^{n-1} \exp(-ax^2-bx) \, dx \]  \hspace{1cm} (A.3)

Thus it is only necessary to numerically evaluate

\[ I_0 = \int_{0}^{\infty} \exp(-ax^2-bx) \, dx \]  \hspace{1cm} (A.4)
Then

\[ I_1 = \frac{1}{2a} - \frac{b}{2a}I_0 \]  \hspace{1cm} (A.5)

and \( I_n \) can be calculated by recurrence using

\[ I_n = \frac{n-1}{2a}I_{n-2} - \frac{b}{2a}I_{n-1} \]  \hspace{1cm} (A.5)

REFERENCES


6. Dr. A. Muleshkov, Mathematics Department, University of Nevada, Las Vegas, NV 89154-0001.

Chapter IV

Data Analysis

IV.1 General discussion

A high polymer may be characterized in terms of a normalized and effectively continuous distribution of a property \( s(\lambda) \) where \( \lambda \) could be its molecular weight, spherical radius, translational diffusion coefficient or some other property. With the assumption of a negligible intermolecular interaction, the measured quantity \( y(\tau) \) can be approximated as a linear superposition of independent contributions that can be written as a Fredholm integral equation of the first kind

\[
y(\tau) = \int s(\lambda) \ K(\lambda,\tau) \ d\lambda ,
\]

where the kernel \( K(\lambda,\tau) \) is a known function and the "spectrum" \( s(\lambda) \) an unknown distribution that needs to be retrieved from the values of \( y \) and \( \tau \).

Dynamic light scattering experiments measure the autocorrelation function of the scattered light intensity, which is given at \( \tau \) as

\[
G^{(2)}_{\text{exp}}(\tau) = \langle I(t')I(t'+\tau) \rangle
\]
The scattered electric field autocorrelation function can be derived using the Siegert relation (II.12.1)

$$G^{(2)}_{\text{exp}}(\tau) = A|G^{(1)}_{\text{exp}}(\tau)|^2 + B. \tag{3}$$

Often $G^{(1)}_{\text{exp}}(\tau)$ is composed of the decays of several modes of motion, as implied in (II.15.7).

$$G^{(1)}_{\text{exp}}(\tau) = \int_0^\infty f(\Gamma) e^{-\Gamma \tau} d\Gamma, \tag{4}$$

where $\Gamma = Dq^2$.

The correspondence between (1) and (4) is obvious. The kernel $K(\lambda, \tau)$ is the decaying exponential $e^{-\Gamma \tau}$ and the unknown "spectrum" $s(\lambda)$ is $f(\Gamma)$, which, being a distribution of decaying modes, reflects the polydispersity of the polymer sample being studied. Thus $s(\lambda)$ can be assumed to have special properties such as non-negativity, smoothness as well as any prior knowledge such as the unimodal or bimodal nature of the distribution $s(\lambda)$.

IV.2 Some Common Techniques of Data Analysis

Data analysis techniques can either be specific to (4) or they can purport to accomplish the inversion of (1) in a more general manner.²

Among the commonly used techniques that seek to solve (4) the first is to invert the Laplace transform using a Fourier transform algorithm, which requires data of an arbitrary high precision over an infinite range of time.³
Another possibility is to assume a specific form for \( G(\Gamma) \) and work out the parameters giving the best fit to the data. Several studies have been made using the Schulz-Zimm distribution of molecular weights.\textsuperscript{4,5,6} This approach works on the condition that the sample at hand has a meaningful relation to the distribution being used as a model.

### IV.3 Method of Cumulants

The method of cumulants seeks to characterize a distribution by fitting the experimental estimates of \( \ln |G^{(1)}(t)| \) to a polynomial\textsuperscript{7}.

The scattered intensity autocorrelation function is expanded as

\[
\frac{1}{2} \ln |G^{(2)}(\tau) - B| = C_0 + K_1 \tau + \frac{1}{2!} K_2 \tau^2 - \frac{1}{3!} K_3 \tau^3 + \ldots. \tag{5}
\]

Here \( C_0 \) is a constant and the quantities \( K_1, K_2, K_3 \), are the cumulants of the distribution \( G^{(1)}(\tau) \) and are given in terms of the moments of the decay constants \( \Gamma \), as

\[
K_1 = \langle \Gamma \rangle, \tag{6}
\]

\[
K_2 = \langle (\Gamma - \langle \Gamma \rangle)^2 \rangle, \tag{7}
\]

\[
K_3 = \langle (\Gamma - \langle \Gamma \rangle)^3 \rangle, \tag{8}
\]

\[
K_4 = \langle (\Gamma - \langle \Gamma \rangle)^4 \rangle - 3\langle (\Gamma - \langle \Gamma \rangle)^2 \rangle. \tag{9}
\]

In view of the relationship \( \Gamma = Dq^2 \), it is apparent that \( K_1 \) is related to the average diffusion coefficient, \( K_2 \) to the width of the distribution of the diffusion coefficients and \( K_3 \) to the skewness of the distribution.
The figure below conveys the limitations of this method by showing three distributions that have the same first three cumulants. It stresses the fact that the interpretation of results obtained from a cumulants fit depends on the particular model chosen. Usually, a reasonably narrow distribution can be characterized by the method of cumulants but problems can arise when the cumulants fail to appreciably converge, or are actually found to diverge.

