REAL TIME MULTIPLE TAU AUTOCORRELATOR AND ITS APPLICATION IN DYNAMIC LIGHT SCATTERING

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DEDICATION

To my parents, my father Luo Binjie and my mother Yang Xinghua

ABSTRACT

Dynamic light scattering (DLS) has recently been extended from a study of translational diffusion coefficients in dilute solution to a means of obtaining distributions in relaxation times over wide ranges of decay times. Many different data analysis algorithms have been developed to extract information on distribution functions (radius distribution, diffusion coefficient distribution, etc.) from photon correlation functions. Obtaining these distribution solutions usually involves the inversion of the Laplace Transform, and this can lead to ill-conditioned Fredholm integral equations of the first kind. These problems can be minimised by using an optimised time scale for the autocorrelation function. The need to handle such a dynamic range within one correlation function led to the development of the Multiple Tau Autocorrelator.

This thesis describes the design and construction of a real time multiple tau autocorrelator and its application in DLS.

An introduction to the theory of DLS is given. The theoretical background of the experiments is discussed and DLS techniques are reviewed. Particular emphasis is placed on experimental techniques and experimental data analysis procedures. The relationship among the intensity, amplitude, and photon count correlation functions are discussed.

Data analysis methods based on obtaining distributions in relaxation times over wide ranges of decay times are discussed. Different hardware correlator system design techniques are reviewed. A correlator based on multiple tau techniques and symmetric normalisation is discussed.

The advantages of using a multiple-instruction-multiple-data (MIMD) system to perform multiple tau autocorrelation is examined. The novel multiple digital signal processor (DSP) architecture for real time implementation of multiple tau autocorrelation is developed based on the task scheduling analysis, interconnection performance, and parallel processing. Detailed explanations of the operation of the Motorola DSP56001 digital signal processor are given, including architecture, addressing modes, instruction sets and peripheral access.

The design and construction of the real time multiple tau autocorrelator is described. Detailed descriptions of hardware circuits and software are given. The correlator has proved satisfactory in its applications. The instrument can also works as spectrum analyser or other real time digital signal processing station.

Two sets of experiments on ternary polymer solutions were carried out using the multiple tau correlator. The results of dynamic light scattering measurements are discussed within the broad framework of the Borsali-Benmouna theory. Experimental data are analysed using the constrained regularisation method. The interdiffusion coefficient and cooperative diffusion coefficient of PS/PMMA/thiophenol and PS/PMMA/toluene system under "optical tracer" conditions are discussed, and the interesting features of polymer polymer interaction as the temperature is varied are also discussed.

Advantages of a multiple tau correlator over a linear correlator in the more complicated ternary polymer solution studies is demonstrated.

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MAIN GLOSSARY

$A(\tau)$	Distribution function of relaxation time
A_+	Amplitude of the fast mode
a	Radius of the particle
B	Photon correlation function baseline
D	Diffusion coefficient
D_C	Cooperative diffusion coefficient describing the relaxation of concentration fluctuations
D_I	Interpenetration diffusion coefficient describing the relaxation of composition fluctuations
D_{S2}	Self diffusion coefficient of polymer 2 in polymer solution
e	Electronic charge
$\boldsymbol{e}_y$	Unit vector in the direction of polarisation vector
$\boldsymbol{e}_z$	Unit vector in the direction of beam propagation
$F(x)$	Kawasakifunction
$G(r)$	Variable accessible experimentally in the Fredholm integral of the first kind, $G(r) = \int K(r,s)A(s)ds$
$A(s)$	Function characteristic for the system under investigation in the Fredholm integral of the first kind
$K(r,s)$	Specific for the experimental method, in our case $K(r,s) = e^{-rs} = e^{-\Gamma t}$, and $r = t$, $s = \Gamma$
$g^{(1)}(t)$	Normalised amplitude or first-order correlation function
$g^{(2)}(t)$	Normalised intensity or second-order correlation function
$G^{(1)}(t)$	Unnormalised amplitude or first-order correlation function
$G^{(2)}(t)$	Unnormalised intensity or second-order correlation function

$G_n(k)$	Photon correlation function
$g_n(k)$	Normalized photon correlation function
$G_e(k)$	Constitutes an unbiased estimator for the photon correlation function $G_n(k)$
$G(k)$	Raw correlation function
$g(k)$	Normalized raw correlation function
$g^{(sym)}(k)$	Symmetric normalised raw correlation function
I	Intensity (expressed as the number of photons reaching the detector in unit time)
k_B	Boltzmann constant
k	Magnitude of the propagation vector $k = \frac{2\pi}{\lambda}$
k_i	Initial wave vector
k_f	Final wave vector
m	Mass of the particle
M	Finite number of samples
n_c	Direct signal in the clipping correlator
n'	Clipped delay signal in the clipping correlator
n^2	Square of average count rate
n_{e0}	Standard monitor channel
n_{ek}	Monitor channel for an individual correlation channel
n_j	Number of photon detection pulses counted during a particular sampling time interval $j\Delta T$
$n(t)$	Number of photons detected in period ΔT
N_1	Degrees of polymerisation of polymers 1 in ternary polymer solution

N_2	Degrees of polymerisation of polymers 2 in ternary polymer solution
p	Quantum efficiency of the detector
$P(q)$	Particle form factor
$\boldsymbol{q}$	Scattering vector
q	Magnitude of the scattering vector $q = \lvert\boldsymbol{q}\rvert = 2k\sin\left(\frac{\phi}{2}\right)$
R_g	Random coil radius of gyration
$R_j(\tau)$	Photon current density correlation function at one point of the photocathode surface
$S_j(\omega)$	Power spectrum of the photocurrent density
t_d	Counting dead time
t_r	Hydrodynamic relaxation time
t	Time
T	Temperature
T_c	Critical temperature of the solution
x	Relative abundance of polymer 2 in ternary polymer solution
$w(\Gamma)$	A continuous distribution function of decay rates Γ
β	Intensity intercept
χ	Polymer-polymer interaction parameter
χ_c	Critical value of the polymer-polymer interaction parameter
ΔT	Sample time
ε	Reduced temperature given by $(T - T_c)/T$
ϕ	Polymer volume fraction
θ	Scattering angle

Γ	Decay rates
η	Viscosity of the solvent
μ	Mean number of detection pulses per sample time ΔT
λ	Wavelength of the incident laser light
ρ	Density of the particle
τ	Lag time
υ	Polymer excluded volume
ω	Angular frequency of the incident laser light
ξ	Dynamic correlation length

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