Fig. 1. Three normalized distributions having the same first three cumulants (mean, variance and skewness). Distribution III is constituted of two monodisperse Dirac δ-peaks. Both axes use arbitrary units.
IV.4 DISCRETE and CONTIN

Two popular data analysis packages that are widely employed by workers in the field of Dynamic Light Scattering are DISCRETE$^{9,10,11}$ and CONTIN$^{12,13,14}$ which seek to be useful for problems encountered in a variety of fields.

DISCRETE

Considering the kernel in (1) to have the form

$$K(\lambda, \tau) = e^{-\lambda \tau}, \quad (10)$$

and assuming that the spectrum consists of discrete peaks of the form

$$\sum_{j=0}^{N} \alpha_j \, \delta(\lambda - \lambda_j) \quad (11)$$

where $\alpha_j$ is the amplitude of each decaying mode $\lambda_j$ and $N$ is the total number of the decaying modes and the baseline is given by $l_0$. The number of exponentials in the sum, i.e. $N$ can be made to be up to nine in the version of the program that is used here. However, the program can be constrained to keep the maximum number of decay modes below a specified number such as two or three, depending on the situation. The program is automatic in that no initial guesses of the values of these three quantities are required, thus eliminating possibilities for bias there. It does not require an infinite range of data nor does
it depend on any prior guesses as to the values of the parameters \( \alpha_j \) and \( \lambda_j \) or number of decaying modes in the solution, \( N \).

DISCRETE is based on the expansion of the solution of a Fredholm integral equation of the first kind in terms of orthogonal eigenfunctions of the kernel. A nonlinear least squares analysis of the raw data is then carried out using the knowledge of the spectral peaks given by this algorithm. The program computes the parameters \( \alpha_j \) and \( \lambda_j \) along with their standard deviations by means of a linear hypothesis test that is corrected approximately for nonlinearity.

The initial subroutine DATAIO reads in \( t \) and \( y \) values and modifies the former if the data are not in regular intervals. It is possible to include input special weights for the least squares fit at this stage as well. In the version used here known as "glfit" the variable NLAMX corresponding to \( N \) is set to three, the flag IWT is set to -2 meaning that the weights to the least squares \( w_k \) are calculated for no baseline as the digital correlator actually computes the baseline for long delay times and information on the measured and calculated baselines is included in the output, which can be subtracted from the intensity autocorrelation function and the square root of the remainder is fed to DISCRETE as the value of the electric field autocorrelation function \( G^{(1)}(q,t) \), which the program reads in as \( y_k \).

\[
w_k = \left[ \sum_{j=1}^{N_k} \alpha_j \exp(-\lambda_j t_k) + ERRFIT \right]^{1}
\]

(12)

The weights are actually calculated by means of a smooth, least squares fit to the \( y_k \) rather than directly from the data to avoid erratic and biased weights. However a smooth curve coming very close to the \( y \) axis near a point \( t_k \) could produce an very large value for \( w_k \). The standard deviation of the fit to the 10 \( y_k \) in the interval where the theoretical curve is closest to the \( y = 0 \) is denoted ERRFIT.
The subroutine FANLYZ uses the raw data for a constrained stepwise least squares analysis and uses a grid search if necessary to get starting values for analysis of transforms, to give LAMF which are the starting values for a final constrained stepwise least squares analysis of raw data in the subroutine YANLYZ.

The output contains the $\alpha_j$ and $\lambda_j$ for the chosen solution and the estimated standard error for values of each of the $\alpha_j$ and $\lambda_j$ obtained by means of a variance-covariance matrix. It also gives $NPHI \geq 0$ which is known as Beale's nonlinearity criterion. If $NPHI \leq 0.1$, the solution is moderately nonlinear and for values greater than one, disastrously nonlinear.

The results summarize up to five chosen solutions, along with the probability that a given solution is a better fit than the next one.

CONTIN

In the case of experimentally obtained data containing noise, the Fredholm integral equation of the first kind in (1) may be represented by,

$$y_j = \int_{\lambda_1}^{\lambda_2} s(\lambda)K(\lambda,t_j)d\lambda + e_j \quad j = 1, \ldots, N_y,$$

(13)

where $K(\lambda,t_j)$ is a known function such as $e^{\lambda t}$ and $s(\lambda)$ is a distribution of particle radii which is to be estimated.

Retrieving $s(\lambda)$ is an ill posed problem. One version of the Riemann-Lebesgue lemma states that usually $K(\lambda, t)$ is absolutely integrable over $\lambda$, i.e.,
Therefore even very small values of $\varepsilon_j \neq 0$ and an arbitrarily large amplitude $A$, there exists an $\omega$ such that $s(\lambda) + A\sin(\omega\lambda)$ still satisfies (1) within the range of experimental errors $\varepsilon_j$. A large set of possible solutions therefore exists for (1), whose members can have arbitrarily large deviations from the time solution.

CONTIN is a constrained Laplace transform inversion program which provides for a number of solutions with different degrees of smoothing as well as a particular "chosen" solution. It employs well known algorithms solving the problem of estimating parameters from noisy measurements $y_k$ as well as systems of linear algebraic equations.

This program uses notions of prior knowledge and parsimony for deciding the best possible combination of a mathematically stable solution and an reasonable physical representation. An example of absolute prior knowledge would be the constraint $s(\lambda) \geq 0$ which would eliminate many oscillating solutions that are indicated by (2). The program provides for the inclusion of statistical prior knowledge of the mean and the covariance of the solution as well as the $\varepsilon_k$. Parsimony implies that of all the possible fits to the data that are consistent with one's prior knowledge (e.g. $s(\lambda)$ is greater than or equal to zero) CONTIN picks the one with the least amount of detail.

As CONTIN is an a voluminous Fortran program containing 66 subprograms, it is only possible to briefly describe its method of analysis.
Method utilized in CONTIN

A quadrature grid of m points is constructed to reduce (13) to a set of linear algebraic equations

\[ y = Cs \]  

with y being the n×1 data vector, s the unknown m×1 vector and the n×m matrix C consisting of elements of the kernel and the weights of the quadrature formula. It is assumed that m ≤ n. The ordinary least squares solution of (3) is \( s_0 \) which minimizes

\[ R_0 = (y - Cs_0)'W(y - Cs_0), \]  

where \( R_0 \) is the weighted sum of squared residuals. In the version of the code used here \( W \) is set to be the n×n least squares weight matrix while the prime denotes the transpose of a matrix. As used here. The solution \( s_0 \) is usually unstable with unconstrained oscillations.

A quadratic programming algorithm is utilized to find the unique regularized solution \( s_\alpha \) constrained to consist of nonnegative elements minimizing the expression

\[ R_\alpha = (y - Cs_\alpha)'W(y - Cs_\alpha) + \alpha (Ds_\alpha)'(Ds_\alpha). \]  

\( R_\alpha \) is known as the regularizer and \( D \) is the matrix of a second difference operator. It increases the sum of the ordinary least squares residuals \( R_0 \) by the sum of the squares of the finite second difference approximations to the second derivatives of the solutions at grid points multiplied by \( \alpha \). The inclusion of the second derivative in the regularizer tends to smooth out spurious oscillations. An optimum setting for \( \alpha \) would not oversmooth the essential features of the distribution. The procedure for optimizing \( \alpha \) is described in [15].
Prior knowledge of a unimodal or bimodal nature of $\alpha$ can be used to completely eliminate spurious oscillations.

Output

The first part of the CONTIN output lists various parameters indicating the goodness of the fit and the number of degrees of freedom in the solution as well as the probability to reject the given solution, which needs to be considered when it exceeds 0.9 or is less than 0.1.

The output gives four moments for each solution along with the percent error in each. The moments are a quadrature approximation to

$$M_j = \frac{\lambda_{\text{max}}}{\lambda_{\text{min}}} \int_{\lambda_{\text{min}}}^{\lambda_{\text{max}}} \lambda^j s(\lambda) \, d\lambda,$$

where $j = -1, 0, 1, 2$

which yield the decaying mode $\lambda$ and its relative amplitude $s(\lambda)$ for each solution. The ratios of the moments are also given, which are weighted averages of $\lambda$. If $\lambda$ were the molecular weight of a polymer sample under study, the ratios of the moments $M_{j+1}$ would respectively yield estimates of the number-, weight-, $z$- and $(z+1)$-average molecular weights. However, actually the $\lambda$ values correspond to values of $\Gamma = D q^2$ and the recovery of the distribution of radii is quite a task.

Finally, the output contains a listing of amplitudes $s(\lambda)$ against $\lambda$, along with error bars on the former are tabulated.
As CONTIN outputs around 30 values of $\lambda$ along with the zero or non-zero amplitude of each and plots the output in the form of peaks, it is often used to gain an insight into the polydispersity of the sample under investigation. With an available theoretical means of generating intensity autocorrelation functions corresponding to various degrees of polydispersity as discussed in Chap. 3, the accuracy of CONTIN in inverting simulated polydisperse autocorrelation functions is investigated in the following chapter.

REFERENCES


2. N. C. Ford, Jr., Light Scattering Apparatus, in *Dynamic Light Scattering*, Ed. R. Pecora, Plenum, New York, 1985. ...


11. DISCRETE - A program for the automatic analysis of multicomponent exponential decay data, S. W. Provencher. Max-Planck-Institut für Biophysikalische Chemie, D-3400 Göttingen-Nicklausberg, Germany.


Chapter V

Results

V. 1 Introduction to the results section

The above schematic describes the principal aims of this work. The purpose of this project is to determine whether the analysis routines used in the laboratory can describe
polydispersity. In order to do this, the Schulz-Zimm distribution (see Chap. 3) is used to calculate intensity autocorrelation functions corresponding to samples of varying degrees of polydispersity. The two data analysis packages used for this purpose are DISCRETE and CONTIN, which were described in Chap. 4. The mode lambda given by DISCRETE and CONTIN corresponds to the decay constant $\Gamma=Dq^2$.

Using the Stokes-Einstein relationship $D=\frac{kT}{6\pi\eta R_H}$, where $\eta$ is the viscosity of the medium and $R_H$ the hydrodynamic radius of the diffusing coil, the CONTIN distribution of $\lambda$-values could in principle be inverted to yield a distribution giving an idea of the shape of the radius distribution, which may then be contrasted with the original Schulz-Zimm distribution.

In the laboratory, experimentally obtained autocorrelation functions are first analyzed using a cumulants fitting routine which is incorporated into the software accompanying the Brookhaven MBI 2030 digital correlator. This is a crude fit and serves to give only rudimentary ideas about the shape of the distribution. Greater trust is placed in outputs of DISCRETE and CONTIN, which are Fortran packages requiring no initial guesses as to the shape of the distribution. The data analysis procedure is to first use DISCRETE to obtain an idea of the correct window to be used for a subsequent CONTIN analysis.

**Introduction to the computing equipment and software used**

Version 1.2 of Mathematica\(^1\), a widely used software for symbolic mathematics, was used on a NeXT computer to make all calculations including the autocorrelation functions using the formulae derived from the Schulz-Zimm distribution in Chap. III. The functions thus obtained were analyzed by means of the Fortran routines DISCRETE and CONTIN on a Sparc workstation for greater speed. The plotting was done using Gnuplot, a popular workstation software for graphical representation of functions and data.
Plan of the results section

First, exponentials with and without noise were analyzed. Subsequently, intensity autocorrelation functions corresponding to $z = 100, 10$ and $1$ were computed to span a wide range of polydispersity. The situations for $z = 50$ and $z = 5$ were also studied but not displayed in this section because for $z = 50$ the results are quite similar to those for $z = 100$ and for $z = 5$ the situation resembles that for $z = 10$. This can be verified by looking at the plots of the various Schulz-Zimm radius distributions.

Further, $z = 5$ and $z = 10$ present similar situations as the corresponding intensity autocorrelation functions reach close to zero during the first five e-folds of decay. The decay for the intensity autocorrelation function for $z = 1$ starts from a much higher value and takes about 15 e-folds to get close to zero. Other values of $z$ were not studied as it is hard to assign them to a clear-cut "monodisperse" or "polydisperse" category.

For each value of $z$, a noiseless intensity correlation function as well as one containing a high level of noise and another a low level of noise were fed to DISCRETE and then CONTIN. DISCRETE was constrained to fit to a maximum of three modes, while the CONTIN window was kept between $\lambda = 100$ to $\lambda = 5000$ as a starting value of $\lambda =0$ often resulted in errors.

Three intensity autocorrelation functions were computed for each value of $z$. One without any noise, the next with a low level of noise and the last with a high level of noise. First, DISCRETE, constrained to finding no more than three modes, was used to find the amplitude ALPHA and the decay rate LAMBDA, along with their uncertainties, of each of the exponentials fitted to the data. Then CONTIN was used to perform a finer grid search. The ratio of the first moment $M(1)$ to the
The zeroth moment $M(0)$ for each peak was recorded. This corresponds to a "number average" for $\lambda$. The ratio of the standard deviation to the mean of each peak was also recorded, giving a measure of its width.

**Noise considerations**

Experimentally obtained autocorrelation functions show a small scatter for values of $G^{(2)}(t)$ in initial channels. The noise increases in subsequent channels while the photon count decreases until the decay finally drops into the baseline, which has a rather constant level of noise. The schemes for adding noise to mimic intensity autocorrelation spectra from light scattering are described within this chapter.

**V.2. Pure Exponentials**

In order to test the effect of noise on DISCRETE and CONTIN, pure exponentials of the form $G^{(2)}(t) = e^{-2\lambda t^2}$ with $\lambda = 2438.2$ were calculated in intervals of $t=0.02$ with $\tau$ ranging from zero to five. The sample time is $0.02/2438.2 = 8.20277$ µ-sec. This value is the same for all exponentials and simulated autocorrelation functions except those for which $z = 1$.

It was thought that a noise level that keeps arbitrarily growing with the decay should be an adequate test for DISCRETE. Noise was calculated and added to $G^{(2)}(\tau)$ according to the scheme: Noisy $G^{(2)}(\tau) = 1000*G^{(2)}(\tau) + B*/Random[-1, +1]*Sqrt[G^{(2)}(\tau)]$.

In Mathematica's notation, Random[-1, +1] represents a pseudo-random number between -1 and +1, which is generated using the starting time of the calculation as a seed. $B$ is a constant that can be varied to keep a control over the level of noise.
V.2.1 Exponential with no noise

Analysis

DISCRETE

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>ALPHA +/- STD ERR</td>
<td>1.000E+03 +/- 2.7E-04</td>
</tr>
<tr>
<td>LAMBDA +/- STD ERR</td>
<td>2.438E+03 +/- 4.8E-04</td>
</tr>
</tbody>
</table>

CONTIN

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>M(1)/M(0) % ERR.</td>
<td>2.4423E+03 1.6E-02</td>
</tr>
<tr>
<td>STD. DEV/MEAN</td>
<td>3.2E-02</td>
</tr>
</tbody>
</table>
Predictably, DISCRETE found the decaying mode to a high degree of accuracy. The CONTIN results suggest that the program tends to look for a peak of a finite breadth rather than a delta peak.

V.2.2 Exponential with a high level of noise

Noise level B=1000.

\[(1000*E^{-1})^2 + B*\text{Random}[\text{Real},\{-1,+1\}]/(E^{-1})]\]

The noise causes the points to scatter above and below the baseline.

This curve has a high noise level which is for trial purpose but on other simulated curves it can be set 'visually' to appear similar to experimentally obtained autocorrelation functions.
A baseline of $2E+05$ was added (by visual inspection).

Discrete yielded

$$\begin{array}{ll}
\text{ALPHA} & \text{STD ERR} \\
1.046E+03 & \pm 6.6E+01 \\
\end{array}$$ $$\begin{array}{ll}
\text{LAMBDA} & \text{STD ERR} \\
2.650E+03 & \pm 1.8E+02 \\
\end{array}$$

CONTIN analysis of the noisy exponential with baseline gave the following results:

$$\begin{array}{llll}
\text{M(1)/M(0)} & \text{% ERR} & \text{STD. DEV./MEAN} \\
2.6997E+03 & 1.5E+01 & 1.6E-01 \\
\end{array}$$

Both DISCRETE and CONTIN find a higher mode than $\lambda = 2438.2$.

V.2.3 Exponential with a low level of noise

Noise level $B=100$, and added a baseline of $2E+04$. 
A wide CONTIN window from $\lambda=100$ to 5000 was chosen as a few times the program failed to calculate moments of the distribution for windows starting at $\lambda=0$.

<table>
<thead>
<tr>
<th>$M(1)/M(0)$</th>
<th>%ERR</th>
<th>STD. DEV./MEAN</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.6243E+03</td>
<td>8.1E+00</td>
<td>1.8E-01</td>
</tr>
</tbody>
</table>
V.3 Intensity autocorrelation functions for various values of $z$

It appears difficult to get Mathematica to compute autocorrelation functions for values of $z$ higher than 100. Therefore it is assumed that $z=100$ approximates a monodisperse distribution i.e. a single exponential distribution and a Schulz-Zimm radius distribution approaching a delta function (this can be verified by looking at Fig. 1 in Chap. III).

The intensity autocorrelation function $G^{(2)}(t)$ is obtained by squaring the “polydisperse” electric field autocorrelation function $P_z(q, t)$, which is computed using (III.2.16) with $P_z(X)$ set as one.

The numerical values used are based on actual values wherever possible, such as the average diffusion coefficient $\bar{D} = 4.52 \times 10^{-8}$ cm$^2$/sec, the magnitude of the scattering wavevector $q = 2.32255 \times 10^5$/cm and the average radius $\bar{r} = 1720 \times 10^{-8}$ cm. The molecular polarizability, $\alpha$, was however set at one.

The quantity assumed to serve the role of the electric field autocorrelation function was therefore

$$G^{(1)}(t) = \left( \frac{4!}{(z+1)^4} \right)^2 CK_{z+5} \left( \sqrt{(z+1)X} \right)$$

with $X = \bar{D}q^2t$. 
V.3.1 Intensity autocorrelation function for z=100 with no noise

A noiseless autocorrelation function for z=100 was computed for values of X ranging from 0 to 7 in intervals of X=0.02. The decay is seen to occur within the first 100 channels so that the autocorrelation function does in fact decay "well into the baseline".

Analysis:

The first 256 channels of the Intensity autocorrelation function were used for a fit and a baseline of 200000 was added.
DISCRETE gave the following mode structure:

\[
\begin{align*}
\text{ALPHA} & \pm \text{STD ERR} \\
5.653E+02 & \pm 6.9E+00 \\
5.593E+02 & \pm 6.9E+00
\end{align*}
\]

\[
\begin{align*}
\text{LAMBDA} & \pm \text{STD ERR} \\
2.139E+03 & \pm 2.3E+00 \\
2.599E+03 & \pm 3.5E+00
\end{align*}
\]

CONTIN gave the following results

<table>
<thead>
<tr>
<th>M(1)/M(0)</th>
<th>% ERR</th>
<th>STD DEV/MEAN</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEAK 1</td>
<td>2.3658E+03</td>
<td>3.9E-02</td>
</tr>
<tr>
<td>PEAK 2</td>
<td>4.8245E+03</td>
<td>3.2E+01</td>
</tr>
<tr>
<td>ENTIRE SOLUTION</td>
<td>2.3682E+03</td>
<td>6.1E-02</td>
</tr>
</tbody>
</table>

The more or less monodisperse nature of the distribution is apparent. Peak 2 of the CONTIN solution is a spurious mode. All such modes are seen to correspond with a much higher value of the percent error than true modes.

The mode structure given by CONTIN is shown below:
The following curve is a replot of CONTIN results with $1/\lambda$ being in the abscissa.
V.3.2 Intensity autocorrelation function for z=100 with low noise

A low level of noise was added to the previous intensity autocorrelation function. The noise was kept proportional to the inverse of the square root of the electric field autocorrelation function. As the orders of magnitude of the values of the electric field autocorrelation function range from 1000 to 0, some other factors were introduced to prevent the noise from being too large or too small. It was found that the scheme $G^{(2)}_{\text{noise}}=G^{(2)} + B/(G^{(1)} + A)$ worked quite well. High values of $B$ would amplify the initially low values of $1/G^{(1)}$ so as to introduce a discernible level of noise in the initial channels. To prevent violent oscillations from occurring in the baseline channels, the factor $A$ is chosen large enough so as to smooth the effect of the noise in the baseline.

The following figure depicts an intensity autocorrelation function generated for z=100. The number of channels and the baseline will remain the same for all the synthetic correlation functions unless otherwise mentioned, i.e. the former fixed at 256 and the latter, at $2 \times 10^5$. The sample time is also 8.20277 μs.
Discrete gives the following mode structure:

\[
\begin{align*}
\text{ALPHA} &\pm \text{STD ERR} & \text{LAMBDA} &\pm \text{STD ERR} \\
1.194E+03 &\pm 6.1E+01 & 2.615E-03 &\pm 1.3E+02 \\
\end{align*}
\]

(NO EXACT FIT TO THE TRANSFORMS FOUND)

DISCRETE finds a higher mode than for an exponential of the form \(e^{-\lambda t}\) with \(\lambda = 2438.2\).

Contin gave the following results

\[
\begin{align*}
\text{M(1)/M(0)} &\quad \% \text{ ERR} & \text{STD DEV/MEAN} \\
2.6840E+03 &\quad 1.0E+01 & 8.6E-02 \\
\end{align*}
\]

The same trend is shown by CONTIN, which finds \(\text{M(1)/M(0)} = 2684\).
MODE STRUCTURE GIVEN BY CONTIN

INVERSE OF CONTIN MODE STRUCTURE
V.3.3 Intensity autocorrelation function for z=100 with high noise

A higher level of noise was added using the same scheme as before (which was used for all synthetic noisy autocorrelation functions discussed here).

![NOISY INTENSITY AUTOCORRELATION FUNCTION](image)

Analysis

DISCRETE found the following mode structure

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{ALPHA} )</td>
<td>1.188E+03 ± 6.1E+01</td>
</tr>
<tr>
<td>( \text{LAMBDA} )</td>
<td>2.624E+03 ± 1.3E+02</td>
</tr>
</tbody>
</table>

CONTIN analysis gave the following results

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( M(1)/M(0) )</td>
<td>2.7225E+03 ± 1.4E+01</td>
</tr>
<tr>
<td>% ERR</td>
<td>1.5E-01</td>
</tr>
<tr>
<td>STD DEV/MAN</td>
<td></td>
</tr>
</tbody>
</table>
A plot of the peaks found by CONTIN is given below:

A plot with $1/\lambda$ in the abscissa with the same amplitude in the ordinate is given below. This may be compared with the Schulz-Zimm distribution for $z=100$ with low noise.
V.3.4 Intensity autocorrelation function for z=10 with no noise

A noiseless intensity autocorrelation function was calculated for z=10.
Analysis

DISCRETE found the following mode structure

\[
\begin{align*}
\text{ALPHA} & + \text{ STD ERR} & \text{LAMBDA} + \text{STD ERR} \\
7.863E+02 & \pm 4.2E+00 & 1.308E+03 & \pm 1.1E+00 \\
1.653E+03 & \pm 1.5E+00 & 2.001E+03 & \pm 2.4E+00 \\
2.528E+02 & \pm 2.7E+00 & 3.251E+03 & \pm 5.9E+00
\end{align*}
\]

CONTIN analysis gave the following results

\[
\begin{align*}
\text{M(1)/M(0)} & \quad \% \text{ ERR} & \quad \text{STD DEV/MEAN} \\
\text{PEAK 1} & \quad 1.0000E+02 & \quad 7.7E+01 & \quad 3.9E-04
\end{align*}
\]
PEAK2  1.9083E+03  1.3E-01  2.7E-01
PEAK3  4.8297E+03  2.9E+01  1.8E-02
ENTIRE SOLUTION  1.9157E+03  1.8E-01  2.8E-01

A plot of the peaks found by CONTIN is given below.

A plot with 1/\lambda in the abscissa with the same amplitude in the ordinate is given below. This may be compared with the Schulz-Zimm distribution of radii for z=10.
INVERSE OF CONTIN MODE STRUCTURE

Amplitude vs. 1/\lambda in sec
V.3.5 Intensity autocorrelation function for z=10 with low noise

A low level of noise was added to the previous intensity autocorrelation function.

Analysis

DISCRETE found the following mode structure.

\[
\begin{array}{cc}
\text{ALPHA} & \text{STD ERR} \\
7.863E+02 & 4.2E+00 \\
1.653E+03 & 1.5E+00 \\
2.528E+02 & 2.7E+00 \\
\end{array}
\quad \begin{array}{cc}
\text{LAMBDA} & \text{STD ERR} \\
1.308E+03 & 2.4E+00 \\
2.001E+03 & 2.4E+00 \\
3.251E+03 & 5.9E+00 \\
\end{array}
\]

CONTIN analysis gave the following results.
A plot of the peaks found by CONTIN is given below.

A plot of $1/\lambda$ in the abscissa with the same amplitude in the ordinate is given below.
V.3.6  Intensity autocorrelation function for z=10 with high noise

A higher noise level was added to the simulated intensity autocorrelation function. The results are in file Intz10.02.
V.3.6 Intensity autocorrelation function for $z=10$ with high noise

A higher noise level was added to the simulated intensity autocorrelation function. The results are in file Intz10.02.

Analysis

DISCRETE gives the following mode structure

| ALPHAT| 2.855E+03 ± 1.4E+02 |
| LAMBDA| 2.097E+03 ± 1.0E+02 |
CONTIN analysis gave the following results

<table>
<thead>
<tr>
<th>M(1)/M(0)</th>
<th>% ERR</th>
<th>STD DEV/MEAN</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1861E+03</td>
<td>1.4E+01</td>
<td>1.7E-01</td>
</tr>
</tbody>
</table>
INVERSE OF CONTIN MODE STRUCTURE

Amplitude

\[ \frac{1}{\lambda \text{ in sec}} \]

\[ 0 \quad 0.0001 \quad 0.0002 \quad 0.0003 \quad 0.0004 \quad 0.0005 \quad 0.0006 \quad 0.0007 \quad 0.0008 \quad 0.0009 \quad 0.001 \]

\[ 0.001 \quad 0.002 \quad 0.003 \quad 0.004 \quad 0.005 \quad 0.006 \quad 0.007 \]

 specialties

\[ \text{inv.02} \]
V.3.7 Intensity autocorrelation function for z=1 with no noise

The Schulz-Zimm distribution of radii corresponding to z=1 is the most polydisperse. The corresponding autocorrelation function is in Intz01.00.

Results

DISCRETE gave the following mode structure

<table>
<thead>
<tr>
<th>ALPHA</th>
<th>STD ERR</th>
<th>LAMBDA</th>
<th>STD ERR</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.982E+04</td>
<td>9.8E+01</td>
<td>5.402E+02</td>
<td>6.9E-01</td>
</tr>
<tr>
<td>3.156E+04</td>
<td>4.3E+01</td>
<td>1.044E+03</td>
<td>2.2E+00</td>
</tr>
<tr>
<td>4.858E+03</td>
<td>5.8E+01</td>
<td>2.279E+03</td>
<td>8.4E+00</td>
</tr>
</tbody>
</table>
CONTIN analysis gave the following results

<table>
<thead>
<tr>
<th></th>
<th>M(1)/M(0)</th>
<th>PERCENT ERROR</th>
<th>STD DEV/MEAN</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEAK 1</td>
<td>9.6577E+02</td>
<td>3.9E-02</td>
<td>4.6E-01</td>
</tr>
<tr>
<td>PEAK 2</td>
<td>4.8475E+03</td>
<td>5.5E+00</td>
<td>1.7E-02</td>
</tr>
<tr>
<td>ENTIRE SOLUTION</td>
<td>9.7516E+02</td>
<td>5.5E-02</td>
<td>5.0E-01</td>
</tr>
</tbody>
</table>

The DISCRETE output seems to confirm the polydisperse character of the original distribution. In a similar manner, CONTIN also gives a fairly broad peak in its output. A spurious peak starts appearing at the end of the CONTIN window. It is characterized by a high level of noise.
V.3.8 Intensity autocorrelation function for z=1 with low noise
Analysis

DISCRETE gave the following mode structure

<table>
<thead>
<tr>
<th>ALPHA ± STD ERR</th>
<th>LAMBDA ± STD ERR</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.484E+04 ± 1.7E+03</td>
<td>8.494E+02 ± 2.6E+01</td>
</tr>
</tbody>
</table>

CONTIN analysis gave the following results

<table>
<thead>
<tr>
<th>M(1)/M(0)</th>
<th>PERCENT ERROR</th>
<th>STD DEV/MEEAN</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.5692E+02</td>
<td>1.1E+01</td>
<td>2.9E-01</td>
</tr>
</tbody>
</table>
INVERSE OF CONTIN MODE STRUCTURE

Amplitude

1/\lambda (in sec)

0 0.001 0.002 0.003 0.004 0.005 0.006 0.007 0.008 0.009 0.01

0 0.001 0.002 0.003 0.004 0.005 0.006 0.007 0.008 0.009 0.01
V.3.9 Intensity autocorrelation function for z=1 with high noise

**NOISY INTENSITY AUTOCORRELATION FUNCTION**

<table>
<thead>
<tr>
<th>G2 (arb. units)</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>3.5e+09</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3e+09</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.5e+09</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2e+09</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.5e+09</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1e+09</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5e+09</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**DISCRETE** gave the following mode structure

**ALPHA ± STD ERR**  **LAMBDA ± STD ERR**

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>5.724E+04 ± 2.4E+03</td>
<td>9.241E+02 ± 3.9E+01</td>
<td></td>
</tr>
</tbody>
</table>

**CONTIN** analysis gave the following results

**M(1)/M(0) PERCENT ERROR STD DEV/Mean**

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>9.2955E+02 ± 1.2E+01</td>
<td>9.6E-02</td>
<td></td>
</tr>
</tbody>
</table>
V.4 Discussion

A lot of workers in photon correlation spectroscopy rely on DISCRETE and CONTIN analyses for characterizing polydispersity as well as for the study of other phenomena than center of mass (CM) diffusion, such as the dynamics of internal modes of polymer coils, whose decay is much faster than that of CM modes. Consequently, it is necessary to examine the output of these routines under various situations. However, there is an acute paucity of any such investigations in the literature. The following discussion seeks to highlight some interesting features of the analyses made on synthetic data designed to look “as real as possible”.

Sensitivity to noise

The first main point is that DISCRETE seems to fit taking into consideration the signal-to-noise ratio of the data. It is apparent that in the case of the noisy autocorrelation functions corresponding to the highly polydisperse case of z=1, DISCRETE found only one mode in the presence of noise. This remark was also noticed in [2] at the end of this project.

It was also seen that the addition of noise does not widen the peak found by CONTIN. In many instances the presence of noise actually narrows the peak. This example is readily seen in the context of exponentials with and without noise where the standard deviation to mean ratio indicating the breadth of each peak is smaller for exponentials with noise.

The likely reason for this behavior is that both programs use weighting of each point of the initial data by the inverse of the mean square error to a crude fit as a smoothing procedure which tends to remove jagged features of the input. As the fit is to a sum exponentials and the initial channels contain a lower level of noise, the fitted curve tends to pass below the actual distribution to which noise was added.
The same tendency was also shown by CONTIN although it is difficult to correlate the breadth of the peak given by the program with polydispersity.

Spurious modes

In all noiseless intensity autocorrelation functions, CONTIN found a small peak at the upper extreme of the window. These spurious modes are always given with large error bars. The possible explanation of this phenomenon is that as the decay of the simulated autocorrelation functions is not purely exponential and that the data given to CONTIN do not have any information on the decay at the origin. CONTIN therefore includes a small, fast mode in order to account for the decay from the zeroth to the first channel. The intensity autocorrelation functions calculated by the BI2030 digital correlator used in the laboratory also do not compute the autocorrelation function at t=0 and the data in the first few channels is not recommended for analysis due to possible contamination with shot noise.

This feature therefore suggests that in order to determine the nature of a fast mode observed in CONTIN output the size of the window should be varied. A larger window will accordingly displace the upper-end artifact as it appears to be merely a response to missing information about the beginning of the decay.

Response to polydispersity

In noiseless polydisperse distributions (corresponding to a low value of z) DISCRETE finds three modes, which is the maximum number of modes it is allowed to find. However, as mentioned before, its resolution is markedly different in presence of noise.
For a monodisperse distribution such as that corresponding to \( z = 100 \), the inversion obtained by both DISCRETE and CONTIN is quite good. For highly polydisperse distributions corresponding to \( z = 1 \), DISCRETE output give no obvious indication of polydispersity in the presence of an arbitrary amount of noise.

It is difficult to obtain an exact idea of the shape of the original radius distribution as given that \( D \sim 1/r, \Delta D \sim \Delta r/r^2 \sim \lambda^2 \Delta r \). The position of the peak within the CONTIN window influences the breadth of the corresponding radius distribution. A higher decaying mode \( \lambda \) will tend to produce a narrower peak in the "radius space".

However, a plot of \( 1/a \) vs. the amplitude was generated for each CONTIN solution. There is a clear tendency for the peaks in these inverse plots to get broader with increasing \( z \). However, the prior knowledge of the initial Schulz-Zimm distribution clearly produces a bias here.

Recovery of the original radius distribution

The recovery of \( f_z(r) \) from the original Schulz-Zimm distribution does not seem to be straightforward. This is as CONTIN seeks to invert the general integral equation of the form

\[
y(t) = \int_a^b s(\lambda) K(\lambda, t) d\lambda
\]

and in this case it is

\[
y(t) = I_z(q, t) = A I_0 N \int_0^\infty \! df_{z} (r) \alpha^2 (r) P(q, r) \exp \left( -q^2 D \left( \frac{1}{r} \right)^2 \right)
\]

Effecting a change of variable, one can set \( \lambda = 1/r \) and thus \( d\lambda = -dr/r^2 \), which is valid as there is only a multiplicative constant to ignore.
Then

\[ y(t) = \int_{0}^{\infty} \frac{s(r)}{r^2} \exp\left(-\frac{\lambda}{r}\right) \, dr \]  

(4)

Thus an equality of the following form can be written

\[ \alpha^2(r) P(q, r) f_z(r) = \frac{s(r)}{r^2} \]

(5)

Assuming the scatterers to be structureless (i.e. point scatterers) and of constant polarizability, the following relationship would be nevertheless valid

\[ f_z(r) = \frac{s(r)}{r^2} = \frac{s(\lambda)}{r^2} \]

(6)

as \( \lambda = \lambda(1/r) \).

Or,

\[ f_z(r) = f_z(\lambda) = \lambda^2 s(\lambda) \]

(7)

This means that a plot of \( s(\lambda) \) against \( \lambda \) having no skewness will result in a curve depicting \( f_z(r) \) as a function of \( r \) having a skew toward the right. The recovery of a skewness thought to result from the Schulz-Zimm distribution may not actually be due to a feature of the original distribution. However, the breadth of the CONTIN peak does give an indication of the original radius distribution.
REFERENCES
